ELEVENTH CONFERENCE ON LUMINESCENCE

(Molecular Luminescence and Luminescence Analysis)

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THE 11th Conference on Luminescence took place September 10-15, 1962 in Minsk with participation of more than 370 persons from thirty cities of the Soviet Union. More than 180 papers were given in the 23 sessions.

In opening the conference, V. L. Levshin, the chairman of the Scientific Council on Luminescence, emphasized the important role of the Council in directing and coordinating the scientific studies on luminescence and its applications being carried out in the various research centers, and in concentrating scientific efforts on the fundamental, current, and promising lines.

The papers read at the conference can be divided into the following classes as to subject:

I. Molecular luminescence:

1. The laser effect. 2. Theory of molecular luminescence. 3. Luminescence of molecular crystals. 4. Quasilinear spectra of frozen solutions. 5. Yield and quenching of luminescence of solutions. 6. Luminescence of vapors of organic compounds. 7. The effect on luminescence of molecular association, the solvent, and other physicochemical factors. 8. Triplet states. 9. Molecular luminescence of inorganic compounds. 10. Luminescence of chlorophyll, proteins, and other biologically important compounds. 11. Molecular luminescence and chemical problems (relation of luminescence to molecular structure, chemiluminescence, etc.).

II. Luminescence analysis:

1. Luminescence analysis in chemistry. 2. Luminescence analysis in biology, medicine, microbiology, and veterinary medicine. 3. Luminescence analysis in technology, industry, and geology. 4. Apparatus and methods of luminescence analysis.

I. MOLECULAR LUMINESCENCE

1. The laser effect. Considerable attention was paid in the conference to a new line of development in optics, quantum light generators (lasers). The Institute of Physics of the Academy of Sciences of the Belorussian SSR presented a series of theoretical papers casting light on a number of new results involving: a) characteristics of absorption and emission at high radiation densities; b) the theory of a resonator containing an active substance. P. A. Apanasevich gave a paper, "The dependence of the absorption, emission, and scattering of radiation on the intensity of the incident radiation" (Institute of Physics of the Academy of

Sciences of the Belorussian SSR, Minsk). He derived by quantum-electrodynamic methods the relation of the absorption and the characteristics of the scattering and photoluminescence to the spectral composition and intensity of the incident non-monochromatic radiation being absorbed by the medium, as well as to the non-optical transitions. Another paper (G. S. Kruglik and P. A. Apanasevich, "The problem of coherent spontaneous emission," Institute of Physics of the Academy of Sciences of the Belorussian SSR) discussed the conditions under which coherent spontaneous emission can be manifested with an intensity proportional to the square of the number of emitting particles. They showed that such an emission is impossible under ordinary conditions. The characteristics of the absorption coefficient at high intensities were taken up in a paper by V. P. Gribkovskii, "Induced anisotropy of the absorption coefficient" (Institute of Physics of the Academy of Sciences of the Belorussian SSR), showing that the absorption coefficients for linearly polarized or natural light agree with that for isotropic radiation only at low or very high intensities.

A paper by **B. I. Stepanov** and his colleagues at the plenary session, "Stimulated emission in an infinite plane-parallel layer," dealt with the resonator theory of lasers, and reviewed studies performed recently by the research group in the Institute of Physics of the Academy of Sciences of the Belorussian SSR. The paper gave results of the solution of the transfer equations and the Maxwell equations for an infinite layer having a negative absorption coefficient in the absence of external radiation. They derived the conditions for steady-state laser action. By taking into account the nonlinear dependence of the absorption coefficient on the radiation density, they could determine the values of the radiation density and the energy liberated within the layer under conditions of steady-state laser action. The conditions for existence of energy fluxes having different directions and frequencies were discussed. A paper by B. I. Stepanov, A. M. Samson, and Yu. I. Chekalinskaya, "The effect of noise on laser action in a finite plane-parallel layer" (Institute of Physics of the Academy of Sciences of the Belorussian SSR) discussed the radiation field within and outside of a resonator in the presence of noise. A paper by A. P. Khapalyuk (Belorussian State University, Minsk), "On the possibilities of laser action in a system of plane-parallel layers" analyzed the characteristic radiation of a

stack of plane-parallel plates having either a positive or negative absorption coefficient.

The problem of the properties of the active substance within the resonator was taken up in a paper by B. I. Stepanov, A. M. Samson, and V. P. Gribkovskii, "The influence of the characteristics of the substance on the properties of the generated radiation" (Institute of Physics of the Academy of Sciences of the Belorussian SSR). A calculation was made in this study of the power absorbed in pumping, the luminescence, and the power and threshold for laser action in a plane-parallel layer having three energy levels. A four-level system in a laser was discussed in a paper by V. L. Broude, V. S. Mashkevich, A. F. Prikhot'ko, N. F. Prokopyuk, and M. S. Soskin, "Stimulated emission in molecular crystals" (Institute of Physics of the Academy of Sciences of the Ukrainian SSR, Kiev). They showed that the optical properties of molecular crystals provide a basis for constructing lasers in such systems. The peculiarities of the emission kinetics of lasers were discussed in a paper by A. M. Samson and V. A. Savva, "Non-steady-state emission in a plane-parallel layer showing laser action" (Institute of Physics of the Academy of Sciences of the Belorussian SSR).

Several papers dealt with experimental studies on lasers. A paper by M. D. Galanin, A. M. Leontovich, E. A. Sviridenkov, V. N. Smorchkov, and Z. A. Chizhikova given in the plenary session, "Characteristics of the emission of a ruby laser" (Institute of Physics of the Academy of Sciences of the USSR, Moscow) studied the kinetics of laser action at room and low temperatures (down to -165° C), and the characteristics of the coherent radiation in a ruby laser. At room temperature, as the pumping intensity was increased, the frequency of the laser pulses increased. As the temperature was lowered, the lifetime of the pulses decreased and their frequency increased (with the pumping kept constant), and finally they went over into continuous emission randomly modulated in time. They studied the characteristics of the coherent emission in the laser action by interference experiments, and found that coherent radiation is emitted from the entire face of the laser crystal.

A report by A. M. Bonch-Bruevich, V. V. Vargin, Ya. A. Imas, G. O. Karapetyan, Ya. É. Karis, M. N. Tolstoĭ, and P. P. Feofilov was given at the plenary session, "Luminescence and stimulated emission of glass activated with neodymium" (State Optical Institute, Leningrad). They studied the absorption and luminescence spectra of glasses containing 0.1-10%neodymium. They observed the generation of stimulated emission in the region of 1.06μ , both in filamentous specimens of diameter 0.1-1 mm enclosed in a glass envelope having a similar refractive index, and in massive specimens (diameter 2-2.5 mm, l = 70mm) prepared from optically homogeneous glass. They observed laser action, both at room and at liquidnitrogen temperatures. The threshold for laser action was 0.4-2 kJ. The spectrum of the generated emission had a rather broad band (60 Å). The kinetics of the laser action took the form of pulses, sometimes occurring at random times, but sometimes occurring at regular time intervals.

The papers were subjected to general discussion.

2. <u>Theory of molecular luminescence</u>. As in the previous conferences, much attention was paid to theoretical problems.

Great interest was aroused by a paper by K. K. Rebane and V. V. Khizhnyakov (Institute of Physics and Astronomy of the Academy of Sciences of the Estonian SSR), which presented the results of theoretical studies on the Mössbauer effect. The authors were able to find an analogy between the Shpol'skiĭ effect, electronic-vibrational transitions in impurity centers in ionic crystals, and the Mössbauer effect. They showed that one can find series of lines in the spectra of impurity centers. They concluded that important information on the structure of organic glasses and crystals can be obtained by studying the Mössbauer effect.

A new variant of the theory of diffusion quenching of the fluorescence of solutions by foreign substances was proposed by B. Ya. Sveshnikov (deceased), A. S. Selivanenko, V. I. Shirokov, and L. A. Kiyanskaya (State Optical Institute, Leningrad). These authors showed that in solving the diffusion equation for the sphericalsymmetry case we can replace Smoluchowski's assumption of an infinitely rapid rate of absorption of the diffusing particles, by that of a finite and relatively small rate. Then the formulas derived from this assumption for the relation of the yield and the lifetime of the fluorescence to the viscosity of the solution explain the experimental curves well. A paper by A. M. Samson (Institute of Physics of the Academy of Sciences of the Belorussian SSR) proposed a generalization of the theory of quenching of luminescence by foreign substances. With the proper choices of the energytransfer probability function, equations were derived both for resonance and diffusion quenching.

L. L. Krushinskii and P. P. Shorygin (Institute of Organic Chemistry of the Academy of Sciences of the USSR, Moscow) reported on an application of a model of a classical linear oscillator with periodically-varying parameters to explain the resonance transformation of light by molecules. Within the framework of this model, they derived an expression to describe the secondary emission analogous to the quantum-mechanical formula of Kramers and Heisenberg. As a result, they showed that if the decay constant γ is larger than the vibration frequency ω_0 of the nuclei, the intensity distribution among the scattering lines as determined from theory agrees qualitatively with the experimental data on resonance scattering. When $\gamma < \omega_0$, it agrees with the distribution characteristic of resonance fluorescence. They also showed that the dependence of γ

on the vibrations of the nuclei can result in appearance of resonance Raman scattering.

