V.E. Zuev Institute of Atmospheric Optics
Siberian Branch, Russian Academy of Science

Institute of Quantum Physics,
Irkutsk National Research Technical University

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Symposium Schedule

Monday, **July 3**	**Tuesday,** **July 4**	**Wednesday,** **July 5**	**Thursday,** **July 6**	**Friday,** **July 7**
09:15-11:15 Opening Ceremony, Invited Speakers **A**	9:15 – 10:45 Invited Speakers **E**	10:00-17:00 Scientific excursion	9:15 – 10:45 Invited Speakers **K**	9:15 – 10:45 Invited Speakers **O**
11:15-11:45 Coffee Break	10:45-11:15 Coffee Break		10:45-11:15 Coffee Break	10:45-11:15 Coffee Break
11:45-13:45 Oral Session **B**	11:15-13:45 Round Tables **F/G**		11:15-13:45 Oral Session **L**	11:15-13:00 Oral Sessions **P** Closing Ceremony
14:00-15:15 Lunch	14:00-15:15 Lunch		14:00-15:15 Lunch	14:00-15:00 Lunch
15:15-17:15 Invited Speakers **C**	15:15-17:15 Oral Session **H**		15:15-17:15 Oral Session **M**	15.00 Departure to Irkutsk
17:15-17:30 Coffee Break	17:15-17:30 Coffee Break		17:15-17:30 Coffee Break	
17:30-19:00 Poster Session **D**	17:30-19:00 Oral Sessions **I/J**		17:30-19:00 Poster Session **N**	
			20:00-22:00 Conference Dinner	

Contents

Session Program 6

Invited Lectures **A**, Monday, July 3, 09:15 14

Oral Session **B**, Monday, July 3, 11:45 17

Invited Lectures **C**, Monday, July 3, 15:15 24

Poster Session **D**, Monday, July 3, 17:30 28

Invited Lectures **E**, Tuesday, July 4, 09:15 65

Round Table **F**, Tuesday, July 3, 11:15 67

Round Table **G**, Tuesday, July 3, 11:15 73

Oral Session **H**, Tuesday, July 3, 15:15 82

Parallel Oral Session **I**, Tuesday, July 3, 17:30 89

Parallel Oral Session **J**, Tuesday, July 3, 17:30 94

Invited Lectures **K**, Thursday, July 6, 09:15 98

Oral Session **L**, Thursday, July 6, 11:15 101

Oral Session **M**, Thursday, July 6, 15:15 109

Poster Session **N**, Thursday, July 6, 17:30 114

Invited Lectures **O**, Friday, July 7, 09:15 149

Oral Session **P**, Friday, July 7, 11:15 151

Author Index 155

E-mail Address Book 159

Session Program

July 3, 2023, Monday

Invited Lectures A, 09^{15} – 11^{15}

Chair: Valery I. Perevalov

Opening Ceremony

A1 The Bimolecular spectra and atmospheric continuum: precise experiment and non-empirical modeling
Mikhail Yu. Tretyakov

A2 Molecular time-domain spectroscopy at NovoFEL: implemented experiments and potential possibilities
Vitaly V. Kubarev

Oral Session B, 11^{45} – 13^{45}

Chair: Leonid A. Surin

B1 Faraday effect on the absorption lines of hydroxyl radical. Experiments with the CW lasers and time-domain experiments at the terahertz NovoFEL
Chesnokov E.N., Plastinina D.M., Kubarev V.V., Koshlyakov P.V.

B2 Water vapour self-continuum absorption within the IR absorption bands: semiempirical dimer-based model
Simonova A.A., Ptashnik I.V.

B3 Water vapor continuum at room temperature in 1.25 μm atmospheric window
Koroleva A.O., Kassi S., Mondelain D., Campargue A.

B4 Continuum absorption of CO-Ar mixture in the far IR range
Galanina T.A., Koshelev M.A., Tretyakov M.Yu., Ivanov S.V.

B5 The last advances in the infrared acetylene spectroscopy
Lyulin O.M., Campargue A., Jacquemart D., Vasilchenko S.S., Perevalov V.I.

B6 Accurate line shape parameters of oxygen fine-structure lines for atmospheric applications
Koshelev M.A., Vilkov I.N., Golubyatnikov G.Yu., Galanina T.A., Sekacheva A.Yu., Serov E.A., Makarov D.S., Tretyakov M.Yu.

B7 Pressure broadening coefficients of the ν_2 Raman band of methane in natural gas
Tanichev A.S., Petrov D.V.

Invited Lectures C, 15^{15} – 17^{15}

Chair: Andrey V. Stolyarov

C1 Diagnostics of the geometry of intermolecular complexes using the combination of advantages of IR and NMR spectroscopy
Peter M. Tolstoy

C2 Rotational dynamics of molecules based on generalized Euler equations
Sergey V. Petrov

C3 Cold ion fragmentation spectroscopy-mass spectrometry for identification of isomeric carbohydrates and lipids
Oleg V. Boyarkin

Poster Session D, 17^{30} – 19^{00}

D1 Integrated intensities of the vibrational-rotational lines of C_2HD in the 6527-6563 cm^{-1} and 6611-6642 cm^{-1} infrared spectral regions
Plastinina D.M., Lipskaya A.S., Chesnokov E.N.

D2 Fourier transform absorption spectrum of SO_2 in 3500-3700 cm^{-1} spectral region
Sharybkina K.K., Vasilenko I.A., Naumenko O.V., Horneman V.-M.

D3 Calculation of vibration-rotation transition frequencies and RKR potentials of the HBr molecule
Velichko T.I., Mikhailenko S.N.

D4 The absorption bands of $^{12}C^{16}O_2$ near 718 nm
Lyulin O.M., Solodov A.M., Solodov A.A., Petrova T.M., Perevalov V.I.

D5 The first observation of the $^{12}C^{16}O_2$ absorption bands near 660 nm
Borkov Yu.G., Solodov A.M., Solodov A.A., Petrova T.M., Perevalov V.I.

D6 Λ- doubling in the 3-0 vibrational band of the $^{15}N^{16}O$ molecule in the ground state
Borkov Yu.G., Sulakshina O.N., Serdyukov V.I., Sinitsa L.N.

D7 Study of the nitrous oxide isotopologues in the 4200-6500 cm^{-1} region
Sinitsa L.N., Serdyukov V.I., Emelyanov N.M., Perevalov V.I.

D8 Absorption spectra of $H_2O:SO_2$ and $H_2O:CO_2$ binary mixtures in aerogel nanopores
Ponomarev Yu.N., Solodov A.A., Solodov A.M., Kuraeva T.E., Petrova T.M.

D9 New spectroscopy of the 1.38 μm water band for CO_2 atmospheres: application to the water vapor retrieval on Mars in SPICAM/MEX and ACS NIR/TGO experiments
Fedorova A.A., Trokhimovskiy A.Yu., Lomakin A.A., Petrova T.M., Deichuli V.M., Montmessin F., Korablev O.I.

D10 Water vapor absorption line parameters in the 4500-4700 cm^{-1} spectral region
Deichuli V.M., Petrova T.M., Solodov A.M., Solodov A.A., Chesnokova T.Yu., Chentsov A.V.

D11 Speed-dependent broadening and shifting of H_2O lines in the subTHz range
Vilkov I.N., Golubyatnikov G.Yu., Koshelev M.A., Chernova A.I., Leonov I.I., Tretyakov M.Yu.

D12 Continuum absorption in gases of nonpolar molecules and their mixtures in the millimeter wave range
Galanina T.A., Koroleva A.O., Amerkhanov I.S., Serov E.A., Koshelev M.A., Tretyakov M.Yu.

D13 Bimolecular absorption of $CO_2 – CO_2$ and CO_2 – Ar in the millimeter wavelength range
Galanina T.A., Koroleva A.O., Amerkhanov I.S., Serov E.A., Koshelev M.A., Tretyakov M.Yu., Chistikov D.N., Finenko A.A., Petrov S.V., Vigasin A.A.

D14 Expanded ro-vibrational analysis of the dyad region of $^{12}CD_4$ and $^{13}CD_4$: Line positions, energy levels and absolute line strengths
Gromova O.V., Ulenikov O.N., Bekhtereva E.S., Bauerecker S.

D15 High–resolution study of the tetradecad stretching vibrational bands of $^{28}SiH_4$
Gromova O.V., Ulenikov O.N., Bekhtereva E.S., Konova Yu.V., Bauerecker S.

D16 Calculation of CO_2 -broadening and -shift coefficients of SO_2 lines in the $\nu_1+\nu_3$ band
Lavrentieva N.N., Nevzorova T.A., Dudaryonok A.S., Lavrentiev N.A.

D17 Air pressure induced nitrogen-dioxide line shift coefficients
Lavrentieva N.N., Dudaryonok A.S.

D18 On the physical meaning of the line contour parameters in the asymptotic line wing theory
Rodimova O.B., Fazliev A.Z.

D19 Description of absorption by dimers within the asymptotic line wing theory
Rodimova O.B., Fazliev A.Z.

D20 Correlation function in the asymptotic line wing theory
Rodimova O.B., Fazliev A.Z.

D21 PQN-code in vibrational spectroscopy
Yuriev M.Yu., Vakhromov V.M., Voloshchenko A.O., Klink L.B.

D22 Deperturbation analysis of the $A^1\Sigma^+$ and $b^3\Pi$ states of LiRb
Bormotova E.A., Pazyuk E.A., Stolyarov A.V., Pashov A.

D23 Specifics of internal rotation in the molecules of aldehydes containing four-membered rings
Styopin S.S., Bataev V.A.

D24 Retrieval of NO_2 tropospheric column by ground-based FTIR observations of direct solar radiation
Makarova M.V., Ionov D.V., Imkhasin H.H., Poberovskii A.V., Polyakov A.V., Kostsov V.S., Makarov B.K., Foka S.Ch.

D25 Multipass dual pattern optical scheme of the ISKRA-V high resolution IR spectrometer onboard Venera-D mission
Volkov P.A., Vinogradov I.I., Spiridonov M.V.

D26 Scientific concept of the DAVUS experiment: Descent in the atmosphere of Venus with an ultraviolet spectrometer
Belyaev D.A., Evdokimova D.G., Spiridonov M.V., Ignatiev N.I., Vinogradov I.I., Vyazovetskiy N.A., Dzuban I.A.

D27 Precision relativistic calculation of the energy spectrum of one-electron quasimolecules as function of a internuclear distance
Danilov A.

D28 Nonlinear dispersion in resonant inelastic X-ray scattering spectra as a tool for studying interatomic interactions
Ignatova N.Yu., Polyutov S.P., Kimberg V.V., Blinov S.N., Krasnov P.O., Gel'mukhanov F.Kh.

D29 Systematic ab initio solution of the vibration-rotation problem by contact transformation theory: the SO_2 benchmark computation up to the first triad
Chang X., Krasnoshchekov S.V.

D30 Cross sections for dissociative recombination of the CF_3^+ ion in collisions with low-energy electrons
Jiang X., Liu H., Zhang Y., Jiang W., Ayouz M., Kokoouline V.A.

D31 Electron scattering cross sections from NH_3: A comprehensive study based on R-matrix method
Chen Y., Jiang X., Yao L., Jiang W., Liu H., Zhang Y.

D32 Multimodal study of optical properties of murine breast tumor
Surkov Yu.I., Serebryakova I.A., Lazareva E.N., Shushunova N.A., Lomova M.V., Ansari A.M., Genina E.A.

D33 Spectral study of the effect of nanocomplexes on biological tissues
Doronkina A.A., Tuchina D.K., Lazareva E.N., Anisimov R.A., Lomova M.V., Kochubey V.I., Yanina I.Yu.

D34 Investigation of changes in the optical properties of rat model tumors during laser plasmon resonance photothermal therapy
Genin V.D., Bucharskaya A.B., Genina E.A., Kirillin M.Yu., Navolokin N.A., Terentyuk G.S., Khlebtsov B.N., Khlebtsov N.G., Tuchin V.V.

D35 Cryospectroscopic and ab initio studies of noncovalent interactions between volatile anesthetics (enflurane, isoflurane) and dimethyl ether. Spectroscopic evidence of trimer formation
Rutkowski K.S., Melikova S.M.

July 4, 2023, Tuesday

Invited Lectures E, $9^{15} – 10^{45}$

Chair: Yury V. Kistenev

E1 Terahertz sensors based on metamaterials and solid-state laser sources
Alexander P. Shkurinov

E2 Spectroscopy of tissues in a wide spectral range from deep UV to THz
Valery V. Tuchin

Round Table F, $11^{15} – 13^{45}$
“Databases and information systems in spectroscopy”

Chair: Elena A. Pazyuk

F1 Simulation of near infrared radiation transfer in the atmosphere and greenhouse gases content retrieval with taking into account new information in spectroscopic databases
Tatiana Yu. Chesnokova (Invited Speaker)

F2 Analysis of the quality of data extracted from publications in W@DIS and GrafOnto information systems
Akhlestin A.Yu., Kozodoeva E.M., Lavrentiev N.A., Privezentsev A.I., Rodimova O.B., Fazliev A.Z.

F3 Internet accessible information systems SPECTRA, S&MPO and HITRAN on the Web
Babikov Yu.L., Mikhailenko S.N.

F4 RITZ energy levels of $^{16}O_3$ deduced from experimental spectra: critical analysis of HITRAN and S&MPO transition frequencies
Tashkun S.A., Mikhailenko S.N., Barbe A., Starikova E.N., Tyuterev V.G.

F5 HAPI2: software for accessing the current version of the HITRAN database
Kochanov R.V.

F6 The status of the information system "Electronic structure of atoms" and the planned expansion into the regions of X-rays, negative ions and isotopes
Zolotarev K.V., Kazakov V.V., Kazakov V.G., Meshkov O.I., Yatcenko A.S.

Round Table G, 11^{15} – 13^{45}
“Spectroscopy in medicine and in gas analysis”

Chair: Valery V. Tuchin

G1 THz spectroscopy for biology, medicine, ecology
Vaks V.L., Domracheva E.G., Chernyaeva M.B., Anfertev V.A., Kistenev Yu.V.

G2 Application of machine learning for terahertz spectra of glioma patient blood plasma analysis
Cherkasova O.P., Vrazhnov D.A., Knyazkova A.I., Konnikova M.R., Nikolaev N.A., Kistenev Yu.V., Shkurinov A.P.

G3 Development of multimodal spectral approaches to study of skin cancer
Genina E.A., Serebryakova I.A., Surkov Yu.I., Lazareva E.N., Zaytsev S.M., Kuzinova Ya.K., Konopatskova O.M., Tuchin V.V.

G4 Breath air analysis using laser IR and terahertz spectroscopy and machine learning
Kistenev Yu.V., Borisov A.V., Vrazhnov D.A., Skiba V.E., Prischepa V.V.

G5 Optical, fluorescence and spectroscopic techniques to assess nanoparticles interaction with red blood cells
Lugovtsov A.E., Korneev K.N., Tuchin V.V., Priezzhev A.V.

G6 Light scattering, capillaroscopy and laser speckle-contrast spectroscopy techniques in the study of blood microrheology and microcirculation
Priezzhev A.V., Lugovtsov A.E., Ermolinsky P.B., Maksimov M.K., Nikitin S.Yu., Gurfinkel Yu.I., Dyachenko P.A.

G7 The study of the optical properties of the lung tissue at the action of e-cigarette liquid
Genin V.D., Yanina I.Yu., Genina E.A. , Mudrak D.A., Navolokin N.A., Bucharskaya A.B., Kistenev Yu.V., Tuchin V.V.

G8 Visualization of changes in lung tissue under the influence of electronic cigarette liquid using spectral OCT
Bucharskaya A.B., Genina E.A., Kistenev Yu.V., Tuchin V.V., Yanina I.Yu.

G9 Telluride-based optically induced terahertz metamaterials
Konnikova M.R., Khomenko M.D., Vasil`evskii I.S., Ozheredov I.A., Bychkov E.A., Shkurinov A.P.

Oral Session H, 15^{15} – 17^{15}

Chair: Leonid N. Sinitsa

H1 Self-perturbed rovibrational lines in the region of the first overtone of HBr. What I have learned from my mistakes
Asfin R.E., Domanskaya A.V., Maul C.

H2 Global modelling of the observed line positions for the spectra of ultraviolet bands: Dunham coefficients for the $A^2\Sigma^+$ excited state of the ^{16}OH molecule
Sulakshina O.N., Borkov Yu.G.

H3 The light OH molecule is still heavy to be deperturbed globally
Kozlov S.V., Pazyuk E.A.

H4 Comprehensive study of CO spectra in Ar bath in the millimeter wavelength range
Serov E.A., Makarov D.S., Vilkov I.N., Golubyatnikov G.Yu., Galanina T.A., Koshelev M.A., Balashov A.A., Simonova A.A., Tretyakov M.Yu.

H5 Rovibronic transition probabilities revisited among $B^2\Sigma^+$, $A^2\Pi$ and $X^2\Sigma^+$ states of CN radical
Kozlov S.V., Terashkevich V.A., Pazyuk E.A., Stolyarov A.V.

H6 The complex character of molecular vibrations as a source for errors in theoretical modeling of spectra of molecules with internal rotation
Bataev V.A.
H7 Effect of symmetry-breaking charge transfer in excited molecules on IR and optical spectra
Ivanov A.I.

Parallel Oral Session I, 17^{30} – 19^{00}

Chair: Petr M. Tolstoy

I1 Calculation of structures, energetics and infrared absorption spectra of hydrogen-bonded dimers and trimers formed by formaldehyde with hydrogen fluoride
Buturlimova M.V., Bulychev V.P., Tokhadze K.G.
I2 Experimental measurement of the van der Waals binding energy in X_{en}-O_2 complexes with velocity map imaging technique
Rogoveshko V.M., Bogomolov A.S., Baklanov A.V.
I3 Spectroscopy of the radiation-induced intermediates resulting from isolated phosphine molecules in low-temperature cryogenic matrices
Shiryaeva E.S., Panfutov O.D., Tyurin D.A., Feldman V.I.
I4 Comparison of algebraic-diagramming construction methods with coupled-cluster methods for calculations of ionization and electron attachment spectra
Trofimov A.B., Skitnevskaya A.D., Belogolova A.M.
I5 High-resolution spectroscopy and selective photoresponse of cold biochromophore anions: theory meets experiment
Bochenkova A.V., Beletsan O.B., Andersen L.H.

Parallel Oral Session J, 17^{30} – 19^{00}

Chair: Oleg V. Egorov

J1 Theoretical study of the evolution of electronic states with inner-level vacancies in Uracil-water system
Skitnevskaya A.D.
J2 Coupling plasmonic and photonic cavity modes in Au/SiO_2/Au nanohole arrays to increase refractive index sensitivity
Shokova M.A., Bochenkov V.E.
J3 Spectroscopic investigation of pyridinium ordering in hybrid low-dimensional perovskite $PyPbBr_3$
Bulanin K.M., Smirnov M.B., Pankin D.V., Roginski E.M., Mikheleva A.Yu., Selivanov N.I., Emeline A.V., Rudakova A.V.
J4 Implementation of up-to-date spectroscopic data on CN radical for laser-induced plasma diagnostics
Zaytsev S.M., Terashkevich V.A., Sushkov N.I.

July 6, 2023, Thursday

Invited Lectures K, 9^{15} – 10^{45}

Chair: Mikhail Yu. Tretyakov

K1 The Mars Atmosphere as revealed by IR spectroscopy in the ExoMars project
Oleg I. Korablev
K2 Microwave spectral lines of atoms and molecules as a probe of the physical properties, kinematics and chemical composition of interstellar clouds
Igor I. Zinchenko

Oral Session L, $11^{15} – 13^{45}$

Chair: Oleg I. Korablev

L1 Long-term FTIR-monitoring of the atmosphere at the St. Petersburg State University
Makarova M.V., Poberovskii A.V., Polyakov A.V., Imkhasin H.H., Ionov D.V., Kostsov V.S., Makarov B.K., Foka S.Ch.

L2 Measuring of methane isotopologues ($^{12}CH_4$ и $^{13}CH_4$) using Raman spectroscopy
Petrov D.V., Tanichev A.S., Matrosov I.I.

L3 Analysis of near-infrared transparency windows of Venus observed by SPICAV IR/Venus Express: spectroscopy uncertainties
Evdokimova D.G., Fedorova A.A., Nazarova A.V., Zharikova M.S., Korablev O.I., Bertaux J.-L.

L4 Multichannel diode laser spectrometer DLS-L for Luna-27 mission
Vinogradov I.I., Spiridonov M.V., Meshcherinov V.V., Kazakov V.A., Lebedev Yu.V., Venkstern A.A., Barke V.V.

L5 CO_2 and H_2O spectroscopy at 2.65-2.7 μm range in the ACS/TGO experiment to study atmospheric structure and water climatology on Mars
Belyaev D.A., Fedorova A.A., Trokhimovskiy A.Yu., Korablev O.I., Montmessin F.

L6 Carbon and nitrogen abundance determination in stellar atmospheres by molecular lines
Ryabchikova T.A., Piskunov N.E., Pakhomov Yu.V.

L7 NO biosignature: transmission and emission spectroscopy for its potential detection with WSO-UV observatory
Tsurikov G.N., Bisikalo D.V.

L8 An affect of H_2O-CO_2 collisional broadening parameterization at 6 μm fundamental H_2O band on retrieval of column water vapor abundance in Martian atmosphere from ACS TIRVIM nadir measurements onboard ExoMars TGO
Vlasov P.V., Ignatiev N.I., Korablev O.I., Fedorova A.A., Shakun A.V., Patsaev D.V., Maslov I.A., Evdokimova D.G., Zasova L.V., Luginin V.C., Trokhimovskiy A.Yu., Grigoriev A.V., Montmessin F.

Oral Session M, $15^{15} – 17^{15}$

Chair: Semen N. Mikhailenko

M1 Spectroscopy in collisions in molecular plasma
Vyacheslav A. Kokoouline (Invited Speaker)

M2 Millimeter-wave coaxial jet spectrometer for study of weakly bound molecular complexes
Surin L.A., Tarabukin I.V., Panfilov V.A.

M3 Lidar-based infrared remote gas sensor for measuring the atmospheric air methane concentration
Meshcherinov V.V., Spiridonov M.V., Kazakov V.A., Rodin A.V.

M4 Coherent quasi-pulse THz molecular crystal source
Sinko A.S., Kargovsky A., Surovtsev N., Shkurinov A.P.

M5 Resonant x-ray scattering: A short review (20 min)
Polyutov S.P., Kimberg V.V., Ignatova N.Yu., Blinov S.N., Krasnov P.O., Gel'mukhanov F.Kh.

Poster Session N, $17^{30} – 19^{00}$

N1 Analysis of $N^{18}O$ isotopolog in the 5200 – 5500 cm^{-1} infrared spectral region
Borkov Yu.G., Sulakshina O.N., Serdyukov V.I., Sinitsa L.N.

N2 LED-based Fourier spectroscopy of $^{14}N^{14}N^{16}O$ in the 9800-12000 cm^{-1} region
Sinitsa L.N., Serdyukov V.I., Emelyanov N.M., Perevalov V.I.

N3 Analysis of water vapor absorption lines in the modern spectroscopic databases in the 16700-17000 cm^{-1} region
Sinitsa L.N., Chesnokova T.Yu.

N4 Collisional transformation of the complex vibrational susceptibility of a linear molecule: the ν_3 band of CO_2 as a guiding example
Kouzov A.P., Filippov N.N., Egorova N.I., Asfin R.E.

N5 Broadening and shifting coefficients of rovibrational lines in the first overtone of HF perturbed by He

Asfin R.E., Diachkova O.O., Katunov T.D.

N6 Line profiles of sodium pressure broadened by helium atoms

Chervinskaya A.S., Dorofeev D.L.

N7 Modification of vibrational parameters of a linear symmetric triatomic molecule by a laser field

Kornev A.S., Chernov V.E., Dorofeev D.L.

N8 Set H_2O-HF dimer warm rotational spectra: new measurements and re-analysis

Golubyatnikov G.Yu., Polyansky O.L., Zobov N.F., Tretyakov M.Yu., Ovsyannikov R.I.

N9 Measurement and calculation of the CO 6th overtone line intensities

Balashov A.A., Bielska K., Li G., Kyuberis A.A., Wojtewicz S., Domyslawska J., Ciurylo R., Zobov N.F., Lisak D., Tennyson J., Polyansky O.L.

N10 The high sensitivity absorption spectroscopy of acetylene near 765 nm

Lyulin O.M., Vasilchenko S.S., Perevalov V.I.

N11 High sensitivity absorption spectroscopy of hydrogen chloride near 770 nm

Vasilchenko S.S., Lyulin O.M., Perevalov V.I.

N12 N_2-, O_2-, air-broadening coefficients and their temperature dependence of CH_3I rovibrational lines for the ν_6 band

Lavrentieva N.N., Dudaryonok A.S., Buldyreva J.

N13 A model of fluorescence quenching induced by hydrogen-bonding in mixtures of protic and aprotic solvents

Feskov S.V., Ivanov A.I.

N14 On the uncertainty of the calculated intensities of water vapor lines in the subTHz frequency range

Ovsyannikov R.I., Tretyakov M.Yu., Koshelev M.A., Galanina T.A.

N15 *Ab initio* quantum defect theory revisited Rydberg's states of H_2

Likharev A.S., Pazyuk E.A., Stolyarov A.V.

N16 Current status of the S&MPO information system

Mikhailenko S.N., Barbe A., Babikov Yu.L., Starikova E.N., Tyuterev V.G.

N17 The 000 and 010 states revisited for ^{18}O-substituted isotopic species of ozone

Starikova E.N., Barbe A., Manceron L., Grouiez B., Burgalat J., Tyuterev V.G.

N18 The $^{13}CH_4$ absorption spectrum at 298 K: Assignment and modeling of the lower part of the Tetradecad in the 4970–5300 cm^{-1} spectral range

Starikova E.N., Sung K., Nikitin A.V., Rey M.

N19 Synthetic $B^2\Sigma^+$-$X^2\Sigma^+$ band spectra of the CN radical: comparison of the equilibrium and multi-temperature models

Terashkevich V.A., Pazyuk E.A.

N20 Convergence of the parameters of the two-temperature model with self-absorption for CN radical spectra fitting on the example of $B^2\Sigma^+$ - $X^2\Sigma^+$ transition

Zaytsev S.M., Terashkevich V.A., Sushkov N.I.

N21 O_2 A-band line parameters for application to CO_2-rich planetary atmosphere

Petrova T.M., Solodov A.M., Deichuli V.M., Solodov A.A., Fedorova A.A.

N22 Water vapor absorption line parameters in the IR spectral region

Deichuli V.M., Solodov A.M., Solodov A.A., Fedorova A.A., Petrova T.M.

N23 Broadening and shift coefficients of the H_2O absorption lines induced by atmospheric air pressure

Deichuli V.M., Petrova T.M., Solodov A.M., Solodov A.A., Starikov V.I.

N24 Look at all Those Surfaces! The Exited States of the Rb Trimer

Bormotova E.A., Likharev A.S., Stolyarov A.V.

N25 Theoretical study of the structure and conformational behavior of some cyclopropane derivatives in the ground and excited electronic states

Styopin S.S., Bataev V.A., Akimov G.A.

N26 Data quality control in IS W@DIS. Filtering wavenumber values in spectral data collections

Akhlestin A.Yu., Lavrentiev N.A., Privezentsev A.I., Fazliev A.Z.

N27 The results of systematization and analysis of plots on the continual absorption of water vapor from publications 1898-2020

Lavrentiev N.A., Rodimova O.B., Fazliev A.Z.

N28 The results of systematization and analysis of plots for the continual absorption of carbon dioxide extracted from publications of 1956-2010

Lavrentiev N.A., Rodimova O.B., Fazliev A.Z.

N29 Measurement of singlet oxygen concentration in ambient atmosphere

Adamenkov Yu.A., Gorbunov M.A., Kalacheva A.A., Shaydulina V.A.

N30 Study of the influence of oxygen on the active medium of an optically pumped rare gas laser using a kinetic 0-D(t) model
Yuriev A.V., Adamenkov Yu.A., Gorbunov M.A., Shaydulina V.A., Kalacheva A.A.

N31 Improved *ab initio* potential energy surface of the ozone molecule near the first dissociation limit including the spin-orbit coupling
Egorov O.V., Kochanov R.V., Tyuterev V.G., Kokoouline V.A.

N32 *Ab initio* potential energy and dipole moment surfaces for disulfur monoxide
Egorov O.V., Rey M., Kochanov R.V., Nikitin A.V., Tyuterev V.G.

N33 Spectra of the formaldehyde molecule in the range of 3800-5100 cm^{-1}
Rodina A.A., Nikitin A.V., Rey M. , Manceron L., Protasevich A.E., Tyuterev V.G.

N34 Current progress in variational calculations of polyatomic hydrocarbons (C_2H_2, CH_4, C_2H_4, C_3H_4, and C_2H_6)
Rodina A.A., Nikitin A.V., Protasevich A.E., Egorov O.V., Rey M., Viglaska D., Galyapin P., Tyuterev V.G.

N35 Refractive index gratings excited by mid-infrared radiation, and local measurements of CH_4 concentration, gas composition, pressure, and temperature in methane-containing gas mixtures
Sahlberg A.-L., Hot D., Kozlov D.N., Li Zh.

July 7, 2023, Friday

Invited Lectures O, $9^{15} – 10^{45}$

Chair: Maksim A. Koshelev

O1 Precision spectroscopy of two-atom molecules at the threshold of their dissociation
Andrey V. Stolyarov

O2 Spectroscopy and dynamics of unstable molecules: ozone puzzle
Vladimir G. Tyuterev

Oral Session P, $11^{15} – 13^{00}$

Chair: Konstantin V. Kazakov

P1 Generalized relativistic pseudopotentials for the light elements simulating the relativistic and QED effects
Mosyagin N.S., Titov A.V., Oleynichenko A.V., Zaitsevskii A., Stolyarov A.V.

P2 *Ab initio* rovibrational energy levels for four isotopologues of triplet (X^3B^1) methylene
Egorov O.V., Rey M., Viglaska D., Nikitin A.V.

P3 Improved ozone vibrational band centers for symmetric and asymmetric isotopologues: *ab initio* calculations including Diagonal Born-Oppenheimer correction
Kochanov R.V., Tajti A., Szalay P.G., Tyuterev V.G.

P4 Energy spectra of light one-electron matter-antimatter quasimolecules
Anikin A.A.

Closing Ceremony

Invited Lectures A
Monday, July 3, $10^{30} - 13^{00}$
Chair: Valerii I. Perevalov

A1

Bimolecular spectra and atmospheric continuum: precise experiment and nonempirical modeling

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Discovered at the end of the 19-th century as a low-frequency component of water vapor absorption in the 8-14 um atmospheric transparency window, the phenomenon of the continuum remained unexplained for about 40 years, until Elsasser hypothesized that the continuum is an accumulated ***far-wing*** contribution of strong water vapor spectral lines from neighbor bands [1]. This hypothesis was generally accepted until the strong negative temperature dependence of the continuum absorption was detected in addition to pure quadratic pressure dependence. To explain the observations, Viktorova and Zhevakin [2] and then Penner and Varanasi [3] and Varanasi et al. [4] suggested that the continuum is caused by ***water dimers.*** Since then a long scientific discussion has been continuing between adherents of the "monomer" (or "far-wings") and the "dimer" nature of the water vapor continuum. Considering the continuum in gases as a bimolecular absorption [5] and revealing bimolecular absorption bands in H_2O continuum spectra [6] should be mentioned as important milestones of the story. The crucial step was the observation of the rotationally resolved water dimer spectrum in water vapor in conditions close to atmospheric ones [7–9] and its independent verification by observation of the envelop of the dimer rotational spectrum [10]. These measurements, supported by sophisticated *ab-initio* calculations [11], left no doubt about the nature of the continuum in the millimeter and submillimeter wave range. However, further study of the continuum within pure rotational and fundamental vibrational H_2O bands revealed that the dimer hypothesis alone not enough: more dimers than allowed by the second virial coefficient of gas equation of state are required to explain the observed absorption, and the far wings hypothesis was revisited [12]. Qualitative analysis of the continuum magnitude and supporting evaluations of its temperature dependence demonstrated that these two mechanisms complement each other and make a comparable contribution to the continuum [13, 14].

In spite of the significant progress in understanding the continuum, available information is still insufficient for constructing a complete predictive, physically justified model. The solution lies in proper calculation of the colliding molecules absorption spectrum not limited by the impact approximation. The semi-classical trajectory-based method [15, 16] seems to be most suitable at the moment for solving the problem. Bimolecular spectra (including the dimeric component) of nonpolar molecules-monomers calculated using this method are amazingly consistent with the experiment [17]. The extension of the method to polar molecules will provide a unique opportunity for simultaneous tracing of (i) the evolution of a monomer dipole during the collision (determining the behavior of resonance line far wings) and (ii) the appearance of a joint transient dipole of colliding molecules (responsible for the bimolecular absorption). The current stage of the project aimed at the solution of this task will be discussed in the lecture.

The work is supported by the RSF (project 22-17-00041, https://rscf.ru/project/22-17-00041).

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A2

Molecular time-domain spectroscopy at NovoFEL: implemented experiments and potential possibilities

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Ultrafast terahertz time-domain molecular spectroscopy in real time has been intensively developed at the NovoFEL, starting from work [1]. Many specific non-stationary effects have been demonstrated [2] and many different spectroscopic techniques have been developed [3–7]. At last time, spectroscopic studies of the OH radical, the most important intermediate short-lived component in many chemical reactions of combustion and explosion, have been carried out at NovoFEL [8–11]. In recent work [12, 13] advantage of using the week magnetic field and heterodyne scheme for very essential increasing of sensitivity was demonstrated.

Ultrahigh-resolution spectroscopy at the NovoFEL was carried out both to fully characterize its radiation [14] and to elucidate the potential capabilities of the laser in this field. In particular, the possibility of creating a high-power ultramonochromatic tunable THz source [15], a super-resolution *comb*-spectrometer [16], and ultra-high resolution coherent spectroscopy was shown. This requires the suppression of NovoFEL radiation instabilities in both the gigahertz [17] and megahertz ranges [18].

