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*NEW DATA ON THE NATURE OF THE QUASILINEAR SPECTRA OF ORGANIC COMPOUNDS**

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I. SOME SPECTROSCOPIC RESULTS

RECENTLY the study of quasilinear spectra has provided a considerable number of interesting new results. The spectra of many new compounds have been studied. Thus, P. P. Dikun[1] has obtained and measured the spectra of about forty derivatives of 1,2-benzanthracene having alkyl and halogen substituents in various postions, both in the fundamental anthracene system and in the additional benzene ring. He showed here that the spectra of isomeric molecules differ considerably in the number, positions, and relative intensities of the lines. Hence, it is quite possible to distinguish them by spectral analysis. The spectra of a number of new compounds not previously studied by our method have been obtained and analyzed, and the fundamental vibrational frequencies determined. These include the polyene and polyphenyl chains (Fig. 1): stilbene (V. L. Levshin and Kh. I. Mamedov,[2] G. V. Gobov[3]), tolan, biphenyl, terphenyl, quaterphenyl, diphenylbutadiene (Gobov,[3] Bolotnikova and Gobov[4]).

Azulene, an isomer of naphthalene, is also of great interest. It has a peculiar structure (Fig. 2) and exhibits unusual spectroscopic properties. Z. S. Ruzevich[5] has obtained and analyzed its quasilinear spectrum at 77°K.

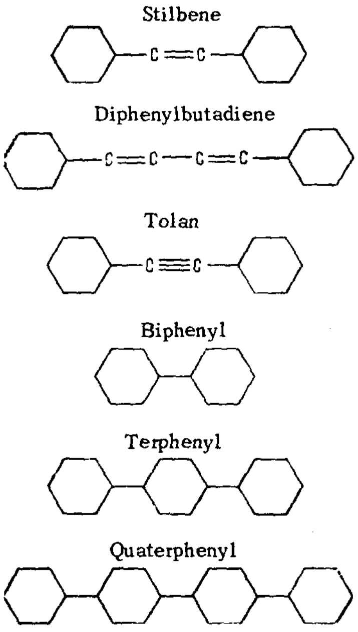

FIG. 1. Structural formulas of polyene and polyphenyl chains.

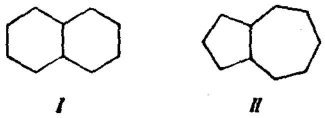

FIG. 2. Structural formulas of naphthalene (I) and azulene (II).

Besides the studies conducted at liquid-nitrogen temperature, others have been carried out at lower temperatures, namely, liquid hydrogen (20°K) and liquid helium (4.2°K). Under these conditions, an important class of polycyclic aromatic hydrocarbons (for the structural formulas, see reference[10], p. 218) has been subjected to detailed analysis: pyrene (L. A. Klimova[6]) and a number of its important derivatives: 3,4- and 1,2-benzpyrene and 3,4,6,7- and 3,4,8,9-dibenzpyrene (É. V. Shpol'skiĭ and L. A. Klimova[7-9]). Finally, as the most complex of the studied compounds, we must cite the phthalocyanines and protoporphyrin. As a sequel to a previously published study (F. F. Litvin and R. I. Personov[11]), some new papers give an especially detailed study and analysis of the luminescence and absorption spectra of metal-free phthalocyanine (R. I. Personov[12]) and also of the uranyl phthalocyanine complex (A. N. Terenin, G. I. Kobyshev, and T. N. Lyalin[13]).

The applications of quasilinear spectra to qualitative and quantitative analysis have also continued to grow. Here, in addition to the development of highly sensitive and precise methods for quantitative analysis for 3,4-benzpyrene, a very important carcinogenic hydrocarbon which is widely distributed under modern urban conditions (B. Muel and G. Lacroix,[14] P. P. Dikun,[15] R. I, Personov[16]), we must cite some interesting studies on the identification of the heavy aromatics in petroleums, bitumens, and gas-bearing clays (A. A. Il'ina et al.,[17] A. A. Il'ina and R. I. Personov[18]).

What are the results of these studies?

As is known, the problem of spectroscopic study is far from completed when we obtain the spectrum and determine the wavelengths of the lines. A photographed or recorded spectrum must be interpreted. From the interpretation of an electronic-vibrational molecular spectrum, above all we must determine the frequencies of the intramolecular vibrations. The system of characteristic vibrational frequencies thus obtained is of value per se as a characteristic of the molecule, while if we can also determine the sym-

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metry of the vibrations, then we can make far-reaching conclusions of the structures of complex molecules. In our first studies, it was important to compare the frequencies obtained by our method with those determined by an independent method, e.g., from Raman spectra. Thus, we could verify that we were actually dealing with spectra of the molecules being studied, rather than with any sort of more complex "centers." After we had convinced ourselves of this with examples of simple molecules, we were then justified in using the results of interpretation of quasilinear spectra as an independent means of study of molecules. All this has been accomplished in the studies which I have just mentioned. Of course, in one article I cannot discuss all the results obtained here. Instead, I shall cite some examples, rather for illustration of the possibilities of our method than for discussion of the problems of molecular spectroscopy associated with these results. I shall devote the rest of the article to a discussion of the problems of the nature and origin of quasilinear spectra.

As the first example, I shall take up one of the problems of the spectroscopy of naphthalene set forth as early as 1954 in an important study by McClure,[19] and then studied by T. N. Bolotnikova, [20] and finally solved by D. P. Craig, [21] (also D. P. Craig and L. E. Lyons [22]) in 1961 and 1962.

In particular, McClure studied the absorption and fluorescence spectra of naphthalene in a solid solution in durene (symmetric tetramethylbenzene), which is completely isomorphous with naphthalene. Owing to the similarity of the molecular and crystallographic parameters of the two substances, naphthalene molecules incorporated into the durene crystal structure form an "oriented gas" to the highest degree of approximation. Under these conditions, McClure found two sequences of lines polarized in mutually perpendicular directions in the fluorescence spectrum. One of these sequences, polarized along the long axis of the naphthalene molecule, begins with the $0'-0''$ line at 31731 cm^{-1}. The other, polarized along the short axis of the molecule, does not start with the $0'-0''$ transition, but according to McClure, its origin is shifted by 509 cm^{-1} (Fig. 3). This frequency 509 cm^{-1} was assigned to one of the totally-symmetric vibrations of naphthalene, since it combines with all the other totally-symmetric frequencies. However, there is considerable disagreement in the literature with regard to the exact value of this frequency, which McClure gives as 509 cm^{-1}. As for the polarization, it was not clear how the superposition of a totally-symmetric vibration on the $0'-0''$ transition could rotate the plane of polarization through $\pi/2$. Bolotnikova [20] has obtained and analyzed the sharp quasilinear fluorescence spectrum of naphthalene in n-pentane at 77°K. As it turned out, this spectrum, when shifted by 177 cm^{-1}, coincides with the spectrum of naphthalene in durene obtained by McClure. In particular, it also contains two systems of lines of differing intensities, which precisely correspond to the two differently polarized systems of lines of naphthalene in durene. The interpretation of the reasons for the different polarization of the second system, Bolotnikova showed, must lie in the fact that there is not one 509 cm^{-1} frequency, but two. While both of these are close to the frequency 509 cm^{-1}, however, they differ appreciably from this value within the limits of possibility of the method. These frequencies are: the totally-symmetric frequency 517 cm^{-1}, which combines readily with the other totally-symmetric frequencies, and the frequency 495 cm^{-1}, which is equal to the shift in the origin of the sequence of polarized lines with respect to the $0'-0''$ transition. Bolotnikova interpreted this 495 cm^{-1} frequency as being a non-totally-symmetric frequency of class β_{1g}. As simple group-theoretical considerations show, this would give rise to precisely the expected change in the direction of polarization. We were greatly satisfied by the confirmation of this interpretation in a remarkable study by D. P. Craig and his associates[21] published in 1961. By using an apparatus having a powerful diffraction grating (of resolving power 300,000), D. P. Craig was the first to resolve the rotational structure of the spectrum of naphthalene vapor. Here, since the contour of the rotation band differs for totally- and non-totally-symmetric vibra-

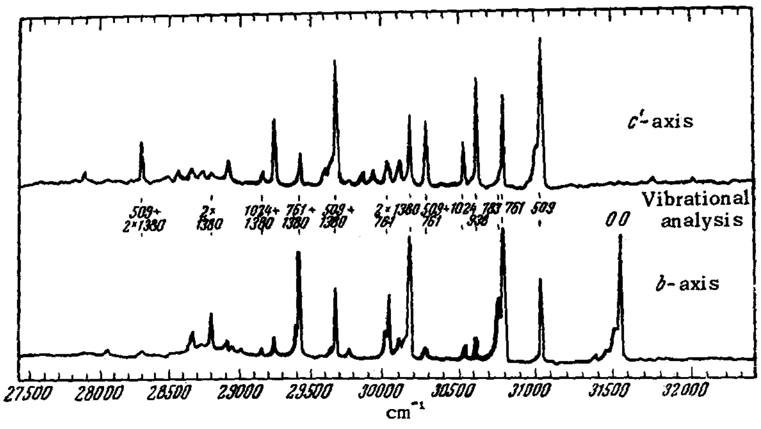

FIG. 3. An analysis of the fluorescence spectrum of naphthalene (according to McClure).

tions, Craig was able to establish indisputably the symmetries of the vibrations, and completely confirmed the interpretation of Bolotnikova.

