U. D. C. 543.421

# Shpol'skii's Method in the Spectroscopy of Polyatomic Molecules

R.N.Nurmukhametov

This review examines various general historical aspects of Shpol'skii's method, together with the results obtained for various classes of organic compound; problems of the relationship between the form of the vibronic spectrum and molecular structure are considered, and various analytical applications of the procedure of quasi-line spectra are described briefly. The bibliography contains 161 references.

CONTENTS

1. Shpol'skii's spectra. Future prospects in research and its applications 180
2. Results from the quasi-line spectra of various classes of compound 182
3. The vibronic spectrum and molecular structure 188
4. Spectroscopic-analytical applications 190

## 1. SHPOL'SKII'S SPECTRA. FUTURE PROSPECTS IN RESEARCH AND ITS APPLICATIONS

A molecule is a quantum system with a discrete set of characteristic energy states, but the electronic spectra of molecules usually have the form of broad bands with little structure.

In practice we study the spectra not of a single isolated molecule, but of a large number of molecules undergoing greater or lesser external perturbation. It might seem that the spectra of vapours should be closest to the spectrum of an individual molecule, but the spectra of vapours of polyatomic molecules are generally extremely unsharp. Without going into all the reasons for the lack of sharpness in the structure of the electronic bands of vapours, we would merely mention as an obvious factor the "spreading" of the vibrational sublevels of the quasi-continuous system of rotational sublevels (due to the small magnitude of $\Delta E_{rot} \simeq 1\ cm^{-1}$). As a result of this and other factors, the unsharp structure cannot be resolved, irrespective of the resolving power of the instrument. It should also be mentioned that many compounds are unstable in the vapour state.

Aromatic polyatomic molecules are usually studied in the condensed phase, in the form of liquid and solid solutions, or pure and mixed crystals. The best spectral resolution in the condensed phase is obtained at low temperatures for crystals and solid solutions. Molecular rotation is restricted at low temperature. Moreover, nonradiative processes are suppressed at low temperatures, leading to an intensification of fluorescence and the appearance of the intercombinationally forbidden $T-S_0$ emission—phosphorescence. For a long time it was assumed that the intramolecular factors leading to loss of sharpness in the structure were the principal factors, so that it was assumed to be impossible to improve the resolution of the structure by altering the molecular environment.

In 1952, Shpol'skii and coworkers[1] obtained the quasi-line spectra of a number of complex aromatic molecules in frozen crystalline solutions. The discovery of the quasi-line spectra of polyatomic molecules stimulated a large number of new studies in the field of the electronic spectroscopy of complex organic compounds. The investigation of the origin of the electronic spectrum of a molecule involves two types of problem: 1) the determination of the frequency of the electronic transition, and its interpretation; and 2) the determination of the mechanism of formation of the band contours, that is the interpretation of its vibrational structure. Problems of the first type were solved with some approximation from spectra with broad bands, but the solution of problems of the second type could be solved only by resolving the structure of the bands. Quasi-line spectra are very characteristic, and they can be used to determine with high accuracy the frequency and intensity of the purely electronic band and the vibrational frequencies combining with the given electronic transition. These spectra reflect more deeply the characteristic features of the electronic and spatial structures of a molecule (this is examined in detail in section 3). Examination of the dependence of the vibronic spectra on structure can be used to find possible answers to the following questions: why is the observed system of electronic bands characteristic of the molecule, what is the mechanism of formation of the bands (the vibrational structure), and what contribution do the various atomic groups constituting the molecule make to its electronic state? The form of the vibrational structure and its degree of resolution are closely related to the nature of the electronic transition, so that the structure can give definite information on the nature of the transition responsible for the electronic band being considered. On the other hand, if we know the relationship between the nature of a transition and the structure of the band, it is possible to predict beforehand the expected form of the vibrational structure and the changes which it undergoes with change in the nature of the electronic transition, which in turn may be changed by definite changes in the structure of the molecule.

The manifestation of the frequency ranges representing a combination or overtone of the normal vibrations makes it possible to examine the problems of the interaction of vibrations and the form of the potential surface. In particular, the decrease in the frequency range in the overtones relative to the additive sum establishes the degree of anharmonicity of the potential curve. The interpretation of the vibrational structure makes it possible to determine which vibrations are involved in the most effective conversion of the electronic excitation energy into vibrational energy. Quasi-line absorption spectra reveal the frequencies of the vibrations of molecules in electronically excited states. Thus the examination of these spectra provides a simple method for determining the vibrational frequencies of excited molecules.

At first, the range of molecules studied was restricted to aromatic polycyclic condensed hydrocarbons. These molecules have a rigid planar structure, and this facilitates

resolution of the vibrational structure of the bands, which, moreover, are determined in the near ultraviolet and visible ranges by the same type of $\pi-\pi^*$ transition. It was not clear whether it was possible to obtain a quasi-line spectrum for molecules containing heteroatoms. In 1958, Shigorin and coworkers[2] reported the quasi-line luminescence spectrum of anthraquinone and its derivatives. Subsequently, Shpol'skii's method was successfuly extended to the molecules of compounds of various classes. A quasi-line structure was not always obtained, particularly for molecules with a non-rigid structure, but a sufficiently clearly resolved vibrational structure, suitable for analysis, was often attained. From the degree of resolution, in turn, it was possible to obtain information on the intramolecular factors leading to loss of sharpness of the bands, and on the spatial structure of the molecules. The stabilisation of certain radicals in solid matrices at low temperatures makes it possible to obtain Shpol'skii's quasi-line spectra not only for molecules, but also for radicals (see R.p. 355).

A large number of studies have been devoted to the vibronic spectra of aromatic molecules, with a chain structure, widely used as scintillating additives (polyphenyls, diphenylpolyenes, arylethylenes, aryloxadiazoles, diarildivinylbenzenes, arylnaphthoxazoles, benzoxazoles, etc.). Shpol'skii's method has been used to study the spectra of aromatic aldehydes, ketones, diketones, various dyes and related compounds (xanthone, acridones, phthalimides, thioindigoids, and indigoids), and *N*-heteroaromatic molecules (the aza-heteroanalogues of triphenylene, quinoline, and bipyridyls). Finally, a quasi-line structure has been obtained for the spectra of the complex molecules of phthalocyanines and porphyrins.

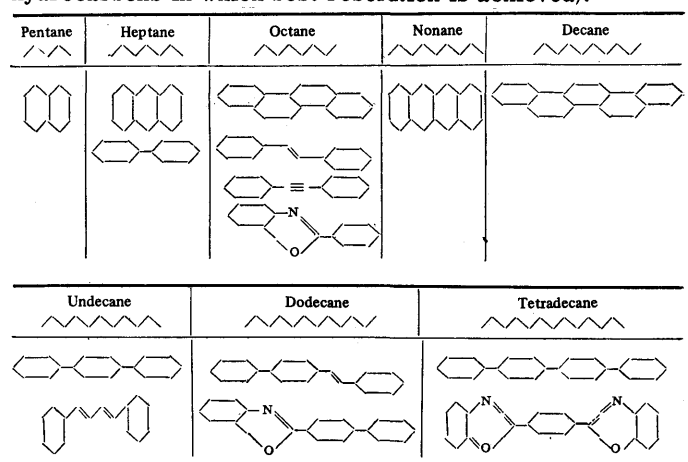
To obtain quasi-line spectra, Shpol'skii and coworkers used a comparatively simple procedure, which can be described briefly as follows: 1) highly dilute solutions with concentrations of $10^{-4}$–$10^{-5}$ M are used, so that there is almost no interaction between the dissolved molecules; 2) inert neutral solvents—saturated n-hydrocarbons—are used as media; 3) the solutions are cooled to low temperature (77, 20, and 4 °K) and are frozen to form a crystalline mass; and 4) the spectra of these frozen solutions are studied.