The study was supported by the Russian Science Foundation (grant No. 19-73-20060).

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Oral Session B
Monday, July 3, $11^{45} – 13^{45}$
Chair: Leonid A. Surin

B1

Faraday effect on the absorption lines of hydroxyl radical. Experiments with the CW lasers and time-domain experiments at the terahertz NovoFEL

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The effect of rotation of the polarization plane in a magnetic field is compared in experiments with a cw laser and in time-domain experiments. The experiments were carried out on narrow absorption lines of the hydroxyl radical (OH) in the gas phase. A cw 1434 nm DFB laser diode was used. The pulse experiments were performed at terahertz NovoFEL. In a longitudinal magnetic field, the OH absorption line splits into a right-hand and left-hand circular polarization components, which leads to a rotation of the polarization plane after the sample.

Hydroxil radicals OH was produced in photochemical reaction in ozone – water vapor mixture. After initiation the photochemical reaction by UV laser pulse the concentration of the OH was monitored by absorption at 1434 nm. The effect of polarization rotation in magnetic field was studied using two nearly crossed polarizes. It was found that the angle of rotation is proportional to the concentration of OH. Typical values of the rotation angle was 10^{-3} for OH concentration $5*10^{13}$cm^{-3} in magnetic field 200G.

In the time-domain experiments, the effect looks like a rotation of the polarization plane of free induction signal (FID) [1, 2] in a magnetic field. After the FEL excitation pulse, the induction polarization plane begins to rotate [3–7]. Large rotation angles are observed; for induction signals with a duration of the order of 10 nsec, the angle can exceed 90 degree [3, 5]. In contrast to experiments with cw lasers, the angle of rotation does not depend on the concentration of absorbing molecules. The modulation effects of free induction in a magnetic field are studied in detail. A nonmonotonic dependence of the angle of rotation on time is shown [7]. The effect of phase switching with a change in the direction of the magnetic field is demonstrated [8].

The study was supported by the Russian Science Foundation (grant No. 19-73-20060).

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B2

Water vapour self-continuum absorption within the IR absorption bands: semiempirical dimer-based model

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An important component of the absorption spectrum of the Earth's atmosphere is the water vapour continuum absorption (or "continuum"). In the case of an equal content of atmospheric gases in the mixture, the value of the so-called self-continuum absorption of water vapour prevails as compared to the continuum formed by other gases. This is caused by the fact that the origin of the continuum is associated with the intermolecular interaction of gas molecules, which is most pronounced for the H_2O molecule due to the formation of intermolecular hydrogen bonds.

Pair interactions of molecules are of the greatest importance for the self-continuum. On the one hand, they cause formation of the simplest H_2O molecular short-lived complexes – H_2O dimers – with characteristic absorption spectra [1]. On the other hand, they lead to changes in the shape of far wings of H_2O lines that go beyond the impact approximation [2]. It is known today that the water dimers make the main contribution to the water vapour self-continuum within the IR absorption bands, while the «line wings» mechanism may dominate in the atmospheric windows. However, a rigorous physically based separation of the contributions of each of these mechanisms to the continuum is currently not available. Therefore, semiempirical models are used for applications to reproduce the water vapour continuum absorption spectra. The MT_CKD continuum model, which extends over a wide spectral region from 0 to 20 000 cm^{-1}, is widely used in many applications [3]. However, within the IR bands, the MT_CKD often provides a weak prediction of the magnitude and (or) spectral features of the water vapour continuum absorption, especially at temperatures above atmospheric (see, for example, [4]).

Here, we propose a semiempirical modification of the water dimer model [5] to reproduce the magnitude and spectral features of the water vapour self-continuum within the IR absorption bands in the frequency region from 50 to 11200 cm^{-1} (from 200 to 0.89 μm) in a wide temperature range from 280 to 430 K. The so-called semiempirical dimer-based model describes the water vapour self-continuum as a set of spectra of bound and quasibound water dimers, simulated using the last available spectroscopic information on transitions in water dimer and the effective equilibrium dimerization constant (characterizing the content of H_2O dimers in the water vapour at given temperature) obtained from fitting. The average deviation of the model from the experimental continuum data in the IR absorption bands is no more than 15% within the spectral and temperature boundaries of the model. The listed characteristics of the semiempirical dimer-based model provide its advantage when comparing with the known continuum models within the IR absorption bands.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (V.E. Zuev Institute of Atmospheric Optics SB RAS).

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B3

Water vapor continuum at room temperature in 1.25 μm atmospheric window

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Water vapour self- and foreign-continua are newly measured in the high energy edge of the 1.25 μm atmospheric window of transparency at room temperature and pressures up to 1 atmosphere. The measurements are carried out in pure water vapour and its mixture with air, nitrogen and oxygen by using highly stable and sensitive cavity ring-down spectroscopy technique (CRDS) [1]. Self- and foreign-continuum absorption cross-sections are retrieved from recorded pressure ramps at fixed frequencies in microwindows of transparency between strong H_2O lines. These microwindows are selected to minimise water monomer spectrum contribution to the total absorption spectrum (although even in this case H_2O lines represents up to 70% of measured absorption for pure water and up to 83% for humidified N_2, O_2 and air).

The spread of previous continuum measurements at lower frequencies (reaching several orders of magnitude in some atmospheric windows [2]), requires a checking of possible systematic errors in data acquisition and analysis. Minimisation of such errors in the presented work is confirmed by (1) the demonstration of the expected pressure dependences both for self- and for foreign-continuum and (2) the consistency of continuum measurements in humidified nitrogen and oxygen with measurements in humidified air.

Presented results agree with previous self-continuum measurements at lower frequencies [2] and with high-temperature measurements of the water-related continuum in air [3]. Together with the previous high-temperature measurements [3, 4], the new data allow to refine information about the temperature dependence of the continuum.

The frequency dependence of the retrieved self- and foreign continuum cross-sections validates in general MT_CKD model [5]. However, an additional weak broad absorption feature is observed in the self-continuum with a centre near 8455 cm^{-1}. It can be tentatively interpreted as due to uncertainties on the resonance line contribution on the derived self-continuum values but, there are also arguments to consider it as possible spectral signature of bound dimers, $(H_2O)_2$. Similar peaks in the continuum spectrum were previously observed near 1600, 3610 and 3750 cm^{-1} and attributed to water dimers [7]. Thus, the detection of the peak at 8455 cm^{-1} may confirm that dimer features are manifested in the entire range of the vibrational-rotational spectrum of water vapor.

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5. https://github.com/AER-RC/MT_CKD/

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* Koroleva A. is an applicant for the best young scientist talk award (oral).

B4

Continuum absorption of CO-Ar mixture in the far IR range

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Physically based modeling of radiation absorption by real gases over wide frequency and temperature ranges are required for the development of climate and radiation transfer models relevant to the atmospheres of terrestrial planets and exoplanets. In particular, the effects associated with non-instant intermolecular interactions, which manifest themselves in the behavior of the far wings of molecular lines and in the spectra of molecular pairs (bimolecular absorption) must be considered. These effects are commonly attributed to the continuum absorption, which is empirically defined as the difference between the observed and calculated resonance spectra of colliding monomers. Classical trajectory based calculations of molecular collisional scattering in combination with highly accurate experimental data demonstrating the smooth continuum pedestal underneath the resonance spectrum seems promising for the development of a physically based model (e.g., [1]). In this work, such experimental data were obtained for the pure rotational spectrum of CO in the Ar bath.

Broadband spectra of the CO–Ar mixture were recorded in the far IR range (40–130 cm^{-1}) by Fourier Transform Spectroscopy using the SOLEIL synchrotron as a high-power radiation source. The spectra were recorded at room temperature and a pressure of 1 atm, with CO content varying within 5-15 %. As a result of the analysis of the resonant part of the absorption, the coefficients of line broadening by Ar pressure were determined. The obtained values agree with the results of calculations by the method of classical trajectories [2] and with the experimental data for the CO fundamental vibration band from [3].

The analysis of the recorded CO-Ar spectra in the range of the pure rotational band of the CO molecule allowed revealing the continuum under resonance absorption. Preliminary analysis of the observed continuum pressure dependence indicates its bimolecular nature. Trajectory based calculations of the collision induced absorption of radiation by the considered molecular system are required to confirm this hypothesis.

Experimental data were obtained in the AILES laboratory at the SOLEIL synchrotron within the framework of project No. 20181852. The spectrum analysis was supported by the Russian Science Foundation (project 22-17-00041, https://rscf.ru/project/22-17-00041). Classical trajectory study was supported by the Russian Ministry of Science and Higher Education within the framework of the state task of the FSRC "Crystallography and Photonics" RAS.

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B5

The last advances in the infrared acetylene spectroscopy

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The immense number of the new high resolution spectral data for the principal isotopologue of acetylene has been obtained by the authors during the last decade. This was achieved due to the utilization of the high sensitive Fourier and CRDS spectrometers from the one hand and due to the development of the acetylene global effective Hamiltonian [1] and the effective dipole moment operator [2] from the other hand. The line lists generated in the result of these works have been included in the HITRAN and GEISA databases. The talk will give an overview of our recent measurements and analysis of the acetylene spectra for a wide spectral range. Several interesting features observed in the acetylene spectra will be presented.

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B6

Accurate line shape parameters of oxygen fine-structure lines for atmospheric applications

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Weak magnetic dipole fine structure lines of molecular oxygen are widely used in microwave radiometric atmospheric measurements for retrieving temperature or pressure distribution. The accuracy of determining the atmospheric parameters depends on the accuracy of the absorption and radiative transfer model used and, in particular, on the underlying spectroscopic parameters of the molecular lines and the continuum.

This work is devoted to experimental study of the shape of the oxygen fine structure lines in the wide range of thermodynamic conditions and the widest possible range of rotational quantum numbers (up to N=43). A temperature interval of about 120 K centered at room temperature is considered. A wide pressure range (0.02–1500 Torr) is covered by three fundamentally different spectrometers [1] having complementary abilities: a conventional direct absorption (video) spectrometer, a spectrometer with a radio-acoustic detector (RAD) and a resonator spectrometer. The signal-to-noise ratio of the experimental recordings reached up to 20000.Various collisional effects manifested in the experimental spectra at significantly different pressures were studied, including (almost immeasurable) pressure shifting and the speed dependence of collisional relaxation rate. The latter was investigated in the framework of the widely used quadratic approximating function [2]. The multispectrum fitting procedure, which applied the simultaneous fitting of the model function to all experimental spectra of a chosen line at a given temperature, was used to minimize possible correlation of the line shape and baseline parameters in the model function. As a result, line center positions were determined with subkHz uncertainty from the analysis of the low pressure spectra from the video and RAD spectrometers [3]. Rotational dependence of the speed-averaged pressure broadening γ_0 and speed-dependent parameter γ_2 were refined confirming the results of our earlier study performed at room temperature [4]. The temperature behavior of γ_2 was studied for the first time. Results from different spectrometers validated each other within the experimental uncertainties. It was demonstrated that the single power law is suitable for both $\gamma_0(T)$ and $\gamma_2(T)$ within the studied temperature range. It was found that the corresponding temperature exponents $n_{\gamma0}$ and $n_{\gamma2}$ showed a significantly different rotational dependence, which also depends on a collisional partner (O_2, N_2).The experimental results for the 118-GHz line are in impressive agreement with the results of the quantum scattering calculations [5]. Intensity of the 118-GHz line was determined from the resonator spectrometer data with a subpercent uncertainty, which allowsassigned a higher (by 3 steps according to the HITRAN classification) intensity accuracy category for all fine structure lines. The new accurate spectroscopic data for the oxygen spectrum are appropriate for calibrating results of quantum chemical calculations and refining the radiative transfer models.

The work was supported by the Russian Science Foundation (project No. 22-72-10118, https://rscf.ru/project/22-72-10118).

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B7

Pressure broadening coefficients of the ν_2 Raman band of methane in natural gas

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Raman spectroscopy has significant potential in natural gas analysis [1–3, and references therein]. This approach is characterized by a high measurement speed, the possibility to detect all molecular compounds using a single device with a non-tunable laser, and the possibility of in situ measurements. The least squares method (or contour fit method) is the most reliable for such multicomponent gas mixtures since it overcomes the problem of mutual overlap of Raman bands [4]. However, Raman bands are sensitive to variations in the density and composition of a gas sample [5–8]. Therefore, the main difficulty of the contour fit method is related to the necessity to provide equal spectral characteristics of Raman bands in the reference spectra and the spectrum of the analyzed mixture for the most accurate measurement [3]. The study of vibrational bands of methane is a priority task since they are the most intense in the Raman spectrum of natural gas.

Simulation of a spectrum is one of the most efficient approaches for this purpose. However, spectroscopic parameters taking into account the influence of pressure and various media are required to calculate a synthetic spectrum. We present experimentally measured pressure broadening coefficients of the methane lines in the ν_2 Raman band range perturbed by main impurities of natural gas. A spontaneous Raman spectrometer based on a 90 scattering geometry was used to record spectra. The obtained spectra were fitted using a spectra simulation algorithm to retrieve the broadening coefficients. The model spectrum was computed as a convolution of a molecular spectrum and an instrument response function. The molecular spectrum was calculated as the sum of the Lorentzian profiles of rotational-vibrational lines. The averaged self-, N_2, CO_2, C_2H_6, C_3H_8, n-C_4H_{10}, and i-C_4H_{10}-broadening coefficients for the S(J) manifolds of the ν_2 band of methane were obtained for the first time. Moreover, we determined the temperature dependence exponents for self-broadening coefficients.

The methane spectrum in natural gas can be simulated in the range of 800–2000 cm^{-1} at different densities using the found broadening parameters. We believe that our data will improve the accuracy of the analysis of methane-bearing gases by Raman spectroscopy.

This work was supported by the Russian Science Foundation (grant No. 19-77-10046).

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Invited Lectures C
Monday, July 3, 15^{15} – 17^{15}
Chair: Andrey V. Stolyarov

C1
Diagnostics of geometry of intermolecular complexes using the combination of advantages of IR and NMR spectroscopy

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The formation and strengthening of hydrogen bonds (H-bonds) manifests itself in striking geometric and spectral characteristics of complexes. So much so that these manifestations constitute the majority of H-bond formation criteria [1], while spectroscopic parameters become essential probes for H-bond diagnostics [2]. For example, bridging proton deshielding in NMR spectra and red-shift of proton donor stretching frequency in IR spectra are among widely known and reliable H-bond predictors. Construction of new predictive correlations is in high demand, especially for the characterisation of soft matter, where the direct information on interatomic distances and complexation energies is hard to obtain. There are two main advantages of using a combination of NMR and IR for the study of H-bonded complexes.

Firstly, all NMR and IR spectroscopic parameters could be roughly divided into two major groups: those that change monotonously upon gradual proton displacement (markers for the proton transfer degree) and those that pass an extremum for short strong H-bonds (markers for the hydrogen bond length or complexation energy). It is clearly advantageous to combine parameters from both groups, which in many cases becomes easier if both types of spectroscopy are considered.

Secondly, experimental measurement of NMR and IR spectra often requires different techniques of sample preparation and different measurement conditions, which leads to only partially consistent spectral data. One of the most dramatic effects is due to the difference in characteristic times: NMR spectral data are averaged over much longer periods of time. This could be a curse or a blessing in disguise: NMR and IR might provide complementary "views" on the same system.

In this presentation we overview the results obtained over the last couple of years, concerning the construction of NMR [3–5] and IR [6–9] hydrogen bond correlations for various intermolecular hydrogen-bonded complexes. We also briefly touch the subject of halogen bonds [10, 11] and NMR/UV-vis combination [12].

This work presents some of the results obtained under support of the Russian Science Foundation (grant Nos. 18-13-00050 (complexes with isolated H-bonds) and 23-13-00095 (complexes with chains of cooperative H-bonds)).

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C2

Rotational dynamics of molecules on a basis of generalized Euler equations

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One of the goals of molecular spectroscopy consists in solution of a rovibrational problem. At the first glance, the solution of this problem can readily be obtained by variational quantum mechanical method. But in reality, quantum mechanical method is restricted. First, the computational cost of such quantum calculations is still too high, so that high precision calculations are available for small molecules only. Second, quantum calculations give numerical results only but don't explain a structure of rotational spectra.

To gain a better understanding of a nature of rotational spectra we use classical mechanics. Dynamical equations of a solid body are generalized to real molecules, i.e., with regard to the interaction between the total rotation of a molecule and intermolecular motion. In the context of this classical approach the model of the soft body is proposed.

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Cold ion fragmentation spectroscopy-mass spectrometry for identification of isomeric carbohydrates and lipids

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Combination of mass spectrometry and photodissociation UV spectroscopy has been used for identification of peptides and drug molecules since a decade. Lipids and carbohydrates are ubiquitous in living organisms but appear to be one of the most difficult type of biomolecules to study on atomic level. Lipids have no well-classified structural units. Carbohydrates contain a variety of isomeric units, but different from peptide, they can be differently interconnected in branched chains. All these properties make identification of these two types of molecules extremely difficult. In addition, they do not absorb, which makes it challenging a use of UV spectroscopy for their identification. We make use of intermolecular hydrogen bonds to distinguish very similar isomeric glycans and isomeric lipids by fragmentation spectroscopy of cryogenically cooled complexes of the molecules with aromatic peptides. An aromatic reporter molecule changes its absorption differently in the complexes with different isomers of a host molecule. We detect these differences and use it for library-based quantifications of isoforms mixed together.

The non-covalent complexes of the analyte molecules with a reporter aromatic molecule are readily formed in solution upon mixing. Soft mode of electrospray ionization allows for transfer of the complexes to the gas phase with little dissociation. The ions of interest are, first, m/z selected by a quadrupole mass filter and then transferred to an octupole ion trapped, where they are cooled to T=10 K in collisions with He buffer gas. Cooling suppresses inhomogeneous spectral broadening, making the spectra structured and more distinguishable. The cold complexes are then irradiated by a 5-ns pulse of UV or IR light, and the appearing fragments are detected by a quadrupole MS. Scanning wavelength of UV/IR laser light while detecting the appearing charged fragments generates a respective spectrum of the complex [1, 2].

We first measure such spectra for a set of isomeric molecules of interest and store them as a library. Next, the spectrum of a mixture of these isomers is measured and mathematically decomposed in the basis set of the library. This allows for quantitative identification of the mixed in solution isomers of the same mass.

The typically achieved accuracy for small saccharides is 1–3%, increasing to 5% for large molecules and/or for sets of small isomers [3]. We demonstrate that such analytical identifications can be done online with HPLC [4–6].

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D1

Integrated intensities of the vibrational-rotational lines of C_2HD in the 6527–6563 cm^{-1} and 6611–6642 cm^{-1} infrared spectral regions

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Using tuning DFB laser diodes, we measured integrated (2,0,0,0,0) and (1,0,1,0,1) band intensities of C_2HD molecule in the 6527 – 6563 cm^{-1} and 6611 – 6642 cm^{-1} frequency ranges. Experiments were performed with a synthesized mixture of isotope acetylene molecules obtained by the reaction of water with calcium carbide. The mixture used in the synthesis was $H_2O : D_2O = 1 : 4$. As a result of the isotopic exchange, the light hydrogen isotope turned out to be predominantly in the form of C_2HD. The isotopic composition of the mixture, according to the results of mass spectrometric analysis, was 4.7% of C_2H_2, 33.9% of C_2HD and 61.4% of C_2D_2.

The measurements were performed with SBF-C53S2 and SBF-C51S2 laser diodes from Shengshi Optical Tech [1] tuned in the previously specified ranges. These ranges include the P3 – P18 and R11 – R44 lines of the C_2HD molecule, as well as a number of C_2H_2 lines. The molecules of C_2D_2 do not have intensive bands in these ranges. The gas pressure in the measurements was 32 Torr and 4 Torr, the laser beam path length in the gas mixture was 3 m. The results of the gas mixture scanning and an empty cell scanning were recorded separately. The contour of each line was approximated by the Voigt function.

The frequencies of the C_2HD lines determined with respect to the reference C_2H_2 lines coincided with those given in [2]. The intensities of the fundamental C_2HD vibrational bands were measured in [3]; however, there are still no data for overtone bands in the literature.

This work was supported by the Russian Science Foundation (grant No. 19-73-20060).

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[*] Plastinina is an applicant for the best young scientist talk award (poster).

D2

Fourier transform absorption spectrum of SO_2 in 3500-3700 cm^{-1} spectral region

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This study is devoted to studying the absorption spectrum of Sulfur dioxide. The spectrum was recorded at room temperature in Infrared laboratory of Oulu on the Bruker IFS-120HR Fourier transform spectrometer in the spectral region from 3500 to 3700 cm^{-1} at an optical path length of 15360 cm and a pressure of 4,73 Torr.

The intensities and positions of the lines were determined by interactive least squares multi-line fitting program. About 5200 rovibrational transitions were assigned to four vibrational bands for the $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ isotopologues. The lines of the $3\nu_1+\nu_3-\nu_1$ hot band of the $^{32}S^{16}O_2$ were assigned for the first time. Three thousand one hundred and sixty accurate experimental energy levels are derived, 1231 of them are new ones. The resulting energy levels were modeled using the effective Watson-type Hamiltonian. The obtained spectroscopic parameters reconstruct the energy levels with accuracy close to experimental uncertainties.

The obtained data have been compared with previous publications [1-4] as well as with variational calculations [5].

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D3

Calculation of vibration-rotation transition frequencies and *RKR* potentials of the HBr molecule

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About 1400 rotation and vibration-rotation frequencies of six isotopologues of the hydrogen bromide molecule (HBr) were collected based on 20 experimental sources. The experimental data set covers the range from 5.7 to 17,942 cm^{-1} with maximum quantum numbers $V_{\max} = 8$ and $J_{\max} = 37$. Fitting of transition frequencies allowed us to obtain a set of mass-independent spectroscopic parameters U_{mj}, Δ^{A}_{mj} and Δ^{B}_{mj}, reproducing rotation and vibration-rotation transition frequencies with an average accuracy of 180 kHz and 0.0015 cm^{-1}, respectively. The calculated vibrational energies were used to calculate the *RKR* potentials of all six isotopologues of the molecule.

The calculated list of transition frequencies is compared with HBr linelist of the HITRAN2020 spectroscopic database [1].

This work was supported by the Ministry of Science and Higher Education of the Russian Federation.

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D4

The absorption bands of $^{12}C^{16}O_2$ near 718 nm

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The absorption spectra of carbon dioxide were recorded in the region from 13500 to 14200 cm^{-1}, using a Bruker IFS 125 HR Fourier transform spectrometer and a 30 meters multipass cell with the White type optical system. The recording was performed at spectral resolution of 0.03 – 0.04 cm^{-1}, room temperature, path length of 1057.95 m and at three pressures of 252, 403 and 582 mbar. The achieved sensitivity (noise equivalent absorption) at the level of $k_\nu = 6\times10^{-10}$ cm^{-1} allowed detection of a number of lines of three 2005*i* - 00001 (*i*=1,2,3) bands of $^{12}C^{16}O_2$ with the intensity values down to 10^{-29} cm^{-1}/(molecule cm^{-2}) at 296 K. The 20053 – 00001 band was observed for the first time. The line intensities for all bands were measured for the first time. The uncertainty of the line position measurements was estimated to be about 0.007 cm^{-1} for the unblended lines with a high value of the signal-to-noise ratio. The uncertainties of the retrieved line intensities for the strongest unblended lines are on the level of 10%. The spectroscopic constants for the three observed bands were fitted to the observed line positions. The vibrational transition dipole moments squared of these bands were fitted to the observed line intensities. A comparison of the measured line positions to those from the HITRAN2020 database was done. Finally a comparison of the measured line intensities to those contained in the HITRAN2020 database as well as in the new version of the Ames line list was also given.

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D5

The first observation of the $^{12}C^{16}O_2$ absorption bands near 660 nm

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The absorption spectra of carbon dioxide were recorded in the region from 15000 to 15300 cm^{-1}, using a Bruker IFS 125 HR Fourier transform spectrometer and a 30 meters multipass cell with the White type optical system. The recording was performed at a spectral resolution of 0.044 – 0.05 cm^{-1}, room temperature, a path length of 1057.95 m and pressures of 185 and 362 mbar. Utilization of a LED as a light source provided a sensitivity (noise equivalent absorption) at the level of $k_\nu = 2.5\times10^{-10}$ cm^{-1} and allowed detection of a number of lines of two 3005i - 00001 (i=2,3) bands of $^{12}C^{16}O_2$ with the intensity values down to 10^{-30} cm^{-1}/(molecule cm^{-2}) at 296 K. These bands were observed for the first time. The uncertainty of the line position measurements was estimated to be about 0.007 cm^{-1} for the unblended lines with a high signal-to-noise ratio. The uncertainties of the retrieved line intensities for the strongest unblended lines are at the level of 15 %. The spectroscopic constants for observed bands were fitted to the observed line positions. The vibrational transition dipole moments squared of these bands were fitted to the observed line intensities. The measured line parameters were compared with the parameters from the HITRAN 2020 database.

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D6

Λ-doubling in the 3-0 vibrational band of the $^{15}N^{16}O$ molecule in the ground state

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The spectrum of the $^{15}N^{16}O$ molecule in the region 5200 – 5500 cm^{-1} was recorded and analyzed in this work. As a result of the analysis, 150 Λ-doublets of vibration-rotational lines were found in the 3-0 band of the main transitions between the electronic states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. For 108 of them, when the splitting value was greater than 4.5×10^{-3} cm^{-1}, it was possible to obtain the positions and relative intensities of each component of the doublet. The frequencies of the registered transitions, weighted in accordance with the experimental uncertainties, were processed by the program code using the non-linear least squares method. As a result of processing, the spectroscopic constants for the v=3 vibrational state of the $^{15}N^{16}O$ isotopologue were found. The Λ-doubling constants for this state are determined for the first time. The obtained results are compared with the well-known database of spectroscopic information HITRAN2020.

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D7

Study of the nitrous oxide isotopologues in the 4200-6500 cm^{-1} region

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Twenty seven bands of $^{14}N^{14}N^{16}O$; $^{15}N^{14}N^{16}O$; $^{14}N^{15}N^{16}O$; $^{14}N^{14}N^{18}O$; $^{15}N^{15}N^{16}O$; $^{15}N^{14}N^{18}O$; $^{15}N^{15}N^{18}O$ nitrous oxide isotopologue were detected in the 4200–6500 cm^{-1} region using a Bruker IFS-125M Fourier spectrometer with a spectral resolution of 0.01 cm^{-1} and a 60 cm multipath cell with a pathlength of 2400 cm. The measurement technique is described in detail in paper [1]. We used a sample of IZOTOP company of NO (80% of $^{15}N^{18}O$ and 20% of $^{14}N^{16}O$) and a trace amount of N_2O isotopologues. Chemical processes inside the sample lead to the appearance of a number of nitrous oxide isotopologues. The partial pressure of the mixture components was determined by comparing the experimental line intensities of the NO and N_2O isotopologues in the recorded spectrum with the line intensities from the HITRAN2020 database [2]. It was found that the partial pressure of all N_2O isotopologues was about 1 mbar.

The line positions of these bands were measured to the uncertainties of 0.0014 cm^{-1}. The spectroscopic constants were fitted using the measured line positions. The root mean squares of the residuals (RMS) of the fits (0.0005–0.0027 cm^{-1}) were close to the experimental uncertainties. Four bands were observed for the first time.

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D8

Absorption spectra of $H_2O:SO_2$ and $H_2O:CO_2$ binary mixtures in aerogel nanopores

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The transmission spectra of nanopores SiO_2 aerogel filled with a mixture of molecular gases $H_2O:SO_2$ and $H_2O:CO_2$ were studied. Previous studies [1, 2] showed that the interaction of SO_2 molecules with a surface water layer leads to the formation of a weakly bound complex of SO_2 molecules and the topmost surface molecules of water, resulting in spectral changes. There is no noticeable effect of CO_2 on the upper water monolayer was noted by the authors.

In nanopores materials, in particular, in SiO_2 aerogel, water molecules are adsorbed on the inner surfaces of nanopores by a layer of several molecules thick [3]. In this case, the molecules on the surface are oriented in such a way that the oxygen atom is bound to the surface, and the hydrogen atoms are outside [4].

Gas molecules filling nanopores interact with the surface layer of molecules with a collision frequency several orders of magnitude higher in comparison with that in free gas [5]. At this rate, the interaction of molecules such as SO_2 and CO_2 with the adsorbed water layer can be more pronounced, including in the characteristics of the absorption spectra.

Studies of the absorption spectra of binary mixtures of SO_2 and CO_2 with water molecules within aerogel nanopores were carried out using a Bruker IFS 125 HR Fourier spectrometer at room temperature in the spectral range of 2000-10000 cm^{-1}.

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D9

New spectroscopy of the 1.38 µm water band for CO_2 atmospheres: application to the water vapor retrieval on Mars in SPICAM/MEX and ACS NIR/TGO experiments

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The 1.38 µm band of H_2O has been used to retrieve the water abundance in the Martian atmosphere since the MAWD spectrometer on Viking 1,2 missions [1]. At present, two experiments on the orbit of Mars, SPICAM IR on Mars-Express and ACS NIR on Trace Gas orbiter, perform measurements of water vapor in this band. The spectrometers provide the monitoring of the seasonal cycle of the column abundance and vertical distribution of H_2O over several Martian years [2-4]. They firstly observed the supersaturation of water vapor in the Martian atmosphere and the high-altitude water during global dust storms of 28 and 34 Martian years [3-5]. All these retrievals used the HITRAN database for the spectroscopic information about the 1.38 µm band. To account for the CO_2 broadening of lines, the broadening scale factor of 1.7 relatively to the air broadening was assumed based on [6, 7]. This could lead to systematic uncertainties of results, as was shown in [8] during the revision of the MAWD data based on HITRAN 2004.

Recent laboratory measurements of the water vapor line broadening for CO_2 atmospheres for lines of three vibrational bands $\nu_1+\nu_3$, $2\nu_2+\nu_3$, and $2\nu_1$ in the 6760-7430 cm^{-1} spectral region [9] allowed us to improve the spectroscopic parameters for the Martian condition. In this work we present the reanalysis of water retrievals in the 1.38 µm band from SPICAM IR and ACS NIR experiments based on the new spectroscopy, estimate the sensitivity of results to new parameters for nadir and occultation measurements, and perform the validation of new linelist using high-resolution ACS-NIR solar occultation observations.

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D10

Water vapor absorption line parameters in the 4500–4700 cm^{-1} spectral region

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The value up to 70% from the absorption of solar radiation in the cloudless atmosphere of the Earth is due to water vapor. In this regard, high-precision information about the parameters of water vapor absorption lines is critical for solving a wide range of problems in climatology, atmospheric optics, and astrophysics.

A Fourier spectrometer Bruker IFS 125 HR [1] was used to measure water transmittance spectra in the spectral region of 4500-4700 cm^{-1}. This region is often used to determine the water vapor content in the Earth's atmosphere. Five measurements with absorption path lengths between 27869 and 72441 cm and buffer gas pressures from 0.115 to 0.592 atm were performed. A multispectrum fitting approach was used applying the traditional Voigt and quadratic speed-dependent Voigt models. There is a good agreement between our intensities and HITRAN data [2], but significant differences are observed for the broadening and shift coefficients of the H_2O absorption lines. The atmospheric transmission was calculated with use of H_2O line parameters from different versions of the HITRAN and GEISA spectroscopic databases and our new data. Model spectra were compared with atmospheric solar spectra measured with a ground-based Fourier spectrometer [3]. It was shown that the use of our new data has improved the agreement between the model and measured atmospheric spectra.

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D11

Speed-dependent broadening and shifting of H_2O lines in the subTHz range

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Radiometric studies in the millimeter (mm) and submillimeter (submm) ranges play an important role in the tasks of remote sensing of the Earth's atmosphere and the underlying surface. The technical capabilities of modern radiometers require high-accurate models of the radiation absorption in the atmosphere. This requires accurate laboratory measurements of the shape parameters of the resonance lines of atmospheric molecules (first of all H_2O) and continuum.

The aim of this work is to increase the accuracy of modeling the resonant absorption of atmospheric water vapor by acquiring new laboratory information about the line profile of all the most intense rotational transitions in the frequency range up to 500 GHz. Line profiles are recorded using two spectrometers [1] differing in the principle of operation and the range of operating pressures, which significantly increases the reliability of the experimental information. The first instrument is a classical direct absorption spectrometer (video spectrometer) based on a frequency-stabilized backward wave oscillator and an InSb bolometer cooled by liquid helium, which allows recording the molecular spectra in the pressure range from fractions of mTorr to about 1 Torr. The second instrument is a spectrometer with radio-acoustic detection of the absorption signal (RAD spectrometer), which operates in the pressure range from several mTorr to tens of Torr. The experimental spectra are analysed using the Voigt profile modified to take into account the dependence of collisional relaxation rate on molecular speed which was investigated in the framework of the quadratic approximating function [2]. The multispectrum fitting procedure, which applied the simultaneous fitting of the model function to all experimental spectra of a chosen line, was used to minimize possible correlation of the line shape and baseline parameters in the model function.

The results of the study are collisional broadening and shifting parameters and their speed dependence measured for the studied water lines at room temperature for several perturbing partners (H_2O, N_2, O_2, Ar). The reliability of the results is well confirmed by the agreement of the data obtained using various experimental techniques. The obtained information can be used for verifying results of theoretical calculations, updating spectroscopic databases and refining the models of atmospheric absorption.

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D12

Continuum absorption in gases of nonpolar molecules and their mixtures in the millimeter wave range

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This work continues the cycle of our recent studies of continual absorption of the millimeter wavelength radiation by atmospheric nonpolar molecules, which began with N_2 [1] and CO_2 [2] continuum measurements. The current objects are CH_4-CH_4, CH_4-CO_2, CH_4-N_2, CO_2-N_2, and N_2-Ar. The measurements are carried out using a resonator spectrometer [3] at pressures up to 2 atmospheres at room temperature in a frequency range of 155-255 GHz with expected extension down to about 80 GHz and up to 350 GHz. In this frequency range, the absorption of all the studied gases is determined by bimolecular absorption under chosen conditions. The only exception is methane with a rotationally induced resonance spectrum of CH_4 monomer that contributes up to 40% to the total observed absorption. The expected bimolecular pressure dependences are experimentally verified and confirmed for all mixtures under consideration. Quadratic frequency dependence of the continuum is observed, except for CH_4-CO_2 and CO_2-N_2 mixtures. This deviation from the quadratic law, which is stipulated in our spectral range by the so-called radiation term, may indicate a significant contribution of dimers to the continuum.

