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HIGH-RESOLUTION MOLECULAR SPECTROSCOPY IN TOMSK: ESTABLISHMENT, DEVELOPMENT, AND CURRENT STATUS

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The paper presents brief information about the establishment and development in Tomsk of high-resolution molecular spectroscopy – the field of science closely related to a study of the optical properties of the atmosphere. The methods and the current state of high-resolution laser spectroscopy and Fourier spectroscopy are described together with new results of mass measurements. The developed theoretical methods for a study of molecular spectra, including methods of their global analysis and information systems of spectral databases, are presented.

Keywords: high-resolution molecular spectroscopy, absorption spectra, laser spectroscopy, Fourier spectroscopy, atmospheric optics, information systems, spectral databases.

INTRODUCTION

The emergence and development of spectroscopy in Tomsk is in many respects associated with Professor N. A. Prilezhaeva, a disciple of the Leningrad Spectroscopic School. Spirit and ideas of this School, in essence, provided the basis for subsequent new directions of fundamental and applied spectroscopic research in Tomsk State University (TSU) and in Siberia as a whole from which, in particular, the independent scientific direction of high-resolution molecular spectroscopy originated.

Putting into operation of the first laser in Tomsk in 1963 preceded the beginning of the laser epoch in Tomsk and of the rapid development of methods of laser spectroscopy, laser sensing of the atmosphere, high- and ultrahigh-resolution spectroscopy, and in this connection, requirements to theoretical methods of extracting physical information from experimental absorption and emission spectra of small and large molecules for solving both fundamental and applied problems sharply increased. The advent of lasers gave a new impetus to investigations on the problem of optical radiation propagation in the atmosphere – the basic scientific direction of the Laboratory of Infrared Radiation (head of the Laboratory V. E. Zuev who later became Academician of the Russian Academy of Sciences) founded at the Siberian Physical-Technical Institute (SPTI) at TSU in 1960. Foundation of this Laboratory was *the bullseye shot*: on its basis the Department of Optoelectronic Devices (1962) and then the Institute of Atmospheric Optics of the Siberian Branch of the Academy of Sciences of the USSR (nowadays V. E. Zuev Institute of Atmospheric Optics of the Siberian Branch of the Russian Academy of Sciences, IAO SB RAS) were founded in 1969.

Since the foundation of the direction of atmospheric spectroscopy at the Institute of Atmospheric Optics of the SB RAS, Academician Vladimir Evseevich Zuev had made the choice in favor of integrated development of methods of theoretical and experimental high-resolution spectroscopy as bases for solving problems of laser radiation propagation in the atmosphere, analysis of gas composition of the atmosphere by local and remote methods, and allowance for the molecular absorption in radiation balance of the atmosphere.

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To implement this complex program, the Laboratory of Statistical Optics (head of the Laboratory S. D. Tvorogov), the Laboratory of Theoretical Spectroscopy (head of the Laboratory Yu. S. Makushkin), and the Group of Laser Spectroscopy (head of the Group V. P. Lopasov) were organized in 1970.

In the process of development of the spectroscopic direction, new laboratories were organized already as parts of the Spectroscopy Department and then Division. In early 1995, the Laboratory of Statistical Optics (headed by S. D. Tvorogov), the Laboratory of Theoretical Spectroscopy (headed by V. I. Perevalov), the Laboratory of Laser Spectroscopy (headed by V. P. Lopasov), the Laboratory of Atmospheric Absorption Spectroscopy (headed by Yu. N. Ponomarev), the Laboratory of Molecular Spectroscopy (headed by L. N. Sinitsa), the Laboratory of Fluorescent Methods of Research (headed by V. M. Klimkin), and the Laboratory of Quantum Electronics (headed by G. S. Evtushenko) were founded.

Until 2005 experimental investigations of high-resolution spectra at the IAO had been performed using a complex of laser spectrometers (laser spectrophotometers and intracavity, optoacoustic, and fluorescent laser spectrometers [1, 2]) that provided high spectral resolution and sensitivity, but operated in limited sufficiently narrow visible and near-IR ranges. In the last decade a complex of Fourier spectrometers has been developed that has allowed large-scale research of the selective and nonselective absorption of molecules in the UV to far-IR ranges to be investigated together with spectral line shapes and their transformation attendant to variations of the pressure and temperature of the examined gas [3–5].

The development of theoretical methods at the IAO SB RAS and TSU and the existing international collaboration are aimed at global modeling of high-resolution spectra of atmospheric gas molecules with accuracy close to that of modern experimental methods [6–8]. These data on several ten to hundred thousand spectral absorption lines of atmospheric molecules and their isotopologues are accumulated in international databases [9, 10] and actively used for solving applied problems of atmospheric optics.

