Meetings and Conferences

PHYSICAL METHODS OF INVESTIGATION OF THE STRUCTURE OF MOLECULES

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Expanded session of the Scientific Council for "Theory of Chemical Structure, Kinetics, and Reactivity" in the Division of Chemical Sciences, Academy of Sciences, U.S.S.R.

THE Scientific Council for "Theory of Chemical Structure, Kinetics, and Reactivity" of the Division of Chemical Sciences of the Academy of Sciences, U.S.S.R. convened on May 14 and 15, 1958 at the Institute of Chemical Physics, Academy of Sciences, U.S.S.R. to hold an expanded session devoted to the status of physical experimental methods for the investigation of the structure of molecules. The session attracted great interest and more than 300 persons participated.

In his opening address, Academician V. N. Kondrat'ev formulated briefly the scope of the broadened session, the presentation of a clear picture of the status of different physical methods for the investigation of the structure of molecules at the scientific institutions of the Soviet Union, the adoption of specific measures for further expansion of the scale of application of these methods, and the disclosure of fields where scientific progress is still noticeably lagging.

The status of diffraction methods in the research on the structure of molecules (x-ray diffraction, electron diffraction, neutron diffraction) was discussed by Prof. A. I. Kitaigorodskii, who divided the diffraction methods into three large groups.

The first group deals with stereochemical problems in the determination of the spatial arrangement of the atoms in the molecule. Here the interatomic distances can be measured with an accuracy to 0.1 A, while the valence angles can be determined accurate to several degrees. Detailed research in stereochemistry has recently uncovered new approaches towards the understanding of the reactivity of the molecule. Diffraction methods can render great help in this field.

The second group involves the study of the relative placement of molecules in crystals. This is the principal method of investigating intermolecular interactions. The accuracy required here is also not too high; x-ray diffraction and neutron diffraction solve such problems with sufficiently good results.

The third group of problems deals with the determination of the interatomic distances and valence angles in molecules with such a degree of accuracy, that the results can be compared with those obtained by theoretical calculations. The prevalent opinion is that this problem is basic to diffraction methods and that principal attention should be paid to it. However, the method is at the limit of its capabilities when used for solving these problems. It is necessary to take into account the crudeness of the theory, the difficulty of introducing corrections for absorption in the sample, and the fact that diffraction methods yield a structure that is an average over all the elementary cells, regular and distorted. In organic chemistry, a substance containing 0.1% of impurities is considered to be quite pure. In such a crystal, however, one encounters one molecule of impurity for each nine molecules along any direction. This impurity distorts the lattice in a volume that exceeds considerably the volume per single molecule. This is why a precise determination of the structure of the molecule can be recommended only for substances of exceptional purity and exceptional crystal quality, i.e., this problem cannot be considered principal in diffraction methods.

When estimating the relative capabilities of electron, x-ray, and neutron diffraction methods, it must be pointed out that the exposures used in these methods are related roughly speaking as $10^{-6} : 1 : 10^6$. The exceedingly long exposures required prevent an extensive use of neutron diffraction. This method can, however, yield important results, for it makes it possible to determine the coordinates of the atoms of light elements down to hydrogen. Electron diffraction also has certain advantages over x-ray diffraction in the determination of the coordinates of the hydrogen atoms, but is greatly inferior to the latter in accuracy. The accuracy of diffraction methods is proportional to the number of reflexes. A good structural result is one in which from 1,000 to 2,000 diffraction dots are used; an electron diffraction pattern rarely contains more than 200. There are

many additional complications. Nevertheless, the electron diffraction method can be a valuable adjunct to x-ray diffraction studies of substances in the solid state. A structural investigation of liquids does not promise any interesting results. A most promising trend is electron diffraction of gases in those cases, when it is necessary to determine experimentally two or three parameters while the remaining parameters can be assumed to be accurately known. The number of problems in which the investigator is interested in the molecule only is quite considerable. Electron diffraction of gases deserves therefore our serious attention.

Progress in diffraction methods is quite slow in our country, owing to a shortage of laboratory centers. It is also difficult to obtain certain types of equipment. In conclusion, A. I. Kitaigorodskii introduced several proposals aimed at further advances in diffraction methods for the study of the structure of molecules.

B. S. Neporent started his talk on electron spectroscopy of molecules by dividing the problems in this field into two large groups: electron spectroscopy of simple molecules, and a study of complex molecules that have continuous spectra.

