

DEVELOPMENTS IN MOLECULAR SPECTROSCOPY IN THE U.S.S.R.

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INTRODUCTION

WITHIN the framework of a single paper it is hardly possible to give an exhaustive, or even a detailed, review of the work on molecular spectroscopy conducted in the U.S.S.R., even for a short period limited to the last 5 or 10 years. If we consider, for example, that over 150 papers on molecular spectroscopy¹ were read at the Tenth All-Union Conference on Spectroscopy, and that these papers²⁻⁹ are only a part of the work completed,† it becomes obviously necessary to limit the subject matter of this article.

Because of its possibilities, problems, and applications — since it is a means of investigating both physical and chemical problems — molecular spectroscopy occupies an intermediate position. Inasmuch as the physical aspect of the subject is treated in this paper, it seems advisable to limit the material by excluding first the work devoted to the spectra of individual molecules or to the solution of particular analytical problems. The extent of such work is great, if we consider that the number of molecules amenable to spectrographic investigation exceeds by thousands of times the corresponding number of atomic structures. We have also limited the scope of the discussion to molecular gases, solutions, fluids, and crystals, while ionic crystals (with certain exceptions), phosphors, and semiconductors are excluded from examination, despite the fact that investigation of these substances by optical methods is essential and of unequivocal scientific interest. The third limitation concerns the spectrum: this article encompasses investigations accomplished in the optical region of the spectrum from the extreme ultraviolet to the far infrared, and work on microwave spectroscopy and electron and nuclear resonance is not included. Finally, the work in the domain of physical optics allied to mo-

lecular spectroscopy — molecular optics and optics of metals, photochemistry, etc. — is not examined, although this work is being carried on in the U.S.S.R. in close association with molecular-spectroscopy research (in the narrow sense) to the same degree as those subjects excluded from examination for the previously enumerated reasons.

Papers on the spectroscopy of molecular vibration (and rotation) are discussed in the first section, electronic molecular spectroscopy in the second, and the basic work on the development of methods and equipment for molecular spectroscopy in the third.

This review, as mentioned, cannot pretend to be complete. In this presentation, limited to examination of basic investigations, every paper cannot be mentioned. Literature references will be given, if possible, to review articles, and in the absence of the latter, to basic or latest publications which cite the entire necessary literature on each subject.

I. MOLECULAR VIBRATION SPECTROSCOPY

A. The Theory of Vibrational Spectra. A great step forward in the theory of vibrational spectra was made by M. V. Vol'kenshtein, M. A. El'yashevich, and B. I. Stepanov, who developed methods of calculating the frequency and intensity of vibrational spectra. This work, begun basically in 1939, was reported in a two-volume monograph, *Vibration of Molecules*,¹⁵ published in 1949 by M. A. El'yashevich and B. I. Stepanov, who, using a rationally selected coordinate system for determining the vibrations of a molecule, offered new methods for deriving and solving old equations by using potential energy constants determined from experimental data on classes of related compounds. The theory of intensity and polarization of bands in vibrational spectra was developed by M. V. Vol'kenshtein on the basis of the additive nature of dipole moments and the polarizability of the bonds in molecules. Results of calculations of vibration spectra of about 100 molecules of organic substances, primarily of the aliphatic hydrocarbon series, are contained in the cited monograph, along with an analysis of the intensities in

*From materials presented by the author at a joint meeting of the United International Commission on Spectroscopy and the Commission on Spectroscopy of the U.S.S.R. Academy of Sciences (August 13, 1958, Moscow).

†A great quantity of work of interest to spectroscopists is being presented also at the All-Union Conference on Luminescence (molecular luminescence).¹⁰⁻¹⁴

the spectra of halide and deuterio-methanes is given.

L. S. Mayants¹⁶ offered a theory of characteristic frequencies in spectra of polyatomic molecules, and gave an analysis of the conditions of the characteristic nature of vibrations and a method for calculating these vibrations. He applied the results to spectra of hydrocarbons and their chlorine derivatives. For the latter, the forms of vibration and the coordinates involved were clarified.

The methods examined were further developed by M. A. Kovner¹⁷ and L. M. Sverdlov,¹⁸ who, with their co-workers, calculated the spectra of a large number of organic substances (aromatic compounds, unsaturated hydrocarbons, and their derivatives).

Recently, M. M. Sushchinskiĭ, together with his co-workers,¹⁹ successfully used machine methods to calculate the vibration spectra of hydrocarbons. He also investigated certain vibration properties of the CH groups in detail.

A natural development of molecular-vibration calculations of hydrocarbons were the investigations of B. I. Stepanov and his co-workers on the spectra of linear chains with periodic structure, and then on the more complex systems of spatial and volume lattices with applicability to the structure of silicon glasses.²⁰

B. Raman Spectroscopy. Systematic investigations of Raman scattering were begun in the U.S.S.R. from the moment of its discovery by L. I. Mandel'shtam and G. S. Landsberg simultaneously with Raman and Krishnan in 1928. Related to the area of the physics of scattering are the known papers by L. I. Mandel'shtam, G. S. Landsberg, E. F. Gross, and others, who studied the basic characteristics of the phenomenon, its temperature dependence, low-frequency spectra, spectra of the higher orders, etc.