The obtained spectra are expected to be used for comparison with results of ongoing bimolecular absorption calculations using a semiclassical trajectory-based method [4,5], which looks promising for detailed understanding of the continuum absorption nature on a much broader scale in terms of frequency, temperature and type of colliding molecules.

The obtained data have independent value for studying the atmospheres of Solar system planets, exoplanets and their satellites, where the continuum absorption can make a considerable contribution to the total absorption and planetary radiation balance.

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* Koroleva is an applicant for the best young scientist talk award (poster).

D13

Bimolecular absorption of CO_2 – CO_2 and CO_2 – Ar in the millimeter wavelength range

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The results of our recent studies of CO_2 – CO_2 and CO_2 – Ar bimolecular absorption in the millimeter wavelength range are reviewed. The study was inspired by the success of the classical trajectory-based formalism recently developed to simulate bimolecular absorption spectra [1-4]. The results of highly accurate laboratory experiments are intended to validate the data of theoretical calculations in the ranges of frequencies and temperature variations accessible for measurements.

The spectra of pure CO_2 and its mixture with Ar were investigated using a resonator spectrometer [5] in the frequency region of 76–255 GHz for several pressures ranging from 375 to 1490 Torr and temperatures within the range of 268–332 K. Parameterization of experimental data reproducing frequency and temperature dependence is proposed. Good agreement of experimental and calculated CO_2 – CO_2 and CO_2 – Ar bimolecular absorption was achieved. Analysis of the frequency and temperature dependence of the continuum revealed a significant contribution of a stable dimer to the observed absorption. Insignificant theoretical underestimation of the observed CO_2-CO_2 and CO_2-Ar continuum by about 20% and 10% respectively is observed, which is probably related to the use of the rigid monomer approximation in the calculations.

Note that the agreement, once achieved, between experimental data and calculations promotes better understanding of the nature of the continuum on a much wider scale. Experimentally validated results of the bimolecular spectra calculations for the whole collisionally induced rototranslational band at temperatures within 200-400 K can be applied for radiative processes modeling of the CO_2-rich planetary atmospheres, such as those of Venus and Mars.

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D14

Expanded ro-vibrational analysis of the dyad region of $^{12}CD_4$ and $^{13}CD_4$: Line positions, energy levels and absolute line strengths

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The high resolution infrared spectra of $^{12}CD_4$ and $^{13}CD_4$ were measured with a Bruker IFS125 HR Fourier transform infrared spectrometer at an optical resolution of 0.003 cm^{-1} and analyzed in the region of 800–1400 cm^{-1} where the ν_2/ν_4 dyads are located. The number of 5560 and 901 transitions with $J^{max} = 31$ and $J^{max} = 23$ were assigned to the $^{12}CD_4$ and $^{13}CD_4$ isotopologues (which is more than three times higher in comparison with the number of assigned transitions known in the literature). The subsequent weighted fit of experimentally assigned transitions was made with the Hamiltonian model which takes into account the resonance interactions between the upper (0001, F_2) and the (0100, E) vibrational states. As a result, a set of 52 fitted parameters (10 parameters of the ground vibrational state, 19 parameters of the (0001, F_2) vibrational state, 9 parameters of the (0100, E) vibrational state, and 14 resonance interaction parameters) was obtained which reproduces the positions of the initial experimental ro–vibrational transitions with the $d_{rms} = 1.8 \times 10^{-4}$ cm^{-1} which is close to the experimental uncertainty of the recorded spectra and is about 615 times better in comparison with the reproduction of the same transition values by the use of parameters from the literature. Line strengths analysis of both isotopologues was made for the first time. The analysis of 1557 experimental lines of the dyad of $^{12}CD_4$ and 131 lines of the dyad of $^{13}CD_4$ was fulfilled with the Hartmann–Tran profile to simulate the measured line shape and to determine experimental line intensities. Sets of 6/1 varied effective dipole moment parameters of $^{12}CD_4/^{13}CD_4$ are determined which reproduce the initial 1557/131 line strengths with the d_{rms} = 4.80% and 4.21%.

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D15

High–resolution study of the tetradecad stretching vibrational bands of $^{28}SiH_4$

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Infrared spectra of SiH_4 isotopologues with the abundances of 92.23 % for $^{28}SiH_4$, 4.68 % for $^{29}SiH_4$, and 3.09 % for $^{30}SiH_4$ were measured in the region of 4100-4500 cm^{-1} with a Bruker IFS 120HR Fourier transform spectrometer and analyzed. For $^{28}SiH_4$ more than 1500 transitions with $J^{max} = 25$ were assigned to the tetradecad stretching bands $\nu_1 + \nu_3$ (F_2), $2\nu_3$ (F_2) and $2\nu_3$ (E). Rotational, centrifugal distortion, tetrahedral splitting, and interaction parameters were determined from the fit of experimental line positions. A set of 31 parameters obtained from the fit reproduces the initial experimental data with the d rms = 3.5×10^{-4} cm^{-1} which is close to the experimental uncertainty.

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D16

Calculation of CO_2-broadening and -shift coefficients of SO_2 lines in the $\nu_1+\nu_3$ band

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Sulfur dioxide exists in the atmosphere of Earth in very small concentrations (about 1 ppm), the most significant its concentrations is in the atmosphere of Venus, where it is the third-most significant atmospheric gas at 150 ppm [1]. It condenses to form clouds, and is a key component of chemical reactions in the planet's atmosphere and contributes to global warming. It has been implicated as a key agent in the warming of early Mars, with estimates of concentrations in the lower atmosphere as high as 100 ppm, though it only exists in trace amounts [2]. On both Venus and Mars, its primary source is volcanic. Sulfur dioxide has been detected in the interstellar medium or circumstellar shells [3].

Calculated SO_2-CO_2 line broadening coefficients in the 150-700 K temperature range and shift coefficients at the room temperature are presented. The data have been evaluated theoretically in the frame of the semi-empirical approach [4] based on the straight-line trajectory approximation within the semi-classical impact theory and including a few-parameter correction to account for the real curved trajectories. The main contribution to the line-broadening coefficients is given by the quadrupole-quadrupole interaction. We also take into account the dipole-quadrupole and polarization (both induction and dispersion) terms of intermolecular potential. Since for every line the power law describes well the SO_2-CO_2 broadening only in a limited temperature range of 200-400 K, traditional temperature exponents as well as parameters of the double power law [5] are determined.

The calculations are performed for the $\nu_1+\nu_3$ band, rotational quantum numbers vary in the ranges of J up to 100 and of K_a up to 20. Being validated by comparison with measurements, these approaches were used to compute extensive line list which could be useful for atmospheric, astrophysical applications and spectroscopic databases.

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D17

Air pressure induced nitrogen-dioxide line shift coefficients

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Detection and measurement capabilities for NO_2 in the Earth's troposphere and stratosphere is of great importance because the nitrogen dioxide plays an important part in the production of photo-chemical smog, it is one of the most common anthropogenic substances emitted into the atmosphere. Besides, the nitrogen dioxide is the main source of ozone in the Earth’s troposphere. For these reasons a precise knowledge of the spectral-line parameters (line positions, absolute intensities, line broadening and shift coefficients, as well as their temperature exponents) is important. While the positions, intensities and widths of rotation-vibration lines are rather well known and presented in the modern spectroscopic data bases, the shifts for the NO_2-N_2, NO_2-O_2 colliding system are needed.

Theoretical line shifts of nitrogen dioxide lines induced by air are reported at the room temperature. Calculations are performed for ~31500 lines in the spectral range of 5700 – 7500 cm^{-1} for the $\nu_1+3\nu_3$, $\nu_1+4\nu_3$, $2\nu_1+3\nu_2+\nu_3$, $3\nu_1+\nu_2+\nu_3$, $2\nu_2+3\nu_3$ and $4\nu_3$ bands, rotational quantum numbers vary in the range of N up to 87, K_a up to 20. Line shifts are calculated in two ways. Nitrogen- and oxygen- induced shifts of nitrogen dioxide lines with rotational quantum numbers $N \leq 35$ were obtained using the semi-empirical method [1] which is based on the semi-classical theory used in conjunction with empirical adjustments [2] to match the available experimental data. Values for the lines with $N > 35$ were obtained by extrapolation of line shifts rotational dependence. The semi-empirical approach is performed by the introduction of empirical correction factor. As soon as the parameters of this factor are determined on some reliable experimental data, calculations correctly reproduce all available measured values on line shifts in various branches and at various temperatures. Being performed for enlarged intervals of N and K_a, these calculations provide complete line-lists of shifts necessary for spectroscopic databases and atmospheric applications.

Vibrational dependence of air pressure-induced shifts in the $\nu_1+3\nu_3$, $\nu_1+4\nu_3$, $2\nu_1+3\nu_2+\nu_3$, $3\nu_1+\nu_2+\nu_3$, $2\nu_2+3\nu_3$ and $4\nu_3$ bands are discussed.

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D18

On the physical meaning of the line contour parameters in the asymptotic line wing theory

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In the theory of the light absorption in a molecular medium developed at the Institute of Atmospheric Optics of the Siberian Branch of the Russian Academy of Sciences [1], the semiclassical representation method in deriving the expression for the absorption coefficient is used, which makes it possible to consider a certain subsystem of variables to be classical, while the rest of the variables remain quantum. In the case when the motion of the center of mass of interacting molecules is declared classical, a kinetic equation is obtained that is valid for arbitrary frequency detunings [2]. The transition in this equation to the asymptotics of large frequency detunings leads to an expression for the absorption coefficient, which is the main one in the so-called asymptotic line wing theory (ALWT). This expression includes the classical and quantum interaction potentials, according to the initial assignment of variables. Their physical meaning is unambiguous - the classical potential controls the movement of the center of mass, the quantum potential refers to the interaction of two molecules, and the classical potential, according to the method of semiclassical representation, is a quantum potential averaged over the quantum variables. Obviously, the quantum mechanical calculation of these potentials is still a very laborious task. Therefore, from the very beginning, ALWT resorted to their parametric assignment.

The classical potential V_{cl} is usually the Lennard-Jones potential. Within the framework of the semiclassical representation, the potential included in the definition of the second virial coefficient is also the potential that controls the motion of the center of mass of the interacting molecules. Therefore, it is natural to take the parameters ε and σ of the potential, which reproduces the temperature dependence of the second virial coefficient, as parameters of the classical potential. These parameters, according to the origin of V_{cl}, depend on temperature, and the temperature behavior of the absorption coefficient is determined by this dependence. Calculations of absorption coefficients performed, for example, for CO-He [3], H_2O [4] systems, agree with experiment. Thus, the physical meaning of the parameters of the classical potential used is confirmed by their connection with the parameters of the potential, appearing in a section of physics other than the interaction of radiation with matter.

Parameters of the so-called quantum potential V_{qu} have so far been found as a result of fitting the calculated values of the absorption coefficient to the experimental ones. The quantity U, which we call the quantum potential for brevity and which we approximate by a set of monomials with an inverse dependence on distance, is in fact the difference of the quantum interaction energies of colliding molecules in different vibrational states. This kind of energy can be obtained in quantum chemical calculations. However, until recently, such calculations were not carried out because of their complexity, and absorption measurements were also needed, falling into the corresponding spectral intervals. Comparisons of this kind turned out to be possible for the CO-Ar system [5], which were used in [6] to check the parameters approximating U when calculating the absorption of CO-Ar in the CO 1-0 band wing. Despite the very approximate data obtained from Fig.2 in [7], the slope and position of the repulsive branch of U fall within the required range of values. The CO_2-He and CO_2-Ar calculations available in [7, 8] make it possible to make additional comparisons. Nevertheless, it is already clear that the parameters related to the quantum potential surface in quantum-chemical calculations and obtained by processing the data on absorption in the spectral band wings are in qualitative agreement with the data of quantum mechanical calculations of the potential surfaces of interacting molecules. Thus, the physical meaning of the potential parameters in the ALWT is beyond doubt.

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D19

Description of absorption by dimers within asymptotic line wing theory

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The derivation of the expression for the absorption coefficient in the asymptotic line wing theory (ALWT) [1, 2] involves consideration of interacting molecules at arbitrary distances between them. Thus, the calculation of the absorption coefficient by ALWT includes both absorption by quasi-bound dimers of initial molecules and absorption by free colliding pairs. Absorption by stable dimers remains outside the calculation, since the latter are molecules different from those for which the calculation is made, and absorption by them must be considered separately. Hence it follows that the difference between the experimental absorption coefficient and that calculated by ALWT includes the absorption by molecules and complexes that do not coincide with the initial absorbing molecules. In the case of self-broadening in the remaining mixture, the leading position in absorption, as a rule, belongs to dimers of the initial molecules.

One example of the application of the above concept is the consideration of the ratio between the absorption by water monomers and dimers in the H_2O rotational band [3]. In this work, the line contour describing the spectral and temperature behavior of the absorption coefficient of water vapor in the range of 8–12 μm was used to calculate the continuum absorption coefficient in the region of 14–200 cm^{-1}. The difference between the continuum absorption measured with a special resonator spectrometer [4] and the data of this calculation revealed spectral features inherent in stable water vapor dimers. They were correlated with the vibrational spectrum of dimers, which follows from quantum mechanical calculations, and the value of their total absorption is in complete agreement with the value of the obtained difference. This successful result was due to the following components: (1) the presence of a contour with a detailed frequency dependence; (2) the availability of detailed data on the vibrational spectra of dimers; (3) the availability of detailed experimental data on continuum absorption. In the following examples, such a fortunate combination of conditions is not always found.

Dimer absorption in the IR spectrum of water vapor was considered from the standpoint of ALWT in [5, 6]. In [5], experimental data were analyzed in addition to [4], and the ALWT results turned out to be in agreement with those obtained by other methods, although condition (3) was not always satisfactory. In [6], absorption by dimers was considered in the IR bands of water vapor at different temperatures using experimental data from [7].

Similar studies of CO_2 spectra run into difficulties with respect to conditions 1 and 3. For example, for pure CO_2 and the well-known band at 4.3 μm, there are practically no sufficiently detailed absorption coefficients published. An analysis of the data presented for this band in [8] gives a result for absorption by $(CO_2)_2$ dimers that qualitatively coincides with the available vibrational spectrum of dimers [9]. In the case of a 15 μm CO_2 band, the line contour for the near wings is known only approximately, and for pure CO_2, data on the absorption coefficient at the center of the system of bands are absent just in the region where vibrational frequencies of dimers are supposed, capturing only one of them [10]. Nevertheless, preliminary calculations show that the absorption by dimers in the IR spectra of molecules important for the atmosphere can be estimated using ALWT besides other methods.

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D20

Correlation function in the asymptotic line wing theory

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As is known, the expression for the absorption coefficient is obtained as the Fourier transform of the correlation function of the dipole moment of a molecule absorbing light. In the simplest case of a harmonic oscillator interacting with an electromagnetic wave for a limited time, the absorption coefficient is described by a Lorentzian contour. The case where the contour differs from the Lorentz one is described in [1], where a specially selected analytical expression for the H_2O correlation function leads to a difference between the contour obtained and the Lorentz one at medium distances from the line center. In [2], the correlation function for the distant wings of CO_2 was calculated directly by the methods of classical molecular dynamics for several million CO_2 molecules in the gas phase.

In the asymptotic line wing theory (ALWT), the absorption process is considered based on general relations describing the interaction of light with matter and, further, the interaction of a light-absorbing molecule with a collision partner. The result of the calculation is the formula for the absorption coefficient and the contour of an individual line without separating the correlation function as such. However, it can be judged indirectly, based on the shape of the contour of a separate line.

In [2], the correlation function for molecular orientations contains a negative spike at its lower boundary, that is, at the boundary of its transition to zero. The analytical correlation function in [1] includes four terms, and those containing $\sin^2$ are responsible for the appearance of a positive spike near its upper boundary. Changing the signs of these terms leads to the behavior of the correlation function on its lower boundary, similar to that in [2]. Moreover, the variation of the parameters characterizing the oscillatory processes during the collision can change the magnitude and shape of this negative spike. Having thus constructed the correlation function, integrating over time and averaging over the intervals between collisions, one can obtain the corresponding contour of a line. Comparison of it with the contour obtained in the framework of ALWT [3] shows that these contours coincide in some spectral intervals. However, one should take into account the fact that, according to ALWT, nonresonant absorption is physically different from resonant absorption. Namely, at resonance, the absorption occurs during the free path, and the collisions only interrupt this absorption. In the nonresonant case, absorption occurs during the collision, and this should be reproduced in the form of a correlation function.

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D21

PQN-code in vibrational spectroscopy

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In the framework of a perturbation formalism based on Polynomials of Quantum Numbers (PQN) [1], we present a computer program that allows one to calculate with required accuracy the vibrational energies and dipolar moment matrix elements for a nonlinear polyatomic molecule. The input data are the harmonic vibrational frequencies, force constants and dipole-moment derivatives. To test our program, we calculated the energies and matrix elements of the dipole moment function for ozone molecules $^{16}O_3$ and $^{18}O_3$ and sulfur compounds SO_2 and H_2S. Obtained results for $^{16}O_3$ and $^{18}O_3$ are in good agreement with experimental data, while for sulfur compounds the theory does not converge well because of a poor choice for anharmonic constants. Despite the still insufficient testing, the current version of the program can serve as an express method for modelling the spectra of polyatomic molecules being a criterion for determining the reliability of the calculated values.

A prospective direction for further investigation is to combine the program with an artificial neural network computing the anharmonic constants and dipole-moment derivatives.

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D22

Deperturbation analysis of the $A^1\Sigma^+$ and $b^3\Pi$ states of LiRb

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There have been many spectroscopic and theoretical studies of the LiRb molecule investigating its electronic structure both using experimental as well as theoretical methods. Among these is a spectroscopic study [1] investigating the depletion spectra of the $A^1\Sigma^+$-$b^3\Pi$ complex of ultracold molecules, observing 41 vibrational levels (see Fig 1, left) with rotational quantum number J=1. Here we have used the coupled-channel deperturbation model to describe the singlet-triplet mixing of each level. We used a 2×2 model Hamiltonian, accounting for the spin-orbit (SO) interaction within the complex. Two different methods were used to represent fitting potentials of the mixed states and SO coupling function. In method 1 both interatomic potentials were approximated using the expanded Morse oscillator function, the coefficients of which were then fitted, in method 2 the initial trial point-wise potentials were constructed and fitted using cubic splines. In both methods, the fit was additionally constrained by minimizing not only the differences between the experimental and theoretical term values, but also the differences between the fitted potentials and SO coupling and their *ab initio* counterparts [2]. As a result, the most experimental terms were fitted with an accuracy of about 0.02 cm^{-1}, which is comparable with experimental accuracy, or better. And only two levels were fit with an accuracy of worse that 0.05 cm^{-1}. Among them is the vibrational level v=9 of the $b^3\Pi$ state, which lies energetically right at the point where the $b^3\Pi$ state intersects with the repulsive branch of $a^3\Sigma^+$ state. Additionally, we were able to determine the mixing coefficients for all experimental levels, with the v_A=3,6 and v_b=10,12 of the $A^1\Sigma^+$ and $b^3\Pi$ states respectively, exhibiting the greatest degree of mixing.

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D23

Specifics of internal rotation in the molecules of aldehydes containing four-membered rings

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Experimental and theoretical studies of the structure of organic molecules containing small cyclic fragments (such as cyclopropane and cyclobutane rings) are of great interest due to the uniqueness of some of their physical and chemical properties.

Previously [1], it was shown that the molecule of cyclobutanecarboxaldehyde (CBCA) is a complicated object for theoretical and experimental investigation of its conformational and vibrational dynamics. The data obtained on the structure of the molecule potential energy surfaces (PESs) suggest the complex nature of the conformational dynamics of this molecule even during transitions to lower vibrational levels: the minimal energy pathways may have a marked curvature or breakings; also, the form of the vibrations can be significantly affected by the behavior of the kinetic energy of the molecule.

In the present work, the authors attempt to qualitatively characterize internal rotation in some model systems containing cyclobutene ring and compare the results with previously obtained for CBCA molecule. Two isomers of C_5H_6O, namely cyclobut-1-ene-1-carbaldehyde (CB1CA) and cyclobut-2-ene-1-carbaldehyde (CB2CA) were chosen as the objects of investigation.

The conformational behavior and geometrical structure of the presented two related molecules were studied using the different methods of quantum chemistry, one- and two-dimensional sections of the PESs along the coordinates of the internal rotation and the closest to it non-planar deformational vibration of the formyl (CHO) group were constructed and analyzed. The possibility of kinematic coupling of these two vibrations and the complexity of their shapes are considered in particular detail. The kinematic interaction of these two low-frequency vibrations of the same symmetry can significantly depend on the relative position of the formyl group and the cycle in the case of CB1CA and CB2CA molecules. This relationship is much more complicated in the case of CBCA molecule.

Such studies are necessary for modeling the IR spectra and obtaining accurate theoretical estimates of thermodynamic functions sensitive to the quality of the description of the low-frequency region of the vibrational spectra.

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D24

Retrieval of NO_2 tropospheric column by ground-based FTIR observations of direct solar radiation

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A high level of air pollution caused by anthropogenic emissions of gas and aerosol components is a key problem for densely populated areas, such as large cities and industrial centers. High concentrations of NO_2 in the ambient air pose a threat to human health and the environment [1]. In the troposphere, NO_2 plays an important role in the formation of photochemical smog, participates in the formation of tropospheric ozone, and is one of the causes of acid precipitation [2].

For a long time St. Petersburg State University (SPbU) has been performing investigations in the field of remote measurements of NO_2 in the atmosphere using ground-based DOAS (Differential Optical Absorption Spectroscopy) and FTIR (Fourier-Transform InfraRed) spectrometry [3,4]. DOAS measurements of scattered solar radiation are one of the methods of passive remote sensing of atmospheric gas composition, allowing, in particular, to obtain information on the tropospheric column (TrC) of NO_2 [5]. Atmospheric monitoring based on the FTIR spectroscopy makes it possible to retrieve the total column (TC) of more than 20 trace gas components of the atmosphere including NO_2 [6,7]. It is important to note that for some species, the informatively of FTIR measurements allows determining not only their total vertical content, but also elements of vertical distribution.

The main goal of this work is to study the possibility of separating the tropospheric part (column) from the total NO_2 column derived from ground-based FTIR solar spectra, including the development and testing of an optimal retrieval strategy for NO_2 TrC. Based on the analysis of high-resolution FTIR solar spectra recorded at the atmospheric monitoring station of SPbU (59.88°N, 29.83°E; 30-35 km east of the central part of the St. Petersburg) during 2009-2022, different strategies for retrieval of the tropospheric NO_2 column from the mid-IR spectra were investigated. Among the three retrieval strategies tested, the strategy based on processing the spectral interval 2914.30-2914.85 cm^{-1} combined with Tikhonov-Phillips regularization showed the best agreement with simultaneous independent DOAS measurements of the tropospheric NO_2 column at the same monitoring station. Based on the results of FTIR and DOAS measurements, the linear trend of tropospheric NO_2 column in the St. Petersburg region for the period 2009-2022 was estimated, as well as the characteristics of its seasonal variations.

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D25

Multipass dual pattern optical scheme of the ISKRA-V high resolution IR spectrometer onboard Venera-D mission

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ISCRA-V (Investigation Sulphurous Components of Rarefied Atmosphere of Venus), being a part of the Venera-D mission lander [1], is a tunable infrared laser absorption spectrometer instrument. The main goal of the ISCRA-V experiment is a study of Venus atmosphere (cloud layer, middle, low, and near-surface atmosphere). The issues of investigation are measuring several Venusian gases concentrations, such as SO_2, OCS, CO_2, H_2O, HCl as well as isotopic ratios $^{34}S/^{33}S/^{32}S$, D/H, $^{18}O/^{17}O/^{16}O$, $^{37}Cl/^{35}Cl$.

The instrument is supposed to use four lasers with the following wavelengths: 7416 nm or 7280 nm (SO_2, CO_2, H_2O), 4823 nm (OCS, CO, CO_2), 3397 nm (HCl), 2630 nm (H_2O, CO_2). In the first two spectral regions an optical path length of 10 m is quite sufficient, while in the last two spectral regions a length of about 25 m is required. For this reason, it was necessary to develop a modified Herriott type multipass optical cell with two different patterns.

The results of Herriott multipass cell modeling are reported, key characteristics of some variants are calculated. A stability analysis of a multipass configuration has been carried out. Instability due to thermal changes, mechanical impact, as well as manufacturing inaccuracy were taken into account. Scattered laser beams light cross-interference effect has been minimized. Criteria for the optimal choice of an optical scheme are formulated. An optical breadboard is under study for experimental checking out the correctness of the calculation. Examples of simulated molecular absorption spectra are given for the current version of the project.

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D26

Scientific concept of the DAVUS experiment: Descent in the atmosphere of Venus with an ultraviolet spectrometer

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We propose a new generation instrument, DAVUS (Descent in the Atmosphere of Venus with an Ultraviolet Spectrometer), for *in-situ* measurements of the atmospheric UV absorbers on board a landing platform of the "Venera-D" mission (to be launched in 2029-2030). The experiment implements active absorption spectroscopy using an integrated UV source: its light penetrates through Venusian gases in an optical cell and further is registered by a spectrometer at the wavelength range from 250 to 400 nm. This spectral interval is sensitive to the molecular absorption lines of minor species, such as SO_2, SO, ClO, which play key roles in the chemistry of the clouds and the lower atmosphere of Venus. For example, sulfur dioxide SO_2, being a volcanic gas, is a chemical precursor of H_2SO_4-acid clouds (47-70 km) enshrouding the planet. In the clouds, SO_2 mixing ratio sharply decreases with altitude: from ~10^5 ppbv at 50 km to ~10^2 ppbv at 70 km [1, 2]. Another subject of interest is an unknown UV absorber situated at wavelengths 300-400 nm when measuring the contrast albedo of Venus clouds. So far, a profound spectral characterization to define this component has been performed neither remotely nor *in-situ*. Sulfurs S_x and dimeric sulfur monoxide S_2O_2, studied by Frandsen et al. (2020) [3], are also considered by DAVUS as probable candidates for the unknown absorber.

While the platform is descending from an altitude of 70 km to the surface, the gaseous and aerosol species fill the multi-pass optical cell. The spectrometer (isolated hermetically and thermally) measures the atmospheric transmission with a high spectral resolution of 0.2 nm. Thus, the considered gases' concentration can be retrieved at an effective footprint length (in the cell) about 2 m with the altitude sampling of ~500 m. An analogous experiment was previously performed by ISAV/VEGA instrument [1], which retrieved SO_2 abundance at the altitude range of 5-60 km, not covering the uppermost cloud layer of 70 km. With DAVUS we improve the sensitivity, spectral resolution and the altitude coverage relative to ISAV measurements. This will enlarge our knowledge about the atmospheric UV absorbers and their linkage with volcanic activity on Venus. A problem of the UV absorption spectroscopy at high pressure and temperature in the lower Venus atmosphere is also discussed.

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D27

Precision relativistic calculation of the energy spectrum of one-electron quasimolecules H_2^+ and He^+-*p* as a function of the internuclear distance

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Due to the increase in the experimental accuracy of spectroscopic studies of molecular systems [1-3], an accurate relativistic calculation of the energy spectrum depending on the internuclear distances for H_2^+ and He^+-*p* systems was made using the dual kinetic balance method [4] for axially symmetric systems. The method has shown itself well in the calculation of heavy quasimolecules (two-center systems) [5-7].

For light systems, non-relativistic calculations are performed using perturbation theory[8]. In this work we present graphs of comparison of our (relativistic) calculation and modern non-relativistic calculations, and spectroscopic results.

The results obtained are important for the study of relativistic effects in systems H_2^+ and He^+-*p* and the possibility of their detection by spectroscopy methods and open up the possibility for studying exotic quasimolecules.

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D28

Nonlinear dispersion in resonant inelastic X-ray scattering spectra as a tool for studying interatomic interactions

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Modern high-power X-ray sources - synchrotrons and X-ray free electron lasers (XFEL) are widely used in studies of the structure of matter and the dynamics of fast processes by resonant inelastic X-ray (RIXS) and Auger (RAS) scattering methods [1]. One of the important applications of the RIXS and RAS spectroscopy methods is the probing of the interatomic interaction in various aggregate states of matter [2]. The distinguishing feature of resonant scattering, the Raman dispersion, is often broken near the absorption resonance. In our work, we have found a simple relationship between deviation from linear Raman dispersion and interatomic potentials. Our theoretical results are illustrated by a corresponding analysis of the experimental RAS spectra of the sulfur hexafluoride (SF_6) molecule.

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D29

Systematic *ab initio* solution of the vibration-rotation problem by the contact transformation theory: the SO_2 benchmark computation up to the first triad

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Perturbation theory has been one from the main approaches for understanding rovibrational spectroscopy and serves as an alternative to the variational method [1]. With the development of the quantum chemistry the second order vibrational perturbation theory (VPT2) has become a standard method for interpreting experimental high-resolution spectra [2]. However, gaining a comprehensive understanding of the spectroscopic characteristics expressed through the perturbation series in a wide spectral region requires an implementation of the high-order perturbation approach, which have to be established not only on a deep understanding of the theory, but also a high-performance program algorithm.

In this work, we employ the high-order contact transformation approach, followed by the Rotational Watson A-reduction up to the 8-th order [3] and based on a straightforward normal ordering of angular momentum operators in the form $J_z^a J_+^b J_-^c$ [4]. For evaluation of vibration-rotation transition intensities a similar procedure is applied for angular momentum operators and Winger D function in order to compute the effective dipole moment operator. The theoretical scheme was implemented in the ANCO program written in Fortran95 using a numerical-analytic algorithm.

To demonstrate the effectiveness of the implemented approach, we compare the spectroscopic parameters (including the octic parameters L) with the theoretical [3, 5] and fitting values [6, 7] from the literature, as well as the modeled rovibrational transitions of SO_2 molecule with HITRAN database up to the first triad.

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* X. Chang is an applicant for the best young scientist talk award (poster).

D30

Cross sections for dissociative recombination of the CF_3^+ ion in collisions with low-energy electrons

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CF_3^+ is the dominant positive ion in CF_4-containing plasma. It is mainly produced by electron-induced dissociative ionization of CF_4

$$e^- + CF_4 \rightarrow 2e^- + CF_3^+ + F$$

with a fast rate coefficient of $9.36\times10^{-8}\exp(-20.4/T_e)$ cm^3 s^{-1} (T_e is the electron temperature) [1]. Low-energy electrons collide with CF inducing dissociative recombination (DR) towards the following dissociation channels [2]

$$e^- + CF_3^+ \rightarrow \begin{cases} CF_2 + F, \\ CF + 2F. \end{cases}$$

This process is one of the major formation routes of CF and CF_2 radicals, playing a key role in the dynamics of the plasma. Corresponding cross section of the process is thus essential data for adequately understanding, characterizing, and modelling CF_4 plasma. However, the rate coefficient for this process is still in controversy. To cross check the experimental measurements and understand the mechanism of the process, a theoretical computation of the CF DR cross section and the rate coefficient is desirable. The approach that initially developed in 2013 [3] is successfully applied in the present study.

Electronic structure calculations were first performed to obtain the C-F bond length and normal mode frequencies. As seen from Table 1, they are in good agreement with the experimental and theoretical results. The normal mode coordinate q is then obtained as the inputs for the e^--CF_3^+ scattering calculations by the R-matrix method.

Table 1. The computed C-F bond length (Å) and vibrational frequencies ω_1, ω_2, ω_3, ω_4 (cm^{-1}) of breathing, umbrella, asymmetric CF stretching, and deformation mode, respectively

	This work	Exp. [4]	Theo. [5]
C-F	1.2305		1.2272
ω_1/A_1'	1038.15	994±16	1044
ω_2/A_2''	829.34	809±14	813
ω_3/E'	1678.65	1667	1683
ω_4/E'	609.09		593

The DR cross section is given by

$$\sigma^{\mathrm{DR}}(E_{\mathrm{el}}) = \frac{4\hbar^2}{4mE_{\mathrm{el}}}\sum_i g_i \sum_{l'\lambda',l\lambda}\left|\frac{\partial S_{l'\lambda',l\lambda}(q_i)}{\partial q_i}\right|\Theta\left(\hbar\omega_i - E_{\mathrm{el}}\right),$$

where m and E_{el} specify the electron mass and the electron scattering energy and g_i is degeneracy of the normal mode I; $S_{l'\lambda',l\lambda}$ is the fixed-nuclei matrix element with initial (final) partial waves $l\lambda$ ($l'\lambda'$) given by the scattering calculations. The Heaviside step function $\Theta(\hbar\omega_i - E_{\mathrm{el}})$ equals to 0 when E_{el} exceeds $\hbar\omega_i$, otherwise 1. Physically, this means the incident electron can excite the ion only if its energy is above the vibrational excitation threshold. To compare with the experimental data from ASTRID storage ring, convolution was performed on the raw cross section with the non-Maxwell–Boltzmann distribution over collision velocities. The convoluted cross sections are in excellent agreements with the experimental curve below the vibrational threshold as seen from Figure 1 [6].

