INFORMATION

XI SYMPOSIUM AND SCHOOL ON HIGH RESOLUTION MOLECULAR SPECTROSCOPY (HighRus–93) JUNE 28–JULY 7, 1993

The regular XI Symposium and School on High Resolution Molecular Spectroscopy was held on board the "Il'ya Repin" ship from June 28 to July 7, 1993. It was organized by the Institute of Atmospheric Optics, SB RAS; the General Physics Institute, RAS; the Scientific Council on Spectroscopy, RAS; and, the Commission on Radiation of the Interdepartmental Geophysical Committee attached to the Presidium of the Russian Academy of Sciences.

110 scientists from the former USSR represented Moscow, St. Petersburg, Tomsk, Novosibirsk, Omsk, Nizhny Novgorod, Ekaterinburg, Kazan, Obninsk, Tumen, Minsk, and Samarkand took part in the Symposium and School as well as 22 foreign scientists from France, USA, Germany, Spain, Italy, and Taiwan.

13 lectures and 106 poster reports were delivered in the framework of the following sessions:

1. Theory of spectra of molecules and radicals.
2. High resolution experimental investigations of spectra of molecules in gas phase.
3. Spectroscopy of intermolecular interactions in gases.
4. Applications of high resolution spectroscopy to atmospheric optics and gas analysis.
5. Experimental technique for high resolution molecular spectroscopy.

Discussions and a "Round table of businessmen" were held on problems and methods of science financing in the CIS (Community of Independent States) and USA as well as organizing of work of small firms making science–intensive production.

Brief review on the materials of the Symposium is given below.

SESSION 1
THEORY OF SPECTRA OF MOLECULES AND RADICALS

As before in theory the main efforts are concentrated on developing the methods describing spectra of non–rigid molecules, radicals, and complexes (the Institute of Atmospheric Optics SB RAS, Tomsk; the Institute of Applied Physics RAS, Nizhny Novgorod; the Institute of Atmospheric Physics RAS, Moscow). The qualitative methods of description and identification of spectra continue to develop (A.V. Burenin, the Institute of Applied Physics, RAS, Nizhny Novgorod; I.M. Pavlichenkov, the State Scientific Center "Kurchatov Institute", Moscow; S.V. Petrov, the Moscow State University). As to employing the theory for processing experimental spectra, two tendencies are outlined here. The first one is the joint description of different spectra: MW, IR, Raman spectra, etc. (A. Perrin, the Molecular Physics and Applications Laboratory, Paris, France; M. Loete and J.–C. Hilico, the Laboratory of Molecular Spectroscopy and Laser Engineering, Dijon, France). Note that adding the MW data to the IR and Raman ones improves by an order of magnitude the extrapolation properties of the parameters that were derived by processing. The second tendency is the global processing of all molecular spectra resulting from transitions between the rotational–vibrational states of the given electron state of a molecule (J.F. Ogilvie, the Institute of Atomic and Molecular Science, Taiwan; J.–L. Teffo, V.I. Perevalov, et al., joint work of the Institute of Atmospheric Optics SB RAS, Tomsk and the Laboratory of Molecular Physics and Applications, Paris, France). This approach enables one to make the extrapolation calculation of hot bands using the experimental data on the lower frequency spectra. In the Moscow State University a group under the leadership of N.V. Stepanov develops successfully the methods describing spectra of pre–dissociation of molecules.

Four lectures were delivered at this session. N.F. Stepanov's lecture was devoted to the methods of describing the spectra of Van der Waals complexes pre–dissociation. J.F. Ogilvie dwelt on the question of the global description of two–atomic molecules spectra and the isotopical function of spectroscopic parameters. A. Perrin presented her report "Recent progress in the analysis of molecules of atmospheric interest: ozon, nitrogen dioxide, and nitric acid". M. Loete summed up the latest achievements in the theory of spectra of spherical top molecules.

SESSION 2
HIGH RESOLUTION EXPERIMENTAL INVESTIGATIONS OF SPECTRA OF MOLECULES IN GAS PHASE

This session dealt with the results of investigations of molecules spectra, radicals, and complexes using the experimental sets and methods: the Fourier spectroscopy; the intracavity laser spectroscopy; the diode laser spectroscopy; the sub–MMW spectroscopy; the CARS–spectroscopy; and, the opto–acoustic laser spectroscopy. The increasing accuracy of the spectra presented should be noted.

In his oral report E.A. Sviridenkov (PhIAS, Moscow) expounded the situation in the intracavity laser spectroscopy and suggested ways of increasing sensitivity of the method. A.F. Krupnov (IAPh, Nizhny Novgorod) drew attention of the audience to the history of developing the MW spectroscopy in Nizhny Novgorod. A.A. Vigasin's lecture (IPhA, Moscow) dealt with studying the carbon gas dimers by means of the CARS–spectroscopy.

The report of P. Helminger and F.C. De Lucia was concerned with the investigation of the rotational spectra of molecules, which are important for understanding the ozone cycle in the upper atmosphere. Their latest results of measuring and interpreting HN_3, H_2O, and HOOH spectra are used in processing of remote sounding results by the methods of the MMW and sub–MMW spectroscopy.

