LINE FLUORESCENCE SPECTRA OF ORGANIC COMPOUNDS AND THEIR APPLICATIONS

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1. A characteristic feature of the electronic spectra of polyatomic organic molecules is their high diffuseness. For example, it has been known for a long time that the fluorescence spectra of organic dyes, as a rule, consist of one broad band of standard form, extending over all or nearly all of the visible spectrum. The so-called "structured" spectra are observed in solutions (in alcohols, hydrocarbon mixtures, etc.) and in the vapor state, principally among aromatic hydrocarbons with condensed benzene rings. These spectra consist ordinarily of three or four bands, each having a width of several hundred cm^{-1}. A certain improvement may be attained, without an essential change in the character of the spectrum, by freezing the solution.

In the ordinarily-used solvents, in particular the special mixtures which give a transparent glass on freezing, the bands become sharper, but their width remains of the order of 200 cm^{-1}.

Until recently, it was possible to eliminate this diffuseness only in a very limited number of cases of the simplest aromatic hydrocarbons (benzene, naphthalene, and some of their derivatives) in the crystalline state at low temperatures. We have in mind the well-known studies of the school of Obreimov and Prikhot'ko (see the review by A. F. Prikhot'ko,[1] in which a complete bibliography is given), and recently also the studies of P. Pesteil[2] in France and McClure and his associates in the United States (see the review by McClure[3]).

Several years ago, the author, in conjunction with A. A. Il'ina and L. A. Klimova,[4] showed that one can use as solvents the neutral, easily crystallizing normal paraffins (pentane, hexane, heptane, etc.), selecting certain of these normal paraffins as solvents for a given substance. Then, with the proper choice of solvent, the luminescence spectra of the finely-crystalline solid solutions obtained on freezing (and, as was subsequently found, also the absorption spectra) acquire remarkable properties. Namely, under these conditions the relatively broad bands of the "structured" spectrum split into a series of lines which are no wider than 2 or 3 cm^{-1}, in favorable cases or 10 cm^{-1} in unfavorable cases. Regularly associated groups of lines (multiplets) appear, an interesting dependence on the solvent is found, etc.

Seven years after the publication of our first report, the number of examples of this type of quasilinear spectra has grown considerably, and at present there are more than thirty known substances for which conditions for the appearance of quasilinear spectra can be found. Together with the polynuclear condensed hy-

drocarbons, these substances include aromatic aldehydes and ketones, anthraquinone and some of its derivatives, and dyes (thioindigo[48]). Very recently, conditions have been found (by F. Litvin and R. I. Personov) for obtaining a quasilinear spectrum of such a complex compound as phthalocyanine and its magnesium derivative; these are substances containing over sixty atoms per molecule, with molecular weights over 500, and analogous in structure to those substances of great biological importance, the porphyrins. Undoubtedly, if any systematic search were undertaken, large classes of organic substances giving this type of spectrum would be found.

We note that the facts which we have found have been completely confirmed in a group of laboratories in the Soviet Union and abroad.[23-28] Finally, the favorable characteristics of the quasilinear spectra are being utilized at present in various directions, namely: the appearance, or conversely the disappearance, of fine structure in the spectrum is used as a very sensitive indicator of intramolecular and intermolecular interactions (D. N. Shigorin and his associates[47-48]); the small widths of the lines and the reproducibility and complete additivity of the quasilinear spectra permit one to use them for qualitative chemical analyses distinguished by complete reliability and the possibility of identification of individual compounds (carcinogenic substances and heavy aromatics in petroleums and bitumens) with a high degree of selectivity as well as with high sensitivity.

2. All of the studies reported up to now were carried out at 77.3° K. It was of great interest to go even lower in temperature and study the same spectra at liquid-hydrogen and liquid-helium temperatures. Through the kindness of Academician P. L. Kapitza, we had the opportunity to perform these studies in the Institute of Physics Problems of the Academy of Sciences of the U.S.S.R. This article gives some results obtained both at 77° K and at lower temperatures.

An example of the experimental apparatus applied is the very simple apparatus used in studies at 20° K (Fig. 1). The solution being studied is placed in a paddle-shaped cuvette in a fused-silica Dewar flask, sealed on with a fused-silica-to-glass graded seal. The hydrogen was siphoned from a large three-liter Dewar into the experimental Dewar, and was added as needed by closing the stopcock K. In the lower silica part of the Dewar, an unsilvered slit was left, through which the frozen solution could be illuminated and the spectrum photographed. The cuvette containing the solution was
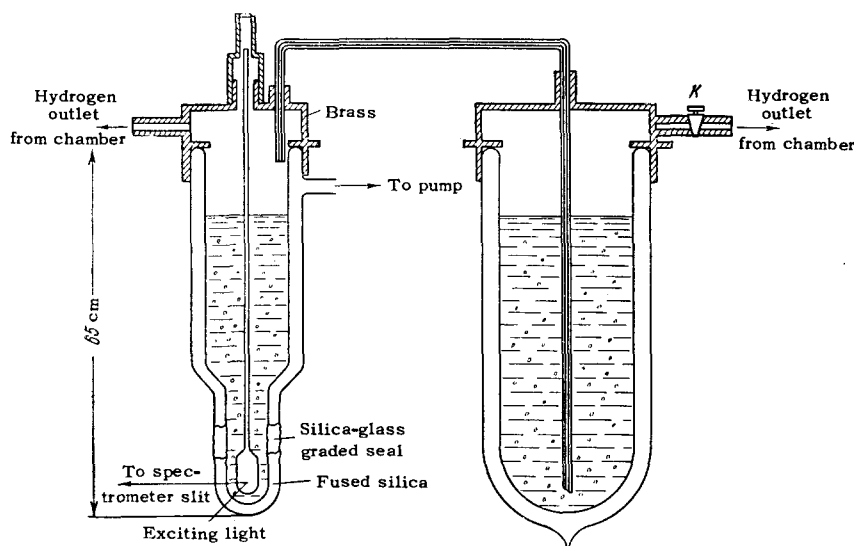
FIG. 1. Describing the experimental apparatus (Shpol'skiĭ and Klimova[19]).

carefully evacuated and sealed. It was found here that the emission intensity increased appreciably after evacuation, indicating quenching of the luminescence by the oxygen.

The region of the spectrum used for excitation (the mercury lines 3135, 3650, 4358 Å) was isolated by uviol glass filters.

Various spectrographs were used in the different studies as systems for dispersion: a small Fuss spectrograph with a Rutherford prism, distinguished by a large aperture with a moderate linear dispersion (25 Å/mm at 4000 Å); a glass three-prism spectrograph ISP-51, preferably with a long-focus camera, F = 840 mm (linear dispersion 10 Å/mm at 4000 Å). Finally, the photographs of spectra at liquid-hydrogen and liquid-helium temperatures were taken in a model spectrograph which we had built, consisting of a State Optical Institute flat diffraction grating (140 × 150 mm, 600 lines per mm), an autocollimating camera, and an astronomical objective (aperture ratio 1:15, F = 1600 mm). The linear dispersion of the apparatus in the second order of the grating was about 4.8 Å/mm.
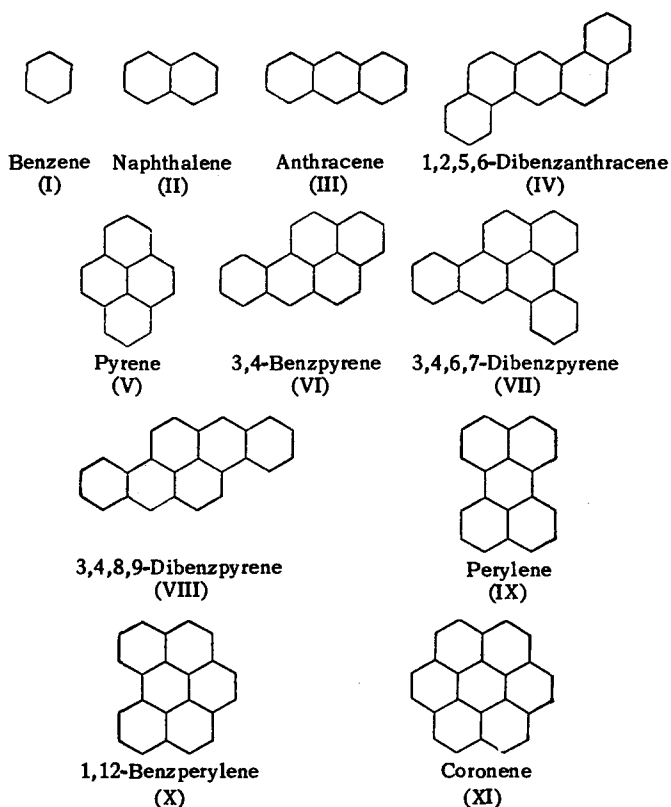
We shall not undertake in this article to give a complete review of the results obtained, but shall discuss only the most characteristic peculiarities of the spectra and the problem of their origin, using some chosen examples. In order to become more fully acquainted with the results obtained with the substances studied, the reader should refer to the original literature.[4-28]

We note that the principal objects of our studies up to now have been the polynuclear aromatic hydrocarbons with condensed benzene rings. These substances are of great interest from various points of view. As a rule, they fluoresce, and in particular, they are suitable materials for study of the resonance transfer of energy between excited and unexcited molecules (the well-known case of the fluorescence of naphthacene as an impurity in anthracene and some other analogous cases). Many of them show a high fluorescene yield, and are widely applied as scintillators. They are dis-

tinguished by very small forces of association, having the character of van der Waals forces. It is interesting to note that, as the number of benzene rings increases, the flat molecules approach closer and closer in structure to graphite, and such complex molecules as coronene and ovalene already are, so to speak, microscopic pieces of a single graphite layer. It is this fact, in particular, which makes the aromatic hydrocarbons interesting for studies of their electrical properties, since graphite in its electrical properties is on the borderline between semiconductors and metals.

Finally, perhaps, the fact is especially important from the practical viewpoint that the aromatic hydrocarbons include the very powerful agents producing malignant tumors, the so-called carcinogenic substances. Especial activity of this type is shown by 3, 4-benzpyrene and 3, 4, 8, 9-dibenzpyrene. In particular, it has recently been found that 3, 4-benzpyrene is rather widely distributed in practice (tobacco tar, smoked products, smoke-polluted air, etc.).[29,51] In view of this, it is important to possess as precise and exhaustive knowledge as possible about the spectra of these substances. Above all, this knowledge is needed for the detection of these substances by spectroscopic methods, and perhaps in the future, for solving the riddle of the reasons for their carcinogenic acitivity. We shall often make use of the spectrum of 3, 4-benzpyrene below as a typical example of a quasilinear spectrum, combining the features of high complexity and clearly-pronounced regularities.