In a paper, "On the time-dependence of reflection and transmission," A. S. Rubanov and A. P. Khapalyuk (Institute of Physics of the Academy of Sciences of the Belorussian SSR, Belorussian State University) discussed a plane-parallel plate (or pile of plates) in reflection and transmission as a linear filter having a complex transfer function determined by the amplitude coefficients for reflection and transmission. This permitted them to describe a non-steady state in reflection (or transmission) using the complex transfer function of the linear filter.

As we know, one can study the propagation of light in media theoretically, taking into account the scattering and photoluminescence on the basis of the transfer equations. The problem becomes much more complicated when we must take into account multiple scattering and luminescence processes. Two papers by K. S. Adzerikho (Belorussian State University, Minsk) discussed these problems on the basis of the characteristics of the light field by using the Stokes parameters. In particular, by solving the differential equations for the Stokes parameters by an iteration method, this author determined the effect of multiple processes on the polarization of the light emerging from the substance.

A paper by Yu. T. Mazurenko (State Optical Institute) discussed the phenomenon of photoluminescence from the standpoint of the second law of thermodynamics for irreversible processes. He showed that thermodynamics does not impose additional limitations on the theoretical methods of calculation for photoluminescent systems, nor thus, on the luminescence yield.

A paper by V. S. Rubanov (Institute of Physics of the Academy of Sciences of the Belorussian SSR), "On energy migration and transfer in a two-component mixture," discussed a two-component mixture showing energy migration and transfer at low acceptor concentrations, using a one-dimensional model. He studied the relation of the efficiency of energy transfer to the intensity of migration, the acceptor concentration, and to the parameters characterizing the molecular properties of the components.

3. Luminescence of molecular crystals. Interest in luminescence and other optical properties of molecular crystals has continually grown. The conference paid much attention to this field of problems. Above all, we must mention here a group of interesting papers presented by the Institute of Physics of the Academy of Sciences of the Ukrainian SSR (Kiev).

A paper at the plenary session by V. L. Broude, E. F. Sheka, and M. T. Shpak, "Exciton luminescence of molecular crystals," analyzed the conditions for appearance and the peculiarities of exciton luminescence in molecular crystals, and showed that the exciton luminescence bands, in distinction from impurity emission bands, are characterized by a steep temperature-dependence of the half-widths; this involves the band nature of the characteristic energy states of the crystal. This provides a firm criterion for distinguishing exciton luminescence in molecular crystals.

A paper by **E**. **F**. **Sheka** reported on experimental studies of the absorption spectra of binary and ternary mixed crystals in the series of deuterated naphthalenes. An analysis of the impurity exciton bands permitted him to determine the mutual influence of the impurity states. The experimental data agree well with the Broude-Rashba theory of absorption in mixed crystals.

M. T. Shpak, A. V. Vasil'ev, and N. I. Sheremet discovered a band corresponding to a direct transition from the exciton band in the luminescence spectrum of crystalline benzene at 20°K.

A paper by V. N. Vatulev, "The effect of the crystal structure on the absorption spectrum and the luminescence of impurities in molecular crystals," showed for the example of anthracene as an impurity in crystals of 9,10-dihydroanthracene and octahydroanthracene that the line spectra of impurities can serve as a sensitive indicator of phase transformations in the crystal, and as a supplementary source of information about this process.

V. I. Gribkov, N. D. Zhevandrov, and E. I. Chebotareva (Institute of Physics of the Academy of Sciences of the USSR) showed in a paper, "A study of the dependence of the polarization of the luminescence of single crystals of stilbene on the wavelength of the emission at liquid-nitrogen temperature," that the marked changes in the polarization observed at room temperature on the short-wavelength side of the luminescence spectrum of a single crystal of stilbene disappear at liquid-nitrogen temperature. This result agrees with the theory of excitons in molecular crystals.

V. L. Zima, V. M. Korsunskii, and A. N. Faidysh (Kiev State University, Kiev) studied anthracene crystals containing as impurities naphthacene, phenazine, acridine, and anthraquinone, and showed that the phenomenological theory of diffusional motion of excitons satisfactorily explains the observed dependence of the quantum yields on the impurity concentration.

A paper that elicited much interest was given by V. P. Kovalev, V. K. Dobrokhotova, Yu. V. Nabořkin, and L. S. Kukushkin: "Emission from molecular crystals containing impurities of differing solubilities in the solid phase" (State Optical Institute, Leningrad, and Low-temperature Physico-technical Institute of the Academy of Sciences of the Ukrainian SSR, Khar'kov). They showed by fluorometric study of the lifetime of emission of an impurity by direct excitation and excitation via the major component that intermediate local states appear in impure molecular crystals, owing to the localization of the exciton at the impurity, and transition from these states to the excited impurity level is hindered.

A paper by Yu. V. Naboikin, S. V. Sverdlov, and

A. A. Avdeenko, "Triplet emission from molecular crystals," dealt with the systematics of molecular crystals from the standpoint of triplet emission. In the discussion on this paper, V. M. Korsunskii and A. N. Faidysh reported that they had discovered triplet-state energy migration in benzophenone crystals containing naphthalene and naphthacene impurities.

Directly bordering on this topic are some papers involved with artificially oriented media (films, polymers) and with energy migration in liquid and solid solutions.

V. L. Broude and E. T. Moïsya (Institute of Physics of the Academy of Sciences of the Ukrainian SSR) reported the results of some studies of exciton processes in one-dimensional systems. They studied the spectra of oriented films at temperatures of 77°K and 20°K, and found that the temperature-dependences of the half-widths of the exciton and molecular bands of χ -isocyanine differed.

In a paper, "On transfer of electronic-excitation energy in liquid solutions of organic substances," E. A. Andreeshchev, S. F. Kilin, I. M. Rozman, and V. I. Shirokov reported on a study of the efficiency of energy transfer between solute molecules in solutions in polystyrene. The results of the measurements were compared with the Förster-Galanin theory of inductive transfer. The experimental values of the transfer parameter exceeded the theoretical values by a factor of 1.5-1.9.

A paper by V. A. Krongauz and I. N. Vasil'ev (Karpov Physico-chemical Research Institute, Moscow) reported on a study of energy-transfer processes by luminescence and radiation-chemical methods. They showed that the protective action of luminophors from certain radiation-chemical effects can be explained by the competition of energy transfer from the solvent to the object substance and the luminophor and from the luminophor to the object substance. The authors expressed some ideas on the mechanism of the energy transfer from the solvent and from the luminophor.

In a paper presented by the United Institute of Nuclear Studies (M. T. Kostyrko, E. N. Matveeva, M. N. Medvedev, M. G. Pisareva, and M. D. Shafranov, "Luminescence of paravinylbiphenyl and parapenta-phenyl"), experimental data were given on the emission from these substances in crystals and polymers when irradiated with $Co^{60} \gamma$ -rays.

4. Quasilinear spectra of frozen solutions. An entire set of papers dealt with the study of absorption and fluorescence spectra and their characteristics by the Shpol'skiĭ method.

The problems discussed in the papers along this line can be divided into the following groups: 1) the nature of the Shpol'skiĭ effect, 2) the possibility of using substances other than the normal paraffins as matrices, 3) the study and analysis of the electronicvibrational spectra of new compounds, and 4) the possibility of using the method for purposes of spectroscopic luminescence analysis.

A long paper by É. V. Shpol'skiĭ (Lenin State Pedagogic Institute, Moscow) at the plenary session paid major attention to the source of the multiplet character of the sharp quasilinear electronic-vibrational spectra of frozen solutions in n-paraffins. He broadly discussed the problem of the methods of incorporation of fluorescent molecules into a crystalline matrix. The peculiarities of behavior of the spectra of different solutions at different temperatures and under different conditions of freezing led to the idea of examining the analogy with inclusion compounds. As we know, the fluorescence spectra of n-paraffin solutions of many aromatic hydrocarbons consist of several identical series of sharp lines. A comparison of the leading portions of the fluorescence and absorption spectra showed that the individual series may involve emission from centers that do not interact with one another, and apparently differ in being incorporated into the polycrystalline matrix of the frozen solvent in different ways. G. M. Svishchev was able to confirm this result. The fluorescence spectrum of nparaffin solutions of coronene at 77°K consists of characteristic doublets. When the solution of coronene is illuminated with monochromatic radiation having the frequency of one of the components of the corresponding doublet in the excitation spectrum, the fluorescence spectrum exhibits only one component. The problem of the temperature-dependence of the widths of the spectral fluorescence lines was taken up in a paper by A. Ya. Khesina (Lenin State Pedagogic Institute, Moscow). She showed that the lines broaden as the temperature increases from 77°K to the melting point of the solvent.

As a rule, normal paraffins are used as solvents in studying the quasilinear spectra. Of interest in this regard is a paper by M. M. Val'dman and G. D. Sheremet'ev (Pedinstitut, Chelyabinsk). Here, in a study of the sharp luminescence spectra of perylene and the diisobutyl ester of 3,9perylenedicarboxylic acid (defektol') at 20.4°K, they used as solvents not only the normal paraffins, but also crystalline dibenzylaminoethanol. Besides, they noted in the same paper an interesting relation of the sharpness of the fluorescence spectra of defektol' to the solvent: the fluorescence spectra are appreciably sharper if one uses as the solvent the n-paraffins having an odd number of carbon atoms (heptane, nonane, undecane) rather than those having an even number of C atoms (octane, decane). V. L. Levshin and Kh. I. Mamedov (Institute of Physics of the Academy of Sciences of the USSR, Moscow, and Institute of Physics of the Azerbaijanian SSR, Baku) showed that one can use isoparaffins, e.g., 2,2,4-trimethylpentane to obtain sharp spectra from α - and

 β -methylnaphthalene. We should note that it would be interesting to try to use also other symmetrical isoparaffins giving a polycrystalline matrix upon freezing.