J.T. Hougen touched the results of investigating the sub–MMW spectra of an acetaldehyde molecule. Experiments in the range from 165 to 417 GHz were made with the RAD–3 spectrometer at the Institute of Applied Physics in Nizhny Novgorod. Molecule of CH_3COH has low–lying torsional modes that in the region of 2000 cm^{-1} form quasi–continuum.

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The global aim of the project is studying the processes of the intramolecular redistribution of vibration energy by high resolution spectroscopy methods.

Investigations in the field of the lower vibration transitions treating water spectrum in bands of the first triad were presented in the reports by G. Graner (the Laboratory of Molecular Physics and Applications, Orsay, France), C. Domingo (the Institute of Substance Structure, Madrid, Spain), and by joint work of the scientists from Germany (the Institute of Physical Chemistry, Giessen), the USA (the University of Ohio), and Russia (the Institute of Atmospheric Optics, Tomsk).

Professor G. Graner detailed all the vibrational levels of the propane molecule nearly 10 μm. Experimental measurements were carried out with the Fourier spectrometer of 0.002 cm^{-1} resolution and the diode laser spectrometer of $1 \cdot 10^{-4}$ cm^{-1} resolution. There were also measured the rotational spectra of excited states (in the spectral region from 8 to 470 GHz). This work reflects the present–day tendency in research of molecular spectra when mutually supplemented spectroscopic information is obtained by different methods and then its joint processing is executed within a scope of one model.

C. Domingo spoke about applying a laser spectrometer of difference frequency to investigation of a discharge in methane. The use of the method of double modulation (radiation of laser and electrical discharge) allowed the weak absorption lines of radical CH_3 to be observed.

S.M. Shchapin (the Institute of Chemistry of High–Pure Substances) reported about creation of the spectra bank for analysis of the super–pure volatile substances by methods of high resolution spectroscopy. At present the absorptional IR spectra of molecules NH_3, PH_3, AsH_3, SiH_4, GeH_4, H_2Se, BCl_3, and H_2O are included in the bank. The measurements were accomplished with Bruker Fourier spectrometers IFS–113 V (resolution up to 0.003 cm^{-1}) and IFS–120 HR (resolution up to 0.002 cm^{-1}). The pulse diode lasers spectrometer of resolution more than 0.001 cm^{-1} was used in the individual spectral regions within the range from 850 to 3000 cm^{-1}.

J.–C. Hilico (the Burgundy University, Dijon, France) informed about results of measuring the spectra of hot bands of methane molecule inside supersonic jet and studying the relaxation mechanisms of vibration energy. The results were obtained together with scientists of the State Scientific Center "Kurchatov Institute". The measurements in the spectrum region of 1260 to 1298 cm^{-1} were implemented on a spectrometer with tunable diode lasers. Vibration temperature reached 1300 K, which allowed the transitions $4\nu_4 - 3\nu_4$ to be observed.

Researches in near IR and visible regions of spectrum were presented by series of joint reports of scientists of the Institute of Atmospheric Optics (Tomsk), the Pierre and Marie Curie University (France), the Institute of Physical Chemistry (Germany), and the University of Ohio (USA). The general result of these researches is analysis of high resolution spectra of HDO, D_2O, $H_2^{18}O$, and H_2S, obtained with use of the Fourier spectrometers with the pathlength of 240 and 430 m and the intracavity laser spectrometers.

SESSION 3
SPECTROSCOPY OF THE INTERMOLECULAR INTERACTIONS IN GASES

Four lectures were delivered at this session. F.C. De Lucia's lecture "Collision spectroscopy between 1 and 1000 K" was devoted to the experimental study of the influence of quantum effects in translational motion of molecules on collision process. To reveal the effect the investigation was carried out at very low temperature. N.N. Filippov's lecture (the State University, St. Petersburg) concerned interference of spectral lines. S.G. Rautian (the Institute of Automatics and Electronics, SB RAS, Novosibirsk) outlined approaches to description of the photoinduced drift of excited particles. V.P. Kochanov (the Institute of Atmospheric Optics, SB RAS, Tomsk) gave an exhaustive review of the non–linear interference effects that occur at absorption in a quasi–degenerated state. An opportunity to observe several new interference effects was substantiated in his lecture.

As before much attention was given to accumulation of experimental data on widths and shifts of spectral lines and their calculations. The French–Russian group under the leadership of A. Barbe (the Reims University, France) and A. Bykov (the Institute of Atmospheric Optics, SB RAS, Tomsk) as well as the Italian group (G. Buffa, et al.) fulfilled great work along this line. When investigating the coefficients of broadening and shift of lines by pressure, the necessity of new methods of calculation arises more and more often. The Dicke effect (narrowing lines due to collisions) should be increasingly taken into account. A. Nadezhdinsky's group (IGPh, RAS, Moscow) presented their reports on this point. In calculating the transparency of atmosphere the necessity to take into account this effect is getting perfectly clear. In measuring shifts Yu. Ponomarev's group (the Institute of Atmospheric Optics, SB RAS, Tomsk) revealed new non–linear effects although failed to find unambiguous interpretation.