3. In order to establish the nature and origin of the studied spectra in frozen crystalline solutions, it is interesting and important to compare these spectra with those of the same substances in the gaseous state (in vapors) and in the form of pure crystals. Data on the spectra of organic compounds in the vapor state are very scanty (see the table in the article by Sponer and Teller[30]). These data are evidence that the spectra of polyatomic organic molecules in the gaseous state consist, in general, of a few highly diffuse bands.

Benzene Naphthalene   Anthracene   1,2,5,6-Dibenzanthracene
(I)   (II)   (III)   (IV)

Pyrene   3,4-Benzpyrene   3,4,6,7-Dibenzpyrene
(V)   (VI)   (VII)

3,4,8,9-Dibenzpyrene   Perylene
(VIII)   (IX)

1,12-Benzperylene   Coronene
(X)   (XI)

This is quite understandable, if we consider the multiplicity of characteristic vibration frequencies of these molecules, and especially, the quasicontinuum of rotational states, which brings about a further diffuseness of the electronic-vibrational bands of these molecules.

Data on the luminescence spectra of pure crystals are more numerous and definite. In this regard, the paper of Birks and Cameron[31] is of fundamental interest. These authors made very careful measurements, taking into account all necessary corrections, of the fluorescence spectra of 41 organic substances in the crystalline state at room temperature. A paper by Ferguson[32] was devoted to the absorption and fluorescence spectra of crystalline pyrene at room temperature and at 77° K. The fluorescence spectra of aromatic hydrocarbons in solid solutions in other aromatic hydrocarbons have been studied by Northrop and Simpson.[33] The results of these studies are in complete agreement with numerous unpublished observations made in our laboratory.

For our purposes, the most important conclusions from all of the studies consist in the following:

1) the spectra of the simplest aromatic hydrocarbons with linearly-condensed benzene rings (naphthalene, anthracene, naphthacene) show a "structured" character. That is, they consist at room temperature of several broad bands ($\Delta\nu = 500 - 1000$ cm^{-1}). Undoubtedly, these bands are of electronic-vibrational origin, that is, they correspond to transitions from some upper electronic state to various vibrational levels of a lower state. More precisely, in view of the

great width of the bands, they are in all probability actually the envelopes of a large number of individual vibrational bands (lines), broadened by interaction with the lattice vibrations.

2) the spectra of polynuclear aromatic hydrocarbons with benzene rings arranged in a plane (pyrene, 3, 4-benzpyrene, coronene, etc.) show no structure. They spread over almost the entire visible region, and their principal maxima occur at much longer wavelengths than in the fluorescence spectra of the same substances in solution or in the vapor state. They show also insignificant maxima or inflections, always located on the short-wave branch of the spectra. This continuous character of the spectra is illustrated by the examples given in Fig. 2, from the study of Birks and Cameron on the spectra of pyrene and 3, 4-benzpyrene. On cooling to liquid-nitrogen temperature, the fluorescence spectrum of 3, 4-benzpyrene does not change at all, while that of pyrene, while it remains continuous, is shifted further to long wavelengths. Owing to this shift, the color of the luminescence of the crystals of the latter substance becomes green at 77° K, although it is blue at room temperature.

Even the external signs, the absence of vibrational structure and the strong shift to longer wavelengths, make the hypothesis highly probable that these spectra possess a distinctive nature, different from the electronic vibrational origin of the structured spectra. This hypothesis is confirmed by a more detailed analysis of the crystalline spectra, which we shall take up now, since it will help us understand more clearly the relation between the crystalline spectra and the discrete quasilinear spectra of interest to us.

In an understanding of the nature of the continuous crystalline spectra, a discovery of Förster and Kasper plays an essential role. They found an interesting phenomenon in the example of the fluorescence spectra of concentrated solutions of pyrene, and designated it as concentration transformation (Konzentrationsumschlag) of fluorescence. The phenomenon of concentration quenching of fluorescence in solutions at high concentrations is well known. However, Förster and Kasper[35] devoted attention to the fact that for pyrene, in going from dilute to concentrated solutions, quenching of the fluorescence is not observed, but rather, a pronounced transformation of the spectrum. (This phenomenon had been observed even earlier for 3, 4-benzpyrene, but was interpreted incorrectly.[35]) In particular, the structured spectrum in the violet, observed in dilute solutions (structured in the sense of the term used above, see p. 372) is gradually quenched on increasing the concentration. However, at the same time, a new spectrum appears, located in the blue region (maximum at $\lambda = 4780$ A), completely without structure. This phenomenon is well illustrated by the spectra given in Fig. 3. Here we see that, while at a concentration of 2×10^{-4} M (solvent = benzene) only the structured spectrum is observed, on the other

FIG. 2. Fluorescence spectra of pyrene and 3,4-benzpyrene (Birks and Cameron[31]).
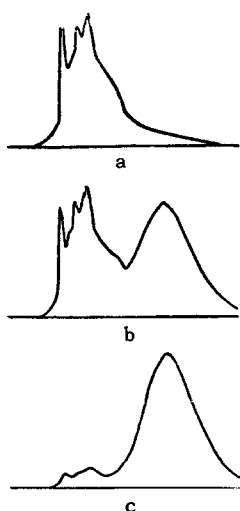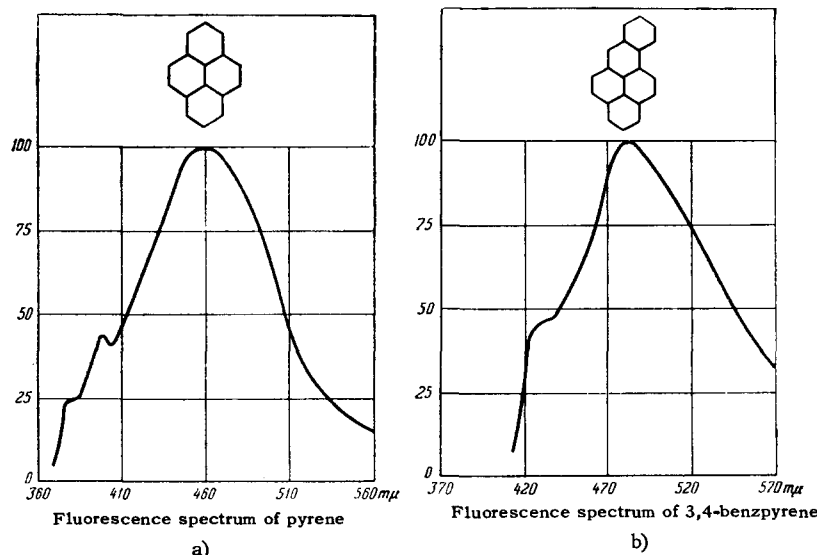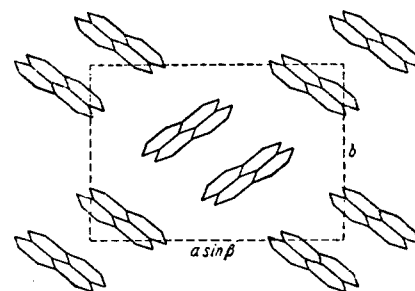

Fluorescence spectrum of pyrene

a)

Fluorescence spectrum of 3,4-benzpyrene

b)

FIG. 3. The concentration transformation of the fluorescence spectrum of pyrene solutions at high concentrations (Förster and Kasper[55]): a)Conc. 2×10^{-4} M; b) 2×10^{-3} M; c) 2×10^{-2} M; at left — violet component (maxima at 3725, 3840, 3920 A); at right — blue component (maximum at 4780 A)

the "blue" spectrum of Förster and Kasper. We must add that in the crystal structure of pyrene, the molecules are arranged in parallel pairs (Fig. 4). Favorable conditions are thus created for pair combination of molecules, and the analogy between the concentrated solution and crystalline pyrene becomes plausible in the highest degree.

FIG. 4. Crystal structure of pyrene (Robertson[5]).

hand, at a concentration of 2×10^{-2} M, the structured spectrum has been almost completely replaced by a continuous broad band shifted into the blue region. Both spectra are observed at intermediate concentrations. Förster and Kasper emphasize that it is remarkable that this transformation of the fluorescence spectrum is not accompanied by a corresponding transformation in the absorption spectrum. Hence, it can not be interpreted as an association phenomenon of the usual type. In the opinion of the authors, this means that we must assume pair association of unexcited molecules with the excited molecules originating in the process of light absorption i. e., within the lifetime of the excited state. Thus, we must consider these pairs to be the carriers of the blue fluorescence.

If we turn now to Fig. 2a, we see that the fluorescence spectrum of crystalline pyrene shown in this figure reproduces essentially all the features of the transformation spectrum in Fig. 3c: the weak maxima on the short-wavelength branch correspond to the last traces of structured spectrum, while the whole broad continuum with a maximum at 4600 A corresponds to

In order to explain the origin of the continuous spectrum of pyrene, an interesting hypothesis has been advanced very recently, which we shall now consider briefly.

According to modern conceptions, the excitation caused by light absorption in the crystal is transferred from molecule to molecule in the form of a neutral excitation wave (i. e., not associated with the motion of charges). Such an excitation wave may be considered to be the motion of a neutral quasiparticle, the exciton. This conception, which was first formulated by Frenkel' and then developed in various directions by Wannier, Mott, and others,[36] has been exceedingly fruitful. In particular, it has permitted A. S. Davydov[37] to develop a theory of light absorption in molecular crystals, which explains the relation between the absorption spectra of the isolated molecule and of the crystal, and which predicts a resonance effect which is important in the interpretation of crystalline spectra, the "Davydov splitting."

However, Lyons[38] recently considered the fact that,

in order to explain the photoelectric properties of molecular crystals, we must take into account the possibility of the appearance of ionized excited states in a molecular crystal, along with the neutral excited states. An estimate of the energy of formation of ionized pairs M^+M^- of neighboring molecules showed that this energy in some cases may turn out not only to be considerably lower than the ionization energy of a free molecule, but even lower than the energy of liberation of an electron within the crystal. That is, it may be lower than the energy spent in the transfer of an electron into the conduction band. This is associated with the fact that the molecules of aromatic compounds have a positive electron affinity. By considering a simple cycle, analogous to those used in the calculation of the ionization energy in alkali halide crystals (see, e. g., Mott and Gurney[39]), Lyons showed the following: the formation of a pair of neighboring ions within a crystal of anthracene by freeing an electron from one molecule and attaching it to a neighboring molecule requires the expenditure of only 2.2 ev, while the complete liberation of an electron within the crystal requires 5.2 ev. Thus it turns out that the lowest level for the formation of pairs of bound ions is even lower than the first singlet neutral exciton level. Hence, it is energetically possible to convert a neutral exciton state into an ionized state, i. e., into a pair M^+M^-, which by the reverse transfer of charge is converted again into a neutral pair.

