X International
Voevodsky
Conference

2022

Physics and Chemistry of Elementary Chemical Processes

September 5-9, 2022,
Akademgorodok,
Novosibirsk, Russia

Book of Abstracts

Organizers

MINISTRY OF SCIENCE AND HIGHER EDUCATION OF THE RUSSIAN FEDERATION
SIBERIAN BRANCH OF THE RUSSIAN ACADEMY OF SCIENCES
VOEVODSKY INSTITUTE OF CHEMICAL KINETICS AND COMBUSTION
NOVOSIBIRSK STATE UNIVERSITY

X INTERNATIONAL VOEVODSKY CONFERENCE

PHYSICS AND CHEMISTRY OF ELEMENTARY CHEMICAL PROCESSES

September 5–9, 2022

Akademgorodok, Novosibirsk, Russia

Dedicated to the 105th anniversary of Academician Vladislav Voevodsky

Novosibirsk ◆ 2022

УДК 54+662.612.3
ББК Г5я431
Ф503

Conference Chair
Acad. Renad Z. Sagdeev (ITC SB RAS)

Vice-Chairs
Prof. Andrei A. Onischuk (ICKC SB RAS)
Prof. Elena G. Bagryanskaya (NIOC SB RAS)

Scientific Secretary
Dr. Alexandra P. Pyryaeva (ICKC SB RAS)

Ф503 Physics and Chemistry of Elementary Chemical Processes : Proceedings of the 10th International Voevodsky Conference. September 5–9, 2022 / Novosibirsk State University. — Novosibirsk : IPC NSU, 2022. — 280 p. DOI: 10.25205/978-5-4437-1350-2

ISBN 978-5-4437-1350-2

10th International Voevodsky Conference (VVV-2022) will be held on September 5–9, 2022 in Akademgorodok, Novosibirsk. This meeting is dedicated to the 105th anniversary of the birth of Academician Vladislav Voevodsky, one of the prominent figures in the early days of Akademgorodok. More than 200 participants from Russia and abroad will be discussing a wide variety of topics related to the physics and chemistry of elementary chemical processes.

УДК 54+662.612.3
ББК Г5я431

ISBN 978-5-4437-1350-2

ORGANIZERS

Voevodsky Institute of Chemical Kinetics and Combustion (ICKC SB RAS)

International Tomography Center (ITC SB RAS)

Institute of Problems of Chemical Physics (IPCP RAS)

Novosibirsk State University (NSU)

Vorozhtsov Novosibirsk Institute of Organic Chemistry (NIOC SB RAS)

Semenov Federal Research Center for Chemical Physics (FRCCP RAS)

Postovsky Institute of Organic Synthesis (IOS UB RAS)

Ministry of Science and Higher Education of the Russian Federation

Siberian Branch of the Russian Academy of Sciences (SB RAS)

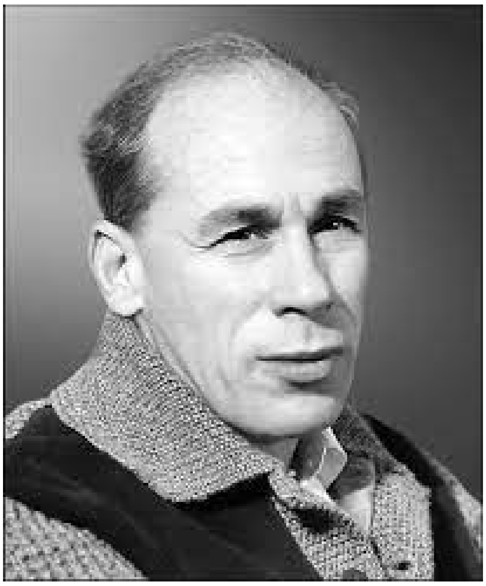
ORGANIZING COMMITTEE

Prof. Matvey V. Fedin (ITC SB RAS)
Prof. Evgeney M. Glebov (ICKC SB RAS)
Prof. Leonid V. Kulik (ICKC SB RAS)
Prof. Nikolay E. Polyakov (ICKC SB RAS)
Dr. Aleksandra V. Kim (ICKC SB RAS)
Dr. Vitaly G. Kiselev (ICKC SB RAS)
Dr. Denis A. Knyazkov (ICKC SB RAS)
Dr. Denis A. Morozov (NIOC SB RAS)
Dr. Andrey G. Shmakov (ICKC SB RAS)
Dr. Victoria N. Syryamina (ICKC SB RAS)
Dr. Mikhail N. Uvarov (ICKC SB RAS)
Dr. Sergey V. Valiulin (ICKC SB RAS)
Dr. Marianna V. Voevodskaya (ICKC SB RAS)
Victoria A. Salomatova (ICKC SB RAS)

PROGRAM COMMITTEE

Acad. Sergey M. Aldoshin (IPCP RAS)
Acad. Valery N. Charushin (IOS UB RAS)
Acad. Mikhail P. Egorov (IOC RAS)
Acad. Mikhail P. Fedoruk (NSU)
Acad. Yuriy N. Molin (ICKC SB RAS)
Acad. Valentin N. Parmon (SB RAS)
Corresponding Member of RAS
Vilen V. Azatyan (FSI FSC SRISA RAS)
Prof. Elmira R. Badamshina (IPCP RAS)
Prof. Alexey V. Baklanov (ICKC SB RAS)
Prof. Alexander V. Chertovich (FRCCP RAS)
Prof. Sergey A. Dzuba (ICKC SB RAS
Prof. Nina P. Gritsan (ICKC SB RAS)
Prof. Oleg P. Korobeynichev (ICKC SB RAS)
Prof. Tatyana V. Leshina (ICKC SB RAS)
Prof. Nikita N. Lukzen (ITC SB RAS)
Prof. Victor A. Nadtochenko (FRCCP RAS)
Prof. Alexander A. Paletsky (ICKC SB RAS)
Prof. Egor V. Verbitskiy (IOS UB RAS)
Prof. Grigoriy V. Zyryanov (IOS UB RAS)

VLADISLAV VOEVODSKY



The name of Academician Vladislav Voevodsky is known throughout the world to the researchers working in chemical physics. His effort and talent were responsible for many key advances in the investigation of gas chain branched reactions, reactions of hydrocarbon cracking, and heterogeneous reactions of radicals and atoms.

Academician Voevodsky was one of the first to realize the potential of the magnetic resonance technique in studying free radicals and other paramagnetic particles. He and his colleagues developed the EPR technique into a powerful experimental method for investigating chemical reactions, founding a new field of science—chemical radiospectroscopy. This work, in turn, led to a breakthrough in the study of many fundamental chemical phenomena, including the free-radical mechanisms of chemical reactions, electron delocalization and transfer, elementary acts in solid and liquid matter radiolysis, mechanisms of photochemical and photobiological processes, and heterogeneous catalysis.

Academician Voevodsky was one of the founders of the Institute of Chemical Kinetics and Combustion (Novosibirsk, Russia) and the Department of Natural Sciences of Novosibirsk State University. For many years he was the Dean of the Department. He raised and inspired a community of worldwide known scientists who continue to work in chemical physics today. His students had a major impact on the development of chemical kinetics and chemical physics—a field of science that describes physics and chemistry of elementary chemical reactions.

The conference in Academician Voevodsky's honor brings together scientists studying elementary chemical processes from all over the world.

CHEMICAL KINETICS AND SPECTROSCOPY

Nature of Compensation Law and “Exotic” Arrhenius Parameters in Denaturation of Proteins

✉ **Alexey V. Baklanov**[1], **Vitaly G. Kiselev**[1, 2]

[1]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2]Novosibirsk State University
Novosibirsk, Russia

✉ baklanov@kinetics.nsc.ru

Proteins possess unique functionality in their native states, operating in the cells of all known organisms. These native states are assembled by folding of a protein chain into a secondary, tertiary or even quaternary structure. Denaturation of proteins provided by unfolding of this structure results in the loss of their functionality, which can be followed by death of the cell and organism. The current work is devoted to theoretical investigation of the nature of two experimentally established phenomena in proteins denaturation provided by heating: the Compensation Law behavior and “exotic” values of the Arrhenius parameters. Exotics of the Arrhenius parameters can be illustrated by the fact that the preexponential factor A for the rate constants of these processes is almost always more than 10^{25} s^{-1} and can reach values up to ca. 10^{130} s^{-1} [1; 2]. These numbers differ drastically from the values of ca. 10^{13}–10^{14} s^{-1} typical for different types of unimolecular reactions of organic molecules [3]. In spite of the spread in values the changes of the Arrhenius parameters E_a and A in a wide manifold of studied proteins compensate each other demonstrating the so-called Compensation Law (CL) behavior [1; 2; 4]. Many hypotheses were suggested for explanation of the CL behavior [4], but this behavior is still not understood.

In the presented work the unfolding of proteins is modeled by dissociation of the dimers of polypeptides (polyglycine) of varied length into the monomeric chains. The “loose” transition state model is suggested, which allows one to calculate the rate constants and the Arrhenius parameters for dissociation of these dimers within the Transition State Theory (TST). The obtained results allowed us to explain the “exotic” values of the Arrhenius parameters and to conclude that the CL behavior is the intrinsic property of the protein denaturation process in a dry or hydrated shape of protein.

[1] Munblit V. Ya., Talrose V. L., Trofimov V. I. (1985). *Termoinaktivatsiia mikroorganizmov* [Thermoinactivation of Microorganisms]. M., Nauka. (in Russ)

[2] Qin Z., Balasubramanian S. K., Wolkers W. F., Pearce J. A., Bischof J. C. (2014). *Ann. Biomed. Eng., 42*, 2392–2404.

[3] Robinson P., Holbrook K. (1975). Unimolecular Reactions. M., Mir. (in Russ.)

[4] Liu L., Guo Q. X. (2001). *Chem. Rev., 101*, 673–695.

Efficiency of the FeEDDS Complex in the Production of OH Radicals

✉ **Yury A. Belikov**[1,2], **Olga A. Snytnikova**[1,3], **Vyacheslav P. Grivin**[2], **Ivan P. Pozdnyakov**[1,2]

[1]Novosibirsk State University
Novosibirsk, Russia
[2]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[3]International Tomography Center SB RAS
Novosibirsk, Russia

✉ y.belikov@g.nsu.ru

At present, the use of Fe(III) complexes with organic carboxylic acids in advanced oxidation processes (AOPs) aimed at wastewater treatment is being widely studied. The complexes show high quantum yields of photolysis along with highly efficient generation of reactive oxygen species, the main of which is the hydroxyl radical •OH under the UV excitation. It is capable of non-selective oxidation of a large number of organic pollutants.

As ligands in such complexes both relatively simple acids (oxalic, puruvic, tartaric, etc.) and more complex ones, such as ethylenediamine-*N*,*N'*-disuccinic acid (EDDS), are studied. Being a structural isomer of ethylenediaminetetraacetic acid, EDDS is biodegradable, which allows one to use it for environmental purposes. However, for the practical application of the system, one needs information about the mechanism of photolysis and the quantum yields of •OH radicals (ϕ_{OH}). This work presents a detailed study of efficiency of both complex photolysis and •OH radicals generation in a wide range of experimental conditions (pH, excitation wavelength, oxygen content, initial ligand and Fe(III) concentrations).

Using steady-state and laser flash photolysis methods in combination with spectrophotometry and liquid chromatography, we got the following results:

1. Primary intermediate is a long-lived (1.8 ms) radical complex [Fe(II)…EDDS•] (λ_{max} = 520 nm), which is formed by the electron transfer from ligand to Fe(III) ion.
2. The value of photolysis' quantum yield is stable in a wide range of initial ligand and Fe(III) concentration, but depends on presence of oxygen. The pH dependence also exists, and it depends on the presence of oxygen too. The value in optimal conditions achieves ~0.8.
3. •OH quantum yield is stable in a wide range of initial ligand and Fe(III) concentration, but depends on pH and has achieved the value of ~0.15 in optimal conditions at neutral pH. High quantum yield makes possible to use the complex in AOPs.

The received results are important for understanding both fundamental photochemistry of the Fe(III) polycarboxylate complexes and for application of such complexes in AOPs of wastewater treatment.

Acknowledgements: this work was financially supported by the Russian Science Foundation (No. 21-43-00004).

Thin-Film Laser Sensor for Detection of Ammonia and Hydrogen Chloride Vapor

✉ **Shirin T. Berdybaeva**, **Eugene N. Tel'minov, Tatyana A. Solodova**

Tomsk State University
Tomsk, Russia

✉ sheirn@mail.ru

Among a wide variety of molecular chemical sensors, luminescent sensors attract the attention of researchers due to their ease of creation and low cost, high sensitivity and high speed of response to the presence of a detectable substance (analyte). When an analyte molecule meets an organic sensor molecule in an electronically excited state, a complex is formed with the transfer of an electronic charge towards the analyte. The luminescence intensity of the sensor molecule decreases [1].

The transition from the fluorescence mode (spontaneous emission) to the threshold lasing mode (transition from enhanced spontaneous emission to stimulated emission) is one of the ways to increase the sensitivity of optical molecular sensors [2]. In work [3], the response time decreased by the factor of 4.

In this work, the dye Nile red (NR) was used as a fluorophore-sensor. This dye is able to quickly respond to changes in the chemical composition of the environment. Ammonia (NH_3) and hydrogen chloride (HCl) were as analyte. The generation characteristics were studied in a sealed cell, which was purged with analyte vapor mixed with inert gases. Registration of the generation intensity was carried out for 0, 10, 20, and 30 seconds after the addition of analyte vapors.

As a result of the studies, the spectra of generation of sensor films under the influence of analyte vapors were obtained. The intensity of generation of the PMMA film from a toluene solution doped with NR decreased in the presence of NH_3 vapor by 70 % within 10 seconds, and after 20 seconds the generation broke down. After the interaction of a PMMA film from a solution of tetrahydrofuran doped with NR with HCl vapor for 10 seconds, the generation intensity dropped by 64 %; after another 30 seconds the generation broke down.

Thus, the possibility of creating solid-state photoexcited laser sensors for ammonia and hydrogen chloride vapors has been shown.

Acknowledgements: this study was supported by the Tomsk State University Development Programme (Priority-2030, No. НУ 2.0.7.22 МЛ).

[1] Zyryanov G. V., Kopchuk D. S. (2014). *Rus. Chemical Reviews*, *83*(9), 783.

[2] Gillanders R. N., Turnbull G., Samuel I. (2018). *In Proc. of the 6th International Conference on Photonics, Optics and Laser Technology*, 323–327.

[3] Berdybaeva Sh. T., Telminov E. N., Solodova T. A. et al. (2021). *Quantum Electronics*, *51*(3), 206–210.

Spectral Properties of Bromocresol Purple

✉ **Nadezhda P. Bezlepkina**[1], **Elena N. Bocharnikova**[1], **Olga N. Tchaikovskaya**[1,2]

[1] Tomsk State University
Tomsk, Russia
[2] Laboratory of Quantum Electronics, Institute of Electrophysics UB RAS
Ekaterinburg, Russia

✉ nadezhda.bezlepkina174833@mail.ru

The growing demand for new optical sensing technologies has stimulated research in this area. Several devices based on optical detection with the use of bromocresol purple (BCP) have been developed to measure pH [1]. Recently, along with optical detectors, chemical sensors based on BCP have been actively investigated. Of particular interest is the application of such sensors in the field of medicine as alternative method of early cancer diagnosis [2]. Therefore, there is a need for a detailed study of the spectral properties of bromocresol purple.

In this work, we investigated the influence of solvent properties on the spectral and luminescent properties of bromocresol purple [3]. Chemically pure solvents were used to obtain the solutions: distilled water, ethanol, toluene, and acetone. Solutions of the investigated compound were prepared by dissolving a dry sample in 10 ml of solvent. Matrix solutions of BCP in distilled water, in ethanol, in toluene and in acetone were obtained this way. The investigation was based on electron spectroscopy methods. The spectral-luminescence characteristics of the BCP solutions were registered on a Cary 5000 and Cary Eclipse spectrophotometer. The measurement error did not exceed 10 %. Using the experimental data, the spectral characteristics of BCP were defined: half-width $\Delta\nu_{1/2}$, molar absorption coefficient ε, lifetime of an excited state τ, oscillator strength f; using the Lippert equation the dependence of the Stokes shift on the solvent polarity was plotted. It is shown that the position and intensity of the absorption bands depend on the solvent in the whole spectral region from 200 to 700 nm. The absorption bands with maxima in the region of 420 ÷ 430 nm and 580 ÷ 590 nm are sensitive to the properties of the solvent. The lowest absorption intensity was registered in the absorption spectrum in toluene. This is due to the fact that toluene is a non-polar solvent, and it weakly interacts with the dye molecule. The absorption spectra of BCP were interpreted using quantum-chemical calculations.

Acknowledgements: this study was supported by the Tomsk State University Development Programme (Priority-2030).

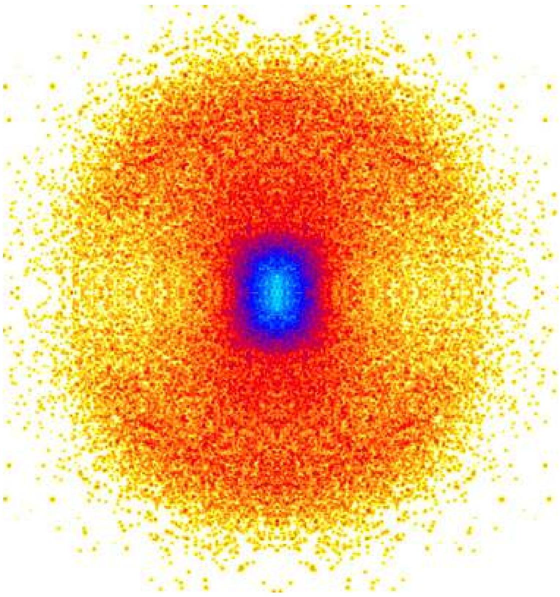
[1] Pinto P. V. (2016). *Sensors and Actuators B-chemical, 223*, 406–410.
[3] Cichero M. C., dos Santos J. H. (2021). *Applied Surface Science Advances, 4.*
[3] Freistat D. M. (1980). *Reagents and preparations for microscopy,* 480.

The Formation of Chemically Bonded Argon via Photoexcitation of Ar-I_2 van der Waals Complex

✉ **Alexandr S. Bogomolov**[1], **Nikolay V. Dozmorov**[1,2],
Sergey A. Kochubei[3], **Alexey V. Baklanov**[1]

[1]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2]Novosibirsk State University
Novosibirsk, Russia
[3]Rzhanov Institute of Semiconductor Physics SB RAS
Novosibirsk, Russia

✉ bogomolov.kinetics@gmail.com



Velocity map image of Ar^+ arising from the complex Ar-I_2

The Van der Waals complex Ar-I_2 is a model system for studying the influence of weakly bonded molecular environment on the photochemistry and photophysics of molecules. Earlier studies of this complex reported in literature were focused only on the processes including transition to the first excited states of iodine molecule. In the current work, the photo-induced processes following the excitation of the complex Ar-I_2 into high-lying Rydberg states and ion-pair states are investigated. The Ar-I_2 van der Waals complex has been generated in supersonic molecular beam. Ions Ar^+ and ArI^+ were observed in a mass-spectrum at the Ar-I_2 van der Waals complex photoexcitation by laser radiation with wavelength ~270 nm ($h\nu \approx 4.6$ eV). It should be noted that the ionization potential of argon is 15.7 eV, which requires four photons of radiation to be used. The four-photon ionization of free Ar atoms is impossible in our experimental conditions (nanosecond laser with pulse energy ca. 1 mJ). The velocity map of Ar^+ (see Fig.) has rings as in the case of diatomic molecule dissociation. It means that Ar^+ is formed from photodissociation of parent ArI^+ ion where the argon ion is covalently bound. The photon energy dependence of the channels giving rise to Ar^+ ions with different kinetic energy has also been investigated. The mechanism of covalently bound Ar^+ ions formation is suggested [1].

Acknowledgments: the reported study was funded by RFBR, project No. 20-52-12014.

[1] Bogomolov A. S., Dozmorov N. V., Kochubei S. A., Baklanov A. V. (2021). *J. Chem. Phys.*, *155*, 124308.

Proton Transfer Processes and Luminescence of ESIPT-Capable Zinc(II) Complexes with Imidazole and Pyrimidine Ligands

Nikita Shekhovtsov[1], **Katerina Vinogradova**[1], **Sofia Vorobyova**[1],
Alexey Berezin[1], **Victor Plyusnin**[2], **Alexey Ryadun**[1], **Dmitry Naumov**[1],
Natalya Pervukhina[1], **Tatyana Kokina**[1], **Anastasiya Ishchenko**[1,3],
Elena Nikolaenkova [4], **Viktor Krivopalov**[4], **Alexei Ya. Tikhonov**[4], ✉ **Mark Bushuev**[1]

[1]Nikolaev Institute of Inorganic Chemistry SB RAS
Novosibirsk, Russia
[2]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[3]Novosibirsk State University
Novosibirsk, Russia
[4]Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS
Novosibirsk, Russia

✉ bushuev@niic.nsc.ru

The excited state intramolecular proton transfer (ESIPT) is a photochemical reaction typical for organic compounds featuring short intramolecular hydrogen bonds of the O–H···N or O–H···O type. To study the impact of coordinated metal ions on the ESIPT reaction, two separate sites, namely the ESIPT site and metal binding site, need to be rationally designed in a single ESIPT-fluorophore molecule. ESIPT-capable zinc(II) complexes with imidazole and pyrimidine ESIPT-fluorophores show anomalous excitation wavelength dependent emission associated with proton transfer processes and direct excitation of the tautomeric form [1–3].

Acknowledgements: the study of the ESIPT reaction was funded by the Russian Science Foundation (grant No. 21-13-00216, https://rscf.ru/en/project/21-13-00216/) and performed at the Nikolaev Institute of Inorganic Chemistry. The authors appreciate the Ministry of Science and Higher Education of the Russian Federation and the Multi-Access Chemical Research Centre SB RAS for providing experimental and computational facilities.

[1] Berezin A. S., Vinogradova K. A., Krivopalov V. P., Nikolaenkova E. B., Plyusnin V. F., Kupryakov A. S., Pervukhina N. V., Naumov D. Y., Bushuev M. B. (2018). *Chem. Eur. J.*, *24*, 12790–12795.

[2] Shekhovtsov N. A., Nikolaenkova E. B., Berezin A. S., Plyusnin V. F., Vinogradova K. A., Naumov D. Y., Pervukhina N. V., Tikhonov A. Y., Bushuev M. B. (2021). *ChemPlusChem*, *86*, 1436–1441.

[3] Shekhovtsov N. A., Vinogradova K. A., Vorobyova S. N., Berezin A. S., Plyusnin V. F., Naumov D. Y., Pervukhina N. V., Nikolaenkova E. B., Tikhonov A. Y., Bushuev M. B. (2022). *Dalton Trans.* DOI: 10.1039/D2DT01232D.

The 1,3-dipolar Cycloaddition to Nitrones and Thier Photorearrangement as Activation Methods of Alkoxyamine Homolysis

✉ **Sergey A. Cherkasov**[1,2], **Dmitriy A. Parkhomenko**[1], **Elena G. Bagryanskaya**[1]

[1] *Novosibirsk Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ scher@nioch.nsc.ru

Radical controlled polymerization in the presence of nitroxide radicals (NMP) is one of the promising methods for obtaining polymers with a narrow molecular weight distribution of given structure and composition. The initiators for this type of polymerization are alkoxyamines, organic compounds with the general formula R1R2NOR3 which are reversibly decomposed by a homolysis reaction into a stable nitroxide radical, and an alkyl macroradical growing in the presence of a monomer. Thus, due to the peculiarities of the mechanism of radical controlled polymerization, the initiator is not consumed over time, but gradually turns into the polymer R1R2NO(M)nR3. This causes a linear increase in the molecular weight of the polymer with the conversion of the monomer, and the resulting polymer chains are close in length. However, this is possible only under optimal conditions, in particular, at some optimal temperature. The optimal polymerization temperature follows from the equilibrium "alkoxyamine-radicals" and the activation energy of the homolysis reaction. The lower the activation energy of homolysis, the lower the temperature at which a favorable equilibrium "alkoxyamine-radicals" is achieved. However, the synthesis of a too labile initiator is extremely difficult. Thus, an ideal alkoxyamine initiator should be labile during polymerization and, at the same time, stable enough for its synthesis. As a solution to this problem, in this work we propose two methods for the activation of non-labile alkoxyamines based on 2,2,5,5-tetramethyl-3-imidazoline-3-oxide-1-oxyl: 1,3-dipolar cycloaddition, and photochemical rearrangement.

Within the framework of this work, the kinetics of 1,3-dipolar cycloaddition to 13 different monomers was studied and the Arrhenius parameters were determined. The influence of the structure of the used monomer on the rate of 1,3-dipolar cycloaddition as well as on the homolysis activation barrier was determined. The photochemical rearrangement was studied by NMR spectroscopy, and the quantum yield and composition of the products were determined. For both methods of activation, their effect on the activation barrier of homolysis of the studied alkoxyamines was determined, and a conclusion was made about their applicability in the context of radical controlled polymerization.

Acknowledgements: this research was funded by RFBR (grant No. 20-33-90133).

Photo-Reversibility and Wavelength Dependence of Excited Intermediates in Nitro-Nitrito Linkage Isomerization of $[Co(NH_3)_5NO_2]Cl(NO_3)$ Crystals Unveiled by Photomechanical Response

✉ **Stanislav A. Chizhik**, **Anatoly A. Sidelnikov, Victor Y. Kovalskii, Pavel A. Gribov**

Institute of Solid State Chemistry and Mechanochemistry SB RAS
Novosibirsk, Russia

✉ stas@solid.nsc.ru

The phenomenon of linkage isomerization in $[Co(NH_3)_5NO_2]^{2+}$ complex, allowing two variants of NO_2 coordination to the metal ion, Co-NO_2 (nitro) and Co-ONO (nitrito), has attracted considerable attention for more than a hundred years [1]. The thermally stable nitro isomer can be isomerized to the nitrite by the UV and visible light with $\lambda < 530$ nm; the reverse nitrito-nitro transformation proceeds as a monomolecular reaction with an activation energy of ~100 kJ/mol. One of the open questions is related to the maximum achievable degree of photoisomerization, i.e., with the possibility of reverse ONO → NO_2 isomerization under the light. Determination of the photostationary state upon irradiation of solutions is impossible because of the parallel photolysis of the complex. It is believed that almost complete transformation is achievable in crystals. However, the exact photostationary nitrito/nitro ratio is unknown due to the insufficient accuracy of spectroscopic and X-ray diffraction methods, including the deformation and cracking of crystals caused by the difference in the crystal parameters.

At the same time, the mechanical effects caused by transformation in crystals can be used for a highly sensitive method for studying such reactions. A methodology has been developed that makes it possible to measure the kinetics of the transformation by the mechanical response it causes (bending and elongation of acicular crystals) with a sensitivity inaccessible to traditional methods [2]. The kinetics of photoisomerization has been studied in the wavelength range 350–523 nm. Evidence of the photoreversibility of photoisomerization was found: the corresponding dependence of the photostationary nitrito/nitro ratio was determined from the dependence of the stationary deformation of crystals on the wavelength; the fraction of the nitrito form reaches a maximum of > 10 % near 400 nm. In addition, the analysis of the effect of crystal deformation on the transformation rate makes it possible to establish the wave-length dependence of intermediate excited states.

Acknowledgements: the study was funded by the Russian Science Foundation (project No. 22-23-01130).

[1] Jörgensen S. M., Anorg Z. (1894). *Chem.,* 5, 147–196.

[2] Ahmed E., Chizhik S., Sidelnikov A., Boldyreva E., Naumov P. (2022). *Inorg. Chem., 61,* 3573–3585.

Unraveling the Mechanism of Gas-to-Particle Conversion in Lower Troposphere: Trap or Trace?

✉ **Galina G. Dultseva**, **Tatyana V. Kobzeva**, **Sergey N. Dubtsov**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ dultseva @kinetics.nsc.ru

Atmospheric organic aerosol is formed in a multistage process starting from photolysis of organic compounds, mostly alkenes and aldehydes which are released from natural and anthropogenic sources [1]. Gas-to-particle conversion is driven by short-lived free radicals, among which OH and HO_2 are the most abundant and well-studied [2]; however, yet poorly studied organic free radicals, either carbon- or oxygen-centered, are essential for predicting the surface functional groups on the formed aerosol particles within the breathable size range, which determines their diverse biological effects. However, the concentrations of organic short-lived free radicals in the troposphere are too low for direct measurement, therefore, for closer acquaintance, we have got to choose to use spin traps or to trace these radicals through the products of their interactions with other species. Laboratory studies of aldehyde photonucleation, with much higher concentrations of the organics than those observed in the troposphere, allowed us to trap and identify the free radicals which accompany photonucleation of aliphatic and aromatic aldehydes. The detailed analysis of gas-phase and aerosol products of this process, in combination with the data collected through atmospheric measurements from the ground level to an altitude of 7 km, allowed us to build up a kinetic model that works both in the photochemical reactor and in the Earth atmosphere. This model was used as a tool to verify the kinetic characteristics of condensable product generation and to determine the major anchors governing this process in the atmosphere [3]. In addition to free radicals, carboxylic acids were determined to be of key importance: being formed through aldehyde oxidation, they catalyze aldehyde polymerization to form solid particles. Within the assumed mechanism, it becomes possible to expect the ranges (successfully, rather narrow sometimes) of free radical concentrations which actually occur in the process under investigation. Thus, substituted phenyl and phenylperoxy radicals were identified by spin trapping under laboratory conditions, and the products of their interaction with specific reagents were traced in real atmosphere.

Thus, an efficient approach to access the mechanism of atmospheric photonucleation of aldehydes combines "trap and trace": trapping free radicals under laboratory conditions and tracing the identified radicals under atmospheric conditions.

[1] Wang G., Iradukunda Y., Shi G. et al. (2021). *J. Environ. Sci.*, *99*, 324–335.
[2] Inomata S. (2021). *ACS Earth Space Chem.*, *5*, 1929–1933.
[3] Dultseva G. G., Dubtsov S. N. (2021). *Atmos. Ocean. Optics*, *34*, 471–474.

Saturation Effect of Secondary Emission Coefficient in MCP-Based Multipliers in Mass-Spectrometry

✉ **Kirill S. Ershov**[1], **Sergey A. Kochubey**[2], **Alexey V. Baklanov**[1]

[1]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2]*Rzhanov Institute of Semiconductor Physics SB RAS*
Novosibirsk, Russia

✉ kershov93@gmail.com

Time-of-flight mass spectrometry (TOF MS) [1], as well as its modification—the so-called velocity map imaging (VMI) [2], is widely used in various chemical and photochemical experiments. In this case, the most commonly used detector for these experimental methods, and the only one in the case of VMI, is a secondary electron multiplier (SEM) based on microchannel plates (MCP). In this work, it is shown that when using such detector, significant distortions in the shape of the mass spectrum can occur due to the saturation effect of the detector sensitivity, which can also occur at a low level of the measured signal. In [3], the mechanism of photodissociation of tungsten hexacarbonyl $W(CO)_6$ was studied using time-of-flight mass spectrometry and measurement of photofragment velocity maps. In this case, photoions of tungsten atoms were recorded, and a large isotope effect was found in favor of light tungsten isotopes. In [3], two possible explanations for the observed isotope effect were proposed: 1) different efficiency of the photodissociation of isotope-containing tungsten hexacarbonyl molecules under the action of the 4th harmonic of the Nd-YAG laser; 2) different efficiency of photoionization at atomic transitions for different isotopes of tungsten. In this work, we consider the "isotope effect", which occurs as the result of signal distortion during the registration of time-of-flight mass spectra using secondary electron multipliers based on microchannel plates. The results obtained in the work showed that the observed effect is associated with the saturation of the detector sensitivity. This conclusion is also confirmed by the results presented in this work for titanium atoms. The results of these experiments, as well as the analysis of the nature of this effect and its quantitative estimates, are presented in this work.

Acknowledgements: the authors express their gratitude to the Russian Federal Ministry of Science and Higher Education for the core funding of this research.

[1] Wiley W. C., McLaren I. H. (1955). *Rev. Sci. Instrum.*, *26*, 1150–1157.
[2] Eppink A. T. J. B., Parker D. H. (1997). *Rev. Sci. Instrum.*, *68*, 3477–3484.
[3] Ershov K. S., Kochubei S. A., Baklanov A. V. (2019). *J. Phys. Chem. A*, *123*, 7751–7757.

Investigation of Degenerate Electron Exchange Reactions Involving Short-Lived Radicals by the Time-Resolved CIDNP Method

✉ **Maksim P. Geniman**

International Tomography Center SB RAS
Novosibirsk, Russia

✉ m.geniman@g.nsu.ru

It is well known that oxidative damage to DNA, usually through structural changes in nucleotides and chain breaks, leads to mutations, cancer and other diseases. Guanine (G) has the lowest ionization potential among the DNA bases, so most oxidants attack G with the formation of the cation radical $G^{+\bullet}$; the oxidative damage of other bases can also migrate to guanine. Guanine radicals can be reduced in the electron transfer reaction with amino acids tyrosine and tryptophan. Depending on the pH value of the solution, the guanine radical exists in different forms, so the rate of its recovery depends on pH.

According to the Marcus theory, the activation energy E_a of the electron transfer reaction is expressed in terms of the difference free energy of the initial and final states $\Delta G°$ and the reorganization energy λ—a parameter that takes into account difference in the solvation energies of the reactants and the transition state and change in the geometry of the reactants when they are converted into products. For a degenerate electron exchange, when the donor and acceptor differ by only one electron, $\Delta G° = 0$ and $E_a = \lambda/4$. The Marcus cross-relation is used to estimate the rate constant of electron transfer reaction from the rate constants of the corresponding degenerate exchange reactions. Therefore, it is interesting to study the reactions of degenerate exchange. The time-resolved CIDNP method can provide information about degenerate exchange reactions involving short-lived radicals. In the temperature range of 8 to 65 °C, the degenerate electron exchange reactions of the guanosine-5'-monophosphate cation $GMPH^+$ with the dication radical $GMPH^{++\bullet}$ at pH = 1.3, of the guanosine-5'-monophosphate anion $GMP(\text{-}H)^-$ with the neutral radical $GMP(\text{-}H)^\bullet$ at pH = 11.3, of the N-acetyl tyrosine anion $N\text{-}AcTyrO^-$ with a neutral radical $N\text{-}AcTyrO^\bullet$ at pH = 11.7, and of the tyrosine anion $TyrO^-$ with a neutral radical $TyrO^\bullet$ at pH = 11.7 were studied. In all cases, the radicals were formed in the reaction of quenching triplet 2,2'-dipyridyl. The rate constant of the degenerate exchange at each temperature was determined in each system. The reorganization energies were calculated using the Arrhenius equation. The rate constants of the reductive electron-transfer reactions for pairs $GMP(\text{-}H)^\bullet/TyrO^-$ and $GMP(\text{-}H)^\bullet/N\text{-}AcTyrO^-$ were found using Marcus cross-relation, the calculated values are higher than the experimental ones.

The rate of nuclear paramagnetic relaxation was found for the 3,5 and β-protons $TyrO^\bullet$ and $N\text{-}AcTyrO^\bullet$, the 8-proton $GMPH^{++\bullet}$ and $GMP(\text{-}H)^\bullet$, the 3,4-protons $DPH^\bullet$ at each temperature. The relaxation rates of the 8-proton in $GMPH^{++\bullet}$ and $GMP(\text{-}H)^\bullet$ coincide over the entire temperature range. In all cases, the dependences of the rate of nuclear paramagnetic relaxation on temperature are described by the Arrhenius dependence.

Properties of Newly Synthesized Sterically Shielded Nitroxides as the Potential Spin Probes in Biological Researches

✉ **Yuriy I. Glazachev**[1], **Andrey I. Taratayko**[2], **Denis A. Morozov**[2],
Irina Zurko[2], **Yuilia F. Polienko**[2], **Igor A. Kirilyuk**[2]

[1]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2]Vorozhtsov Institute of Organic Chemistry SB RAS
Novosibirsk, Russia;

✉ glaza@kinetics.nsc.ru

Nitroxides are a broad family of stable free radicals with one unpaired electron localized on the unbonding orbital of the N–O group. These radicals have found broad application in various fields of science and technology. The broad majority of commonly used nitroxides have a cyclic structure with four methyl substituents adjacent to the N–O group. Recently, nitroxides with methyl groups replaced with bulkier alkyl substituents have attracted much attention. These so-called sterically shielded nitroxides demonstrated much higher stability against chemical reduction to diamagnetic compounds with components of biological systems than their tetramethyl analogs did. The advantage of these reduction-resistant radicals over conventional tetramethyl-substituted nitroxides is especially obvious when they are used for the EPR measurements inside living cells, or *in vivo* for functional imaging using the MRI or EPRI techniques.

We presented a series of newly synthesized nitroxides with a variety of such substituents. The observed reduction rate constants in ascorbic acid/glutathione system varied from 10^{-2} up to $10^{-5} M^{-1} s^{-1}$. The partition coefficient of nitroxide in water/octanol system varied from few units up to few thousands. The lineshape of the EPR spectra was also analyzed, since it is important in the EPRI method. As a result, we obtained the series of spin probes that can be used for corresponding research. Additionally, it allowed us to propose the future radical synthesis toward desired nitroxide properties.

Acknowledgements: the work was financially supported by the Russian Scientific Foundation (grant No. 19-13-00235) and the Russian Foundation for Basic Research (No. 18-53-76003 ЭРА_а).

Photochemistry of Sodium Thiosulfate in Aqueous Solutions: a Lot of Radicals

✉ **Evgeni M. Glebov**[1,2], **Ivan P. Pozdnyakov**[1,2],
Vjacheslav P. Grivin[1], **Victor F. Plyusnin**[1,2], **Nikolai B. Egorov**[3]

[1]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2]*Novosibirsk State University*
Novosibirsk, Russia
[3]*Tomsk Polytechnic University*
Tomsk, Russia

✉ glebov@kinetics.nsc.ru

Sodium thiosulfate $Na_2S_2O_3$, often called *hypo* (from "hyposulfite"), is widely used in various industries. Photochemical applications of thiosulfate are infrequent, but quite important. It is known to be of interest: 1) for systems that photochemically split hydrogen sulfide into hydrogen and sulfur, 2) as an additive for photovoltaic solar cells, and 3) in photochemical synthesis of thioperrhenates. Literature on the thiosulfate photochemistry is old and discrepant.

A mechanistic study of sodium thiosulfate dianion ($S_2O_3^{2-}$) photolysis in aqueous solutions was performed using stationary and nanosecond laser flash photolysis [1]. $S_2O_3^{2-}$ photochemistry was found to be oxygen-dependent. Quantum yield of $S_2O_3^{2-}$ disappearance was measured; it was found to depend on the irradiation wavelength and presence of dissolved oxygen in solutions. The photochemical properties were explained by means of model containing two primary reactions, namely photoionization and photodissociation of thiosulfate to $S^{\bullet-}$ and $SO_3^{\bullet-}$ radical anions. In the presence of dissolved oxygen, we were forced to propose the formation of a weak complex formed by thiosulfate and dioxygen, $[S_2O_3^{2-}\ldots O_2]$. The photoexcitation of this complex directly yields $S_2O_3^{\bullet-}$ and $O_2^{\bullet-}$. Kinetic behavior of intermediate absorption in laser flash photolysis experiments was found to be rather complicated because of the presence of an aquated electron and several sulfur-containing radical anions. In oxygen-free solutions these radicals are $S_2O_3^{\bullet-}$, ${}^{\bullet}S_4O_6^{3-}$, $S^{\bullet-}$, and $SO_3^{\bullet-}$. In the presence of dissolved oxygen $SO_2^{\bullet-}$, $SO_5^{\bullet-}$ and $S_2O_5^{\bullet-}$ radicals as well as superoxide anion radical should be added to explain the kinetics of intermediate absorption. The existence of the $S_2O_5^{\bullet-}$ radical anion was proposed for the first time. Several rate constants of these radicals' reactions were measured.

Acknowledgements: the work was supported by the Russian Foundation of Basic Research (grants No. 20-33-90217, 20-03-00708).

[1] Glebov E. M., Pozdnyakov I. P., Grivin V. P., Plyusnin V. F., Isaeva E. A., Egorov N. B. (2022). *J. Photochem. Photobiol. A: Chem.*, *427*, 113818.

Catalytic Processing of Coalbed Methane into Useful Chemical Products to Reduce the Carbon Footprint and Anthropogenic Impact on the Climate

✉ **Zinfer R. Ismagilov**[1,2], **Ekaterina V. Matus**[2], **Ilyas Z. Ismagilov**[2]

[1] *The Federal Research Center of Coal and Coal Chemistry of SB RAS*
Kemerovo, Russia
[2] *Boreskov Institute of Catalysis SB RAS*
Novosibirsk, Russia

✉ zinfer1@mail.ru

Methane emissions into the atmosphere lead to an increase in the greenhouse effect and the destruction of the Earth’s ozone layer. As a greenhouse gas, methane has a high impact on the climate change. Its direct radiation effect is 26 times higher than that of carbon dioxide.

A huge reserve of coalbed methane in the Kuznetsk Basin (~13 trln m3) has high potential for impacting the global warming, besides the commercial value.

In this paper we present a review of scientific foundations and technologies for the integrated processing of methane into useful chemical products and our latest results in catalytic approach for coalbed methane processing. We consider the catalytic tri-reforming of methane — a process that combines steam reforming, dry reforming and partial oxidation of methane — the most attractive for processing of methane consisting a variable composition of methane-air mixture. The thermodynamic analysis of the tri-reforming of (CH_4 + O_2 + CO_2 + H_2O) and its constituent reactions — steam reforming (CH_4 + H_2O), dry reforming (CH_4 + CO_2), partial oxidation (CH_4 + O_2), autothermal reforming (CH_4 + O_2 + H_2O), and steam carbon dioxide reforming (CH_4 + CO_2 + H_2O) — are presented. The equilibrium compositions of the conversion products of various types of coalbed methane in tri-reforming are revealed, depending on their concentration characteristics, for selection and optimization of the reaction conditions.

Catalysts for the processing of coalbed methane are synthesized and for the first time systematically studied by a complex of the *ex situ* and *in situ* physical and chemical methods, the regularities of their formation and genesis of the active component have been revealed.

A number of special methods for designing the catalytic systems are under development, including the use of the effects of mutual enhancement of the action of metals and modification of the composition of the carrier. Our approaches for elucidation of the relationship between the conditions of promotion (composition, content, method of introducing the promoting additive) and the physicochemical characteristics (dispersion, morphology, phase composition, etc.) of the catalyst are presented.

Acknowledgements: the research was supported financially by the Russian Science Foundation (project No. 22-13-20040, https://rscf.ru/project/22-13-20040/) and by the Regional Government of the Kemerovo Region — Kuzbass.

Charge Transfer Symmetry Breaking in Excited Quadrupolar Molecules in Protic Solvents

✉ **Anatoly I. Ivanov**

Volgograd State University
Volgograd, Russia

✉ anatoly.ivanov@volsu.ru

A threshold-type dependence of the fluorescence quenching of a centro-symmetric acridine-dione in the mixtures of protic (methanol) and aprotic (DMF) solvents is analyzed theoretically. The following assumptions are made: 1) fluorescence quenching occurs due to the formation of an H-bond between the fluorophore and the protic solvent, and 2) only sufficiently long clusters of methanol molecules can form strong complexes with the fluorophore and cause an excited state charge transfer symmetry breaking and a strong fluorescence quenching. The assumptions provide for explaining the observed absence of quenching at methanol concentrations below 9 M. The developed theory provides both quantitative description for the concentration dependence of the fluorescence yield and non-exponential fluorescence decay kinetics measured experimentally [1]. Since charge transfer dissymmetry degree is sensitive to the interaction energy between fluorophore and the clusters, this opens up new possibilities for studying the details of H-bond clustering in protic solvents.

A model of H-bond effect on charge transfer symmetry breaking in excited quadrupolar fluorophores is proposed. Such fluorophore has two symmetrically arranged H-bond acceptors. The effect of H-bonding is described in terms of two quantities: 1) free energy of H-bond formation by an excited symmetric fluorophore with a protic solvent, and 2) a parameter determining the susceptibility of the H-bond strength to the charge of the H-bond acceptor. The model bases on the fact that an increase in fluorophore dissymmetry makes one acceptor more negative and the other less negative. This results in strengthening of the H-bond on one branch and weakening on the other. An analytical solution of the mathematical model is obtained. Regardless of the strength of the H-bond, the effect of the H-bonding on the symmetry breaking degree is shown to be small, as long as the free energy of formation of the weaker H-bond is negative. A strong effect is expected only if this free energy becomes positive, that is, when the H-bond is formed on only one arm. An unexpected result of weakening of the dissymmetry degree caused by the strengthening of the H-bond is predicted and discussed. An approach for quantitative determination of the susceptibility of the H-bond strength to the charge of the H-bond acceptor is proposed.

Acknowledgements: the study was performed within the grant of the Russian Science Foundation (grant No. 22-13-00180).

[1] Bondarev S. L., Raichenok T. F., Tikhomirov S. A., Kozlov N. G., Mikhailova T. V., Ivanov A. I. (2021). *J. Phys. Chem. B*, *125*, 8117–8124.

In Situ XPS and PM IRRAS Study of Methanol and Ethanol Oxidation Over Pt(111)

✉ **Vasily V. Kaichev, Alexandra V. Selivanova, Andrey A. Saraev**

Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia

✉ vvk@catalysis.ru

The oxidation of methanol on a Pt(111) single crystal was studied using X-ray photoelectron spectroscopy (XPS) and polarization-modulation infrared reflection absorption spectroscopy (PM IRRAS). Both methods make it possible to study a catalyst directly under reaction conditions. XPS provides for determination of the chemical state of a catalyst and the presence of reaction intermediates on its surface, including adsorbed carbon atoms [1]. A distinctive feature of PM-IRRAS is its ability to simultaneously record vibrational spectra of species adsorbed on the catalyst surface and molecules in the gas phase over the catalyst [2; 3]. The combined use of these methods allowed us to obtain detailed information on the mechanism of the catalytic reaction under study.

The experiments were performed at a temperature range between 300 and 600 K. It was shown that the oxidation of methanol starts at approximately 350 K, and methanol is oxidized mainly to CO_2 and methyl formate. CO was not found among gas-phase products within the whole temperature range. A small amount of formaldehyde was detected in the gas phase only at 350–450 K. On the platinum surface, methyl formate, CO, formates, carbonates, and carbon atoms were detected under the reaction conditions. Their concentrations depended on the reaction temperature and the methanol/oxygen molar ratio. Formates were detected only at 300 K, which indicates their low thermal stability. Both CO and formate are the key intermediates in the total oxidation of methanol, which can proceed via two different pathways: a CO-based route and a non-CO-included route. Carbonates are formed from formates and demonstrate extremely high thermal stability. This leads us to the supposal that not only CO, but also carbonates can poison the platinum surface and prevent the oxidation of methanol.

Similar picture was observed in the study of ethanol oxidation. The main reaction products were CO, CO_2, acetaldehyde, and acetic acid. The yield of CO depends on the concentration of oxygen in the gas phase. The overall mechanisms of the oxidation of methanol and ethanol on platinum are discussed.

[1] Bukhtiyarov V. I., Kaichev V. V., Prosvirin I. P.(2005). *Topics in Catalysis*, *32*, 3–15.

[2] Rupprechter G. (2007). *Advances in Catalysis*, 51, 133–263.

[3] Selivanova A. V., Kremneva A. M., Saraev A. A., Kaichev V. V., Bukhtiyarov V. I. (2021). *Applied Surface Science*, *535*, 147717.

Study of Polymerization of Fluorine Monomer (1-(2,3,4,5,6-Pentafluorophenyl)prop-2-en-1-one)

✉ **Polina M. Kaletina**[1,2], **Andrey S. Vinogradov**[1],
Inna K. Shundrina[1], **Tatyana V. Mezhenkova**[1], **Elena G. Bagryanskaya**[1]

[1] *Vorozhtsov Novosibirsk Institute of Organic Chemistry of SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ kaletina@nioch.nsc.ru

Polymers based on vinyl ketones are highly photodegradable. Such polymers often find application as packaging, films or imaging and sensing materials. Fluorine polymers are known for their properties. These include thermal stability, chemical inertness and low water absorption. A new monomer (1-(2,3,4,5,6-pentafluorophenyl)prop-2-en-1-one) was synthesized in the laboratory of halogen compounds of the NIOCh SB RAS. On the one hand, it is a vinyl ketone, and on the other hand, it has a fluorinated aromatic ring.

Typically, both classes of polymers (vinyl ketones and fluoropolymers) are synthesized by radical polymerization. During polymerization, it was found that a side reaction occurs in the system. This is a dimerization process known for this type of compounds. Nevertheless, the polymer was obtained and the conditions for purification from the byproduct were selected.

RAFT polymerization is used to expand the application or to modify the resulting polymers based on vinyl ketones. This method of living controlled polymerization has proven itself well in the polymerization of vinyl ketones. For example, when using ATRP polymerization, side coordination occurs between the monomer and the metal catalyst. Therefore, a number of the RAFT polymerization experiments were carried out on 1-(2,3,4,5,6-pentafluorophenyl)prop-2-en-1-one. It has been shown that the resulting polymer has lower dispersion compared to conventional radical polymerization. However, part of the monomer turns into a dimer, because this reaction occurs under heating.

One way to solve this problem is to use photoinduced electron transfer—a reversible addition-fragmentation chain transfer polymerization (PET-RAFT). This method does not require thermal initiator therefore polymerization can be carried out at room temperature with much less dimer formation.

Acknowledgements: this study was supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 14.W03.31.0034).

[1] Cheng C. et al. (2007). *Journal of the American Chemical Society*, *33*, 10086–10087.
[2] Lee I. H. et al. *Polymer Chemistry*, *21*, 3351–3356.

Nanostructured Germanium Formed by Ion Implantation Method as an Anode for lithium-Ion Batteries

✉ **Sergey M. Khantimerov, Tatiana P. Gavrilova, Vladimir I. Nuzhdin,**
Valerii F. Valeev, Alexey M. Rogov, Andrey L. Stepanov

Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS
Kazan, Russia

✉ khantim@mail.ru

Further wide commercialization of the lithium-ion batteries (LIB) technology is impossible without the development of effective electrode systems and methods for their quick recharge. Currently, the possibility to use germanium (Ge) as a LIB anode is intensively studied due to theoretically much more advanced characteristics of Ge compared to carbon [1]. However, the internal stresses arising in such materials during cycling lead to the destruction of electrodes. To solve this problem, nanostructured germanium anodes of various configurations can be used.

Here we present the investigation of nanostructured germanium that consists of intertwining nanowires with a diameter of ~30 nm formed applying the method of low-energy high-dose implantation of a single-crystal germanium substrate with silver ions [2]. Electrochemical properties study of the resulting material during its lithiation/delithiation process demonstrates high reversible capacity (1,080 mAh/g) and its retention of about 80 % after 1,000 cycles. The possible use of the obtained material as the anode of a lithium-ion battery is discussed.

Acknowledgements: this work is supported by the Russian Science Foundation (grant No. 19-79-10216).

[1] Gavrilin I. M., Kudryashova Yu. O. et al. (2021). *Journal of Electroanalytical Chemistry, 888*, 115209.

[2] Stepanov A. L., Khantimerov S. M. et al. (2021). *Vacuum, 194*, 110552.

Spin Exchange in Biradicals as a Model to Study Long-Range Interactions

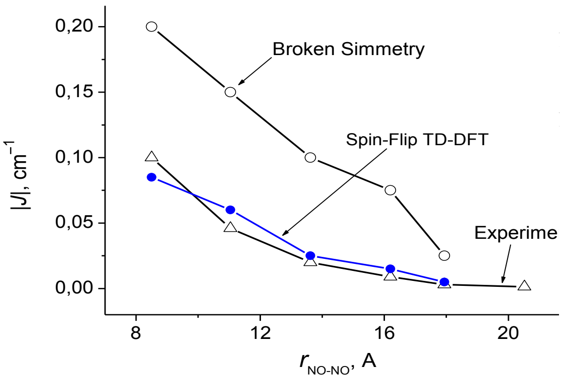
✉ **Alexander I. Kokorin**

Semenov Federal Research Center for Chemical Physics RAS
Moscow, Russia
Plekhanov Russian University of Economics
Moscow, Russia

✉ alex-kokorin@yandex.ru

About 60 years ago, V. V. Voevodsky announced his idea concerning the importance of energetically weak long-range interactions on the pathway and mechanism of chemical reactions. Among the first scientists who started experimental studies in this area were his PhD students — Yury Molin and Kirill Zamaraev. Among other tested physical and chemical processes, the electron spin exchange (eSE), in particular, intramolecular spin exchange (IMSE) in stable biradicals was chosen as a promising object of studies. Indeed, IMSE in biradicals is rather weak, the EPR technique provides for quantitative measurements of the exchange integral value $|J|$ from 2 to ca. 300 G (6–900 MGz), and a numerous number of the synthesized nitroxyde biradicals of different types and structures permit to vary all necessary parameters and features.

In practice, all the investigated biradicals exist in liquid solutions in two or several "effective" conformations k which are characterized by the value of J_k and a life-time τ_k of this conformation [1]. Between these conformers, there are transitions which are well-described by the theory developed by V. N. Parmon and G. M. Zhidomirov [1; 2]. The EPR study of biradicals allowed us to quantitatively characterize the intramolecular dynamics of the system and the efficiency of interaction between long-range linked unpaired electrons in nitroxide biradicals. One example of the experimental correlations is shown in Figure below. Some actual properties of nitroxide biradicals were published in [3; 4] and will be discussed in the report.



Electron spin exchange integral value $|J|$ as a function of the distance $r_{\text{NO-NO}}$ between the unpaired electrons in biradicals *X-Y*: experimental and DFT calculated

Acknowledgements: the research was supported by the FR Program of the Russian Federation No. 122040500068-0.

[1] Parmon V. N., Kokorin A. I., Zhidomirov G. M. (1980). *Stable biradicals*. Nauka, Moscow.

[2] Parmon V. N., Zhidomirov G. M. (1974). *Molec. Phys., 27*, 367–375.

[3] Kokorin A. I. (2004). *Appl. Magn. Reson., 26*, 253–274.

[4] Kokorin A. I. (2020). In: *Nitroxides. Brief History, Fundamentals, and Recent Developments* by G. I. Likhtenstein, Ch. 5, pp. 93–118. Springer, New York.

Chemistry of Nuclear Spin Isomers of Symmetric Molecules for New Scientific and Practical Applications

✉ **Igor V. Koptyug**

International Tomography Center SB RAS
Novosibirsk, Russia

✉ koptyug@tomo.nsc.ru

Unlike other types of molecular isomerism, nuclear spin isomerism is much less studied. The existence of the nuclear spin isomers of molecules (NSIM) has a quantum nature and is associated with the Pauli principle, which imposes strict restrictions on the total wave function of symmetric molecules. The most widely known nuclear spin isomers are those of the H_2 molecule, namely orthohydrogen (o-H_2) and parahydrogen (p-H_2), for which the total nuclear spin of two hydrogen atoms is equal to one ($I = 1$) or zero ($I = 0$), respectively. At the same time, other symmetric molecules also have two or more NSIM.

The unique properties of NSIM are of major interest in a broad range of scientific disciplines and practical applications. One of the most advanced areas of activity is the utilization of p-H_2 to achieve a dramatic NMR signal enhancement in the context of a range of the so-called nuclear spin hyperpolarization techniques. Unfortunately, efficient NSIM enrichment procedures currently only exist for H_2 and D_2. This largely hinders the progress in extending the research to NSIM of other molecules. While several techniques for enrichment of NSIM of polyatomic molecules have been demonstrated, none of them is able to provide the quantities of enriched gases comparable to those available for H_2.

This presentation demonstrates the wide range of potential applications of NSIM, along with the results of the recent efforts to develop novel NSIM enrichment protocols. The parahydrogen-based NMR signal enhancement is very useful in the mechanistic studies of catalytic reactions, which now also covers heterogeneous hydrogenations catalyzed by a variety of types of solid catalysts, including supported metals, immobilized metal complexes, single-metal-atom and intermetallic catalysts, and more [1; 2]. Hyperpolarization is also highly useful in the advanced studies of chemical reactions [3] and operating catalytic reactors [1] by the NMR-based spectroscopic and imaging (MRI) techniques. Parahydrogen is widely explored to produce hyperpolarized biocompatible substances for advanced biomedical imaging, including natural metabolites and drugs. The ortho-to-para NSIM ratio of gaseous molecules provides a glimpse at the past of the Universe in terms of the conditions of the formation of space objects several billions of years ago. The field is developing rapidly, and novel possibilities continue to emerge [4].

[1] Pokochueva E. V. et al. (2021). *ChemPhysChem*, *22*, 1421–1440.
[2] Skovpin I. V., et al. (2022). *Catal. Sci. Technol.*, DOI: 10.1039/D1CY02258J.
[3] Burueva D. B., Eills J. et al. (2020). *Angew. Chem. Int. Ed.*, *59*, 17026–17032.
[4] Them K., Ellermann F. et al. (2021). *J. Am. Chem. Soc., 143*, 13694–13700.

Effect of Cu(I) Additive on Sorption by Imidazole Based Ionic Liquids Studied by *In Situ* ATR-FTIR Spectroscopy

✉ **Evgeny P. Kovalev, Anton S. Shalygin, Oleg N. Martyanov**

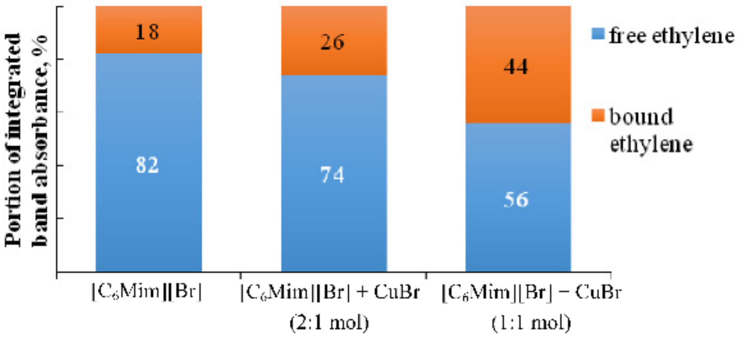
Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia

✉ kovalev-e@catalysis.ru

Ionic liquids (ILs) are low temperature molten salts which have a number of unique physical and chemical properties. ILs are assumed to be applied in the selective separation of ethane and ethylene [1]. In order to improve the separation efficiency, additives of transition metals could be used, e.g., Cu (I) and Ag (I) capable of forming π-complexes with alkenes [2].

FTIR spectroscopy is a convenient method that allows one to investigate the mechanisms of interaction between the sorbed gas molecules and IL, which remains an important aspect for designing new materials [3].

During the study of ethylene sorption by [C_6Mim][Hal] ILs (Hal = Cl, Br, I) with additions of Cu(I) halides, it was found that as the content of the Cu(I) in the IL increases, a change of the band shape of ethylene out-of-plane bending vibrations is observed, with the proportion of interacting ethylene enhancing (see Fig.). The alteration is likely to occur in the contributions of various mechanisms of ethylene sorption.



Effect of CuBr on ethylene sorption by [C6Mim][Br]. Temperature is 25 °C, ethylene pressure is 20 atm

Acknowledgements: this work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project No. AAAA-A21-121011390053-4).

[1] Moura L., Santini C. C., Costa Gomes M. F. (2016). *Oil Gas Sci. Technol.—Rev. d'IFP Energies Nouv., 71*(23).

[2] Safarik D. J., Eldridge R. B. (1998). *Ind. Eng. Chem. Res., 37*, 2571–2581.

[3] Kovalev E. P., Shalygin A. S., Shubin A. A., Kozhevnikov I. V., Prikhod'ko S. A., Adonin N. Y., Kazarian S. G., Martyanov O. N. (2022). *J. Mol. Liq., 348*, 118082.

Negative Apparent Activation Energies, V-Shaped Temperature Dependences, and Pressure Dependence of “Simple Metathesis Reactions” with “Negative Barriers”

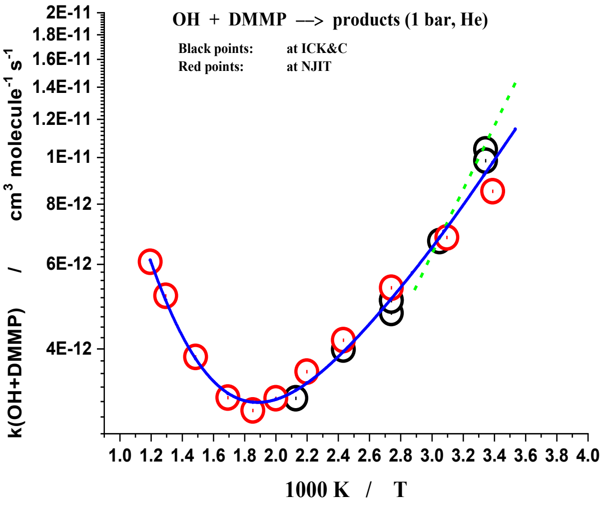
Xiaokai Zhang[1], **Pavel V. Koshlyakov**[2], **Eugeniy N. Chesnokov**[2], ✉ **Lev N. Krasnoperov**[1,2]

[1] *New Jersey Institute of Technology*
Newark, USA
[2] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia

✉ lev.n.krasnoperov@njit.edu

Elementary chemical reactions which exhibit “negative apparent activation energies” (i.e., the reactions which slow down with temperature) are discussed. Discovered early negative apparent activation energies in the reactions of small hydrocarbon free radicals with hydrogen halides (R + HX, R = CH_3, C_2H_5, C_3H_7, etc., X = I, Br, Cl) stirred momentous controversy in the kinetics and thermodynamics’ community in view of the importance as an individual issue of fundamental chemical kinetics and, particularly, due to the tremendous impact on the determination of the C-H bond strengths in hydrocarbons [1].

These observations were explained based on the concept of reactions having a “negative” or “submerged” barrier, i.e., reactions having “transition states” with the ground state lying below the ground state of the reactants [2]. Beyond explaining the negative temperature dependences of such reactions, the theory also predicts V-shaped temperature dependences and bath gas pressure dependences at high pressures.



Recently, we discovered a new class of reactions which exhibit all features predicted for the reactions with negative barriers [3]. These are reactions of hydroxyl radicals with organophosphorus compounds. Three such reactions were experimentally studied, reactions of OH with trimethyl phosphate (TMP), dimethyl methyl phosphonate (DMMP), and trimethyl phosphite (TMPi). In all cases, V-shaped temperature dependences were observed (negative at low and positive at elevated temperatures). An example (reaction OH + DMMP) is shown in Figure. For this reaction, the bath gas pressure dependence was also observed (1–30 bar, He).

[1] Gutman D. (1990). *Acc. Chem. Res.*, *23*(11), 375–380.
[2] Krasnoperov L. N. et al. (2006). *J. Phys. Chem. A*, *110*(9), 3110–3120.
[3] Zhang X. et al. (2022). *Molecules, 27*(7), 2301; (2021). *RSC Advances*, *11*(23), 14121–14131.

Spectroscopic Evidence for the Substantial Catalyst Deactivation under "Ligand-Free" Suzuki-Miyaura Reaction with Aryl Chlorides

✉ **Anna A. Kurokhtina**, **Elizaveta V. Larina, Nadezhda A. Lagoda, Alexander F. Schmidt**

Irkutsk State University
Irkutsk, Russia

✉ kurokhtina@chem.isu.ru

Operando kinetic study combining kinetic control of the reaction proceeding with simultaneous spectroscopic monitoring of the concentration of a catalyst form during a catalytic reaction is an extremely helpful tool for elucidation of the role of this form in catalysis. We applied this approach to investigate catalyst transformations in thoroughly studied Suzuki-Miyaura reaction, where the most challenging aryl chlorides were used as substrates under so-called ligand-free conditions, i.e., when no phosphines, amines, carbenes or any other strong organic ligands are added. The combination of gas chromatography for kinetic control of the reaction product accumulation and UV/Vis-spectroscopy for measurements of the concentration of Pd compounds having the absorbance in this region was applied. Using $Pd(acac)_2$ as the catalyst precursor (absorption maximum at 328 nm) in the reaction with 1,4-dichlorobenzene or chlorobenzene, it was demonstrated that the precursor concentration predictably decreases during the reaction, and no additional well-defined maximum is observed. However, a smooth increase of absorbance at 350–400 nm provided for the proposing formation in the reaction mixture of Pd nanoparticles (PdNPs) with no significant amounts of Pd (II) molecular complexes. The formation of Pd black was observed only when the reaction stopped. Using the method of least squares and proposing that all Pd loaded presents in two spectroscopically fixed forms, i.e., $Pd(acac)_2$ and PdNPs, the set of molar extinction coefficients for proposed PdNP was found. Analyzing the literature data [1], PdNPs with 5 nm diameter were most probably formed under the reaction conditions, and their amount in the reaction solution passed through the maximum during the reaction. By the analysis of the dependencies plotted in various coordination systems, including the rate of product formation and concentrations of the reaction product and Pd species (precursor and PdNPs), it was demonstrated that under the Suzuki-Miyaura reaction PdNPs are an inactive catalyst form. At the same time, the concentration of Pd molecular complexes responsible for the catalytic activity was negligible in comparison with total amount of Pd loaded and was not observed spectroscopically.

Acknowledgements: this work was supported by the Russian Science Foundation (project No. 19-13-00051).

[1] Ershov B. G.., Sukhov N. L., Troitsky D. A. (1994). *Zh. Fiz. Khim.*, *68*, 820–824.

Ligand-to-Metal Charge Transfer Excited States in Organometallics

✉ **Galina V. Loukova**

Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia

✉ gloukova@mail.ru

Organometallic compounds are an important class of materials in many areas of science and technology. Most organometallic compounds dissipate excitation energy very rapidly in a non-radiative fashion, and only a small fraction has excited states with moderate lifetimes from which luminescence can typically occur. One of the key problems in photophysics and photochemistry of organometallic complexes is the assignment and characterization of their higher-lying and lower-lying excited states. Most organometallic complexes possess metals in low oxidation states; so far, in the UV-vis spectrum, low-energy metal-to-ligand charge transfer (MLCT) transitions dominate.

Ligand-to-metal charge transfer (LMCT) excited states play an important role in photophysics and photochemistry of metal complexes; however, knowledge of photophysical properties of complexes having pure LMCT excited states, unlike MLCT, metal-centered, ligand-centered or other excited states, accounts almost silent observations. LMCT excited states of organometallic compounds are the extremely rare and much less studied type of electronically excited states. [1–5] Perhaps, only early-transition metal complexes in high oxidation states exhibit readily identifiable LMCT excited states. The examples to be discussed illustrate a rich variety of photophysical and photochemical behavior exhibited by organometallic species in their pure LMCT excited states. The principle emphasis is given to the investigations on solvatochromism, the relation between LMCT transition energies and differences in oxidation and reduction potentials, relation between emission quantum efficiency and lifetime, electron-exchange (Dexter) resonant energy transfer, and photolysis of organometallic compounds in their LMCT excited states.

Acknowledgements: the study was carried out in accordance with the state contract No. 0089-2019-0003 (state No. AAAA-A19-119070790003-7).

[1] Loukova G. V. (2022). In: Springer Handbook of Inorganic Photochemistry, Chpt. 19. Eds. D. Bahnemann, A. O. T. Patrocinio, pp. 465–499. Springer Handbooks.

[2] Loukova G. V., Smirnov V. A. (2000). *Chem. Phys. Lett., 329*, 437–442.

[3] LoukovaG. V., Strelets V. V. (2001). *Collect. Czech. Chem. Commun., 66*, 185–206.

[4] Loukova G. V. (2002). *Chem. Phys. Lett.*, *353*, 244–252.

[5] Loukova G. V., Vasiliev V. P., Milov A. A., Smirnov V. A., Minkin V. I. (2016). *J. Photochem. Photobiol. A: Chem.*, *327*, 6–14.

LMCT States of Sophisticated Group 4 Metallocene Dicarboranyls

✉ **Galina V. Loukova**[1], **Alexey A. Milov**[2]

[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia
[2] *Southern Scientific Center RAS*
Rostov-on-Don, Russia

✉ gloukova@mail.ru

Ligand-to-metal charge transfer (LMCT) excited states are the rarest and least studied. We have conducted a lasting study [1–3] on molecular photonics of group 4 bent metallocenes, having rare ^{3}LMCT excited states. Some results are given below.

Optical properties	d^0 metallocenes						
	Cp_2MMe_2	**Cp_2MCl_2**			**$M(CpCMe_2CB_{10}H_{10}C)_2$**		
		Ti	**Zr**	**Hf**	**Ti**	**Zr**	**Hf**
absorption LMCT: $S_0 \to S_1$	**Me → M**	**Cp, Cl → M**			**Cp → M**		
λ_{max} /nm		517	335	307	466	334	316
luminescence: $T_1 \to S_0$	**no** ($T_1 \rightsquigarrow S_0$)						
λ_{00} /nm		595	408	377	525.5	386	373
λ_{max} /nm		649	459	424.5	602	441	419

Note: Cp—cyclopentadienyl.

We have obtained and systematically analyzed a large array of data for calculating the geometry of a d^0-metallocene using the example of structurally complex titanocene dicarboranyl Ti(η^5:η^1-Cp-$CMe_2CB_{10}H_{10}C)_2$ and demonstrated good agreement of the most of the calculated structural data with the available X-ray data.

Photophysical and structural characteristics of the d^0 metallocenes enantiomers are simulated for the first time using the example of a triad of coordination compounds of group 4 M(η^5:η^1-Cp-$CMe_2CB_{10}H_{10}C)_2$ (Ti, Zr, Hf). Using Hf(η^5:η^1-$CpCMe_2CB_{10}H_{10}C)_2$ as an example, the changes in the structure and the dipole moment of the metal complex at the transition from the ground state to the ^{1}LMCT state are evaluated for the first time. It has been found that one-step enantiomerization between opposite M(η^5:η^1-$CpCMe_2CB_{10}H_{10}C)_2$ enantiomers does not occur under thermal conditions.

Acknowledgements: the research was financially supported by the State Contract 0089-2019-0003 (reg. No. AAAA-A19-119070790003-7) and the SSC RAS state contract 01201354239.

---

[1] Loukova G. V. (2022). In *Springer Handbook of Inorganic Photochemistry*, Chpt. 19; Eds. D. Bahnemann, A. O. T. Patrocinio, pp. 465–499. Springer Handbooks.

[2] Loukova G. V. (2010). In *Organometallic Compounds: Preparation, Structure and Properties*; Ed. H. F. Chin, pp. 159–196. Nova Sci. Publ., N. Y.

[3] Loukova G. V.(2002). *Chem. Phys. Lett.*, *353*, 244–252.

[4] Loukova G. V., Milov A. A., Vasiliev V. P. (2018). *Russ. Chem. Bull., Int. Ed.*, *67*, 2323–2325.

Ways of Mechanical Energy in Cellulose: A Simple Study

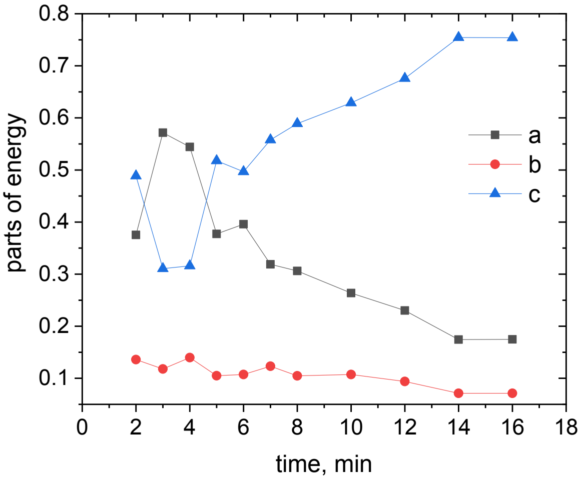
Aleksey Bychkov[1], ✉ **Anna Matveeva**[1,2], **Vladimir Bukhtoyarov**[1],
Ekaterina Podgorbunskikh[1], **Oleg I. Lomovsky**[1]

[1] *Institute of Solid State Chemistry and Mechanochemistry SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ matveeva@solid.nsc.ru

Mechanical treatment can be applied in different tasks: size reduction, destroying of complex material microstructure or specific impact at the level of individual molecule. All these processes often occur simultaneously, but the ratio between them can be different. So, if we want to optimize this technology for mechanical treatment of plant raw materials, we must understand which part of the applied energy goes at a desired channel. The construction of such description can be very difficult, and thus it is an unpopular research theme.

Here we propose a simple approach to the estimation of mechanical energy expenditure ways at processing of alpha-cellulose. Our approach is based on two main assumptions: 1) part of the total applied energy spent on the material destruction does not change during the experiment; 2) destruction goes at three ways, as shown in Figure: size reduction (a), amorphization of crystal structure (b), and depolymerization (c).



We found that the main processes are size reduction and depolymerization, and they have an opposite tendency: the size reduction part decreased in time, but the depolymerization part increased. This is an intuitively clear result, what proved the viability of our approach.

Acknowledgements: the study was carried out with financial support of the Russian Science Foundation (projects No. 19-73-10074, 21-13-00046).

[1] Bychkov A. L., Matveeva A. G. (2022). *Chemical Education.* (in press)

Thermal Stability of Dinitrotriazolopyridines and Dinitrobenzotriazoles: Interplay of Thermal Analysis and Computational Chemistry

✉ **Igor N. Melnikov**[1], **Vitaly G. Kiselev**[1–3], **Igor L. Dalinger**[4],
Nikita V. Muravyev[1], **Alla N. Pivkina**[1]

[1]Semenov Federal Research Center for Chemical Physics RAS
Moscow, Russia
[2]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[3]Novosibirsk State University
Novosibirsk, Russia
[4]Zelinsky Institute of Organic Chemistry RAS
Moscow, Russia

✉ igor.n.melnikov@yandex.ru

Understanding the thermal stability of novel hazardous materials is of great importance for storage and safety issues. The objects of present study are recently synthesized heterocyclic derivatives of pyridine and benzene, viz., 6,8-dinitrotriazolopyridine (DTP), 2-amino-6,8-dinitrotriazolopyridine (ADTP) [1], 5,7-dinitrobenzotriazole (DBT), and 4-amino-5,7-dinitrobenzotriazole (ADBT) [2]. These compounds exhibit high decomposition onset temperatures (> 290°C) [1; 2]; however, the nature of their thermal stability is poorly studied. Therefore, we investigated the mechanism and kinetics of thermal decomposition for the title compounds. Thermal stability of DTP and ADTP in the condensed phase was studied using differential scanning calorimetry at elevated pressures (2.0 MPa). The thermokinetic analysis was performed using the isoconversional and model-fitting analysis. The thermolysis of DTP occurs in the melt with the kinetic parameters $E_a = 135.1 \pm 0.4$ kJ/mol and $\log(A, \mathrm{s}^{-1}) = 10.37 \pm 0.03$. Thermal decomposition of ADTP as low (0.13–2 K/min) and high (5–20 K/min) heating rates is described by very high kinetic parameters. The obtained results indicate that thermolysis of ADTP is complicated by parallel physical processes—most importantly, melting. The experimental kinetics was complemented by theoretical mechanistic insights obtained at a modern reliable level of theory (DLPNO-CCSD(T)/aVQZ). In all cases, the nitro-nitrite rearrangement and C-NO_2 bond cleavage are the most important initial decomposition channels. The nitro-nitrite rearrangement is an energetically preferred reaction with the activation energy ~240 kJ/mol (DTP, ADTP) and ~270 kJ/mol (DBT, ADBT). However, due to higher preexponential factors, the C-NO_2 bond cleavage is a dominant decomposition reaction at high temperatures (> 230 °C) with the activation barriers ~280 kJ/mol (DTP, ADTP) and 300 kJ/mol (DBT, ADBT).

Acknowledgements: this work was supported by the Ministry of Science and Higher Education of the Russian Federation (project No. 075-15-2020-803 to ZIOC RAS).

[1] Starosotnikov A. M. et al. (2019). *ChemistrySelect, 4*, 1510–1515.
[2] Ehlers D. et al. (2015). *Chem. Eur. J., 21*, 16073–16082.

Photochemical Processes of Nickel(II) Xanthate Complex in CCl_4

✉ **Alexander V. Mikheylis**[1], **Vyacheslav P. Grivin**[1], **Victor F. Plyusnin**[1,2]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ mikheylis@kinetics.nsc.ru

Many transition metal dithiolate complexes ($M(S_2R)_2$) are known to be photoactive in the presence of electron acceptors such as halocarbons. However, the mechanisms of their phototransformation were studied only by the methods of stationary photolysis and EPR [1]. Based on these data, it was assumed that photolysis proceeds with the formation of free dithiolate radicals ($^{\bullet}S_2R$), which arise when they are detached from the coordination sphere of the excited complex. Using laser flash photolysis, we showed [2–3] that an important detail in the photochemistry of dithiolate complexes is the formation of radical complexes ($M(S_2R)(^{\bullet}S_2R)$). The disappearing of these intermediates can proceed via various channels and is associated with the appearance of more complicated particles: dimers, trimers, and tetramers.

In this paper, we report the results of a study of the photochemistry of the nickel (II) xanthate complex ($Ni(S_2COEt)_2$ = $Ni(xan)_2$) in CCl_4 solutions by using the methods of stationary and laser flash photolysis. The change in the absorption spectrum, the dependence of quantum yields of $Ni(xan)_2$ disappearance on the concentration of CCl_4 in CH_3CN solutions, and the wavelength of the exciting light were determined by the method of stationary photolysis. The mechanism of photochemical reactions has been studied using laser flash photolysis. After a laser pulse (XeCl, 308 nm, 5 ns), broad bands of the radical complex $[ClNi(S_2COEt)(^{\bullet}S_2COEt)]$ appear in spectrum with maxima at 370 and 450 nm. This intermediate rapidly reacts with a molecule of the starting complex to form a dimer. The dimer formation rate constant $k_1 = 2 \times 10^9\ M^{-1}s^{-1}$ is close to the diffusion limit. The disappearance of dimeric particles occurs in the millisecond time range and is associated with their recombination. The products of this process are disulfide $(S_2COEt)_2$ and the $Ni(S_2COEt)Cl$ complex. Finally, due to the slow disproportionation reaction, $Ni(S_2COEt)Cl$ is converted into a precipitate of Ni(II) chloride insoluble in CCl_4.

Acknowledgment: the projects was financially supported by the Russian Foundation of Basic Investigation (grants No. 20-03-00708 and 20-33-90193).

[1] Jeliazkova B. G., Sarova G. C. (1997). *Polyhedron*, *16*, 3967–3975.
[2] Kolomeets A. V. et al. (2011). *JPPA: Chem.*, *220*, 164–172.
[3] Plyusnin V. F. et al. (2011). *J. Phys. Chem. A.*, *115*, 1763–1773.