The Shpol'skii method has been widely applied for analysis of the electronic-vibrational spectra of organic compounds. In the conference, studies were reported in which sharp spectra were obtained from a number of new compounds: azulene (Z. S. Ruzevich, Lenin State Pedagogic Institute, Moscow), dianthrylethylene (V. K. Dobrokhotova, V. A. Kul'chitskii, and Yu. V. Naboikin, Lowtemperature Physico-technical Institute, Khar'kov), biphenyl, terphenyl, quaterphenyl, and diphenylbutadiene (G. V. Gobov and T. N. Bolotnikova, Pedinstitut, Chelyabinsk, and Lenin State Pedagogic Institute, Moscow) 3,9-perylenecarboxylic acid ester (M. M. Val'dman and G. D. Sheremet'ev), indigo, N.N'-dimethylindigo, 5.5'-dichloroindigo, tetrachloro- and tetrabromoindigo (R. N. Nurmukhametov, D. N. Shigorin, and Yu. I. Kozlov, Karpov Physicochemical Scientific Research Institute, Moscow).

A paper of **T**. N. Bolotnikova and G. V. Gobov dealt with a study of the luminescence spectra of biphenyl, terphenyl, quaterphenyl, stilbene, and diphenylbutadiene. They followed the change in the extent to which neighboring vibrational frequencies were manifested as the length of the molecule was increased. They found a similarity of the spectra of solutions of terphenyl and quaterphenyl with those of stilbene and diphenylbutadiene, respectively. That is, the replacement of the inner benzene rings by -CH=CH- groups has little effect on the nature of the electronic-vibrational spectrum.

P. A. Teplyakov (Odessa) used the Shpol'skiĭ method to interpret the phosphorescence spectrum of phenanthrene in the normal paraffins (from n-hexane to n-nonane) under the assumption advanced previously by a number of authors that emission occurs from two metastable levels.

R. I. Personov (Lenin State Pedagogic Institute, Moscow), in developing his previous studies, obtained the fluorescence and absorption spectra of metal-free phthalocyanine in various n-paraffins at 77°K. The sharpness of the spectra of the solutions of phthalocyanine in octane, nonane, and decane permitted him to distinguish differences in the effect of the solvent on the two regions of the long-wavelength absorption spectrum involving different electronic transitions. A detailed study of the spectra of n-paraffin solutions of pyrene was reported in a paper by L. A. Klimova (Lenin State Pedagogic Institute, Moscow). She was able to obtain sharp absorption spectra of pyrene in the region of the second electronic transition. It turned out that the vibrational frequencies of the second excited state practically do not differ from those

of the molecule in the first excited electronic state. A painstaking analysis of the exceedingly complex fluorescence spectrum showed that a number of frequencies that had previously been assigned as nontotally-symmetric are active in this spectrum.

A number of papers were concerned with the application of quasilinear spectra for luminescence analysis. V. L. Levshin and Kh. I. Mamedov obtained and studied sharp fluorescence and phosphorescence spectra from α - and β -methylnaphthalene, and remarked that the existence of the fine structure increases the possibilities for luminescence analysis of crude oils and other complex mixtures. In order to ascertain the possibility of using the Shpol'skii method in analysis of complex mixtures, V. K. Dobrokhotova, V. A. Kul'chitskii, and Yu. V. Naboikin studied the fluorescence spectra of two-component frozen hexane solutions of a mixture of naphthalene and dianthrylethylene. They showed that with excess naphthalene concentration and excitation in the 313 m μ region (where naphthalene molecules absorb), the emission spectrum of dianthrylethylene becomes diffuse. In the paper they noted that one must take into account the possibility of energy-migration processes in analysis of mixtures.

5. Yield and quenching of luminescence of solutions. Studies on the subject of radiationless deactivation of excited states of luminescent molecules are necessary to solve the cardinal question of luminescence, that of the reasons why some compounds luminesce and others do not. A number of papers were concerned with this line of research.

V. V. Zelinskii presented a paper at the plenary session (State Optical Institute), "The dependence of processes of radiationless deactivation of luminescence on the positions of the spectra." On the basis of an analysis of a wealth of experimental material, the author proved a hypothesis, which he had advanced previously together with L. G. Pikulik and V. P. Kolobkov, that there is a correlation between the effects of various factors on the fluorescence yield (and also the phosphorescence yield) and on the position of the maximum in the fluorescence spectrum. L. G. Pikulik entered the discussion to furnish new experimental data in favor of the close mutual connection between the effects of the solvent on the spectra and on the yield.

Considerable interest was aroused by a paper by V. L. Ermolaev (State Optical Institute), "Pathways of radiationless deactivation of excited aromatic molecules in glassy solutions." On the basis of prior studies of sensitized phosphorescence, literature data on the effect of deuteration on the phosphorescence of organic compounds, and measurements made in this study of the quantum yield and lifetime of the ordinary and the sensitized phosphorescence of naphthalene, biphenyl, and their deuterated derivatives, the author concluded that processes of radiationless deactivation proceed via the lowest triplet state. The probabilities of radiative and radiationless transitions from the triplet state were determined in the study. Yu. V. Morozov (Institute of Radiation and Physicochemical Biology of the Academy of Sciences of the USSR, Moscow) showed for organic dyes (acridine orange and trypaflavin) that the fundamental process of radiationless deactivation in a molecule is direct conversion to the ground state. The probability of quenching from the triplet level determines only the phosphorescence yield. There is no contradiction between the results of these studies, since they were obtained from compounds of different classes. Apparently, primarily the structure of the molecule determines the predominance of the one or the other deactivation process. V. V. Zelinskii, I. A. Zhmyreva, and V. P. Kolobkov (State Optical Institute) measured the temperature-dependence of the absolute quantum yield of solid organoluminophors to investigate deactivation processes. They showed that in dyes of the fluorescein group, the quantum yield of the total emission is near unity when α -phosphorescence occurs. Lowering of the temperature leads to disappearance of the α -phosphorescence and a decrease in the total quantum yield.

Problems of the luminescence yield are closely connected with the problem of the existence of the Stokes cut-off (the change in the form of the emission spectrum when excited in the anti-Stokes region). This problem was the topic of a paper by G. P. Gurinovich, E. K. Kruglik, and A. N. Sevchenko (Institute of Physics of the Academy of Sciences of the Belorussian SSR, Minsk), who showed that there is no Stokes cut-off at all in most studied cases (they studied dyes and phthalimide derivatives in various solvents). In the cases in which they observed a deformation of the spectrum under anti-Stokes excitation, they could ascribe it to the existence of several types of luminescent centers in the solution.

S. V. Volkov, L. A. Limareva, and V. I. Shirokov (State Optical Institute) compared the decay laws in the presence of impurity quenching and concentration quenching, and reported on a new fluorometric apparatus having modulation frequencies of 11.2 and 131 Mc. The presence of two modulation frequencies permits one to study deviations of the decay law from exponentiality. They showed that for concentrated solutions of fluorescein in glycerin, the deviation of the decay law from exponential is less marked than in quenching by absorbing impurities. This was explained by the occurrence of multiple energy transfer in the concentration quenching. A paper by T. M. Vember, "On the mechanism of the effect of aromatic amines on the fluorescence and photochemical oxidation of anthracene compounds," showed that the extent of quenching depends on the electron density in the anthracene ring system and in the benzene ring of the aromatic amines. He concluded that the quenching of the fluorescence in the cases examined is due to electron transfer from the quenching agent to the excited molecule.

A. N. Nikitin, G. S. Ter-Sarkisyan, B. M. Mikhailov, and L. E. Minchenkova (Institute of Organic Chemistry of the Academy of Sciences of the USSR, Moscow) found an increase in the quantum yield of fluorescence of the polyenes that they studied (substituted hexatrienes) upon going from heptane solutions to solutions in benzene and toluene. Since the oscillator strength and the fluorescence lifetime decreased here, the authors concluded that the molecules of the studied compounds when in the excited state form complexes with the molecules of the aromatic solvents.

The absolute quantum yield of fluorescence and the absorption and emission spectra of fourteen coumarin derivatives were studied in a paper by **P. I. Petrovich** and **N. A. Borisevich** (Research Institute of Organic Intermediates and Dyestuffs, Moscow, and Institute of Physics of the Academy of Sciences of the Belorussian SSR, Minsk). These compounds are of interest in that they are used for optical bleaching of fabrics, the bleaching effect here being due to their blue fluorescence. The authors mentioned the most promising substances, having high quantum yields and favorable positions of the fluorescence spectrum, in particular 7-aminocoumarin.

6. Luminescence of vapors of organic compounds. The study of the luminescence of polyatomic molecules in the gas phase is of highest importance for the theory of luminescence. Studies along this line were represented by five papers.

N. A. Borisevich (Institute of Physics of the Academy of Sciences of the Belorussian SSR) gave a paper at the plenary session presenting some results obtained in a study of excited states in the gas phase, using the universal relation between absorption and emission spectra, and based on studying the temperature-dependence of the absorption coefficient of the vapors. The major part of the paper was concerned with the peculiarities characteristic of the fluorescence yield of rarefied vapors. In line with the formula according to which the fluorescence yield is defined as the ratio of the differences in the mean energies of the molecules leaving the excited state radiationlessly and with emission of fluorescence, these differences were found for a number of molecules of various groups of compounds (perylene, 1-aminoanthraquinone, β -naphthylamine, anthracene, and some phthalimide derivatives). He showed that the stated energy differences under certain conditions can serve as a measure of the activation barrier of radiationless transitions.