This subdivision is connected with the substantial difference between the methods of investigation. The study of a developed vibrational spectrum of a molecule, consisting of well resolved lines is a purely spectroscopic problem. The low-selectivity spectra of the complex molecules is a more difficult problem, in which it is impossible to confine oneself to obtaining the spectral characteristics. It is necessary to resort to luminescent investigations and to investigations of the state of polarization, of the glow of the molecules, of the action of the solvent, of the effect of complex formation, etc. Such investigations are carried out quite extensively in the U.S.S.R. and occupy a prominent position in the world's science. For many systems, reliable results have already been obtained on various molecular characteristics of interest to chemists: the mobility of the electron shell, the probability of the thermal activity upon variation of the electron state, the production of the biradical state, etc. A study has been made, for example, of the suppression of the photochemical processes in many synthetic materials based on organic compounds, a factor that lengthens the service life of such materials.

The Institute of Chemical Physics of the U.S.S.R. Academy of Sciences is engaged in studies on the spectra of radicals, aimed at determining the role of radicals in chemical reactions. However, we lag foreign science in this very promising field as far as the scale of the research goes.

High-level research on spectra of organic substances in the crystalline state is being done under the leadership of A. F. Prikhod'ko. It has been possible to obtain interesting data on the reactivities of molecules.

Research on complex molecules in the gas phase is being carried out on a small scale (Moscow State University and Leningrad State University). The spectra of adsorbed molecules are investigated, and the changes in the spectra yield information on the energy properties of the adsorption phenomena.

The most research is being done on polyluminescence — optical investigations involving luminescence of complex molecules and resulting in spectra that have no vibrational structure. This work is done essentially by Soviet scientists who use original methods to study the transfer of excitation energy from one molecule to another and to measure the concentration of the investigated molecules in the solid, liquid, or gaseous state.

In conclusion, B. S. Neporent noted that the status of spectroscopic apparatus, from the point of view of assortment and quality of instruments produced, is satisfactory, but the volume of production is frequently inadequate.

E. V. Shpol'skii devoted his lecture to the spectroscopy of polyatomic organic molecules. The lecturer defines "spectroscopy" as the production and measurement of sharp spectra, from which wavelengths can be determined with an accuracy to not less than 0.1 A. If such a spectrum is obtained, it is possible to determine from it the energy levels, to ascertain the symmetry of various states, to determine the transition probability, etc.

Until recently, more attention has been paid to absorption spectra than to emission spectra. Yet emission spectra, obtained by optical excitation, i.e., luminescence spectra, help solve many important problems. Such spectra of organic molecules disclose not only the allowed transitions, but also forbidden ones and help study the probabilities of many energy processes in the molecules. It is customary to assume that to obtain sharp spectra it is necessary to investigate the substance in gaseous state. In the case of polyatomic organic molecules the situation is just the opposite: gas spectra of such molecules are quite smeared out, owing to the abundance of natural oscillations and the presence of a quasi-continuum of the rotational states in the polyatomic molecules. Consequently, it is necessary to reduce the temperature, and to strive as close as possible to absolute zero, i.e., to proceed to the observation of crystal spectra. Such investigations are carried abroad out at hydrogen

and helium temperatures, and it is proposed to begin the study of spectra at helium temperatures in this country in the nearest future. When using single crystals, this procedure permits the use of polarized light, thus greatly facilitating the interpretation of the results.

However, spectroscopy of molecular crystals has two very serious shortcomings. First, the interaction of the molecules in the crystal lattice causes the appearance of the so-called lattice lines. Second, in complex molecules such as condensed aromatic hydrocarbons (pyrene, coronine, etc.), the spectra are smeared out even at helium temperatures, owing to the strong resonance effects (the sharing of electrons). The California group found a way out by preparing a substitution solution of the investigated substance in an isomorphous crystal solvent, so that the investigated molecules could be fixed at sufficient distances from each other. It was necessary in this case that the crystal solvent be transparent in the region where the spectrum of the dissolved substance was located. This occurs very rarely (McClure found only three pairs of substances that give solid solutions satisfying the above requirement).

E. V. Shpol'skii used the freezing of weak solutions of the investigated hydrocarbons in normal paraffins (pentane, hexane, and higher). In this case the luminescence spectra (singular and triplet) of the polynuclear atomic hydrocarbons, in pure substances in crystalline state (polycrystalline and single-crystal), which produce even at low temperatures a single wide continuum extending over several thousands of reciprocal centimeters, and split up even at nitrogen temperature (77°K) into a multitude of narrow lines. At the hydrogen temperature (20°K) there occurs a further narrowing of the lines and new fine details appear. The sharpness of the lines is such that it is possible to undertake a vibration analysis of the spectra (coronene, pyrene, 3, 4-benzpyrene) and to carry out in many cases a qualitative analysis of natural mixtures and artificial products. Whatever absorption spectra could be obtained appeared in the first absorption region, like the luminescence spectra.