Among the recent papers, we point out first those by P. P. Shorygin and his co-workers²¹ on resonance Raman scattering excited near the absorption band or within it. They have discovered that the intensity of scatter bands grows faster than it theoretically should. The study of this phenomenon is being continued by other investigators also. In addition to the obvious practical interest, investigations of this kind are very useful in explaining the mechanism of Raman scattering and its connection with, or more accurately, the conditions of, its transition into resonant fluorescence. Theoretical investigation of these problems was undertaken by L. N. Ovander,²² and B. I. Stepanov, and P. A. Apanasevich.²³

A large group of investigations, belonging to the school of G. S. Landsberg, deals with the problem, essential to theory and practice, of the line width of Raman scattering. A number of papers on this subject were published by P. A. Bazhulin and his co-workers,^{24,25} as well as by Kh. E. Sterin,²⁶ who, in particular, established the curious fact that the line widths of totally symmetric vibrations of benzene and cyclohexane in vapors and solutions were equal, and showed that it was impossible to explain this width by the action of intermolecular forces. I. I. Sobel'man²⁷ in his theoretical investigations associated the line width with random rotational motions of the molecules, while the thorough experimental investigations of P. A. Bazhulin and N. I. Rezaev²⁵ led them to conclude that the line widths, depending on their nature, could be due to both rotational motions of the molecules and intramolecular processes (interacting vibrations).

The methods worked out by M. M. Sushchinskiĭ²⁸ for the measurement of Raman spectra and, in particular, for rapid determination of the width and intensity of the lines, were fundamental for the study of Raman spectra of a large number of hydrocarbons, systematized in the monograph by G. S. Landsberg, P. A. Bazhulin, and M. M. Sushchinskiĭ,²⁹ in which data (frequency, maximum and integral intensities, line widths, and polarization) were collected for almost 280 substances. A considerable portion of these data was obtained by the authors. Carefully thought out principles of systematizing the spectra of Raman scattering are extremely important for the work developing recently on the documentation of molecular spectra.

Simultaneous investigation of intensities and degrees of polarization of characteristic lines permitted Ya. S. Bobovich and M. V. Vol'kenshteĭn,³⁰ P. P. Shorygin,³¹ and M. M. Sushchinskiĭ and V. I. Tyulin³² to investigate the properties of the polarizability tensor and, in particular, to establish a sharp increase in the derived polarizability tensor as a consequence of conjugation in the molecule. These investigations were recently extended to a new, broad class of compounds.³³

Let us mention the thorough, systematic investigation of Raman spectra of various classes of organic substances, including their deuterium derivatives, being conducted by V. T. Aleksanyan, Kh. E. Sterin, and others, in collaboration with chemists B. A. Kazanskiĭ and others.³⁴

Substantial results were achieved in the spectroscopic investigation of Raman scattering of intermolecular interactions. In a large amount of work in this direction, started in 1934 by G. S. Landsberg and his students and co-workers (F. S.

Baryshanskaya, V. I. Malyshev, S. A. Ukholin), and continued to the present, the properties of hydrogen bonds were studied in various states of matter — in fluids, with gradual transition to vapor and solution through the critical state, in crystals as a function of temperature, etc. A review of these papers is given by V. I. Malyshev.³⁵ A large cycle of work on the investigation of organic and inorganic crystals is being carried out by E. F. Gross and his co-workers,³⁶ Sh. Sh. Raskin,³⁷ A. I. Stekhanov,³⁸ and others. From this, in particular, new results were obtained for low-frequency and second-order scattering,³⁹ and a special study was made of the development of the hydrogen bond and other intermolecular interactions. A number of investigations of spectra of substances having a hydrogen bond were carried out by M. I. Batuev.⁴⁰ The theory of the spectroscopic development of the hydrogen bond was discussed in papers by B. I. Stepanov,¹⁵ N. D. Sokolov,⁴¹ and recently by V. M. Chulanovskii.⁴²

Reciprocal molecular influences in solutions and mixtures not connected with specific forces of the hydrogen-bond-type were investigated by Ya. S. Bobovich and V. M. Pivovarov,⁴³ who established unique density anomalies and offered explanations regarding the universal influence of the medium as well as the influence of the intermolecular forces on the properties of electron levels. These authors, as well as P. A. Bazhulin, his co-workers,⁴⁴ and others, investigated the "anomalous" temperature dependence, which varied for the different lines of a particular substance. These phenomena continue to be studied intensively.

Unique interactions occurring in glassy substances were studied by means of Raman scattering spectra of silicate glass by E. F. Gross and V. A. Kolesova, M. F. Vuks, and V. A. Ioffe, as well as by Ya. S. Bobovich and T. P. Tulub. From these studies it was possible to establish the characteristic features of various structural groups and to draw certain conclusions with regard to the structural details of various glasses. A discussion of these papers is given in a review article by Ya. S. Bobovich and T. P. Tulub.⁴⁵ Spectra of several oxides in glassy state were studied and conclusions, based on the comparison of spectra of glasses and melts, were formed regarding their molecular structure by T. A. Sidorov, N. N. Sobolev, and their associates.⁴⁶

C. Infrared Spectroscopy. A characteristic feature of infrared spectroscopy is its extremely rapid development in recent years, especially since the appearance of industrial spectroscopic equipment. Up to this time, among the scientific

institutions of the entire world, only a small number of laboratories had apparatus of this type. These laboratories built this equipment themselves and used it to carry out a limited number of investigations. From the great bulk of modern work on molecular infrared spectroscopy in the U.S.S.R., we select for examination only the investigations or sequences of investigations relating to the solution of spectroscopic problems or to the study of broad physical or physico-chemical problems.