A paper by V. V. Gruzinskii (Institute of Physics of the Academy of Sciences of the Belorussian SSR) dealt with the application of the universal relation to structured spectra of molecules. The calculated temperatures of the excited molecules permitted the determination in a simple manner of the electronictransition frequency and the vibrational heat capacity of β -naphthylamine and perylene vapors. He showed that the quantum yield in perylene vapor is practically independent of the size of the exciting quantum. Hence, the inversion point was determined by the action of the foreign gases on the fluorescence spectrum, rather than on the quantum yield. The values of the inversion point and the electronic-transition frequency obtained from the universal relation practically coincide with the 0-0 transition for perylene vapor.

A study of the temperature-dependence of the absorption spectra of complex and semicomplex molecules was the subject of a paper by V. A. Tolkachev (Institute of Physics of the Academy of Sciences of the Belorussian SSR). On the basis of a method permitting one to express the distribution of molecules in the excited state in terms of the equilibrium distribution, he obtained a relation between the absorption coefficient and the mean effective excitation energy. The derived relation is applicable to spectra of complex and semicomplex molecules. For all the studied substances, the effective energy generally proved not to equal the value of the exciting quantum. The smallest deviations here were observed in the Stokes excitation region, and the largest in the anti-Stokes region.

Studies on the effect of temperature on the quantum yield of luminescence of vapors of organic compounds were reported by V. P. Klochkov (State Optical Institute). The author observed both the usual decrease in the yield and also a small increase, in agreement with the dependence of the quantum yield of fluorescence of the studied substances on the frequency of the exciting quantum. It turned out that the effects of foreign gases on the shapes of the fluorescence spectra differed when the excitation was carried out at different wavelengths. Here the size of the effect decreased as one approached a certain wavelength (the inversion point).

A paper by V. T. Korotkevich (Institute of Physics of the Academy of Sciences of the Belorussian SSR) reported some results obtained in a study of a series of methylated and ethylated phthalimide derivatives in the gas phase.

The reported studies on luminescence of vapors aroused a lively discussion, in which V. L. Levshin, B. S. Neporent, N. A. Borisevich, etc., participated.

7. The effect of luminescence of molecular association, the solvent, and other physicochemical factors. A long paper by V. L. Levshin (Institute of Physics of the Academy of Sciences of the USSR) at the plenary session was concerned with concentration quenching of luminescence of solutions. He showed in the paper that concentration quenching results from a number of processes. In many cases, molecular association is of decisive significance. He discussed various forms of the effect of association, taking into account diffusion of excited particles and diffusion of excitation energy. The important role of migration of energy to nonluminescent associations in the process of con-

centration quenching was demonstrated also in a paper by B. Ya. Sveshnikov (deceased), V. I. Shirokov, and L. A. Limareva (State Optical Institute), "The mechanism of concentration quenching in solutions of fluorescein, rhodamine B, and trypaflavin in glycerol." A paper by L. V. Levshin and V. G. Bocharov, "A study of molecular association of rhodamine 6G in binary solvents" (Moscow State University) explained the observed concentration effects by molecular association and the solvent effect. In a paper, "On the application of the phenomenon of concentration quenching of luminescence to determine the degree of association of molecules in solution," A. S. Selivanenko and M. V. Fock (Institute of Physics of the Academy of Sciences of the USSR) proposed a method of calculation of the relative number of aggregates. E. G. Baranov and V. L. Levshin (Institute of Physics of the Academy of Sciences of the USSR), in a paper "Concentration quenching in alcoholic solutions of rhodamine 6G," compared the onset of association with the trend in the concentration quenching. Yu. V. Morozov (Institute of Radiation and Physico-chemical Biology of the Academy of Sciences of the USSR, Moscow) reported on the peculiarities of the luminescence of dimers of acridine orange and rhodamine B.

Thus, the conference showed that the process of molecular association is being widely and successfully studied by luminescence methods. Such studies are of great interest, particularly in regard to the important role which the association process seems to play in living nature, and to the possibilities which it furnishes for study of biological objects.

Several papers dealt with the effect of the solvent and other physicochemical factors on luminescence of solutions. V. V. Zelinskii (State Optical Institute) showed in a paper, "Spectroscopic scales of solvents," that solvents can be arranged in a series such that their effect on the spectra of solutes varies monotonically. The author considered here that the position of a solvent on the scale involves its chemical nature rather than its macroscopic characteristics. The effect of the state of aggregation on spectra was investigated in a paper by O. P. Kharitonova (Institute of Physics of the Academy of Sciences of the Ukrainian SSR), who studied the spectra of 2,6-dimethylnaphthalene in the vapor, in solution, and in the crystal. In a paper, "A quantitative study of the temperature-dependence of the absorption and fluorescence spectra of complex molecules in solution," I. V. Piterskaya and N. G. Bakhshiev (State Optical Institute) attempted a quantitative interpretation of the observed regularities, starting with a theory describing the effect of the universal intermolecular interactions on the spectra. The effect of temperature on the spectroluminescent characteristics of complex molecules was also taken up in a paper by L. F. Gladchenko and L. P. Pikulik (Institute of Physics of the Academy of Sciences of the Belorussian SSR), who interpreted the spectral

shifts and other temperature effects by taking into account the mobility of the molecules in the medium. Experimental data on the effect of ten different solvents on the absorption and fluorescence spectra of some five-membered heterocyclic compounds were reported by L. M. Kutsyna, L. A. Ogurtsova, and O. P. Shvaïka (All-Union Scientific Research Institute of Monocrystals, Khar'kov); these data permitted the authors to conclude that the specific interactions play the major role, rather than the universal interactions. The effects of the solvent, the pH, and other related problems, were also dealt with in papers by A. P. Kilimov, L. N. Zvegintseva, and I. K. Brandesov (Institute of Physics of the Siberian Division of the Academy of Sciences of the USSR, Krasnoyarsk) and a number of other papers.

Considerable interest was aroused among the participants in the conference by a paper by **B. S. Neporent** and **O. V. Stolbova** (State Optical Institute), "Orientation of molecules under the influence of light." The authors found a subtle effect of photodichroism involving the disturbance of an isotropic orientational distribution of molecules in solution under the influence of polarized light. They discussed the relation between the experimentally-observed photodichroism and the macroscopic parameters of the medium and certain characteristics of the molecules.

8. Triplet states. Among the papers involved with the study of triplet states, we must especially mention a paper by A. K. Piskunov, R. N. Nurmukhametov, D. N. Shigorin, V. I. Muromtsev, and G. A. Ozerova (Karpov Physicochemical Scientific Research Institute, Moscow), "A study of triplet states of molecules by the EPR method and luminescence." The combination of two powerful methods of investigation permitted the authors to obtain a number of new results, in particular involving the relation between the lifetimes of triplet states of molecules and their structures. The especial value of the EPR method consists in the fact that with it, in addition to studying the molecules themselves in various states, one can get information on their interactions with the solvent and with the radicals which appear upon ultraviolet illumination.

A continuation of some well-known studies of energy migration between triplet levels was furnished in a paper by V. L. Ermolaev and E. B. Sveshnikova (State Optical Institute), "Inductive-resonance energy transfer from aromatic molecules in the triplet state." Here, using a large volume of data, they studied the phenomenon of radiationless energy transfer from molecules in an excited triplet state to unexcited molecules, raising the latter to an excited singlet state. In particular, they proved the existence of energy transfer from triplet to singlet levels for some biologically important compounds (tryptophan, chlorophyll). A study of the probabilities of transitions in molecules from the fluorescent to the phosphorescent state was the subject of a paper by A. V. Aristov and the late **B. Ya. Sveshnikov** (State Optical Institute), "On the effect of the temperature on the probability of transition of a molecule to the phosphorescent state." This paper prposed a new method of determining the probability of transition of a molecule from the fluorescent to the phosphorescent state, based on studying the nonlinear relation of the luminescence intensity to the intensity of the exciting light. The proposed method makes it possible to use a new equation, which, together with the previously known equation, constitutes a complete system of equations for calculating all the probabilities of transitions within the framework of the system of Jablonski.

Studies of triplet excited states using triplet-triplet absorption were reported in two papers given by the Institute of Physics of the Academy of Sciences of the Belorussian SSR: "Some results of application of pulse spectroscopic methods to the study of porphyrins," by G. P. Gurinovich and A. I. Patsko; and "Absorption spectra of excited organophosphors," by V. A. Pilipovich and N. I. Tursunov. The former paper gave results of measurements of triplet-triplet absorption spectra of a number of porphyrins and their metal derivatives. They determined the lifetimes of the molecules in the metastable state, and studied the kinetics of accumulation and depletion of particles in the metastable state. They advanced the hypothesis that photochemical reactions can occur under these conditions. The latter paper showed that upon lowering of temperature, the triplet-triplet absorption increases, and energy-level diagrams were constructed for a number of organophosphors. They discovered another triplet energy level. Another paper by V. A. Pilipovich and N. I. Tursunov, "On the temperature-dependence of the quantum yield of phosphorescence of organophosphors," showed that the relative quantum yield of phosphorescence declines with lowering of temperature for the organophosphors having α - and β -bands. A paper by M. D. Khalupovskii (Lenin State University of Daghestan, Makhach-Kala) showed from a study of the rise in intensity of separate narrow regions of phosphorescence spectra that the mean rise time of phosphorescence is not unambiguously related to the mean decay time in the general case.

