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XX SYMPOSIUM ON HIGH-RESOLUTION MOLECULAR SPECTROSCOPY (HighRus-2023)

Experiments on Molecular Spectroscopy at the Novosibirsk Terahertz Free Electron Laser

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Abstract—The unique parameters of the Novosibirsk free electron laser (NovoFEL) allow unique experiments on the spectroscopy of molecules to be performed at the Shared Resource Center. The radiation parameters of terahertz NovoFEL are article described in detail. The molecular spectroscopy experiments performed on this laser are given with the corresponding references in which they are described. Possible but as yet unperformed experiments on terahertz NovoFEL in the field of ultra-high-resolution molecular spectroscopy are considered.

Keywords: free electron laser, terahertz radiation, ultrafast molecular spectroscopy, ultra-high resolution molecular spectroscopy

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INTRODUCTION

The unique Novosibirsk free electron laser (NovoFEL) facility has been operating for 20 years. It currently consists of three lasers in the terahertz, far-infrared, and infrared ranges of wavelengths [1, 2]. In addition to work related to developing original devices and ways of generating radiation (i.e., of the facility itself), most of its working time is now occupied by user experiments at special stations where the NovoFEL operates as a source of radiation with fixed parameters. Fortunately, the one most popular among users is the terahertz NovoFEL, which is simplest in terms of physical design and configuration, due to the current rapid development of this range of wavelengths. The other two FELs are used occasionally for some user experiments, but most of the time they are used to test ways of generating radiation in different FEL schemes. Due to the more complex scheme for obtaining the desired active medium (an electron beam of a certain density at a higher energy), much more time is needed to set up these FELs. A round-the-clock operating mode, similar to that of synchrotron storage rings, is also required for effective user operation. However, it is not yet available on the NovoFEL.

User experiments performed at the NovoFEL can be divided into two parts. The first part includes experiments using at least one of the unique NovoFEL parameters, and ideally a combination of them. A number of such experiments are possible only at the NovoFEL. The second part includes experiments where these unique parameters are not of fundamental importance. Analysis shows it is often preferable to use other alternative sources for these experiments, since every advantage (unique parameter of the NovoFEL) has a negative side. The high energy parameters of the NovoFEL are thus accompanied by the bulkiness of the installation and the complexity of its configuration. Another important advantage of an FEL over quantum devices is our ability to smoothly adjust the wavelength, due to the many more degrees of freedom of the active medium. These produce a number of specific instabilities in the radiating system that must be suppressed when making precise experiments.

Experiments on terahertz molecular spectroscopy certainly belong to the first most important group of user experiments at the NovoFEL, since they actually use all the unique parameters of its radiation. The radiation parameters of terahertz NovoFEL are described in detail in the next section of this work. Although this data can be found in articles published at different times, on this occasion it has been collected in one place with the aim of giving potential users a quick and correct understanding of the terahertz NovoFEL's radiation. This is followed by a section with a brief description of the molecular spectroscopy experiments performed at the NovoFEL. This section is written as an abstract because details of these extensive experiments are best obtained from the original published articles. Finally, the last section dis-

cusses potential but still unperformed experiments at the NovoFEL in the field of super-resolution molecular spectroscopy.

OPERATING PRINCIPLES AND RADIATION PARAMETERS OF THE TERAHERTZ NovoFEL

To correctly understand the observed parameters of NovoFEL radiation, let us qualitatively consider the basic principles of generating radiation in a free electron laser. In order to emit an electromagnetic wave, an individual electron must move with acceleration along a certain curvilinear trajectory. The radiation will obviously be much stronger if it is produced synchronously in some periodic resonant system. FELs typically use periodic magnetic field undulators for this purpose. The NovoFEL uses planar magnetic undulators in which electrons oscillate in the same plane. The electric vector of the emitted linearly-polarized electromagnetic wave will be in the same plane. As is shown below, linear polarization of NovoFEL radiation is useful for spectroscopic applications, since polarization experiments are usually the ones most sensitive.

An electromagnetic wave moves along the undulator's axis at the speed of light, while the axial projection of the speed of a relativistic electron moving along a sinusoidal trajectory will obviously be less than the speed of light. It is then obvious that the resonant radiation of an electron in the undulator, in which the radiation fields from its periodic poles add up in phase, will be observed when the electromagnetic wave overtakes the electron at the one period-pole of the undulator exactly by the wavelength of the radiation. This condition of the resonance automatically determines the wavelength of the maximum emission of an individual electron in the undulator and a first approximation of the wavelength of the FEL's radiation. The electron trajectories are bent more upon a gradual increase in the magnetic field of the undulator, which increases the wavelength of its radiation. This way of changing the wavelength smoothly is the one used most often in FELs, including terahertz NovoFELs. The energy of the relativistic electrons also changes along with the field of the undulator when the wavelength of the NovoFEL radiation must be changed appreciably. However, such a change is really only possible for a shift by a given interval of wavelengths. This is because, in contrast to changing the undulator field, we must adjust the NovoFEL electron-optical system after each such shift.