I have taken up this seemingly special case in such detail because it permits us to draw a number of theoretically-important conclusions. First, since the rotation of the plane of polarization owing to superposition of a β_{1g}-type vibration is a characteristic of the spectrum of the gas, the described results show that the naphthalene molecules in the paraffin matrix which we have used are actually in a molecularly-disperse and undeformed state. That is, they are in the state of molecules of an oriented gas. We should consider this to be one of the most sensitive proofs of the correctness of our concepts on the nature of quasilinear spectra as being purely molecular spectra. Second, these results excellently illustrate the possibilities of the quasilinear-spectrum method in solving intricate spectroscopic problems.

Quite naturally, this method permits us not only to assert that the parameters and symmetry of a molecule are maintained when incorporated into a foreign matrix, but it also gives us some criteria for determining very small deformations of molecules. These criteria involve the selection rules. In order to demonstrate this by concrete examples, I shall discuss some results from two new studies: that of Mme. L. Pesteil and Mme. Madeleine Rabaud on the spectroscopy of phenanthrene and deuterophenanthrene in an n-pentane matrix at 20° K,[23] and the above-mentioned study of L. A. Klimova on the spectroscopy of pyrene at 20° and 4°K.[6] One of the excellent photographs obtained by L. A. Klimova is shown in Fig. 4 (see insert).

In this study, as is usual, a vibrational analysis was carried out in addition to the measurement of the wavelengths. This permitted the determination of the normal vibrational frequencies of the molecule. However, it happened that when the work had been practically completed, a study was published by Mecke and Klee,[24] who had made a painstaking study at high resolution of the Raman and infrared spectra of pyrene itself and some of its derivatives. Comparison with the results of Klimova showed that for frequencies having the same symmetry both methods, our method of quasilinear electronic-vibrational spectra and the method of purely vibrational spectra used by Mecke and Klee, gave results agreeing within limits of ±1 cm^{-1}, or even less, the absolute values of the frequencies ranging from 406 to 3043 cm^{-1} (the vibration frequency of the C-H bond) (Table I).

The study of Pesteil and Rabaud gave analogous results for the case of phenanthrene. Here they could compare the results of analysis of the electronic-vibrational spectrum with the purely vibrational spectra studied by Mathieu. It would be wrong to suppose that the value of these studies consists only in verifying the validity of our method of determining the normal frequencies of molecules. It is of no less value to compare the results of application of selection rules to both cases, permitting the drawing of more detailed conclusions.

In this regard, a historic remark made by Mecke and Klee[24] in their paper is of great interest. Almost exactly 100 years ago, when spectroscopy, and particularly molecular spectroscopy, was still taking its first steps, Tyndall remarked that the existence of definite characteristic frequencies in a system of particles was still not sufficient to ensure that the light of these same frequencies would be absorbed intensely. Tyndall wrote in 1865, "The atoms and molecules of every gas have certain definite rates of

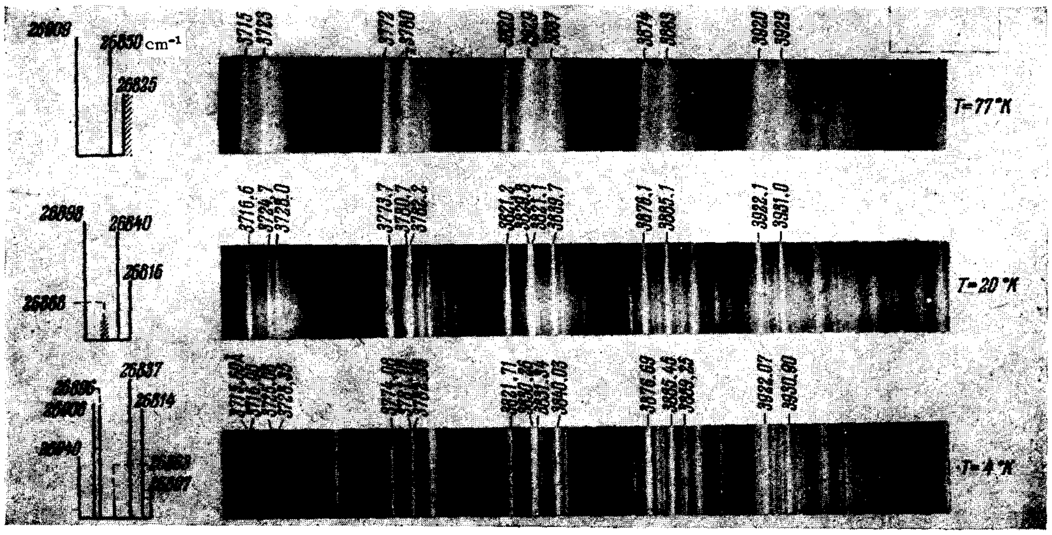

FIG. 4. The fluorescence spectrum of pyrene in hexane at various temperatures (portions of the spectrum). Plane diffraction grating. Linear dispersion ≈ 5 Å/mm (L. A. Klimova).

Table I.

Order No.	Fundamental vibrational frequencies of pyrene observed in the fluorescence spectrum		Vibrational frequencies observed in the Raman spectrum (Mecke and Klee[24])			The corresponding frequencies observed in the infrared spectrum (Mecke and Klee[24])			Type of vibration (Mecke and Klee[24])
	$\Delta\nu$, cm^{-1}	Intensity	$\Delta\nu$, cm^{-1}	Intensity	Symmetry type	$\Delta\nu$, cm^{-1}	Intensity	Symmetry type	
			349						ω
1	406	s	406	w	α_g				ω
2	456	m				456	vw	β_{1u}	Γ
3	498	m				497	m	β_{3u}	ω
4	559	w	558	w					
5	590	w	591	m	α_g	589	w	i	ω
6	678	w				675	vw	i	
7	736	s				734	m	i	
8	802	s							
9	945	w				945	vw	i	
10	1028	w							
11	1067	m	1067	w	α_g				δ?
12	1107	s	1108	w	β_{1g}				
13	1143	m	1142	m	α_g				δ
14	1183	w	1184	w	α_g				ω?
15	1232	m				1283	vw	i	
16	1240	w	1239	vs	α_g				
			1308						
17	1325	m	1327	vw					
18	1366	m	1369	w	β_{1g}				
19	1369	w							
20	1405	vs	1407	vs	α_g				ω
21	1500	m	1500	vw					
22	1551	m	1551	vw					
23	1595	m	1594	s	β_{1g}				ω
24	1631	m	1631	vs	α_g				ω
		w	2872	m					
25	3043	w	3046	m	β_{1g}				

Notation: vs—very strong; s—strong; m—medium; w—weak; vw—very weak; i—frequencies inactive by symmetry in the infrared spectrum; ω—vibrations of carbon atoms in the plane of the molecule; Γ—vibrations of carbon atoms out of the plane of the molecule; δ—vibrations involving change in the angle between two adjacent carbon atoms and a hydrogen atom bound to one of these carbon atoms.

oscillation, and those waves of aether are most copiously absorbed, whose periods of recurrence synchronize with the periods of the molecules amongst which they pass." However, in 1872 he wrote, "that an agreement in period alone is not sufficient to cause powerful absorption and radiation—that in addition to this the molecules must be so constituted as to furnish points d'appui to the aether."[26]

If we bear in mind the small amount of information and the primitive character of the theoretical concepts of that era, we must be amazed at the remarkable physical intuition of Tyndall, who for good reason was successor to Faraday's chair at the Royal Society of Great Britain. Indeed, we know well now what are these "points d'appui" that must be present for "absorption and radiation" of light to occur. In particular, in modern terms, the existence of definite energy levels is not sufficient for the frequencies corresponding to the transitions between these levels to appear in the spectrum. In order that these frequencies should be manifested, definite selection rules must be satisfied. In turn, these selection rules depend on the symmetry of the molecule. Here, the higher the symmetry is, the greater the number of transitions between the levels which are forbidden, and correspondingly, the smaller the number of frequencies which can be observed experimentally. Since the symmetry plays the decisive role, we have a reliable guide. This is group theory, which is coming more and more into use in physics. In particular, group theory permits us to calculate for every point group the maximum number of possible vibrations of each symmetry class. It often turns out, however, that the number of normal vibrations obtained by vibrational analysis of a quasilinear spectrum is smaller than the number of totally-symmetric vibrations predicted by group theory. Thus, for example, for naphthalene the number of A_1 vibrations is nine according to group theory (five for the carbon skeleton and four for the hydrogens), but a vibrational analysis gives only seven vibrations with frequencies below 1700 cm^{-1}; in the case of acenaphthene, in line with its lower symmetry, the number of A_1 vibrations is 21 according to group theory (11 C-C vibrations 10 C-H vibrations); vibrational analysis gives 13 vibrations with frequencies below 1700 cm^{-1}. The fact that in these cases and in a number of others the observed number of frequencies is smaller than that predicted by group theory need not cause concern, for two reasons: first, the analysis was only taken as far as 1700 cm^{-1}, beyond which more frequencies undoubtedly occur; second, for various reasons the number of observed frequencies can actually be somewhat smaller than that predicted by group theory.

