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All-Union School on new methods in molecular spectroscopy

The Scientific Councils of the USSR Academy of Sciences on Chemical Kinetics and Structure and on the Spectroscopy of Atoms and Molecules organised in October, 1989, an All-Union School on New Methods in Molecular Spectroscopy. Its aim was to acquaint the participants in the enormous progress achieved in this field during the last 10–15 years as a result of the development of experimental, mainly laser, techniques.

More than 400 persons from 42 cities of the Soviet Union took part in this School. It involved the delivery of 23 lectures and 9 round table discussions. Major specialists in the field of molecular spectroscopy were invited to deliver lectures.

The lectures by R I Personov (Institute of Spectroscopy, USSR Academy of Sciences, Troitsk) examined the principles and the wide variety of applications of the selective laser spectroscopy of molecules and matrices — the selective excitation of luminescence and the method for recording the narrow stable minima in absorption bands. These methods, which have nowadays come to be widely used, make it possible to discover the fine structure in inhomogeneously broadened spectral bands and to increase the "spectral resoluton" by a factor of 10^3-10^4. This leads to fundamentally new possibilities for a wide variety of theoretical and practical applications. Together with the fundamental principles of selective methods, a wide variety of their applications were considered. They include the fine structure of the luminescence and absorption spectra of molecules of different classes, a wide variety of intermolecular interactions, one- and two-quantum photochemical reactions in the condensed phase, the Stark and Zeeman effects in the spectra of complex molecules, the spectra of adsorbed molecules, the problems of increasing the memory of optical memory devices with the aid of methods for the recording of minima, etc.

The lecture by O M Sarkisov (Institute of Chemical Physics, USSR Academy of Sciences, Moscow) was devoted to the physical principles of the method of the laser-induced luminescence, its experimental realisation, and its application to the study of elementary atomic-molecular processes in the gas phase. The interaction of atoms and radicals, the distribution of energy in the products of elementary chemical reactions, the transmission of energy in collisions, and unimolecular reactions with participation of molecules subjected to high vibrational excitation were examined. The same range of problems but using other laser methods such as the intraresonator laser spectroscopy (IRLS) and the method of modulated intraresonator laser absorption was examined in the lectures by E A Sviridenkov (The Physical Institute, USSR Academy of Sciences, Moscow) and O M Sarkisov and Yu M Gershenzon (Institute of Chemical Physics, USSR Academy of Sciences, Moscow). It was emphasised in the former lecture that, by virtue of the extremely high sensitivity of the IRLS, it is possible to investigate "forbidden" optical transitions and high overtones and to apply these methods to the solution of various problems in chemical physics; in the latter lecture, the possibility of achieving an ultrahigh resolution in the spectra by virtue of magnetic and electrical modulation of the intraresonator laser absorption was demonstrated. Examples of the highly sensitive recording of chemically active radicals were also presented.

The lectures by A N Rubinov (Institute of Physics, Academy of Sciences of the Belorussian SSR, Minsk) were devoted to advances in the spectroscopy of molecules in liquid solutions. It was established that the electronic absorption and luminescence spectra of dye solutions are inhomogeneously broadened and that the broad continuous bands are due to the fluctuations in the solvation shell. A model was proposed for a polar solvent, which explains the static and dynamic inhomogeneous broadening of the spectra of dyes as well as a number of other spectral features. It was shown how it is possible to investigate the hydrogen bond between the electronically excited dye molecules and the solvent with the aid of picosecond spectroscopy by measuring the rate of rotation of molecules.

The lecture by E E Nikitin (Institute of Chemical Physics, USSR Academy of Sciences, Moscow) was devoted to a new aspect of laser molecular spectroscopy with a short time resolution. The idea of the method consists in the application of ultrashort laser pulses lasting $10^{-14}-10^{-13}$ s, i. e. tens and hundreds of femtoseconds. This leads to unique possibilities for the investigation of intramolecular movements and the dynamics of the transition state; in the simplest cases, it is possible to obtain information about the movement of fragments of the transition complex on the real time scale. It is difficult to overestimate the usefulness of femtosecond spectroscopy for the development of chemical physics.

The gas-dynamic method for the attainment of low temperatures — the method of the ultrasonic stream expanding adiabatically into a vacuum — has come to be widely used during the last 10 years. The lecture by A M Pyndik (Institute of Spectroscopy, USSR Academy of Sciences, Troitsk) was devoted to this topic. Any gaseous substance can be cooled to temperatures of several degrees Kelvin (and sometimes to a fraction of a degree Kelvin) under the conditions of an ultrasonic stream. It is then easy to achieve fairly high concentrations (from 10^{12} to 10^{15} cm^{-3}) which permit the use of various spectroscopic methods such as fluorescence, phosphorescence, multiphotonionisation, Raman light scattering, and many others. Since at low temperatures the molecules are in the lowest vibrational and rotational states, this creates many advantages for the spectroscopic investigation. These include the narrowing of the absorption band by two orders of magnitude, the disappearance of "hot" bands, an increase in optical selectivity, and the possibility of attaining appreciable concentrations of "van der Waals" molecular complexes.

One of the effective spectroscopic methods for the study of such compounds under the conditions of ultracold streams and beams is the microwave spectroscopy in the centimetre and millimetre ranges, to which the lecture by A F Krupnov (Institute of Polymer Physics, USSR Academy of Sciences, Gorky) was devoted. At the present time, the wavelength range used in modern microwave spectroscopy has greatly expanded, as a result of which cold equilibrium gases, molecular ions, the interstellar space, etc. have become the objects of study by this procedure. Microwave spectroscopy not only makes it possible to measure frequencies with a very high accuracy

but also to create on this basis a new generation of frequency standards.