Modelling Ultrafast Fluorescence Dynamics: Dependence of the Solvent Response Dynamics on the Fluorophore Nature

✉ **Alexey E. Nazarov, Anatoly I. Ivanov**

Volgograd State University
Volgograd, Russia

✉ nazarov.alexey@volsu.ru

A theory of time-resolved fluorescence spectra describing molecules with non-parabolic free energy curves of the excited and ground states is presented [1]. The model includes the description of the solvent relaxation and relaxation of intramolecular high-frequency vibrations. The relaxation of the solvent is described classically and high-frequency vibrations at the quantum level. The excited adiabatic electronic term of a covalently linked perylene-dimethylaniline (PeDMA) is essentially non-parabolic. The reorganization of both intramolecular vibrations and the solvent strongly affects the absorption and fluorescence spectra and their influence on spectral dynamics is highly entangled. Within this theory the analysis of the spectra of PeDMA in a series of solvents of different polarity is performed. The investigation shows that the developed theory and the modern fluorescence upconversion spectroscopy provides a possibility to disentangle the relaxation of intramolecular high-frequency vibrations and the dynamics of the solvent. The developed approach allows one to determine the solvent relaxation function of hexane from the experimental fluorescence spectral dynamics of PeDMA.

The vibrational relaxation for PeDMA was determined due to the fact that the vibrational structure of the fluorescence spectra in non-polar hexane is sufficiently pronounced. It was found that the vibrational relaxation is accelerated with increasing the solvent polarity. This acceleration is well seen for the mode with the frequency $h\nu = 175$ meV. The relaxation time constant of another mode is estimated to be 0.05 ps for both polar and non-polar solvents.

The fluorescence spectral dynamics of the two dyes, PeDMA [1] and coumarin 153 [2], detected with the same setup have been analyzed using similar theoretical approaches. The comparison of fluorescence spectral dynamics of these two dyes shows that the solvation dynamics depends on the fluorophore.

Acknowledgements: the study was performed with financial support of the Russian Science Foundation (grant No. 22-13-00180, https://rscf.ru/en/project/22-13-00180/).

[1] Nazarov A. E., Rosspeintner A., Angulo G., Ivanov A. I. (2022). *J. Mol. Liq.*, *360,* 119387.

[2] Fedunov R. G., Yermolenko I. P., Nazarov A. E., Ivanov A. I., Rosspeintner A., Angulo G. (2020). *J. Mol. Liq.*, *298,* 112016.

Effective Multicomponent Approach to Indolizin-1-ols: Chemical and Spectral Particularities of the Products

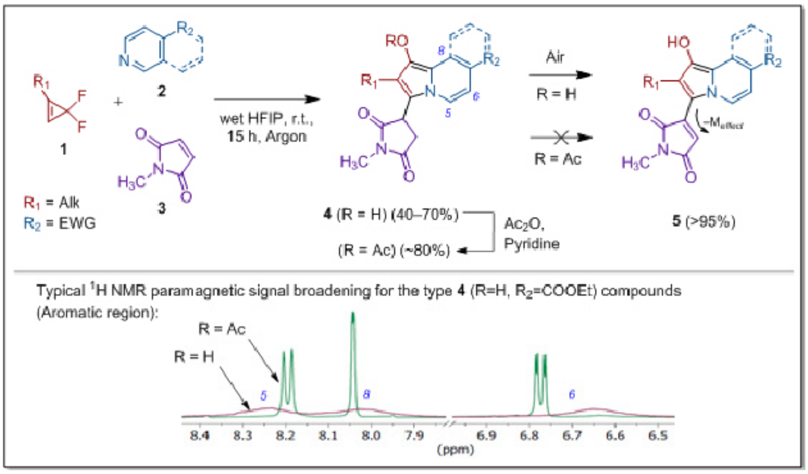
✉ **Ilya V. Nechaev**[1], **Georgij V. Cherkaev**[2], **Aleksei B. Sheremetev**[1]

[1] *Zelinsky Institute of Organic Chemistry RAS*
Moscow, Russia
[2] *Enikolopov Institute of Synthetic Polymeric Materials RAS*
Moscow, Russia

✉ zbx@bk.ru

In this study, a three-component methodology for synthesis of novel indolizin-1-ol derivatives was developed [1]. It was shown that indolizin-1-ol moiety causes oxidative instability of the molecules, containing it. Thus, as one can see in Figure, succinimides **4** (*R* = *H*) are easily and almost quantitatively oxidized by air to afford brightly colored maleimides **5**. The formed products **5** are stabilized toward oxidation due to the emerging conjugation and transition of –M effect onto the electron-rich indolizine moiety.

It was found that acylation of the OH group of the compounds **4** fully suppress their ability for aerobic dehydrogenation to maleimides **5**.



For indolizin-1-ols, the ease of homolytic cleavage of the O–H bond leads to the formation of stable radicals: paramagnetic species that critically affect the shape of the NMR spectra. The paramagnetic broadening was completely eliminated by functionalization of the OH group. These spectral features correlate with the aerobic reactivity of the products **4** and confirm the homolysis of the O–H bond as the initial step of the oxidative transformations of 1-hydroxyindolizines. Kinetics of the aerobic dehydrogenation has been studied and the temperature and R_2-substituent dependences were shown.

[1] Nechaev I. V., Cherkaev G. V., Solyev P. N., Boev N. V. (2021). Synthesis and Aerobic Dehydrogenation of Indolizin-1-ol Derivatives. *J. Org. Chem.*, *86*, 4220–4235.

Mechanism of UVC Photodegradation of Carbamazepine in Aqueous Solutions

✉ **Mikhail V. Novikov**[1,2], **Olga A. Snytnikova**[1,3],
Roman G. Fedunov[1,2], **Vadim V. Yanshole**[1,3], **Ivan P. Pozdnyakov**[1,2]

[1] *Novosibirsk State University*
Novosibirsk, Russia
[2] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[3] *International Tomography Center SB RAS*
Novosibirsk, Russia

✉ suzugamori.ren.san@gmail.com

Carbamazepine (CBZ) is an antiepileptic drug from the group of "pharmaceuticals and personal care products" (PPCPs). Since the beginning of the 1960s, it has been used as a medicinal preparation. By the late 1990s, carbamazepine like many other pharmaceuticals was causing concern due to detection in urban water supplies, surface waters, and drinking water [1]. Its effect on living organisms begins to manifest even at low concentrations, with which current water treatment systems are not able to cope effectively [2]. Thus, CBZ is a representative of a group of priority micropollutants in natural waters.

In this work, the mechanism of direct UV photolysis of tricyclic antidepressant carbamazepine (CBZ) at neutral pH was revealed by the combination of nanosecond laser flash photolysis, steady-state photolysis coupled with high resolution LC-MS and DFT quantum-chemical calculations. Both the detection of short-lived intermediates and the detailed identification of final products were done for the first time. The quantum yield of CBZ photodegradation (282 nm) is about 0.1 % and 0.18 % in air-equilibrated and argon-saturated solutions. The primary stage is photoionization with the formation of CBZ cation radical followed by a fast nucleophilic attack by a solvent molecule. The main products of photodegradation are compounds of hydroxylation and/or rearrangement of the original CBZ, as well as their subsequent photochemical transformations. The obtained results can be important for understanding the behavior of tricyclic antidepressants in the processes of UVC disinfection and in natural waters under the action the sunlight.

[1] Zhou S., Xia Y., Li T., Yao T., Shi Z., Zhu S., Gao N. (2016). Degradation of carBamazepine by UV/Chlorine Advanced Oxidation Process and Formation of Disinfection By-Products. *Environmental Science and Pollution Research*, *23*(16), 16448–16455.

[2] Qiang L., Cheng J., Yi J., Rotchell J. M., Zhu X., Zhou J. (2016). Environmental Concentration of Carbamazepine Accelerates Fish Embryonic Development and Disturbs Larvae Behavior. *Ecotoxicology*, *25*(7), 1426–1437.

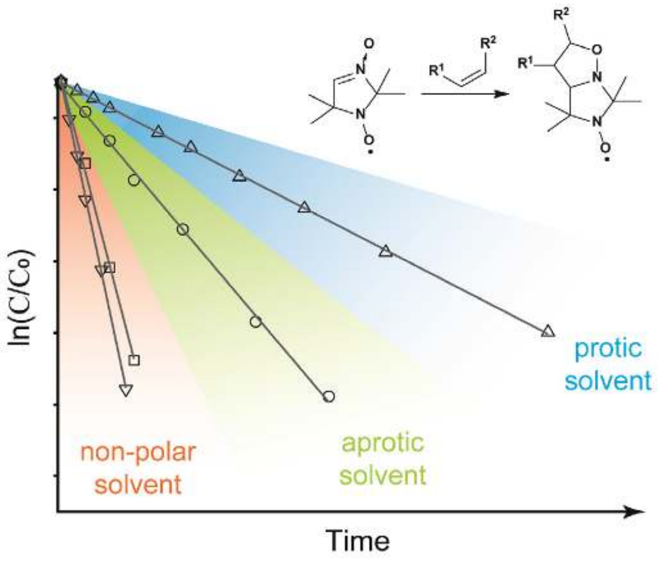
The Kinetic Solvent Effect on 1,3-Dipolar Cycloaddition of 2,2,5,5-Tetramethyl-3-imidazoline-3-oxide-1-oxyl

✉ **Dmitriy A. Parkhomenko**[1], **Sergey A. Cherkasov**[1,2],
Polina M. Kaletina[1,2], **Yuliya F. Polienko**[1]

[1] *Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ parkhomenko@nioch.nsc.ru

The use of 2,2,5,5-tetramethyl-3-imidazoline-3-oxide-1-oxyl as a controlling agent in Nitroxide Mediated Polymerization provides for the activation of alkoxyamine homolysis by 1,3-dipolar cycloaddition of a vinyl monomer [1]. Polymerization can be carried out in a medium with different polarity and hydrogen bonding capacity which affects the rate of 1,3-dipolar cycloaddition reaction. In the present study, the solvent effect on the rate of this reaction was experimentally and theoretically investigated for six different dipolarophiles: styrene, n-butyl acrylate, acrylonitrile, methyl vinyl ketone, maleic anhydride, and N-phenyl maleimide. It was shown that an increase in both solvent polarity and hydrogen bonding capacity leads to a decrease in cycloaddition reaction rate. The strength of the solvent effect is determined by the dipolarophile's structure: cycloaddition of non-polar dipolarophiles is slightly affected by solvent polarity, while in the case of polar dipolarophiles reaction proceeds up to one order of magnitude slower in a polar protic solvent when compared with a non-polar one. The correlation of reaction rate coefficients with Kamlet-Taft solvent parameters was found.



Acknowledgements: the work was supported by the Russian Science Foundation (grant No. 20-73-00350) and the Ministry of Science and Higher Education of the Russian Federation (grant No. 14.W03.31.0034).

[1] Edeleva M. et al. (2019). *Chem. Commun., 55*, 190–193.
[2] Cherkasov S. A. et al. (2021). *ChemPlusChem, 86*, 1080–1086.
[3] Cherkasov S. A. et al. (2022). *ChemPlusChem*, doi:cplu.202200119.

Spectral Properties and Kinetics of Interaction with the Fluoride Ion for Aryl-Substituted Boron Subphthalocyanines

✉ **Arina A. Petukhova**, **Tatiana V. Dubinina**, **Natalia E. Borisova**

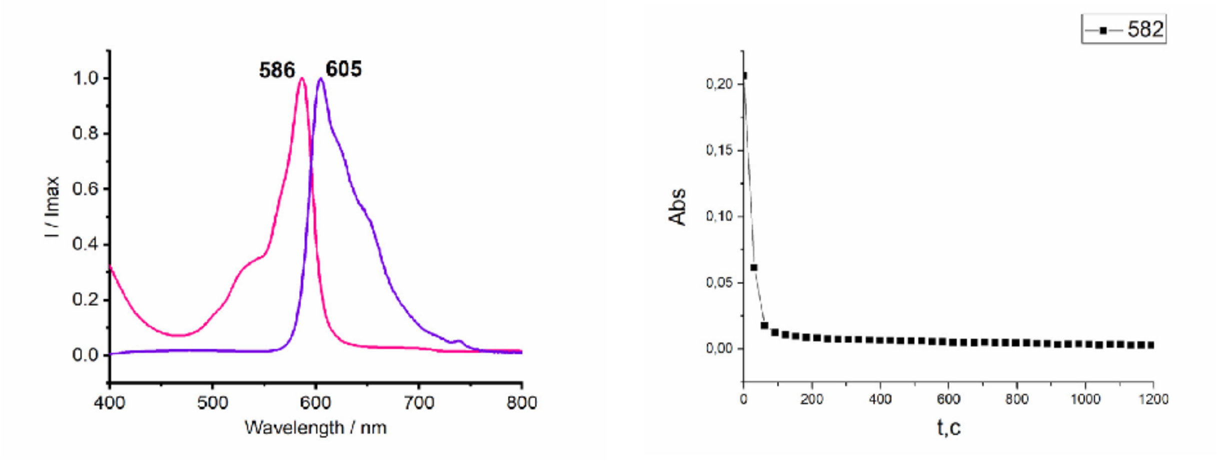
Lomonosov Moscow State University
Moscow, Russia

✉ arisha.petukhova@mail.ru

Subphthalocyanines are macroheterocyclic compounds with a 14π-electron conjugation system. Due to the cone-shaped structure that suppresses aggregation in solution, subphthalocyanins are highly soluble in most organic solvents. Subphthalocyanines have intense absorption and fluorescence in a visible region, which allows them to be considered promising for use in organic electronics. The introduction of substituents to the periphery of the subphthalocyanine macrocycle provides for controlling optical properties (the position of absorption/fluorescence maxima), improving solubility. The objects of the study were phenyl- and 3-thienyl-substituted boron subphthalocyanines.

A bethochromic shift of the absorption maxima (586 and 592 nm) and fluorescence (598 and 605 nm) was observed going from phenyl to thienyl-substituted subphthalocyanine. This is probably due to the destabilization of the subphthalocyanine's HOMO orbital and a decrease in the energy gap of the HOMO-LUMO with the introduction of an electron-donating heteroaromatic substituent. There was also an increase in the fluorescence quantum yield from 14 % (phenyl-substituted) to 17 % (thienyl-substituted).

Of interest was the study of the kinetics of the interaction reaction of subphthalocyanine with a fluoride ion (the reaction is selective to this particular ion). It was found that the decoloration of the subphthalocyanine solution, probably accompanied by the opening of the macrocycle, occurs in less than 5 min. In this case, using the isomolar series method, it was shown that a complex of subphthalocyanine with fluorine is formed in a ratio of 1:1.



Absorption and luminescence spectra for thienyl-substituted complex (λ_{ex} = 369 nm) (left).
The kinetic curve of the Q band intensity drop under the action of $Bu_4N^+F^-$ in acetonitrile (right)

Fast Photophysics Processes and Transient Species in Photochemistry of $Ni(S_2P(i\text{-}Bu)_2)_2$ Complex in CCl_4

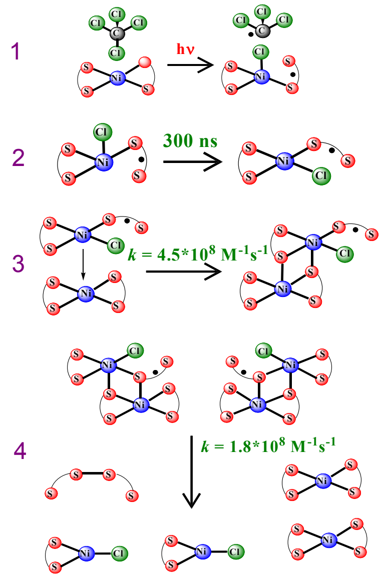
✉ **Victor F. Plyusnin, Aleksandr V. Mikheylis, Vjacheslav P. Grivin**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ plyusnin@kinetics.nsc.ru

Femtosecond spectroscopy and nanosecond laser flash photolysis were used to study the photophysical and photochemical transformations of *bis*-diisobutyl-dithiophosphinate Ni(II) complex ($Ni(S_2P(i\text{-}Bu)_2)_2$ in CCl_4 solutions [1]. The radiation of second harmonic (405 nm) of Ti:Sapphire laser transfers $Ni(dtpi)_2$ complex to excited CTLM state. Its decay in CCl_4 is described by two exponents with time 0.58 and 2.0 ps. The first process involves fast transitions from CTLM state to lower-lying (d, d^*) state and then to "hot" ground state. The second time corresponds to the vibrational cooling of this "hot" ground state.

The study of photochemistry was performed with laser flash photolysis at 308 nm. In this case, an electron transfer from the excited $Ni(dtpi)_2$ complex to a solvent molecule leads to the appearance of primary intermediate, the [ClNi(dtpi)(•dtpi)] complex in which a •dtpi radical is coordinated with a nickel ion via one sulfur atom. In fast reaction with $Ni(dtpi)_2$, this complex forms a long-lived dimer $ClNi(dtpi)(^\bullet dtpi)[Ni(dtpi)_2]$ (see Fig.). This intermediate for a few hundred microseconds decays in the reaction of recombination with the formation of $(dtpi)_2$ disulphide and ClNi(dtpi) complex. The quantum chemical calculations allowed us to determine the geometry of intermediate complexes arising in the photochemistry of $Ni(S_2P(i\text{-}Bu)_2)_2$ complex.



The scheme of photochemical transformation of $Ni(S_2P(i\text{-}Bu)_2)_2$ complex in CCl_4. *(1)* Excitation of $Ni(S_2P(i\text{-}Bu)_2)_2$ complex and electron transfer to CCl_4 molecule; *(2)* Change of the geometry of $Cl_{ax}Ni^{II}(dtpi)(^\bullet dtpi)$ complex to $Cl_{eq}Ni^{II}(dtpi)(^\bullet dtpi)$ state; *(3)* Reaction of $Cl_{eq}Ni^{II}(dtpi)(^\bullet dtpi)$ and initial $Ni(S_2P(i\text{-}Bu)_2)_2$ complex resulting in $ClNi^{II}(dtpi)(dtpi^\bullet)[Ni^{II}(dtpi)_2]$ dimer formation; *(4)* Final reaction of two $ClNi^{II}(dtpi)(^\bullet dtpi)[Ni^{II}(dtpi)_2]$ dimers resulting in the formation of final products

Acknowledgment: the research was financially supported by the Russian Foundation of Basic Investigation (grants No. 20-03-00708 and 20-33-90193).

[1] Solovyev A. I., Mikheylis A. V., Plyusnin V. F., Shubin A. A., Grivin V. P., Larionov S. V., Tkachenko N. V., Lemmetyinen H. (2019). *J. Photochem. Photobiol. A: Chem.*, *381*, 111857.

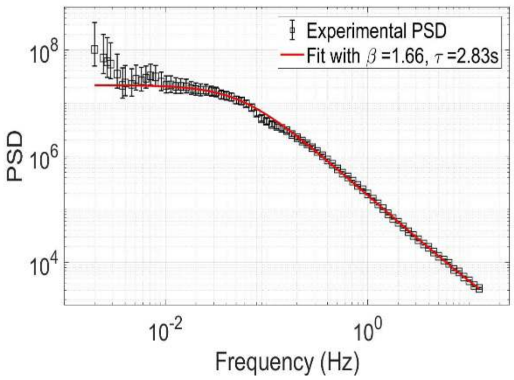
Presence of Maximal Characteristic Time in Photoluminescence Blinking of MAPbI3 Perovskite

✉ **Eduard A. Podshivaylov**[1], **Sudipta Seth**[2], **Jun Li**,[2] **Marina Gerhard**,[3]
Alexander Kiligaridis,[2] **Ivan G. Scheblykin**,[2] **Pavel A. Frantsuzov**[1]

[1]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2]Chemical Physics and NanoLund, Lund University
Lund, Sweden
[3]Faculty of Physics and Materials Sciences Center Renthof
Marburg, Germany

✉ podshivailov@kinetics.nsc.ru

Materials and devices based on crystals with the perovskite structure were paid much attention in the last decade. High efficiency of converting light into electricity, the ability to create numerous substances with such structure, and unusual elastic properties make perovskites indispensable in many applications.



Like systems with quantum-confined effects, perovskite microcrystals [1] and films [2] exhibit the phenomenon of long-term changes in luminescence intensity, referred to as blinking. To date, the reason for this behavior in perovskites is unknown.

The present research consisted in studying the blinking signal using the spectral power density (PSD), which was determined using the well-known Welch method. Using the example of MAPbI3 microcrystals, PSD has been shown to take the form of a power law with saturation at low frequencies. Accordingly, there is a characteristic time corresponding to the saturation frequency. For blinking systems presence of such characteristic time has been observed for the first time.

The dependence of the spectral power density parameters on the pump radiation intensity has been investigated. A small correlation has been found between the exponent of the power dependence and the characteristic time. A comparison with the blinking of a conventional two-level system with random switching was made.

Additionally, the dependence of the truncation time for the ON-OFF switching times distribution on the threshold value has been studied.

[1] Seth S., Podshivaylov E. A., Li J., Gerhard M., Kiligaridis A., Frantsuzov P. A., Scheblykin I. G. (2021). *Adv. Energy Mater., 11*(44), 2102449.

[2] We X., Ho-Baillie A., Huang S., R. Sheng, Chen S., Ko H., Green M. A. (2015). *Nano Letters*, *15*(7), 4644–4649.

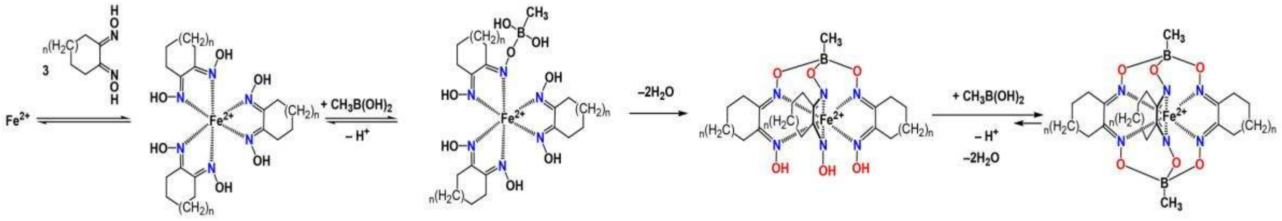
Kinetics of the Template Synthesis and Acidic Decomposition of the Methylboron-Capped Iron(II) Tris-Dioximate Clathrochelates: Dramatic Changes in the Kinetic Parameters and Schemes in Passing From Six- to Eight-Membered Alicyclic α-Dioximes

✉ **Alexander L. Pomadchik, Alexander S. Belov, Anna V. Vologzhanina, Yan Z. Voloshin**

Nesmeyanov Institute of Organoelement Compounds RAS
Moscow, Russia

✉ pom17@yandex.ru

Reaction of the template synthesis of the boron-capped iron(II) macrobicyclic complexes (clathrochelates) of a general formula $FeD_3(BR)_2$ (where D^{2-} is the alicyclic α-dioximate dianion, R is the apical substituent) are known [1–3] to be the unique objects for studying of the kinetics of their coordination-driven self-assembly from three chelating and two cross-linking ligand synthones on the iron(II) ion as a matrix (Scheme). These reactions proceed in the quantitative yields even in diluted solutions, thus giving the intensively colored ($\varepsilon \sim 2 \cdot 10^4$ mol $^{-1} \cdot$L$\cdot$cm^{-1}) clathrochelate products with their absorption maxima from 440 to 460 nm, whereas the initial ligand synthones are optically silent in a given range. This allows an easy studying of both their synthesis and decomposition using a photometric method. We performed these reactions for the methylboron-capped iron(II) clathrochelates—the derivatives of alicyclic six-, seven- and eight-membered α-dioximes. Their ring size was found to dramatically affect the kinetic schemes and parameters of the template synthesis and acidic decomposition reactions of these clathrochelates. If general schemes of their coordination-driven self-assembly persist, those for six- and seven-membered α-dioximes contain a rate-determining stage, whereas that for their eight-membered analogue has three initial consecutive stages with close reaction rates. Passing from a six-membered chelating synthon to its seven-membered analogue causes a decrease in the synthesis reaction rates by approximately three orders of magnitude. These kinetic effects were explained using the single-crystal XRD data for the initial α-dioximes and for their methylboron-capped macrobicyclic iron(II)-encapsulating derivatives as well.



trigonal-antiprismatic geometry trigonal-prismatic geometry

Acknowledgments: this work was supported by RFBR (grant No. 20-03-00127).

[1] Voloshin Y. Z., Kostromina N. A., Krämer R. (2002). *Clathrochelates: Synthesis, Structure and Properties*. Elsevier: Amsterdam, The Netherlands.

[2] Pomadchik A. L., Belov A. S., Lebed E. G., Voloshin Y. Z. (2020). *Russ.J.Inor.Chem.*, *65*, 1503–1512.

[3] Pomadchik A. L., Belov A. S., Lebed E. G., Belaya I. G., Vologzhanina A. V., Voloshin Y. Z. (2021). *Molecules*, *26*(13), 4019.

Structure of Mixed Molecular Clusters and Its Effect on Laser Induced Intracluster Dynamics

✉ **D. G. Poydashev**[1], **O. S. Ablyasova**[1–3], **E. A. Ryabov**[1]

[1] *Institute of Spectroscopy*
Troitsk, Moscow, Russia
[2] *Helmholtz-Zentrum Berlin für Materialien und Energie*
Berlin, Germany
[3] *Albert-Ludwigs-Universität Freiburg*
Freiburg, Germany

✉ poydashev@isan.troitsk.ru

The dynamics of intracluster processes was measured in the pump-probe experiments for $(CF_3I)_nXe_m$ and $[Fe(CO)_5]_nXe_m$ mixed molecular clusters. These mixed clusters produced by expansion of a mixture with Xe carrier gas from pulsed nozzle tend to have a shell structure: strongly bonded molecules in the core of the cluster are surrounded by weakly bonded atomic shells.

Photochemical reactions induced in such clusters by femtosecond UV laser pulses proved to be sensitive to laser intensity. XeI^+ ions are formed much more effectively with stretched from 150 fs to 2.2 ps UV laser pulses during the multiphoton ionization (MPI) process of $(CF_3I)_nXe_m$ mixed clusters. Real-time kinetics for XeI^+ and I_2^+ ions formed from these mixed clusters allow us to conclude that the presence of atomic shells in the mixed cluster prevent ultrafast (in 100 fs time domain) formation of products which require particles from the core of the cluster. In contrast to I_2^+ ions formed in 1 ps from pure $(CF_3I)_n$ clusters [1], a rate for XeI^+ and I_2^+ ions in the case of mixed cluster is ~50 ps [2]. We believe the latter time constant is a good estimate on dissociation rate of the shell of the mixed cluster.

Dissociative ionization has a significant impact on the process of probing weakly bonded cluster beams by means of MPI. It could lead to high kinetic energy of obtained ion products and, therefore, mark the mechanism of ion formation process as well as the origin of produced ions. The kinetic energy of Xe^+ ions formed during the MPI of dissociated shells of the mixed cluster was measured, and it equals to several electronvolts in the experiment with $[Fe(CO)_5]_nXe_m$ mixed clusters. The mechanism of dissociation of Xe shells was revealed: these atoms are dissociated from the surface of the mixed cluster as small Xe_n clusters.

[1] Apatin V. M., Kompanets V. O., Lokhman V. N., Ogurok N.-D. D., Poydashev D. G., Ryabov E. A., Chekalin S. V. (2011). *JETP Letters*, *94*(7), 570–573.

[2] Poydashev D. G., Ablyasova O. S., Ryabov E. A. (2022). *JETP Letters*, *115*(9), accepted for publication.

New Approaches to Determination of the Quantum Yield of Hydroxyl Radical Generation and Its Reactivity with Persistent Contaminants

✉ **Ivan P. Pozdnyakov**[1,2], **Yuliya E. Tyutereva**[1,2], **Mikhail V. Novikov**[1,2],
Olga A. Snytnikova[1,3], **Vaycheslav P. Grivin**[1,2], **Victor F. Plyusnin**[1,2]

[1] *Novosibirsk State University*
Novosibirsk, Russia
[2] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[3] *International Tomography Center SB RAS*
Novosibirsk, Russia

✉ ipozdnyak@kinetics.nsc.ru

Fe (III) carboxylate complexes are photoactive natural compounds which are intensively studied and are considered to be one of the promising systems for the degradation of pollutants in the so-called advanced oxidation processes (AOPs). They demonstrate high quantum yields of photolysis and efficient generation of $^{\bullet}$OH radicals under the action of UV radiation. However, there is very little information on the quantum yields of $^{\bullet}$OH radicals (ϕ_{OH}) upon excitation of such systems. At the same time, the ϕ_{OH} values and the reactivity of $^{\bullet}$OH with respect to the target compounds are the most important parameters for the application of any photosystem in AOPs. This work presents valid approaches to determining the ϕ_{OH} values during the UV photolysis of natural Fe(III) carboxylate complexes and determining the rate constants of hydroxyl radical reactions (k_{OH}) with priority environmental pollutants.

The first approach is based on the use of the $FeOH^{2+}$ hydroxocomplex as a reference system with a well-known ϕ_{OH} value and benzene as a selective trap for $^{\bullet}$OH radicals. For the first time, ϕ_{OH} was determined for the most popular Fe(III)-oxalate photosystem in a wide range of initial parameters (pH, excitation wavelength, concentration of oxalate and Fe(III) ions). Also, the oxidative potential of the oxalate photosystem was tested on a set of resistant organic herbicides, and the quantum yields of photodegradation of these herbicides were compared with the ϕ_{OH} value.

The second approach is based on application of the method of laser flash photolysis using the $FeOH^{2+}$ complex as a standard source of hydroxyl radicals at pH 3, and methylviologen dication (MV^{2+}) as a selective probe for the $^{\bullet}$OH radical. The use of MV^{2+} makes it possible to determine the k_{OH} values even for those compounds which do not themselves form optically detectable adducts in the reaction with hydroxyl radicals. The applicability of this approach has been tested on a wide range of resistant organic herbicides, and its main advantages and disadvantages are discussed in comparison with existing stationary and time-resolved methods.

Acknowledgements: this work was financially supported by the Russian Science Foundation (No. 21-43-00004).

UV-Photoexcitation of Oxygen-Isoprene Collision Complexes as a Source of Singlet Oxygen

✉ **Alexandra P. Pyryaeva**,[1] **Kirill S. Ershov**[1], **Sergei A. Kochubei**[2], **Alexey V. Baklanov**[1]

[1]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2]Rzhanov Institute of Semiconductor Physics SB RAS
Novosibirsk, Russia

✉ pyryaeva@kinetics.nsc.ru

The interaction of oxygen molecules with molecular environment provides strong enhancement of UV-absorption by oxygen and other molecules, which takes place when molecules collide in the gas phase. Thus, isoprene C_5H_8 (the most widespread biogenic organic compound in the Earth atmosphere after methane), being transparent at wavelengths $\lambda > 240$ nm, absorbs in the presence of molecular oxygen due to the collision-induced absorption in C_5H_8-O_2 collision complexes [1].

Oxygen collision-induced absorption also dramatically changes oxygen photochemistry causing new photochemical processes such as formation of singlet oxygen species $^1O_2$ which possess high chemical reactivity and play important role in nature. Recently, we have observed $^1O_2$ formation as result of the isoprene-oxygen collision complexes photoexcitation in the gas phase within the spectral region 253.5−355 nm at oxygen elevated pressure [2]. Singlet oxygen has been detected with its NIR luminescence centered near 1.27 µm. The $^1O_2$ photogeneration is found to be a one-photon process. We have measured the $^1O_2$ quantum yield within the UV-C region (253−278 nm) and supposed it is governed mainly by O_2 molecules photoexcitation to the Herzberg III ($^3\Delta_u$) state via C_5H_8-O_2 collision complexes enhanced absorption. So, excited triplet O_2 gives rise to $^1O_2$ because of triplet-triplet annihilation in the collisions with unexcited O_2 molecules. In the UV-B (308 nm) region the $^1O_2$ appearance is attributed to the excitation of a double spin-flip (DSF) transition in C_5H_8-O_2 complex. In the UV-A region (355 nm), besides DSF isoprene sensitizes $^1O_2$ formation as result of O_2-assisted excitation to the triplet state. We suppose that DSF may result in $^1O_2$ formation in widespread wavelength region depending on oxygen collisional partner X in any oxygen-containing media. Relying on the obtained data we made estimations of the role of this new process in the Earth atmosphere.

Acknowledgements: this work was financially supported by the Russian Foundation for Basic Research (grant No. 16-13-10024).

[1] Pyryaeva A. P., Goldort V. G., Kochubei S. A., Baklanov A. V. (2014). *Chem. Phys. Lett., 8*(13), 610–611.

[2] Pyryaeva A. P., Ershov K. S., Kochubei S. A., Baklanov A. V. (2020). *J. Phys. Chem. A*, *124*, 8469−8477.

Colloidal Quantum Dots as a New Type of Luminofors

✉ **Vladimir F. Razumov**

Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia

✉ razumovvf@list.ru

The development of efficient luminophors is an urgent task for fundamental and applied chemistry. Since the 1930s, widespread inorganic crystallophors, the glow of which is caused, as a rule, by the presence of absorbing light crystalline substance of small quantities of luminescent ions, for which are used cations of transition and rare earth metals. The characteristics necessary for varying target are achieved by selecting the chemical composition of activators of luminescence. In the second half of the XX century scientists began to actively implement another class of luminophors—molecular organic luminophors, the spectral luminescent properties of which are achieved by chemical design of the structure of the luminescent molecules using the arsenal of methods for fine chemical synthesis, and the required performance characteristics via the use of polymer binder. In recent years, there is increasing attention from the fundamental and practical point of view to the new class of luminophors—the so-called colloidal quantum dots (CQD), fluorescent properties of which are specified by the average size of nanoparticles of crystalline semiconductor. Their size can vary in the range of 2–10 nm, and the width of individual nanoparticles at room temperature in the luminescence spectra is only 20–30 nm, and the spectrum situation may vary in the range of ca. 100 nm relative to the band gap of a massive semiconductor.

Thus, a limited set of luminescent quantum dots based on semiconductors of the AIIBVI, AIIIBV or AIVBVI type easily cover the spectral range from 350 to 3,500 nm by varying their size. In contrast to organic molecular luminophors, CQD potentially have much greater thermal stability and photostability, and also have a number of functional advantages due to the unique variation of its spectral characteristics. Therefore, now it can find application in light-emitting diodes, displays, solar cells, optical amplifiers, lasers, chemo- and biosensors, and biomedical diagnostics. The more distant prospect of using CQD is associated with molecular electronics and quantum computing. A number of new physical phenomena such as quantum size effects, multiple exciton generation, a blinking of fluorescence, inhomogeneous spectral broadening was discovered in CQD.

The report details the fundamental basis of luminescent properties of CQD, discussed the problems and prospects of their application.

Acknowledgements: the research was financially supported by the Russian Science Foundation (grant No. 21-73-20245).

Experimental Measurement of the van der Waals Binding Energy in $(Xe)_n$-O_2 Complexes with the Velocity Map Imaging Technique

✉ **Vladislav M. Rogoveshko**[1,2], **Alexandr S. Bogomolov**[2], **Alexey V. Baklanov**[2]

[1]Novosibirsk State University
Novosibirsk, Russia
[2]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ v.rogoveshko@g.nsu.ru

Interest to the van der Waals complexes of xenon with oxygen is attracted by the known application of xenon as an anesthetic agent [1]. This effect is very surprising because xenon is an inert gas. The mechanism of this anesthetic action is still unknown. There is an assumption that the complexes of xenon with oxygen can play an essential role in this anesthetic effect. This dictates interest to the binding energy and structure of the van der Waals complexes of oxygen with xenon. In the current work the measurements of the binding energy are carried out with the approach suggested in paper [2], which is based on the use of the velocity map imaging of the photofragments arising in photodissociation of van der Waals complexes.

In these experiments van der Waals oxygen-xenon complexes are generated in a cold supersonic molecular beam. UV-laser radiation used for excitation of complexes is also used for resonance-enhanced photoionization O atoms arising in the photodissociation of O_2 in complexes. The distribution of O^+ photoions over kinetic energy and the angular anisotropy of their recoil were measured using the velocity map imaging technique. The comparison of the kinetic energy and angular distribution of O atoms formed from an oxygen-xenon complex with those observed for the photodissociation of non-bonded oxygen molecule allows us to extract the binding energy of the complex Xe-O_2.

Experimental evidence of the formation of more complicated complexes of xenon with oxygen complexes was also obtained. It was observed that the shift in kinetic energy of atoms increases with xenon concentration in the expanded gas mixture. Also, the velocity maps of xenon atoms were measured. The results indicate the formation of xenon clusters $(Xe)_n$ and complexes of these clusters with the oxygen molecule $(Xe)_n$-O_2.

[1] Cullen S. C., Gross E. G. (1951). *Science, 13*, 580.

[2] Vidma K. V., Bogdanchikov G. A., Baklanov A. V., Chestakov D. A., Parker D.H. (2010). *J. Chem. Phys.*, *133*, 194306.

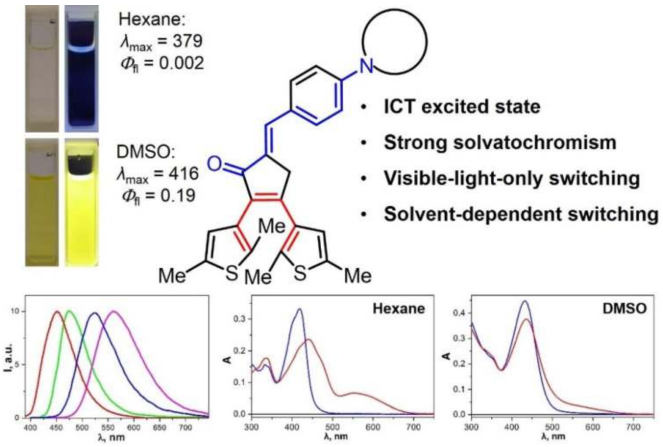
Solvent Dependent Photochromism and Emission of Diarylethenes with a π-Conjugated Push-Pull System

✉ **Veronika V. Semionova**[1], **Evgeni M. Glebov**[1], **Valerii Z. Shirinian**[2], **Andrei G. Lvov**[3,4]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Zelinsky Institute of Organic Chemistry RAS*
Moscow, Russia
[3] *Favorsky Irkutsk Institute of Chemistry SB RAS*
Irkutsk, Russia
[4] *Irkutsk National Research Technical University*
Irkutsk, Russia

✉ semveronica22122gmail.com

Introduction of the push-pull system between carbonyl and dimethylamino groups in the ethene bridge of diarylethene (DAE) provides access to the fluorescent switches responsible for various stimuli (UV and visible light, solvent polarity, pH). A study of luminescent and photochromic properties of three cyclopentenone-based derivatives was performed (see Figure, [1]). The intramolecular charge transfer (ICT) excited state is responsible for emission, determining strong dependence of emissive properties vs. solvent polarity. The kinetic behavior of luminescence was explained by the model based on the equilibrium between two isomers of the DAEs open form. Dialkylaminobenzylidene moiety conjugated with cyclopentenone bridge provides a unique combination of bidirectional manipulation by visible light only and complex switching behavior.



Solvatochromic and photochromic properties of luminescent DAEs

Acknowledgement: the work is supported by the Russian Foundation of Basic Research (grant No. 20-03-00708).

[1] Glebov E. M., Semionova V. V., Lazareva S. K., Smolentsev A. B., Fedunov R. G., Shirinian V. Z., Lvov A. G. (2022). *J. Lumin.*, *241*, 118472.

Addition of Br_2 to a Triple Bond: Radical Rather than Ionic Mechanism

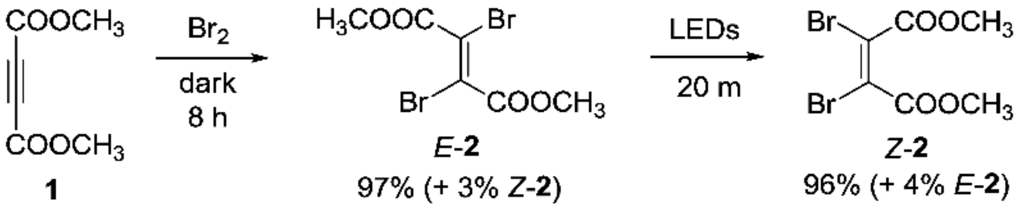
Andrey V. Shernyukov, **George E. Salnikov**, ✉ **Alexander M. Genaev**

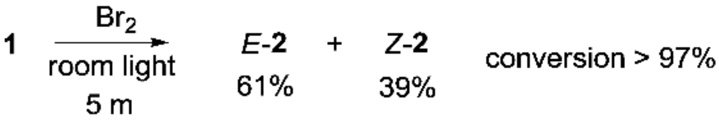
Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS
Novosibirsk, Russia

✉ genaev@nioch.nsc.ru

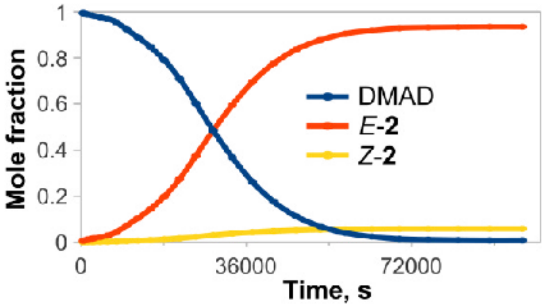
It is commonly believed that the bromination of alkynes proceeds by an ionic mechanism, through bromenium ions.

We studied the bromination of dimethyl acetylenedicarboxylate (DMAD) **1**. It was found that in complete darkness, a slow selective bromination of DMAD occurs, while at the slightest illumination the reaction becomes fast and non-selective.





$$\mathbf{1} \xrightarrow[\text{room light, 5 m}]{Br_2} E\text{-}\mathbf{2}\ (61\%) + Z\text{-}\mathbf{2}\ (39\%) \quad \text{conversion} > 97\%$$



But even with light shielding, the DMAD's bromination kinetics are S-shaped, caused by the induction period. It suggests the free radical chain mechanism.

With the addition of a Br• radical scavenger, *tert*-butyl nitrite, the DMAD bromination reaction does not proceed at all, which indicates its radical nature even in complete darkness.

Acknowledgements: the work was supported by the Russian Foundation for Basic Research (grant No. 20-03-00187).

The Impact of Excilamps Radiation on the Photodegradation of Some Phenol Derivatives

✉ **Irina V. Sokolova,** **Anastasia A. Fedorova**

Tomsk State University
Tomsk, Russia

✉ sokolova@phys.tsu.ru

Due to the presence of the OH group and its propensity to form hydrogen bonds, phenol and its derivatives are model compounds which have been the subject of extensive spectroscopic investigation. The addition of other substituents is expected to affect the structure and properties of phenol in different ways, depending on its location and nature. It is also important that phenol and its derivatives constitute a wide class of water pollutants because of their stability and solubility in water. There are many conventional methods to destroy phenols, but each method has its shortcomings. Chemical oxidation methods are expensive and lead to contamination of water with other toxic pollutants. Biodegradation can only be used for dilute wastewater. Ultraviolet (UV) radiation with quantum energy comparable to the energy of a chemical bond is a unique tool for initiating and performing many physical and chemical processes on the surface and in the volume of various media. UV radiation can be used not only for disinfecting water and air, i.e., for removal of pathogenic microorganisms, but also for decomposition of complex organic compounds. In this regard, a study of the efficiency of different UV radiation sources which may influence various electronically excited states of organic molecules becomes relevant. Such sources are exciplex lamps which are increasingly used for toxicant photolysis [1]. The influence of UV radiation on the spectral properties of 2,6-di(hydroxymethyl)-4-methylphenol and 4-cyanophenol in water solutions has been studied. The pulsed excilamps were used as the UV radiation source: KrCl (222 nm), XeBr (282 nm), XeCl (308 nm). It was established that the process of phototransformation of compounds occurred faster when concentration decreased. The use of the flow-through photoreactor [2] leads to a more effective degradation of the examined compounds than irradiation in stationary conditions. The degree of photodegradation depended on the exposure time. The effect of hydrogen peroxide and humic acids additives on the processes of phenol photodegradation were also discussed. The method of ecotoxicant photodegradation with application of the UV radiation sources can be used both independently and in combination with other modern technologies.

Acknowledgement: The work was supported by the Ministry of Education and Science of Russia (project No. 0721-2020-0033).

[1] Boichenko A. M. et al. (2011). *Techn. and Appl.*, STT, 512. (in Russ.)
[2] Vershinin N. O. et al. (2013). *J. Appl. Spectrosc., 80*, 600–603.

Low-Frequency Raman Spectroscopy of Phospholipid Membranes

✉ **Nikolai V. Surovtsev**

Institute of Automation and Electrometry SB RAS
Novosibirsk, Russia

✉ snv@iae.nsk.su

Various experimental techniques are applied to the phospholipid bilayers, being models of biological membranes, candidates for biosensors, and cargos for drug delivery. Raman spectroscopy, a noninvasive and label-free experimental technique, is one of those. However, the low-frequency (< 100 cm^{-1}) Raman spectroscopy was not used for phospholipid membranes before. A number of peculiar features in the terahertz vibrational spectrum, which is manifested in the low-frequency Raman spectrum, are expected for 2D-like objects with the nanometer thickness as phospholipid bilayers. One can believe that the low-frequency Raman spectrum should have information about the thickness breathing mode of the phospholipid layers and the acoustic-like excitations. Our recent works reviewed in the present report reveal this. Manifestation of the low-frequency Raman features, their relation to the elastic modulus and layer thickness, their temperature dependences, sensitivity to the phase state and to domain coexistence are discussed in the present work.

Study of 4-nitrophenol Reduction over Graphene Oxide Modified with Ag and CeO_2 Nanoparticles by *In Situ* UV-Vis Spectroscopy

✉ **Aleksey V. Taratayko**, **Grigory V. Mamontov**

Laboratory of Catalytic Research, Tomsk State University
Tomsk, Russia

✉ taratayko1997@mail.ru

Nowadays, the Ag-based catalysts are in the focus of green chemistry as advantageous systems due to their relatively low cost, low-temperature activity, nontoxicity, and facile preparation and modification procedures [1]. Graphene, a two-dimensional carbon nanomaterial, and its derivatives (e.g., graphene oxide (GO), reduced graphene oxide (RGO)) are considered promising environmentally benign adsorbents and catalyst supports. This work aims to synthesize the Ag-CeO_2/GO systems and study their catalytic activity in 4-nitrophenol (4-NP) reduction to 4-aminophenol (4-AP) at room temperature and atmospheric pressure.

The graphene oxide was synthesized according to the modified Hummers' method [2]. Silver- and/or ceria-containing catalysts were synthesized by the deposition-precipitation technique. The synthesized samples were characterized by a complex of physical-chemical methods. Catalytic activity was tested in 4-NP reduction to 4-AP by applying $NaBH_4$ as reducing agent at room temperature and atmospheric pressure.

According to the TGA and XRD results, the structure of the synthesized GO support corresponds to the graphene oxide. The average size of Ag and CeO_2 nanoparticles in the catalysts is about 20 nm. The UV-visible spectra for suspension of catalysts in water indicate the reduction of catalysts in the reducing medium and the evolution of SPR band of metallic Ag nanoparticles. The catalytic experiments were carried out in the *in situ* cell with monitoring of the UV-visible spectra of the solution to control concentrations of the substrate ($\lambda = 400$ nm) and product ($\lambda = 300$ nm). Kinetics curves were analyzed within the model of pseudo-first order reaction. The calculated rate constants are 0.796 and 1.747 min^{-1} for Ag/GO and Ag-CeO_2/GO, respectively. The Ag-CeO_2/GO catalyst shows the highest catalytic activity in the synthesized catalysts series and stability during six conversion cycles.

To sum up, the considered synthesis technique provides for preparing the Ag-CeO_2/GO catalysts that are advantageous and environmentally benign systems for catalytic processes such as nitroarenes reduction under mild conditions.

Acknowledgements: this work was supported by the grant of the President of the Russian Federation (No. MK-460.2021.1.3).

[1] Wen C., Yin A., Dai W.-L. (2014). *Appl. Catal. B*, *160–161*, 730–741.

[2] Qu J. C., Ren C. L., Dong Y. L., Chang Y. P., Zhou M., Chen X. G. (2012). *Chem. Eng. J.*, *211–212*, 412–420.

The Use of Iron Oxalate Complexes and Potassium Persulfate for Photodegradation of Para-Arsanilic Acid

✉ **Yuliya E. Tyutereva**[1,2], **Petr S. Sherin**[2,3], **Victor F. Plyusnin**[1,2], **Ivan P. Pozdnyakov**[1,2],
Evgeniya V. Polyakova[2,4], **Vyacheslav P. Grivin**[1,2], **Olga V. Shuvaeva**[4]

[1]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2]*Novosibirsk State University*
Novosibirsk, Russia
[3]*International Tomography Center SB RAS*
Novosibirsk, Russia
[4]*Institute of Inorganic Chemistry SB RAS*
Novosibirsk, Russia

✉ i.tiutereva@g.nsu.ru

Iron oxalate complexes and potassium persulfate are often used to increase the efficiency of photodegradation of organic pollutants, as they demonstrate good absorption of solar UV radiation and effective generation of active oxidative hydroxyl and sulfate radicals. In this work, these photoactive additives were used for the photodegradation of para-arsanilic acid (p-ASA).

p-ASA is a representative of arsenic-containing organic compounds used as feed additives. This compound is widely used in agriculture to combat intestinal parasites [1]. Although the feed additives themselves have low toxicity, the products of their biological and (photo)chemical decomposition—inorganic arsenic compounds and organic by-products—demonstrate significant toxicity to living organisms. In this regard, there is interest in developing methods, including photochemical methods, for removing p-ASA and its analogues from aqueous solutions.

In the course of the work, we obtained data on the quantum yields of active radicals, the rate constants of their reactions with the target compound, and optical properties of the secondary organic radicals formed [2]. The conditions allowing one to achieve complete degradation of not only p-ASA, but also its main aromatic photoproducts are determined. It is shown that under these conditions mainly inorganic arsenic As(V) is formed, which can then be removed by known sorption methods. The data obtained is important for understanding the effectiveness of photodegradation of p-ASA under UV irradiation in water treatment processes using the abovementioned additives.

Acknowledgements: the work was financially supported by the Russian Science Foundation (grant No. 21-43-00004).

[1] Jones F.T. (2007). *Poult. Sci., 86*, 2–14.
[2] Tyutereva Yu. E et al. (2021). *J. Photochem. Photobiol. A: Chem., 420*, 113507.

Photochemistry of $[IrCl_6]^{3-}$ Complex in Aqueous Solutions

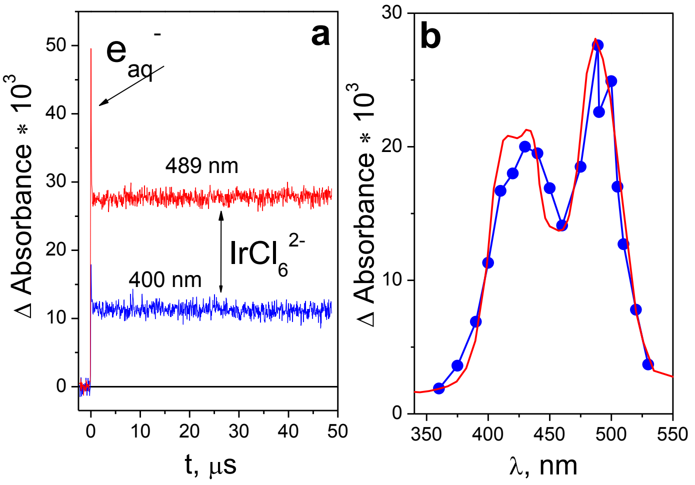
✉ **Grigory I. Zhdankin**[1,2], **Vjacheslav P. Grivin**[1], **Victor F. Plyusnin**[1,2], **Evgeni M. Glebov**[1]

[1] Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2] Novosibirsk State University
Novosibirsk, Russia

✉ g.zhdankin@g.nsu.ru

Areas of light-activated platinum metal complexes are solar energy, conversion, photocatalysis, molecular machine development, antitumor therapy (photochemotherapy, PCT). Therefore, for their successful application, a comprehensive and detailed knowledge of the photophysical and photochemical mechanisms of processes is necessary. In this work we report the first study of $[IrCl_6]^{3-}$ photochemistry in aqueous solutions by means of stationary and laser flash photolysis (266 nm, 5 ns).

In the laser flash photolysis experiment we observed photoionization of $[IrCl_6]^{3-}$ with the formation of an aquated electron and $[IrCl_6]^{2-}$ complex having characteristic absorption in the visible spectral range (Figure).



Laser flash photolysis (266 nm) of $[IrCl_6]^{3-}$ in H_2O (5×10^{-4} M, 1 cm cell, air-saturated solutions). *a*— examples of kinetic curves, *b*— intermediate absorption spectrum (blue dots and line) and normalized $[IrCl_6]^{2-}$ spectrum (red line)

However, in the stationary photolysis experiments we did not observe formation of $[IrCl_6]^{2-}$. The resulting photochemical process was photoaquation. It means that two-quantum processes were responsible for the photoionization in the laser flash photolysis experiments. The study of photolysis mechanism is in progress.

Acknowledgements: the work was supported by the Russian Science Foundation (grant No. 22-33-00248).

Correlation between the Reactivity and Selectivity of Low-Spin and High-Spin Oxo-Iron(V) Complexes in the Oxidation of (+)-Sclareolide

✉ **Alexandra M. Zima, Dmitrii E. Babushkin,**
Oleg Y. Lyakin, Konstantin P. Bryliakov, Evgenii P. Talsi

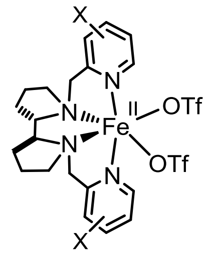
Boreskov Institute of Catalysis SB RAS

Novosibirsk, Russia

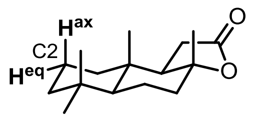
✉ zima@catalysis.ru

The milestone discovery of the Fe(PDP)-type catalyst system [1] has been an inspiration for the subsequent progress of bioinspired catalyst systems for C=C and C–H oxidation of complex organic molecules [2]. In recent years, the main mechanistic peculiarities of catalyst systems based on non-heme Fe complexes with aminopyridine ligands, including the key role of perferryl intermediates, have been reliably established. However, disclosing the correlations between the electronic structure (and spin state) of key perferryl intermediates and their selectivity profile remains the subject of experimental and theoretical studies.

Notably, while perferryl intermediates in the Fe(PDP)-based catalyst systems exhibit clear "reactivity-selectivity" relationship in the enatioselective epoxidation of olefins [3], such correlations in C–H oxidation reactions have been elusive until recently. Herewith, we report on the first example of "reactivity-selectivity" correlation in Fe(PDP) catalyzed C–H oxidation of (+)-sclareolide (**S**).



X = H, EWG, EDG
Fe(PDP) (X = H)



(+)-sclareolide (**S**)

The catalyst systems exhibiting the most reactive oxoiron(V) intermediates in the series, have been found to display the lowest (51–55 %) C2 oxidation regioselectivity (to yield alcohol and ketone, $\mathbf{S}^{2(eq)\text{-}OH}$ and $\mathbf{S}^{2=O}$). Contrastingly, the systems featuring the least reactive intermediates, exhibit the highest C2 oxidation regioselectivity (64–65 %). The chemoselectivity of C2 oxidation, assessed by the $\mathbf{S}^{2(eq)\text{-}OH}/\mathbf{S}^{2=O}$ ratio, also increases with decreasing reactivity of the oxoiron(V) intermediates (from 1.6 up to 5.0). These results demonstrate that besides steric effects, electronic effects may play an important role in directing the C-H oxidation chemo- and regioselectivity, which should be taken into account when designing biomimetic catalyst systems for late-stage oxidation of complex substrates of natural origin.

Acknowledgements: the work was financially supported by the Russian Science Foundation (grant No. 22-13-00225).

[1] Chen M. S., White M. C. (2007). *Science*, *318*(5851), 783–787.
[2] Vicens L., Olivo G., Costas M. (2020). *ACS Catal.*, *10*(15), 8611–8631.
[3] Zima A. M., Lyakin O. Y., Bryliakov K. P., Talsi E. P. (2019). *Chem. Cat. Chem.*, *11*(21), 5345–5352.

CHEMICAL PHYSICS IN BIOLOGY AND MEDICINE

Electron and Energy Transfer Processes in Linked Systems with Chiral Drugs. Spin Chemistry and Photochemistry Investigation

✉ **Aleksandra A. Ageeva**[1,2], **Ilya M. Magin**[1,2], **Alexander B. Doktorov**[1], **Victor F. Plyusnin**[1,2],
Alexander A. Stepanov[1], **Nikolay E. Polyakov**[1], **Tatyana V. Leshina**[1]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ al.ageeva@gmail.com

Photoinduced elementary processes in chiral linked systems consisting of drugs and tryptophan (Trp) residues attract considerable attention due to several aspects. Firstly, these models allow one to trace full and partial charge transfer underlying the binding of drugs to enzymes and receptors. On the other hand, Trp fluorescence is widely used to establish the structure and conformational mobility of proteins due to its high sensitivity to the microenvironment. Therefore, the study of mechanisms of Trp fluorescence quenching in various systems has both fundamental and practical interest. In order to study the elementary processes, in this work the model systems are studied, including (S)- and (R)-ketoprofen (KP) bound to the amino acid Trp using fluorescence spectroscopy and CIDNP techniques. According to the data in literature, two mechanisms of Trp fluorescence quenching in biomolecules are possible: electron transfer (ET) and singlet-singlet energy transfer (SSET). The analysis of the CIDNP effects of KP-Trp diastereomers indicates an intramolecular ET between the Trp donor in the singlet excited state and the KP acceptor in the ground state.

In this work, we made an attempt to estimate the contribution of the processes of ET and SSET in dyad diastereomers using the CIDNP effects and fluorescence quenching. Assuming that the fraction of the ET channel in diastereomers is proportional to the ratio of CIDNP enhancement coefficient, and using the radical pair theory, modified by Prof. Doktorov, we estimated the concentration ratio of biradical-zwitterions BZ(SS)/BZ(RS) to be 7.5. The analysis of the fluorescence spectra of diastereomers indicates stereoselective quenching of Trp in the dyad, and the ratio of fluorescence quenching constants (S,S)/(R,S) is 2. This suggested that the (R,S)-diastereomer is predominantly quenched by the SSET mechanism, while the ET contribution is more significant for the (S,S)-diastereomer. Quantum-chemical calculations of distances between the chromophores in diastereomers, as well as the experimental 1D NOE data, showed that shorter distances are typical for the (R,S)-diastereomer. Thus, it was shown that the stereoselectivity of ET and SSET can be due to both differences in distance between partners and orientation of the transition dipole moments of KP and Trp in diastereomers of the dyad.

Acknowledgements: the work was supported by the Russian Science Foundation (project No. 18-13-00047).

Lanthanide Complexes with Lipids as Non-Linear NMR Sensors of the Local Temperature Due To Both Paramagnetic Lanthanide-Induced Shifts and Relaxation Rates

✉ **Sergei P. Babailov**[1,2], **Olga Yu. Selyutina**[2]

[1]Nikolaev Institute of Inorganic Chemistry SB RAS
Novosibirsk, Russia
[2]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ babajlov@niic.nsc.ru

NMR techniques have previously been used to determine physical and chemical properties of paramagnetic lanthanide (Ln) compounds in "pure" homogeneous aqueous and organic solutions {these systems are characterized by a linear dependence of paramagnetic lan-thanide-induced shifts (LISs, ΔδLIS) on 1/T} [1]. In this study, we investigated the temperature dependences of paramagnetic lanthanide-induced shifts (LISs, ΔδLIS) and of the transverse relaxation rate enhancements (TRRE, R2) of signals in such heterogeneous medium as liposomes {in complex systems of phospholipids POPC, DPPC, DMPC, and DOPC with Ln cations}. It was established by NMR that the dependence of LIS on 1/T is conditionally fragmented into several segments with different slope angles (which corresponds to reorganization of the structure of complexes due to phase transitions in micelles). The obtained results indicate that Ln complexes with phospholipids can be used as tunable non-linear temperature sensitive probes for local temperature determination and advanced disease diagnostics using the NMR/MRI "shifting" technologies [2].

Temperature dependence of TRRE was measured using the examples of unsaturated POPC lipid and saturated DPPC and DMPC lipids. It was demonstrated that for unsaturated POPC lipid viscosity do not depend on the temperature. In addition, for DPPC and DMPC lipids viscosity do not depend on the temperature below phase transition temperature, but near the phase transition temperature a dramatic increase of viscosity was observed {according to the Curie—Spin contribution to the paramagnetic TRRE}. The obtained results show that Ln-phospholipid complexes could be used as non-linear sensors for determining local viscosity and temperature of a lipid membrane using the NMR/MRI relaxational technologies.

Acknowledgements: the work was supported by the Russian Science Foundation (research project No. 20-63-46026).

[1] Babailov S. P. (2022). *Progr. Nucl. Magn. Reson. Spectr.*, *52,* 1–21.
[2] Selyutina O. Yu., Kononova P. A., Babailov S. P. (2020). *New J. Chem.*, *44*, 18378–18372.

Trityl Radicals as Spin Labels and Spin Polarizing Agents in Dynamic Nuclear Polarization

✉ **Elena G. Bagryanskaya**, **Victor M. Tormyshev**

Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS
Novosibirsk, Russia

✉ egbagryanskaya@nioch.nsc.ru

The distance distribution information obtained by means of pulsed dipolar EPR spectroscopy provides an important contribution to many studies in structural biology. Increasingly, such information is used in integrative structural modeling where it delivers unique restraints on the width of conformational ensembles [1]. Application of pulsed dipolar EPR spectroscopy is only possible when the spin labels based on nitroxides, triarylmethyl (TAM) radicals, copper or gadolinium complexes are used. During the last years, several new approaches for the application of pulsed dipolar EPR spectroscopy were developed: highly stable nitroxide spin labels for in-cell measurements, TAM spin labels with narrow linewidths which increase sensitivity [2], and high-field ENDOR spectroscopy in W-band for pairs of triarylmethyl and fluorine labels [3].

The review of the synthesis of TAM spin probes [2] and their application to distance measurements of the membrane proteins in *E. coli* using Finland and OX063 trityl labels [4; 5] and studding protein aggregates [6]. In addition, recently TAM-based biradicals have been used for quantum computer experiments [8] and as spin agent for Dynamic Nuclear Polarization [9].

Acknowledgement: This research was supported by the Russian Science Foundation (No. 21-14-00219).

[1] Schiemann O. et al. (2021). *J. Am. Chem. Soc., 143*(43), 17875–17890.
[2] Tormyshev V. M., Bagryanskaya E. G. (2021). *Russian Chemical Bulletin*, *12*, 2278–2297.
[3] Asanbaeva N. B. et al. (2022). *Phys. Chem. Chem. Phys., 24(10)*, 5982–6001.
[4] Joseph B. et al. (2021). *Chemistry - A Europ. Journ., 27*, 2299–2304.
[6] Ketter S. et al. (2022). *J. Magn. Reson. Open*, *10-11*, 100041.
[7] Bretschneider M. et al. (2020). *Journ. Phys. Chem. Lett. 11*(15), 6286–6290.
[8] Sato K. et al. (2019). *The Journal of Physical Chemistry A*, *123*(34), 7507–7517.
[9] Bothe S. et al. (2018). *J. Phys. Chem. C*, *122*(21), 11422–11432.

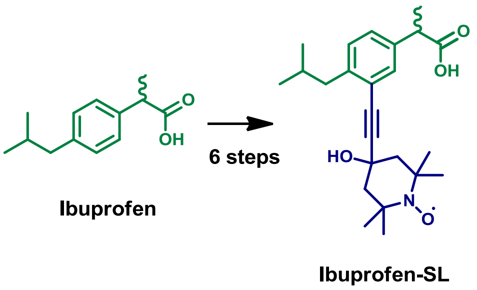
Preparation of Spin-Labeled Ibuprofen and Its Interaction with 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine Bilayer

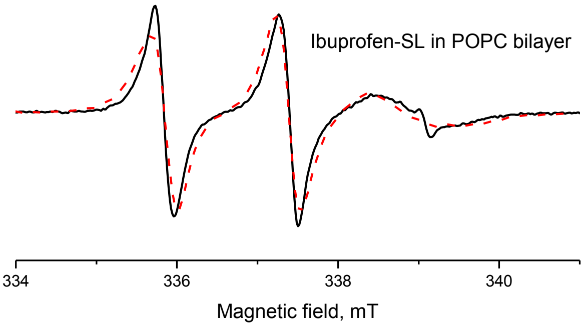
✉ **Denis S. Baranov, Anna S. Smorygina, Sergei A. Dzuba**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ baranov@kinetics.nsc.ru

Ibuprofen, along with aspirin and paracetamol, is the most significant non-steroidal anti-inflammatory drug, which in various dosage forms is widely used as an analgesic and antipyretic drug. For studying its interaction with biological membranes and protein using the EPR spectroscopy, the synthesis of its spin-labeled analog would be desirable. Here, a simple sequence of transformations of ibuprofen, such as nitration, esterification, reduction, Sandmeyer reaction, Sonogashira cross-coupling, oxidation and saponification was developed for the synthesis of spin-labeled ibuprofen. The spin label TEMPOL in spin-labeled ibuprofen is attached to the benzene ring. The EPR spectra of spin-labeled ibuprofen showed its interaction with 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine bilayer. Using the ^2H electron spin echo envelope spectroscopy, it was shown that spin-labeled ibuprofen is embedded into the hydrophobic bilayer interior.





Acknowledgements: the research was performed under the financial support of the Russian Science Foundation (grant no. 21-13-00025).

Nuclear Spin Dependent Enzymatic Synthesis of ATP in Strong Magnetic Fields

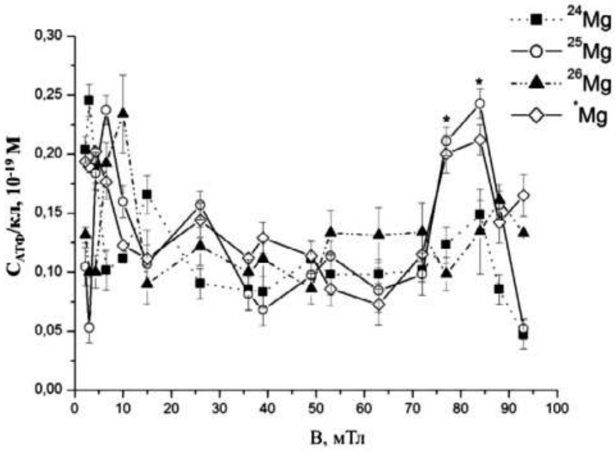
✉ **Vitaliy Berdinskiy, Elina Kaepkulova, Ulyana Letuta**

Orenburg State University
Orenburg, Russia

✉ vberdinskiy@yandex.ru

The synthesis of ATP (adenosine triphosphate—the main source of energy in all living organisms) proved to be a ^{25}Mg nuclear spin dependent process *in vitro* and *in vivo* [1–4].

The well-known HFI mechanism of a singlet-triplet conversion of ion-radical pairs is able to explain the magnetic field dependencies of ATP synthesis in low magnetic fields. However, it is unable to explain those in strong magnetic fields B ~ 80 mT. To explain these effects, a new model and a theory of S-T conversion for equivalent electron spins interacting with a nuclear spin was proposed. This S-T conversion has shown to be inevitably accompained by the redistribution of charge density decreasing Coulomb repulsion of interacting particles. Theoretical results qualitatively coincide with the experimental ones for the ATP production in bacterial cells *Escherichia coli*.



Magnetic field dependences of intracellular ATP content in *E. coli* bacteria grown on the M9 medium with magnesium isotopes ^{24}Mg, ^{25}Mg, ^{26}Mg and natural magnesium Mg. The data is given per cell. The range of magnetic fields is 0.8–98 mT

[1] Buchachenko A. L. (2009). *Magnetic Isotope Effect in Chemistry and Biochemistry.* Nova Science Publishers, New York.

[2] Buchachenko A. L. (2014). *Magneto-Biology and Medicine.* Nova Science Publishers, New York.

[3] Letuta U. G., Avdeeva E. I. (2017). *Doklady Biochemistry and Biophysics*, *474*, 196–200.

[4] Letuta U. G., Berdinskiy V. L., Udagawa C., Tanimoto Y. (2017). *Bioelectromagnetics*, *38*, 511–518.

[5] Letuta U. G. (2021). *Archives of Microbiology*, *203.5*, 1853–1861.

Double Electron-Electron Resonance of Molecular Clusters in Biological Membranes

✉ **Sergei A. Dzuba**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉ dzuba@kinetics.nsc.ru

Double electron-electron resonance spectroscopy (DEER, also known as PELDOR) is sensitive to spin-spin dipolar interactions between spin labels at the nanoscale range of distances. Most often, DEER is applied to study distances between two spin labels attached to the same molecules. Here, we report the results of DEER studies of nano-clusters containing large number of molecules; such clusters naturally appear in biological membranes.

Plasma membrane is known to be highly compartmentalized, with lipids and proteins organized in specific domains (so-called lipid rafts), and with cholesterol (Chol) as an important constituent. Lipid rafts are assumed to be involved in different cellular processes, such as signal transduction, membrane trafficking, and protein activity. DEER was applied here to spin-labeled cholestane 3β-doxyl-5α-cholestane (DChl), which structure resembles that of Chol. DChl was diluted in bilayers comprised of saturated dipalmitoyl-glycero-phosphocholine (DPPC) and unsaturated dioleoyl-glycero-phosphocholine (DOPC) phospholipids, with Chol added in different proportions. The DEER data was described in terms of enhanced local concentrations which allowed us to detect clustering of DChl molecules. Lateral distribution in the clusters was found to change drastically with Chol content: in absence of Chol the DChl molecules are randomly distributed in the clusters, while in presence of Chol the distribution becomes quasi-regular. The found superlattice parameter was 3.7 nm. The found regularity of DChl lateral distribution was interpreted by raft sub-structuring, with DChl molecules embedded between the substructures.

Free fatty acids play various roles in biological membranes. Their functioning depends on intermolecular interactions. DEER was applied to study spin-labeled stearic acids in gel-phase phospholipid bilayers composed of DPPC/DOPC mixtures or of palmitoyl-oleoyl-glycero-phosphocholine (POPC) lipids. The results showed that in all cases stearic acids are assembled into the lipid-mediated lateral clusters with a characteristic intermolecular distance of ~2 nm. On presence of antimicrobial peptides (AMP) the lateral distribution in clusters was found to change, which indicates the AMP impact on the lateral lipid organization in membranes.

Acknowledgements: this work was supported by the Russian Science Foundation (grant No. 21-13-00025).

In Vitro Studies of Antidiabetic Potential of Nitrosyl Iron Complex with Thiosulfate Ligands

✉ **Irina I. Faingold[1], Yuliya V. Soldatova[1], Anastasia V. Smolina[1],**
Darya A. Poletaeva[1], Nataliya A. Sanina[1,2]

[1] Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia
[2] Medicinal Chemistry Research and Education Center, Moscow Region State University
Mytishchy, Russia

✉ ifaingold@mail.ru

The widespread prevalence of type 2 diabetes mellitus (T2DM) and the lack of effective therapy determine the relevance of this study, making the task of finding effective antidiabetic agents one of the most important for medicinal chemistry. Modern clinical drugs for the T2DM treatment have a symptomatic effect, exhibit serious side effects, their long term use leads to resistance; thus, a combination therapy and individual selection of drugs are required. Many biological systems are involved in the pathogenesis and progression of T2DM. Therefore, the most promising approach to the development of effective drugs for the treatment of T2DM is the search for pharmacologically active compounds that are selective for a complex of therapeutic targets of T2DM: oxidative stress, non-enzymatic glycosylation of proteins, and the polyol pathway of glucose metabolism. This approach is one of the most topical for modern medicinal chemistry.

In this work, we studied the iron nitrosyl complex with thiosulfate ligands $Na_2[Fe_2(S_2O_3)_2(NO)_4]\cdot 4H_2O$ (complex 1) synthesized in the Laboratory of Structural Chemistry IPCP RAS. Binuclear dinitrosyl iron complexes with functional sulfur-containing ligands are structural synthetic analogs of the active center of non-heme iron-sulfur proteins; they are considered to be natural reservoirs of nitric oxide (NO). Due to their ability to donate NO without additional activation under physiological conditions, these compounds are of considerable interest for the development of potential antidiabetic drugs. Antidiabetic effect of complex 1 was carried out in an *in vitro* study. It was found that complex 1 acts on the therapeutic targets of T2DM: it inhibits the processes of lipid peroxidation (IC_{50} = 0.4 mM) and non-enzymatic glycosylation of albumin protein (IC_{50} = 47.4 ± 7.6 μM), also reduces the catalytic activity of the aldose reductase: enzyme of the polyol pathway of glucose metabolism ($K_i = 5.25\cdot 10^{-4}$ M). We present for the first time that one of the mechanisms of the antioxidant action of complex 1 is its ability to scavenge free radicals due to NO donation. The data obtained indicate the prospects for further study of iron nitrosyl complexes in order to create a new class of effective drugs for treatment of T2DM and its complications.

Acknowledgements: the study of antidiabetic potential of complex 1 was supported by the Russian Science Foundation (project No. 22-24-00764). Synthesis of the nitrosyl iron complex with thiosulfate ligands was supported by the State Task (No. AAAA-A19-119071890015–6).

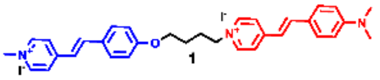
Sensing of Nucleic Acid and Associated Cellular Components with Organic Fluorescent Chemosensors

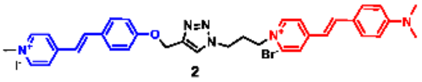
✉ **Olga A. Fedorova**[1], **Maria A. Ustimova**[1], **Nelly S. Chmelyuk**[2],
Maxim A. Abakumov[2], **Yuri V. Fedorov**[1]

[1]Nesmeyanov Institute of Organoelement Compound RAS
Moscow, Russia
[2]Pirogov Russian National Research Medical University
Moscow, Russia

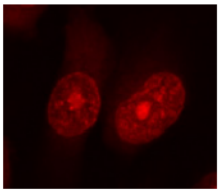
✉ fedorova@ineos.ac.ru

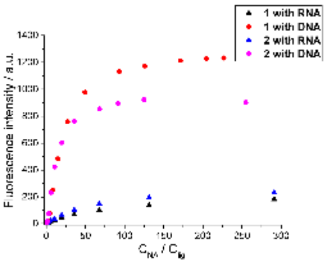
Cyanine dyes in particular styryl dyes exhibit a remarkably high affinity towards nucleic acids along with a significant change in their photophysical properties upon the DNA binding. These properties are used for DNA detection and quantification in a variety of methods and techniques such as the polymerase chain reaction, DNA fragment sizing, DNA staining, DNA damage detection, flow cytometry, and evaluation of biological activity. Although interactions of several styryl dyes with DNA have already been described, only relatively few investigations include sufficient data to deduce the binding modes. In this respect, DNA-binding properties of mono- and bis-styryl dyes were investigated in the presence of calf thymus DNA. To access the factors that influence the DNA association in the series of these ligands, the structure of the molecules was varied by either changing size of the heterocyclic moiety or altering the position of the styryl substituents. The major binding mode for the monostyryl dyes is intercalation, for bisstyryl dyes the interaction with DNA through the minor groove binding was found.

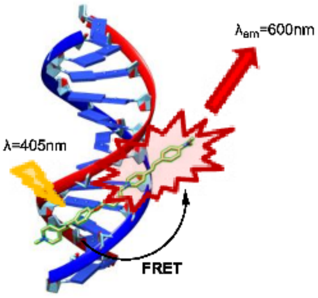




Fixed A549 cells + dye **1**







Recently, we showed that asymmetric bi(styryl) dyes are fluorescence turn-on probes for intracellular DNA/RNA distribution. These fluorogenic dyes possess the properties of highly soluble in water, cell permeable, high photoresistance and not toxic to cells, therefore, being promising dyes for biological and biochemical non-toxic applications.

Acknowledgements: this work was supported by the RSF project № 21-73- 20158.

Salts of Guanine and Xanthine: High-Pressure and Low-Temperature Study

✉ **Anna A. Gaydamaka**[1,2], **Sergey G. Arkhipov**[1,2], **Boris A. Zakharov**[1,2],
Nikita E. Bogdanov[1,2], **Sergey V. Rashchenko**[1,3], **Anna I. Semerikova**[1,3],
Ekaterina S. Smirnova[1,4], **Anna G. Ivanova**[1,4], **Elena V. Boldyreva**[1,2]

[1] *Novosibirsk State University*
Novosibirsk, Russia
[2] *Boreskov Institute of Catalysis SB RAS*
Novosibirsk, Russia
[3] *Sobolev Institute of Geology and Mineralogy SB RAS*
Novosibirsk, Russia
[4] *FSRC "Crystallography and Photonics" RAS*
Moscow, Russia

✉ gaydamaka@catalysis.ru

The study of anisotropy in the wide temperature and pressure range can provide information about intermolecular interactions in the structure. Crystals made of small RNA or DNA fragments can serve as models of the effect of pressure on nucleic acids and oligonucleotides, similar to how the crystals of amino acids are used to model proteins. Guanine is remarkable for its unique ability to form assemblies. In particular, the oligonucleotides enriched with guanine can form quadruplexes in the presence of alkali and earth-alkaline metals. Potassium cations are of special biological importance because they form natural quadruplexes, which are present in telomeric parts of the chromosome. In this contribution $2Na^+\cdot C_5H_3N_5O^{2-}\cdot 7H_2O$ was characterized by single-crystal X-ray diffraction in the pressure range of 1 atm — 2.5 GPa [1], as well as in the temperature range 100–300 K; $K^+\cdot C_5H_4N_5O^-\cdot H_2O$ was characterized by the single-crystal X-ray diffraction in the pressure range of 1 atm — 7 GPa, as well as in the temperature range 100–300 K [2]; $Li^+\cdot C_5H_3N_4O_2^-\cdot 2H_2O$ was characterized by the single-crystal X-ray diffraction and Raman spectroscopy in the pressure range of 1 atm — 5.5 GPa. ThetaToTensor software was used to calculate the coefficients of thermal expansion tensors and compressibility tensors and to represent graphically characteristic surfaces of tensors [3]. The anisotropy of strain on temperature and pressure variations was compared, the similarities and the differences are discussed concerning the intermolecular interactions.

Acknowledgements: the research was supported by the project AAAA-A21-121011390011-4 and program "Priority2030" (NSU). The equipment of REC MDEST (NSU), PETRA-III (Hamburg), and advanced laboratory diffractometer XtaLAB Synergy-DW (FSRC "Crystallography and Photonics" RAS). was used.

[1] Gaydamaka A. et al. (2019). *Cryst. Eng. Comm.*, *21*, 4484–4492.
[2] Gaydamaka A. et al. (2021). *Acta Crystallographica Section B*, *77*, 808–818.
[3] Bubnova R. S., Firsova V. A., Filatov S. K. (2013). *Glass Physics and Chemistry*, *39*(3), 347–350.