The spectroscopic cluster formed in Tomsk continues to generate new directions of research on molecular spectroscopy and creates conditions for the development of new scientific structural and creative associations. Investigations on high-resolution spectroscopy launched at the IAO SB RAS and continued in TSU have returned like a boomerang again in TSU, but already on the new level joining efforts of researches involved in vibrational-rotational spectroscopy at the IAO SB RAS and in electronic spectroscopy and molecular photonics in TSU. Thus, the Laboratory of Quantum Mechanics of Molecules and Radiation Processes founded in 2013 on the basis of TSU united into one creative group scientists from the IAO SB RAS, TSU, and University of Reims (France). It has allowed interdisciplinary problems of IR and electronic spectroscopy of not only gaseous media, but also complex organic systems to be formulated and solved, including a study of their electronic structures and molecular spectral and optical properties in a wide range of conditions for isolated and interacting quantum systems with application to biophotonics and synthesis of perspective photosensitive materials and light emitting organometallic materials.

In this paper a brief review is presented of the current state of experimental methods and techniques of high-resolution molecular spectroscopy, theory of rotational-vibrational spectra of molecules of planetary atmospheres, and development of international spectroscopic databases with active participation of Tomsk scientists.

1. THEORY OF VIBRATIONAL-ROTATIONAL SPECTRA AND SPECTROSCOPIC DATABASES

The effective operator method based on degenerate perturbation theory is traditionally used for a description and analysis of high-resolution spectra of molecules. Great attention at the IAO SB RAS was focused on the development and analysis of this method. The superoperator degenerate perturbation theory was proposed and subsequently generalized to the case of quasi-degenerate zeroth approximation [11, 12]. Great attention was paid to a study of ambiguity of the effective Hamiltonians – a consequence of the nature of the degenerate perturbation theory. Reduced forms of effective Hamiltonians with parameters unambiguously retrieved from an experiment were proposed for spherical [13], symmetric [14], asymmetric top [15, 16], and linear molecules. Great attention was also paid to the development of the theory of high-resolution spectra of non-rigid molecules [20]. To remove divergence of series in the perturbation theory in the case of non-rigid molecules, the method of generating functions was proposed [21, 22]. The problem of summing divergent series in the perturbation theory is so far in the focus of attention of theoretical

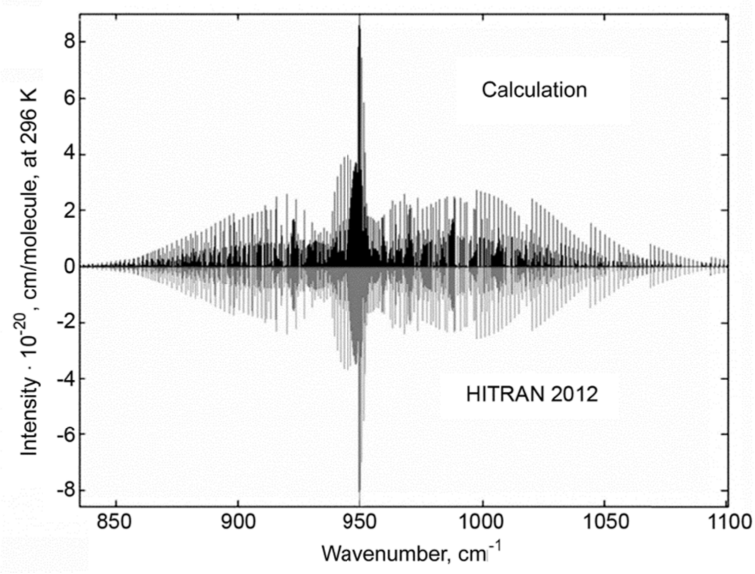

Fig. 1. Comparison of the intensity diagrams of high-resolution spectra of the C_2H_4 molecule in the range 850–1100 cm^{-1} calculated using the variational approach [25] with the spectrum from the HITRAN database [26] (experiment).

researchers of the Institute [23]. The isotopic substitution theory was developed in [24] for spectra of polyatomic molecules.