M. M. Sushchinskii lectured on "Methods of Vibrational Spectroscopy." Thirty years have passed since the discovery of Raman scattering, and infrared spectra have been investigated for 50 years. Infrared spectra of nearly 20,000 substances have been obtained, and Raman spectra are available for more than 2,000 substances.

The list of products is continuously expanding: organic and inorganic substances, various commer-cial products, natural substances, and various biological objects. Studies are made on gases, liquids, solids, glasses, and polymers. The lecturer pointed out the inadequate level of most researches: the investigators confine themselves to plotting the spectrum without interpretation and without attempts to obtain from their curves the physical characteristics of the molecules. This is frequently explained by the fact that the regularly available instruments, ISP-51 and IKS-11, do not permit a detailed study of vibrational spectra.

M. M. Sushchinskii briefly described the long known capabilities of the methods of vibrational spectroscopy (determination of number of definite structural groups in the molecule, determination of interatomic forces, explanation of the electron-optical properties of the molecule), and then listed the following recent new research trends:

(1) Establishment of the presence of rotary isomers, a helpful procedure in the investigation of high-polymer compounds.

(2) Spectroscopy of compressed gases.

(3) Study of infrared spectra in polarized light, which sometimes permits location of the bonds in polymers and biological objects.

(4) Investigation of the rotational structure of infrared vibrational spectra and purely rotational Raman spectra, which makes it possible to determine the moments of inertia of molecules and hence the interatomic distances and valence angles.

(5) Raman spectra, taken near the region of the natural electron absorption of the molecule, yield information on the electrostatic properties of the molecules (P. P. Shorygin).

(6) Infrared spectra of molecules adsorbed on the surface (A. N. Terenin) clarify the nature of adsorbing centers.

(7) Owing to the tremendous volume of experimental material, the documentation of vibrational spectra assumes great importance.

Comparison and foreign works shows that the ideas and the skill of the leading Soviet investigators are the equal of those abroad, but that the working conditions are much worse here than, for example, in the U. S. The shortage of help, the inadequacy of the technical equipment, and the great lack of interest on the part of theoretical physicists in molecular spectroscopy are to blame.

The paper by V. I. Divanov-Klokov was devoted to infrared spectroscopy of compressed gases. When a pure gas or a mixture of gases are compressed, the interaction between a given molecule and its neighboring one can lead to a change in the symmetry, causing in turn a removal of the forbiddenness of certain transitions (forced absorption).

It was established that the intensity of absorption corresponding to vibrational frequencies of hydrogen, nitrogen, or oxygen increases in proportion to the square of the pressure, indicating an interaction between two molecules.

In 1955 Kittelar observed in gas mixtures absorption frequencies corresponding to differences and sums of all the vibration frequencies of the corresponding molecules. This was treated as a simultaneous vibrational transition in two molecules. It turned out to be more convenient technically to carry out these experiments in liquid mixtures. This was followed by an experimental verification of earlier assumptions on the possibility of simultaneous electron transitions in two colliding oxygen molecules.

The lecturer noted that little material was accumulated during the ten years elapsed since the beginning of these investigations. This was attributed to great difficulties with apparatus, since the observation turned out to be possible in the most favorable case (mixture of a polar and a non-polar gas) only at pressures on the order of 20 atmos. To observe the effect in a mixture of non-polar gases it is necessary to have hundreds of atmospheres, and in the case of electron transitions in oxygen, the necessary pressure amounts to thousands of atmospheres.

The spectroscopy of compressed gases can yield information on intermolecular interactions, particularly on the formation of unstable complexes. Considerable progress has been made in the theory of forced absorption. No theory of simultaneous transitions has been developed so far. Experiments in this field have been successful in the U.S.S.R. only at the INEOS, (Institute of Elementary Organic Compounds) Academy of Sciences, U.S.S.R. (I. V. Obreimov).

Further progress in the research is greatly hindered by the lack of apparatus capable of plotting a spectrogram within one or two minutes, by difficulties in producing sufficiently low temperatures, and by the lack of high-pressure cuvettes (up to 3500 atmos).

