

*PROBLEMS OF THE ORIGIN AND STRUCTURE OF THE QUASILINEAR SPECTRA
OF ORGANIC COMPOUNDS AT LOW TEMPERATURES**

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1. In this article I shall discuss the electronic spectra of polyatomic organic compounds. It is precisely the electronic spectra, from among all other types of molecular spectra, that should be of greatest interest since they manifest all the degrees of freedom of the molecule. Nevertheless, until very recently they have aroused very little interest on the part of physicists, insofar as the spectra of polyatomic molecules are concerned. The reason for this is the highly diffuse structure of the electronic spectra of polyatomic molecules and the consequently limited possibilities of using them to get information on the structure of molecules and to study molecular processes.

The fundamental result of the studies in our laboratory, a result that has created possibilities for varied applications, is our success in finding a method of obtaining electronic spectra from a rather broad class of organic compounds in the form of series of bands so narrow that in most cases we can quite rightly call them lines. The appearance of these spectra, which we shall call "quasilinear," depends on the use of low temperatures: liquid nitrogen (77.3°K), liquid hydrogen (20°K), or liquid helium (4.2°K). However, the interaction of the emitting or absorbing molecules with the surrounding medium plays just as important a role as the low temperature does in the resolution of the broad bands devoid of individuality into quasilinear spectra strictly specific for the given molecules. Hence, the problem of the origin of the quasilinear spectra is also of essential physical interest. We shall pay major attention to this problem in the following discussion, rather than to the applications of the quasilinear spectra.

The problem of the nature and origin of the broad bands in the electronic spectra of polyatomic molecules cannot be discussed here in its full scope. Considerable advances have been made recently in understanding the origin of these spectra, owing to the studies of B. S. Neporent and B. I. Stepanov.^[3,4,5] Among other matters, these studies have provided a convenient spectral classification of polyatomic molecules as related to characteristics of their spectra. We shall consider here the case of "simple" polyatomic molecules, in B. S. Neporent's terminology (these may actually consist of a very large number of atoms). Under the most favorable conditions, in the case of the so-

called "structured spectra," we still find bands having widths of the order of several hundreds of cm^{-1} , or sometimes even over a thousand. An especially important point is that the diffuseness of these spectra vanishes neither in the gaseous state (even at the lowest pressures), nor in the crystalline state, in the latter case even at the lowest temperatures provided that the substance is studied in the form of pure crystals.

The reasons for the diffuseness of the spectra under these very simple conditions are qualitatively not difficult to understand. In the gaseous state, the molecules can rotate freely, and the large moments of inertia of polyatomic organic molecules give rise to a quasicontinuum of rotational states. In most cases, these states are not resolvable even by gas microwave spectroscopy with its great resolving power, not attainable by optical methods. This is just the reason why in solutions, where the rotation of the molecules is hindered, the spectra of polyatomic molecules become more discrete than in the gas state. An example of such a relation between the spectra in the vapor and in solution for the case of the highly-symmetrical planar molecule coronene ($\text{C}_{24}\text{H}_{12}$) is shown in Fig. 1.*

For another reason, the problem of obtaining narrow-line spectra is also not solved by going to the pure crystals. In this case, strong electron-phonon interactions lead to a broadening of the levels, such that the indi-

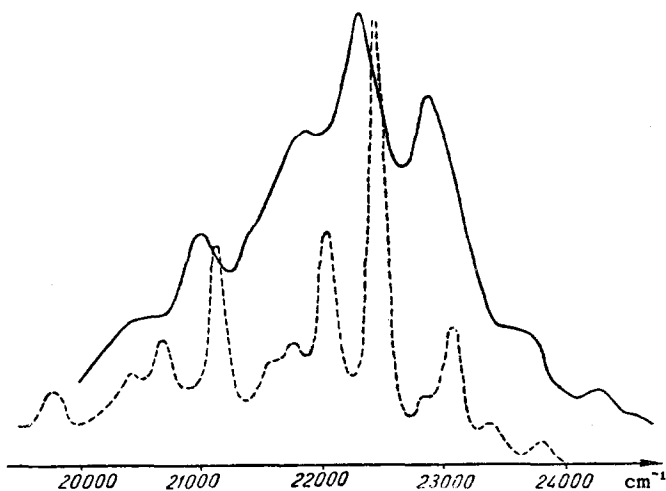


FIG. 1. Fluorescence spectrum of coronene: a) in the vapor; b) in octane solution, $T = 300^\circ\text{K}$.

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*The author wishes to express sincere thanks to V. P. Klochkov, who has kindly made the measurements of these spectra.

vidual lines merge into broad bands which are not resolved even at the lowest temperatures. This has been shown, for example, in the study of A. F. Prikhot'ko and M. T. Shpak for the case of the simple aromatic hydrocarbons stilbene and tolan. When studied in the form of the pure crystals, these compounds retained their rather broad bands even down to 20°K.

We must mention the anomalous spectra often observed in complex substances in the crystalline state. These cases are characterized by the following phenomenon: whereas the absorption and luminescence spectra have a certain degree of structure and approximately obey the law of mirror symmetry in solution at low concentrations, the fluorescence spectrum in the crystalline state completely loses its structure and similarity to the absorption spectrum, and is strongly shifted toward the red. Without stopping to discuss this phenomenon in detail, we note that such spectra are currently ascribed to "resonance dimers," i.e., dimers arising during the lifetime of the excited state (Förster^[7]), while the corresponding transitions are said to involve electron transfer (Lyons^[8]). As an example of this type of spectrum, Fig. 2 gives the fluorescence spectrum of 3,4-benzpyrene^[9] in the crystalline state. As we see, this spectrum is continuous, with slight hints of maxima on the short-wavelength side, and extends over almost the entire visible region.