Obviously, these ionized states and the transitions between them are analogous to the charge-transfer spectra discussed by Mulliken,[40] with the difference that in the latter case, a partial ionization appears even in the ground state.

Ferguson[32] has advanced a hypothesis, according to which the continuous fluorescence spectrum of pyrene is also considered to be a charge-transfer spectrum. He assumed that in the light-absorption process the geometry of the molecule is changed in such a way that neighboring pairs of molecules may approach, thus facilitating the formation of an ionized pair M^+M^-. This hypothesis is still of a quite preliminary nature, and has not been supported by any calculations. However, if we take into account the distinctive character of the crystalline continuous spectra and their diffuse nature, which is not resolved even at low temperatures, and their indubitable origin through the sharp transformation of the fluorescence spectrum from the structured (i. e., electronic-vibrational) spectrum, we must consider the hypothesis of charge transfer as being worthy of attention in any case.

With regard to the crystalline spectrum of 3, 4-benzpyrene, it has the same character as the continuous spectrum of pyrene. The transformation of the spectrum of this substance at high concentrations, similar to that of pyrene, has also been noted in the literature.[35] In view of this, all that has been said above about the crystalline spectrum of pyrene is valid also for the

spectrum of 3, 4-benzpyrene. However, from the standpoint of the problem of the nature of the sharply-discrete quasilinear spectra which we have discovered and studied, the fact of principal importance is that the continuous crystalline spectra are not merely smeared-out electronic-vibrational spectra, but have a different origin, and are diffuse in nature. Further, the close approach and the arrangement of molecules in parallel pairs in the structures of pure crystals (as in pyrene) facilitates the appearance of diffuse spectra, and hinders the manifestation of discrete, i. e., electronic-vibrational, spectra.

In our studies, as has been said already, we have not studied the continuous crystalline spectra of aromatic compounds, but have used the properties of these spectra, especially the strong shift to longer wavelengths, in order to establish firmly the presence or absence of precipitation of crystallites of the substance being studied from the solution.

4. Aromatic hydrocarbons, including those which show continuous fluorescence spectra in the crystalline state (e. g., pyrene or 3, 4-benzpyrene), give structured spectra in solution at low concentrations, i. e., spectra consisting of several broad bands. Lowering the temperature to 77° K ordinarily increases the sharpness of the bands. However, in those cases in which the solvents are alcohols or special mixtures giving glassy masses on freezing, the spectra obtained on cooling in liquid nitrogen are not fundamentally different from those obtained in the same solvents at room temperature, although they are somewhat sharpened. In the studies conducted with A. A. Il'ina,[41,42] we studied the luminescence spectra of both 3, 4-benzpyrene and of a number of other derivatives of pyrene in solutions at 77° K. At the time when these spectra were obtained, they established a record for sharpness in spectra of solutions. However, the width of the bands was $150 - 200$ cm^{-1}, many times greater, as we shall see, than the width of the "lines" of the quasilinear spectra. Figure 5 gives as examples the spectra of 3, 4-benzpyrene and 3, 4, 6, 7-dibenzpyrene in paraffin oil at 77° K. The wavelengths for 3, 4-benzpyrene are given in Table I, and an approximate vibrational analysis is given of the frequency differences with respect to the band at 4035 A, which is ascribed to the $0'-0''$ transition. A comparison of columns 4 and 5 shows that the strongest completely-symmetric frequencies, which may be determined precisely from the quasilinear spectrum, are quite clearly reproduced in this spectrum (see below, p. 381-10).

Considering the coarseness of the determination of the maxima of broad bands, we must consider this agreement as being unexpectedly good.

On comparing the spectrum given in Fig. 5 of 3, 4, 6, 7-dibenzpyrene with that of 3, 4-benzpyrene, we see that both spectra have analogous structures and are located in the very same part of the spectrum, although they are somewhat shifted with respect to one another.
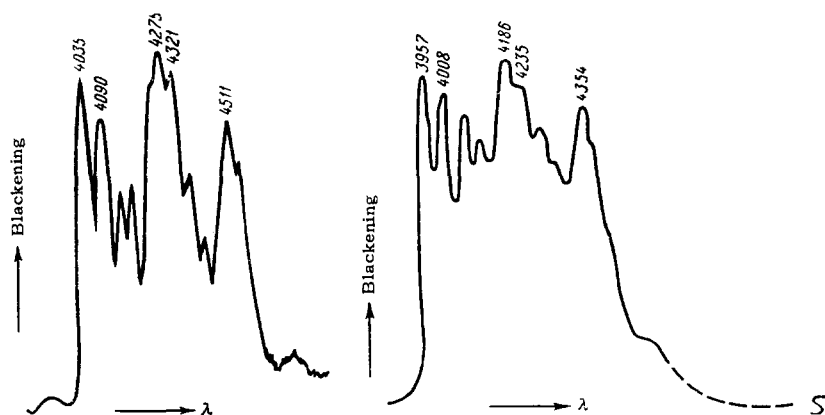
FIG. 5. Fluorescence spectra of 3,4-benzpyrene (left) and 3,4,6,7-dibenzpyrene (right) in paraffin oil, T = 77°K. (Il'ina and Shpol'skiĭ[42]).

TABLE I. The fluorescence spectrum of 3, 4-benzpyrene in paraffin oil at 77° K.

Serial No.	A	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	Close frequencies in the quasi-linear spectrum
	3970	25190		
1	4035	24785	0 (transition 0—0)	
2	4090	24450	335	335 (very strong)
3	4143	24140	645	637 (moderate)
4	4177	23940	845	853 (moderate)
5	4247	23545	1240	1237 (very strong)
6	4275	23390	1395	1389 (very strong)
7	4321	23145	1640	1636 (moderate)
8	4383	22815	1970 (1640+ +335=1975)	1636+335=1971
9	4437	22540	2245	—
10	4511	22170	2615	—
11	4594	22010	2775 (1390 × 2 =2780)	1389 × 2 = 2778
12	4590	21785	3000	

This fact is of great negative significance in chemical analysis by means of fluorescence spectra, since with the great width of the bands, these spectra may mask each other.

5. We proceed now to discuss the quasilinear spectra. Figure 6 presents very clearly the character of these spectra and their relation to the spectra obtained from the pure substance in the crystalline state and from solutions in such commonly-used solvents as alcohols (including spectra at low temperatures). In this figure, a collection of photographs is given of fluorescence spectra of the aromatic hydrocarbon perylene(p. 373, IX)[20,21] under various conditions. We see here that in the crystalline state (Fig. 6a) the fluorescence spectrum both at room temperature and at 77° K is continuous with a diffuse maximum at 6150 A, i. e., in the orange-red region.

It is essential that, on lowering the temperature to 77° K, this continuous spectrum is not resolved into bands or lines. That is, it possesses the same properties as the analogous crystalline spectra of pyrene or 3, 4-benzpyrene. In solution at low concentrations, even at room temperature, the continuous spectrum is replaced by a structured spectrum strongly shifted toward shorter wavelengths. The relation between these structured and continuous spectra of perylene is completely analogous to the relation between the "vio-
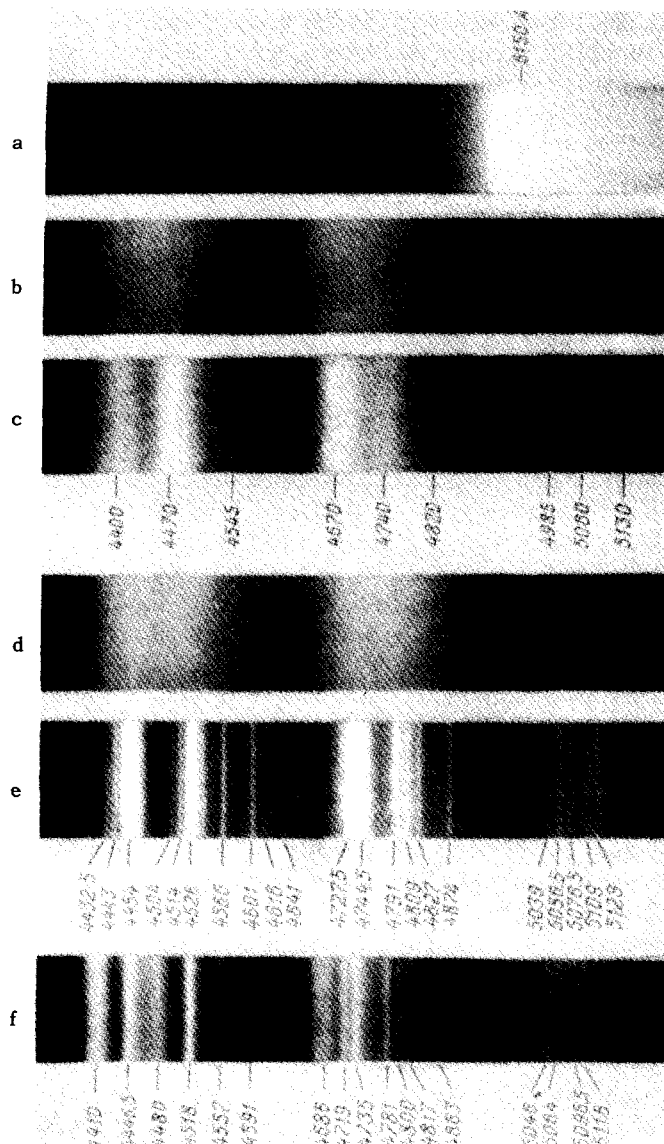

FIG. 6. Fluorescence spectra of perylene under various conditions (Shpol'skiĭ and Personov[20]): a) Crystalline at T = 291° and 77° K; b) in ethyl alcohol at T = 293° K; c) the same at 77° K; d) in n-hexane at T = 293° K; e) the same at T = 77° K; f) in n-heptane at T = 77° K.

let" and "blue" spectra of pyrene. Undoubtedly, the structured spectrum is the diffuse electronic-vibrational spectrum of the perylene molecule, while the continuous crystalline spectrum is of the same nature as the analogous crystalline spectra of pyrene and 3, 4-benzpyrene.

Further, we see from the figure that the bands in the spectrum in alcoholic solution are greatly sharpened on lowering the temperature to 77° K, forming a regular sequence. However, the width of these bands is still of the order of 200 cm^{-1}. On the other hand, in frozen hexane and heptane solutions, each of the bands observed in alcohol solution is resolved into several "lines," whose wavelengths may be determined reliably with an accuracy of tenths of Angstoms. We note here that the spectrum in the frozen hexane solution shows the greatest sharpness, while that in heptane is appreciably more diffuse.