Since the middle 90s of the last century, the direction of global modeling of high-resolution spectra of molecules has actively been developed in the Laboratory of Theoretic Spectroscopy of the IAO SB RAS. Here global modeling means a description of high-resolution spectra of molecules by one and the same theoretical model in wavelength ranges from microwave to visible ones. It is important to note that the purpose of modeling is obtaining the accuracy of calculations of the spectral line parameters comparable with that of the present-day experiments. Two directions are being developed: the effective operator method based on the perturbation theory and the variational approach based on *ab initio* calculated potential energy surfaces and dipole moments. The developed models make it possible to calculate the parameters of spectral lines on transitions between highly excited vibrational-rotational states, including those for high-temperature spectra. We note that recording of high-temperature spectra is a challenging and sufficiently time-consuming procedure, and it is practically impossible to encompass in one experiment a wide range of temperatures.

The effective operator method is semiempirical, and its effective application is possible in the presence of sufficiently large array of input experimental data. The variational approach can be implemented in both theoretical and semiempirical variants. However, it requires more powerful computers and its accuracy is inferior to line center calculations by several orders of magnitude. As for the line intensities, the present-day *ab initio* calculations of the dipole moment surface make it possible to calculate the line intensities with accuracy close to experimental one. As an example of the efficiency of the variational approach, a comparison between the intensity diagram for ethylene plotted on the basis of the calculated ethylene spectrum and the HITRAN database [26] is shown in Fig. 1 borrowed from [25]. We note that this database comprises mainly experimental data. As follows from the figure, the two diagrams are practically bird's eye view indistinguishable. The high-resolution spectra of the methane [27, 28] and ethylene [25, 29] molecules were modeled using the variational approach, and the list of high-temperature lines of the methane molecule was presented in [30].

Global modeling of the high-resolution spectra of carbon dioxide [31, 32], acetylene [33], nitrous oxide [34], and nitrogen dioxide [35] molecules was successfully performed within the framework of the effective operator method. For the carbon dioxide molecule, modeling was done for all twelve stable isotopic modifications [36]. For nitrous oxide, the main isotopic modification $^{14}N_2{}^{16}O$ was modeled [34] as well as four rare isotopic modifications $^{14}N^{15}N^{16}O$ [37], $^{15}N^{14}N^{16}O$ [37], $^{14}N_2{}^{18}O$ [38], and $^{15}N_2{}^{16}O$ [39].

The global modeling makes it possible to develop three versions of the carbon dioxide spectroscopic databank (CDSD) for the spectral line parameters: the version for atmospheric applications CDSD-296 [36] and the two versions for high-temperature applications CDSD-1000 [40] and CDSD-4000 [41]. This databank is widely used in different applications. The CDSD-296 version was included in HITRAN [26] and GEISA [42] international spectroscopic databases, and the CDSD-1000 version was involved into the high-temperature (HITEMP) international database [43]. The use of the high-temperature databases makes it possible to follow the spectrum evolution with temperature.

The CDSD-1000 databank was repeatedly tested experimentally on the example of the high-temperature low-resolution spectra of carbon dioxide [44, 45]. We note that when the accuracy of the experiment increases, the experimental spectrum approaches to the spectrum simulated using CDSD-1000. The authors who tested the spectral line parameter databank [45–47] claimed that it seemed not necessary to continue measurements of the transmission of the $CO_2/H_2O/N_2$ mixture in the temperature range 500–1700 K at atmospheric pressure; to generate these data, the HITEMP database could be used with confidence.

The free high-temperature nitrous oxide spectroscopic databank (NOSD-1000) (ftp.iao.ru/pub/NOSD/) and nitrogen dioxide spectroscopic databank (NDSD) (ftp.iao.ru/pub/NDSD/) have been developed on the basis of the results of global modeling of high-resolution spectra of the N_2O and NO_2 molecules. The program complex was developed at the IAO SB RAS that provides retrieval of the spectral line parameters in spectra of any arbitrary origin. This program complex together with professional skills of researchers made it possible to analyze a lot of experimental spectra of atmospheric gas molecules. The spectroscopic data obtained were involved into the HITRAN [26] and GEISA [42] international databases.

In addition, the Institute became a member of the Virtual Atomic and Molecular Data Center (VAMDC) [48] established under the 7th European Framework Program. Data presentation standards and interfaces that allowed users to extract the required data from the databases belonging to the participants of this association in a unified form were developed in the association. In addition to the spectroscopic databanks, spectroscopic information systems have been created at the IAO SB RAS that are in high demand not only in our country, but also abroad. Among them are "Spectroscopy of Atmospheric Gases (Spectra)" (http://spectra.iao.ru/), "Spectroscopy and Molecular Properties of Ozone" (http://smpo.iao.ru), "HITRAN on the Web" (http://hitran.iao.ru), and "Scientific Portal on Spectroscopy SP@DIS" (http://www.saga.iao.ru/). These information systems make it possible to obtain the required spectroscopic data and to simulate different spectral functions for different mixtures of gases under different thermodynamic conditions. The transmission spectrum of the H_2O, CO_2, CO, N_2O, and NO_2 gas mixture simulated using the Spectra system is shown in Fig. 2.