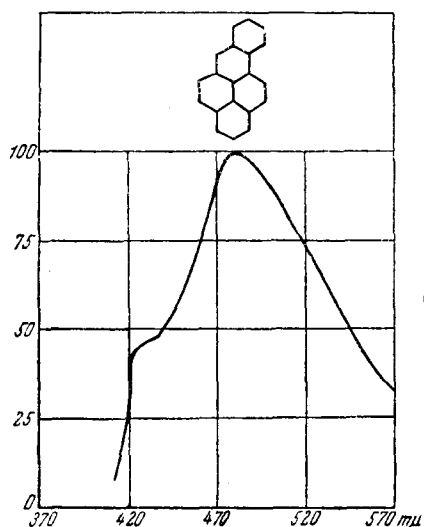


FIG. 2. Fluorescence spectrum of crystalline 3,4-benzpyrene (Birks and Cameron^[9]).

2. However, whatever the mechanism might be of the molecular interaction creating such a diffuseness in the crystal spectrum or even giving rise to an anomalous continuous spectrum, an increase in the distance between the emitting molecules must lead to a great decrease in this interaction. If, in addition, the molecules maintain one and the same orientation throughout the crystal structure, or at least a limited number of selected orientations (e.g., two mutually-

perpendicular orientations), then we may observe an undistorted or only slightly distorted spectrum. Such a situation may occur through the inclusion of the emitting (or absorbing) molecules in a foreign crystal structure, which must satisfy a number of conditions. Namely: first, it must interact as weakly as possible with the emitting molecules; second, it must form a rigid matrix for the incorporated molecules, in which these molecules must be located without deformation but without extra looseness, so that they may be fixed in strictly defined orientations; third, it must be transparent in the spectral region of emission and absorption of the incorporated molecules. Clearly, it is not easy to find such matrices for every molecule of interest. However, if we succeed in this, we can expect that the incorporated molecules will form a system to which we can apply the model of an "oriented gas." This means that under such conditions the incorporated molecule may retain the electronic and vibrational levels characteristic of its free state. As is known, this is generally not the case in pure crystals.

It would seem natural to create such an oriented-gas condition by means of isomorphous replacement of certain molecules of the solvent crystal by molecules of the substance being studied. Here, since we are imposing a condition of isomorphism, both substances (the activator and the matrix) must be similar in composition, structure, and chemical properties, according to the ordinary ideas on isomorphism.

Experimentally, the oriented-gas condition in mixed crystals of aromatic hydrocarbons satisfying the requirement of isomorphism has been achieved by McClure and Sidman for two or three pairs of substances (see, e.g., the review^[10]), including naphthalene in durene (symmetrical tetramethylbenzene); and by Prikhot'ko and Shpak for stilbene in dibenzyl and in tolan. It was shown in all these cases that under such conditions the dissolved molecules actually behave like an oriented gas, and in particular, they give nearly linear spectra. In some cases, the problem is that of studying the spectra of molecules in states resembling the free state as closely as possible, rather than studying the molecular mechanism of light absorption by the crystal (which is independently of great interest). In such cases, this mixed-crystal method obviously has great advantages over the study of pure crystals. However, the use as the host crystal of a substance belonging to the same class of compounds as the substance being studied introduces a highly essential limitation. Besides, since the solvent crystal must be transparent throughout the region of absorption and luminescence of the solutes, this strict condition, together with the requirement of isomorphism, reduces the number of suitable pairs to a few singular cases.

In the studies of McClure and Sidman, as well as those of Prikhot'ko and Shpak, all three conditions of "isomorphism in the narrow sense" according to

Grimm* were completely satisfied. However, our studies have shown that among organic substances the formation of mixed crystals is possible under conditions much broader than the conditions formulated by Grimm for "isomorphism in the broad sense."

3. The gist of our studies consists in the establishment and application of the important fact that the oriented-gas condition may be achieved by using as the matrix a substance belonging to a completely different class of compounds from that of the impurity molecules being studied (for brevity, we shall often refer to the latter molecules as the activator). In particular, it has proved possible to find suitable matrices for a large class of organic compounds among the normal paraffins, i.e., saturated compounds of the series $C_nH_{2n+2} = CH_3CH_2CH_2 \dots CH_2CH_3$, the molecules of which form linear (unbranched) chains, e.g., n-pentane, n-hexane, etc.

The successive compounds of this series differ by one CH_2 group, and form a large set of molecules having analogous properties, but differing lengths. They all crystallize easily. A very important point is that these substances are not only chemically neutral, but also are transparent even into the far ultraviolet. As we shall see, experiment has shown that in this case, the conditions for isomorphism are not satisfied at

*The most detailed résumé known to the author of the experimental facts and theoretical conceptions on isomorphism in relation to the structure of atoms and molecules is that of Grimm and Wolff.^[17] This résumé, however, is based mainly on the subject matter of inorganic compounds; it clearly reveals the great complexity of the phenomena even among inorganic compounds, for which the conditions would seem to be considerably simpler than among organic substances. As generalizations, these authors found it necessary to formulate separately the conditions for isomorphism in the "narrow" and "broad" senses.

As for "isomorphism in the narrow sense," according to Grimm, "Ability to form mixed crystals is determined by the following three conditions:

- a) the chemical types of structure must be identical;
- b) the crystal-structure types must be identical;
- c) the atomic or ionic distances in the crystals must be similar; the required degree of approximation depends on the temperature and the type of bonding."

We must note that these authors mean by "identical chemical type" (Grimm and Wolff, §77) a type of compound whose stoichiometric formulas may be reduced to the same general form, e.g., the form MX for $NaCl$, PbS , MgO , etc., or the form $MM'X_4$ for $BaSO_4$, $KMnO_4$, etc.