Inasmuch as this quasilinear spectrum corresponds to transitions to various vibrational levels of the ground state, it is natural to attempt a vibrational analysis, i. e., to determine the vibrational frequencies themselves from the spectrum. Such an analysis becomes easy to perform, since, as is shown by ample experimental material, transitions involving emission in a condensed material always take place from the lowest excited electronic level, independently of the level to which the molecule was excited upon absorption of light (see M. Kasha[53]). Because of this, the determination of the vibrational frequencies of the molecule in the ground state is reduced to a search for the differences between the frequency of the line corresponding to the $0'-0''$ transition (i. e., the transition between the upper and lower vibrationless electronic levels) and the frequencies of the following lines. Obviously, the $0'-0''$ transition generally corresponds to the line of shortest wavelength in the fluorescence spectrum. However, the most irreproachable method for identifying the $0'-0''$ transition consists in determining the frequencies which coincide in the absorption and luminescence spectra.

In the case of perylene, such a control is essential, since the short-wavelength line in the fluorescence spectrum is considerably weakened by reabsorption. The frequency of the $0'-0''$ transition determined in this way for perylene is equal to 22445 cm^{-1} (λ = 4454.0 A).

In electronic-vibrational spectra, together with the frequencies of the normal vibrations, we commonly observe their overtones and combination frequencies. This permits us to reduce the observed frequencies (which are sometimes numbered in the hundreds, as we shall see) to a small number of characteristic frequencies of the molecule.

As an example, a vibrational analysis is given in Table II of the first fifteen frequencies in the fluorescence spectrum of perylene. We see that the observed frequencies may be represented in terms of five fre-

TABLE II. The fluorescence spectrum of a solution of perylene in n-hexane at 77° K.

No. of line	Wave-length (A)	Frequency of line (cm^{-1})	Intensity	$\Delta\nu$(cm^{-1})	Possible interpretation
1	4454	22445	Very intense	0	0—0
2	4526	22088	Very intense	357	0—358
3	4541	22015	Moderate		
4	4566	21895	Intense	550	0—550
5	4601	21728	Intense	717	0—358 × 2
6	4616	21658	Moderate		
7	4641	21541	Moderate	904	0—358—550
8	4656	21472	Weak		
9	4682	21352	Weak	1093	0—550 × 2
10	4727.5	21147	Very intense	1298	0—1298
11	4744.5	21071	Very intense	1374	0—1375
12	4791	20867	Very intense	1578	0—1578
13	4009	20789	Intense	1656	0—1298—358
14	4827	20711	Intense	1734	0—1375—358
15	4854	20596	Very weak	1849	0—1298—550

quencies, within an accuracy of some tenths of one percent. A vibrational analysis of the complete fluorescence spectrum of perylene at 77° K permits us to reduce the fifty observed lines to the same five frequencies: 358, 556, 1298, 1375, 1578, and their combinations.

In order to elucidate the nature of the quasilinear spectra, and to compare the results obtained from them with the electronic-vibrational spectra of the same molecules obtained in other ways, it has been convenient to study the quasilinear spectra of the simplest aromatic hydrocarbons. Such a study has been carried out by T. N. Bolotnikova,[13-15] who obtained and analyzed the quasilinear spectra of a series of substances including naphthalene and anthracene, which have been studied in great detail under the most varied conditions: in the vapor state, in the pure crystalline state, in crystalline solid solutions, as well as by infrared and Raman spectra. The study of Bolotnikova has not only provided an answer to the question posed on the nature of the quasilinear spectra, but has given us a number of interesting new results. In numerous previous studies, the spectrum of naphthalene has been subjected to especially detailed study, and its interpretation has been carried rather far. Bolotnikova showed that naphthalene in pentane solution gives an excellent quasilinear spectrum even at 77° K, with wavelengths which may be measured precisely. The same result was found in a study performed independently of Bolotnikova, and published almost simultaneously by Mme. L. Pesteil and Mlle. A. Ciais.[25]

The analysis of the spectrum obtained, as carried out by Bolotnikova,[14] permitted the establishment of two developed vibrational sequences with a period of 1386 cm^{-1}. The first sequence is weak, beginning with the $0'-0''$ band (31731 cm^{-1}), and the second is strong; the appearance of the latter is associated with the excitation of a vibrational mode with a frequency of 495 cm^{-1}. These two sequences correspond exactly with two sequences polarized in mutually perpendicular planes, which were established by McClure[3] in the

spectrum of a solid solution of naphthalene in durene at 20° K. This fact is essential, since durene (symmetrical tetramethylbenzene) is completely isomorphous with naphthalene, and hence, the naphthalene molecule in this case exists in a state as close as possible to the state of an "oriented gas" at high rarefaction.

Finally, very recently D. P. Craig (London) has been able to resolve completely the rotational structure of the spectrum of naphthalene vapor by use of a spectrograph with a powerful diffraction grating (resolving power of the order of 300,000). Thus he obtained precise data on the energy levels (and in particular, on the $0'-0''$ transition) of the free molecule. The calculation for the asymmetric-top molecule naphthalene (all three moments of inertia being different), which was necessary in the interpretation, was performed on an electronic computer. This study, carried out under extraordinary conditions, has completely confirmed the results of Bolotnikova. Confirmation was found, in particular, for the interpretation given by Bolotnikova for the frequency 495 cm^{-1}, differing from that of McClure. She interpreted this frequency, which changes the polarization state of the second sequence in the fluorescence spectrum of naphthalene, as the frequency of a not-completely-symmetric vibration of the type β_{1g}.* Thus we may consider it completely proved that naphthalene in frozen solution in pentane shows the undistorted system of vibrational spectra corresponding to free molecules.

An analogous situation occurs also in the case of anthracene. As was shown by Bolotnikova, this substance gives a sharp quasilinear spectrum at 77° K in hexane and in heptane. Of these, the heptane solution gave the sharpest spectrum. With a shift of this spectrum by 385 cm^{-1} toward shorter wavelengths, it coincides well with the spectrum of mixed crystals of anthracene in naphthalene, i. e., with a spectrum obtained under conditions in which the anthracene molecule exists in the oriented-gas state. A vibrational analysis showed that the measured lines of anthracene in hexane may be easily interpreted as combinations of the following frequencies: 390, 1165, 1265, 1407, 1567, 1645. These frequencies are the independently-determined frequencies of the completely-symmetric vibrations of the anthracene molecule.

According to a report by L. Pesteil and A. Ciais, they were able also to interpret the spectrum of a frozen hexane solution of acenaphthene, a molecule having the structure

CH$_2$————CH$_2$,
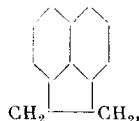
*The results cited from the study of D. P. Craig were reported by Professor Craig in a lecture given at Moscow University on Feb. 18 of this year. In this lecture, the results of his studies were compared with those of Bolotnikova.

and thus to obtain especially many valuable data on this molecule.[25] However, these studies have not yet been completely published.

6. Thus, in the examples discussed above of simple aromatic hydrocarbons, the emission spectrum of a frozen solution in a paraffin may be considered to be the electronic-vibrational spectrum of the emitting molecules. This spectrum is sufficiently sharp to obtain precise data on the vibrational energy levels of the ground state; in addition, it is free from effects complicating the interpretation of the spectra of pure crystals (Davydov splitting, lattice frequencies).

In the case of more complex molecules, in particular those of the polynuclear aromatic hydrocarbons, such as pyrene, 3, 4-benzpyrene, coronene, and others, matters are more complex. The characteristic peculiarity of the quasilinear spectra of such molecules is the presence of closely-spaced groups of lines (doublets, or more generally, multiplets), which are re-
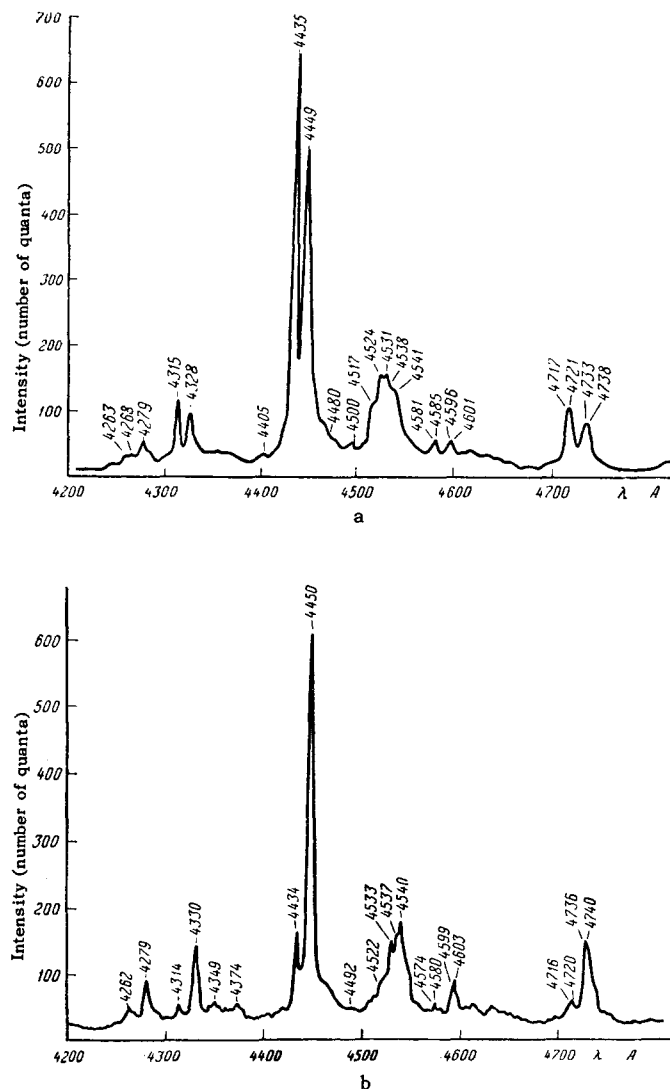

FIG. 7. Fluorescence spectrum of coronene at T = 77° K: a) in n-heptane (Shpol'skiĭ and Klimova[8]); b) in n-hexane.

3.4-benzpyrene in: a) paraffin oil and b) n-heptane.