From among these papers let us first mention the original method offered by P. V. Slobodskaya and M. L. Veingerov⁴⁷ for determining the duration of the excited state of molecules from the thermal relaxation time of a gas exposed to infrared radiation of a specific wavelength. For this purpose an optical-acoustic receiver, developed long ago by M. L. Veingerov, was used, and measurements of bands of carbon monoxide gas were refined to indicate the phase shift between the intensity of the modulated radiation and the signal from the receiver microphone. M. L. Veingerov's receiver, having served as a basis for sensitive gas-analysis methods developed both in the U.S.S.R. and abroad, has been recently used by him in the study of the "reverse" optical-acoustic effect from cold bodies.⁴⁷

The form and width of lines in infrared absorption spectra was studied by V. M. Chulanovskii and his co-workers,⁴⁸ who found that a number of bands of chloroform and bromoform have a form close to that due to dispersion, and that the decay is determined by the rate of vibrational energy transfer from the molecules to the surrounding media. Knowledge of the form of the bands is highly essential at the present time for the determination of their width and intensity.

V. M. Tatevskii, Yu. P. Pentin, and others⁴⁹ investigated the phenomenon of rotational isomerism with infrared spectra by comparing spectra obtained from fluid and cold crystalline states and reached conclusions as to the number and stability of various rotational isomers in alkali halides.

As indicated, the number and variety of investigations devoted to spectra of individual molecules is tremendous. Let us mention here the cycle of investigations by D. N. Shigorin,⁵⁰ who, simultaneously using infrared and electronic absorption spectra, luminescence, and Raman scattering, reached a number of conclusions concerning the structure and properties of complex organic molecules, and in particular the unique role of the intramolecular hydrogen bond in a molecule with chain coupled π electrons. Systematic investigation of spectra of a number of substances by various spec-

troscopic methods was carried on also by V. M. Tatevskii and co-workers,⁵¹ Yu. N. Sheinker and co-workers,⁵² and A. V. Iogansen.⁵³ The latter, having developed a means of accounting for the instrumental error of the spectrometer on the results of measurements, offered a method of group analysis for petroleum products without preliminary calibration of the spectrometer.

From the number of investigations of infrared spectra carried out outside the generally accepted region of 2 to 15 μ , let us mention first of all the work of N. G. Yaroslavskii and associates,⁵⁴ who used a device which they constructed themselves to study spectra of water vapor in the region of 50 to 1500 μ , and discovered new lines there. In the short-wave infrared region (from 1 to 3 μ) K. P. Vasilevskii and B. S. Neporent,⁵⁵ using their high-resolution equipment, also investigated the spectra of water vapor from the point of view of applicability of different versions of the law of absorption with an unresolved structure of the spectrum.

The methodology of infrared spectra with their selective sensitivity to effects on various structural elements of molecules is being successfully used for the study of the most varied intermolecular interactions. Among this kind of work we shall point out the investigations by G. S. Landsberg's associates, A. A. Shubin⁵⁶ and V. I. Malyshev,⁵⁵ on the hydrogen bond, which is related, as already mentioned, to the cycle of analogous work being carried out by the combination scattering method. In addition to the characteristics of bonds between various molecules obtained in these studies, let us note V. I. Malyshev's establishment of the unique pass spectra of fogs, which are apparently related to the anomalous dispersion in water sprays.

V. M. Chulanovskii with his co-workers,⁵⁷ investigating the structures of liquids by their infrared spectra, established a connection not only between the band locations and the types of intermolecular bonds in liquids (saturated or averaged, of the solvate type), but also the dependence of the integral intensities of the basic valence vibrations and harmonics on the type of these bonds, and offered a classification of intermolecular bonds on the basis of the spectral features observed. Among these works let us point out the investigations of M. O. Bulanin,⁵⁸ who showed that the band structure of valence vibrations of liquid water is connected with intramolecular and not intermolecular processes, a fact which is significant in modern theory regarding the structure of liquid water. He also established, on the basis of the spectra, the conservation, in liquid phase (solutions), of rota-

tional mobility of compact hydrogen-containing molecules similar to water or hydrogen halides.⁵⁹

Of significant interest is the great cycle of investigations by A. N. Terenin and associates (N. G. Yaroslavskii, A. N. Sidorov, V. I. Filimonov, and others)⁶⁰⁻⁶⁴ on the spectroscopic study of adsorption phenomena accompanied by the formation of donor-acceptor bonds of adsorbed molecules with the surface of the adsorbent. Infrared spectroscopy methods have disclosed the great importance of the role of the surface OH groups, determining the activeness of such adsorbents as silica gel, porous glass, and aluminosilicates. Comparison of the spectra of adsorbents with group spectra of a number of organic molecules with electronic acceptors such as $AlCl_3$ made it possible to clarify the nature of molecular deformation during adsorption. Work in this area is being carried on also by A. A. Babushkin and his associates, and others.⁶⁵

A. N. Terenin and A. N. Sidorov,⁶⁶ having investigated the adsorption of a number of organic vapors evaporated from layers of phthalocyanines, demonstrated with infrared spectra the great role of the central atom of metal in intermolecular interactions, in which these important molecules, analogous to those of chlorophyll, participate.