The radiation from single electrons is negligible, so we must also consider the radiation from many electrons or an electron beam. It is obvious that the radiation of an electron flux uniform in density will be zero, due to the mutual compensation of radiation from individual electrons separated by half the wavelength. In reality, it is always non-zero because of statistical fluctuations of the electron density that produce incoherent weak synchrotron radiation which is an analog of spontaneous radiation in quantum lasers. As is well known, coherent laser radiation is more powerful than spontaneous N_f times, where N_f is a very large number equal to the number of photons in the emitted laser mode. In FEL, electron radiation becomes coherent when, under the influence of a fluctuation electromagnetic wave at a resonant frequency, they are grouped with a period equal to the wavelength of the resonant electromagnetic radiation, like electrons in millimeter-wave devices. This grouping occurs around the zero points of the field with a negative derivative; i.e., the transverse current wave of grouped electrons and the transverse wave of the electromagnetic field, the interaction of which determines the radiation, are phase-shifted by $\pi/2$. Thus, the current is a reactive load on the field exactly at the resonant frequency, and the emission of electrons is again zero. However, if the radiation frequency differs slightly from the resonant frequency, the waves slipping relative to each other give a non-zero power of interaction. Calculations show that the optimum value of the phase slip along the length of the undulator is 2.61 rad for a plane wave. However, plane waves have zero intensity and are not used in practice. As in quantum lasers with open resonators, the fundamental mode at anything but the longest wavelengths has the form of a Gaussian beam in an NovoFEL, where the phase also varies along the length according to a known law. There is also an optimum size of a Gaussian beam for interaction with electrons, when its Rayleigh length is 0.255% the length of the undulator, and the maximum gain is observed for a phase slip of 5.55 rad. [3]. It is interesting that with a phase slip 2.61 rad, the FEL gain is almost exactly zero for such an optimum Gaussian beam. Note first that this fundamentally important physical shift in the frequency of FEL radiation from the resonant frequency has a very low magnitude ($\sim 10^{-5}$). Second, it is automatically set by the FEL generator itself. It is therefore often completely ignored in describing the operating principles of an FEL, or an abstract value of 2.61 rad is given.

Let us next consider the two most important factors that determine the laser generation of the NovoFEL: the pulse-periodic mode of its operation and the formation of radiation by its optical resonator. The pulse-periodic mode is determined by a requirement of laser generation: raising the density of the active medium to such a level that the unsaturated gain of the mode in the optical cavity exceeds its losses. This requires a current of relativistic electrons of tens of amperes. The power of a relativistic beam with an energy of tens of MeV and such a current would be hundreds of megawatts. To accelerate it would require a very high constant electric voltage that is impossible for technical reasons. All FELs therefore operate in the pulse-periodic mode with a duty cycle of around 10^3–10^4, and their short bunches of electrons are accelerated in the synchronized field of high-fre-

quency resonators. Most of the world's FELs operate according to a scheme with additional low-frequency modulation of radiation in which rare bursts of pulses are generated. What makes the NovoFEL unique is that it typically generates a continuous sequence of short pulses of radiation. The mode of LF modulation is also possible when we must reduce electron beam losses in some complex NovoFEL regimes, or (more often) when users need to observe the effects on samples from exposure to high pulsed NovoFEL radiation power at low non-destructive average radiation power. In addition, the NovoFEL has a pulse durations tens of times longer than other FELs, due to the use of relatively low-frequency RF resonators in a linear electron accelerator. These factors have a beneficial effect on the NovoFEL parameters that are important for spectroscopy, since they greatly increase the spectral intensity of NovoFEL radiation and the monochromaticity of its mode lines.

The effect the optical cavity has on NovoFEL radiation is even stronger than in quantum lasers, though it is often underestimated or overlooked against the backdrop of the larger accelerator-electronic part of the installation. Unlike quantum lasers, where radiation in the optical cavity is accumulated to trigger stimulated emission in an active medium that has already been prepared in one way or another, intracavity radiation in an FEL first forms an active medium (a grouped electron beam) and then interacts with it in a coherent manner, as in stimulated emission. As in quantum devices, certain mode structures form in the FEL cavity that are determined by the boundary conditions on the mirrors and side walls of the cavity. We must first consider the effect the pulse-periodic operating regime has on the mode structure of NovoFEL radiation. There are several possible ways of synchronizing periodic electron bunches with light pulses circulating inside a resonator. The main option on the terahertz NovoFEL is to have the electronic pulses follow with a frequency exactly the same as the period of revolution of a light pulse equal to a high accuracy of $2L/c$, where L is the length of the optical resonator and c is the speed of light. Different electron bunches, though initially independent and passing through the resonator only once, emit coherent photons in the operating mode of the laser resonator as well, since their density (grouping) is modulated and synchronized by an intracavity light pulse. In the stationary mode, at each period of revolution of the intracavity pulse, a small part (several percent) of its power exits through holes in the mirrors and is useful NovoFEL radiation. The remaining part of the power in the same period is completely restored to the previous level in a coherent manner as a result of interacting with the electron beam. The output pulses of NovoFEL radiation will always have a high degree of coherence with one another, due to their laser nature. According to the Fourier transform, the NovoFEL emission spectrum will be a set of narrow longitudinal synchronized modes separated by frequency interval $\delta\nu = c/2L$ inside a uniform contour of amplification with width $\Delta\nu \sim 1/\Delta t$, where Δt is the duration of coherence within one pulse. With full intrapulse coherence, we observe the so-called Fourier limit of the width of the amplification circuit when Δt is equal to the duration of a pulse. Such a set of synchronized longitudinal modes with the same transverse structure is usually called a super mode. If the NovoFEL pulses are not coherent with one another, the NovoFEL radiation spectrum will take the form of a wide, uniformly broadened continuous line equal to the gain contour of the active medium. Since all conventional spectral instruments have resolution insufficient to resolve lines of ultrafine mode structure, users often consider such an unresolved contour to be NovoFEL monochromatic. This is partly because the spectral contour of the NovoFEL radiation can be considered a quasi-continuous line, due to the propinquity of mode lines in experiments with low spectral resolution. However, the true spectrum of NovoFEL radiation is by no means continuous: its mode lines are much narrower than the distances between them. In principle, this has been assumed on a qualitative level since the first theoretical work on an FEL. As with any other laser, the true monochromatic nature of an FEL is apparent from the width of its mode lines. Measuring these widths in the pulse-periodic FEL mode has a number of specific features and became possible only recently, after the invention of a special device: an ultra-long resonant Fabry-Perot interferometer [4], which in the time-domain regime is capable of measuring mode line widths of any value. We know that the limiting linewidth for this quantity in quantum lasers is determined by the ratio of the power of incoherent spontaneous emission to that of coherent stimulated emission. In order of magnitude, it is equal to the inverse number of photons in the emitted mode. Only certain laser frequency standards approach this limit, and the lines in conventional lasers are much wider because of different technical fluctuations. The situation with monochromaticity in an FEL is somewhat worse than in quantum lasers, since the large fluctuating number is not that of photons in the mode but the number of electrons in a grouped electron bunch, which is several orders of magnitude smaller. In a terahertz NovoFEL, one electron emits about 100 photons, and the limiting monochromaticity is estimated at $\sim 10^{-10}$. The actual measured monochromaticity of NovoFEL mode lines in a typical mode is 2.2×10^{-8} (linewidth, 40 kHz), two orders of magnitude below the theoretical limit because of different technical factors. This monochromaticity corresponds to a 25 μs period of coherence, a 7 km length of coherence, and an average of 140 coherent sequential pulses [4]. Note that these parameters were obtained in the normal NovoFEL regime without any special stabilization of its technical fluctuations. It is likely that the monochromaticity of the NovoFEL mode lines could be improved consid-