By the use of mixed solvents, Shpol'skii's method was extended to compounds which do not dissolve directly in n-hydrocarbons. Thus the spectra of phthalocyanines was obtained with a solution in acetone[3], which was then diluted with n-hydrocarbons. When a benzene solution of perylene was diluted with hexane, the spectrum obtained did not differ from the spectrum of the pure hexane solution[4]. Indigo and indigoids were dissolved in hexane by means of a dioxan solution[5]. A similar technique was used to obtain the spectra of *N*-substituted acridones[6,7].

The range of matrices in which a quasi-line structure can be obtained has been extended. Sponer, Kanda, and coworkers[8-10] showed that these spectra are also obtained in a cyclohexane matrix. Sheremet'ev and Val'dman[11] obtained the quasi-line spectrum of perylene in dibenzylaminoethanol. We showed for the example of pyrene in poly-2-methylpropene[12,13] that it is possible to resolve a quasi-line structure in a polymeric matrix. It has been reported[4] that the spectra of pyrene show a quasi-line structure in hexanol at 77 °K.

A remarkable characteristic feature of quasi-line spectra is the frequently observed multiplet structure of the vibronic bands, so that the spectrum consists of the superposition of several identical molecular spectra, displaced relative to one another. The degree of resolution and the multiplet structure of the bands are found to be very characteristic of the solute–solvent system. Analysis of the characteristic features of quasi-line spectra established one important reason for the loss of sharpness in the spectra of solid solutions—non-uniform perturbation of the electronic levels of the dissolved molecules by the field of the environment (as a result of non-uniformity of the matrix) leading to dispersion of the energies (frequencies) of the electronic transitions in the set of molecules. Experiment shows that it is possible to eliminate this dispersion by choice of a suitable solvent. Although there is no general rule for the selection of a solvent in which we can expect the best resolution of the structure for a given compound, in some instances it is possible to use a relationship established by Bolotnikova[14-16], who showed that the best resolution of the spectra of polyacenes is observed in those hydrocarbons whose molecular dimensions are close to those of the polyacene. Thus the best resolution was obtained in pentane for naphthalene, in heptane for anthracene, and in nonane for naphthacene (Table 1). A similar result was obtained for the angular hydrocarbons chrysene[17], picene[18], and benzanthracene[19]. Gobov[20,21] showed that this rule is applicable for the biphenyl–terphenyl–quaterphenyl series, for the diphenylpolyenes stilbene and diphenylbutadiene, and for various benzoxazoles[22] (see Table 1). It is not a universal rule, however. As

Table 1. The role of correspondence in the dimensions of the molecules of the solvent and the luminophor in improving the resolution of the vibrational structure of electronic bands. The upper row gives the carbon frameworks of the n-hydrocarbon molecules, and the lower row gives the frameworks of the luminophor molecules (under the n-hydrocarbons in which best resolution is achieved).




an illustration, we would point out that the spectrum of 1,4-distyrylbenzene, whose molecule is longer, by the length of the styryl group, than that of stilbene, is most clearly defined in hexane[23], and not in n-hydrocarbons with a longer chain. The high sensitivity of the structure to the solvent, concentration, and method of freezing, and in some instances to the presence of impurities, provides an effective indicator for the study of the fine effects of intermolecular interaction.

We shall not consider in detail experimental data on the investigation of the nature of the multiplet structure[24-26]; these are discussed in detail in reviews by Shpol'skii[4,27-30]. The aim of the present review is to examine the progress made in the study and interpretation of the vibronic spectra of molecules of various classes, and the new information which has been obtained on the relationship between electronic spectra and structure (the manifestation, in the spectra, of the characteristic features of the electronic transition and the electronic and spatial structures of the molecules, particularly in the excited state). A quasi-line structure cannot be obtained for all molecules. In the present review an attempt is made to determine which factors of the intramolecular structure influence the resolution (or lack of resolution) of the structure.

The high sensitivity and characteristic nature of quasi-line spectra have provided a basis for a number of spectroscopic-analytical methods for the qualitative and quantitative determination of substances in various products. These problems will be examined in section 4.

## 2. THE QUASI-LINE SPECTRA OF VARIOUS CLASSES OF COMPOUND

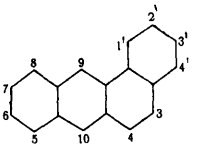
Aromatic polycyclic condensed hydrocarbons. The compounds of this class which have been studied by Shpol'skii's method are given in Table 2; for all of these, a quasi-line structure has been obtained in a suitable solvent. A general characteristic feature of the vibrational structure of the electronic bands for compounds of this class is that the frequencies of the normal vibrations of the carbon framework predominate. The vibrational frequencies active in the luminescence spectra correspond to the vibrations of the molecule in the ground electronic state and are equal to or very close to the frequencies active in the Raman spectrum of the same compound. Another characteristic feature of the structure of the electronic bands of aromatic hydrocarbons is the appearance of common frequencies with very similar values. An analogous picture of very similar frequencies is observed in the infrared spectra of various aromatic hydrocarbons, so that the spectra are not characteristic, and are unsuitable for analytical purposes. We shall not deal in detail with the problems of the relationship between the vibronic spectra and the structure of molecules of this class, since this has already been done[62].

Table 2. Aromatic condensed hydrocarbons with quasi-line spectra which have been studied.

| Compound | References | Compound | References |
|---|---|---|---|
| Benzene | 8,31,32 | 1,2,4,5-Dibenzpyrene | 48 |
| Naphthalene | 15,33-35 | 3,4-Naphtho-6,7-benzpyrene | 47 |
| Anthracene | 14,16,36,37 | 3,4,8,9-Dibenzpyrene | 48 |
| Naphthacene | 14,16,37 | 1,12-Benzperylene | 49,50 |
| Phenanthrene | 38-41 | Perylene | 51-53 |
| Benzanthracene | 19 | Triphenylene | 54,55 |
| Chrysene | 17 | Fluoranthene | 56 |
| Dibenzanthracene | 14 | Fluorene | 8,57,58 |
| Pyrene | 14,42,43 | Acenaphthene | 58,59 |
| 1,2-Benzpyrene | 44 | Rubicene | 60 |
| 3,4-Benzpyrene | 45 | Azulene | 61 |
| Picene | 18,46 | Pentacene | 46 |
| Penthaphene | 46 | Benznaphthalene | 46 |

Aromatic hydrocarbon radicals. Grajcar and Leach[63] obtained absorption spectra ($\nu_{0-0} = 21\,580\ cm^{-1}$) and fluorescence spectra ($\nu_{0-0} = 21\,630\ cm^{-1}$) showing considerable structure for the benzyl radical at 77°K in a methylcyclohexane + 3-methylpentane (2:3) matrix. The fluorescence spectra showed vibrational frequencies of 570, 965, 1050, 1295, and 1460 $cm^{-1}$, some of which are close to the vibrational frequencies of benzene. Ripoche[64] studied the fluorescence spectra at 88°K for benzyl radicals, again produced by the photolysis of toluene, in new matrices—cyclopentane, methylcyclopentane, and methylcyclohexane. Under these conditions he obtained quasi-line spectra with a large number of quasi-lines; he made a detailed vibrational analysis and assigned the frequencies to definite types of normal vibration. Vibrational frequencies were distinguished at 363, 532, 820, 872, 982, 1017, 1087, 1145, 1376, 1439, 1475, 1540, and 1593 $cm^{-1}$ (in cyclopentane). Mileshina and coworkers[65] obtained the quasi-line fluorescence spectrum of the diphenylmethylene biradical in a hexane matrix at 77°K. This spectrum is due to a $T^* \rightarrow T_0$ transition (the ground state of diphenylmethylene is a triplet state) and is interpreted by means of the frequencies 630, 800, 1012, 1170, and 1600 $cm^{-1}$, which are close to the vibrational frequencies of the benzene ring, active in the fluorescence spectra of the benzyl and triphenylmethyl radicals.