Successful work of spectroscopic researchers from the IAO SB RAS would be impossible without wide international collaboration. Scientists from the Institute carried out research in collaboration with scientists from France, China, USA, Japan, England, Germany, and Belgium. The International Scientific Association on High-Resolution Spectroscopy (Spectroscopie d'Absorption de Molécules d'Intérêt Atmosphérique, SAMIA), establisted by the Russian Academy of Sciences, the Russian Foundation for Basic Research, the French National Center for Scientific Research, and the Chinese Academy of Sciences had been working from 2009 till 2012. The Institute of Atmospheric Optics played the main role in this Association from the Russian party. Currently, this Association has been transformed into the CNRS International Associated Laboratory SAMIA.

2. EXPERIMENTAL HIGH-RESOLUTION ABSORPTION SPECTROSCOPY OF MOLECULES

2.1. Laser spectroscopy

The program of the development of methods of laser spectroscopy launched at the IAO SB RAS by its founder Academician V. E. Zuev was focused on the methods which provided:

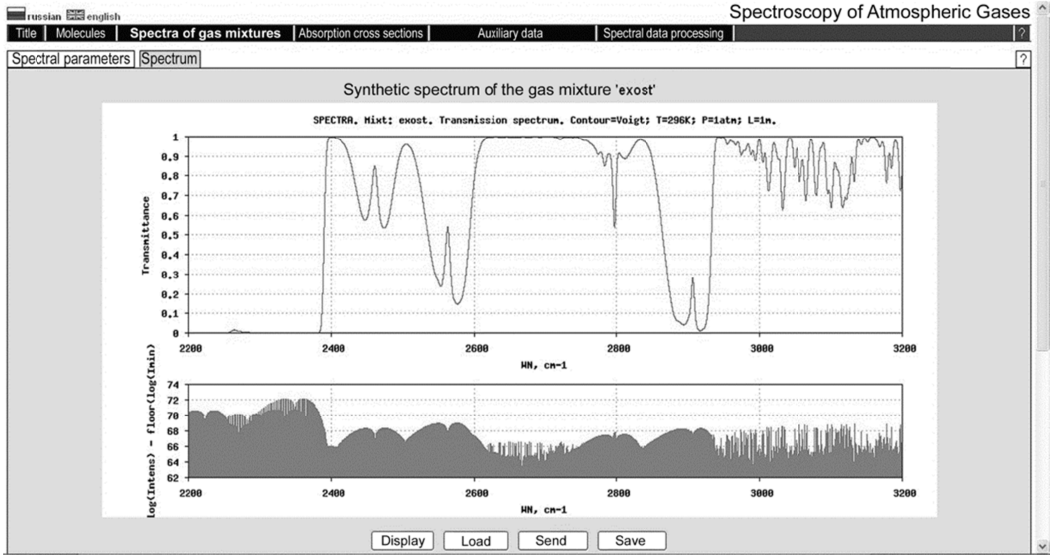

Fig. 2. Low-resolution (4 cm^{-1}) spectrum of the gas mixture (40% H_2O, 40% CO_2, 10% CO, 5% N_2O, 3% NO, and 2% NO_2) simulated by the SPECTRA information system [49] for a total gas pressure of 1 atm, an optical path length of 1 m, and a temperature of 296 K. View from the monitor screen.

– high spectral resolution 10^{-2}–10^{-4} cm^{-1} necessary for a study in detail of the structure of complex spectra, line shapes, regularities of absorption line broadening and shifting under the pressure, and effects of interference of lines in the spectrum;

– high sensitivity to the absorption coefficient to 10^{-9} cm^{-1}, which makes it possible to detect weak absorption lines that cannot be recorded in the transmission spectra of solar radiation by the atmospheric column, but are significant for taking into account losses of laser radiation energy on long near-ground paths;

– high rate of recording of the spectra (by the method of intracavity laser spectroscopy), which allows the spectra of short-living chemical compounds to be observed during time periods 10^{-6}–10^{-3} s.

Among these methods are:

1) method of laser spectrophotometry,
2) method of intracavity laser spectroscopy,
3) method of laser optoacoustic spectroscopy.