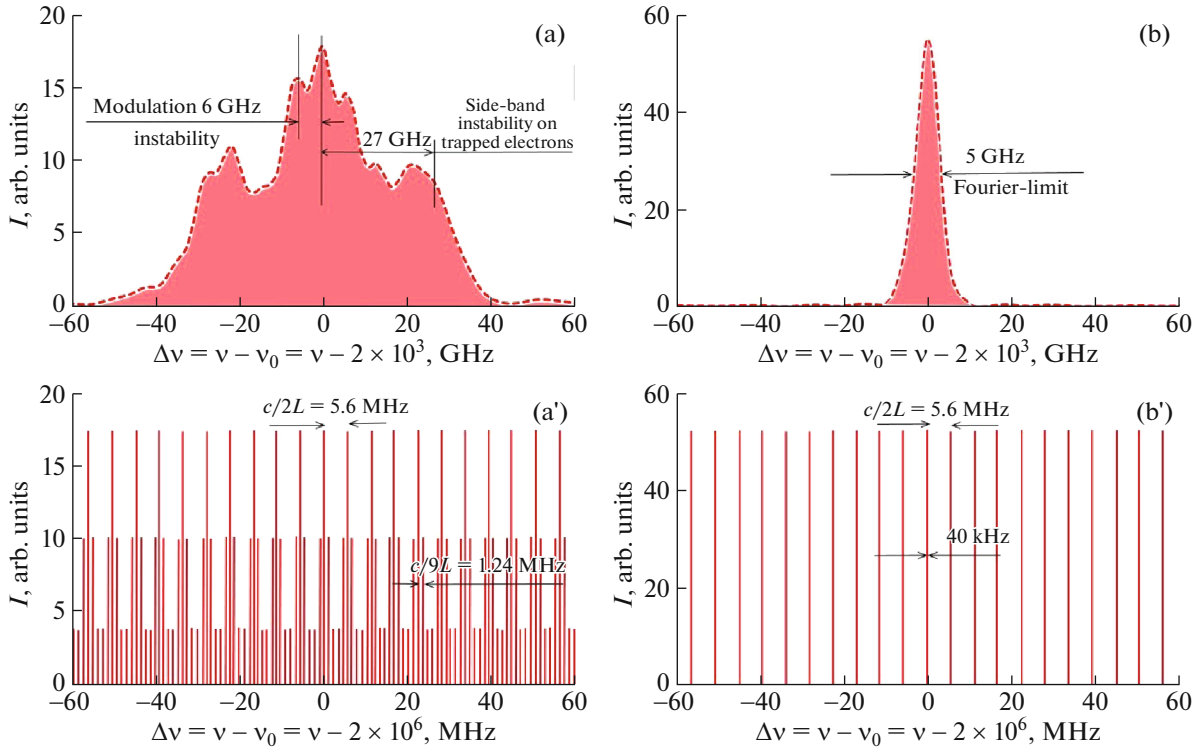

Fig. 1. (a) Characteristic spectrum of terahertz NovoFEL radiation near a central frequency of 2 THz in the resonant unstable regime; (a') spectrum sweep near the center for the regime with low-frequency mode instability; (b) terahertz NovoFEL spectrum in the stabilized stable regime; (b') spectrum sweep near the center for a regime without low-frequency mode instability.

erably, though stabilizing technical fluctuations in a facility as large as the NovoFEL would be much more expensive than in desktop quantum lasers.