Lively discussions followed the first five lectures.

M. A. El'yashevich supported A. I. Kitaigorodskii's proposal to organize research on specific groups of substances by different methods. Such investigations are frequently hindered by the lack of the necessary pure substances. A radical solution to the problem of research at hydrogen and helium temperatures must be found. New electronic computers are necessary for theoretical work in the field of molecular structure.

Comrade **Makarov** discussed the application of electron beams to the study of excitation levels of molecules. Such investigations call for apparatus with mechanical workmanship of very high grade. It is necessary to organize production of suitable equipment in the plants.

Comrade **Zamkov** called for further research on the application of the Kerr effect. This procedure makes it possible to obtain rapidly accurate data for the determination of the structure of molecules and for analytical purposes. No suitable apparatus has yet been produced, and should be manufactured as soon as possible.

Comrade **Levin** spoke of the unhappy state in the manufacture of modern infrared spectrometers. An impression is gained that plants are afraid of complicated electronic circuits. The proposed organization of a card file of molecular spectra should be rapidly put into practice.

E. V. **Shpol'skii** noted the obvious unfavorable situation in theoretical research in the field of electronic and electron-vibrational spectra. The attention devoted by theoretical workers to nuclear physics is understandable and justified, but this does not mean that it is necessary to refrain from work on solid-state physics. So far there are no centers for systematic training of young theoreticians, whose interests would lean towards these difficult problems. Semiqualitative model representations are very important to experimenters, and of great help in their work. It is also necessary to develop classical computational methods with use of the most modern computational techniques. The most important problem is to bridge the gap between us and the U. S. with respect to the number of cryogenic installations. It is necessary to publish an atlas of absorption spectra.

N. D. **Sokolov** also noted that among the 70 or 80 theoreticians, who graduate every year from the Physics Faculty of the Moscow State University, only one or two remain to work in molecular physics. Certain changes are necessary in the training of theoretical physicists, so that the students do not get the idea that molecular physics is an "uninteresting" field. N. D. Sokolov supported the proposal of A. I. Kitaigorodskii that a new journal, "The Structure of Matter," be published.

B. S. **Neporent** acquainted the participants of the session with the work of the Commission on Spectroscopy on documentation of molecular spectra. Foreign catalogues should be acquired in the near future to accelerate this work. In spite of the general high level of Soviet spectroscopic research, we rarely publish work in which experimental mastery is combined with so high a theoretical level.

It is necessary to organize theoretical groups in laboratories. To improve the apparatus situation substantially, it is necessary to broaden the instrument-building base.

Ya. L. Gol'dfarb recalled that for five or ten years principal attention was concentrated in chemistry on the nature of the bond. What is of primary importance now is the dependence of the reactivity on the stereochemistry of the molecules in the ground and in the transition states. In the development of physical methods of help to chemists, it is therefore necessary to remember above all the stereochemical problems. Interchange of experience must be organized so that workers in various institutes can turn to others where some method is being developed for advice or for material help. It is necessary to welcome initiative shown by the Scientific Council in demonstrating to a large circle of persons the various tools that physics places at the disposal of chemistry.

G. L. Slonimskii has emphasized that all modern methods acquire particular significance in the investigation of the structure of polymers. It is here that the greatest number of physical measurements are carried out and that the least are reported. It is advisable to devote a special session of Scientific Council to the results of the investigation and the structure of high-molecular substances by various physical methods.

A. A. Brandt delivered a lecture on the electric methods of investigating the structure, properties, and interaction of molecules. Measurement of the dielectric constant makes it possible to determine the value of the dipole moment, the period of dipole oscillations, the relaxation time, etc. Measurement of the electric losses makes it possible to measure small concentrations of polar groups, inaccessible to infrared spectroscopy. Losses in crystals are determined by the density of packing, i.e., experiment in this field give information on the interaction and structure of molecules. This uncovers a way towards solving problems of importance to radio engineering, such as the production of new materials with low losses. Unfortunately, existing methods of measuring losses are still insufficiently accurate. To increase the significance of electric methods of research on the structure of molecules it is necessary to have closer contact between physicists and chemists. It is necessary to train radio-physicists in the measurement of different properties of matter. It is necessary to produce standard apparatus for the measurement of dielectric constants, to publish a collection of materials on the dielectric properties of matter, and to organize a laboratory for research on the electric properties of matter.

Comrade **Ivanov** supported the proposed development of apparatus for the measurement of electric characteristics of matter in a wide range of frequencies and temperatures.