However, it turns out that in the cases of phenanthrene and pyrene the number of frequencies obtained by vibrational analysis of the quasilinear spectra is considerably larger than the number of totally-symmetric vibrations predicted by group theory, and the problem arises of finding the reasons for this discrepancy. The situation is as follows: for phenanthrene, having the low symmetry C_{2v}, group theory predicts at most 23 totally-symmetric vibrations, whereas L. Pesteil and M. Rabaud [23] assigned the 52 lines in the fluorescence spectrum and the 41 lines in the phosphorescence spectrum observed at 20°K to 39 frequencies. In the spectrum of pyrene, whose molecule has the higher symmetry D_{2h}, the number of totally-symmetric A_g vibrations is 13 according to group theory. L. A. Klimova, who carried the measurements to frequencies considerably higher than 1700 cm^{-1}, assigned the 112 lines observed in one sequence to 25 frequencies (Fig. 4). To explain this excessive number of normal frequencies, we might suggest one of the following two reasons: a) the molecules of phenanthrene and pyrene in the frozen paraffin matrix are somewhat deformed, and hence certain selection rules cease to be effective and vibrations are manifested which are forbidden for the given symmetry group; b) owing to certain perturbations, the discussion of which would lead us too far afield, a non-totally-symmetric vibration can be manifested (β_2 in the case of phenanthrene or β_{1g} in the case of pyrene). The participation of such a vibration will result in rotation of the dipole by $\pi/2$ in the plane of the molecule, and in the appearance of a sequence of lines polarized in the perpendicular direction, similarly to the case of naphthalene.

As yet there are not enough experimental data to solve the problem in favor of either hypothesis, but the problem has been clearly formulated, and we may hope that such data will appear in the immediate future.

We can easily note some simple regularities in comparing the vibrational frequencies obtained by vibrational analysis of the quasilinear spectra of different polynuclear aromatic hydrocarbons. These include the existence of common frequencies among different hydrocarbons and the effect of the molecular symmetry on the intensities of these common frequencies. Thus, for example, although the coronene molecule consists of seven condensed benzene rings, these rings are so arranged that the coronene molecule belongs to the same symmetry class D_{6h} as the benzene molecule itself. An analysis of the coronene spectrum shows that the frequency having the highest intensity is 992 cm^{-1}. This exactly coincides with the most intense totally-symmetric frequency of benzene, which is interpreted as the "breathing" frequency of the molecule. On the other hand, isomeric molecules, though consisting of the same number of benzene rings in somewhat differing condensed arrangements, can show no common frequencies at all, or only a small number of such frequencies with widely differing intensities. This can be expected in those cases in which one of the molecules has a higher symmetry than the other. Then the more symmetrical molecule will exhibit new selection rules, whereby the most intense frequencies of the less symmetrical molecule can become forbidden. Interesting examples of this relation are given by comparison of sets of normal frequencies of two isomeric derivatives of pyrene: 3,4- and 1,2-benzpyrene. Of these, the latter molecule has a higher symmetry (C_{2v}) than the former (C_1). Upon comparing the frequencies of the two molecules, it turns out that, for example, the most intense frequency 1389 cm^{-1} of 3,4-benzpyrene is manifested very weakly by 1,2-benzpyrene; the same relation holds for the three other common frequencies of the two molecules. This fact is of great practical significance in analysis by quasilinear spectra; owing to this difference, the spectra of isomeric molecules differ so greatly from one another that they cannot be confused.

Some interesting facts emerge from comparison of the results of analysis of the spectra of the above-described chain molecules containing benzene rings with or without conjugation (see Fig. 1). Thus, for example, one can always find in these molecules a frequency 1000 cm^{-1} and the neighboring 998 and 980 cm^{-1}, as well as a frequency 1600 cm^{-1}. The former is very near to the above-mentioned "breathing" frequency of the benzene ring, while the latter, 1600 cm^{-1} is near an intense non-totally-symmetric frequency of the benzene ring. The presence of conjugation in the diphenylpolyenes shifts the breathing frequency to 1000 cm^{-1}, while it remains almost exactly unchanged in bibenzyl and tolan without conjugation. For some other regularities, see the original reference [4].

As the last example, I shall take up the spectroscopic study by Personov on phthalocyanine.

First—a few words on these remarkable molecules. We denote as the phthalocyanines a series of pigments of extraordinary stability. Metal-free phthalocyanine has the composition $C_{32}H_{18}N_8$. That is, it consists of 58 atoms and is the source substance for the series of metal compounds $C_{32}H_{16}N_8M$, M = Be, Mg, Fe, Cu, etc. In addition to their value as pigments, the phthalocyanines are important through their structural analogy with those natural compounds, the porphyrins, chlorophyll, and hemoglobin. The structural formula of metal-free phthalocyanine is given in Fig. 5. The dimensions of phthalocyanine molecules (15 Å) are such that it has been repeatedly reported that

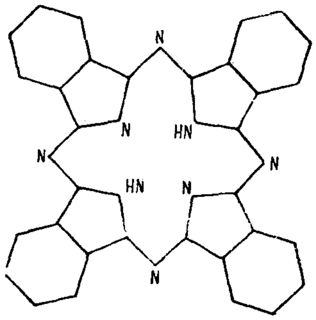

FIG. 5. Structural formula of phthalocyanine.

these molecules could be "seen" in the electron microscope. Previously Personov and Litvin had studied the emission spectrum of metal-free phthalocyanine and of the magnesium complex of phthalocyanine (Fig. 6, see insert). A new detailed study has been made of the fluorescence and absorption spectra of the former of these compounds.

As we have stated, the phthalocyanines are distinguished by their extraordinary stability. Indeed, copper phthalocyanine sublimes without decomposition at 580°C. This stability is manifested spectroscopically in two respects. First, the concomitant planar, inflexible shape of the molecule gives rise, even at 77°K, to a remarkable sharpness of the fluorescence and absorption lines, as we can see well from Fig. 6. Second, whereas aromatic hydrocarbons ordinarily show abundantly the overtones and combination frequencies in addition to the fundamental frequencies, phthalocyanine shows only the fundamental frequencies, as Personov has shown. This indicates that the intramolecular bonds in phthalocyanine remain almost harmonic, in spite of the strong perturbation introduced by the electronic excitation.

I am limiting myself to these examples, insofar as the topic at hand is the result of study of individual molecules.

II. THE RESONANCE SPECTRUM AND THE NATURE OF THE MULTIPLETS

Now I shall take up briefly the problem of the nature of the so-called "multiplets." By "multiplets" (doublets or more complex groups) we mean groups of lines repeated throughout the spectrum without change in the frequency spacings (see, e.g., [10]). These groups are observed in quasilinear luminescence spectra, and are repeated with the same frequency differences throughout the region of the absorption spectrum corresponding to the first quantum transition. While we shall use the term "multiplets," we shall not ascribe these groups to the removal of any type of degeneracy, but shall consider them to result from the superposition of a series of spectra having somewhat differing values for their purely-electronic (0′—0″) transitions, but maintaining the same vibrational frequencies (diagram in Fig. 7). Indeed, the intramolecular vibrational frequencies determined from each such sequence coincide without exception with one another (for one of the many examples, see [7]). Furthermore, although the structure of the multiplet of the same substance in different solvents can vary in the number, spacing, and relative intensities of the components, the vibration frequencies of the molecule, as determined in each case with respect to their particular 0′—0″ transition, also agree among themselves. For all these reasons, we consider the different spectra which are superposed to form the multiplets to belong to different spatially-separated "centers." These consist of molecules of the same type, but subjected to locally-varying influences of the crystal field of the fundamental crystal structure. This interpretation agreed excellently with all the known facts, but was without direct experimental confirmation. G. M. Svishchev has recently provided such a confirmation by a direct experiment.[27]

The chosen object of study was coronene, whose fluorescence spectrum consists of doublets (Fig. 8, see insert). The spacing between the doublet components when the solvent is normal hexane is 86 cm^{-1}. In heptane, the doublets are retained, but the spacing between the components declines to 70 cm^{-1}. By using a quartz double monochromator, Svishchev was able to isolate from the continuous ultraviolet spectrum of an ultrahigh-pressure xenon lamp a finely monochromatized beam, with which he excited the fluorescence of coronene in frozen hexane and heptane solu-

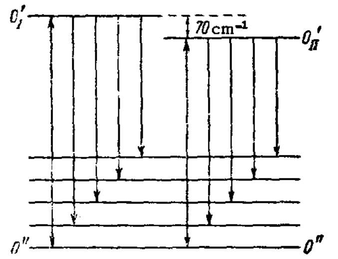

FIG. 7. Diagram of the origin of the doublets.

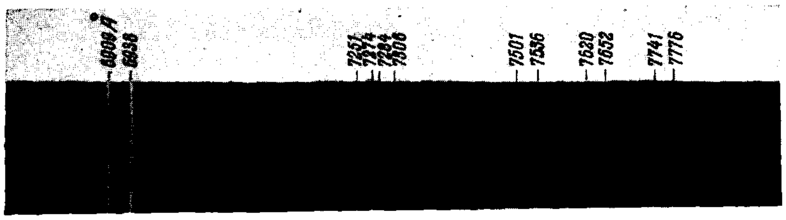

FIG. 6. The fluorescence spectrum of phthalocyanine in n-octane at 73.3°K. ISP-67 spectrograph with a camera having F = 1500 mm. Linear dispersion 20 Å/mm at 6900 Å.

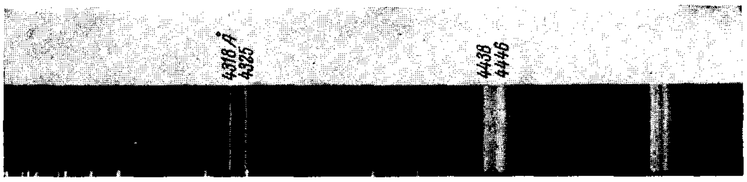

FIG. 8. A portion of the fluorescence spectrum of coronene in n-octane at 77.3°K. ISP-67 spectrograph with a camera having F = 1500 mm. Linear dispersion 3.5 Å/mm at 4200 Å.

tions. In turn, this fluorescence was resolved into a spectrum, using a three-prism ISP-51 spectrograph as a monochromator. Here a photomultiplier operating as a photocounter was placed at the monochromator exit as a detector. This arrangement permitted the recording of the resonance spectrum, in complete analogy with the experiments of Wood with the resonance spectra in sodium and iodine vapors.