The radiation spectrum of a terahertz NovoFEL described above (Fig. 1b) corresponds to the stabilized operating regime of the NovoFEL, when various instabilities that can alter the spectrum of its radiation are suppressed [5–7]. Three types of instabilities have been observed at the terahertz NovoFEL: two fast instabilities at high frequencies (modulation instability and instability on trapped electrons) [5, 6] and one specific mode instability at very low frequency $c/(9L) = 1.24$ MHz associated with the excitation of mode axis oscillations at the periodicity frequencies of a stable open terahertz NovoFEL resonator [7]. All instabilities appear in the NovoFEL spectra as modes at the side frequencies for low-frequency instability, or as side super-modes surrounding a stabilized super-mode (Fig. 1a). For simplicity, all three instabilities are depicted in Fig. 1a as existing simultaneously. This situation is possible but quite rare, since all three instabilities are independent of one another in a first approximation and usually observed separately. High-frequency instabilities were especially evident in the first experimental modes of the NovoFEL, where its radiation pulses were longer than 200 ps [6]. In contrast to the NovoFEL regimes used today with pulse durations of around 100 ps, where they are somewhat suppressed, the instabilities had time to develop fully. The physics of these instabilities was considered in the works mentioned above. Here we will limit ourselves to noting the successful suppression of high-frequency instabilities by special negative detuning of the frequency of repetition of electron pulses from the frequency of rotation of an intracavity light pulse [5, 6]. There is no instability in the low-frequency mode if the electron beam is carefully adjusted to the axis of the intracavity super mode and the spread of energy is minimized [7] (Fig. 1b). Despite the halving of the NovoFEL's total output power during stabilization by frequency detuning (≤2 times), its spectral power grows and reaches a maximum during stabilization [5], since the NovoFEL gain contour narrows more (by 5–7 times) than the drop in power. It is therefore always advantageous to work in a stabilized mode when making spectroscopic measurements on the NovoFEL. In addition to very good coherence, this also ensures strong responses (signals) from resonance phenomena. Note too that the spectral pattern of NovoFEL radiation in the form of narrow mode lines is a reflection of its fundamental laser nature and is virtually independent of the presence or absence of instabilities. Powerful NovoFEL radiation in a resonant mode with developed HF instabilities can be considered the simultaneous generation of several (5–7) well-coherent

Table 1. Parameters of terahertz NovoFEL radiation and the main parameters of the electron beam in the single-turn accelerator-recuperator mode

Parameter (unit dimensions)	Value	Notes
Wavelength (μm)	90–400	Laser generation at the 3rd harmonic is possible at long waves (>200 μm)
Frequency (THz)	0.75–3.3	
Relative spectral width of the gain loop (FWHM, %)	0.2–3	The minimum value is in the stabilized regime; the maximum is in the resonant regime
Monochromaticity: relative width of mode lines (FWHM)	2×10^{-8}	
Pulse duration (ps)	70–120	
Pulse repetition frequency (MHz)	5.6 11.2 22.5	1 intracavity pulse, 2 intracavity pulses, 4 intracavity pulses
Maximum peak power (MW)	0.9	At a frequency of 5.6 MHz and a wavelength of 130 μm
Maximum average power (W)	300 500	at 5.6 MHz at 22.5 MHz
Polarization of radiation	Linear	
Shape and size of beams at stations	Centimeter-sized Gaussian beams	Beam sizes vary at different stations
Electron energy (MeV)	12	
Maximum peak electron current (A)	20	
Maximum average electron current (mA)	20	

lasers, the phases of which are not synchronized or coherent with one another.

A similar situation with coherence is observed when two or four intracavity light pulses are created in the NovoFEL's optical cavity. This is achieved by doubling or quadrupling the rate of repetition of electronic pulses from 5.6 to 11.2 or 22.5 MHz. Since the intracavity pulses are separated in space and time, they must not be coherent with one another. However, partial coherence is possible in a number of FELs with many intracavity pulses when (a) the rate of repetition of the electronic pulses is kept constant with good accuracy and (b) the electronic pulses have a surge in the amplitude of the current that is much shorter than the emitted wavelength. Intracavity light pulses are automatically phase-locked with one another through electron bunches and are usually partially coherent [8]. According to the Fourier transform, a fine structure of the radiation spectrum should appear in the radiation spectrum, due to additional modulation of the ultrafine 5.6 MHz mode structure at electronic pulse repetition frequencies of 11.2 or 22.5 MHz. The linewidth of such modulation will be equal to the inverse number of coherent intracavity pulses. In the limit of their complete coherence, the ultrafine mode structure at a frequency of 5.6 MHz is replaced with an ultrafine mode structure that has a frequency of 11.2 or 22.5 MHz. In reality, the two conditions mentioned above for the coherence of intracavity pulses on a terahertz NovoFEL are not satisfied. so is no fine mode structure of radiation from the NovoFEL. The NovoFEL radiation spectrum is identical at frequencies of 5.6, 11.2 and 22.5 MHz, since only the power of the radiation changes. It should ideally double and quadruple in correspondence with two or four independent lasers incoherent with each other with a frequency of 5.6 MHz. This property of no coherence between two intracavity NovoFEL light pulses at a frequency of 11.2 MHz is used in a unique way of measuring coherence in each sequence of pulses at frequencies of 5.6 MHz with virtually any degree of accuracy [3].

Radiation from NovoFEL lasers inside a radiation-protected room is transported to safe user premises in the form of Gaussian beams through long transport channels of an open optical type, filled with a nitrogen-air mixture constantly dried of water vapor at atmospheric pressure [9]. The radiation parameters of terahertz NovoFEL described above are listed in Table 1.