Reduction-Resistant Nitroxides

✉ **Igor A. Kirilyuk**

Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS
Novosibirsk, Russia

✉ kirilyuk@nioch.nsc.ru

Nitroxide spin probes and spin labels are broadly applied in biophysical and biomedical researches. Natural antioxidants and enzymatic systems may reduce nitroxides to diamagnetic compounds [1]. These undesired reactions may complicate the EPR studies of biological samples using nitroxides. Some modern research areas, such as in-cell EPR/PELDOR measurements and *in vivo* NMR and EPR imaging, require especially high stability of the paramagnetic agent. Introduction of several bulky alkyl substituents larger than methyl group to α-carbons of nitroxyl group is a fruitful approach to increase the resistance of nitroxides to reduction. Some of these so-called sterically shielded (or sterically hindered) nitroxides demonstrate more than two orders of magnitude lower decay rates in the presence of ascorbate than similar tetramethyl-substituted nitroxides [2]. Their lifetimes in tissue homogenates may exceed those of triarylmethyl (TAM) radicals.[3]

Impressive progress in molecular design and synthesis of new sterically shielded nitroxides was achieved in the recent few years, and redox properties of the new nitroxides were studied [4–7]. Alternative mechanisms of decay of sterically shielded nitroxides in biological systems are discussed. The peculiarities of the EPR spectra were shown, and the nature of additional hyperfine splitting was investigated. Some examples of application of sterically shielded nitroxides are given.

[1] Kocherginsky N., Swartz H. (1995). *Nitroxide Spin Labels: Reactions in Biology and Chemistry*. Boca Raton, FL: CRC Press.

[2] Paletta J. T. et al. (2012). *Org. Lett.*, *14*, 5322–5325.

[3] Jagtap A. P. et al. (2015). *Free Radical Res.*, *49*, 78–85.

[4] Dobrynin S. A. et al. (2018). *J. Org. Chem.*, *83*, 5392–5397.

[5] Dobrynin S. A. et al. (2021). *Molecules*, *26*(19), 5761.

[6] Zhurko I. F. et al. (2020). *Molecules*, *25*(4), 845.

[7] Taratayko A. I. et al. (2012). *Molecules*, *27*(6), 1922.

Nuclear Spin Catalysis in Biochemical Reactions Driven by Biomolecular Motors

✉ **Vitaly K. Koltover**

Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia

✉ koltover@icp.icp.ac.ru

The magnetic isotope effect (MIE) was discovered in chemistry about fifty years ago [1]. Not long ago, MIEs were discovered in living nature, in the experiments with cells enriched with different isotopes of magnesium [2]. Furthermore, the catalytic MIEs were discovered in the experiments with myosin, the most important molecular motor of bioenergetics utilizing the energy of ATP to perform mechanical work. The rate of enzymatic hydrolysis of ATP in the reaction media enriched with magnetic isotope ^{25}Mg is twice as high as it is in the reaction media enriched with the nonmagnetic isotope ^{24}Mg or ^{26}Mg. A similar nuclear spin effect was detected in the experiments with zinc as the enzyme cofactor. The rate of the ATP hydrolysis with the magnetic ^{67}Zn increases by 40–50 %, compared to that with the nonmagnetic ^{64}Zn or ^{68}Zn. Similar catalytic effects of the magnetic ^{25}Mg were found in the experiments with H^+-ATPase isolated from yeast mitochondria and Mg-dependent ATPase of the myometrium plasma membrane [3]. The MIE unambiguously indicates that there is a limiting step in the chemo-mechanical process catalyzed by the molecular motors, which depends on the electronic spin state, and this step is accelerated by the nuclear spin of the magnetic isotope. The nuclear spin catalysis may be explained as follows. The energy released from the hydrolysis of ATP (~0.54 eV) is not enough for the electron-conformational transition of the enzyme macromolecule to the singlet excited state. This energy is sufficient for a transition to the lower triplet state (S = 1), but such transition from the ground state (S = 0) is prohibited by the spin conservation law. The nuclear spin of isotope removes this forbiddance, thereby accelerating the chemo-mechanical cycle in the enzymatic reaction. Detailed mechanisms of MIE in living cells and enzymatic reactions need further investigation.

Acknowledgements: the work was supported by the Ministry of Science and Higher Education of Russian Federation (No. AAAA-A19-119092390041-5).

[1] Buchachenko A. L., Sagdeyev R. Z., Salikhov K. M. (1978). *Magnetic and Spin Effects in Chemical Reactions.* Nauka, Novosibirsk. (in Russ.)

[2] Avdeeva L. V., Koltover V. K. (2016). *Moscow Univ. Chem. Bull.*, *71*, 160–166.

[3] Koltover V. K. (2021). *Russ. Chem. Bull.*, *70*, 1633–1639.

Multielemental (Boron, Gadolinium) Nanobiocomposites for Multichannel Theranostics

Tatyana V. Kon'kova[1], **Nadezhda V. Klushina**[1], **Igor D. Evseev**[2], ✉ **Boris G. Sukhov**[1]

[1] Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2] Novosibirsk State University
Novosibirsk, Russia

✉ boris_sukhov@mail.ru

A methodology for the synthesis of hybrid inorganic-organic nanobiocomposites, which are various multielement inorganic nanoparticles (with a complex of neutron-capturing, magnetic, photoactive, and other properties) encapsulated in biotargeted polymer macromolecules, is being developed [1–6].

The nanobiocomposite with a complex of magnetic and potentially neutron-capturing properties was synthesized. This composite is gadolinium borate nanoparticles encapsulated in Siberian larch arabinogalactan macromolecules which can pass through the blood-brain barrier.

Thus, the resulting nanocomposite is a promising tool for multichannel theranostics (contrast-enhanced magnetic resonance imaging, neutron-stimulated gamma-tomography, magnetic hyperthermia, dual boron, gadolinium neutron capture therapy), including brain tumors.

[1] Trofimov B. A., Sukhov B. G. et al. (2003). Nanocomposites with Magnetic, Optical, Catalytic and Biologically Active Properties Based on Arabinogalactan. *Doklady Chemistry*, *393*, 287–288.

[2] Trofimov B. A., Sukhov B. G. et al. (2007). Pd(0)-Arabinogalactan Nanocomposites As Catalysts For Dimerization Of Acetylenic Compounds. *Doklady Chemistry*, *417*, 261–263.

[3] Myachina G. F., Korzhova S. A. et al. (2009). Nanocomposites of Silver and 1-vinyl-1,2,4-triazole Copolymer with Sodium Methacrylate. *Doklady Chemistry*, *427*, 199–201.

[4] Myachina G. F., Kon'kova T. V. et al. (2010). Gold Nanoparticles Stabilized with Water-Soluble Biocompatible Poly(1-vinyl-1,2,4-triazole). *Doklady Chemistry*, *431*, 63–64.

[5] Petrova M. V., Kiryutin A. S. et al. (2011). A Theoretical and Experimental Study of NMR Contrasting Properties of Nanocomposites Based on Ferric Oxides Stabilized by Arabinogalactan Matrix. *Appl. Magn. Res.*, *41*, 525–536.

[6] Lesnichaya M. V., Sukhov B. G. et al. (2017). Chiroplasmonic Magnetic Gold Nanocomposites Produced by One-Step Aqueous Method Using K-carrageenan. *Carbohydr. Polym.*, *175*, 18–26.

Interactions of the Antiviral Drug Glycyrrhizin and Coronavirus E-Protein with Membrane Mimetics by Solution NMR Studies

✉ **Polina A. Kononova** [1,2], **Olga Yu. Selyutina** [2], **Nikolay E. Polyakov** [2]

[1] *Novosibirsk State University*
Novosibirsk, Russia
[2] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia

✉ kononova_polina@bk.ru

Glycyrrhizin is the main active component in licorice root. Liquorice root is a popular medicinal herb with nutritional and therapeutic values. There is a lot of data on its antiviral activity, including activity against the SARS-coronavirus [1]. The mechanism of its antiviral action remains unclear. One of the possible mechanisms of the antiviral action of glycyrrhizin against COVID-19 is also considered to be the prevention of fusion of the virus envelope with the plasma membrane of the host cell [2]. E-protein inhibition reduces viral pathogenicity, suggesting that E-protein is a potential antiviral target [3]. The role of E-protein in functioning and pathogenesis of coronaviruses in general and SARS-CoV-2 in particular is unclear. The hypothesis of a targeted effect of glycyrrhizin on the coronavirus E-protein was tested.

The interaction of glycyrrhizin with model lipid membranes was studied by the NMR method. Bicelles DMPC/DHPC (molar ratio 1:2, $q = 0.5$) was used as a membrane mimetic. The Nuclear Overhauser Effect NMR spectroscopy (NOESY) was used to determine the localization of glycyrrhizin molecules in lipid bilayer. The transmembrane domain of SARS-CoV-2 E-protein (ETM) was used to study lipid-mediated effect of glycyrrhizin on viral proteins. Localization of ETM in lipid bilayer was also studied by the NOESY technique.

The experiments have shown the presence of interaction between glycyrrhizin and the transmembrane domain of the SARS-CoV-2 E-protein. Also, it was possible to observe the incorporation of E-protein into the membrane mimetics.

Acknowledgements: this work was financially supported by the Council on Grants of the President of the Russian Federation (Project No. MK-1580.2021.1.3).

[1] Chrzanowski J., Chrzanowska A., Graboń W. (2021). Glycyrrhizin: An Old Weapon Against a Novel Coronavirus. *Phytother Res., 35*(2), 629–636.

[2] Selyutina O. Y. et al. (2021). Effect of Glycyrrhizic Acid on Phospholipid Membranes in Media with Different pH. *Russ Chem Bull*, *70*(12), 2434–2439.

[3] Mandala V. S. et al. (2020). Structure and Drug Binding of the SARS-CoV-2 Envelope Protein Transmembrane Domain in Lipid Bilayers. *Nat. Struct. Mol. Biol.*, *27*(12), 1202–1208.

Lipid Peroxidation Processes Involving Thiosemicarbazones

✉ **Vladimir E. Koshman**[1,2], **Ekaterina A. Shelepova**[1,2],
Olga Yu. Selyutina[2], **Nikolay E. Polyakov**[2]

[1] *Novosibirsk State University*
Novosibirsk, Russia
[2] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia

✉ kosmanvova2010@mail.ru

Thiosemicarbazones (TSCs) have a wide range of biological activities, including anticancer, and are of great interest to scientists from various fields of science. Their anticancer activity has long been attributed to their ability to inhibit ribonucleotide reductase. However, recent studies indicate a significant role of oxidative stress in the anti-tumor activity of TSCs. This aspect of their biological activity is currently very poorly understood and is of great interest for medicinal chemistry [1].

In this work, the processes of lipid peroxidation involving chelate complexes with iron and copper ions were studied using the thiosemicarbazones di-2-pyridylketone-4,4-dimethyl-3-thiosemicarbazone (Dp44mT), di-2-pyridylketone 4-cyclohexyl-4-methyl-3-thiosemicarbazone (DpC) and novel thiosemicarbazone AOBP as examples. The interaction of chelate complexes with the lipid bilayer and their role in the lipid peroxidation reaction were studied on model systems by ^{1}H NMR methods and molecular dynamic simulation using GROMACS software.

Experiments were performed in model systems (linoleic acid micelles and DHPC/DLPC bicelles). The redox properties of Dp44m, DpC, and AOBP complexes with iron and copper in the lipid peroxidation reaction and the role of the natural antioxidant ascorbic acid in this process were studied. The interaction of TSCs complexes with the lipid membrane was also studied. It was found that complexation of Dp44mT with iron almost completely inhibits the peroxidation reaction, while complexes with copper retain oxidative activity. At the same time, in the presence of ascorbic acid, the activity of Dp44mT complexes with iron significantly increases. It was revealed that the complexation of Dp44mT with iron ions inhibits the formation of the OH-radical in the Fenton reaction. In the presence of ascorbic acid, OH-radical formation was observed. The increase in the oxidative activity of Dp44mT complexes with iron ions in the presence of ascorbic acid is due to the cyclic oxidative-reductive reaction with Dp44mT complexes. Complexation of iron with DpC also inhibits lipid peroxidation.

[1] Lu B., Chen X. V., Ying M. D., He Q. J., Cao J., Yang B. (2018). *Frontiers in Pharmacology*, *8*, 992.

Perylene-(Cyanine Dye) Dyad as NIR Agent for Theranostics

✉ **Alexey V. Kozlov**[1], **Daria V. Revina**[1,2], **Lev R. Sizov**[1],
Alexander Yu. Rybkin[1], **Nikolai S. Goryachev**[1,2]

[1] Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia
[2] Lomonosov Moscow State University
Moscow, Russia

✉ lexsetlex@gmail.com

Oncological diseases remain one of the most major medical and social problems that requires the development of highly effective methods of therapy. One of such methods is photodynamic therapy (PDT) that has been used in clinical practice for more than 30 years and has shown its high effectiveness. However, photosensitizers (PS) used in modern clinical practice for PDT, have a number of disadvantages that do not allow one to fulfill the full potential of this method. In recent years, there has been a significant increase in interest in the creation of PSs that implement photodynamic action by generating various radical forms (the so-called type I PDT mechanism), instead of singlet oxygen (type II PDT mechanism). From this point of view, the creation of type I PSs based on organic donor-acceptor structures is the most promising. For example, fullerene-dye dyads have been studied as a potential type I PSs [1; 2].

In the present work, we synthesized covalently-linked dyad of a non-fullerene acceptor—perylenediimide (PDI) with cyanine dye IR780. The structure was confirmed by the ^{1}H NMR, H-H COSY NMR and HRMS spectra.

It was shown that the dye and acceptor in the obtained structure have small influence on each other, which is expressed in the low efficiency of fluorescence quenching of the dye moiety and the absence of changes in the absorption spectra of each moiety of the dyad. Although we observed a fluorescence signal from IR780 (in the region > 780 nm) upon excitation in the blue region (~490 nm), no fluorescence was detected for the native dye IR780 in the same conditions. We believe the observed signal is caused by the Förster energy transfer mechanism from the photoexcited PDI to IR780 moieties. It is shown that the dyad practically does not form singlet oxygen upon excitation in the NIR region of the spectrum; however, at the same time, its ability to generate superoxide anion-radical increases significantly compared to the native dye IR780. Thus, the observed increase of the superoxide generation efficiency and high fluorescence signal in the NIR region show promising potential of such perylene-(cyanine dye) dyads as agents for theranostics and other biomedical applications.

Acknowledgements: the work was financially supported by the Russian Science Foundation (grant No. 21-73-00274).

[1] Rybkin A. Y. et al. (2020). *Dyes and Pigment*, *180*, 108411.
[2] Kozlov A. V. et al. (2021). *Mendeleev Communications*, *31*, 807–809.

Using Spin Chemistry and Photochemistry in the Chiral Model Systems to Study the Role of D Amino Acids in the Alzheimer's Disease

✉ **Tatyana V. Leshina**[1], **Aleksandra A. Ageeva**[1,2], **Victor F. Plyusnin**[1,2], **Ilya M. Magin**[1,2],
Olga Yu. Selyutina[1], **Nikolay E. Polyakov**[1]

[1]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2]Novosibirsk State University
Novosibirsk, Russia

✉ leshina@kinetics.nsc.ru

Today it is considered established that the occurrence of a number of neurodegenerative diseases, including Alzheimer's disease, is preceded by the replacement of L amino acids with D analogues in vital proteins and peptides [1]. Replacing L amino acids with D analogues for reasons not yet established leads to fatal changes in the structure of proteins: they lose their ability to normally fold and form highly disordered conglomerates, which ultimately block the passage of nerve impulses. These highly disordered oligomers and fibrils cannot be studied by traditional high-resolution NMR and X-ray methods. Therefore, the current trend is to study the nature of differences in proteins with L and D isomers of amino acids by the example of short peptides by the *in silico* methods [1]. This report presents a modification of the abovementioned approach. The modified version is associated with the use of the photoinduced processes in model chiral linked systems—donor-acceptor dyads with L or D residues of tryptophan (Trp) or other donors in order to study the difference between the reactivity of optical isomers in the intramolecular photoinduced electron (PET) or hydrogen atom transfer in the solutions. Quenching of the excited states of isomers with different optical configurations occurs in the dyads, where acceptors are the well-known non-steroidal anti-inflammatory drugs (NSAIDs): (R/S) naproxen and (R/S) ketoprofen. The choice of NSAIDs is not accidental, since the derivatives of these compounds are now being tested as drugs against the Alzheimer's disease. The joint application of spin effects, including those calculated using the modified radical pair theory, fluorescence quenching techniques and molecular modeling demonstrated a real difference in the structure and efficiency of PET in diastereomers with L/D Trp residues. Additionally, a photoinduced chiral inversion that proceeds by a radical mechanism was found. In the light of the problem stated above, it is important that homo diastereomers (S,S) are less prone to chiral inversion than their hetero analogues (R,S). As a result of the study, it was possible to establish some analogies between the processes in model systems and amyloid Aβ42 which is considered the main protein that injures brain cells in the Alzheimer's disease. Thus, the first results give hope that the use of model systems that can be investigated using a number of physical methods is promising for the study of some factors in the Alzheimer's disease.

Acknowledgements: the work was supported by the Russian Science Foundation (18-13-00047).

[1] Raskatov J. A., Teplow D. B. (2017). *Sci. Rep.*, *7*, 12433–12439.

[2] Ageeva A. A., Doktorov A. B., Polyakov N. E., Leshina T. V. (2022). *Int. J. Mol. Sci.*, *23*, 3060–3078.

The Effect of Terahertz Radiation on the Transport Characteristics of Albumin: Binding with Metal Ions

✉ **Eugenia F. Nemova**[1], **Tatyana V. Kobzeva**[2], **Galina G. Dultseva**[2]

[1] *Institute of Laser Physics SB RAS*
Novosibirsk, Russia
[2] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia

✉ endy@ngs.ru

The effects of THz radiation on biological systems are extensively studied over a broad range of biological systems from cell cultures to entire organisms [1]. However, the molecular effects of THz radiation on the molecules of biological significance remain poorly understood yet. In our previous studies, we detected the THz-caused structural rearrangement in albumin molecules that manifested itself in the changes of albumin binding with oxygen, ozone, and nitrogen oxide. Coupling between albumin molecules under aerobic and anaerobic conditions was also found to change, as determined by means of EPR [2]. Since the transport of metal ions (mainly calcium, magnesium and copper) is one of the most biologically significant functions of albumin molecules *in vivo*, in order to reveal the molecular effect underlying the THz-induced changes, in the present work we studied albumin binding with metal ions. We chose to use Ni^{2+}, Cu^{2+} and a larger ion Cd^{2+} as probes to test the steric settings at the binding sites. Bovine serum albumin was deposited as a film on a quartz substrate and irradiated with a THz laser. After albumin interaction with metal ions in solution, the sample was investigated by means of EPR. The parameters of the detected EPR spectra (line width, intensity, hyperfine splitting) were used to quantify the steric conditions for metal ion binding. Binding with cadmium ions was studied by means of high performance liquid chromatography. The detected changes caused by THz irradiation were compared with the results obtained previously for O_2, O_3, NO binding with the albumin. Metal ion binding was also accessed by means of a simple semi-empirical simulation to reveal functional groups that are directly responsible for binding. It has been determined that THz irradiation of albumin molecules partially removes steric hindrance for binding large metal ions, which may lead to significant biological consequences.

[1] Tseilikman V., Komelkova M., Kondashevskaya M. V. et al. (2021). *Int. J. Mol. Sci.*, *22*, 13235.
[2] Nemova E. F., Cherkasova O. P., Nikolaev N. A. et al. (2020). *Biophysics*, *65*, 479–485.

Reduced Nicotinamide Adenine Dinucleotide is the Natural UV Filter of the Bird Eye Lens

✉ **Nataliya A. Osik**[1,2], **Ekaterina A. Zelentsova**[1,2], **Yuri P. Tsentalovich**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Physics department, Novosibirsk State University*
Novosibirsk, Russia

✉ n.osik@tomo.nsc.ru

The most important functions of the human eye lens are focusing light on the retina and absorbing ultraviolet radiation. The latter is achieved by high content of the molecular UV filters—kynurenine and its derivatives. Absorbing ultraviolet light, these metabolites protect the retinal tissue from photoinduced damage and significantly reduce chromatic aberrations. Thus, UV filters in the lens directly affect visual acuity. So far, such compounds have been found only in the lenses of human, some primates, and squirrels. Of great interest is the metabolomic composition of the lens of birds and especially birds of prey which possess a particularly sharp vision. It is known that in the lenses of some birds there is absorption of UVA light (315–400 nm). However, its molecular nature has not been revealed to date, as well as the metabolomic composition of the avian lens tissue has not been studied.

The purpose of the present work is to establish the features of the bird lens metabolome responsible for visual acuity. Quantitative metabolomic analysis of the lenses of 11 different bird species, including waterfowl (gulls, grebes) and birds of prey (hawks, shrike), was carried out by ^{1}H NMR spectroscopy. The lenses of black kite and grebes were found to contain unusually high concentrations of nicotinamide adenine dinucleotide reduced (NADH) up to 2.7 μmol per a gram of tissue. The metabolite effectively absorbs UVA radiation, does not form triplet states and other reactive intermediates after photoexcitation, and is extremely photostable. The measured value of the quantum yield of NADH photodegradation was $(1.9 \pm 0.3) \times 10^{-5}$ and $(2.3 \pm 0.4) \times 10^{-5}$ under anaerobic and aerobic conditions respectively. The metabolomic extract of the black kite lens has an intensive absorption band in the UVA region, which is provided by the presence of NADH. While for the bird species, such as marsh harrier and rock dove in the lenses of which no NADH was detected, the absorption of UVA light was not observed at all.

Thus, in the present work, for the first time it was established that NADH is the effective natural UV filter of the avian lens. The presence of a UV filter in the lens can be possibly associated with the reduction of chromatic aberrations and an increase in the quality of bird vision.

Acknowledgements: the project was supported by RSF (No. 21-74-00068).

Investigation of the Antibacterial Action of Silver Nanoparticles after Inhalation Delivery in Laboratory Mice

✉ **Maria E. Plokhotnichenko**[1], **Sergey V. An'kov**[1,2], **Anatoly M. Baklanov**[1],
Evgueniya V. Nefedova[3], **Nikolay N. Shkil**[3], **Sergei V. Valiulin**[1],
Alexandra P. Pyryaeva[1], **Galina G. Dultseva**[1]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Vorozhtsov Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[3] *Siberian Federal Scientific Center of Agro-BioTechnologies RAS*
Krasnoobsk, Russia

✉ mairy-jewel@yandex.ru

According to the data of the World Health Organization, bacterial infections are among 10 main causes of death annually. In particular, this situation is due to the emergence of bacterial resistance to the applied antibacterial medicines. Therefore, special attention is being paid in the recent decade to the development of methods to treat drug resistant infections.

In the present work, we studied the antibacterial action of silver nanoparticles of 10–30 nm in size after their aerosol delivery to laboratory mice. For this purpose, we used an inhalation bench developed at the ICKC SB RAS. The bench includes a generator of dry aerosol particles which operates through ultrasonic spraying of a solution of the substance under investigation, inhalation chambers of "nose-only" and "whole-body" types, as well as measurement equipment—the diffusion aerosol spectrometer DSA-M and optical aerosol spectrometer OSA, providing for the real-time determination of the dose delivered to animals. Silver nanoparticles were generated by ultrasonic spraying of the Agrovit preparation (Vektor-Vita company).

Antibacterial efficiency of the inhalation delivery of silver nanoparticles was studied with the model of sepsis in laboratory mice, caused by bacterial species *Klebsiella pneumonia* and *Staphylococcus aureus*. Inhalation of silver nanoparticles demonstrated excellent curative antibacterial effect. Mice infected with 0.5 mL of bacterial suspension with the concentration of 10^6 CFU/mL receiving no treatment died within the first 24 h, while the mice treated with the aerosol were alive during the whole observation period of 7 days. After 8 h from the introduction of infection, the number of CFU in the blood of animals receiving aerosol treatment was determined to be an order of magnitude lower than in the animals that were not subjected to inhalation.

Acknowledgement: this research was funded by the Russian Science Foundation (project No. 22-23-00921).

Glutathione and Albumin as the Main Blood Components Involved in the Transformation of Nitrosyl Iron Complexes

✉ **Olesya V. Pokidova**[1], **Nina S. Emel'yanova**[1,2], **Alexandra Yu. Kormukhina**[2],
Veronika O. Novikova[1], **Alexander V. Kulikov**[1,2], **Natalia A. Sanina**[1–3]

[1] Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia
[2] Lomonosov Moscow State University
Moscow, Russia
[3] Scientific and Educational Center "Medical Chemistry" of Moscow State Regional University
Mytishchi, Russia

✉ pov@icp.ac.ru

Dinitrosyl non-heme iron complexes (DNICs) are a stable depot of nitrogen monoxide (NO), a signaling molecule involved in the regulation of many physiological processes. In this work, the interaction of their synthetic analogs, a promising cardiotropic and cytostatic compounds of the composition $[Fe(SC(NH_2)_2)_2(NO)_2]_2[Fe_2(S_2O_3)_2(NO)_4]$ and $[Fe(SC(NHCH_3)_2)_2(NO)_2]BF_4$ [1,2], with reduced glutathione (GSH) and bovine serum albumin (BSA) in aqueous solutions was studied by experimental and theoretical methods.

It was found that the studied complexes react with GSH to form a new binuclear DNIC with two GS^- ligands. The resulting complex is a more prolonged NO donor than the initial ones. It was shown that the products of aerobic decomposition of complexes ($[Fe(NO)_2]^+$ and $[Fe(NO)(NO)_2]^+$ fragments) can bind in the hydrophobic pocket of the BSA. As a result of this interaction, DNICs with high molecular weight are formed with Cys34 and His39 as ligands. According to the EPR- and UV-spectroscopy data, the interaction of complexes with protein leads to their significant stabilization. In addition to coordination binding, the studied complexes can be adsorbed on the protein surface due to weak intermolecular interactions, resulting in prolonged generation of NO.

We believe that the resulting compounds formed in the model systems are the pharmacologically active forms of complexes in the body.

Acknowledgements: the study of the transformation of complexes in model systems is supported by the Presidential Grant (No. MK-1634.2021.1.3). The synthesis of complexes is performed in accordance with the State Task (state registration No. AAAA-A19-119071890015-6).

[1] Sanina N. A., Aldoshin S. M., Shmatko N. Y., Korchagin D. V., Shilov G. V., Knyazkina E. V., Ovanesyan N. S., Kulikov A. V. (2015). *New Journal of Chemistry*, *39*, 1022–1030.

[2] Shmatko N. Yu., Korchagin D. V., Shilov G. V., Ovanesyan N. S., Kulikov A. V., Sanina N. A., Aldoshin S. M. (2017). *Polyhedron*, *137*, 72–80.

The Influence of Moderate Magnetic Field on the Generation of Radicals by Mixture of Some Choline Derivative with Hydroperoxides

✉ **Natalia V. Potapova**, **Oleg V. Kazakov, Olga T. Kasaikina**

Semenov Federal Research Center for Chemical Physics RAS
Moscow, Russia

✉ pot.natalia2010@yandex.ru

The interaction of external magnetic fields (MF) with living organisms and the influence of magnetic and electromagnetic fields on chemical and especially biological processes are a rapidly growing area of investigation. It is known that the main contribution to magnetic effects in biosystems is made by the reactions of radicals, radical ions, and other paramagnetic particles. Hydroperoxides (LOOH), the primary amphiphilic products of lipid oxidation form mixed micelles with surfactants (S), and cationic surfactants (S^+) were found to catalyze the decay of LOOH {mLOOH..nS^+} into free radicals in mixed micelles. Acetylcholine chloride (ACh), known as a neurotransmitter, regulates numerous fundamental functions of central and peripheral nervous system. ACh contains quaternary ammonium cation (R_4N^+) similar to cationic surfactants, but it has no bulky hydrophobic substituent. Nevertheless, in organic media, ACh forms supramolecular mixed nanoaggregates with LOOH and similarly to S^+ catalyzes the decomposition of LOOH into free radicals.

In this work, we studied the impact of endogenous substances containing (R_4N^+), namely choline (Ch) and L-carnitine (LCh), comparing to ACh on the radical generation via LOOH decomposition a) in the bulk solution in organic media; b) the effect of the magnetic field of permanent magnets (0.61 T) on these processes; c) the effect of Ch, LCh and ACh adsorption on cellulose on their catalytic activities in LOOH decay. a) by dynamic light scattering, ACh and Ch were found to disperse in organic media only in the presence of LOOH whereas LCh formed nanoaggregates both itself and together with LOOH of the same size of 100 nm. Ch, similar to ACh, caused the catalytic decomposition of LOOH into radicals in mixed aggregates with LOOH; b) in magnetic field (0.61 T), the decrease in the rate of radical initiation was observed only in the cases of ACh and Ch; c) adsorbed on microcrystalline cellulose ACh and Ch retain the ability to catalyze the radical decay of LOOH and initiate radicals whereas adsorbed LCh does not affect the LOOH decay. Carnitine, unlike other choline derivatives, is an internal salt, making peroxide difficult to incorporate and difficult to break down. It is possible that the magnetic field influences the properties of the double electric layer and the orientation of the peroxide bond in microaggregates. Apparently, these properties of ACh, along with cation-π interactions with binding sites, play role in physiological functions which ACh performs in living organisms.

Acknowledgements: this study was partly supported by the Russian Foundation for Basic Research (grant No. 20-03-00753).

Prediction of the pH Range of the PsbS-Dependent Photoprotective Response in Chloroplasts of *Lobosphaera incisa*

✉ **Vasily V. Ptushenko**

Belozersky Institute of Physico-Chemical Biology, Lomonosov Moscow State University
Moscow, Russia
Emanuel Institute of Biochemical Physics RAS
Moscow, Russia

✉ ptush@belozersky.msu.ru

Plants need to balance between light harvesting used for photosynthesis and photoprotection in excess of light. One of the key mechanisms used by oxygenic phototrophs for rapid balancing is non-photochemical quenching (NPQ) of excited chlorophyll molecules. In land plants, PsbS protein located in the photosynthetic membrane plays a crucial role in NPQ. Excessive light energy leads to acidification of the intrathylakoid space (lumen) and, hence, to protonation of some PsbS lumen-exposed acidic groups. In turn, this causes PsbS transition to the NPQ-inducing state. Although the mechanism of PsbS-dependent NPQ is still unknown, the amino acid residues serving as pH indicators are known for some model objects (Arabidopsis, spinach [1; 2]).

For algae (except for Charophyta), participation of PsbS in photoprotection has not yet been directly shown, although the PsbS gene was found in the genome of green algae. Only a few years ago, PsbS protein was detected in the model alga *Chlamydomonas reinhardtii*, as well as high-light-induced differential expression of PsbS gene [3; 4]. The latter indirectly indicates PsbS participation in the photoprotection. In this work, the amino acid sequence of PsbS from green alga *Lobosphaera incisa* was determined, and a three-dimensional structure was predicted. Using the methods of molecular dynamics and continuum electrostatics, pK values for lumen-exposed amino acid residues were calculated. It was shown that PsbS-dependent NPQ in *L. incisa* could be induced at lower values of the transmembrane ΔpH than in higher plants, which may indicate a more effective PsbS-dependent photoprotection in green alga.

Acknowledgements: the work was supported by the Russian Science Foundation (grant No. 22-24-00323).

[1] Fan M., Li M., Liu Z., Cao P., Pan X., Zhang H. et al. (2015). *Nature Structural & Molecular Biology*, *22*, 729–735.

[2] Li X.-P., Phippard A., Pasari J., Niyogi K. K. (2002). *Funct. Plant Biol.*, *29*, 1131–1139.

[3] Tibiletti T., Auroy P., Peltier G., Caffarri S. (2016). *Plant Physiology*, *171*, 2717–2730.

[4]. Correa-Galvis V., Redekop P., Guan K., Griess A., Truong T. B., Wakao S. et al. (2016). *Journal of Biological Chemistry*, *291*, 17478–17487.

Study of Self-Associates of Polysaccharide Macromolecules in Aqueous Solutions by Dynamic Light Scattering

✉ **Alena A. Pudova**[1], ✉ **Maksim V. Zelikman**[2]

[1] Novosibirsk State University
Novosibirsk, Russia
[2] Institute of Solid State Chemistry and Mechanochemistry SB RAS
Novosibirsk, Russia

✉ a.pudova1@g.nsu.ru
✉ zelikman_mv@mail.ru

Dextrans and arabinogalactan (AG) belong to the class of natural polysaccharides and are used in various industries.

Dextrans with molecular weights of 10, 40 and 70 kDa are hydrophilic polysaccharides characterized by good water solubility and low toxicity. The literature describes a large number of examples in which dextrans conjugate with various drugs [1]. Arabinogalactans are a class of polysaccharides found in a wide variety of plants. The branched structure of AG, which distinguishes it from polysaccharides already used in pharmaceuticals, made it possible to use AG as a host molecule for drugs and to create inclusion complexes based on it [1].

The purpose of our work is to study the molecular mechanisms of the formation of supramolecular systems of polysaccharides with lipophilic drug molecules in aqueous solutions, which can be used as a system for their "delivery". The inclusion of drug molecules in such complexes makes it possible to increase water solubility and bioavailability and significantly reduce the effective dosages and toxic effects [2]. In the primary models of intermolecular complexes, we studied the effect of self-association in aqueous solutions of these polysaccharides.

The characteristics of polysaccharide solutions were studied in water and $LiNO_3$ solutions at various temperatures and concentrations by dynamic light scattering (DLS). In all cases, a significant degree of self-association is shown in units of change in their molecular weights (kDa) and the dependence of these characteristics on the indicated conditions.

[1] Khvostov M. V. et al. (2019). The Use of Natural Polysaccharides in Pharmaceuticals. *Bioorg. Chem.*, *45*(6), 563–575.

[2] Dushkin A. V. et al. (2019). Supramolecular Drug Delivery Systems Based on Plant Metabolites. Physico-Chemical, Pharmacological Properties and Features of Mechanochemical Production. *Chemistry for sustainable development*, *3,* 133–244.

Scientific adviser—PhD., prof. A. V. Dushkin

Cryospectroscopic and *Ab Initio* Studies of Non-Covalent Interactions Between Sevoflurane and Selected Acceptor-Targets

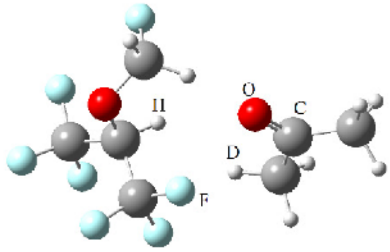
Sona M. Melikova, ✉ Konstantin S. Rutkowski

Saint Petersburg State University,
St. Petersburg, Russia

✉ k.rutkovsky@spbu.ru

Volatile halogenated hydrocarbons and ethers reveal strong analgesic and anesthetic effects. Among these compounds, sevoflurane belongs to the most safety anesthetics for purposes of invasive surgery. The halogenated compounds mentioned above, possess at least one CH group which can act as weak CH donor in interactions with targets of acceptor property [1–3]. One of the simplest acceptors including O atom with lone electron pair are acetone (ACT) and dimethyl ether (DME).

In the present report, the attention focuses on the features of non-covalent interactions between sevoflurane and such targets as DME and ACT. As an experimental tool effective in detection of weak complex formation, FTIR spectroscopy of cryosolutions has been chosen. The mixtures of sevoflurane and DME or ACT were dissolved in liquefied noble gases (Kr (~120–165 K) or Xe (~170–185 K)). Additional perspective feature of noble gases, especially Xe, is their excellent anesthetic effect which is not accompanied by any nephro- and hepatotoxicity complications. H-bond-type interactions resulted in characteristic changes on selected vibrational bands of both moieties. Ab initio calculations (mp2/6-311++g(d,p)) were performed to obtain geometric and spectroscopic parameters of sevoflurane, stable forms of heterodimers (complexation energy withing: –(5.5–6.0) kcal/mol), and to interpret characteristic changes in the IR spectrum related to complex formation.



Acknowledgements: the work was supported by the RFBR grant (No. 20-03-00536).

[1] Melikova S. M., Rutkowski K. S. (2021). *Opt. and Spectrosc.*, *129*(4), 493–500.
[2] Rutkowski K. S., Melikova S. M., Rospenk M. (2020). *J. Molec. Struct.*, *1221*, 128852.
[3] Rutkowski K. S., Melikova S. M., Rospenk M. (2017). *Spectrochim. Acta A*, *184*, 163–168.

The Interaction of Quinone-Chelators with Lipid Membrane: ^{1}H NMR and MD Study

✉ **Olga Yu. Selyutina**, **Anna V. Mastova, Nikolay E. Polyakov**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ olga.gluschenko@gmail.com

The interaction of a pharmacophore with cell membranes is a topic of great interest in biology and pharmacology due to its possible relevance in the pathway of action. Substituted anthraquinones known as anthracycline antibiotics (doxorubicin, daunomycin, emodin, etc.) are widely used in cancer therapy [1]. The two mechanisms by which these quinones act in the cancer cell are proposed. First is the intercalation into DNA duplexes, and second is the generation of ROS which destroy cellular membranes by stimulating lipid peroxidation [2–4]. The latter is also considered the reason of anthraquinones side effects, such as cardiotoxicity [5]. Thus, the interaction of anthraquinones with the cell membrane is of interest from the point of view of their mechanism of action.

In the present work, the study of different quinones interaction with the model lipid membrane was done using the ^{1}H NMR spectroscopy and molecular dynamics simulations. The NOESY technique was applied to determine the localization of anthraquinones in lipid membrane, and the results were correlated with the MD simulation data. Small isotropic DMPC/DHPC bicelles were used as a model membrane in solution of the ^{1}H NMR experiments. It was demonstrated that all studied quinones are able to penetrate into the hydrophobic part of the lipid bilayer. This result was also confirmed by the molecular dynamics simulations of DMPC bilayer with quinone molecules.

Acknowledgements: this work was financially supported by the Russian Science Foundation (grant No. 21-73-10037).

[1] Powis G. (1989). *Free Radic. Biol. Med.*, *6*, 63–101.

[2] Kankeu C., Clarke K., Passante E., Huber H. J. (2017). *J. Mol. Med.*, *95*, 239–248.

[3] Bhattacharya B., Mukherjee S. (2015). *J. Cancer Ther.*, *6*, 849.

[4] S Hrelia., Fiorentini D., Maraldi T., Angeloni C., Bordoni A., Biagi P.L., Hakim G. (2002). *BBA Biomembr.*, *1567*, 150–156.

[5] Mandal B., Singha S., Dey S. K., Mazumdar S., Kumar S., Karmakar P., Das S. (2017). *RSC Adv.*, *66*, 41403–41418.

Quantitative Metabolomic Profiling of Blood Serum During the Autophagy Modulation by NMR Spectroscopy

✉ **Olga A. Snytnikova**[1], **Oyuna S. Kozhevnikova**[2], **Yuri P. Tsentalovich**[1]

[1] International Tomography Center SB RAS
Novosibirsk, Russia
[2] The Federal Research Center Institute of Cytology and Genetics SB RAS
Novosibirsk, Russia

✉ snytnikova_olga@tomo.nsc.ru

Metabolites play a key role in the life of living organisms. The use of modern omics technologies, such as metabolomic profiling, makes it possible to obtain information about metabolic changes in the body under various conditions. The information obtained can make a significant contribution to the deciphering of the complex mechanisms of metabolic processes, and to the understanding of molecular pathways related to the development of diseases in living cells and organisms. Autophagy is involved in the maintenance of cellular homeostasis, the removal of damaged proteins and organelles, and is necessary to maintain cell metabolism in conditions of energy and nutrient deficiency. A decrease in autophagic activity plays an important role in age-related diseases. Today, the response of metabolic pathways to autophagy modulation remains poorly understood.

The aim of this study was to investigate the changes of metabolomic composition of blood serum during the induction and inhibition of autophagy processes by high-field NMR spectroscopy. We used two strains of Wistar and OXYS rats, which allowed us to demonstrate changes in the blood serum metabolome not only under the condition of autophagy processes, but also in pathology, since the OXYS rat strain is a unique genetic model of accelerated senescence and the development of age-related diseases. For the first time, quantitative characteristics of changes in the concentrations of a wide range of metabolites under autophagy were obtained. 55 metabolites have been identified in blood serum, including amino acids, antioxidants, osmolytes, etc.; the range of variation and quantitative content in the concentrations of metabolites were determined. By statistical analysis the correlations between the metabolomic compositions of the studied groups were established. The results show that starvation leads to a significant increase of the concentration of a number of metabolites, mainly related to the energy metabolism. More pronounced metabolomic changes were observed for OXYS rats. Under autophagy inhibition, the level of 19 metabolites (such as citrate, tryptophan, glutamate, and betaine) decreased, while the level of 6 metabolites increased (mannose, 2-OH-3-methylbutyrate, etc.). For some metabolites, the combined effects of starvation and autophagy inhibition depended on the animal genotype.

Acknowledgements: this work was supported by RFBR (project No. 20-03-00234).

NMR-Based Metabolomic Profiling of Brain in Rat Model of Alzheimer's Disease

✉ **Olga A. Snytnikova**[1], **Natalia G. Kolosova**[1],
Darya A. Telegina[2], **Ekaterina D. Savina**[1], **Yuri P. Tsentalovich**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *The Federal Research Center Institute of Cytology and Genetics SB RAS*
Novosibirsk, Russia

✉ snytnikova_olga@tomo.nsc.ru

The incidence of Alzheimer's disease (AD) is growing dramatically against the background of the aging of the world population. This study is aimed at the solution of an urgent scientific problem—identifying the metabolic predictors and markers for the development of (AD), its most common (~95 %) sporadic form. Changes in concentrations of low molecular weight metabolites reflect the disturbances in metabolic cycles during the development of Alzheimer's disease, so the identification of the most promising metabolomic biomarkers is very important from a prognostic point of view. The study was performed with the use of the OXYS rat line, a model of early aging, one of the manifestations of which is the development of a complex of AD signs. Using the method of metabolomic profiling with application of an analytical platform based on NMR spectroscopy, a comparative quantitative analysis of brain metabolites of OXYS rats was carried out in the "preclinical" period preceding the development of signs of AD (at the age of 20 days), during their manifestation (3 months) and active progression (18 months). Wistar rats of the same age were used as controls. In each group of animals, a metabolomic profile of 59 compounds was established, including amino acids, organic acids, antioxidants, osmolytes, glycosides, purine and pyrimidine derivatives. The range of variation in the concentrations of metabolites was determined; their quantitative content was established in the form of an average concentration value and a standard deviation in each group of samples. A statistical analysis was carried out to establish correlations between the metabolic composition of the study groups. We observed common metabolic patterns with aging in both Wistar and OXYS rats' brains involved in energy-generating pathways as well as metabolic shifts neurotransmitters. Thus, there is an increase in the concentration of inhibitory neurotransmitters (GABA-glycine) and a decrease in excitatory (glutamate), and in OXYS rats at an accelerated pace. Taken together, these shifts in neurotransmitter metabolism with age can impair neuronal transmission and lead to memory loss.

Acknowledgements: this work was supported by RSF (project No. 22-24-20035).

Aerosol Inhalation Delivery of Ceftriaxone in Mice

✉ **Sergey V. Valiulin**[1], **Andrey A. Onischuk**[1], **Anatoly M. Baklanov**[1],
Sergey V. An'kov[1,2], **Sergey N. Dubtsov**[1], **Alexander A. Alekseev**[1],
Galina G. Dultseva[1], **Nikolay N. Shkil**[3], **Tatyana G. Tolstikova**[1,2]

[1]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2]*Vorozhtsov Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[3]*Siberian Federal Scientific Center of Agro-BioTechnologies RAS*
Krasnoobsk, Russia

✉ valiulin@kinetics.nsc.ru

The pulmonary route of drug administration is a non-invasive and effective approach to deliver therapeutic agents both locally and systemically. The main benefits from the inhalation delivery are: rapid onset of action, in contrast to oral application, and ease of administration, non-invasive needle-free systemic delivery and high patient acceptability, in contrast to injections. In the present work, aerosol formation and pulmonary delivery are studied for the antibiotic drug ceftriaxone, which is currently delivered mainly by injection. For this purpose, an inhalation set-up designed and built by us was used, which includes: a generator of dry aerosol particles, inhalation chambers, and measuring equipment that provides for determining the delivered inhalation dose in real time. Studies have been performed on the pharmacokinetics of ceftriaxone after inhalation, intravenous and intraperitoneal administration.

Chromatographic measurements show that inhaled ceftriaxone is accumulated in the respiratory system. The absorption to blood from the respiratory system can be described by the first-order kinetics with the rate constant $kresp = 0.050 \pm 0.005\ \mathrm{min}^{-1}$. The lung-to-blood adsorption is characterized by the first-order rate constant $klung = 0.025 \pm 0.005\ \mathrm{min}^{-1}$, while the absorption to blood through peritoneal barrier is characterized by the first-order rate constant $kP = 0.035 \pm 0.005\ \mathrm{min}^{-1}$. The elimination rate constant is determined from aerosol delivery experiments to be $ke = 0.025 \pm 0.005\ \mathrm{min}^{-1}$, which is in good agreement with that measured for intravenous and intraperitoneal administration.

To investigate the antibacterial efficiency of the ceftriaxone aerosol form, outbred male mice were infected with the archival strains of *K. pneumonia* 82 and *S. aureus* ATCC 25 953. After the intraperitoneal injection of bacterial suspension, all the infected animals demonstrated increased bacterial burden, however, aerosol treatment, as well as injection delivery, caused a significant reduction of the bacterial concentration in animals. Aerosol, intravenous and intraperitoneal treatment of the infected animals resulted in approximately equal therapeutic effects. Thus, the developed ceftriaxone aerosol form is efficient against *K. pneumonia* and *S. aureus* in mice.

Acknowledgements: this research was funded by the Russian Science Foundation (Project No. 19-73-10143).

Physico-Chemistry of Dinitrosyl Itron Complexes as a Determinant of Their Biological Activity

✉ **Anatoly F. Vanin**

Semenov Federal Research Centre for Chemical Physics RAS
Moscow, Russia

✉ vanin@chph.ras.ru

The so-called "oxidative" mechanism of mononuclear form of dinitrosyl iron complexes (M-DNICs) with thiol-containing ligand formation was considered. The complexes are proposed to be formed from neutral NO molecules, Fe^{2+} ions and thiol (RS^-) ligands based on the disproportionation reaction of NO molecules binding with Fe^{2+} in pairs. Then a protonated form of nitroxyl anion (NO^-) appearing in the reaction released from iron ligand sphere and the next neutral NO molecule is included instead which leads to M-DNIC with thiol-containing ligand formation. This results in its resonance structure of M-DNIC described as $[(RS^-)_2Fe^{2+}(NO)(NO^+)]$, in which nitrosyl ligands are represented by NO molecules and nitrosonium cation (NO^+) in equal proportion. The hydrolysis of nitrosonium cations in the complexes is prevented by electron density transferring from thiol sulfur atoms characterized by high π-donor activity to iron-dinitrosyl groups. Similar resonance structure is characteristic of the binuclear form of DNICs with thiol-containing ligands (B-DNICs). The experiments with solutions of B-DNICs with glutathione or N-acetyl- L-cysteine demonstrated that these complexes release both NO and NO^+ in case of decomposition in the presence of acid or after oxidation of thiol-containing ligands in them. The level of released NO from decomposed B-DNICs was measured via optical absorption intensity of NO in gaseous phase, while the number of released nitrosonium cations was determined based on their inclusion into S-nitrosothiols or their conversion into nitrite anions. Biomedical researches showed that NO molecules released from DNICs usually have positive and regulatory effects on living organisms (vasodilating and hypotensive actions, positive effect on healing various type of wounds, inhibiting platelet aggregation, etc.), while nitrosonium cations have cytotoxic effect (suppressing the development of experimental endometriosis in rats or preventing coronavirus infection in hamsters).

Study of the Stability of ZIF-8 Particles in Some Buffers and Physiological Media

✉ **Anastasiya A. Yazikova**[1,2], **Artem S. Poryvaev**[1,2], **Daniil M. Polyukhov**[1],
Olga A. Chinak,[3] **Vladimir A. Richter**[3], **Olesya A. Krumkacheva,**[1] **Matvey V. Fedin**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia
[3] *Institute of Chemical Biology and Fundamental Medicine*
Novosibirsk, Russia

✉ a.yazikova@tomo.nsc.ru

Targeted drug delivery systems are promising platforms for improving the treatment of cancer. Metal-organic frameworks (MOFs) and, in particular, the ZIF-8 (zeolitic imidazole framework) nanoparticles are considered to be good nanoplatforms for this route. It is provided by properties such as easy and high guest loading, pH sensitivity and lots of possibilities for surface modification. However, the significant drawback of ZIF-8 is poor stability in some buffers and blood serum. We report a new experimental approach which is a combination of electron paramagnetic resonance (EPR) and spin probe method. Thus, direct and quantitative characterization of guest release from ZIF-8 in different physiological media and buffers can be held. For this purpose we used ZIF-8 with encapsulated nitroxides, which was exposed to physiological media, and the *in situ* kinetics of guest escape was monitored by EPR. The release of spin probes drastically changes the EPR spectral shapes, thus, providing for quantitative characterization of leaked species. We demonstrate that the guest release from ZIF-8 particles in blood-mimicking solutions is a concentration-dependent process dictated by albumin, and nearly full guest release from nanoparticles in fetal bovine serum (FBS) occurs within a few minutes. Significant deceleration of this process and stabilization of ZIF-8 in FBS can be achieved by additional adsorption of guest inhibitors (exemplified by aromatic hydrocarbons) prior to contact with physiological media. The proposed methodology provides further perspectives for the optimization of MOF-based platforms for efficient drug delivery.

Acknowledgments: this work was supported by the Russian Science Foundation (No. 20-73-10239).

Effect of pH on Mechanisms and Products of Photodamage to Tryptophan and Tyrosine Residues in the Free State and a Model Protein

✉ **Yuliya S. Zhuravleva, Peter S. Sherin**

International Tomography Center SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉ zhuravleva@tomo.nsc.ru

Cross-linking of proteins in living tissues largely contributes to the development of various diseases and molecular pathways of ageing. This is essentially important in the case of cataract—the progressive opacification of an eye lens—proceeding via extensive protein aggregation. The latter may proceed via different reactions, including cross-linking, mechanisms of which are still mostly unclear. Tryptophan (Trp) and tyrosine (Tyr) residues are amino acids with low redox potentials and are known for their participation in photo-induced oxidation and cross-linking of proteins via radical reactions. Recently, it has been discovered that Trp/Tyr cross-links are present in human cataract lenses and, therefore, may directly contribute to the development of this disease.

The oxidative stress is considered the main cause of cataract, and it may lead to the acidification of tissue. Thus, the variation of pH during the cataract progression may affect the rate of cross-linking and the accumulation of aggregation products. In this work, we studied the effect of pH on the reaction mechanisms between Trp/Tyr radicals ($Trp^{\bullet}$/$Tyr^{\bullet}$) in free state and in a model protein, lysozyme.

The photodamage was sensitized by kynurenic acid (KNA), a UV-A chromophore present in the human eye lens. We found that the protonation of $Trp^{\bullet}$ in free state under acidic conditions accelerates the transfer of back electron from KNA radical by a factor of two. This leads to more efficient restoration of initial reagents and reduction of the yield of all products, including Trp-Trp cross-links. However, this protonation effect is absent in the case of $Tyr^{\bullet}$ within the pH range of 3–7 due to its very low pKa (< 0).

Protein globule significantly affects the paths of radical reactions due to steric hindrance and changes in charges on the protein surface with pH variation. We found that the effect of $Trp^{\bullet}$ protonation is significantly reduced within lysozyme globule resulting in a minor variation in the yield of protein degradation within pH 3–7. However, the media acidification results in tremendous differences in the product composition from the domination of Trp-Trp cross-linking at pH 7 to the prevalence of oxygenation (Trp + O) at pH < 5. This drastic change indicates a strong competition between cross-linking and oxygenation for radicals within the protein. Thus, variation of pH within a living tissue may significantly affect the direction of radical reactions and requires further studies under the conditions simulating cell environment.

COMBUSTION AND ENERGETIC MATERIALS

Explosive Decomposition of High Explosives with Inclusions of Ultrafine Metal Particles under the Influence of Pulsed Laser Radiation

✉ **Boris P. Aduev, Denis R. Nurmukhametov,**
Gennadiy M. Belokurov, Igor Yu. Liskov, Nataliya V. Nelubina

Federal Research Center for Coal and Coal Chemistry SB RAS
Kemerovo, Russia

✉ lesinko-iuxm@yandex.ru

It has been established that the role of ultrafine (~100 nm) metal inclusions (Al, Ni, Fe) in explosives (PETN, RDX) is to change its optical characteristics. It is a result of absorption of laser radiation by the metal core of the inclusions followed by heating of the core. When the critical radiation energy density in the explosive shell surrounding the inclusion is exceeded, an exothermic chemical reaction is initiated. It is shown that the nature of the dependence of the laser initiation threshold (1,064 nm, 532 nm, 14 ns) of the explosion of blasting explosives on the mass fraction of ultrafine metal particles is related to the nature of change in pressure in the energy absorption layer which is determined by the conditions of gas dynamic unloading. The dependence of laser initiation threshold for explosion of brisant explosives on the size of inclusions of ultrafine metal particles is related to the dependence of the radiation absorption index on the particle size. The dependence of laser initiation threshold of an explosion of polycrystalline PETN samples with the inclusions of ultrafine metal particles on the wavelength is related to the radiation absorption efficiency coefficients. For the same values of the extinction index, the thresholds for initiating an explosion when exposed to different wavelengths are the same. In thin (1 mm) PETN samples with inclusions of ultradisperse aluminum particles, under laser irradiation the regularities of explosive decomposition are manifested which differ from the regularities during normal detonation. With a decrease in the sample density, the thresholds of laser initiation of an explosion, as well as the velocities and pressures of shock waves generated during the explosion of samples in air, increase. The primary product during laser initiation of an explosion of explosives (PETN, RDX) with inclusions of ultrafine particles of Al, Ni and Fe is NO^{2*} — radicals formed in "hot spots" as a result of the dissociation of the explosive molecule. The luminescence spectra at the explosion stage are of a thermal nature and are associated with a chemical reaction in the core of the explosive molecules. Based on the studies carried out and the analysis of their results, the model of laser initiation of the explosive decomposition of brisant explosives with inclusions of ultrafine metal particles is proposed.

Features of the Physicochemical Mechanism of Combustion, Explosion and Gas Detonation Reactions, Development of Chemical Methods of Process Control

✉ **Vilen V. Azatyan**

Scientific Research Institute for System Analysis RAS
Moscow, Russia

✉ vylenazatyan@yandex.ru

The increased interest in the processes of combustion, explosion and detonation of gases is determined by their strategic role in technology, energy and everyday life. The specificity of the reactions underlying these processes is as well one of the topical problems of the theories of chemical kinetics and combustion. At the same time, the fundamental problems of chemical and physicochemical aspects of these phenomena began to be solved only in the last three decades. It was generally accepted that combustion during self-heating was caused only by heat release. The role of reaction chains was ignored and denied even in fundamental monographs and encyclopedias. Using a hypothetical model of a one-stage reaction, it was only possible to formally describe the reaction kinetics under the conditions corresponding to the accepted calculation parameters. However, in the works of the Russian Academy of Sciences in cooperation with the Ministry of Emergency Situations, it was shown that the generally accepted one-stage model contradicts the fact that the combustion, explosion, and detonation of gases occur. It was found that in all combustion modes the reactions are solely chain reactions. The laws of these non-isothermal chain reactions that determine the course of these processes are revealed. It has been established that even in a laminar flame, the characteristic reaction time is less than 10^{-4} s. In detonation, this time is less than 10^{-6} s. Extremely high velocities and accelerations are determined by the previously unknown law of the temperature dependence of the chain reaction rates which is expressed as an exponent that contains in its positive exponent the Boltzmann factor with the activation energy of the limiting stage. The law of the "exponent in a positive exponent" also determines the multiplication of free atoms and radicals during combustion and explosion. The concentrations of active particles in the flame exceed the equilibrium values by many orders of magnitude due to the conversion of most of the reaction enthalpy into the energy of free valences of atoms and radicals.

Examples of the application of the developed chemical methods for controlling all the characteristics of combustion, explosion and detonation of gases are given. The methods also use the resonance of intramolecular vibrations of the additive and the intermediate particle. A strong effect of heterogeneous reactions of atoms and radicals on flame propagation and explosion was revealed. It is shown that it is necessary to take into account these reactions to achieve the reliability of mathematical modeling of combustion.

Features of Flame Propagation Caused by Heterogeneous Reactions of Intermediate Particles

✉ **Vilen V. Azatyan**[1], **Mikhail I. Alymov**[2], **Vyacheslav M. Prokopenko**[2],
Sergey K. Abramov[2], **Vladimir B. Kazansky**[3]

[1] *Scientific Research Institute for System Analysis RAS*
Moscow, Russia
[2] *Merzhanov Institute of Structural Macrokinetics and Materials Science*
Chernogolovka, Russia
[3] *Zelinsky Institute of Organic Chemistry RAS*
Moscow, Russia

✉ vylenazatyan@yandex.ru

Flame propagation is one of the main modes of gas-phase combustion, passing under certain conditions into explosion and detonation. Despite the strategic role in technology and importance for the theory of combustion, the implementation of this combustion mode, as well as its main regularities, until recently could not be explained. Combustion accompanied by self-heating was considered as a single stage reaction of the initial molecules, caused only by an increase in temperature. The role of reaction chains was ignored. The dependence of flame velocity on the dimensions of the reactor was explained only by a change in heat removal. To describe the rate of the process, the calculated parameters were hypothetically selected according to the observed combustion rate and according to a conventionally accepted equation. In a series of our works, however, it was shown that due to very high activation energies exceeding 200 kJ/mol, the rates of intermolecular reactions are thousands of times lower than the rates of real combustion reactions. It was found that the combustion of gases during any self-heating proceeds only through chain mechanisms. One of the important stages of chain processes is the chemisorption of atoms and radicals, because of which active particles are removed from the reaction medium, and thus the only combustion path is blocked.

To reveal and study the role of heterogeneous recombination of active particles in flame propagation, the process was carried out with varying the efficiency of heterogeneous recombination, all other parameters of the system being kept unchanged. For this purpose, the reactor was preliminarily rinsed with solutions providing a specified efficiency of heterogeneous recombination. It was found that over the surfaces created in this way, flame velocities differ up to ten times. This means that the walls affect combustion not only by removing heat, but even more so by breaking the reaction chains. An important feature of combustion was also a change in the characteristics of the flame because of its impact on the surface. The pulsating mode of combustion also depends on the properties of the surface. The obtained results indicate the need to consider heterogeneous reactions both in the theory of flame propagation and in practice, for example, when selecting materials for combustion chambers. It also follows from the obtained data that the results of numerical simulation of gas combustion can be reliable only if heterogeneous reactions of atoms and radicals and their role in the formation of concentration and temperature gradients are taken into account.

Effect of Modifier Additives on Burning Rate and Condensed Combustion Products Parameters of Composite Aluminized Propellant

✉ **Natalia S. Belousova, Oleg G. Glotov, Polina G. Korchemkina**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
Novosibirsk State Technical University
Novosibirsk, Russia

✉ nata.bel@kinetics.nsc.ru

The objects under study were model composite propellants consisting of ammonium perchlorate (AP ≈ 60 % by weight), aluminum (≈ 20 %), active binder (≈ 20 %) and optionally a modifier additive (1.0–3.5 % over 100 %). Components: AP—sieve fraction 500–630 µm or 180–250 µm; AVl: ASD-4 [1]; binder—methylpolivinyl-tetrazole polymer plasticized with nitroether-nitramine plasticizer [1; 2]; additive—one of the following substances: TiB_2, $AlMgB_{14}$, $(NH_4)_2TiF_6$, NH_4BF_4, $Ca_3(PO_4)_2$. Experiments on the combustion of composite propellants were carried in a pressure vessel (bomb) in nitrogen at a pressure of 0.35 MPa. The bomb has a volume of 0.33 liters and working pressure up to 3 MPa. The bomb is provided with 30 mm diameter windows for video recording of the combustion process, a pressure control system; it is designed to collect condensed combustion products (CCP) into the liquid. The experiments are aimed at determining the propellant's burning rate and the characteristics of agglomerates leaving the burning surface. The video record of the combustion process was made at a shooting speed of 24 fps. The sampling of CCP was carried out into a 100 ml glass poured with distilled water and placed inside the bomb. The following agglomerate characteristics were determined: mass (as the mass of the particles with size larger than 80 µm), size distribution function and mean sizes, and combustion completeness. The effects of additive modifiers on registered parameters were revealed. Some of the effects found are of practical interest for burning rate control and improvement of the CCP characteristics. However, none of the five tested additives resulted in simultaneous reduction in mass and size of the agglomerates. It was concluded that the work should be continued for searching new additives capable of reducing the aluminum agglomeration intensity.

[1] Kizhnyaev V. N., Golobokova T. V., Pokatilov F. A., Vereshchagin L. I., Estrin Y. I. (2017). Synthesis of Energetic Triazole- and Tetrazole-Containing Oligomers and Polymers, *Chemistry of Heterocyclic Compounds, 53*(6,7), 682–692. https://doi.org/10.1007/s10593-017-2109-6

[2] Arkhipov V. A., Gorbenko T. I., Zhukov A. S., Pesterev A. V. (2011). Tin Chloride Effect on the Burning Rate of the Heterogeneous Condensed Systems. *Chemical Physics and Mesoscopy, 13*(4), 463–469. (in Russ.)

The Effect of Diffusion on the Combustion of a Sphere of Polymethyl Methacrylate in Air

✉ **Tatyana A. Bolshova,** **Oleg P. Korobeinichev, Andrey G. Shmakov**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ bolshova@kinetics.nsc.ru

In practice (during fires), the combustion of gases, liquids and solids under the free convection conditions mainly proceed in the diffusion mode. Such combustion is accompanied by the formation of a flame, the main feature of which is a separate supply of fuel and oxidizer to the reaction zone. The process of mixing fuel and oxidizer is caused by convective mixing and molecular diffusion. At a low flow rate, the fuel and oxidizer enter the combustion zone due to molecular diffusion, and at a high flow rate, convective mixing becomes the prevailing process. When burning real objects with a complex curvilinear surface, the existence of both regimes is possible. The aim of this work is to study the propagation of flame along a curved surface under the conditions of free convection. The object of research was a sphere made of cast polymethyl methacrylate (PMMA) with the diameter of 40 mm. PMMA is a synthetic polymer of methyl methacrylate (MMA, $C_5H_8O_2$), a thermoplastic transparent plastic widely used in industry, construction and everyday life. The study of fire propagation through such polymers is an urgent task of fire safety.

The combustion of a PMMA sphere has been studied experimentally and using the CFD simulations (ANSYS Fluent[1]). Temperature and concentration profiles of the main products near the combustion surface were obtained experimentally. The calculation of the gas flow around a solid body was carried out on the basis of the system of complete Navier-Stokes equations for a multicomponent mixture, taking into account the diffusion, heat exchange between the surface and gas, the kinetic mechanism for the gas phase [2], the pyrolysis reaction on the surface of the sphere [3], radiation, and convection losses. As a result of calculations, the fields of temperatures, the gas flow velocity and concentrations of substances were obtained. The experimental data and calculation results are in good agreement with each other. The variation of the MMA and O_2 diffusion coefficients showed that the degree of diffusion effect on combustion depends on the velocity field of the gas flow formed near the sphere surface.

[1] Academic Research, ANSYS 2021 R1 http://www.ansys.com/

[2] Seshadri K., Williams F. A. (1978). *Journal of Polymer Science: Pol. Chem. Ed. 16*, 1755–1778.

[3] Trubachev S. A. et al. (2021). *Proc.Comb.Inst.*, *38*, 4635–4644.

Experimental and Kinetic Modeling Study of the Positive Ions in Ethylene Flames

✉ **Andrey V. Cherepanov**, **Denis A. Knyazkov**, **Vitaly G. Kiselev**,
Ilya E. Gerasimov, **Andrey G. Shmakov**

Novosibirsk State University
Novosibirsk, Russia
Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ a.cherepanov1@g.nsu.ru

The flame is weakly ionized plasma. Understanding the behavior of ions in a flame is momentous for the development of new diagnostic methods and new ion-sensitive technologies for controlling combustion processes. In this work, the spatial distribution of positive ions (cationic structure) in premixed ethylene/oxygen/argon flames stabilized on a flat-flame burner at atmospheric pressure was measured by molecular beam mass spectrometry in a wide range of equivalence ratios $\phi = 0.4 \div 1.5$. Numerical calculations of the cationic structure of these flames, as well as profiles of the rate of production of the main flame ions, have been carried out using the Cantera software (V. 2.5.1) [1]. A detailed ion chemistry mechanism was used for calculations. The mechanism was developed on a basis of ion chemistry models available in the literature [2] and supplemented with reactions for the $C_3H_5^+$ cation that is abundant in ethylene flames. A comparison of the experimental and simulation data has shown that the mechanism correctly describes the relative content of the most abundant oxygen-containing cations (CH_5O^+, $C_2H_3O^+$) in flames, as well as of the $C_3H_5^+$ cation detected experimentally in a rich flame ($\phi = 1.5$). The chemistry of $C_3H_3^+$—a key cation in fuel-rich flames—was also revisited. Two structure isomers of $C_3H_3^+$ (cyclic and linear) together with the reactions involving these cations and an isomerization reaction are added in the mechanism. The updated mechanism has demonstrated to correctly predict the relative mole fraction of the $C_3H_3^+$. Several abundant cations with the general formula C_xH_y were also detected in the fuel-rich flame ($\phi = 1.5$). The obtained data will serve as a basis for further development of the ion chemistry mechanism in fuel-rich hydrocarbon flames.

Acknowledgements: this work was supported by the Ministry of Science and Higher Education of the Russian Federation (project No. 075-15-2020-806).

[1] Goodwin D. G., Speth R. L., Moffat H. K., Weber B. W. (2018). Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes. Version 2.5.1. https://doi.org/10.5281/zenodo.1174508.

[2] Knyazkov D. A. et al. (2022). Cationic Structure of Premixed Near-Stoichiometric CH4/O2/Ar Flames at Atmospheric Pressure: New Insights from Mass Spectrometry, Quantum Chemistry, and Kinetic Modeling. *Combustion and Flame, 241*, 112106.

Estimation of the Characteristic Time Scale of Physicochemical Processes in a Flame by the PIV

✉ **A. A. Chernov**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
Siberian State University of Geosystems and Technologies
Novosibirsk, Russia

✉ chernov@kinetics.nsc.ru

In the modern theories, the flame movement rate in a turbulent field of low and medium intensity in the mode of chemical reaction is described with the formula of dependence of the turbulent flame propagation rate on laminar speed values, the Markstein length and chemical time scale [1; 2]. In this paper, we present the dependence of the chemical time scale for premixed methane-air, dimethyl ether (DME)-air and methyl methacrylate-air flames (Le = 1 ÷ 2.5) depending on the equivalent ratio, initial temperature and inhibitor concentration.

Local laminar premixed flame burning velocities and chemical time scale were measured at the initial temperature of 300, 358, 366 K and atmospheric pressure using the particle image velocimetry (PIV). Premixed flames were stabilized on the Mache-Hebra type Bunsen burner with the nozzle diameter of 1 cm. The experimental setup was described previously in [3]. Gas flows were monitored by the MKS Instruments mass-flow controllers. The inhibitor was supplied into the mixing chamber of the burner by a stepper motor. The entire installation was thermostated. To study the dynamic structure of the flame the method of Particle Image Velocimetry (PIV) was applied with an inter-frame delay no more than 20 ÷ 100 μs. Registration and processing of stroboscopic images of particles in the selected flow section was carried out using the POLIS system consisting of two pulsed Nd:YAG lasers (532 nm, pulse duration 5 ns, pulse energy 40 mJ, beams are reduced to one axis), a CCD camera 1360 × 1024 pixels.

The results of the experiments show that with an increase in the burning rate, the chemical time scale decreases regardless of the experimental conditions and the type of fuel.

[1 Fogla N., Creta F., Matalon M. (2015). *Combustion and Flame*, *162*, 2758.

[2] Zimont V. L. (2000). *Experimental Thermal and Fluid Science*, *21*, 179.

[3] Knyazkov D. A., Bolshova T. A., Shvartsberg V. M., Chernov A. A., Korobeinichev O. P. (2021). *Proceedings of the Combustion Institute*, *38*, 4625–4633.

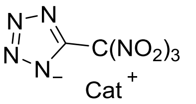
Energetic Polynitrogen Heterocycles: Synthesis and Performance

✉ **Leonid L. Fershtat**[1], **Daniil A. Chaplygin**[1], **Dmitry M. Bystrov**[1], **Nikita V. Muravyev**[2]

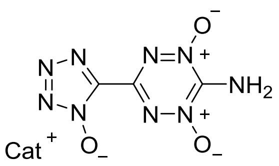
[1] Zelinsky Institute of Organic Chemistry RAS
Moscow, Russia
[2] Semenov Federal Research Center for Chemical Physics RAS
Moscow, Russia

✉ fershtat@bk.ru

Polynitrogen heterocycles are of paramount importance in the design and preparation of novel organic materials. As a rule, polynitrogen heterocycles exhibit an optimal set of functional properties enabling their potential of application in energetic materials science [1]. Herein, we present recent achievements of our research group in the synthesis of structurally diverse polynitrogen heterocyclic compounds incorporating tetrazole [2] and tetrazine rings. An estimation of crucial physicochemical parameters along with an application potential of the synthesized compounds as energetic materials is also discussed.



T_d: 112-136 °C
ρ: 1.70-1.85 g cm^{-3}
[N + O]: 82-88%
ΔH^o_f: 140-726 kJ mol^{-1}
D: 8.2-9.2 km s^{-1}
P: 29-38 GPa



T_d: 160-212 °C
ρ: 1.75-1.78 g cm^{-3}
[N + O]: 77-83%
ΔH^o_f: 413-779 kJ mol^{-1}
D: 8.5-8.8 km s^{-1}
P: 31-33 GPa

Acknowledgements: this work was supported by the Russian Science Foundation (project No. 21-73-10109).

[1] Zlotin S. G., Churakov A. M., Egorov M. P., Fershtat L. L., Klenov M. S., Kuchurov I. V., Makhova N. N., Smirnov G. A., Tomilov Yu. V., Tartakovsky V. A. (2021). *Mendeleev Commun., 31*, 731–749.

[2] Chaplygin D. A., Larin A. A., Muravyev N. V., Meerov D. B., Kosareva E. K., Kiselev V. G., Pivkina A. N., Ananyev I. V., Fershtat L. L. (2021). *Dalton Trans., 50*, 13778–13785.

Burning Times of Boron, Aluminum Diboride and Aluminum Dodecaboride Microparticles

✉ **Oleg G. Glotov**[1,2], **Valeriy V. Zamashchikov**[1],
Natalia S. Belousova[1,2], **Igor A. Bedarev**[3], **Grigory S. Surodin**[1]

[1]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2]*Novosibirsk State Technical University*
Novosibirsk, Russia
[3]*Khristianovich Institute of Theoretical and Applied Mechanics SB RAS*
Novosibirsk, Russia

✉ glotov@kinetics.nsc.ru

The commonly used tools for studying the combustion of metal fuel particles, including boron, are gas burners [1; 2]. This paper presents an original experimental set up that also includes a gas burner. However, our technique has a number of features that give advantages over others, namely, preheating the gas mixture up to a temperature of 600 K and creating a combustion environment with high oxygen content, introducing the tested particles into the flame directly with a working premixed combustible gas mixture (no carrier stream of inert gas). These features make it possible to create combustion conditions that simulate conditions in a technical device. Gas flame parameters are calculated using the ChemKin software. The sampling of combustion product particles is performed immediately after the flame using AQFA-type filters made of quartz fiber. The use of laser illumination and video shooting at 3,200 fps allowed us to record the streaks of moving particles, both burning (behind the flame front) and cold (without flame). As a result of the analysis of the streaks, the burning time of the micron size particles of boron, aluminum and aluminum borides was determined. A modified mathematical model of boron particles combustion was developed based on the PSU (Pennsylvania State University) model [3]. Verification of the model was carried out using burning times measured in the experiments.

[1] Veith J., Pfitzner M. (2016). Combustion of Boron Particles in Premixed Methane/Air Flames, Propellants Explosives Pyrotechnics, 41, 260–266. https://doi.org/10.1002/PREP.201500069.

[2] Chintersingh K. L., Nguyen Q., Schoenitz M., Dreizin E. L. (2016). Combustion of boron particles in products of an air–Acetylene flame, Combustion and Flame, 172, 194–205. http://dx.doi.org/10.1016/j.combustflame.2016.07.014.

[3] Ulas A., Kuo K. K., Gotzmer C. (2001). Ignition and Combustion of Boron Particles in Fluorine-Containing Environments. Combustion and Flame, 127(1–2), 1935–1957.

Effect of the Prescription Configuration on Properties of Nanothermite Composition Bi_2O_3/Al/1Me-3H

✉ **Vladimir V. Gordeev, Maxim V. Kazutin, Nicolay V. Kozyrev**

Institute for Problems of Chemical and Energetic Technologies SB RAS
Biysk, Russia

✉ gordeev.vladimir92@yandex.ru

Nanothermites are considered a promising material for the creation of micro-sized pyrotechnic devices. However, high sensitivity of nanothermites to friction and electrostatic discharge complicates their use. Phlegmatic materials are used to reduce the sensitivity of pyrotechnic mixtures. In the case of nanothermite mixtures, the introduction of these materials leads to a significant reduction in combustion performances. The use of additives of different nature allows one to preserve or improve the combustion performances of nanothermites, and in some cases reduce sensitivity of the composition, but the available data do not allow us to form an unambiguous concept of the effect of additives on the properties of nanothermites, which complicates the understanding of the mechanism of combustion nanothermite/additive systems.

In this work, a nanothermic pair of Bi_2O_3—Al with the addition of high-energy 1-methyl-3-nitro-1,2,4-triazole (1Me-3H) material was studied with different formulation compositions: I—the ratio of the components of the mixture corresponded to the maximum calculated heat of explosion of the composition (*Q*) at a given content of 1Me-3H; II—the ratio of components of the mixture corresponded to the maximum calculated pressure value (*P*) developed during combustion composition in a closed volume; III—the ratio of components of the Bi_2O_3 : Al nanothermite (88 : 12 %) corresponding to the maximum calculated value of *Q* and remained constant in the mixture; IV—the ratio of nanothermite components Bi_2O_3 : Al (86 : 14 %), corresponding to the maximum calculated value of *P* and remained constant in the mixture.

For prescription configurations I, III, IV, it is possible to increase the relative explosion force (*F*) of the composition by 22–29 % compared to the base nanothermite pair. In case of the prescription configurations II, the explosion force of the composition is at the level of base mixture with an additive content of up to 7 % after which there is a decrease in *F*. Combustion rate compositions for configurations I and II remain at the level of base nanothermite, and for configurations III and IV are characterized by an increase in the rate of combustion by 100–200 m/s. The combustion rate of the studied compositions in a thin layer (0.1 mm), regardless of the prescription configurations, remains at the level of basic nanothermic composition.

Acknowledgements: the research was carried out within the state assignment of Ministry of Science and Higher Education of the Russian Federation (project No. FUFE-2021-0005).

3-(4'-R-3'-Furazanyl)-5-(nitropyrazolyl)-1,2,4-oxadiazoles— a New Class of HEDMs

✉ **Tigran E. Khoranyan**, **Olga V. Serushkina**, **Irina A. Vatsadze**, **Kyrill Yu. Suponitsky**, **Konstantin A. Monogarov**, **Tatiana K. Shkineva**, **Igor L. Dalinger**

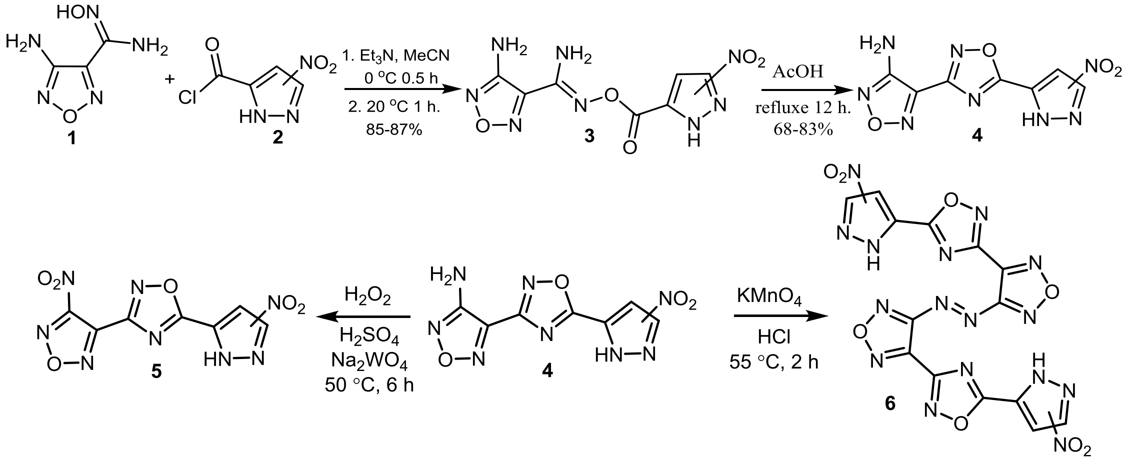
Zelinsky Institute of Organic Chemistry RAS
Moscow, Russia

✉ horanyan@ioc.ac.ru

One of the modern trends in synthesis of new high-energy density materials (HEDMs) is the construction of a molecule consisting of linear-connected five-membered nitrogen-oxygen heterocycles. This approach allows one to modify the properties by varying the type of heterocycles and the way of their connecting.

We synthesized a new energy ensemble of three different types of heterocycles: pyrazole, 1,2,4-oxadiazole and 1,2,5-oxadiazole. The reaction of aminofurazan amid-oxime **1** with nitropyrazolecarbonyl chloride **2** get acylamidoximes **3**. The formation of the 1,2,4-oxadiazole ring was achieved by boiling the obtained acylamidoximes **3** in acetic acid.

We found that the treatment of amines **4** using a mixture of $H_2O_2/H_2SO_4/Na_2WO_4$ leads to nitrocompounds **5**. By the action of $KMnO_4$ in HCl on the initial aminofurazans **4**, it was possible to carry out their oxidative dimerization and obtain azofurazans **6** (see Fig.).



Nitrofurazan's compounds **5** were studies by the X-ray diffraction analysis. For compounds **5** and **6**, the following parameters were studied by experimental and computational methods: density, heat resistance, sensitivity to shock and friction, pressure and detonation velocity. It is shown that all these compounds are superior to TNT in terms of energy efficiency, having comparable values of mechanical sensitivity.

[1] Khoranyan T. E., Serushkina O. V., Vatsadze I. A., Suponitsky K. Yu., Monogarov K. A., Shkineva T. K., Dalinger I. L. (2022). *Russ. Chem. Bull.* (accepted for publication)

Modern Predictive Quantum Chemical Calculations for Thermochemistry and Decomposition Kinetics of Energetic Materials

✉ **Vitaly G. Kiselev**[1–3], **Nikita V. Muravyev**[3], **Konstantin A. Monogarov**[3], **Alla N. Pivkina**[3]

[1] *Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia
[3] *Semenov Federal Research Center for Chemical Physics RAS*
Moscow, Russia

✉ kiselev@phys.nsu.ru

Highly accurate theoretical values of bond energies and activation barriers of primary decomposition reactions are crucial for reliable predictions of thermal decomposition and the detonation-related phenomena of energetic materials (EM). However, due to the prohibitive computational cost, high-level *ab initio* calculations had been impractical for a large number of important EMs of medium size including, for example, CL-20. The widely used DFT calculations very often could not provide the uniform "chemical accuracy" (~1 kcal/mol) and, ultimately, the convincing mechanistic evidence on the decomposition pathways of important EMs.