The conference showed that studies on triplet states are being conducted on a broad front in the Soviet Union, as is quite justified by the importance and timeliness of this problem, which is of great significance in bioenergetics, quantum electronics, and other lines of science. We must especially note the fruitfulness of the application in this field of various optical and other methods of study which supplement and enhance the scope of one another.

9. <u>Molecular luminescence of inorganic compounds</u>. The Conference paid much attention to problems of luminescence of inorganic compounds.

A paper by N. A. Tolstoĭ and A. P. Abramov (State Optical Institute) at the plenary session, "Emission kinetics of chromium luminophors," presented results of a detailed study of the concentration-dependence of the intensity of the secondary emission lines in ruby (involving inveraction between chromium ions), as well as of the relaxation spectra of the emission. The authors concluded that the secondary lines are emitted by centers consisting of pairs of chromium ions (dimers) sensitized by single chromium ions (monomers). In the discussion of this paper, Z. L. Morgenshtern (Institute of Physics of the Academy of Sciences of the USSR) spoke of some measurements which she had performed together with E. E. Bukke on the luminescence yield of ruby. When excited in the absorption bands, the quantum yield was high (~ 0.8), while when excited in the R-lines, it was unity.

A paper by S. G. Zazubovich, N. E. Lushchik, and Ch. B. Lushchik (Institute of Physics and Astronomy of the Estonian SSR, Tartu), "Electronic-vibrational processes and polarized luminescence of mercury-like centers in cubic crystals," reported results of some studies begun in the last few years on spectroluminescent regularities in ionic crystals. The authors studied the polarization spectra, the azimuthal dependence of the degree of polarization, polarization diagrams, and excitation and emission spectra of emission centers in alkali-halide crystals activated with "mercurylike" ions. The results of the studies permitted the authors to conclude that the mercury-like centers in ionic crystals are an intermediate case between free ions and solutions of complex molecules with respect to ease of establishment of an equilibrium distribution among the electronic states.

A study of the luminescence of sodium nitrite at low temperatures was reported by A. F. Yatsenko and Yu. A. Kulyupin (Institute of Physics of the Academy of Sciences of the Ukrainian SSR). The experimental results on the absorption and luminescence permitted the authors to propose that the luminescence of sodium nitrite is intrinsic, rather than due to impurities, the nitrite ion being responsible for the absorption and luminescence spectra.

A paper by I. S. Gorban' and V. M. Kosarev (Kiev State University) reported a study of the optical and photochemical properties of PbI_2 crystals in which photochemical transformations are occurring, as reflected in the photoluminescence spectra. The authors studied the general characteristics of the quenching of the luminescence by radiation, and found characteristic signs permitting sorting of the crystals into photochemically active and inactive ones. The data obtained suggest the possibility of using PbI_2 crystals as a substance capable of remembering light signals.

Some interesting information on the luminescence of platinocyanide compounds was reported in a paper by A. M. Tkachuk (State Optical Institute), who studied crystals and solutions of lithium, potassium, magnesium, and barium platinocyanides. The author observed phenomena of thermoluminescence, photoconductivity, and a dependence of τ on the intensity of the exciting light at high excitation densities. He showed that the characteristics of the emission of frozen solutions are determined by the structure of the micro-crystals that precipitate from the solution upon freezing.

M. U. Belyĭ and I. Ya. Kushnirenko (Kiev State University), studied the spectroscopic characteristics of aqueous solutions of the halides of arsenic, gallium, and selenium at room and at low temperatures. The absorption and luminescence spectra of the solutions of some of the salts exhibited a complex structure. M. U. Belyĭ and B. A. Okhrimenko (Kiev State University) reported the results of studies of the structural peculiarities of the spectral characteristics of luminescent solutions of electrolytes. The objects of study were the ions Pb^{+2} and Bi^{+3} .

Continuing their earlier studies on the luminescence of uranyl compounds, A. N. Sevchenko, L. V. Volod'ko, and D. S. Umreïko (Belorussian State University) reported the results of a study of the temperature- dependence of the absorption and fluorescence spectra of uranyl compounds over a wide temperature range. These studies made it possible to solve a number of questions involving both the nature of the spectra and the mechanism of the fluorescence process. With a large amount of experimental data, the authors confirmed the ideas that they had previously expressed on the complex nature of the electronic absorption spectra of uranyl compounds.

Directly bordering on this series of studies was a long paper at the plenary session by A. N. Sevchenko, V. V. Kuznetsova, and V. S. Khomenko (Institute of Physics of the Academy of Sciences of the Belorussian SSR), "Luminescence of solutions and crystals of organic complexes of the rare earths." The authors generalized and supplemented the results of their previous studies on the laws of intramolecular energy transfer. The authors related the changes that they found in the character of the luminescence spectrum of the rare-earth organic complexes upon going from one compound to another, or from the solution to the crystal, to the change in the relative position of the lowest excited levels responsible for the light emission in the rare-earth ion and the organic addend. Some problems of intramolecular migration of excitation energy were discussed in a paper by G. N. Lyalin and G. I. Kobyshev (Scientific Research Institute of Physics of Leningrad State University, Leningrad). They made an encompassing study of the optical properties of the complex of phthalocyanine with the uranyl cation, which they had synthesized for the first time.

10. Luminescence of chlorophyll, proteins, and other biologically important compounds. Physical methods of investigation are used ever more widely in solving biological and biochemical problems. Two sessions were reserved for problems of luminescence of biologically important compounds. Basically, all the papers involving luminescence of biological compounds could be divided into two types: those involving the study of photosynthetic pigments (chlorophyll and its analogs), and those involving the study of protein systems.

A long paper of a semi-review type was given by L. A. Tumerman (Institute of Radiation and Physicochemical Biology of the Academy of Sciences of the USSR) on the primary processes of conversion of light energy in photosynthesis and their relation to the luminescence of chlorophyll. The author devoted much time to some experimental facts which could be interpreted from the standpoint of the "electron current" theory. In the author's opinion, a semiconductor mechanism involving the quasicrystalline structure of the photosynthetic apparatus of plants plays a great role in the primary stage of photosynthesis. The paper aroused a lively discussion (T. N. Godnev, V. B. Evstigneev, G. P. Gurinovich, V. L. Broude, etc.).

Spectroluminescent studies of the products of photochemical reactions of chlorophyll and its analogs, the porphyrins, under model conditions were reported in papers by Yu. E. Erokhin and A. A. Krasnovskii (Bakh Institute of Biochemistry of the Academy of Sciences of the USSR, Moscow), and by G. P. Gurinovich, M. V. Pateeva, and A. M. Shul'ga (Institute of Physics of the Academy of Sciences of the Belorussian SSR). In the former paper, a painstaking study was made of the luminescence spectra of the photoreduced forms of a number of biologically important compounds in various solvents and at various pH values (at room and liquid-nitrogen temperatures). The latter paper attempted to relate the tendency of molecules to undergo photochemical transformations to their structures. On the basis of the obtained data, the authors drew some conclusions on the concrete mechanism of the photochemical reduction of the porphyrins.

On the basis of a study of the spectra and luminescence intensity of bacteriochlorophyll and bacterioviridin and their temperature-dependences, A. A. **Krasnovskii** and Yu. E. Erokhin (Bakh Institute of Biochemistry of the Academy of Sciences of the USSR, Moscow) attempted to relate the peculiarities of the spectra of bacteria to the state of aggregation of the pigments in the living cell. It was noted in the discussion that such an explanation is plausible, but does not follow unequivocally from the results given (N. D. Zhevandrov, V. B. Evstigneev, T. N. Godnev, etc.).

V. B. Evstigneev (Bakh Institute of Biochemistry of the Academy of Sciences of the USSR) made a painstaking comparison of the spectroluminescent properties of chlorophylls a and b and the corresponding water-soluble chlorophyllins and pheophorbins. The spectroscopic properties of these compounds are similar, so as to permit the use of the water-soluble analogs of chlorophyll as model systems for studying the photochemical reactions in an aqueous medium.

A paper by F. Ya. Sid'ko and N. S. Eroshin (Insti-

tute of Physics of the Siberian Division of the Academy of Sciences of the USSR, Krasnoyarsk), "On the problem of luminescence of chlorophyll solutions," reported a study of the dependence of the absorption spectra and luminescence intensity of chlorophyll in alcohol-water solutions [on the degree of aggregation. -Tr.]. The authors noted a mutual relation between the absorption spectra and the degree of aggregation of the pigment molecules. A number of critical remarks were made concerning the paper (L. A. Tumerman, A. V. Karyakin).

Much attention was paid at the conference to problems of luminescence of proteins. A substantial paper on the primary photochemical reactions in proteins was given by Yu. A. Vladimirov and D. I. Roshchupkin (Moscow State University). These authors found that ultraviolet illumination of the aromatic amino-acids and their glycine dipeptides and proteins leads to a rapid weakening of the luminescence, depending on the temperature, the medium, and the pH of the solution. They expressed some ideas on the mechanism of these photochemical transformations, and tried to construct a diagram of the electronic transitions in molecules of the aromatic amino-acids and proteins. A paper by A. V. Karyakin and L. A. Chmutina (Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR) dealt with the luminescence of the soy protein glycinin. The authors were able to observe the luminescence of this compound in the visible at a certain acidity of the medium. They proposed some hypotheses on the nature of this luminescence (the authors ascribed it to emission by the carboxyl groups of the protein).