Along with these conditions for "isomorphism in the narrow sense" determining the possibility of forming solid solutions (mixed crystals), Grimm and Wolff (op. cit., §80) found it convenient to introduce the concept of "isomorphism in the broad sense." The conditions for and meaning of this type of isomorphism are formulated by the authors in a rather indefinite manner: "We shall call hereinafter all substances of identical chemical-structure type (for definition, see above, - É. Sh.) and identical crystal-structure type isomorphous in the broad sense, and add that the degree of isomorphism will become greater and the manifestations of chemical similarity will become more numerous and marked as the lattice dimensions approach each other." (Under-scored everywhere by É. Sh.)

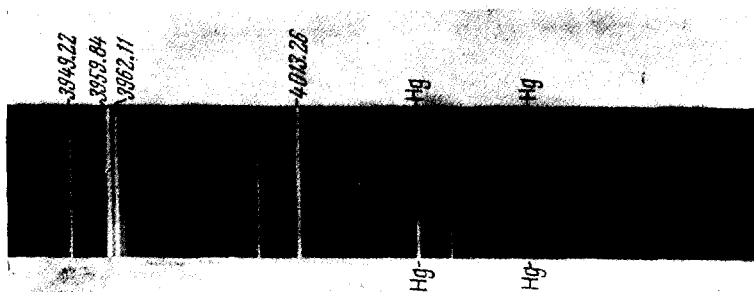
all, either in Grimm's "strict" sense, or in his "broad" sense. However, the very fact that solid solutions are formed (as evidenced by the appearance of molecular electronic-vibrational spectra) under conditions considerably broader than those for isomorphism in the "broad sense" indicates the necessity of a fundamental revision of the pertaining theories for the case of organic compounds.

We shall return below to a more detailed discussion of the mechanism of formation of an oriented-gas system in this case, but shall just note now that the frozen-paraffin-solution method is distinguished both by simplicity and effectiveness. And since the crystalline paraffins provide the investigator with matrices having an exceedingly broad set of molecular dimensions, the possibilities for using the method to obtain linear spectra are correspondingly great. Here not only the so-called "structured spectra," but also the anomalous spectra shown above, which exhibit a continuum in the pure crystalline state, are split into spectra consisting of hundreds of lines of "atomic" breadth. Figure 3 gives as an example the spectrum of the complex substance 3, 4, 6, 7-dibenzpyrene at liquid-helium temperature.^[12]

When we had proved the possibility of obtaining linear spectra from a broad set of substances by this method, we still had to verify that these spectra really belong to the activator molecules. The test consisted in determining the vibrational frequencies from these spectra for a number of molecules such as benzene, naphthalene, anthracene, and certain others for which these vibrational frequencies were well known from the analysis of the purely vibrational spectra (infrared and Raman). This important work has been carried out in our laboratory by T. N. Bolotnikova, and also in the laboratories of Professor Pestel in Marseilles (see, e.g.,^[19]) and Professor Rousset in Bordeaux.^[26] In all cases, excellent agreement of frequencies was found, as determined by both methods. This not only confirmed for us the fact that we are dealing in our systems with a "frozen gas," but also indicated that it is correct to use the spectra obtained by the described method to determine the vibrational frequencies of the normal state in cases in which these frequencies are unknown.

At present, this method has been used to carry out analyses of the vibrational frequencies of a number of complex organic compounds belonging to various classes: polycyclic condensed aromatic hydrocarbons, polyene and polyphenyl chains, certain dyes,^[25] aromatic aldehydes and ketones, and certain other classes. Besides the simplicity of this method, other great advantages are the small amount of material required to obtain a spectrum (of the order of 1 ml, or possibly even less with cuvettes of suitable construction), the high degree of accuracy, and the possibility of simultaneous determination of both low ($\sim 10\text{ cm}^{-1}$) and high frequencies.

FIG. 3. A portion of the fluorescence spectrum of 3,4,6,7-dibenzpyrene, $T = 4.2^\circ\text{K}$. (Shpol'skiĭ and Klimova^[12]).



4. Let us consider now the problem of the origin of the quasilinear spectra. First of all, the natural question arises of why the normal paraffins in particular have such remarkable properties with regard to the spectroscopy of the rather broad class (and possibly even considerably broader) of polyatomic organic compounds cited above. Undoubtedly, the chemical inertness and complete optical transparency of the paraffins (even into the far ultraviolet) play important roles. However, this is far from all. We may see this from the results of a series of recently published studies of the spectra of various substances (including benzene) in matrices of frozen noble gases (Ar, Kr, Xe)^[14] at 4.2°K . The spectra obtained under these conditions were considerably more diffuse than those in paraffin solutions at the same temperature.

In addition, with noble-gas matrices the spectra of benzene show highly differing shifts (up to 500 cm^{-1}) in different matrices. No analogous effect has been observed in paraffin matrices. This all shows that the combination alone of low temperatures, inertness, and transparency of the normal paraffins is insufficient to explain the remarkable sharpness of the quasilinear spectra of organic substances, often highly complex ones.

To determine the mechanism of origin of these spectra, we must first of all decide whether the dissolved substance at low temperatures in a paraffin matrix exists in a molecularly-dispersed state, or separates out on lowering the temperature in the form of some sort of aggregates or even microcrystallites (especially in case of poor solubility). Fortunately, the very nature of the luminescence spectra directly contradicts the latter alternative, for practically all the studied substances give fluorescence spectra in the crystalline state in the form of a continuum as described above, even at the lowest temperatures. This is in sharp distinction from the discrete linear spectra observed in frozen paraffin solutions.