In fact, if one carries out the excitation in the usual way with a light filter, i.e., with a beam containing a wide frequency range, the spectrum consists of doublets, since the exciting light overlaps with the frequencies of the region of the absorption spectrum between the purely electronic 0—0 levels with room to spare (see Fig. 7). However, if one carried out the excitation under the above-described conditions, using a sufficiently pure monochromatic exciting radiation and varying the wavelength of this radiation continuously, the fluorescence spectrum undergoes a characteristic transformation. We must bear in mind the fact that these spectra are always of resonance type. That is, the leading doublet in the absorption spectrum exactly coincides with the leading doublet in the fluorescence spectrum. Then, when the exciting wavelength exactly coincides with the short-wavelength component of the absorption-spectrum doublet, the fluorescence spectrum consists only of the short-wavelength components. However, when the exciting wavelength coincides with the long-wavelength component of the absorption spectrum, the fluorescence spectrum again consists of only one component, now the long-wavelength one. This experiment shows that, at least in the case of coronene, the different components of the multiplets (doublets in this case) actually belong to different spectra independent of one another; the superposition of these spectra generates the pattern of apparent multiplets.

Hence it follows that with sharply monochromatic excitation the pattern of the spectrum, i.e., the distribution of intensity among the multiplet components (in the limiting case, the disappearance of certain components) can be altered considerably, depending on the exciting wavelength. This explains certain peculiar phenomena heretofore not explained. Thus, for example, it has been noted that when one excites the fluorescence through different absorption filters transmitting the same spectral region, the intensity distribution among the doublet (multiplet) components can vary appreciably. In view of the sharpness of the absorption lines of the material being studied, very small variations in the transmission spectrum of the filter are sufficient to give appreciable changes in the relative intensities of the "partial fluorescence spectra" which are superimposed to produce the multiplet. Also, these phenomena recall greatly, though in cruder form, the widely-known observations of Wood regarding the excitation of resonance spectra in iodine vapor with varying wavelength of excitation.

Obviously, some observations made by the author together with A. A. Il'ina [39] are of the same class of phenomenon; these were made prior to the discovery of the quasilinear spectra, and naturally, were not interpreted correctly at that time. Here the fluorescence spectrum of 3,4-benzpyrene in paraffin oil at 77°K was studied. When excited by a mercury lamp through a light filter transmitting the 3650 Å region, the spectrum consists of a series of bands of width 150—200 cm^{-1} having sharp maxima. However, if one uses as the filter the narrowly monochromatic filter of the Zeiss set "for mercury lines" transmitting only the 4043-4078 Å violet lines but not the shorter-wavelength region of the spectrum, the bands become appreciably narrower, and their maxima are shifted by about 70 cm^{-1} to longer wavelengths. At that time, the observation seemed to contradict the fact that the fluorescence spectrum is independent of the exciting wavelength. However, in fact, the same characteristics are manifested here, though in a very blurred fashion, as those leading to the redistribution of intensity among the multiplet components in the quasilinear spectra when one changes the spectral composition of the exciting light.

However, the problem remains unsolved why the frequency spacings of the purely-electronic transitions corresponding to the individual multiplet centers are exactly maintained in all experiments, i.e., the problem of the nature of the local variations in the crystal field giving rise to the multiplets. The solution of this interesting problem will permit us to make some very detailed conclusions on the internal structure of the crystalline medium enclosing the emitting centers. I have discussed this problem in a recent article, in which I indicated a possible relation of this problem with a number of interesting physicochemical problems.

In conclusion, I shall note that the very fact of the occurrence of a 0′—0″ resonance transition in the solid crystalline state is not trivial, and requires explanation. However, this problem will be discussed in Sec. IV of this article.

III. THE CRYSTAL-CHEMICAL PROBLEM

I shall take up now a very important set of problems on the origin of the quasilinear spectra. The pertinent problems can be divided into two large groups: a) the crystal-chemical problem, i.e., the problem of the state of the molecules being studied in the crystal structure of the solvent; b) the solid-state physics problem, or the problem of the interaction of the active absorption and emission "centers" with the solvent crystal, and thus, the problem of the reasons for the quasilinear nature of the spectra. It is all the more opportune to discuss these problems, in that now, when we can consider the molecular nature of the spectra to be firmly established and the accumulation of factual information on individual molecules is advancing, the overall physical problems involved in the quasilinear spectra have come up for treatment.

In proceeding to discuss the crystal-chemical problem, I should mention that in the course of development of crystal spectroscopy, it proved convenient to study polyatomic molecules by incorporating them in a foreign crystal structure at low temperatures. In these cases, the substance chosen as the solvent crystal is isomorphous with the one being studied, since one naturally assumed that isomorphism is a necessary condition for the preservation of translational symmetry, and thus, for formation of a crystalline solid solution. Here the isomorphism was understood "in the classical sense": both components of the isomorphous pair had to belong to the same type of chemical compound. That is, they were compounds having structural formulas of the same type, and had to be as similar as possible in crystallographic properties. However, the possibility of using this method was very limited, since the cases of isomorphism as this phenomenon is usually understood are relatively rare among organic compounds. Then, when we add the requirement that the solvent crystal should be transparent in the region of interest, the possibilities become even more limited.*

The method which we have used to obtain quasilinear spectra also consists in using crystalline matrices at low temperatures. However, this method differs quite essentially from the above-described isomorphous-substitution method, since it unexpectedly turned out to be possible to use solvent crystals of one particular type as the matrices enclosing the molecules being studied. The latter compounds could be rather diverse, regardless of the chemical and crystallographic properties of these substances (of course, within known, but rather broad limits). I am referring to the normal paraffins which we have used, with their zigzag unbranched molecules of varying lengths.

Since in obtaining a quasilinear spectrum we must work with a frozen crystalline solution (the special solvents in the form of mixtures freezing to glassy masses, e.g., the well-known E. P. A. mixture, do not permit one to obtain a quasilinear spectrum), the obvious problem arises: to explain how substances differing so greatly from one another and from the paraffins in composition and in molecular and crystal structure can give crystalline solid solutions. Apparently, one should not speak of isomorphism in this case, with all the indefiniteness of this property, especially in the field of organic compounds.

This situation indicates that we have a problem whose solution is of interest beyond the limits of spectroscopy.

In discussing this problem, we can justly take the reverse route and consider the appearance of a quasilinear spectrum to be a reliable sign of a molecularly-disperse distribution of the substance being studied. In this way we can make some general conclusions based on existing information. In particular, it has been established that when the solvent is one of the normal paraffins, the best conditions for appearance of a quasilinear spectrum occur under the condition that the dimensions of the long axis of the incorporated molecule are as close as possible to the dimensions of the paraffin solvent. This rule is analogous to Goldschmidt's rule, which has been tested against a large volume of experimental material, according to which inorganic compounds can form a wide range of mixed crystals if the corresponding radii differ by no more than 15%. In the case of the paraffin-aromatic complexes, we have also shown that if the dimensions of the "guest" and "host" molecules differ within certain limits, the molecular dispersion is maintained, but the spectrum sometimes becomes more poorly resolved.

A second important condition concerns the similarity of the geometrical shapes of the "guest" and "host" molecules. This rule has no analog in the inorganic field, in which the ions replacing one another are spherical in shape. However, in the case of our paraffin complexes, this condition seems most obvious when the guest molecules are condensed linear aromatic compounds with varying numbers of benzene rings, e.g., naphthalene, anthracene, and naphthacene. Figure 8 compares the structural formulas of anthracene and naphthacene with the chains of the normal paraffins in which these substances give the best-resolved spectra. The geometric similarity of the zigzags of the paraffin molecules and the incorporated aromatic molecule is striking. It shows that each projection of the one molecule exactly corresponds with a recess in the other, so that the most favorable conditions occur for closest packing of the two molecules, which differ greatly in all other features.

The idea that analogy of shape ("symmorphism") can act as a fundamental, if not the only condition for

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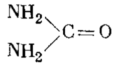
*Recently V. L. Broude and E. F. Sheka have obtained results of interest in the spectroscopy of pure crystals in a case of ideal isomorphism occurring through isotopic substitution of certain atoms of the structure.

formation of a homogeneous mixed crystal or solid solution is not new. Sixty years ago the Italian physical chemist Giuseppe Bruni proposed a principle for solving a number of structural problems, according to which one can draw conclusions on the structural details of an organic compound if it forms a solid solution with another compound of previously known structure, regardless of any possible other differences between the two compounds. Thus, he solved a number of problems involving the presence of cis- or trans-isomerism and analogous problems. Many of his conclusions, which at that time were unexpected and controversial among chemists, have since been confirmed by x-ray structural analysis. The point that we should note in these conclusions of Bruni is that the standard molecules or templates were chain molecules having zigzag structures of the normal-paraffin type (besides the paraffins themselves, e.g., the fatty acids). Thus the impression arises that there is something specific and characteristic of long-chain zigzag molecules in particular, which makes it possible to obtain with them mixed crystals with components differing strongly in their physicochemical properties, but similar geometrically.