A number of investigators dedicated their efforts toward the study of the structure of glassy substances. Information on the silicon skeletal structure of glasses of various composition was obtained by infrared transmission and reflection spectra by V. A. Florinskaya, N. A. Sevchenko, and Yu. V. Glazkov.⁶⁷⁻⁶⁸ A group of papers by M. V. Vol'kenshtein and associates was devoted to the study of the glassification process by spectral methods. The glassification theory they offered, built on the assumption that certain degrees of freedom of intermolecular interaction freeze, agrees with data on infrared absorption and on temperature quenching of luminescence.⁶⁹

Measurement of infrared spectra, as we know, is the basic spectroscopic method of investigating polymers, allowing the study of their structural details, the character of forces forming and binding polymer molecules, their behavior during heating or deformation, the degree of crystallinity of such substances as polyethylene, etc. We shall not enumerate and examine all work in this area. We point out, however, that a large group of recent investigations in this area, carried out by M. V. Vol'kenshtein, O. B. Ptitsyn, V. N. Nikitin, V. M. Tatevskii, K. V. Nel'son, and others, was reported at the Tenth and Eleventh Conferences on Spectroscopy and published in the proceedings of the conferen-

ces.^{7,9} We will note that the rotational isomeric theory of polymeric structure advanced by M. V. Vol'kenshtein⁷⁰ was verified by B. Z. Volchek and V. N. Nikitin,⁷¹ who showed, with polarized infrared spectra, that rotational isomerization takes place when a polymer is stretched.

II. ELECTRONIC MOLECULAR SPECTROSCOPY

Electronic spectroscopy is no longer the basic means for investigating vibrational structure of spectra that it has been in past decades. This is a result of the development of methods of vibrational spectroscopy (especially infrared), which in many cases simplify experimental procedure and especially the theoretical refinement of results relating to molecular vibration spectra. At the same time, progress in science places before electronic spectroscopy new problems, which cannot be solved as effectively by other methods. We are speaking of the investigation of complex organic and especially aromatic molecules as the principal link between various systems in which these molecules act as centers of some transformation of light energy or other forms of energy into light; i.e., we refer to the "energy" of complex particles, which occupies a place of importance in the investigations by Soviet spectroscopists.

A. Spectra of Simple Diatomic and Triatomic Molecules. In this area the work of recent years has been concentrated around the use of spectral characteristics for the determination of molecular constants and the study of various processes in which the molecules being studied participate. Earlier, V. N. Kondrat'ev⁷² and his associates successfully used spectroscopic methods to investigate the kinetics of reactions and, in particular, investigated electronic spectra of radicals OH, C₂, SH, CH. The classical papers of A. N. Terenin⁷³ on the spectroscopic study of photodecay of molecules in salt vapors are well-known.

From among recent papers we mention the investigation by N. A. Prilezhaeva and V. I. Danilova,⁷⁴ who have shown, by measurement of illumination yield, that the predissociation in spectra of diatomic molecules does not begin in a narrowly limited region in which diffuse absorption spectra are observed, but develops gradually in a wide region of the spectrum, as observed earlier for polyatomic molecules.

I. V. Veits and V. L. Gurvich,⁷⁵ spectroscopically investigating the equilibrium constants of oxides and salts of a number of elements of groups II and III in flames, determined their dissociation energies and established the basic electronic states

for the molecules of oxides of the group II elements.

V. I. Dianov-Klovok in several papers⁷⁶ devoted to the investigation of electronic spectra of liquid oxygen came to the conclusion that the bands in the region of 3300 to 1200 Å should be attributed to (O₂)₂ complexes, which are also responsible for the magnetic properties of liquid oxygen.

A. V. Yakovleva and I. I. Gromova⁷⁷ investigated the conditions of fluorescence excitation of nitrogen in the extreme ultraviolet region (1300 Å) as a function of the intensity of the excitation light and gas pressure, and came to the conclusion that initial fluorescence states are due to collisions between excited molecules.

A number of papers (M. S. Khokhlov,⁷⁸ V. D. Mikhalevskii and K. I. Mochalov, V. V. Prokof'eva,⁷⁹ V. I. Elizar'eva⁸⁰) was devoted to the determination of the discharge-zone temperature of diatomic molecules and radicals (OH, N₂, CO, CN) varying in the type of rotational structure of their spectra. It was established^{78,79} that there was a deviation from the equilibrium temperature, as measured by the OH and CN radicals, arising as a result of reaction. M. Z. Khokhlov found that the approach of the "temperature" of the hydroxyl to the temperature of neutral gas, occurring under increased pressure, is not so much connected with the increase in the number of collisions as with the increase in temperature in the discharge zone and with the predominance of the process of hydroxyl formation as a consequence of thermal dissociation of water molecules.

A. V. Leskov⁸¹ examined the possibilities of analytical application of diatomic molecular spectra and cited intensity tables for many of them.