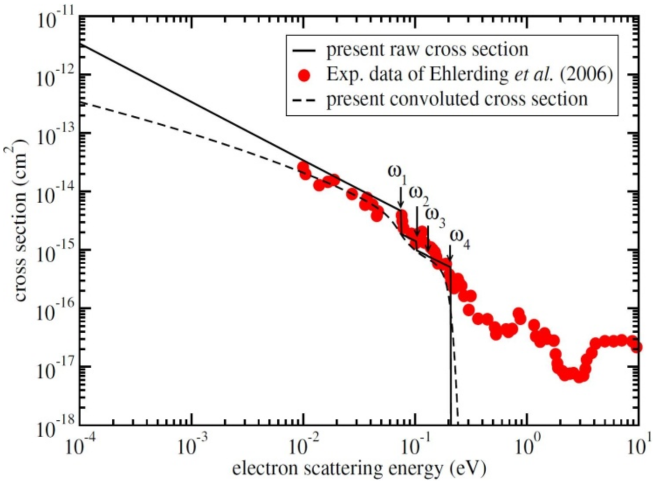

Figure 1. The computed DR cross sections. Experimental measurements are given for comparison.

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D31

Electron scattering cross sections from NH_3: A comprehensive study based on R-matrix method

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Burning NH_3 as a carbon-free fuel for future power generation to reduce greenhouse-gas emissions has gained special attention in recent years [1]. However, Poor combustion and nitrogen dioxide emissions have hindered the commercial development of NH_3 [2]. Cold plasma-assisted combustion technology has been experimentally proved to solve above problems. The overall efficiency of the combustion was improved and the ignition of the flame speeded up in this way. Nevertheless, the mechanism underlying plasma-assisted combustion is still unknown. Cold plasma is known to generate a large number of energetic electrons driving the plasma-based technologies. One of the fundamental processes in this context is the collision between electrons and NH_3, which plays a crucial role in understanding the dynamics behind the plasma-assisted combustion. Accordingly, it is necessary to obtain the electron-impact cross section sets for NH_3 to construct the plasma model of the combustion.

We performed a comprehensive cross-sectional computation on the electron scattering from NH_3 using the frame of the R-matrix method in this study. Table 1 listed the obtained position and width of the two resonances and compared with those previously reported data. They are in good agreement with the experimental and theoretical results, which indicates the accuracy of our model in describing the electron-NH_3 scattering process.

Table 1. Comparison of the calculated resonances with the experimental and theoretical results

Symmetry	$^2A_1$		^2E	
	Position(eV)	Width(eV)	Position(eV)	Width(eV)
This work	5.51	0.0097	10.912	0.0277
Exp.[3]	5.59±0.05			
Exp.[4]	5.7		10.5	
Exp.[5]	5.5		10.7	
Exp.[6]	5.7		10.6	
Theo.[7]	4.19	0.011	10.5	0.033

Cross section sets for total elastic, differential, momentum transfer, total ionization, and electronic excitation are presented. The electron-impact dissociation of NH_3 to NH_2+H and NH+H_2 was considered for the first time by summing up the cross sections for the molecular dissociative excitations to the correlated dissociation channels. The excitation cross section for each vibrational mode of NH_3 which remains controversial was computed by applying the theoretical approach combining the fixed-nuclei R-matrix method, normal mode approximation and the vibrational frame transformation. For the convenience of plasma modeling, the uncertainty of the section sets calculated in this study was estimated. All the obtained scattering cross section data with uncertainties in the present study is shown in Figure 1.

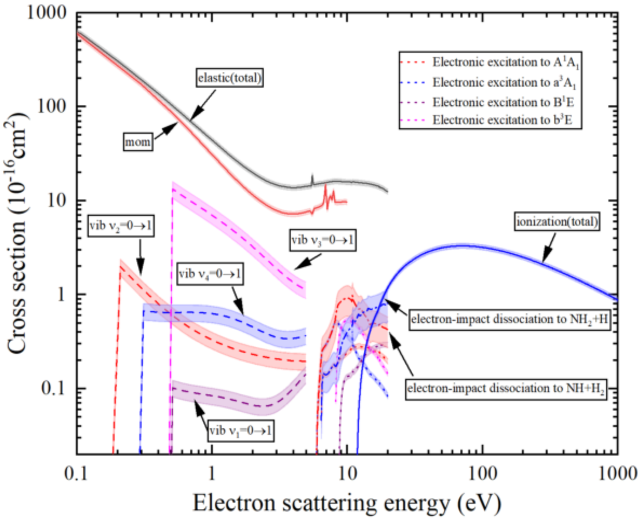

Figure 1. Summary of the computed electon-NH_3 collisional cross sections in the present study. The uncertainties are specified by the ribbons.

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D32

Multimodal study of optical properties of murine breast tumor

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The mouse breast tumor model is often used to develop cancer imaging and treatment methods [1,2]. In this study, a multimodal approach was applied to the study of the optical properties of healthy tissue and a model breast tumor *ex vivo* in laboratory mice. The study included spectrometry in the range from 350 to 2500 nm, refractometry in the range from 450 to 1550 nm, Raman spectroscopy (RS) in the range from 400 to 1800 cm^{-1}, optical coherence tomography (OCT) and ultrasound scanning. Based on the measured spectra of total transmission and diffuse reflection, and the dispersion dependences of the refractive index of samples of healthy and tumor breast tissues *ex vivo*, the absorption coefficient (μ_a) and transport scattering coefficient (μ_s') were calculated using the algorithm described in detail in Ref. [3]. To assess the change in lipid content during the development of a breast tumor, the so-called “analytical optical clearing” approach was used, described in Ref. [4].

The experiments were carried out on Balb/c female white laboratory mice weighing 30 ± 5 g. Model breast tumors were obtained by injecting a suspension of 4T1 cells in an amount of 500,000 cells/50 µl into the mouse mammary region. Tissue samples for refractometric and spectral measurements were excised 4 weeks after inoculation of the model tumor.

Ultrasound and OCT images of the sections of healthy and tumor tissue *in vivo* showed changes in the tissue structure during tumor development. A decrease in the scattering of tumor tissue compared to healthy breast tissue, a decrease in lipid content by more than 50%, and an increase in the content of water and proteins were shown. A decrease in the refractive index of the tumor tissue was also obtained.

This work was supported by the Russian Foundation for Basic Research (grant No. 20-52-56005).

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D33

Spectral study of the effect of nanocontainers on biological tissues

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Spectroscopic techniques have been finding increasing applications in the field of biomedicine especially in the field of disease diagnosis and monitoring in spite of the rapid emergence of several molecular biology based techniques. Currently, this methods are being actively developed, which are distinguished by their speed, low invasiveness and availability [1, 2]. Nanocontainers for targeted delivery help in the implementation of such methods [3]. In such cases, porous particles of calcium carbonate are used as carriers, for example, which have a slight cytotoxic effect on living cells [4, 5]. Or nanocontainers with dyes are used in photodynamic therapy to slow down the growth of tumor tissue [6, 7]. However, it is important to know the optical properties of tissues in the area of photodynamic exposure both for containers with dye and without, since this makes it possible to evaluate the effect of nanocontainers on the optical properties of tissues in the area of irradiation, which must be taken into account when calculating the loading of dye into containers.

This study shows the change in optical parameters, such as the absorption coefficient, scattering coefficient, anisotropy factor, of biological tissues before and after the introduction of nanocontainers taken from the area of tumor development. The measurements were performed *ex vivo* at room and physiological temperatures, which makes it possible to approximate the obtained data to the actual conditions during photodynamic therapy.

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Investigation of changes in the optical properties of rat model tumors during laser plasmon resonance photothermal therapy

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Currently, along with traditional methods of tumor treatment (surgery, chemotherapy, radiotherapy, photodynamic therapy), methods based on the use of modern nanotechnologies and, in particular, laser plasmon resonance photothermal therapy (PPTT) are attracting more and more attention. The principle of operation of PPTT is based on the accumulation of plasmon resonance nanoparticles in tumor tissues and their local heating by irradiation with a laser of the appropriate wavelength, which makes it possible to reduce the dose of laser radiation and reduce the damage caused to healthy tissues surrounding the tumor.

In this study, kidney cancer and liver cancer cell cultures obtained from the bank of tumor strains of the Russian Cancer Research Center named after N.N. Blokhin. Model tumors were subcutaneously inoculated into albino male rats. Gold nanorods (GNRs) with an absorption maximum at a wavelength of 800 nm were injected intratumorally. Irradiation was performed percutaneously using an 808 nm diode laser. After irradiation, the optical properties of individual layers (capsule, periphery, and central part) of a mature tumor and skin of rats were measured in the spectral range of 350-2200 nm. Using the inverse adding-doubling method [1], the absorption coefficient and the reduced scattering coefficient were calculated. Modeling of photon propagation in the skin and tumor before and after the introduction of the GNR suspension was carried out by the Monte Carlo method and was used to assess the absorption of laser radiation energy in the tumor.

The work was supported by the Russian Foundation for Basic Research (grant No. 20-52-56005).

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D35

Cryospectroscopic and *ab initio* studies of noncovalent interactions between volatile anesthetics (enflurane, isoflurane) and dimethyl ether. Spectroscopic evidence of trimer formation

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Volatile halogenated hydrocarbons and ethers reveal strong analgesic and anesthetic effects. Among these compounds, enflurane and isoflurane belong to isomers which often used for purposes of invasive surgery. These halogenated compounds possess two CH groups 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 is dimethyl ether (DME). The attention focuses on the features of noncovalent interactions between these isomers (particularly isoflurane) and DME. As an experimental tool effective in detection of weak complex formation, the FTIR spectroscopy of cryosolutions has been chosen.

Cryospectroscopic measurements, performed with isoflurane dissolved in liquefied Kr and Xe, have shown that the basic features of the temperature changes in the region of CH stretching bands are defined by two largely populated rotamers [4]. However, at T~118 – 130 K only one the most stable conformer lettered by *a*, with two CH groups contrarily oriented, possess c.a. 90 % of the whole population. Thus, it contributes predominantly to the IR spectrum registered in liquefied Kr.

In the case of enflurane, the FClCH and CHF_2 groups act as CH donors of somewhat different strength when interacting with dimethyl ether ($(CD_3)_2O$). It is worth noting that the complexes formed are stabilized by so called blue-shifting H-bonds predominantly. In the case of isoflurane one can expect that both CH groups will interact with molecular acceptors in a similar way. Somewhat stronger complexes are expected to be formed when H atom of CHFCl-group is engaged in H-bonding type interactions. In this report, the results on the cryospectroscopic temperature studies of isoflurane + dimethyl ether (DME) mixtures dissolved in liquefied Kr are presented at a wide range of concentrations. Ab initio calculations were made to obtain geometric and spectroscopic parameters of stable forms of dimers and trimer, and to interpret temperature and concentration changes revealed in the IR spectrum of the system studied. To avoid the overlapping effect in the region of CH stretching vibrations the wholly deuterium substituted form of DME was used.

The calculations have been performed using the computer resources of the Resource Centre of SPbGU (http://cc.spbu.ru). The spectroscopic measurements were partly performed on the apparatus of the Resource Center Geomodel of SPbGU.

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Invited Lectures E

Tuesday, July 4, 9^{15} – 10^{45}

Chair: Yury V. Kistenev

E1

Terahertz sensors based on metamaterials and solid-state laser sources

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In my lecture, I will talk about the basic principles of building terahertz sensor devices that can be used to study small impurities in the atmospheric air, including human waste products and pathogens. Increased sensitivity of sensors is achieved by using dielectric metamaterials, which contribute to the concentration of the electric field near the characteristic anomalies in the absorption and refraction spectra of complex organic molecules. I will talk about methods to achieve extreme concentration detection of impurity substances in the atmospheric air. Important for practical application is not only the sensor itself, but also the corresponding source of terahertz radiation, which is tuned to the optimal resonance of the molecule-sensor system.

Spectroscopy of biological tissues in a wide range of wavelengths from deep UV to THz

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Principles and novelties in the field of tissue optical spectroscopy with enhanced properties at immersion optical clearing will be presented as well as discussion of new fields of clinical applications for spectroscopic monitoring of metabolic substances, delivery of drugs and labeling agents. Optical clearing method is based on controlling the optical properties of tissue through the use of immersion optical cleaning agents, which impregnate the living tissue of interest and make them transparent for a limited time [1-3]. The enhancement of the spectroscopy probing depth and spectral image contrast for different human and animal tissues will be demonstrated using spectrophotometry from deep UV to THz, fluorescence, photoacoustic and Raman spectroscopies.

Experimental data on enhanced spectroscopic data collection using glucose, glycerol, PEG, Omnipaque^{TM}, albumin and other optical clearing agents for normal and pathological tissues (cancer and diabetes mellitus) will be presented. Perspectives of immersion optical clearing/contrasting technique aiming to enhance imaging of living tissues by using different spectroscopic and imaging modalities working in the ultra-broad wavelength range from free electron beam excitation (Cherenkov light emission) to terahertz waves will be discussed.

The research was carried out with the support of a grant under the Decree of the Government of the Russian Federation No. 220 of 09 April 2010 (agreement No. 075-15-2021-615 of June 4, 2021).

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Round Table F
“Databases and information systems in spectroscopy”
Tuesday, July 4, $11^{15} – 13^{45}$
Chair: Elena A. Pazyuk

F1 (Invited Talk)

Simulation of near infrared radiation transfer in the atmosphere and greenhouse gases content retrieval with taking into account new information in spectroscopic databases

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The accuracy of greenhouse gases remote sensing by spectroscopic methods depends on quality of absorption line parameters used as input information in the atmospheric radiative transfer modeling. The spectroscopic databases are regularly updated, and the continuing validation of the absorption line parameters is required. The discrepancies in CH_4, CO, and H_2O atmospheric total content, retrieved from the measured atmospheric solar spectra, can reach 4% and higher [1-3] due to the use of different versions of HITRAN[4], GEISA[5], and ATM[6] spectroscopic databases.

One of the effective ways to estimate the quality of spectroscopic line parameters is to compare the simulated spectra with the atmospheric spectra measured with a high resolution at different atmospheric conditions. It allows not only revealing the spectroscopic database, which gives minimal residual between measured and simulated spectra, but also identifying incorrect line parameters in the databases from the shape of the residual.

The atmospheric spectra are simulated with the HITRAN2020 and GEISA2020, ATM latest issues, and a comparison with the atmospheric solar spectra recorded by a Fourier spectrometer [7] in the NIR spectral region is made. The spectral intervals used for the CH_4, CO, and H_2O atmospheric content measurements are analyzed. The atmospheric content of the gases is retrieved with use of different spectroscopic databases.

The author would like to thank V.I. Zakharov, N.V. Rokotyan, K.G. Gribanov, I.V. Zadvornyh for providing the atmospheric solar spectra measured with the FTIR spectrometer at the Kourovka observatory.

The research has been supported by the Ministry of Science and Higher Education of the Russian Federation (V.E. Zuev Institute of Atmospheric Optics of Siberian Branch of the Russian Academy of Sciences).

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Analysis of the quality of data extracted from publications in information systems W@DIS and GrafOnto

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Information systems W@DIS and GrafOnto appeared as a tool for extracting, storing, analyzing and evaluating the quality of primary and expert spectral data extracted from information sources. Data is extracted from tables, files, graphs and figures. Both of these systems are related to the results of seven spectroscopic problems [1]. The data on the states, transitions and spectral parameters of the lines and the properties of such data are located in the databases (DB) W@DIS, and the data on the spectral functions in the GrafOnto DB.

The key properties in IS W@DIS are properties that characterize the quality of data obtained in the analysis of reliability and assessment of confidence in expert data. Reliability analysis is based on the rules of selection and sifting of non-identifiable energy levels and transitions, but on the calculation of pair ratios, including the analysis of the degree of disordering of wave numbers and energy levels [2] and filtering of transitions [3]. The need to assess the credibility of expert data is due to the non-formality of their choice.

The quality of spectral functions in IS GrafOnto largely depends on the quality of printing when printing a picture and, to a lesser extent, on the recognition procedure. The collection contains 6400 graphs and only 8% of them are associated either with tables or with the authors of the results. A significant error occurs when graphs are implicitly quoted. Quantification of the difference between the citing and cited graphs is determined by the original method [4].

Attributive, contextual and semantic search of spectral data sources, integration of data sources, semi-automatic finding of a cited graph and selection of a cited graph for an arbitrary graph of the GrafOnto system are available to users.

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F3

Internet accessible information systems SPECTRA, S&MPO and HITRAN on the Web

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The information systems SPECTRA [1], S&MPO [2] and HITRAN on the Web are currently a real working tool for solving different problems of molecular spectroscopy. All three systems provide access to lists of the spectral line parameters (SLP) of molecules and allow you to calculate frequency profiles of various spectral functions both for individual molecules and for mixtures of various molecules and their isotopic modifications. The results of the work can be saved in the system or uploaded to the user's computer in text or graphical form. This talk presents the main functionality of the systems, their current state and prospects for further development.

The SPECTRA system provides access to the most well-known banks of spectroscopic information HITRAN [3] and GEISA [4], as well as to other lists of SLP for a number of molecules (H_2O, CO_2, N_2O, CO, CH_4, NO, NO_2, OH, H_2S).

The S&MPO system is focused on working with ozone molecule (O_3) data only. Most of the information provided by the system is the result of many years of Russian-French cooperation on the study of the ozone molecule. In addition to the SLP lists, the system has experimental absorption spectra; a function for comparing calculated and experimental spectra is available.

The HITRAN on the Web system provides access only to the HITRAN database. The functionality of the system is identical to the capabilities of the SPECTRA system. The system was created as part of the implementation of Russian-American cooperation supported by the CRDF Foundation in 2010-2011. Currently, the system works with the SLP database of the HITRAN2020 version [3] and updates of 2022-2023.

In 2015-2019, the program code of the systems was completely rewritten using the tools and technologies relevant at that time.

Over the years, the development of systems has been supported by grants from the RFBR and CRDF, as well as the "5–100" Program to improve the competitiveness of the Russian Universities. Currently, the work is supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of the state task. The support from the Russian Science Foundation (grant no. 19-12-00171-P) is acknowledged.

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RITZ energy levels of $^{16}O_3$ deduced from experimental spectra: critical analysis of HITRAN and S&MPO transition frequencies

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The most complete, carefully selected and calibrated data set of experimental microwave and infrared transition frequencies of $^{16}O_3$ was compiled from the literature sources reviewed in [1], private communications and new measurements [2] currently in progress. The dataset consists of over 75000 entries covering the 0.3–7999.0 cm^{-1} spectral range. It was used to obtain a set of more than 28500 experimental energy levels using the RITZ computer code [3] based on the fundamental Ritz-Planck-Einstein principle. These levels reproduce the measured data with the accuracies compatible with the measurement uncertainties: the root-mean-square (obs.-calc.) value of the fit is 0.001 cm^{-1} in the mid-IR range and about 30 kHz or even better in the MW range, with the overall dimensionless weighted standard deviation of 1.22. This means that the rovibrational spectral transitions can be computed from the RITZ levels with nearly experimental accuracy. The experimental levels were used to critically analyze the $^{16}O_3$ transition frequencies in the current versions of the HITRAN (hitran.org) [4] and S&MPO (smpo.tsu.ru) [5] databanks. The discrepancies obtained in these comparisons will be discussed.

This work was supported by the Russian Science Foundation (grant No. 19-12-00171-P).

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F5

HAPI2: software for accessing the current version of the HITRAN database

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This talk presents the second generation of the HITRAN Application programming Interface (HAPI2) software. HAPI2 is a set of Python software libraries integrated with the HITRANonline web portal [1] that facilitates the collection of spectroscopic data and basic spectral modeling using this data. HAPI2 extends the capabilities of its predecessor (https://hitran.org/hapi, [2]) to all sections of the HITRAN database [3], including experimental absorption cross sections; collision-induced absorption, partition functions, and also provides data in JSON format on quantum transitions, molecules, isotopologues and data sources. Along with enhanced access to data from HITRAN, HAPI2 provides fast codes for the calculation of the spectral functions from line-by-line data, as well as codes for absorbance calculation for non-Voigt line profiles.

The HAPI2 library is open source software available in the Github repository https://github.com/hitranonline/hapi2.

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F6

The status of the information system "Electronic structure of atoms" and the planned expansion into the regions of X-rays, negative ions and isotopes

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The report describes the main opportunities provided to support scientific research and training of specialists by the information system "Electronic Structure of Atoms" [1]. Detailed information is provided on the volume and characteristic features of the database of the Internet information resource, including data on neutral atoms, single and multiple ions, transuranic atomic systems, information on the classification of levels and transitions [2]. The means of visualization of scientific data implemented in the system are considered, including their representation in the form of spectrograms, Grotrian diagrams and quantograms. Quantum diagrams are a new type of diagrams of the electronic structure of atomic systems, focused on computer generation in combination with interactive dynamic representation of the results [2]. The effectiveness of the application of the information system "Electronic structure of atoms" for various scientific tasks, including the analysis of the electronic structure of atomic systems and for the training of specialists is discussed. A further expansion of the information system may be the creation of an online system for processing X-ray fluorescence spectra for a wide range of multidisciplinary studies using synchrotron radiation. It is also planned to expand the data bank to the areas of multiple and negative ions and stable isotopes.

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Round Table G
“Spectroscopy in medicine and in gas analysis”
Tuesday, July 4, 11^{15} – 13^{45}
Chair: Valery V. Tuchin

G1

THz spectroscopy for biology, medicine, ecology

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Nowadays the various applications (ecology, biology, medicine etc) impose requirements to revealing the trace gas concentrations in multicomponent gas mixture. The atmospheric molecular components, produced in trace-concentration, can influence to weather and climate changes owing to their high chemical activity [1]. The approach based on revealing the metabolic profile of disease or pathologies and search of set of metabolites-markers of diseases in biological liquids (blood, urine, saliva, etc.), vapors (exhaled breath) is developed in medicine [2]. Therefore the development of methods allowing to detect the gases in trace concentrations is current of importance.

A spectroscopy based on nonstationary effects such as inducing and decaying the free dumping polarization in a gas sample at the interaction of radiation and gas molecules can be considered as a high sensitive method of investigating the multicomponent gas mixtures. If a polarization is created in a gas sample under resonant conditions, then after the generator is taken out of resonance, the polarization wave will radiate the same electromagnetic field mode that excited it. This is realized by periodically switching the phase or frequency of the probing radiation, which resonantly interacts with the gas, and it leads to the processes of non-stationary radiation and absorption, i.e., to the periodic appearance and decay of the induced macroscopic polarization. The devices can be realized in mode with phase switching or fast sweeping modes of the probing radiation [3].

The THz high resolution spectroscopy imposes the strong requirements to such components of spectrometer as radiation sources and receivers. The development of semiconductor technology including quantum cascade lasers will allow achieving a high level for production of the radiation sources and detectors for terahertz spectroscopy.

THz high resolution spectroscopy is successfully used in ecology as well as medicine diagnostics. The One of the substances influencing to atmosphere state is chloroform emitted owing to natural processes (producing by water phytoplankton or fungus) or anthropogenic activities. The spectra of the chloroform in a gas phase in the 2-mm wavelength sub-ranges were measured and missing spectroscopic data were supplemented.

The contents of thermal decomposition products of the urine samples (urine of cancer patient before and after chemotherapy and healthy volunteers; urine of rats with artificially induced dysbacteriosis and healthy rats) were studied with using the terahertz nonstationary gas high resolution spectroscopy for revealing the markers of pathological states.

The THz gas spectroscopy method is a prospective method for investigation of atmosphere pollutants or hazardous substances in trace concentrations and biological samples.

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G2

Application of machine learning for terahertz spectra of glioma patient blood plasma analysis

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Gliomas, one of the most severe malignant tumors of the central nervous system, have a high mortality rate and an increased risk of recurrence [1]. Therefore, early glioma diagnosis and the control of treatment have great significance [2]. The blood plasma samples of glioma patients, patients with skull craniectomy defects, and healthy donors were studied using terahertz time-domain spectroscopy (THz-TDS) [3]. An analysis of experimental THz data was performed by machine learning (ML). The ML pipeline included (i) THz spectra smoothing using the Savitzky–Golay filter, (ii) dimension reduction with principal component analysis and t-distribution stochastic neighbourhood embedding methods; (iii) data separability analyzed using Support Vector Machine (SVM), Random Forest (RF), and Extreme Gradient Boosting (XGBoost) [4]. The ML models’ performance was evaluated by a k-fold cross validation technique using ROC-AUC, sensitivity, and specificity metrics. It was shown that tree-based ensemble methods work more accurately than SVM. RF and XGBoost provided a better differentiation of the group of patients with glioma from healthy donors and patients with skull craniectomy defects. THz-TDS combined with ML was shown to make it possible to separate the blood plasma of patients before and after tumor removal surgery (AUC = 0.92). Thus, the applicability of THz-TDS and ML for the diagnosis of glioma and treatment monitoring has been shown.

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G3

Development of multimodal spectral approaches to study of skin cancer

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Modern optical technologies combined with optical clearing of tissues based on reducing light scattering in tissues by partially replacing interstitial fluid with biologically compatible hyperosmotic immersion agents, increase the effectiveness of optical cancer diagnostics methods [1].

In this study, a combination of high–resolution ultrasound examination and optical methods (Raman spectroscopy, optical coherence tomography (OCT), and backscattered diffuse reflectance spectroscopy) with biocompatible optical clearing agents was used for the study of basal cell carcinoma in humans and model melanoma in mice.

The study involved light-skinned volunteers with basal cell carcinoma and benign neoplasms and volunteers with high pigmented health skin. Differentiation of neoplasms was carried out using morphological research. It was found that the skin scattering in the area of neoplasms is significantly reduced compared to healthy skin, there was an increased content of hemoglobin in the oxygenated form. For cancer, a characteristic feature was a low content of lipids and keratin. In the area of benign neoplasms, increased content of proteins, nucleic acids, lipids, and keratin was observed. The sizes of neoplasms were evaluated using ultrasound examination, and their internal structure was visualized using OCT.

Experimental assessment of differences between model melanoma and healthy skin in mice was performed using diffuse reflectance spectroscopy in combination with biocompatible optical clearing agents and chemical and physical penetration enhancers. At 420 nm, 545 nm, and 575 nm, the relative changes in the diffuse reflectance ratio ($R_{benign}/R_{melanoma}$) after clearing were 314%, 205%, and 204%, respectively.

This work was supported by the Tomsk State University Development Program “Priority-2030”.

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G4

Breathe air analysis using laser IR and terahertz spectroscopy and machine learning

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The report is devoted to development on new implementations of medical diagnostics using breath air analysis by IR and THz laser spectroscopy, and machine learning. This problem is connected with the informative features extraction and finding effective classification methods. The informative features can be associated with two ways of a breath air sample analysis: (i) the sample absorption spectrum profile, (ii) contained in the sample volatile molecular compounds concentration profile. The latter approach requires effective methods of the spectroscopy inverse problem solution when the breath air sample molecular composition is not a priori known. A choice of acceptable classification methods is defined by the ability to work well with small-volume datasets.

We will demonstrate examples of above-mentioned problems' solution.

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G5

Optical, fluorescence and spectroscopy techniques to assess nanoparticles interaction with red blood cells

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Different types of nanoparticles (NP) have been shown to be biocompatible and promising for various biomedical applications [1]. In particular, iron oxide NP and nanodiamonds (ND), magnetic ND, zinc oxide, aluminum oxide, titanium dioxide and silicon NP have been proposed for their application for biomedical imaging, photodynamic therapy and targeted drug delivery [2-4]. It is presumed that in order to reach the goal these particles should be intravenously administered into the blood. In principle, NP can affect the properties of blood cells, in particular, erythrocytes such as their ability to reversibly aggregate and deform in shear flow when moving along blood vessels and capillaries.

There are a few possible mechanisms of the NP interaction with erythrocytes, in particular, potential opportunity of the particles to adsorb on the cell's membranes and their partial penetration into the internal content of the cells. All these phenomena can result to membrane rigidity and internal cell viscosity alterations which in turn lead to changing the red blood cells deformability – the ability of the cells to change their shape flexibly and reversibly by passing through the capillaries with diameter less or equal than the cells size. Another consequence of the NP interaction is that their adsorption on the surface membrane leads to a decreasing the area of possible direct cell contacts and results in impairment of erythrocytes spontaneous and reversible aggregation. In turn, both deformability and aggregation properties determine the viscosity of blood on which the blood circulation crucial depends. Thus, before clinical applications it is necessary to verify the NP on safety including regarding deformability and aggregation microrheologic parameters of the blood.

In this work we tested blood samples *in vitro* incubated with different NP with variety of sizes and surface functionalization. The basics of laser difractometry, diffuse light scattering aggregometry, as well as optical trapping techniques to study the effect of NP on blood microrheologic parameters are discussed [5]. To investigate the mechanisms of the NP interaction with erythrocytes we used the fluorescent microscopy and spectroscopy technique erythrocytes. Comparing of the spectra of the erythrocytes measured before and after the incubation with NP demonstrated membrane adsorption and/or intracellular penetration of some types of the NP. Using fluorescent microscopy, we obtained the images of erythrocytes samples and NP clearly showing the membrane adsorption of the latter.

The effect of NP on blood microrheology is demonstrated. Incubation of blood with NP at high concentrations of the latter does negatively affect both aggregation and deformability of the cells, the effect being dependent on the particle concentration, size and surface functionalization. Basing on the measurement results one can conclude that the NP can be administered into blood in ambient conditions at low concentrations (above 30 μg/ml), without significant complication of the blood rheological conditions. However, under certain conditions, this effect can be very significant, and it is necessary to check the hemocompatibility of each type of nanoparticles in vitro.

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G6

Methods of light scattering, capillaroscopy and laser speckle-contrast spectroscopy in the study of microrheology of blood and microcirculation

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The composition of the blood, as well as the parameters characterizing the structure and dynamics of blood and tissues surrounding blood microvessels, are the factors that determine the fluidity of the blood and the efficiency of the transport and delivery of gases (oxygen and carbon dioxide) and nutrients throughout the volume of the human body. Age-related changes in the body and most socially significant diseases are accompanied and largely determined by the deviation of these parameters from normal values. Thus, the ability to measure and control these parameters in normal conditions and their changes in pathology is important for an adequate assessment of the state of patients, ways to improve the treatment procedure and to correct the microrheology and microcirculation of the blood of patients.

In modern hemorheological studies, laser and optical methods are widely used, which allow performing a comprehensive study of deviations from the norm of various parameters associated with the structure and dynamics of blood, through visualization and measurement. In particular, the following ones are used: diffuse light scattering (DLS); laser diffractometry (LD); optical tweezers (OP), videocapillaroscopy, speckle-contrast spectroscopy, two-photon tomography, and fluorescence imaging. The first three methods are used for in vitro measurements using fresh EDTA-stabilized blood samples drawn from healthy donors or patients suffering from various diseases, such as diabetes mellitus and arterial hypertension. The last four methods are used for in vivo measurements and imaging. Also, parameters associated with erythrocyte aggregation are measured in model solutions of certain plasma proteins known as aggregation agonists or inhibitors to study the mechanisms of aggregation. In particular, the forces of aggregation and disaggregation of individual erythrocytes are measured using the OP, the aggregation index, the characteristic aggregation time and the critical shear stress in whole blood samples are measured with an aggregometer using the DLS method.

In our work, the conventional LD (ektacytometry) method used to measure the average value of the deformability of erythrocytes in a sample is improved in such a way that it becomes possible to measure the parameters of cell distribution in deformability, which is important for the clinical application of the method. The blood flow in capillaries is imaged using the digital capillaroscopy techniques, which allows for determining several parameters of the flow in nail-bed capillaries of human individuals. Also, in vivo imaging of blood flow in larger areas of the microcirculatory system in laboratory animals is performed using the laser speckle-contrast spectroscopy method.

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G7

The study of the optical properties of the lung tissue at the action of e-cigarette liquid

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The use of e-cigarettes has become widespread in recent years. Liquids for vaping include different components, the main of which are polypropylene glycol and glycerol. These components are hyper-osmotic optical clearing agents. The aim of this work was to study changes in optical properties of lung tissue under action of e-cigarette liquid.

Aerosol of e-cigarette liquid without nicotine (Alliance, Russia) was used. Concentration of components was the following: glycerol – 60%, propylene glycol – 40%.

The experimental setup consisted of an inhalation chamber with a special device for aerosol pumping. A 150 ml Janet syringe was attached to the vaper iJust 3 (Shenzhen Eleaf Electronics Co., China) via a hose with a small filter, when the vaper generates steam, it was drawn into the syringe and injected into the inhalation chamber.

In *ex vivo* studies, the lungs of Wistar rats (20 samples) placed in e-cigarette liquid for 1 hour. For *in vivo* study, 12 animals were divided into two groups - experimental and control, 6 rats in each. The rats of the experimental group were placed in the inhalation chamber and aerosol of e-cigarette liquid was pumped into it at the rate of 1.5 liters for 10 minutes. Then a 2-minute break was taken. Thus, during the entire procedure, which included five inhalations of 10 minutes each, the rats received 7.5 liters of aerosol each. Rats of the control group were intact. The animals were withdrawn from the experiment one hour after inhalation, and their lungs were taken. Twenty samples were obtained from each group for the spectral study.

The spectra of total transmission and diffuse reflection coefficients of the samples were measured in the wavelength range of 350–2500 nm using a spectrophotometer UV-3600 with an integrating sphere LISR-3100 (Shimadzu, Japan). Average thickness of the samples was 0.50±0.13 mm. The absorption and reduced scattering coefficients of the lung tissue were calculated using the inverse addition-doubling method [1].

Significant changes were observed in the scattering spectra of the lung tissues after the exposure in the e-cigarette liquid (*ex vivo* group). A decrease in the values of the reduced scattering coefficients in comparison with the control values was associated with optical clearing effect. In the *in vivo* group, there was an increase in scattering, which can be caused by the expansion of the alveoli and thickening of the alveolar septa. At the same time, the immersion effect was insignificant due to the short period of action.

This work was supported by the Tomsk State University Development Program “Priority-2030”.

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G8

Visualization of changes in lung tissue under the influence of electronic cigarette liquid using spectral OCT

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The relevance of this study is due to the wide prevalence of lung diseases such as lung cancer and respiratory viral infections [1-3]. The method of optical coherence tomography (OCT), and in particular spectral OCT, is actively used in such fields of medicine as ophthalmology, cardiology, oncology, dermatology, dentistry, etc. [4-6]. Modern non-invasive research methods allow detailed and dynamic 3D visualization of anatomical structures in living organisms; however, these methods have limited resolution, which is insufficient for visualizing tissue and cellular structures. OCT has significant capabilities for detailing lung microstructures.