To implement each of these methods, series of laser spectrometers were developed and improved together with the improvement of frequency-tunable lasers operating in the UV, visible, and IR ranges. The developed models of the laser spectrometers were prototypes for a series of high-sensitive laser gas analyzers with concentration sensitivity on the level of ppm–ppt. A detailed review of the development and application of these methods to investigations on spectroscopy of molecules and the atmosphere is presented in [2]. Here we only briefly describe their essential features and possibilities.

2.1.1. Laser spectrophotometry

Laser spectrophotometry is natural generalization of the classic method with the difference that the laser in this case is not only the radiation source, but also the spectral device to a certain extent. Therefore, the main requirements to laser sources lie in obtaining radiation with a narrow spectrum and controllable frequency; moreover, both the spectrum width $\delta\nu$ and the frequency tuning (change) $\Delta\nu$ should be by 5–10 times less than the width of the examined spectral line (~0.01–0.05 cm^{-1} at atmospheric pressure). The spectrophotometric method is unique among the methods of laser

TABLE 1. Specifications of Laser Spectrophotometers

Laser active medium	Spectral range, cm^{-1}	Spectral resolution, cm^{-1}	Threshold sensitivity, cm^{-1}	Optical path length, m
Ruby	14395–14405	0.001	10^{-8}	60–4000
Dye	16500–16900	0.0007	$5\cdot10^{-9}$	110–10000
Alexandrite	12500–14000	0.005	10^{-8}	60–4000
Neodymium glass	9240–9520	0.0001	10^{-7}	12–228

spectroscopy. Its advantage is that the absorption coefficient is determined from the data of direct measurement of the transmission of the medium and does not require calibration.

The first high-speed laser spectrometer was realized at the IAO SB RAS in 1970 [50]. A ruby laser was used with thermal and electro-optical wavelength tuning in the process of generation and a multipass gas cavity with White's optical system that allowed the path length to be obtained up to 300 m for a distance between the mirrors of 5.5 m. The measurement techniques were refined using this spectrometer and pioneer results were obtained in absorption spectroscopy of the atmospheric water vapor.

The second spectrometer was developed on the basis of a running-wave neodymium glass ring laser [51]. Laser radiation was extremely narrow (less than 2 MHz) and was tuned in the 0.7 cm^{-1} range during a lasing pulse. The total 9240–9500 cm^{-1} tuning range of the laser frequency was attained by rotation of the dispersion prism placed inside the cavity. The position of the laser line was determined by the diffraction spectrometer with an error of 0.08 cm^{-1}. Precise frequency measurements (0.001 cm^{-1}) were carried out using a thermostabilized and evacuated Fabry–Perot interferometer with a base of 103.5 mm. The 3-m long absorption cavity with White's mirror system (optical path length of 280 m) was used in this spectrometer.

The second generation of spectrometers is a more perfect complex based on a 30-m long multipass cavity providing the path length up to 4 km [52]. A Spectra-Physics-370 cw dye laser and ruby and alexandrite pulse lasers were used as radiation sources. Active stabilization and radiation frequency tuning of the pulse lasers were performed using the special scanning Fabry–Perot interferometer; in this case, the error in determining the initial frequency did not exceed 0.004 cm^{-1}. The $5\cdot10^{-3}$–$7\cdot10^{-4}$ cm^{-1} spectral resolution and the 1–2% error in measuring the transmission were obtained.

A significant advantage of the experimental basis for laser spectroscopy was the development of the spectrophotometric complex on the basis of the 110-m long cavity [52] with the Barskaya three-mirror optical system [53]. The set of mirrors and the laser sources encompassed spectral ranges 235–270, 350–800, 1045–1075, 2090, 2650, 2936, 5300, and 10600 nm, and the optical path length changed from 110 to 10000 m.

The use of diode lasers with continuous radiation frequency tuning in the spectrophotometric method made it possible to design a mobile meter of the methane concentration in the atmosphere used to study methane emissions from bottom sediments of gas hydrates in Lake Baikal, Kuzbass mines, and plant biota [54]. Specifications of the family of the laser spectrophotometers are presented in Table 1.

2.1.2. Intracavity laser spectroscopy

The method of broadband intracavity (IC) spectroscopy proposed in 1970 by E. A. Sviridenkov and A. F. Suchkov [55] consists in suppressing laser radiation at frequencies of the absorption lines of the material put inside the broadband laser cavity. In this case, the laser radiation intensity spectrum has sharp dips at frequencies of the absorption lines that are subsequently recorded by conventional spectral devices. The method of IC spectroscopy is characterized by high sensitivity to the absorption (10^{-7}–10^{-9} cm^{-1}) that makes it efficient for a study of weak atomic and molecular spectra.