A. V. Kleinberg,⁸² using the redistribution of intensities in the fluorescence band spectrum of fluorescence upon dilution of nitric oxide with another gas, investigated the process of energy transfer through collisions of the nitric oxide molecules with molecules of other gases.

A. A. Shishlovskii and his associates⁸³ undertook an extensive optical investigation of salt solutions. As a result of a thorough spectroscopic investigation of thallium, lead, and other salts, he developed a method of structural analysis of electrolyte solutions.

B. Spectra of Complex Polyatomic Molecules. A thorough discussion of earlier papers on spectra of complex polyatomic molecules can be found in an exhaustive monograph by A. N. Terenin Photochemistry of Dyes,⁸⁴ as well as in a book by S. I. Vavilov The Microstructure of Light,⁸⁵ which contains an analysis of the studies on the general properties of electron systems responsible for the

radiation and absorption of light by complex molecules. These investigations are introduced by Vavilov's papers on the study of the nature of elementary radiators. In his investigations of polarized fluorescence (performed together with P. P. Feofilov⁸⁶ who is still continuing this work) means were developed for determining the multiplicity and mutual orientation of the virtual oscillators that are responsible for optical transitions, and the aggregate of which represents the electronic system of a complex molecule.

Important investigations on the multiplicity of electronic states of complex molecules were made by A. N. Terenin,⁸⁷ who in 1943 identified the metastable phosphorescent states of aromatic molecules with triplets. As we know, G. N. Lewis and his associates came to the same conclusion independently.

Theoretical papers on the calculation of spectra of polyatomic molecules with conjugate bonds were done using the free electron method by M. G. Veselov and T. N. Rekashevaya,^{88,89} and others. M. V. Vol'kenshtein, L. A. Borovinskiĭ, and S. M. Zazykova⁹⁰ studied the diamagnetic anisotropy of conjugated ring compounds as well as the intensities of Raman spectra. The applicability of free electron models, the introduction of necessary corrections, and the relation of this method to others are examined by M. V. Adamov, M. G. Veselov, and G. K. Rebane,⁹¹ as well as by L. A. Borovinskiĭ.⁹²

The amount of information obtainable by investigating spectra of complex molecules is sharply raised by simultaneous examination of absorption and emission spectra. Essential here is spectral symmetry, discovered by V. L. Levshin in 1930. He and his associates recently made a number of new investigations in this region.⁹³

B. S. Neporent⁹⁴ discovered a regular variation of spectral relationships with the degree and character of interaction of vibrational and electronic states, and classified complex molecules according to their spectroscopic characteristics. Investigating the complex aromatic molecule as a quantum electronic system connected with the vibrational degrees of freedom which follow classical laws, he described the form of the bands of complex molecules by using one generalized nuclear coordinate.⁹⁵ This model was developed also by B. I. Stepanov and his associates.⁹⁶ From a somewhat different point of view — by examining a center of illumination with definite energy levels and interacting with the medium — the problem of the bands was solved by S. I. Pekar,⁹⁷ A. S. Davydov and V. M. Agranovich,⁹⁸ and A. F. Lubchenko.⁹⁹

The most general problems on the relationship between absorption and luminescence spectra were examined recently in papers by B. I. Stepanov, M. N. Alentsev, and B. S. Neporent.¹⁰⁰⁻¹⁰² It was shown that the form of the luminescence spectrum should coincide with the form of the thermal-radiation spectrum, and it was pointed out that the relations of the form and symmetry of the spectra depended on the selection of the coordinate system.

An important source of information on the properties of complex molecules and their dependence on various factors is the spectral fluorescence radiation curve together with absorption and radiation spectra. The problem of the drop in fluorescence in the anti-Stokes region is the subject of discussion by S. I. Vavilov and P. Pringsheim, in which L. D. Landau, E. I. Adirovich, and others (see reference 103) participated. Recently V. V. Antonov-Romanovskii, B. I. Stepanov, and M. V. Fock¹⁰⁴ undertook one more theoretical examination of this problem for a system with three energy levels. Extension of the results obtained to include complex molecules with their unique internal bonds requires, however, a special substantiation. In recent years, investigations of the falling branch of the yield curve in the anti-Stokes region have continued. N. A. Borisevich, P. I. Kudryashov, B. Ya. Sveshnikov, and others^{105,106} showed that this drop, which follows from the Vavilov law, occurs also for vapors of complex aromatic compounds. They also showed that the anti-Stokes excitation appears even in phosphorescence spectra, despite the long duration of excited states in this case. Also continued were investigations of the Stokes branch of the yield curve, which for vapors is a falling one as a consequence of the increase in the probability of non-radiative transitions.⁹⁵ These investigations were used for the study of internal conversion of excitation energy, as well as for a detailed investigation of the vibration energy transfer processes in molecular collisions.¹⁰⁷

Investigations of fluorescence decay for vapors of a number of aromatic compounds by paramagnetic gases (oxygen, nitrous oxide), undertaken by A. N. Terenin and associates,¹⁰⁸ substantiated the existence of collision-induced transitions into a metastable triplet state. The probability of spontaneous transitions of this nature was thoroughly studied by B. Ya. Sveshnikov¹⁰⁹ in his investigations of spectra and kinetics of phosphorescence of solutions of aromatic compounds. The relationships of such transitions with spectral characteristics of molecules were also studied by V. V. Zelinskiĭ and associates¹¹⁰ with a large quantity of experimental data.