This study demonstrates the possibility of using spectral OCT to visualize changes in the lung tissue after exposure to e-liquid vapor. It is shown that the changes observed using OCT correspond to morphological changes in the structure of the lung tissue.

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Telluride-based optically induced terahertz metamaterials

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In recent years, photonics of phase change materials (PCMs) has become a new area of research, since the optical and dielectric properties of PCMs change during the amorphous-crystalline phase transition [1]. One of the most promising classes of PCMs are tellurides [2]. Activation of the telluride phase transition is possible by thermal, electrical or optical effects on the material [3]. The phase transition principles can be used in terahertz (THz) metamaterials [4], affecting their spectral characteristics [3]. By controlling the fraction of crystals in a PCM film, multilevel energy-independent states of switching the amplitude, frequency, or polarization of a THz wave with a long storage time can be realized.

We investigated the optical and THz permittivity properties of telluride-based PCMs thin films during insulator-to-metal transition. Studies of the amorphous and crystalline phases as well as THz spectra are presented and studied using Lorentz and Drude models. It is assumed that the tellurides state can be tracked by the intensity of the characteristic Raman peaks. Molecular dynamics simulations demonstrate that during crystallization the characteristic modes intensity of amorphous state decreases. For example, the 155 cm^{-1} mode for $GeTe_2$, attributed to Te-Te stretching, disappears during complete crystallization. We demonstrate that the properties of telluride-based metasurfaces can be specified at the initial design stage and modified at the experimental stage. It has been shown that this PCMs characteristic is especially interesting for achieving dynamic and tunable functionality of the metasurfaces, in particular for controlled modulation of the amplitude, frequency, and polarization of THz radiation. Such active "THz sensors" can be used to increase the sensitivity of THz methods to various groups of biomolecules, viruses and bacteria.

This work was supported by the Russian Science Foundation (grant No. 22-29-01054) in part of the PCM material characterization; by the Ministry of Science and Higher Education within the State assignment FSRC “Crystallography and Photonics” RAS in part of developments and prospects of THz photonics; and by the Ministry of Science and Higher Education (grant No. 075-15-2021-1412) in part of the sensor creation.

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Oral Session H
Tuesday, July 4, $15^{15} – 17^{15}$
Chair: Leonid N. Sinitsa

H1

Self-perturbed rovibrational lines in the region of the first overtone of HBr. What I have learned from my mistakes

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The sequence of the spectra of pure HBr at different sub-atmospheric pressure was recorded in the region of the first overtone with a Bruker IFS 120 HR Fourier spectrometer at resolution of 0.003 cm^{-1}. The rovibrational lines of $H^{79}Br$ and $H^{81}Br$ with the same line index m were fitted with Voigt profiles simultaneously. This profile was found to describe adequately the experimental lines. The self-broadening and self-shifting coefficients as well as the intensities of the lines were obtained [1]. It was not found the statistically significant difference between both broadening and shifting coefficients for different isotopologues.

The obtained broadening coefficients are in good agreement with literature data, however they have a smaller error, about 1%. It should be noticed that the HITRAN values in P-branch, which are mirroring from R-branch, differ essentially from the experimental ones. To the best of our knowledge, the shifting coefficients [1] were reported for the first time. The intensities of the line are in the reasonable agreement with literature and HITRAN values.

Unfortunately, some methodical errors were made during the experiment. Particular two aperture sizes were used during recording of the different spectra. This led to unexpected results. The influence the aperture size on the spectra and the ways to remedy the described situation are discussed.

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H2

Global modelling of the observed line positions for the spectra of ultraviolet bands: Dunham coefficients for the $A^2\Sigma^+$ excited state of the ^{16}OH molecule

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A global treatment of the available experimental data on transition frequencies both in the $A^2\Sigma^+$ state and in the $A^2\Sigma^+-X^2\Pi$, and $B^2\Sigma^+-A^2\Sigma$ electronic systems of ^{16}OH molecule was carried out. In this analysis, a global model with vibrational dependences of the parameters of the effective Hamiltonian for the diatomic molecule in different electronic state was used. As a result of the fit, a set of the 'Dunham-type' coefficients for $A^2\Sigma^+$ electronic state was obtained. They reproduce the experimental dataset within estimated experimental uncertainties. The determined 'Dunham-type' coefficients were employed to generate the potential energy curve in the $A^2\Sigma^+$ electronic state using the RKR method.

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H3

The light OH molecule is still heavy to be deperturbed globally

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The hydroxyl radical OH is one of the first diatomic molecule discovered in the cold interstellar medium. The OH spectra is often observed in stellars, Sun, Earth and other planet atmospheres as well as a working body of a cosmic masers. It is also important intermediate product of high energy collisions and photodissociation.

To use the emission and absorbtion OH spectra in a diagnostic of high temperature enviroments the rovibronic term values and optical transition probabilities are required in a wide range of the excitation energy. It obviously means that all intramolecular interactions should be properly taken account in a global deperturbation analysis. It is not trivial to realize even for the lowest electronic states of OH since the strong competition between spin-orbit coupling, electronic-vibrational, electronic-rotational and ro-vibrational interactions is taking place. Moreover, the last two perturbations rapidly increase as the rotational excitation of the light OH molecule increases.

In this work we have studied options to improve the current deperturbation model based on the conventional band-by-band effective Hamiltonian approach [1] using the reduced coupled-channel (RCC) model [2] which explicitly accounts for spin-orbit, electronic-rotational and ro-vibrational interactions. It was found that taking into account for the 2-nd order mass-dependent non-adiabatic correction for both vibrational and rotational kinetic energy terms is crucially important for such light molecule as hydroxyl. Indeed, using this slightly modified version of the RCC model [3], all experimental rotational levels belonging to the lowest v=0-2 vibrational levels of the ground state $X^2\Pi$ could be represented within the experimental uncertainty [4]. However, the RCC model still fails to describe the higher vibrational levels with the appropriate spectroscopic accuracy.

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H4

Comprehensive study of CO spectra in Ar bath in the millimeter wavelength range

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The results of thorough analysis of experimental spectra of pure CO and its mixture with argon recorded in the 105–245 GHz frequency range at room temperature are presented. The spectra were recorded using 3 different spectrometers which jointly cover a pressure range from 0.02 up to 1500 Torr. The motivation of this work is the development of a physically based approach to modeling molecular spectra in a broad range of gas thermodynamic conditions. In such a model the effects beyond the limits of impact approximation, including bimolecular absorption, should be taken into account.

As the first step, we determine “classical” parameters of R(0) and R(1) lines, such as intensity, unperturbed line position, collisional broadening and shifting, speed dependence of collisional broadening and shifting, as well as line mixing manifesting itself in the line core region. The detailed description of this step can be found in [1,2]. We demonstrate that broadening and shifting parameters, obtained from spectra recorded by three spectrometers with different absorption measurement principles, depend linearly on pressure within the data uncertainty in the whole pressure range. This proves the correctness of the used line profiles and the low impact of systematic errors. The obtained coefficients are compared with the data from HITRAN [3], *ab initio* calculated values and results of other studies. The line mixing coefficients for the rotational lines of CO are experimentally determined for the first time.

The spectra obtained at relatively high pressures (200–1500 Torr) include not only the total contribution of the rotational lines, but also the smooth pedestal which is traditionally referred to the continuum. The second step of our work is the analysis of this continuum absorption. The retrieved continuum demonstrates the expected continuum-like dependence on the partial pressures of CO and Ar, which enables determination of the self- and foreign-continuum components. Both components have a quadratic frequency dependence, which is conditionedin the studied spectral range by the so-called radiation term. The continuum coefficients for the CO-CO and CO-Ar pairs are determined for the first time. Also, we estimated a possible uncertainty of the continuum absorption due to the uncertainty of the resonant lines far wings contribution.

The obtained data on the resonant lines are valuable for validating results of *ab initio* quantum-scattering calculations [1, 4]. The retrieved continuum is supposed to be compared with the model based on the semi-classical trajectory-based formalism [5, 6]. We believe that joint theoretical and experimental investigation of CO spectra with high accuracy is the way to determine in detail the nature of the continuum and to develop an accurate physically based absorption model which is relevant for remote sensing applications. The model would serve as a prototype for physically based modeling of the atmospheric continuum.

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H5

Rovibronic transition probabilities revisited among $B^2\Sigma^+$, $A^2\Pi$ and $X^2\Sigma^+$ states of CN radical

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The work presents the refined line list for $B^2\Sigma^+$-$X^2\Sigma^+$, $A^2\Pi$-$X^2\Sigma^+$ and $B^2\Sigma^+$-$A^2\Pi$ rovibronic transitions of CN radical, frequently encountered in deep space and re-entry observations as well as exoloited in the spectroscopic diagnostic of high temperature gas-phase processes.

The required accurate permanent dipole moments for the $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$ states and the corresponding transition dipole moment functions between them were *ab initio* evaluated over a wide range of internuclear distances $R(\text{Å})\in[0.7; 4.0]$ using alternative quantum-chemistry methods SA-CASSCF/ic-MR-CI/d-aug-cc-pVnZ(n=4,5) and MR-ACPF/aug-cc-pCVnZ(n=5,6). The results of both methods are found to be self-consistent within few percents of error.

The *ab initio* dipole moments obtained were then used to compute the matrix elements of rovibronic transitions within the framework of a global deperturbation model [1], which explicitly accounts for spin-orbit and electron-rotational interactions between all three states of the complex $X^2\Sigma^+\sim A^2\Pi\sim B^2\Sigma^+$. Using these matrix elements and energies, spontaneous Einstein emission coefficients were systematically evaluated for all dipole allowed transitions of various CN isotopologues lying in the energy range from 0 to 60 000 cm^{-1}.

The obtained information was tabulated in the ExoMol database format [2] and used to simulate the emission spectra using the ExoCross program [3]. The comparison of the obtained synthetic spectra, e.g. for the $A^2\Pi$-$X^2\Sigma^+$ band (0-0) with the result of a similar simulation using the data [4] currently recommended for use by ExoMol shows a good agreement. Moreover, the transition moment ratio of 2.0 ± 0.2 for the experimentally observed [5] interference of the $B^2\Sigma^+$-$X^2\Sigma^+$(8-11) and $B^2\Sigma^+$-$A^2\Pi$ (8-7) bands is reproduced by the present calculation with an absolute value of 2.85, which is two times better than that obtained in work [4].

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H6

The complex character of molecular vibrations as a source for errors in theoretical modeling of spectra of molecules with internal rotation

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In the experimental studies of the structure and conformational dynamics of non-rigid molecules based on the methods of vibrational or electron-vibrational spectroscopy, the heights of barriers to conformational transitions are obtained by solving inverse vibrational problems.

In this case, the vibrational Schrödinger equation is solved using the variational principle, and the desired structural information (conformer energy differences and conformational transition barriers) is obtained from the optimal effective potential functions. The described problems are mathematically incorrect: they usually do not have a unique solution and, moreover, their solutions are often unstable with respect to small variations in the initial data.

The described approach remains productive only if the set of coordinates used (in practice it is usually one coordinate — a one-dimensional approximation) for constructing the PES (Potential Energy Surface) sections properly represents the selected nuclear motions of the molecular system. Analysis of the shape of the PES often allows one to qualitatively evaluate the adequacy of the chosen coordinate to the problem being solved, for example, by the degree of curvature of the minimal energy path without much effort. The data on the shape of the PES are obtained from quantum-chemical calculations, and largely due to this, the use of quantum chemistry methods in the processing of experimental data from molecular spectroscopy has become the modern standard for such studies.

However, the kinetic part of the Hamiltonian does not lend itself to such a simple analysis. An example of insufficient consideration of the features of the kinetic part of the Hamiltonian is the almost twofold discrepancy in the estimates of the barrier to internal rotation in the benzaldehyde molecule, obtained by various methods of quantum chemistry and from three sets of experimental data [1].

Using the example of molecules containing planar fragments (benzene, furan, and others rings), the report discusses the structural features of molecular systems in which internal rotation can have a multimode character due to the relatively large off-diagonal elements of the matrix of kinematic coefficients B. The author presents an attempt, by comparing the results of one- and two-dimensional vibrational problems based on quantum-chemically calculated PES cross sections, to evaluate possible errors in the one-dimensional model and the stability of the inverse problem for internal rotation, which has a complex character.

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H7

Effect of symmetry-breaking charge transfer in excited molecules on IR and optical spectra

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Many quadrupolar dyes with a D-π-A- π -D or A- π -D- π -A structure, where D and A are electron donor and acceptor groups, experience symmetry breaking (SB) after optical excitation. SB is the concentration of electronic excitation on one D-π-A branch, which is initially evenly distributed throughout the molecule. This transformation of the electronic subsystem occurs in parallel with changes in the vibrational subsystem, which is tracked using time-resolved infrared spectroscopy (TRIR) [1]. In this report, a general theory of vibrational spectra variations of molecules undergoing symmetry breaking after photoexcitation is presented [2]. The approach is based on the expansion of the electron−vibrational interaction in a series in powers of the displacements of the vibrational modes and the dissymmetry parameter. The theory reveals the nature of the changes in the frequencies and intensities of the time-resolved IR bands as the symmetry breaking progresses. In particular, the intensities and the splitting of the IR bands associated with local vibrations of small groups of atoms symmetrically located in the left and right arms of the molecule are calculated. The theory explains the regularities of influence of symmetry breaking on the IR band intensities and the splitting of the frequencies observed recently using time resolved infrared spectroscopy.

This model can reproduce the IR spectral dynamics observed in the −C≡C− and −C≡N stretching region with a D−π−A−π−D dye in polar solvents using a single set of molecular parameters [3]. This approach allows estimating the degree of asymmetry of the excited state in different solvents and its change during symmetry breaking. Additionally, the relative contribution of different mechanisms responsible for the splitting of the symmetric and antisymmetric −C≡C− stretching bands, which are both IR active upon symmetry breaking, can be determined.

An approach is developed that allows estimation of parameters of an excited quadrupolar molecule responsible for changes in vibration frequencies in states with symmetry breaking by charge transfer from time-resolved IR spectra. The approach is tested on a molecule like A-π-D-π-A composed of an electron-accepting group A coupled with electron-donating group D by means of π-conjugated bonds, a D pyrrolopyrrole core, and two cyanophenyl acceptors. The expression derived for the IR spectrum of a molecule with symmetry breaking is shown to perfectly describe experimental data. The numerical values of the parameters of asymmetry in a series of solvents with different polarities and the solvent-independent parameters of the molecule itself are determined [4].

Types of possible changes in IR spectra with increase in molecule’s asymmetry are classified within the earlier developed theory of symmetry breaking and its manifestation in nonstationary IR spectra. Physical interpretation of the revealed trends is presented, and the latter are compared with currently available experimental data [5].

Effect of symmetry breaking on the fluorescence spectra is briefly discussed [6, 7].

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Parallel Oral Session I
Tuesday, July 4, 17^{30} – 19^{00}
Chair: Petr M. Tolstoy

I1

Calculation of structures, energetics and infrared absorption spectra of hydrogen-bonded dimers and trimers formed by formaldehyde with hydrogen fluoride

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Hydrogen-bonded complexes formed by H_2CO and HF may serve as model complexes of wide classes of carbonyl-containing and hydrogen halide molecules. Equilibrium nuclear configurations of $(H_2CO)_2$ and $H_2CO\cdots HF$ dimers and two stable $H_2CO\cdots(HF)_2$ and four stable $(H_2CO)_2\cdots HF$ trimers were determined using the MP2/aug-cc-pVTZ *ab initio* method. The binding energies of complexes, the cooperativity of H-bonding effects in complexes of different composition and the structural changes upon formation of dimers and trimers were examined. Anharmonic values of frequencies and intensities for infrared absorption bands were computed using the second-order perturbation theory and variational approaches. The calculated spectral parameters relating to the H–F, C = O, and C–H stretches and the in-plane HF librations of $H_2CO\cdots HF$ were used to identify the spectrum of this heterodimer recorded in the matrix-isolation experiment in liquid N_2 at $T = 8$ K [1]. The changes in the spectral parameters of absorption bands upon formation of dimers and trimers were derived from comparison of the data obtained in the same approximation for the complexes and monomers [2]. For each complex, sufficiently strong and characteristic bands, including the H–F stretching band, were determined, which can be used for spectroscopic detection of these systems. It was found that three predicted trimers have sufficiently large binding energies and their H–F stretching bands are significantly shifted from strong bands of monomers and dimers, which can facilitate their experimental observation. The blue shifts of C–H stretching bands upon complexation were analyzed and explained. To study the isotope effects in the spectra of the considered complexes upon H/D substitution, the frequencies and intensities of absorption bands of $(D_2CO)_2$ and $D_2CO\cdots DF$ dimers and $D_2CO\cdots(DF)_2$ and $(D_2CO)_2\cdots DF$ trimers were calculated in the same approximation [3].

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I2

Experimental measurement of the van der Waals binding energy in $(Xe)_n$–O_2 complexes with velocity map imaging technique

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Interest to the van der Waals complexes of xenon with oxygen is provided by the known application of xenon as an anesthetic agent [1]. This effect is very surprising because xenon is inert gas. The mechanism of this anesthetic action is still not known. 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 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 velocity map imaging of the photofragments arising in photodissociation of van der Waals complexes. Also, the partition functions of complexes Xe–O_2 and Xe_2-O_2 were calculated to estimate the concentration of such complexes on anesthesia conditions.

In these experiments the 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 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 oxygen molecule $(Xe)_n$–O_2.

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[*] V. Rogoveshko is an applicant for the best talk award (oral).

I3

Spectroscopy of the radiation-induced intermediates resulting from isolated phosphine molecules in low-temperature cryogenic matrices

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Phosphorus-containing molecules, in particular phosphine, have been identified in interstellar space and proposed as a source of phosphorus for the origin of life on our planet [1]. Reduced forms of phosphorus, due to their resistance to oxidation, are rare on Earth, but the situation is changing outside of it. The presence of a wide variety of rather simple phosphorus-containing molecules in interstellar space stimulates model experimental studies of their radiation-induced reactions with other common substances and the origin of more complex molecules. Meanwhile, the mechanism of radiolytic decomposition of phosphine has been poorly studied up to now. The application of matrix isolation method makes it possible to "freeze" the resulting highly reactive species and characterize them by common spectroscopic methods and the astrochemical applications of this approach were reviewed recently [2].

FTIR spectroscopy was used as the main method for studying the radiolysis of phosphine in solid noble gas matrices. The PH_3/Ng (1/1000, Ng = Ar, Kr, Xe) and PH_3/SF_6/Ng (1/1/1000) mixtures were used in this work. The deposited samples were irradiated with X-rays at 4.3 K. To refine the identification of the products of phosphine radiolysis, we have applied the ab initio quantum-chemical calculations at the CCSD4T level with the L2a_3 basis set.

Radiolysis of isolated phosphine molecules in the noble gas matrices leads to the appearance of new IR absorption bands [3]. Radiation-induced absorption bands with maxima at 1103, 1098 and 1092 cm^{-1} in Ar, Kr and Xe matrices, respectively, were assigned to the $PH_2^{\bullet}$ bending vibration. Also, we observed additional bands in this region with a blue shift of about 5–7 cm^{-1} in all used matrices (maxima at 1109, 1104 and 1099 cm^{-1} in Ar, Kr and Xe, respectively), which were attributed to the radicals that can be trapped in different matrix sites (e.g., single-substitutional and double-substitutional). Other strong absorptions in the regions of P-H stretching with at least four components in all studied noble gas matrices were assigned to "free" PH and caged [PH…H_2] pair on the basis of kinetic arguments. The behavior of these absorptions upon annealing of irradiated samples in a Kr matrix also appears to confirm this assumption. Furthermore, we observed for the first time absorptions attributed to $PH_3^{+\bullet}$ radical cation, which are quite prominent in the presence of electron scavenger (SF_6). The comparison with computational data and possible mechanism of the formation of different species are discussed.

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I4

Comparison of algebraic-diagramming construction methods with coupled-cluster methods for calculations of ionization and electron attachment spectra

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Computational schemes based on the algebraic-diagrammatic construction (ADC) approximation for Green's functions [1] are practically important methods for studying electronic transitions and various excited states of molecules, including states with detached and attached electrons [2, 3]. They successfully compete with the coupled-cluster methods within the framework of the equations-of-motion (EOM-CC) approach, which – due to a number of circumstances – are more common today. The presentation deals with the third-order ADC schemes (ADC(3)), which are in many respects similar to the EOM-CC models accounting for singly and doubly excited configurations (EOM-CCSD). This group of methods provides for results that are sufficiently accurate for many applications at relatively low computational costs which scale with the number of molecular orbitals n as n^5-n^6. A common feature here is the key computational step in the form of an eigenvalue problem for a secular matrix defined within the space of singly and doubly excited configurations. The latter describe the final states of the system and may generally differ from the initial state in terms of the number of electrons.

In this work, the first rigorous comparison of the accuracy of the IP-ADC(3) and IP-EOM-CCSD schemes for the ionization problem, as well as the EA-ADC(3) and EA-EOM-CCSD schemes for the electron attachment problem was carried out using the data of the full configuration interaction method (FCI). It is shown that the energies of transitions to "main" states with dominant one-hole (1*h*) and one-particle (1*p*) configurations in the case of the electron detachment and attachment processes, respectively, have in ADC(3) and EOM-CCSD a comparable accuracy. At the same time, the energies of transitions to "satellite" states of the two-hole-one-particle (2*h*-1*p*) and two-particle-one-hole (2*p*-1*h*) types differ significantly, having in EOM-CCSD considerably larger error than in ADC(3).

The theoretical analysis shows that the main and satellite configurations are treated consistently in the ADC(3) method respectively through third and first order of perturbation theory (PT), while in the EOM-CCSD method they are treated respectively through second and first order. Thus, the differences in transition energies observed for satellite states can only be explained by partial summations of higher-order contributions beyond the first order. Further analysis leads to the conclusion that the problem is caused by second-order contributions to the diagonal elements of the satellite block of the EOM-CCSD secular matrix, which shift all energies of satellite transitions upward. It is also obvious that the treatment of satellite transitions in ADC(3) schemes at the exact first-order level appears to be more balanced than in the EOM-CCSD methods.

The described situation is common to all types of the EOM-CCSD method including those for treatment of the excitation and double ionization processes and requires special care when calculating spectra or treating other problems that do not exclude the states of a satellite- or mixed satellite-main-state-type. Obviously, due to the above features, the EOM-CCSD method cannot provide a correct description of such states. The latter is demonstrated by a number of failed attempts to interpret photoelectron spectra using the SAC-CI method (equivalent to the EOM-CCSD method) known from the literature. By contrast, the ADC(3) method in all cases makes it possible to correctly reproduce the spectrum at a qualitative level and explain the nature of the observed bands.

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I5

High-resolution spectroscopy and selective photoresponse of cold biochromophore anions: theory meets experiment

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Photoinduced electronic and nuclear dynamics are often strongly coupled in the excited-state decay channels of biomolecular systems [1–3]. Internal conversion and light-induced electron transfer can be modulated by vibrational excitation, suggesting a way for controlling molecular functions. By using time-resolved action absorption spectroscopy of cryogenically cooled molecular ions combined with high-level *ab initio* calculations, we provide direct evidence of such control through achieving an unprecedented vibrational resolution in the photoresponse of the deprotonated Green Fluorescent Protein (GFP) chromophore – a key molecular unit in bioimaging of living cells.

Action-based absorption measurements of GFP chromophore anions cooled at 6K are performed in electrostatic ion-storage ring SAPHIRA (Aarhus, Denmark) through detection of specific mass-selected fragment ions, as well as prompt neutrals from electron detachment, which are both operational via resonance-enhanced multiphoton excitation. We present direct spectroscopic evidence for an energy barrier in S_1 that hinders internal conversion, thus allowing fluorescence, and see the influence of the electronic continuum $D_0 + e^-$, close to S_1. With the improved energy resolution and by simulating absorption and vibrational autodetachment (VAD) spectra using extended multiconfigurational quasi-degenerate perturbation theory (XMCQDPT2) [4], we disclose four characteristic spectral regions with competing electronic and nuclear decay channels and reveal the co-existence of mutual energy-borrowing mechanisms between nuclei and electrons mediated by specific vibrational modes. We also identify the $S_0 – S_1$ band origin [5] and discuss a remarkable agreement between the vibronic profiles of the protein and its chromophore, which suggests their similar photophysics. This paves the way for direct control over the functioning of light-sensitive proteins via selective vibrational excitation.

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Parallel Oral Session J
Tuesday, July 4, 17^30^ – 19^00^
Chair: Oleg V. Egorov

J1

Theoretical study of the evolution of electronic states with inner-level vacancies in uracil-water system

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When a molecular inner-valence electron is ionized, the resulting cation-radicals store considerable internal energy, allowing for a number of relaxation scenarios. If the amount of energy is sufficient, the fastest and thus most probable relaxation processes involve the ejection of the second electron that carries away excess energy. This electron can be ejected from the same molecule via the well known Auger decay if the energy of inner-valence single ionization is higher than the lowest energy of double ionization. This decay is usually followed by fragmentation of the molecule. In the environment, the phenomenon referred to as intermolecular Coulombic decay (ICD) can occur which implies that the relaxation energy from the primary ionized molecule is transferred to the neighboring one causing ejection of a secondary electron from the latter. Thus ICD prevents fragmentation of the initially ionized molecule and facilitates cleavage of the intermolecular bond. If the excess energy is sufficient, relaxation can also lead to electron transfer mediated decay (ETMD) in which two vacancies are created on neighboring molecules while the originally ionized molecule is returned to its neutral form.

The ICD was first suggested theoretically by Cederbaum and coworkers [1] and almost 10 years later discovered experimentally [2].The studies of the last two decades have proven that ICD and related phenomena such as ETMD are rather general and occur in many systems [3]. Moreover, recent experiments assisted by our calculations have shown that such effects are operative in biosystems [4, 5].The role of hydrogen bonding and donor-acceptor interactions between the involved neighboring molecules are considered in our recent publication [6] and represent the subject of the present work. In this research, propagator (or Green's function) methods within the algebraic-diagrammatic construction (ADC) approximation are used to treat the ionization and double ionization in molecules and molecular clusters and model the spectra in wide energy diapasons. In the presentation, the results revealing the aforementioned relaxation processes in the uracil-water system are discussed in some detail. The competing relaxation mechanisms of biological systems with inner-valence vacancies located on carbon and heteroatoms are considered, as well as the relaxation scenario after ionization of the water environment.

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Coupling plasmonic and photonic cavity modes in Au/SiO_2/Au nanohole arrays to increase refractive index sensitivity

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Surface plasmon resonance, a collective coherent oscillation of electron density in noble metals, offers a number of important applications for nanomaterials. For instance, the sensitivity of surface plasmon resonance to the refractive index of the environment can be used for the detection of biomolecules with very low detection limit [1,2]. The refractive index sensitivity, one of the primary characteristics of such sensors, is defined by the structure of a sensing layer. One of the most promising plasmonic nanostructures to be used for biosensors is a nanohole array in thin metal films [3-5]. Such materials can be relatively easy fabricated using the colloidal lithography approach. Enhancing the refractive index sensitivity of such systems is important and highly timely.

In this work, by using numerical Finite-difference time-domain simulations, we study the factors affecting the refractive index sensitivity of Au/SiO_2/Au nanostructures with nanohole arrays in SiO_2 and the top Au layers. We show that the sensitivity of such nanostructures can be enhanced by more than 20% compared to the system with only one Au layer. We demonstrate how coupling of the plasmon modes and photonic cavity modes affect the reflectance spectra and the refractive index sensitivity.

The observed non-monotonous dependence of the sensitivity on the dielectric spacer thickness can be used to optimize the performance of the biosensors based on the nanohole topology.

This work was supported by the Russian Science Foundation (grant No. 22-23-00454).

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J3

Spectroscopic investigation of pyridinium ordering in hybrid low-dimensional perovskite $PyPbBr_3$

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The versatile study of hybrid organic-inorganic perovskites is due to their special optoelectronic properties. These materials have become promising materials for highly efficient and inexpensive solar cells [1]. Methods of optical vibrational spectroscopy, such as Raman spectroscopy and infrared absorption spectroscopy, have repeatedly been shown to be extremely effective in studying the structure and properties of perovskites [2, 3].

The Raman and infrared spectra of $PyPbBr_3$ perovskite at various temperatures were recorded and analyzed. Based on XRD data on the structure of $PyPbBr_3$ using computer simulation, the parameters of unit cells differing by mutual position of nitrogen in the pyridinium ion were calculated. Vibrational spectra for the proposed conformers having the lowest formation energies were obtained and analyzed by quantum-mechanical calculations. Comparative analysis of the calculation results with experimental spectroscopic data made it possible to determine the most preferable configurations present in the real sample at different temperatures.

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J4

Implementation of up-to-date spectroscopic data on CN radical for laser-induced plasma diagnostics

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Spectra of CN radical is widely observed and investigated in laser-induced breakdown spectroscopy (LIBS). LIBS is an analytical technique based on optical breakdown in the ambient gas or liquid medium or onto the surface of solid sample followed by spectral analysis of laser-induced plasma [1]. The standardless (calibration-free) elemental analysis of plasma requires determination of its parameters including temperature as well as taking into account the possible chemical reactions between plasma species under local thermodynamic equilibrium (LTE) assumption. Besides elemental analysis, the accurate extraction of rotation temperature ($T_{\rm rot}$) from CN spectra is desirable for the non-LTE medium since $T_{\rm rot}$ is commonly assumed to be close to translation one ($T_{\rm tr}$). The goal of the present study was the checking of the performance of up-to-date CN line list for plasma diagnostics.

The violet system ($B\,^2\Sigma^+$ - $X\,^2\Sigma^+$ transition of CN radical, sequence $\Delta\upsilon = 0$, spectral range 378.7-389 nm) has been investigated. Samples mixed from urotropine and eriochrome black T (mass ratio 9:1, respectively) were used as the target for laser ablation and plasma generation in air with the help of Nd:YAG pulse laser ($E = 4.5$ mJ/pulse, $\tau \sim 6$ ns, spot size of the focused beam was 300 μ). The plasma emission collected with a parabolic mirror condenser onto the optical fiber and then guided to the 25 μ slit of a Czerny-Turner imaging spectrometer ($f = 520$ mm) with the blazed grating (2400 mm^{-1}, $\lambda_{\rm blaze,\ 1st\ order} = 270$ nm). The spectrometer was equipped with an ICCD camera (time resolution up to 10 ns) for spectra registration and the system provided the resolution of 0.037 nm (2.5 cm^{-1}, FWHM of the instrumental profile) near 384 nm allowing the recognition of rovibronic structure of the transition. The set of the twelve CN spectra at the different delays after laser pulse (200 ns – 6 us) corresponding the different plasma temperature and optical density was obtained.

We have implemented the algorithm developed previously [2] for modeling of atomic spectra of laser-induced plasma for simulation of molecular spectra of CN. The up-to-date energy level list [3] as well as the line list with transition probabilities [to be published] were introduced into calculations. We fitted the experimental spectra by model ones using the CRS2-LM algorithm available from NLopt [4] cross-platform library. The instrumental profile as well as the self-absorption of CN emission within the approximation of 1D uniform light source with the length l were carefully taken into account. We have tried both models with LTE (one-temperature $T = T_{\rm exc} = T_{\rm vib} = T_{\rm rot}$) and without one (non-LTE, two-temperature with the separation of the term energies into electronic, vibration and rotation parts; both of the cases with the constraints $T_{\rm exc} = T_{\rm vib} \neq T_{\rm rot}$ and $T_{\rm exc} = T_{\rm rot} \neq T_{\rm vib}$ were examined). The fitted temperatures cover the range from 3500 to 6500 K. We revealed that the CN spectra at the early stages of plasma evolution can be explained by simple LTE model, while the non-LTE one was necessary for accurate approximation of experimental data at the middle and late stages. The difference between $T_{\rm vib}$ and $T_{\rm rot}$ rises drastically within the plasma evolution from 1 to 3 μs and reaches 2000 K at the delays 3-6 μs. The square mean relative error of intensity approximation was ~4 % higher than the experimental uncertainty but correlated with the last one at the mid and late delays after laser pulse and reaches 6 % for the best case. Thus, we can conclude that our CN line list is highly suitable for accurate approximation of high-temperature experimental spectra of CN radical introducing the transitions from the levels with the high J values (up to 71.5 at least) and accurate diagnostics of extremely hot environments containing CN species.

This work was supported by the Russian Science Foundation (grant No. 23-13-00207).

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Invited Lectures K
Thursday, July 6, $09^{15} – 10^{45}$
Chair: Mikhail Yu. Tretyakov

K1

The Mars Atmosphere as Reveled by IR spectroscopy in the ExoMars TGO ACS Experiment

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Since 2018, ESA-Roscosmos ExoMars Trace Gas Orbiter (TGO) monitors Mars' atmospheric composition and climate with the Russian-led instrument, the Atmospheric Chemistry Suite (ACS) [1]. With spectral resolving power of $\lambda/\Delta\lambda \approx 30{,}000$ and high signal-to-noise ratio, ACS offers the best characteristics to detect minor gases. A selection of ACS results will be presented.

The search for organic compounds in the atmosphere of Mars – the remote search for life – has been going on since the middle of the 20th century. Methane occupies a special place: on the Earth it is predominantly produced by living organisms. After 2011, it has been measured by NASA's Curiosity rover, showing a "background» of 0.2–0.5 ppbv and rare bursts, up to 20 ppbv. In the ACS spectra we see faint lines of other gases, but not the methane features. A stringent upper limit of ≤0.02 ppbv was established [2, 3], an order of magnitude less than Curiosity's background. With a lifetime of ~300 years, methane shall accumulate in the atmosphere. To reconcile the TGO upper limits and the Curiosity detections, an as yet unknown mechanism for the rapid methane destruction, which does not affect the well-established chemistry of other active species of the Martian atmosphere (CO, O_3) is needed.