It follows from all this that the substance (activator) exists in the paraffin matrix as a molecularly-dispersed solid solution. However, in such a case we must examine what peculiarities in the molecular structure of the normal paraffins make possible the formation of a solid solution of an aromatic hydrocarbon in spite of the violation of the conditions for isomorphism (even in the "broad sense") between the solvent and the

solute, or as we shall say, between the matrix and the activator.

A great many interesting and important pertinent facts have been known for a long time in organic crystal chemistry, and in particular, in the study of solid solutions. However, since these facts are not well known to physicists and spectroscopists, we shall take the liberty of giving an account of them here.

The normal paraffins of general formula $\text{C}_n\text{H}_{2n+2}$ consist of linear chains of carbon atoms. The distance between neighboring carbon atoms in these chains is equal to the length of the aliphatic C—C bond in the diamond structure, namely, 1.54 \AA . On the other hand, x-ray diffraction study of the paraffins has shown that the unit cells of all the paraffins have the same dimensions in the directions of the a and b axes, $a = 7.45\text{ \AA}$, $b = 4.97\text{ \AA}$. The unit-cell dimension in the c -axis direction coincides with the molecular length in the case of the fundamental modification (the so-called type A, see below), and increases linearly with the number of carbon atoms in the paraffin molecule. These dimensions are manifested in the x-ray patterns as a definite period l . However, in addition to this long period whose value differs from compound to compound, the x-ray analysis shows another short period in the c direction, $\Delta d = 2.5\text{ \AA}$, identical in all paraffins. However, since the length of the C—C bond in normal paraffins is 1.54 \AA , the appearance of a short period of 2.5 \AA might be explained only by assuming that the carbon atoms in the paraffin chain have a zigzag configuration, as shown in Fig. 4.* The arrangement of the long paraffin chains in the unit cell is shown in Fig. 5.

Let us discuss now the problem of the state of the activator in the paraffin matrix. The simplest and most graphic relation occurs in the case in which the activator is a molecule of an aromatic hydrocarbon having a condensed "linear" arrangement of benzene rings (naphthalene, anthracene, naphthacene). It turns out that one of the conditions for "isomorphism in the broad sense" (according to Grimm) is satisfied in

*It is curious to note that the appearance of a diffraction maximum corresponding to a period $\Delta d = 2.5\text{ \AA}$ results from the fact that each long paraffin molecule acts as a diffraction grating of period Δd , owing to its internal periodicity.

However, the long period obviously corresponds to the sequence of molecules arranged one after another parallel to the c axis.

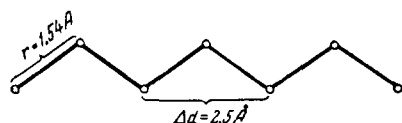


FIG. 4. Zigzag structure of a paraffin chain giving rise to an internal period of $\Delta a = 2.5 \text{ \AA}$.

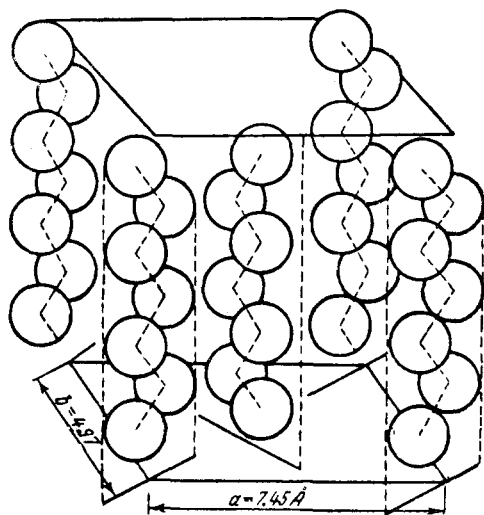


FIG. 5. Arrangement of paraffin chains in the unit cell.

these systems, namely the similarity of dimensions of the molecules of the activator and the matrix.

In fact, in those cases providing the linear spectrum having the narrowest lines, we find good agreement between the dimensions of the long axes of the molecules of the aromatic substances, on the one hand, and the paraffin providing the best conditions for appearance of a linear spectrum, on the other hand. This is illustrated by the two examples of anthracene and naphthacene, and the paraffins heptane and nonane, respectively; the carbon skeletons are shown in Fig. 6, and the linear dimensions of the molecules including hydrogen atoms are given in the following table^[15] (all dimensions in \AA):

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

On the other hand, when the dimensions of the activator and matrix molecules do not agree, the spectrum becomes poorer: the lines broaden and finally spread out into bands. Thus, for example, the spectrum of naphthalene in hexane and in heptane is poorer than that in pentane, owing to the greater degree of freedom in the geometric arrangement of the molecule. However, if the dimensions of the matrix molecule are less than those of the activator molecule, the deterioration of the spectrum is obviously due to the deformation of the activator molecule. An example of this is the spectrum of anthracene (molecular length 10 \AA) in pentane (molecular length 7.36 \AA). Here the

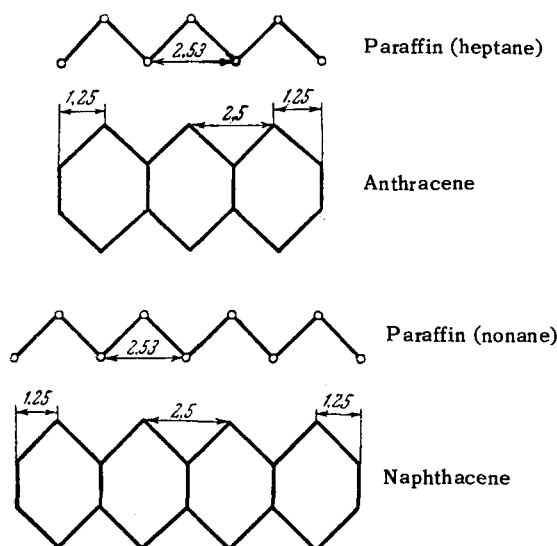


FIG. 6. Relation of the dimensions and shapes of the activator molecules and the paraffin matrix under the conditions most favorable for the appearance of the best resolution in the quasilinear spectra.

bands are relatively more diffuse than in the spectrum in hexane, for which the molecular dimensions agree completely.