EXPERIMENTS ON ULTRAFAST MOLECULAR TERAHERZ SPECTROSCOPY

When considering the potential capabilities of the terahertz NovoFEL in the field of molecular spectroscopy,

an important criterion for selecting experiments is their uniqueness. This allows us to justify the use of NovoFEL, which is expensive to operate, instead of other simpler and cheaper sources of terahertz radiation. By uniqueness we mean not just the originality of the experiments, but a certain expansion of terahertz spectroscopy in terms of procedures, conditions, and objects of study. The radiation parameters of the terahertz NovoFEL described above are particularly suited for the pulsed ultrafast spectroscopy of molecules in the given time domain. Ultrafast spectroscopy is required for spectral measurements of such single-shot unstable phenomena as combustion or explosion, especially in the diagnostics of short-lived radical molecules, which are an important intermediate component of many chemical reactions.

Here we should immediately note the fundamental difference between true ultrafast measurements at NovoFEL in real time, from various stroboscopic technologies, such as step-scan mode Fourier transform spectrometers or the currently common terahertz time-domain spectrometers based on femtosecond lasers. Like a conventional stroboscopic oscilloscope, these methods allow us to measure fast, but only strictly repeating phenomena, and repeating them many times, since these measurements are carried out at many points in time, shifted from the beginning of the phenomenon, which actually takes quite a long time. At the same time, it is often impossible to distinguish real time changes in the signal from measurement artifacts without special control of the stability of the measured signal by some parallel method, which, as a rule, is impossible. Therefore, these methods only work for a priory stable rapid phenomena.

Moreover, a feature of linear direct ultra-fast real-time measurements is the ability to accumulate signals that fluctuate in magnitude as a whole (which is completely impossible in stroboscopic methods) to statistically increase the signal-to-noise ratio without degrading the spectral resolution. As is known, ultrafast detectors that are broadband in carrier and detected frequencies always have low sensitivity and, therefore, a low signal-to-noise ratio. Therefore, whenever possible, our measurements use the accumulation of hundreds and thousands of signals to increase measurement accuracy, especially since at the megahertz pulse repetition rates of NovoFEL this takes little time.

The physical basis of molecular spectroscopy at terahertz NovoFEL is the effect of free induction radiation of molecules. The frequency of the NovoFEL super-mode is tuned to any molecular rotational transition of the molecule under study in the ground vibrational state or to several characteristic transitions at once. After exciting a molecule with such a short pulse, it emits for some time at its characteristic frequencies. The power of this radiation of free induction of a molecule (Free Induction Decay, abbreviated as FID) is measured by direct or heterodyne detection in real time. For such time-domain spectroscopy, ultrafast detectors based on Schottky diodes [10, 11] and digital broadband direct oscilloscopes from LeCroy and Keysight Technologies are mainly used since the signals are in the nanosecond and subnanosecond ranges. Most often, practical experiments require spectroscopic detection of a particular known molecule, the transitions of which can be found in one of the modern databases (analytical spectroscopy). In this case, it is necessary to calculate the characteristic time signal of the free induction of a molecule for a given spectral excitation. An excellent computational model is the semiclassical Lorentz dispersion theory, in which the characteristics of transitions are taken from databases compiled from quantum mechanical calculations, and each transition is then considered a classical oscillator with given parameters. The FID time signal of illuminated molecular transitions is, according to the Fourier transform, a complete time analogue of their frequency spectra. More precisely, complex fields (characterized by amplitude and phase) in time and frequency representations are complete analogues. In the case where NovoFEL illuminates many sufficiently strong transitions of a molecule, a single free induction power signal, which in this case is very individual, is sufficient to identify it.

In complex spectroscopic experiments, when the molecular composition is unknown in advance, a solution to the problem of general spectroscopy is required, when a complex spectrum is found from the measured complex time signal of free induction (two field projections on the complex plane) and the molecular composition is deciphered with a certain accuracy from it. When molecules are illuminated at high quantum number transition frequencies with multiple sublevels, their FID signals are very individual—the overlap integral of the FID signals of two different molecules typically does not exceed 1%.

The diagram of an ultrafast heterodyne polarization spectrometer is shown in Fig. 2 [12]. In it, in two perpendicular polarizations, two FID signals are simultaneously measured, phase shifted by $\pi/2$: cosine and sine projections of the complex field. The spectrometer can measure both single-pulse spectra and spectra accumulated over multiple pulses. The spectral resolution of the spectrometer is directly proportional, according to the Fourier transform, to the time of spectrum measurement or the duration of the FID signals in the measuring and reference heterodyne channels (Fig. 3). As the fastest spectral measurement (300 ps), this figure shows an experiment on measuring the spectra of single terahertz NovoFEL pulses in the modulation instability mode (Fig. 4) [13]. The same figure shows the same NovoFEL spectrum measured with a Fourier transform spectrometer with approximately the same resolution. It can be seen that all the characteristic features of single-pulse spectra disappear when averaging over many pulses in Fourier