In the spectral rage, where the methane features should be present (2900–3300 cm^{-1}) we have detected CO_2 lines missing from spectroscopic databases [4]. The frequencies of observed lines coincided with the theoretically calculated P-, Q-, and R-branches of the magnetic dipole or electric quadrupole band of CO_2 [5]. This $\nu_2+\nu_3$ band, which is forbidden for electric dipole absorption, has never been observed or calculated numerically before. A new active compound of the atmosphere of Mars, HCl was confidently identified [6]. Its relative content reached 4 ppbv after the global dust storm of MY34, while outside the dusty season; its content was ≤0.1 ppbv. The ACS spectra were also checked for the presence of yet undetected species.

The ACS/TGO reported the first CO altitude profiles. Carbon monoxide does not condense and its relative content changes while CO_2 seasonally condenses and sublimes into and from the polar caps. Photochemical production of CO is balanced by its loss reaction with OH, which recycles CO into CO_2. CO is therefore a tracer of the OH-catalyzed chemistry that contributes to the stability of CO_2 [7, 8].

The loss of water is a key issue in the Mars' history. Photodissociation and subsequent dissipation of hydrogen from the upper atmosphere depends on the supply of water from below. ACS observations allowed for systematic study of the water vertical distribution [9, 10]. During dusty season, water vapor reaches the photodissociation heights, traversing cold layers of the atmosphere often in a state of deep supersaturation [9, 11]. It suggests that the stratospheric cold trap, efficient on the Earth, does not work on Mars. Measurements of water vapor, CO_2 and CO isotopologues vertical profiles made it possible to refine estimates of the total loss of water and volatiles from Mars based on isotope ratios [12–14].

This study was partially supported by the Russian Science Foundation (grant No. 23-12-00207).

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K2

Microwave spectral lines of atoms and molecules as a probe of the physical properties, kinematics, and chemical composition of interstellar clouds

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As of March 2023, about 290 molecules have been detected in the interstellar medium or circumstellar shells [1]. The largest molecules detected by radio spectroscopy contain 19 atoms. In addition, spectral lines of some atoms and ions, including the radio recombination lines (RRL) of some highly excited atoms [2] are observed at millimeter, submillimeter and longer wavelengths. Since the main constituent of cold dense interstellar clouds, molecular hydrogen, is unobservable there, spectral lines of these molecules, atoms and ions represent the main source of information about the chemical composition as well as physical conditions and processes in these objects (e.g. [3]).

Here we discuss the main approaches to analysis of radio astronomical observations of spectral lines in interstellar clouds and capabilities of such analysis. Spectral line observations make it possible to determine the main physical parameters of the clouds. For example, symmetric top molecules are good “thermometers” [4], because relative population of their K-ladders is governed by collisions. The relative abundance of the isomers $H^{13}CN$ and $HN^{13}C$ is also a temperature indicator [5]. The gas density and temperature can be derived from observations of several transitions of a molecule based on non-LTE excitation analysis. An optically thin emission of the molecules with a known abundance (e.g., $C^{18}O$) gives information on the total gas column density and mass. An example of such a study is presented in [6]. Investigation of the line Doppler shifts and line profiles provide an information on the cloud kinematics. For example, broad non-Gaussian line wings indicate high-velocity flows. An asymmetric dip on the line profile can be an indicator of collapse. A convenient tool for studies kinematics is the so-called position-velocity diagram. Special opportunities for studies of the physical parameters and processes in interstellar clouds provide cosmic masers (e.g., [7]). Detailed studies of the kinematics of cold clouds require accurate laboratory frequencies of some molecules. For this purpose, a Lamb-dip spectrometer was developed at the IAP RAS [8]. Clouds of atomic hydrogen and their interaction with the molecular and ionized gas are investigated in the 21 cm line [9].

An important direction of research is an investigation of the molecular inventory in the clouds and its relation to the physical conditions. In particular, the relative abundances of some molecules can serve as a chemical clock, indicating age of the cloud. An interesting feature is the enhanced abundance of deuterated molecules (e.g., [10]), which exceeds the cosmic D/H ratio by orders of magnitude.

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Oral Session L

Thursday, July 6, 11^{15} – 13^{45}

Chair: Oleg I. Korablev

L1

Long-term FTIR-monitoring of the atmosphere at the St. Petersburg State University

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Global climate change is one of the most important scientific, societal and economic contemporary challenges. In order to assess the significance of such changes and to better understand the physical and chemical processes involved, continuous, consistent, long-term monitoring of the atmospheric composition is indispensable. Ground-based high-resolution Fourier Transform InfraRed (FTIR) measurements of direct solar radiation are of particular interest for climate research allowing atmospheric gaseous composition and multiple climate processes to be monitored in detail.

Atmospheric FTIR-monitoring makes it possible to retrieve the total column (TC) of more than 20 trace gas components of the atmosphere [1,2] For some species, the informatively of FTIR measurements allows us to determine not only their TC, but also elements of volume mixing ratio (VMR) profile. The formalism for solving such an ill-posed problem of atmospheric sounding which requires some a priori information was developed by Tikhonov (3) and Rodgers (4).

The present study provides an overview of 14 years of atmospheric FTIR monitoring carried out at St. Petersburg State University (SPbU) in the framework of the Network for the Detection of Atmospheric Composition Change (NDACC) from 2009 to 2022. St. Petersburg site is a mid-latitude observational station located at 59.88°N, 29.83°E, 20m asl [5]. The instruments for atmospheric monitoring including Fourier Transform Spectrometer (FTS) Bruker IFS 125HR (spectral resolution up to 0.002 cm^{-1}) are installed in the suburban Peterhof campus of SPbU which is located about ~35 km southwest from the center of St. Petersburg. In order to retrieve TC and/or VMR profile of atmospheric gases, FTIR spectra are being processed by the SFIT4 retrieval code [6] which implements Optimal Estimation and Tikhonov–Phillips regularization algorithms. In the current work we are focusing on:

- characterization of the FTIR-system installed at the St. Petersburg site including information on typical FTS setups for atmospheric measurements, and techniques for FTS alignment control;
- information on retrieval strategies for long-lived (CH_4, N_2O, CO_2 and OCS) and short-lived (CO, HCN, C_2H_6, H_2CO, CH_3OH, HCOOH, C_2H_2, NH_3, and NO_2) trace gases which have been developed/modified taking into account the specific features of our FTIR-system and weather/climate conditions for St. Petersburg site;
- results of fourteen-year FTIR monitoring including estimates of long-term trends and characteristics of seasonal variations of CH_4, N_2O, CO_2, OCS, CO, HCN, C_2H_6, H_2CO, CH_3OH, HCOOH, C_2H_2, NH_3, and NO_2 in the atmosphere.

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L2

Measuring of methane isotopologues ($^{12}CH_4$ и $^{13}CH_4$) using Raman spectroscopy

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At present, the gas analysis technique based on Raman spectroscopy is being actively developed. The main advantage of this method is the ability to measure *in situ* all molecular species whose concentration exceeds the sensitivity threshold of the spectrometer. Despite the relatively low signal intensity, modern Raman spectrometers have a detection limit of less than 1 ppm (0.0001%) [1]. Such accuracy, coupled with high measurement speed, makes it possible to use Raman spectroscopy for real-time mud gas monitoring [2]. This approach measures the concentrations of C_1-C_5 alkane vapors and the $^{13}C/^{12}C$ and D/H ratios of methane isotopologues. Using this data, it is possible to determine many parameters of the hydrocarbon source, evaluate the production potential and optimize the production process. Previously, it was shown that Raman spectroscopy makes it possible to determine with high accuracy the concentrations of C_1-C_6 alkanes together with the main non-hydrocarbon species [3]. In this regard, providing an additional opportunity to measure the isotopic composition of methane will increase the diagnostic potential of Raman gas analyzers and expand fields of their application.

An analysis of the intensities and shifts of the $^{13}CH_4$ bands relative to $^{12}CH_4$ showed that the best range for this task is the interval of 2850–3100 cm^{-1}, where the Q-branches of the ν_1 and ν_3 bands are located. During the work, we compared the calculated intensities and wavenumbers of the lines for $^{12}CH_4$ and $^{13}CH_4$ from the MeCaSDa database [4] with the experimental spectra in the indicated range. The Raman spectrometer developed by us with a resolution of ~0.4 cm^{-1} was used to obtain experimental data. The results obtained showed that the data for the ν_3 band lines are in good agreement. In turn, for the lines of the ν_1 band intensities in the calculated and experimental spectra are slightly different. Despite this, we tested two methods for measuring $^{13}CH_4/^{12}CH_4$ using the Q-branches of the ν_1 and ν_3 bands. The measurement error for $\delta^{13}C(1\sigma)$ was ~3 ‰.

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L3

Analysis of near-infrared transparency windows of Venus observed by SPICAV IR/Venus Express: spectroscopy uncertainties

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Remote sensing of water vapor content in the deep Venus atmosphere and the surface is obstructed by a cloud layer (47–70 km)of sulfuric acid (H_2SO_4) and a strong absorption of the primary atmospheric constituent (96.5%), carbon dioxide (CO_2), at high pressure and temperature (+475°C, 92 bar at the surface). There are only narrow intervals, i.e. "transparency windows", in the near-infrared between strong CO_2 absorption bands where radiation of the surface and the lower atmosphere escapes to outer space [1]. This weak thermal emission can be observed at the Venus' night side. In 2006-2014 the IR channel of SPICAV (SPectroscopy for the Investigation of the Characteristics of the Atmosphere of Venus) spectrometer on board the Venus Express space mission performed numerous observations of the Venus transparency windows at 0.9-1.0, 1.1, 1.18, 1.28 and 1.31 µm with a high resolving power of ~1400 [2].This emission originates from the hot surface and the first-scale height of the atmosphere (0-20 km) [3] and several windows coincide with H_2O absorption bands. Thus, the SPICAV IR dataset is exclusive one to investigate H_2O in the Venus deep atmosphere [4, 5] and to study the surface. Changes in the brightness of short-wavelength transparency windows might indicate ongoing volcanic activity [6, 7].

In this work we use a line-by-line radiative transfer model with multiple scattering for 0.9-1.3 µm spectral range following the previous works [4, 5]to synthesize SPICAV IR spectra. The computations are performed by the SHDOMPP program [8] based on the spherical harmonic discrete ordinate method for the plane-parallel geometry. Vertical profiles of CO_2, temperature and pressure are defined by the VIRA database [9]. The cloud layer is set according to the model [10]. The H_2O mixing ratio is assumed constant. The work study errors of retrievals of water vapor mixing ratio and surface brightness in IR that occur due to spectral uncertainties of different input optical parameters. Parameters of molecular and cloud aerosol scattering and emissivity of different surface material have low spectral dependence. Refractive indices of cloud aerosol particles depend on concentration of H_2SO_4-H_2O solution. Fine spectral features of a high-resolution synthetic spectrum are associated with correct lists and line shapes assumption of CO_2 and H_2O lines. The high pressure and temperature conditions require a modulation of absorption lines' far wings[4]. The additional CO_2 continuum absorption formed by the superposition of the lines' far wings is not described theoretically. It is set by adding a correction factor [5] slowly depending on a wavelength. Different line lists or shapes entails additional fitting of this parameter.

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* Evdokimova D. is an applicant for the best young scientist talk award (oral).

L4

Multichannel diode laser spectrometer DLS-L for Luna-27 mission

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Lunar soil studies are planned onboard the “Luna-27” polar landing probe of the “Luna-Resource” mission scheduled for 2027-2028. DLS-L spectrometer was designed to study products pyrolytically evolved from soil samples in a vicinity of the Lunar probe landing site. The DLS-L aims in an independent measurement of pyrolytical output dynamics and integral content of H2O and CO2, as well as in retrieving isotopic ratios D/H, $^{18}O/^{17}O/^{16}O$, $^{13}C/^{12}C$ for isotopologues of H_2O and CO_2.

There are three main sources of volatiles on the Moon: degassing of the lunar mantle, interaction of solar wind protons with surface rocks, and shock degassing of falling meteorites and comets [1]. The composition of the forming volatiles and their isotopologues will be unique in each case. The DLS-L data would help for further understanding of physics and chemistry of the Lunar regolith, as original data of near-polar Lunar soil first-ever direct study. These studies will provide key scientific information for understanding the source of volatiles on the Moon and an answer to the question of the supply of volatiles for future lunar exploration missions.

The DLS-L device is based on tunable diode laser absorption spectroscopy technique (TDLAS) in mid-IR range [2]. On-ground calibration of the DLS-L has been carried out for IR regions of 2.64 μm (for H_2O isotopologues absorption lines), 2.68 μm (H_2O and CO_2 main molecules), 2.78 μm (CO_2 isotopologues).

The device is capable of operating in two different modes. In the first operating mode of the device, the content of gas mixture components, retrieved with sub-percentage error, in combination with a high speed of the working algorithm execution makes it possible to effectively carry out measurements directly during the pyrolysis, comparing the intensity of the gases output with the soil sample heating temperature. In other words, it allows us to observe the dynamics of pyrolytic extraction of regolith samples in real time. In the second operating mode, long-term measurements of a specially accumulated gas sample in the analytical cell makes it possible to retrieve integral parameters and isotopic ratios D/H, $^{18}O/^{17}O/^{16}O$, $^{13}C/^{12}C$ for H_2O and CO_2 molecules with the accuracy of about 1%.

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L5

CO_2 and H_2O spectroscopy at 2.65-2.7 µm range in the ACS/TGO experiment to study atmospheric structure and water climatology on Mars

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In this paper, we report highly sensitive spectroscopic measurements by the Atmospheric Chemistry Suite (ACS)on board ExoMars Trace Gas Orbiter (TGO) in the regime of solar occultation in the Martian atmosphere [1], allowing to retrieve the altitude distribution of temperature, CO_2 and H_2O densities. ACS consists of three infrared spectrometers, near-IR (NIR, 0.73-1.6 µm), middle-IR (MIR, 2.3-4.2 µm) and thermal-IR (TIRVIM, 1.7-17 µm), operating on the Martian orbit since April 2018. The middle-IR channel (ACS-MIR), an echelle spectrometer, has been performing the solar occultation measurements with high spectral resolving power $\lambda/\Delta\lambda > 25\,000$ and a signal-to-noise ratio exceeding 1000. Measuring the atmospheric transmission spectra, the instrument senses CO_2 absorption band around 2.7 µm in an extremely broad altitude range, from 10 to 180 km, covering the troposphere, the mesosphere and the thermosphere of Mars [2]. In parallel, the strong H_2O band at 2.66-2.67 µm is also observed for the first time up to 120 km [3].

In the paper, we discuss our scheme of the temperature and CO_2, H_2O density retrievals validating with atmospheric models and with simultaneous measurements by the ACS-NIR channel, which senses below 100 km [4]. The algorithm of retrievals considers an inverse problem to fit a modelled transmission spectrum to the measured one applying the temperature derivatives of the absorption cross sections that possess the rotational molecular lines. It allows us to derive the atmospheric CO_2 density and temperature in parallel for each sounded altitude, while the pressure is obtained on a basis of the hydrostatic equilibrium consumption.

Our measurements cover several seasons between the middle of the 34th Martian Year (MY) till the middle of MY 36, observations from May 2018 to February 2022, including the global dust storm in MY 34. The selected data set comprises about 800 sessions of solar occultation with revealed seasonal variability of the temperature, CO_2 and H_2O density profiles. Thanks to the high resolution ACS spectroscopy, an increased water vapor abundance is observed even at the upper mesospheric altitudes (80-120 km), for the first time, during the dust storm and perihelion seasons [3, 4].

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L6

Carbon and nitrogen abundance determinations in stellar atmospheres by molecular lines

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We propose a simultaneous analysis of the C_2 and CN molecular lines (bands) in 5100-5200 and 7930-8100 Å spectral regions for accurate determination of the carbon (C) and nitrogen (N) abundance in the atmospheres of the solar-like stars. This analysis is based on the recent updating of the molecular constants for both molecules. The improved molecular data were taken from [1] for C_2 molecule and from [2] for CN. These data are included in Vienna Atomic Line Database (VALD) [3], which is widely used by astronomy spectroscopists. We showed that molecular data analysis in spectra of few well-studied stars including Sun provides C and, in particular, N abundances consistent with those derived from the atomic lines. The proposed approach give a strong support for using a combination of C_2 and CN molecular lines for accurate nitrogen abundance determination keeping in mind difficulties in the analysis of the N I atomic lines which are weak and heavily blended in the observed spectra of the solar-like stars.

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NO biosignature: transmission and emission spectroscopy for its potential detection with WSO-UV observatory

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Searching for potentially habitable exoplanets is a complex multi-parameter problem. The following necessary (but not sufficient) habitability conditions are commonly considered: exoplanet should be terrestrial type planet (exo-Earth, super-Earth, sub-Neptune), the existence of liquid water is possible on its surface, there is no strong greenhouse effect in its atmosphere [1]. Meanwhile, one of the considerable habitability factors is the presence of N_2-O_2 dominant atmosphere on an exoplanet. This factor may point out already existing geological and biological processes on it [2,3]. Among the indicators of such an atmosphere, the spectral features of which can potentially be detected using ground-based and space telescopes, one can single out molecules of NO, N_2O, NO_2, N_2-O_2 dimers [2].

Planned for the launch WSO-UV space observatory [4, 5] can play a significant role in searching for potential biomarkers on terrestrial type exoplanets. We investigate the nitric oxide molecule and determine the possibility of its detection in the atmospheres of exoplanets using the spectrographs of this observatory [6]. It is known from satellite observations of the Earth's atmosphere [7] that the strongest spectral features of NO in the near ultraviolet range are γ bands ($A^2\Sigma^+$ - $X^2\Pi$ electron transition, 203–248 nm).

In this work calculations of light transmission and fluorescence in the strongest vibrational γ-bands for the atmospheres of typical exo-Earths, super-Earths and sub-Neptunes are made. Each vibrational band consists of 12 separate branches × 80 rotational lines [8]. In addition, the ground $X^2\Pi$ state consists of two sub-states: $X^2\Pi_{1/2}$ and $X^2\Pi_{3/2}$ (due to the presence of spin-orbit interaction), each of which is split into two (Λ-doublet). Also, in calculations the absorption of light in the atmosphere by O_2, O_3, NO_2, N_2O, SO_2 molecules in the considered spectral range, Rayleigh scattering for N_2, O_2, CO_2, Ar, and resonant self-absorption in individual NO γ-bands are taken into account.

Based on the results of the work, it was shown that the detection of NO transmission and emission signals in the γ-bands in the atmospheres of nearby (< 5 pc) terrestrial exoplanets is possible using the LSS spectrograph ($R = 1000$) of the WSO-UV observatory - within a reasonable observational time (< 120 observational hours, signal to noise ratio is equal to 3). At the same time, the imposed restrictions and possible ways to solve them for detecting this signal on more distant exoplanets are presented.

This work was supported by the Russian Science Foundation (project No. 22-12-00364).

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L8

An affect of H_2O-CO_2 collisional broadening parameterization at 6 μm fundamental H_2O band on retrieval of column water vapor abundance in Martian atmosphere from ACS TIRVIM nadir measurements onboard ExoMars TGO

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The Thermal InfraRed channel (TIRVIM) [1] is a double-pendulum Fourier-transform spectrometer and one of the three instruments of the Atmospheric Chemistry Suite (ACS) designed by Space Research Institute (IKI) in Moscow [2] onboard the joint ESA-Roscosmos mission ExoMars Trace Gas Orbiter (TGO) [3]. ACS TIRVIM is designed to monitor the Martian atmosphere in the 1.7–16 μm spectral range in nadir and solar occultation modes of observation at a great variety of local times, covering almost a complete Martian Year (MY) during its operation. Besides the main scientific goal of TIRVIM in nadir mode (5–16 μm range) – monitoring of thermal structure of the atmosphere up to 60 km of altitude, surface temperature and column dust and water ice clouds content – the instrument is also capable of observing fundamental H_2O band at 6 μm which provides information about water vapor abundance in the Martian atmosphere.

The significant problem of nadir water vapor retrieval is correct approximation of H_2O spectroscopic parameters in CO_2-rich atmospheres since there are not enough measurements for H_2O broadened by CO_2 in this spectral region (1300–1800 cm^{-1}). The most of approaches use simple scaling of H_2O air broadening HWHM from HITRAN database [4]: by 1.3 factor in 2.3 μm H_2O band in the Venus atmosphere [5], by 1.5 factor in rotation bands in the range 28–42 μm [6]; and there are also attempts to measure and simulate H_2O-CO_2 collisional broadening in the considered 5–8 μm spectral range [7,8].

We present an analysis of how different parameterization of H_2O-CO_2 collisional broadening affects the retrieved column water vapor abundance from TIRVIM nadir observations in the 1300–1800 cm^{-1} spectral range. Since the effect is significant and retrieved column vapor content vary by 25% in some cases, it is important to know exact line parameters for H_2O broadened by CO_2 in order to reduce inaccuracy and get correct atmospheric water vapor abundance on Mars.

This work is supported by the Ministry of Science and Higher Education of the Russian Federation.

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Oral Session M
Thursday, July 6, 15^{15} – 17^{15}
Chair: Semen N. Mikhailenko

M1 (Invited Speaker)

Spectroscopy in collisions in molecular plasma

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Recent progress in theoretical methods for spectroscopy of molecular ions will be reviewed. Spectroscopy of molecular ions and corresponding experimental and theoretical techniques are important for understanding and modeling many different types of molecular plasma environments with a wide interval of temperatures 10-105 K: planetary atmospheres, interstellar medium, technological plasma, strong laser radiation interacting with air constituents, etc. The focus will be on processes taking place in collisions or half-collisions: spectroscopy in molecular photoionization and photodetachment, spectroscopy in electron-molecule collisions, such as rovibronic excitation and dissociative recombination.

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M2

Millimeter-wave coaxial spectrometer for study of weakly bound molecular complexes

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A design is presented for a millimeter-wave direct absorption spectrometer with molecular jet for studies of the rotational spectra of weakly bound molecular complexes. The molecular jet is injected coaxially with the millimeter-wave radiation, which makes two passes of the vacuum chamber (and thus the molecular jet). This is accomplished by passing the radiation through a wire grid polarizer and reflecting it back across the chamber using a rooftop mirror. The pulsed valve (General Valve Series 9, 1.0-mm orifice) is mounted in the centre of the rooftop reflector. Feedhorns and Te1flon lenses are used to focus the radiation on to the rooftop reflector and the detector. The cell is evacuated by a 5-axis magnetically levitated turbopump with drag stage for a pump speed of up to 3000 l/s (Pfeiffer Vacuum ATH 3204 M) and a multi-stage Roots pump (Pfeiffer Vacuum ACP 40) with a pumping speed of 37 m3/h. The spectrometer operates in the frequency range of 50-170 GHz, but could be used at lower and higher frequencies. The instrument utilizes microwave frequency synthesizer (Rohde&Schwarz SMF100A) with active frequency multipliers (Radiometer Physics AFM). The detectors for the spectrometer are Schottky diode detectors (Virginia Diodes). Phase-sensitive detection is achieved by FM modulation of the frequency synthesizer and use of a lock-in amplifier at twice the modulation rate. The output of the lock-in is processed by a boxcar integrator. The spectrometer is operated under computer control through a Ethernet/LAN interface which allows communication between a PC, the signal generator and the receiver. The instrumental resolution of spectrometer is 30–50 kHz and the uncertainty in the frequency measurements is estimated to be 3–5 kHz. The recorded spectra will be presented and a potential of newly build spectrometer will be discussed.

M3

Lidar-based infrared remote gas sensor for measuring the atmospheric air methane concentration

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An important indicator of the greenhouse effect, chemical reactions involving organic compounds and a widely used energy carrier is methane. The modern development of unmanned aerial vehicles (UAV) provides a good opportunity to find and observe leaks of natural gas or landfill gas, control emissions of methane from swamps and permafrost. Thus, this component of the atmospheric air was selected as the target gas for testing the presented lidar, suitable for installation on UAV. The possibility of installation on UAVs is an important economic factor for the potential use of the device.

Since the standard speed of the UAV is 50-70 km/h, and the spatial resolution of sensing should be at least 1 m, a technique should allow processing the received signal with a frequency of 10-100 kHz and its sensitivity should provide the registration of an excess of the natural background of methane by a few tens %. Wavelength-modulation laser absorption spectroscopy combined with quadrature detection of radiation scattered from the surface meets these requirements [1].

The amplitude ratio of 2f-signal and 1f-signal characterizes the absorption of the measured gas and allows calculating of this gas concentration. In remote measurements of laser radiation scattered from the surface, the total intensity of the detected radiation can vary by an order of magnitude, therefore, normalization of the 2f-signal to the 1f-signal is necessary. For the correct operation of this technique the laser radiation frequency should be stabilized at the centre of the absorbing line with $\sim 10^{-3}$ cm^{-1} accuracy. Such high stability is achievable using the 3f-signal [2].

Field device specifications	
Dimensions	275x175x85 mm^3
Weight	3,5 kg
Power consumption	20-35 W from batteries or on-board source

The method was tested in laboratory conditions; a laboratory prototype of the device was created for this reason [2]. The next stage of work was the creation of a field device that meets the requirements for installation on UAVs with a payload mass of 3-4 kg [3].

Fig.1. The first package of the field instrument unit onboard UAV.

An instrument for remote sensing of methane concentration and the first field results obtained during 2022-2023 are presented.

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M4

Coherent quasi-pulse THz molecular crystal source

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In recent years, narrowband terahertz (THz) sources have been indispensable in various fields of photonics, one of the main ones being: creating compact and convenient table-top free-electron lasers; THz resonant nonlinear spectroscopy and the construction of THz LIDARs suitable for monitoring small gaseous components of the atmosphere at kilometer tracks in real time for the purpose of environmental control. One of the ways to generate THz radiation is a nonlinear source usage. Certain molecular crystals have resonant phonon modes falling in the low-THz frequency range. Despite the widespread point of view that low-energy phonons negatively affect the generation of THz radiation, at the same time, in a nonlinear medium with high-Q lattice vibrations at THz frequencies, one can expect both the presence of noncritical phase matching and an increase in nonlinearity in the resonance frequency region [1].

Molecular-crystalline guanylurea hydrogen phosphite $(NH_2)_2CNHCO(NH_2)H_2PO_3$ (GUHP) exhibits high-Q vibrational resonances at THz frequencies [2-4]. We report on the excitation the molecular phonon subsystem and a temperature and axis orientation dependent multicycle quasi-pulse THz generation with a strongly phonon-coupled emission pattern in GUHP crystal. A THz generation model based on the resonant both Raman and IR vibrational response of a high-Q molecular-crystalline medium is constructed, where Stimulated THz emission in a molecular crystal can be polarization selectively generated, on the one hand, by simultaneous excitation of nonlinear processes of the second and third order, and, on the other hand, by ballistic excitation of a free damped dipole oscillator.

We have also investigated the possibility of quasi-pulse THz generation in molecular crystals of phthalic acid: potassium, rubidium, cesium, ammonium and sodium acid phthalate; ortho-sulfobenzoic acid crystal and sucrose single crystal.

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[*] A. Sinko is an applicant for the best young scientist talk award (oral).

M5

Resonant x-ray scattering: a short review

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Scattering of photons, electrons, and neutrons is utilized in many experimental probes for investigation of the structure of matter and of dynamical processes. We focus here on two spectroscopic techniques, initially enabled by the appearance of x-ray synchrotron radiation light sources. Elemental selectivity of X-ray spectroscopy, greatly simplifying the spectrum (compared to optical and ultraviolet spectroscopy), gives detailed information about the local electronic structure in complex systems since, conceptually, an atom projected contribution to the electronic states can be determined. This makes resonant inelastic x-ray scattering (RIXS), that we present, unique tool in studies of local structure of disordered system like molecules and liquids [1-6].

In our talk, the most important achievements in investigations of coupled electron-nuclear dynamics in free molecules and structural aspects in studies of molecules and liquids are outlined. A special attention will be paid to such a feature of RIXS as unique opportunity to study matter not only in static but also in dynamics using technique of variable scattering duration [1]. The concept of the scattering time varied by the detuning from X-ray absorption resonance allows us to study the electronic-vibrational dynamics and ultrafast dissociation in real time with a femtosecond time resolution [1,2] without using pump-probe methods with short (femtosecond) x-ray pulses. There is yet another powerful method for studying ultrafast dynamics, namely, core-hole clock technique [4,7]. This method is used to study the charge-transfer dynamics at interfaces and surfaces with the lifetime of the core hole as an internal reference clock to follow the charge-transfer process. One of the main numerical methods used in our simulations of RIXS and RAS spectra and dynamics is the time-dependent wave packet technique. The advantages of this method relative to the time-independent approach are most pronounced in the case of dissociative states. The developed theory with the corresponding software allowed us to investigate intra- and intermolecular interactions faraway from equilibrium and to extract from the experimental RIXS data potential energy surfaces [1]. Recently we achieved an experimental realization of the Einstein-Bohr recoiling double-slit gedanken experiment by using RAS from molecular oxygen in an electron-ion coincidence arrangement [1]. Our results are fully compatible with quantum mechanical complementarity. Not so long ago resonant X-ray spectroscopy started to be used for the solution of such a fundamental problem as structure of liquids. Unlike the gaseous and crystalline media, a liquid is more difficult object of study due to its inherent disorder and the fluctuations of the local structure. Therefore, the use of complementary physical methods (to conventional small-angle X-ray and neutron scattering) is necessary to obtain a consistent picture of liquids. Recently we successfully applied the X-ray absorption and RIXS to get insight in the local structure of such important liquids as water, methanol and acetic acid [1]. Coherence of RIXS process and related momentum conservation law [1] allowed to extract from the experimental data the band structure, the dispersion laws of phonons and magnetic excitations as well as parameters of electron-phonon interaction of solids. Due to increase of resolving power of RIXS we evidence significant progress in RIXS studies of magnetic properties and collective excitations in high-temperature superconductors [1,3,6].

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Poster Session N
Thursday, July 6, 17^{30} – 19^{00}

N1

Analysis of $N^{18}O$ isotopologue in the 5200–5500 cm^{-1} infrared spectral region

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Continuing the investigation of various nitric oxide isotopic species [1, 2], high resolution infrared spectrum of $N^{18}O$ was analyzed in the 5200-5500 cm^{-1} region. On a Bruker IFS-125M Fourier spectrometer with a spectral resolution of 0.0056 cm^{-1} the vibrational band 3-0 was recorded to the first time.

As a result of the analysis, 99 Λ-doublets of vibration-rotational lines were found in the 3-0 band of the main transitions between the electronic states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. For 58 of them, it was possible to obtain the positions and relative intensities of each component of the doublet. The whole set of 157 registered transitions frequencies, weighted in accordance with the experimental uncertainties, were processed by the program code using the non-linear least squares method. This processing made it possible to determine spectroscopic constants for the state v=3 vibrational state of the $N^{18}O$ isotopologue. The Λ-doubling constants for this state are determined for the first time. The obtained results are compared with the well-known database of spectroscopic information HITRAN2020.

The research was supported by the Russian Science Foundation (contract No. 23-23-00184).

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N2

LED-based Fourier spectroscopy of $^{14}N^{14}N^{16}O$ in the 9800–12000 cm^{-1} region

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Five bands of $^{14}N^{14}N^{16}O$ nitrous oxide isotopologue ($2\nu_1+2\nu_2+3\nu_3$; $3\nu_1+3\nu_3$; $\nu_1+4\nu_3$; $\nu_1+5\nu_3$) were studied in the 9800-12000 cm^{-1} region using a Bruker IFS-125M Fourier spectrometer with a spectral resolution of 0.05 cm^{-1} and a 2400 cm path length in a multipath cell. Gas pressure was 95 mbar. LED EDEN-1L53-R served as a source of radiation, has provided a high signal-to-noise ratio and made it possible to record weak lines with an intensity of the order of $1\cdot10^{-26}$ cm/molecule. The measurement technique that uses LEDs is described in detail in paper [1]. Each spectrum was obtained by averaging over 24840 scans.

The line parameters (line centers, intensities and halfwidths) were determined using the Wxspe software package, which allows an automatic search and processing of peaks using methods of pattern recognition theory [2]. The contour parameters were adjusted by the least squares method using Voigt profile. The parameters of upper vibration states were obtained for the studied absorption bands.

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N3

Analysis of water vapor absorption lines in the modern spectroscopic databases in the 16700–17000 cm^{-1} region

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The H_2O absorption lines parameters in modern spectroscopic databases were validated on basis of measured spectra in the visible region of 16700-17000 cm^{-1}. The H_2O transmission spectra were simulated with the HITRAN2016, HITRAN2020 [1], GEISA2020 [2] databases and W2020 H_2O linelist [3]. A comparison of the simulated spectra with the laboratory spectra of pure water vapor and H_2O-N_2 mixture, recorded using a Fourier spectrometer with light-emitting diodes of high luminance [4], is made. The parameters of 65 H_2O absorption lines from the HITRAN2020 database were corrected on the basis of the measurements. The positions of 32 lines, intensities of 51 lines and self-broadening coefficients of 10 lines were improved. The ratio of the HITRAN2020 broadening coefficients to the experimental values is close to 1, whereas the air pressure-induced line shift coefficients in the spectroscopic databases are, on average, two times higher than the experimental values, and therefore, our previously obtained experimental values of N_2 pressure-induced line shift coefficients [4] were used to simulate the transmission spectra of H_2O-N_2 mixture.

It was shown that the spectra, calculated with new corrected data, agree better with the measured spectra and give minimal residual in the 16700-17000 cm^{-1} region.

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N4

Collisional transformation of the complex vibrational susceptibility of a linear molecule: the ν_3 band of CO_2 as a guiding example

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We report results of a joint analysis of pressure effects on both parts of the complex vibrational susceptibility of an ensemble of linear vibrating rotators. While the imaginary part of susceptibility which determines the absorption band shape was numerously studied for different systems, the transformation of the real part remains - to the best of our knowledge - unexplored. Its comprehension, especially for frequencies close to anomalous dispersion, might be useful to control phase-matching conditions when coherent optical responses are generated.