Several lectures were devoted to the vibrational spectroscopy of molecules. Yu A Kuritsyn (Institute of Spectroscopy, USSR Academy of Sciences, Troitsk) talked about the methods of high resolution diode laser IR spectroscopy. E A Ryabov (Institute of Spectroscopy, USSR Academy of Sciences, Troitsk) dealt with a new phenomenon — the laser multiphoton vibrational excitation of molecules. For a sufficiently high emission intensity, the molecule absorbs a large number of IR quanta and can be excited up to the dissociation limit. The use of multiphoton excitation for the study of intramolecular dynamics, the non-equilibrium selective IR photochemistry, the laser isotope separation, and chemical synthesis under non-equilibrium conditions was discussed.

The lectures by B V Lokshin (Institute of Organoelement Compounds, USSR Academy of Sciences) were devoted to chemical applications of IR Fourier spectroscopy. During the last decade, this method has been rapidly introduced into practice as a result of progress in the field of computers and lasers and the creation of new effective algorithms for the Fourier transformation. The possibilities of the method for the analysis of substances in those cases where the application of traditional spectroscopy is limited by the energy, resolution, or the duration of the experiment were demonstrated: the determination of contaminants in the atmosphere, the identification of gas-chromatographic fractions, the measurement of the spectra of microspecimens, adsorbed molecules, and aqueous solutions, the study of electrochemical processes, semiconductors, molecules isolated in matrices at low temperatures, phase transitions, and polymer oxidation and degradation processes, and kinetic research. The application of IR Fourier spectroscopy to the measurement of photothermal ionisation IR emission and reflection spectra, IR circular dichroism, photoacoustic spectra, and near infrared Raman spectra was discussed. It was shown that the presence in the apparatus of a built-in computer creates new possibilities such as the treatment and transformation of the spectra, differential spectroscopy, and the creation and use of libraries of spectroscopic data.

Resonance Raman spectroscopy (RRS) was discussed in the lecture by G E Blyumberg (IKhBF,† Academy of Sciences of the Estonian SSR, Tallin). The principal features of resonance Raman spectra, the spectral profiles, and the information which can be extracted from them about vibronic interactions in the electronically excited state, the correspondence between the vibrational modes in the ground and excited states, the evolution of the system in the excited vibronic state, etc. were examined. A model was proposed for the behaviour of a molecular electronically excited impurity centre in the crystal participating in the multimodal interaction with the medium.

The lecture by D P Chernyakovskii (Yaroslavl' Polytechnic Institute, Yaroslavl') was devoted to electrochromism as a method for spectroscopic analysis. It dealt with the application of electrochromism spectra to the determination of the electrical parameters of molecules in the ground and electronically excited states, to the study of the migration of the electronic excitation energy, to the study of the thermomobility of macromolecules in polymer systems, to the observation of the shift of the chemical equilibrium in an electric field, etc.

The new trends in the application of vibrational spectroscopy to the study of adsorbed complexes and surface layers were reviewed in the lecture by V I Lygin (Moscow State University, Moscow). It was emphasised that the application of new methods, in the first place Fourier spectroscopy and Raman spectra with laser excitation, has raised surface research to a qualitatively new level. They make it possible to investigate virtually all types of catalysts and adsorbents even at a very low (down to 10^{-2} of a monolayer) degrees of surface coverage. By virtue of the application of the highly sensitive Fourier spectroscopy, it is possible to separate the spectrum of the surface layers from that of the bulk phase, to obtain differential spectra at different surface coverages, and to investigate the kinetics of adsorption and surface reactions. The measurement of the diffuse scattering spectra has led to appreciable progress in the study of highly scattering powdered adsorbents. New possibilities have arisen following the application of the method of incomplete internal reflection to the study of film adsorbents, membranes, electrochemical processes, etc.

Together with lectures on optical spectroscopy, two lectures devoted to methods of "electronic" spectroscopy were delivered. One of these, by Yu V Chizhov (Leningrad State University, Leningrad), concerned molecular photoelectron spectroscopy. It was emphasised that the modern techniques of the physical experiment, particularly the high monochromaticity of laser radiation, make it possible to increase greatly the accuracy of the measurement of the energy levels in molecules and to investigate various interactions between the electronic states in chemical compounds.

Another lecture was delivered by V I Panov (Moscow State University, Moscow). It reported new methods for the investigation of the surface, which permit the study of its microtopography and its atomic and electronic properties with atomic spatial resolution. These methods are based on the use of the scanning tunnel microscope (STM) and the atomic force microscope (AFM). The question of the application of the STM to the study of the atomic structure and of the electronic properties of single surface lattices of layered crystals, and to the observation of surface diffusion and the observation of single adsorbed atoms and molecules on the surfaces of solids was discussed in detail. The special interest in this method arose because of the possibility of a detailed study of the changes in the electronic and atomic properties of atoms in adsorption and catalysis. The ability of the method to determine the character of the chemical bonds formed by single atoms within a single unit cell was demonstrated in relation to the reaction of H_3 with the surface of silicon.

The possiblity of using the AFM in the study of the relief and interatomic interactions of non-conducting substances was demonstrated in the lecture. In contrast to the STM, it is possible to determine by this method the interatomic interaction constants for single atoms and molecules. Thus the combinaton of these methods permitted for the first time the observation of single atoms and the investigation of their electronic properties and of their interatomic interactions with atomic spatial resolution.

On the whole, the school was successful. The round table discussions, devoted to problems in modern spectroscopy of greatest current interest, in particular kinetic spectroscopy with time resolution, new spectroscopic instruments, and the spectroscopy of the surface, were very popular. In the concluding session, the participants expressed the unanimous view that it is essential that schools on new methods in molecular spectroscopy should be held regularly.

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