Substituted aromatic hydrocarbons. The introduction of substituents influences the electronic structure, electronic transitions, symmetry, and spatial configuration of the molecule, and alters its dimensions and the nature of its interaction with solvent molecules. All this is reflected not only in the position and intensity of the electronic bands, but also in the nature of the vibrational structure and its degree of resolution. Let us consider first the spectra of alkyl, halogeno, and vinyl derivatives of aromatic hydrocarbons. Kharitonova[66] studied the quasi-line spectra of $\alpha$- and $\beta$-methylnaphthalenes in hexane at 20°K. Dikun[67,68] obtained the quasi-line spectra of ~ 40 derivatives of 1,2-benzanthracene with alkyl and halogeno substituents.



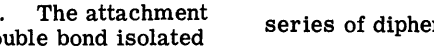

Fenina[19,69] carried out a more detailed study and interpretation of the vibrational structure of the fluorescence spectra of 1,2-benzanthracene and all its monomethyl derivatives, and from the quasi-line spectra determined the frequencies of the long-wave $^1L_b$–$^1A_1$ transition. The maximal long-wave displacement (450 $cm^{-1}$) was observed when the $CH_3$ group was introduced into position 9 or 10, a marked displacement was observed for the 3-methyl derivative (300 $cm^{-1}$), approximately equal medium displacements of 100 $cm^{-1}$ were observed for substitution in the 1'-, 2'-, 4'-, and 7-positions, a small displacement was observed for the 3'-, 5-, 8-, and 4-$CH_3$ derivatives, and 6-$CH_3$-benzanthracene even showed a slight short-wave displacement. The values of the displacements only in a few instances agree with the predictions of the theory of the influence of alkyl substituents on the energy of the electronic transitions of benzanthracene. On the basis of an analysis of the quasi-line absorption spectra it was concluded that the frequency of the $^1L_a$–$^1A_1$ transition in benzanthracene is 1600–1700 $cm^{-1}$ higher than the frequency of the $^1L_b$–$^1A_1$ transition. The spectra of all the derivatives

except the 3-methyl derivative were sharper in octane. The spectra of the 3-methyl derivative are equally sharp in hexane and heptane, and less sharp in octane.. The sterically hindered substituents in positions 9 and 1′ produce a marked decrease in the sharpness of the structure. Utkina [70-72] made a systematic study of anthracene derivatives, and showed that the introduction of alkyl substituents (methyl, ethyl, and propyl) lowers the frequency of the electronic transition by about 700–750 $cm^{-1}$, and the introduction of two alkyl substituents produces a displacement which is approximately twice this value. The attachment of an allyl radical with the $-CH=CH_2$ double bond isolated from the $\pi$ system of the anthracene nucleus produces the same displacement of the spectra as alkyl radicals. When the double bond is conjugated (in 9-vinylanthracene), however, the long-wave displacement of the band amounts to about 2000 $cm^{-1}$, that is by an amount characteristic of an increase in the $\pi$ system by a double bond in the direction of the electronic transition being considered. The structure of the fluorescence spectrum is less sharp, the greater the steric hindrance in the molecule. A particularly marked decrease in sharpness is observed as a result of the introduction of vinyl groups. The phenanthrene derivative retene gave a quasi-line structure very similar to the structure of the spectra of the unsubstituted molecule. A quasi-line structure was also obtained for halogenopyrenes. The introduction of halogens improves the resolution of the structure considerably. Val'dman [11] obtained a quasi-line fluorescence spectrum for a complex derivative of perylene—di-isobutyl perylene-3,9-dicarboxylate. Hydrocarbon derivatives containing the electron-donating groups $NR_2$, NR, OR, and SR (aromatic amines, ethers, and thioethers) will be examined below.

N-Heteroanalogues of aromatic hydrocarbons have been studied by Shpol'skii's method to a much smaller extent, apparently due to the difficulties encountered in the resolution of their structure. In the first place, many of these compounds either do not show fluorescence, or show only weak fluorescence in non-polar solvents, because of strong deactivation due to singlet–triplet conversion with the participation of excited $n-\pi^*$ states [73-76]. Secondly, thanks to the presence of the $n$ electrons of the N atom, these molecules readily undergo association with polar molecules, traces of which are almost always present in hydrocarbon solvents.

Mamedov described the quasi-line phosphorescence spectra of quinoline in hexane [77] and pentane [78] and of 5,6-benzquinoline in hexane [78]. Ruziewicz [79,80] resolved the structure of the phosphorescence bands of 1,4-diazotriphenylene and 1-azotriphenylene. El-Sayed [81] reported the quasi-line structure of the luminescence band of pyridazine in hexane.

Polyphenyls and diphenylpolyenes. Gobov [20,21,82-84] described the structure of the luminescence spectra of biphenyl, terphenyl, and quaterphenyl at 77 °K, and showed that the best resolution of the structure for the longer polyphenyl molecules is obtained in the hydrocarbons with longer chains: in hexane and heptane for biphenyl, in undecane for terphenyl, and in cetane ($C_{15}H_{30}$) for quaterphenyl. The fluorescence band of the O–O transition has a frequency of 33 355 $cm^{-1}$ in biphenyl, and lower values of 30 715 $cm^{-1}$ in terphenyl and 28 080 $cm^{-1}$ in quaterphenyl, that is the frequency is reduced by about 2600 $cm^{-1}$ with increase in the size of the molecule by one phenyl unit. A common characteristic of the structures of the fluorescence spectra of polyphenyls is the predominance of the frequency of the antisymmetric pulsating vibration of the benzene ring at 1600 $cm^{-1}$. In the spectra of terphenyl and quaterphenyl it forms intense progressions, determining the periodic form of the structure. The range of their fluorescence bands is determined by the overtones $4 \times 1600$ $cm^{-1}$. Biphenyl gives a structured phosphorescence band with $\nu_{0-0} = 22\,905$ $cm^{-1}$; visible phosphorescence is not observed for terphenyl and quaterphenyl.