Here we report on the advantages in theoretical thermochemistry and kinetics of EM achieved with the use of novel local modifications of the coupled cluster (DLPNO-CCSD(T)). These render feasible high-accuracy calculations on caged polynitroamino and polynitro EMs, e.g., CL-20 and octanitrocubane (ONC). For all important species studied, the obtained values of bond energies are at least 10 kcal/mol more accurate than those reported in the literature so far. We also studied in detail the gas-phase thermochemistry of novel high-energy polynitro derivatives of 5/6/5 heterocyclic frameworks comprised of fused tetrazine and two triazole or pyrazole rings. To this end, we proposed and benchmarked a "bottom-up" approach. First, highly accurate multi-level procedures W2-F12 and/or W1-F12 in conjunction with the atomization energy approach were utilized for smaller species. In turn, for medium-sized species (up to 24 non-H atoms), these values were complemented with the enthalpies of isodesmic reactions calculated using DLPNO-CCSD(T)/aVQZ. In a more general sense, the latter approach is a viable step beyond the commonly used DFT procedures and represents a new level of predictive computational thermochemistry and kinetics for important EMs.

We also proposed a new approach for the determination of standard (solid) state enthalpy of formation of EM based on complementary high-level quantum chemical calculations (W1-F12 and W2-F12) of the gas-phase values and advanced thermal analysis techniques yielding sublimation enthalpies. We performed a massive benchmarking of the proposed procedure on a large set of EMs.

Acknowledgements: this work is supported by the Russian Science Foundation (project No. 22-13-00077). The support of the Supercomputer Center of Novosibirsk State University is also acknowledged.

Kinetics and Mechanism of Thermal Decomposition of Triphenyl Phosphate in Flow Reactor

✉ **Andrey G. Shmakov**[1], **Alexander M. Mebel**[2], **Oleg P. Korobeinichev**[1], **Denis P. Porfiriev**[3],
Ksenia N. Osipova[1], **Ilya E. Gerasimov**[1], **Denis A. Knyazkov**[1], **Bin Yang**[4]

[1]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2]Florida International University
Miami, Florida, USA
[3]Samara National Research University
Samara, Russia
[4]Tsinghua University
Beijing, China

✉ shmakov@kinetics.nsc.ru

The main method for reducing the combustibility of polymeric materials is the introduction of flame retardants into them. An important scientific problem is to understand the mechanism of action of a flame retardant during the polymer combustion. The purpose of this work was to experimentally and theoretically study the conversion of triphenyl phosphate (TPP) during its thermal decomposition in an inert medium, i.e., under conditions which are characteristic of the flame zone near the surface of the polymer.

The high-temperature pyrolysis of TPP vapor in Ar was studied by using thermal flow reactor at a pressure of 1 atm. Mass spectra of products of thermal decomposition of TPP vapors were measured by probe molecular beam mass spectrometry at 300–1,000°C. Using the G3(MP2, CC) model chemistry, along with the B3LYP method in the framework of density functional theory (DFT) with the 6-311G(d, p) basis set, the calculations were performed to optimize the geometry of all structures on the considered potential energy surfaces of TPP and products of primary and secondary decomposition of TPP. The kinetic rate constants of the thermal decomposition reaction of TPP were also calculated using the RRKM theory and the method of the main kinetic equation (RRKM-ME) implemented in the MESS program code, thermochemical parameters for TPP and products of primary and secondary decomposition of TPP in temperature range 200–6,000 K were obtained. Based on the results of calculations, as well as the mechanisms of transformation of the phenyl and phenoxyl radicals from the literature, a combined detailed chemical-kinetic mechanism that describes the pyrolysis of TPP in inert medium was created.

The comparison of the results of numerical calculations of the TPP pyrolysis products composition in the reactor showed that the developed mechanism quantitatively predicts the dependence of the TPP concentration on the reactor temperature distribution, and for intermediate compounds, this mechanism finely describes the experimentally observed trends in the conversion of phosphorus-containing substances on the reactor temperature.

Acknowledgements: this work is supported by the Russian Foundation for Basic Research (project No. 21-53-53026).

Ignition and Pyrolysis of Coal Microparticles under the Action of Pulsed Laser Radiation

Yaroslav V. Kraft[1], ✉**Boris P. Aduev**[1], **Denis R. Nurmukhametov**[1],
Valeriy D. Volkov[1], **Zinfer R. Ismagilov**[1,2]

[1]*Federal Research Center for Coal and Coal Chemistry SB RAS*
Kemerovo, Russia
[2]*Boreskov Institute of Catalysis SB RAS*
Novosibirsk, Russia

✉lesinko-iuxm@yandex.ru

The paper presents the results of studies on establishing the patterns of development of thermal processes in coals of the Kuznetsk coal basin of marks B, DG, G, Zh and K (Russian coal classification system) in air and coal mark *B* in an inert medium under the action of laser pulses. Coal particles with a size of < 63 µm were used, the distribution maximum fell on a particle size of ~20 µm.

The emission spectra of the particles' surface of the studied grades of coal were measured under the action of single laser pulses (1,064 nm, 120 µs) with different energy densities in air medium. It has been established that the emission spectra of the surface of coal particles during the action of a single laser pulse in an air medium have a non-elementary character. At the energy density of the laser radiation corresponding to the ignition detection threshold, the emission of the CO flame and excited H_2^* and H_2O^* molecules contribute to the spectra. With an increase in the energy density of laser radiation, the emission of carbon particles contributes to the spectra. It is shown that for coal particles there are three stages of ignition with characteristic time intervals.

The results of the study of pyrolysis of pelletized samples of coal mark *B* under the action of pulsed laser radiation (1,064 nm, 120 µs, 6 Hz, 1.2–2.0 J/cm^2) are also presented. H_2, CH_4, H_2O, CO and CO_2 were found in the composition of gaseous pyrolysis products of coal samples. It has been established that with an increase in the energy density per pulse from 1.2 to 2.0 J/cm^2, the volume fraction of H_2 in the composition of gaseous pyrolysis products increases, while the volume fraction of CO_2, on the contrary, decreases. The volume fractions of CO and CH_4 are close to constant. It is shown that the volume of combustible gases formed per unit mass of the reacted sample increases linearly with increasing radiation energy density, while the volume fraction of combustible gases (H_2, CH_4, and CO) in the mixture of gaseous pyrolysis products at a laser radiation energy density of 2.0 J/cm^2 is 93 %. It is also shown that with an increase in the energy density of laser radiation, the fraction of the reacted coal sample increases linearly. The influence of the coal mineral component on the yield of combustible gases during laser pyrolysis and on the structure of the coal sample surface that is formed as a result of exposure to laser radiation has been established.

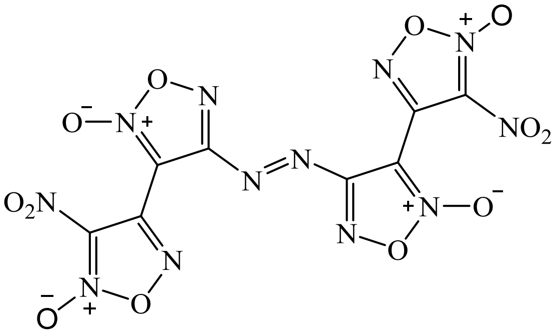
Thermally Stable and High-Performance Energetic Materials Based on the Azo-Bridged Bifuroxan Core

✉ **Alexander A. Larin**[1], **Nikita V. Muravyev**[2], **Leonid L. Fershtat**[1]

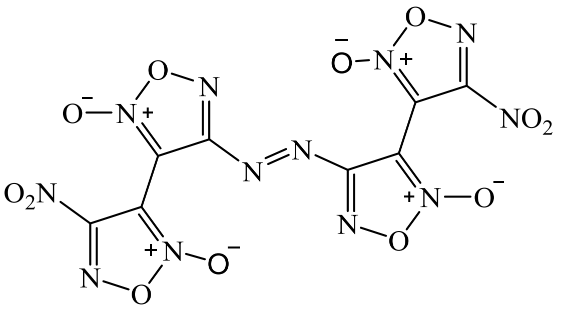
[1] *Zelinsky Institute of Organic Chemistry RAS*
Moscow, Russia
[2] *Semenov Federal Research Center for Chemical Physics RAS*
Moscow, Russia

✉ roby3@mail.ru

Polyheterocyclic systems are of great interest as potential components of high-energy formulations of a new generation [1]. In this work, the most powerful energetic materials, azo-bridged bifuroxans (see Figs. 1a, 1b) in particular, were studied. These hydrogen-free molecules ($C_8N_{12}O_{12}$) exhibit outstanding heats of formation, high thermal stabilities and acceptable sensitivities, compared with benchmark explosives (CL-20, PETN, HMX). In addition, a complex investigation of physicochemical and detonation parameters for two target energy-rich structures was performed. Structure in Fig. 1a exhibited decent thermal stability (decomposition temperature > 200 °C), moderate sensitivity to mechanical stimuli along with a notable nitrogen-oxygen content (79 %), positive oxygen balance to CO (+14.0), high density (1.88 $g \cdot cm^{-3}$) and excellent heat of formation (> 1000 $kJ \cdot mol^{-1}$). Therefore, these energetic compounds may be considered as promising candidates for a variety of energetic applications.



1a



1b

Acknowledgements: this work was supported by the Russian Science Foundation (project No. 19-73-20074).

[1] Larin A. A., Shaferov A. V., Epishina M. A., Melnikov I. N., Muravyev N. V., Ananyev I. V., Fershtat L. L., Makhova N. N. (2020). *ACS Appl. Energy Mater.*, *3*, 7764–7771.

Equation of State of Moon and Asteroid Matter

✉ **Igor V. Lomonosov**, **Vadim V. Kim, Afanasii V. Ostrik**

Institute of Problems of Chemical Physics of RAS
Chernogolovka, Russia

✉ director@icp.ac.ru

The equation of state (EOS) is the fundamental property of matter defining its individual properties. EOS governs the system of gas dynamic equations and defines significantly the accuracy and reliability of the results of numerical modeling. In practice, it is required for numerical modeling of numerous processes arising under the conditions of extreme energy densities.

Knowledge of the properties of the matter of the Earth, planets and other objects of the Solar system at high pressures is the subject of fundamental research. This information is also of great practical importance for solving the problem of asteroid hazard. In this paper, we describe the EOS problem of the substance of the Moon surface—regolith, and the asteroid matter—ordinary chondrite. We propose the method for constructing EOS for regolith and chondrite for the high pressure region, discuss the EOS model and obtained results.

Shock Initiation of Detonation in Heterogeneous Explosives Based on Nitromethane

✉ **Valentina M. Mochalova**[1], **Alexander V. Utkin**[1], **Mikhail Shakula**[1,2], **Vladimir Lavrov**[1]

[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia
[2] *Moscow Institute of Physics and Technology*
Dolgoprudny, Russia

✉ roxete20000@mail.ru

The liquid explosive nitromethane (NM) is of great interest for the study of detonation processes. Its detonation properties are well investigated and are determined by a chemical reaction occurring uniformly throughout the entire volume of a shock-compressed substance [1]. The addition of various microballoons dramatically changes its critical diameter and sensitivity to shock-wave action [2]. This is a consequence of the appearance of hotspots in which the rate of chemical reaction increases, and decomposition of the explosive becomes heterogeneous in volume. The mixtures of NM with calibrated glass microspheres are ideal for research, analysis and numerical modeling, since hotspots of the same size and temperature are obtained under compression.

In this work, the influence of glass microballoons on the shock initiation of detonation and critical diameter of nitromethane is investigated. In the experiments, NM with a density of 1.12 g/cc and hollow glass microballoons with an average diameter of 70 μm and a density of 0.14 g/cc are used. A VISAR interferometer recorded particle velocity profiles and measured detonation velocity in a mixture of gelled NM with microballoons. Studies have shown that when we add 5 wt.% of microballoons, a sharp decrease in the critical diameter of gelled NM from 16,5 mm to 5 mm is observed. The threshold of shock-wave sensitivity has also significantly dropped. In NM, it exceeds 7.7 GPa, and the addition of microballoons reduces the initiation pressure several times. It was found that at 5 wt.% of microspheres, a shock wave with an amplitude of 2 GPa leaded to the initiation and development of detonation. Moreover, the character of initiation is different from that observed in NM, where the period of induction is clearly expressed. But in the mixture of gelled NM and microballoons (95/5), the reaction begins immediately after the shock jump.

Acknowledgements: this work was supported by Russian Foundation for Basic Research (project No. 20-03-00245a (experiments)) and performed in accordance with the program of Ministry of Science and Higher Education of the Russian Federation No. AAAA-A19–119071190040–5 (calculation).

[1] Dremin A. N., Savrov S. D., Trofimov V. S., Shvedov K. K. (1970). *Detonation Waves in Condensed Media*. Nauka.

[2] Lee J. J., Frost D. L., Lee J. H. S., Dremin A. (1995). *Shock Waves, 5*, 115–119.

Screening of Energetic Cocrystals Using Thermal Analysis

✉ **Nikita V. Muravyev**[1], **Igor N. Melnikov**[1], **Konstantin A. Monogarov**[1],
Leonid L. Fershtat[2], **Igor L. Dalinger**[2], **Kyrill Yu. Suponitsky**[3], **Alla N. Pivkina**[1]

[1] *Semenov Federal Research Center for Chemical Physics RAS*
Moscow, Russia
[2] *Zelinsky Institute of Organic Chemistry RAS*
Moscow, Russia
[3] *Nesmeyanov Institute of Organoelement Compounds RAS*
Moscow, Russia

✉ n.v.muravyev@ya.ru

Co-crystallization is an important crystal engineering approach to design diverse materials with improved functional properties. The co-crystal concept is well-developed in pharmaceutical industry, but it is relatively new for energetic materials design. In this study we compiled a dataset of previously published energetic co-crystals (ECCs) and categorized ECCs by the typical patterns of thermal behavior (ECC vs. neat coformers). Then, for a smaller dataset (~30 entries) of chemically diverse co-crystals, we applied and modified the available thermal screening approaches. Finally, we report a unified procedure that meets the criteria of high-throughput screening. With the suggested approach several pairs with promising energetic materials were screened and new co-crystals are found and reported.

Acknowledgements: this research was supported by the Ministry of Science and Higher Education of the Russian Federation (agreement with Zelinsky Institute of Organic Chemistry RAS No. 075-15-2020-803).

Study of Shock Compressibility and Shock-Induced Temperature of Oxides by Mach Cumulative Explosive Generators

✉ **Dmitry N. Nikolaev, Alexandr V. Shutov, Igor V. Lomonosov**

Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia

✉ nik@ficp.ac.ru

The development of shock waves generators based on Mach reflection of shock wave started in early 1970s. In this presentation, the results of the last 10 years of our research are presented. A number of improvements has been introduced. Fully cylindrical design with sophisticated detonation distributor makes it possible to generate a conical imploding detonation wave using easy-to-made cylindrical geometry of the explosive charge and metal liner. Detonation distributor produced by the CNC milling machine provides perfect symmetrical convergence of the shock wave. The implemented double Mach reflection (DMR) regime provides flat and steady 1D shock wave in a sample. Besides, 2-staged generators have been developed, providing further rise of the shock parameters. The experimental development was supported by a 3D numerical simulation of explosion devices. Thus, a set of generators makes it possible to achieve pressures from 200 to 2,000 GPa, which can be compared with laser shock and electromagnetic launching techniques.

In addition, a set of diagnostic tools was developed, including fast optical fiber-gauges measuring wave velocities and optical pyrometry.

The results of the study of shock wave properties of the Earth mantle oxides, such as Al_2O_3, TiO_2, MgO, FeO, are presented. In porous samples, shock compressibility was measured. In monocrystalline—optically transparent samples—the Hugoniot temperatures were also measured. The obtained data was compared with the calculated equations of state and other available experiments, and allowed us to draw some conclusions about high-pressure melting curves of the studied substances.

Acknowledgements: This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Institute for High Temperatures of the Russian Academy of Sciences, project No. 075-15-2020-785). All the experiments were carried out by using the equipment of Moscow Regional Explosive Center for collective use of the Institute of Problems of Chemical Physics RAS.

Influence of Dispersion of Coal Particles on the Characteristics of Laser Ignition

✉ **Boris P. Aduev**[1], **Denis R. Nurmukhametov**[1], **Yaroslav V. Kraft**[1], **Zinfer R. Ismagilov**[1,2]

[1] *Federal Research Center for Coal and Coal Chemistry SB RAS*
Kemerovo, Russia
[2] *Boreskov Institute of Catalysis SB RAS*
Novosibirsk, Russia

✉ lesinko-iuxm@yandex.ru

In this work we studied laser ignition (1,064 nm, 120 µs) of coal particles of various grades with a size of 0.25–50 µm. The objects of study were dispersed particles of brown coal, hard coals of grade DG, G, Zh, K (Russian coal classification system) with a narrow granulometric distribution from ~0.25 to 60 µm. Coal samples with bulk density $\rho = 0.5$ g/cm^3 were used.

It was found that the dependence of the ignition threshold H_{cr} on particle size at all three stages of ignition is determined by two tendencies. Firstly, a decrease in the particle size from the maximum values to 10 µm leads to a decrease in the ignition threshold. Secondly, at values < 10 µm, an increase in ash content and decrease in carbon content in the studied coal particles are observed, which leads to an increase in ignition threshold values at particle sizes d ~ 1–2 µm. As a result of the action of two tendencies, a minimum of the ignition threshold $H_{cr}^{\min}$ is formed in a particle size range of 1–5 µm:

- 1÷2 µm for brown coal;
- 2 µm for coal grade DG;
- 4 µm for coal grade G;
- 0.7 µm for coal grade Zh;
- 2 µm for coal grade K.

The dependences of ignition thresholds of coal particles of various sizes with a narrow granulometric distribution on the content of volatile matter are qualitatively similar to those obtained earlier [1; 2] for the samples with a wide particle size distribution. This shows the generality of the mechanisms of laser ignition of particles of any size, taking into account the quantitative threshold differences. For technical applications, it should be taken into account that the "dangerous", easily flammable particle size range for coal grades B, DG, G, Zh and K should be taken to be the range of $d = 1 \div 5$ µm.

[1] Aduev B. P., Nurmukhametov D. R., Kraft Y. V., Ismagilov Z. R. (2020). *Optics and Spectroscopy, 3*, 429–435.

[2] Aduev B. P., Nurmukhametov D. R., Kraft Y. V., Ismagilov Z. R. (2020). *Chemistry for Sustainable Development, 6*, 518–526.

Experimental and Numerical Study of the Structure of $NH_3/H_2/O_2/Ar$ Flames at Elevated Pressures

✉ **Ksenia N. Osipova**[1,2], **Andrey G. Shmakov**[1]

[1]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2]Novosibirsk State University
Novosibirsk, Russia

✉ k.n.osipova23@gmail.com

Transition to carbon-free fuels is one of the most important problems for modern energetics. Despite the fact that hydrogen use can mitigate the zero-carbon target, its direct application in transportation systems is associated with problems of fire and explosion safety. Hydrogen carriers, e.g., ammonia, are considered a prospective solution. Unlike hydrogen, the infrastructure of ammonia storage, transportation and distribution are well-developed and have many years of exploitation experience. Nevertheless, pure ammonia has poor combustion properties, which can be improved by hydrogen addition. Moreover, hydrogen can be produced via ammonia cracking.

The scope of the present work was to obtain new experimental data on the structure of $NH_3/H_2/O_2/Ar$ flames ($\phi = 0.8$, 1.0 and 1.2) at 4 and 6 atm and to compare them with the numerical results obtained using four published mechanisms (Models).

For flame structure measurement, a molecular beam mass-spectrometric setup with soft electron impact ionization was used. Flames were stabilized on the flat burner ($T_0 = 368$ K). For high pressure measurements, the burner was placed at the chamber pressurized with N_2. The temperature profiles were measured using thin S-type thermocouples with a diameter of 0.03 mm. PREMIX code from CHEMKIN package was used for numerical modeling. A comparison with the experimental data revealed that recently developed Model 4 [1] has the best predictive capability.

Ammonia molecule has fuel-bonded nitrogen which inevitably enhances NO_x formation. Both experimental and numerical data showed that NO is mainly present in the post-flame zone, while concentration of N_2O and NO_2 is negligible. Moreover, the transition to rich blends reduces NO concentration in the post-flame zone as well as peak-concentration of NO, N_2O and NO_2. Pressure increase has the same effect on NO_x concentration. Model 4 showed good agreement for NO mole fraction profile; however, for N_2O and NO_2 larger discrepancies were observed. The numerical analysis indicated that N_2O and NO_2 mainly form from NO. Thus, the NO- submechanism needs to be refined.

Acknowledgements: this work is supported by the Ministry of Science and Higher Education of the Russian Federation (project No. 075-15-2020-806).

[1] Zhang X., Moosakutty P., Rajan R. P., Younes M., Sarathy S. M. (2021). *Combust Flame, 234*, 11653.

Gaseous Products of the Methane Pyrolysis in Laser Initiated Cr/Al_2O_3 Nanoparticle Evaporation Process in Methane-Argon Medium

✉ **Aleksandr N. Pyryaev**[1,2], **Vladimir N. Snytnikov**[1], **Valeriy N. Snytnikov**[1,2]

[1] Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
[2] Novosibirsk State University
Novosibirsk, Russia

✉ pyrayevcat@gmail.com

During the last few decades, laser initiated evaporation process has become widely used to produce nanoparticles and coatings for electrical conductivity and catalytic purposes [1] including hydrogen generation from light alkanes [2]. Laser radiation allows one to supply a high density of energy in the reaction zone and to intensify the dissociation and reassociation of the reactant molecules. Consequently, there is a greater number of different chemical bonds to produce a wider range of different products and materials, including gaseous products. There are many difficulties associated with gaseous product analysis in laser initiated process of Cr/Al_2O_3 nanoparticles formation in the methane-argon medium at low pressure. In this work some solutions for the procedure of chromatographic analysis of gaseous products synthesized during methane pyrolysis in a two-phase system gas-nanoparticle are presented, and some optimization approaches for intensification of methane pyrolysis stimulated by laser synthesis of catalytically active nanoparticles are proposed.

Laser synthesis of Cr/Al_2O_3 nanoparticles was conducted in a self-designed evaporation cell in methane-argon medium using continuous gas-discharge CO_2 laser with maximum output power of up to 120 W. The previously prepared tablets of pressed Cr/Al_2O_3 powder were used as evaporation target. The gaseous products of the methane pyrolysis reaction were characterized by chromatographic complex including a LKhM-80 (USSR) chromatograph with NaX nozzle column and a Kristall 5000 chromatograph (Khromatek, Russia) with a capillary column (Agilent Technologies, HP-Al-KCl sorbent). Special sampling system capable of capturing gas mixture from the evaporation cell in real time mode with compensation of chamber vacuum was created.

The experiments were carried out using several CH_4/Ar ratios, gas supply configuration and laser settings to optimize the pyrolysis process. The main products of pyrolysis were hydrogen (maximal obtained reaction yield was ca. 4 %) and amorphous carbon (soot) without any intermediate hydrocarbons (ethane, propane, acetylene, etc.). The experimental parameters' variation, such as pressure in evaporation cell and methane-argon ratio, gives some quantitative variation in the products of reaction.

[1] Spreafico C., Russo D., Degl'Innocenti R. (2022). *Journal of Intelligent Manufacturing, 33*, 353–385.

[2] Snytnikov V., Snytnikov Vl., Masyuk N., Markelova T., Parmon V. (2021). *Instruments and Experimental Techniques, 64*(3), 474–482.

Transfer of Soot Aerosol of Siberian Forest Fires of 2019 in the Stratosphere

✉ **Ilya I. Romanchenko**[1], **Alexandr A. Cheremisin**[1],
Valery N. Marichev[2], **Pavel V. Novikov**[1,3], **Dmitry A. Bochkovskiy**[2]

[1]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2]*Zuev Institute of Atmospheric Optics SB RAS*
Tomsk, Russia
[3]*Krasnoyarsk Institute of Railway Transport*
Krasnoyarsk, Russia

✉ ilya-romanchenko@mail.ru

Currently, due to possible climatic consequences, significant attention is paid to the issues of stratospheric pollution by aerosols of volcanic origin and soot aerosol from aircraft. In the last decade, another source of stratospheric pollution has been discovered—pyrocumulative emissions arising from powerful and extensive forest fires.

In summer of 2019, numerous severe forest fires were recorded on the territory of Eastern Siberia. Along with this, summer and autumn LIDAR observations in Tomsk showed that there are dense aerosol layers in the stratosphere at an altitude of 10 to 16 km. The analysis of air currents showed that smoke from fires, even if they got to such high altitudes, had to be carried east, in the opposite direction from Tomsk. Initially, preference was given to the hypothesis that this aerosol appeared over Western Siberia as a result of the transfer of volcanic aerosol after the eruption of Raikoke on June 21, 2019. We carried out a more thorough analysis of the origin of aerosol layers observed in the stratosphere over Tomsk in summer and autumn of 2019.

In the paper we present the results of calculations of backward isentropic trajectories of air masses. They were constructed in the HYSPLIT software package using GDAS meteorological data containing global data of the satellite measurements of wind speed in the atmosphere. Data from the CALIOP space LIDAR on the CALIPSO satellite was also used, which made it possible to localize the appearance of aerosol plumes along the trajectories of air masses. Radiometric data of the VIIRS system from the Suomi NPP satellite and data on the brightness temperature in the far-infrared region (8.6 microns) obtained from the Himawari-8 satellite was also used. This data made it possible to obtain information about the geographical localization of forest fires in vast areas of the Northern Hemisphere.

As a result of a comprehensive analysis of ground and satellite data, it is shown that the aerosols observed over Tomsk in summer and autumn of 2019 were formed as a result of pyrocumulative soot emissions during forest fires in Siberia.

Synthesis and Study of Properties of ZrO_2-Based Catalysts

✉ **Maria A. Savastyanova**, **Konstantin O. Ukhin, Natalia B. Kondrashova, Victor A. Valtsifer**

Institute of Technical Chemistry UB RAS
Perm, Russia

✉ mariysav75@gmail.com

Transition metals and their oxides are well-known as catalysts for oxidation-reduction processes. An important stage for the creation of a highly efficient catalytic system is search and development of the carrier synthesis methods which have a direct impact on their structure and catalytic properties [1; 2].

Zirconium dioxide has a number of valuable properties (chemical resistance, high temperature resistance to destruction and sintering) which determine its use as a carrier for catalytically active particles of various high-temperature processes, as well as the presence of weak acidic and basic centers, stability in oxidizing and reducing atmospheres that determines its use as a catalyst [3].

This paper presents the results of the study of properties of combined ZrO_2-based catalysts modified by transition metal oxides (copper/zinc and nickel/zinc).

The effect of the method of doping with copper, nickel and zinc compounds on the phase composition, porous structure, particle size and catalytic activity of synthesized catalysts is studied.

It was found that the samples obtained by template hydrothermal synthesis, followed by the template removal (CTAB) have a specific surface area of 35 m^2/g (copper/zinc) and 29 m^2/g (nickel/zinc), which is higher than the textural characteristics of commercial zirconium dioxide (8.7 m^2/g). The phase composition of these samples is a mixture of monoclinic form and high-temperature cubic modification of ZrO_2. The crystallite sizes in these samples are 15.2 and 20.1 nm. It is shown that the sample containing nickel and zinc oxides exhibits the greatest catalytic activity.

[1] Dong R., Wang H., Zhang Q., Xu X., Wang F., Li B. (2015). *CrystEngComm journal*, *17*(38), 7406–7413.

[2] Dey S., Dhal G. C., Mohan D., Prasad R. (2017). *Bulletin of Chemical Reaction Engineering & Catalysis*, *12*(3), 393–407.

[3] Kouva S., Honkala K., Lefferts L., Kanervo J. (2015). *Catalysis Science & Technology*, *5*(7), 3473–3490.

Proton Radiography of Explosively Driven Targets and Static Objects

✉ **Nikolay S. Shilkin**[1], **Victor B. Mintsev**[1], **Dmitry. N. Nikolaev**[1], **Denis S. Yuriev**[1],
Alexey V. Kantsyrev[2], **Anton V. Bogdanov**[2], **Vsevolod A. Panyushkin**[2],
Alexey V. Skobliakov[2], **Dmitry. S. Kolesnikov**[2], **Roman O. Gavrilin**[2], **Alexander A. Golubev**[2,3]

[1]Extreme States of Matter department, Institute of Problems of Chemical Physics of RAS
Chernogolovka, Russia
[2]National Research Center Kurchatov Institute-ITEP
Moscow, Russia
[3]Private Institution Science and Innovations SC Rosatom
Moscow, Russia

✉ shilkin@ficp.ac.ru

We report our experimental results on proton radiography of explosively driven targets and static objects. The experiments were conducted on a proton microscope with the use of magnetic optics PUMA [1] equipped with a small blasting chamber. The PUMA microscope was developed for non-destructive investigation of static and dynamic objects with areal density up to 20 g/cm^2. Proton beams with the energy of 800 MeV were provided by the TWAC-ITEP terawatt accelerator facility. The field of view of the microscope was about 20 mm. A typical beam was composed of three or four bunches with the intensity ca. 10^{10} protons per bunch. A set of compact explosive generators [2] for the investigation of gas-dynamic processes at high pressures and temperatures was developed to fulfill the conditions of proton radiography experiments at PUMA. The experimental results on shock-compressed non-ideal plasma of argon and xenon and detonation of condensed explosives are presented. The results on proton radiography of static objects are also discussed.

[1] Kantsyrev A. V. et al. (2014). *Instrum.Exp. Tech., 57*, 1–10.
[2] Mintsev V. B. et al. (2018). *Contrib. Plasma Phys.*, *58*, 93–98.

Discharge Setup for Generation and Study of Plasmoid above the Water Surface: First Results

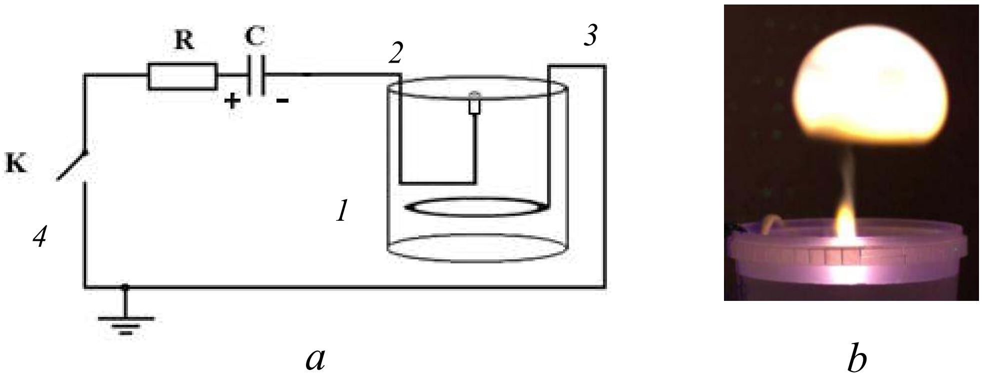
✉ **Egor A. Shishkin, Alexander A. Cheremisin, Vladimir P. Isakov**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ egor.shishkin.1996@mail.ru

The discharge technologies are widely used in many industries: for the synthesis of various compounds, such as fullerenes, nanotubes, and for the production of ozone and surface treatment. Discharge phenomena are also widespread in nature. For example, there are linear and ball lightings. Many discharge processes are poorly understood. This paper presents a high-voltage pulsed discharge setup for generation of plasmoids above the water surface. This object evoked a considerable interest during the last decade.

The scheme of the developed and created discharge setup is shown in Figure, *a*. A plasmoid (Figure, *b*) was created by discharging a high-voltage capacitor bank through the discharge cell. The battery voltage was 5.5 kV, the capacity was 1 mF.



a) electrical scheme; *b)* photo of the plasmoid. *1*—discharge cell, *2*—central electrode located above water surface, *3*—second electrode submerged into water, *4*—key *K*; *C*—capacitor bank, *R*—resistance limiting discharge current

As a result of the discharge, a brightly luminous plasmoid was formed with a lifetime of up to 0.6 s. The mechanism of plasmoid formation, its structure, and the nature of its long life are still poorly understood. At present, we have studied the dependence of the shape and lifetime of the plasmoid on the electrical voltage and other parameters of the setup. The schemes for registration of the dispersed phase inside the plasmoid have been developed. The first results indicating the formation of aerosol particles inside the plasmoid are obtained.

Effect of Me/B-Powder on Ignition and Combustion of HEMs

✉ **Ivan V. Sorokin**[1], **Alexander G. Korotkikh**[2]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Tomsk Polytechnic University*
Tomsk, Russia

✉ sorokin@kinetics.nsc.ru

The study of the ignition and combustion characteristics of high-energy materials (HEMs) is important for solving a number of practical problems related to the assessment of explosion safety and calculation of transition processes in power installation for various purposes (rocket and space technologies, weapons, pyrotechnics). To improve the ignition and combustion characteristics of HEM, combustion catalysts, powders of various metals or their oxides are used. In order to increase the combustion heat and ignition characteristics of HEM, boron-based powders or metal borides are used.

This paper presents the experimental data on the experimental characteristics of ignition and combustion of HEM based on ammonium perchlorate, butadiene rubber, and metal fuel base on Me/B-powder. It was shown that the use of 15.7 wt.% the mixed ultrafine powders (UFP) based on Al/B, Ti/B, Ni/B or Fe/B in HEM reduces the ignition delay time by 7–50 % compared to boron-based HEM within the range of heat flux density from 60 to 200 W/cm^2. Based on the experimental data of the ignition delay time versus heat flux density, the formal activation energy, the multiplication of the specific heat flux of the reactions by the pre-exponent and the ignition temperature are calculated. These could be used in mathematical modeling of the ignition for composite solid propellant containing metal fuels. We carried out a series of combustion measurements for metallized HEM compositions in the range of nitrogen pressure of 0.5–5.0 MPa. The burning rate and power exponent were determined for test HEM compositions in a constant pressure bomb. It was established that the complete replacement of amorphous boron by mechanical mixture of Fe/B, Ti/B and Al/B in HEM increases the burning rate of the HEM sample by 1.2–3.4 times depending on pressure. The mechanical mixture of Al/B UFP is the most effective to increase the burning rate of HEMs based on AP and butadiene binder.

[1] Gong L., Li J., Li Y., Yang R. (2020). *Propellants, Explosives, Pyrotechnics, 45*, 1634–1644.

[2] Korotkikh A. G., Sorokin I. V., Selikhova E. A., Arkhipov V. A. (2020). *Combustion and Flame, 222*, 103–110.

[3] Liang D., Xiao R., Liu J., Wang Y. (2019). *Aerosol Science and Technology, 84*, 1081–1091.

A Pocket Model with a Tetrahedral Cell for Aluminum Agglomeration in Composite Propellants

✉ **Ivan V. Sorokin**[1], **Oleg G. Glotov**[1,2], **Alexandr A. Cheremisin**[1]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State Technical University*
Novosibirsk, Russia

✉ sorokin@kinetics.nsc.ru

Knowledge of the initial size distribution of agglomerates is important for modeling of many processes in a rocket engine, such as predicting the slag accumulation, etc. The agglomeration models are developed to give size distribution for the condensed particles leaving the burning surface. There are various agglomeration models in the literature which can be classified depending on the approach: empirical, physical, pocket, packing-based, statistical, etc. [1–3]. The most known model is the Cohen pocket model [4]. In this model, an elementary spatial propellant cell is a cube at the vertices of which there are particles of an oxidizer, and the volume between them—the "pocket"—is filled with a binder and metal particles forming an agglomerate.

This paper presents a new model for estimating the size of metal agglomerates. Based on an the empirical analysis of the propellants structure,the tetrahedral pocket model is proposed, in which the propellant pocket corresponds to the internal volume of a triangular pyramid (regular tetrahedron). Oxidizer particles are located at the vertices of the tetrahedron, the internal volume is filled with a mixture of fuel-binder and metal.

The paper presents a comparison of the experimental data with the results of calculations using the tetrahedral model proposed, the Cohen model [1], as well as the empirical correlations of Hermsen, Salita, Beckstead, Grigoriev, and Duterque. The comparison was carried out for a composite solid propellant based on ammonium perchlorate, binder and aluminum powder. It was shown that tetrahedral pocket model in many cases gives better results for predicting the agglomeration diameter than other approaches.

Acknowledgements: the work was financially supported by the Grant of the Ministry of Science and Higher Education of the Russian Federation (No. 075-15-2020-781).

[1] Gallier S., Propellants, Explosives, Pyrotechnics **2009**, 34, pp. 97-105.

[2] Grigor'ev V. G., Kutsenogii K. P., Zarko V. E. (1981). Combustion, Explosion, and Shock Waves, 4, 356–362. (in Russ.)

[3] Rashkovsky S. A. (1998). Combustion Science and Technology, 136, 149–169.

[4] Cohen N. S. (1983). AIAA Journal, 21, 720–730.

Influence of Forming Spark Plasmoids on Kinetics of Propane-Oxygen Mixture Combustion in a Closed Volume

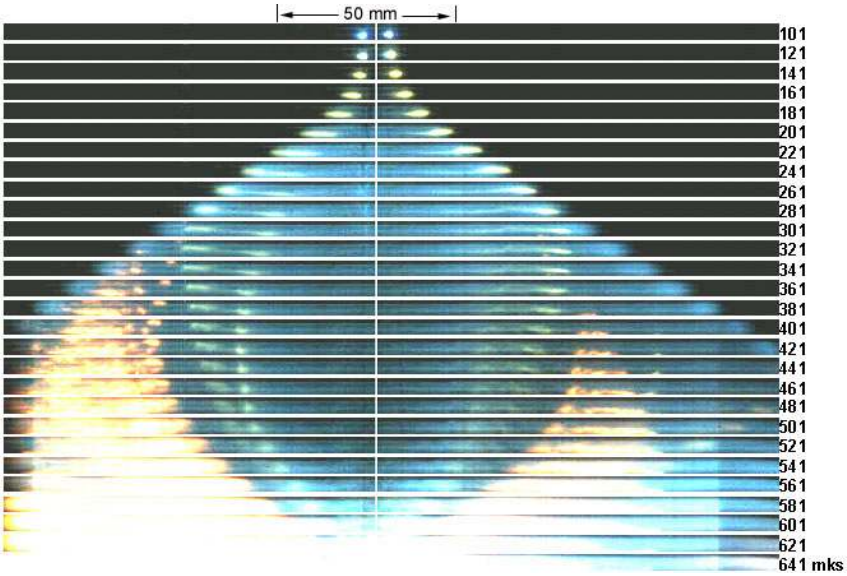
✉ **Vyacheslav S. Teslenko, Alexey P. Drozhzhin**

Lavrentyev Institute of Hydrodynamics SB RAS
Novosibirsk, Russia

✉ vteslenko@mail.ru

Basing on the principles of ecological safety, automobiles all over the world have been actively switching to gas fuel.

This work deals with the research of the propane-oxygen mixture combustion for one- and two-dimensional variants of combustion processes developing in a closed volume depending on the number of initiation sparks. The experimental set-up was performed according to the scheme presented in [1].



The Figure demonstrates one of the photographic records of initiation and combustion of stoichiometric propane-oxygen mixture taking place in a tube with the length L = 54 cm, and inner diameter 5 mm. The initiation was realized synchronously by two sparks in the middle part of the tube (L/2). The distance between the sparks was 7 mm.

The photographic record clearly shows that the symmetric combustion occurring at speed 200–240 m/s is led by two spark plasmoids; then, due to the backward motion of plasmoids, the combustion accelerates to 1,800 m/s.

Similar processes take place in a two-dimensional variant, but they have more complex dynamics. Therefore, the presented one-dimensional variant is more informative. It is shown that it is possible to decrease time duration of full gas combustion in the model cylinder of internal combustion engine (ICE) 72 mm in diameter to 350 µs.

The obtained results are the basis for new technological development increasing a maximum permissible number of revolutions of ICE and efficiency coefficient.

[1] Teslenko V. S., Drozhzhin A. P. (2021). Propane Multipoint Ignition and Combustion in an ICE Cylinder Simulator. *Thermophysics and Aeromechanics, 28*(5), 703–710. http://swsl.hydro.nsc.ru/.

The Influence of Synthesis Parameters on the Characteristics of MOs/CB Composites and Their Effectiveness for the Thermal Decomposition of Ammonium Perchlorate

✉ **Konstantin O. Ukhin**[1], **Irina I. Lebedeva**[1], **Maria A. Savastyanova**[1],
Natalia B. Kondrashova[1], **Victor A. Valtsifer**[1], **Vladimir N. Strelnikov**[1], **Ivan G. Mokrushin**[2]

[1] Institute of Technical Chemistry UB RAS
Perm, Russia
[2] Perm State University
Perm, Russia

✉ ukhin_k@mail.ru

At present, different catalysts are employed in the thermal decomposition of ammonium perchlorate (AP), and transition metal oxides and their composites are preferable materials for catalytic applications [1]. This study is focused on application of combined transition metal (iron and cobalt) oxide catalysts deposited on the surface of a carbon carrier for the decomposition of ammonium perchlorate (AP). Catalyst samples with different contents of iron and cobalt oxides were prepared by the impregnation and chemical precipitation methods at varying calcination temperatures.

Structural and morphological features of the synthesized catalysts were studied by applying the XRD, SEM, and BET methods. It was found that at increased heat treatment temperature contributes to an increase in crystallinity of the oxide phases. Partial reduction of Co_3O_4, initially to CoO at 600 °C and then to metallic cobalt Co at 700 °C, was observed. Under chemical deposition conditions with an increase in the heat treatment temperature, the specific surface area and pore volume of the catalysts decrease to the values corresponding to the carbon carrier. The reason for that could be the nonporous structure of metal oxides, the textural characteristics of which decrease with an increase in the size of crystalline blocks of metal oxides. In an inert atmosphere, the isolated particles of Fe_3O_4 and Co_3O_4 spinels uniformly distributed on the carbon carrier surface are formed. For the catalysts obtained by the impregnation method, high thermal decomposition temperatures not only speed up the process, but also promote aggregation and sintering of the oxide particles. The results of the DSC study showed that synthesized composite catalysts possess excellent catalytic properties for the thermal decomposition of AP. Furthermore, the appearance of reduced forms of metals in the composition of the active catalytic component of the catalysts increases their catalytic activity and the thermal effect of the AP thermolysis reaction.

Acknowledgements: the reported study was funded by RFBR and Perm Territory (project No. 20-43-596007).

[1] Ukhin K. O., Kondrashova N. B., Valtsifer V. A. et al. (2021). *Propellants Explosives Pyrotechnics, 46*, 1696–1708.

Instability of Detonation Waves in Mixtures of Tetranitromethane with Methanol and Nitrobenzene

✉ **Alexander V. Utkin**, **Valentina M. Mochalova,**
Daniil Ya. Rapota, Vasiliy A. Sosikov, Sergey I. Torunov

Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia

✉ utkin@icp.ac.ru

Detonation waves in homogeneous explosives are unstable at certain kinetics of a chemical reaction [1; 2]. At the same time, it is necessary to distinguish between the loss of stability of a one-dimensional flow realized in the absence of boundaries influence and instability at the edge of charge. The consequence of manifestation of instability of the first type is the formation of a cellular structure of the detonation front. The second type of instability the authors called [3] the reaction termination wave.

Experimental studies of the relationship of various types of detonation waves instability in mixtures of tetranitromethane with nitrobenzene and methanol have been carried out. The registration of wave profiles and glow of the detonation front were made by the interferometer VISAR and high-speed cameras. It is shown that in mixtures of tetranitromethane with methanol, cellular instability of the detonation front and reaction termination waves appear simultaneously at a concentration of 50 wt.%. Whereas in mixtures with nitrobenzene, the reaction disintegration waves first occur at a concentration of nitrobenzene less than 65 wt.%, and only then, with an increase in concentration, cellular instability occurs. Thus, it is shown that the relationship between different types of detonation instability in liquid explosives is not strictly deterministic.

[1] Shchelkin K. I., Troshin Ya. K. (1963). *Gas Dynamics of Combustion*. Izd. Akad. Nauk SSSR, Moscow.

[2] Voitsekhovskii B. V., Mitrofanov V. V., Topchiyan M. E. (1963). *Structure of the Detonation Front in Gases*. Izd. Sib. Otd. Akad. Nauk SSSR, Novosibirsk.

[3] Dremin A. N., Savrov S. D., Trofimov V. S., Shvedov K. K. (1970). *Detonation Waves in Condensed Media*. Nauka, Moscow.

Development of Fire-Extinguishing Powder Compositions for Automatic Means of Explosion Containment

✉ **Igor V. Valtsifer**, **Artem Sh. Shamsutdinov, Anna V. Pyankova**

Institute of Technical Chemistry UB RAS
Perm, Russia

✉ valtsifer.i@itcras.ru

Automatic means of localizing explosions are used in mines which are dangerous due to the formation of an explosive concentration of methane and presence of suspended coal dust. Their effectiveness directly depends on the rate of creation of a flame-extinguishing barrier from particles of the fire-extinguishing powder (FEP), which overlaps the cross section of the mine. Explosion containment systems are able to suppress the source of ignition at the initial stage during deflagration, when propagation of the flame front passes at subsonic combustion rates.

Elimination of flame leakages outside the flame-extinguishing powder damper can be carried out only with the help of rapid ejection of FEP towards the flame front movement through the spray nozzle system.

In order to reduce the ejection time and, therefore, to reduce time necessary for creating a localizing barrier, FEP was created with decreased interaction forces between the particles of the powder composition and with lower energy value required to start the flow process.

During the study, we found that manufacturing of FEP with lower flow energy value is possible due to the use of modified silicon dioxide with spherical monodispersed particles of a size of ca. 55 nm. This composition has high flowability (specific flow energy 8.04 mJ/g, cohesion 0.340 kPa), superhydrophobicity (apparent contact angle 168°) and low moisture absorption. By means of the proposed one-step synthesis method for super hydrophobic silicon dioxide manufacturing, the surface properties were achieved without any additional post-synthetic modification. It makes synthesized particles quite promising functional filler for FEP designed for automatic means of localizing explosions.

Field tests of the developed FEP demonstrated the prospects of these researches.

Acknowledgements: the study was financially supported by the Perm Region Government within the framework of the scientific project "Fire Extinguishing Powder Composition of the Combined Gas Generating Effect" 03.18.2021 No. C-26/543.

Study of Laser Pyrolysis of Coals with Analysis of Gaseous Products

✉ **Boris P. Aduev**[1], **Yaroslav V. Kraft**[1], **Denis R. Nurmukhametov**[1],
Valeriy D. Volkov[1], **Zinfer R. Ismagilov**[1,2]

[1]*Federal Research Center for Coal and Coal Chemistry SB RAS*
Kemerovo, Russia
[2]*Boreskov Institute of Catalysis SB RAS*
Novosibirsk, Russia

✉ lesinko-iuxm@yandex.ru

The paper presents the results of a study of the action of pulsed laser radiation (1,064 nm, 120 μs, 10 Hz, 1.5 J/cm^2) on coal samples in an argon medium. The objects of study were coals of the Kuznetsk coal basin, grades D, OS, SS, T and A (Russian coal classification system). We used pelleted samples made from coal particles with a size of < 63 μm, the distribution maximum was at a particle size of ~20 μm.

The products of laser pyrolysis of pelletized coal samples in argon medium are H_2, CH_4, H_2O, CO, and CO_2 molecules. The dependences of the composition of gaseous products of pyrolysis of coal samples on their technical and genetic characteristics (the yield of volatile matter, the degree of coalification, the atomic ratio H/C and O/C, the aromaticity index) have been established.

Data on the yield of combustible gases per unit mass of reacted coal samples were obtained, and the fraction of reacted coal samples were determined. It is shown that with an increase in the chemical maturity of coals, the yield of combustible gases per unit mass of the reacted sample increases, while the proportion of the reacted sample, on the contrary, decreases.

During laser pyrolysis of pelleted coal samples in an argon medium, correlations between the yield of combustible gases per unit mass of the reacted sample, the fraction of the reacted sample, and the technical, genetic characteristics of coals (the yield of volatile matter, the degree of coalification, the atomic ratio H/C and O/C, aromatic index) are observed. For the yield of combustible gases per unit mass of the reacted coal sample, the strongest correlation was found for the aromaticity index. For the fraction of the reacted coal sample, the strongest correlation was found for the yield of volatile matter.

In addition, it is shown that the volume fraction of combustible gases (H_2, CH_4, CO) in the mixture of gaseous products of laser pyrolysis of coals increases with the increasing chemical maturity of coals.

It is notable that the formation of coal tar was detected during laser pyrolysis of pelleted samples of coal grades D, OS, SS, and T in an argon medium.

Erroneous Use of Balance Equations in Combustion Theory of Energetic Materials

✉ **Vladimir E. Zarko**[1,2], **Alexander B. Kiskin**[1]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Tomsk State University*
Tomsk, Russia

✉ zarko@kinetics.nsc.ru

In this work the problem of erroneous use of the balance equations in studies dealing with the determination of energetic materials (EMs) high temperature kinetic parameters and calculation of dependency of burning rate on radiant flux is discussed.

High temperature kinetic parameters are widely used in calculations of ignition and combustion characteristics. Unfortunately, classical thermal analysis methods (heating rate ca. 1 K/s) could not provide adequate data for evaluating the EM burn rate, since typically the EM's heating rate during combustion is much higher than 1,000 K/s. The solution to the problem was proposed by A. G. Merzhanov [1], who suggested determining the kinetic parameters from calculation of ignition criterion when using the data on the EM ignition delays. This criterion states that at the ignition instant the heat flux generated by the condensed phase (global) reaction equals in magnitude to the external heat flux. Unfortunately, mathematical justification for that approach has not been performed. In present work the numerical calculations were performed using mathematical model of EM's ignition, and the results of virtual experiments were processed using Merzhanov's ignition criterion. It was found [2] that the use of simple heat balance gives wrong magnitude of kinetic parameters, and ignition criterion should be complemented with the fitting coefficient that depends on the values of heat flux and kinetic parameters.

The dependencies of burn rate on initial temperature and radiant flux are widely used in technical applications and for verification of combustion models. In some earlier works [3; 4], the assumption has been made on the basis of simplified heat balance equation that the combustion of transparent EM under radiant flux q_r equals to the combustion at enhanced initial temperature $T_o^* = T_o + q_r/\rho_{cr}(q_r)$, where ρ — density, *c* — heat capacity, and $r(q_r)$ — burn rate. Processing the dependencies $r(T_0)$ and $r(q_r)$ obtained in physical experiments [3] has shown that using a simplified heat balance equality gives incorrect results, and the explanation has been found very recently based on a detailed combustion modeling that showed the necessity to implement properly fitting coefficients into the balance equation.

[1] Merzhanov A. G. (1967). *Combustion and Flame, 11*(3), 201–211.
[2] Zarko V. E., Knyazeva A. G. (2020). *Combustion and Flame*, *221*, 453–461.
[3] Konev E. V. (1965). *Combustion, Explosion, and Shock Waves, 1*(2), 53–56.
[4] Assovsky I. G. (2005). *Physics of Combustion and Internal Ballistics*. M.: Science.

MAGNETIC RESONANCE SPECTROSCOPY AND MAGNETIC FIELD EFFECTS

Ligands Effects on the Magnetic Anisotropy in Hetero/Homoleptic Cobalt(II) Complexes by NMR Spectroscopy and Quantum Chemical Calculations

✉ **Dmitry Yu. Aleshin**, **Alexander A. Pavlov**, **Igor A. Nikovskiy**,
Yulia V. Nelyubina, **Valentin V. Novikov**, **Ekaterina A. Khakina**

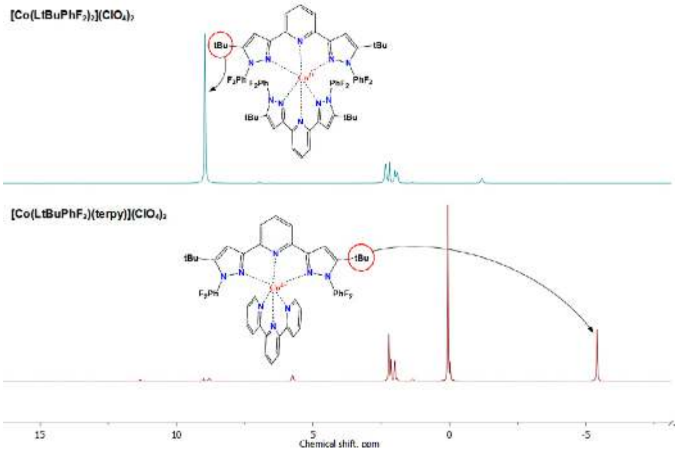
Nesmeyanov Institute of Organoelement Compounds RAS
Moscow, Russia

✉ dima.aleshin26@gmail.com

Nowadays paramagnetic NMR is firmly gaining positions in different areas, such as pseudocontact shift probes in structural biology, PARACEST agents in magnetic resonance imaging and characterization of paramagnetic intermediates in catalysts [1]. Magnetic tensor anisotropy and its orientation in molecules is the key characteristic of a metal complex that determines its magnetic properties. In this perspective, the knowledge of ligand effects on the magnetic anisotropy is viewed as potentially prominent.

We report an interesting case of the dramatic change in magnetic susceptibility tensor caused by the minor change of the ligand field (see Fig.). Such interesting behavior was found according to the NMR chemical shift dependence in the spectra of paramagnetic compounds.

In poster we discuss the nature of such behavior based on the CASSCF method and the AOM model.



^{1}H NMR spectra of hetero- and homoleptic complexes at room temperature

Acknowledgements: this study was supported by the Russian Science Foundation (project No. 22-73-00148).

[1] Ott J. C., Suturina E. A., Kuprov I., Nehrkorn J., Schnegg A., Enders M., Gade L. H. (2021). *Angewandte Chemie*, *60*(42), 22856–22864.

EPR Spectra Detection by Heat Release Using PVDF Films

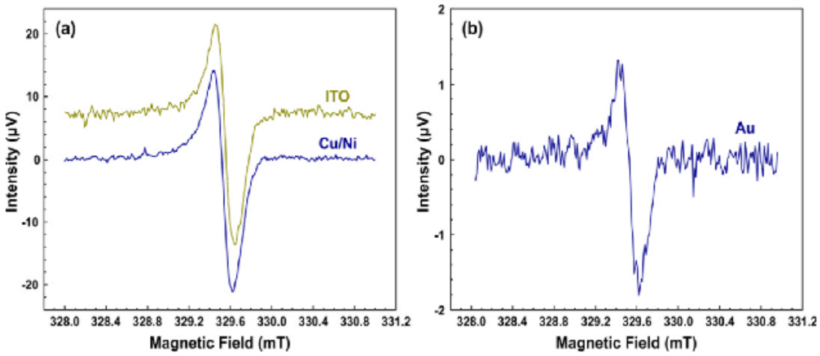
✉ **Oleg A. Anisimov, Anatoly R. Melnikov, Samat B. Zikirin,**
Evgeny V. Kalneus, Vladimir I. Ivannikov, Yury A. Grishin

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ anisimov@academ.org

The energy absorption by the sample during EPR resonance leads to a detuning of the resonator and reflection of the MW power that is recorded by a crystal detector located outside the resonator. Since the absorption of energy by the sample leads to its heating, this heating can be used for recording EPR spectra instead of a standard way. This method of detection is especially advantageous for recording the EPR spectra of recombining radical pairs, when the change in the heat released during the resonance is determined by difference in the recombination energy of pairs in states with different spin multiplicity. This difference can exceed by several orders of magnitude the heat released due to spin reorientation at resonance. One can use pyroelectrics that can transform the change in heat released into a change in electric current as very sensitive sensors to measure heat variations.

In this work, we investigated three types of PVDF (polyvinylidene difluoride) standard pyroelectric films with indium tin oxide (ITO), Cu/Ni, and Au coatings to determine their sensitivity for detecting the EPR signals. A comparative study based on the calculation of the noise-equivalent power and specific detectivity from experimental spectra showed that the Au-coated PVDF film is the most promising active element for measuring the EPR signal. Using the best achieved sensitivity, we gave an estimation whether this is sufficient for using a PVDF-based pyrodetector for indirectly detecting the EPR spectra by the recombination heat release or not.



(*a*) EPR spectra of DPPH powder registered by a pyrodetector based on an active element with Cu/Ni coating (dark blue) or ITO coating (dark green, vertically shifted). The thickness of PVDF film is 28 μm. Modulation amplitude is 0.15 mT, modulation frequency is 115 Hz, time constant is 0.3 s, MW power is 200 mW, temperature is 298 K. DPPH weight is 2.2 μg (ca. $3 \cdot 10^{15}$ spins) and 2.8 μg (ca. $4 \cdot 10^{15}$ spins) for Cu/Ni and ITO coating, respectively. Spectrum recording time is 400 s (Cu/Ni coating) and 1,280 s (ITO); *(b)* the same as *(a)* for an active element with Au coating. The thickness of PVDF film is 12 μm. DPPH weight is 0.23 μg (ca. $3 \cdot 10^{14}$ spins). The spectrum recording time is 2,000 s

Acknowledgements: the work was financially supported by the Russian Foundation for Basic Research (project No. 19-29-10020).

Elementary Operations of Quantum Computation Algorithms by Using Phase-Modulated Microwave Pulses

✉ **Marsel Arifullin**, **Vitaliy Berdinskiy**

Orenburg State University
Orenburg, Russia

✉ arifullinm@mail.ru

New and most promising schemes of quantum computers based on solid-state systems have been proposed based on high-spin paramagnetic ions with a total spin $S > 1/2$ in a zero magnetic field [1–3]. Qubits and qutrits in such high-spin systems are driven by high-frequency pulses with different phases. Spin-orbital interactions in high spin ($S \geqslant 1$) paramagnetic ions embedded in crystal leads to zero fields splitting of ground state [4]. If there are no magnetic field, then three spin states of ions (Ni^{2+}, for example) are ground state $|0\rangle = 2^{-1/2}|\,\alpha_i\beta_j + \beta_i\alpha_j\rangle$ and two excited states $|A\rangle = 2^{-1/2}|\,\alpha_i\alpha_j + \beta_i\beta_j\rangle$ and $|B\rangle = 2^{-1/2}|\,\alpha_i\alpha_j + \beta_i\beta_j\rangle$. All these states are well-known naturally entangled Bell states [1].

Radio frequency or microwave pulses allows one to manipulate populations and coherencies of those states, and change their magnetic properties at a zero magnetic field [1]. Thus, all three spin states $|0\rangle$, $|A\rangle$ and $|B\rangle$ can be used as qubits. However, a pair of degenerate states $|A\rangle$ and $|B\rangle$ is more preferable due to the absence of magnetic decoherence mechanisms. Practical usage of paramagnetic crystals with embedded high spin ions needs neither strong magnetic fields, nor vacuum or laser equipment.

Resonant radiofrequency or microwave pulses having different polarizations and phases are able to produce spin manipulations similar to CNOT, Phase Shift, and Quantum Fourier Transformations and others gates. For spin paramagnetic sublevels, the first transition of alignment to polarization controlled by radio frequency pulses, should be accompanied by the appearance of macroscopic magnetization even in zero magnetic fields [4–5].

Acknowledgements: the work was funded by RFBR (project No. 18-37-00374).

[1] Abragam A., Bleaney B. (1970). *Electron Paramagnetic Resonance of Transition Ions*. Clarendon press, Oxford.

[2] Nielsen M., Chuang I. (2010). *Quantum Computation and Quantum Information*. Cambridge: Cambridge University Press.

[3] Pileio G. (2010). Relaxation Theory of Nuclear Singlet States in Two Spin-1/2 Systems. *Progress in Nuclear Magnetic Resonance Spectroscopy, 56*, 217–231.

[4] Arifullin M. R., Berdinskiy V. L. (2020). *Physics of the Solid State*, *62*, 440–444.

[5]. Arifullin M. R., Berdinskiy V. L. (2020). High-Spin Paramagnetic Ions as Qubits and Qutrits for Quantum Computations. *Russ. Phys. J.*

Photochemical Properties of Thiosemicarbazones and Its Chelate Complexes

✉ **Alina S. Arkhipova**[1,2], **Viktor A. Timoshnikov**[2], **Nikolay E. Polyakov**[2], **Olga Yu. Selyutina**[2]

[1]Novosibirsk State University
Novosibirsk, Russia
[2]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ alinaarkhipova@349gmail.com

Some thiosemicarbazones (TSCs) possess anti-cancer properties. The main mechanism of action described in the literature is the inhibition of ribonucleotide reductase. In addition, TSCs are able to form chelate complexes with metal ions, such as iron, copper and zinc [1]. This feature is associated with another mechanism of anti-cancer action, based on uncontrolled generation of active oxygen radicals. These mechanisms have been actively studied for a long time. Besides, recent studies have shown that some TSCs demonstrate an increase of the antitumor activity in photoinduced reactions [2]. However, a detailed mechanism of action was not described.

In this work, we investigated the photochemical properties of Di-2-pyridylketone-4-cyclohexyl-4-methyl-3-thiosemicarbazone (DpC), 2,2-pyridylphenylketone-4-acridyl-3-thiosemicarbazone (AOBP), Di-2-pyridylketone-4-acridyl-3-thiosemicarbazone (AODP), and their chelate complexes with metal ions in the reactions involving electron donors and acceptors by NMR and chemically induced dynamic nuclear polarization (CIDNP) methods.

Using the NMR and CIDNP methods, it was shown that DpC and their complexes with iron ions exhibit electron donor properties under the UV light irradiation at 308 nm in the presence of an electron acceptor — quinone AQDS. Based on CIDNP spectra, it was revealed that these reactions proceed via the free radical mechanism. A S-centered TSC radical has been detected. On the other hand, chelate complexes with copper and zinc show high photochemical stability. It was shown that DpC and their chelate complexes do not exhibit acceptor properties. Similar experiments were carried out with TSCs AOBP and AODP at various pH values. These compounds exhibited electron-donor and electron-acceptor properties in photochemical reactions. These results provide for a deeper understanding of the role of metal ions in the anticancer activity of the TSC chelators, as well as assessing the prospects for their use in photodynamic therapy.

[1] Kalinowski D. S., Quach P., Richardson D. (2009). *Future Medicinal Chemistry*, *6*, 1143–1151.

[2] Osman A. H., Aly A. A. M., Zidan A. S. A., Al-Jadabib K. S. T. (2019). *United Journal of Chemistry*, *2*, 49–56.

Influence of Metal Ions on the Radical Yield in Photochemical Reactions Involving Quinone-Chelators

✉ **Simon V. Babenko**, **Olga Yu. Selyutina**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ babenko@kinetics.nsc.ru

Anthracycline quinones are widely used in medicine as highly effective cytotoxic agents in chemotherapy and photodynamic therapy of tumors. Some of these quinones are able to form chelate complexes with different ions, such as Zn^{2+}, Ca^{2+}, Fe^{2+}, and these chelate complexes in certain cases enhance the generation of radical species [1].

In this study, we explore the ability of such anthraquinone derivative, 2-phenyl-4-(butylamino) naphtho[2,3-h]quinoline-7,12-dione (Qc) to generate radical species in photoreactions with biologically relevant electron donors or their synthetic analogs, as well as the influence of chelate complexes with metal ions on the yield of radical species. In particular, we report about 5 fold increase in the radical yield in the photoreaction between Qc and electron donor, 1,4-dihydropyridine (DHP), as a result of addition of Cu^{2+}. However, not all metal ions, despite forming chelate complexes, lead to increase in radical yield. In fact, Qc forms a complex with Fe^{3+} ions with complex formation constant over 10^7 M^{-1}, but no increase in the radical yield is observed.

In this study we use the chemically induced dynamic nuclear polarization (CIDNP) approach — a highly informative NMR-based technique for monitoring radical photoreactions. The main advantage of CIDNP is its high spectral resolution which provides for differentiating between products of radical reactions, and, therefore, to obtain information even on complex radical reactions involving multiple pathways. Additionally, CIDNP intensity is generally proportional to the concentration of radical species. Thus, the influence of metal ions on the yield of radical ions or free radicals generated by quinone can be assessed quantitatively.

Acknowledgements: this work was funded by the Russian Science Foundation (grant No. 21-73-10037).

[1] Markova I. D., Polyakov N. E., Selyutina O. Yu., Fedenok L. G., Fedotov K. Yu., Slepneva I. A., Leshina T. V., Pokrovsky A. G., Vasilieva N. V., Weiner L. M., *Z. Phys. Chem.*, *213*, 369–389.

Validation of Structural Grounds for Anomalous Molecular Mobility in Ionic Liquid Glasses

✉ **Olga D. Bakulina, Michail Yu. Ivanov**

Novosibirsk State University
Novosibirsk, Russia
International Tomography Center SB RAS
Novosibirsk, Russia

✉ o.bakulina@tomo.nsc.ru

Heterogeneities in ionic liquids (ILs) have been in focus of many experimental and theoretical studies over the past decade. Apart from being a fundamentally important phenomenon, such heterogeneities have a potential of being used in many practical applications, including heterogeneous catalysis, drug delivery, new reaction pathways, chemical syntheses, etc.

The electron paramagnetic resonance (EPR) spectroscopy is the method of choice that provides unique information at molecular level. In this approach, the paramagnetic probe has to be dissolved in IL in negligible "non-perturbing" concentrations, and in the majority of situations, nitroxide radicals are the most suitable and sufficient for obtaining the required information.

Our group has recently developed a versatile EPR approach to study IL heterogeneities and nanostructuring at temperatures below the melting and/or glass transition points (T_m and T_g respectively) in particular [1; 2]. Unprecedented suppression of molecular mobility was evidenced near the glass transition, which was assigned to unusual structural rearrangements of ILs on the nanometer scale. Indeed, pulse and continuous wave EPR clearly indicated the occurrence of heterogeneities near T_g, which exist within a rather broad temperature range of ~50 K. In fact, the detailed nature of observed structural anomalies is still unclear, and additional information about this phenomenon is highly required.

In this work two deuterated imidazolium-based ILs were synthesized to reduce electron-nuclear couplings between the radical probe and alkyl chains of IL. Also, molecular mobility in these glasses was investigated. The obtained trends were found closely similar to those of deuterated and protonated analogs, thus, excluding the relaxation-induced artifacts and reliably demonstrating structural grounds of the observed anomalies in heterogeneous IL glasses.

Acknowledgements: the work was supported by the Russian Science Foundation (grant No. 19-13-00071).

[1] Ivanov M. Yu., Prikhod'ko S. A., Adonin N. Yu., Kirilyuk I. A., Adichtchev S. V., Surovtsev N. V., Dzuba S. A., Fedin M. V. (2018). *J. Phys. Chem. Lett.*, *9*, 4607–4612.

[2] Ivanov M. Yu., Fedin M. V. (2018). *Mendeleev Commun.*, *28*, 565–573.

The Study of the Oxidation Mechanism of 5-Hydroxymethylfurfurol by NMR Spectroscopy

✉ **Egor D. Blinov**, **Oleg A. Kotelnikov, Olga V. Vodyankina,**
Tamara S. Kharlamova, Konstantin L. Timofeev, Maxim D. Zagvozkin, Vera P. Tuguldurova

Tomsk State University
Tomsk, Russia

✉ egir.blinov@gmail.com

5-hydroxymethylfurfural (HMF) is one of the key compounds obtained during the processing of biomass. The catalytic oxidation of HMF produces a number of valuable compounds, including 2,5-furandicarboxylic acid (FDCA). FDCA is a "green" alternative to terephthalic acid and a precursor to a new type of polymer—polyethylenefuranoate [1]. At this moment, the processes occurring during the catalytic oxidation of HMF under various conditions and using various catalysts are not completely clear.

In this work, using NMR spectroscopy (Bruker AVANCE III HD, 400 MHz), intermediate and side products formed in the HMF oxidation reaction depending on the reaction conditions were identified. In this work, we studied four initial reaction mixtures consisting of: 1) 0.025 M HMF and 0.05 M NaOH; 2) 0.025 M HMF and catalyst (1 % Pt/UiO-66); 3) 0.025 M HMF, 0.05 M NaOH, 1 % Pt/UiO-66 and 4) 0,05 M HMF, 0,2 M $NaHCO_3$ and 0,5 M H_2O_2. The reaction conditions were the same for the first three mixtures: the solvent was H_2O, 100 °C, 5 atm., 3 h. The fourth reaction mixture was studied *in situ* at 20 °C to obtain kinetic dependences.

The analysis of the NMR spectra of the reaction mixtures in neutral and alkaline media revealed the key role of base in the formation of the target product FDCA during the catalytic oxidation of HMF in the presence of 1 % Pt/UiO-66. Under the studied conditions, the formation of the target product is possible only at high pH values. Moreover, the oxidation proceeds as HMF → HMFCA (5-hydroxymethylfuran acid) → FFCA (5-formyl-2 furancarboxylic acid) → FDCA. It was found that the main side products of the catalytic oxidation of HMF are the products of hydration, oligomerization, and the Cannizzaro reaction of carbonyl groups of the starting reagents and intermediates. Also, it has been found that in the presence of alkali, HMF furan ring opening can occur to give either levulinic and formic acids or oligomeric compounds called humins. For the process of formation of levulinic and formic acids from HMF, the kinetic parameters were calculated.

Acknowledgements: this work was supported by RSF (grant No. 19-73-30026).

[1] Cheng F. et al. (2021). *Frontiers of Chemical Science and Engineering*, *15*(4), 960–968.

Spin Statistical Factor in the Reaction of Distant Electron Transfer

✉ **Vsevolod I. Borovkov**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ borovkov@kinetics.nsc.ru

The rate of bimolecular reaction between paramagnetic particles generally depends on the total electron spin of the reactants. Such asymmetric reactivity of organic radicals is the origin of many spin polarization phenomena in chemistry.

In chemical kinetics, the spin dependence is usually described by introducing the so-called spin statistical factor $\sigma < 1$, which, to a first approximation, is equal to the statistical weight of reactive states of a pair of reactants among all possible spin states. For diffusion-controlled reactions, the observed reaction rate constant k is expressed in this case as $k = \sigma \cdot K_D = \sigma \cdot 4\pi RD$, where D is the sum of the reagents' diffusion coefficients, K_D and R are, correspondingly, a *hypothetical* rate constant and effective reaction radius that would be if the spin dependence *disappeared*. The σ value can be used to estimate the intersystem crossing rate within the encounter complex of the reactants.

To develop a quantitative kinetic model of a spin-selective reaction, it is important to have information about the corresponding spin factor and its dependence on the conditions under which the studied reaction takes place. For reactions between neutral organic radicals in which short-ranged covalent bonds are formed, the expected value of K_D can be estimated more or less accurately. For electron transfer between some particular donor and acceptor, the effective radius R can be significantly larger than the sum of the van der Waals radii of the reactants. Thus, careful measurements to determine both the parameter K_D and the spin statistical factor σ are required.

This presentation discusses the problem of determining the spin factor in reactions between triplet oxygen molecules and solvated electrons or radical anions in liquids:

$$e^{-} + {}^{3}\mathrm{O}_2 \rightarrow {}^{2}\mathrm{O}_2^{-\bullet} \text{ and } \mathrm{A}^{-\bullet} + {}^{3}\mathrm{O}_2 \rightarrow \mathrm{A} + {}^{2}\mathrm{O}_2^{-\bullet}$$

The expected value of the spin factor would be $\sigma = 1/3$. In the experiments, however, the σ value increases with slowing down the diffusion of reactants. This effect originates from the dipole-dipole interaction of the spins of unpaired electrons in $^{3}O_2$ molecule, since this interaction causes mixing of reactive doublet and non-reactive quartet spin states. It was found that even though this dipole-dipole interaction results in a very rapid paramagnetic relaxation of oxygen molecules with a characteristic time of $T_1 \approx 8$ ps [1], the doublet-quartet mixing in the reaction encounter complex involving the $^{3}O_2$ molecule proceeds on a much longer timescale. The possible reasons for that are discussed.

[1] Teng C.-L., Hong H., Kiihne S., Bryant R. G. (2001). *J. Magn. Reson.*, *148*, 31–34.

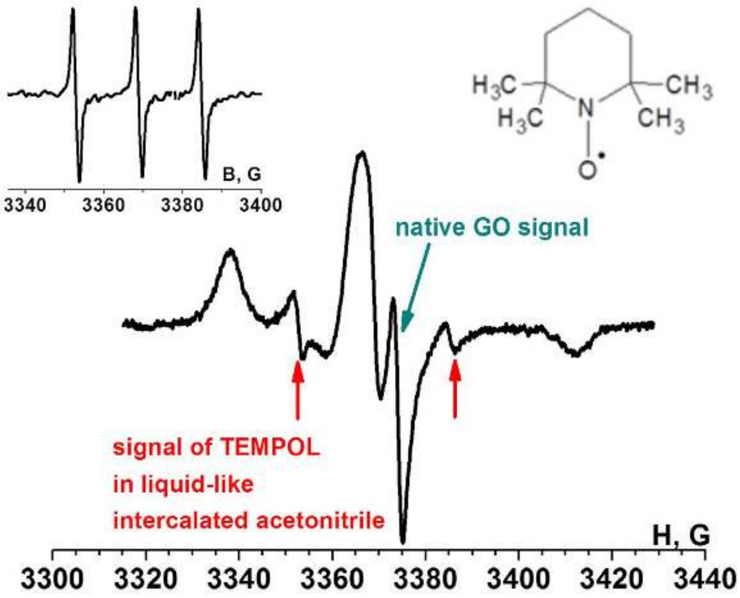
Capability of Spin Probe Technique in Determining of Molecular Organization of Graphite Oxide Materials

✉ **Natalia A. Chumakova**[1,2], **Dmitry A. Astvatsaturov**[1,2], **Andrey Kh. Vorobiev**[2], **Tatiana S. Yankova**[2], **Anastasiya T. Rebrikova**[2], **Mikhail V. Matveev**[2]

[1] Semenov Federal Research Center for Chemical Physics
Moscow, Russia
[2] Lomonosov Moscow State University
Moscow, Russia

✉ harmonic2011@yandex.ru

Graphite oxide (GO) is a layered material formed by graphene planes decorated with oxygen-containing groups. GO swells easily in polar liquids with intercalation of the liquids into the inter-plane space. It is known that intercalated substances do not demonstrate the “liquid — solid” phase transition which is characteristic for bulk liquids. Membranes formed by GO were found to possess highly selective permeability for liquids and hydrated ions; the reasons of this phenomenon are not clear.



The EPR spectrum of a spin probe TEMPO in the system “GO — acetonitrile”; insert is EPR spectrum of TEMPO in bulk acetonitrile

Up to now, the detailed study of molecular organization of GO materials was hindered by lack of suitable experimental methods. In the report it is shown that X-EPR spectroscopy of spin probes is a promising method for such investigations. The report demonstrates the capability of the spin probe technique for studying of the phase state of polar substances intercalated between the graphene planes, and for quantitative characterization of the orientational alignment of GO membranes. As an illustration, Figure shows the EPR spectrum of a spin probe TEMPO in the system “GO — acetonitrile”. The spectrum is superposition of three signals, namely, the native signal of GO and two signals of TEMPO characterized by fast and slow rotational mobility. Fast rotation is typical for the radicals dissolved in liquid media; hence, there is liquid-like acetonitrile in between the graphene planes. However, the shape of the spectrum indicates lower mobility of intercalated acetonitrile in comparison with the bulk one.

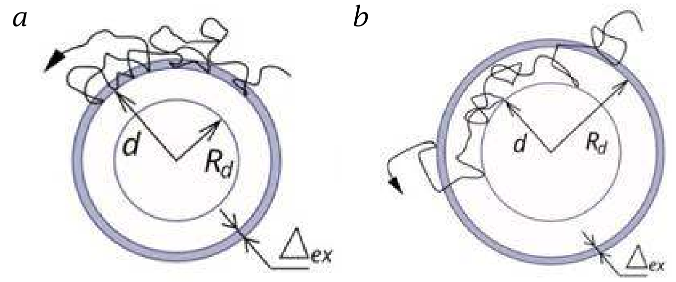
The Influence of Spin Relaxation and Locally Strong Spin Exchange on Magneto-Spin Effects in Radical Pairs in High Magnetic Fields

✉ **Alexander B. Doktorov**

Voevodsky Institute of Chemical Kinetics and Combustion, SB RAS
Novosibirsk, Russia

✉ doktorov@kinetics.nsc.ru

Based on the generalization of gyroscopic model description of electron spin evolution of radical pair available in the literature, the recombination yield and stationary chemically induced electron spin polarization (CIDEP) in high magnetic fields are analytically investigated. The general model includes into consideration arbitrary recombination (from singlet and triplet states), additional dephasing rates, arbitrary exchange interaction, and both transverse and longitudinal spin relaxation, and is valid for any model of the system. Using the Green function formalism, we formulated a general approach to the calculation of recombination yield and stationary chemically induced electron spin polarization (CIDEP) in the case of spherically symmetric system and contact recombination. For this case, an approximation for calculation of the spin effect for locally strong exchange dephasing induced by non-local exchange interaction of radicals is developed. It has been shown that longitudinal spin relaxation essentially influences the effective radius of dephasing induced by non-local exchange interaction of the radicals.



Contribution of the exchange interaction (filled area is exchange interaction "zone"). Δ_{ex} is the exchange interaction layer thickness, d is distance of closest approach of radicals, R_d is dephasing radius, J is contact value of exchange interaction: *a* — locally weak exchange interaction $\left(R_d \le d, \quad j_c = 2J\frac{\Delta_{ex}^2}{D} << 1\right)$. Dephasing is due to re-contacts and can be integrally strong $\left(j_e = 2J\frac{\Delta_{ex} d}{D} > 1\right)$; *b* — locally strong exchange interaction ($R_d > d, j_c \geqslant 1$). The dephasing occurs on a single passage through the exchange interaction "zone"

Shaping of MOFs: Optimization of ZIF-8 Composites upon EPR Control

✉ **Aleksandr A. Efremov**[1,2], **Artem S. Poryvaev**[1], **Daniil M. Polyukhov**[1], **Matvey V. Fedin**[1,2]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ a.efremov@tomo.nsc.ru

Shaping of metal-organic frameworks (MOFs) is one of the crucial steps toward their industrial application. A number of methods for producing pellets containing MOF-micro/nanoparticles have been developed up to date; however, the uptake rates of guest molecules by such shaped MOFs and their dependence on the preparation procedure were not analyzed in detail. Since the optimization of the uptake rates is vital for practical use, in this work we employ a spin-probe Electron Paramagnetic Resonance (EPR) to study solvent diffusion into ZIF-8 based pellets. This approach allows one to selectively monitor the impregnation of ZIF-8 particles embedded in the pellet, and corresponding diffusion coefficients can be obtained for the molecules of interest.

We established that the diffusion properties of obtained pellet strongly depend on the preparation procedure even in case of the same binder and plasticizers. We explained the phenomenon via the decreasing on-surface MOF blockage by binder. Particle size of ZIF-8 plays role in the uptake of guest molecules as well. ZIF-8 nanoparticles usage instead of macroparticles for pellets preparations leads to faster uptake rate.