Nevertheless, one can hardly speak in these cases of the formation of a crystalline substitutional solid solution in the usual sense. Hence, it is convenient to discuss as a new possibility the properties of some special chemical systems discovered less than 25 years ago. These are called molecular compounds or inclusion compounds, in which it is precisely the geometry which plays the decisive role. There are several types of these compounds.* Characteristic of all of them is the formation of a homogeneous system, the "compound", in which two completely different molecules can be combined without participation of chemical bonding forces, owing to the fact alone that one molecule, the "guest," is situated in some cavity surrounded by molecules of the other component, the "host." If at the same time the purely geometrical characteristics of the guest molecule, i.e., its dimensions and shape, are identical with or as close as possible to the corresponding geometrical characteristics of the cavity in the host, a stable compound can arise. However, here the components are bound not by covalent bonds, but rather either by simple van der Waals forces or at most by hydrogen bonds.

Such a compound has little in common with ordinary solid solutions, even in that in many cases one need only disrupt the surrounding structure made by the "host" for the "guest" to emerge unchanged. This is quite evident from the example of one of the six known types of "inclusion compounds," the so-called "clathrate compounds". When hydroquinone (otherwise called quinol), which is widely known as a photographic developer, crystallizes from methyl alcohol, a particular type of crystal structure is formed (the so-called β-hydroquinone), whose characteristic peculiarity consists in the formation of approximately spherical cavities of diameter about 4 Å. Molecules of such gases as SO_2 or H_2S or noble-gas molecules can be "imprisoned" in these cavities, provided that their van der Waals radii are about 2 Å. Thus, for example, helium ($R = 1.5$ Å) and neon ($R = 1.6$ Å) have radii too small, and they slip out through the hexagons of oxygen atoms forming one of the "walls" of the cavity, but argon (1.8 Å), krypton (2 Å) and xenon (2.0 Å) form stable compounds, since their sufficiently large atoms are retained within the "cells". Such odorous gases as SO_2 or H_2S are also imprisoned, and lose their odors. However, one need only break up the "compound" formed by dissolving it in water or melting it for the inert gases to emergy noisily, or for the liberated hydrogen sulfide or sulfur dioxide to make its presence known by its odor. This just shows that, although we can even ascribe a formula to the "compound" of the type, e.g., $C_6H_4(OH)_2M$, where $M = Ar$, He, H_2S, etc., in fact no chemical bond is formed, and the captive atoms or molecules are held only by van der Waals forces.

Of even greater interest for comparison with our systems is another type of inclusion compounds, the canal complexes. These complexes were discovered and studied in the example of the complexes: urea


$(NH_2)_2C{=}O$

= host, normal paraffin C_nH_{2n+2} = guest; and also urea with derivatives of the normal paraffins (higher alcohols, fatty acids, etc.) as guests. The structure of these complexes has been worked out by x-ray diffraction analysis, which revealed the following. While urea ordinarily crystallizes in the tetragonal system, when crystallized together with a normal paraffin, the urea is rearranged into a hexagonal structure. Here the cavities appear in the form of canals of hexagonal cross-section along the c axis. These canals can have any length, since the individual small urea molecules are joined by hydrogen bonds. The canal diameter, 5 Å, exactly fits the diameter of the cross-section of a zigzag paraffin chain. The entire structure remains unchanged, regardless of the length of the paraffin chain cocrystallized with the urea, but the number of urea molecules per paraffin molecule increases in strict proportion to the number of carbon atoms in the paraffin molecule. Obviously, the only possible arrangement of the paraffin chain in the canal consists in laying it along the canal parallel to the c axis. An essential point is that only the normal paraffins with their straight zigzag chains turn out to fit without hindrance in a canal of 5 Å diameter. The isomers consisting of the same num-

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*See the monograph of F. Cramer,[28] one of the most active researchers in this field.

ber of carbon atoms, but having branch points within the chain, are too "fat," cannot be fitted into the canals, and no compounds are formed (branching at the ends does not interfere with "compound" formation).

The consequence of all these properties is a remarkable ability of canal complexes, which is of great practical value, and of especial interest to us (for reasons to be given below): strict selectivity in the choice of "guests" for complex formation. This property has been the basis of a large number of patents describing methods of separation of normal and branched paraffins. These methods are of considerable technical interest, since they permit separations which cannot be attained either by crystallization or by distillation.*

I have emphasized in the treatment above that when the properties of the components differ as greatly as they do in the systems that we have studied, the formation of true solid solutions is improbable. Further, I shall show below that certain unusual properties of our systems recall so much the properties of the inclusion compounds that a working hypothesis is quite justified that the normal-paraffin-based complexes which we use in our method are one of the types of these compounds. I have formulated this as a hypothesis still, since, first, inclusion compounds in which normal paraffins play the role of the "host" have not yet been described by anyone, in so far as I know; and second (and most important), there are still no direct proofs of the idea that we are actually dealing with such systems here. Hence, in particular, the question remains open whether we can assign our systems (if they are actually inclusion compounds) to one of the known types of these compounds, or whether they are new types of inclusion compound.

Before I go on to describe the facts that can serve as grounds for our hypothesis, it is useful to cite a general characteristic of inclusion compounds which I have taken from the cited monograph of Cramer:[28]

> "In inclusion compounds we are dealing with a purely spatial formation of bonds between partners. Here no primary or secondary valence bonds are formed, but one molecule spatially encloses another. The enclosed molecule is as if surrounded by a stable framework, and cannot leave its place, although it is not bound directly to the other framework molecule. The necessary cavity can occur either within an individual molecule, which requires relatively large molecules (of molecular weight above 1000), or it can occur in a spatial structure owing to the mutual arrangement of many small molecules. This sort of compound must hence be considered from a quite special standpoint. The formation of these compounds does not depend either on chemical affinity nor on definite functional groups; conversely, the following assumptions are significant here:
>
> 1) The framework substance must possess cavities of molecular dimensions: in the case of molecular structures, these cavities need not exist previously, but often they may be formed in the presence of the addend (underscoring mine—É. Sh.)
>
> 2) As the addend must fit into the cavities, its spatial configuration is of decisive importance; spatial correspondences here play the role of chemical reactivity.
>
> It is self-evident that when the spheres of action of the molecules forming the inclusion compound are in close spatial contact, they also interact ... However, above all, the purely spatial configuration of the components of the compound is still important."

The following facts which we have used favor the identification of the paraffin complexes as being inclusion compounds:

a) The possibility of formation of homogeneous systems of the mixed-crystal type when there is such a great chemical and crystallographic dissimilarity between the components that not even the broadest conditions for isomorphism can be satisfied.

b) Analogy of shape, as is especially clear in the case of the linear aromatics, and similarity of dimensions; as we see from Fig. 9, the zigzag shape of the normal paraffin and the edge of the aromatic molecule fit one another so exactly that the "lock and key" principle is satisfied.

c) Striking selectivity. The observations of other laboratories and ours have revealed the following. One can prepare a solution in any solvent, e.g., methyl or ethyl alcohol, benzene, or any other suitable solvent, provided that the frozen solution shows the

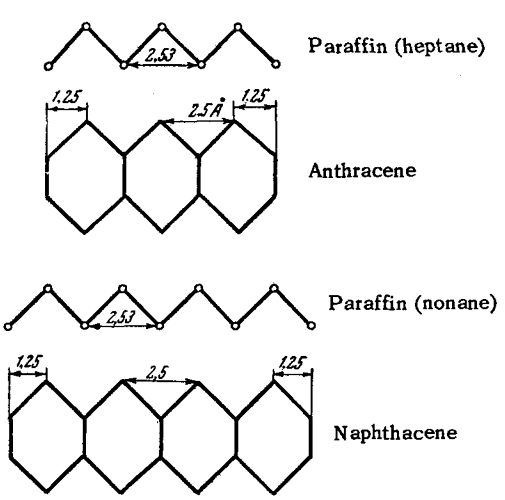

FIG. 9. The relation of the dimensions and shapes of the molecules of the activator and the paraffin matrix under the conditions favoring the highest resolution of the quasilinear spectra.

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*For examples, see the monograph of Cramer.[28]

usual broad bands in its spectrum. However, if we add to the same liquid solution even a small amount of a suitable (in molecular dimensions) normal paraffin, the entire remarkable quasilinear spectrum appears at once; the guest molecules, as it were, choose for themselves "apartments" in which they can arrange themselves with especial comfort. This amazing property is completely analogous to the properties described in Cramer's monograph, on which are based the methods of separation of normal from branched paraffins by formation of the inclusion compounds with urea. Muel and Lacroix,[14] who developed a method of quantitative analysis for 3,4-benzpyrene, have used it in practice as follows: the final fraction from chromatography of tobacco tar, which contains the 3,4-benzpyrene, was obtained in a cyclohexane solution, and gave a diffuse spectrum. Addition of 10% normal octane was enough to bring about distinct manifestation of the quasilinear spectrum.

d) Of great interest are some observations on the melting of a frozen solution while under ultraviolet illumination. These observations are based on the sharp difference between the fluorescence spectra of the polycyclic aromatics in the crystalline and the molecularly-disperse states. Thus, for example, coronene in the crystalline state gives a green emission with a continuous spectrum, while in the molecularly-disperse state it gives a blue-violet emission with a discrete spectrum. If one melts the solution while illuminating it through a black-light filter, one first observes the appearance of a multitude of shining green points which disappear upon further warming. Obviously, owing to the breakdown of the paraffin structure, the coronene molecules are freed from "captivity," and the coronene crystallizes out because of its low solubility in the cold solvent, and redissolves in the liquid paraffin upon further warming.