Along with the investigations of level structure and of the mechanism of energy transformations inside molecules, or molecular energetics, electronic spectra play an important role in the investigations of intermolecular interactions, which determine many physical properties of matter. These investigations can be divided naturally into two categories: the study of excitation-energy transfer processes between molecules (migration or "intermolecular energetics"), and the investigation of changes in spectra to study molecular interaction, which is sometimes expressed as the influences of the medium on the studied absorption or emission center.

Investigations of energy migration, initiated in the U.S.S.R. by S. I. Vavilov and his associates with the well-known papers on the concentration decay and concentration depolarization of fluorescence,⁸⁵ have been continued up to the present time. Systematic investigations in this direction are being continued by V. L. Levshin and his associates,¹¹¹ and in recent times this work revealed methods of separating and independently studying the physicochemical (association, etc.) and physical (migration of energy) factors that determine the concentration dependence of fluorescence. M. D. Galinin¹¹² suggested a classical examination of the energy-transfer process (the quantum theory was given by Ferster), based on the concept of interacting molecules as resonance-bonded dipoles and, using along with spectral methods direct fluorometric measurements of the duration of the excited state, carefully investigated various cases of energy transfer: between identical molecules (energy of migration), between fluorescing and nonfluorescing molecules (resonant decay), and between various fluorescing molecules (sensitized fluorescence), establishing the dependence of these processes on optical characteristics of the molecules (degree of similarity of the oscillators, determining the probability of resonance transition), and of course, on diffusion and other external factors.

Of special interest are the investigations of A. N. Terenin and V. L. Ermolaev,¹¹³ who discovered and investigated the sensitized fluorescence phenomenon, i.e. the transfer of energy from a molecule in the excited triplet state to another in a singlet normal state, both having simultaneous spin flip. With this it was possible to show that the energy transfer process occurs through contact between the donor and acceptor molecules, and not via the resonance mechanism, as occurs during energy migration in the fluorescence state.

V. M. Chulanovskii and O. V. Sverdlova¹¹⁴ investigated the interaction between identical mole-

cules of aromatic compounds according to their effect on the form of the absorption spectra of benzene solutions. B. S. Neporent and V. P. Klochkov¹¹⁵ discovered and investigated the interaction of unexcited molecules in the gas phase, in which the conditions of the experiment (high temperatures and low density) excluded the formation of complexes and associations. These interactions were investigated also for mutual shielding of aromatic molecules against disturbance of their π -electron systems through collisions with light gas atoms.

The latter papers refer already to the study of the effect of the medium on the spectral characteristics of molecules. Also pertinent in this respect are the investigations of the effect of the solvent on the spectra of the dissolved substance. M. D. Galanin and Z. A. Chizhikova,¹¹⁶ as well as B. S. Neporent and N. G. Bakhshiev,¹¹⁷ investigated the influence of the solvent on the values of the Kravets absorption integral, and found that for complex aromatic molecules the influence of the solvent can be accounted for by introducing corrections for the dependence of the internal field in the solutions on the refractive index of the solvent and on other characteristics of the system.

C. Electronic Spectra of Crystals. The uniqueness of the spectra of crystals with ordered and strong interactions between their particles makes it mandatory to segregate papers on the investigation of solid state spectra (monocrystalline and polycrystalline, pure and impure) in a separate class — solid state spectroscopy — on par with atomic and molecular spectroscopy. Therefore we limited this brief examination to certain investigations chiefly connected with the study of crystal molecules in which spectra of individual molecules occur. From the number of investigations on inorganic crystalline substances, we shall dwell only on those of special spectroscopic interest.

Significant success was achieved in the investigation of spectra and optical properties of molecular crystals at low temperatures, in which the spectra of many substances acquire a developed fine structure. This work, largely concerned with aromatic compounds, was begun by I. V. Obreimov as far back as 1929. It had been set up by him in the Academy of Sciences of the Ukrainian S.S.R., where it is continued to this day and carried out at present over a broad experimental and theoretical front (see the review article by A. F. Prikhot'ko¹¹⁸).

The staff of the laboratory headed by A. F. Prikhot'ko, using the methodology developed at the laboratory, is carrying on investigations of absorption and luminescence spectra of crystals

in polarized light, accompanying these investigations with measurements of dispersion of crystals with methods suggested by I. V. Obreimov¹¹⁹ and developed in the laboratory to a state in which they can be used at low temperatures (20 to 70°K). Parallel extensive investigations are being carried out in the same area by a group of theoreticians.

From the well-known results of these studies we mention first the investigations of I. V. Obreimov, A. F. Prikhot'ko, and K. G. Shabalda^{120,121} on spectra of crystals and molecules of naphthalene, and the theoretical work of A. S. Davydov,¹²² in which it was shown, by accounting for the molecular interaction in molecular crystals, that along with "molecular" levels there were also "crystalline" levels and splitting, determined by the properties of the elementary cell of the crystal (Davydov splitting). Without accounting for these results, investigation of molecular crystals spectra are no longer possible.