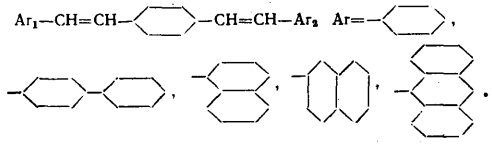
As early as 1935, Hausser and coworkers [85] made a systematic study of the absorption and luminescence spectra of a series of diphenylpolyenes  with $n = 1-7$. They observed a regular displacement of the spectra towards longer wavelengths with increase in the number of polyene groups in the molecule. The structures of the fluorescence spectra of diphenylpolyenes are very similar and are described by a series formula $\nu = \nu_0 - 1550\,n_1 - 1660\,n_2$, where $n_1 = 0.1$, $n_2 = 2.3$, and $\nu_0$ has values 29 730 $cm^{-1}$ for stilbene ($n = 1$), 27 250 $cm^{-1}$ for diphenylbutadiene ($n = 2$), 24 900 $cm^{-1}$ for diphenylhexatriene ($n = 3$), 22 135 $cm^{-1}$ for $n = 4$, and 19 870 $cm^{-1}$ for $n = 5$. The vibrational structure of the spectra of stilbene was subsequently studied many times. Gobov [83] and Levshin and Mamedov [86] resolved the vibrational structure of the fluorescence band and the long-wave absorption at 77 °K in octane. Malykhina and Shpak [87] studied the quasi-line spectra in polarised light for an octane–stilbene single crystal, and Dyck and McClure [88] made a similar study of a bibenzyl–stilbene single crystal. The frequency of the $S_1^*-S_0$ transition for stilbene is 30 034 $cm^{-1}$ in octane and 29 903 $cm^{-1}$ in bibenzyl. All the authors cited showed that the form of the spectrum is determined chiefly by the progressions of the frequency of the stretching vibration of the ethylene group ($\nu_{C=C}$ = 1640–1659 $cm^{-1}$ in fluorescence, and 1600 $cm^{-1}$ in absorption). The spectrum also shows another seven frequencies, observed independently and in combination with the above frequency; most of these seven frequencies are assigned to the skeletal vibrations of the benzene rings.

The structured fluorescence spectra of stilbene, diphenylbutadiene, and diphenylhexatriene show considerable resemblances to the spectra of polyphenyls. Their structure has a similar periodic form, determined by the progressions of the frequency of the stretching vibration of the ethylene and polyene groups. This frequency lies at 1640 $cm^{-1}$ in stilbene, 1616 $cm^{-1}$ in diphenylbutadiene, and 1600 $cm^{-1}$ in diphenylhexatriene (for the latter, only a coarse vibrational structure is observed; the spectrum [89] consists of broad bands with $\Delta\nu \simeq 400$ $cm^{-1}$). The band for the O–O transition in stilbene (30 034 $cm^{-1}$) is very close to the band for terphenyl (30 715 $cm^{-1}$), and the band for diphenylbutadiene (27 948 $cm^{-1}$) is very close to the band for quaterphenyl (28 080 $cm^{-1}$), so that the replacement of the internal phenyl units in the polyphenyl chain by an ethylenic bond does not alter significantly the position of the absorption and fluorescence bands of this chain $\pi$ system. This is true, however, only for the initial members of the polyphenyl series; with further increase in the length of the polyphenyl chain, the decrease in the frequency of the long-wave transition is much smaller than that for increase in the length of the polyene chain in diphenylpolyenes [90].

Arylethylenes. Fluorescence spectra of arylethylenes in n-hydrocarbons at 77 °K, with the most clearly defined structures, were obtained [89,91] for phenylstilbene in undecane and dodecane, and for di-$\alpha$-naphthylethylene, di-$\beta$-naphthylethylene, $\alpha$-naphthyl-$\beta$-naphthylethylene, and $\beta$-naphthylphenylethylene in hexane. The fluorescence

spectrum of diphenylstilbene in all n-hydrocarbons can be resolved only into broad bands ($\Delta\nu \simeq 300$ cm$^{-1}$). Decrease in temperature to 20°K did not lead to additional resolution of the structure of the spectrum of phenylstilbene; only a slight decrease in the width of the bands was observed[89]. A characteristic common feature of the vibronic spectra of arylethylenes is the periodic form of the structure. The period interval is a frequency in the range 1600–1640 cm$^{-1}$, assigned to the stretching vibration of the ethylenic bond. The frequency decreases with increase in the weight of the aryl radicals and with increase in the efficiency of the conjugation (estimated from the decrease in the frequency of the electronic transition). In the fluorescence spectra it has the value 1640 cm$^{-1}$ for stilbene, 1635 cm$^{-1}$ for β-naphthylphenylethylene, 1620 cm$^{-1}$ for phenylstilbene, 1610 cm$^{-1}$ for α-naphthyl-β-naphthylethylene, and 1600 cm$^{-1}$ for di-α-naphthylethylene. The width of the fluorescence band for these molecules is determined by the range $4 \times 1600$ cm$^{-1}$, and the maxima in the fluorescence spectrum at room temperature are separated from one another by about 1600 cm$^{-1}$.

Diaryldivinylbenzenes



The fluorescence spectra have been studied[23] at 77°K in hexane, heptane, octane, nonane, undecane, and heptadecane solutions. A well resolved vibrational structure was obtained for most compounds. The narrowest bands were obtained for solutions of distyrylbenzene and di-β-naphthyldivinylbenzene in hexane. The bands in the fluorescence spectra of bis(biphenyl)-, di-β-naphthyl, β-naphthylphenyl-, α-naphthylphenyl-, and biphenylphenyldivinylbenzenes were found to be more diffuse, but the fluorescence spectrum of dianthryldivinylbenzene has very narrow bands. The poor resolution of the structure for the latter compounds is due to the appreciably non-planar structure of the molecule, resulting from considerable steric hindrance. A common characteristic feature of the structured spectra of diaryldivinylbenzenes is the periodic form of the structure, in which the frequencies of the range 1550–1520 cm$^{-1}$, corresponding to the stretching vibrations of the divinylbenzene group and its overtones, predominate.

Arylacetylenes. Gobov[83] described the structure of the luminescence and absorption spectra of tolane in n-octane. The fluorescence spectrum was interpreted by means of the frequencies 260, 524, 700, 1000, 1150, 1493, 1600, and 2232 cm$^{-1}$; the same frequencies, with the exception of 524 cm$^{-1}$ and 1493 cm$^{-1}$, were distinguished in phosphorescence. The 2232 cm$^{-1}$ frequency, which is the most characteristic of the spectrum and combines with the other frequencies, shows appreciable anharmonicity and is assigned to the stretching vibration of the acetylenic group. In the absorption spectrum the frequency is lowered to 2150 cm$^{-1}$. The 1000 cm$^{-1}$ and 1600 cm$^{-1}$ frequencies were interpreted as characteristic frequencies of the benzene rings.

The structures of the long-wave absorption, fluorescence, and phosphorescence spectra of phenylacetylene have been described[92]. The triple bond vibrational frequency, whose value is lowered to 2100 cm$^{-1}$ as a result of kinematic factors, is also active in the luminescence spectra. This frequency, however, does not predominate in the spectrum, and the frequencies of the benzene ring, particularly the 1600 cm$^{-1}$ and 1000 cm$^{-1}$ frequencies, are equally active. In agreement with the low intensity of the long-wave absorption band, a relatively low intensity is observed for the O–O band, indicating an electronic transition partly forbidden by symmetry. The superposition of the incompletely symmetrical vibration at 600 cm$^{-1}$ partly removes the forbidden character. This is characteristic of benzene derivatives such as phenylacetylene, styrene, biphenyl, and naphthalene. The transition is not forbidden in phosphorescence. Phenylacetylene and tolane are characterised by a difference in the $S_1^* - T$ splitting of 10 000 cm$^{-1}$, which is the same as that in the polyacene series. Bagratishvili and coworkers[93] obtained the quasi-line fluorescence and phosphorescence spectra of bi-β-naphthyl, whose molecule is appreciably non-planar due to steric hindrance. The band structure contains many "naphthalene" frequencies.