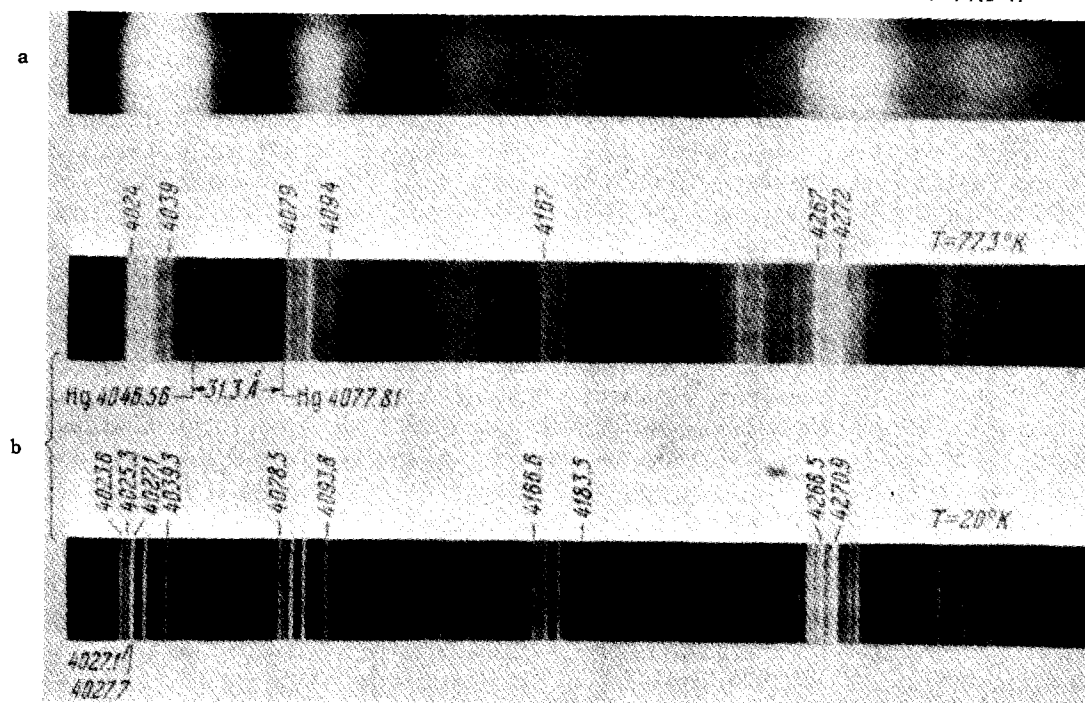FIG. 8. Fluorescence spectra of frozen solutions of 3,4-benzpyrene in different solvents at T = 77°K and 20°K (Shpol'skiĭ and Klimova[19]).

peated throughout the spectrum without change in the distances between components.

As an example, we shall discuss first the fluorescence spectrum of coronene in hexane and heptane (Fig. 7). From this figure,[8] which is a record of the spectra on the recording photoelectric spectrometer of Neporent and Klochkov,[43] we see that the spectrum consists in both cases of clearly-marked doublets. In the hexane solution, the spectrum begins with the very weak doublet 4246 — 4262 A, with the frequency difference 86 cm^{-1}.* If each line of this doublet is assigned to the corresponding $0'-0''$ transition, then, as is shown in the figure, the entire spectrum may be represented as two sequences of frequencies, 0, 365, 992, 1435, . . . , shifted by 86 cm^{-1} with respect to each other. In the heptane solution, the $0'-0''$ transition also corresponds to a weak doublet, but the distance between the components of the first and following doublets is 72 cm^{-1}. Hence, in this case the spectrum may be considered to be the superposition of two spectra shifted by 72 cm^{-1} with respect to each other (instead of 86 cm^{-1}, as in hexane). However, in both cases, in hexane and in heptane, the frequencies in each of the sequences are one and the same. The same frequencies are also obtained in octane solution, where the distance between components of the doublets is

*The weakness of the first doublet can obviously be explained by the fact that the $0'-0''$ transition in the coronene molecule, which belongs to the symmetry class D_{6h}, is forbidden by symmetry. In the condensed state, this transition is weakly permitted, due to small distortions of the molecule by the field of the solvent.

38 cm^{-1}. It follows from all this that the frequencies common to all cases, independent of the solvent, belong to the coronene molecule, and comprise a sequence of its vibrational frequencies in the ground state. Attention is called to the change in the intensity distribution between the components of the doublets on going from the solvent hexane to heptane. We shall return to this problem below.

A considerably more complex picture exists in the case of 3, 4-benzpyrene. In Fig. 8, fluorescence spectra of this substance are given, taken under various conditions in a spectrograph with a diffraction grating of high resolution (4.8 A/mm). The upper spectrum, taken with a solution in paraffin oil at 77° K, gives a representation of the form exhibited by the spectra which we designate as "structured," when taken at the high resolution necessary to reveal the details of the quasilinear spectra. The spectra in other commonly-used solvents (alcohols, chloroform etc.) have exactly the same form at 77° K. Although the presence of a sequence of discrete bands is visible even here, the bands themselves are spread out into broad regions of continuous spectrum.

The following two spectra (Fig. 8) are the fluorescence spectra of the same substance in n-pentane at 77° and 20° K. As we can see, the broad bands of the "structured" spectrum are resolved here into groups of sharp lines, which are completely distinct even at 77° K. On comparing the spectrum at 20° K with that at 77° K, we see that the decrease in temperature results, above all, in a further narrowing of the lines. For ex-

ample, the pair of lines 4027.06 — 4027.73, with a separation of only 0.67 A, is quite clearly resolved on the original photograph. Further, new lines appear at 20° K; in particular, the weak continuous background observed at 77° K is resolved into lines at 20° K.

Even a simple visual inspection of the spectrum discovers clear regularities in it: the lines in the spectrum form groups, or "multiplets," the first multiplet then being repeated throughout the spectrum with the distance between components maintained. This is illustrated in Table III by the example of three multiplets, while in Fig. 9, several of these repeating multiplets are indicated by brackets, and the distances between corresponding lines are shown. Analogously to what we did in the case of coronene, we shall ascribe the entire first multiplet to the $0' - 0''$ transitions in the various sequences shifted relative to one another. The basis for this is the precise agreement of the wavelengths of the first multiplet in the fluorescense spectrum with those of the leading multiplet in the absorption spectrum.[9,10] In such a case, we can identify the distances indicated in the figure between corresponding lines in the first and following multiplets with the vibrational frequencies in the ground state, these frequencies being repeated in all the sequences. The high precision with which these frequencies are reproduced may be seen from Table III, in which the wavelengths

and corresponding frequencies are given as examples, together with the interpretation for the multiplets indicated in Fig. 9. The complete table, including about 200 measured lines from one heptane solution alone, was given in the original reference.[19] These 200 frequencies may be reduced without any forcing to the following seventeen frequencies (Table IV), which appear either as frequencies of normal vibrations or as their overtones or in combinations.

The strongest frequencies (335, 1345, 1389) are found in combinations with other frequencies up to 17 times. Without doubt, this creates confidence in their reality. This confidence is strengthened further by the fact that the frequencies determined from spectra in different solvents coincide with a high degree of precision.[9,10,19]

Finally, there is another control. All of the hydrocarbons studied show a persistent luminescence, as well as the luminescence of short lifetime ($\tau \sim 10^{-8}$ sec). This persistent luminescence is due to transitions from the lowest metastable triplet level to the vibrational levels of the ground state. An analysis of the spectrum of this persistent luminescence leads to a few strongest frequencies which appear also in the fluorescence spectrum.[9,10,18]

Any broad generalizations about the results obtained for the vibrational frequencies of complex molecules

TABLE III. Vibrational levels of 3, 4 benzpyrene. Solvent: heptane. T = 20° K.

| Serial No.	λ (Å)	ν (cm^{-1})	$\Delta\nu$	Interpretation
1	4023.60	24847		$(0-0)_1 = \nu_1$
2	4025.37	24835	12	$(0-0)_2 = \nu_2$
3	4027.06	24825	22	$(0-0)_3 = \nu_3$
4	4027.73	24821	26	$(0-0)_4 = \nu_4$ Multiplet
5	4031.98	24795	48	$(0-0)_5 = \nu_5$ $0' \rightarrow 0''$
6	4035.77	24771	76	$(0-0)_6 = \nu_6$
7	4039.28	24750	97	$(0-0)_7 = \nu_7$
8	4043.23	24726	121	$(0-0)_8 = \nu_8$
...	....	.....	...	....
12	4078.62	24512		$\nu_1 - \nu_{12} = 24847 - 24512 = 335$
13	4080.40	24500	12	$\nu_2 - \nu_{13} = 24835 - 24500 = 335$
14	4082.06	24490	22	$\nu_3 - \nu_{14} = 24825 - 24490 = 335$
15	4083.05	24485	27	$\nu_4 - \nu_{15} = 24821 - 24485 = 336$
16	4086.95	24460	52	$\nu_5 - \nu_{16} = 24795 - 24460 = 335$
17	4090.64	24438	74	$\nu_6 - \nu_{17} = 24771 - 24438 = 333$
18	4094.83	24415	97	$\nu_7 - \nu_{18} = 24750 - 24415 = 335$
19	4098.63	24391	121	$\nu_8 - \nu_{19} = 24726 - 24391 = 335$
				Average. 335
...	....	.....	...	....
34	4135.42	24175		$\nu_1 - \nu_{34} = 24847 - 24175 = 672$
35	4136.91	24166	9	$\nu_2 - \nu_{35} = 24835 - 24166 = 669$
36	4140.00	24149	26	$\nu_4 - \nu_{36} = 24821 - 24149 = 672$
37	4143.51	24126	49	$\nu_5 - \nu_{37} = 24795 - 24126 = 669$
38	4144.77	24120	55	$\nu_7 - \nu_{38} = 24750 - 24120 = 670$
				Average. 670 = 335 × 2
...	....	.....	...	....
47	4166.60	23994		$\nu_1 - \nu_{47} = 24847 - 23994 = 853$
48	4168.68	23982	12	$\nu_2 - \nu_{48} = 24835 - 23982 = 853$
49	4170.39	23972	22	$\nu_3 - \nu_{49} = 24825 - 23972 = 853$
50	4171.18	23967	27	$\nu_4 - \nu_{50} = 24821 - 23967 = 854$
51	4175.62	23943	51	$\nu_5 - \nu_{51} = 24795 - 23943 = 853$
52	4183.53	23897	97	$\nu_7 - \nu_{52} = 24750 - 23897 = 853$
53	4187.37	23874	120	$\nu_8 - \nu_{53} = 24726 - 23874 = 852$
				Average. 853
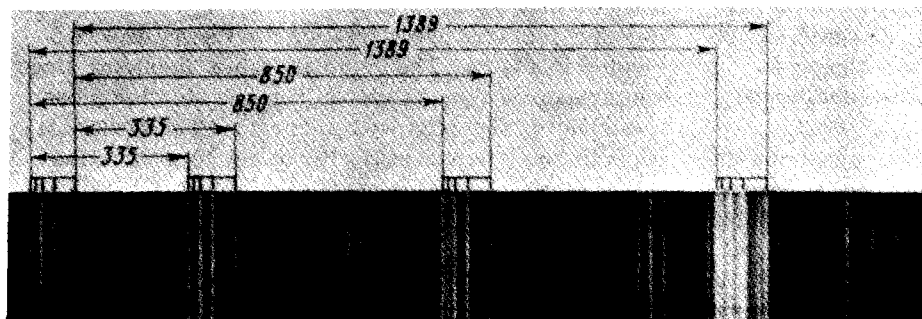
FIG. 9. Showing the interpretation of the fluorescence spectrum of 3,4-benzpyrene in n-heptane, T = 20°K (Shpol'skiĭ and Klimova[19]).