Considerable extend of the temperature range of measurements in the direction of low temperatures allowed the influence of quantum effects in translational motion of molecules on the collision process to become clear.

Another effect causing discrepancy between the experimental and measured spectra is lines interference that was considered in reports of M. Tonkov's group (the State University, St. Petersburg). The approaches proposed by them give hope for success in describing the nature of this effect, but detailed calculations want developing quantum models. Direct methods of measuring velocity of rotation relaxation, that were reflected in F.C. De Lucia report, give assistance in developing such models.

The reports of S.D. Tvorogov and co–authors (the Institute of Atmospheric Optics, SB RAS, Tomsk) were devoted to developing the theory of spectral lines wings that had been advanced by them earlier. They proposed the method of deriving the kinetic equations when terms that give a center and wing of a line emerge in an explicit form in case of corresponding asymptotic passage. Anomalous behavior of an intermediate part of the profile, that was found experimentally under high pressures, gained the theoretic explanation.

The spectroscopic researches of complexes gained further development. The results obtained testify to considerable transformation of these calculations in the case of collisions of the complexes with other particles (K. Tokhadze, the State University, St. Petersburg). M. Cherkasov from the Institute of Atmospheric Optics, SB RAS (Tomsk) put forward a new universal method of calculation of a relaxational matrix parameters .

When discussing the results, the deficient development of the scattering matrixes calculation methods, that are necessary for investigation of the spectral effects of molecular collisions, was noted. Simultaneously, the participants expressed their wish to have empirical methods which would enable one to make fast calculations of the spectra of complex systems.

SESSION 4

APPLICATIONS OF THE SPECTROSCOPY OF HIGH RESOLUTION TO ATMOSPHERIC OPTICS AND GAS ANALYSIS

Applications of the diode laser spectrometers to solving atmospheric–optics tasks (A. Fried, the National Center of Atmospheric Researches, USA) and medical ones (A. Nadezhdinsky's group, IGPh RAS, Moscow) were presented most fully.

M. Spiridonov (the Institute of General Physics, RAS, Moscow) reported about application of the diode laser spectroscopy to analysis of processes that occur in the working space of CO_2 laser.

V.V. Kuznetsov and T.B. Mamchenko (the Scientific–Production Union "Taifun", Obninsk) and V.M. Klimkin (the Institute of Atmospheric Optics, SB RAS, Tomsk) told the audience about applications of the high resolution spectroscopy to monitoring the pollutants in the air and water spaces. The report of D.N. Kozlov, et al., dealt with application of CARC–spectroscopy to determining the temperature profiles in gas discharge.

There were presented three banks of spectroscopic information together with the automation control systems and an access to this information: the bank of spectroscopic information on two–atomic molecules RADEN (Moscow State University) and the banks with information on the spherical top molecules, T.D.S (the Institute of Atmospheric Optics, SB RAS, Tomsk and Laboratory of Molecular Spectroscopy and Laser Engineering, Dijon, France) and GEISA–93 (the Institute of Atmospheric Optics SB RAS, Tomsk and the Laboratory of Meteorological Dynamics, Palaiseau, France).

A number of reports concerned the problem on laser radiation propagation through the atmosphere. The other papers proved theoretically the feasibility of sensing different atmospheric pollutants.

SESSION 5

EXPERIMENTAL TECHNIQUES FOR HIGH RESOLUTION MOLECULAR SPECTROSCOPY

The reports concerned with the experimental equipment contained basically familiar and well proved methods. Especially it refers to the diode laser spectroscopy, that was most fully presented at the Symposium. The lecture "Atmospheric trace gas monitoring using high frequency modulation spectroscopy with semiconductor laser" by P. Werle (the Fraunhofer Institute, Garmish–Partenkirchen, Germany) was one of illustrations of that. It included the majority of up–to–date methods of increasing sensitivity and precision. Use of the HF modulation allowed measurements of NO_2 content in the air at the level of 10 ppt.

A. Mantz (USA) used the Fabry and Perot interferometer with piezoceramic modulation for the diode laser frequency stabilization, which provided high and long–time stability of the device.

V. Gorbatenko, B. Dumesh, et al., (the Institute of Spectroscopy, RAS, Troitsk) presented to the audience the MMW spectrometer based on a free electrons laser or the orotron, which featured low energy of electrons and high spatial frequency of beam modulation. Registration of absorption was executed by changes of the collector current. According to authors the sensitivity on absorption equalled 10^{-9} cm^{-1}.

S.A. Kovalenko, E.A. Sviridenkov, et al. (the Physical Institute, RAS, Moscow) reported that owing to investigations of non–linear processes in wide–band lasers they succeeded in improving sensitivity of the intracavity laser spectroscopy by a factor of 10^2 and brought it up to 10^{-11} cm^{-1} in the absorption coefficient.

S.M. Chernin (the Physical Institute, RAS, Moscow) presented the matrix multipath optical systems that were demonstrated by him in operation during the Symposium.

At present the Proceedings of the Symposium come out in the SPIE (Vol. 2205).

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