G. M. Barenboim and A. N. Domanskii (Institute of Cytology of the Academy of Sciences of the USSR, Leningrad) studied the reaction of oxygen with excited aromatic amino-acids and related compounds (in the paper, "Quenching of the photo- and radioluminescence of aromatic amino-acids, proteins, and nucleic acids by oxygen and nitric oxide"). They showed that the rate of quenching of the luminescence depends on the nature of the biomolecule, the solvent, and the quenching agent, increasing linearly with the concentration of the latter. They advanced the hypothesis that the quenching involves the facilitation of singlet-triplet transitions by paramagnetic gases (O_2 , NO, etc.) and the formation of a labile peroxide complex.

A study of concentration quenching and concentration depolarization of tryptophan in water-glycerol solutions, and the difference in the rate of these processes in solutions of different viscosity led S. V. Konev, M. A. Katibnikov, and T. I. Lyskova (Laboratory of Biophysics and Isotopes of the Academy of Sciences of the Belorussian SSR, Minsk), to think that exchange of excitation energy in kinetic collisions plays a considerable role in the concentration effects.

The papers heard at the biological sessions and also the discussion of results of the studies revealed a promising situation in the application of spectroluminescent methods of investigation to solve biological problems.

11. Molecular luminescence and chemical problems. Several papers on chemiluminescence were presented by the Institute of Chemical Physics of the Academy of Sciences of the USSR (Moscow) at the 11th Conference. A paper by R. F. Vasil'ev and A. A. Vichutinskii, "A study of chemiluminescence in liquid-phase oxidation reactions," gave an explanation for the enhancement of chemiluminescence by oxygen in radical reactions; the essence of this amounted to the fact that when O_2 is introduced, the free radicals of the chemical system are transformed into peroxide radicals. Upon recombination, highly luminescent oxygen-containing products are formed. Another paper by R. F. Vasil'ev and A. A. Vichutinskii, "The role of energy-transfer processes in chemiluminescence" showed that the chemiluminescence accompanying the oxidation of hydrocarbons is increased by introduction into the system of small concentrations of activators (chlorophyll, anthracene, etc.). Apparently, this is to be explained by energy transfer to the activator. A paper by L. M. Postnikov, V. F. Shuvalov, and V. Ya. Shlyapintokh, "The nature of the chemiluminescence in the low-temperature oxidation of acetaldehyde" demonstrated the possibility of determining the rate of reaction and its dependence on various parameters from the chemiluminescence kinetics. A study of exceedingly weak chemiluminescence in the visible using a photomultiplier operating as a photon counter was the subject of a paper, "A study of exceedingly weak emission (chemiluminescence) in fermentation processes," by Yu. A. Vladimirov, F. F. Litvin, and T'an Man-ch'i (Moscow State University).

A considerable number of the papers were concerned with the problem of the relation of luminescence to the structure of molecules. Among these, we must note some papers presented by the Institute of Monocrystals (Khar'kov) and the Karpov Physicochemical Institute (Moscow), as well as a paper by Ya. A. Terskii, B. M. Bolotina, V. G. Brudzya, and D. A. Drapkina (Institute of Chemical Reagents, Moscow), "The effect of substituents on the luminescent properties of azomethines." Of interest was a study of intramolecular proton-transfer photoreactions in hydrogen-bond bridges in azomethine compounds, reported in a paper by Yu. I. Kozlov, R. N. Nurmukhametov, D. N. Shigorin, and V. A. Puchkov (Karpov Physico-chemical Scientific Research Institute, Moscow).

Data on the relation of the optical properties of tetrabenzoporphin and its complexes with magnesium, zinc, and cadmium to their structures were given in a paper by K. N. Solov'ev, S. F. Shkirman, and T. F. Kachura (Institute of Physics of the Academy of Sciences of the Belorussian SSR), "Spectroluminescent properties of benzoporphyrins." In particular, the authors showed that the inclusion of the benzene rings in the conjugated system of the porphin ring has practically no effect on the size of the singlet-triplet spacing, which amounts to about 3000 cm^{-1} .

Bordering on the problems of the relation of luminescence to molecular structure was an interesting paper by A. S. Cherkasov and K. G. Voldaĭkina (State Optical Institute), "Luminescence of vinylanthracenes and configurational change in the molecules in the excited state," which showed a relation between the spectra and the existence of isomerism in 2-vinylanthracene (due to the partial double-bond character of the single bond joining the vinyl group to the anthracene ring), and also demonstrated a change in the equilibrium content of the isomers upon transformation to the excited state.

II. LUMINESCENCE ANALYSIS

1. Luminescence analysis in chemistry. Luminescence methods have at present found a firm place in the arsenal of analytical chemistry, owing to their exceedingly high sensitivity. In modern technology, hyperpure materials are acquiring an ever larger role, and problems arise thereby of determining infinitesimal quantities of impurities. The work is being conducted both along the line of searching for new luminescent reagents, and that of perfecting methods already known.

A paper was given at the conference by E. A. Bozhevol'nov and G. V. Serebryakova (Institute of Chemical Reagents, Moscow), concerned with ways of searching for luminescent reagents (for cations). The authors showed that certain principles of searching for colorimetric reagents which have been established rather firmly are applicable also to luminescent reagents. In particular, ideas of functional-analytic groupings have proved useful, i.e., characteristic combinations of atoms in the molecule of an organic reagent causing it to interact with a given ion. Likewise useful is the hypothesis of analogy, according to which the action of organic reagents of the type, e.g., of R-OH, R-SH, R-NH₂ is analogous to the action of water, hydrogen sulfide, and ammonia, respectively. There are luminescent reagents which acquire the power to luminesce upon binding a cation (their molecules are not rigid in structure). In such a case, the search is simplified by building models of the molecules in order to determine the conformational isomers.

A paper by N. A. Gorbacheva and M. A. Konstantinova-Shlezinger (Institute of Physics of the Academy of Sciences of the USSR) dealt with the determination of uranium by means of the width of the luminescent band on a chromatogram. The paper showed that on an alumina column the width of the band for uranyl nitrate is proportional to its concentration. They studied the effect of foreign cations and anions, and developed a method of determining uranium in rocks. In a paper by A. I. Ivankova, D. P. Shcherbov, and B. T. Taskarin (KazIMS, Alma-Ata) the optical properties of the chloride and bromide complexes of a number of metals with rhodamine 6G and rhodamine S at various pH values were studied. They showed that one can determine mercury by luminescence, using rhodamine S. A paper by R. N. Plotnikova, D. P. Shcherbov, E. A. Shilenko, S. A. Voinov, and É. D. Korabel'nikova (KazIMS, Alma-Ata) showed the great convenience of using an incandescent lamp to excite luminescence in determinations of microgram amounts of metals. For this purpose they selected a combination of liquid crossed light filters made of copper and chromium salts. The simplicity of the method makes it feasible in any factory laboratory.

A study of the properties of a new luminescent reagent for magnesium, bis-salicylalethylenediamine. was reported in a paper by G. V. Serebryakova and E. A. Bozhevol'nov (Institute of Chemical Reagents, Moscow). The method shows high selectivity and exceedingly great sensitivity: 0.0001 µg of magnesium in 5 ml dimethylformamide. It has proved possible to determine by a luminescence method submicrogram amounts of copper (S. U. Kreingol'd and E. A. Bozhevol'nov, Institute of Chemical Reagents, Moscow). They proposed two methods for luminescence determination of copper. The first is based on the quenching of the fluorescence of fluorescein-complexone by heavy metals. The second, more sensitive method is based on the catalytic action of copper in the alkali degradation of Lumogen Orange-Red.

The luminescence analysis of some forms of raw materials and products of the rare-metal industry was dealt with in a paper by V. M. Vladimirova, N. K. Davidovich, and G. I. Kuchmistaya (State Institute of Rare Metals, Moscow). They developed methods for determining selenium and tellurium in arsenic. In the study, they discovered and investigated a reaction of univalent thallium with rhodamine 6G (in the presence of TiCl₃). The reaction is highly sensitive and selective. On the basis of this reaction, they developed methods for analysis of ores, concentrates, and minerals.

L. F. Kuznetsova reported that the inner-complex compounds of tetracycline and terramycin with europium luminesce with an emission spectrum characteristic of europium. Obviously, the luminescence of the europium complexes described in the paper is due to the well-known effect of intramolecular migration of excitation energy.

In the above-mentioned paper by A. N. Sevchenko, V. V. Kuznetsova, and V. S. Khomenko involving the problem of intramolecular energy migration, methods were also described for luminescence determination of europium, terbium, samarium, and dysprosium. On the basis of a study of the spectroluminescent characteristics of a large number of rare-earth complexes, the authors selected some complex-forming agents for various analytical purposes. 2. Luminescence analysis in biology, medicine, microbiology, and veterinary medicine. Along with other physical methods, luminescence is at present widely entering into practice in biological studies. The application of luminescence microscopy has been especially widely developed in cytology (the study of the cell), microbiology, and immunology. We must mention the increasing introduction of precise, objective methods of recording into biology.