The session of May 15 opened with a lecture by **A. M. Prokhorov**, devoted to gas radiospectroscopy and electronic paramagnetic resonance. The advantage of gas radiospectroscopy is that one can work with small quantities of matter: a small cavity need be filled with gas at a pressure of 10^{-2} mm mercury. Absorption takes place at centimeter waves. The object of study are simple molecules with electric and magnetic dipole moments. Complicated molecules give a large number of overlapping weak lines. Isotope substitutions shift the lines. From the intensity is is possible to estimate the value of the potential barrier of the torsional vibration about a single bond. A recent development is a theory whereby these barriers are determined from frequency measurements. If the molecule contains nuclei with non-vanishing electric quadrupole moments, the splitting of the lines of the rotational spectrum make it possible to determine the constant of the quadrupole bond of the free molecule. These data can be compared to measurements of the quadrupole bond in the solid state, carried out by the method of the nuclear quadrupole resonance. The lecturer has noted that the number of problems solved by gas radiospectroscopy is not very extensive. It is therefore meaningful to make use of this method only if a specific research plan has been formulated. The lecturer then described the capabilities of electronic paramagnetic resonance as regards the study of the structure of molecules and the kinetics of chemical reactions. It becomes possible to clarify the valence state of paramagnetic ions and to observe transition from one valence to the other. In liquids it is possible to study the solvate shells and processes of complex formation. It is easy to observe a small number of free radicals, occurring in chemical reactions. The significance of research in the free radicals for chemistry cannot be overestimated, for here is a literally unchartered territory as far as work is concerned. This is why electronic paramagnetic resonance is gaining more and more recognition. The essential problem here is the acquisition of modern apparatus and good magnets.

L. A. Blyumenfel'd devoted his paper to applications of electronic paramagnetic resonance in biology and in the study of methylorganic compounds. In the laboratory of V. V. Voevodskii (Institute of Chemical Physics, Academy of Sciences, U.S.S.R.) an investigation of organic compounds containing strontium and chromium has led to far-reaching conclusions concerning the electron structure of

these compounds. A recently-observed interesting phenomenon is that the hyperfine structure of paramagnetic-resonance lines depends on the nature of the solvent and on small additives of various substances to the solvent. The theory of this phenomenon has not been developed but is apparently will prove useful for research on the possibility of formation of solvate complexes etc.

Another intersting trend in the work of this laboratory is research in radiation chemistry — the study of free radicals formed by gamma irradiation of hydrocarbons and high polymers.

Irradiation of frozen hydrocarbons produces a large yield of alkyl free radicals, the structure of which is determined uniquely from the hyperfine structure of the absorption lines. It is also possible to observe in these experiments signals of free atomic hydrogen. Both the free radicals and the atomary hydrogen can be stored in frozen state for many days. When the temperature is increased it is possible to observe the recombination kinetics.

Electron paramagnetic resonance is used in L. A. Blyumenfel'd's laboratory to study the mechanism of fermentative catalysis. Definite conclusions have been drawn concerning the structure of albumen ferments: it has been ascertained that an excess electron obtained in one manner or another is delocalized to a considerable extent over the albumen molecule. This makes it possible to tackle the problem of changes produced in albumens by muscular contractions etc. In conclusion, L. A. Blyumenfel'd noted the need for regular production of spectrometers for the study of electronic paramagnetic resonance.

A report by **B. M. Kozyrev** on the work done at the Laboratory for Electronic Paramagnetic Resonance in Kazan' was read by N. D. Sokolov. Information was obtained in this laboratory on the symmetry of local electric fields that act on the ion from the solvate shell, on the lower boundary of the lifetime of the solvates, and on the partially-covalent character of the bonds between the central ion and the molecules of the solvate shells. The character of the chemical bonds between paramagnetic ions and their surroundings can be studied also in glass-like systems. An investigation is being made of the influence of adsorption of paramagnetic gases (O_2 and NO) on the width of the absorption line in diphenyl pycril hydrazil at various temperatures. Above $0°C$, the adsorbed oxygen forms on the surface of the free radical a so-to-speak two dimensional liquid; when the temperature is reduced, the motion of the adsorbed O_2 molecules "freezes." In addition, work is being done on proton resonance in carbons and other carbon-con-

taining substances and apparatus for observing the quadrupole resonance is under study. At the Kazan' State University and the Kazan' Branch of the U.S.S.R. Academy of Sciences, extensive theoretical and experimental research is being done on spin-lattice relaxation in salt crystals and in electrolyte solutions.