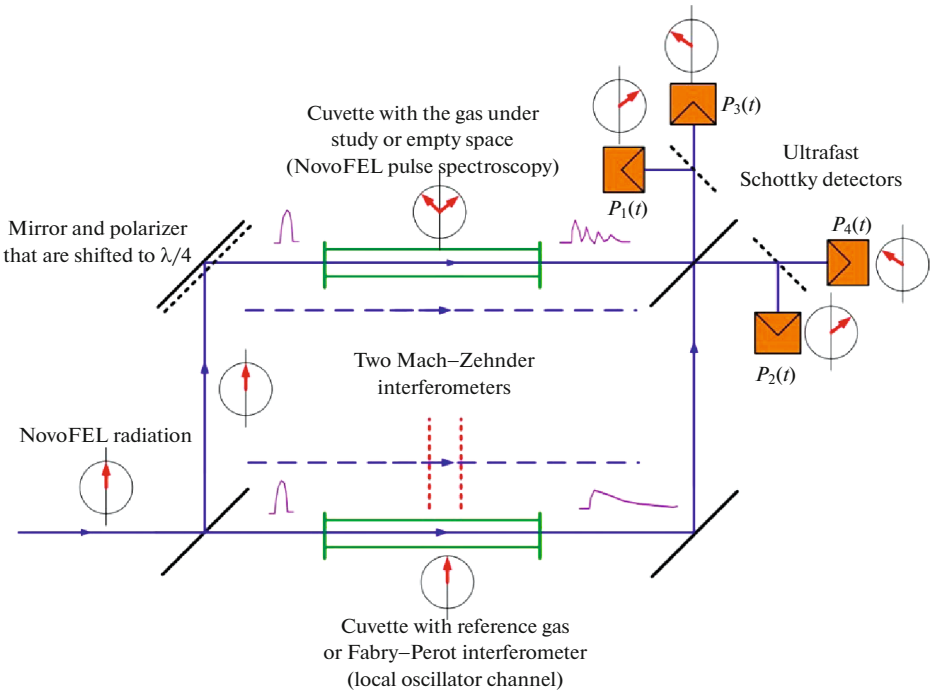

Fig. 2. Optical design of a heterodyne polarization spectrometer. Arrows in circles indicate the direction of the polarization of the radiation's electric field.

measurements. A part of the NovoFEL excitation pulse, extended using a Fabry–Perot interferometer (FPI), was used as a heterodyne signal. In general, this method of creating a heterodyne signal is the most universal, since it works at all NovoFEL wavelengths. However, creating a very long (>10 ns) heterodyne signal using FPI is a very difficult task (see next section), and the amplitude of a longer signal is greatly reduced. Therefore, where possible, we used molecular heterodyne cells filled with hydrocyanic acid (HCN) vapor or carbon monoxide (CO) at low pressure with well-known frequency spectra.

In addition to the possibility of obtaining complete information about a complex radiation field of molecules and linking its frequencies to that of a known local oscillator, heterodyne measurements have another important advantage over simple measurements of free induction radiation power. The latter is proportional to the square of the concentration of emitting molecules, while the heterodyne signal is proportional to the FID field and the first power of the concentration. As the concentration falls, the power of the FID radiation drops much faster than the heterodyne signal. This allows us to increase the sensitivity in heterodyne measurements by at least two orders of magnitude [14].

Another important way of increasing the sensitivity and individuality of the spectra of molecules with a magnetic moment is to use a magnetic field. The cardinal difference between our fast coherent and quasi-stationary measurements is the much stronger effect of the magnetic field. A magnetic field of only a few hundred Gauss is enough to obtain a full-scale Zeeman effect that rotates the plane of radiation polarization by more than 90°. By observing FID radiation in a polarization perpendicular to the polarization of a powerful pulse of NovoFEL excitation, we can almost completely prevent it from entering the detector sys-

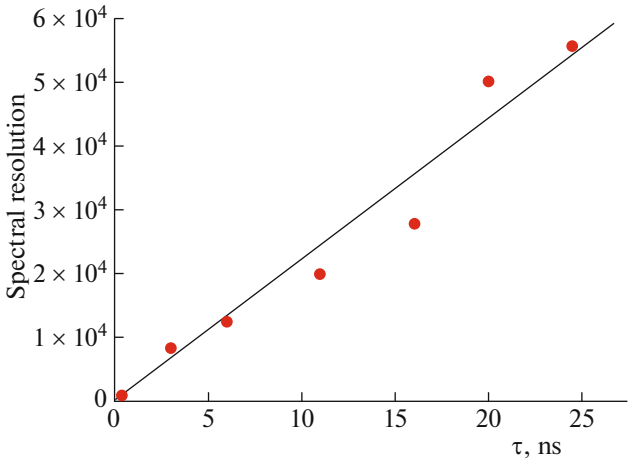

Fig. 3. Spectral resolution of a heterodyne polarization spectrometer, depending on the period of measuring. The leftmost experimental point has a resolution of 1000 with a 300 ps period of measuring, obtained in an experiment on the spectroscopy of individual NovoFEL pulses in the mode of modulation instability.

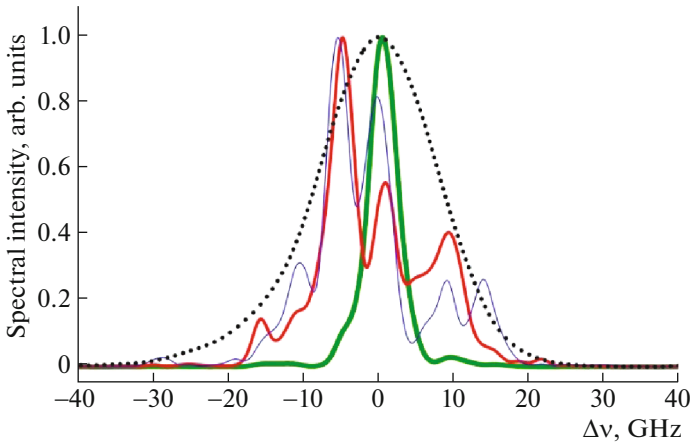

Fig. 4. Spectra of individual NovoFEL pulses in the regime of modulation instability (three solid lines) and the NovoFEL spectrum recorded under the same conditions with a Fourier transform spectrometer (averaged over many pulses) at the same spectral resolution (dashed line; side frequencies not detected).

tem. This allows us to use detectors with much greater sensitivity (e.g., Schottky detectors with the optimum antenna and detectors based on superconductivity) that cannot withstand excitation pulse power three orders of magnitude greater. In addition, the magnetic field splits the lines on values of the projection of the magnetic moment, adding to the modulation of the FID signal characteristic of a detected molecule.