While these very advantageous geometric correspondences are quite graphic and important, they do not settle the entire matter. It turns out that, in spite of considerable differences in crystal lattice, molecular structure, and chemical properties between the aromatic substance and the paraffin, there are strong features of correspondence. We can thus refer to them as approximate "molecular isomorphism."* In fact, a structure analysis of the linear aromatic hydrocarbons (see Robertson,^[15] where the references to the original literature are given) has shown that here the *a* and *b* axis dimensions remain the same, while the *c* axis increases by 2.5 \AA (just as in the paraffins) with the addition of each new benzene ring to the aromatic molecule. This is shown in Fig. 6. Thus, we find not only approximate equality of length between the activator and matrix molecules in the cases in which the quasilinear spectra are best resolved, but also geometric similarity of the zigzag structures ("synmorphism").

We see that such features of form analogy may play an essential role in the formation of substitutional solid solutions from: first, the qualitative consideration that this "synmorphism" must favor the formation of the mixed crystal, since it facilitates the fulfillment of a basic principle of organic crystal chemistry, that of "closest packing" (see Kitaigorodskii^[18]); second, this is also corroborated by the studies of Giuseppe Bruni, dating back as far as the beginning of this century (cited here on authority of^[16,17], since Bruni's monograph^[23] was not accessible to the author). Bruni himself was motivated by an interest in the opposite di-

*Bruni (see below) has called this property "synmorphism."

rection. On the basis of the fact that analogy of form of the molecules (symorphism) is necessary for the inclusion of a foreign molecule in the crystal structure, Bruni used the fact of formation of a mixed crystal to draw conclusions on the structure of one of two compounds crystallizing together, when the structure of the other compound is known with certainty. It is most interesting to note that Bruni had the courage to defend the correctness of the conclusions thus drawn, even in cases in which they contradicted chemical data. However, many of his conclusions have been subsequently confirmed by x-ray structure analysis. In particular, he was able to make especially definite conclusions, confirmed in all cases, on whether configurations were cis or trans, on the basis of co-crystallization with normal paraffins, whose molecules have zigzag structures corresponding to the trans-configuration. This is illustrated by the example^[16] given in Fig. 7.

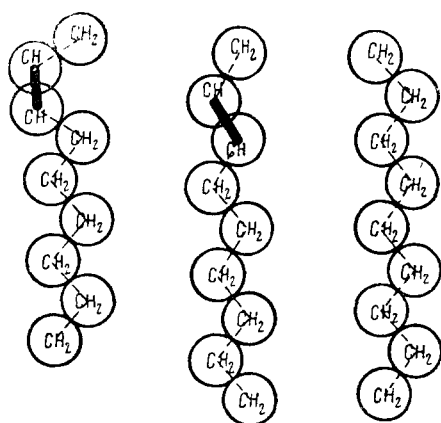


FIG. 7. At left: cis-configuration; in center: trans-configuration; at right: normal paraffin chain.

5. We consider now certain peculiarities of the spectra of organic compounds in frozen paraffin matrices. In many cases, the interaction between the emitting molecule and the crystal structure of the solvent is so weak that the activator may be considered to be actually an oriented gas, whose spectrum is not at all distorted by the crystalline matrix, except possibly for a small shift in the purely-electronic transition. However, in most cases, complications arise, consisting in the appearance in the spectrum of groups of closely-spaced lines having frequency differences from 3–5 to several tens of cm^{-1} . These groups are repeated throughout the luminescence spectrum without variation in spacing in the frequency scale; for the present, we shall conditionally call them “multiplets.” In the simplest case, e.g., coronene, these groups consist of pairs of lines (doublets), but in other cases the number of components can be considerably greater. Here, in the cases in which a sharp spectrum can be obtained in several solvents, the pattern of the spectrum varies according to the solvent. Thus, for example, coronene at 77°K in hexane, heptane, and octane

always exhibits doublets, but the frequency difference between the components varies from 86 cm^{-1} to 40 cm^{-1} ; on the other hand, 3,4-benzpyrene in various solvents shows a variation of both the number of components and of the spacings between them.

Let us discuss now the problem of the origin of these multiplets. In connection with the interpretation of the doublet spectrum of coronene, Bowen^[24] advanced the hypothesis that the relative displacement of the components of a multiplet is due to the fact that the activator molecules can be fixed in the matrix in two mutually-perpendicular orientations. This hypothesis, however, cannot explain the origin of multiplets consisting of a large number of components (as many as 7–8) or certain other facts. A detailed analysis of the various possible explanations of the origin of the multiplets has been given elsewhere.^[1] Without repeating this analysis here, we note that in any explanation we must keep in mind the following important facts, which we have firmly established for a large number of examples:

1) The entire first multiplet exhibited in emission, whatever its number of components, is always in its entirety a resonance multiplet. That is, every line in the first multiplet in emission corresponds to an absorption line of exactly the same frequency.

2) The head multiplet is repeated further throughout the emission spectrum with exact maintenance of the frequency differences between the components. This may be given an interpretation such that each line of the head multiplet is the origin of a resonance series of vibrational frequencies, and all these series are exact copies of one another, but are relatively shifted by the amount of the multiplet splitting (Fig. 8, see insert).