Benzoxazoles and naphthoxazoles. The quasi-line fluorescence spectra of 2-phenylbenzoxazole, 2-biphenylylbenzoxazole, 2-styrylbenzoxazole, 1,4-di-(2′-benzoxazolyl)-benzene, and 1,4-di-(2′-benzoxazolyl)-ethylene in n-hydrocarbon solutions at 77°K have been described and interpreted[22]. It was shown that the fluorescence spectrum is determined by the $\pi-\pi^*$ transition, and that the $\pi$ system of these molecules is isoelectric with the $\pi$ system of the corresponding arylethylenes, for example the phenylbenzoxazole and stilbene molecules are $\pi$ isoelectronic. The interaction of the unshared pairs of electrons of the O and N heteroatoms appears to lead to mutual exclusion of their influence on the $\pi$ electronic system. The similarity in the $\pi$ electronic structures leads not only to similar electronic bands and identical luminescence and scintillation properties, but also to an identical mechanism of formation of the vibrational structure of the bands. The structure of the spectra is characterised by a periodicity. The period corresponds to the stretching vibrations of the internal connecting group. In the phenylbenzoxazole molecule this is the C–N bond of the oxazole ring, and the predominant frequencies in the structure are those at 920, 1550, and 1610 cm$^{-1}$, which, according to the interpretation of the vibrational spectra[94] are the characteristic vibrations of the oxazole ring. In the molecules of 2-biphenylylbenzoxazole and 1,4-di-(2′benzoxazolyl)-benzene, the internal connecting group consists of a C=N bond and a phenyl ring; in the structure of the spectrum, the 1600 cm$^{-1}$ vibrational frequency of the phenyl ring is correspondingly more active. In the molecules of 2-styrylbenzoxazole and 1,4-di-(2′-benzoxazolyl)-ethylene, this frequency is replaced by the vibrational frequency of the ethylenic group at 1640 cm$^{-1}$. The structures of the absorption spectra of these compounds have been obtained and analysed[95]. Very clearly defined structures were observed for the vibronic fluorescence and absorption spectra[96] of phenylnaphthoxazoles; the biphenylylnaphthoxazoles showed a less clearly defined structure. Their electronic bands were found to be similar to the bands of the corresponding naphthylphenylethylenes and biphenylnaphthylethylenes.

Aromatic amines, alcohols, and ethers. The electronic long-wave absorption and luminescence bands of amino- and *N*-dialkylamino-derivatives of aromatic hydrocarbons in solution at room temperature have the form of broad structureless bands. In vitreous solutions at low temperature, these are resolved into a number of comparatively broad bands. Ermolaev[97] described fluorescence and phosphorescence spectra of this type, with a

coarse vibrational structure, for a number of aromatic amines in EPA solutions (petroleum ether + ethanol + 3-methylbutane) at 77°K. For those compounds in which the amino-group is not included in the rigid framework and is capable of rotating relative to the C–N axis (for example in aniline, dimethylaniline, diphenylamine, and triphenylamine), it is not possible to observe greater resolution of the structure in n-hydrocarbon solutions compared with vitreous solutions. When the amino-group is rigidly fixed in the molecule, however, a quasi-line structure can be obtained. The spectra of carbazole in hexane and heptane have been obtained[98], and the quasi-line spectra of acridan have been described[7]. The fluorescence and phosphorescence spectra of these molecules show purely electronic bands of high intensity, indicating that the transitions are allowed. The skeletal vibrations, particularly that of the benzene ring at 1600 $cm^{-1}$, are active in the structure. Attempts to obtain an effectively resolved structure for the electronic bands of aromatic alcohols and ethers, such as phenol, naphthols, anisole, methoxynaphthalenes, etc. in n-hydrocarbon solutions did not give positive results. When the –O– or –S– bridge is part of a rigidly fixed structure, quasi-line spectra can be obtained (diphenylene oxide and diphenylene sulphide)[98]. The quasi-line fluorescence and phosphorescence spectra of diphenylene oxide have been described[100]. The quasi-line spectra of diphenylene oxide and carbazole have been studied[99,100].

Aldehydes and ketones. The luminescence spectra of aliphatic aldehydes—formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde—and ketones—acetone, diethyl ketone, methyl ethyl ketone, cyclohexanone, cyclopentanone, and cycloheptanone—in the vapour state and in n-hydrocarbon solutions frozen at 77°K have been studied[101]. Emission bands with little structure were observed in the vapours and solutions; slight improvement in the structure in solutions was observed for the aldehydes on going from butyraldehyde to acetaldehyde. The emission was attributed to the $T_{n-\pi^*}-S_0$ transition. The $n-\pi^*$ phosphorescence and long-wave $n-\pi^*$ absorption spectra of aromatic aldehydes and ketones (benzaldehyde, acetophenone, benzophenone, and their derivatives) are resolved in n-hydrocarbons at 77°K to give a few broad bands, as in the vitreous solutions[102,103]. The only frequencies which can be clearly distinguished in their structure are those of the stretching vibration of the C=O group, which form an intense progression. In the phosphorescence bands this frequency has the value 1680–1660 $cm^{-1}$, corresponding to the vibration in the ground electronic state, but in the absorption bands it is lowered to 1200 $cm^{-1}$, indicating a considerable decrease in the strength of the C=O bond in the excited $n-\pi^*$ state. In this state there is also a significant increase in the equilibrium distance in the C=O group, and this determines the nature of the distribution of the band intensities. When the keto-group forms part of a rigid structure, a quasi-line structure can be observed for the $n-\pi^*$ phosphorescence. Shigorin and Shcheglova[104] reported the quasi-line phosphorescence spectrum of anthrone, and we reported that of anthraquinone[2,25]. A detailed analysis of the quasi-line structure of the $n-\pi^*$ phosphorescence spectrum of anthraquinone was carried out[25]. It was shown that the $\nu_{C=O}$ frequency forms predominant progressions and combines with all other vibrational frequencies active in the spectrum. In aromatic aldehydes and ketones with $\pi-\pi^*$ phosphorescence, it is possible to obtain a quasi-line structure for its band, as shown for the example of biphenylaldehyde and α- and β-naphthaldehydes[105].

Derivatives of anthraquinone and other quinones. Shigorin and coworkers[106–111] studied the influence of the intramolecular interaction of various atomic groups in these compounds on the quasi-line luminescence and long-wave absorption spectra. It was shown that the introduction of various β-substituents (β-halogeno[2,25], β-carboxy, β-carbalkoxy[106], and β-alkyl[107]) into the anthraquinone molecule does not alter the nature of the luminescence band. The luminescence spectra of β-substituted anthraquinones are determined by the $n-\pi^*$ phosphorescence and exhibit a vibrational structure similar to that of the spectrum of anthraquinone, in which a progression of the vibrational frequency of the CO group of the anthraquinone ring predominates. The β-substituents produce only a slight change in the position of the spectrum and the multiplicity of its bands. The introduction of α-substituents (α-alkyl, α-aryl[107], and α-halogeno[108]) leads to a marked long-wave displacement of the absorption bands and to the appearance of a fluorescence band, often with an indistinct structure. Particularly marked changes are produced by α-hydroxy substituents and their ethers[111]. For the former, this can be attributed to the production of a stable intramolecular hydrogen bond with the formation of a quasi-aromatic ring. The formation of a ring of this kind has been assumed to be responsible for the production of a quasi-line structure in the absorption and fluorescence spectra of 1,4-dihydroxyanthraquinone and 1,2,5,8- and 1,4,5,8-tetrahydroxyanthraquinones, which are displaced considerably towards longer wavelengths compared with the spectra of anthraquinone. The influence of the nature and position of the substituent on the structure of the spectra for a series of naphthoquinone derivatives has been studied[110], and the dependence of the spectra of quinones on the number and relative arrangement of the keto-groups in the aromatic ring (anthrone, phenanthrenequinone, and anthraquinone) has been investigated[104].