Molecular spectroscopy experiments at the NovoFEL began in 2011. Let us briefly list the main works that describe specific experiments in detail. Chesnokov et al. [15] described the world's first direct detection of FID radiation from molecules in the terahertz region using the example of an HDO + H_2O mixture and isotopic mixture $H^{81}Br$ + $H^{79}Br$. A universal scheme for a polarization heterodyne spectrometer was proposed in [12]. A free induction signal with a record long duration of 180 ns was obtained in [16] for an isotopic mixture of $H^{81}Br$ + $H^{79}Br$ at low pressure corresponding to a maximum Doppler spectral resolution of several megahertz and the limit where we can still ignore the hyperfine mode structure of NovoFEL radiation (Fig. 5). The nature and effect of the characteristic spike in the FID emission of a molecule was explained in [17], using an NO_2 molecule with many lines in the molecular bands around 81.8, 67.3, and 52.6 cm^{-1}. Like a spectrum, this spike can serve as a fingerprint to detect the molecule. Non-Faraday rotation of the plane of polarization of FID radiation from a paramagnetic NO molecule was studied in [18] in the region of its molecular bands at 66.8 and 65.2 cm^{-1}. Rotation of the plane of polarization of more than 180° is shown by a magnetic field of less than 1 kG. A gas cell with HCN was used for sensitive heterodyne measurements of CH_3OH (70.8 cm^{-1}) and HBr (49.9 cm^{-1}) in [19]. The first experiments on detecting the short-lived OH radical without a magnetic field are described in [20]. The dynamics of its birth and relaxation in a fast photochemical experiment ("spectral cinema") were traced by measuring its FID signals after several dozen pulses of NovoFEL excitation. The effect of a magnetic field on the emission of paramagnetic NO and OH molecules was described in [21]. The authors of [22, 23] described and explained the FID signals of the OH radical in a magnetic field (Fig. 6). The effect of reversing the FID signal of a molecule to the opposite direction of the magnetic field was described in [24], using the example of the OH radical. This effect is used in all our magnetic measurements to subtract spurious signals that do not depend on the direction of the field. Finally, the sensitivity of magnetic heterodyne measurements of the OH radical was raised by at least two orders of magnitude in [25], relative to earlier homodyne measurements. Two serial FPIs 12 and 50 mm long served as a heterodyne pulse expander.

POSSIBLE EXPERIMENTS IN THE FIELD OF ULTRA-HIGH-RESOLUTION TERAHERTZ MOLECULAR SPECTROSCOPY

The previous section considered spectroscopic experiments with resolutions of no more than $\nu/\Delta\nu \sim 3.5 \times 10^5$, corresponding to the time needed to measure the signal of free induction of molecules: 180 ns, the interval between adjacent NovoFEL pulses. The maximum spectral resolution of NovoFEL is equal to the inverse relative width of the mode lines (5×10^7) and corresponds to the interval occupied by 140 coherent NovoFEL pulses. The spectral potential of the NovoFEL not obtained in terms of resolution is more than two orders of magnitude. Special spectral objects ("cold molecules") and the corresponding special equipment to create them are needed to realize this potential, since the spectral resolution we have

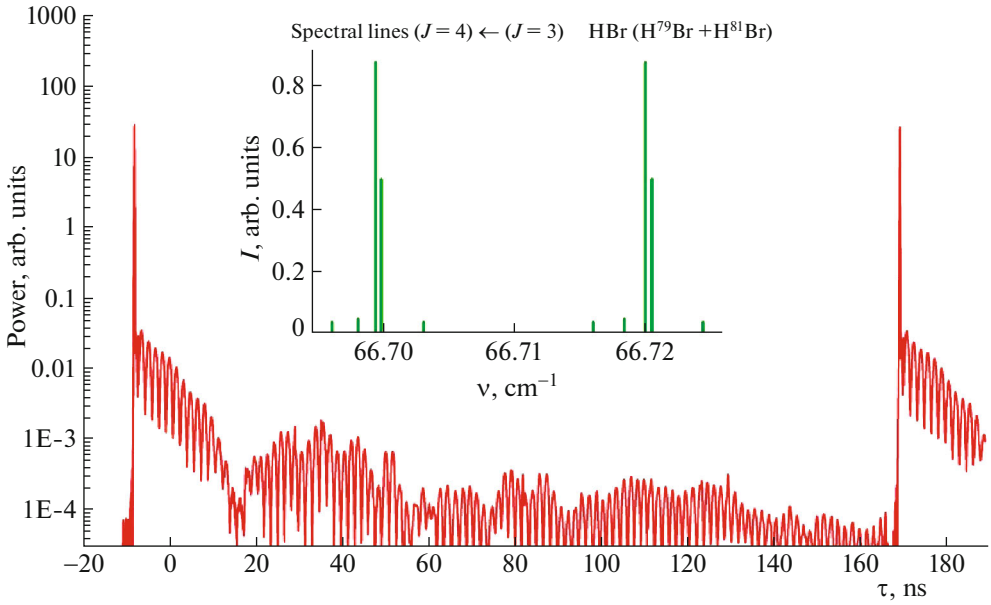

Fig. 5. Free induction signal of a natural isotopic mixture of HBr molecules between two powerful short NovoFEL excitation pulses. The tab shows the spectral lines that produce this signal. High frequency modulation is isotopic line splitting.

now corresponds approximately to the Doppler broadening of molecular lines at room temperature. Of course, we improve the resolution even more by measuring the position of the center of gravity of the Doppler-broadened lines more accurately. However, this is usually done for ratios of line width to instrumental function of no more than 20–30.