TABLE IV. Table of fundamental frequencies of 3, 4-benzpyrene.

1	217	Weak	10	1163	Moderate
2	335	Very strong	11	1237	Very strong
3	455	Weak	12	1288	Moderate
4	613	Moderate	13	1345	Very strong
5	637	Moderate	14	1389	Very strong
6	755	Very weak	15	1417	Strong
7	813	Moderate	16	1586	Moderate
8	853	Moderate	17	1636	Moderate
9	1085	Very weak			

would be premature because of the insufficient number of molecules studied. However, one fact is worth mentioning. This is that different hydrocarbons show certain close frequencies. One of the most interesting examples of this is the fact that in coronene, which consists of seven benzene rings forming a molecule of the same D_{6h} symmetry as benzene, the frequency 995 cm^{-1} appears most strongly. This frequency is very near to the completely-symmetric (breathing) frequency 992 cm^{-1} of the ground state of the benzene molecule.* Another example: the strongest frequency of the 3, 4-benzpyrene molecule at 1389 cm^{-1} is close to the completely-symmetric frequency a_{1g} of the anthracene molecule (1400 cm^{-1}), of pyrene (1405 cm^{-1}), and of naphthalene (1386 cm^{-1}). There are a number of other examples.

We should note that an analogous maintenance of frequencies of groups of atoms in different molecules is manifested also in infrared spectra, where we also observe the influence of the surroundings on the vibrational frequencies in the ground state to be slight. Among other observations, it is interesting to note that the "breathing" frequency of benzene, which in the first excited state is equal to 928 cm^{-1}, appears in many molecules consisting of linked benzene rings [for example, biphenyl, $C_6H_5-C_6H_5$, diphenylmethane $(C_6H_5)CH_2-(C_6H_5)$, and in general in cases in which benzene rings are separated from each other by such groups as CH_2 or $-CH_2-CH_2-$].

7. The problem of the nature of the quasilinear spectra and of the correspondence between these spectra and the electronic-vibrational spectra of free molecules requires a special study. Obviously, a system consisting of a frozen crystalline solvent and lumines-

*An interesting semi-quantitative explanation of this fact has been given by N. I. Zhirnov.[12]

cing molecules is analogous to an inorganic crystal phosphor. In either case, we have a crystalline matrix and activating centers introduced into it in small concentration. However in the case of interest to us, that of phosphors based on molecular crystals activated by organic molecules, the conditions are immeasurably simpler than in the case of inorganic phosphors, in which the matrices are ionic or covalent crystals, and the activators are the ions of luminescent atoms. In the latter case, all of the ingredients of the phosphor interact very strongly with each other. On the other hand, in a frozen paraffin matrix, the interaction forces of the molecules with each other and with the introduced organic molecule are small in comparison with the intramolecular forces. This is why the answers to many questions which are very essential to an understanding of the mechanism of the process, although often posing difficult problems among inorganic phosphors, can be solved with considerably greater ease in the present case of organic phosphors with molecular structures. Besides, we shall see below that there is a certain analogy between the inorganic and organic crystal phosphors, in spite of the essential difference in conditions. For convenience, we shall use the terminology applied to inorganic phosphors, and refer to the luminescing impurity molecules as the activator, and to the surrounding molecules of the fundamental structure as the solvent or matrix.

First, the question of which component of the phosphor is responsible for the light absorption may be answered immediately in this case: all paraffins absorb only in the Schumann ultraviolet. Hence, only the impurity molecules are responsible for the absorption of the exciting light (which does not extend beyond the middle ultraviolet or the visible region).

The following question is highly essential: the site in which the activator molecules occur. Are they distributed on the surfaces or within the crystallites of the matrix? Do they enter into the crystal structure, forming a substitutional solid solution, or are they distributed in the interstices? Are they distributed in solitary fashion, or do they form groups of two or more molecules? At present, we cannot consider as finally settled the whole complex of problems mentioned above and other associated problems. However, there exists material which will permit us to make some plausible conclusions.

The examples of spectra measured in our laboratory of various substances in various solvents show that the most favorable conditions for the appearance of a quasilinear spectrum occur when the dimensions of the activator molecule are approximately equal to those of the solvent molecule. Hence, we may conclude with a high degree of probability that the active molecules giving the quasilinear spectrum are not only within the solvent crystal, but enter into its crystalline structure, replacing the paraffin molecules. We shall discuss this problem in somewhat greater detail for the examples of the linear aromatic hydrocarbons studied by T. N. Bolotnikova.[14-15] The carbon skeleton of the molecules of normal paraffins in the crystalline state forms a planar zigzag chain, at whose corners the carbon atoms are placed (Fig. 10a). The hydrogen atoms occur in planes perpendicular to the chain axis.
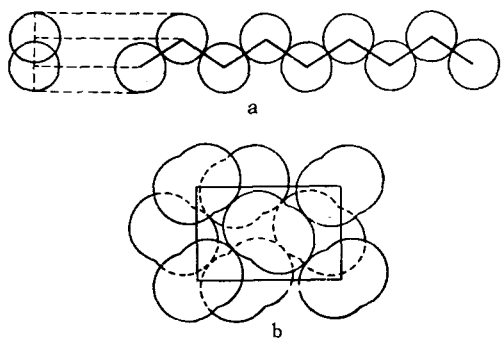
FIG. 10. a) Structure of the molecule of a normal paraffin; b) packing of molecules in the crystal structure projected on a plane perpendicular to the axes of the molecules.

The adding of each two CH_2 links to the paraffin molecule increases the length of the chain by 2.53 A, agreeing well with the 2.5 A periodicity in the chain of benzene rings in the aromatic compounds. The cross section of the chain perpendicular to the axis is approximately a circle of radius 2.62 A. The distance between the hydrogen atoms along the short axis of the aromatic molecule is 5.5 A, in good agreement with the diameter of the cross section of the cylinder corresponding to the space occupied by the paraffin molecule. In those cases in which a quasilinear spectrum is obtained, there is also a good agreement between the dimensions of the long axes (including the hydrogen atoms) of the aromatic molecule, on the one hand, and of the paraffin which gives the best conditions for the appearance of the quasilinear spectrum, on the other hand. This is illustrated by the following table, in which the numbers give the dimensions of the long axes of the molecules in Angstrom units.

On the other hand, when the dimensions of the paraffin molecule are too large, the lines of the spectrum are smeared out. Thus, for example, the spectrum of naphthalene in hexane and in heptane is poorer than that in pentane, in agreement with the increase in the difference between the dimensions of the molecules of

Activator	Paraffin
Naphthalene 7.2	Pentane 7.36
Anthracene 10.0	Heptane 10.0
Naphthacene 12.8	Nonane 12.8

activator and matrix: the bands in hexane are broader than in pentane, while in heptane, they are again broader than in hexane. Also conversely, when the dimensions of the activator molecule (i. e., the long axis) are greater than those of the matrix molecule, the spectrum loses its sharpness. An example of this is the spectrum of anthracene (10 A) in pentane (7.36 A), in which the bands are broadened in comparison with those in the spectrum of anthracene in heptane, where there is complete agreement of dimensions. These relations of dimensions are most remarkable; it is difficult to assume that they might be coincidental. This assurance is confirmed by the fact that this regularity has a simple graphic meaning: the sharpest spectrum is obtained when the space filled by the activator molecule corresponds precisely with that of the matrix molecule, so that the activator molecule may be fixed in a definite position within the matrix with minimum deformation, but without excess freedom of arrangement.

In the case of molecules with nonlinear condensed arrangements of benzene rings, the conditions are not so simple. However, a relation between the long axes of the activator and matrix molecules, which is favorable for the appearance of the quasilinear spectrum, occurs also among these more complex molecules, at least in the cases which we have studied. Thus, for example, pyrene (molecular length 7 A) gives the sharpest spectrum in hexane (8.75 A), while 3, 4-benzpyrene (10 A) gives the sharpest spectra in heptane (10 A) and octane (11 A). On the other hand, in cases in which the solvent used is a paraffin with a considerably longer molecule (e. g., pentadecane, with a molecular length of 21 A), the spectrum is smeared out so much that it becomes indistinguishable from the spectra in alcoholic and other analogous solutions giving broad bands.

The above-mentioned analogy with inorganic crystal phosphors consists in the fact that the quality of the phosphor, or even the possibility of forming it, depends on the relation of the dimensions of the ions or atoms of the activator to those of the cations of the matrix, in cases in which a substitutional solid solution is formed by "isomorphous" replacement of these cations. Correspondingly, it depends on the relation of the dimensions of the activator to those of the free interstices between lattice positions, when the activator atoms are distributed over interstitial positions (see the interesting discussion of the conditions in the latter case for the example of zinc sulfide phosphors activated by atoms of copper and other atoms, in the paper of Riel[44]).

It is interesting also to note that especially favorable conditions for formation of luminophors occur in layer structures. In this case, the possibility of introduction of activating atoms (or ions) within the crystal structure depends on the fact that large interstices occur between the separate layers filled with atoms or ions; the activator atoms may be distributed in these interstices without deforming the crystal structure. It is possible that a similar sort of effect occurs also in our paraffin luminophors.

Finally, there is even a closer analogy between the luminescence of impurity molecules which we have studied and the alkaline-earth luminophors (MgO, SrO, MgS, etc.) activated by trivalent samarium ions and other rare-earth ions. In this case, favorable conditions are created for the appearance of fluorescence with a line spectrum. Such a "linear fluorescence" has in fact been studied by Tomaschek,[45] who showed that the spectrum of this fluorescence depends very strongly on the surroundings, which influence the location of the spectrum and the number of lines in it. Unfortunately, the extreme complexity of the fluorescence spectrum of rare-earth ions and the strong field in the crystal structures studied make any sort of thorough interpretation of the spectra essentially impossible.

8. We proceed now to a discussion of the reasons for the appearance of "multiplets" in the quasilinear spectra. We saw above that the character of the splitting varies not only as a function of the nature of the activator (e. g., the doublets of coronene at 77° K, the multiplets of benzpyrene, etc.), but also of other factors. For example, on lowering the temperature from 77° K to 20° K, the number of components in the benzpyrene multiplet increases. Further, in those cases in which the spectrum retains its sharpness, a definite dependence of the character of the splitting on the solvent is observed in several solvents. Finally, "splitting" due to removal of degeneracy is excluded in this case. This may be seen from the fact that a molecule of low symmetry, such as 3, 4-benzpyrene, in which degenerate vibrations generally do not exist, gives multiplets with a large number of components.