At the plenary session a review paper was presented by M. N. Meisel', E. M. Brumberg, T. M. Kondrat'eva, I. Ya. Barskii, and A. V. Gutkina (Institute of Radiation and Physicochemical Biology of the Academy of Sciences of the USSR, Moscow, and Institute of Cytology of the Academy of Sciences of the USSR, Leningrad), "Luminescence microscopy in radiobiological studies." Luminescence microscopy has proved to be an invaluable aid in finding the initial physicochemical and structural lesions in cells, especially in the nucleoprotein structures of the nucleus and cytoplasm. Luminescence cytochemistry has made it possible to reveal the alteration in material exchange in irradiated cells, especially in phosphorus, fat, and lipid exchange. Of especial interest is ultraviolet luminescence microscopy, which permits the recording of changes in the intrinsic luminescence of cells in the ultraviolet region of the spectrum. Also mentioned was the practical value of using luminescence microscopy in radiobiology to develop means and methods of cure and protection from radiation injury.

A paper by R. I. Pinto (Institute of Cytology of the Academy of Sciences of the USSR, Leningrad) gave data on changes in the intensity of the secondary fluorescence of blood cells under X-irradiation. A luminescence-microscope study of lymph nodes in radiation sickness was reported by V. M. Manteifel' (Institute of Radiation and Physicochemical Biology of the Academy of Sciences of the USSR).

A. V. Zelenin, N. G. Khrushchov, E. A. Lyapunova, N. E. Vorotnitskaya, and V. E. Barskii (Institute of Radiation and Physicochemical Biology of the Academy of Sciences of the USSR) discussed in their paper the modern theories of the nature of the formation of acridine orange complexes with cytoplasmic structures. They showed in the paper that with a correct choice of pH, fluorochroming with acridine orange reveals only RNA. They discussed the problem of the nature of the red granules that appear in cells when fluorochromed with acridine orange, and suggested that these granules result from the interaction of the dye with the transport fraction of the RNA. V. G. Kondratenko and M. N. Malatyan (Institute of Radiation and Physicochemical Biology of the Academy of Sciences of the USSR) reported on the luminescence-microscopic demonstration of mitochondria in living cells by the method of vital fluorochroming. In this study an intrinsic ultraviolet luminescence of bone-marrow cells was found.

The ultraviolet fluorescence of mitochondria of

spermatids of certain acrididae was dealt with in a paper by E. M. Brumberg, I. Ya. Barskii, I. A. Chernogryadskaya, and M. S. Shudel' (Institute of Cytology of the Academy of Sciences of the USSR). They proposed that the ultraviolet fluorescence of the cytoplasm of cells involves the coenzymes of the mitochondria, possibly the phosphopyridine nucleotides. E. M. Brumberg, I. Ya. Barskii, E. M. Pil'shchik, and M. V. Nikolaeva (Institute of Cytology of the Academy of Sciences of the USSR) studied the ultraviolet fluorescence of the cytoplasm of liver cells of white rats at various stages of embryogenesis.

V. E. Barskii, A. V. Zelenin, and E. A. Lyapunova (Institute of Radiation and Physicochemical Biology of the Academy of Sciences of the USSR) reported that the nuclei of normally-functioning animal cells show a weak ultraviolet fluorescence in the $310-370 \text{ m}\mu$ region (the fluorescence of cells is mainly due to the emission from the protoplasm). However, the intensity of the fluorescence can be increased by removing the nucleic acids by acid hydrolysis. Here the nuclei of tumor cells fluoresce more strongly than those of healthy cells. The authors concluded that the ultraviolet fluorescence of the nuclei that appears after removal of the nucleic acids is due to the presence of the cyclic amino-acids, especially tryptophan, in the nuclear proteins.

A paper by A. A. Zotikov (Institute of Radiation and Physico-chemical Biology, Academy of Sciences, USSR) attempted to estimate quantitatively the intensity of luminescence of the nuclei of the protozoa Tetrahymena, both normal and irradiated with $\operatorname{Co}^{60} \gamma$ -rays. For this purpose, a microscope-fluorimeter was assembled, based on a MUF-3m microscope with a FÉU-29 photomultiplier and a modulation photometer. He used acridine orange as the fluorochrome. A relation was found between the luminescence intensity of the onecelled organisms and the radiation dose.

An interesting report on the bioluminescence of plankton microorganisms of the Pacific Ocean was given by I. I. Gitel'zon, R. I. Chumakova, O. G. Baklanov, A. S. Artemkin, and V. F. Shatokhin (Physics Institute, Siberian Division, Academy of Sciences, USSR). The authors showed from a large number of bathyphotometric measurements performed aboard the research ship Vityaz' of the Academy of Sciences of the USSR that bioluminescence of the sea was observed in every region included in the itinerary. They also studied the bioluminescence of plankton microorganisms in the laboratory, and showed here that there is no correlation between bioluminescence and the division of bacteria, while bioluminescence is correlated with respiration only in the early stages of the oxidative chain. An estimate showed that only 0.1% of the energy liberated by the cell in the metabolic process takes part in bioluminescence. The maximum in the bioluminescence spectrum lies near 480 m μ .

The method of luminescence-marked antibodies is

widely applied in luminescence immunochemistry.* It consists in fluorochroming a serum containing specific antibodies and in treating a microscope preparation with this serum. If the preparation contains the sought antigens, they are readily revealed by the luminescence of the complex of the antigen with the fluorochromed antibody. A new, rapid, simple, and effective method of obtaining luminescent conjugates from anti-plague and cholera serums was proposed in a paper by P. K. Tabakov, E. V. Chibrikova, I. I. Shurkina, and E. I. Vel'ner (Scientific Research Institute of Microbiology, Saratov). By a choice of the alcohol concentration added to the serum, the authors were able to shorten the time for preparation of the luminescent conjugates from 3-4 weeks to 3-4 days. The method can be carried out in any laboratory. The authors of a paper, "On the problem of increasing the sensitivity of the indirect luminescent-antibody method," N. A. Kuz'min, P. A. Emel'yanenko, and Yu. N. Stepanich considered the reason for the frequent failures of the indirect luminescent-antibody method to be the use of antispecific sera containing immune globulins of other species of animals. One observed a brighter luminescence of microbes if one uses immune globulins together with the anti-specific serum for which they had been used as the antigen in preparing the serum (paired sera). In a study by P. I. Pritulin, the luminescent-antibody method was used to study the changes that typhoid bacteria undergo in an animal organism at various stages of the infection process. The luminescent-antibody method has made possible a study of pathogenesis (P. I. Pritulin) and of immunogenesis (P. I. Pritulin and B. A. Komarov) of paratyphus in animals. They followed the distribution of the bacteria in various parts of the organism at various stages of the disease. During the infection process, the antibodies initially interact only with the original microbes, but later also with related microorganisms. In the opinion of the authors, this polyspecificity of the antibodies can be explained by a change in the antigenic structure of the bacteria causing the disease. The development of a luminescent-antibody method for diagnosis of swine erysipelas and listerellosis of agricultural animals was reported by O. A. Polyakova (All-Union Institute of Experimental Veterinary Medicine of the All-Union Academy of Agricultural Sciences, Moscow). V. M. Kartasheva (All-Union Scientific Research Institute of Veterinary Sanitation of the All-Union Academy of Agricultural Sciences, Moscow) reported on the determination of the pathogenic bacteria of tuberculosis, typhus, and brucellosis in milk using luminescence-marked antibodies and other luminescence methods.

^{*}Antibodies are specific protein substances produced by an organism upon introduction of the so-called antigens, e.g., bacterial toxins. The antibody forms a complex with the antigen and destroys its biological activity.

A number of papers at the conference were concerned with luminescence in medicine. Ya. L. Rappoport, G. D. Knyazeva, and M. A. Milaeva (Institute of Chest Surgery of the Academy of Medical Sciences of the USSR, Moscow) used luminescence methods to study the breakdown of the blood-brain barrier under artificial circulation, and the reversibility of the changes in various organs under deep cooling of the organism in order to estimate the amount of blood supply to the various organs. These studies permitted the authors to improve significantly methods of surgery on the heart and the major blood vessels. Under laboratory conditions with animals, methods were developed for operative treatment of myocardial infarction in which the ischemic zone is revealed by a luminescence method.

A paper by V. I. Ermolov (Institute of Obstetrics and Pediatrics, Rostov-on-Don) showed that luminescence microscopy has a considerable advantage over ordinary bacterioscopy in the analysis of cerebrospinal fluid for diagnosis of tubercular meningitis. The importance of this is noted in connection with the fact that the use of powerful therapeutic preparations lowers the viability and number of the bacteria and interferes with the diagnosis. Studies by V. Kh. Anestiadi and E. G. Zot (Medinstitut, Kishinev) showed that in pathological-anatomical studies, luminescence methods considerably facilitate the diagnosis of atherosclerosis, especially in its early stages. The application of luminescence in gynecology to diagnose cancer was dealt with in a paper by I. A. Makarenko (Medinstitut, Minsk). The author noted the practical value of the luminescence method, especially in mass prophylactic examinations.

A spectroluminescent study of solutions of the antibiotic griseofulvin was the subject of a paper by A. V. Markovich, A. A. Nevinskii, and N. M. Ivanov (Scientific Research Institute of Antibiotics, Leningrad). The authors used luminescence to determine the concentration of griseofulvin in the blood serum of persons after it had been administered. É. Baumyanis, I. Vitols, Z. Orvid, Ya. Popens, É. Silin'sh, and Ya. Éĭdus (Institute of Experimental Medicine of the Latvian SSR, Riga) reported on the spectrofluorometric determination of certain cyclic hormones in biological media. The method is already in use in clinical-laboratory practice. In a paper by E. A. Galashin and V. V. Filippovskii, "A fluorescence method for determining the bands of aromatic amino-acids in paper chromatograms," they used for development of the chromatograms both the ultraviolet fluorescence of the aromatic amino-acids and their phosphorescence in the visible (with photographic recording of the luminescence, using interference filters).