Esters of dicarboxylic acids. Ivanova[111] recorded the structure of the fluorescence spectra of two diethyl esters of ω,ω′-dicarboxylic acids. Distinct resolution of the structure of the spectrum of $C_2H_5OOC.(CH=CH)_6COOC_2H_5$ was observed in n-octadecanol (half-width of the bands about 30–50 $cm^{-1}$), with initial $\nu_{0-0}$ band at 20023 $cm^{-1}$. The fluorescence bands of the ester $C_2H_5COO(CH=CH)COOC_2H_5$ were found to be more diffuse ($\Delta\nu \simeq 150$ $cm^{-1}$) and approximately the same in dodecane, cetane, and octadecanol. The most characteristic frequencies in the structure of the spectra were 1550 $cm^{-1}$ and 1140 $cm^{-1}$, assigned to the stretching vibrations of the polyene chain. The long-wave absorption and fluorescence bands are determined in these esters by a $\pi-\pi^*$ transition, so that the characteristic frequencies of the carboxyl group do not appear distinctly in the structure.

Xanthone and acridones. The xanthone molecule contains two oxygen atoms joined in different ways to the π system, and the interaction of these atoms is responsible for a number of remarkable characteristic features. Under the influence of the electron-donating –O– bridge, the energies of the $n-\pi^*$ transitions are increased, and the energies of the $\pi-\pi^*$ transitions are decreased, so that the $n-\pi^*$ absorption band is partly overlapped by the $\pi-\pi^*$ band, although it remains a long-wave band, and the $T_{n-\pi^*}$ and $T_{\pi-\pi^*}$ levels have very similar energies, so that inversion of the positions of the $T_{n-\pi^*}$ and $T_{\pi-\pi^*}$ levels is observed[112] under the influence of solvent. In n-hydrocarbon solutions, xanthone exhibits short-lived $n-\pi^*$ phosphorescence, and in alcohol it exhibits long-lived $\pi-\pi^*$

phosphorescence. In hexane and heptance solutions at 77°K a quasi-line structure was obtained for the $n-\pi^*$ phosphorescence bands and two absorption bands, associated with the $\pi-\pi^*$ transitions ($\nu_{S_2^*-S_0}$ = 29 575 cm$^{-1}$ and $\nu_{S_3^*-S_0}$ = 35 370 cm$^{-1}$). Under the same conditions, however, the $n-\pi^*$ absorption band remains diffuse. This makes it possible to define more precisely one of Kasha's distinguishing criteria for $n-\pi^*$ and $\pi-\pi^*$ bands, which says that in a condensed phase the $n-\pi^*$ bands are diffuse, whereas the $\pi-\pi^*$ bands have more structure. The example of xanthone shows that this is true only for the $n-\pi^*$ absorption bands, but not for $n-\pi^*$ phosphorescence.

The vibrational structure of the phosphorescence spectrum of xanthone has a very characteristic periodic form, determined by the fact that the $\nu_{C=O}$ frequency forms intense progressions and combines with all other vibrational frequencies. The values of the frequencies decrease in the overtones, indicating anharmonicity of the vibration of the C=O group. In the $\pi-\pi^*$ absorption bands, this predominance of one of the frequencies, which would be close to the frequency of vibration of the C=O group, is not observed.

In the acridone molecule the –NH– bridge is a stronger electron-donating substituent, so that the lower excited $S_1^*$ and $T$ levels are $\pi-\pi^*$ levels. Acridone itself does not dissolve in n-hydrocarbons, but its $N$-substituted derivatives can be studied in hexane by diluting the latter with a dioxan solution[7]. For the $N$-methyl, $N$-ethyl, and $N$-phenyl derivatives of acridone it has been possible to obtain a quasi-line structure for the $\pi-\pi^*$ phosphorescence band, in which the frequencies of the skeletal vibrations are active. Although the vibrational frequency of the C=O group appears in the spectrum, it is not the predominant frequency.

Phthalimides and naphthalimides. Although the absorption and phosphorescence spectra of phthalimide and its $N$-substituted derivatives in solid glasses at 77°K show a coarse vibrational structure[113-115], the first attempts to obtain the quasi-line structure of the absorption bands in n-hydrocarbons were unsuccessful[114,115]. This was due chiefly to the low solubility of the phthalimides in n-hydrocarbons. Phthalimide itself is almost insoluble, and its $N$-substituted derivatives readily precipitate from solution on cooling to 77°K, so that the concentration is insufficient for observation of the absorption spectrum of the solution, We were able[116] to obtain the quasi-line structure of the phosphorescence spectrum of $N$-methylphthalimide in hexane at 77°K; the spectrum consisted of a large number (more than 30) of closely situated quasi-lines. There are no predominant frequencies in the structure, and intervals close to the frequency of the stretching vibration of the C=O group do not appear distinctly. This characteristic feature of the structure is an important additional argument for assigning the phosphorescence of phthalimide to the $\pi-\pi^*$ transition.

The molecule of naphthalimide differs from that of phthalimide in its more extensive $\pi$ system, and this leads to a different arrangement of the singlet and triplet $n-\pi^*$ and $\pi-\pi^*$ levels and the production of fluorescence in naphthalimide. In hexane at 77°K the fluorescence spectrum consists of a broad diffuse band, on which a number of narrow intense bands are superimposed. Better resolution of the structure could not be obtained in n-hydrocarbons, however.

Thioindigoids and indigoids. Nurmukhametov and coworkers[5,117,118] studied the vibronic spectra of thioindigoid and indigoid dyes, to investigate the nature of the electronic transition determining their colours. The fluorescence spectrum of thioindigo[118,119] is resolved in hexane and heptane into 12 narrow bands, which are less distinct in other n-hydrocarbons, beginning at octane. These bands were interpreted from the initial resonance O–O band at 18 308 cm$^{-1}$ (in hexane) by means of the frequencies 220, 480, and 1540 cm$^{-1}$. The last frequency is the most characteristic in the spectrum, and it combines with the other frequencies, and this determines the two-fold repeated form of the structure of the emission band. The nature of the distribution of intensity in the spectrum indicates that the transition is allowed by symmetry and the Franck–Condon principle. The 1540 cm$^{-1}$ frequency is assigned to the stretching vibration of the central ethylenic group. A similar structure is observed in absorption, interpreted by means of the frequencies 220, 480, and 1500 cm$^{-1}$. Although the molecule contains two carbonyl groups, their characteristic frequencies, which according to the infrared spectra of thioindigo should have the value 1650 cm$^{-1}$, do not appear in the structure. A possible explanation is that the long-wave transition of the thioindigo molecule is a $\pi-\pi^*$ transition, in which the excitation energy is concentrated to a large extent on the C=C group, and not on the C=O groups, as in an $n-\pi^*$ transition. This interpretation of the spectrum of thioindigo agrees with its ready cis-trans photoisomerisation, established by Rogers, Margerum, and Wyman. Photoisomerisation requires concentration of the excitation energy in the C=C bond.

The structure of the spectra of various derivatives of thioindigo and related molecules[13], whose formulae are given in Table 3, have also been studied. Their spectra preserve the general characteristic features of the thioindigoid spectrum.