A natural development of the work under discussion are the numerous investigations of the spectra of frozen crystals of a large number of aromatic compounds. In these investigations, owing to combination of the study of spectra and dispersion measurements, essential information was obtained on the oscillator strength and the orientations of basic electronic transitions relative to the axes of the molecule and the crystal. In a number of theoretical papers the properties of crystalline (free exciton) and molecular (localized exciton) levels were examined in detail, and the laws of molecular interaction in the lattice, etc., were investigated. The structural transformations of crystals were also subjected to experimental study. At present, interesting investigations of the influence of elastic deformation of crystals on their spectra are being carried on. The interest in attaining decreased molecular interaction led to the investigation of monocrystalline solutions of certain aromatic substances in others; both theoretical and experimental work was done on the influence of the solvent on the molecules of the dissolved substance, as well as on problems of energy migration from the solvent to the dissolved substance (localization of the exciton), or between the molecules of the dissolved substance found at relatively large distances. Investigations of luminescence acquire a significant role in such experiments. The transition to solution is accompanied in many cases by an improvement in the structure of the absorption and luminescence spectra. These and following works up to the most recent ones are examined in the cited review by A. F. Prikhot'ko,¹¹⁸ which also contains a detailed bibliography.

In the program for the detailed study of electronic-vibrational spectra of molecules of complex aromatic substances, of special interest are the investigations of E. V. Shpol'skiĭ and associates,¹²³ who established that frozen, snowlike solutions of these substances (coronene, pyrene, benzpyrene, and other polyatomic hydrocarbons, and even anthraquinone) in certain saturated hydrocarbons exhibit excellent line structure in absorption and fluorescence spectra. Structured spectra appear only with specific dimensional ratios of the molecules of dissolved substance to the molecules of the solvent, whereas the fine structure details of these spectra depend on the properties of the solvent molecules. The nature of the phenomena determining the existence in frozen snowlike solutions of discrete spectra is of separate scientific interest. Independent of this, the possibilities of investigating the structural details of electronic and vibrational levels of polyatomic aromatic molecules, which this method affords, are of very great interest, inasmuch as it is practically free of limitation in the selection of solvent, a limitation inherent, for example, in the "oriented gas" method.

From the investigations of inorganic crystals we should mention the work of E. F. Gross and his associates,¹²⁴ who discovered and investigated absorption line spectra, and then almost simultaneously with V. A. Arkhangel'skaya and P. P. Feofilov,¹²⁵ the emission line spectra of several crystalline semi-conductors at low temperatures. These spectra were attributed to the excitation of the exciton and reverse transitions, although V. A. Arkhangel'skaya and P. P. Feofilov, as well as V. L. Broude and others,¹²⁶ turned their attention to the dependence of the absorption lines of certain salts on the properties of the investigated sample, which, possibly, supports the point of view that there is a connection between the observed spectra and lattice defects or impurities.

Interesting investigations of absorption and emission centers introduced in cubic crystals of NaF, CaF₂, and others were carried out by P. P. Feofilov,¹²⁷ who used polarization methods that he had worked out with S. I. Vavilov for the study of molecular luminescence systems. Here the orientation of color centers in isotropic cubic crystals was discovered, and the distribution of the so-called "F₂-centers" relative to the axes of the crystal was explained which made it possible to ascertain the nature of these centers. Analogous investigations of fluorite crystals activated with europium permitted determination of the nature of the oscillators responsible for the individual transitions in this atom. From the investigation of the

Zeeman effect in such crystals conclusions were reached on the nature of the oscillators responsible for the formation of lines in a number of rare earth atoms.¹²⁸

A series of investigations of luminescence spectra of uranyl salt crystals was undertaken by A. N. Sevchenko and other,¹²⁹ who analyzed the spectra of a number of salts and studied the processes of temperature quenching of luminescence in them. Recently, A. N. Sevchenko and L. V. Volod'ko¹³⁰ investigated the spectra of luminescence of a number of complex uranyl salt crystals and established that the majority of the lines in their spectra are connected with lattice vibrations.

III. METHODOLOGICAL INVESTIGATIONS

The most important methodological problem of contemporary spectroscopy is the exclusion of instrument error, i.e., determination of the true spectra of the studied emission recorded by the spectroscopic apparatus. Work in this direction was recently completed by A. V. Iogansen⁵³ for absorption spectra and by M. M. Sushchinskii²⁸ for Raman spectra, in which it is necessary to take into account also the width of the excitation line. Further investigations were carried out by I. V. Peisakhson,¹³¹ S. G. Rautian, G. G. Petrash, and others. These authors pointed out that the possibility of excluding instrument error, or the accuracy with which the apparatus function is computed, i.e., reduction of the measurements to the ideal spectroscopic apparatus, depends on the accuracy with which it is possible to measure the spectrum, i.e., on the level of interference. I. S. Abramson and A. I. Mogilevskii,¹³² as well as others, examined the problem of accounting for the enumerated factors as well as calculating the time constant of the recording device, which introduces additional errors into measurement results, depending on the spectrum scanning rate. The general examination of the status of the problem and methods of accounting for these factors was given in a review article by O. D. Dmitrievskii, B. S. Neporent, and V. A. Nikitin¹³³ and in a review by S. G. Rautian.¹³⁴ As a result of these investigations, it is possible to select optimum operating modes for the apparatus and to account for the distortion of the spectra by the apparatus.