N. D. Sokolov noted the high level of the work of the Kazan' group, where a genuine collaboration between theoreticians and experimenters has been established. There are still many unsolved problems in the theory of radiospectroscopy. Among the most important ones is that of quadrupole interactions, theoretically very difficult, which can yield important data on the character of bonds, on the distribution of the electron density, etc.

N. D. Sokolov then took the floor to deliver a paper on the use of nuclear magnetic resonance in chemical research. If a constant external magnetic field H_0 is imposed on a specimen, containing nuclei with non-zero magnetic moment μ, this magnetic moment can become oriented in different manners relative to the external field, each orientation corresponding to a definite energy level. The distances between the neighboring levels are $\mu H_0/I$, where I is the nuclear spin. If the constant magnetic field is modulated by a weak radio-frequency field at a frequency given by $h\nu = \mu(\mu/I)H_0$, the orientation changes, i.e., resonance absorption of the energy of the radio-frequency field takes place. Strictly speaking, the field in which the nucleus is located is not equal to H_0. It is less than H_0 by a value σH_0, due to the influence of the electron shell. The constant of magnetic screening, σ, is sensitive to variations in the number of electrons surrounding the given nucleus. For example, protons having different electron surroundings give somewhat different resonant frequencies, and this manifests itself in a fine splitting of the line of nuclear magnetic resonance. In addition to this fine splitting (chemical shifts), one can observe in the magnetic spectra a hyperfine multiplet structure, due to the interaction between paramagnetic nuclei of different atoms with each other through the electron spins. A characteristic quantity is also the spin-lattice relaxation time, determine from the rate of change of the signals under definite conditions, and also the spin-spin relaxation time, determined from the widths of the signals.

Measurement of the chemical shifts makes it possible to determine the structure of the molecules. Thus, a molecule of ethyl alcohol contains three different protons: the proton of the CH_3, group, the proton of the CH_2 group, and the proton

of the OH group. The nuclear magnetic resonance spectrum of ethyl alcohol, when properly resolved, therefore consists of three lines, whose intensities are related as 3:2:1. An analysis of the hyperfine multiplet structure discloses not merely the presence of similar groups, but also their location. Research of this type is carried out in our country at present at the Leningrad University under the leadership of F. I. Skripov and at the Moscow University under Yu. S. Konstantinov, using flourine containing compounds. Research on chemical shifts in proton resonance is being done extensively abroad.

A deeper study of the structure of the molecule by this method requires a theoretical analysis of the connection between the values of the chemical shifts and the structural molecule. Only the first steps have been made in this direction thus far.

Interesting results were obtained in the study of the hydrogen bond by means of proton magnetic resonance. The speed of the reaction can be estimated from the form of the signal. A. I. Rivkind uses the sensitivity of the spin-lattice relaxation time to the presence of paramagnetic impurities to determine the character of the interaction of the solvate shell with the central ion.

It must be noted that the level of Soviet research in the field of nuclear magnetic resonance lags considerably the parallel work abroad. This is explained by the lack of apparatus.

The character of the requirements imposed on nuclear magnetic spectrometers suitable for the study of the structure of molecules is detailed in the paper by **N. M. Ievskaya**. It is necessary to distinguish between broad lines and narrow lines of nuclear magnetic resoance. Broad lines have widths from 0.1 to 10 gausses. To record such lines, the apparatus must discern from 0.01 gauss to 1 gauss. Since experiment is carried out in fields on the order of 10 gausses, the resolution of the apparatus should be in this case from 10^{-4} to 10^{-6}. This is a requirement imposed on the homogeneity of the field, on its stability, and on the stability of the frequency of the field. When working with broad lines the signals obtained are weak and it therefore becomes necessary to take use more material, on the order of 10 cm^3. In this case 1 cm^3 should contain from 10^{16} to 10^{18} nuclei of the investigated element. When studying the chemical shifts it is necessary to deal with lines ranging from 0.1 to 100 milligausses in width. The resolution required in this case is from 10^{-6} to 10^{-9}. It is impossible to obtain such great homogeneity in large volumes; the specimens must be on the order of 0.1 cm^3. In these experiments 1 cm^3 of the specimen should contain 10^{17} to 10^{18} nuclei of

the investigated element. The chemical shifts increase with increasing mass number. The chemical shifts for hydrogen nuclei do not exceed 10 milligausses, i.e., the spectrometer resolution must be better than 10^{-7}. A resolution of 10^{-5} to 10^{-6} is sufficient to observe the chemical shifts of fluorine. This is exactly the resolution of our best apparatus "home made" by the researchers themselves in Leningrad, Moscow, and Kazan'. Yet in the U. S. the Varian company produces commercial nuclear magnetic spectrometers, which have excellent characteristics. Our lag in this field will not be overcome until the laboratories are provided with modern equipment. In the conclusion of her lecture N. M. Ievskaya made several specific recommendations for intensification of work in nuclear magnetic resonance.