The concept of the infinite-order relaxation matrix Γ, which couples different rotational transitions (lines) forming a vibrational band, allows us to simultaneously calculate both terms of susceptibility by applying a certain model of Γ. The results are reported for compressed CO_2, for which the quantum strong-collision model (SCM) [1, 2] was successively tested both for IR absorption and Raman spectra [3] as well as for the time-domain responses [4]. Moreover, the use of SCM leads to compact susceptibility expressions [1] that do not require matrix inversion.

At low pressures, the SCM exactly reproduces the resolved line structure of a vibration-rotation absorption band which, as pressure is raised, transforms into a smoothed Bjerrum doublet and then coalesces into a quasi-lorentzian line exhibiting the pressure narrowing effect.

The transformations of the real susceptibility are following. Initially, it consists of resolved dispersion terms, but, as the line structure is smoothed by pressure, an unexpected triplet is formed with a hump near the band origin at ν_0. This feature survives till the doublet absorption band structure remains resolved. As the gas density is further increased, the line mixing manifests itself in the appearance of a single dispersion curve centred at ν_0. The line mixing reduces both the absorption band width and the spectral interval occupied by anomalous dispersion. However, the far periphery of normal dispersion remains unaffected and continues to scale as $|\nu - \nu_0|^{-1}$.

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N5

Broadening and shifting coefficients of rovibrational lines in the first overtone of HF perturbed by He

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The parameters of rovibrational lines perturbed by He appeared in spectroscopic database HITRAN2016 [1], however there are still some lacks, especially in the experimental data [2, 3]. Here we present the experimental values of broadening and shifting coefficients for the lines in the first overtone of HF perturbed by He. Additionally, the analogous parameters were measured in the fundamental band.

The spectra were recorded at the room temperature with a Bruker IFS-125 HR spectrometer with a resolution of 0.005 cm^{-1}. A small amount of HF was admitted into a stainless cell with sapphire windows and successively diluted with He. The total pressure of the mixture was in the range of 1–11 atm. Each line in the overtone and fundamental bands of HF was fitted with a Voigt profile. The Doppler widths were fixed according to known relations. The broadening and shifting coefficients were obtained from linear dependences of Lorentzian widths and line centers, respectively, on the total pressure. Using different initial pressure of HF (0.7 – $\sim 1\cdot 10^{-4}$ atm) allowed us to evaluate line parameters in the large interval of rotational numbers $J = 0\ldots10$ in the overtone band and $J = 0\ldots11$ in the fundamental band. Most of the values, especially for the overtone transition, are novel.

The obtained data were compared with existing literature data of HF-He system as well as with HCl-He, HBr-He, and HI-He systems [4, 5].

The studies were carried out using the equipment of the resource center “Geomodel” of the Science Park of the Saint Petersburg State University.

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N6

Line profiles of sodium pressure broadened by helium atoms

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Resonance lines of alkali metal atoms are a well-known feature of the spectra of brown dwarfs and exoplanets [1, 2]. These lines are broadened by collisions with neutral atoms of helium and hydrogen, making them an important tool for determining the temperatures, densities, and albedos of these celestial objects. Theoretical calculations of these line profiles are crucial for developing accurate measurement methods [3, 4].

In the present work sodium resonance lines pressure broadened by helium atoms are calculated in the quasistatic approximation. The model Hamiltonian for the Rydberg electron in the NaHe molecule is constructed according to the method of Bottcher and Dalgarno [5].

The model Hamiltonian was constructed as a combination of the electron kinetic energy, interaction between sodium ion and helium, interaction between Rydberg electron and helium, interaction between sodium ion and Rydberg electron, and 3-particle interactions between the Rydberg electron, Na+ and He. The potentials above are described in details in [6].

The Schrodinger equation with this Hamiltonian was numerically solved with the use of the finite element method. The line profile of the transition 3s → 3p (T = 403K) was calculated and compared with the experimental data [8].

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N7

Modification of vibrational parameters of a linear symmetric triatomic molecule by a laser field

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In recent years, the motion of nuclei in polyatomic molecules under the action of high-intensity laser fields has been actively studied. In particular, experiments [1–4] are devoted to studying the rearrangement of nuclei and Coulomb explosion in the processes of dissociative ionization of triatomic molecules CO_2, OCS, H_2O, and D_2O. The modification of vibrational parameters (frequency and bond length) of diatomics by a linearly polarized monochromatic was first studied theoretically by Zon in [5] and generalized to the nonlinear symmetric *ABA* triatomics (H_2O and SO_2) in [6].

Here, we extend our theory to the linear $D_{\infty h}$ symmetric triatomics, particularly, $^{12}C^{16}O_2$ and $^{12}C^{32}S_2$. Such molecules have two non-degenerate longitudinal vibrational Σ_g, Σ_u modes and single doubly degenerate transverse P_u mode.

We used the normal-modes formalism and the laser-dressing concept. Namely, the laser field influenced on nuclear motion indirectly via polarization of electronic shells. We found that the relative shift of any vibrational parameter in the first order in laser intensity *I* is described by a simple formula depending on the angle between molecular axis *z* and polarization vector **u**. We obtained the parameters of the formula by using derivatives of molecular polarizabilities with respect to normal coordinates. The latter are calculated with NWChem package by CCSD(T) method using Pople's valence-split 6-311++G(3df,3pd) basis set. We found that frequently used Dunning's correlation-consistent basis sets turned out to be invalid for deformed molecules with multiple bonds.

As a result, the laser field removes double degeneracy of P_u mode if $\mathbf{u} \nparallel Oz$. The $P_{u\parallel}$ mode corresponds to bending vibrations in the (z, $\mathbf{u}$) plane, the $P_{u\perp}$ one in the perpendicular direction. The difference between $P_{u\parallel}$ and $P_{u\perp}$ reaches maximum if $\mathbf{u} \perp Oz$. For the frequency shifts, $\Delta P_{u\parallel}/\Delta\ P_{u\perp} \approx 2$. However, within $\sim I$ corrections, the linear shape of the molecule will be preserved. Thus, the laser field reduces $D_{\infty h}$ symmetry of a triatomic molecule to D_{2h}. This is the key difference between linear triatomics and non-linear ones [6]. Additionally, in the case of longitudinal orientation of the molecule with respect to **u** vector, the laser field increases the *A*–*B* bond length by 0.43%, for $^{12}C^{16}O_2$, and by 1.3%, for $^{12}C^{32}S_2$.

Obtained results may be used to calculate laser-modified Franck–Condon factors. Those quantities are required in theoretical description of filamentation and various laser-chemistry phenomena.

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N8

H_2O-HF dimer warm rotational spectra: new measurements and re-analysis

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Studies of H_2O-HF [1, 2] are of increased importance as a similar but easier to study system, which will teach us how to deal with the more important and more complicated water dimer. The advantage of H_2O-HF over water dimer [3] is that the high resolution spectrum in the equilibrium gas phase at relatively high temperatures could be observed and accurately measured. The advantage of the millimeter and submillimeter-wave region is that the pure rotational spectra of the dimer in the ground state and in multiple thermally populated vibrational states could be observed. The experimental values of the dimer rotational constants retrieved from these spectra can be compared with corresponding values calculated *ab initio* for all vibrational states, which provide the important characterisation of accuracy of the modelling of both H_2O-HF and H_2O-H_2O spectra.

In this presentation we report our first steps of the resumed investigation of the rotational spectrum of the H_2O-HF dimer in the millimeter and submullimeter-wave region, which has been paused for more than 30 years [4] because of the lack of sufficiently accurate instruments for the spectrum modelling on the *ab initio* basis.

In course of this work positions of more than 100 lines of the dimer spectrum in the 158-345 GHz range were refined (uncertainty is reduced by about order of magnitude) and several lines were newly measured at warm equilibrium gas phase using two spectrometers with complementary abilities, namely, video spectrometer and spectrometer with radio-acoustic detection of absorption. Obtained data are refitted together with all other information on the spectrum available from previous works. Effective Hamiltonian constant values characterising the dimer intermolecular dynamics are refined. Further steps of the detailed study of the dimer are discussed.

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N9

Measurement and calculation of the CO 6th overtone line intensities

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Intensities of 14 ro-vibrational lines in the sixth overtone (7–0) band of carbon monoxide ($^{12}C^{16}O$) are measured in the visible range between 14300 and 14500 cm^{-1} using a frequency-stabilized cavity ring-down spectrometer [1]. This is the first observation of such a high and weak vibrational overtone spectrum of CO molecule. A theoretical model for intensity calculations is constructed and tested based on the use of a high accuracy *ab initio* dipole moment curve and a semi-empirical potential energy curve [2].

Studies of high overtone transitions provide a challenge to both experiment and theory as the lines are very weak: integrated intensity at 296 K is below 2×10^{-29} cm/molecule. An agreement between theory and experiment within the experimental uncertainty of a few percent is obtained. This success became possible only after issues with stability of the Davidson correction to the MRCI (multi-reference configuration interaction) calculations were solved.

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N10

The high sensitivity absorption spectroscopy of acetylene near 765 nm

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Using the Cavity Ring-Down Spectrometer (CRDS) of V.E. Zuev Institute of Atmospheric Optics SB RAS the acetylene spectra were recorded in the 12933 - 13297 cm^{-1} region with the sensitivity of 2×10^{-11} cm^{-1} at room temperature and at four pressures of 2, 5, 9 and 15 Torr. Sixteen bands of $^{12}C_2H_2$ and one band of $^{12}C^{13}CH_2$ were assigned in these spectra. Five bands were observed for the first time. The band and line assignments were performed using the results of the line positions and relative line intensities predictions with the global effective Hamiltonian and effective dipole moment operators of Refs. [1,2]. It was suggested the alternative assignments of the five observed bands compared to those of Ref. [3]. The line positions and intensities were recovered from the recorded spectra. The line intensities in this region are reported for the first time. The line positions were modeled using the traditional power series expression in terms of the angular momentum quantum number for an isolated band. The line intensities were modeled using the vibrational transition dipole moment squared and the Herman-Wallis parameters.

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N11

High sensitivity absorption spectroscopy of hydrogen chloride near 770 nm

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Using the Cavity Ring-Down Spectrometer (CRDS) of V.E. Zuev Institute of Atmospheric Optics SB RAS the hydrogen chloride spectra were recorded in the 12943- 13295 cm^{-1} region with sensitivity of 4×10^{-11} cm^{-1}. The lines P(4) – P(12) of the 5-0 band of two $H^{35}Cl$ and $H^{37}Cl$ isotopologues were assigned in these spectra. The positions, intensities, self-broadening and self-pressure-induced shift coefficients of these lines were measured. The measured line positions are in a good agreement with those presented in the HITRAN2020 database. The measured line intensities are 1.3 times greater than those from the HITRAN2020 database. The measured self-broadening coefficients are in a good agreement with the HITRAN2020 values for the small angular momentum quantum numbers and slightly exceed the HITRAN2020 values for the large angular momentum quantum numbers.

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N12

N_2-, O_2-, air-broadening coefficients and their temperature dependence of CH_3I rovibrational lines for the ν_6 band

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The modern radiative-transfer models require precise knowledge of spectroscopic parameters (line positions, intensities, broadening and shifting coefficients and their temperature dependencies) even for minor compounds of the terrestrial atmosphere, including methyl iodide with the background concentration from 0.2 to 2 ppt [1]. This gas is found to be one of the halocarbons that participate in marine clouds formation [2], thus influencing the terrestrial radiation budget. Besides being the most abundant iodine-containing atmospheric compound [1], CH_3I has the lifetime long enough to transport iodine into the upper troposphere [3], where it is photolyzed, giving reactive iodine [4] and partly reacts with O_3 causing the destruction of the ozone layer [4] .

CH_3I-nitrogen and CH_3I-oxygen line-broadening coefficients at 296 K are calculated for the ^RR, ^PR, ^RP, ^PP, ^RQ and ^PQ sub-branches of the ν_6 band in a wide range of rotational quantum numbers ($0 \le J \le 70$, $K \le 20$) by a semi-classical [5] and a semi-empirical [6] methods. The computed values compare very favourably with the available experimental data and therefore can be safely employed as estimates of broadening coefficients missing in databases for high J and K. The theoretical room-temperature data for CH_3I-N_2 and CH_3I-O_2 are further combined to obtain the air-broadening values required for atmospheric applications. The calculated results demonstrate an excellent consistency with both existing sets of CH_3I-air measurements.

Temperature-dependence exponents of the traditional power law relating line-broadening coefficients at experimental and reference temperatures are deduced for CH_3I-N_2, CH_3I-O_2 , CH_3I-air lines in the ν_6 band from theoretical estimates in the temperature interval 200–400 K recommended for HITRAN. Perfectly linear fits in log-log coordinates indicate that this simple law is sufficient and more advanced models such as the double-power law are not applicable. Calculations are performed by a semi-empirical method employing room-temperature-adjusted model parameters which remain valid for other temperatures. In the absence of measurements at not-room temperatures, these data can be extremely useful for atmospheric applications involving methyl iodide, in particular for the terrestrial atmosphere.

As the vibrational dependence of CH_3I lime broadening coefficients is shown for both perturbing molecules to be small the CH_3I-air line-broadening coefficients and their temperature exponents calculated for the ν_6 fundamental can be used for other perpendicular and parallel bands.

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N13

A model of fluorescence quenching induced by hydrogen-bonding in mixtures of protic and aprotic solvents

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Fluorescent properties of symmetric electron-donor-acceptor dyads are currently in focus of extensive experimental and theoretical research, since kinetics and quantum yield of their fluorescence are highly sensitive to interactions with the environment [1, 2]. Of particular interest is the role of hydrogen-bonding interactions between the fluorophore and solvent in liquids. Hydrogen bonds are known to be able to break the excited-state symmetry, leading to intramolecular charge transfer between two branches of the dyad and causing subsequent fast nonradiative deactivation [3–5] of the fluorophore. Recent experimental studies on a centrosymmetric dyad, an acridine-dione derivative AD, revealed unexpected behavior of its time-dependent fluorescence profiles in protic and aprotic solvents. The observed fluorescence of AD did not exhibit any spectroscopic evidence of quenching in aprotic solvents (even highly polar), but manifested strong quenching in alcohols [6]. In binary mixtures of protic (MeOH) and aprotic (DMF) solvents, on the other hand, the quenching was detected only at fairly high concentrations of methanol, [MeOH] > 9 mol/L. These results are unusual for this type of the reaction and require detailed analysis and explanation.

In this report, we consider a new mechanism of nonradiative deactivation in symmetric electron-donor-acceptor dyads in mixtures of protic and aprotic solvents. The mechanism is consistent with the general HBIND scheme [4], but also takes into account important peculiarities of H-bond clustering in methanol and N,N-dimethylformamide. We develop a model of the AD fluorescence quenching considering formation of weakly and strongly bound complexes of AD with MeOH clusters in solution. The key components of the model are the H-bond cooperativity effect in methanol clusters and the statistics of MeOH clustering in mixtures with DMF. The proposed model is shown to give both qualitative and quantitative description of available experimental data, particularly, the observed dependence of the AD fluorescence yield on the concentration of methanol in the mixture. Non-exponential time-dependent profiles of AD fluorescence intensity at different [MeOH] are also well reproduced with this model.

In this report, new possibilities for experimental studies of H-bond structures in liquids are discussed in context of the proposed approach. The efficiency of nonradiative deactivation in symmetric dyads is sensitive to the strength of H-bonding interactions between the dyad and solvent clusters, so that the fluorescence yield is expected to depend on the average length of H-bond cluster in solution. This opens up a possibility for spectroscopic studies of H-bond clustering both in neat alcohols and in their mixtures with other solvents.

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N14

On the uncertainty of the calculated intensities of water vapor lines in the subTHz frequency range

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The uncertainty of the continuum is one of the main factors limiting the accuracy of reconstructing atmospheric parameters from remote sensing data both in the microwave [1] and in the near infrared ranges [2]. For lack of information for physically based continuum modelling (see, e.g., [3] and references there) the continuum is still determined empirically as the difference between the observed absorption and the calculated spectrum of H_2O monomer and, therefore, the uncertainty of the continuum is determined by the uncertainty of the H_2O monomer spectrum calculation. Our estimates [4] show that the uncertainty of the magnitude of the continuum component associated with the interaction of water molecules with dry air molecules (foreign continuum) in the region of the H_2O rotational band reaches 100% if the code of possible errors of the line parameters indicated in HITRAN [5] is taken as the basis for calculations.

In this work we analyse intensities of the pure rotational spectral lines of the main isotopologue of a water molecule in the frequency range from 0 to 1.75 THz, which are potentially significant for modelling the continuum in the subTHz range. All lines stronger than 10^{-28} cm/molec are considered. We compare linelists available from the most known open sources such as HITRAN, GEISA, ExoMol, and JPL catalogue. The calculations on the basis of extensive experimental measurements in the far and middle infrared ranges using the method of effective Hamiltonians, the variational method, and scarce experimental data in the range under consideration are taken into account. We demonstrate that for lines in the ground vibrational state with the intensity of more than 10^{-27} cm/molec, the intensity uncertainty is less than 2%, and reaches 5–10% for weaker lines. For strong (more than 10^{-26} cm/molec) lines in the ν_2 state, the uncertainty ranges from 2 to 5% and increases to 5–10% for weak lines. For all lines in vibrational states $2\nu_2$, ν_1 and ν_3, the uncertainty is no more than 5-10%. The presented data show that most of the considered lines can be assigned a higher (by 1-2 steps according to the HITRAN classification) intensity accuracy category.

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N15

Ab initio quantum defect theory revisited Rydberg’s states of H_2

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The Quantum Defect Theory (QDT) implementation for *ab initio* quantum-chemical modeling of highly excited electronic states of atoms and molecules has a long and successful history. The hydrogen dimer (H_2) is the first case when the QDT machinery could manage to describe the energy and radiation properties of Rydberg’s diatomic states at the almost spectroscopic level of accuracy.

The development of computational capabilities of using the arithmetic of quadruple and even higher accuracy has provided the recent advent of more precise potential energy curves (PECs) for the ground and all excited electronic states of the H_2 molecule converging up to fourth dissociation limit [1,2]. In a combination with a highly accurate PEC available for the ground state of molecular cation H_2^+ [3] it became possible to evaluate, due to the famous Milliken’s equation, the molecular quantum defect functions and their first derivatives with respect to internuclear distances R under the extremely high accuracy and over a very wide range of R. This opens a new opportunities for the detailed description of energetic, radiative and electric properties of highly excited electronic states of H_2 istotopomers in the framework of the multi-channel QDT.

In this work the single-channel quantum defect functions $\mu_{l\Lambda}(R)$, together with $d\mu_{l\Lambda}/dR$, were systematically extracted from *ab initio* Born-Oppenheimer PECs and their first derivatives with respect to R available for the Rydberg’s states of the H_2 molecule [1,2]. A comparative analysis of the asymptotic behavior of the $\mu_{l\Lambda}(R)$ functions in the unified He I atom limit and on the dissociation $1s$+nl threshold has discovered at small R-values the drop-down points corresponding to the states with large angular moment of Rydberg’s electron l and localized for each state the internuclear distance where configuration interaction and l-mixing effect are both taking place. The adiabatic correction function [4] and non-adiabatic energy shifts were calculated for the particular states under the single-channel QDT approximation and compared with the literature data as well.

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N16

Current status of the S&MPO information system

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S&MPO (Spectroscopy and Molecular Properties of Ozone) is an Internet accessible information system [1]. The system provides access to spectroscopic information of the ozone molecule. Significant updates of the lists of the spectral line parameters [2-5] have been made in recent years. In 2015-2019, the program code of the system was rewritten using the tools and web technologies relevant at that time. Since then new functionalities have been added particularly for graphical comparisons between calculated and experimental spectra. A major update is progress for the line positions and energy values of $^{16}O_3$. The line lists for $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$ isotopologues are also improved for in the MW, terahertz and far-infrared range using recent experimental measurements [6,7].

The report will present the modern capabilities of the system and the current state of the database of spectral line parameters.

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N17

The 000 and 010 states revisited for ^{18}O-substituted isotopic species of ozone

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High resolution infrared spectra ozone, enriched with ^{18}O oxygen, were recorded in the range 50-720 cm^{-1} on the Bruker IFS125HR Fourier transform spectrometer of the AILES Beamline at Synchrotron SOLEIL [1-4]. The experimental setup and the recorded data have been described in [5].

The analyses of these newly measured spectra have permitted to significantly extend the set of previously observed transitions and quantum numbers for six isotopologues $^{16}O^{16}O^{16}O$, $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{16}O$, $^{16}O^{18}O^{18}O$, $^{18}O^{16}O^{18}O$, $^{18}O^{18}O^{18}O$.

As a result of simultaneous treatment of the observed transition frequencies with the available microwave data [6], new parameters of vibrational states (000) and (010) were obtained for these isotopic species of ozone. The complete line lists calculated with the new parameters will be included in the S&MPO database [7].

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N18

The $^{13}CH_4$ absorption spectrum at 298 K: Assignment and modeling of the lower part of the Tetradecad in the 4970–5300 cm^{-1} spectral range

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Here we present the spectral analysis of the lower part of the $^{13}CH_4$ Tetradecad in the 4970-5300 cm^{-1} region. As continuation of our previous work at 80 K [1], we have characterized the same region at room temperature in this work capturing a wider range of J-manifolds. For this, we have analysed spectra of ^{13}C-enriched CH_4 sample recorded at Doppler-limited resolution at 298 K with a high-resolution Fourier-transform spectrometer, covering the entire Tetradecad region in the 4970-6200 cm^{-1}.

Using the effective Hamiltonian and dipole moment parameters for the Tetradecad [2-4] obtained from the analyses of the cold Fourier Transform Spectroscopy (4970-5853 cm^{-1}) and Differential Absorption Spectroscopy (5853-6200 cm^{-1}) spectra, a calculation was performed for 298 K. In 4970-5300 cm^{-1} range a list of 1624 lines was created, out of which 1497 lines assigned belonging to four bands of the Tetradecad were having J_{max} extended up to 16 from 11 in the previous work. The line positions were fitted with a *rms* deviation of 2.1×10^{-3} cm^{-1}. Measured line intensities for 692 transitions were modelled using the effective dipole transition moments approach with a *rms* deviation of about 9%.

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N19

Synthetic $B^2\Sigma^+$-$X^2\Sigma^+$ band spectra of the CN radical: comparison of the equilibrium and multi-temperature models

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Considering high-temperature gas-phase systems: space objects (e.g. stellar atmosphere) and laser-induced plasma it is often necessary to take into account the non-equilibrium conditions by distinguishing vibrational and rotational temperatures in order to describe experimentally observed distribution of intensities. High-precision data on the frequencies of rovibronic transitions for the CN radical, were received in frame of the reduced coupled-channel (RCC) deperturbation analysis [1] of the first three electronic states: $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, as well as the probabilities of the corresponding $B^2\Sigma^+$-$X^2\Sigma^+$, $B^2\Sigma^+$-$A^2\Pi$, $X^2\Sigma^+$-$A^2\Pi$ rovibronic transitions obtained within the same RCC model. It is expected that these data can be used not only in the case of thermal equilibrium, but also in cases where the Boltzmann distribution is not applicable.

For example, the spectra of the $B^2\Sigma^+$-$X^2\Sigma^+$ (violet) system were simulated assuming non-local thermodynamic equilibrium (non-LTE approach). The work demonstrates the implementation of one-temperature (equilibrium) and two-temperature approaches by means of the ExoCross [2] program. It has been found that even a small difference between the vibrational and rotational temperatures can in some particular cases (corresponding to local perturbations) lead to a pronounced redistribution of the relative intensities in the band spectra.

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N20

Convergence of the parameters of the two-temperature model with self-absorption for CN radical spectra fitting on the example of B $^2\Sigma^+$ - X $^2\Sigma^+$ transition

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Cyano radical is an important molecule in astrochemistry due to its presence in interstellar medium, carbon stars and comets. Obviously, CN spectra can be a diagnostic tool for the investigation of the parameters of these objects. This is the reason of the extensive theoretical and experimental studies of CN molecule under terrestrial conditions. Today, a several spectroscopic data are available on CN: molecular constants [1] and Franck-Condon factors [2], experimental-perturbative-variational line list [3], energy list obtained with coupled-channel deperturbation treatment of the X $^2\Sigma^+$~A $^2\Pi$~B $^2\Sigma^+$ complex [4] supported by the corresponding line list [to be published]. However, the precise experimental data used for theoretical calculations are commonly obtained at the low-temperature (~300 K) which can be very far from extraterrestrial conditions. To check the validity of the extrapolation of calculated PECs and transition strengths into the high-J field the high-temperature experimental spectra are needed. The laser-induced plasma is such a source which provides the temperatures from ~1500 to 50000 K and can be used for simulation of the processes in the carbon stars atmospheres, for example.

Since 1991 [5], a number of efforts on modeling of CN spectra retrieved from laser plasma were made. However, the careful assessment of the quality of approximation as well as the convergence of the fitted parameters within the one or two temperature models are still absent to our best knowledge. Moreover, there were no efforts to take into account the self-absorption effect, especially, for the non-LTE case.

We have compared the performance of the different data for the approximation of the set of CN spectra (B $^2\Sigma^+$ - X $^2\Sigma^+$ transition, sequence $\Delta v = 0$, spectral range 378.7-389 nm) obtained from laser-induced plasma of mixture of urotropine and eriochrome black T at the different conditions. The line list [1] from the ExoMol database is not suitable for the accurate fitting of the spectra (discrepancies in the frequencies near the (4,4) and (5,5) band "heads" and in the intensities for the high-J (J>50.5) transitions of the (0,0) band were observed). Comparison between the simulated spectra without self-absorption obtained with LIFBASE [2, 1], Exocross [6, 3] and our [7, 4] programs shows a good agreement between LIFBASE and our simulations, while the Exocross algorithm seems inappropriate for the cases with the high difference between T_{rot} and T_{vib} (~2000 K). With the help of the our up-to date line list with transition probabilities, our algorithm [7] for spectra modeling and stochastic optimization algorithm CRS2-LM [8] we have stated, that the self-absorption effect took place at the early and middle delays after laser pulse, while it was not occurred at the late delays. The most interesting case occurred at the middle delays when the necessity of the two-temperature (T_{rot}, T_{vib}) model supported by self-absorption (1D uniform light source with the length l) was evident. To prove it we have examined the optimizer trajectory in the parameter space and the loss function surface. The square mean relative error of the intensity approximation reached 6 % for the best case. For estimation of the random error of the fitted parameters, the randomization of the experimental data according to normal probability distribution with the experimental SDs of intensities was made. The relative random errors for T_{rot} and T_{vib} were at the level of 2-3 % (2*SDs) proving the appropriateness and convergence of our models.

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N21

O_2 A-band line parameters for application to CO_2-rich planetary atmosphere

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The O_2 absorption spectra induced CO_2 pressure in the 13000–13180 cm^{-1} spectral region were studied. The measurements were performed using the Bruker IFS 125HR FTIR spectrometer at room temperature, at the spectral resolution of 0.01 cm^{-1} and in the wide pressure range of carbon dioxide. The multispectrum fitting procedure has been applied to the measured spectra to recover the spectral line parameters. Two lineshape models were used: traditional Voigt profile and quadratic speed-dependent Voigt ones. We observed deviations from the Voigt profile due to speed-dependent broadening and line mixing effects. The weak line mixing coefficients were determined from fits using the speed-dependent + line mixing models.

The values of the broadening and shift coefficients for O_2–CO_2 in the spectral range 13000–13180 cm^{-1} were obtained for the first time. These data are planned to be used in the calculation of the Martian atmosphere transmission.

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N22

Water vapor absorption line parameters in the IR spectral region

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The content of different gases (H_2O, CO_2, HDO, O_2, CH_4, etc.) in planetary atmospheres is often measured in the IR, where data from HITRAN, GEISA, and other databases [1, 2] are used as a source spectroscopic information. These bases are adapted for research in the Earth's atmosphere. The atmospheres of Mars and Venus mainly consist of CO_2; its content exceeds 95%. Therefore, to model the absorption spectra of these planets' atmospheres the CO_2-pressure broadening and shift coefficients should be known for different gases, including water vapor.

Only few studies of spectral lines for the H_2O–CO_2 system have been published [3–7]. The broadening and shift coefficients were experimentally studied in two spectral regions, 2.7 μm (3060–4370 cm^{-1}) and 6 μm (1350–2300 cm^{-1}), and calculated for a broader range (1300–5000 cm^{-1}) in 2019 in [3]. We analyzed the broadening and shift coefficients of H_2O absorption lines in the 10100–10800 cm^{-1} spectral range in [7]. In this work, we continue the study in the 3760– 4160 and 6760–7430 cm^{-1} regions.

The absorption spectra of the mixtures of water vapor and carbon dioxide at five different partial pressures of both gases have been recorded using the Bruker IFS 125HR FTIR spectrometer at room temperature. The multispectrum fitting procedure has been applied to these spectra to recover the spectral line parameters. To obtain the spectral lines parameters the quadratic speed-dependent Voigt profile was used. The water vapor line broadening and shift coefficients for lines of fife vibrational bands ν_1, ν_3, $\nu_1+\nu_3$, $2\nu_2+\nu_3$, and $2\nu_1$ were obtained. The calculations of Mars atmosphere transmission with new data were made.

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N23

Broadening and shift coefficients of the H_2O absorption lines induced by atmospheric air pressure

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Water vapor is one of the most important constituents in the atmosphere. It has an important impact on the atmospheric radiation due to the strong absorption of the infrared radiation. The accuracy of the H_2O content retrieval directly depends on the accuracy of the line parameters. Many works have shown that the inaccuracies of the water vapor parameters are the major source for systematic errors in the ground based remote sensing [1–3]. All parameters of the absorption lines including the broadening and shift coefficients are important. It is observed that the small changes in the half-width can have large effects on the uncertainty of the retrieved data (see, for example, [4] and references in it).

High-resolution H_2O absorption spectra were recorded with the Bruker IFS 125 FTIR spectrometer [5] covering H_2O transitions from 5090 to 7490 cm^{-1} at a spectral resolution of 0.01 cm^{-1}. The multispectrum fitting procedure has been applied to these spectra to recover the spectral line parameters. The $H_2{}^{16}O$ line broadening and shift coefficients for 439 lines of 7 vibrational bands $2\nu_3$, $\nu_2+\nu_3$, $2\nu_2+\nu_3$, $\nu_1+\nu_3$, $\nu_1+\nu_2$, $\nu_1+2\nu_2$, and $2\nu_1$ were measured. The spectral line parameters were derived from measurements using quadratic speed-dependent Voigt (qSDV) profiles. The uncertainty of the broadening coefficients for the unblended H_2O absorption lines was estimated to be 1–3%.

The calculations of broadening and shift coefficients were performed in a framework of the semi-classical method and by using an empirical function whose parameters were taken from the literature. The uncertainty of calculations was estimated to be 5% for the air broadening half-widths on average. The results from this investigation provide new information for noted 439 lines perturbed by air pressure.

The results obtained were compared with the literature data.

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N24

Look at all those surfaces! The exited states of the Rb trimer

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Molecules in the ultracold regime have continued to attract the attention of scientists as they offer unique insights for instance how quantum states affect chemical reactions. As of now alkali-metal dimers are a well-known candidate for laser cooling and synthesis, with most having been synthesized and cooled. For many of these molecules, the focus has now shifted to atom+dimer collisions and, thus, to trimers.

In this work, the potential energy surfaces (PESs) as well as transition dipole moments (TDMs) of low-lying doublet states of the Rb_3 molecule were obtained for the T-geometry within the framework of *ab initio* calculations performed in the C_{2v} symmetry. The Rb atoms were described using a core polarization potential and effective core potential approach. The molecular orbitals were optimized within a multi-reference self-consistent field calculation, using an active space consisting of 20 orbitals. In the following configuration interaction calculations all sub-valence electrons, save the three valence electrons, were kept on doubly occupied orbitals.

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N25

Theoretical study of the structure and conformational behavior of some cyclopropane derivatives in the ground and excited electronic states

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Structure and conformational dynamics of cyclopropanecarboxaldehyde (CpCHO), cyclopropanecarboxylic acid fluoride (CpCFO), and cyclopropanecarboxylic acid chloride (CpCClO) molecules were investigated in the ground (S_0) and lowest triplet (T_1) and singlet (S_1) electronic states by various *ab initio* quantum chemistry methods (MP2 and CASPT2 in cc-pVTZ basis set).

Calculations of equilibrium geometric parameters indicate that all considered molecules in S_0 state are represented by *cis*- and *trans*-conformers with C_s symmetry. Our calculations of the structure of these molecules in the S_1 and T_1 states predicted the significant conformational changes being in result of electronic excitation: the rotation of cyclopropyl group and the pyramidalization of the carbonyl fragment (CCXO, X=H, F, Cl) that is planar in the S_0 state.

For modeling low-frequency vibrations one-dimensional (1D) and two-dimensional (2D) potential energy surfaces sections of molecules along the coordinates of low-lying vibration modes were constructed. Obtained vibrational energy levels in harmonic, 1D and 2D anharmonic models are compared. In studying the shapes of the potential energy surfaces (PES) of molecules, special attention is paid to the properties of the sections along the non-rigid vibrational coordinate corresponding to internal rotation. The constructed sections were used for solving a series of anharmonic quantum-mechanical vibrational problems. Analysis of the shape of the PES sections in the ground electronic state shows that the internal rotation is well separated from other molecular vibrations.

However, analysis of the kinetic part of the Schrödinger equation shows that the internal rotation may be related to the low-frequency deformational vibration of the substituent (CHO, CFO and CClO). This relationship can be judged from an analysis of the change in kinematic factors $\boldsymbol{B}_{ij}$ in the two-dimensional problem that takes into account these two studied nuclear motions. This dependence appears differently in the *cis* ($\varphi_{tors} = 0°$) and *trans* ($\varphi_{tors} = 180°$) conformers.

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N26

Data quality control in IS W@DIS. Filtering values wavenumbers in spectral data collections

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For most users of spectral data related to molecular spectroscopy and used by them in applied research, only expert data is of primary interest. Trust in expert data is determined by the credibility of the experts who generate this kind of data. And such trust is not always justified. The authors propose an information system [1] within which users can obtain detailed information about the quality of the data they use expert arrays.