The studied ways of shaping procedure optimization upon EPR control yields robust pellets with the pore filling rates comparable to those for powdered ZIF-8. The proposed methodology yielded highly permeable ZIF-8-based pellets and is promising for future application in shaping of various MOFs.

Acknowledgements: this work was supported by the Russian Science Foundation (grant No. 22-73-10239).

A CIDNP Study of the Reduction of Short-Lived Thymine Radicals by Aromatic Amino Acids

✉ **Natalya N. Fishman**[1], **Olga B. Morozova**[1],
Hans-Martin Vieth[1,2], **Alexandra V. Yurkovskaya**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Institut für Experimentalphysik, Freie Universität Berlin*
Berlin, Germany

✉ n_s@tomo.nsc.ru

As a model for chemical DNA repair, the reduction of thymine radicals in their reaction with aromatic amino acids has been studied by the time-resolved chemically induced dynamic nuclear polarization (CIDNP) technique. To generate the thymine radicals in a wide pH range in aqueous solution, pulsed laser irradiation was applied to a solution containing the photosensitizer 3,3′,4,4′-tetracarboxy benzophenone (TCBP), thymine, and amino acid (tryptophan, N-acetyl tryptophan, tyrosine or histidine). As a preliminary step, the photoinduced oxidation of thymine by triplet-excited 3,3′,4,4′-tetracarboxy benzophenone was studied and thymine radical intermediates were characterized by means of CIDNP. It was shown that proton-coupled electron transfer (PCET) from neutral thymine to the triplet excited photosensitizer in neutral aqueous solution (pH 6.3) leads to the formation of a neutral thymine radical; its formation is preceded by the formation of an elusive cationic thymine radical on the geminate stage of the reaction. In contrast, in basic solution (pH 11.7) a thymine anion reacts with the triplet excited photosensitizer by electron transfer resulting in the formation of a TCBP radical anion and a neutral thymine radical. The latter deprotonates rapidly, and a thymine radical anion is formed at these conditions. The complementary measured magnetic field dependences of CIDNP have confirmed the reaction mechanism. The reduction of the neutral thymine radical at pH 6.3 and to the thymine radical anion at pH 11.7 by tryptophan was revealed by comparing CIDNP kinetic data in the photoreactions of triplet TCBP and thymine with the respective data obtained for triplet TCBP and thymine and tryptophan (or N-acetyl tryptophan). The rate constants for the reduction of neutral and anionic thymine radicals by tryptophan and N-acetyl tryptophan were determined from quantitative analysis of the CIDNP kinetics, which is sensitive to the rates of fast radical reactions. We also have qualitatively investigated the kinetics of the reduction of thymine radicals by tyrosine or histidine in a wide pH range in aqueous solution, since it turned out that this reaction gives a large amount of by-products in the presence of tyrosine or histidine.

Acknowledgements: the experimental part of this work was supported by the Russian Science Foundation (project No. 20-63-46034), and the theoretical modelling was supported by the Ministry of Science and Higher Education of the Russian Federation (Grant No. 075-15-2021-580).

$Li_3V_2(PO_4)_3$-Based Composites as Potential Cathode Materials for Lithium-Ion Batteries: ESR Measurements

✉ **Tatiana P. Gavrilova**[1], **Sergey M. Khantimerov**[1], **Ivan V. Yatsyk**[1], **Julia A. Deeva**[2], **Tatiana I. Chupakhina**[2], **Nicolay M. Lyadov**[1], **Nail M. Suleimanov**[1]

[1]Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS
Kazan, Russia
[2]Institute of Solid State Chemistry UB RAS
Ekaterinburg, Russia

✉ tatyana.gavrilova@gmail.com

The compounds based on lithium-vanadium phosphate $Li_3V_2(PO_4)_3$ can be used as a cathode material in metal-ion batteries due to the stability of their crystal structure with respect to the change in the valence state of transition ion caused by the processes of intercalation/deintercalation of an alkaline element during the charge/discharge process of the electrochemical cell. Thus, the investigation of physical properties of $Li_3V_2(PO_4)_3$-based structures is of great interest. Here we present the investigations of magnetic and electrochemical properties of $Li_3V_2(PO_4)_3$-based composites, including $Li_3V_2(PO_4)_3/Li_3PO_4$ (LVPO/LPO) and $Li_3V_2(PO_4)_3/C$ (LVPO/C).

LVPO/LPO solid solutions were obtained by the thermal hydrolysis method [1] or hydrothermal method with the subsequent annealing in Ar atmosphere. In comparison, the mesoporous sample of LVPO/C was synthesized by the soft-template method [2]. The investigations of electrochemical properties showed the discharge capacity retention after one hundred charge/discharge cycles for all samples and an increase in the discharge capacity in LVPO/LPO composite with an increase in lithium deficiency.

The magnetic properties of LVPO/LPO and LVPO/C composites were investigated using magnetometry and the electron spin resonance (ESR) methods. As-prepared samples demonstrated the paramagnetic properties due to the presence of V^{4+} ions ($3d^1$, $S = 1/2$) because of non-stoichiometry (lithium deficiency) of the sample. The degree of non-stoichiometry depends on the composition of a sample (including the amount of Li_3PO_4 salt), and its increasing is accompanied by an increase in the amount of V^{4+} ions that can be directly detected using the ESR method. The ESR measurements of lithiated and delithiated LVPO/C samples showed the complete reduction of vanadium ions to the valence state V^{3+} after the first charge/discharge cycle, indicating the reversible intercalation of all lithium ions to the structure during the first delithiation/lithiation cycle in the investigated composite.

Acknowledgements: this work is supported by the Russian Science Foundation (grant No. 19-79-10216).

[1] Gavrilova T., Khantimerov S. et al. (2021). *Magnetochemistry*, *7*(64), 1–9.
[2] Gavrilova T. P., Khantimerov S. M. et al. (2021). *Solid State Commun.*, *323*, 114108.

Magnetic Properties of $CaCu_3Ti_4O_{12}$: Fe Solid Solutions

✉ **Tatiana P. Gavrilova**[1], **Adilya R. Yagfarova**[1], **Ildar F. Gilmutdinov**[1,2], **Ivan V. Yatsyk**[1], **Julia A. Deeva**[3], **Tatiana I. Chupakhina**[3], **Farit G. Vagizov**[2], **Rushana M. Eremina**[1]

[1] *Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center RAS*
Kazan, Russia
[2] *Institute of Physics, Kazan Federal University*
Kazan, Russia
[3] *Institute of Solid State Chemistry UB RAS*
Ekaterinburg, Russia

✉ tatyana.gavrilova@gmail.com

$CaCu_3Ti_4O_{12}$: Fe (1; 3 %) solid solutions were prepared according to the standard solid-state synthesis technique. Based on Mössbauer spectroscopy, electron spin resonance and magnetometry experimental data we suggested that Fe ions substitute Ti^{4+} and Cu^{2+} positions in octahedral and planar oxygen environment, respectively. Such type of substitution leads to the appearance of three types of iron magnetic centers: divalent Fe^{2+} centers in planar environment and trivalent Fe^{3+} centers in symmetrical and distorted octahedral positions which strongly affects the magnetic properties of the investigated samples.

The highest value of the antiferromagnetic interaction was observed in $CaCu_3Ti_4O_{12}$:Fe (3 %) sample, where the highest value of the Weis constant and the maximum of ZFC-FC splitting (the splitting between temperature dependencies of magnetization measured in zero-field cooling and field cooling regimes) was observed. At low temperatures $T < T_N$ the paramagnetic phase in $CaCu_3Ti_4O_{12}$: Fe (1; 3%) goes into magnetically ordered state (canted antiferromagnetic or ferrimagnetic state), which is confirmed by a significant drop in the integral intensity of the electron spin resonance spectra when the temperature decreases. At the same time, the isothermal magnetization measurements as a function of the external magnetic field above the Néel temperature T_N showed the existence of hysteresis loops proving the ferrimagnetic or canted antiferromagnetic ordering with uncompensated residual magnetic moment in $CaCu_3Ti_4O_{12}$: Fe (3 %). Moreover, the multiple positive and negative slopes in the Arrott plot in $CaCu_3Ti_4O_{12}$: Fe (3 %) sample were observed, which can indicate the field-induced phase transition or metamagnetic transitions with multiple values of the upper and lower critical fields denotig a significant competition between antiferromagnetic and ferromagnetic moments.

Based on all experimental data, we suggest that two factors simultaneously affect the magnetic properties of $CaCu_3Ti_4O_{12}$:^{56}Fe (3 %) sample. This effect appears in a significant ZFC-FC splitting, the highest value of the Weis constant and clearly visible metamagnetic transition and can be related with the simultaneous existence of significant amount of Fe^{3+} ions in distorted octahedral positions and Fe^{2+} ions in planar environment in this sample.

ESR-Spectroscopy in Ionic Liquids: High Pressure Investigations on the Rotational Dynamics of Some Nitroxides

✉ **Guenter Grampp**[1], **Boryana Mladenova**[2], **Daniel Kattnig**[2]

[1] *Institute of Physical & Theoretical Chemistry, Graz University of Technology*
Graz, Austria
[2] *Living Systems Institute and Department of Physics, University of Exeter*
Exeter, UK

✉ grampp@tugraz.at

Ionic liquids (ILs) are molten salts of mainly organic cations and inorganic or organic anions, liquid at room temperature. They are of interest, not only from scientific point of view but also for chemical industrial productions. Environmental friendly industrial productions based on so-called "Green Chemistry" principles mainly use ionic liquids as solvent to avoid classical toxic organic solvents. But, few reports exist on ESR-spectroscopic investigations using ionic liquids as solvents. We would like to report on ESR-measurements using various nitroxides (TEMPO; TEMPOL and TEMPAMINE) in different ionic liquids. We have constructed a high-pressure system for use in electron spin resonance (ESR) spectroscopy. The apparatus allows the application of pressures of up to 100 MPa to solutions and with several key solvent properties (viscosity, dielectric constant, relaxation times, refractive index) being pressure dependent, reaction dynamics may be probed via pressure variations.

Rotational correlation times τ_{rot}: Using the high viscosity of ionic liquids, the rotational correlation times, τ_{rot}, of uncharged TEMPO-derivatives and of charged Fremy's salt are measured as a function of temperature [1,2] **and** pressure [3]. Therefore, experimental values of both activation energies and activation volumes are obtained. The rotation correlation times vary between 54 and 1470 psec at 300 K. Activation volumes vary from 38.5–56.6 Å^3. Within a temperature range of 280–380 K, the rotational tumbling is very well described by the Stokes-Einstein-Debye law. This study is distinguished from similar studies by the fact that proton super-hyperfine coupling constants could be resolved for all nitroxides in the ionic liquids by carefully optimizing the experimental details. As a consequence, many rotational correlation times reported here are smaller than those found previously. Furthermore, the temperature dependence of the nitrogen ESR coupling constants is reported and discussed in detail.

[1] Bogdanov A. V., Mladenova Kattnig B. Y., Vorobiev A. Kh., Grampp G., Kokorin A. I. (2020). *J. Phys. Chem. B, 124*, 11007–11084.

[2] Mladenova Kattnig B. Y., , Chumakova N. A., Kattnig D. R., Grigorev I. A., Grampp G., Kokorin A. I. (2021). *J. Phys. Chem. B, 125,* 9235–9243.

[3] Mladenova Kattnig B. Y., Kattnig D. R., Grampp G. (2022). *J. Phys. Chem. B, 126,* 906–911.

Study of the ^{13}C NMR Chemical Shifts of Nitrobenzene in Acid Mixtures

✉ **Timur Yu. Ivanenko**[1,2], **Alexander A. Kondrasenko**[1,3],
Ivan V. Peterson[1], **Anatoly I. Rubaylo**[1,2]

[1] Institute of Chemistry and Chemical Technology SB RAS
Krasnoyarsk, Russia
[2] Siberian Federal University
Krasnoyarsk, Russia
[3] Reshetnev Siberian State University of Science and Technology
Krasnoyarsk, Russia

✉ timivonk@gmail.com

Acid-catalyzed alkylation reactions are widely used in industrial processes and in laboratory practice. The course of these reactions largely depends on the acidity of the solution used. A practical interest lies in the discovery and improvement of methods for comparing Bronsted acids of various strengths in non-aqueous solutions.

We have carried out studies of nitrobenzene as an indicator compound by ^{13}C NMR in mixtures with different ratios of acetic, phosphoric and sulfuric acids.

It can be assumed that in the studied systems there is a shift in the equilibrium of nitro and aci-nitro forms of the indicator in solution. In this case, the reason for the change in chemical shifts is the apparent change in electron density on carbon atoms. The increase in the chemical shift of ^{13}C at ortho and para positions and its decrease for ipso-carbon do not contradict general considerations about the mesomeric effect.

To verify the assumptions made, it is necessary to use the data of ^{1}H NMR spectroscopy, since the chemical shift of protons depends practically only on the electron density. The development of methods for conducting experiments in such systems is a more complex task than ^{13}C NMR spectra.

[1] Catalan J., Yanez M. (1979). Protonation and Proton Affinities of Monosubstituted Benzenes: A Theoretical Study, *Journal of the Chemical Society, Perkin Transactions 2*, *6*, 741–746.

[2] Stasyuk O. A. (2016). How Amino and Nitro Substituents Direct Electrophilic Aromatic Substitution in Benzene: An Explanation with Kohn-Sham Molecular Orbital Theory and Voronoi Deformation Density Analysis, *Phys. Chem. Chem. Phys.*, 11624–11633.

[3] Eckert-Maksic M. (1997). Theoretical Model Calculations of the Absolute Proton Affinities of Benzonitrile, Nitroso- and Nitrobenzene. *Journal of Molecular Structure: Theochem*, *417*, 131–143.

Dynamic Equilibrium in Photoexcited Molecular Systems

✉ **Yuri E. Kandrashkin**

Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center RAS
Kazan Russia

✉ yuk@kfti.knc.ru

Light absorption in molecular systems often produces a dynamic equilibrium between several excited states. In the case of photoexcited molecules, such states are metastable triplet states, as well as charge-transfer states. Each of these states is characterized by its own set of local interactions. For example, in molecular dyads composed of rigidly bound chromophore groups, these states are mainly determined by the parameters of the fine structure. In the case of dynamic equilibrium, the transitions between different localized triplet states cause changes in spectral and kinetic properties of the observed spin system, which can be studied using the electron paramagnetic resonance spectroscopy.

We have recently proposed a two-site model that enables one to describe such phenomena [1–3]. One of the important concepts of this model is the existence of some common state $\rho = (k_B\rho_A + k_A\rho_B)/(k_A + k_B)$, which is characterized by the average spin-Hamiltonian H of the two triplet states. Here, k_A and k_B are the hopping rate constants. It was shown that due to reversible transitions, most of the matrix elements of the density matrix ρ can be neglected. To describe the observed phenomena, it is enough to include only those matrix elements that are diagonal in the basis of the eigenfunctions H. They are repopulated with the following rates:

$$K_{ij} = \frac{8k_A k_B \left|(H_A - H_B)_{ij}/2\right|^2}{(k_A + k_B)[(k_A + k_B)^2 + (H_A + H_B)_{ij}{}^2/4]}$$

Here, i and j are the indices of the spin sublevels, H_A and H_B are the spin-Hamiltonians of the sites A and B. The obtained expressions provide a simple relation between spectral and kinetic parameters of the excited molecules and enable the identification and study of excited states of molecules in dynamic equilibrium.

Acknowledgements: the project was financially supported by the Government Assignment for the FRC Kazan Scientific Center RAS.

[1] Kandrashkin Y. E. et al. (2020). *J. Chem. Phys.*, *153*, 094304.
[2] Kandrashkin Y. E. et al. (2019). *J. Phys. Chem. Lett.*, *10*, 4157–4163.
[3] Kandrashkin Y. E. et al. (2020). *J. Phys. Chem. C*, *124*, 3939–3951.

---

^{2}H NMR Study of Hydrogen Bond Dynamics and Phase Transition in a Model Ionic Liquid Electrolyte

✉ **Alexander E. Khudozhitkov, Daniil I. Kolokolov**

Novosibirsk State University
Novosibirsk, Russia
Boreskov Institute of Catalysis
Novosibirsk, Russia

✉ alexandr.khudozhitkov@gmail.com

^{2}H NMR method is a versatile tool that provides for probing dynamics and phase behaviour in solid state. This method has been successfully utilized in various systems ranging from zeolites to proton conductors and polymers. Recently, we have developed a robust approach for gaining access to the structure and dynamics in liquid, supercooled and crystallized protic ionic liquids (PILs) by using the solid state ^{2}H NMR line shape and spin relaxation analysis. Herein, we exploit this approach to perform a comprehensive solid state ^{2}H NMR study of the PIL over a broad temperature range of 133–436 K delivering information about the hydrogen bond dynamics and phase transition in the model ionic liquid electrolyte triethylammonium bis(trifluoromethanesulfonyl)imide [TEA][NTf_2]. Deuterium is located in the N-D group of [TEA] cation so we can directly follow the dynamics of hydrogen bond between cation and anion. ^{2}H NMR spectra line shape at 133–223 K consists of two Pake doublets with notably different deuterium quadrupole coupling constants (DQCC) Q_{Ia} = 172–175 kHz and Q_{Ib} = 144–145 kHz. It indicates at two possible ways of hydrogen bond formation. The density function theory (DFT) calculations provided for determining the geometry of ion pair responsible for these signals. In the 233–283 K temperature region the coexistence of liquid and solid state can be observed. We show that melting transition is governed by two sets of thermodynamic parameters. For the initial process below 238 K $\Delta H_1^{\ominus} = 110 \pm 20$ kJ·mol^{-1}, close to the second melting transition we obtained $\Delta H_2^{\ominus} = 22 \pm 5$ kJ·mol^{-1}, indicating that less energy is required to reach the second melting transition. In order to probe motional behavior of [TEA][NTf_2] we measured the deuteron spin-lattice $(T_1)_D$ and spin-spin $(T_2)_D$ relaxation times of the N–D molecular vector for the isotropic and anisotropic components. From fitting the temperature dependence of spin relaxation times, we determine the geometry, activation barriers and rates of motions exhibited by the [TEA] cation.

We compare our results with previously reported data regarding ionic liquids with anions of varying strength: [TEA][OTf] and [TEA][OMs]. Our results prove that the stronger hydrogen bonds between cation and anion lead to the lower enthalpy change between solid and liquid state, higher activation barrier of tumbling motion and lower amplitude of librational motion.

Acknowledgements: this work was supported by the Russian Science Foundation (grant No. 21-13-00047).

PHOTO-SABRE Polarization on *Trans*-Azobenzene Using Parahydrogen under Light

✉ **Alexey S. Kiryutin**[1], **Vitaly P. Kozinenko**[1,2], **Alexandra V. Yurkovskaya**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ kiryutin.aleksey@gmail.com

Parahydrogen can be used to hyperpolarize nuclear spins providing for the enhancement of signals in nuclear magnetic resonance and magnetic resonance imaging by up to five orders of magnitude. This method is applicable when a pairwise hydrogenation reaction occurs; the singlet spin order (population imbalance between the singlet and triplet states of the spin pair) of parahydrogen can be transferred into and redistributed across the nuclear spin system of the target molecule. Of particular interest are the reversible hydrogenation reactions happening in catalytic complexes: in this case, a dihydrogen molecule H_2 that is dissolved in a solution can reversibly bind to the metal center, typically stabilized iridium ion. It is possible to transfer its nuclear spin order to another target molecule that binds to the same complex simultaneously with hydrogens. The method is called SABRE (Signal Amplification By Reversible Exchange) [1], and it enables the polarization of a wide variety of substrates, including important biomarkers which can be used as contrast agents for bio-imaging.

Azobenzene is an interesting molecule which exists in two isomeric forms, trans-ABZ and cis-ABZ. The stable form trans-ABZ can be easily converted to cis- form by light irradiation; the amount of cis-ABZ is determined by the wavelength of light. Recently, it was shown [2] that cis-ABZ can be polarized in SABRE process, but trans-ABZ was not polarized.

Here we present a study on PHOTO-SABRE of cis- and trans-azobenzene under light illumination at the ultralow magnetic field. We have detected strong ^{15}N and ^{1}H polarization of trans-azobenzene and measured decay time of strong polarization in the field range from 100 nT to 9.4 T. During SABRE process also long-lived states (LLS) of cis- and trans$^{15}N_2$-azobenzene populates. We have optimized the conditions for the LLS population and measured relaxation rate of LLS in trans-$^{15}N_2$-azobenzene, which can be up to 17 minutes [3].

Acknowledgements: this work was supported by the Russian Science Foundation (grant No. 20-62-47038).

[1] Adams R. W. et al. (2009). Science, *323*(5922), 1708.

[2] Sheberstov K. F. et al. (2021). *Chem. Phys. Chem.*, *22*(14), 1527.

[3] Sheberstov K. F., Vieth H. M., Zimmermann H., Rodin B. A., Ivanov K. L., Kiryutin A. S., Yurkovskaya A. V. (2019). *Sci. Rep.*, *9*(1), 20161.

Shaped EPR Pulse Techniques with Different Type of Spin Labels

✉ **Mikhail Kolokolov**[1,2], **Sergey L. Veber**[1], **Anatoly R. Melnikov**[1],
Matvey V. Fedin[1], **Elena A. Bagryanskaya**[3], **Olesya A. Krumkacheva**[1]

[1] International Tomography Center SB RAS
Novosibirsk, Russia
[2] Novosibirsk State University
Novosibirsk, Russia
[3] Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS
Novosibirsk, Russia

✉ m.kolokolov@tomo.nsc.ru

EPR (Electron Paramagnetic Resonance) spectroscopy is an essential method of investigating molecular conformations in structural biology. In recent years, EPR has made another step forward by introducing shaped pulses which have been widely used in NMR for decades before [1]. Unlike rectangular pulses commonly used in EPR, shaped pulses have their phase and amplitude defined as a function of time, giving precise control of the spin evolution. The most important advantage of using shaped pulses is a significant increase in excitation band (up to 1 GHz and higher). This leads to a higher modulation depth and, thus, increases the sensitivity of the EPR experiments severalfold [2]. Increasing the excitation band also allows one to perform experiments with total excitation of EPR spectra, such as the SIFTER experiment.

This work describes the implementation of shaped pulses in a commercial Bruker EPR spectrometer operating on X- and Q-bands in ITC SB RAS. A home-built arbitrary waveform generator (AWG) module operating on gigahertz frequency is presented. Technical difficulties limiting the efficiency of shaped pulses and ways of overcoming them are described.

The generation of high-frequency-shaped pulses was validated using a spectrum analyzer. Then AWG was integrated into the spectrometer bridge's ELDOR channel to increase the sensitivity of PELDOR experiments. Pulse parameter optimization is described. The Q-band PELDOR experiments with rectangular and shaped pulses were performed on a human ribosome complex and DNA-duplex with attached nitroxide-nitroxide spin labels. A significant increase in the modulation depth and signal-to-noise ratio under the WURST pulse shape is demonstrated. During the integration of AWG into the main channel, the synchronization problem between AWG and spectrometer has emerged; it was necessary to add a high-speed digitizer. For the first time, shaped pulses were used in a SIFTER experiment on fullerene spin labels excited by the laser.

Acknowledgements: this work was supported by RFBR (grant No. 19-29-10035).

[1] Spindler P. E., Zhang Y., Endeward B., Gershernzon N., Skinner T. E., Glaser S. J., Prisner T. F. (2012). Shaped Optimal Control Pulses for Increased Excitation Bandwidth in EPR. *J. Magn. Reson.*, *218*, 49–58.

[2] Bahrenberg T., Rosenski Y., Carmieli R., Zibzener K., Qi M., Frydman V., Godt A., Goldfarb D., Feintuch A. (2017). Improved Sensitivity for W-band Gd(III)-Gd(III) and Nitroxide-Nitroxide DEER Measurements with Shaped Pulses, *J. Magn. Reson.*, *283*, 1–13

Fast Field Cycling Relaxometry of Long-Lived Spin States to Probe Weak Ligand-Protein Binding

✉ **Vitaly P. Kozinenko**, **Alexey S. Kiryutin**, **Alexandra V. Yurkovskaya**

International Tomography Center SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉ vitaly.kozinenko@gmail.com

The survey of the interactions between biological molecules in living organisms (i.e., metabolites, proteins, nucleic acids) constitutes a crucial analytical field of interactomics which provides a powerful tool for biology and medical diagnostics. The nuclear magnetic resonance (NMR) spectroscopy with its ability to non-intrusively probe dynamical processes has proved to be one of the most perspective methods to detect the interactions between biological molecules. The characterization of weak interactions between metabolites and macromolecules is of particular interest, as it is not always amenable to the existing approaches. Such interactions can be identified with the help of high-resolution relaxometry, which is the study of the dependence of proton relaxations rates on strength of the external magnetic field [1]. We propose the extension of this approach that utilizes the preparation of the spin states immune to rapid dipolar relaxation, which makes them perfect probes for the study of slow dynamical processes. The relaxation time of such long-lived states (LLS) at low magnetic fields can reach more than ten-fold excess over the relaxation time of longitudinal magnetization [2].

We performed experiments with a number of small biological molecules, namely, citric acid, dipeptide alanine-glycine, and others, acting as ligands and human serum albumin as a target protein. For the considered ligands we optimize the preparation of long-lived spin order at high magnetic field with the consecutive fast field cycling of the sample in the range from 1 mT to 16 T. The addition of even a small amount of binding protein results in a drastic decrease of the relaxation time of the long-lived state at low magnetic fields, which provides a robust tool for the detection of weak binding process. We also propose a theoretical model, which describes the field dependence of LLS for arbitrary metabolite/protein concentration ratio, which provides for a detailed characterization of their interaction. The proposed approach can become a valuable contribution to the field of the NMR interactomics.

Acknowledgements: the work was supported by the Russian Foundation for Basic Research (grant No. 20-53-15004).

[1] *J. Am. Chem. Soc.* 2021, *143, 25*, 9393–9404.
[2] *J. Chem. Phys.* 2005, *122*, 214505.

Photoexcited Triplet States as Spin Labels: Methodology Aspects for the Pulsed Dipolar EPR Spectroscopy and Application to Biomolecules

✉ **Olesya A. Krumkacheva**[1], **Natalya E. Sannikova**[1], **Ivan O. Timofeev**[1], **Alexey S. Chubarov**[2], **Michael K. Bowman**[3,4], **Elena G. Bagryanskaya**[3], **Matvey V. Fedin**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Institute of Chemical Biology and Fundamental Medicine SB RAS*
Novosibirsk, Russia
[3] *Vorozhtsov Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[4] *University of Alabama*
Tuscaloosa, USA

✉ olelesya@tomo.nsc.ru

Photoexcited triplet states of organic molecules are promising spin labels with advanced spectroscopic properties for Pulsed Dipolar Electron Paramagnetic Resonance (PD EPR) spectroscopy. Strong triplet hyperpolarization led to a drastically enhanced sensitivity compared to common DEER with nitroxide observer.

Recently proposed triplet fullerene labels have shown great potential for the Double Electron-Electron Resonance (DEER) distance measurement as "observer spins" due to a high quantum yield of the triplet state, hyperpolarization and relatively narrow EPR spectrum [1]. This work [2] demonstrates the applicability of fullerene labels to other PD EPR techniques, such as Relaxation Induced Dipolar Modulation Enhancement (RIDME) and Laser Induced Magnetic Dipolar spectroscopy (LaserIMD). In particular, a specific contaminating signal in LaserIMD experiments was observed, explained and mitigated. Comparative analyses of the signal-to-noise (SNR) ratios were performed for all employed methods. DEER on fullerene-triarylmethyl pair shows best performance, which provides for the state-of-the-art DEER acquisition at 100 nM with SNR~35 within reasonable 42 hours.

Photoexcited triplet states are also actively used within biological complexes as photosensitizers for the photodynamic therapy (PDT) of cancer. In this work, we propose the pulsed dipolar EPR spectroscopy in combination with other EPR methods as a tool to determine and characterize binding sites of photosensitizer to biopolymers. The report shows that the pulsed dipolar EPR spectroscopy provides valuable information on the structure and function of PDT candidate complexes, exemplified with photosensitizer bound to human serum albumin (HSA) [3] and G-quadruplex DNA.

Acknowledgements: this work was supported by Russian Science Foundation (20-73-10239).

[1] *Angewandte Chemie International Edition* **2019**, *58*(38), 13271–13275.
[2] *Phys. Chem. Chem. Phys.* **2022**, *24*, 4475–4484.
[3] *J. of Photochem. and Photobiol. B: Biology* **2020**, *211*, 112008.

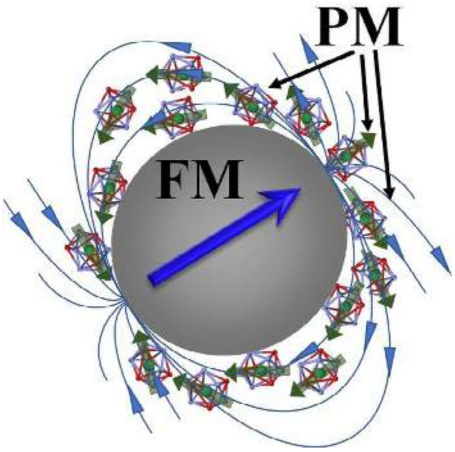
Functionalization of Er^{3+} Single-Ion Magnet Using Ferromagnetic Microparticles

✉ **Ekaterina I. Kunitsyna**, **Roman B. Morgunov**

Institute of Problems of Chemical Physics of RAS
Chernogolovka, Russia

✉ kunya_kat@mail.ru

Single-ion magnets (SIM) are promising objects for the development of platforms for quantum computing and information storage [1]. In SIM, relaxation occurs rather quickly, so it cannot be measured with a SQUID magnetometer and does not correspond to the conditions of quantum decoherence required for quantum calculations. The solution to this problem is the application of an external magnetic field (electromagnet), which shifts the relaxation time to the desired frequency range. In our work, we propose to use the residual field of a ferromagnetic particle to create an external field. The use of PrDyFeCoB ferromagnetic microparticles with a predetermined magnetization that is retained makes it possible to control the local rate of spin relaxation in complexes covering microparticles (see Fig.).



Model of a composite material based on PrDyFeCoB microparticles (MP) and Er^{3+} complex (PM). The internal field of particles is indicated by an arrow. The Er^{3+} complex is located in the region of the stray field of microparticles

In this work, the frequency dependences of magnetic susceptibilities, individual microparticles, and individual SIM powder, as well as their composite, were studied. The comparison of the dependences $\chi'(f)$ and $\chi''(f)$ in a mixture of the SIM complex and microparticles showed the presence of a peak in a zero external field at 2 K; the pure complex did not show slow relaxation in the absence of a field though. The stray field of PrDyFeCoB microparticles turned out to be sufficient to observe slow spin relaxation in the SIM complex. Two processes that affect relaxation were considered: orbital hybridization caused by chemical interaction between the compound and the metal surface; and the magnetic dipole interaction provided by residual magnetization of the matrix. It has been found that the magnetic relaxation of the [Er(HL)(L)]4CHCl3H2O complex can be controlled using a preliminarily applied external magnetic field.

Acknowledgements: the work was supported by the program of the Institute of Problems of Chemical Physics RAS AAAA-A19-119092390079-8.

[1] Leuenberger M. N., Loss D. (2001). *Nature*, *410*, 789–793.

MAS NMR Spectroscopy for Acidity Characterization and Olefin Reaction Monitoring on Zn-Modified zeolites

✉ **Zoya N. Lashchinskaya**, **Anton A. Gabrienko, Sergei S. Arzumanov, Alexander G. Stepanov**

Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia

✉ lashchinskaya@catalysis.ru

MAS NMR spectroscopy is an exceptionally powerful technique capable of providing exhaustive data concerning the properties of solid acid catalysts and their performance in hydrocarbon conversion. As an example, we present our results of the investigation of zeolite acidity characterization and olefin (ethene and n-butene) transformation on Zn-ZSM-5 and Zn-BEA catalysts with ^{1}H, ^{31}P, and ^{13}C MAS NMR spectroscopy. It has been found that zinc-modified zeolites are effective catalysts for the transformation of light olefins (C_2–C_4), the abundant feedstock produced from naphtha and liquified petroleum gas [1]. However, the lack of comprehensive information about the nature of the active sites and the reaction mechanism hinders the implementation of such catalysts on an industrial scale. Here, we aim to demonstrate the capabilities of MAS NMR to provide the required data.

The successful use of MAS NMR to address the following issues was demonstrated.

1. Quantification of the zeolite Brønsted acid sites (BAS) by using ^{1}H MAS NMR with an internal standard approach [2]. The state of Zn species was determined indirectly by the change in BAS content upon the modification.

2. Qualitative characterization of the catalyst BAS and LAS (Lewis acid sites) with ^{31}P MAS NMR spectroscopy of adsorbed on the zeolite trimethylphosphine probe. We found that the introduction of Zn^{2+} cations did not change the strength of the zeolite BAS [3].

3. Monitoring olefin reactions on Zn-modified zeolites using the ^{13}C CP/MAS NMR technique. The structures of the surface intermediates and the mechanisms of ethene and n-butene transformation were determined [4; 5].

The key feature of the experimental procedure was sample preparation in sealed glass ampoules acting as microreactors. Such methodology provides reliable data for zeolite catalyst performance under controlled conditions [6].

[1] Ono Y. (1992). *Catal. Rev.-Sci. Eng.*, *34*, 179–226.
[2] Gabrienko A. A. et al. (2017). *ACS Catal.*, *7*, 1818–1830.
[3] Gabrienko A. A. et al. (2020). *ChemCatChem*, *12*, 478–487.
[4] Lashchinskaya Z. N. et al. (2020). *ACS Catal.*, *10*, 14224–14233.
[5] Lashchinskaya Z. N. et al. (2022). *J. Phys. Chem. C*, published.
[6] Gabrienko A. A. et al. (2015). *J. Phys. Chem. C*, *119*, 24910–24918.

EPR Study of Stable Bicyclic Functionalized Nitroxides: Aza-nortropinone-5-Methyl-3-oxo-6,8-dizabicyclo[3.2.1]-6-octane 8-oxyls

Larisa N. Grigorieva, Alexsei Ya. Tikhonov,
✉ **Konstantin A. Lomanovich, Dmitrii G. Mazhukin**

Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS
Novosibirsk, Russia

✉ lomanovich@nioch.nsc.ru

In recent decades, bicyclic nitroxyl radicals have caught chemists' attention as selective catalysts for the oxidation of alcohols and amines and as additives and mediators in directed C-H oxidative transformations. In this regard, the design and development of synthetic approaches to new functional bicyclic nitroxides is a relevant and important issue. It has been reported that imidazo[1,2-b] isoxazoles formed during the condensation of acetylacetone with 2-hydroxyaminooximes having a secondary hydroxyamino group are recyclized under mild basic catalyzed conditions to 8-hydroxy-5-methyl-3-oxo-6,8-diazabicyclo[3.2.1]-6-octenes. The latter, containing a sterically hindered cyclic N-hydroxy group, upon oxidation with lead dioxide in acetone virtually quantitatively form stable nitroxyl bicyclic radicals of a new class, which are derivatives of both 2,2,6,6-tetramethyl-4-oxo-piperidine-1-oxyl (TEMPON) and 3-imidazolines.

The EPR spectra recorded for degassed solutions in toluene represent triplets with hyperfine coupling (hfc) constant aN of ~1.855 mT, for one of which, a fine structure is observed due to the presence of a hyperfine interaction with hydrogen atoms in the CH2- and CH3- groups. due to the asymmetry of all carbon atoms, the hfc constants for all the different types of hydrogen atoms differ from each other and are in the range from 0.095 to 0.217 mT for methylene protons in the carbonyl and decrease from 0.054 mT for protons of the CH2 group on the six-membered ring closest to the radical center down to ~0.001 mT for the most distant protons of the aliphatic ring.

[1] Grigor'eva N., Tikhonov A. Ya., Lomanovich K. A., Mazhukin D. G. (2021). Stable Bicyclic Functionalized Nitroxides: The Synthesis of Derivatives of Aza-nortropinone–5-Methyl-3-oxo-6,8-diazabicyclo[3.2.1]-6-octene 8-oxyls L. Molecules, 26(10), 3050. DOI: 10.3390/molecules26103050

Review of Magnetic and Spin Effects in Charge Separated States in the Triads “Electron Donor—Hard Molecular Bridge—Electron Acceptor”

✉ **Nikita N. Lukzen**

International Tomography Center SB RAS
Novosibirsk, Russia

✉ luk@tomo.nsc.ru

The recombination of biradicals formed in the course of photoinduced charge separation in a rigidly bound triad “electron donor — molecular bridge — electron acceptor” for a number of acceptors and donors with different rigid molecular bridge in a magnetic field is considered. The recombination of such biradicals into the ground diamagnetic state is spin-selective. The kinetics of formation and recombination (decay) of such charge separated states (CSS) has been studied in detail experimentally and theoretically in the range of magnetic fields from 0 to 1,800 mT using flash photolysis with a resolution of tens of nanoseconds. It was shown that for several triads, the so-called J-resonance is observed, which has a width of several mT, which indicates the intersection of the singlet (S) and triplet (T) levels separated by an exchange interaction in a zero magnetic field. The magnetic field dependences of the CSS recombination kinetics were modeled quantum-mechanically taking into account the five strongest hyperfine interactions and the anisotropic hyperfine interaction with the nitrogen nucleus. Both incoherent and coherent hyperfine interactions have shown to contribute to the S/T spin conversion in all magnetic fields. Based on the analysis of the kinetic curves, it was found that the nanoviscosity in a polytetrahydrofuran solution, compared to a tetrahydrofuran solution, increases significantly less than the macroscopic viscosities of a polytetrahydrofuran solution vs tetrahydrofuran solution. The nanoviscosity changes by a factor of 24, while the macroscopic viscosity changes by a factor of ~1,000.

Acknowledgements: the work was financially supported by the Russian Foundation for Basic Research (RFBR grant 21-53-12023-ННИО-а).

Solid State Photo-CIDEP in Chiral Linked Systems

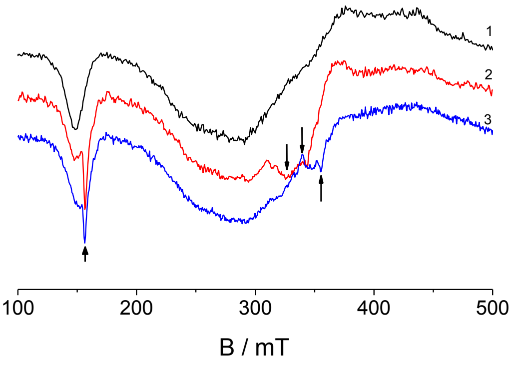
✉ **Ilya M. Magin**[1,2], **Mikhail Yu. Ivanov**[2,3], **Nikolay E. Polyakov**[1], **Alexander I. Kruppa**[1],
Matvey V. Fedin[2,3], **Tatyana V. Leshina**[1]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk,Russia
[3] *International Tomography Center SB RAS*
Novosibirsk, Russia

✉ magin@kinetics.nsc.ru

Photoinduced charge transfer processes in diastereomers are currently being intensively studied as models for the binding of chiral drugs to chiral amino acid residues located in the active centers of enzymes and receptors. Thus, a direct detection of paramagnetic forms of diastereomers formed upon UV irradiation is of considerable interest. In the present study, we use photochemically induced dynamic electron polarization (photo-CIDEP) to detect paramagnetic particles resulting from UV irradiation of dyads containing the well-known NSAID (R/S)-ketoprofen (KP) with various electron donors.

We attempted to observe biradicals and biradical zwitterions formed in chiral dyads at 80–100 K in toluene glass solution under UV irradiation using photo-CIDEP—a direct method of the paramagnetic particles detection. The systems under study were dyads containing an electron acceptor (R/S)-ketoprofen and hydrogen and/or electron donors: (S)-N-methyl pyrrolidine (Pyr), cholesterol (Chl) and (L)-tryptophan (Trp). Benzophenone (BP) and KP were also studied as an example of systems that demonstrate triplet CIDEP.



CIDEP spectra in toluene glass. *1*—(S)KP-(S) Pyr; *2*—(R)KP-(S)Trp 3) (S)KP-(S)Trp

In all three dyads, under UV irradiation the TR EPR spectra demonstrated the wide CIDEP spectra, which we attributed to triplet state of KP. However, dyads (R/S)KP-(S)Trp demonstrate additional, narrow CIDEP signal, which we ascribed to biradical zwitterion.

Acknowledgements: this work was supported by the Russian Science Foundation (grant No. 18-13-00047).

Photoinduced Oxidation of Lipid Membrane in the Presence of Non-Steroidal Anti-Inflammatory Drug Ketoprofen

✉ **Anna V. Mastova**, **Olga Yu. Selyutina**, **Nikolay E. Polyakov**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ mastova-anna99@yandex.ru

The damage of cell membranes induced by photosensitive drugs attracts significant attention of researchers in various fields of medicine. Ketoprofen (KP) is known to be the most photosensitive among the non-steroidal anti-inflammatory drugs. The phototoxic side effects of KP and other non-steroidal anti-inflammatory drugs are associated with the action of free radicals, but there is insufficient information about the nature of these radicals. In the present study, free radicals formed upon KP irradiation in lipid membrane were studied using the NMR and CIDNP methods, as well as molecular dynamics simulation. Our study confirmed the effective penetration of KP into the lipid bilayer and showed a significant effect of the nature of the medium on the photolysis mechanism. If in a homogeneous solution the main channel of KP photolysis is free radical mediated monomolecular decomposition with formation of radical pair of benzyl and $CO_2H^\bullet$ radicals, then the reaction route shifts towards the bimolecular reaction of KP photoreduction in lipid membrane [1]. In addition, the effect of presence of electron donor (amino acid tryptophan) on the lipid oxidation has been studied. It was found that photoreaction of KP with tryptophan proceeds more efficiently than with lipid molecules. However, in contrast to a homogeneous solution in phosphate buffer saline, where the amino acid tryptophan accelerates the photodecomposition of KP due to intramolecular hydrogen transfer, tryptophan in a lipid membrane significantly reduces the rate of photodegradation due to a reversible electron (or hydrogen) transfer reaction [2]. Also, it was found that S-ketoprofen interacts stereoselectively with tryptophan enantiomers in lipid membrane.

Acknowledgements: this work was supported by the Russian Science Foundation (grant No. 18-13-00047).

[1] Mastova A. V., Selyutina O. Y., Polyakov N. E. (2022). *Membranes*, *12*(3), 251.
[2] Mastova A. V., Selyutina O. Y., Polyakov N. E. (2022). *Membranes*, *12*(5), 460.

Nitroxide Radicals in Starch Films: Structure-Feature Correlations

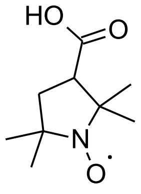
✉ **Anna Matveeva**[1,2], **Timofey Kuskov**[2], **Andrey I. Taratayko**[3], **Yulia F. Polienko**[3],
Ekaterina Podgorbunskikh[1], **Igor O. Lomovsky**[1]

[1] Institute of Solid State Chemistry and Mechanochemistry SB RAS
Novosibirsk, Russia
[2] Novosibirsk State University
Novosibirsk, Russia
[3] Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS
Novosibirsk, Russia

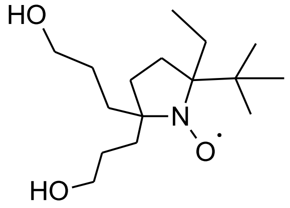
✉ matveeva@solid.nsc.ru

Polysaccharides, such as cellulose, starch or chitin/chitosan, are perspective renewable materials for food storage, drug delivery and drug release systems. The ability to form ordered (crystalline) regions alternating with disordered (amorphous) regions makes it possible to change physical properties of the resulting materials (flexibility, brittleness, density, air permeability) over a wide range.

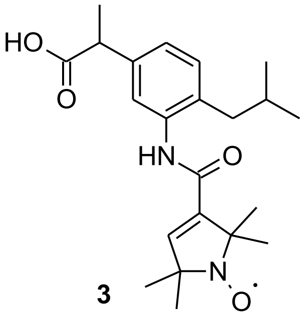
The main problem is to find structure-feature correlations. For example, native starch can be formed in so-called A, B and C polymorphic forms, depending on the certain type of plant source: potatoes, corn, manioc, etc. Further, native raw material can be modified in different ways. In present work, we study a mechanically-induced amorphization at all tree polymorphic types of native starch. Indeed, mechanical treatment changes the initial crystallinity degree [1]. Now we show that this treatment also affects the crystallinity degree of the starch films obtained by gelatinization of treated raw material.



1



2



3

Parallel EPR measurements on encapsulated nitroxides **1**, **2**, **3** show that aggregate state and local concentration of the label in films depends on the type of initial crystal structure and the mechanically-induced crystallinity degree, similar to [2].

Ackowledgements: the study was carried out with financial support from the Grant of the Government of the Novosibirsk Region (project No. GR-9).

[1] Dome K., Podgorbunskikh E., Bychkov A., Lomovsky O. (2020). *Polymers*, *12,* 641–653.
[2] Biliaderis C. G., Vaughan D. J. (1987). *Carbohydrate Polymers*, *7*, 51-70.

Atomize: Open-Source Modular Software for Working with Scientific Devices and Combining Them into a Spectrometer

✉ **Anatoly R. Melnikov**

International Tomography Center SB RAS
Novosibirsk, Russia
Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS
Novosibirsk, Russia

✉ anatoly.melnikov@tomo.nsc.ru

Remote control of spectrometers is usually carried out using home-written programs, which are often restricted to doing a certain experiment with a specific set of devices. In contrast, such programs as fsc2 [1] and Atomize [2] are much more flexible, since they are based on the modular approach for communication with device and scripting language for data measuring. For each available device, there is a special module that allows us to control it using high-level functions with self-explanatory names like *oscilloscope.get_curve()*. This makes it easy to set up a new experiment or modify already existing one without detailed knowledge about the internals of the program or exactly how the devices are controlled by the computer.

Herein, we report the current status of Atomize, open-source modular software for working with scientific devices. At the moment there are more than 200 device specific, general, and plotting functions available for over 25 different devices, including 4 series of devices. Additionally, the Python programming language is used inside the experimental scripts, which opens up almost unlimited possibilities for raw experimental data treatment. Atomize has been tested on Ubuntu 18.04 LTS, 20.04 LTS, and 22.04 LTS and is currently used for controlling several pulsed and continuous wave EPR spectrometers using a broad range of different devices. The source code, detailed documentation, and examples of experimental scripts can be found at https://github.com/Anatoly1010/Atomize.

[1] http://fsc2.org.
[2] https://github.com/Anatoly1010/Atomize.

Temperature Jump Spectroscopy under Pulsed THz Radiation: A Way to Measure T_1 of Magnetically Concentrated Substances

✉ **Anatoly R. Melnikov**[1,2], **Alexander Maryasov**[3], **Yaroslav V. Getmanov**[2,4],
Darya Shevchenko[4], **Matvey V. Fedin**[1,2], **Sergey L. Veber**[1,2]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia
[3] *Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[4] *Budker Institute of Nuclear Physics SB RAS*
Novosibirsk, Russia

✉ anatoly.melnikov@tomo.nsc.ru

Spin-lattice and spin-spin interactions play an important role in a number of physical phenomena with applied potential, i.e., magnetic relaxation in single-molecule magnets (SMMs), entanglement of a quantum system with its environment, and decoherence of magnetic qubits. In particular, for the technological application of SMMs, the low rate of spin-lattice relaxation (T_1) is one of the critical factors that requires fundamental understanding. To determine T_1 of SMM, the magnetic susceptibility of a macroscopic sample is usually measured by alternating current SQUID magnetometry. Another direct method is pulsed EPR spectroscopy, which requires diamagnetically diluted samples to suppress spin-spin interactions.

Temperature jump spectroscopy can be used as an alternative to SQUID magnetometry and pulse EPR. This is a type of time-resolved (TR) EPR spectroscopy that records changes in microwave (MW) absorption caused by pulse heating of a sample. The sign and shape of the resulting signal reflect the difference in the EPR signals of the spin system before and after the external stimulus. Traditional TR EPR spectroscopy uses laser radiation in the visible range to photochemically generate non-equilibrium-populated triplet states. The use of far infrared radiation (30–60 cm^{-1}) does not cause photochemical reactions, but heat the sample initiating spin dynamics.

Herein, we propose a numerical approach for modeling spin dynamics under continuous MW irradiation and a T-jump induced by pulsed THz radiation and exemplify it with the results obtained for cobalt(II) bis[tris(pyrazolyl)borate] with 100 % cobalt(II) ion content. Numerical modeling is based on solving the Liouville—von Neumann equation in the Julia programming language. The T_1 values were determined over a wide temperature range at several magnetic field positions of the powder spectrum. T-jump experiments were carried out at the EPR spectroscopy endstation [1] utilizing pulsed THz radiation of the Novosibirsk Free Electron Laser [2].

[1] Veber S. L. et al. (2018). *J. Magn. Reson.*, *288*, 11–22.
[2] Kulipanov G. N. et al. (2015). *IEEE T. THz Sci. Techn.*, *5*, 798–809.

Time-Resolved CIDNP Characterization of Kynurenic Acid Radicals Generated in Photoinduced Reactions with Tryptophan and Tyrosine

✉ **Olga B. Morozova**[1], **Maksim P. Geniman**[1,2],
Natalya N. Fishman[1], **Alexandra V. Yurkovskaya**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ om@tomo.nsc.ru

Kynurenic acid (KNA) is endogenous UV-A chromophore of the human eye lens able to sensitize photodamages to eye lens proteins. To study radical species of KNA, a time-resolved chemically induced dynamic nuclear polarization (TR CIDNP) was used. Recently we have established that at neutral pH tryptophan (Trp) reacts with triplet KNA via proton-coupled electron transfer (PCET) [1; 2], which involves the sequential transfer of both electron and proton from Trp to the KNA triplet, while the mechanism of the reaction between the triplet KNA and tyrosine (Tyr) is H-transfer. In neutral solution, KNA (anion) can exist in three tautomeric forms: keto-, enol, and oxo-quinolinate one, and triplet quenching can lead to the formation of three tautomeric radical structures. In order to determine the pathways of H/H^+ transfer in quenching reactions, we performed DFT calculations of the ^1H hyperfine coupling constants (HFCCs) for various tautomeric forms of KNA radicals, and compared them with the intensities in the ^1H geminate CIDNP spectra detected during the photoreactions under study. From the best-fit proportionality relationship between HFCCs and CIDNP intensities it was found that two out of three possible tautomeric forms of KNA anion radical are formed as a result of H/H^+ transfer to carbonyl oxygen of keto-form or oxo-quinolinate form. H/H^+ transfer to nitrogen of enol form was ruled out. The geminate CIDNP spectra were also detected during the photo-induced reactions of Trp and Tyr with 4-hydroxy quinoline (4HQN), a hydrophobic core of KNA, which radical exists in a single tautomeric form. For HFCCs of this radical and geminate CIDNP intensity, proportionality relationships with high determination coefficient were obtained. The high potential of TR CIDNP has led to a deep understanding of subtle details of photochemical reaction.

Acknowledgements: this work was supported by RFBR (project No. 19-29-10028 and 20-03-00234).

[1] Zhuravleva Y. S., Morozova O. B., Tsentalovich Y. P., Sherin P. S. (2020). *J. Photochem. Photobiol. A*, *396*, 112522.

[2] Morozova O. B., Yurkovskaya A. V., Sherin P. S. (2021). *Phys. Chem. Chem. Phys.*, *23*, 22483–22491.

Kinetics of Base Pair Opening-Closing Process in DNA Duplex Containing OxoG:C Pair and OxoG:A Mismatch

✉ **Sergey S. Ovcherenko**[1,3], **Andrey V. Shernyukov**[1], **Dmitry M. Nasonov**[1,3],
Anton V. Endutkin[2], **Dmitry O. Zharkov**[2,3], **Elena G. Bagryanskaya**[1]

[1] *Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[2] *Institute of Chemical Biology and Fundamental Medicine SB RAS*
Novosibirsk, Russia
[3] *Novosibirsk State University*
Novosibirsk, Russia

✉ ovcheren@nioch.nsc.ru

8-oxoguanine is known to be one of the most common and major DNA lesions resulting from the reactive oxygen species modifying guanine. When this lesion is located opposite to adenine in a base pair, the change from 8-oxoguanine's anti- to syn- conformation leads to the formation of the Hoogsteen base pair with adenine. The repair of this lesion is initiated by specific enzymes, namely 8-oxoguanine glycosylases which locate and excise the damaged base by means of flipping it outside the DNA double helix to the enzyme's active site. There are several models of how DNA glycosylase locate a damaged base and the role of the base pair opening-closing kinetics in this process [1]. However, there is no exact match in the literature that confirms one model and refutes the others [2].

NMR spectroscopy provides the exact experimental detection of the DNA base pair opening–closing rate constants at the single base pair level through the analysis of the water-iminoproton exchange rate. Iminoproton exchange with water occurs in two steps, namely opening of a base pair followed by proton exchange from the open conformation. Application of the water magnetization transfer technique permits the determination of exchange rate constants within the range that is most common for iminoprotons of a normal DNA duplex.

As a part of the study of the role of the opening-closing kinetics of 8-oxoG:A and 8-oxoG:C DNA base pairs in the recognition of 8-oxoguanine lesion by formamidopyrimidine-DNA glycosylase in the current work in the absence of enzyme, we obtained the kinetics constants for the base pair opening-closing process in the DNA duplexes containing 8-oxoG:A and 8-oxoG:C base pairs in two different sequence contexts and compared them with the values for the canonical G:C base pair in the same sequence contexts. The results obtained by NMR spectroscopy using the water magnetization transfer technique [3] are presented and discussed.

Acknowledgements: this work was supported by the Russian Science Foundation (No. 21-14-00219).

[1] Cao C. et al. (2004). *Nature Struct. & Molec. Biol.*, *11*(12), 1230–1236.
[2] Li R., Mak C. H. (2020). *The J. of Phys. Chem. B*, *124*(27), 5559–5570.
[3] Hwang T. L. et al. (1998). *Journal of biomolecular NMR*, *11*(2), 221–226.

The Reduction of Ag(I) by N,N-bis(silatranylmethyl)amines: EPR Study

✉ **Dmitry V. Pavlov**, **Boris A. Gostevsky, Nataliya F. Lazareva**

Favorsky Irkutsk Institute of Chemistry SB RAS
Irkutsk, Russia

✉ pavlov@irioch.irk.ru

In continuation of investigations of amines containing a tetra- or penta-coordinated group Rn-N(CH2SiX3)3-n in the α-position, we studied their interaction with AgNO3 by the EPR method. Mixing equimolar solutions of silver nitrate and N-substituted N,N-bis(silathranylmethyl)amines in acetonitrile leads to the reduction of silver. The nitrate salts of corresponding amines were isolated.

$$RNCH_2Si(OCH_2CH_2)_3N + AgNO3 \rightarrow Ag + Rn^+HCH_2Si(OCH_2CH_2)_3N{\cdot}NO_3^-$$
$$2\ MeCN \rightarrow NCCH_2CH_2CN$$

The electron transfer reaction from the amine produces a formation of the amine radical cation and metal silver. At the same time, an intermolecular hydrogen atom transfer from acetonitrile to the nitrogen atom of the amine occurs, which leads to the formation of an ammonium cation and a CH_2CN radical that subsequently recombines to form a $CNCH_2CH_2CN$ dimer.

In the case of N-alkyl-N,N-bis(silatranylmethyl)amines, like methyl, benzyl, i-propyl, the signals of radical cations are recorded at 285–295 K and then quickly decrease. The hyperfine structure and the value of hyperfine coupling constants non-equivavalent methylene groups of silatranyl substitutants (*R* = i-Pr, *aN* = 17.36, *aH(2)* = 4.73 G, *aH(2)* = 20.24 G, *aH(R)* = 10.34 G, g-factor 2.0047), indicate a partial redistribution of the spin density due to the influence of the solvent.

In the case of aromatic substituents at the nitrogen atom, the spectrum of the reaction mixture already at 230 K shows narrow signals of the formed silver nanoparticles (*R* = Ph, Δ*H* = 7.6 G, g-factor 2.0045).

Behavior of Biomolecules in Phospholipid Membranes Studied by the NMR, CIDNP and Molecular Dynamic Techniques

✉ **Nikolay E. Polyakov**, **Anna V. Mastova**, **Olga Yu. Selyutina**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ polyakov@kinetics.nsc.ru

The NMR, CIDNP and molecular dynamic techniques can provide unique information on the interaction of biomolecules with cell membranes. In particular, a considerable attention is paid to the mechanisms of stereoselectivity in the interaction of chiral drugs with the active sites of enzymes and cell receptors. The first reason is difference in therapeutic activity of enantiomers of common drugs. Another reason is the interest in the role of chiral inversion of amino acids involved in various peptides in development of many diseases, including Alzheimer's, Parkinson's, type II diabetes, and a number of other pathological conditions. In our study we used an elementary chemical process—electron transfer (ET)—to simulate individual stages of ligand-receptor and enzyme-substrate interactions. In particular, the studies of photoinduced ET in chiral donor-acceptor dyads consisting of nonsteroidal anti-inflammatory drug (R/S)-ketoprofen and (L)-tryptophan showed stereo and spin selectivity of the ET in diastereomers [1].

The present study is devoted to the interaction of (S)-ketoprofen with L- and D-enantiomers of tryptophan in homogeneous aqueous solution and in phospholipid membranes [2]. The study was done using the NMR technique and molecular modeling. These approaches confirm the efficient penetration of ketoprofen into the lipid bilayer and binding with tryptophan molecule. The short-lived paramagnetic intermediates formed during the photoinduced ET from electron donor tryptophan to ketoprofen have been detected using the chemically induced dynamic nuclear polarization (CIDNP) technique. It was found that S-ketoprofen interacts stereoselectively with tryptophan enantiomers in a lipid membrane. The formation of the ketyl radical of ketoprofen under irradiation leads to the oxidation of membrane lipids and may cause ketoprofen phototoxicity. However, in contrast to a homogeneous solution in phosphate buffer saline where amino acid tryptophan accelerates the photodecomposition of KP due to intramolecular hydrogen transfer, tryptophan in a lipid membrane significantly reduces the rate of photodegradation due to the reversible electron (or hydrogen) transfer reaction. The stereoselectivity in the rate of KP and lipids decomposition under the UV irradiation of S-ketoprofen in the presence of tryptophan enantiomers in lipid bilayer has been detected.

Acknowledgements: this work was supported by the Russian Science Foundation (grant No. 18-13-00047).

[1] Ageeva A. A., Magin I. M., Doktorov A. B., Plyusnin V. F., Kuznetsova P. S., Stepanov A. A., Alekseev A. A., Polyakov N. E. (2021). *Int. J. Mol. Sci.*, *22*, 6198.

[2] Mastova A. V., Selyutina O. Y., Polyakov N. E. (2022). *Membranes*, *12*, 460.

Blatter-Radical-Grafted Mesoporous Silica as Prospective Nanoplatform for Gas Sorption and Spin Manipulation

✉ **Artem S. Poryvaev**[1], **Anastasiya A. Yazikova**[1,2], **Daniil M. Polyukhov**[1], **Aleksandr A. Efremov**[1,2], **Matvey V. Fedin**[1]

[1] International Tomography Center SB RAS
Novosibirsk, Russia
[2] Novosibirsk State University
Novosibirsk, Russia

✉ poryvaev@tomo.nsc.ru

Mesoporous silica is a robust and promising adsorbent for gas capture and purification, and the efficiency/selectivity of these processes can be greatly enhanced by modification of the sorbent surface with organic molecules to yield specific sorption sites. Here, we report a new type of modified SBA-15 silica-based adsorbent for nitrogen monoxide (NO), a gas that is of high environmental importance. SBA-15 was decorated with stable Blatter-type radicals via grafting, and interactions with NO were studied using *in situ* Electron Paramagnetic Resonance (EPR) spectroscopy. The developed material shows a formation of diamagnetic adduct upon the NO sorption, which can be decomposed to the initial state upon heating. The capability of reversible NO capture paves new ways for rational design of Blatter radical-based adsorbents for environmental applications.

On the other side, the pulse EPR study revealed that Blatter's type organic radicals grafted into the mesoporous silica show advanced relaxation properties at room temperature. Moreover, electron spin decoherence time exceeds that in many other qubit candidates, providing for efficient spin manipulation at ambient conditions.

Thus, tuneable multifunctional nature of such composite materials promotes them as promising nanoplatforms for developing new spin-based quantum bits and efficient nitrogen monoxide sorbents.

Acknowledgements: this work was funded by RFBR (grant No. 20-53-12005).

Reaction Operators for Radical Pairs

✉ **Peter A. Purtov**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉ purtov@kinetics.nsc.ru

Spin chemistry concerned with electron and nuclear spins behavior as well as with the manifestation of magneto-spin interactions in chemical reactions is developed quite well both experimentally and theoretically. Most frequently spin chemistry deals with radical pair reactions in liquid solutions. Commonly the recombination of radical pairs occurs at the immediate contact of radicals, when the overlap of radical pairs orbitals is considerable, and singlet-triplet transitions take place in the intervals between re-contacts, when the exchange interaction is insignificant. However, in some reactions, e.g., in electron transfer, the reaction and spin evolution proceed simultaneously. To describe such processes, a phenomenological exponential model was developed about 50 years ago. According to this model, the evolution of the spin density matrix of a radical pair (RP) obeys the equation:

$$\begin{gathered}\frac{\partial\rho(t)}{\partial t}=-\frac{i}{\hbar}\left[\hat{H},\rho\right]-\frac{K_S}{2}\left(Q_S\rho+\rho Q_S\right)-\frac{K_T}{2}\left(Q_T\rho+\rho Q_T\right),\\ Q_S=|S\rangle\langle S|,\ \ Q_T=|T_0\rangle\langle T_0|+|T_-\rangle\langle T_-|+|T_+\rangle\langle T_+|.\end{gathered} \qquad (1),$$

In the spin chemistry, eq. (1) are widely used to describe various effects. Although these equations are phenomenological, it describes the observed effects well. In [1] the exactly solvable model is used to verify eq. (1). However, in the spin chemistry, the cases are possible where the processes are reversible (e.g., electron transfer). Thus, eq. (1) needs to be generalized. In the present work, we have derived the exactly solvable model that contains both reversible and irreversible processes. Expression for the reaction operator of this model is more complex due to the expanded basis of spin states. The reaction operator of eq. (1) is a particular case. These operators coincide only in the limiting case of the fully irreversible recombination process. This work continues the study begun in [2; 3]. It is considered a more common exactly solvable model. Expression for the reaction operator of this model is more complex due to the expanded basis of spin states. The reaction operator of the eq. (1) is a particular case. These operators coincide only in the limiting case of the fully irreversible process of recombination.

Simultaneous consideration of recombination from the singlet and triplet states is much more complicated. Here we also built an exact model. However, in this more general case, the equation (1) is not always justified even for an irreversible process. The applicability limits of the approximation are indicated. A more general case of reversible recombination is studied [4].

[1] Purtov P. A. (2010). *Chem. Phys. Letters*, *496*, 335.
[2] Sosnovsky V., Purtov P. A. (2014). *Chem. Phys. Letters*, *608,* 136.
[3] Purtov P. A. (2017). *Zeitschrift fur Physikalische Chemie*, *231*(2), 225–238.
[4] Purtov P. A., *Chem. Phys. Letters* (in press)

Analysis of DNP Cross-Talk Experiments for Several Nuclei

✉ **Bogdan A. Rodin**[1–3], **Alexandra V. Yurkovskaya**[1,2], **Daniel Abergel**[3]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia
[3] *Laboratoire des biomolécules, École normale supérieure, Sorbonne Université*
Paris, France

✉ phagost@gmail.com

Dynamic nuclear polarization (DNP) is an efficient and versatile method that enables one to increase signal intensity in nuclear magnetic resonance (NMR). Hyperpolarization of nuclear spins is achieved by transferring the high electron polarization to the former through microwave (mw) irradiation. Admittedly, this transfer is achieved through three main mechanisms, namely, the solid effect (SE) that involves forbidden electron-nuclear transitions, the cross effect (CE) and thermal mixing (TM) [1]. The TM description of DNP assumes the existence of several thermal reservoirs with different spin temperatures, such as the nuclear Zeeman, electron Zeeman, and nuclear non-Zeeman reservoirs. It was recently proposed [2] that in the experiments involving two nuclear spin species and electrons, the TM regime may be dominant if a) both nuclei reach a common spin temperature under the mw irradiation and b) both nuclei reach a common spin temperature (different from the lattice) when either of the nuclei is initially depolarized. This phenomenon of polarization transfer between nuclear reservoirs is called cross-talk. It was concluded that the TM regime is achieved when the concentration of radicals is relatively high ($\geqslant$ 50 mM for TEMPOL).

In this work we investigate the cross-talk phenomenon under the TM conditions using Provotorov's equation [3]. Surprisingly, it was found that D plays important role in the polarization transfer, and it has to be included into the model to correctly describe the visible effects. Also, it was revealed that D spins play important role in the repolarization experiments, contrary to the previous statements [4]. A detailed study of the dependencies on both nuclei and radical concentrations is presented. Using these data and Provotorov's equations, we estimated such parameters as non-Zeeman heat capacities, rate constants of temperature exchange between nuclear and electron non-Zeeman reservoirs, as well as the relaxation rate of non-Zeeman reservoir. We believe that this work will provide better insight into the mechanisms of polarization transfer.

Acknowledgements: this research was supported by the Russian Foundation for Basic Research (Grant No. 20-53-15004).

[1] Wenckenbach T. (2016). *Essentials of Dynamic Nuclear Polarization*. Spindrift Pub., 1717.

[2] Guarin D. et al. (2017). *J. Phys. Chem. Lett.*, *8*(22), 5531–5536.

[3] Provotorov B. N. (1962). *J.E.T.P., 42*, 882–888.

[4] Stern Q. et al. (2021). *Science Advances*.

Mechanistic Insight into Heterogeneous Hydrogenation of Methylenecyclobutane with the Use of Parahydrogen

✉ **Oleg G. Salnikov**[1,2], **Dudari B. Burueva**[1], **Larisa M. Kovtunova**[2],
Kirill V. Kovtunov[1], **Igor V. Koptyug**[1]

[1] International Tomography Center SB RAS
Novosibirsk, Russia
[2] Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia

✉ salnikov@tomo.nsc.ru

In spite of all accumulated knowledge there is still a number of unanswered questions regarding the mechanisms of hydrogenation reactions. Parahydrogen-induced polarization (PHIP) can provide unique information about the mechanisms of reactions involving hydrogen. PHIP is based on pairwise addition of two H atoms from the same parahydrogen (p-H_2) molecule to the same substrate molecule. This leads to a significant enhancement and characteristic antiphase lineshape of the NMR signals of the corresponding ^1H nuclei.

In this work, PHIP technique was applied for a mechanistic study of methylenecyclobutane (MCB) hydrogenation over Rh, Pt and Pd catalysts supported on TiO_2 [1]. The reaction leads to the formation of up to 11 products. At lower temperatures (150–350 °C), the major reaction product was methylcyclobutane, while higher temperature of 450 °C favors branched products: isoprene, 2-methyl-1-butene and 2-methyl-2-butene. Based on the absence of PHIP effects for isoprene, we propose that it is produced via direct cleavage of the C_4 ring without adsorption of MCB via the C=C bond. Formation of other products starts with adsorption of the reactant via the C=C bond. PHIP results show that cyclic products 1-methylcyclobutene and methylcyclobutane are formed via the sequential steps of H atoms addition and elimination. Acyclic products are obtained through fission of the C_4 ring to 1,4-pentanediyl and 2-methyl-1,4-butanediyl species which then may isomerize to adsorbed alkenes followed by either desorption, pairwise hydrogen replacement or H_2 addition. The differences in PHIP signal patterns of 2-methyl-1-butene formed from MCB and 2-methyl-2-butene allowed us to establish that 2-methyl-1-butene is produced from MCB via 2-methylbutylidene species, while in the case of 2-methyl-2-butene used as a reactant 2-ethyl-1,3-propanediyl species serve as an intermediate. Altogether, the obtained results demonstrate unique features of the PHIP technique as of tool for mechanistic studies of hydrogenation reactions.

Acknowledgements: this work was supported by the Council on Grants of the President of the Russian Federation (grant No. MK-2826.2022.1.3) and the Russian Foundation for Basic Research (grant No. 19-33-60045).

[1] Salnikov O. G. et al. (2022). *ChemPhysChem*, *23*, e202200072.

Crystallization of Paramagnetic Compounds in the Gradient Magnetic Field of a Superconducting Magnet

Arkady A. Samsonenko[1,2], **Natalya A. Artiukhova**[1,2], **Alexey S. Kiryutin**[1], **Ivan V. Zhukov**[1,2], **Victor I. Ovcharenko**[1], **Sergey L. Veber**[1,2]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ a.samsonenko@g.nsu.ru

The magnetic field force acting on substances can to some extent compensate for the gravitational force. The most known example of levitation in a magnetic field is probably the levitation of a frog [1]. Unlike diamagnetic compounds, the levitation of paramagnetic ones is impossible for fundamental reasons [2]. Despite the fact that full compensation of the gravitational force is not possible in the case of paramagnetic compounds, the residual "effective" acceleration can be significantly reduced. As a result, it can improve the quality of the obtained crystals. Another advantage of the crystallization in a gradient magnetic field is different strength of the magnetic field acting on the crystals of different paramagnetic compounds. This results in the possibility of spatial separation of these compounds inside the magnet.

In this work, the field profile of the NMR magnet with the proton frequency of 300 MHz was characterized in detail. The magnetic force acting on samples with different magnetic permeability was also calculated. The estimate of the magnetic field magnitude required to achieve the levitation conditions of different compounds was obtained. The experimental setup designed to carry out crystallization in the magnetic field of the NMR magnet was described. The purpose of this work is to demonstrate the features of paramagnetic compounds crystallization in a gradient magnetic field. Copper sulfate crystals were used as a model system. The advantages of this crystallization method are discussed.

[1] Ratera I. E. et al. (2012). *Chem. Soc. Rev., 41*, 303–349.
[2] Tolstikov S. et al. (2014). *Chem. Eur. J., 20,* 2793–2803.

Multicenter EPR-Based Approach to Studying the Localization of Photosensitizers in Biomolecules

✉ **Natalya E. Sannikova**[1,2], **Alexey S. Chubarov**[3],
Michael K. Bowman[4,5], **Matvey V. Fedin**[1], **Olesya A. Krumkacheva**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia
[3] *Institute of Chemical Biology and Fundamental Medicine SB RAS*
Novosibirsk, Russia
[4] *Vorozhtsov Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[5] *Department of Chemistry & Biochemistry, University of Alabama*
Tuscaloosa, USA

✉ sannikova.epr@gmail.com

Photodynamic therapy (PDT) is a promising treatment of cancer. The effectiveness of PDT depends on the ability of photosensitizers (PS) to bind to transport proteins, such as human serum albumin (HSA), and on their localization in such complexes. Therefore, the development of informative methods of studying the structure of PS complexes with biomolecules is an important task. Chlorin E6 (Ce6) is a widely used PS in clinical practice, but its localization in HSA has not been reliably determined.

In this work, we proposed a new approach to study the localization of PS in complex with HSA by the electron paramagnetic resonance (EPR) spectroscopy. This approach involves using several orthogonal labels in combination with photoexcited molecules: the $\mathrm{Cu^{II}}$ ion bound to the N-end of HSA and a MTSL nitroxyl label selectively introduced into Cys-34. We demonstrated that Laser-IMD (laser-induced magnetic dipole) spectroscopy provides for obtaining the distance distribution between the photoexcited triplet state of Ce6 and stable orthogonal labels $\mathrm{Cu^{II}}$ or MTSL. Besides, the distance between two photoexcited triplet states of PS was measured using a LIRIDME (laser-induced relaxation induced dipolar modulation enhancement) pulse sequence for the first time. Finally, the proposed approach allowed us to determine all the binding sites of Ce6 with high accuracy. We found that Ce6 binds to HSA at two different sites: FA1 (subdomain IB) and FA7 (subdomain IIA).

Acknowledgements: this work was supported by the Russian Science Foundation (grant No. 20-73-10239).

Molecular Mobility of Nanocellulose Gels Studied by the Paramagnetic Probe Method

✉ **Irina A. Shilova, Svetlana I. Kuzina, Alfa I. Mikhaylov**

Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia

✉ ishil@icp.ac.ru

Molecular mobility of cellulose nanoparticles in hydrogel isolated from macrocrystalline cellulose was estimated from **correlation time** *t* (seconds) and **radical rotation frequency** $n = (t)^{-1}$. The EPR spectra of solid solutions at 77 K showed that NR is a triplet with the anisotropic HFI constant A_{ii} = 3.85–3.9 mT, g-factor = 2.0045, and the integral intensity ratio1:1:1. Correlation time *t* was $3{\cdot}10^{-7}$ s at 77 K. The triplet shape of the spectrum was the evidence of complete dissolution of NR and the formation of true solution in both media. The triplet of nitroxyl radicals retained in the water matrix at 77–265 K and in the water-alcohol solution—at 77–180 K. Thus, the temperature of rotation of radicals was by 85° lower in the presence of alcohol than in water. Provided free rotation of the radicals of PMP at 300 K, fully isotropic triplets with a_{iso} = 1.7 mT, *g* = 2.0045, and the intensity ratio 1:1:1 were recorded in solution. Narrow lines of the isotropic triplets (DH_i = 0.15–0.22 mT for water and water-alcohol systems of gel) justified high hydrophobicity and weak interaction of radicals with the environment. Correlation time *t* was estimated from the EPR spectra registered at different temperatures [1]. The high pre-exponential factor, namely, 10^{18} s^{-1} for water and the water system of hydrogel can be interpreted in terms of "water compensation effect" [2]. The effect is as follows: water molecules are squeezed out from the nearest environment of the active center to provide the rearrangement and disorder in water structure, and, consequently, the growth of entropy of the system. Therefore, the compensation effect provides a smoother temperature dependence of active centers than it would be with the participation of the activation energy without the entropy factor. In terms of thermodynamics, the effect consists in that essential changes in enthalpy and entropy compensate each other, and the changes in free energy are relatively small. It is known that water molecules appear as clusters or ensembles in both liquid and solid state, and molecules are strongly interlinked by hydrogen bonds in such clusters and ensembles. Considering hydrogen bond value ~5 kcal/mol, one can suppose that nanoparticles form two hydrogen bonds inside a water cluster in water gel. The activation energy of particle rotation is 11 kcal/mol. If alcohol is added, one hydrogen bond breaks, and the activation energy of radical rotation decreases to ~5 kcal/mol.

[1] Vasserman A. M., Kovarskii A. L. (1986). *Spin Probes and Lables at Polymer Physicochemistry*. M.: Nauka.

[2] Volkenshtein M. V. (1975). *Molecular biophysics*. M.: Nauka.

Anchored Complexes of Rhodium and Iridium in the Hydrogenation of Alkynes and Olefins with Parahydrogen

✉ **Ivan V. Skovpin**[1], **Larisa M. Kovtunova**[1,2], **Anna V. Nartova**[2], **Ren I. Kvon**[2], **Valerii I. Bukhtiyarov**[2], **Igor V. Koptyug**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Boreskov Institute of Catalysis SB RAS*
Novosibirsk, Russia

✉ iskovpin@tomo.nsc.ru

Additionally to the use as a NMR sensitivity boosting technique, parahydrogen-induced polarization (PHIP) is a powerful tool for studying hydrogenation reaction mechanisms, since it provides means for detecting short-lived reaction intermediates and, thus, can shed light on possible routs of dihydrogen addition. For a long time this technique was applied only for the investigations of homogeneous hydrogenation reactions, because heterogeneous catalysts were not expected to account for the necessary condition of PHIP observation—the pairwise addition of both atoms of a dihydrogen molecule. Recently, however, it was shown that PHIP can be observed in hydrogenation reaction over heterogeneous catalysts [1].

Several catalysts synthesized by covalently binding Rh and Ir complexes to the NH_2- and PPh_2-functional groups of the linker chains on functionalized silica gel surface were compared in the gas-phase hydrogenation of propyne and propene. Their stability, activity and product selectivity were evaluated. Furthermore, the use of parahydrogen in the reaction provided useful mechanistic information by delivering nuclear spin hyperpolarization of the reaction products with the associated enhancement of their NMR signals. In contrast to Rh-based catalysts which showed a pronounced tendency to reduction, for Ir-based catalysts, the XPS analysis did not reveal any indication of the formation of metal phase under the reducing conditions upon hydrogenation of propyne or propene at 120 °C. Catalysts with a π-acceptor ligand PPh_2- demonstrated greater activity in the gas-phase hydrogenation of propyne/propene in comparison with σ-donor ligand NH_2-. Furthermore, the NMR signal enhancement of up to ca. 700- (Rh) and 800-fold (Ir) were achieved. Remarkably, the Ir metal complex bound via the phosphine moiety demonstrated high stability in the gas-phase hydrogenation of propyne along with high catalytic activity and pairwise H_2 addition selectivity, yielding substantial quantities of strongly hyperpolarized propene.

Acknowledgements: this work was supported by the RFBR grant No. 19-29-10003_mk. The authors also express their gratitude to the Russian Ministry of Science and Higher Education for granting access to NMR equipment.

[1] Koptuyg I. V., Kovtunov K. V., Burt S. R., Anvar M. S., Hilty C., Han S., Pines A., Sagdeev R. Z. (2017). *J. Am. Chem. Soc.,* V., *129*, 5580–5586.

DEER of Spin-Labeled Stearic Acids in Model Phospholipid Membranes Reveals Alternative Cluster Formation in Two Opposing Leaflets

✉ **Ana S. Smorygina, Sergey A. Dzuba, Elena A. Golysheva**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ anna.smor.mr@gmail.com

Free fatty acids are essential components of biological membranes important for their functioning: they increase the membrane fluidity, serve as energy supply and a source of structural components, and participate in lipid metabolism and other biological processes. In this work, we studied the synthetic membranes clustering of molecules of spin-labeled stearic acids in model. Membranes were prepared either of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) lipids or of equimolar mixture of 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) and 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) lipids. The stearic acid molecules contained the spin label at the 5th or 16th position of the carbon atom in the acyl residue.

The main approach was a pulsed version of EPR—double electron-electron resonance spectroscopy (DEER, also known as PELDOR). DEER spectroscopy is based on an electron spin echo phenomenon; it is used to determine the nanoscale distances between spin labels and study spatial distribution of spin labels.

Local concentrations of the DSA molecules found from DEER data turned out to exceed remarkably their mean concentrations χ for both DOPC/DPPC and POPC bilayers. This enhancement unambiguously implies lateral (nano)clustering. The characteristic distance between the DSA molecules in clusters was found to be ~2 nm. However, for 5-DSA, the local concentration of stearic acid turned out to be lower than that for 16-DSA, which was explained by the formation of sub-clusters in two opposing leaflets. The polar heads of 5-DSA molecules in each sub-cluster repel each other, thus, reducing the lateral density of spin labels along the acyl chain.