All of this is so reminiscent of the properties of inclusion compounds that the hypothesis that they are formed when the host crystal is any of the normal paraffins seems very plausible. Of course, with molecules having an angular or planar arrangement of benzene rings, such as perylene, pyrene, coronene, or such molecules large in two dimensions as the phthalocyanines and the porphyrins, one-to-one correspondence between guest and host molecules cannot occur. However, I should note that in accordance with the cited general characteristics of inclusion compounds, the cavities for incorporation need not exist already in the host crystal: "often they are formed in the presence of the addend." This is the first point, but secondly, just as occurs in the urea-n-paraffin complexes, a given size of guest molecule corresponds to a number of host molecules in proportion to the ratio of their dimensions. Finally, I shall note that, in view of the layer-type crystal structure of the paraffins, large planar guest molecules may possibly be fitted between the layers: the spacing of about 4 Å between successive paraffin molecules is quite sufficient for fitting a planar molecule there.

One need hardly prove that structural and crystal-chemical studies in this field are of outstanding interest. It is also obvious that the study of quasilinear spectra should make possible the drawing of some very detailed conclusions on the structures of the systems being studied.

Finally, I would like to mention the outstanding interest in this new field of inclusion compounds, which, as is becoming ever clearer, play a very important role in nature, especially in biological processes.

IV. ON THE THEORY OF THE QUASILINEAR SPECTRA

Up to now, we have been guided by a model of an oriented gas in interpreting our spectra. The justification for this is the fact that the vibration frequencies determined from the quasilinear spectra for the atoms of the molecule coincide to a high degree of accuracy with those found independently from the purely vibrational spectra (infrared and Raman) in the cases in which the latter are known. Consequently, as regards the framework of heavy (in comparison with the electrons) nuclei, the model of unperturbed molecules has been confirmed without question even to the finest details, as have been discussed in Sec. I. However, for a complete interpretation of the spectrum, we must also take into account the properties of the electron shell. As we have seen, the fixation of the molecule in the crystal structure shows practically no influence on the vibration frequencies of the nuclei. However, there are some positive signs of an effect of the host structure on the incorporated impurity molecule with regard to the electron shell. First of all, this effect is manifested in a shift of the entire spectrum by 150—200 cm^{-1} with respect to the spectrum of the free gas molecule, i.e., by the amount of the weak van der Waals bond. Thus, the discussion of the mechanism of origin of a quasilinear spectrum in its entirety becomes a highly interesting solid-state physics problem.

During the last 20 years, there has been no lack of theoretical papers on the problem of the mechanism of luminescence of inorganic crystal phosphors within the framework of solid-state physics. The interest in this problem obviously involves the great practical importance of the crystal phosphors. One need only mention daylight fluorescent lamps, television tube screens, and radar instruments. We should acknowledge as a great advance the clear qualitative picture of the luminescence mechanism of certain important types of crystal phosphors (see, e.g.[29]). However, even in cases in which it has been possible to establish definitely the nature of the emission "centers" (e.g., in the thallium-activated alkali-halide phosphors), the possibilities of experimental verification of the very cumbersome mathematical calculations [30-32] have turned out to be exceedingly limited, owing to the structureless character of the spectra. In the final analysis, the achievement of the theory has been considered to be the explanation of the actually important, but not very comforting fact that the emission bands remain diffuse down to temperatures near absolute zero (cf. [32]).

In complete contrast to this unfavorable situation are the conditions for emission in our organic mixed crystals. Undoubtedly, in this case we are also concerned with a crystal phosphor, but based on molecular, rather than ionic crystals. The nature of the emission "centers" in this case is identified easily and quite reliably, while the narrow width and the richness of the lines, as well as the high sensitivity of the spectra to the environmental conditions, make these systems a potential source of a wealth of information on processes occurring within the crystalline solid. An advantage of no little importance from the standpoint of the theoretician is the fact that the fundamental crystal structure absorbs in the far ultraviolet, while the impurity molecules absorb in the visible or near ultraviolet. This gives considerable room for use of approximate methods.

In spite of all these advantages, the problem of explaining the origin of the quasilinear spectra within the framework of solid-state physics has not attracted the attention of theoreticians until very recently. Thus a heartening step is found in the studies of K. K. Rebane and V. V. Khizhnyakov [33] of the Institute of Physics and Astronomy of the Academy of Sciences of the Estonian S.S.R. They were the first to take up the problem of providing a theory for the quasilinear spectra, taking into account the interaction between the impurity molecule and the rest of the crystal. Below I shall only briefly deal with the physical assumptions of this study, omitting the mathematical part.*

Perhaps it is somewhat curious, but in any case very important, that a severe problem arises even at the beginning, involving the possibility in principle of obtaining a highly-resolved quasilinear spectrum in a crystalline solid, particularly with regard to the strict resonance character of the leading lines of this spectrum. In fact, the usual crudely qualitative explanation of this fact ascribes it to the notion that in the crystalline state the impurity molecules are fixed in identical positions at great distances from one another. First, this eliminates possible interactions of identical closely-spaced molecules, which could result in diffuseness owing to a weak removal of degeneracies, and second (and especially important), it eliminates the effect of the rotational degrees of freedom, whose levels are spaced so closely for large molecules that they form a quasicontinuum. This broadening effect of molecular rotation on a spectrum is quite visible in Fig. 10, which shows the fluorescence spectra of the large but very "firm" molecule coronene in the vapor and in octane solution at room temperature.

However, the argument that a large number of degrees of freedom disappear when the molecules are condensed in a crystal is inexact.[33] In fact, although the translational and rotational motions disappear here, the collective lattice vibrations arise instead. For a macroscopic crystal, the number of these vibrations is enormous, and as we can easily see, they must form a quasicontinuous series, such as occurs in the rotational states in a gas. Obviously, the excitation of an impurity molecule incorporated into a crystal must unavoidably result in part of the energy of the electronic transition being transformed into these lattice vibrations. However, in such a case it is still not clear how the spectrum of the crystal is freed from the broadening influence of these vibrations, an influence which should give the same effect as the quasicontinuum of rotational states in a gas.

In this regard, Rebane and Khizhnyakov considered the analogy between the mechanism whereby the γ-lines appear with their natural widths in a crystalline solid in the Mössbauer effect [34] and the narrow "lines" in an optical quasilinear spectrum. As it turned out, this analogy extends much further than the external similarity of the phenomena.

In view of the interest and importance of the problem, I shall take it up in somewhat greater detail, and shall begin with the Mössbauer effect. As we know, when γ-quanta are emitted, part of the energy of the quantum transition is spent in imparting the kinetic energy of recoil to the emitting nucleus. For a free

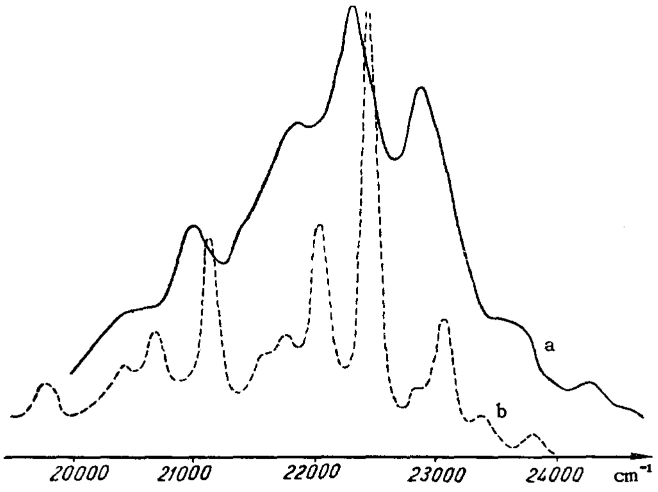

FIG. 10. The fluorescence spectra of coronene: a) in the vapor, T = 400°K; b) in octane solution, T = 300°K.

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*K. K. Rebane and V. V. Khizhnyakov have kindly provided me with the text of their paper at the 11th Conference on Luminescence, for which I am sincerely grateful.

nucleus at rest, the energy of the emitted photon will consequently be smaller than the energy of the quantum transition by an amount $R = p_\gamma^2/2M$, where M is the mass of the nucleus. Thus the line emitted must be shifted to lower frequencies with respect to the line of the recoil-less transition by the same amount R (in energy units). Correspondingly, in resonance absorption, likewise in view of the law of conservation of momentum, the energy of the incident photon must be larger than the energy of the quantum transition by the same amount R. In the case of free nuclei in a gas, these shifts are accompanied by the Doppler shifts as well, owing to the thermal motion of the nuclei of the source and the absorber. Consequently, the emission and absorption curves become diffuse in form, and their maxima are displaced by an amount 2R, as is shown in Fig. 11. Parenthetically, we note now that the evident analogy of this picture with the luminescence and absorption curves when a Stokes shift occurs is not fortuitous, although the nature of the 2R shift differs in this case.

If the emitting nucleus is incorporated in a crystal structure, the recoil momentum of the nucleus is transmitted to the neighboring atoms. This involves transfer of part of the energy to the lattice vibrations. That is, in other words, the nuclear transitions are accompanied by the creation of phonons in the crystal. However, Mössbauer showed that there is a finite probability of particular transitions not involving a change in the internal state of the crystal. In these transitions, the energy of the emitted photon is exactly equal to the energy of the quantum transition in the nucleus, and the spectrum consists of an exceedingly narrow line, practically with its natural width uncomplicated by any broadening.