The first intracavity laser spectrometer based on a ruby laser was developed at the IAO SB RAS in 1972 [56]. Later on, a series of IC spectrometers was developed for the high-frequency spectral range based on new laser media

TABLE 2. Specifications of Intracavity Laser Spectrometers

Laser active medium	Spectral range, cm^{-1}	Spectral resolution, cm^{-1}	Threshold sensitivity, cm^{-1}	Spectral range per pulse, cm^{-1}
Ruby	14395–14405	0.02	10^{-8}	0.5–3
Dye	16500–16900	0.05	10^{-7}	20–100
Neodymium glass	9100–9520	0.02	10^{-8}	50–100
Neodymium glass	7350–7400	0.05	10^{-7}	5–10
F_2^+–LiF	10400–10500	0.05	10^{-7}	50–100
F_2^-–LiF	8000–9000	0.05	10^{-8}	50–100
$KZnF^3:Cr^{3+}$	12207–12272	0.05	8×10^{-8}	5–20

characterized by wide uniform laser gain profile, including neodymium glass [57], dyes, and alkali halide crystals with color centers operating in the bands 1050–1090, 890–960, and 1090– 1250 nm, respectively [58].

IC spectroscopy is characterized by a number of factors that make it especially efficient for a study of highly excited states of atoms and molecules and molecular kinetics:

– high threshold sensitivity to the absorption;

– small sizes of cavities that allow different excitation methods (high-temperature heating, electric charges, external fields) to be used;

– high speed of operation (a wide spectral range is recorded for about 1 ms).

Extensive investigations of the molecular absorption spectra were carried out using the developed IC spectrometers at wavelengths greater than 9000 cm^{-1}. The high sensitivity of the spectrometers made it possible to record several thousands of new weak molecular absorption lines, several tens of new vibrational-rotational bands of H_2O, CO_2, C_2H_2, CH_4, H_2, and NH_3 molecules and their isotopologues. The absorption spectra of $D_2{}^{16}O$, $H_2{}^{16}O$, and $HD^{16}O$ vapors were studied at temperatures 300–1000 K using the intracavity laser spectrometers based on the neodymium laser with a threshold absorption sensitivity of 10^{-8} cm^{-1} and a spectral resolution of 0.035 cm^{-1}, and the line shifts in the $\nu_1 + \nu_2 + \nu_3$ and $\nu_2 + 2\nu_3$ H_2O bands in the range 9403–9414 cm^{-1} were measured. Specifications of the developed spectrometers (Table 2) and results of investigation of the spectra can be found in [2, 58, 59].

2.1.3. Laser optoacoustic spectroscopy

The method of laser optoacoustic spectroscopy (LOAS) belongs to the group of methods based on the direct detection where the detector of the absorbed power is the sample itself. Its characteristic features that favorably distinguished it from other well-known methods of laser absorption spectroscopy are:

1. Recording of an OA signal against zero background. The OA signal in the absence of absorption in the sample is equal to zero.
2. The signal-to-noise ratio increases in proportion to the radiation source power. The principal limitation on the power is imposed only by the phenomenon of the saturated absorption.
3. The OA signal is proportional to the spectral absorption coefficient that essentially simplifies the experimental data processing.
4. The concentration characteristic is linear when the concentration changes by 4–5 orders of magnitude.
5. The measured value is an intensive parameter of the sample under study, i.e., it does not depend on the sample sizes; measurements are carried out in a small volume of the measurement chamber.
6. Principal limitation of the threshold sensitivity is determined by temperature fluctuations in the medium under study.

The development of LOAS at the IAO SB RAS was initiated by A. B. Antipov, and the first domestic monograph [60] devoted to LOAS was published in 1984. The highest LOAS resolution was obtained using dye and diode lasers with continuously tunable wavelength [60, 61]. The resonance OA detector in the form of a differential Helmholtz resonator [62] was successfully used in spectrometers with diode lasers.

To study the absorption spectra and the spectral line parameters of a number of molecules (CH_4, C_2H_4, etc.), the use of two differential OA detectors of the Helmholtz resonator type in the diode laser spectrometer turned out to be successful. This spectrometer equipped with a semiconductor TEC-100 laser having an output power of 3 mW for a radiation source provides a threshold sensitivity of $2\cdot10^{-9}$ cm$^{-1}\cdot$Hz$^{-1/2}$ W. This makes it possible to measure the absorption cross sections to $4\cdot10^{-23}$ cm^2/molecule typical for very weak lines. Detailed studies of the structure of the absorption spectra and of the parameters of spectral line profiles of methane and ethylene were carried out in [61, 63] in the 6030–6300 cm^{-1} tuning range of the spectrometer, and several hundreds of the ethylene spectral lines missing in the HITRAN database were recorded.