3) When we compare the frequency differences (splittings) in the multiplets of various activators in several solvents, we find that different activators in the same solvents exhibit exactly the same frequency differences, and indeed with the intensity distribution characteristic of each solvent. This shows that the amount of splitting depends not so much on the activator as on the solvent.

4) While the value $\Delta\nu$ remains strictly constant, the intensity distribution in a multiplet can vary as a function of external factors, as for example, the rate of freezing. There is always an element of chance, but only in the intensity distribution as a function of the conditions of freezing.

The combination of these facts, we believe, indicates the following:

a) The “multiplets” are not really multiplets, i.e., they are not groups of lines arising from the removal of some sort of degeneracy in a given atom or molecule. On the contrary, in this case the “multiplets” apparently arise from the grouping of a few relatively displaced electronic-vibrational sequences belonging

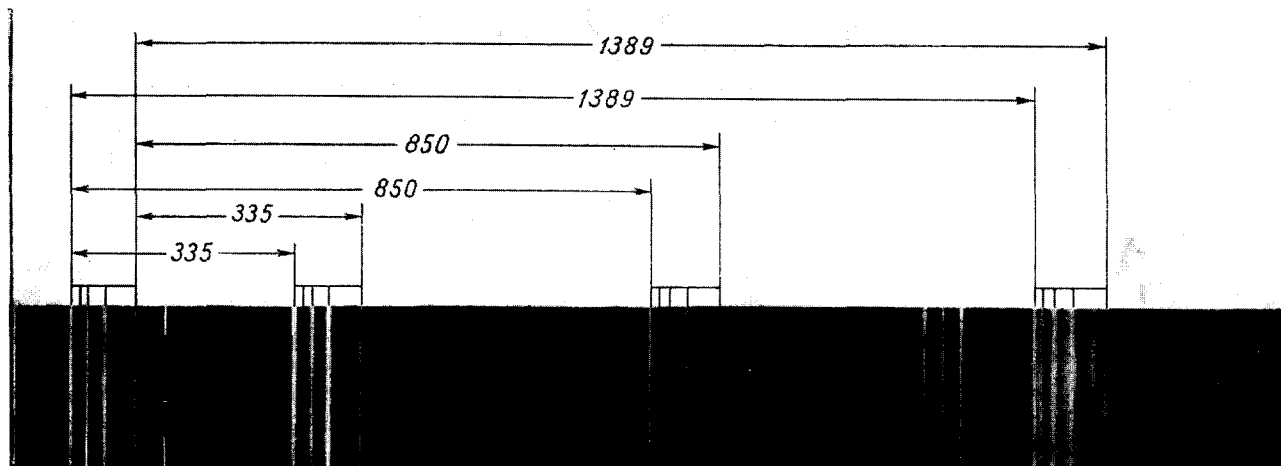


FIG. 8. Interpretation of the fluorescence spectrum of 3,4-benzpyrene in n-heptane, $T = 20^\circ \text{K}$ (Shpol'skii and Klimova).¹

to molecules in differing spatial arrangements.

b) We must consider the source of the variety of sequences to be local differences in the crystal field in which the emitting molecules are situated; these differences influence the energy of the purely-electronic transition, but have no effect on the vibrational levels.

These conclusions seem indisputable to us. However, they still do not solve the problem of just what changes in the internal structure of the crystalline solvent give rise to the variations in the local field leading to discrete differences in the energy of the purely-electronic transition.

This fact (i.e., the discreteness) is quite essential, and it must be emphasized very strongly. As has been said, the conditions of freezing can influence the intensity distribution among the multiplet components, but not at all their frequencies. With slow cooling, the intensities of certain components may even decrease to zero, but then the entire resonance series vanishes simultaneously. That is, the given line is absent in every multiplet, while all the other frequencies strictly maintain their original values. This shows that the local variability of the field is in turn due to a discretely variable and exactly reproducible set of causes.

The problem of the causes of these discrete variations is of great interest, both from the standpoint of spectroscopy and from that of the fine structure of the solid state, if we may so call it. The discovery of these causes is a problem still awaiting complete solution. However, it is already quite in order to discuss the possible sources of the local variations in the molecular field in the crystalline solvent.

Here we must note first of all that these sources may be of differing origins. Thus, for example, in case of polymorphism, rapid freezing may lead to the coexistence of different polymorphic modifications in the frozen solvent. Consequently, the shift in the electronic-transition energy of a given activator molecule will depend on which particular modification it is situated in.

The question naturally arises of just what is known about polymorphism in the normal paraffins.

If we refer to the literature, we find that the normal paraffins (and probably, long-chain organic molecules in general) are actually polymorphic as a class, according to Robertson,^[15] the most authoritative specialist in the application of x-ray structure analysis to the study of the structures of organic molecules. The polymorphism, which in this case has been confirmed both by x-ray and by thermal data and microscopic studies, is manifested in a peculiar way. In particular, it turns out that there is a certain normal form (class A, according to Robertson), in which the molecules are arranged with their long axes perpendicular to the (001) plane of the rectangular unit cell. In this modification, the period l obviously coincides with the length of the molecule. Besides this normal form, there are at least two other forms of lower symmetry (B and C, according to Robertson). In these, the molecular axes are inclined at constant small angles to the (001) plane, and the periods are correspondingly shorter than in the A form. However, since the number of possible crystalline forms of a given substance is limited to two or three, this factor also cannot fully explain the number of components of the multiplets, since this number may be as large as eight.

In discussing the problem at hand, we must naturally take into account all the physical and structural properties of the normal paraffins. In the case of the normal paraffins, as we have seen, the geometry of the molecules and the conditions of spatial packing play important roles. However, these conditions in turn are governed by the fact that the paraffins which we use are long chains whose basic skeletons consist of carbon atoms linked by covalent forces. We must now consider what other properties such molecules possess, besides those mentioned, and we must search among these properties for ones which might explain the different peculiarities of our quasilinear spectra, in particular their multiplet structure.