Initially, this remarkable phenomenon was explained simply by the idea that in such transitions the recoil is transmitted to the crystal as a whole. And since the mass of the crystal is enormous in comparison with that of an individual nucleus, the energy transfer under these conditions must be negligibly small. Hence such transitions are usually called recoil-less transitions.

However, a painstaking analysis of the situation has shown that this explanation is inexact, and the existence of transitions without changes in the internal state of the crystal (without generation of phonons), in which the momentum is transferred to the crystal as a whole, cannot be understood on the basis of classical mechanics of elastic collisions. Indeed, we cannot doubt that at the moment of emission, recoil is first taken on by the emitting nucleus. Then, owing to the elastic bonds of the emitting atom with the other atoms of the structure, this recoil is finally transformed into collective vibrations of the crystal, increasing its store of thermal energy. That is, the recoil must involve phonon transitions. How it happens that these transitions exert no influence on the width of the γ-line emitted is just not clear.*

Some have attempted to explain it with the idea that the bonds in the crystal are so strong that the atom undergoing the recoil should carry with it the entire crystal. However, this proved false. Further, a simple calculation based on the classical dynamics of collisions has shown [36] that on the average the crystal receives from recoil just as much energy as a free atom does, i.e.,

$$\overline{\Delta E} = R = \frac{p_\gamma^2}{2M}.$$

This means that, since the crystal structure is considered classically, the bonds should exert no effect on the γ-line. The apparent contradiction with experiment, which shows the existence of "recoil-less" γ-lines, can be resolved if the problem is a quantum, rather than classical problem. Hence, any effect of the bonds will be manifested when the lattice vibrations are described by small quantum numbers, i.e., at low temperatures. The analysis which Lipkin [36] carried out in the cited study leads to the conclusion that the incorporation of the emitting nucleus into the crystal structure creates conditions for "recoil-less" emission, not because the nucleus is frozen in the crystal and cannot undergo recoil, but mainly because the bonds in the crystal give rise to zero-point oscillations which are absent in the gas, and these create a limiting value for transfer of energy to the crystal structure. However, according to the "sum rules"† derived by this author, the area under the energy distribution curve in the final state E_f must be the same for the cases of the "gas" and the crystal.

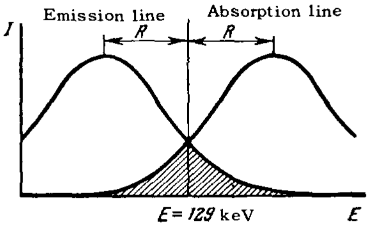

FIG. 11. Positions and shapes of the emission and absorption bands of the γ-rays for the 129 keV transition in Ir^{191} at 300°K (Mössbauer, Usp. Fiz. Nauk 72, 658 (1960), Fig. 1).

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*Hereinafter we shall follow the physically very lucid studies of H. Lipkin.[35,36]

†These sum rules are the following:

$$\langle E_f \rangle = E_i + R, \qquad \text{(a)}$$

$$\langle E_f^2 \rangle - \langle E_i \rangle^2 = 2R \frac{p_L^2}{3M}. \qquad \text{(b)}$$

Here R is the recoil momentum of a free atom in emission of a γ-photon, $R = p^2\gamma/2M$, and p_L is the momentum of the atom before emitting the γ-photon. The brackets denote the statistical "moments": $<E_f>$ is the first moment, i.e., the mathematical expectation (mean value); $<E_f^2>$ is the second moment (dispersion); $p(E_f)$ characterizes the spectrum of the final state of the crystal structure; E_i is the energy of the initial state of the crystal structure. Formulas (a) and (b) coincide with the corresponding formulas derived from the classical dynamics of collisions.

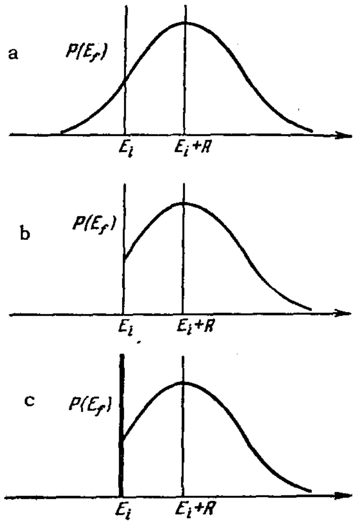


FIG. 12. On the theory of the Mössbauer effect. a) The classical spectrum of a gaseous source; b) the portion of the previous spectrum corresponding to positive energy transfer; c) the same spectrum as in b), but with the addition of a δ-function (from Lipkin[36]).

Hence, this requirement can be satisfied only if the missing area in the case of the crystal occurs in the form of a delta-function at $E = E_i$, which then corresponds to the Mössbauer "recoil-less" line (Fig. 12). So as not to digress too far from our main topic, we shall limit ourselves to this very sketchy presentation, referring those interested in the systematic development of this author's ideas to the original article. The point of the final conclusion is that emission in the form of a broad quasicontinuum and in the form of the Mössbauer line are two independent processes which can occur alternatively, each with its own probability. This, then, is the answer to why the lattice vibrations exert no influence on the width of the recoil-less line.

If we now turn to the mechanism of emission of the optical quasilinear spectrum, we see that here, as Rebane and Khizhnyakov have formulated it especially clearly, literally the same problem arises as in the case of the Mössbauer effect, that of explaining why the inevitable collective lattice vibrations have no effect on the spectrum. First of all, let us specify what properties of the spectrum we are concerned with. Namely, these are: 1) the appearance in a crystalline solid of a spectrum having lines of width of the order of a few cm^{-1}, instead of the usually observed bands of widths of hundreds of thousands of cm^{-1}; 2) the strict resonance character of the leading ($0'-0''$ transition) line of the spectrum.

In the optical region of the spectrum, the recoil momentum upon emission of a photon is infinitesimally small in comparison with the recoil in γ-emission. Consequently, the appearance of resonance in emission and absorption in the optical region of the spectrum involves no difficulties in the case of free molecules (in a gas). However, when the molecule is incorporated in a crystal structure, the conditions are altered, and the influence of the crystal vibrations must affect the $0'-0''$ transition, just as it affects the widths of the lines.

In fact, we can easily see that the role played by the recoil momentum in emission of a γ-photon must be played by the inevitable "thermal" losses giving rise to the Stokes shift in the case of the fluorescence spectrum in a solid. Even if these losses exerted no effect on the width of the lines, they would have to disturb the resonance between the leading lines in the absorption and luminescence spectra, just as the recoil momentum disturbs the resonance in the case of γ-fluorescence. Still, in the quasilinear spectra the frequencies of the $0'-0''$ lines in absorption and emission always coincide within the limits of error of measurement, i.e., $1-0.1\ \mathrm{cm}^{-1}$, or in other words, $10^{-4}-10^{-5}$ eV. This characteristic of the quasilinear spectra is of great practical significance, since it is precisely this which permits us to carry out a vibrational analysis of the electronic-vibrational spectrum very simply. Of course, in essence it cannot be separated from the mechanism of origin of the narrow lines, but the existence of this characteristic shows especially clearly that the phenomenon of appearance of a quasilinear spectrum has little in common with the trivial phenomenon of narrowing of lines due to simple lowering of temperature.

We shall discuss this problem in more detail, and take up first the case of inorganic crystal phosphors. In this case, the appearance of the Stokes shift has been interpreted very clearly, owing to the use of the so-called method of configurational coordinates, first used by F. Seitz 25 years ago. In cases in which the crystal phosphor contains a well-localized "center" (a classic example might be an alkali-halide crystal phosphor activated with the thallium ion Tl^+), we can construct a model of the potential curves analogous to that used in the theory of diatomic molecules. However, we must bear in mind the essential difference between the two cases. In the theory of diatomic molecules, the potential curve represents the relation of the potential energy of the molecule to the distance between the nuclei. Near the minimum, the curve is a parabola, corresponding to the model of a harmonic oscillator, and the minimum corresponds to the equilibrium distance of the nuclei. In the case of the crystal phosphor, the curve represents the total lattice energy as a function of some configurational coordinate characterizing the arrangement of the neighboring atoms (or ions) with respect to the "center." Of course, one cannot completely characterize such an arrangement with one coordinate; one would actually need a multidimensional surface. However, for qualitative arguments we can use even a single coordinate. For example, in the case of a well-localized center, showing a rapid decline of the interaction between the center and the atoms of the crystal structure, the essential role is played only by the motion along the radius vector from the center, and the configurational coordinate can be taken as the distance from the center to the neighboring molecules of the crystal

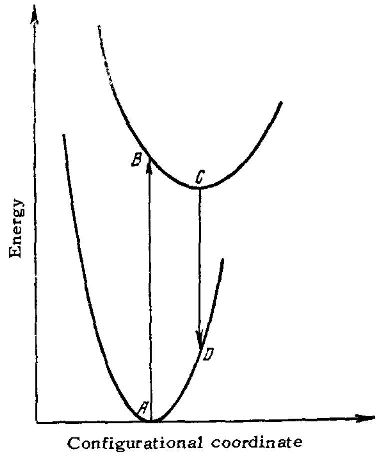


FIG. 13. Diagram of the configurational-coordinate method.

structure (the "breathing coordinate"). Obviously, electronic excitation of the center alters the elastic forces of interaction between the center and the crystal structure. Hence, the minimum of the curve for the excited state is shifted with respect to the minimum of the lower curve, as is shown in Fig. 13.