A feature of IS W@DIS is the implementation of quality control of expert data using a set of traditional methods and methods proposed by the authors of the report. The use of new methods requires the availability of a complete set of published spectral data. These original methods include estimation of the disorder of compared data arrays [2], decomposition of expert data [3], and filtering of wavenumber values using empirical (reference) energy levels. In [3], when decomposing expert arrays, experimental data on wave numbers contradicting each other were used. Filtering the values of the wave numbers in the primary data made it possible to obtain reliable results of assessing the trust in expert data on the isotopologues of the water molecule. The result of filtering is also the selection of experimental energy levels that did not fall into the array of empirical levels. Arrays of such energy levels are available in the W@DIS IS. The report discusses the results of filtering for H_2O, H_2S, SO_2 molecules and their application for decomposition of expert data.

In the last 15 years, about a dozen works have appeared in which the values of empirical energy levels are calculated for two- (CH, OH, ZrO, TiO, …), three- (H_2O, H_2S, HOCl, …) and four- (NH_3, C_2H_2) atomic molecules. It is planned to use filtering for the entire set of molecules with empirical energy levels.

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N27

The results of systematization and analysis of plots on the continual absorption of water vapor extracted from publications 1898-2020

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A feature of the study of continuum absorption is that in most cases the results of the studies are presented in graphical form, and the presentation of the results in tabular form is not often used in articles. This feature initiated our work on the creation of the information system GrafOnto, which systematizes figures from publications in this subject area. Published figures containing primitive plots in the Cartesian coordinate system are represented by numerical arrays (Graf) and a description of the properties for each graph (Onto).

The report discusses the statistics of such graphs related to the water molecule [1-3] and its mixtures with molecular nitrogen and argon. In particular, the number of plots characterizing the properties of water vapor in the absorption and transmission processes is 2610, and these plots are included in 482 composite plots and 60 composite figures. Plots describing the absorption of radiation characterize the frequency and temperature dependence. Statistics of plots and related publications related to continual absorption in transparency windows and in the region of absorption bands are given, describing the number of primitive primary plots and the number of works from which they were extracted. The statistics of plots characterizing the temperature dependence of the absorption coefficients for three temperature ranges is considered.

A separate topic of the report is the study of the quality of citing plots in IS GrafOnto. A method for estimating the difference between the citing and cited plots is proposed. The statistics of pairs of citing and cited plots on the continuum absorption of water vapor are given.

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N28

Results of systematization and analysis of graphs on the continual absorption of carbon dioxide extracted from publications of 1956-2010

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The report discusses the statistics of plots related to carbon dioxide (984) [1-3] and its mixtures with argon (166), helium (207), neon (8) and xenon (13), molecular nitrogen (301), hydrogen (10), deuterium (6) and oxygen (11). The number of graphs in the GrafOnto system is indicated in parentheses in the listing of mixtures above. In particular, 984 plots characterizing the properties of carbon dioxide in the absorption and transmission processes are included in 294 composite plots and 50 composite figures. Plots describing the absorption of radiation characterize the frequency and temperature dependence. Statistics of plots and related publications related to continual absorption of carbon dioxide in transparency windows and in the region of absorption bands are given, describing the number of primitive primary graphs and the number of works from which they are extracted.

Information is provided on the number of plots characterizing the temperature dependence of absorption coefficients for three temperature ranges, and the number of publications containing figures from which they are extracted.

A separate topic of the report is the description of the functionality of the GrafOnto information system, which provides attributive and contextual search for plots, integration of primitive plots into composite plots, detailed statistics on substances and characteristics of continual absorption.

The results of a study of the quality of citing plots characterizing the continual absorption of carbon dioxide and its mixtures in the GrafOnto IS are presented. A method for estimating the difference between the citing and cited plots is proposed. The statistics of pairs of citing and cited plots on the continuum absorption of carbon dioxide are given.

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N29

Measurement of singlet oxygen concentration in ambient atmosphere

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We represent the results of Singlet Oxygen (SO) measurements conducted in ambient atmosphere. SO (O_2 ($a^1\Delta$)) is the lowest metastable level of oxygen molecule with electron energy 0.98 eV and radiative lifetime about 4400 seconds. Because of this set of features SO rises interest in laser physics, chemistry, biology and ecology. Traditionally measurements SO concentration are conducted on radiative transition to the ground state O_2 ($a^1\Delta$) → O_2 ($X^3\Sigma$) at 1268 nm. However, this method is impossible while measuring SO concentration in ambient atmosphere due to Solar radiation. In this work we have measured SO concentration with the help of diode laser spectroscopy methods on electron transition O_2 ($a^1\Delta$) →O_2 ($b^1\Sigma$) at 1505 nm. We have observed two lines of SO transition with vibronic transition 8–8 and 10–10. The SO lines were identified using water vapor lines wavelengths from HITRAN database. The dependence of SO lines intensity due to weather conditions is discussed.

N30

Study of the effect of oxygen on the active medium of an optically pumped rare gas laser using the kinetic 0-D(t) model

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The optically pumped rare gas laser (OPRGL) is a new type of optically pumped gas laser with high quantum efficiency, which can convert the high output power of a diode laser into the output power of a gas laser with good beam quality. In [1], the first generation at a wavelength of 893,1 nm was demonstrated. According to published open sources, there has been a significant step in the world in studying the properties of the active medium on the model of a laser source based on a mixture of inert gases with optical pumping. The discharge was optimized and became stable at atmospheric pressure and efficient in the production of metastable atoms [2, 3].

A mixture of argon (3%) and helium (97%) is used as the OPRGL active medium. The main purpose of using helium is to increase the collisional relaxation from the pump level to the upper laser level in order to create the largest population inversion.

In present paper we represent a development of a kinetic model of the laser active medium of OPRGL. This model is necessary for the analysis of the discharge conditions, which will further allow optimizing the experimental stand and scaling to create an efficient laser facility.

The plasma kinetic model includes particles of argon (18 species), helium (5 species) and oxygen (13 species). The model includes more than 500 reactions describing the interaction of these particles. Oxygen was added to the model to take into account the effect of impurities on the discharge kinetics.

To compare the experimental data, an experiment was carried out in which the radiation of a probing tunable diode laser was passed through the active medium. Comparison between theoretical and experimental results is demonstrated.

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N31

Improved *ab initio* potential energy surface of the ozone molecule near the first dissociation limit including the spin-orbit coupling

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For the correct accounting for the ozone (O_3) molecular dynamics and the structure of the bound states near the first dissociation (D_e) limit, it is crucial to have the precise potential energy surface (PES) on a wide grid of nuclear configurations. The electronic ground state PES of O_3 published in [1] has proven to be quite accurate for spectroscopic calculations and it had some advantages compared to the previous ones for the long-range calculations of the O_3 dynamics [2] and reaction rate coefficients [3, 4]. However, the behavior of this PES needs further improvements in the long-range region, primarily to agree better with the empirical $D_e = 1.143$ eV derived in [5] from the thermochemical data observed by Ruscic et al. [6]. In this report we present the results on the improvement of the *ab initio* PES [1] towards the D_e limit.

To achieve a good agreement with the empirical D_e value, large-scale *ab initio* calculations were done using the MOLPRO package. The complete active space (CAS) was formed from the total number of the electrons (24) and 15 molecular orbitals. Under such *ansatz* and the aug-cc-pV6Z orbital basis set, the *ab initio* D_e agreed with the empirical one within experimental uncertainties without any additional adjustments.

The spin-orbit coupling (SOC) contribution was included by forming the state-average CAS(18, 12) based on the 9 electronic states approaching in the D_e limit (3 singlets, 3 triplets, and 3 quintets). The SOC matrix elements were calculated using the icMRCI electronic wavefunctions and the full Breit-Pauli SO-operator. The final agreement with the empirical D_e limit was estimated as less than 10 cm^{-1}.

The described scheme of the *ab initio* calculations was employed for the whole grid of the nuclear configurations constructed in the scattering (Jacobi) coordinates. The radial dependence of the potential energies in the long-range region ($R = 6 - 12\ a_0$) was analyzed. The draft of the full-dimensional PES for this region is presented. The connection with the accurate under the D_e limit *ab initio* PES [1] is discussed.

The study was supported by the Russian Science Foundation (project No. 19-12-00171-P).

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N32

Ab initio potential energy and dipole moment surfaces for disulfur monoxide

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The line list for the main isotopologue of disulfur monoxide ($^{32}S_2{}^{16}O$) was variationally computed using both accurate *ab initio* potential energy (PES) and dipole moment surfaces (DMS). The *ab initio* PES [1] used in this work was based on the potential energies converged with respect to the orbital basis set size CCSD(T), with the inclusion of corrections due to the scalar relativistic effects, DBOC, and high-order electronic correlations. This PES allowed to describe the experimental band origins of $^{32}S_2{}^{16(18)}O$ within the error of 0.5 cm^{-1}. To construct the DMS, the *ab initio* dipole moment values were calculated *via* the finite difference approximation as the first derivative of the potential energy with respect to the electric field using the CCSD(T)/aug-cc-pV5Z approach. The final line list covers the 0–1800 cm^{-1} region and contains more than one million transitions with the intensity cutoff value of 10^{-25} cm/molecule.

The simulated absorbances in the regions of the ν_2 (380 cm^{-1}) and ν_3 (679 cm^{-1}) fundamental bands agree well with the available recorded ones published in [2] and [3], respectively. The integrated intensities of the strongest cold and hot bands located in the 0–1800 cm^{-1} region are presented.

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N33

Spectra of the formaldehyde molecule in the 3800–5100 cm^{-1} range

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A comprehensive study of vibration-rotation spectral patterns of the formaldehyde molecule will be reported. Vibrational energy levels of H_2CO were computed using variational nuclear motion calculations from *ab initio* and empirically optimized full 6-dimensional potential energy surfaces in the electronic ground state. *Ab initio* calculations were carried out using extended electronic structure coupled-cluster method accounting for the dynamic electron correlations including triple and quadruple excitations as well as relativistic and diagonal Born-Oppenheimer corrections [1]. Effective Hamiltonian and effective dipole transition moments for the ro-vibrational polyads were derived from the *ab initio* surfaces using high-order contact transformations (CT) [2,3]. The analyses of experimental spectra recorded at T=160–165 K and various pressures were performed for the region of the 3-rd vibrational polyad. The experimental setup was described in [4]. The line positions and intensities were obtained by nonlinear least-squares fits with the SpectraPlot software [5] and analyzed using the CT-models for the effective Hamiltonian and effective dipole transition moments. Fifteen new vibrational levels were derived from these analyses in a good agreement with calculations [1]. In the range 4500-4700 cm^{-1}, a line list with the quantum identification was produced. It can be useful for a global modeling of the formaldehyde spectra and for an improvement of the line parameters in the databases [6-8].

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N34

Current progress in variational calculations of polyatomic hydrocarbons (C_2H_2, CH_4, C_2H_4, C_3H_4, and C_2H_6)

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The prediction of the rovibrational energy levels of the acetylene molecule was studied using both the *ab initio* [1] and new empirically refined potential energy surfaces (PESs). The refinement of the PES was done by the fit of the available experimental data on the main $^{12}C_2H_2$ isotopologue. The quality of the refined PES was analyzed by the variational calculations of the rovibrational energy levels of four isotopologues ($^{13}C_2H_2$, $^{12}C_2D_2$, $^{13}CH^{12}CH$, and $H^{12}C^{12}CD$) including their isotopic shifts for some lower energy levels with $J \leq 5$. Although under the Born–Oppenheimer approximation the isotopic shift should be independent on the PES, we found that the refined PES gave more accurate results than those based on the *ab initio* one. The accuracy of the isotopic shift calculation was estimated as an order of magnitude better than the accuracy of the energy levels calculation.

In the case of CH_4, the rovibrational energy levels in the region of the tetradecade polyad were computed with a high accuracy using the *ab initio* PES without any empirical corrections. It was found that the prediction of the vibrational energy levels up to 17000 cm^{-1} strongly depended on shape of the PES.

A novel methodology [2] for computing parameters of the effective both Hamiltonian and dipole moment was applied with respect to C_2H_4. The obtained for each polyad effective parameters will be used to improve the assignment of the C_2H_4 absorption spectra, measured particularly, around 7000 cm^{-1}.

The full-dimensional *ab initio* PESs for two structural isomers of the hydrocarbon C_3H_4 (D_{2d}–propadiene and C_{3v}–propyne) were developed up to the 5th order inclusively. The application of the rigid (D_{3d}) approximation for the variational calculations of the line list of C_2H_6 was discussed with respect to the new contraction approach implemented in the variational TENSOR code and presented previously *ab initio* PES and DMS [3].

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N35

Refractive index gratings excited by mid-infrared radiation and local measurements of CH_4 concentration, gas composition, pressure, and temperature in methane-containing gas mixtures

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Combustion-relevant molecular species, which lack easily accessible electronic transitions in the UV- and visible spectral ranges, but resonantly absorb radiation via strong mid-IR rovibrational transitions in fundamental vibrational bands, can be selectively excited using frequency-tunable mid-IR laser radiation. In particular, local temporally- and spatially-resolved highly-sensitive laser diagnostics of either directly CH_4 concentrations, or gas parameters, by using CH_4 as probe molecules present in small amounts in a gas mixture, with no influence on its properties, can be provided by the technique utilizing Laser-Induced Gratings (LIGs), or spatially-periodic modulations of the refractive index [1]. In this case, it becomes possible to instantly determine several parameters of the gas [e.g., 2-5], like the sound velocity and thermal diffusivity, in a single laser shot measurement.

It is investigated how different gas parameters can be measured using mid-infrared resonantly excited LIGs in CH_4-containing gas mixtures. In the experiments, nanosecond pulses of 3-μm tunable narrowband laser radiation were used to generate LIGs upon excitation of a selected transition of the v_3 band of CH_4. For diffraction by LIGs, continuous-wave probe laser radiation was employed, that made it possible to record temporal evolution of the grating diffraction efficiency (LIG signals). Probe radiation in the visible range ensured a high sensitivity of signal recording. The specificity of the LIG signal temporal profiles with respect to the mixture composition, pressure, and temperature of a selected buffer gas is studied in terms of its use for determination of these characteristics.

The results demonstrate that the LIG technique with mid-IR excitation in methane-containing gas mixtures provides measurements of low local concentrations of CH_4 (down to ~50 ppm in N_2 at ambient temperature and in a broad range of pressures). The technique also makes it possible to use CH_4 as an effective probe molecule in binary gas mixtures for sensitive local determination of gas parameters based on LIG signal temporal profiles.

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Invited Lectures O
Friday, July 7, 09^{15} – 10^{45}
Chair: Maksim A. Koshelev

O1

High-resolution diatomic spectroscopy near the dissociation threshold

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Bound, quasi-bound and continuum rovibronic states located near the dissociation threshold play a key role in the formation of stable molecular ensembles in photo-association, magneto-association and stimulated Raman adiabatic passage (STIRAP) of colliding ultracold atoms [1]. The same molecular states are also tightly involved in the contra verse process, namely: photo and collisionally induced the dissociation of molecules normally taking place at the elevated temperature. Laser-induced fluorescence of the so-called non-diagonal electronic transitions combined with a high-resolution Fourier-transform spectroscopy (FTS-LIF) often can provide all three bound-bound, bound-quasibound and bound-continuum parts of the molecular spectra, simultaneously.

Here we focus on global deperturbation analysis of diatomic states converging to the common atomic limit. The main challenge of the rigorous deperturbation treatment of these mutually perturbed states is based on the issues [2]:

(1) all bound, quasi-bound and continuum states should be simultaneously treated within the framework of the exactly same (uniform) quantum-chemical approximation (model);

(2) the conventional adiabatic approximation completely breakdowns on the dissociation: non-relativistic states become degenerate; hence, spin-orbit and hyperfine interactions should be taken into accounted explicitly;

(3) the last bound levels are localized in the extremely wide range of internuclear distance (R>100-1000 Å)

(4) highly accurate *ab initio* electronic structure calculations are needed to have got the reliable estimates of potential energy curves and non-adiabatic matrix elements of all states treated in a wide range of R.

By the example of high-resolution FTS-LIF spectra of KCs [3-5] molecule and sub-Doppler laser spectroscopy of the K2 dimer produced in the molecular beam [6], we demonstrate that the developed coupled-channel deperturbation model which takes into account for spin-orbit coupling effect and Fermi-contact hyper fine interactions can manage to represent both non-adiabatic energies and radiative transition probabilities of the fully mixed electronic states localized near the dissociation threshold with the unprecedentedly high spectroscopic accuracy.

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O2

Spectroscopy and dynamics of unstable molecules: ozone puzzle

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Unstable species represent well-known difficulties for experimental measurements of molecular spectra and for a precise determination of transition probabilities. In this context a development of theoretical methods including *ab initio* calculations of the dipole moment and potential energy surfaces supporting molecular dynamics are of a particular importance. Various approaches to determine accurate line intensities, temperature dependence of the partition functions in non-LTE conditions [1], metastable states beyond the dissociation threshold and their lifetimes as well as molecular formation and fragmentation processes [2] will be outlined. Specific puzzling issues for the case of the ozone molecule [3-8] including recent application to isotopic effects in the dynamics will be discussed.

The support from the Russian Science Foundation (grant No. 19-12-00171-P) is acknowledged.

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Oral Session P
Friday, July 7, 11^{15} – 13^{00}
Chair: Konstantin V. Kazakov

P1

Generalized relativistic pseudopotentials for the light elements simulating the relativistic and QED effects

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The relativistic pseudopotential (RPP) method is often used in calculations of electronic structure, spectra, and various physico-chemical properties of compounds of heavy elements because it allows one to reduce drastically the computational efforts in comparison with the calculations with the Dirac-Coulomb(-Breit) Hamiltonian without significant loss in accuracy. The generalized (Gatchina) versions of the RPPs (GRPPs) were developed at NRC "Kurchatov Institute" - PNPI. They allow one to increase significantly the accuracy of RPP calculations due to the use of different RPP components for valence and outer core electrons with the same spatial and total angular momenta, etc. [1]. Here, the GRPPs are constructed for light elements without excluding any electrons from explicit treatment ("empty-core GRPP") to simulate the standard relativistic effects, Breit corrections to Coulomb interactions between electrons, and quantum electrodynamic (QED) contributions described by the self-energy and vacuum polarization diagrams [2]. Thus, the nonrelativistic kinetic energy and Coulomb interelectronic interaction operators should be used in the further calculations with these GRPPs. The errors of the GRPP simulation and the contributions of different effects are demonstrated in atomic numerical self-consistent-field calculations in Table 1. Unlike them, direct relativistic calculations with the Dirac–Coulomb(–Breit) Hamiltonian are difficult for molecules, clusters, and crystals due to four-component representation for the wave-function, etc. On the other hand, widely used nonrelativistic calculations with Schrödinger Hamiltonian neglect the relativistic effects which can be essential for some tasks (spin-orbit splittings, spin-forbidden electronic transition moments [3], etc.).

Table 1. The transition energies between the states of carbon averaged upon nonrelativistic configurations from Hartree–Fock–Dirac–Breit (HFDB) calculations with accounting for the QED effects, the different contributions to them, and the GRPP errors (in cm^{-1})

Nonrelativistic configuration	HFDB+QED (Fermi nucleus)	Finite nucleus contribution	QED effects	Breit effects	Relativistic effects	GRPP errors
$1s^22s^22p^2 \rightarrow$						
$1s^22s^22p^13s^1$	52418	0	3	-4	-43	1
$1s^22s^12p^3$	70850	0	-8	-7	120	1
$1s^22s^22p^1$	80614	0	3	-5	-35	0
$1s^22s^12p^2$	145440	0	-7	-11	104	2

This work on the GRPP generation at NRC "Kurchatov Institute" - PNPI has been supported by the Russian Science Foundation (grant No. 20-13-00225).

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P2

Ab initio rovibrational energy levels for four isotopologues of triplet ($\tilde{X}\,^3B_1$) methylene

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The rovibrational energy levels of four isotopologues of triplet ($\tilde{X}\,^3B_1$) methylene (CH_2, CHD, CD_2, and $^{13}CH_2$) were variationally calculated up to ~10000 cm^{-1} using the developed accurate *ab initio* potential energy surface (PES). The triplet methylene has the large-amplitude bending vibration and quasilinear properties because of the lower barrier to linearity (~2000 cm^{-1}). The constructed PES was based on the RHF-UCCSD(T)/aug-cc-pCV6Z method with the inclusion of the corrections due to the scalar relativistic effects, DBOC and high-order electronic correlations. For the first time, the obtained *ab initio* height of the barrier to linearity (1924.6 cm^{-1}) agreed well with that from the empirical PES published almost 40 years ago (1931±30 cm^{-1}) [1]. The available experimental band origins for the three isotopologues (CH_2, CD_2, and $^{13}CH_2$) were reproduced with errors less than 0.1 cm^{-1} while the total root mean square deviation with the empirical transitions including those for CHD was 0.115 cm^{-1}.

According to our results, the rovibrational energy levels strongly overlap at rather small rotational quantum numbers. This restricts the use of the polyad model for triplet methylene. The effect of the rovibrational interactions cannot be ignored even for the ground vibrational state (000) at $K_a \geq 5$. The possibility of the use of the effective Watson *A*-reduced Hamiltonian and the generating-function approach to predict the rovibrational energy levels of triplet methylene was discussed by comparing with the accurate variational calculations. The results were prepared for publication [2].

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P3

Improved ozone vibrational band centers for symmetric and asymmetric isotopologues: *ab initio* calculations including Diagonal Born-Oppenheimer correction

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In this work, we analyzed the previously calculated Diagonal Born-Oppengheimer Corrections (DBOC) on a common grid of configurations for symmetric ($^{16}O^{16}O^{16}O$, $^{17}O^{17}O^{17}O$, $^{18}O^{18}O^{18}O$, $^{16}O^{18}O^{16}O$, $^{18}O^{16}O^{18}O$) and asymmetric ($^{18}O^{16}O^{16}O$, $^{18}O^{16}O^{18}O$) isotopologues in the ground electronic state. This is a continuation of the previously published work devoted to the symmetric isotopologues [1].

Based on the *ab initio* electronic energies computed at a grid of nuclear geometries, a single analytical mass-dependent model was created for corrections to the Born-Oppenheimer ground state potential energy surface (PES) for ozone [2]. Based on the constructed model, simultaneous calculations of the vibrational band centers will be reported providing a significant improvement for the BO PES-based predictions up to 2700 cm^{-1} for all eighteen isotopic species of the ozone molecule.

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P4

Energy spectra of light one-electron matter-antimatter quasimolecules

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Ongoing development of experimental technique in spectroscopy of light three-body atomic systems brings stimulus to theoretical studies of this many-body problem. Due to the fact that quantum electrodynamics (QED) theory for such a case is not yet well elaborated, researches are made to develop numerical solutions of the problem.

One of the fundamental challenges of physics is the search of the global CPT-symmetry violation, which is carried out, in particular, in the field of precision atomic and molecular spectroscopy. One of the direct ways for testing CPT-invariance is to compare spectra of matter and antimatter - a problem that gained attention after experiments such [1], in which antihydrogen atoms were synthesized. Due to the experimental conditions and features of the antimatter synthesis it is required to study the so-called quasimolecular systems that emerge in collisional processes.

One way to describe energy spectrum of one-electron quasimolecule is to solve nonrelativistic two-center problem and use nonrelativistic quantum electrodynamics (NRQED) to obtain relativistic corrections [2]. A different approach is to use the Born-Oppenheimer approximation to obtain the one-electron Dirac equation with the Coulomb potential of the two nuclei at a fixed internuclear distance. There are a number of ways to find the energy spectrum of the system, for example, partial-waves and Dirac-Sturm expansions [3,4]. In the present work a different method is used which is based on the expansion of the wave function in a finite basis set of B-splines generalized to the axially-symmetric systems (A-DKB) [5]. Using this method energy spectra of antiproton-helium and proton-antiproton ions are obtained.

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Author Index

A

Adamenkov Yu.A. 141, 142
Akhlestin A. 67, 138
Akimov G. 138
Alkhuder O. 23
Amerkhanov I. 38, 39
Andersen L.H. 93
Anfertev V. 72
Anikin A. 154
Anisimov R. 61
Ansari M.A. 59
Asfin R.E. 23, 81, 117
Ayouz M. 56

B

Babikov Yu.L. 68, 128
Baklanov A.V. 90
Balashov A.A. 84, 121
Barbe A. 69, 128, 129
Barke V. 104
Bataev V. 50, 87, 137
Bauerecker S. 41, 42
Bekhtereva E.S. 40, 41
Beletsan O.B. 92
Belogolova A.M. 92
Belyaev D. 52, 104
Bertaux J.-L. 103
Bielska K. 121
Bisikalo D. 107
Blinov S.N. 54, 112
Bochenkov V. 95
Bochenkova A.V. 92
Bogomolov A.S. 89
Borisov A.V. 75
Borkov Yu. 31, 32, 83, 113
Bormotova E.A. 48, 136
Boyarkin O.V. 27
Bucharskaya A.B. 62, 78, 79
Bulanin K.M. 95
Buldureva J. 125
Bulychev V.P. 88
Burgalat J. 129
Buturlimova M.V. 88
Bychkov E. 80

C

Campargue A. 19, 20
Chakalov E.R. 24
Chang X. 55
Chen Y. 57
Chentsov A. 37
Cherkasova O. 73
Chernov V. 119
Chernova A.I. 37
Chernyaeva M. 72
Chervinskaya A. 118
Chesnokov E.N. 16, 28
Chesnokova T.Yu. 36, 67, 116
Chistikov D. 39
Ciurylo R. 121

D

Danilov A. 54
Deichuli V. 35, 36, 133, 134, 135
Diachkova O.O. 117
Domanskaya A. 81
Domracheva E. 72
Domyslawska J. 121
Dorofeev D. 119, 120
Doronkina A. 61
Dudaryonok A.S. 42, 44, 124
Dyachenko P.A. 78
Dzuban I. 52

E

Egorov O. 143, 144, 146, 151
Egorova N. 116
Emeline A.V. 95
Emelyanov N. 33, 114
Ermolinsky P.B. 77
Evdokimova D. 52, 102, 107
Fazliev A.Z. 45, 46, 47, 68, 139, 140, 141
Fedorova A. 35, 102, 104, 107, 134, 135
Feldman V. 91
Feskov S. 125
Filippov N.N. 116
Finenko A. 39
Foka S. 51, 101

G

Galanina T.A. 19, 21, 38, 39, 84, 127
Galyapin P. 146
Gel'mukhanov F.Kh. 55, 113
Genin V.D.. 62, 78
Genina E.A. 61, 62, 74, 78, 79
Golubiatnikov G.Yu. 21, 37, 84, 120
Gorbunov M.A... 141, 142
Grigoriev A.. 107
Gromova O.V. 40, 41
Grouiez B.. 129
Gurfinkel Yu.I. 77

H

Horneman V.-M.. 29
Hot D. 147

I

Ignatiev N. 52, 107
Ignatova N.Yu. 54, 112
Imkhasin H. 50, 100
Ionov D.. 50, 100
Ivanov A. 88, 126
Ivanov S... 19

J

Jacquemart D. 20
Jiang W.. 56, 57
Jiang X.. 56, 57

K

Kalacheva A.A... 141, 143
Kargovsky A.. 111
Kassi S. 18
Katunov T.D... 118
Kazakov V. 71, 103, 110
Khlebtsov B.N. 62
Khlebtsov N.G.. 62
Khomenko M.. 80
Kimberg V.V. 54, 112
Kirillin M.Yu.. 62
Kistenev Yu.V. 73, 75, 78, 79
Klink L... 48
Knyazkova A. 73
Kochanov R.V. 71, 143, 144, 152
Kochubey V. 61
Kokoouline V.A..................................... 57, 109, 144
Konnikova M... 73, 80
Konopatskova O.M. 74
Konova Yu.V. 41
Korablev O................................ 36, 98, 102, 105, 107
Korneev K.N. 76
Kornev A.. 119
Koroleva A. 18, 38, 39
Koshelev M.A. 19, 21, 37, 38, 39, 84, 126
Koshlyakov P.V. 17
Kostin M.A. 23
Kostsov V.. 50, 100
Kouzov A. 116
Kozlov D. 147
Kozlov S.. 83, 85
Kozodoeva E. 67
Krasnoshchekov S.V. 56
Krasnov P.O. 54, 112
Kubarev V.V. 16
Kubarev V. 14
Kuraeva T... 34
Kuzinova Y.K. 74
Kyuberis A.A. 121

L

Lavrentiev N.A........................... 43, 67, 138, 139, 140
Lavrentieva N.N. 42, 43, 124
Lazareva E.N... 59, 61, 74
Lebedev Yu. 103
Leonov I.I. 37
Li G. 121
Li Zh.. 148
Likharev A.S. 127, 136
Lipskaya A. 27
Lisak D... 121
Liu H. 56, 57
Lomakin A. 35
Lomova M.V. 59, 61
Luginin M. 107
Lugovtsov A.E. 76, 77
Lyulin O. 20, 30, 122, 123

M

Makarov B. 50, 100
Makarov D.S. 21, 84
Makarova M. 50, 100
Maksimov M.K. 77
Manceron L. 129, 145
Maslov I. 107
Matrosov I. 102

Maul C. 82
Melikova S.M. 64
Meshcherinov V. 103, 110
Meshkov O. 71
Mikhailenko S.N. 30, 69, 128
Mikheleva A.Yu. 95
Mondelain D. 18
Monmessin F. 35, 104, 108
Mosyagin N.S. 150
Mudrak D.A. 78
Mulloyarova V.V. 23

N
Naumenko O.V. 28
Navolokin N.A. 62, 78
Nazarova A. 102
Nevzorova T.A. 42
Nikitin A.V. 130, 144, 145, 146, 152
Nikitin S.Yu. 77
Nikolaev N. 73

O
Oleynichenko A.V. 150
Ovsyannikov R.I. 121, 126
Ozheredov I. 80

P
Pakhomov Yu. 106
Panfilov V. 110
Panfutov O. 90
Pankin D.V. 95
Pashov A. 49
Patsaev D. 107
Pazyuk E.A. 48, 84, 85, 127, 132
Perevalov V.I. 21, 31, 32, 34, 115, 123, 124
Petrov D. 23, 101
Petrov S.V. 26, 39
Petrova T. 30, 31, 35, 36, 133, 134, 135
Piskunov N. 105
Plastinina D.M. 16, 27
Poberovskii A. 50, 100
Polyakov A. 50, 100
Polyansky O.L. 120, 122
Polyutov S.P. 54, 112
Ponomarev Yu.N. 34
Priezzhev A.V. 77
Prischepa V.V. 76
Privezentsev A. 67, 138
Protasevich A. 145, 146
Ptashnik I.V. 18

R
Rey M. 131, 144, 145, 146, 151
Rodimova O.B. 44, 45, 46, 67, 139, 140
Rodin A. 111
Rodina A. 145, 146
Roginski E.M. 95
Rogoveshko V.M. 89
Rudakova A.V. 96
Rutkowski K.S. 63
Ryabchikova T. 105

S
Sahlberg A.-L. 147
Saparbaev E. 26
Sekacheva A. 21
Selivanov N.I. 95
Serdyukov V. 32, 33, 113, 114
Serebryakova I.A. 59, 74
Serov E.A. 21, 38, 39, 84
Shaidulina V.A. 142
Shakun A. 107
Sharybkina K. 28
Shaydulina V.A. 142
Shiryaeva E. 90
Shkurinov A.P. 65
Shkurinov A. 74, 81, 112
Shokova M. 94
Shushunova N.A. 59
Simonova A.A. 17, 84
Sinitsa L.N. 33, 114, 115
Sinko A. 111
Skiba V.E. 75
Skitnevskaya A.D. 91, 94
Smirnov M.B. 95
Solodov A.A. 30, 31, 34, 36, 133, 134, 135
Solodov A.M. 30, 31, 34, 36, 133, 134, 135
Spiridonov M. 52, 103, 110
Starikov V.I. 136
Starikova E.N. 69, 128, 129, 130
Stolyarov A.V. 48, 86, 128, 137, 149, 151
Styopin S. 49, 137
Sulakshina O.N. 32, 82, 113
Sung K. 130
Surin L. 109
Surkov Yu.I. 59, 74

Surovtsev N. 111
Sushkov N.I. 97, 133
Szalay P.G. 152

T

Tajti A.. 152
Tanichev A. 22, 101
Tarabukin I. 109
Tashkun S. 69
Tennyson J. 121
Terashkevich V.A. 85, 96, 131, 132
Terentyuk G.S. 62
Titov A.V. 150
Tokhadze K.G. 89
Tolstoy P.M. 23
Tretyakov M.Yu. 14, 20, 22, 38, 39, 85, 120, 126
Trofimov A.B. 91
Trokhimovskiy A. 35, 104, 107
Tsurikov G. 106
Tuchin V.V. 63, 66, 75, 76, 79, 80
Tuchina D. 61
Tupikina E.Yu. 23
Tyurin D. 90
Tyuterev Vl.G. 70, 129, 130, 143, 145, 146, 147, 150, 153

U

Ulenikov O.N. 40, 41

V

Vakhromov V. 47
Vaks V. 72
Vasil’evskii I. 80
Vasilchenko S. 20, 122, 123

Vasilenko I. 28
Velichko T.I. 29
Venkstern A. 103
Vigasin A. 40
Viglaska D. 146, 151
Vilkov I.I. 21, 37
Vilkov I.N. 84
Vinogradov I. 51, 52, 103
Vlasov P. 107
Volkov P. 51
Voloshchenko A. 47
Vrazhnov D.A. 73, 75
Vyazovetskiy N. 53

W

Wojtewicz S. 121

Y

Yamaletdinov R. 26
Yanina I.Yu. 62, 78, 79
Yao L. 57
Yatcenko A. 72
Yuriev A.V. 142
Yuriev M. 47

Z

Zaitsevskii A. 150
Zasova L. 107
Zaytsev S.M. 74, 96, 132
Zhang Y. 56, 59
Zharikova M. 102
Zinchenko I.I. 100
Zobov N.F. 120, 121
Zolotarev K. 71
Zviagin A. 26

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