Table 3. Vibronic spectra (at 77°K) of arytoxadiazoles, arylbenzoxazoles, thioindigoids, and indigoids (absorption and fluorescence).

| Compound | References | Compound | References |
|---|---|---|---|
| 2,5-Aryloxadiazoles | | 2-Phenylnaphth-[2,1d]- | 97 |
| Biphenyl- | 92 | 2-Biphenylylnaphth-[2,1d]- | 97 |
| Bis(biphenylyl)- | 92 | 1,4-Di-(2-benzoxazolyl)benzene | 22, 96 |
| Phenyl-β-naphthyl- | 92 | 1,4-Di-(2-benzoxazolyl)ethylene | 22, 96 |
| Di-β-naphthyl- | 92 | Thioindigoids and indigoids | |
| Phenyl-α-naphthyl | 92 | Thioindigo | 120, 121 |
| Di-α-naphthyl- | 92 | 5,5′-Dimethyl- | 120, 121 |
| α-Naphthyl-β-naphthyl- | 92 | 6,6′-Dichloro- | 120, 121 |
| α-Naphthylstyryl- | 92 | 6,6′-Diethoxy- | 120, 121 |
| Arylbenzoxazoles and arylnaphthoxazoles | | 5,5′-Dinitro- | 120, 121 |
| | | 6,6-Dinitroindigo | 122 |
| 2-Phenylbenz- | 22, 96 | 5,5′,7,7′-Tetrabromo- | 122 |
| 2-Biphenylylbenz- | 22, 96 | 5,5′,7,7′-Tetrachloro- | 122 |
| 2-Styrylbenz- | 22, 96 | 5,5′-Dichloro- | 122 |
| 2-Phenylnaphth-[1,2d]- | 97 | NN′-Dimethyl- | 122 |

Although the indigo molecule differs from that of thioindigo only in the replacement of S atoms by NH groups, the colours differ significantly: crystals of the former are deep blue, whereas those of the latter are red. For isolated indigo and thioindigo molecules, the differences in absorption are much smaller. Study of the structure of the vibronic spectra of these molecules has made possible

a more valid explanation of their common and individual properties. Indigo does not dissolve directly in n-hydrocarbons. The structure of the fluorescence and absorption spectra were obtained at 77 °K by diluting the dioxan solution with hexane in the ratio 1 : 15.[5,117] The form of the structure is similar to that for thioindigo, but the range of the spectrum is shorter, the number of bands is smaller (6), and the intensity of the O–O band with frequency 16 440 $cm^{-1}$ relative to the other vibronic bands is much higher. The definite similarity in the quasi-line spectra of thioindigo and indigo indicates that their colours are determined by electronic transitions of the same character, and the main contribution to the excited state is made by the C=C group, whose vibrational frequency is most characteristic for the structure of the band due to this transition. The –NH– bridges in indigo are stronger auxochromes than the –S– bridges in thioindigo, leading to a more marked (by 1900 $cm^{-1}$) bathochromic shift in the band and a higher intensity for the O–O band.

Study of indigo derivatives (see Table 3)[5,117] showed that halogeno substituents have little influence on the structure and position of the fluorescence spectrum, showing their greatest influence on the relative intensity of the O–O band and leading in some instances to a more diffuse structure. Methylation of the NH group leads to a marked bathochromic shift and a decrease in the sharpness of the structure of the electronic bands. The low solubility of the indigoids is due to their marked association, and this is due chiefly to strong intermolecular hydrogen bonds, as shown by Shigorin and coworkers for the example of indigo molecules, which are associated by means of hydrogen bonds. This association is also responsible for the significant difference in the colours of indigo and thioindigo (the molecules of the latter cannot form hydrogen bonds with one another).

Porphyrins and phthalocyanines. Personov and Litvin[120,121] were the first to apply Shpol'skii's method successfully to compounds of these classes, which are of considerable biological importance. The three broad fluorescence bands observed under ordinary conditions for phthalocyanine without metal are resolved in octane at 77 °K into more than 30 bands, lying in the range 6840–7775 Å, with characteristic doublet splitting ($\Delta\nu$ between doublets 60 $cm^{-1}$). The 6939/6910 Å doublet has absorption bands which coincide by resonance. The spectrum of the long-wave absorption band is approximately the mirror image of the fluorescence spectrum and extends from 6939 Å to 6248 Å. Quasi-line long-wave absorption and fluorescence spectra have also been obtained for magnesium phthalocyanine; each is resolved into more than 30 bands, and there is a complex multiplet structure. The fluorescence spectrum of protoporphyrin in octane consists of a large number of doublets with $\Delta\nu = 20$ $cm^{-1}$, and can be interpreted satisfactorily by means of the vibrational frequencies 240, 740, 790, 985, 1135, 1225, 1345, 1550, and 1585 $cm^{-1}$.

Personov[121] made a detailed study of the quasi-line spectra of phthalocyanine in octane, nonane, and decane at 77 °K, and gave a detailed vibrational analysis. He pointed out the change in the distance between the doublets in different solvents, and on the basis of the fine details of the structure he concluded that in the range of the long-wave absorption, the fine structure of the overlapping bands of two electronic transitions with $\lambda_{0-0}$ (I) = 6907/6917 Å (in decane) and $\lambda_{0-0}$ (II) = 6506/6530 Å (in decane) is observed.

Shkirman and Solov'ev[122] obtained the quasi-line absorption and fluorescence spectra of tetrabenzoporphin and tetrazaporphin in octane at 77 °K. Because of their low solubilities, the former was dissolved first in chlorobenzene, and the latter in a pyridine–acetone mixture. The tetrazaporphin bands consist of complex multiplets, in which two components are the most intense. The intense doublet of the O–O band is observed at 6115/6134 Å with $\Delta\nu = 51$ $cm^{-1}$. The fluorescence and absorption spectra are almost mirror images and were interpreted by means of 17 vibrational frequencies. The quasi-line spectra of tetrabenzoporphin consist of characteristic doublets with intense resonance lines at 6580/6594 Å, with an interval $\Delta\nu = 32$ $cm^{-1}$ between them. The fluorescence and absorption spectra are not mirror images. The quasi-line spectra of porphin and dihydroporphin (chlorin) in octane and decane at 77 °K have been described[123]. These compounds were dissolved in n-hydrocarbons through a buffer benzene solution. The fluorescence and absorption spectra of porphin consist of series of triplets with a resonance triplet of the O–O transition at 6127/6134/6149 Å (in octane). The structure of the fluorescence spectrum was interpreted by means of the frequencies 155, 310, 720, 786, 955, 974, 1014, 1057, 1176, 1222, 1263, 1319, 1361, 1389, 1409, 1456, 1497, 1539, 1605, and 1615 $cm^{-1}$. The spectrum of chlorin contains approximately the same frequencies, with the exception of the frequencies 786, 1176, 1319, 1456, and 1605 $cm^{-1}$. These frequencies of porphin are assigned to the symmetry species $b_{1g}$. Since in porphin the O–O transition is assumed to be forbidden by symmetry, these frequencies remove the forbidden character. The symmetry of the chlorin molecule is lower, and the transition is allowed by symmetry, so that only the completely symmetrical vibrations are active in its spectrum.

The absorption and luminescence spectra of azo-compounds and azomethine compounds have been studied in n-hydrocarbons and other solvents[124–127]. It was established that arylazo-compounds with general formula Ar-N=N-Ar′ become fluorescent only when an *o*-hydroxy substituent is introduced into the aryl ring; intramolecular hydrogen bonding then leads to the formation of a six-membered ring containing the –N=N– azo-group. The luminescence spectra of hydroxyazo-compounds are resolved only into a few broad bands. A similar picture is observed for the spectra of hydroxyazomethine compounds, in which the hydroxyl group is introduced into the aldehyde ring and forms a stable intramolecular hydrogen bond. Azomethines also become fluorescent when the $-N(CH_3)_2$ substituent is introduced into the *p*-position of the phenyl rings. From the example of α-hydroxyanthraquinones, hydroxyazo-compounds, and hydroxyazomethine compounds, it may be concluded that when an intramolecular hydrogen bond is formed, the electronic bands usually have a diffuse structure, but the increase in symmetry in the dihydroxy- and tetrahydroxyanthraquinones is accompanied by improved resolution of the structure. A less sharp structure compared with the spectra of benzophenones is also observed for *o*-hydroxybenzophenones.