When the center is excited, in accordance with the Franck-Condon principle, there is an instantaneous transition from the lower curve to the upper curve along the vertical line (AB), i.e., without change in the distance between the center and its surroundings. For this reason, the system finds itself in a state with excess potential energy, and thus vibrations about the center arise, and are rapidly transformed into normal lattice vibrations. After an interval of time of the order of 10^{-12} sec, the representative point moves over to the minimum of the upper curve, and from there, after $\sim 10^{-8}$ sec, it undergoes a transition to D on the lower curve. Here also the system (center + surroundings) turns out to be "heated" above the equilibrium temperature; vibrations arise, and are again transformed into normal lattice vibrations. Thus the optical absorption and emission of the center involve creation of phonons in the crystal. As for the Stokes shift, it can be determined directly from the diagram as the difference AB − CD.

We shall now bear in mind the fact that the number of normal lattice vibrations (oscillators) is enormous (being equal to $3N - 6$, where N is the number of molecules in the crystal). Hence, although the energy of each oscillator is quantized, their superposition forms a quasicontinuous sequence, provided that the energy transferred is not too small. Since the energy of the quantum transition is divided between the emitted photon and this quasicontinuous spectrum of lattice vibrations, a diffuse spectrum consequently appears.

With some necessary changes, we can transfer these ideas to the case in which we are interested, that of a molecular crystal containing inclusions in the form of more or less complex molecules (rather than simple ions, as in the inorganic crystal phosphors). First of all we note that, owing to the weakness of the interactions between the host crystal and the impurity molecule, the latter is situated in a well-localized potential well. This localized character is considerably more perfectly marked in this case than in the case of a foreign ion in an ionic structure. We might even say that we are concerned here with an ideal local center, in which the internal bonds are many times greater than the bonds with the surrounding host crystal. Hence we can consider independently the motion of the molecule as a whole, as characterized by the set of coordinates Q of its center of gravity, and the motion of the electrons and nuclei within the molecule, as characterized by the set of their coordinates q with respect to the center of gravity. If we consider the excitation of the molecule in the adiabatic approximation (i.e., using the semiclassical Franck-Condon principle on the basis of the ordinary "molecular" potential curves), we arrive at a representation of the local vibrations (q coordinates), which are the intramolecular vibrations of the "center". They do not enter into the quasicontinuous spectrum of the crystal, and the latter plays the role of a thermostat with respect to them.

We get a different picture if we consider the motion of the molecule as a whole with respect to the crystal, as characterized by the set of coordinates Q of the center of gravity. To do this, we can use the configurational-coordinate method, and repeat what was described above on the influence of the lattice vibrations on the purely-electronic transition. The result of these interactions must be an inevitable broadening of the electronic-vibrational spectrum, not to be distinguished from the ordinary broadening of an impurity electronic spectrum in a crystalline medium. The source of this broadening, we emphasize, is the creation of phonons in the crystal, accompanying the electronic transition in the impurity molecule. Consequently, in general the usual electronic transitions in an impurity molecule cannot give sharp lines or resonance lines. Such lines can appear only in special transitions, which must be phononless, in complete analogy with the Mössbauer "recoil-less" transitions. Obviously, in both cases we are concerned with a quantum phenomenon, and this fact is precisely the reason why we must use low temperatures.

A basis for the possibility of "phononless" transitions, and correspondingly of "phononless" lines, has been provided in different ways, independently of one another, by E. D. Trifonov and by K. K. Rebane and V. V. Khizhnyakov.

Trifonov[37] has made a purely mathematical analysis of the expression for the probability of a vibrational state arising in a crystal when a purely-electronic transition with an energy $\hbar\omega_0$ takes place in an impurity center. It turned out that the integral giving the probability density of the final vibrational state of the crystal diverges. Here, this divergence involves a δ-type singularity at the point $\omega = \omega_0$. This proves the possibility of a "phononless" transition at this frequency.

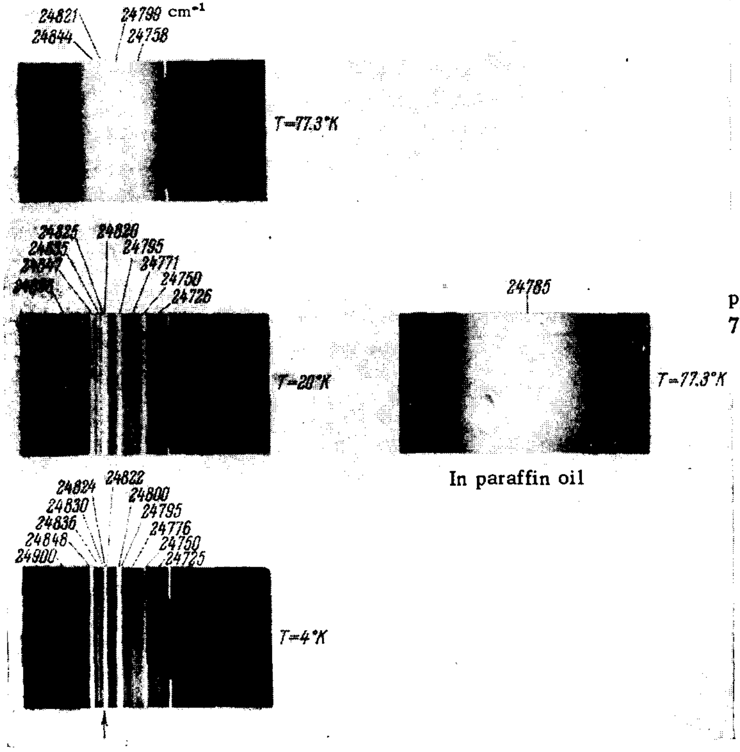
Rebane and Khizhnyakov [38] have made a detailed analysis of the conditions for appearance of an optical quasilinear spectrum. They calculated in the Franck-Condon approximation the probability of a transition from the initial state of the crystal to some final state in which an electronic transition has occurred in the impurity center. Thus, Rebane and Khizhnyakov studied the nature of the spectrum which appears, taking into account the effect of the lattice oscillators. It turned out that among all the possible combinations of oscillator states, there are some for which the internal state of the crystal does not change when a transition occurs between them. Namely, these are the transitions between oscillator states having the same vibrational quantum numbers: 0—0, 1—1, 2—2, etc. Since the internal state of the crystal does not change in these transitions, they result in the appearance of a narrow "phononless" line. In fact, owing to the non-ideality of the crystal, different impurity centers exist under slightly differing conditions, entailing the appearance of a certain statistical width. Further, if there is a small difference between the oscillator frequencies of the normal and excited states, this can lead to the appearance of a "hyperfine" structure in the lines. Thus, the observed phononless lines must be actually quasilines.

In all other transitions, in which the quantum numbers of the oscillators in the initial and final states differ, a diffuse spectrum must arise. Thus, according to the theory of Rebane and Khizhnyakov, under these conditions an "additive spectrum" appears in the optical region, consisting of a diffuse background plus lines, exactly as takes place in the Mössbauer effect. These authors formulate the fundamental result of their theory as follows: "The treatment carried out shows that the reason for the appearance of Shpol'skiĭ's quasilinear spectra is the same as that of the Mössbauer effect: interaction with the lattice vibrations does not broaden the phononless lines, but basically amounts to the appearance of a background."

Further, Rebane and Khizhnyakov studied the influence of the temperature on the ratio of intensities of the lines and background. It turned out that a rapid redistribution of intensity in favor of the background takes place as the temperature rises, and conversely, lowering of the temperature leads to a marked increase in the intensity of the lines at the expense of the background.

While special experiments have not yet been set up to test the theory of Rebane and Khizhnyakov quantitatively, the existing data show good qualitative agreement with this theory. These data are:

a) The appearance of a continuous background (more exactly, a diffuse broad band) together with the lines, and a rapid decrease in the intensity of this background with decreasing temperature. As a rule,



In paraffin oil

FIG. 14. The leading multiplets of the spectrum of 3,4-benzpyrene in n-heptane at various temperatures and in paraffin oil at 77.3°K.

at 77°K the background and the lines are observed at the same time; at 20°K the background is appreciably weaker, while at 4°K it has practically vanished. Fig. 14, which shows the leading multiplet of 3,4-benzpyrene in heptane, is one of the numerous examples of this phenomenon (see insert).

b) The possible existence of "hyperfine" structure in the quasilines. The usual width of the lines even at liquid-helium temperatures is of the order of $1-5$ cm^{-1}, i.e., of the order of $10^{-4}-10^{-5}$ eV. This is three or four times greater than the radiation width. Such a great broadening, as has been shown, can be partly due to imperfection of the crystal or imperfection in the manner of incorporation of the impurity molecule into the fundamental structure. However, possibly this broadening is due, at least to a considerable degree, to an unresolved "hyperfine" structure of the quasilines, in accordance with the theory of Rebane and Khizhnyakov. In a number of cases, one can distinctly see that there are possibilities for further resolution, even at 4°K. Thus, for example, in the same leading multiplet of 3,4-benzpyrene, the 24820 cm^{-1} line, which has a barely resolvable structure at 20°K, is resolved at 4°K into a triplet, one of whose components (24824 cm^{-1}) has an exceedingly narrow width. Further lowering of the temperature (boiling helium under reduced pressure) and increased resolving power of the apparatus will undoubtedly permit us to resolve many quasilines into their components, or actual lines. The possibility is not excluded of creating such favorable conditions that lines having a width differing little from the radiation width will be observed.

To sum up all that I have said in this article, we see that the quasilinear spectra present broad possibilities, both for practical applications and for studies in the fields of spectroscopy, crystal chemistry, and solid-state physics.

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