3. HIGH-SENSITIVE FOURIER SPECTROSCOPY

Nowadays panoramic study of the high-resolution absorption spectra of molecular gases from the UV to far-IR range is carried out mainly with the Fourier spectrometers. Commercial spectrometers, as a rule, are equipped with optical chambers having path lengths of several tens of meters that provide the threshold sensitivity to 10^{-6} cm^{-1}. To increase the sensitivity while retaining high spectral resolution, either long multipass chambers or radiation sources whose output power is by 2–3 orders of magnitude higher are used. Let us consider examples of implementation and application of these approaches on the example of experimental complexes developed at the IAO SB RAS.

3.1. Fourier spectrometer with the 30-m long gas chamber

One of such experimental spectroscopic complexes based on the Bruker IFS 125 HR Fourier spectrometers and the 30-m long gas chamber equipped with White's multipass system was put into operation at the IAO SB RAS in 2010 [64]. It was intended for a study of the absorption spectra in a wide spectral range from UV to far-IR with a threshold sensitivity of ~10^{-9} cm^{-1} and an optical path length of 730 m. Results of comparative analysis of the specifications of this complex and foreign systems developed at the National Institute of Standards and Technology (USA), Kitt Peak National Laboratory (USA), University of Reims (France), and the Rutherford Laboratory (UK) presented in [64] showed that its characteristics are analogous to or exceed the corresponding characteristics of the above-listed analogs. Extensive investigations of the absorption spectra of the H_2O, CH_4, CO_2, C_2H_4, and SO_2 molecules with resolution from 0.03 to 0.005 cm^{-1} were carried in [65–67] using this complex. Figure 3 illustrates the sensitivity attained and details of recording of the CO_2 absorption spectrum in the 9250–9500 cm^{-1} spectral range.

L. Wang *et al.* [68] analyzed the CO_2 spectra in this range. They succeeded in a more precise determination of the intensities of some bands and recording of the absorption lines of new vibrational bands due to an increase in the optical path length and in the signal-to-noise ratio. The noise equivalent absorption equal to $7.1\cdot10^{-10}$ cm^{-1} was determined in the range 9250–9500 cm^{-1} where several absorption bands were observed, four of which were recorded and identified for the first time: three belonged to the main isotopic modification of CO_2 (30032–10001, 30033–10002, and 22232–02201), and the fourth absorption band (20032–00001) belonged to $^{16}OC^{18}O$, which for optical path length of 726.7 m made it possible to record lines with intensity of 10^{-29} cm/molecule [65].

3.2. Fourier spectroscopy using light emitting diode sources

When using radiation sources with high spectral brightness (light-emitting diodes, LED) in the 11000–22000 cm^{-1} short-wavelength range, we succeeded in the sharp increase of the sensitivity of the Fourier spectrometers. The maximum signal-to-noise ratio equal to 45 000 was obtained with the Bruker IFS 125 M Fourier spectrometer for signal accumulated during a day [69]. This corresponded to the threshold sensitivity of $1\cdot10^{-8}$ cm^{-1} and made it an effective device for a study of expensive isotopologues of molecules.

The power of radiation emitted by modern commercial LED in the narrow spectral range of the order of 1 000 cm^{-1} is sufficiently high (0.3–3 W). The intensity of the modern LED does not decrease when approaching the high-frequency range, whereas the intensity of heat sources decays exponentially in the same range; thereby, the ratio of

TABLE 3. Spectra of the H_2O and CO_2 Isopotologues Studied Using the Fourier Spectrometer with LED Radiation Sources

Range, cm^{-1}	H_2O^{16}	H_2O^{17}	H_2O^{18}	HDO	D_2O	$^{16}OC^{16}O$	$^{18}OC^{18}O$	$^{16}OC^{18}O$
10 000–11 000	+			+	+			
11 200–12 200	+		+	+	+	+	+	+
12 800–14 000	+	+		+	+			
14 800–15 600	+			+	+			
15 200–16 300	+	+		+	+			
16 300–17 000	+			+	+			
17 000–18 000	+	+	+	+	+			
18 000–20 500	+							
20 000–22 200	+							
21 000–23 000	+							