The second large group of investigations to be discussed relates to the development of methods for determining optical constants of substances by measurements of diffuse reflection, transmission, scattering, or radiation by finely dispersed particles of the substance being investigated or by bodies that carry this substance in the form of

volume or surface impurities. A special conference, the proceedings of which were published,¹³⁵ was called to consider these problems. The status of the problem and the work completed up to 1956 are discussed in a report read at the conference by B. I. Stepanov.¹³⁶ The investigations discussed, begun about 30 years ago in the Soviet Union, were recently intensively continued in theoretical investigations by B. I. Stepanov and O. P. Girin, G. V. Rozenberg, V. V. Antonov-Romanovskii, A. P. Ivanov, and Yu. I. Chekalinskaya, in which the problem was examined both in the framework of transport theory as well as with conceptual models of the scattering body as a layered system. As a result, it was possible to establish the connection between the experimentally measured parameters and the optical constants of the layer material. Investigations carried out by A. S. Toporets,¹³⁷ A. P. Ivanov,¹³⁸ and Z. V. Zhidkova¹³⁹ demonstrated the possibility of qualitative, and in certain cases also quantitative, determination of the optical characteristics of substances from experimental data.

The determination of optical constants from absorption measurements meets difficulties, especially in the infrared region of the spectrum, connected with the impossibility of obtaining sufficiently thin samples. In this connection, methods were developed recently for determining optical constants of substances from spectra of their specular reflection. T. P. Kravets and his associates¹⁴⁰ developed a method using the reflection of radiation emission from the boundary of a radiating body with two other bodies having different indexes of refraction. L. D. Kislovskii,¹⁴¹ using the possibility of approximating reflection spectra in the form of the resonance curve of a damped oscillator, suggested a simple method of determining optical constants from a single measurement of the specular-reflection spectrum, as well as a method for constructing absorption and dispersion curves for a substance from measurement of its reflection at several points. The methods were successfully used for various solid and liquid substances.

From the number of papers devoted to the technological development of spectroscopic research, the first to be mentioned should be the successful work of F. M. Gerasimov and his associates,¹⁴² who developed methods for preparing and testing diffraction gratings, and provided the possibility of making a number of devices having almost maximum resolution and covering a wide region of the spectrum from the extreme ultraviolet to the far infrared.

We already mentioned the diffraction spectrometers for the infrared region up to $1500\mu^{54}$ and the high resolutions for photoelectric regions of 1 to $3\mu^{55}$. Photoelectric diffraction spectrometers for the visible and ultraviolet regions (including vacuum) are being produced by industry.¹⁴³ Photoelectrical spectrometers have been developed in laboratories for the measurement of weak illumination, luminescence,¹⁴⁴ and Raman scattering. The work of M. M. Sushchinskii,¹⁴⁵ and Ya. S. Bobovich and D. B. Gurevich¹⁴⁶ served as the basis for the industrial manufacture of photoelectrical equipment for the measurement of Raman spectra. Among these is the recording spectrometer DFC-12 having a double monochromator with diffraction gratings (after B. A. Kiselev¹⁴⁷), which in combination with low-pressure mercury lamps makes it possible to obtain Raman spectra of such materials as strongly scattering glasses, powders, gases, etc.

For everyday laboratory use industry is manufacturing spectrometers for the infrared region from 2 to 15μ , single beam (IKS-12) and double beam (IKS-14), spectrographs (ISP-51), and photoelectric spectrometers (ISP-51 and PS-381) for the measurement of Raman spectra, spectrometers (SF-2 and SF-4) for measurement of spectra in the visible and ultraviolet regions, etc. A review of spectroscopic equipment being produced by industry in the U.S.S.R. is given in reports by V. K. Prokof'ev.^{143,148}

From the number of spectroscopic devices developed in laboratories, we also mention the high-speed spectrophotometer developed in the I. V. Obreimov laboratory by V. I. Dianov-Klokov and I. A. Palitsyna¹⁴⁹ with which the electronic absorption spectra of a large number of organic compounds have been measured. Equipment with polarization devices for microspectroscopic investigations is being produced by industry for the visible region, and is being constructed in the laboratories^{150,151} for the infrared.

In conclusion let us note the work of L. A. Tuzerman, M. D. Galanin, and A. M. Bonch-Bruevich and associates (see review, reference 152) on the development of reliable and accurate fluorometric devices which will permit determination of the duration of fluorescence up to 10^{-10} to 10^{-11} sec, i.e., measurement of the probability of transition in intense electronic spectra. A. M. Bonch-Bruevich gave a careful analysis of the method and basic causes of measurement error of this nature. The original apparatus ("taumeter") for oscillographic measurements of duration of the order of 10^{-3} to 10^{-7} sec was developed and used in many investigations by N. A. Tolstoi and P. P. Feofilov.¹⁵³

¹ G. S. Landsberg, Сочинения (Works), U.S.S.R. Acad. Sci. Press, Moscow, 1958 p. 457.

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⁵ VIII Conference on Spectroscopy, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **17**, 523-668 (1953); **18**, 249-300 (1954).

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¹⁸ L. M. Sverdlov, reference 7, pp. 278, 282; reference 9, p. 1023.

¹⁹ R. I. Podlovchenko and M. M. Sushchinskii, reference 7, p. 99; reference 9, pp. 1073-1078.

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