It was also found that stearic acid molecules in the bilayers of different compositions are immersed to different relative depths: in the POPC bilayer, spin labels have a three-dimensional spatial distribution, while in the DOPC/DPPC bilayer their distribution is close to two-dimensional. The CW EPR spectra taken at room temperature support the conclusions on the cluster formation of the DSA molecules obtained here by DEER spectroscopy at cryogenic temperatures.

Acknowledgements: this work was supported by RSF (grant No. 21-13-00025).

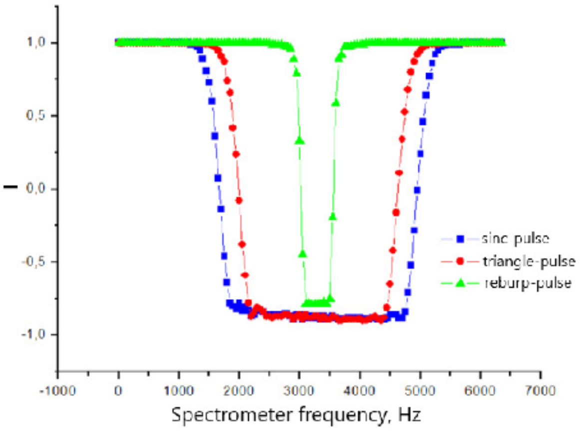
Constant Adiabaticity Inverting Pulses

✉ **Aleksandr V. Snadin**[1,2], **Nikita N. Lukzen**[1,2], **Alexey S. Kiryutin**[1,2], **Konstantin L. Ivanov**[1]

[1] International Tomography Center SB RAS
Novosibirsk, Russia
[2] Novosibirsk State University
Novosibirsk, Russia

✉ snadin1999@mail.ru

Adiabatic inversion methods are well-suited for broadband excitation in NMR and EPR. The idea of adiabatic inversion is to use a pulse (radiofrequency pulse in the case of NMR or microwave pulse in the case of EPR) with time-dependent frequency ω varied in such a way that a passage through resonance is performed, $\omega = \omega_0$. When the passage is slow enough, the spin vector S always follows the effective field ω_{eff} in the rotating frame, which has a z-component equal to the frequency off-set $\Delta(t) = \omega_0 - \omega$ and the x-component equal to ω_1, which is given by the strength of the oscillating B_1 field. If we assume that initially $\Delta > 0$ and $\Delta \gg \omega_1$, the effective field ω_{eff} and the spin vector S are both parallel to the z-axis. Passage through resonance means that Δ changes its sign and so does the spin vector, i.e., the spin is inverted.



Excitation profiles of water protons for different pulses. The Reburp-pulse is also inverting, it does not have a constant adiabaticity parameter, and was taken for comparison

Various RF inverting pulses have been constructed for NMR experiments with a constant adiabaticity parameter, which provide for obtaining selective and rectangular spin inversion profiles. The constructed pulses were experimentally tested on a 700 MHz NMR spectrometer using water protons in the presence of a relaxant (10 mM copper (II) sulfate ($CuSO_4$)). Due to different time dependences of the RF field amplitude, it was possible to achieve selective excitation profiles of different widths. Pulses with a constant adiabaticity parameter were compared with widely used inverting pulses of a certain shape to compare inversion, selectivity. It is shown that these pulses can be used for MRI.

Acknowledgements: the work was financially supported by the Russian Foundation for Basic Research (grant No. 21-53-12023-ННИО-а).

ZIF-8 Nanoparticles Stability in Cell Culture Media

Anna S. Spitsyna[1,2], **Artem S. Poryvaev**[1], **Natalya E. Sannikova**[1],
Anastasiya A. Yazikova[1], **Igor A. Kirilyuk**[2], **Sergey A. Dobrynin**[2],
Olga A. Chinak[3], **Matvey V. Fedin**[1], ✉ **Olesya A. Krumkacheva**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[3] *Institute of Chemical Biology and Fundamental Medicine SB RAS*
Novosibirsk, Russia

✉ olesya@tomo.nsc.ru

Metal-organic frameworks, porous coordinated compounds, are promising materials in different fields due to high variety of possible features and tunability. In particular, zeolite imidazolate framework-8 (ZIF-8) is capable of hosting proteins, nucleic acids and photosensitizers, emerged as a potential drug carrier. With biocompatibility, pH-dependent drug release and adjustable pore size being ZIF-8 main advantages, this framework was applied in photodynamic therapy, cancer treatment, protein delivery, etc. Many of these applications include studying ZIF-8 uptake by cells making the interaction of ZIF-8 nanoparticles with a cell culture media somewhat inevitable. The systematic investigation of ZIF-8 stability in various cell culture media has not been performed, despite the fact that this information is essential for *in vitro* studies.

In this work [1], we report a quantitative investigation of the ZIF-8 nanoparticles' stability in most common cell culture media. With this purpose, ZIF-8 nanoparticles containing sterically shielded nitroxide probes with high resistance to reduction were synthesized and studied using the Electron Paramagnetic Resonance (EPR). Degradation of ZIF-8 in cell media was monitored by tracking the cargo leakage. It was shown that nanoparticles degrade, at least partially, in all studied media, although the degree of cargo leakage varies widely. We found a strong correlation between the amount of escaped cargo and the total concentration of amino acids in the environment. We also established the role of individual amino acids in ZIF-8 degradation. Finally, 2-methylimidazole preliminary dissolved in cell culture media partially inhibits the degradation of ZIF-8 nanoparticles. The guidelines for choosing proper cell culture medium for in vitro study of ZIF-8 nanoparticles have been formulated.

Acknowledgements: this work was supported by the Russian Science Foundation (No. 20-73-10239).

[1] Spitsyna A. S., Poryvaev A. S., Sannikova N. E., Yazikova A. A., Kirilyuk I. A., Dobrynin S. A., Chinak O. A., Fedin M. V., Krumkacheva O. A. (2022). *Molecules*, *27*, 3240.

Study of the Features of Hydrogenation Reactions of Unsaturated Hydrocarbons with Parahydrogen

✉ **Sergey V. Sviyazov**[1,2], **Dudari B. Burueva**[1,2],
Oleg G. Salnikov[1,2], **Vitaly P. Kozinenko**[1,2], **Igor V. Koptyug**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉ s.sviyazov@tomo.nsc.ru

One of the most promising methods for hyperpolarization of nuclear spins is the parahydrogen-induced nuclear polarization (PHIP). In the PHIP method, parahydrogen, the nuclear spin isomer of molecular hydrogen with a total nuclear spin $I = 0$, is used as a source of hyperpolarization. The essence of the PHIP method is that spin correlation of parahydrogen atoms can be partially preserved in the products and intermediates of a hydrogenation reaction with parahydrogen.

Recently, a promising catalytic system for the selective hydrogenation of alkynes has been developed — a Pd catalyst deposited on a defective graphite-diamond composite with monoatomic distribution of Pd (Pd_1/ND@G) or with clustered metal distribution (Pd_n/ND@G). Both catalysts have shown remarkable performance in selective hydrogenation of propyne. It was shown that the Pd_1/ND@G catalyst with a single-atom Pd distribution is much more active in the pairwise addition of hydrogen to propyne compared to the Pd_n/ND@G catalyst — for Pd_1/ND@G, the maximum observed enhancement of the NMR signal for propylene was about 89, while for Pd_n/ND@G — 15. Thus, we can conclude that the use of catalysts with monoatomic distribution of the active component is promising for obtaining hyperpolarized substances due to the PHIP effect.

Moreover, in this work, the polarization of ^{13}C spins at natural abundance in a hyperpolarized gas was achieved. The hyperpolarized propane was obtained in propylene hydrogenation with parahydrogen over Rh/TiO_2 catalyst. Next, the ^1H polarization was transferred to ^{13}C nuclei of propane using the PH-INEPT family of pulse sequences. The maximum observed ^{13}C polarization was 0.07 ± 0.01 % and 0.030 ± 0.006 % for the methyl group of [1-^{13}C]propane and the methylene group of [2-^{13}C]propane, respectively.

The selective hydrogenation of acetylene with parahydrogen was proposed as a promising approach for the enrichment of nuclear spin isomers of ethylene. In this work, the Wilkinson's catalyst was used for production of ethylene in $CDCl_3$. It was shown that in the ^1H NMR spectra of the solution immediately after bubbling of parahydrogen, the ^{13}C satellite signals of ethylene are observed, which indirectly confirms the enrichment of ethylene spin isomers. The maximum observed ^1H polarization was 1.2 %.

Acknowledgements: this work was supported by the Russian Foundation for Basic Research (grant No. 19-29-10003).

3D ^{15}N Visualization of a Drug Hyperpolarized by SABRE Approach

✉ **Alexandra I. Svyatova**[1–3], **Ivan V. Skovpin**[1], **Nikita V. Chukanov**[1,2],
Eduard Y. Chekmenev[4,5], **Andrey N. Pravdivtsev**[6], **Jan-Bernd Hövener**[6], **Igor V. Koptyug**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State Universit*
Novosibirsk, Russia
[3] *Institute of Cytology and Genetics SB RAS*
Novosibirsk, Russia
[4] *Karmanos Cancer Institute (KCI), Integrative Biosciences (Ibio), Wayne State University*
Detroit, USA
[5] *Russian Academy of Sciences*
Moscow, Russia
[6] *Department of Radiology and Neuroradiology Section Biomedical Imaging,*
MOIN CC, Universitätsklinikum Schleswig-Holstein, Universität Kiel
Kiel, Germany

✉ alexandra.svyatova@tomo.nsc.ru

Biomedical studies use the magnetic resonance imaging (MRI) as a non-destructive and non-invasive tool for visualization of internal organs and tissues, and of metabolic processes in living bodies. The main limitation of MRI is its sensitivity because of small nuclear spin polarization. This problem can be solved using the hyperpolarization (HP) methods. One of such methods is the signal amplification by reversible exchange (SABRE). SABRE-based approaches allow one to perform the heteronuclear MRI of heterocyclic compounds, e.g., vitamin B3 [1] or fampridine [2], despite the fact that conventionally heteronuclei are not used for signal detection because of their low gyromagnetic ratio and natural abundance.

In this work, we used ^{15}N-labeled fampridine hyperpolarized by the SABRE-based approach for the 2D and 3D ^{15}N MRI. Fampridine has therapeutic value (it treats symptoms of multiple sclerosis). As a result of HP, we obtained ^{15}N signal intensity enhancement $\varepsilon = 2{,}000$ in a magnetic field of 9.4 T. Also, we compared the values of ε achieved for ^{15}N-labeled and non-labeled fampridine. While ε is higher for non-labeled substrate, molar polarization is higher for the ^{15}N-labeled one. High values of signal intensity allowed us to perform the 3D ^{15}N MRI with a signal-to-noise ratio of up to 90.

The implementation of HP methods for heteronuclear MRI expands the range of MRI applications, e.g., real-time monitoring of metabolism or differentiation of normal and cancerous/necrotic tissues.

Acknowledgements: this work was supported by the Russian Foundation for Basic Research (grant No. 19-29-10003).

[1] Svyatova A. I., Skovpin I. V. et al. (2019). *Chem. Eur. J.*, *25*(36), 8465–8470.
[2] Skovpin I. V., Svyatova A. I. et al. (2019). *Chem. Eur. J.*, *25*(55), 12694–12697.

Comparative Study of Membrane-Active Trichogins in Lipid Membranes

✉ **Victoria Syryamina**[1], **Sergei A. Dzuba**[1,2], **Fernando Formaggio**[3], **Marta De Zotti**[3]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Physics department, Novosibirsk State University*
Novosibirsk, Russia
[3] *ICB-CNR, Padova Unit, Department of Chemistry, University of Padova*
Padova, Italy

✉ v_syryamina@kinetics.nsc.ru

Membrane-active peptides (MAPs) are a promising class of therapeutics because of their ability to inhibit pathogen growth. When MAPs are bound to a lipid membrane, its local structure and integrity are perturbed making the membrane to be prone to local defects. The character of these perturbations determines the peptide activity, and is of interest for further drug design.

By exploiting the spectroscopy of the Electron Paramagnetic Resonance (EPR), we studied the relationship in the character of peptide/membrane interaction and the activity for the short-length decapeptide trichogin. This peptide is a well-studied, low-cost and convenient template for drug design [1]. Thus, trichogin analogs of different activity and selectivity to pathogens were examined in a membrane consisting of zwitter-ionic lipids that mimics the membrane of mammalian cells, and in membrane consisting of negatively charged lipid that mimics the pathogens' membrane. By use of spin-labeled trichogin analogs we studied the peptide self-assembling process and the topography of lipid bilayers, and by using the trichogin analogs and spin-labeled fatty acids we studied the peptide-induced structural rearrangements in the membrane plane.

For the native trichogin, stepwise specific oligomerization accompanied by the drill-like motions was found; this peptide also results in lateral reorganization in the membrane plane with pronounced clustering of fatty acids. It is likely that these smaller lipid-like molecules compensate for defects around the peptide in the membrane, which facilitates the activity of the parent peptide. For the inactive trichogin form, we did not find any pronounced oligomerization and peptide-induced lateral changes. Finally, the trichogin analog with selectivity and activity against cancer cells did not demonstrate any effect in the zwitter-ionic membrane, but caused perturbations in charged membrane.

In sum, the obtained results indicate the correlation between the peptide activity and peptide-induced structural changes in the lipid membrane.

Acknowledgements: the work was supported by the Russian Science Foundation (project No. 21-73-00011).

[1] De Zotti M. et al. (2012). *Amino Acids*, *43*, 1761–1777.
[2] Dalzini et al. (2016). *Sci reports*, *6*, 1–14.

Redox Activity of Quinone-Chelator Q1 and Its Chelate Complexes with Iron Ions in Cancer Cells Media. EPR Study

✉ **Viktor A. Timoshnikov**[1], **Irina A. Slepneva**[1],
Olga A. Chinak[1,2], **Olga Yu. Selyutina**[1], **Nikolay E. Polyakov**[1]

[1] Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2] Institute of Chemical Biology and Fundamental Medicine SB RAS
Novosibirsk, Russia

✉ timoshnikov@kinetics.nsc.ru

Quinones-chelators have been used for a long time for cancer treatment [1; 2]. These drugs have two main anticancer mechanisms of action: inhibition of topoisomerase II; redox activity and generation of reactive oxygen species (ROS), which can disrupt the performance of cells, tissues, and organs [3; 4]. In this work, we studied the effect of the chelator 2-phenyl-4-(butylamino)naphtho[2,3-h] quinoline-7,12-dione (Q1) and its complexes with Fe(III) ions on the generation of ROS in cancer cell cultures. The EPR method with spin traps DEPMPO and CP-H was applied.

The experiments were carried out in HEPES buffer solutions ($pH = 7.4$) with 2 % DMSO of cancer cell cultures: MOLT-4 (suspension), A549, and MDA-MB-231 (adhesive).

Semiquinone radicals Q1 were detected for all cell lines in deoxygenated solutions, which indicates the transmembrane activity of quinone and participation in redox reactions. In addition, incubation of cell cultures with quinone Q1 increased the yield of DEPMPO-superoxide spin adducts. A similar effect was observed upon the incubation of cell cultures with $Fe(NO_3)_3$. In addition, the successive incubation of cultures with quinone and iron salt has shown an additive effect of spin adducts yield. However, upon the incubation with the Q1-Fe(III) complex, the signal level was not higher than in the case of incubation with pure Q1. This phenomenon can be explained by the low transmembrane activity of the complex compared to the ligand. The next stage of our work was to study the effect of Q1 and its Q1-Fe(III) complexes on the yield of the nitroxyl radical of the CP-H trap. It was shown that the addition of quinone and also $Fe(NO_3)_3$ significantly increases the rate of radical generation. The maximum efficiency was observed in the case of A549 cells. It was also found that the rate of radical generation in the case of chelate complexes is lower than in the presence of pure quinone, which also confirms the low transmembrane activity of the Q1-Fe(III) complexes.

Acknowledgements: this work was funded by the grant from the Russian Science Foundation (No. 21-73-10037).

[1] Dikalov S. (1993). *Biochem. Biophys. Res. Commun., 195,* 113–119.
[2] Miura T. (1991). *Pharmacol. Toxicol., 69*, 296–300.

---

^{1}H and ^{19}F NMR Signal Enhancement Enabled by Spin Polarization-Induced NOE and Parahydrogen-Induced RASER

✉ **Ivan A. Trofimov**[1,2], **Oleg G. Salnikov**[1,2], **Andrey N. Pravdivtsev**[3],
Eduard Y. Chekmenev[4], **Igor V. Koptyug**[1]

[1] International Tomography Center SB RAS
Novosibirsk, Russia
[2] Department of Natural Sciences, Novosibirsk State University
Novosibirsk, Russia
[3] University Medical Center Schleswig-Holstein and Kiel University
Kiel, Germany
[4] Wayne State University
Detroit, USA

✉ i.trofimov@tomo.nsc.ru

One of the ways to improve sensitivity of NMR is to create nuclear spin hyperpolarization, i.e., highly non-equilibrium population of nuclear spin states. One of several hyperpolarization techniques is the parahydrogen-induced polarization (PHIP) that allows one to produce hyperpolarized substrates via pairwise addition of parahydrogen molecules to asymmetric unsaturated precursors in high and low magnetic fields (PASADENA and ALTADENA conditions, respectively). It was earlier demonstrated that non-linear interaction of hyperpolarized substrate magnetization with the LC circuit of NMR probe may lead to a long-lasting NMR signal (RASER effect) during the PHIP experiments. Recently, it was discovered that substrate specificity of the PHIP technique may be overcome in PASADENA experiments by parahydrogen and the RASER induced nuclear Overhauser effect (PRINOE)—net hyperpolarization of hyperpolarized molecules may be transferred to other molecules in a solution via cross-relaxation [1].

Here we broaden the scope of the PRINOE approach in multiple directions. While previous demonstration of PRINOE effects relayed in the PASADENA regime, here we show that it can also be performed in the ALTADENA regime (in the field of Earth). Control experiments allowed us to establish the genesis of PRINOE under ALTADENA conditions. Frequency selective saturation of RASER-active resonances was shown to increase the PRINOE efficiency. The screening of target molecules demonstrated the correlation of the observed NMR signal enhancement (*SE*) with T_1 relaxation time. The greatest ^{1}H NMR signal enhancement was observed for furan and chloroform which in average provided $SE = -4.5 \pm 1.0$ for furan and $SE = -3.7 \pm 0.7$ for chloroform. The presented PRINOE technique is not limited to ^{1}H NMR—we show that it can be employed for boosting the NMR signals of heteronuclei, such as ^{19}F. The greatest ^{19}F NMR signal enhancement was observed for 1,1,1,3,3,3-hexafluoroisopropanol that provided maximal $SE = -7.9$.

Acknowledgements: this work was supported by the Council on Grants of the President of the Russian Federation (grant MK-2826.2022.1.3).

[1] Korchak S. et al. (2021). *Angew. Chem. Int. Ed.*, *60*, 20984-20990.

NMR-Based Quantitative Metabolomics of Biological Tissues

✉ **Yuri P. Tsentalovich, Olga A. Snytnikova, Vadim V. Yanshole,
Lyudmila V. Yanshole, Ekaterina A. Zelentsova**

*International Tomography Center SB RAS
Novosibirsk, Russia*

✉ yura@tomo.nsc.ru

A metabolome — a complete set of small-molecular-weight compounds in a tissue — reflects the actual state of tissue and may significantly vary depending on the age, diet and health status. Quantitative metabolomics is probably the most promising and sought-after branch of metabolomics, which is actively developing and integrating into novel applications in biology and medicine. Unlike qualitative (where only the presence of certain metabolites is detected) and semi-quantitative (the ratio of metabolite levels in the "case" and "control" samples is estimated) metabolomics, the quantitative measurements imply the determination of absolute values of metabolite concentrations in a biological tissue (typically, in moles per gram of tissue).

High-field NMR spectroscopy is one of the most suitable tools for quantitative metabolomics, allowing one to determine the concentrations of 50–80 metabolites in a tissue from a single NMR spectrum. In this report, we discuss an optimal workflow of the metabolomic studies, including sample collection, sample preparation, analytical measurements, and post-analytical data treatment. During the last few years, we successfully applied the metabolomic approach to the solution of a wide range of medical and biological tasks: 1) the mechanisms of development of ophthalmological diseases in humans (cataract, keratoconus); 2) the study of pathogenesis of metabolic diseases in model animals (mice, rats); 3) the influence of water temperature, salinity, level of dissolved oxygen, and anthropogenic pollution on fish metabolome; 4) the determination of post-mortem interval for forensic science; 5) the mechanism of animal adaptation for survival under extreme conditions (low temperature, hypoxia); 6) the mechanism of extremely acute eyesight of birds of prey.

Acknowledgments: this work was supported by the Russian Science Foundation (No. 22-23-00021).

Development and Characterization of the Impulse THz Heating Method Using EPR of Magnetoactive Compounds

✉ **Sergey V. Tumanov**[1,2], **Anatoly R. Melnikov**[1,2], **Natalia A. Artiukhova**[1,2], **Artem S. Bogomyakov**[1,2], **Oleg A. Shevchenko**[3], **Yaroslav V. Getmanov**[2,3], **Victor I. Ovcharenko**[1], **Matvey V. Fedin**[1,2], **Sergey L. Veber**[1,2]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia
[3] *Budker Institute of Nuclear Physics SB RAS*
Novosibirsk, Russia

✉ tumanov@tomo.nsc.ru

The possibility of a fast temperature change of the sample in a controllable way makes it possible to study the related phenomena, such as thermally induced trapping of metastable states in magnetoactive compounds or thermally activated catalytic and biological processes. The Electron Paramagnetic Resonance (EPR) spectroscopy station at the Novosibirsk Free Electron Laser (NovoFEL) makes it possible to study the influence of terahertz radiation on the spin state of paramagnetic systems. Changes in the compound temperature due to radiation absorption are inevitable consequences of such exposure. However, the process of sample heating at the NovoFEL EPR station itself is of great interest because of the record-setting power of THz radiation at NovoFEL along with the possibility of using small compound samples. Together these two factors result in a significant heating rate. The magnetoactive complex [$Cu(hfac)_2L^{Et}$] was chosen as a model system for studying the heating process. The advantages of this complex in the scope of the goal are a sharp spin transition and significant differences between the spin states above and below the transition temperature.

In this work, the heating process of [$Cu(hfac)_2L^{Et}$] is studied. We have shown the setup ability for pulsed heating with > 60 K amplitude at the 7.3 K/ms heating rate. The results are promising for further studying of thermally induced metastable states and other thermally activated processes.

Acknowledgements: this work was funded by RFBR (grant No. 20-33-90190).

X-band EPR Spectrometer Based on MW Bridge with 300 W Solid-State Amplifier and AWG Unit

✉ **Sergey L. Veber**[1,2], **Nikolay P. Isaev**[2,3], **Anatoly R. Melnikov**[1–3],
Konstantin A. Lomanovich[2], **Mikhail V. Dugin**[4], **Mikhail Yu. Ivanov**[1,2],
Dmitriy N. Polovyanenko[2], **Michael K. Bowman**[2,5], **Elena G. Bagryanskaya**[2]

[1] *International Tomography Center of SB RAS*
Novosibirsk, Russia
[2] *Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[3] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[4] *Micran*
Tomsk, Russia,
[5] *Department of Chemistry & Biochemistry, University of Alabama*
Tuscaloosa, USA

✉ sergey.veber@tomo.nsc.ru

Technical advances of the modern EPR spectrometers set up the frontiers of the EPR-related methodologies and approaches. Considering the EPR spectrometers of conventional microwave bands, such as X- and Q-, high-power amplifiers, arbitrary wave generators, and fast digitizers are the essential units required for the up-to-date pulse EPR techniques.

Herein we describe a X-band EPR spectrometer constructed in the Magnetic Resonance Laboratory of Biomolecular Systems (NIOCH SB RAS) and featuring all the required equipment to perform state-of-art pulse EPR experiments. Among the general construction of the spectrometer, the scheme of the microwave bridge is considered in details, including a pulse-forming and pulse-monitoring unit and low-noise amplifier with a pulse protection circuit. Modular open source software Atomize (https://github.com/Anatoly1010/Atomize) is used to control the spectrometer including AWG and fast digitizer cards featured high-speed data streaming. The wideband dielectric EPR resonator was developed to fit the requirements for AWG experiments with chirp pulses. The spectrometer is designed to have high dynamic range, low coherent noise, and to capture the direct dimension efficiently. These capabilities were demonstrated for both rectangular and AWG pulse experiments.

Acknowledgements: this work was supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 14.W03.31.0034).

Application of the EPR Method in Studying of the Mn Behavior during the Diagenesis of Lacustrine Carbonate Sediments

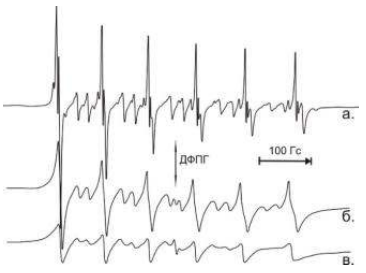
✉ **Yulia S. Vosel**[1], **Sergey S. Vosel**[2,3], **Dmitriy V. Stass**[2,3]

[1] *Sobolev Institute of Geology and Mineralogy SB RAS*
Novosibirsk, Russia
[2] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[3] *Novosibirsk State University*
Novosibirsk, Russia

✉ vosel@igm.nsc.ru

The processes of diagenesis play a significant role in the redistribution of microelements in sediments. Thus, the increase in the uranium and the decrease in the manganese content downwards through the section of organic carbonate sediments are caused by the redox processes involving microorganisms [1]. Manganese of oxide phases, being reduced in the lower layers, migrates with interstitial waters upwards through the section, where it is anew oxidized by oxygen and precipitated.

To determine the amount of oxides and hydroxides of Mn, a sequential leaching scheme is used. The fault of the used scheme is that a large amount of manganese hydroxides is decomposed at the stage of carbonate dissolution [2]. At the same time, this manganese is involved in redox processes. Hence, independent procedures are required, allowing one to separate manganese within the carbonate composition from that in oxide phases. To do this, from the obtained amount of Mn released into solution during leaching, the amount of Mn present in calcite, determined by the EPR method, was subtracted.



EPR spectra of Mn^{2+} in calcite: reference sample *(a)*, sediments of Lake Alyaty *(b)* and Tsagan-Tyrm *(c)*

The spectra of sediments were obtained by means of a Bruker EMX spectrometer in the X-ray spectral region. The view of spectra is typical for Mn^{2+} ions in calcite: six doublets of the hyperfine structure (HFS) of 94 G HFS constant and pairs of lines of forbidden transitions (see Fig) [3]. The amount of Mn^{2+} ions was measured by the integrated intensity of the spectrum determined by double integration of the low field HFS doublet and compared to the intensity of the standard sample.

[1] Klinkhammer G., Palmer M. (1991). *Geochim. Cosmochim. Acta*, *55*, 1799–1806.

[2] Fedotov P., Spivakov B. (2008). *Rus. Chem. Rev.*, *77*(7), 649.

[3] Vlasova M., Kakazei N. (1979). *Electron Spin Resonance in Mechanically Destroyed Solids.* Naukova Dumka, Kiev. (in Russ.)

Electron Spin Resonance *In Situ* Study of Ni Catalyst in Catalytic Transfer Hydrogenation Reaction Conditions

✉ **Stanislav. S. Yakushkin, Irina T. Kandarakova,**
Nikolay S. Nesterov, Alexey A. Philippov, Oleg N. Martyanov

Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia

✉ stas-yk@catalysis.ru

Ni catalysts are widely used in chemical industry in hydrogenation and other processes. [1]. One of the promising replacement for molecular hydrogen for these processes are formic acid and lower alcohols [2], with the type of reactions known as catalytic transfer hydrogenation (CTH). Heterogeneous Ni catalysts are known to be active in CTH [3]. In the Boreskov Institute of Catalysis a novel method of synthesizing high-load Ni-containing catalytic systems using the supercritical antisolvent (SAS) method [4] was proposed.

Interaction between heterogeneous catalysts' surface and a reaction media can be considered the most important subject to study for modern catalysis. Many industrial catalytic processes, including CTH, proceed at high temperature and pressure, under supercritical conditions. To study the catalyst in these conditions it is important to apply phisico-chemical methods *in situ*, as the properties of the catalyst and the reaction media may change significantly at elevated temperature and pressure.

Electron spin resonance (ESR) is a unique tool to study not only paramagnetic species, but also strongly coupled systems, ferromagnetic particles, clusters, which provides for carrying out experiments in a wide range of temperatures and pressures. Earlier in the Boreskov Institute of Catalysis ESR was used to detect supercritical water local dynamic using vanadyl as a spin probe [5] for the first time.

In this work ESR was applied *in situ* to study Ni catalysts under the conditions of CTH reaction. It was shown the partial reduction of nickel oxide on the surface of metallic nanoparticles takes place in the presence of supercritical 2-propanol.

Acknowledgements: the research was supported by the Russian Science Foundation (project No. 21-73-00244 https://rscf.ru/en/project/21-73-00244/).

[1] Jalama K. (2017). *Catal. Rev. - Sci. Eng., 59*, 95–164.

[2] Gilkey M. J., Xu B. (2016). *ACS Catal., 6,* 1420–1436.

[3] Philippov A. A. et al. (2019). *Catal. Today*, 0–1.

[4] Nesterov N. S., Paharukova V. P., Yakovlev V. A., Martyanov O. N. (2016). *J. Supercrit. Fluids, 112*, 119–127.

[5] Trukhan S. N., Yudanov V. F., Martyanov O. N. (2011). *J. Supercrit. Fluids, 57*, 247–250.

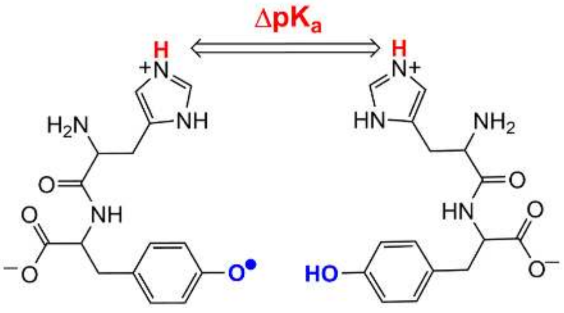
Kinetic Evidence for the Transiently Shifted Acidity Constant of Histidine Linked to Paramagnetic Tyrosine Probed by Intramolecular Electron Transfer in Oxidized Peptides

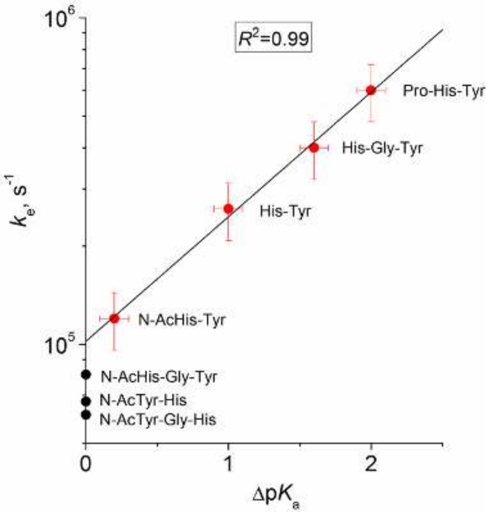
Olga B. Morozova[1], **D. V. Stass**[1,2], ✉ **Alexandra V. Yurkovskaya**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Institutte of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia

✉ yurk@tomo.nsc.ru

As a model for chemical DNA repair the reduction of thymine radicals in their reaction with aromatic amino acids has been studied by the time-resolved chemically induced dynamic nuclear polarization (CIDNP) technique. The kinetics of electron transfer (ET) from tyrosine (Tyr) to short-lived histidine (His) radicals in peptides of different structures was monitored using time-resolved chemically induced dynamic nuclear polarization (CIDNP) to follow the reduction of the His radicals using NMR detection of the diamagnetic hyperpolarized reaction products. In aqueous solution over a wide pH range, His radicals were generated *in situ* in the photo-induced reaction with the photosensitizer, 3,30,4,40-tetracarboxy benzophenone. Model simulations of the CIDNP kinetics provided pH-dependent rate constants of intra- and intermolecular ET, and pH dependencies of the reaction under study were interpreted in terms of protonation states of the reactants and the product, His with either protonated or neutral imidazole. In some cases, the increase of pKa of imidazole in the presence of a short-lived radical center at a nearby Tyr residue was revealed. Interpretation of the obtained pH dependencies made is possible to quantify the degree of paramagnetic shift of the acidity constant of the imidazole of the His residue in the peptides with a Tyr residue in its paramagnetic state, and to correlate this degree with the intramolecular ET rate constant — a higher intramolecular ET rate constant corresponded to a greater acidity constant shift.





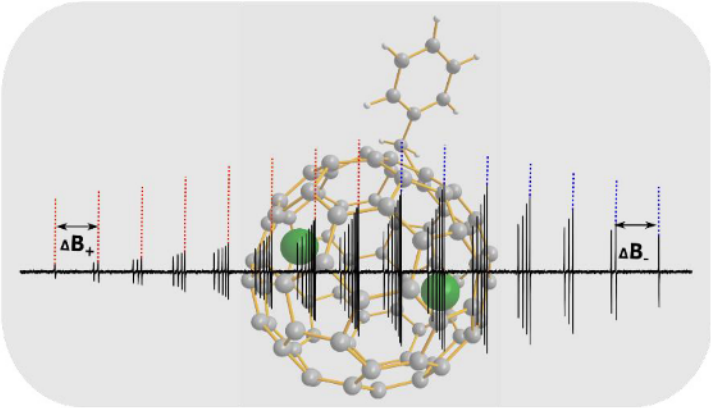
Endohedral Fullerene $Sc_2@C_{80}(CH_2Ph)$ as a Standard Sample for Field Calibration

✉ **Ruslan B. Zaripov**, **Yuri E. Kandrashkin**

Zavoisky Physical Technical Institute, FRC Kazan Scientific Center RAS
Kazan Russia

✉ rb.zaripov@knc.ru

Endohedral fullerenes $Sc_2@C_{80}(CH_2Ph)$ have unique spectral characteristics due to the large hyperfine interaction (509 MHz) of a delocalized electron (S = 1/2) with two equivalent ^{45}Sc nuclei (I = 7/2) [1; 2]. The EPR spectrum consists of 64 well-resolved lines divided into 15 groups depending on the projection of the total spin of the scandium nuclei. The total EPR spectrum width is of about 0.25 Tesla. In this regard, we show that this sample can be used as a standard for magnetic field calibration. In the EPR spectrum of endofullerene, each group has a reference line with the maximum possible total nuclear spin located on the right edge of the group. It is shown that these reference lines are equidistant in the regions of the spectrum with low and strong fields and, therefore, can serve as a reference for calibrating the magnetic field. The calibration procedure is tested by using the Q-band EPR. The results showed high accuracy of the procedure for correcting linear and nonlinear displacements of the magnetic field.



Q-band EPR spectra recorded at liquid solution. The dotted lines show the reference lines. Also different splitting (ΔB_{-}) between these lines for the right and left parts of the spectrum are indicated

Acknowledgements: the research was supported financially by RSF (project No. 22-43-04424).

[1] Zaripov R. B., Kandrashkin Yu. E., Salikhov K. M., Büchner B., Liu F., Rosenkranz M., Popov A. A., Kataev V. (2020). *Nanoscale*, *12*, 20513.

[2] Kandrashkin Yu. E., Zaripov R. B., Liu F., Büchner B., Kataev V., Popov A. A. (2021). *Physical Chemistry Chemical Physics*, *23*, 18206.

Field Dependence of ^{1}H Optical Nuclear Polarization in Organic Molecular Crystal Powder: Experiments and Modeling

✉ **Ivan V. Zhukov**[1], **Alexey S. Kiryutin**[1], **Hans-Martin Vieth**[1,2],
Jörg Matysik[3], **Alexandra V. Yurkovskaya**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Fachbereich Physik, Freie Universität Berlin*
Berlin, Germany
[3] *Institut für Analytische Chemie, University of Leipzig*
Leipzig, Germany

✉ i.zhukov@tomo.nsc.ru

Optical nuclear polarization (ONP) is the effect of nuclear spin hyperpolarization build up as a result of the optical cycle “excitation-relaxation” of a dye molecule incorporated in a host molecular crystal structure. To show ONP, the optical cycle of a dye molecule must proceed through an optically excited triplet state $|T_1>$ characterized by the strong non-equilibrium populations of the electron spin sublevels $|T_{1X}>$, $|T_{1Y}>$, $|T_{1Z}>$, i.e., the optical electron polarization (OEP) defined with respect to the molecular-fixed frame [1]. The electron spin sublevels of the excited triplet state are coupled to local nuclear spins through hyperfine interaction (HFI) which transfers part of this strong non-equilibrium electron spin order to the local nuclear spins. The transfer might be either coherent (which is especially pronounced in the level avoided crossing (LAC) region) [1], i.e., mediated by the static HFI of a local magnetic nucleus with the excited tripled state of a trapped dye molecule, or incoherent [2], i.e., mediated by the time-dependent HFI of a local magnetic nucleus with mobile triplet excitons. Recently, a complete theoretical approach has been developed, which is focused on description of the static ONP field dependence in terms of level crossing and level avoided crossings [3].

Previously, ONP studies were preferably done using single crystals, allowing one to investigate in detail the LAC-ONP field and orientation effects. These investigations impose quite strict requirements on the experimental setup and on the quality of crystals used, and are challenging to implement. On the other hand, ONP studies on powder samples are relatively simple to implement, both in static and MAS conditions. However, to extract quantitative data on the properties of the system under study, a challenging numerical modeling should be exploited. The results of experiments and numerical modeling of on ^{1}H ONP field dependence studies are to be presented.

Acknowledgements: the reported study was funded by the RFBR and DFG, project No. 21-53-12023.

[1] Stehlik D., Doehring A., Colpa J. P., Callaghan E., Kesmarky S. (1957). *Chemical physics*, *7*, 165–186.

[2] Allgeier J., Macho V., Stehlik D., Vieth H.-M., Auch W., von Schuetz J. U. (1982). *Chemical Physics Letters*, *86*, 522–527.

[3] Sosnovsky D. V., Ivanov K. L. (2018). *Molecular Physics*, *19*, 2740–2755.

MOLECULAR DYNAMICS

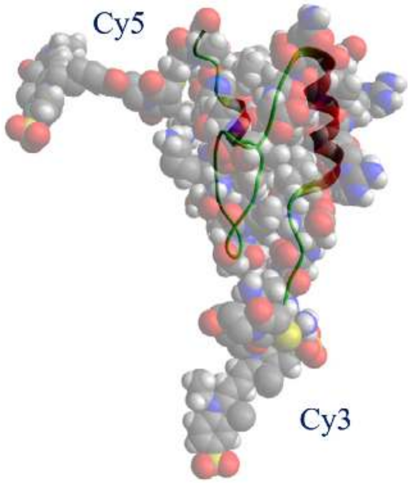
Modeling of FRET-Experiments on Protein Folding

✉ **Vladimir A. Andryushchenko,** **Sergei F. Chekmarev**

Kutateladze Institute of Thermophysics SB RAS
Novosibirsk, Russia

✉ vladimir.andryushchenko@gmail.com

A key question in the application of the Förster resonance energy transfer (FRET) to studying protein folding is how dyes can affect the process of folding. Understanding of these effects is particularly important for small proteins, for which dyes can be comparable in size with the protein. Moreover, the FRET experiment requires a support from simulations in order to interpret the results of measurements.



In this work, we modeled FRET experiments on folding of the BBL domain, the protein that consists of 45 amino acid residues [1; 2]. The FRET protein construct is a system that is presented by the protein and two dyes Cy3- and Cy-5 maleimides at the protein termini, as it is in the experiment and as shown in Figure. This study was conducted by the molecular dynamics simulation (MD)—the protein and dyes were described at atomic level of resolution, an explicit solvent was used, and a brute-force modeling of folding trajectories from an extended state of the protein was performed. The protein and 25,000 water molecules (TIP3P) modeling the solvent were placed in a cube with a 95 A edge and periodic boundary conditions. The simulations were performed by the MD method in the framework of the CHARMM program [3].

It was found that at T = 280 K, T = 300 K and T = 350 K the native states of the protein and the FRET-construct are stable. Fifteen MD folding trajectories for both the protein and FRET-construct were generated for each temperature. It has been found that the presence of dyes does not change the overall picture of folding except that the FRET-construct folds considerably slower than the original protein. It also means that the folding kinetics of the FRET-construct remain to be two-state single-exponential kinetics which are observed for the original protein. The FRET-efficiency histograms constructed on the basis of simulated MD-trajectories have a tendency to converge and are found in agreement with the experimental histograms. In addition, the influence of dyes on the structure of solvent molecules near the protein, as well as on the corresponding charge distribution, was studied.

[1] Huang F. et al. (2009). *Proc. Natl. Acad. Sci.*, *106,* 16239–16244.
[2] Liu J. et al. (2012). *Proc. Natl. Acad. Sci.*, *109,* 179–184.
[3] Brooks B. R. et al. (2009). *J. Comput. Chem.*, *30,* 1545–1614.

Volumetric Properties of Binary Mixtures of Carbon Tetrachloride with Tert-Butyl Alcohol: A Molecular Dynamics Simulation Study

✉ **Alexey V. Anikeenko**[1], **Nikolai N. Medvedev**[1,2]

[1] Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2] Novosibirsk State University
Novosibirsk, Russia

✉ anik@kinetics.nsc.ru

Carbon tetrachloride (CCl_4) is a typical non-polar solvent. *tert*-Butyl alcohol (TBA) is of great interest because of its anomalous properties at small concentrations in water. The nature of those anomalies is elusive and they are usually related with the hydrogen bond network of water. In this work, we compare volumetric properties of TBA in water and in CCl_4 where no solvent-specific structure exists.

We prepared molecular dynamics models of CCl_4–TBA mixtures in the whole range of TBA mole fractions, from 0.0 to 1.0, at 300 K and 1 bar. The total number of molecules in the models was 10,000. To better reproduce experimental excess molar volume and excess molar enthalpy of the CCl_4-TBA mixture we made a slight modification of the OPLS interatomic potentials. A small variation of Lennard—Jones cross-interaction of the H-atoms of CH_3 groups with the chlorine atoms markedly improved the agreement with the experimental data.

The behavior of the apparent volume of TBA in a CCl_4 solution is calculated. Its rapid decrease in the mole fraction range from 0 to 0.1 is observed, followed by a slower linear decline to the value in pure alcohol. The Voronoi molar volumes of both components are calculated, which are proper (real geometric) volumes related to the components of the solution [1]. It turned out that the Voronoi molar volume of TBA rapidly falls in the interval up to 0.1 and then decreases linearly to the value in pure alcohol. A similar behavior of the calculated volumes was also observed for aqueous solutions of TBA [1]. However, the volume of CCl_4 varies almost linearly, which is somewhat different from the behavior of water in water-alcohol solutions. It is discussed that some similarity of the properties of TBA in water and CCl_4 solutions is related with a noticeable association of TBA molecules at low concentrations. However, the driving force for association is different. Small clusters of TBA in CCl_4 are stabilized by alcohol-alcohol hydrogen bonds. In water, the TBA clusters are larger and they are determined by the hydrophobic effects.

Acknowledgements: the work was financially supported by the RSF grant (No. 22-23-00620).

[1] Kadtsyn E. D., Nichiporenko V. A., Medvedev N. N. (2022). *Journal of Molecular Liquids*, *349*, 118173.

Sedimentation of Soot Particles in Dark and under Illumination in a Rarified Gas Medium

✉ **Alexander A. Cheremisin**[1], **Andrey V. Kushnarenko**[1,2]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia,
[2] *Institute of Space and Information Technologies, Siberian Federal University*
Krasnoyarsk, Russia,

✉ aacheremisin@gmail.com

The study of sedimentation of aerosol particles is important for understanding and predicting many industrial and natural processes. But simulating the motion of particles with complex shape and surface temperature different from the temperature of the gas medium is a significant problem. This is the case of photophoresis.

This report presents the results of a computational experiment to study the influence of the fractal dimension of soot aerosol clusters on their sedimentation in a rarefied gas medium under illumination and without it. Illumination significantly changes the behavior of particles because of the gravito-photophoretic force arising. The latter has a gas-kinetic nature and is caused by absorption of the radiation energy fluxes of infrared and visible ranges by cluster.

The experiment is based on the application of the previously developed Monte Carlo method [1] to solve the problem of heat and mass transfer for particles of complex shape and aerosol clusters in the approximation of the free molecular regime. The algrithm solves the non-linear problem of heat and mass transfer and estimates the force effect on the cluster from the rarefied gas medium — the photophoretic force, its moment and four tensors for the calculation of the viscous friction force and its moment. Then the equations of translational-rotational motion of the aerosol cluster are integrated.

The experiment was carried out on the ensembles of clusters of different fractal dimensions. It is shown that there is a significant influence of illumination on the nature of sedimentation of soot aerosol clusters which absorb light well. In the case of clusters containing the same number of particles and having the same fractal dimension, the rate of their sedimentation in the absence of illumination is close to each other. The experiment demonstrates that there is a relationship between the cluster velocity and its fractal dimension. Under illumination, due to the influence of the photophoretic force, a significant spread of velocities in the cluster ensemble is observed. Moreover, some of the clusters even begin to move upwards, against gravity.

[1] Cheremisin A. A. (2010). Transfer Matrices and Solution of the Heat-Mass Transfer Problem for Aerosol Clusters in a Rarefied Gas Medium by the Monte Carlo Method. *Russian Journal of Numerical Analysis and Mathematical Modelling*, *25*(3), 209–233.

Motion of He, Ne, and Ar Atoms and HF Molecules inside the C_{60} Cage

✉ **Alexey I. Chichinin**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ chichinin@kinetics.nsc.ru

Much of this work was stimulated by the discussion on the quantized rotation and ortho–para conversion of single water molecules permanently entrapped inside closed fullerene C_{60} cages (see experimental and theoretical studies [1–4] and references therein). Of particular interest is, firstly, the observed splitting of the ground state of ortho-H_2O raising the three-fold degeneracy into two states with degeneracy 2 and 1 [1] and, secondly, the enrichment of para water at low temperatures due to conversion of the fullerene-encapsulated para water to ortho water [2].

In the present study, we try to attribute both effects to interaction between the "vibrational" and rotational motions of water. *Ab initio* calculations of He, Ne, Ar, HF, and H_2O molecules entrapped inside C_{60} cage are reported. We choose not only the water molecule, but molecules with different masses and rotational degrees of freedom. The program Orca was used on the B3LYP D3BJ TZV def2/J level of theory. The "vibrational" energies of three noble atoms inside C60 are represented in the table below, they are characterised by quantum numbers *n* and *L*, as in hydrogen atom. The energies are given in cm^{-1}, they are calculated by using both WKB (Wentzel—Kramers—Brillouin) approximation and the direct solution of the radial part of the Schrödinger equation.

	He + C_{60}			**Ne + C_{60}**			**Ar + C_{60}**		
n	$L = 0$	$L = 1$	$L = 2$	$L = 0$	$L = 1$	$L = 2$	$L = 0$	$L = 1$	$L = 2$
1	204,0			130,9			257,5		
2	461,2	588,3		304,8	440,5		599,6	770,1	
3	715,6	846,8	981,3	478,9	615,2	741,4	940,3	1110,0	1279,3
4	982,6	1122,8	1267,0	654,3	792,0	919,8	1279,8	1448,8	1617,3

The Ne + C_{60} system has almost the same reduced mass as $H_2O + C_{60}$, hence, their "vibrational" energies should be similar. The movement of HF and H_2O molecules inside C_{60} was analysed similarly. In the model of "quick rotation" the movement in the case of HF changes from the two-dimensional vibrational oscillator (when F atom is close to the wall of the cage) to the free rotation (when F atom is close to the centre of gravity). A more realistic model, in which H atom rotates with a speed comparable with the speed of F atom, permit rather small range of spherical θ angles for the rotation of H atom. Hence, it was found that the fullerene cage shifts the rotation levels of the two molecules, in moderate agreement with the experiment.

[1] Goh K. S. K. et al. (2014). *PCCP*, *16*, 21330.
[2] Meier B. et al. (2018). *Phys. Rev. Lett.*, *120*, 266001.
[3] Mamone S. et al., *J. Chem. Phys.*, *140*, 194306.
[4] Beduz C. et al. (2012). *Proc. Natl. Acad. Sci. USA*, *109*(32), 12894.

Germanium Nanowires Layer Formed by Ion Implantation and Incoherent-Light Pulse Annealing

✉ **Bulat F. Farrakhov**[1], **Andrei L. Stepanov**[2], **Yakhya V. Fattakhov**[1],
Dmitry A. Konovalov[2], **Vladimir I. Nuzhdin**[2], **Valery F. Valeev**[2]

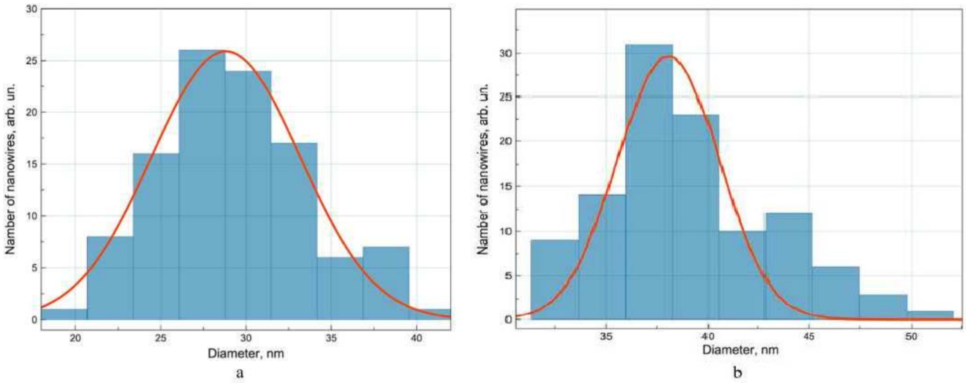
[1] *Laboratory of Medical Physics, Zavoisky Physical-Technical Institute*
FCR Kazan Scientific Center RAS
Kazan, Russia
[2] *Group of Nanooptics and Nanoplasmonics, Zavoisky Physical-Technical Institute*
FCR Kazan Scientific Center RAS
Kazan, Russia

✉ bulat_f@mail.ru

The study addresses the monocrystalline c-Ge substrates implanted by Ag^+ ions with the energy of 30 keV, irradiation dose of 7.5×10^{16} ion/cm^2, and annealed by incoherent-light pulse. By scanning electron microscopy and optical spectroscopy measurements, it was shown that after ion implantation an amorphous porous Ag:PGe layer of a spongy structure with nanowires on the c-Ge substrate were formed. The spongy pulse light annealed structure of the Ag:PGe layer was not destroyed, however, the diameters of nanowires increased by about 1.5 times.

Monocrystalline 150 μm thick c-Ge (100) n-type plates were selected as substrates [1]. The implanted Ag:PGe samples were annealed in air by ILP by special Impuls-6 equipment with halogen lamps located in a sealed reaction chamber as heating elements. Annealing of implanted Ge was performed with one light pulse, duration 5 s. The power density of the light pulse was 30 W/cm^2. The surface sample temperature was measured to be ca. 600 °C.

The surface morphology of the Ag:PGe samples was studied using Merlin (Carl Zeiss) scanning electron microscope (SEM). Optical reflection spectra were measured by the AvaSpec-2048 spectrometer (Avantes). Figure shows histograms of the nanowire.



a

b

Histograms of the nanowire diameters for the c-Ge implanted by Ag^+ ions at E = 30 keV, J = 8 mkA/cm^2, $D = 7.5 \times 10^{16}$ ion/cm^2 *(a)* and the same implanted sample treated by ILP annealing *(b)*

[1] Stepanov A. L., Farrakhov B. F., Fattakhov Ya. V. et. al. (2021). *Vacuum*, *186*, 110060.

The Voronoi Analysis of Solutions Volumetric Properties

✉ **Evgenii D. Kadtsyn**, **Vladislav A. Nichiporenko**

Novosibirsk State University
Novosibirsk, Russia
Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ e.kadtsyn@g.nsu.ru

Volumetric properties are thermodynamic properties calculated from system density, like partial molar volume. They are often used in solution chemistry to investigate solution structure. Their concentration behavior and its possible features can shed light on molecular processes occurring in a solution. On the other hand, volumetric properties are thermodynamic characteristics which have no direct geometrical sense (except the total system volume). That makes their structural interpretation rather speculative. To draw structural conclusions, a relation between volumetric properties and microscopic molecular volumes is highly desirable.

In our previous works, such relations were derived. We introduced the concept of the component Voronoi molar volume, which is the mean value of the Voronoi volume of component molecules in a solution. We expressed solution volumetric properties via the Voronoi molar volumes of components. Our expressions allowed us to analyze volumetric properties from molecular volumes' point of view. It is possible to consider solute and solvent contributions to properties separately and search for reasons of appearance of the features such as partial volume minima.

In the present work, our approach was expanded to aqueous alcohol solutions. Molecular dynamics models of methanol, ethanol, and 1- and 2-propanols were obtained, and the Voronoi tessellation was performed. The Voronoi molar volumes of components were shown to decrease over the whole studied concentration range. Partial molar volumes of alcohols' were evaluated, and all of them have a minimum at small concentrations. The analysis of separate contributions revealed their reason connected with the finishing of water volume decrease.

Acknowledgements: the work is financially supported by the RSF grant No. 22-23-00620.

[1] Kadtsyn E. D., Nichiporenko V. A., Medvedev N. N.(2022.) *J. Mol. Liq.*, *349*, 118173.

[2] Kadtsyn E. D., Nichiporenko V. A., Medvedev N. N. (2021). *Journal of Structural Chemistry*, *62*(1), 61–72. (in Russ.)

Molecular Dynamics Study of the Anticancer Drug Dioxadet Transfer Across the Lipid Membrane DOPC

✉ **Alexandra V. Kim**, **Elena A. Yakush**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉ kim@kinetics.nsc.ru

Dioxadet is a drug used in chemotherapy for abdominal cancer, it was developed at the Petrov Research Institute of Oncology, St Petersburg. To identify the mechanism of dioxadet transport across the cell membrane we performed a molecular dynamic simulation with free energy and permeability calculations.

During the previous step of the study we created several models of dioxadet and showed that dioxadet readily dissolves in water and forms associates. In this study, we used the model with a DOPC lipid bilayer as a membrane. The Gibbs free energy profile at different temperatures of 300, 305 and 310 K was calculated to estimate its permeability. Since the ΔG sign in the membrane is negative, dioxadet prefers to be inside the membrane. In the middle of the membrane, in the gap between the lipid tails, there is a small energy barrier which height increases with increasing temperature. The enthalpy and entropy contribution profiles to the free energy say that the system loses in entropy, but gains in enthalpy when the drug is transferred to the membrane. Large enthalpy is caused by large partial charges on the atoms of the aromatic ring of dioxadet, which interact with polar heads of the lipids. The diffusion coefficient profile and resistivity profile were also calculated, see our similar calculations for other molecules in [1; 2]. It is shown that when a dioxadet molecule passively diffuses across the membrane, its near-surface region offers the greatest resistance. The barrier in the central non-polar region practically does not play any role. The membrane permeability for dioxadet was found to be $P = (0.6 \pm 0.1)\cdot 10^{-3}$ cm/s at $T = 300$ K. When a second dioxadet molecule is added to the membrane, its permeability becomes almost doubled due to a decrease in the resistance of the bilayer surface.

[1] Kim A. V., Shelepova E. A., Selyutina O. Yu., Meteleva E. S., Dushkin A. V., Medvedev N. N., Polyakov N. E., Lyakhov N. Z. (2019). *Molecular Pharmaceutics*, *16*(7), 3188–3198.

[2] Kim A. V., Shelepova E. A., Evseenko V. I., Dushkin A. V., Medvedev N. N., Polyakov N. E. (2021)., *Journal of Molecular Liquids*, *344*, 117759.

Molecular Dynamics, Molecular Mechanics and DFT Modeling of the Conformational Properties of Spin-Labeled Chitosan in Water

✉ **Victor B. Luzhkov**[1,2], **Vladimir B. Krapivin**[1]

[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia
[2] *Lomonosov Moscow State University*
Moscow, Russia

✉ vbl@icp.ac.ru

The modification of polysaccharide chitosan by stable nitroxide radicals provides biomaterial possessing many useful biological properties [1]. In this report, we considered conformational dynamics of a spin-labeled chitosan in water which has been systematically explored using the microscopic force-field (FF) molecular dynamics (MD) simulations, FF molecular mechanics, and density functional theory (DFT) calculations with implicit water model [2]. The low-molecular-weight chitosan oligomers of 2–6 D-glucosamine (GA) subunits, and two stable nitroxide radicals – 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO) and 2,2,5,5-tetramethylpyrroline-1-oxide [1] were considered.

Eight conformers in total for rotation about the β(1→4) glycosidic bond were found for the GA—GA dimer from the MM-FF and DFT calculations. Populations of the conformers were accessed from the MD simulations at $T = 300$ K in the periodic box with explicit TIP3P water molecules. The bent structures with the shape of left and right helix with a small helix pitch were formed upon the elongation of chitosan chain. The gas phase calculations predict greater stability of the bent conformations, whereas the calculations with inclusion of solute-solvent interactions give a linear structure of polysaccharide in water. The found activation barriers for rotations around the glycosidic bond show that transitions between the bent structures only occur via the linear conformation of chitosan. This was supported by 50-ns MD simulations of chitosan hexamers. The free energies of transition states ~26–28 kJ mol^{-1} from the DFT results agree with the lifetimes of chitosan conformers in the MD simulations. According to the MD calculations, the nitroxide substituents do not form intra-molecular hydrogen bonds with saccharide rings in water. Nitroxide moieties enhance the variety of visited conformational states of neutral and protonated monosubstituted chitosan chains, but the linear conformation remains most populated. Overall, the polar environment has strong influence on the stability of chitosan rotamers.

[1] Sen' V. D., Sokolova E. M., Neshev N. I., Kulikov A. V., Pliss E. M. (2017). *React. Funct. Polym.*, *53*, 111–118.

[2] Krapivin V. B., Luzhkov V. B. (2021). *Russ. Chem. Bulletin, International Edition, 70*, 1523–1532.

The Structure of Ionic Liquids in Terms of Intermolecular Voids

✉ **Nikolai N. Medvedev**[1], **Ekaterina A. Shelepova**[1,2]

[1] Voevodsky Institute of Chemical Kinetics and Combustion, SB RAS
Novosibirsk, Russia
[2] Novosibirsk State University
Novosibirsk, Russia

✉ nikmed@kinetics.nsc.ru

The all-atom and coarse-grained MD models of a number of ionic liquids (ILs) are studied. The modern MD models make it possible to reliably reproduce the existing experimental data. However, the main value of MD modeling is that it gives the coordinates of the atoms of the simulated system, which makes it possible to study the structural features of solutions which cannot be extracted from the experiment. In our work, special attention is paid to the analysis of intermolecular voids. The Voronoi—Delaunay method is used with the help of which it is possible to calculate the empty volumes related to different components of the system: anions, cations (separately to their heads and alkyl tails) and dissolved gas molecules, as well as to select and estimate the sizes of real interatomic voids. The distributions of radii of the interstitial spheres are studied, separately for the entire ionic liquid and for its components with charges of different signs. A conclusion about specific spatial correlations of anions and cations is made [1]. For comparison, we obtained models of the same mixtures at the same density, but without charges on the molecules. A significant difference in the mutual arrangement of molecules corresponding to anions and cations is shown. It turns out that for the system considered as a whole, the interatomic voids are the same for the ionic liquid and its neutral analog. This means that spatial distribution of molecules is determined mainly by the impermeability of atoms, while electrostatic interactions dictate only the features of mutual arrangement of components within a given spatial distribution [2]. The models of ILs with gas molecules dissolved in them were calculated and studied [3]. The empty volumes related to different components of ionic liquids were found; it was shown that the regions of alkyl substituents are the loosest. It was also shown that gas molecules contribute an additional empty volume that is localized exclusively in their nearest environment.

Acknowledgements: the research was financially supported by the RFBR grant No. 20-33-90144.

[1] Shelepova E. A., Paschek D., Ludwig R., Medvedev N. N. (2020). *J.Mol.Liq.*, *299*, 112121.
[2] Shelepova E. A., Paschek D., Ludwig R., Medvedev N. N. (2021). *J.Mol.Liq.*, *329*, 115589.
[3] Shelepova E. A., Medvedev N. N. (2022). *J. Mol. Liq.*, *349*, 118127.

Concentration-Dependent Charge Scaling as a Simple Method of Force Field Correction in MD Simulation of Aqueous Alcohol Solutions

✉ **Vladislav A. Nichiporenko**, **Evgeniy D. Kadtsyn**

Novosibirsk State University
Novosibirsk, Russia
Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ v.nichiporenko@g.nsu.ru

In molecular dynamics investigations, the choice of a force field is the main problem. The modern force fields are good enough to reproduce physical properties of a wide range of substances with rather high accuracy. However, this accuracy is not enough for structure investigations, especially in working with mixtures. In this case, either more resource-intensive methods or force field correction are required.

Alcohol-water solutions are an example of such case where the use of standard force fields gives insufficient accuracy to predict properties. The polarity of such solutions is known to change dramatically with the concentration increase. In standard MD simulations, however, all molecular parameters, including atomic charges, have to be fixed. We suggest a simple method of force field correction to eliminate this problem — a concentration-dependent charge scaling with linear concentration variation of scaling factor. To simplify the method we scale charges for alcohol molecules only. We have shown that even our simplest form of force field correction allows us to obtain models with much higher accuracy of properties' predictions than when using standard force fields. The method was constructed to reproduce the concentration behavior of density, but it was shown to reproduce such fine volumetric characteristics as alcohol partial molar volume, as well as other characteristics, e.g., dielectric permittivity, excess enthalpy, and even chemical potentials.

Acknowledgements: the work was financially supported by the RSF grant No. 22-23-00620.

Probing the Structural Mobility of UiO-66 (Zr) MOF in the Presence of Guest Molecules by Means of ^{2}H NMR Spectroscopy

✉ **Mikhail S. Plekhanov**, **Alexander E. Khudozhitkov**, **Daniil I. Kolokolov**

Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉ m.plekhanov@g.nsu.ru

Metal-organic frameworks (MOFs) are actively studied compounds consisting of metal clusters connected to each other by organic linkers to form ordered porous structures. These compounds have many promising applications, such as catalysis, adsorption, separation of mixtures of hydrocarbons, and drug delivery.

UiO-66 (Zr) is one of the most promising MOFs due to its outstanding chemical and thermal stability. UiO-66 (Zr) consists of zirconium clusters connected by 1,4-benzodicarboxylic acid struts which build up a 3D porous network formed by tetrahedral (effective diameter d = 8 Å) and octahedral (d = 11 Å) cages interconnected by narrow windows ($d \sim 6$ Å). Notably, the rotational mobility of terephthalic linkers can change the size of a window affecting a diffusion of guest molecules through the framework and altering the MOF functional properties.

Depending on the activation conditions UiO-66 (Zr) can exist in two forms: hydroxylated and dehydroxylated. Recently, it has been shown that dehydroxylated form exhibits a high selectivity for butane isomers separation (D_n/D_{iso} = 1,000). However, mechanism of this phenomenon remains unclear. One possible explanation is that the diffusion rate is determined by the rotational dynamics of linkers, which can depend on both the form of the framework and adsorbed molecules.

In this work we have investigated this possibility by probing the UiO-66 (Zr) linkers' mobility depending on the type of the adsorbed guest molecules (*n*-butane or isobutane) and the form of the inorganic node (hydroxylated or dehydroxylated). The linkers' mobility was studied by solid state ^{2}H NMR using a UiO-66 (Zr) variant with deuterated linkers. Numerical analysis of the experimental ^{2}H NMR spectra line shapes measured at different temperatures yielded the temperature dependence of the linkers' rotation rates for all samples. These dependencies were used to show the effects of guest molecules and hydroxylation state on the structural mobility of framework.

In the results it is shown that rotational dynamics depend both on the form of the framework and the type of guest molecules. Energy barrier for linker rotation in the presence of *n*-butane is shown to be greater than for isobutane by 5 kJ/mol. It is shown that energy barrier in dehydroxylated form is greater than in hydroxylated by 11 kJ/mol for both kinds of guest molecules. Besides, we observed a phenomenon of spatial coordination of guest molecules in the pores of framework.

On the Reason for the Increased Solubility of CO_2 in [C_nMIM][NTf_2] Ionic Liquids.

Ekaterina A. Shelepova, ✉ **Nikolay N. Medvedev**

Novosibirsk State University
Novosibirsk, Russia
Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ nikmed@kinetics.nsc.ru

Ionic liquids (ILs) have many unique properties, which explain the increased interest of researchers. In particular, one of these properties is the selectivity of carbon dioxide dissolution: it dissolves in ILs much better than N_2, CH_4, and O_2. The literature data shows that high solubility of CO_2 in ILs has entropic rather than enthalpic nature; i.e., it is related to the structure of the solution. The solubility of gases, in particular CO_2, in ILs is often connected with the intermolecular empty volume. In this work, we study the structure and intermolecular voids in the CO_2, O_2, N_2, and CH_4 solutions in [C_nMIM][NTf_2] ILs based on molecular dynamic simulations.

We calculated the radial distribution functions between the dissolved gas molecules and various components of the ILs. It was shown that CO_2 molecules prefer to be located mainly near anions, and there are fewer of them near the imidazole ring than near the alkyl chains of cations. Other gases are located near the non-polar alkyl chains, which is especially noticeable in ILs with long alkyl substituents. For all investigated gases it is shown that the additional empty volume appears near the dissolved gas molecule. Thus, all considered gases locally loosen the ILs. At the same time, CO_2 creates a noticeably smaller amount of the additional empty volume compared to other studied gases which are less soluble in the investigated ILs. It can be assumed that the dissolution of these gases requires larger energies to form a cavity where the gas molecule is placed, which leads to their lower solubility. Apparently, this is the reason for various solubility of these gases.

Acknowledgements: the study was funded by RFBR according to the research project No. 20-33-90144

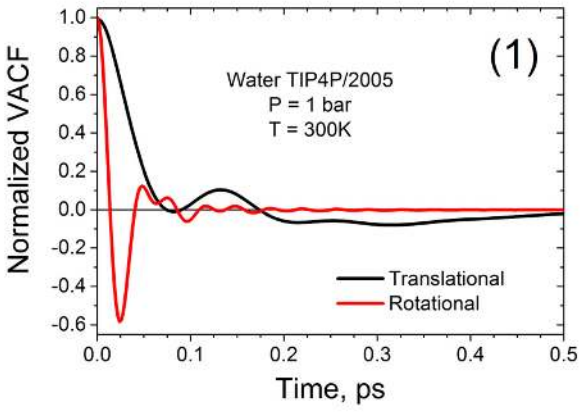
Autocorrelation Functions of Translational and Rotational Velocities of Water Molecules and Their Spectra in Computer Models

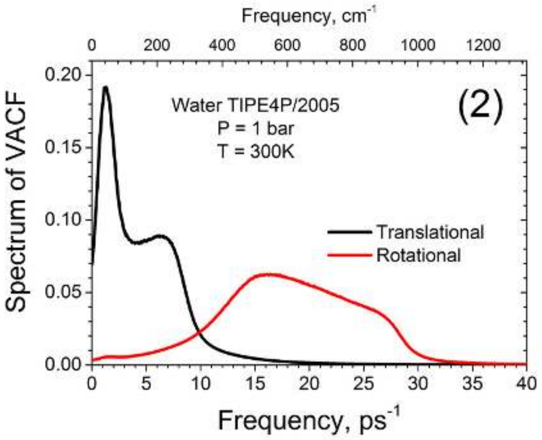
✉ **Vladimir P. Voloshin**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ voloshin@kinetics.nsc.ru

Molecular dynamics simulation provides the researcher with complete structural information— the coordinates and velocities of each atom of the simulated system. This makes it possible to directly calculate the autocorrelation functions of the velocities of atoms and molecules and the spectra of their vibrations [1]. Figure (1) shows the normalized autocorrelation functions of the translational velocities of the centers of mass of TIP4P/2005 water molecules and the rotational velocities of the same molecules. Already from this Figure it can be seen that the period of the main rotational oscillations is significantly less than the translational ones. Detailed information about the oscillations is presented in Figure (2). The spectra shown were obtained using the Fourier transform of the autocorrelators. These spectra confirm that the frequency of rotational oscillations is significantly higher than that of the translational ones. Moreover, the rotational spectrum contains only one maximum, while the translational spectrum has a high low-frequency maximum and lower high-frequency maximum. In our work, we have shown that the high-frequency maximum describes single-particle oscillations of water molecules relative to their nearest environment, while the low-frequency maximum describes collective oscillations of various scales. The wide maximum of the rotational spectrum combines the oscillations of molecules with different local environments. The high-frequency slope of this maximum is formed by molecules with a large number of strong hydrogen bonds, while the low-frequency slope is formed by molecules with weak bonds or no bonds at all.





[1] Voloshin V. P., Naberukhin Yu. I. (2022). Autocorrelation Functions of Translational and Rotational Water Velocity. *Russian J. Phys. Chem. A*, *96*(7), in press.

The Molecular Dynamics Study of a Dioxadet Drug Properties in Water

✉ **Elena A. Yakush, Alexandra V. Kim**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉ elenayakush43@gmail.com

In the late 1980s, the Petrov Research Institute of Oncology, Russia, developed a drug belonging to the group of ethylenimines. In experimental studies carried out using a wide range of transplanted tumors, it revealed a significant resorptive and contact activity. The drug passed the complete pre-clinical and clinical trials and was approved for medical use under the name Dioxadet [1].

To characterize the drug more thoroughly, a study of its physico-chemical properties in solution by the molecular dynamics methods was carried out.

Several models were created with the help of such online resources as ATB, PRODRG, and SwissParam. Also, the AmberTools software package was used, and quantum chemical electron density calculations were carried out in Gaussian. Thus, five different models were obtained and used to calculate the Gibbs free energy of solvation (the molecular dynamics method of alchemical desolvation and MBAR postprocessing). The calculation of the Gibbs free energy of solvation was also performed by quantum-chemical means, which allowed us to say that the previous calculations were qualitatively correct. The obtained values of the Gibbs free energy of solvation are negative, i.e., the solvation process of gaseous dioxadet in water is beneficial. The comparison of the solubility energy values for one molecule and three (almost saturated solution) was made, and showed that the energy increases in absolute value, so the joint dissolution of dioxadet molecules is beneficial. The classical molecular dynamic simulation of three molecules in water was performed and spatial distribution of the molecules relative to each other revealed that it is typical for the dioxadet molecules to form associates in water. Enthalpy and entropy calculations were also made in different ways, making it possible to estimate their contributions to the Gibbs energy.

[1] Zhikhoreva A. A. et al. (2018). Morphological Changes in the Ovarian Carcinoma Cells of Wistar Rats Induced by Chemotherapy with Cisplatin and Dioxadet. *Biomed. Opt. Express*, *9*, 5817.

ORGANIC PHOTOVOLTAICS

Tuning the Hole Mobilities in Ordered Small-Molecule Semiconductors by Side-Chain Engineering and Fluorine Substitution

Ilya E. Kuznetsov[1], **Denis V. Anokhin**[1,2], **Alexey A. Piryazev**[1,2], **Maxim E. Sideltsev**[1],
Azaliya F. Akhkiamova[1,2], **Dmitry A. Ivanov**[1,3], ✉ **Alexander. V. Akkuratov**[1]

[1] *Institute of Problems of Chemical Physics of RAS*
Chernogolovka, Russia
[2] *Moscow State University*
Moscow, Russia
[3] *Institut de Sciences des Matériaux de Mulhouse*
Mulhouse, France

✉ akkuratow@yandex.ru

Organic electronic devices, such as organic solar cells, organic photodetectors, organic field-effect transistors, etc., have attracted significant attention over the last several decades due to their low-cost and unique characteristics, e.g., lightweight, flexibility, and transparency [1]. The performance of organic electronics devices is mainly affected by the charge transport characteristics of used organic semiconductor materials. Charge carriers transport in organic semiconductors can be improved by enhancing their crystallinity and self-ordering ability in solid state [2]. However, the majority of crystalline organic materials demonstrate poor solubility in organic solvents which hamper the production of devices using high-throughput printing technologies. In this regard, the development of soluble small molecules with crystalline or liquid-crystalline ordering is considered an effective approach to obtain materials combining advanced optoelectronic properties, good solubility, and improved charge transport characteristics.

In this work, we report the synthesis of four novel low molecular compounds based on alternate thiophene and benzothiadiazole blocks exhibiting crystalline or liquid-crystalline properties. It has been found that variation of side chains position in terminal thiophene rings and fluorine loading into benzothiadiazole moieties allow one to tune the optoelectronic properties of compounds as well as the microstructure of thin films. According to the GIWAXS data, thermal treatment of certain samples led to the reorganization of morphology which resulted in significant increase in hole mobilities of these materials. Annealing of fluorine-containing oligomer M4 induced the formation of domain structure of films, which hole mobility was one order of magnitude higher as compared to the untreated films. These findings provide a valuable insight into the structure-property relationships for designed small molecules featuring them as promising semiconductor materials for further developing of high-performance organic electronics.

Acknowledgements: this work was funded by Russian Science Foundation (grant No. 21-73-10182).

[1] Hashemi S. A., Ramakrishna S., Aberle A. G. (2020). *Energy Environ. Sci.*, *13*, 685–743.
[2] He Z., Zhang Z., Bi S., Chen J., Li D. (2020). *Sci. Rep.*, *10*, 4344.

Organic Cation Dynamics and Spectral Features in Hybrid Metal Halide Perovskites

✉ **Vasilisa E. Anikeeva**[1,2], **Kirill N. Boldyrev**[1], **Olga I. Semenova**[3], **Marina N. Popova**[1]

[1] *Institute of Spectroscopy RAS*
Troitsk, Moscow, Russia
[2] *HSE University*
Moscow, Russia
[3] *Rzhanov Institute of Semiconductor Physics SB RAS*
Novosibirsk, Russia

✉ vanikeeva@hse.ru

Hybrid metal halide perovskites are prospective materials for different application in photovoltaics, such as highly efficiently solar cells [1], highly sensitive photodetectors [2], LEDs [3], and lasers [4]. The success of using these compounds in different devices is due to the optical and optoelectronic properties—optimal for solar spectra band gap, a high carrier mobility, large diffusion lengths [5]. Many properties important for photovoltaics are closely related to the features of the phonon spectrum and the electron-phonon interaction.

In this work, we present an infrared and terahertz spectra of methyl ammonia lead iodide/bromide in a wide temperature region (5–330 K). $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ large single crystals were synthesized in the Institute of Semiconductor Physics. Spectral measurements were made by using the Bruker IFS 125HR Fourier spectrometer.

Due to the complex structure of the studied samples, we observed many spectral features in all frequency ranges (15–9,000 cm^{-1}). Changes in spectra at the temperature of 160 K for iodide sample and at the temperature of 155 K for bromide sample correspond to the structural phase transitions from tetragonal to orthorhombic phase. There is an additional restructuring at the temperature of 149 K for bromide crystal; it is associated with the transition to another orthorhombic phase, from the *Imma* phase to the *Pnma* phase. The temperature dependence of peak positions in spectra is a hysteretic dependence, which means that the phase transitions mentioned above are first-order phase transitions. Moreover, upon further cooling, at the temperature 100 K we observed the phonon line narrowing and appearance of visible dips in the reststrahlen band which correspond to a glassy slowing of the rotational dynamics of the $CH_3NH_3^+$ molecular cation [6].

Acknowledgements: the work was supported by the Russian Science Foundation (grant No. 19-72-10132).

[1] https://www.nrel.gov/pv/cell-efficiency.html.
[2] Lian Z., Yan Q. et al. (2015). *Sci Rep.*, *5*, 16563.
[3] Kim H., Zhao L., Price J. S. et al. (2018). *Nat Commun.*, *9*, 4893.
[4] Liu Z., Huang S., Du J. et. al. (2020). *De Gruyter.*, *9*, 2251–2272.
[5] Brenner T., Egger D., Kronik L. et al. (2016). *Nat. Rev. Mater.*, *1*, 15007.
[6] Boldyrev K., Anikeeva V. et. al. (2020). *J. Phys. Chem. C*, *124*, 23307.

Does singlet fission take place in tetracene dimer?

✉ **Alexandr S. Bogomolov**[1], **Vladislav M. Rogoveshko**[1,2], **Alexey V. Baklanov**[1]

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2]*Novosibirsk State University*
Novosibirsk, Russia

✉ bogomolov.kinetics@gmail.com

Singlet fission (SF) is a process of singlet exciton conversion into two triplet excitons which takes place in different materials. Big interest to SF is provided by the perspectives of its use in organic photovoltaics for conversion of solar energy into electric energy. The presence of SF provides for enhancement of the quantum yield of triplet excitons which give rise to electron-hole pairs. According to the estimates by Hanna and Nozik [1] the use of this phenomenon can shift the so-called Schockley-Quisser limit for energy conversion efficiency to the higher values by 30 %. This dictates the interest to the nature of SF phenomenon. The most studied SF materials are polyacenes. In theory the structural unit responsible for SF phenomenon is a dimer of polyacene. But the current studies of SF are mainly carried out not with the dimers but with the solid films which have complex structure which complicates the interpretation of experimental data. Another problem of the current studies that the SF process is detected indirectly as the decrease of luminescence yield and lifetime because it reflects the singlet exciton population.

In the presented work we study the formation of the triplet tetracene (Tc) excitons from the singlet exciton in Tc monomers and dimers isolated in molecular beam. Tc dimers and monomers are resonantly excited by pulsed dye laser in spectral range of $S_0 \rightarrow S_1$ transition. Further, the exited Tc molecules are ionized with a probing pulse of UV laser. Changing delay time between two laser pulses, we directly detect the short-living singlet exited states of Tc as well as long-living triplet states. We have found that triplet state of Tc with the same photoionization spectrum appears after excitation of both monomer and dimer of Tc. Taking into account that excitation of singlet state in monomer gives rise to triplet state via intersystem crossing (IC). We conclude that IC process can be a source of the observed triplet exciton in dimer as well. Moreover, this interpretation is also applicable to many experimental data from literature which were considered to be due to SF phenomenon.

Acknowledgements: the reported study was funded by RFBR (project No. 20-52-12014).

[1]. Hanna M. C., Nozik A. J. (2006). *J. Appl. Phys.*, *100*, 074510.