Among these properties, we shall discuss especially the ability to form the so-called rotational isomers, a characteristic of long-chain molecules having atoms linked by single bonds. Briefly speaking, the essence of the matter is the following. The planar zigzag form of the carbon skeleton of a normal paraffin, which we discussed above, is the stablest form in the crystalline state, but it is not the only form. In addition, we also find a series of other relatively stable forms in which certain parts of the molecule are rotated with respect to others. Hence the potential-energy curve of the molecule as a function of the rotation angle shows a discrete set of minima. Obviously, molecules of this sort have the same composition, i.e., they are isomers. However, in addition, these molecules differ both in their configuration and by virtue of the fact that their internal energies may vary by an amount of the order of 1 kcal, or about 0.05 eV. However, the presence of a rotational isomer instead of a normal paraffin molecule at any site within the crystal amounts to a lattice defect. If an activator molecule is located near this defect site, it will be subjected to the action of the locally-altered field, which in turn will bring about a shift in the electronic levels.

We might make the following objection to this. It is usually considered that the rotational isomers exist only in the gaseous and liquid states, but the crystalline state (as is usually stated) should contain only molecules of the stablest planar form. The basis for this statement is the fact that the vibrational (infrared and Raman) spectra of a given substance exhibit differing numbers of separate frequencies in the liquid and the crystalline states. In particular, the crystalline state manifests fewer characteristic frequencies than the liquid state. This is then ascribed to the existence in the crystalline state of only the normal "planar" form of the molecule, while the liquid state contains the rotational isomers as well. We can see an example of this difference in the infrared spectra of the two normal paraffins shown in Fig. 9.*

However, it seems to me that under our conditions of freezing, it is still possible to retain the rotational isomers in the solid state. Indeed, we ordinarily carry out the freezing process with catastrophic speed (from the standpoint of crystallization conditions), i.e., within one or two minutes. Even in the cases which we consider slow freezing, it hardly takes longer than ten minutes. Under such conditions, the rotational isomers might be retained in the crystalline state owing to a sort of "quenching." Finally, if we bear in mind the fact that the sensitivity of the electronic-vibrational spectra surpasses that of the purely vibrational infrared and Raman spectra by six to eight orders of magnitude, then the commonly advanced argument of the absence of rotational isomers in the crys-

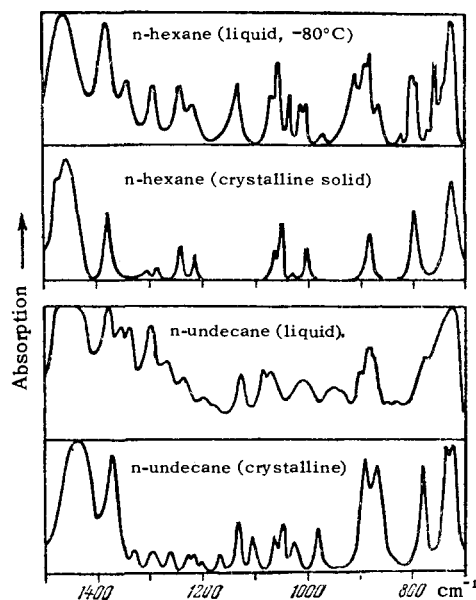


FIG. 9. Infrared spectra of the normal paraffins.

talline state under our conditions of study cannot be considered to be convincing. On the contrary, the fact seems unavoidable to us that, inasmuch as rotational isomers generally exist, as must be considered to be proved, the method of quasilinear spectra in crystalline solutions must exhibit the highest sensitivity for their detection.

However, this is still not all. When we examine the conditions under which an activator molecule exists in the frozen paraffin matrix, we find it reasonable to take into account another important peculiarity of liquids, most distinctly manifested among the normal paraffins and other chain- or rod-like molecules, e.g., the higher normal alcohols, the normal fatty acids, etc. I have in mind the so-called quasicrystalline structure of liquids. As we know, a liquid occupies a position intermediate between a gas and a crystalline solid. We ordinarily emphasize the properties of liquids in which they resemble gases. However, it has recently been shown quite clearly, especially by Ya. I. Frenkel',^[20] that it is no less important to bear in mind the properties of liquids in which they resemble solids. In particular, as early as the late twenties, the American physicist G. W. Stewart showed that the diffraction phenomena observed when an x-ray beam passes through a liquid (the so-called haloes) are not due to the presence in the liquid of microcrystallites, but rather, are due to an ordered spatial arrangement of the molecules. In discussing the reasons for such an ordered arrangement of the molecules in a liquid, Stewart stated that the shape of the molecules must play an important role. Thus, if a molecule has a cigar- or rod-like shape, the probability of parallel grouping of molecules will be greater than that of any other grouping, and it is not at all remarkable if molecules of elongated shape turn out to be arranged in parallel. This

*As we can see from Fig. 9, this difference is at least dubious for undecane.

parallel orientation of rod-like molecules has been subsequently confirmed by a number of highly-varied other phenomena: the formation of monomolecular layers of fatty acids on water surfaces (Langmuir and Adam), and the parallel orientation of chain molecules adsorbed on the surface of a metal or at a phase boundary (Trillat).