V. L. Tal'roze stated certain ideas on the organization of regular production of high-grade radiospectroscopic apparatus.

E. I. Fedin remarked that a new method of investigating molecular and crystalline structure of solids — nuclear quadrupole resonance — did not yet acquire in our country a status commensurate with its significance and with the potentialities of the method. Nuclear quadrupole resonance is unique as regards to sensitivity to chemical effects. While chemical shifts in nuclear magnetic resonance give only the fine structure of the line, requiring resolution to 10^{-8}, similar effects shift the frequency of the quadrupole resonance by several megacycles, the frequency itself being on the order of 30 Mcs. Crystal effects cause splitting of the absorption lines of tens and hundreds of kcs at line widths on the order of 1 to 3 kcs. In the laboratory of A. I. Kitaigorodskii (Institute of Elementary Organic Compounds, Academy of Sciences, U.S.S.R.) a quadrupole radio spectrometer was placed in operation during the last year and projects are under way in this field. The first favorable results were obtained recently in Leningrad and Kazan'. Nuclear quadrupole resonance eliminates the difficulties involved with stabilization of the magnetic field, but the effect is weak. It is necessary to cover a broad band of frequencies (from 1 Mcs to 1,000 Mcs) and to measure the resonance frequencies accurately. Progress is slowed by the lack of many instruments, the acquisition of which ahould be arranged for.

K. V. Vladimirskii spoke about his investigations, which uncovered the possibility of research on chemical shifts not only in hydrogen and fluorine, but in all nuclei with magnetic moments. Usually experiments on chemical shifts are performed under conditions close to stationary, when it is im-

possible to attain the sensitivity necessary for the observation of all nuclei. In a specially selected non-stationary mode (deep modulation of the magnetic field of a relatively high frequency) it becomes possible to obtain spectra which are just as easy to read as those obtained with slow coverage of the resonance region. It turns out that the requirements for apparatus are less stringent in this case. One can measure chemical shifts, for example, in silicon-29 etc., a very important factor in chemistry.

M. A. El'yashevich expressed a few opinions on progress in radiospectroscopic methods. It is necessary to solve quickly the problem of providing suitable apparatus, to join forces of the interested workers, and put an end to home-made equipment. The most important theoretical problem is that of quadrupole interactions, a problem involving complicated mathematical computations of multi-electron systems.

E. V. Shpol'skii indicated that many fine effects, studied by magnetic-resonance methods can be studied with sufficient reliability by using the fine structures of the electron spectra plotted at low temperatures. It has been established that the occurrence of intramolecular hydrogen bonds removes the fine structure. The same effect is obtained by the formation of a glass-like state. Naturally, it is necessary to have diffraction gratings of high resolution, but they are easier to prepare than radiospectrometers.

L. L. Dekabrun spoke of the many advantages of the pulse technique of observation of nuclear resonance ("spin-echo"). If two successive radio frequency pulses of suitably selected frequency and spacing are applied to a specimen, a "spin-echo," which is a pulsed nuclear-resonance signal is produced in the receiving equipment. This relaxes substantially the requirements concerning the homogeneity of the magnetic field, and the apparatus becomes simple and reliable. The procedure is indispensable if the relaxation times play the principal role, and also in research of exploratory character. Steps must be taken towards the application of pulse methods to nuclear resonance.

Ya. G. Dorfman delivered a paper on magnetochemistry. Strictly speaking magnetic methods of molecular research should include not only the measurement of susceptibility but also all varieties of magnetic-resonance experiments. Unfortunately radiospectroscopic investigations are usually separated from purely magnetic ones.

Statistical methods of measuring the susceptibility are applicable to liquids and solids. Meas-urements of susceptibilities of gases and vapors are still in the development stage. For such a simple object as methane, various authors give experimental values that differ by a factor of more than three. Recently radiotechnical methods have been developed for the measurement of susceptibility, and these increase substantially the speed of the experiment. Apparently this method can be used to measure the susceptibility of not only the end products of the reaction, but also of the products produced furing the time of reaction.