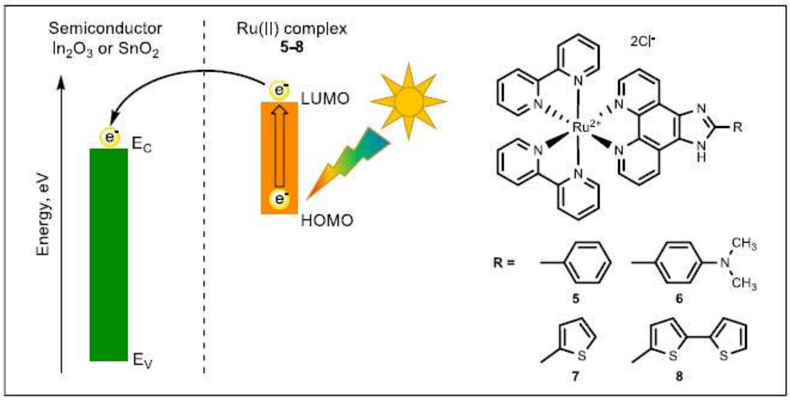
New Heterobimetallic Ruthenium(II) Complex with Imidazo[4,5-f][1,10]phenanthroline-Based Ligand: Synthesis, Optical and Electrochemical Properties

✉ **Yuri V. Fedorov**[1], **Sergey D. Tokarev**[1], **Marina N. Rumyantseva**[2],
Abulkosim Nasriddinov[2], **Anna A. Moiseeva**[2], **Olga A. Fedorova**[1], **Gediminas Jonusauskas**[3]

[1] Nesmeyanov Institute of Organoelement Compounds RAS
Moscow, Russia
[2] Lomonosov Moscow State University
Moscow, Russia
[3] Laboratoire Ondes et Matière d'Aquitaine – UMR CNRS 5798, University of Bordeaux
Talence, France

✉ fedorov@ineos.ac.ru

In this work, the optical characteristics and conductivity of hybrids based on nanocrystalline SnO_2 or In_2O_3 semiconductor matrixes and heteroleptic Ru(II) complex under photoactivation with visible light were studied. The heteroleptic Ru(II) complexes were prepared based on 1H-imidazo[4,5-f][1,10]phenanthroline and 2,2'-bipyridine ligands. Nanocrystalline semiconductor oxides were obtained by chemical precipitation with subsequent thermal annealing and characterized by the XRD, SEM and single-point BET methods. The heteroleptic Ru(II) complexes, as well as hybrid materials, were characterized by the time-resolved fluorescence and X-ray photoelectron spectroscopy. The results showed that the surface modification of SnO_2 nanoparticles with heteroleptic ruthenium complexes led to an increase in conductivity upon irradiation with the light appropriate for absorption by organometallic complex. In the case of In_2O_3, the deposition of Ru (II) complexes resulted in a decrease in conductivity: apparently, due to the special structure of the surface layer of semiconductor.



Picture illustrating the processes occurring
after the excitation of ruthenium (II) complexes 5–8 on the surface of SnO_2 or In_2O_3

Acknowledgements: this work was supported by the Russian Scientific Foundation (grant No. 19-73-20187).

Out-of-Phase Electron Spin Echo Spectroscopy of Short-Living Charge-Transfer State in Organic Photovoltaic Composite of P3HT and Semiconducting Carbon Nanotubes

Aina V. Kulikova, Elena S. Kobeleva, ✉ Leonid V. Kulik

Voedodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ chemphy@kinetics.nsc.ru

Carbon nanotubes (CNT) are an interesting alternative to fullerenes or small molecules as an electron acceptor material for active layer of organic solar cell. Promising results were obtained some time ago for bulk heterojunction blend of poly-3-hexylthiophene (P3HT) and semiconducting CNTs (s-CNT) with specially separated s-CNT from statistical mixture of metal CNT and s-CNT [1]. However, paramagnetic intermediates of photoelectric conversion (either free photogenerated charges or charge-transfer states) were not detected for such blends. Thus, the mechanism of photoelectric conversion in such polymer/s-CNT systems is unclear, which complicates their further optimization.

Using the out-of-phase electron spin echo (ESE) technique with photoexcitation of P3HT/s-CNT blend by laser flash we detected the signal of the charge-transfer state. The two-pulse sequence π/4–τ–π–τ–echo was used. No out-of-phase ESE signal was detected in the same experiment with pristine P3HT film without s-CNT. The appearance of the out-of-phase ESE signal is a solid proof that spin-correlated pair P3HT^{+}/s-CNT^{-} is formed upon photoexcitation. The out-of-phase ESEEM trace for this system is surprisingly close to that of P3HT/PC$_{70}$BM [2], which implies similar distance of initial charge separation of 3–4 nm. However, the decay of the out-of-phase electron spin echo signal with delay-after-flash (DAF) increase for P3HT/s-CNT blend is much faster, with characteristic time of 10 μs at 30 K. It points at higher geminate recombination rate for this system, which may be one of the reasons of relatively poor photovoltaic performance of P3HT/s-CNT blend [1].

[1] Ren S. et al. (2011). *Nano Lett.*, *11*, 5316.
[2] Lukina E. A. et al. (2016). *PCCP*, *18*, 28585.

Synthesis and Photovoltaic Properties of Novel (X-DADAD)$_n$ Conjugated Polymers with Fluorene and Phenylene Blocks

✉ **Ilya E. Kuznetsov**[1], **Maxim E. Sideltsev**[1],
Vladimir G. Kurbatov[1], **Mikhail V. Klyuev**[2], **Alexander V. Akkuratov**[1]

[1] Institute for Problems of Chemical Physics RAS
Chernogolovka, Moscow, Russia
[2] Ivanovo State University
Ivanovo, Russia

✉ kusnetsovilja@gmail.com

Conjugated polymers are promising semiconductor materials for organic photovoltaic devices based on p-n junction. Organic solar cells (OSCs)[1], organic light-emitting diodes [2], organic photodetectors [3], etc. attracted considerable attention in the recent years due to their important advantages over inorganic analogues, such as flexibility, lightweight, stretchability and semitransparency. Furthermore, organic photovoltaic devices can be produced over large areas using low-cost and high throughput printing technologies [4]. Here we report the synthesis and investigation of novel fluorene- and phenylene-based conjugated polymers with TBTBT molecular framework consisting of thiophene (T) and benzothiadiazole (B) building blocks. It has been demonstrated that variation of X building blocks with branched side chains in (X-TBTBT)$_n$-type structures, as well as introducing fluorine into the main chain, strongly affect optical, electronic and physicochemical properties of the resulted polymers. The investigation of photostability of polymer thin films in accelerated tests showed that fluorine-containing polymers are promising materials for organic solar cells with long-term operation stability. The phenylene-based polymer with fluorine-loaded TBTBT block provided power conversion efficiency of 7 % in organic solar cells, which can be further improved by the optimization of morphology of the active layer.

Acknowledgements: this work was supported by the Russian Foundation for Basic Research (project No. 20-03-00309) and Ministry of Science and Higher Education of the Russian Federation within the projects No. AAAA-A19-119101590029-0. We acknowledge the participation of Dr. P.M. Kuznetsov in the characterization of organic solar cells. The authors also gratefully thank Dr. Troshin P. A. for providing the equipment of FMEM laboratory at IPCP RAS.

[1] Xu Y., Yuan J., Zhou S., Seifrid M., Ying L., Li B., Huang F., Bazan G. C., Ma W. (2019). *Adv. Funct. Mater.*, *29*, 1806747.

[2] Han D., Khan Y., Ting J., King S. M., Yaacobi-Gross N., Humphries M. J., Newsome C. J., Arias A. C. (2017). *Adv. Mater.*, *29*, 1606206.

[3] Xu X., Zhou X., Zhou K., Xia Y., Ma W., Inganäs O. (2018). *Adv. Funct. Mater.*, *28*, 1805570.

[4] Chang J. S., Facchetti A. F., Reuss R. (2017). *IEEE J. Emerg. Sel. Topics Circuits Syst.*, *7*, 7–26.

Thienonaphtalimides as Promising Additive to Organic Solar Cells

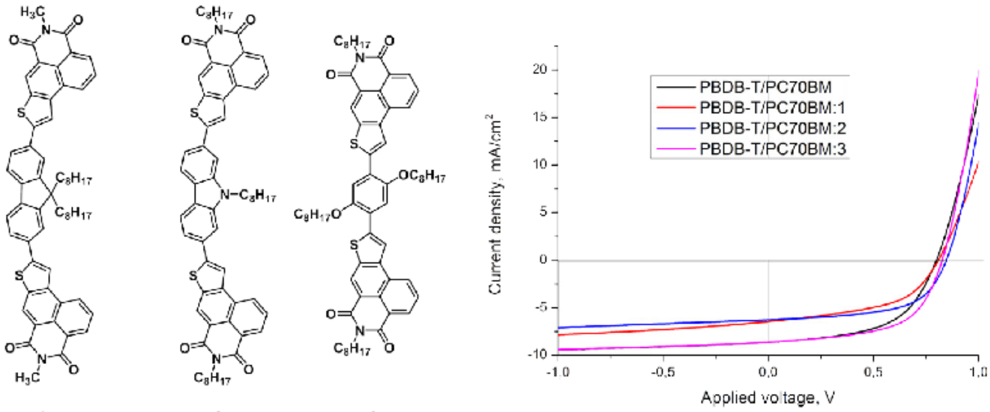
✉ **Danil A. Nevostruev**[1,2], **Olga L. Krivenko**[1], **Denis S. Baranov**[1],
Maxim S. Kazantsev[3], **Vladimir A. Zinoviev**[4], **Alexey A. Dmitriev**[1,2], **Leonid V. Kulik**[1]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia
[3] *Vorozhtsov Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia
[4] *Rzhanov Institute of Semiconductor Physics SB RAS*
Novosibirsk, Russia

✉ nevostruev@kinetics.nsc.ru

Searching for and application of new materials for organic photovoltaics (OPV) is a promising field of investigation. Fundamental compounds, such as poly(3-hexylthiophene) (P3HT) and fullerene derivative (PC60BM), have shown good performance in the active layer of OPV, leading to PCE of 6 %, but nowadays more perspective donors and acceptors exist. One of these is the polymer PM6 and non-fullerene acceptor Y6, which allows one to increase the photovoltaic performance up to 15.7 % [1].

Different polycondenced compounds were probed in organic electronics, and among the most famous types of chemical compounds are perylene- and naphtalimides. In our laboratory, donor molecules based on thienonaphtalimides, bridged with various π-linkers (see Fig.) were synthesized.



1 2 3

Structures of synthesized thienonaphtalimides (left) and J–V curves of binary and ternary blends (right)

As it was found, the additive of 5 % of **3** in the PBDB-T/PC70BM active layer leads to a small increment of PCE (from 17.57 % to 17.68 %), which could be explained by the amplification of crystallinity of donor polymer PBDB-T (see Fig.).

[1] Yuan J. et al. (2019). *Joule*, *3*, 1140–1151.

New D-π-A Compounds as Electron Transport Materials for Perovskite Solar Cells

✉ **Alexander S. Steparuk**[1], **Ekaterina F. Zhilina**[1], **Roman A. Irgashev**[1,2],
Gennady L. Rusinov[1,2], **Sofia A. Petrova**[3], **Danila S. Saranin**[4], **Alexey E. Alexandrov**[5],
Alexey R. Tameev[1,5]

[1] *Postovsky Institute of Organic Synthesis UB RAS*
Ekaterinburg, Russia
[2] *Ural Federal University named after the first President of Russia B. N. Yeltsin*
Ekaterinburg, Russia
[3] *Institute of Metallurgy UB RAS*
Ekaterinburg, Russia
[4] *National University of Science and Technology MISiS*
Moscow, Russia
[5] *Frumkin Institute of Physical Chemistry and Electrochemistry RAS*
Moscow, Russia

✉ assteparuk@ios.uran.ru

Over the past decade, perovskite solar cells (PSCs) have attracted considerable attention from researchers worldwide, since PSCs are promising photovoltaic materials due to their low cost of production, as well as high efficiency [1].

Four new compounds **ISC 1-4** with D-π-A structure containing thieno[3,2-*b*]indole as an electron-donating unit and benzo[*b*]thieno[2,3-*d*]thiophen-3(2*H*)-one as an electron-accepting unit, were readily synthesized using a simple three-step protocol based on our original strategy, which we used previously for the obtaining of different thieno[3,2-*b*]indole-based D-π-A compounds [2]. Thermal stability, optical and electronic properties of these materials were investigated. In thin solid films of **ISC 1-4**, the electron mobility measured using the conventional CELIV technique was within the range of 10^{-6} $cm^2 \cdot V^{-1} \cdot s^{-1}$. The **ISC 1-3** substances were found to be applicable as electron transport materials in PSCs. For the **ISC 1** based perovskite solar cell, the PCE of 12.02 % was demonstrated under the AM 1.5 G irradiation.

Acknowledgements: the synthesis and analytical study of organic materials was performed with the financial support of RSF (project No. 19-13-00234). The study of solar cells was carried out with the financial support of RSF (project No. 18-13-00409).

[1] Kumar N. S., Naidu K. C. (2021). *Journal of Materials Chemistry*, *7*, 940–956.

[2] Alexandrov A. E., Tameev A. R., Steparuk A. S., Irgashev R. A., Rusinov G. L. (2019). *Russ. Chem. Bulletin*, *68*, 1204–1207.

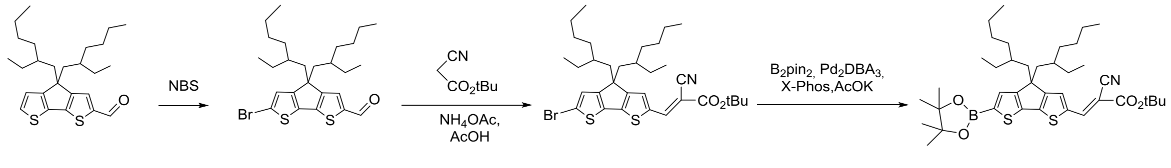
Building Block Based on 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’] dithiophene: Approach to the Novel Effective Photovoltaic Materials

✉ **Olga O. Ustimenko**[1,2], **Maksim S. Mikhailov**[2],
Ekaterina A. Knyazeva[2], **Oleg A. Rakitin**[2]

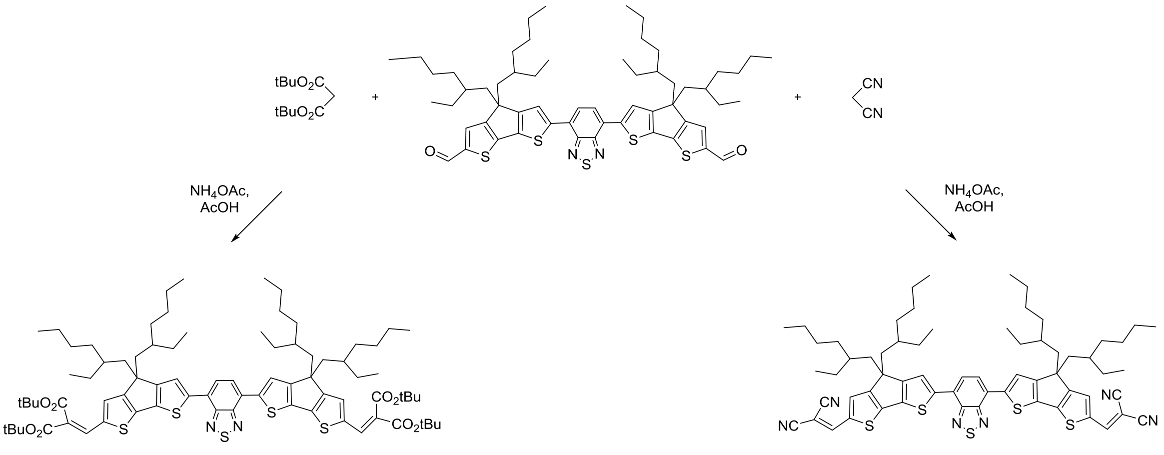
[1] *Lomonosov Moscow State University*
Moscow, Russia
[2] *Zelinsky Institute of Organic Chemistry RAS*
Moscow, Russia

✉ oustimenko99@gmail.com

Due to the growing demands of mankind in renewable energy, the search for approaches to new photovoltaic materials based on organic compounds is now one of the topical issues of fundamental science. The work of the above stated photovoltaic elements sensitized with dyes of various structural types is usually based on the different electron transfer processes between donor (D), acceptor (A) and π-spacer (π) fragments of the dye molecule. The role of the π-spacer is to supply the electron transfer in an appropriate direction and to enlarge the π-conjugated chain. Currently, 4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene is considered one of the most promising building blocks combining outstanding π-spacing properties with the the difficulties of synthesis. Thus, new approaches to different building blocks on its basis are being actively developed now [1; 2]. As a result of the synthesis including three successive stages, we have obtained a previously undescribed universal π-acceptor building block that combines a proven architecture with the prospect of conducting cross-coupling reactions with various donor and acceptor fragments.



The second part of this work was the synthesis of symmetrical dyes of the structural type A^1-π-A-π-A^1 based on the previously obtained building block.



© Ustimenko O. O., Mikhailov M. S., Knyazeva E. A., Rakitin O. A., 2022

The recorded absorption spectra in the visible and UV ranges, as well as the calculated energy values of the boundary orbitals for the target compounds, have revealed that all of them can be used as potentially effective photovoltaic materials.

[1] Gudim N. S., Knyazeva E. A. et al. (2021). Molecules, 26, 4931.
[2] Mancilha F. S., Neto B. A. D. et al. (2006). Eur. J. Org. Chem., 4924.

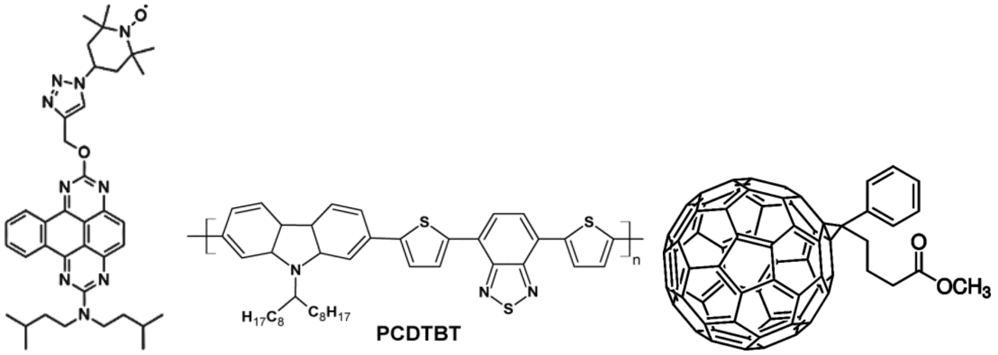
Tetraazapyrene Functionalized Nitroxide Radical TEMPO and Its Application in Polymer:Fullerene Photovoltaic Cells

✉ **Mikhail N. Uvarov**[1], **Denis S. Baranov**[1], **Danil A. Nevostruev**[1], **Aina V. Kulikova**[1,2],
Dmitrii E. Utkin[2,3], **Maxim S. Kazantsev**[4], **Vladimir A. Zinoviev**[3], **Leonid V. Kulik**[1]

[1]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2]*Novosibirsk State University*
Novosibirsk, Russia
[3]*Rzhanov Institute of Semiconductor Physics SB RAS*
Novosibirsk, Russia
[4]*Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia

✉ uvarov@kinetics.nsc.ru

The nitroxide radical TEMPO has been functionalized by the tatraazapyrene heterocyclic core developed previously [1]. The compound synthesized, the radical R1 (see Fig.), was added into spin-coated active layers of conventional and inverted polymer:fullerene PCDTBT:PCBM-based organic photovoltaic cells (OPC). The solubility in chlorobenzene of the radical R1 is weak as compared to the donor-acceptor composite components PCDTBT and PCBM; therefore, the surfaces of the OPC active layers could be easily modified by the radical during spin-coating of the three-component solution. Because of the radical R1 thin interface layer was formed within the manufactured OPC, the values of power conversion efficiency for the inverted OPC were improved; however, the IV-characteristics of conventional OPC were distorted by s-shape. These effects appear because the radical R1 thin layer has electron-blocking and simultaneously hole-transporting properties. Therefore, the functional interface layer of the radical R1 could be deposited by one-step procedure of spin-coating.



R1 **PCBM**

The structures of the synthesized radical R1,
semiconducting polymere PCDTBT and fullerene C_{60} derivative PCBM

[1] Baranov D. S., Krivenko O. L., Nevostruev D. A. et al. (2019). *Dyes and Pygments*, *168*, 219–227.

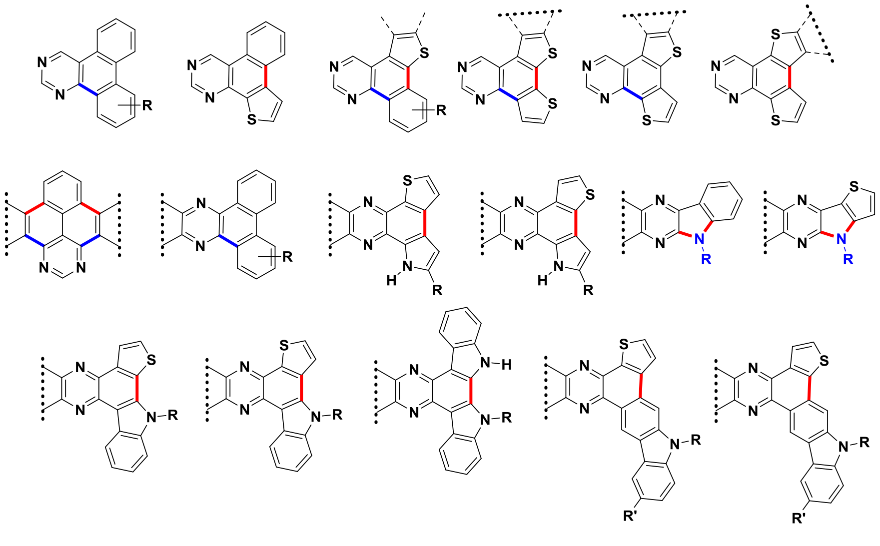
S_N^H-Reactions and Other Cross-Dehydrogenative Coupling Processes for the Construction of 1,3-/1,4-Diazine-Based Polycyclic Systems

✉ **Egor V. Verbitskiy, Gennady L. Rusinov, Valery N. Charushin**

Postovsky Institute of Organic Synthesis UB RAS
Ekaterinburg, Russia
Ural Federal University
Ekaterinburg, Russia

✉ verbitsky@ios.uran.ru

Polycyclic(hetero)aromatic compounds are ubiquitous structural motifs, which are to be found in a variety of enhanced materials for organic electronics and pharmaceutical applications [1; 2]. In the report, we speak about new synthetic approaches to polycyclic systems based on pyrimidine and pyrazine. The main emphasis is focused on the utilization of the nucleophilic aromatic hydrogen substitution reaction (S_N^H-reaction) and other cross-dehydrogenative coupling processes. Photophysical and electrochemical properties, as well as the outlook of the feasible application of the resulting systems (see Figure), are also discussed in this contribution.



Scope of structures of 1,3-/1,4-diazine-based polycyclic systems

Acknowledgements: this work has been supported by the Russian Scientific Foundation (grant No. 18-13-00409 P).

[1] Verbitskiy E. V., Rusinov G. L., Charushin V. N. (2017) Diazatriphenylenes and Their Thiophene Analogues: Synthesis and Applications. *ARKIVOC*, *1*, 356–401.

[2] Borissov A., Maurya Y. K., Moshniaha L., Wong W.-S., Żyła-Karwowska M., Stępień M. (2022). Recent Advances in Heterocyclic Nanographenes and Other Polycyclic Heteroaromatic Compounds. *Chem. Rev.*, *122*(1), 565–788.

QUANTUM AND THEORETICAL CHEMISTRY

The Quantum-Chemical Modeling of Adamantane Olefination with Ethylene, Propylene, and Butylene

✉ **N. I. Baranov**[1], **R. E. Safir**[1], **E. I. Bagrii**[2], **A. G. Cherednichenko**[1], **K. V. Bozhenko**[1]

[1] Peoples' Friendship University of Russia
Moscow, Russia
[2] Topchiev Institute of Petrochemical Synthesis RAS
Moscow, Russia

✉ 1042182094@rudn.ru

High reactivity of double-bonded adamantane derivatives offers extensive opportunities for their utilization as starting materials for the synthesis of various functional adamantane derivatives. The purpose of this work was to study theoretically the reactions of ionic alkylation of adamantane with alkenes in the presence of aluminum chloride as catalyst. The geometric parameters of the substances, thermodynamic quantities, and normal vibration frequencies were estimated in the Gamess US program in the B3LYP-D3(BJ)/6-311++G** approximation. The evidence for the fact that the found structure belongs to the energy minimum was the absence of imaginary harmonic frequencies in the IR spectrum. The intrinsic reaction coordinate (IRC) method was used to confirm the correspondence of the transition state to a certain reaction. The thermal corrections were calculated for 298 K and 1 atm. Changes in the Gibbs free energy upon chemical transformations can be seen in the Table.

Gibbs Free Energies of Reactions	**ΔG, kcal/mol**
Ad + C_2H_4 = Ad-CH=CH_2 + H_2	7.92217238
Ad + C_3H_6 = Ad-CH=CH-CH_3 + H_2	13.1060753
Ad + 1-C_4H_8 = Ad-CH=CH-CH_2-CH_3 + H_2	10.6394756
Ad + 1-C_4H_8 = Ad-CH_2-CH=CH-CH_3 + H_2	8.19197347
Ad + 1-C_4H_8 = Ad-CH_2-CH_2-CH=CH_2 + H_2	12.2709777
Ad + 1-C_4H_8 = Ad-CH=CH-CH=CH_2 + 2H_2	24.9122745

These findings make it possible to conclude that adamantane alkylation resulting in alkenes formation is a multistage process with proton moving.

[1] Bagrii E. I. (1989). Adamantany: poluchenie, svoistva, pri- menenie [Adamantanes: Obtaining, Properties, Application]. Moscow: Nauka.

[2] Baranov N. I., Bagrii E. I., Safir R. E. et al. (2022). Pet. Chem., 62, 352–375. https://doi.org/10.1134/S0965544122020153.

Bending Crystal Phenomena: Computational Insight

✉ **Alexandr S. Dubok**, **Denis A. Rychkov**

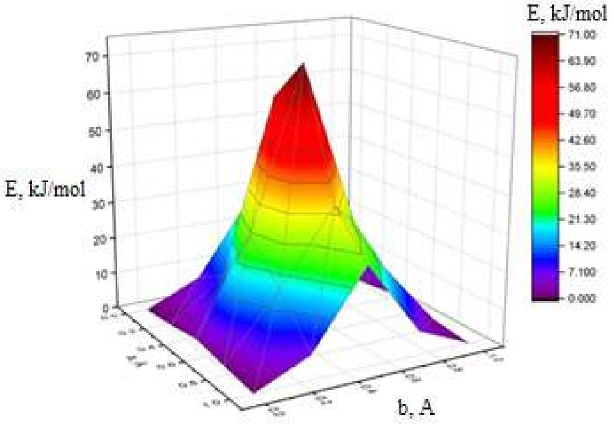
Institute of Solid State Chemistry and Mechanochemistry
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉ a.dubok1@g.nsu.ru

Molecular crystals can be used as flexible and efficient materials for electronics (Organic Field-Effect transistors), photonics (organic light emitting diodes), and other areas [1]. When developing a material one should keep in mind it's functional characteristics, including mechanical properties. Therefore, methods for their prediction are required.

Bending organic crystals are often described as layered structures, the layers being strongly bonded inside, weakly connected to each other though [2]. However there are some examples of bending crystals which do not satisfy these description [3]. Moreover, the number of known bending crystals, according to our estimations, hardly exceeds one hundred, whereas the number of structures in crystal databases is more than one million. This raises the question: taking into account that layered organic crystals are common, why bending ones are so rare?

Computational methods, on the one hand, are capable of giving qualitative evaluations. On the other hand, they can reveal the relationships and processes underlying on the atomic level, in many cases being unavailable for conventional experimental methods. In this research we focused on studying plastic bending properties in organic crystals with the aid of quantum and molecular mechanic methods attempting to develop the methods for predicting bending crystals.



Positional energy surface for bending sliding

To better capture the structure-properties correlations, we chose a system of *pyrazinamide* polymorphs which contains a bending and a non-bending form [2]. Then we computed the layer energies and PES (see Fig.) for layer sliding and revealed noteworthy relations between them and the ability to bend.

Acknowledgements: this research was funded by the Russian Science Foundation (grant No. 21-73-00094, https://rscf.ru/en/project/21-73-00094/).

[1] Brooks J. S. (2010). *Chem. Soc. Rev., 39*(7). 2667–2694.
[2] Reddy C. M. et al. (2006). *Cryst. Growth Des., 6*(12). 2720–2731.
[3] Thomas S. P. et al. (2017). *Angew. Chemie Int. Ed., 56*(29). 8468–8472.

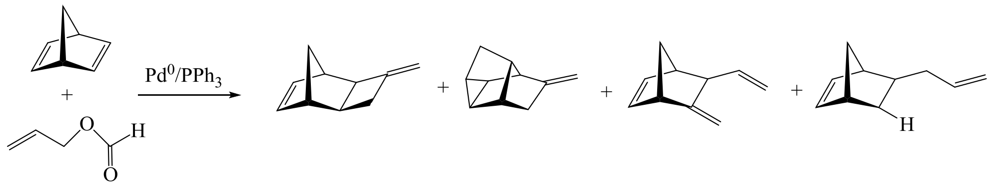
On the Accuracy of DFT Methods for Calculating the Activation Characteristics of the Pd-catalyzed Allylation of Norbornadiene

✉ **Karen T. Egiazaryan**, **Ravshan S. Shamsiev**

MIREA—Russian Technological University, Lomonosov Institute of Fine Chemical Technologies
Moscow, Russia

✉ mccubas369@gmail.com

More recently, an increasing number of studies have been devoted to studying the reaction of norbornadiene (NBD) allylation in the presence of metal complex catalysts [1], which leads to various carbocyclic products (see Fig.). Post-experimental theoretical modeling [2] using the DFT-PBE/L11 method allowed us to study in detail the mechanism of this reaction. At the same time, the question of reliability of the used calculation method remains debatable, since the obtained values of activation barriers turned out to be noticeably overestimated ($\Delta G^{\neq}_{298} > 30$ kcal/mol). The aim of this work was to study the influence of the basis set and the type of exchange-correlation functional on the activation and structural characteristics of intermediates and transition states corresponding to the critical points of the energy profiles of the Pd-catalyzed allylation of norbornadiene.



The main products of Pd-catalyzed allylation of NBD

The calculations were carried out within the scalar-relativistic approximation using the L1, L11, L2, def2-SVP, def2-TZVP, def2-QZVPP basis sets and the *BLYP*, *OLYP*, *PBE*, *BP86*, *B3LYP*, *PBE0*, *B97*, ω*B97X* functionals. According to calculations, the expansion of the basis set does not significantly affect the value of $\Delta G^{\neq}_{298}$ for the routes of products formation products. The replacement of GGA-functionals by hybrid ones leads to an even greater increase in the values of $\Delta G^{\neq}_{298}$ (by ~2 kcal/mol). The Grimme dispersion correction (D3) for GGA or hybrid functionals leads to a strong underestimation of $\Delta G^{\neq}_{298}$ (by ~10 kcal/mol). Moderate values of $\Delta G^{\neq}_{298}$ were obtained using the LRC-functional—ω*B97X-D3*.

Acknowledgements: this work was financially supported by the MIREA—Russian Technological University (grant "For young scientists").

[1] Durakov S. A., Melnikov P. V., Marzinkevich E. M., Smirnova A. A., Shamsiev R. S., Flid V. R. (2021). *Russ. Chem. Bull.*, *70*(1), 113–121.

[2] Shamsiev R. S., Egiazaryan K. T., Flid V. R. (2022). *Russ. Chem. Bull.*, *71*(5), 905–914.

Kinetics of Polaron Capture by Traps in a Lithium Niobate Crystal

✉ **Stanislav Fedorenko**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ fedorenk@kinetics.nsc.ru

Small-polaron transport plays a key role in the formation of remarkable properties of Lithium Niobate crystals (LN) attractive for practical application. Modern time-resolved light induced absorption spectroscopy experiments make it possible to observe the relaxation kinetics of polaron population over a wide range of times [1]. However, the interpretation of experimental data from a microscopic point of view is very difficult due to the complexity of the mechanism of interaction of various types of charge carriers and their capture on traps. Phenomenological analysis of kinetics with the help of widely used Kohlrausch—William—Watts stretched exponential functions does not give anything new from the point of view of physics [2]. Monte Carlo simulation, unfortunately, does not provide an answer for the microscopic detailing of the kinetic mechanism of polaron capture into traps, without which it is impossible to understand the general kinetic patterns of the process [3].

To correct the situation, we solve the problem of determining the kinetics of polaron relaxation starting from a microscopic description of the polaron dynamics by means of stochastic jumps given by the Markus—Holstein non-adiabatic probability. We focus on the case of Fe doping in LN, when all photo-induced charges are generated from Fe^{2+} centers, which makes it possible to exclude hole polarons from consideration. In this formulation of the problem, three active players remain in the system: free and bound polarons, which can reversibly transform into each other, and Fe^{3+} traps, on which both types of polarons are irreversibly captured.

We have solved this problem analytically. Explicit dependences of the kinetics of free and bound polarons on the microscopic interaction parameters, temperature, and concentration of impurity sites and vacancies were obtained.

[1]Imlau M., Badorreck H., Merschjann C. (2015). *Appl. Phys. Rev.*, *2,* 040606.

[2] Guilbert L., Vittadello L., Bazzan M., Mhaouech I., Messerschmidt S., Imlau M. (2018). *J. Phys. Condens. Matter*, *30,* 125701.

[3] Vittadello L., Guilbert L., Fedorenko S., Bazzan M (2021). *Crystals*, *11,* 302.

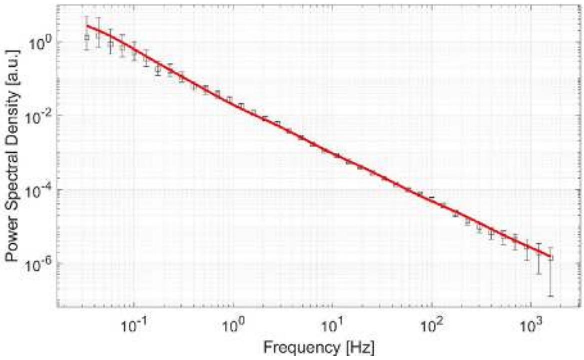
Quantitative Theoretical Model of Single Quantum Dot Blinking

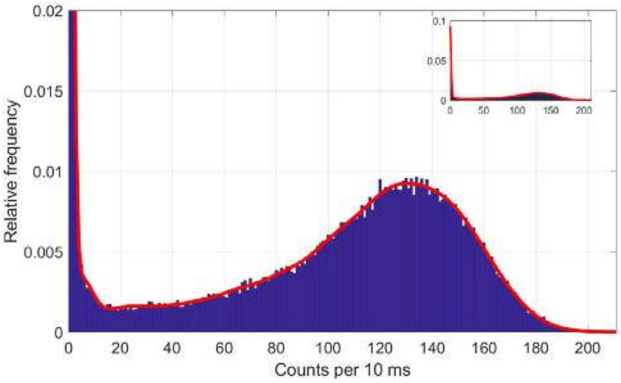
Eduard A. Podshivaylov, ✉ Pavel A. Frantsuzov

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia

✉ frantsuzov@kinetics.nsc.ru

Several decades have passed since the first experimental observation of a single semiconductor quantum dots luminescence blinking. To date, three main mechanisms describing this phenomenon are known in the literature: the charging mechanism [1], the trapping mechanism [2], and the hot carriers trapping mechanism. [3]





Historically, the first model within the trapping mechanism was proposed by Marcus and Frantsuzov [2]. It is assumed that the quenching of luminescence occurs due to the trapping of one of the carriers, which leads to non-radiative recombination. The trapping rate in the model is related to spectral diffusion and fluctuates with time, resulting in an emission intensity blinking.

Further development of this idea was the multiple recombination centers (MRC) model [4]. A finite number of recombination centers that can be described by the photoactivated stochastic two-level systems set is assumed to exist. Switching of such centers leads to a change in the trapping rate, resulting in a good correspondence between the theory and the experiment.

Nevertheless, until now, there is no model that quantitatively describes both the spectral power density (PSD) and the probability density function (PDF) of the blinking intensity.

We present a new model based on trapping mechanism that can fit quantitatively both the power spectral density and the probability density function. Without abandoning the basic ideas of the MRC model, this model connects fluctuations in luminescence signal with long-term changes in the value of the electron-phonon interaction.

[1] Efros Al. L., Rosen M. (1997). *Phys. Rev. Lett., 78*, 1110.

[2] Frantsuzov P. A., Marcus R. A. (2005). *Phys. Rev. B.*, *72*, 155321.

[3] Galland C., Ghosh Y., Steinbrück A., Sykora M., Hollingsworth J. A., Klimov V. I., Htoon H. (2011). *Nature*, *479*, 203–208.

[4] Frantsuzov P. A., Volkán-Kacsó S., Jankó B. (2009). *Phys. Rev. Lett.*, *103*, 207402.

DFT Approach for the Calculation of NMR and IR Spectral Parameters of Olefins on Zn-Modified Zeolites

✉ **Anton A. Gabrienko**, **Alexander A. Kolganov**,
Zoya N. Lashchinskaya, **Alexander G. Stepanov**

Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia

✉ gabrienko@catalysis.ru

Zn-modified zeolites have demonstrated their promising properties for converting light C_2–C_4 olefins to methyl-substituted benzenes [1–4]. For further advances in developing effective catalysts based on Zn-zeolites, reliable information concerning the mechanisms of olefin transformations is needed. Such research can be performed by means of solid-state NMR and FTIR spectroscopy. However, the interpretation of the spectra is a very challenging task, since the detected chemical shifts (^{13}C) and wavenumbers for detected intermediates and products are affected by the interaction of hydrocarbon molecules and zeolite active sites. The application of DFT that could provide the spectral parameters and stabilization energies can be helpful for solving the problem of the ^{13}C NMR signal and IR band assignment. The keystone is the methodology for this type of calculations concerning its application to the adsorbed hydrocarbon species.

Here, we report an approach for calculating the ^{13}C chemical shift and wavenumber values examined for a variety of olefinic species adsorbed on Zn-modified BEA and ZSM-5 zeolites. It has been inferred that the reliable result is achieved by performing the following steps: 1) zeolite framework optimization with periodic DFT (pPBE), 2) cluster geometry optimization with hybrid GGA (PBE0), and 3) calculation of the NMR and IR parameters. TPSS/cc-pVTZ method has been found to provide the best computational cost/accuracy ratio. The advantage of the linear regression method for converting the calculated chemical shielding constant to the chemical shift has been demonstrated.

Additionally, the linear correlation between the adsorption energy of C_2–C_4 olefins on Zn^{2+} sites of zeolites and spectral parameters has been revealed. The higher the adsorption energy, the larger the red-shift of the $\nu_{C=C}$ band and the lower the downfield shift of the ^{13}C NMR signal for a C-2 atom. This finding provides the basis for a new method of measuring hydrocarbon adsorption energy using spectroscopic techniques.

[1] Bonnin A., Comparot J. D., Pouilloux Y. et al. (2021). *Appl. Catal. A-Gen.*, *611*.
[2] Pan T., Wu Z. J., Zhou K. Y. (2020). *Ind. Eng. Chem. Res.*, *59*, 12371–12380.
[3] Chen X., Dong M., Niu X. et al. (2015). *Chin. J. Catal.*, *36,* 880–888.
[4] Schweitzer N. M., Hu B., Das U. et al. (2014). *ACS Catal.*, *4*, 1091–1098.

Structure and Properties of the $EuErCuTe_3$: *Ab Initio* Calculation

✉ **Maxim V. Grigoriev**[1], **Vladimir A. Chernyshev**[2], **Anna V. Ruseikina**[1], **Thomas Schleid**[3]

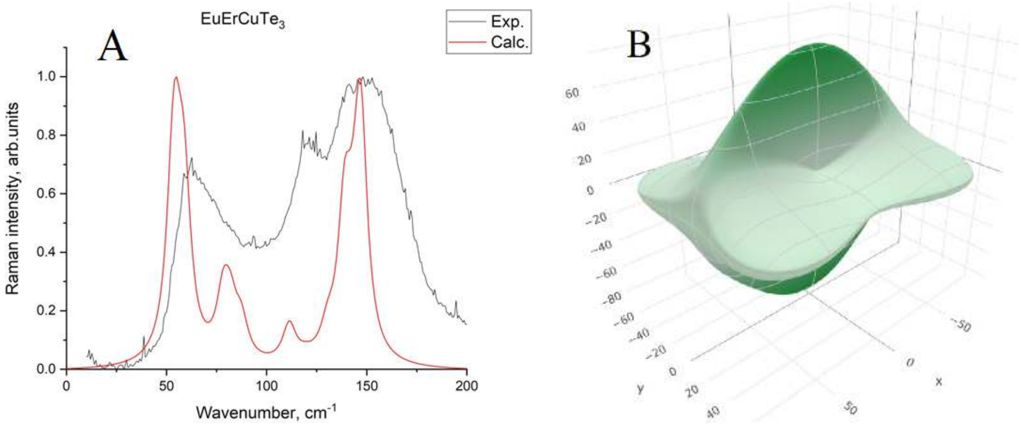
[1] *University of Tyumen*
Tyumen, Russia
[2] *Ural Federal University*
Ekaterinburg, Russia
[3] *University of Stuttgart*
Pfaffenwaldring, Germany

✉ ma.v.grigorev@utmn.ru

For the first time an *ab initio* calculation of $EuErCuTe_3$ (*Cmcm*) was carried out. The crystal structure, band structure, phonon spectrum, and elastic properties were calculated. The calculations were performed within the framework of DFT with hybrid functionals which take into account the contribution of non-local exchange in the Hartree-Fock formalism. The program CRYSTAL17 was used. The results of the calculation of the crystal structure are in good agreement with the experimental data (see Table).

Lattice constants (Å) and band gap value (eV) of $EuErCuTe_3$

	A	B	C	GAP
Calc.	4.3333	14.3268	11.1892	1.85
Exp.	4.3069	14.3093	11.1943	–



A—the Raman spectrum, *B*—dependence of the Young's modulus (GPa) on the direction in the crystal

The frequencies and types of the infrared, Raman, and "silent" modes were determined from the calculation. From the analysis of the displacement vectors which were obtained from the *ab initio* calculation, the degree of participation of ions in the phonon modes was determined.

The results of modeling the Raman spectrum are in good agreement with the experiment. The anisotropy of elastic properties is illustrated by the dependence of the Young's modulus on the direction in the crystal (see Fig.). The calculations predict a low-frequency phonon spectrum, which is promising for using $EuErCuTe_3$ as a matrix for activation by rare-earth ions.

First-Principles Relativistic Calculations of the Magnetic Properties of Lanthanide Complexes: Are Quantitative Predictions Possible?

✉ **Nina P. Gritsan, Alexey A. Dmitriev, Elena A. Pritchina, Evgeny M. Kadilenko**

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉ gritsan@kinetics.nsc.ru

Lanthanides are of fundamental importance for contemporary chemistry and for application in materials science. In particular, lanthanides have become the corner-stone components of molecule-based functional magnetic materials due to their large magnetic moments, large anisotropies, and slow relaxation [1]. Recently, a breakthrough in the field of single-molecular magnetism occurred when the blocking temperature of the dysprosium metallocenes exceeded the temperature of liquid nitrogen [2]. The growing amount of detailed experimental data requires high-level quantum chemical calculations to understand temperature dependences of magnetic susceptibility and relaxation of magnetization of the single-molecule magnets (SMMs) and to establish the relationship of their chemical structure with magnetic and relaxation properties.

In the case of lanthanides, correct account for relativistic effects is essential. Therefore, we performed high-level SA-CASSCF and CASPT2 calculations accompanied by a non-perturbative account of the spin-orbit coupling (SOC). This report presents and discussws the results of calculations for a number of lanthanide complexes: single-ion magnets (SIM) and dinuclear SMMs containing lanthanide and 3d-metal cations. The calculation results, namely wave functions and energies of the magnetic sublevels, are used to calculate magnetic susceptibility and magnetization, the spin-Hamiltonian parameters for pseudo-spin states, matrix elements of the transition magnetic moments between the lowest-energy magnetic sublevels, etc. The latter data is used to model and explain the results of static and dynamic measurements, which are demonstrated using the experimental results of our colleagues and data in literature.

An even more complicated problem is the understanding and modelling of properties of lanthanide complexes with paramagnetic ligands, which are also promising as SMMs [1]. The report also presents and discusses the results of the calculations for lanthanide complexes with radical anions [3].

Acknowledgements: this work was supported by the Russian Science Foundation (project No. 22-13-00077).

[1] *Lanthanides and Actinides in Molecular Magnetism* (2015); Eds. R. A. Layfield, M. Murugesu. Wiley, Weinheim, Germany.

[2] Guo F.-S., Day B. M., Chen Y.-C. et al. (2018). *Science, 362*, 1400–1403.

[3] Booth C. H., Kazhdan D. et al. (2010). *J. Am. Chem. Soc.*, *132*, 17537–17549.

Peculiarities of HCl Sorption from Air by Weak Base Anion Exchanger with Ethylenediamine Functional Groups: Experimental Study and DFT Simulation

✉ **Yauheni G. Kosandrovich**, **Aliaksandr L. Pushkarchuk**,
Tatsiana V. Bezyazychnaya, **Larisa N. Shachenkova**, **Vladimir S. Soldatov**

Institute of Physical and Organic Chemistry NAS RB
Minsk, Belarus

✉ kosandrovich@ifoch.bas-net.by

Fibrous ion exchangers are successfully used to purify air from different toxic compounds, including HCl [1; 2]. At the same time, the literature data on the features of interactions and structural characteristics of sorption complexes “functional group — water molecules — HCl” are scarce. Here we present the results of an experimental investigation of HCl sorption from air by polymeric anion exchanger on the base of polyacrylonitrile fiber with ethylenediamine functional groups (PAN-EDA), and computer simulation of the structures of HCl sorption complexes with amino groups of this anion exchanger using DFT/B3LYP/D3/6-31G(3d ,p) level of theory. Firefly (PC GAMESS) software package was used for the DFT calculations.

From the experimental sorption results we found that: 1) critical relative air humidity for PAN-EDA ion exchanger in the processes of HCl sorption from air is 25–30 %; 2) the maximum HCl sorption value exceeds the anion exchange capacity (S_{max}^{HCl} = 5.2 mmol/g; E_{base} = 4.0 mmol/g), i.e., a superequivalent sorption is observed.

The cluster consists of two functional groups (PAN-2EDA), and different number of water and HCl molecules were chosen for the DFT simulation. The geometric characteristics of sorption complexes PAN-2EDA + nH$_2$O + mHCl (n — number of water molecules (from 2 to 14); m — number of HCl molecules (from 1 to 6)) with functional groups of the anion exchanger have been found. It was established that: 1) dissociation of first HCl molecules in the phase of PAN-EDA ion exchanger with the transfer of protons to the N atoms of the terminal aminogroup occurs at a water content of 2–3 H_2O molecules per functional group; 2) at a maximum water content (6–7 H_2O molecules per functional group) and the maximum number of HCl (4–6) structuring of the system is observed: non-covalent bonds are formed between the HCl molecules with formation of HCl chains, which explains the superequivalent sorption observed in sorption experiments.

[1] Soldatov V. S. (2011). Ion exchangers for air purification. In: I*on Exchange Solvent Extraction, A Series of Advances*; A. K. Sengupta (Ed.), pp. 45–117. CRC Press Taylor and Francis Group, USA.

[2] Kosandrovich E. G. (2012). Fibrous Ion Exchangers. In: *Ion exchange technology I: Theory and Materials*; Inamuddin and Mohammad Luqman (Eds.), pp. 299–371. Springer, UK.

Integral Encounter Theory (IET) of the Reversible Reaction A + A ↔ C, Taking into Account the Force Interaction between the Reactants

✉ **Alexander A. Kipriyanov**[1], **Alexey A. Kipriyanov**[2]

[1]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[2]*Novosibirsk State University*
Novosibirsk, Russia

✉ alexander.kipriyanov@yandex.com

The currently developed regular method for deriving binary non-Markovian kinetic equations for a wide class of chemical reactions was initially established when considering many-particle systems consisting of point particles. Such consideration corresponds to the neglect of force interactions between the reactants (the ideal "gas" of the reactants). Taken somewhat later, the force interaction was taken into account at the final stage of the derivation of equations in the framework of the binary approximation.

The construction of a theory that takes into account chemical and force interaction on equal bases, starting with a many-particle description of the reacting system, was carried out earlier for irreversible association reactions A + A → C and A + B → C. Despite the fact that taking into account the force interaction in the reacting pairs for these reactions formally corresponds to the replacement of the reaction interaction by the total one, the consistent derivation of the kinetic equations was a non-trivial problem due to different analytical properties of the reaction and force interaction operators. Consistently taking into account the force interaction between the reactants in a reversible associative-dissociative reaction A + A ↔ C for the general case of spatially inhomogeneous systems is not obvious, since the decay channel of the reactant C cannot be formally associated with any pair of force interaction.

Within the framework of the many-particle approach under discussion, a hierarchy of equations for one-particle and two-particle correlation patterns was obtained in the thermodynamic limit. Solving the equations neglecting the contributions of three-particle correlations made it possible to obtain closed non-Markovian kinetic equations for local concentrations within the framework of the Integral Encounter Theory (IET). In full accordance with the principles of the general kinetic theory, these equations have an integro-differential form and contain inhomogeneous sources that describe the decay of the initial pair correlations. Despite the fact that the obtained non-Markovian kinetic equations are valid in a narrow time interval, they have the correct Markovian limit corresponding to the kinetic law of mass action, ensure the fulfillment of the particle number balance law, and lead to correct equilibrium concentrations.

Acknowledgements: the authors are grateful to Prof. A. B. Doktorov for useful discussions.

Non-Markovian Kinetic Effects in the Liquid-Phase Reaction A + A ↔ C

✉ **Alexander A. Kipriyanov**[1], **Alexey A. Kipriyanov**[2], **Alexander B. Doktorov**[1]

[1]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS
Novosibirsk, Russia
[2]Novosibirsk State University
Novosibirsk, Russia

✉ alexander.kipriyanov@yandex.com

The development of a consistent theory of liquid-phase bimolecular reactions is one of the main directions of theoretical research which makes it possible to understand the causes forming the kinetics and mechanisms of reactions. At the moment, the most recognized methods for deriving kinetic equations tested on exactly solvable models, as well as confirmed by the results of computer simulations, are the methods based on a many-particle description of the reacting system. The most efficient of them, providing for generalization to multistage reactions and consideration of a realistic structure of reactants, was a method based on adapting the approaches of non-equilibrium statistical mechanics and non-stationary scattering theory to chemical systems.

This method in its modern formulation leads to the integro-differential kinetic equations of the Modified Encounter Theory (MET). The reduction of the resulting equations to a differential form with an inhomogeneous source allows one to interpret the equations in terms of the Generalized Encounter Theory (GET). Previous studies for the irreversible reactions A + A → C and A + B → C made it possible to establish the effect of the accumulation of macroscopic correlations caused by the dependence between the evolutions of reaction pairs during free walks in the reservoir. This work is devoted to the study of these effects within the framework of MET and GET for a much more complex system of the reversible reaction A + A ↔ C.

On the basis of a *hierarchy* of equations for correlation patterns in the thermodynamic limit and T-operators obtained earlier, a procedure for extracting the contributions from binary channels (two-particle correlations) into the evolution of three-particle completely correlated patterns is carried out. This made it possible to obtain non-Markovian kinetic equations in the Effective Pair Approximation (EPA). Further calculation of the evolution of effective pairs made it possible to obtain the non-Markovian integro-differential kinetic equations MET. The interpretation of these equations from the point of view of the Encounter Theory concepts confirmed the effect of dependence of pair encounters of reactants in solution. The presence of revealed macroscopic correlations in binary theory is of great importance. However, non-stationary non-Markovian effects can manifest themselves rather weakly in the kinetics of the considered bimolecular reaction in the region of implementation of the Markovian theory.

Size-Dependent Activity of Platinum Nanoparticles: Theoretical Insights from CO Adsorption and Methanol Dehydrogenation

✉ **Svetlana S. Laletina**[1,2], **Mikhail Mamatkulov**[2], **Aleksey M. Shor**[1],
Elena A. Shor[1],**Vasily V. Kaichev**[2], **Ilya V. Yudanov**[2,3]

[1]Institute of Chemistry and Chemical Technology (ICCT) SB RAS,
Federal Research Center "Krasnoyarsk Science Center SB RAS"
Russia
[2]Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
[3]Institute of Solid State Chemistry and Mechanochemistry SB RAS
Novosibirsk, Russia

✉ shkulepo@rambler.ru

Size and shape of metal nanoparticles (NPs) determine their properties, including chemical activity. A detailed understanding of if and how the reactivity of such NPs scales with the size is crucial for the rational design of new nanosized catalysts with enhanced catalytic properties [1,2].

Using DFT calculations, the size dependence of CO adsorption was studied on Pt_n clusters, where n = 38–314 atoms. These computational results suggest that a nanosized transition to a pronounced higher (comapred to single-crystal) adsorption activity occurs for Pt NPs at particle size ca. 200 Pt atoms. To elusidate the structural effects connected with low-coordinated sites on the particle edges and vertexes, the concept of generalized coordination numbers was adapted to include the second coordination sphere [2].

Further, the size and structure effects on Pt nanoparticles were studied using methanol dehydrogenation as a model surface reaction [3]. The effect of cluster morphology is manifested by higher adsorption energy of the COH_x intermediates on vertexes and edges of model nanoparticles compared to the close-packed terraces. Moreover, due to the size effect, the adsorption sites of Pt_{79} nanoparticles (1.2 nm in diameter) exhibit considerably higher adsorption activity than the same sites of Pt_{201} (1.7 nm). Thus, particles with a size of ca. 1 nm are shown to be more active due to the superposition of two effects: (i) higher surface fraction of low-coordinated adsorption sites, and (ii) higher activity of these sites compared to particles with a size of ca. 2 nm.

[1] Yudanov I. V., Genest A., Schauermann S., Freund H. J., Rösch N. (2012). Size Dependence of the Adsorption Energy of CO on Metal Nanoparticles: A DFT Search for the Minimum Value. *Nano Lett.*, *12*(4), 2134–2139.

[2] Laletina S. S., Mamatkulov M., Shor E. A., Kaichev V. V., Genest A., Yudanov I. V., Rösch N. (2017). Size-Dependence of the Adsorption Energy of CO on Pt Nanoparticles: Tracing Two Intersecting Trends by DFT Calculations. *J. Phys. Chem. C*, *121*(32), 17371–17377.

[3] Laletina S. S., Mamatkulov M., Shor A. M., Shor E. A., Kaichev V. V., Yudanov I. V. (2022). Size and Structure Effects on Platinum Nanocatalysts: Theoretical Insights from Methanol Dehydrogenation. *Nanoscale*, *14*, 4145–4155.

Influence of Subsurface Carbon on Methane Oxidation on Pd(100)

✉ **Svetlana S. Laletina**[1,2], **Vasily V. Kaichev**[2]

[1] Institute of Chemistry and Chemical Technology SB RAS,
Federal Research Center "Krasnoyarsk Science Center SB RAS"
Krasnoyarsk, Russia
[2] Boreskov Institute of Catalysis
Novosibirsk, Russia

✉ shkulepo@rambler.ru

The catalytic oxidation of methane over Pd-based materials is a very important industrial process [1–3]. Today approximately 23 % of electricity in the world is produced by combustion of natural gas that mainly consists of methane [3]. Under the reaction conditions not only palladium oxide, but also palladium carbide can be formed [2]. Changing the state of palladium affects its catalytic properties. In this work, we consider the effect of dissolved carbon on the reaction mechanism of methane oxidation on palladium using theoretical calculations. The calculation was performed by the Vienna *ab initio* simulation package VASP using a Pd(100) slab-model.

We developed a mechanism of methane oxidation based on 17 elementary steps. The mechanism takes into account the dissociative adsorption of methane and oxygen on metallic palladium, dissolution of carbon into subsurface layers, formation of palladium carbide, and formation of the main reaction products: CO, CO_2, H_2, and H_2O. Thermal effects and activation energies of individual steps were calculated for pure palladium and palladium with dissolved carbon in the octahedral cavities of the metallic palladium lattice. In full agreement with the literature data, the position of C atoms in the octahedral centers is found to be energetically more favorable in comparison with the smaller tetrahedral centers. The effect of C_{sub} is manifested by lower adsorption energy of intermediates compared to clean surfaces. The presence of C in the subsurface layer of Pd lowers the adsorption energies of the intermediates of the methane decomposition/oxidation reaction by up to 0.4 eV, excepting adsorption of water molecule. The endothermicity of the first ($CH_4 \rightarrow CH_3 + H$) and last stages of methane decomposition ($CH^* \rightarrow C^* + H^*$) increases by about 0.3 eV, transforming the latter from exothermic to weakly endothermic. The activation barrier of the last stage of decomposition also increases by 0.3 eV. In addition, the presence of C_{sub} facilitates the removal of CO_2 and H_2O from the surface.

Thus, we can conclude that the dissolved carbon in the subsurface layers of palladium affects on its catalytic activity. It slows down the methane dehydrogenation on the Pd(100) surface, but facilitates oxidation of the intermediates and removal of products from the surface.

[1] Gélin I. P., Primet M. (2002). *Appl. Catal. B: Env.*, *39*(1), 1–37.
[2] Kaichev V. V., Vinokurov Z. S., Saraev A. A. (2021). *Catal. Sci. & Tech., 11*(13), 4392–4397.
[3] Ghosh B. K., Mekhilef S., Ahmad S., Ghosh S. K. (2022). *Sustainability*, *14*, 4036.

Ir Spectroscopic Study and *Ab Initio* Calculations of the Formation of H-Complexes of 1,2,3-Benztriazole with Proton Acceptor Molecules

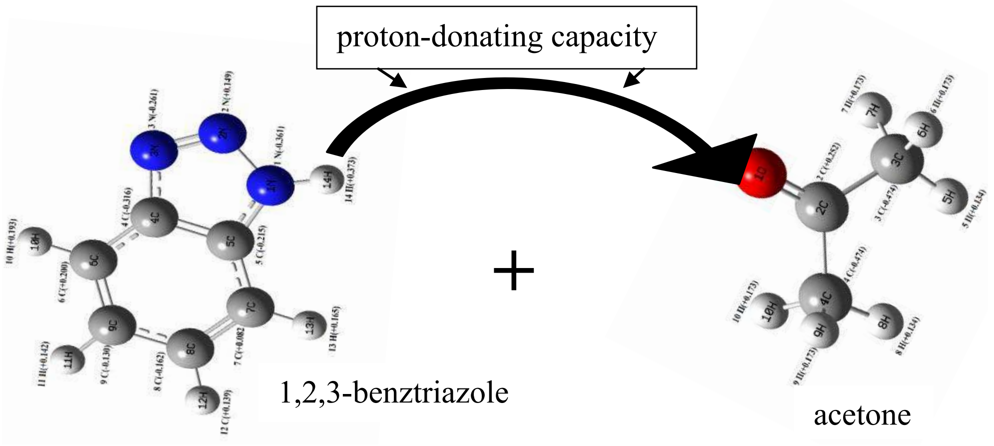
✉ **Nikolai L. Lavrik**

Voevodsky Institute of Chemical Kinetics and Combustion, SB RAS
Novosibirsk, Russia

✉ lavrik@kinetics.nsc.ru

Aromatic heterocyclic compounds (AHC) are widespread in nature and form the basis for many natural biologically active compounds and drugs. In this connection, there is an increasing interest towards studying the donor and acceptor characteristics that determine the degree of participation of heterocyclic compounds in the intermolecular hydrogen (H) bonding.

Among the products of chemical synthesis of AGS, the derivatives of triazole molecules, which have a wide spectrum of pharmacological action, are of significant interest. Due to the relevance of practical application of triazole derivatives, it is of interest to study the proton-donating ability (PDA) of this molecule.



The aim of the present work was to study the efficiency of proton-donating capacity of 1,2,3-benztriazole molecule. The measure of PDS was the value of enthalpy (energy) of H-bond formation between this molecule and acetone, dioxane, DMFA, and DMSO molecules. The H-bond formation energy was determined from the IR spectroscopy data. The molecular structure and charge values of the studied molecules and H-complexes were calculated by the electron density functional method B3LYP/6-31G using the Gaussian software package. As a result, it was found that for 1,2,3-benztriazole molecules the strongest H-bond occurs in the H-complex 1,2,3-benztriazole—DMSO. This result is explained by the fact that during the formation of the H-complex *H-N...O* to the bond *N...O* the greatest charge transfer from the *O* atom takes place. Thus, in the question of the **nature of the H-bond (electrostatic or covalent?)** for the studied H-complexes the contribution of the covalent component should be considered.

A DFT Study of Decomposition of Dinitrosyl Iron Complex $Fe(NO)_2(SCH_2)_2^+$ in Water

✉ **Victor B. Luzhkov**[1,2], **Vladimir B. Krapivin**[1], **Natalia A. Sanina**[1,2]

[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia
[2] *Lomonosov Moscow State University*
Moscow, Russia

✉ vbl@icp.ac.ru

The iron-sulfur-nitrosyl complexes have interesting chemical and biological properties and such promising biomedical applications as nitric oxide (NO) donors [1]. In this report we consider the mechanisms of anaerobic decomposition in water [2] of a model cationic dinitrosyl iron complex (DNIC) $Fe(NO)_2(SCH_2)_2^+$ (**1**) with a small thioformaldehyde ligand using the density functional theory (DFT) methods and polarizable continuum model of water. The electronic structures and harmonic frequencies of molecules have been calculated using the M06 and TPSSH functionals and the def2-TZVP basis set. In the DFT calculations of electronic structures and molecular properties, the polar solute-solvent interactions had been included in the SCF equations for solute. The explored reaction paths involve reactions of ligand abstraction and replacement by water molecules, and dimerization of intermediate products. Search of the equilibrium structures and transition states (TS) along the reaction paths was performed. In calculations of molecular geometries of known DNIC, TPSSH gives better agreement with the experimental Fe–S bond lengths than M06. The coordination patterns of the central iron change in course of reactions from three to four and five ligands in intermediate products. The atomic vibrations corresponding to imaginary frequencies in TS are in line between Fe and the atom S of the leaving SCH_2 group.

The free-energy calculations have predicted that the concerted associative mechanism of the thioformaldehyde ligand removal has a ~10–20 $kJ{\cdot}mol^{-1}$ lower activation barrier in water than cleavage of coordination Fe–S bond in dissociative mechanism. The dimerization of the intermediate products in dissociative path is uphill in the Gibbs free energy by several tens $kJ{\cdot}mol^{-1}$. The replacement of NO by H_2O under anaerobic conditions is thermodynamically unfavorable compared to the hydrolysis of thioformaldehyde. Large differences between the reaction potential energies in TPSSH and M06 results are alleviated by the inclusion dispersion correction in the TPSSH calculations. In general, the found data have demonstrated the importance of inclusion of solvent effects in calculations of molecular structures.

[1] Vanin A. F. (2021). *Int. J. Mol. Sci.*, *22*, 10356.

[2] Krapivin V. B., Luzhkov V. B., Sanina N. A., Aldoshin S. M. (2022). *Mendeleev Com.* (accepted, in press)

Modeling of the Transformation of Glucose into 1,6-anhydro-beta-D-glucopyranose

✉**Sergey G. Mamylov, Igor O. Lomovsky, Oleg I. Lomovsky**

Institute of Solid State Chemistry and Mechanochemistry SB RAS
Novosibirsk, Russia

✉mamylov@solid.nsc.ru

The interaction of quercetin with glucose in order to obtain glycoside is the way to improve the transport of flavonoid in biological systems. Solid state synthesis by mechanochemical activation of quercetin and glucose reagents makes it possible to simplify the synthesis of glycosides. The thermal analysis of the reaction mixture shows that the initial stage of thermal interaction is the primary transformation of glucose.

The mass loss of the sample corresponds to the cleavage of one water molecule from a glucose molecule. The analysis of the literature shows that one of the probable products of primary glucose transformation is 1,6-anhydro-beta-D-glucopyranose, known as levoglucosan. The reaction of glucose dehydration with the formation of levoglucosan and a water molecule was considered.

Quantum chemical modeling (Gaussian-09, b3lyp/6-31G* method, SSCC SB RAS) of beta-D-glucopyranose and levoglucosan was carried out. An assumption about the location of this molecule in the system of products was made. Next, the Gibbs potential of the reagent and products was calculated by the Gaussian. At the next stage, the transition state of the transformation of glucopyranose into levoglucosan was determined. Transition state is the initial glucopyranose ring with a modified and noticeably shifted primary alcohol carbon atom C6. The latter forms a grouping of C6 with its adjacent hydroxyl group and the hydroxyl group of the carbon atom C1 shifted towards it. The Gibbs energy values were obtained along the reaction path from the reagent, through the transition state to the product for the transformation process “glucose-levoglucosan”.

Acknowledgements: the work was supported by the RNF grant No. 21-13-00046 and Project of ISSCM SB RAS No. FWUS-2021-0005. This study was conducted using the resources of the General-Purpose Computing Center “Siberian Supercomputer Center,” Institute of Computational Mathematics and Mathematical Geophysics SB RAS.

Theoretical Study of Conductance through Monoatomic Nanowires

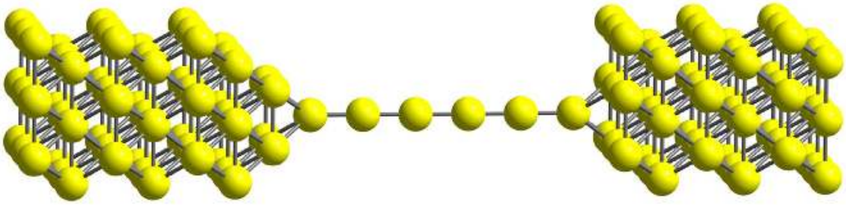
✉**Irina V. Mirzaeva**, **Svetlana G. Kozlova**

Nikolaev Institute of Inorganic Chemistry SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉dairdre@gmail.com

Molecular electronics attract an increasing interest of researchers from various fields of science. Advances in the field of cluster chemistry make it possible to synthesize the systems which can be considered promising molecular devices [1]. However, modeling of electronic transport through such systems is a rather difficult task. A common simplification is the use of monoatomic wires as electrodes. However, the properties of the monoatomic nanowires themselves are not yet sufficiently studied.

Here we present the theoretical studies of geometry, electronic structure and transport properties of Cu, Ag, Au and Pt monoatomic nanowires. Geometry and electronic structure were studied using the BAND 2021 program [2], including both scalar and spin-orbit levels of relativistic corrections. Transport properties of monoatomic nanowires between bulk electrodes (see Fig.) were studied with the SIESTA package [3] using the non-equilibrium Greens functions approach including only scalar relativistic effects.



Monoatomic nanowire between bulk contacts

Acknowledgements: the work was supported by the Russian Science Foundation (project No. 22-23-00245).

[1] Gabuda S. P., Kozlova S. G., Mironov Yu. V., Fedorov V. E. (2009). *Nanoscale Res Lett, 9*, 1110–1114.

[2] BAND 2021, *SCM, Theoretical Chemistry*. Vrije Universiteit, Amsterdam, The Netherlands. http://www.scm.com.

[3] *SIESTA 4.1.5*, http://siesta-project.org/.

Jahn–Teller Exchange Clusters in “Breathing” Crystals. The Theory of Thermo- and Photoinduced Spin Crossover-Like Transitions

✉**Vitaliy Morozov**

International Tomography Center SB RAS
Novosibirsk, Russia

✉moroz@tomo.nsc.ru

Compounds of “breathing” crystals family [1] containing the Jahn—Teller exchange clusters are well-known for the ability to demonstrate numerous spin crossover-like transitions. The transitions can be induced by the change of temperature, photo illumination or applying external pressure. On the basis of the random field distributions approach developed in the Ising magnets theory, we suggest a new theoretical description of thermal transitions for these molecular systems. The developed approach involves not only pure crystals, but also the case of random impurities of the non-Jahn—Teller metals in the “breathing’ crystals. The impurities decrease the cooperative effects in thermal transitions of the Jahn—Teller exchange clusters making the transitions smoother.

Interaction of polymer chains is known to be one of the important physical factors affecting magneto-structural transitions in “breathing” crystals compounds. We show the inclusion of inter-chain interaction can result not only in strengthening spin crossover like cooperative transitions of exchange clusters, but sometimes to slow down the thermal transitions [2].

Relaxation kinetics of photoexcited states in “breathing” crystals usually manifest a *self-decelerating character* in contrast to analogue of this phenomenon—the LIESST effect (Light-Induced Electron Spin-State Trapping [3]) well-studied for the Fe(II) spin-crossover compounds. The self-decelerating kinetics phenomenon is associated with a few relaxation rates of different types of photo-excited states in the crystals.

The suggested kinetic approach qualitatively explains the difference of relaxation kinetics at various initial excitation intensity observed in the experiments on photoexcitation of “breathing” crystals [4].

We also discuss an additional mechanism of the polychromatic relaxation observed due to a macroscopic distribution of relaxation rates inside the inhomogeneously photoexcited samples of “breathing” crystals.

[1] Ovcharenko V. I., Bagryanskaya E. G. (2013). *Spin-Crossover Materials. Properties and Applications*; Ed. M. A. Halcrow, pp. 239–280. Wiley.

[2] Morozov V. A., Sagdeev R. Z. (2017). *Russ. Chem.Bull. (Int. Ed.), 66*(2), 201–207.

[3] Hauser A. (2004). *Top. Curr. Chem., 234*, 155–198.

[4] Fedin M. V., Maryunina K. Yu., Sagdeev R. Z., Ovcharenko V. I., Bagryanskaya E. G. *Inorg.Chem., 51*(1), 709–717.

Electronic Structure of Halogen-Substituted Zinc Phthalocyanines

✉ **Anton S. Nizovtsev**

Nikolaev Institute of Inorganic Chemistry SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉anton.nizovtsev@gmail.com

Owing to their unique physical and chemical properties, transition metal(II) phthalocyanines (MPc) are widely used in various hi-tech fields, such as molecular electronics, sensorics, and solar energy conversion. The electronic structure features of metal phthalocyanines depends on the nature of the central atom and substituents in the macrocycle, which allows one to tune properties of MPc-containing functional materials.

In this contribution, the electronic structure of unsubstituted and halogen-substituted zinc phthalocyanines, ZnPcX_n (X = F, Cl, Br, I; n = 0, 4, 8, 16), are systematically studied with the use of the advanced methods of quantum chemistry allowing us to accurately predict the positions of electronic energy levels of such complex chemical systems. The impact of the introduction of halogen atoms into the phthalocyanine core of considered compounds on their molecular and electronic structure features are established and discussed.

Acknowledgements: the work was supported by the Russian Science Foundation (project No. 21-73-00276).

Determination of Thermodynamic Stability of $pTol_2S_2$ Polymorphs at High Pressures Using Computational Techniques

Valeriya Yu. Smirnova, ✉Denis A. Rychkov

Institute of Solid State Chemistry and Mechanochemistry SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉rychkov.dennis@gmail.com

The study of molecular crystals under pressure is an important direction in modern solid state chemistry, as it helps to obtain new phases, study individual interactions, and better understand the nature of crystal structures formation [1]. While experimental data is critical at high pressure, a complete experimental screening of a compound for polymorphism is very resource intensive, thus, there is a growing need to support theoretical work. Organic disulfides are interesting for obtaining multifunctional lubricant additives based on them. Di-p-tolyl disulfide $(CH_3{-}C_6H_4{-}S{-})_2$, also called $pTol_2S_2$, is a typical lubricant, thus, extreme conditions are important for possible phase transitions.

The experimental work shows that when $p\text{-}Tol_2S_2$ single crystals are compressed at pressures above 1.6 GPa, the α-phase that is stable at low pressures passes into the high-pressure β phase. Recrystallization of single crystals at pressures above 0.45 GPa transforms the α-phase into a more stable γ-phase under given conditions [2]. These experiments show structural, but not thermodynamic stability ranges.

The aim of this study was to determine the regions of thermodynamic stability of di-p-tolyl disulfide $(CH_3{-}C_6H_4{-}S{-})_2$ polymorphs in the 0.0–3.0 GPa pressure range using various computational methods, including FF and DFT [3].

In this work we show how different computational methods can be used to define thermodynamic stability of different phases. Alpha form proves to be the most stable in the range under 0.30 GPa, while beta and gamma phase are comparable in energy in 0.3–0.4 GPa, followed by preferable gamma phase in the next pressure region of 0.4–3.0 GPa. Transition state energies for all phase transitions were roughly estimated from phase diagram.

Acknowledgements: this work was supported by the FWUS-2021-0005 project.

[1] Orgzall I., Emmerling F. et al. (2008). *J. Phys. Condens. Matter.*, *20*, 295206.
[2] Sobczak S., Katrusiak A. (2017). *J. Phys. Chem. C.*, *121*, 2539–2545.
[3] Rychkov D. A. (2020). *Crystals*, 2020, *10*, 81.

Computational Study of Direct Chemical Phenol Glycosylation Mechanism

Irina S. Tretyakova[1,2], ✉**Denis A. Rychkov**[1,3], **Alexander S. Kil'met'ev**[4], **Igor O. Lomovsky**[1]

[1] *Institute of Solid State Chemistry and Mechanochemistry SB RAS*
Novosibirsk, Russia
[2] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS*
Novosibirsk, Russia
[3] *Novosibirsk State University*
Novosibirsk, Russia
[4] *Novosibirsk Institute of Organic Chemistry SB RAS*
Novosibirsk, Russia

✉rychkov.dennis@gmail.com

Glycosylation is a chemical reaction between a carbohydrate and another molecule with any functional group which can act as a glycosyl acceptor forming *glycoconjugate* as a reaction product. Glycoconjugates are extremely important for different fields, including biochemistry, organic synthesis, pharmaceutics, etc. [1]. This type of chemical species is extensively studied in terms of drug delivery and dietary supplements due to the significant improvement of solubility and bioavailability of different small biologically active molecules, such as flavonoids, provided by it [2].

Nevertheless, classical organic synthesis of glycosylated flavonoids, including flavonoid rutin, contains multiple stages and is complicated by the necessity to protect flavonol molecules from oxidation in the liquid phase. Direct solid-state synthesis of glycosylated flavonol and its derivatives, if possible, may resolve this issue. Thus, the aim of this study was to evaluate the possible reaction path of flavonols with carbohydrates using the reaction between glucose and phenol as a simple model, calculate energy barriers and estimate stable products using the modern DFT approach.

The present work provides a clear view of the reaction mechanism and particular path of phenol direct chemical glycosylation through the formation of glucose carbocation (C_1 carbocation with free *p*-orbital is attacked by phenyl -OH group), providing formation of C-O bond and H^+ proton migration to the nearest functional group. All performed calculations prove the concept of possible direct glycosylation of flavonols in the solid state using the mechanochemical synthesis, which coincides with our preliminary results on quercetin [3].

Acknowledgements: this work was funded by the Russian Science Foundation (project no. 21-13-00046).

[1] Colombo C., Pitirollo O. et al. (2018). *Molecules*, *23*, 1712–1720
[2] Magar R. T., Sohng J. K. (2020). *J. Microbiol. Biotechnol*, *30*, 11–20.
[3] Orlov D. V., Lomovsky O. I. et al. (2018). *IOP Conf. Ser. Mater. Sci. Eng.*, *292*.

Computational Study of Elastic, Brittle and Plastic 4-Bromophenyl 4-Bromobenzoate Crystals via the Molecular Mechanics Approach

Ilona A. Isupova, ✉Denis A. Rychkov

Institute of Solid State Chemistry and Mechanochemistry SB RAS
Novosibirsk, Russia
Novosibirsk State University
Novosibirsk, Russia

✉rychkov.dennis@gmail.com

The phenomenon of different mechanical properties of molecular crystal polymorphs which bother attention of multiple research groups is relatively new [1]. Current research methods in this area are mainly experimental, involving X-ray diffraction, vibrational spectroscopy and surface methods. Nevertheless, computational methods may answer multiple questions of these phenomena, including the exact estimation of intermolecular interactions in crystal structures. Current theoretical explanation is vague and does not contain quantitative criteria [2]. In this work, we implement simple molecular mechanics (MM) methods for studying the phenomena of different mechanical properties of 4-bromophenyl 4-bromobenzoate polymorphs.

This system contains three polymorphs with known crystal structures which were studied experimentally and theoretically [3; 4]. Our idea was focused on applying different theoretical methods to these structures: classical crystallographic analysis, the BFDH morphology prediction model, calculation of intermolecular energies using the MM method.

Preliminary results show different stability of the three forms, thus, coinciding well with the literature data. For two forms of 4-bromophenyl 4-bromobenzoate, distinct layers were found and their energies (as well as interlayer energies) were calculated. Interlayer energy as a function of distance between layers was calculated for two forms. The observed energies were correlated with macroscopic properties of 4-bromophenyl 4-bromobenzoate polymorphs and previous experimental and theoretical studies.

Acknowledgements: this work was supported by the Russian Science Foundation (grant No. 21-73-00094, https://rscf.ru/en/project/21-73-00094/).

[1] Reddy C. M., Gundakaram R. C. et al. (2005). *Chem. Commun.*, *1*, 3945–3947.
[2] Reddy C. M., Padmanabhan K. A. et al. (2006). *Cryst. Growth Des.*, *6*, 2720–2731
[3] Saha S., Desiraju G. R. (2018). *Chem. Commun.*, *54*, 6348–6351.
[4] Masunov A. E., Wiratmo M. et al. (2020). *Cryst. Growth Des.*, *20,* 6093–6100.

New Vision of Spin Nutation

✉**Kev M. Salikhov**

Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center RAS
Kazan, Russia

✉kevsalikhov@mail.ru

It is shown that the Torrey nutation theory based on the Bloch equations for the magnetization vector, in principle, cannot be used to describe the "nutation" of interacting spins (including the splitting of spin energy levels in a zero magnetic field). The Bloch equations assume that the vector of the magnetic moment of the spins completely sets the state of the spins. But this is true only for non-interacting particles with the spin $S = 1/2$. Using the example of the simplest system with the spin $S = 1$, a systematic consideration of the response ("nutation") of spins to the sudden activation of an alternating magnetic field was carried out. A detailed analysis of the dependence of "nutation" is carried out on the spin-spin interaction and the nature of the excitation of spins by an alternating field. Under the conditions when spin-spin interactions are comparable to the energy of interaction of spins with an alternating field, the motion of spin magnetization is described as a sum of contributions oscillating with different frequencies which are equal to the frequencies of transitions between the spin-Hamiltonian eigenstates in a rotating coordinate system.

For the first time, the Heisenberg's mathematical apparatus was used to describe the "nutation" of spins. In this approach, the equations of motion are written directly for the quantities measured in the experiment. For spins, the complete orthogonal set of quantities is the dipole moment and multipole polarizations. To demonstrate the potential of this description of "nutation", a specific case of paramagnetic particles with spin $S = 1$ is considered. Taking into account the splitting energy in a zero magnetic field, the associated equations of motion for the dipole and quadrupole moments are obtained. They can be called generalized equations of the magnetic polarization of spins. These equations show that in the presence of spin-spin interactions, a reversible mutual transformation of dipole and quadrupole moments occurs. This leads to oscillations of the length of the spin magnetization vector, the projections of which are usually observed in the experiment. Therefore, the oscillations of the magnetization projections observed in the experiment reflect both nutation of the magnetization vector and modulation of the length of this vector due to the mutual transformation of the observed dipole polarization, and the quadrupole polarization is not observed in conventional experiments.