3. Luminescence analysis in technology, industry, and geology. Luminescence methods of quality control of production in various branches of industry are widespread at present, and are being successfully devel-

oped in many laboratories. Of great significance are the methods of luminescence defectoscopy, which have become widespread in the USSR and abroad; these methods permit one relatively simply to find defects in the parts of mechanisms and machines which could be found only with great difficulty by other methods. A substantial paper by A. S. Borovikov (State Research Institute, Civil Air Fleet), "Research and development in luminescence defectoscopy'' emphasized the real necessity of further refinement of luminescence defectoscopy in connection with the great increase in the role of refractory non-ferromagnetic materials in thermal power engineering, air transport, etc. Major attention was paid to the development of luminescence and dye variants of the color method of defectoscopy, using film-forming "developers." He gave concrete recipes and recommendations.

Daylight fluorescent pigments have found wide application for marking of various objects involved in transportation (airplanes, airport buildings, beacons, buoys, moorings, road signs and signals, etc.), and have made it possible to increase their visibility distances by a factor of three or four, and thus to improve safety of travel. A substantial review paper on the chemical nature of these pigments and their applications was given by V. K. Matveev, L. S. Karmanova, and E. D. Anorova (Institute of Organic Chemistry of the Academy of Sciences of the USSR and State Research Institute of the Civil Air Fleet). V. K. Matveev also reported on a method developed for preparing in pure form Lumogen Light-Green, which has found wide application in luminescence chemical analysis.

The use of luminescence methods of control in the process of rubber production was reported in two papers by V. N. Provorov and V. D. Zaĭtseva (Scientific Research Institute of Rubber, Moscow). In one of these, luminescence control methods were used to detect inhomogeneities of distribution of the ingredients in light-colored rubber compositions based on natural rubber. In the second paper, the uniformity of the distribution of the fixative on the form was studied by luminescence methods; this is one of the fundamental factors in improving the quality of latex articles made by the ionic-precipitation method.

As is known, the dyeing of fabrics in the textile industry is determined not only by the spectroscopic properties of the dyes used, but also by the sensitivity of the spectra to various sorts of intermolecular interactions. This problem was taken up in a paper by R. N. Nurmukhametov and L. V. Bondareva (Karpov Physicochemical Scientific Research Institute, Moscow), "Luminescence spectra of polycyclic diketones in lavsan fibers and in solution."

The mass character of the studies and analyses in geological surveys, which require speed of operation and reliability, makes luminescence analysis irreplaceable in solving many geological-survey problems. This is especially true in studying the petroleum resources of the country. Characteristically, crude oils of different origins have different spectroluminescent characteristics. Thus, T. A. Botneva (Lenin State Pedagogic Institute, Moscow) has made a study of the luminescence of approximately 300 samples taken from sites in the Tatar, Orenbury, Kuibyshev, Saratov, Volgograd, Gur'ev, and Astrakhan regions, dated as formations of the Devonian, Jurassic, and Cretaceous periods. The results that she obtained clearly demonstrate all the variety in the spectroluminescent properties of crude oils, and permit one, in the opinion of the author, to systematize the crude oils and to establish a relation between the intensity and color of the emission of a crude oil and its relative content of bituminous substances. This, in turn, is related to the differing origins of the crude oils.

The problem of the origin of the luminescence of crude oils was discussed also in other papers (A. A. Il'ina, R. I. Personov, T. A. Alekseeva, and E. B. **Proskuryakova**, Lenin State Pedagogic Institute, Moscow, and All-union Research Institute of Petroleum Exploration). The use of the fluorescence and phosphorescence line spectra of the naphthene-aromatic fractions of natural bitumens made possible the identification of a number of emission bands with the corresponding bands of 1,12-benzperylene in mixture with other hydrocarbons of similar type.

V. N. Florovskaya and L. P. Ovchinnikova (Moscow State University) reported on a study of bitumens from volcanic sedimentary rocks from the II'men massif of the Ural Mountains. The luminescence spectrum of the bitumen in n-hexane shows the bands of individual hydrocarbons of the aromatic series. A clear pattern of the distribution of the bitumens in the samples is seen when they are examined through a luminescentspecimen microscope. The authors feel that the existing information on the luminescence of bitumens is concerned mainly with free bitumen.

The study of the composition and spectroluminescent characteristics of combined bitumen is a problem for future investigations. The first results of these studies involve a study of the substance determining the color and luminescence of the mineral hackmanite (V. N. Florovskaya, R. B. Zesin, L. I. Ovchinnikova, and T. A. Teplitskaya, Moscow State University). A freshly-broken piece of hackmanite has a brilliant crimson color, which disappears within several minutes of exposure of the mineral to sunlight, and reappears after several days in the dark. A colored specimen of the mineral has an orange-red luminescence, while the bleached mineral has a light blue luminescence. The authors consider that the cited light-sensitive properties of hackmanite can be explained by the presence in the mineral of organic pigments occurring in the combined state, which undergo photochemical transformations. T. A. Teplitskaya (Moscow State University) also gave a report, "Some results of the emission of luminescence by porphyrins in minerals."

In the discussion of the papers, **T. É. Baranova** reported some additional information on luminescentbituminological analysis of crystalline rocks. **V. I. Tyurin** reported on the results of a study of the correlation of oil-bearing carbonate strata by means of the thermoluminescence of the limestones. Thermoluminescence has been used to determine the age of granites, for correlation of limestones, and for revealing ore-bearing veins in prospecting for gold ores, etc.

4. Apparatus and methods of luminescence analysis. It has become a good tradition at the conferences on luminescence to discuss problems of methods of luminescence research and luminescence analysis. Much attention was paid to problems of photometry, colorimetry, and luminescence microscopy.

R. F. Vasil'ev (Institute of Chemical Physics of the Academy of Sciences of the USSR, Moscow) told in his paper of an apparatus of great aperture ratio, assembled from a replica-grating monochromator (working area $150 \times 140 \text{ mm}^2$, 600 lines/mm). The electronic part of the apparatus was assembled entirely from widely-distributed standard instruments. Its high sensitivity is ensured by the great aperture ratio of the monochromator, which was assembled according to the scheme of Fasti (F = 300 mm), by the high slits (70 mm), and by the choice and refrigeration of the photomultiplier.

The discussion that took place after the paper (**Z. M. Sverdlov** et al.) showed that this type of apparatus using standard amplifying equipment is also in use in a number of other laboratories.

M. S. Shipalov reported on two absorptiometers designed and built in the Bakh Institute of Biochemistry for the rapid, objective estimation of concentrations in solutions of substances absorbing in the ultraviolet. The measurements are made from the change in intensity of a luminescent screen excited by a special bactericidal-type lamp. The measurements made in the instruments constructed showed quite satisfactory sensitivity and reproducibility of results. Such substances as adenosine triphosphate and uridine can be determined reliably in amounts of the order of 0.3-0.5 mg/liter.

Z. M. Sverdlov reported on a photoelectric fluorimeter-absorptiometer (FAS-1) having a special accessory for studying the luminescence of bitumens developed in the All-union Research Institute of Geology. The use of the instrument in the study of various bitumens and crude oils made it possible to obtain a series of objective characteristics from which one could determine the composition of the solutions being studied. FAS-1 also finds various applications in clinical studies. Regular production of the instrument will begin in the immediate future at the <u>Geologorazvedka</u> (Geological Survey) plant. The FAS-1 instrument was demonstrated in action at the conference.

The binocular microscope MBS-1 is widely used at present in luminescence-microscopic studies of minerals. However, no good excitation sources suitable for geological practice have yet been produced by industry. A low-voltage (18 volts) low-power ultraviolet source UFOB-1 intended for use in a luminescence illuminator has been specially designed at the Moscow Electric Lamp Factory, under assignment of the Allunion Research Institute of Geology. A test of an illuminator designed with use of the UFOB-1 lamp in combination with the MBS-1 microscope showed that it was quite suitable for study and identification of many important minerals (Z. M. Sverdlov).

In order to study rapidly-varying processes, special instruments have been built recently in various laboratories: spectrovisors, which make it possible by use of an oscillograph tube to observe and record the spectra of short-lived products of chemical reactions. Such an instrument, adapted for rubber production control, was reported by A. N. Faïdysh, L. E. Chechik, A. D. Chugaĭ, and I. Sh. Shkolyar (Krasnyĭ Rezinshchik (Red Rubber Worker) factory, Kiev).

Problems of errors in luminescence measurements and methods of eliminating them in the case of "thick" micro-objects were dealt with in a paper by G. M. Svishchev. He suggested a new design of a microspectrometer in which the studied object is excited by a microbeam of light. Of considerable interest in the study of the luminescence of moving micro-objects was an apparatus containing an electron-optic converter, as proposed by M. Ya. Korn et al, for photographing rapidlymoving biological micro-objects under the microscope. The use of the electron-optic converter permits one to take motion pictures of luminescent microobjects in cases in which powerful illuminators cannot be used for some reason or another.

At the Conference, the problem was actively discussed of the state of luminescence instrument making in the country. It was noted that thus far the Council on Luminescence has paid little attention to the coordination of instrument-making studies, with the result that sometimes whole series of defective luminescence instruments are manufactured. By a resolution of the conference, the Council was instructed to call a conference devoted to discussion and coordination of studies on luminescence instrument making.

Translated by M. V. King