Magnetic susceptibility can usually be represented in the form $\chi = \chi_{p0} + \chi_d + \chi_p$, where χ_{p0} is the orientational paramagnetic susceptibility, χ_d the diamagnetic susceptibility (the Langevin precession), χ_p the paramagnetic term connected with the deformation of the electron shells. χ_{p0} is connected directly with the measurement of the number of unpaired spins; the value of χ_d must be taken into account to determine χ_{p0}. The diamagnetic correction for light molecules is small, but in many cases it cannot be neglected. A way out can be found by combining measurements of χ with the use of paramagnetic resonance. At a sufficient intensity of the radio-frequency field it is possible to "turn off" the orientation term and to measure only χ_d, thus estimating the dimensions of the orbit. Furthermore, when investigating mixtures of substances it is possible to "turn off" individual components of the mixture. No such work has been performed anywhere. The lecturer reports on the results of his latest investigations: he has found out that χ_d exhibits a pronounced dependence on the electric polarizability, i.e., χ_d can be calculated for a large number of molecules with great accuracy. This makes it possible to determine χ_p, something no one has engaged in. Knowledge of χ_p will make it possible to estimate the asymmetry of the electron shell. All this is outwardly reminiscent of Pascal's scheme, but the Pascal experiments has no physical meaning while the proposed additive scheme is based on modern concepts of the mechanism of the phenomenon. Magnetochemistry can deepen substantially the results of research on the electronic structure of free radicals, obtained with the aid of paramagnetic resonance. A very promising study is that of magnetic properties of molecules during the course of chemical reactions. In conclusion, Ya. G. Dorfman noted the quite unsatisfactory situation with respect to magnetochemical research in the Soviet Union and proposed certain measures to improve the situation.

N. D. Sokolov agreed with the poor opinion of the state of our magnetochemistry and support

Ya. G. Dorfman's proposals. N. D. Sokolov praised highly the establishment of a linear connection between the magnetic susceptibility and the electric polarizability.

M. A. El'yashevich again called for close contact between different fields of research and for a rapid elimination of the lag in some of the neglected sections of our science, such as magnetochemistry. Another area is radiospectroscopy of molecular beams.

A paper on mass-spectrometric research on the structure of molecules was read by V. L. Tal'-roze. Although mass spectrometry gives less data on the structure than optics or radiospectroscopy, the information it does yield is sometimes unique. The principal data that can be obtained are the ionization potential of the molecule and the binding energy of the molecule. Ionization is effected by electron impact in deep vacuum, and is followed by mass spectroscopic analysis of the resultant ions. The ionization potentials can be estimated in this case accurately only if the electron beam is sufficiently monochromatic. This problem has not been fully solved, but it becomes possible to obtain satisfactory accuracy. Recently the accuracy has been increased through the use of photoionization. The binding energy is more difficult to determine, owing to the indeterminacy in the states of the electron-impact products. It becomes necessary to complicate the research substantially by carrying out a series of measurements and by leaning on thermochemical data. In addition to the binding energy and the ionization potential, it becomes possible to obtain qualitative information on the structure of molecules by splitting them with a beam of electrons having energies on the order of several thousands electron volts and by subsequent analysis of the fragments. Here we can speak only of the positions of the double bonds, and of the positions of the large atom groups that are bound to carbon or to other heavy atoms. The position of the hydrogen and of several other atoms cannot be established, since strong regroupings occur inside the excited ion during such an ionization. Investigations of this type, cannot be carried out with the mass spectroscopes produced by our industry. It would be necessary to organize production of additional adapters for the regular-production instruments, permitting rapid conversion of the mass spectroscopes to the measurement of ionization potentials and binding energies. As to the analytic applications of mass spectroscopy, the situation in this field is satisfactory from the point of view of quality. We lag behind the U. S. or England in the number of projects and in the use of mass spectroscopy in manufacture.

In his concluding remarks, Academician V. N. Kondrat'ev noted that several years ago our lag in research on the structure of molecules was considerably greater than now, and that the situation has been substantially improved. Many investigators, whose interests have been hitherto confined to apparatus, begin to be interested in molecular structure once they start operating the apparatus. There is no doubt that when more equipment becomes available the lag in some fields will be rapidly overcome.

On May 22 the scientific council adopted an extensive resolution concerning the proceedings of its broadened session of May 14-15.

Translated by J. G. Adashko