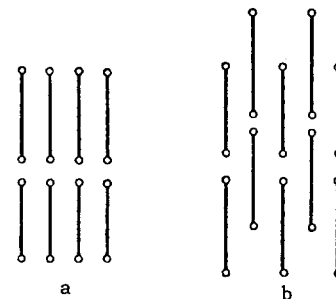
However, we must not imagine that the ordered arrangement of the molecules extends throughout the volume of the liquid. On the contrary, at each instant small ordered groups can exist at numerous points within the liquid, while the regions between these groups will not be so highly ordered. Stewart has denoted these ordered groups of molecules, especially those of chain-like form, as "cybotactic groups." In the limiting case of especially long chains, the cybotactic groups are transformed into "swarms" of macroscopic dimensions, responsible for the peculiar properties of the so-called liquid crystals and anisotropic liquids.

The cybotactic groups are a certain type of "assembly parts" or "blocks" or "building bricks" which play an important role in the formation of a real crystal. As is known, a macroscopic "single crystal" as grown is an assemblage of this sort of blocks, rather than a strictly regular periodic sequence of molecules.

Our hypothesis on the role of anomalous paraffin molecules (rotational isomers) in the origin of the "multiplets" is essentially supplemented by taking into account the existence of short-range order and "blocks." In fact, on the one hand, there is an especially crucial proof of the existence of ordered groups in a liquid in the particular case of chain- or rod-like molecules, e.g., the normal paraffins (pentane, hexane, heptane, etc., up to pentadecane). Here the x-ray diffraction patterns show sharp maxima. Now, knowing the experimental geometry, if we use the Bragg equation $\lambda = 2d \sin \vartheta$ to determine the value of d , the repeat period or "lattice parameter" of the quasi-crystalline group, we find that d is about 5 Å. However, this is just the diameter of the packing cylinder of paraffin molecules. This shows that the cybotactic group in the paraffin case consists of long molecules arranged more or less in parallel (for a review and references to the original research, see [21]).

However, two cases are possible with a parallel arrangement of chain molecules: the molecules may be arranged like matches in a box, i.e., so that their ends of the same kind lie in a single plane (Fig. 10a), or in such a way that they retain their parallel orientation, but their ends are arranged at random (Fig. 10b). The two arrangements differ in their x-ray diffraction patterns in that additional diffraction maxima appear in the former case, corresponding to the length of the molecule, or twice the length (in the case of the fatty acids). It is precisely the former case which corre-

FIG. 10. Two possible parallel arrangements of chain molecules (a and b).



sponds to the x-ray diffraction patterns of the normal paraffins in the liquid state.*

According to our hypothesis, a molecule of an organic activator must be incorporated in a suitable group. On the other hand, the actual existence of rotational isomers among the paraffin molecules is also an unquestionable fact. Thus, even before crystallization, we have in the solution a certain number of types of discrete luminescence centers, which are preserved during the transition to the solid state.†

Unfortunately, there is no hope of experimentally confirming this picture by x-ray structural studies. In fact, whereas the cybotactic groups in the case of the normal paraffins are probably very small, this periodicity would have to extend over many millions of molecules in order to be detected by x-ray methods.

On the other hand, the great sensitivity of the electronic transitions to the external field conditions and the exceedingly narrow lines in our linear spectra make it possible to detect changes within dimensions of almost literally two or three molecular diameters. Thus the only possibility of testing such a hypothesis involves precisely the use of spectroscopic methods.

The following important fact has been known for a long time in our own and other laboratories using our methods, but has not been explained thus far. However, it now becomes comprehensible. Namely, if the sol-

*Both cases occur in liquid crystals consisting of very long molecules. The state corresponding to the former case is termed the smectic state, while the latter is termed nematic.

†Recently H. Spöner and her associates^[22] studied the quasi-linear triplet-singlet spectrum of benzene molecules in a cyclohexane matrix frozen at 77° and 4° K. At 4° K, this spectrum consisted of doublets with $\Delta\nu = 59 \text{ cm}^{-1}$, maintained precisely throughout the spectrum exactly as occurs in our experiments in all cases in which the lines are grouped in "multiplets." The authors attribute the appearance of the doublets to the formation of cybotactic groups consisting of four molecules (corresponding to the four molecules in the cyclohexane unit cell). These groups may consist either of matrix molecules alone (C-C-C-C), or of mixed groups (C-B-C-C) or (C-B-C-B-C); here the position of the B molecule with respect to the C molecule probably plays no role. Thus in this interpretation, the appearance of the doublets is explained by the formation of two discrete types of "centers": molecular and dimeric centers with respect to benzene molecules. Here the relative displacement of the spectra is explained by the influence of the surroundings on the energy of the purely-electronic transition.

vent does not give a fine structure, the multiplet is replaced by a corresponding broad band. However, if we add to such a solvent a normal paraffin whose molecules are of suitable length, even in small amount, the entire finely-structured spectrum appears simultaneously. This phenomenon was used in a study by Muel and Lacroix^[19a] concerning the development of a method for quantitative analysis for 3,4-benzpyrene using quasilinear spectra, as follows: 3,4-benzpyrene in cyclohexane solution does not give a fine structure on freezing; the addition to the cyclohexane of no more than 10% n-octane leads to the appearance of a quasilinear spectrum exactly reproducing the multiplet structure characteristic of frozen octane solutions. The most plausible explanation of this fact, strange at first glance, we suppose, consists in the peculiarity of a long chain, such as in octane, to form cybotactic groups, which incorporate the activator molecules.

This suggests the possibility of using activator molecules as intentionally added indicators or probes permitting us to make apparent subtle changes or defects in the internal structure of the solid state, by well-known analogy with what is currently being done with the Mössbauer effect.

I have attempted in this article to discuss the conditions for appearance of quasilinear spectra in paraffin matrices, adducing various physical, physicochemical, and crystal-chemical data. We may hope that further study of these spectra will not only supplement our knowledge of the spectra and structure of a number of molecules which are important in practice and interesting theoretically, but will also provide quite a bit of information of value in the study of the structure of the solid state.

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