Note that the exponential decay of the free induction signal of cold molecules over a period of 140 coherent NovoFEL pulses will be compensated for by the coherent excitation of molecules from 140 consecutive pulses. For example, the magnitude of the FID signal of cold HBr molecules will be on the same order as in Fig. 5 (i.e., it is quite measurable). However, the waveform of the molecule's free induction will be without modulation, since individual lines of the molecule will be excited by different NovoFEL mode lines when configured appropriately. Modulation will appear when using a local oscillator in form of a cell with a cold heterodyne gas or a terahertz gas laser. Through this modulation the measured lines can be linked to the local oscillator line and all other important advantages of heterodyne measurements described in the previous section can be enjoyed.

Another means of high-resolution spectroscopy closer to the ones currently used was proposed in [26]. The idea was to convert pulse-periodic NovoFEL radiation into continuous tunable monochromatic radiation. As was shown in [26], this can be done using three serial resonant FPIs 1/10, 1/100, and 1/1000 of length L of the NovoFEL optical resonator. Resonant FPI length $L/10$ is now used to diagnose NovoFEL radiation, especially the parameters shown in Figs. 1a', 1b'. Each FPI passes through every tenth line of radiation arriving at its input, so one central mode line of the longitudinal super-mode remains. The power of this monochromatic line, which corresponds to quasi-continuous radiation, is $(1/1000)K$ of the average power of the NovoFEL, where $K \approx 0.2$–0.3 is the coefficient of real losses in the FPIs. The maximum monochromatic tunable radiation power of the NovoFEL is thus 60–100 mW, and at least 10 mW in a wide range of wavelengths. Note that the typical power of continuous THz radiation sources used in high-resolution spectroscopy is tens of nanowatts and approaches microwatts in the long-wavelength range. Even after a ×1000 thinning of the NovoFEL modes, the power that remains is at least 1000 times greater than that of desktop alternative sources. Since the signal-to-noise ratio of even strong THz lines is unity (<10) in modern experiments even with the most sensitive helium bolometers, we believe it is relevant to raise the power of the source. Of course, we must stabilize the lengths of all FPIs, including that of the NovoFEL's optical cavity, to obtain such a source. However, this is quite feasible if we use feedback systems and piezo displacements.

At the NovoFEL, we can also perform experiments on the so-called comb spectroscopy currently popular at synchrotrons [27]. The spectrum of molecules is depicted as dips in the lines of the comb structure (Fig. 1b'), due to absorption in a molecular gas. This technique does not have the highest spectral resolution. To improve it, we must minimize the distances between the lines of the comb structure. This can be done on the NovoFEL by specially tuning the stable generation of longitudinal modes with enhanced side frequencies (Fig. 1a') [7].

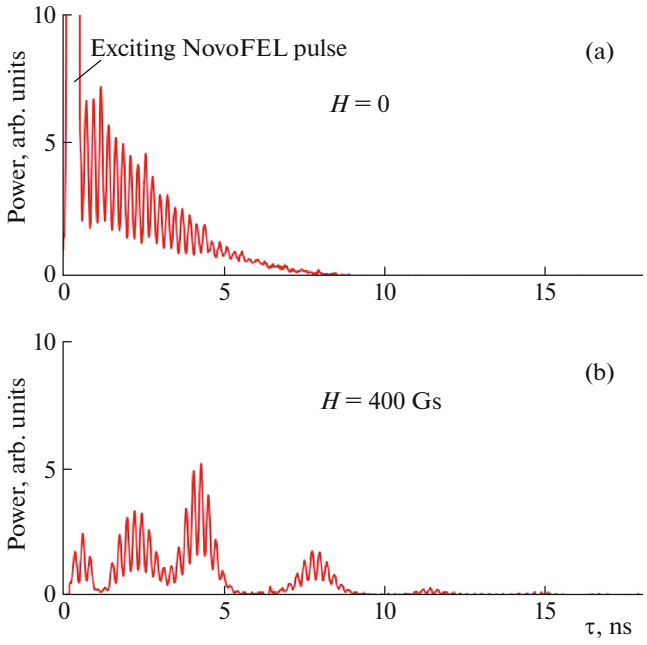

Fig. 6. OH radical free induction signal: (a) without a magnetic field and (b) in a weak magnetic field for polarization perpendicular to the polarization of an NovoFEL excitation pulse that is completely suppressed. The high-frequency modulation of both signals is the Λ-splitting of OH lines, independent of the magnetic field. Depending on the magnitude of the magnetic field, the low-frequency modulation is the beating effect of lines split by the Zeeman effect and non-Faraday rotation of the plane of polarization.

CONCLUSIONS

The high spectral power, wide range of smooth tuning, and laser quality of terahertz NovoFEL radiation allow us to conduct unique experiments in the field of molecular spectroscopy. Many unique techniques for ultrafast time-domain spectroscopy of molecules and NovoFEL radiation have been obtained. The great potential of the NovoFEL in the field of ultra-high-resolution terahertz spectroscopy has been demonstrated.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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