We shall discuss this problem with the same substances, coronene and 3, 4-benzpyrene, as examples. The spectrum of coronene, as we have seen, may be considered as a superposition of two spectra shifted with respect to each other. Here we observe in different solvents a dependence of the magnitude of the splitting on the solvent. At first glance, this dependence gives the impression of a relation between the value of the splitting of the doublet $\Delta\nu$ and the mass of the solvent molecule, namely, $\Delta\nu = 86, 72, 38$, in hexane, heptane, and octane, respectively. One of the possible assumptions is that the energy of the emitted photon is partly spent in generating slow vibrations of solvent molecules as a whole with respect to one another (the so-called Gross vibrations, which are of the order of tens of cm^{-1}). However, this hypothesis does not withstand criticism for two reasons: first, the change in the frequency as a function of the mass of the solvent molecule is too rapid; in fact, the ratio of molecular weights $C_6H_{14} : C_7H_{16} : C_8H_{18} = 86 : 100 : 114$. Then, since the classical frequency is inversely proportional to the square root of the mass, the frequency for hexane and octane, for example, should not change by more than 10%, instead of the actually observed 50%. Second, since $kT = 60$ cm^{-1} at 77° K, we should observe at such a temperature "violet" satellites in addition to the "red" satellites, analogously to the situation occurring in Raman scattering. However, in fact this is not observed.

Another source of doublet splitting is the already-mentioned resonance effect observed in crystalline spectra, called the "Davydov splitting." The Davydov doublet splitting is observed in crystalline spectra, in the absence of other degeneracies, in cases in which the unit cell of the crystal contains two molecules. However, if we proceed on the basis of the most natural assumption that the solute is homogeneously distributed throughout the solvent, then at low concentrations (the commonly-used concentrations are of the order of $10^{-5} - 10^{-7}$ M) the distances between the fluorescing molecules will be too great for dipole-dipole interaction ($\sim R^{-3}$) of the excited molecules to give a noticeable effect.

We may add to what we have said on the magnitude of $\Delta\nu$ the effect of the sharp change in the intensity distribution between the components of the doublets on going from one solvent to another, as mentioned above (for example, in coronene a reversal of the order of intensities of the components is observed on going from hexane to heptane). Then it will be more proper to describe the observed changes in the doublets in different solvents as a variability of spectrum depending on the solvent, rather than as a phenomenon associated with intramolecular processes in the luminescing molecules.

If we consider now the spectra of pyrene and 3, 4-benzpyrene, we shall no longer see any clear relation between the magnitude of $\Delta\nu$ and the mass of the solvent molecules. Here, the number of components in the multiplets is different in different solvents, varying from one to five.[9]

We must still consider the possibility of explaining the multiplets as being due to the establishment of an equilibrium distribution over closely-spaced energy levels of the excited state. In fact, this equilibrium should be established in a time interval considerably shorter than the lifetime of 10^{-8} sec of the excited state. In fact, this factor also cannot give us the required explanation, since the distance between the extreme components of the multiplet in coronene is of the order of 100 cm^{-1} (86 cm^{-1} in hexane), and in benzpyrene is 150 cm^{-1}, whereas at 20° K, $kT = 15$ cm^{-1}, and at 4° K, $kT = 4$ cm^{-1}.

A study of the same hydrocarbons at 20° K has given a series of essential new results. The lowering of the temperature by a factor of almost four led to certain changes in the spectra. Thus, for example, in the case of coronene, a change in the intensity distribution between the components of the "multiplets" is observed, and new lines appear. It turned out here that the new lines also are arranged in the same vibrational series as the series found at 77° K. Thus the number of series for coronene was increased to five or six. Second, it turned out that the intervals 86, 72, 38 cm^{-1}, each of which had been considered to be characteristic of the doublets in some given solvent, were actually found in all solvents, such that in hexane we find not only the interval 86, but also 72 cm^{-1}, while in heptane, not only 72, but also 86 cm^{-1}, etc.

Thus, it has been confirmed that the change in the "splitting" of bands of coronene in different solvents is reduced simply to a redistribution of the intensities between the same vibrational series, and the set of possible intervals between the series remains one and the same. Figure 11 illustrates this for the example of one of the "multiplets" of coronene in hexane and heptane. We see that in each group of lines we find not one interval, but at least, three intervals: 86, 72, 38 cm^{-1}, which are the same in all solvents.

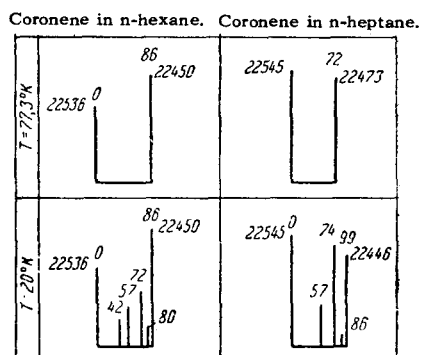Coronene in n-hexane.   Coronene in n-heptane.

FIG. 11. Multiplets of coronene in different solvents at 20° K (Shpol'skiĭ and Klimova[19]).

Analogous results were also obtained at 20° K in the case of benzpyrene. Here, as we have seen, we also observe a number of series, this number corresponding to the number of components in a "multiplet." Here the intervals between the components form a series of values among which we find some which are close to or coincident with the intervals between the series for coronene in various solvents (for example, 54, 75, 85, 101 cm^{-1}). This shows that the number and relative displacements of the series are determined, at least basically, not by the properties of the luminescing molecules, but by the properties of the solvents.

We must add to this the above-mentioned fact that in the absorption spectra, all of the lines of the leading multiplet are in resonance coincidence with the lines of the 0'—0" "multiplet" in the luminescence spectrum, although there can be no question here of a quasi-equilibrium distribution over the energy levels. We may see easily that all of this picture, though confused at

first glance, becomes perfectly clear if we assume that the series forming the "multiplets" belong to different, spatially-separated luminescing molecules. In such a case, the origin of the multiformity of series, and in general of the variability of the spectra, may be local differences in the crystal field in which the luminescing molecules are situated.

The following experiment demonstrates this especially clearly. Spectra were photographed of the fluorescence of solutions of 3, 4-benzpyrene and pyrene at 77° K, frozen by two methods: the ordinary rapid freezing, and slow freezing. It turned out that in the latter case the character of the emission changes, as the eye may see directly: the emission becomes weaker, other conditions remaining the same, and its color is somewhat changed, changing from blue-violet to light blue. Figure 12 shows schematically what changes take place in the spectrum on slow freezing. We see that under these conditions the short-wavelength components of the "multiplets" in the spectra of benzpyrene in hexane and pyrene in heptane disappear, and even the components of longest wavelength are greatly weakened.
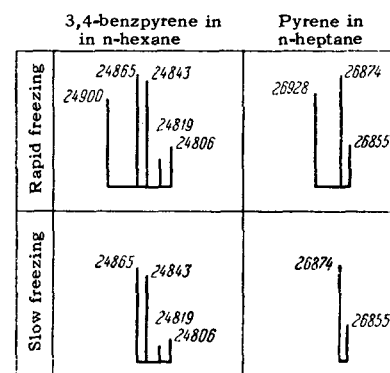

FIG. 12. Change in fluorescence spectra in crystalline frozen solutions as related to the rate of freezing (Shpol'-skiĭ and Klimova[19]).

A visual examination of the frozen solution shows that it differs even in external appearance from the pressed snow obtained by rapid freezing. In particular, "frost patterns" are formed on the walls of the cuvette upon slow freezing, indicating the formation of coarser crystals.

It appears to us that the described experiment may be qualitatively explained as follows. Only in the crystalline state obtained with careful crystallization does the carbon skeleton of the paraffin molecules have the form of a planar zigzag, as discussed above, on entering into the crystal structure. This is the stablest form, but there exists in addition a series of other forms in which some parts of the molecule are twisted with respect to other parts. These anomalous molecules are obviously isomers, namely the rotational isomers of the given paraffin. The potential-energy curve of the paraffin as a function of the rotation angle has a discrete set of minima, each of which corresponds to a particular rotational isomer. In the gaseous or liquid state, the normal paraffins are complex mixtures of rotational isomers. Something like quenching

takes place during rapid freezing: the molecules are in part unable to transform into the stables planar form, and thus enter into the crystal structure in the form of rotational isomers. Obviously, each such anomalous molecule is a "lattice defect," and the local field in its immediate vicinity is different from the field near the normal planar paraffin molecules. In addition, the luminescent molecules which occur near the various "lattice defects" are subject to different perturbations, with which the appearance of the "multiplets" may be associated. Clearly, on the contrary, under slow freezing a greater fraction of the paraffin molecules will be able to transform into the stablest planar form, and the spectrum will become simpler. The picture described here is apparently an inevitable consequence of reliably-established facts concerning the nature of the normal paraffins. On the other hand, there are also other sources of "lattice defects," which may also exert an influence on the local field in the sites of the luminescing molecules.

Thus we see that the fluorescence spectrum of a frozen crystalline solution, while essentially retaining its individuality, is a structure-sensitive property. In particular, there is the fact emphasized above that the multiplet structure is a feature superimposed on the character of the spectrum by the micro-crystalline structure. In addition, the high resolution of the described spectra, even at liquid-nitrogen temperature, and the weakness of the interactions in molecular crystals (especially in crystals of normal paraffins) result in the remarkable possibility of completely clear isolation of the spectrum belonging to the molecule being studied from the complications introduced by the properties of the crystalline solvent.

9. So far we have discussed only the applications of the quasilinear spectra in the determination of the vibrational levels of the ground state of luminescent molecules. We saw here that the multiplet structure of the spectrum and its dependence on the solvent not only does not decrease the accuracy of the determination of the vibrational levels, but on the contrary, opens up a way for substantially increasing the accuracy, since we have as many independent ways to determine each vibrational level as there are components in the multiplets (see Table III).

The high sensitivity of the quasilinear spectrum to the influence of intramolecular and intermolecular force fields makes it possible to reveal very subtle effects due to the interaction of molecules. An example of this is the possibility of detecting hydrogen-bonding in the electronic-vibrational spectra, whereas the spectroscopic investigation of hydrogen-bonding has been limited up to now to the vibrational spectra: the infrared and Raman spectra.
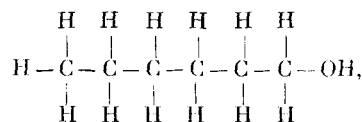
As is known, the hydrogen bond is a distinctive type of bond which is formed with the participation of a hydrogen atom, and which occupies an intermediate position in the scale of bonding energies between the strong

chemical bonds and the weak van der Waals bonds. The energy of the hydrogen bond is estimated to be only 5 or 6 kcal. It appears between molecules or within one molecule, between groups of atoms XH and YZ:

$$\begin{array}{c} X \\ | \\ H \dots \dots YZ, \end{array}$$
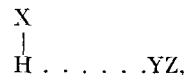
where Y is an electronegative atom, e. g., O, N, Cl. Spectroscopically, the hydrogen bond is manifested in vibrational spectra by a lowering of the frequency of the valence-bond vibration of XH and by the appearance of broad bands in the vibrational spectrum together with the lines (under certain conditions, by broad bands alone). Thus, for example, in water and alcohols the valence-bond vibration of the OH group, which has a frequency of 3647 cm^{-1}, is shown as a line in the Raman spectra only at high temperatures, at which the thermal motion has broken most of the hydrogen bonds, or in dilute solutions in CCl_4. At temperatures near room temperature, the line corresponding to the OH-group vibrations is replaced by a broad band. The problem of the origin of this diffuse band cannot be considered yet as having been finally solved; there are various interpretations, and perhaps each of these contains a part of the truth. However, the very fact of the appearance of this diffuseness in vibrational spectra is a widely-used spectroscopic criterion for the hydrogen bond. In a solid, the presence of hydrogen bonds leads to a decrease in the distance between molecules of about 1 A, i. e., by about 25% in comparison with the distances in hydrocarbons. This leads to the formation of more compact structures, and obviously, to an increase in the interaction between molecules.