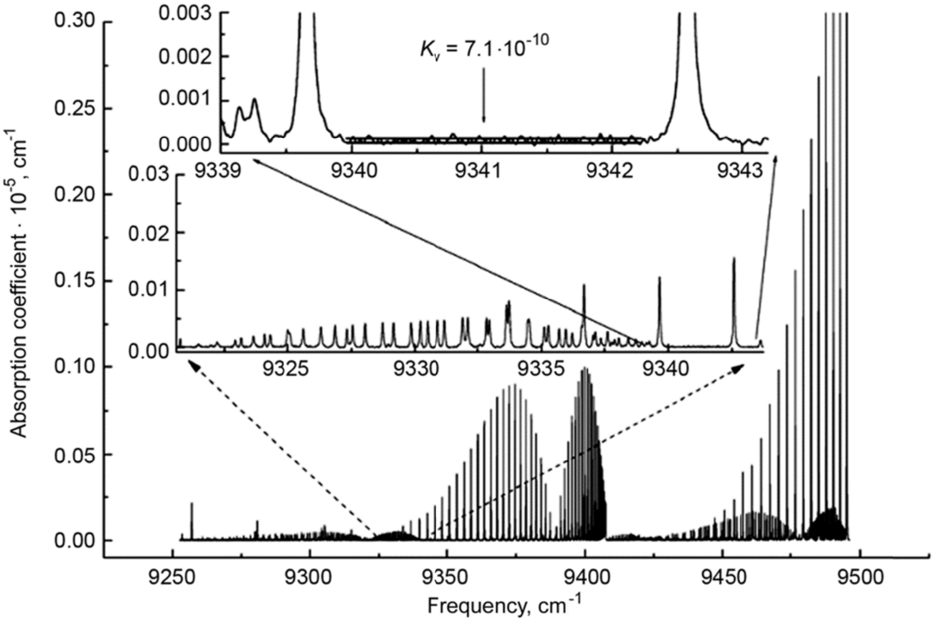

Fig. 3. Carbon dioxide absorption spectrum in the 9250–9500 cm^{-1} spectral range.

the LED intensity to the halogen lamp intensity in the UV range reached 300. When approaching the UV range, the sensitivity of the Fourier spectrometer with a LED source is by 3 orders of magnitude higher than the sensitivity of a spectrometer with a heat source due to the fact that the LED noise is by 3–10 times less that the noise of the heat source.

The absorption spectra of the carbon dioxide and water vapor isotopologues were measured in [69–71] at wavelengths exceeding 9000 cm^{-1} using the high-sensitive Fourier spectrometers with LED sources. The complete list of the examined isotopologues is presented in Table 3.

CONCLUSIONS

Integration of science and education in Tomsk creates conditions for solving permanently appearing basic and applied problems in the fields of optics and spectroscopy and makes it possible to collaborate with leading domestic and foreign research centers for molecular IR and electronic spectroscopy and quantum chemistry. The basis for such collaboration is the modern experimental techniques corresponding to the international standards as well as the comprehensive approach to processing and analysis of large arrays of experimental data using original theoretical models. As a result of this approach, the community of spectroscopists from the IAO SB RAS and TSU has established strong scientific collaboration with spectroscopic laboratories of universities in France (Paris, Reims, Dijon, and Grenoble), England (London), China (Hefei and Shanghai), Finland (Helsinki and Oulu), Sweden (Stockholm), USA (Harvard), and with all academic institutes of the Russian Academy of Sciences and leading universities of the Russian Federation. The joint work on photophysics of porphyrins and their derivatives has recently been launched with the University of Helsinki [72]. The work on up-conversion of nanoparticles for solving visualization problems (biophotonics) in biological systems and developing solar cells and 3D displays [73] has been initiated with the Royal Institute of Technology in Stockholm. We note that the initial integration of education, science, and industry was previously and continues to be now a constant source of interdisciplinary applications of spectroscopy. Academician A. È. Kontorovich, a graduate of the Department of Optics and Spectroscopy of Tomsk State University, in his letter of congratulations on the 60th anniversary of the Department wrote wonderful words that once again emphasized great contribution and profound influence of the Tomsk Spectroscopy School on the formation of new, including interdisciplinary, directions of scientific and applied research and technology. He wrote that as fate would have it, he had changed his profession. However, for nearly half a century of his scientific work, various spectroscopic methods had been and still remain the tool that he always uses in his research. However, this thing is not the most important. Exactly Great School, general physical and mathematical education, ability to learn and to master new fields of research, and prophecy to research creative work are the main things that gave him the Faculty and the Department, have already helped him and continue to help in his work. He said with certainty that he still felt himself to be one of many hundreds of students of the Faculty and the Department [74].

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