Palladium Atoms and Clusters at Ceria Nanoparticles: A DFT Study

✉**Elena A. Shor**, **Aleksey M. Shor, Vladimir A. Nasluzov**

Federal Research Center “Krasnoyarsk Science Center SB RAS”,
Institute of Chemistry and Chemical Technology SB RAS
Krasnoyarsk, Russia

✉eshor1977@gmail.com

CeO_2-based materials are well-known for their catalytic activity in various industrial processes. Peculiar catalytic properties of ceria are attributed to the high mobility of its lattice oxygen. Transition metal atoms supported at ceria surface or incorporated in its framework can further enhance the redox performance and oxygen storage capacity of CeO_2. In turn, cerium oxide can affect the properties of adsorbed metal species, in particular, favors to the dispersion of metal particles and suppresses their sintering at elevated temperatures. In line with the experimental techniques, computational modelling is often utilized to investigate elementary processes occurred at the ceria surface [1]. Present theoretical study is aimed at evaluating of oxygen vacancy formation energy—a measure of lattice oxygen mobility—in dependence of the nature of adsorbed metal atom (Pd or Ag), size of the metal particle (atomic or tetrameric) and its position (intra- of extraframework). The denucleation of M_4 metal moieties at oxide surface is modelled as well.

Surface sites of the CeO_2 substrate were represented by a stoichiometric nanoparticle $Ce_{21}O_{42}$ exposing {100} and {111} nanofacets. A generalised-gradient corrected exchange-correlated functionals PW91 and PBE were utilised with the Hubbard-type on-site corrections U ($U = 4$) for Ce4f states providing an improved description of the Ce^{3+} ion formation in redox transitions [2].

As previously was found for Ag particles [3], the adsorption of Pd atom and $Pd_{2\text{-}4}$ clusters is about 2 times stronger at O_4-pocket of the {100} facet of the $Ce_{21}O_{42}$ model than at its {111} facet. The adsorption energies of Pd and Pd_4 species at a partially reduced ceria nanoparticle $Ce_{21}O_{41}$ are by 1 eV smaller. Our calculations show that palladium clusters Pd_2-Pd_4 anchored at {100} facet are readily decomposed via the migration of one atom to the {111} facet. The activation barriers for such processes are low, and stability of the newly formed denucleated structures is high. Extraframework Pd moieties disfavors formation of O vacancies. This effect is more pronounced for single atoms and is reduced for Pd clusters. On the opposite side, intraframework Pd species results in spontaneous depletion of the first O atom and reduces the formation of the second O vacancy.

[1] Bruix A., Neyman K. M. (2016). *Catal. Lett.*, *146*, 2053–2080.

[2] Nasluzov V. A., Ivanova-Shor E. A., Shor A. M., Laletina S. S., Neyman K. M. (2021). *Materials*, *14*, 6888.

[3] Nasluzov V. A., Ivanova-Shor E. A, Shor A. M., Neyman K. M. (2019). *Surf. Sci.*, *681*, 38–46.

Magnetostructural Correlations in Magnetoactive Chain-Polymer Cu(II) Complexes with Alkyl-Pyridyl-Substituted Nitronyl Nitroxides

Svyatoslav E. Tolstikov[1], ✉**Kristina A. Smirnova**[1,2], **Gleb A. Letyagin**[1],
Artem S. Bogomyakov[1], **Galina V. Romanenko**[1], **Victor I. Ovcharenko**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia

✉k.smirnova@tomo.nsc.ru

Complexes of Cu(hfac)$_2$ (hfac — hexafluoroacetylacetonate) with pyridyl-substituted nitronyl nitroxide radicals exhibit magnetic effects similar to the classical spin crossover [1]. Thereby, such systems are promising materials for sensible molecular devices. To obtain complexes with desired magnetic properties, it is crucial to study how the structure of the complex affects the character of its spin transition.

The purpose of this work is to study magnetostructural correlations in new Cu(hfac)$_2$ complexes with alkyl-pyridyl-substituted nitronyl nitroxide radicals L^R (R = Me, MeO, and Et; *i*-Pr, *n*-Pr, *n*-Bu and cyclopenthyl — CP) by magnetic measurements and X-ray crystallography.

X-ray crystallography experiments proved that centrosymmetric dimers {[Cu(hfac)$_2$L^R]$_2$} bonded by {Cu(hfac)$_2$} fragments form the chain-polymer {[Cu(hfac)$_2$L^R]$_2$[Cu(hfac)$_2$]}$_n$ structure of the investigated compounds. The tridentate bridging radical is coordinated by oxygen atoms of the nitroxyl fragment and a nitrogen atom of the pyridine ring. Magnetic measurements showed a significant reduction of the effective magnetic moment μ_{eff} under temperature decrease, indicating the presence of the magnetic transition. For complexes with L^R, where R = Et, *n*-Pr, *i*-Pr, CP, the transition occurs at 220, 190, 170, and 300 K respectively, while for L^{Me}, L^{MeO}, $L^{n\text{-Bu}}$ the transition is incomplete at temperatures up to 350 K.

The structural data obtained at 335–30 K proved the radical shifts from axial to equatorial orientation only in the dimer fragments. This process facilitates the strong antiferromagnetic exchange coupling between spins of the paramagnetic sites. We revealed that the phase transition temperature correlates with the temperature at which the disorder of an alkyl substituent vanishes.

Acknowledgements: this work was supported by the Russian Foundation for Basic Research (project No 18-13-00380).

[1] Tolstikov S. E. et al. (2015). *Polyhedron*, *100*, 132–138.

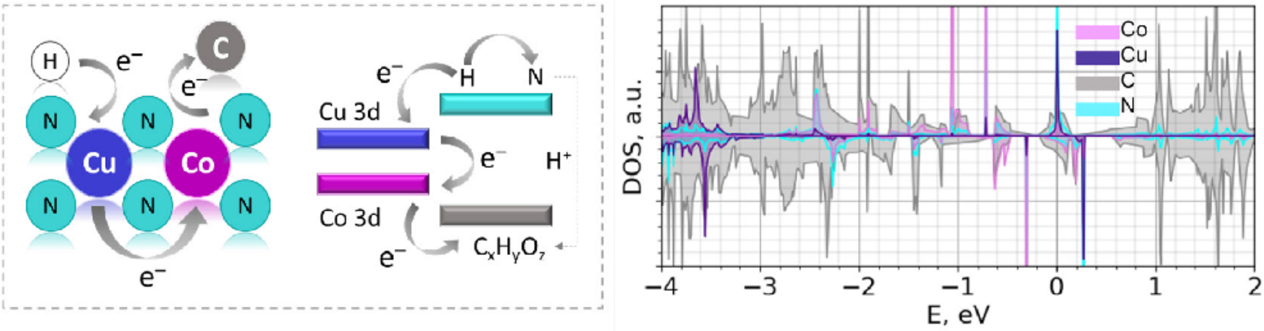
Targeted Electronic Structure Modification in Catalysis: A Case Study of Dual-Metal Catalyst for CO Hydrogenation

✉**Olga A. Syzgantseva**, **Maria A. Syzgantseva**

Lomonosov Moscow State University
Moscow, Russia

✉osyzgantseva@gmail.com

The targeted modification of chemical and electronic structure of hybrid organic-inorganic compounds is a powerful tool for modulating the properties of materials in various applied fields [1], including catalysis where it can be used to decrease the reaction barriers and alternate its pathways. The mixed-metal strategy has a peculiar place among such approaches [2], since it allows one to easily change the reducibility characteristics of a catalytic material [3], including the ionization potentials and work-function, as well as electron localization and adsorption patterns of the reaction intermediates [1–4]. This is particularly important for the redox reactions [4–5], such as CO hydrogenation. In this report, the chemical approaches [1–3] for targeted electronic structure modification are outlined and further illustrated by the case of the CoCu dual-metal nitrogen-doped graphene-based (Cu/Co-CN) catalyst for selective formation of ethanol from syngas. The synergistic effect of Co and Cu increases the density-of-states near the Fermi level and facilitates the electron injection towards the adsorbates, which provides for reaching a space-time yield toward $C_{2+}OH$ of 851.8 mg/(g·h), ranking this catalyst among the best in this class [5].



Electronic structure features and working principles of the Co/Cu-CN catalyst

Acknowledgements: Lomonosov Moscow State University and Siberian Supercomputer Centers are gratefully acknowledged for providing supercomputer facilities.

[1] Syzgantseva M. A. et al. (2020). *ACS Appl. Mater. Interfaces*, *12*, 17611–17619.
[2] Syzgantseva M. A. et al. (2019). *JACS, 141*, 6271–6278.
[3] Helali Z. et al. (2017). *Theor. Chem. Acc.*, *136*, 100.
[4] Syzgantseva O. A. et al. (2012). *J. Phys. Chem. C*, *116*, 6636–6644
[5] Chen G. et al. (2022). *CCS Chemistry*, DOI: https://doi.org/10.31635/ccschem.022.202201930.

Si(111) Strained Layers Structure on Ge(111) Surface

✉**Ruslan A. Zhachuk**[1], **José Coutinho**[2], **Vasily A. Cherepanov**[3,4], **Bert Voigtländer**[3,4]

[1]*Institute of Semiconductor Physics SB RAS*
Novosibirsk, Russia
[2]*Department of Physics & I3N, University of Aveiro, Campus Santiago*
Aveiro, Portugal
[3]*Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich*
Jülich, Germany
[4]*ARA-Fundamentals of Future Information Technology*
Jülich, Germany

✉zhachuk@gmail.com

The importance of stress and strain fields on surface physics is well recognized. They can have a strong impact on surface reconstruction, stability of surface planes, step bunching, and surface diffusion. The close chemistry of Si and Ge, combined with a lattice mismatch of about 4 %, make the Ge/Si system a prototypical model to study the effect of interfacial elastic strain. Ge epitaxy on Si(111) has been extensively studied and follows the Stranski-Krastanov growth mode. Here, the formation of compressively strained Ge islands on Si(111) substrates has attracted much interest due to their prospective use as template structures in nanoelectronics and nanophotonics.

However, the film growth at the tensile strain is much less studied. As a model system, we studied the growth of tensile strained Si(111) on the Ge(111) surface by first principles calculations combined with low-energy electron diffraction and scanning tunneling microscopy [1]. We show that the calculated Si(111) surface reconstructions and their respective energy ordering as a function of strain match the experimental observations. Namely, it is shown that under tensile strain the Si(111) surface exhibits domains of adatom-based $c(2\times4)$ reconstruction, separated by domain walls. This contrasts with the relaxed and compressive strain regimes where dimer-adatom-stacking fault structures are seen. An atomic model for the domain wall that separates neighboring $c(2\times4)$ domains is proposed, showing low surface energy and good agreement with the experimental microscopy and diffraction data. According to the calculations, the formation of domain walls on a pure Si(111) surface always implies an energy penalty, suggesting that their appearance is unfavorable under thermodynamic equilibrium conditions. We suggest that Ge/Si intermixing can stabilize the domain walls, hence explaining this apparent contradiction.

[1] Zhachuk R., Coutinho J., Dolbak A., Cherepanov V., Voigtländer B. (2017). *Physical Review B*, *96*, 085401.

Pentamer with Interstitial Atom as the Universal Building Block of (110), (331), (113) Silicon and Germanium Surfaces

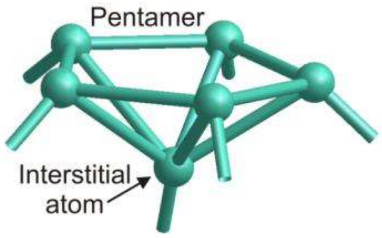
✉**Ruslan A. Zhachuk**[1], **Alexander A. Shklyaev**[1,2], **José Coutinho**[3]

[1] *Institute of Semiconductor Physics SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia
[3] *University of Aveiro*
Aveiro, Portugal

zhachuk@gmail.com

Due to the technological importance, semiconductors Si and Ge have been a benchmark for studying surface physics. The major stable surfaces of Si and Ge are: (001), (111), (110), (113) and (331). These surfaces are reconstructed, i.e., the topology of interatomic bonds between the surface atoms is different from that in crystal bulk. While the structure of clean (001), (111) and (113) surfaces is the most studied, and their atomic and electronic structures are well-established, much less was known about the structure of (110) and (331) surfaces.

In this series of works [1-9] we solved the building block structure of (110) and (331) silicon and germanium surfaces from the first-principles calculations based on the density functional theory and a comparison of results with the available experimental scanning tunneling microscopy and spectroscopy data. The building block structure consists of an interstitial atom that holds together five atoms of the surrounding pentamer (see Fig.), and a closely integrated rebonded area. The interstitial atom forms six covalent bonds with its nearest neighbors, which is not typical for the atoms of group IV elements such as Si and Ge. The formation of pentamers with interstitial atoms on (110) and (331) surfaces is similar to the one previously found on (113) surfaces of Si and Ge. Thus, we demonstrated that the reconstructed (110), (113) and (331) surfaces form a family, members of which are stabilized by pentamers with interstitial atoms. All their surface structures are consistently described on a single basis.



A pentamer structure

[1] Zhachuk R., Teys S. (2017). *Phys. Rev. B*, *95*, 041412.
[2] Zhachuk R., Coutinho J. (2017). *JETP Letters*, *106*, 346.
[3] Zhachuk R., Coutinho J., Palotás K. (2018). *J. Chem. Phys.*, *149*, 204702.
[4] Zhachuk R. A., Shklyaev A. A. (2019). *Appl. Surf. Sci.*, *494*, 46.
[5] Zhachuk R., Coutinho J. (2019). *J. Exp. Theor. Phys.*, *128*, 94.
[6] Zhachuk R. (2020). *Data in Brief*, *28*, 104847.
[7] Zhachuk R. A., Dolbak A. E., Shklyaev A. A. (2020). *Surf. Sci.*, *693*, 121549.
[8] Zhachuk R. A. (2020). *J. Exp. Theor. Phys.*, *131*, 322.
[9] Zhachuk R. A., Coutinho J. (2020). *Appl. Surf. Sci.*, *533*, 147507.

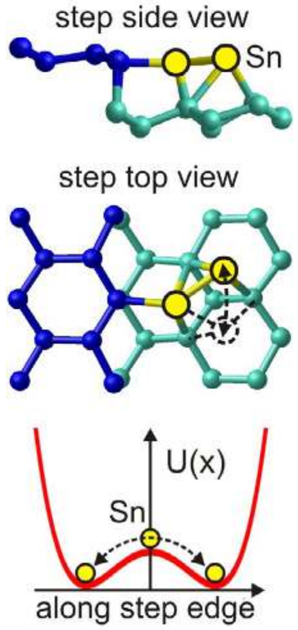
Dynamics of Sn Adatoms at the Single Steps on the Si(111)-$\sqrt{3} \times \sqrt{3}$-Sn Surface

✉**Ruslan A. Zhachuk**[1], **Dmitry I. Rogilo**[1], **Alexey S. Petrov**[1], **Dmitry V. Sheglov**[1],
Alexander V. Latyshev[1,2], **Stefano Colonna**[3], **Fabio Ronci**[3]

[1] *Institute of Semiconductor Physics SB RAS*
Novosibirsk, Russia
[2] *Novosibirsk State University*
Novosibirsk, Russia
[3] *CNR–Istituto di Struttura della Materia*
Roma, Italy

✉zhachuk@gmail.com

Among other chemical elements used in silicon-based heterostructures for micro- and photoelectronic applications, Sn attracts particular interest, since it belongs to the same group as Si and Ge. In this work the atomic structure of well-ordered single steps on the reconstructed Si(111)−$\sqrt{3} \times \sqrt{3}$−Sn surface and the dynamics of Sn adatoms in the vicinity of these steps was studied [1]. The work was performed using low-temperature scanning tunneling microscopy (STM) and *ab initio* calculations based on the density-functional theory (DFT). The STM tip was used to record the tunneling current versus time on top of oscillating adatoms, keeping the feedback loop turned off. The dynamics of adatoms detected as the telegraph noise present in the tunneling current was registered near the steps at $T = 80$ K. The atomic structure model of the single steps consisting of Sn atomic chains along the steps was developed based on DFT calculations and comparison of experimental and calculated data. The results of our calculations show that this structure leads to the formation of potential double wells near the steps acting as traps for Sn atoms (see Fig.). The thermally activated flip-flop motion of Sn atom in the double well explains the fluctuating STM current recorded near the steps.



Atomic structure of a step and schematic of the potential along the step edge

[1] Zhachuk R. A., Rogilo D. I., Petrov A. S., Sheglov D. V., Latyshev A. V., Colonna S., Ronci F. (2021). *Physical Review B*, *104*, 125437.

SPINTRONICS

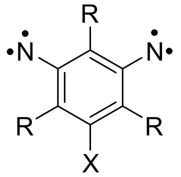
Effect of Spin-Orbit Coupling on the Sign of Magnetic Anisotropy of Quintet Dinitrenes

✉**Alexander V. Akimov**[1], **Denis V. Korchagin**[1], **Anton Savitsky**[2],
Sergei V. Chapyshev[1], **Eugenii Ya. Misochko**[1]

[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russian Federation
[2] *Technical University Dortmund*
Dortmund, Germany

✉shura@icp.ac.ru

In comparison with the conventional EPR spectroscopy (X-band, 9 GHz), the W-band 94 GHz EPR spectroscopy allows one to determine the sign of the ZFS parameters of high spin nitrenes [1; 2]. We report on the W-band EPR spectroscopic studies of dinitrene belonging to a class of quintet 1,3,5-tribromophenylene-2,4-dinitrenes **1c** obtained as in the photolysis of diazide in frozen solution. The main aim of the research was to understand the factors affecting the sign and magnitude of *D* in aromatic tetraradicals with large SOC and quintet spin multiplicity. For this purpose, a number of models phenylenedinitrenes 1b and 1d–f (see Fig.) has been additionally studied by the quantum chemical methods.



1a R = X = H
1b R = Br, X = N_3
1c R = Br, X = F
1d R = Br, X = CN
1e R = Br, X = Cl
1f R = Br, X = Br

Structures of quintet phenylenedinitrenes **1a-f**

In general, our experimental (W-band EPR spectroscopy) and theoretical (quantum chemical calculations and tensor analysis) studies show in which cases high-spin nitrenes may have negative ZFS owing to the presence of heavy atoms at appropriate sites nearby the nitrene centers and exhibit the bistability property as organic single-molecule magnets.

Acknowledgements: the work was financially supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779).

[1] Akimov A. V., Masitov A. A., Korchagin D. V., Chapyshev S. V., Misochko E. Ya., Savitsky A. (2015). W-Band EPR Studies of High-Spin Nitrenes with Large Spin-Orbit Contribution to Zero-Field Splitting. *J. Chem. Phys.*, *143*, 084313.

[2] Korchagin D. V., Akimov A. V., Savitsky A., Chapyshev S. V., Aldoshin S. M., Misochko E. Ya. (2018). Steric Heavy Atom Effect on Magnetic Anisotropy of Triplet Tribromophenyl Nitrenes. *J. Phys. Chem. A.*, *122*, 8931–8937.

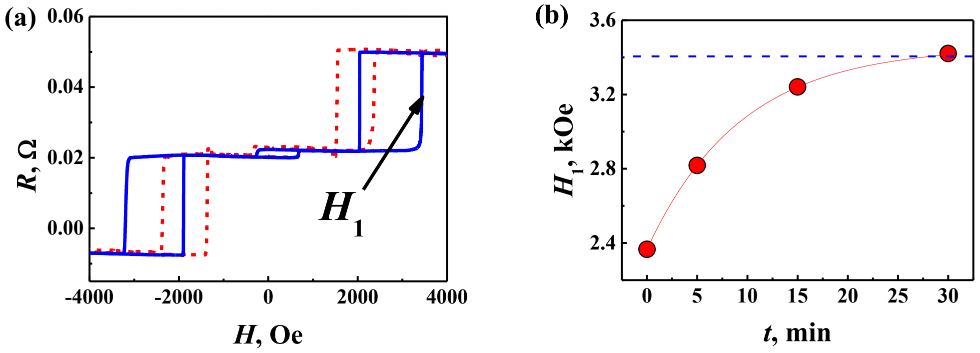
Slow Relaxation of the Anomalous Hall Effect in GdFeCo/Ir/GdFeCo

✉**Maxim V. Bakhmetiev**[1], **Roman B. Morgunov**[1], **Oksana V. Koplak**[1], **Stéphane Mangin**[2]

[1] *Institute of Problems of Chemical Physics*
Chernogolovka, Russia
[2] *Institut Jean Lamour, Université de Lorraine*
Nancy, France

✉bakhmetiev.maxim@gmail.com

Heterostructures GdFeCo/Ir/GdFeCo with two ferromagnetic layers manifest a spin-orbit torque (SOT). These samples are synthetic ferrimagnets (SF) with perpendicular magnetic anisotropy. The angular dependence of resistance allowed us to decompose the resistance to classic, planar and the spin-Hall components. We have analyzed the possibility of magnetization reversal caused by the spin polarized electron current. The SOT-MRAM logic elements are basic for the energy saving magnetoresistive memory [1]. Fig. 1*(a)* shows the dependences of electrical resistance corresponding to the anomalous Hall effect (AHE) on the magnetic field at the same “in-plane” orientation of the magnetic field. Solid line represents field dependence of the in-plane hysteresis of resistivity *R* in the initial sample, and dashed line is the in-plane field dependence *R(H)* in the sample preliminary magnetized in perpendicular orientation and turned to in-plane configuration.



Dependence of electrical resistance on the magnetic field *(a)* In the sample not magnetized before resistance recording (solid line), *(b)* in the sample perpendicularly magnetized in magnetic field 1 T and rapidly turned into the in-plane orientation. Solid line is exponential approximation

Slow (~30 min) relaxation of the coercive field determined from the $R(H)$ dependence is observed upon reorientation of the GdFeCo/Ir/GdFeCo two-layer structure in the magnetic field after saturation of the sample by 1 T (Fig. 1*(b)*).

Acknowledgements: the project was funded by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779).

[1] Shao Q., Li P. et al. (2021). *IEEE Trans. Magn.*, *57*.

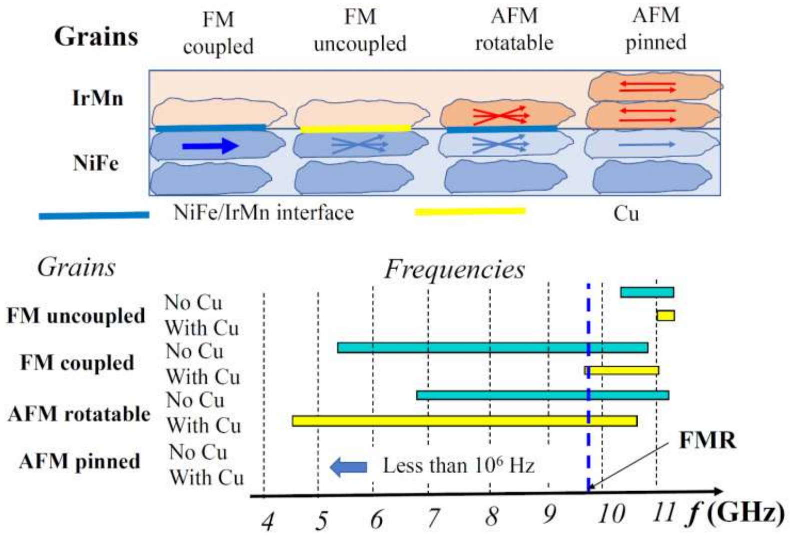
Frequency of Magnetization Reversal of Grains NiFe and IrMn in Exchange-Biased Thin Films NiFe/Cu/IrMn

✉**Maxim V. Bakhmetiev**[1], **Artem D. Talantsev**[1], **Roman B. Morgunov**[1,2]

[1] *Institute of Problems of Chemical Physics*
Chernogolovka, Russia
[2] *Sechenov First Moscow State Medical University*
Moscow, Russia

✉bakhmetiev.maxim@gmail.com

A set of partially uncoupled NiFe/Cu/IrMn exchange biased thin films with variable thickness of non-magnetic Cu spacer is characterized by the ferromagnetic resonance (FMR) and Brillouin light scattering (BLS) techniques applied complementary to reveal the time-scale dependent effects of uncoupling between ferromagnetic and antiferromagnetic layers on high-frequency magnetization dynamics. The results correlate with interfacial grain texture variations and static magnetization behavior. Two types of crystalline phases with correlated microwave response are revealed at the ferro-antiferromagnet interface in NiFe/Cu/IrMn thin films (see Figure).



Schematics of the magnetization reversal frequency ranges determined from FWHM of the grain magnetization reversal energy barrier distributions

The first phase forms as well-textured NiFe/IrMn grains with NiFe (111)/IrMn (111) interface. The second phase consists of amorphous NiFe/IrMn grains. Intercalation of NiFe/IrMn by Cu clusters results in relaxation of tensile strains at the NiFe/IrMn interface leading to larger size of grains in both the NiFe and IrMn layers.

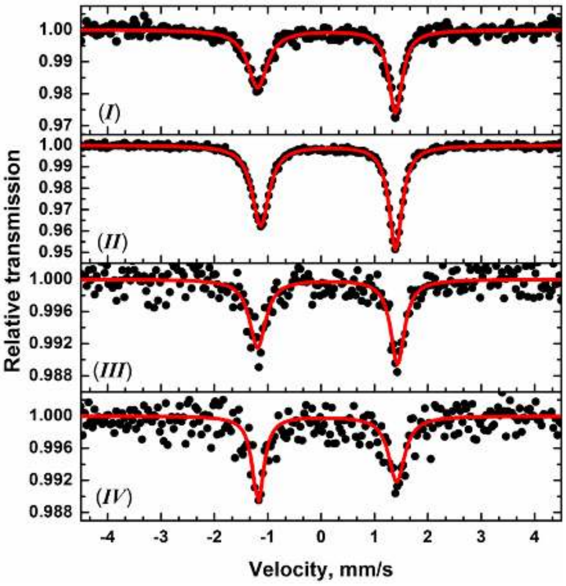
The X-ray Crystallographic and Mössbauer Study of the Halide Salts of $[Fe^{III}(3\text{-}OMe\text{-}Sal_2trien)]^+$ Spin-Crossover Cation

✉**Maxim A. Blagov**[1,2], Nataliya G. Spitsyna[1], Nikolay S. Ovanesyan[1], Sergey V. Simonov[3]

[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia
[2] *Lomonosov Moscow State University*
Moscow, Russia
[3] *Institute of Solid State Physics RAS*
Chernogolovka, Russia

✉max-blagov@mail.ru

The four halide salts of $[Fe^{III}L]^+$ (L=3-OMe-Sal_2trien^{2-}) spin-crossover cation were synthesized for the first time: $[FeL]F\cdot 4H_2O$, $[FeL]Cl\cdot 5H_2O$, $[FeL]Br\cdot 5H_2O$ and [FeL]I. Structures of the salts have $P\bar{1}$ symmetry at 150 K and iron(III)-ligand bond lengths comply with low-spin state (LS, $S = 1/2$). The Mössbauer spectra parameters (ΔE_Q—quadrupole splitting and δ—isomer shift) at room temperature also correspond to the LS electronic configuration of iron(III) center (see Fig). Presumably, the crystal packing features and the halide anion stabilize the LS spin state of spin-crossover cation. Moreover, the new polymorphic LS phase of [FeL]I was revealed, while the previously described LS phase in [1] shows a peculiar correlation between the structure and magnetic properties.



Mössbauer spectra for the *(I)* $[Fe(3\text{-}OMe\text{-}Sal_2trien)]F\cdot 4H_2O$ [ΔE_Q = 2.585(6) mm/s, δ = 0.103(3) mm/s]; *(II)* $[Fe(3\text{-}OMe\text{-}Sal_2trien)]Cl\cdot 5H_2O$ [ΔE_Q = 2.528(2) mm/s, δ = 0.131(1) mm/s]; *(III)* $[Fe(3\text{-}OMe\text{-}Sal_2trien)]Br\cdot 5H_2O$ [ΔE_Q = 2.62(1) mm/s, δ = 0.121(7) mm/s]; *(IV)* $[Fe(3\text{-}OMe\text{-}Sal_2trien)]I$ [ΔE_Q = 2.60(2) mm/s, δ = 0.12(1) mm/s] salts at 296 K. Fit line denotes in red color.

Acknowledgements: this work was performed in accordance with the State Assignment, state registration No. AAAA-A19-119092390079-8, the instrumental base of the Center for Collective Use and the Computer Center IPCP RAS was used. The study was partially carried out within the State Assignment for ISSP RAS.

[1] Shvachko Y. N., Spitsyna N. G., Starichenko D. V. et al., *Molecules*, *25*(21), 4922.

Magnetic Properties of Cobalt Dioxolene Complexes with Tetradentate N-donor Base

✉**Maxim Chegerev**[1], **Denis V. Korchagin**[2], **Andrey G. Starikov**[1], **Nikolay N. Efimov**[3],
Gennady V. Shilov[2], **Vladimir I. Minkin**[1], **Sergey M. Aldoshin**[2]

[1] *Institute of Physical and Organic Chemistry, Southern Federal University*
Rostov-on-Don, Russia
[2] *Institute of Problems of Chemical Physics RA S*
Chernogolovka, Russia
[3] *Kurnakov Institute of General and Inorganic Chemistry RAS*
Moscow, Russia

✉mchegerev@sfedu.ru

Investigation of metal complexes with redox-active ligands (*o*-benzoquinones and their imines) is one of the intensively developing fields of organometallic and coordination chemistry. Valence tautomerism (VT), also called a redox-isomerism, is a unique phenomenon observed in metal coordination compounds that involves a reversible intramolecular electron transfer between a metal center and a redox-active ligand (or ligands), caused by the action of temperature, pressure, irradiation, or electric field. The compounds capable of VT represent promising candidates for the design of molecular switches, photoresponsive devices or key substructures of molecular electronics and spintronics.

In this work, a family of octahedral complexes [(Me_2TPA)Co(36-Cat)] **1**, [(Me_2TPA)Co(36-Cat)]PF_6 **2** and [(Me_2TPA)Co(diox-$(OMe)_3$)]BPh_4 **3** (Me_2TPA = bis(6-methyl-2-pyridyl)methyl)-(2-pyridylmethyl)amine; 36-Cat = dianion of 3,6-di-*tert*-butylcatechol; diox-$(OMe)_3$—2,5-di-*tert*-butyl-6-oxy-3,4,4-trimethoxy-cyclohexa-2,5-dienone) have been synthesized and their magnetic properties were investigated. The neutral complex **1** was found to form a hexa- (CoO_2N_4) and pentacoordinated (CoO_2N_3) isomers possessing different structure and magnetic behavior. One electron oxidation of **1** gives rise to the ionic complex **2** demonstrating a thermally induced VT transition ($_{LS}Co^{III}$-Cat → $_{HS}Co^{II}$-SQ) in the solid state. An aerial oxidation of **1** results in the formation of ionic complex of $_{HS}$-Co^{II} bearing cyclohexadienonate ligand—**3**. Compounds **1** and **3** were found to demonstrate slow magnetic relaxation at applied fields of 1,500–2,500 Oe.

Acknowledgements: this work was supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779).

Multinuclear Complexes of Metal Phthalocyanines and Related Macroheterocycles with Transition Metals and Clusters

✉**Maksim A. Faraonov, Dmitry V. Konarev**

Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia

✉maksimfaraonov@yandex.ru

Metal phthalocyanines and related compounds are widely used to obtain photoactive and magnetic materials. One way to modify the structures and properties of such materials is to coordinate various fragments to the central metal atom of a metal macrocycle. Coordination complexes attract much attention of the researchers, because the introduction of additional metal center into the phthalocyanine system leads to a change in its electronic structure. As a result, complexes with unique optical and magnetic properties and even synergy of such properties can be obtained.

In the present work, we have developed methods for the synthesis of coordination compounds of tin (II) phthalocyanine and related macrocycles with transition metals and clusters due to the formation of a tin–metal σ-bond [1; 2]. It has been established that such compounds can have different macrocycle charge state.

Of particular interest are formally neutral compounds in which charge transfer from the transition metal to the macrocycle with the formation of a paramagnetic radical trianion ligand (for example, $\{CpFe^{II}(CO)_2Sn^{II}(Macrocycle^{\bullet 3-})\}$) is observed. In such complexes, dense dimeric or one-dimensional packing of the macrocycles is observed, which leads to strong magnetic interactions in the systems (exchange interaction J up to −180 K). These compounds are soluble even in non-polar organic solvents and have intense absorption in the visible and near-IR regions due to the presence of the macroheterocycles.

Metal macroheterocycle in neutral or radical anion state can replace one or two carbonyl ligands in transition metal clusters ($Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$ and others); paramagnetic clusters can also be formed in such reactions. Moreover, paramagnetic decamethylchromocene cations, $Cp^*_2Cr^+$ ($S = 3/2$), can act as countercations.

Acknowledgements: the complexes based on substituted phthalocyanines and tetrapyrazinoporphirazines were obtained and studied with the support of RSF (project No. 21-73-10207). The complexes of phthalocyanines were obtained and studied with the support of the Russian Science Foundation (project No. 21-13-00221).

Spin State Switching in Copper-Nitroxide Based Molecular Magnets Using Low-Energy Photons

Sergey L. Veber[1], **Sergey V. Tumanov**[1], **Anatoly R. Melnikov**[1], **Kseniya Yu. Maryunina**[1],
Yaroslav V. Getmanov[2], **Oleg A. Shevchenko**[2], **Victor I. Ovcharenko**[1], ✉**Matvey V. Fedin**[1]

[1] *International Tomography Center SB RAS*
Novosibirsk, Russia
[2] *Budker Institute of Nuclear Physics SB RAS*
Novosibirsk, Russia

✉mfedin@tomo.nsc.ru

Molecular magnets switchable by external stimuli are perspective systems for realization of high-density magnetic memory and quantum information processing devices. Among them, copper(II)-nitroxide based complexes Cu(hfac)$_2$L^R (also called "breathing crystals") exhibit spin-crossover-like (SCO-like) behavior and can be switched between two magnetostructural states by temperature, pressure or light [1]. Light-induced switching is the most promising for potential applications, and long-lived photoinduced states at cryogenic temperatures have been experimentally evidenced, similar to LIESST in classical iron-based SCO compounds. However, the absorption spectrum of copper-nitroxide compounds is drastically different. While iron-based SCO compounds most often feature well-defined d-d or charge-transfer bands in the UV-vis region, copper-nitroxide magnets show poorly resolved broad bands spreading at least to the near IR region. At the same time, ultrafast photoswitching (< 50 fs) and excited state relaxation point out at existence of low-lying excited states [2]. These specifics altogether imply that a very low-energy radiation quanta, far-IR-to-THz range, can possibly induce photoswitching of copper-nitroxide magnets.

We report that as low energy as mid-IR is sufficient to switch the breathing crystal Cu(hfac)$_2$L^{Pr} from ground to excited long-lived state, which was observed at temperature below 10 K with FTIR or EPR detection. Furthermore, Novosibirsk Free Electron Laser (NovoFEL) provides unique opportunity of tunable excitation within 1040-1180 cm^{-1}, yielding solid confirmations of the low-energy photoswitching. Thus, we showed that the excitation energy necessary for photoswitching of breathing crystals can be drastically downscaled from UV-vis to mid-IR region (~20 times). At the moment, this is a rather fundamental finding; however, decent advantages of using low-energy quanta may lead to the new and promising potential applications.

Acknowledgements: this work was supported by the Russian Science Foundation (No. 22-13-00376).

[1] *Coord. Chem. Rev.* 2015, *289–290*, 341; *Angew. Chem. Int. Ed.* 2008, *47*, 6897.
[2] *Angew. Chem. Int. Ed.* 2014, *40,* 10636; *Inorg. Chem.* 2017*, 56,* 11729.

Calculations on a Quantum Computer Performed at IPCP RAS

✉**Eduard B. Fel’dman**

Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia

✉efeldman@icp.ac.ru

Quantum computers based on quantum phenomena, such as superposition and entanglement [1], are expected to perform the tasks which surpass the capabilities of modern classical digital computers [2]. First quantum computers were created quite recently and are limited to the noisy intermediate-scale quantum (NISQ) technology. Quantum calculations create new possibilities for solving problems in various branches of science, such as molecular and atomic calculations, structural chemistry, magnetic resonance, and so on. Although the accuracy of today’s calculations on quantum computers is insufficient owing to the errors of quantum gates, it is still possible to perform quantum calculations for some relatively simple tasks. Taking into account the fantastic advantages of quantum computers over their classical counterparts, which are expected to be released in the future, the development of quantum algorithms is a challenging and useful task.

Quantum algorithms are based on the Solovay—Kitaev theorem [1], according to which every unitary operator can be represented as a product of one- and two-qubit gates. A quantum algorithm can be represented as a circuit consisting of specially tailored gates that allows one to solve the given problem. A lot of such algorithms were worked out in the Institute of Problems of Chemical Physics recently. In some cases we not only solved a particular task, but also developed a method of correction of errors connected with the errors of a quantum computer. All calculations were conducted on the 5-qubit quantum processor of IBM superconducting quantum computer. The following developed algorithms should be mentioned: the algorithm for solving a system of three linear algebraic equations [3], calculation of the number π on a quantum computer [4], and simulation of multiple quantum NMR dynamics of a spin dimer on a quantum computer [5]. In all cases, solutions obtained on the quantum computer coincide with good accuracy with known theoretical results.

Acknowledgements: this work was funded by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779).

[1] Nielsen M. A., Chuang I. L. (2010). *Quantum Computation and Quantum Information*. Cambridge Univ. Press, Cambridge.

[2] Preskill J. (2018). *Quantum*, *2*, 71.

[3] Doronin S. I., Fel’dman E. B., Zenchuk A. I. (2020). *Quant. Inf. Proc.*, *19*, 68.

[4] Bochkin G. A., Doronin S. I., Fel’dman E. B., Zenchuk A. I. (2020). *Quant. Inf. Proc.*, *19*, 257.

[5] Doronin S. I., Fel’dman E. B., Kuznetsova E. I., Zenchuk A. I. (2022). *Appl. Magn. Reson.*, *53*(7–9).

Magnetic Materials Based on Sandwich Lanthanide Complexes with Phthalocyanines

✉**Yulia G. Gorbunova**[1,2], **Alexander G. Martynov**[2], **Marina A. Polovkova**[2],
Lyudmila A. Lapkina[1], **Gayane A. Kirakosyan**[1,2], **Dmitry V. Konarev**[3], **Aslan Yu. Tsivadze**[1,2]

[1]*Kurnakov Institute of General and Inorganic Chemistry RAS*
Moscow, Russia
[2]*Frumkin Institute of Physical Chemistry and Electrochemistry RAS*
Moscow, Russia
[3]*Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia

✉yulia@igic.ras.ru

Sandwich lanthanide phthalocyaninates are very promising molecular materials with unique physico-chemical properties, including magnetic ones. Different types of such materials have been developed recently in our group, and the obtained results are discussed in the report.

Thus, the introduction of crown ethers into homoleptic Tb(III) and Dy(III) trisphthalocyanates provides for their solubilisation in aqueous medium and application as NMR thermosensors in physiological temperature range (303–323 K) due to high temperature sensitivity of lanthanide induced shifts, achieving values of $\Delta\delta/\Delta T$ up to 1.1 and 0.55 ppm/K respectively [1–3].

Heteroleptic trisphthalocyaninates bearing two adjacent crown-substituted ligands act as the receptors which can bind potassium cations. This process results in switching of the coordination polyhedron of the corresponding lanthanide cation from square-antiprismatic to square-prismatic. In turn, it results in a spectacular increase in the axial component of the magnetic susceptibility tensor providing a new tool of supramolecular control of the magnetic properties of lanthanide complexes [4]. Octopus-like Tb(III) bisphthalocyaninate bearing eight thioacetate-terminated tentacles in one ligand and crown-ether rings in another ligand can form self-assembled monolayers on gold surface. Face-on orientation provides for subsequent binding of crown-phthalocyanines via potassium ion bridges, providing a heterogeneous bilayer with expanded redox-behaviour where distinct redox-states can be read out using optical density measurements [5]. The proposed approach can be used in a wide range of switchable materials, including single-molecule magnets, conductive, and optical devices, etc.

Acknowledgements: the work was supported by the Ministry of Science and Higher Education of Russia (grant No. 075-15-2020-779).

[1] Babailov S. P. et al. (2021). *Sensors Actuators, A Phys., 331*, 112933.
[2] Martynov A. G. et al. (2022). *Polyhedron, 219*, 115792.
[3] Babailov S. P. et al. (2022). *J. Porphyrins Phthalocyanines, 26*, 334–339.
[4] Martynov A. G. et al. (2021). *Inorg. Chem., 60*, 9110–9121.
[5] Shokurov A. V. et al. (2022). *Small, 18*, 2104306.

Effect of Dihalide Substituents on Crystal Structure and Magnetic Properties of Cation $[Mn^{III}(3,5\text{-diHal-sal}_2323)]^+$ Complexes with BPh_4 Anion

✉**Anna V. Kazakova**[1], **Aleksandra V. Tiunova**[1,2], **Denis V. Korchagin**[1], **Eduard B. Yagubskii**[1]

[1] Institute of Problems of Chemical Physics RAS
Chernogolovkay, Russia
[2] Lomonosov Moscow State University
Moscow, Russia

✉kazakova@icp.ac.ru

A series of tetraphenylborates of mononuclear Mn(III) cation complexes with hexadentate ligands, the products of the reaction between a N,N′-bis(3-aminopropyl)ethylenediamine and salicylaldehydes with different haloid substitutions at 3,5 positions, have been synthesized: $[Mn(3,5\text{-diCl-sal}_2323)]BPh_4$ (**1**) and $[Mn(3,5\text{-Br,Cl-sal}_2323)]BPh_4$ (**2**), $[Mn(3,5\text{-diF-sal}_2323)]BPh_4$ (**3**), and two polymorphic modifications (**4** and **5**) of $[Mn(3,5\text{-Br,F-sal}_2323)]BPh_4$. Their crystal structure, dielectric constant (ε) and magnetic properties have been studied. Ligand substituents have a dramatic effect on the structure and magnetic properties of the complexes. The complexes **1** and **2** are isostructural, but have fundamentally different properties. Complex **1** demonstrates two structural phase transitions related to sharp spin crossovers from the high spin (HS) state to the HS:LS intermediate phase at 137 K and from the intermediate phase to the low spin (LS) state at 87 K, while complex **2** exhibits only one spin transition from the HS to the HS:LS intermediate phase at 83 K. Complex **3** exhibits a gradual and complete spin conversion with $T_{1/2} = 141$ K between a high spin ($S = 2$) and a low spin ($S = 1$) states. Two polymorphic modifications of the complex $[Mn(3,5\text{-Br,F-sal}_2323)]BPh_4$ have fundamentally different magnetic properties: one of the modifications (monoclinic, **4**) shows a gradual and complete spin transition with $T_{1/2} = 137$ K, while the other (triclinic, **5**) remains in a high spin state over the entire investigated temperature range of 2–300 K. The magneto-structural relationships were traced in comparison with dichloro-, dibromo- difluoro- and mixed Br,Cl- and Br,F-substituted $[Mn(3,5\text{-R,R'-sal}_2323)]$ complexes with tetraphenylborate anion [1].

Acknowledgements: the work was carried out with the financial support of the Ministry of Education and Science of Russia (grant No. 075-15-2020-779).

[1] Tiunova A. V., Kazakova A. V., Korchagin D. V., Shilov G. V., Zorina L. V., Simonov S. V., Zakharov K. V., Vasiliev A. N., Yagubskii E. B. (2021). *Chem. Eur. J.*, *27*, 17609–17619.

Single Ion Magnets Based on Cobalt(II) Carboxylate Complexes

✉**Mikhail A. Kiskin**[1], **Stanislav A. Nikolaevskii**[1], **Nikolay N. Efimov**[1],
Alexander E. Baranchikov[1], **Sergey L. Veber**[2], **Igor L. Eremenko**[1]

[1]*Kurnakov Institute of General and Inorganic Chemistry RAS*
Moscow, Russia
[2]*International Tomography Center SB RAS*
Novosibirsk, Russia

✉mkiskin@igic.ras.ru

Single ion magnets (SIMs) are subject to significant research efforts from chemists and physicists due to their prospective applications in high-density information storage and molecular spintronics devices. To implement slow magnetic relaxation of paramagnetic metal-containing compounds, it is necessary for the metal ion to possess magnetic anisotropy (*D*). Magnetic anisotropy is determined by the electronic structure of a metal ion, as well as the electronic and spatial characteristics defined by its ligand environment. It has been proven that by controlling the geometry of the coordination environment of a 3d-metal ion, i.e., adjusting its crystal field and spin-orbit interaction, one can achieve relatively weighty values of the barrier to reorientation of magnetization. A related and no less important task facing the researchers is the development of approaches associated with an increase in the relaxation times of the magnetization of such complexes. This can be achieved by minimizing the dipolar spin-spin interactions between metal centers through magnetic dilution. Magnetic dilution with preservation of the original SIM structure should be carried out in an isostructural diamagnetic matrix, for instance, in a zinc complex of analogical composition, although, unfortunately, not all known SIMs are based on "magnetic" 3d-metal ions correspond to the isostructural analogues of such diamagnetic compounds.

The report discusses the results of studies on the synthesis of cobalt(II) carboxylate complexes, approaches to controlling the coordination environment of the metal center, crystal packing, and magnetic dilution in order to improve the operational characteristics of SIMs.

Acknowledgements: the work was financially supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779).

Operando MRI Study of a Heterogeneous Reactor Using Parahydrogen-Induced Polarization with Antiphase-to-Inphase Signal Shape Conversion

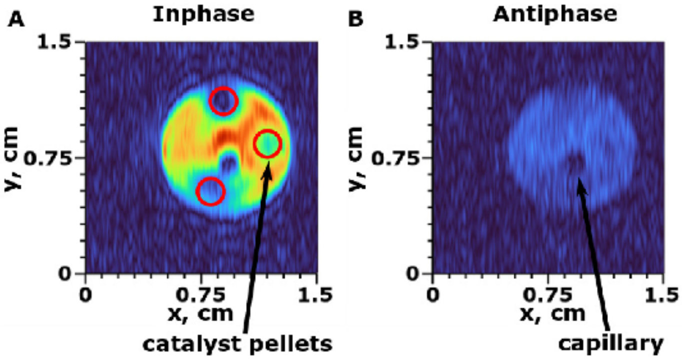
✉**Elizaveta S. Kononenko**[1,2], **Alexandra I. Svyatova**[1,2], **Ivan V. Skovpin**[1,3],
Larisa M. Kovtunova[1–3], **Igor V. Koptyug**[1]

[1]*International Tomography Center SB RAS*
Novosibirsk, Russia
[2]*Novosibirsk State University*
Novosibirsk, Russia
[3]*Boreskov Institute of Catalysis SB RAS*
Novosibirsk, Russia

✉elizaveta.kononenko@tomo.nsc.ru

The magnetic resonance imaging (MRI) methods can be used for operando studies of heterogeneous catalytic processes in the gas phase. As the spatial distribution of reactants and reaction products is not uniform, MRI allows one to get a more detailed understanding of the heterogeneous reactor operation. However, there are many factors, including low spin density, magnetic field inhomogeneities, fast diffusion and short relaxation times of gases, which complicate such studies and make it essential to use hyperpolarization. Spin hyperpolarization techniques in general, and parahydrogen-induced polarization (PHIP) in particular, provide a major increase in the intensity of NMR signals. At the same time, an antiphase lineshape of NMR signals associated with PHIP at high magnetic fields is disadvantageous for MRI experiments because it leads to mutual cancelation of the positive and negative parts of such signals [1].

Results of this work demonstrate the importance of antiphase-to-inphase signal shape conversion in MRI experiments to utilize the signal enhancement provided by hyperpolarization to the maximum possible extent. This approach, implemented for the first time in an MRI study of an operating model reactor, allowed us to achieve a 10-fold improvement in signal-to-noise ratio compared to the usual experiment performed on an antiphase signal. This made it possible to visualize catalyst beads in the 3D MR image obtained (Fig. A).



A slice of a 3D MR image of hyperpolarized propane in a model reactor obtained with *(A)* and without *(B)* conversion of an antiphase signal to an inphase one

Acknowledgements: this work was supported by the Russian Foundation for Basic Research (grant No. 19-29-10003).

[1] Barskiy D. A. et al. (2017). *J. Phys. Chem. C.*, *121*, 10038–10046.

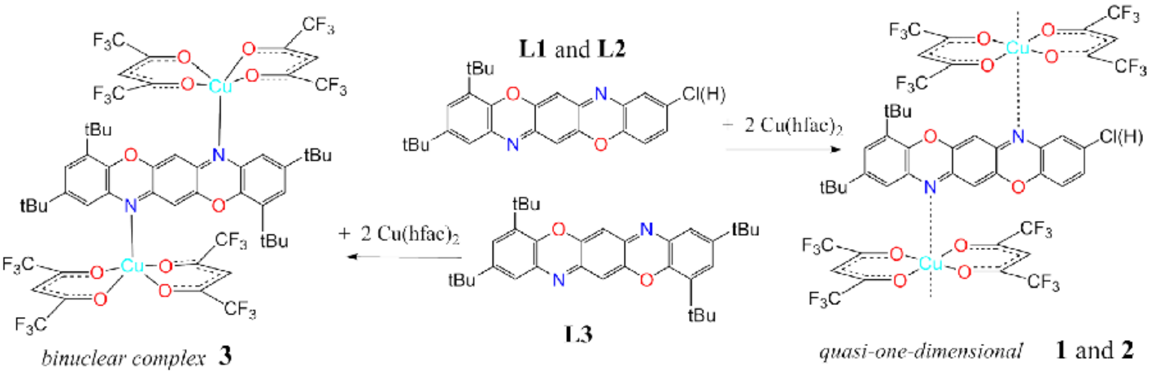
Evidence of Field-Assisted Slow Magnetic Relaxation in Cu(II) Complexes with Pentaheterocyclic Triphenodioxazines

✉**Denis V. Korchagin**[1], **Evgeny P. Ivakhnenko**[2], **Pavel A. Knyazev**[2], **Oleg P. Demidov**[3], **Alexander V. Akimov**[1], **Roman B. Morgunov**[1], **Nikolay N. Efimov**[4], **Andrey G. Starikov**[2], **Andrey V. Palii**[2], **Vladimir I. Minkin**[1], **Sergey M. Aldoshin**[1]

[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia
[2] *Institute of Physical and Organic Chemistry, Southern Federal University*
Rostov on Don, Russia
[3] *North Caucasus Federal University*
Stavropol, Russia
[4] *Kurnakov Institute of General and Inorganic Chemistry*
Moscow, Russia

✉korden@icp.ac.ru

Novel copper(II) complexes were obtained by the reaction of sterically crowded triphenodioxazines with Cu(II) hexafluoroacetylacetonate. The compounds with L1 (**1**) and L2 (**2**) are quasi-one-dimensional complexes in which $Cu(hfac)_2$ moieties are co-crystallized with triphenodioxazine molecules through only weak Cu...N intermolucular interactions (Cu…N 2.69–2.75Å). At the same time, a binuclear Cu(II) complex (**3**) is formed with the L3 ligand, in which Cu(II) ions are bound to the ligand by covalent interactions (Cu…N 2.33Å).



The magnetic AC susceptibility data show that in spite of absence of the zero-field splitting in Cu(II) ions with $S = 1/2$, all complexes demonstrate slow magnetic relaxation behavior at a weak applied magnetic field (H_{DC} ~ 500 Oe) for **1**, **2** and H_{DC} = 2,500 Oe for **3**. The studied systems represent new examples of quite rare family of the $S = 1/2$ systems exhibiting slow magnetic relaxation with a potential of promising applications in molecular spin devices or as molecular quantum bits.

Acknowledgments: this work was supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779).

Spin Exchange between Triplet ^{3}CS and ^{3}LE States in NI-PXZ Dyad Revealed by TR EPR

✉**Ivan V. Kurganskii**[1,2], **Xue Zhang**[3], **Jianzhang Zhao**[3], **Matvey V. Fedin**[1]

[1]*International Tomography Center SB RAS*
Novosibirsk, Russia
[2]*Novosibirsk State University*
Novosibirsk, Russia
[3]*Dalian University of Technology*
Dalian, P. R. China

✉kurgansky@tomo.nsc.ru

The control over the photoexcited triplet state formation plays a key role in quantum information science and spintronics. Moreover, development of the ways of increasing the singlet-triplet transition quantum yield is important for photodynamic therapy and design of new triplet-triplet annihilation upconversion based devices. There are several mechanisms of intersystem crossing (ISC) within organic molecules: spin-orbit ISC—the most common one, which quantum yield can be enhanced by heavy atom effect; radical pair (RP) ISC and spin-orbit charge transfer (SOCT) ISC. The latter two occur within donor-bridge-acceptor (DbA) chromophore dyads as a result of the charge separation (CS) and following charge recombination from the ^{3}CS to a triplet locally excited (^{3}LE) state. The SOCT ISC is the most promising mechanism, since it requires only synthesis of purely organic compounds, readily tunable for particular application. However, SOCT ISC is understudied. There is no model of it that could cover all its features observed in the experiments. One of the phenomena is discussed in this report.

We studied a naphthalimide-phenoxazine (NI-PXZ) dyad by the time-resolved EPR spectroscopy—a technique providing various information about a short-lived triplet state. The unique spectral lineshape of ^{3}(NI-PXZ) and its dynamics correspond well to the spin exchange between its ^{3}CS and ^{3}LE [1]. This conclusion concurs with the findings of other experimental techniques and DFT calculations provided by our colleagues. Thus, for the best of our knowledge, it is the first observation of the spin exchanging ^{3}CS and ^{3}LE in a DbA dyad, an important one for further design of the SOCT ISC compounds.

The measurements were performed at 80 K using a self-made X-band TR EPR spectrometer based on Bruker EMX. The molecules dissolved in 2MeTHF:TOL (1:3, v/v) mixture were efficiently excited by the 355 nm laser light.

Acknowledgements: this work was supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779).

[1] Zhang X., Kurganskii I. et al. (2022). *Chem.Eur. J., accepted for publication*

Adiabatic Approach to Polarizing ^{15}N Nuclei with SABRE at High Magnetic Fields

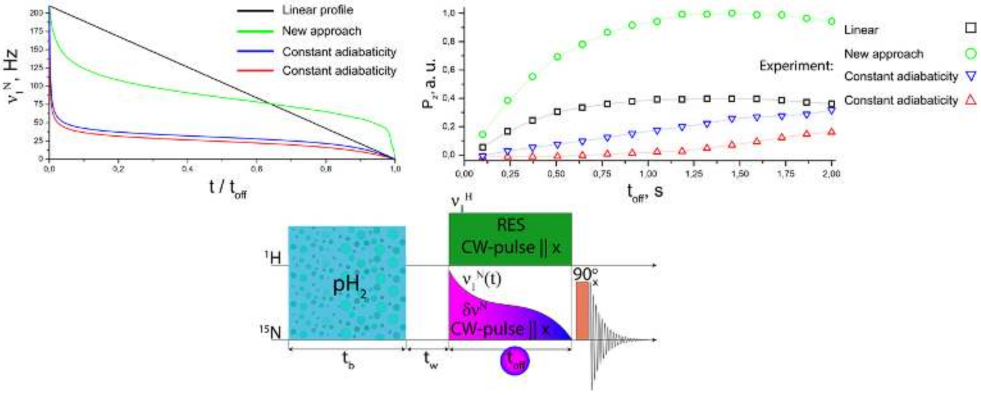
✉**Danil A. Markelov**[1,2], **Vitaly P. Kozinenko**[1,2], **Alexandra V. Yurkovskaya**[1]

[1] International Tomography Center SB RAS
Novosibirsk, Russia
[2] Novosibirsk State University
Novosibirsk, Russia

✉d.markelov@tomo.nsc.ru

Parahydrogen induced polarization (PHIP) is a well-established tool to dramatically enhance weak nuclear magnetic resonance (NMR) signals in NMR-spectroscopy and imaging (MRI). A version of PHIP, termed Singal Amplification by Reversible Exchange (SABRE) is based on the reversible interaction of parahydrogen and substrate molecules with an organometallic complex. To perform SABRE in a high magnetic field it is necessary to irradiate the sample using radiofrequency (RF) pulses with adiabatic amplitude modulation on ^{1}H and ^{15}N nuclear channels.

Here we analyze SABRE pulse sequences in a high magnetic field (9.4 T) and optimize experimental parameters such as: RF-pulse amplitudes and frequencies, the RF-pulse amplitude switching profile. We also propose a new approach to calculating the RF-pulse amplitude switching profiles based on the SABRE spin dynamics calculation. Such calculation considers both presence of spin relaxation and reversible chemical exchange of parahydrogen and substrate with the SABRE complex by means of the Liouville equation. We demonstrate experimentally that in some cases our approach for calculating RF-amplitude switching profile leads to almost three-fold increase in ^{15}N hyperpolarization efficiency as compared to linear and constant adiabaticity amplitude switching. The proposed optimization procedure of the experimental SABRE parameters allowed us to achieve ^{15}N NMR-signals enhancement of 4,000.



^{15}N polarization in high-filed SABRE pulse sequence (bottom). Left picture corresponds to the RF-amplitude switching profiles, right picture — ^{15}N polarization for different switching profiles

Acknowledgements: the work was financially supported by the Russian Ministry of Education and Science (contract No. 075-15-2021-580).

Anionic Compounds of Hexaazatriphenylene-Based Ligands: Synthesis, Structure and Properties

✉**Maxim V. Mikhailenko**[1], **Aleksandr F. Shestakov**[1],
Salavat S. Khasanov[2], **Dmitrii V. Konarev**[1]

[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia
[2] *Institute of Solid State Physics RAS*
Chernogolovka, Russia

✉mmv@icp.ac.ru

Hexaazatrinaphtylene (HATNA), hexaazatrianthracene (HATA) and hexaazatriphenylenehexacarbonitrile (HATCN6) belong to the class of hexaazatriphenylene-based (HAT) ligands. These compounds can coordinate up to three metal centers and they can be chemically reduced to anionic radical states, which makes them promising ligands in the design of magnetic assemblies.

We have developed a special synthetic procedure and successfully obtained first HATNA and HATA dianionic compounds and first HATCN6 trianionic compound in the form of $[(\mathrm{HAT})^{-n}]\bullet 3\mathrm{FeCl}_2$ ($n = 2$ or 3) molecular complexes with high-spin iron ($S_{Fe} = 2$). All compounds were fully characterized by the optical spectroscopy, RSA, EPR and SQUID-magnetometry methods.

The investigation of magnetic properties of the complexes shows the existence of the antiferromagnetic exchange between Fe atoms through the dianionic ligand in HATNA and HATA compounds with the Weiss temperature of −98 and −80 K; exchange value of −4.6 and −4.7 cm^{-1}, respectively. The appearance of an unpaired electron delocalized on HATCN6 ligand in the trianionic complex leads to the emergence of the antiferromagnetic coupling between metal and ligand magnetic spins with the J value of −163 cm^{-1}. Such a strong antiferromagnetic exchange becomes the reason for parallel orientation of Fe spins and for the formation of a high-spin molecular complex with $S = 11/2$. A positive Weiss temperature of +23 K is observed for this trianionic HATCN6 compound.

All the complexes are also studied using DFT calculations.

Acknowledgements: the work was supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075–15-2020-779).

[1] Konarev D. V., Khasanov S. S., Mikhailenko M. V., Batov M. S., Otsuka A., Yamochi H., Kitagawa H., Lyubovskaya R. N. (2021). *Eur. J. Inorg.Chem., 1*, 86–92.

[2] Mikhailenko M. V., Khasanov S. S., Shestakov A. F., Kuzmin A. V., Otsuka A., Yamochi H., Kitagawa H., Konarev D. (2022). *Chem. Eur. J., 28*, e202104165.

Paramagnetic Quantum Dots InP@ZnS Doped with Manganese Ions

✉**L. M. Nikolenko**[1], **V. F. Razumov**[1,2], **D. N. Pevtsov**[1,2],
V. Yu. Gak[1], **A. V. Akimov**[1], **A. V. Aybush**[3]

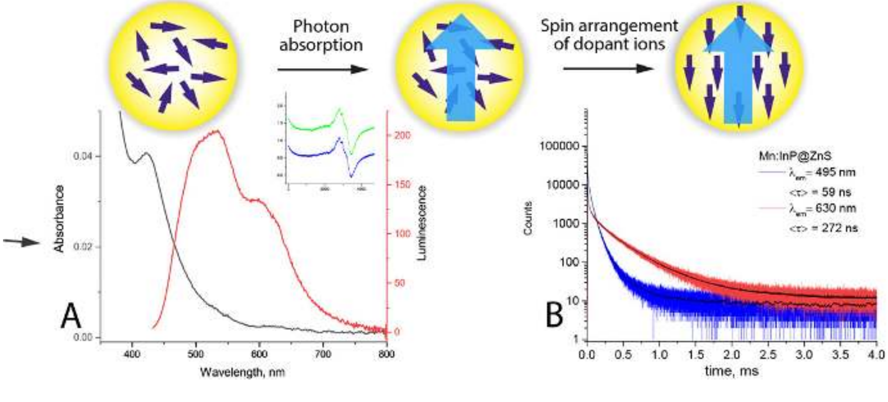
[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia
[2] *Moscow Institute of Physics and Technology*
Dolgoprudny, Russia
[3] *Semenov Federal Research Center for Chemical Physics RAS*
Moscow, Russia

✉nav@icp.ac.ru

Colloidal quantum dots doped with paramagnetic ions (PQD) represent a new class of functional materials for spin photonics. Photoinduced arrangement of dopant ion spins is possible in such systems. This unusual effect is caused by strong exchange interaction of an electron and a hole due to their localization in a space smaller than the size of the exciton. As a result, the spins of the electron (1/2) and hole (3/2) are directed in the same direction in the ground state of the exciton in the PQD. Thus, the exciton created by photon absorption has a magnetic moment equal to 2 and causes the magnetization of the PQD.

In our work, we studied the spectral and luminescent properties of the PQD, including the excitation-luminescence matrices, the luminescence decay kinetics, and transient absorption spectra. A new long-wavelength band attributed to the Mn ion emission is a characteristic feature of the luminescence spectra of PQDs (Fig. 1*A*). The average lifetime of the Mn^{2+} ion emission (272 ns) is much longer than that of the intrinsic emission of InP nuclei (59 ns) (Fig. 1*B*).

The experimental data confirm the incorporation of Mn^{2+} into the InP crystal lattice, which is promising for the development of photocontrolled magnetic devices.



A. Absorbance (*1*) and luminescence (*2*) spectra of Mn:InP@ZnS PQDs (In:Mn = 1,25:1) in *n*-hexane. EPR spectra are in the inset. *B*. Luminescence decay curves of Mn:InP@ZnS PQDs in *n*-hexane probed at 495 and 630 nm

Acknowledgements: the project was financially supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779).

Spin Effects in Molecular Quantum Cellular Automata

✉**Andrei V. Palii**, **Denis V. Korchagin, Sergei M. Aldoshin**

Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia

✉andrew.palii@uv.es

The systems we focus on are the square planar mixed-valence (MV) clusters regarded as molecular cells in quantum cellular automata (QCA), which act as a current-free alternative to the traditional CMOP electronics.

In almost all studies dealing with QCA only charge degrees of freedom have been analyzed. Recently we have demonstrated [1] that by polarizing one of the cells acting as a "driver-cell" one would be able not only to polarize the neighboring ("working") cell but also, under some conditions, to switch the ground state from the spin-singlet to the spin-triplet. The proposed electronic model of the cell includes three parameters: two transfer parameters t_n and t_d describing the one-electron transfer processes occurring along the sides and along the diagonals of the molecular square, and the Coulomb energy gap U between the diagonal-type and the side-type charge configurations. The considered most topical case is that of the strong Coulomb interaction, when $U >> t_n, t_d$. By evaluating the effect of the neighboring driver cell on the ground spin-state of the working cell, we have demonstrated that within the range of parameters $0 < t_d/U < 1/4$ the electrostatic field of the driver cell that is strong enough can induce spin-switching from $S = 0$ to $S = 1$.

Another class of molecules we discuss includes the MV molecular squares in which electronic pair is delocalized over four paramagnetic centers ("spin cores"). The presence of spin cores gives rise to the appearance of such magnetic interactions as double exchange and the Heisenberg—Dirac—Van Vleck (HDVV) exchange. The detailed analysis of the cell based on the transition-metal tetramer of the type of $d^2–d^2–d^1–d^1$ [2] shows that depending on the relative strength of the double exchange and the HDVV exchange the ground state of an isolated cell can be either localized spin-triplet or delocalized spin-singlet. Due to different sensitivities of these states to the electrostatic field of the driver cell, the latter has shown to produce switching between different spin-states.

The findings listed above make us think that by combining the ideas related to seemingly completely different areas of the QCA-based molecular electronics and the molecular spintronics, one can, in principle, create a multifunctional device with such two beneficial functions as the cell-cell response and the spin switching. The work was performed with funding from the Ministry of Science and Higher Education of the Russian Federation (Grant No. 075-15-2020-779).

[1] Palii A., Tsukerblat B., Clemente-Juan J. M., Coronado E. (2016). *J. Phys. Chem. C, 120*, 16994–17005.

[2] Palii A., Clemente-Juan J. M., Aldoshin S., Korchagin D., Rybakov A., Zilberg S., Tsukerblat B. (2020). *J. Phys. Chem. C, 124*, 25602–25614.

EPR Study of Nitrenephenylverdazyl Radicals

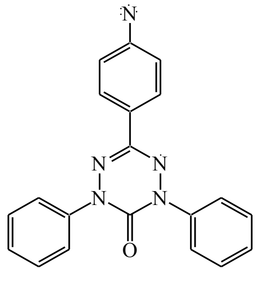
✉**Alexander S. Shmakov**[1], **Alexander V. Akimov**[2],
Denis V. Korchagin[2], **Eugenii Ya. Misochko**[2]

[1] Lomonosov Moscow State University
Moscow, Russia
[2] Institute of Problems of Chemical Physics RAS
Chernogolovka, Russia

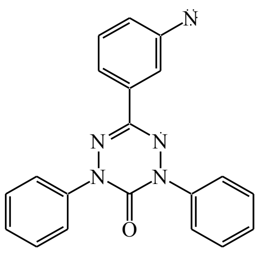
✉shmakovchem@mail.ru

The conjugation of several spin centers in one molecule can lead to the formation of a high-spin state, when the spins are added, and a low-spin state, when they are subtracted [1]. Revealing the structural features which determine the overall spin of the system is an interesting and actual task.

The present work is devoted to the study of the magnetic properties of two nitrenephenylverdazyl radicals, namely those with the *para*-(**1**) and *meta*-(**2**) positions of the nitrene groups. The magnetic parameters were determined using X-band EPR spectroscopy. There are slight structural differences in these compounds, but different conjugation of two unpaired electrons on the nitrene center with one unpaired electron in the verdazyl ring leads to a different total spin of the system. In the *para* position, the total spin of the system is S = 3/2, and in the *meta* position S = 1/2. High-level quantum-chemical calculations showed good agreement with the obtained experimental results.



1



2

Acknowledgements: the work was financially supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779).

[1] Allen T. L., Lahti P. M. (2011). Q-Band EPR Spectroscopy of Photogenerated Quartet State Organic Nitreno Radicals. *The Journal of Physical Chemistry A, 115*(19), 4922–4928.

New Erbium (3+) Hexafluoroacetylacetonates with Spirocyclic Photochromes: Synthesis, Structure, Properties

✉**Valeriya P. Shtefanets**[1,2], **Gennady V. Shilov**[2], **Nikolay N. Efimov**[3],
Elena A. Yurieva[2], **Natalia A. Sanina**[2], **Sergei M. Aldoshin**[2]

[1] *Moscow Institute of Physics and Technology (National Research University)*
Dolgoprudny, Russia
[2] *Institute for Problems of Chemical Physics RAS*
Chernogolovka, Russia
[3] *Kurnakov Institute of General and Inorganic Chemistry RAS*
Moscow, Russia

✉shtefanets.vp@phystech.edu

The functionalization of monomolecular magnets (MMM)—viz metal complexes with various organic ligands—in order to give them additional (photo-, conductive, etc.) properties is a “hot topic”in the chemistry and physics of new materials. For example, the reversible photocyclization of complexes containing a photochromic component in the molecule upon UV or visible light irradiation can cause “switching on/switching off” the slow MMM relaxation [1].

Heavy lanthanide ions are increasingly being used for the design of MMMs due to their significant magnetic anisotropy and greater sensitivity to the surrounding crystal field [2]. It has been established that in a number of such molecular systems, the quantum tunneling mechanism of relaxation is controlled by photoisomerization [3; 4]. However, due to the high degree of coordination of 4f ions, systems with a weak modification of magnetic properties have been obtained so far [5–8].

In this work, new Er (3+) hexafluoroacetylacetonates with spirocyclic photochromes were synthesized. Their structure, magnetic properties, and photochemical activity were studied.

Acknowledgements: the work has been performed with financial support of the Ministry of Science and Higher Education of Russian Federation, Project “Fundamentals of Spin Technologies and Directed Design of ‘Smart’ Polyfunctional Materials for Spintronics and Molecular Electronics” (agreement No. 075-15-2020-779).

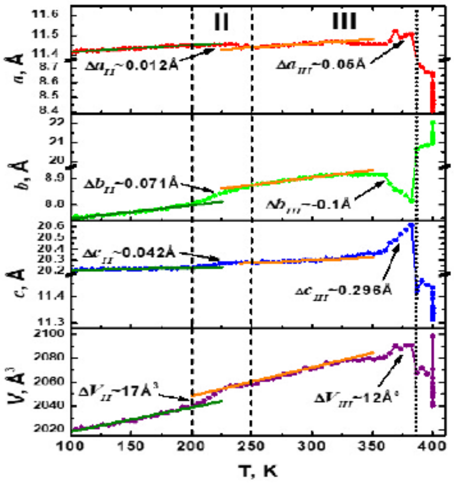
[1] Fetoh A. et al.(2016). *Scientific reports*, *6*(1), 1–6.
[2] Nakano M. et.al. (2011). *Chem. Soc. Reviews*, *40*(6), 3239–3248.
[3] Pinkowicz D. et al. (2014). *Chemistry –A Eur. J.*, *20*(39), 12502–12513.
[4] Cosquer G. et al. (2015). *Dalt. Trans.*, *44*(13), 5996–6002.
[5] Cosquer G. et al. (2018). *Inorganics*, *6*(1), 9.
[6] Pinkowicz D. et al. (2014). *Chem. Eur. J*, *20*, 12502–12513.
[7] Cosquer G. et al. (2015). *Dalt. Trans.*, *44*, 5996–6002.
[8] Fetoh A. et al. (2019). Inorg. *Chemistry*, *58*(4), 2307–2314.

Anionic Spin-Crossover Complex of Fe(III) with Space Symmetry Transition and Thermal Hysteresis around Room Temperature

✉**Nataliya G. Spitsyna**[1], **Maxim A. Blagov**[1,2]

[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia
[2] *Lomonosov Moscow State University*
Moscow, Russia

✉spitsina@icp.ac.ru



The dependences of K[Fe(5Cl-thsa)$_2$] salt unit cell parameters based on XRPD data in the temperature range 100–400 K for *a*, *b*, *c* and *V*. Roman numerals **II** and **III** indicate the SCO step numbers according to magnetic measurements. The short dashed lines (---) mark borders of the distinct SCO steps. The dotted line (·····) at ~387 K indicates the orthorhombic-to-monoclinic structural phase transition (*Pbcn* → *P*2$_1$/*n*). Note that the Y-axes for *a*, *b*, and *c* parameters contain breaks

The 2D spin-crossover potassium salt of the $N_2S_2O_2$-coordination Fe(III) anion K[Fe(5Cl-thsa)$_2$] (5Cl-thsa–5-chlorosalicylaldehyde thiosemicarbazone) is synthesized and characterized structurally and magnetically over a wide temperature range [1]. The salt exhibits a complete three-step cooperative SCO transition in the temperature range 2–440 K both in the heating and cooling modes: the first step occurs in a temperature range from 2 K to 50 K, the second abrupt hysteretic step occurs from 200 to 250 K with $T_{1/2} = ½\cdot(T_{1/2}\uparrow + T_{1/2}\downarrow) =$ $= 230$ K ($T_{1/2}$ = temperature of 50 % HS to LS conversion) and a 6 K hysteresis loop, the third gradual step occurs from 250 K to 440 K.

A peculiar effect of structural lagging was revealed (see Fig.), associated with the discrepancy between the expected significant increase in the iron(III)-ligand bond lengths with an increase in the HS concentration by 57 % at the second stage of SCO transitions. This non-trivial phenomenon was investigated in detail applying magnetization measurements, the ^{57}Fe Mössbauer spectroscopy, and DFT calculations.

Acknowledgements: the work was funded by the the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779), the instrumental base of the center for collective use and the computer center of the IPCP RAS was used.

[1] Spitsyna N. G., Blagov M. A., Lazarenko V. A. et. al. (2021). *Inorganic Chemistry.*, *60*, 17462–17479.

Computer Modeling of Polyspin Organic Molecules Based on Bis-Triangulenes and Stable Radicals

✉**Andrey G. Starikov**[1], **Maxim Chegerev**[1], **Alyona Starikova**[1],
Vladimir I. Minkin[1], **Sergey M. Aldoshin**[2]

[1] Institute of Physical and Organic Chemistry, Southern Federal University
Rostov-on-Don, Russia
[2] Institute of Problems of Chemical Physics of RAS
Chernogolovka, Russia

✉agstarikov@sfedu.ru

In order to search for 'metal-free' magnetic systems which can serve as the basis for molecular electronics devices, a systematic computer simulation (DFT, B3LYP/611++G(d,p)) of polycyclic organic molecules containing stable radical groups was carried out. The considered systems contain four paramagnetic centers, the nature and strength of exchange interactions between which can be controlled by varying the length of the central polycyclic (acene) fragment. The calculated magnetic properties indicate the presence in the studied compounds of ferromagnetic interactions between radical groups and their antiferromagnetic coupling with paramagnetic triangulene centers of polycycles. The presence of exchange channels differing in nature, but similar in strength in one molecule indicates the existence of spin entanglement in the considered compounds.

All the proposed magnetically active molecules are a combination of well-known structural fragments. The methodology developed in recent years for the introduction of various radical groups into organic molecules [1] makes it possible to expect synthesis of predicted polyradical systems that have prospects for use in organic electronics and spintronics.

Acknowledgements: this work was supported by the Ministry of Science and Higher Education of the Russian Federation (grant No. 075-15-2020-779).

[1] Tretyakov E. V., Ovcharenko V. I., Terent'ev A. O., Krylov I. B., Magdesieva T. V., Mazhukin D. G., Gritsan N. P. (2022). *Russ. Chem. Rev.*, *91*, 1.

[Mn(5-Hal-sal$_2$323)]$_2$[ReCl$_6$] (Hal=Cl, Br): the First Mn(III) Molecular Complexes to Exhibit both Spin Crossover and Single-Ion Magnet Effects

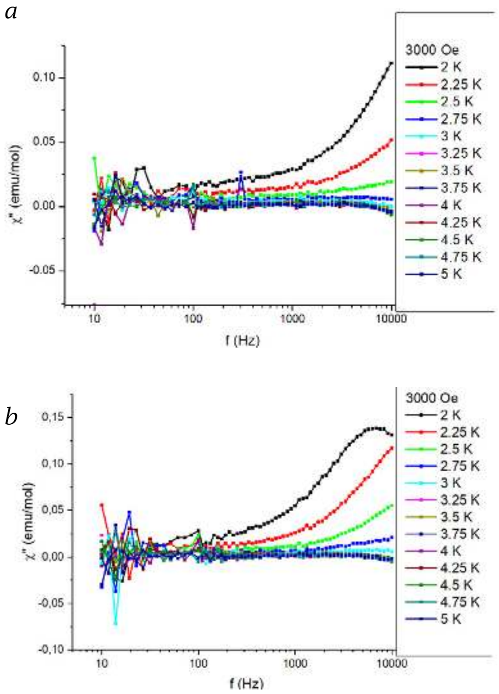
✉ **Aleksandra V. Tiunova**[1,2], **Anna V. Kazakova**[1],
Denis V. Korchagin[1], **Gennady V. Shilov**[1], **Eduard B. Yagubskii**[1]

[1] *Institute of Problems of Chemical Physics RAS*
Chernogolovka, Russia
[2] *Lomonosov Moscow State University*
Moscow, Russia

✉ a_tiunova96@mail.ru

At present, the main class of Mn(III) spin-crossover compounds is cationic complexes of Mn(III) with the sal$_2$323 ligand and its derivatives, which were first obtained in 2003, and the first spin transition in this class was discovered in 2006. Since that time, active investigations of these complexes aimed at studying the effects of substituents on the phenolate nucleus of the ligand, the nature of counterions and solvate solvents on the spin behavior of the complexes have begun. In this work, we used for the first time a doubly charged paramagnetic anion [ReCl$_6$]$^{2-}$ as a counterion in the Mn(III) cationic complexes with a monohalosubstituted ligands (5-Cl(Br)-sal$_2$323). To the best of our knowledge, all complexes of the [Mn(sal$_2$323)]$^+$ family synthesized so far contain singly charged anions. An important argument in favor of choosing the [ReCl$_6$]$^{2-}$ as a counterion was the fact that this anion is a field-induced single-ion magnet, like its analogs [ReBr$_6$]$^{2-}$ and [ReI$_6$]$^{2-}$. Thus, one could expect the formation of complexes combining the Mn(III) spin crossover and [ReCl$_6$]$^{2-}$ single-ion magnetism in the same crystal lattice. Only a few compounds are known in the literature in which the spin transition coexists with single-molecule magnetism.

The bicomponent ion-pair molecule complexes [Mn(5-Cl-sal$_2$323)][ReCl$_6$] (**1**) and [Mn(5-Br-sal$_2$323)][ReCl$_6$] (**2**) were synthesized. Their crystal structures and magnetic properties were studied. The compounds are isostructural and show a thermally induced spin transition at high temperature associated with the cationic subsystem and a field-induced frequency dependent on magnetic susceptibility at low temperature, associated with the anionic subsystem.



The frequency dependency of the $\chi''(\nu)$ for complexes **1** (a) and **2** (b) at temperatures of 2–5 K under the magnetic field of H = 3,000 Oe

Acknowledgement: the work was financially supported by the Ministry of Education and Science of Russia (grant No. 075-15-2020-779).

AUTHOR INDEX

CONTENTS

Chemical Kinetics and Spectroscopy

Chemical Physics in Biology and Medicine

Combustion and Energetic Materials

Magnetic Resonance Spectroscopy and Magnetic Field Effects

Molecular Dynamics

Organic Photovoltaics

Quantum and Theoretical Chemistry

Spintronics

Scientific publication

PHYSICS AND CHEMISTRY OF ELEMENTARY CHEMICAL PROCESSES

Proceedings
of the X International Voevodsky Conference VVV-2022

September 5–9, 2022
Akademgorodok, Novosibirsk, Russia

Proofreader *T. A. Markova*
Layout designer *A. S. Tereshkina*
Cover design *E. V. Neklyudova*

Signed to print on 5.09.2022.
Format 60 × 84 1/8. Publ. sign. 34.75. Conv. print. sheets 32.3.
Circulation 26 pcs. Order No. 189.

Novosibirsk State University Publishing Centre.
630090, 2 Pirigov Str., Novosibirsk, Russia

ISBN 978-5-4437-1350-2

9 785443 713502