We shall relate these properties of the hydrogen bond to the fact that in alcoholic (ethanol, methanol) solutions, the fluorescence spectra of aromatic hydrocarbons are highly diffuse, even at low temperatures, and the lines which are well resolved in paraffin solutions fuse together into broad bands. This fact makes it quite plausible to assume that the smearing-out of the lines in this case is also due to the hydrogen bonds occurring between the alcohol molecules, forming a network of hydrogen bridges. The following observation may confirm this hypothesis. In the higher alcohols, for example hexyl alcohol,

$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - OH,$$

the role of the OH group, which is responsible for the appearance of hydrogen bonds, is decreased because of the great length of the hydrocarbon part of the molecule. Undoubtedly, this explains the fact that the ratio of the intensity of the line corresponding to the vibrations of the OH group to the intensity of the bands in the Raman spectra of the higher alcohols increases with increasing length of the hydrocarbon part of the

alcohol molecule.[46] An analogous phenomenon was recently found in our laboratory in the case of the quasilinear spectra. Thus, for example, the fluorescence spectrum of pyrene shows the usual diffuse form for alcohol solutions in ethanol at 77° K. However, in hexyl alcohol at the same temperature, it shows the doublets characteristic of the quasilinear spectrum of pyrene.

Some interesting observations on the influence of intramolecular interactions on the quasilinear spectra of anthraquinone derivatives have been published by D. N. Shigorin and his associates.[47] Anthraquinone
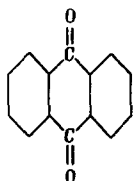
gives a sharp quasilinear spectrum in hexane, heptane, and octane at 77° K. This spectrum[47] clearly shows a frequency, on the average equal to 1664 cm^{-1}, independently of the solvent. This frequency, as is known from studies of infrared spectra,[49] belongs to the valence-bond vibration of the C=O group. The agreement of the characteristic C=O vibration frequency in anthraquinone, as determined from the quasilinear fluorescence spectra and the infrared spectra, is an interesting fact in itself. This is because it serves as a proof of the correctness of the interpretation of the quasilinear spectra as being the electronic-vibrational spectra of the ground state. However, especially interesting results were obtained from a study of the spectra of the anthraquinone derivatives. In organic chemistry, depending on the position of the substituent (R), we may distinguish α-derivatives (α) and β-derivatives (β):
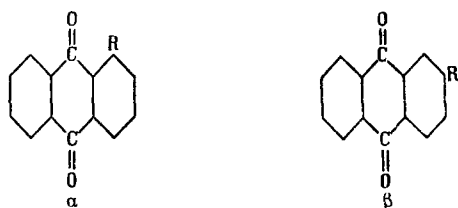
It happens that when the substituent (R = Cl, NH$_2$, CH$_3$) is in the β-position, the spectrum retains its sharpness; the most intense frequency determined from the spectrum is also retained. This frequency is 1664 cm^{-1}, i. e., the frequency of the valence-bond vibration of the C=O group.

However, if the substituent is in the α-position, its influence on the spectrum depends essentially on the nature of the substituent. Thus, for instance, if the substituent is the hydroxyl group (α-hydroxyanthraquinone)
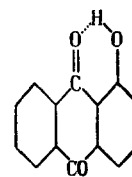
an internal hydrogen bond is formed. Then the fluorescence spectrum completely loses its fine structure and is also strongly shifted toward the red. On the other hand such substituents as methyl (CH$_3$), phenyl (C$_6$H$_5$), and methoxyl (CH$_3$O) cause practically no change in the fluorescence spectrum of anthraquinone, even when they are in the α-position.

Halogen atoms as substituents in the α-position show a considerable influence on the spectrum, shifting it and smearing out the bands. Here the degree and character of the influence may be related to the electronegativity differences of the halogens, varying in going from fluorine to iodine and with the change in the dimensions of the atoms.

This study may serve as an illustration of the possibility of detecting intramolecular interactions by their influence on the structure of the quasilinear spectra.

Interesting results have been obtained by R. N. Nurmukhametov, D. N. Shigorin, and N. S. Dokunikhin[48] in a study of the fluorescence spectrum of the dye thioindigo. The molecule of this dye is rather complex, and in distinction from the aromatic hydrocarbons discussed above, contains heteroatoms:
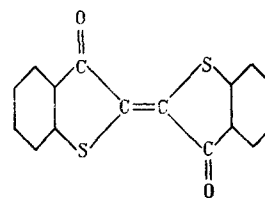
The fluorescence spectra of thioindigo in hexane and heptane at 77° K show a distinct line structure. It was possible to interpret the frequencies of the observed lines in terms of only three frequencies: 220, 480, and 1540 cm^{-1}. Of these, the most characteristic is the frequency 1540 cm^{-1}, which appears independently and in combinations with the two other frequencies and their overtones six times. This frequency is close to the vibration frequency 1535 cm^{-1} ascribed to the valence-bond vibration of the ethylenic group C=O in stilbene
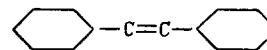
On these grounds, the authors interpreted the 1540 frequency in thioindigo as being the frequency of the valence-bond vibration of the ethylenic link C=C. It is interesting to note that, in spite of the presence in the thioindigo molecule of two carbonyl groups C=O, the fluorescence spectrum of this dye shows not the

carbonyl frequency (which is 1650 cm^{-1} for thioindigo on the basis of measurements of the infrared spectra[49]), but rather, the ethylenic (C=C) frequency. This fact agrees with observations on the photo-chemical behavior of thioindigo.[49] The point is that there are two isomers of this dye, trans and cis:
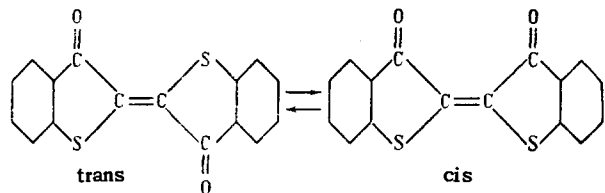
These two forms are separated by a potential barrier, such that the molecule must acquire energy in order to surmount it, e. g., by absorption of light. In fact, the mutual transformation of these two forms of the molecule on irradiation (photoisomerization) has been found by Rogers and his associates.[50] It appears that upon illumination by yellow light, the equilibrium between the isomers is shifted to the right (trans → cis), and on illumination by blue light, to the left. Of these forms, only the trans isomer fluoresces, as may be explained by steric hindrance occuring in the cis isomer, in which the two C=O groups are situated alongside one another, and hence, interfere with the coplanarity of the molecule.

The phenomenon of photoisomerization of the thioindigo molecule agrees with the concept of the localization of the excitation energy in the ethylenic bond, as is shown in the quasilinear fluorescence spectrum. Obviously, in order that photoisomerization may take place, the symmetry-related parts of the molecule must be rotated with respect to one another. This is made possible by the localization of energy in the C=C bond, which is accompanied by the breaking of the second bond and the appearance of torsional oscillations.

The examples given show that there exist undoubted possibilities for applying the quasilinear spectra in the study of molecular interactions and in solving structural problems.

10. We shall not discuss here the topic of the applications of quasilinear spectra for purposes of chemical analysis, since our previous article was devoted to this subject.[16] Here we shall limit ourselves to a few remarks. Since the cited article was published, a number of studies have been carried out, and in part published. These studies have demonstrated in concrete examples the possibilities of practical application of the quasilinear spectra. At present, these applications are proceeding mainly in two directions: 1) the determination of carcinogenic substances in polluted air, in tars (in particular, tobacco tar), and in certain smoked foods (L. M. Shabad and P. P. Dikun[29]); 2) the determination of the heavy aromatics in petroleums and bitumens (A. A. Il'ina and her associates, R. I.

Personov). As regards qualitative analysis, the quasilinear luminescence spectra provide an ideal method for rapid, absolutely reliable identification of certain individual substances at exceedingly low concentrations. Different substances which are similar in structure or isomeric, one being carcinogenic while the others are not, may show overlapping luminescence spectra under ordinary conditions (in alochol or oil solutions); an example is given by 3, 4-benzpyrene and 1, 12-benzperylene. In view of the high selectivity of the quasilinear spectra of these substances, these spectra permit us to distinguish them simply and without error. This characteristic of the quasilinear spectra thus represents their great advantage.*

The application of the quasilinear spectra in quantitative analysis, as in all cases dealing with emission spectra, is a considerably more difficult problem, and in any case, requires further study. In the case of the quasilinear spectra, the problem is not limited to the determination of the relation between the concentration of the substance being determined and the intensity of its spectral lines. Rather, when multiplets are present in the spectrum, great caution is necessary in the selection of the lines used in the analysis, since certain components of the multiplets show anomalous behavior upon change of concentration (L. Pesteil and A. Ciais[28]).

The last remark will be concerned with the limitations of the method. This subject has been discussed in part in our previous article.[16] Of course, as with every method, the application of the quasilinear spectra has its limitations. It may seem obvious that in a given case there is an unavoidable limitation due to the lack of solubility of the substances in question in normal paraffins. Actually, the situation is more favorable, since there exists a certain phenomenon already noted by Bowen,[23] and designated by him as specificity. It appears, for example, that perylene may be extracted from rock samples with benzene or chloroform. Then, on addition of an excess of the proper paraffin hydrocarbon (e. g., hexane) to the solution and freezing, the spectrum retains all of the characteristics of a frozen hexane solution. The same is true of acetone solutions. Finally, the fact already mentioned above of the appearance of structure in the spectra of frozen solutions in hexyl, heptyl, and other higher alcohols shows that there are probably other classes of solvents besides the normal paraffins showing the property of manifesting fine structure in the spectra at low temperatures.

The increase in the group of substances whose spectra show line structure, the compiling of a correspond-

ing atlas of spectra, and finally, new applications of the method — these are the further problems in this interesting field.

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