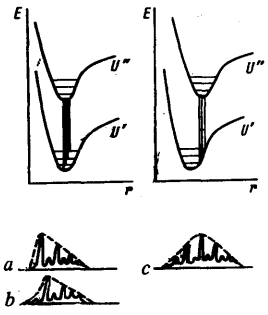
Shpol'skii's method has been used chiefly to resolve the structures of the electronic bands of luminescent molecules. In principle, however, it can also be used to obtain the quasi-line absorption spectra of non-fluorescent molecules. This can be illustrated by azobenzene, which does not exhibit luminescence. Dyck and McClure studied the absorption spectrum of an azobenzene–bibenzyl mixed crystal at 77 °K and 4 °K and found that whereas the long-wave $n-\pi^*$ absorption band does not show a resolved structure, the position and vibrational structure of the $\pi-\pi^*$ absorption band are similar to those of the absorption band of stilbene. Finally, triplet–triplet absorption bands have been observed under the conditions of Shpol'skii's method[128,129].

## 3. THE VIBRONIC SPECTRUM AND THE STRUCTURE OF MOLECULES

Electronic transitions in molecules differ in the type of excited state ($n-\pi^*$ or $\pi-\pi^*$) realised in the transition; in whether the transition is allowed or forbidden by symmetry or the Franck–Condon principle; and in whether the transition can take place between states with the same multiplicity—singlet–singlet or triplet–triplet—or different multiplicities—singlet–triplet. All these features determine the nature of the electronic transition, which has a significant influence on the form of the vibrational structure.

When the transition is allowed by symmetry, the band due to the purely electronic transition in the system of vibronic bands is clearly distinguished in the spectrum and has a comparatively high intensity (if it is forbidden by other reasons, for example by the Franck–Condon principle). The frequencies of the completely symmetrical vibrations, chiefly those of the framework containing the electronic system excited in the transition, predominate in the structure of the band. In the case of hydrocarbons these are the vibrational frequencies of the carbon framework of the $\pi$ system. The values of the frequencies in the fluorescence and phosphorescence spectra (in which the vibrations of the ground electronic state appear) coincide with or are very close to the values of the frequencies found in the Raman spectrum of the same compound. In the absorption spectra, however, the same vibrations may have slightly altered frequency values, and this makes the identification of the type of the vibrations difficult. Thanks to the mirror symmetry rule, however, identification is often possible, so that the change in the vibrational frequencies in different electronic states can be estimated. The structure may reveal not only the completely symmetrical vibrations, but also a certain type of incompletely symmetrical vibration, namely those in which the transition is still allowed by symmetry but in which the direction of its polarisation changes. This was shown in a series of papers by Zimmerman and Yoop[130-135] on the study of the polarisation absorption and fluorescence spectra at −180°C for alcoholic solutions of naphthalene, phenanthrene, anthracene, tetracene, tetraphene, chrysene, pyrene, perylene, and azulene. Dörr and coworkers[136-138] showed that the incompletely symmetrical vibrations which rotate the plane of polarisation of the vibronic oscillator through 90° appear in the phosphorescence spectra of a number of aromatic hydrocarbons. Shpak and Malykhina established that the fluorescence spectrum of stilbene contains two mutually perpendicular polarised band series. Naphthalene, phenanthrene, and pyrene provide examples of molecules in whose quasi-line spectra it has been possible to observe incompletely symmetrical vibrations. Bolotnikova found that the fluorescence spectrum of naphthalene in pentane at 77°K shows the 495 $cm^{-1}$ frequency of the vibration with symmetry $b_{1g}$; the frequencies of the completely symmetrical vibrations combine with it to form a second series of bands which are polarised, in agreement with McClure's studies, in a direction perpendicular to that for the first series of bands, beginning from the initial purely electronic O–O band. Analysis of the quasi-line fluorescence and phosphorescence spectra of phenanthrene enabled Pesteil and Rabaud[40] to distinguish in the spectrum the frequencies of the normal vibrations, the number of which is greater than the total number of completely symmetrical vibrations. On this basis, using data from the vibrational spectra, these authors assigned some of the frequencies to definite incompletely symmetrical vibrations. Klimova[43] established that the spectra of pyrene show the frequencies of incompletely symmetrical vibrations.

When the transition is forbidden by symmetry, the purely electronic band either is not observed or has a low intensity. The forbidden character resulting from symmetry is removed in this instance by the superposition of a definite type of incompletely symmetrical vibration on the electronic transition. The corresponding vibronic band is more intense than the purely electronic band and serves as the origin for progressions of the frequencies of the completely symmetrical vibrations. These electronic bands are characterised by example *b* (see Figure) of the distribution of band intensity along the spectrum, if in the excited state the equilibrium interatomic distances are close to the distances in the ground state. This type of vibrational structure (low intensity of the purely electronic band, removal of the forbidden character by a quantum of the incompletely symmetrical vibration, and distribution of the band intensity along the spectrum according to example *b*) is observed in the spectra of the molecules of benzene, coronene, and triphenylene, which have an O,O transition forbidden by symmetry. A similar picture is observed in the spectra of biphenyl and naphthalene, where the purely electronic transition is partly forbidden.




Different examples of the distribution of intensity in the vibronic bands: *a*) for an electronic transition allowed by symmetry and $r_0' = r_0''$; *b*) for a transition forbidden by symmetry and $r_0' = r_0''$; *c*) for a transition between states with $r_0'' > r_0'$; $u'$ and $u''$ are the potential curves of the ground and excited states, and $r_0'$ and $r_0''$ the equilibrium distances in these states.

If however the electronic transition takes place into a state with significantly altered equilibrium distances, the purely electronic transition is forbidden or greatly weakened as a consequence of the Franck–Condon principle, and the system of bands for this transition is characterised by example *c* of the distribution of intensity within this system (see Figure). This is observed for the $n-\pi^*$ transitions of carbonyl-containing molecules, as shown for a number of aromatic aldehydes and ketones, anthraquinone, etc.

Thus from the relative intensity of the purely electronic band it is possible to obtain information on the degree of allowed character (or forbidden character) of the electronic transition, and from the form of the intensity distribution it is possible to obtain information on the forbidden character of the transition.

The form and degree of resolution of the structure are closely related to the nature (type) of the electronic transition, and this is reflected in one of the distinguishing criteria for $n-\pi^*$ and $\pi-\pi^*$ bands. Kasha [73] pointed out that the structure of $n-\pi^*$ bands is usually exceptionally sharp for vapours, but is much less sharp in the condensed phase (liquid and solid solutions), whereas the structure of the $\pi-\pi^*$ bands is more diffuse in vapours, and improvement in the resolution of the structure is observed in solutions, particularly at low temperatures. It should be noted that these differences do not always emerge clearly. For example, for molecules with a non-rigid and non-planar structure, both the $n-\pi^*$ and $\pi-\pi^*$ bands are often structureless (the influence of spatial configuration on structure will be examined below). In those instances, however, where structural factors do not lead to a decrease in the sharpness of the bands, the formulated criterion for bands due to $n-\pi^*$ transitions is applicable only for singlet-singlet transitions, that is for the $n-\pi^*$ absorption bands and for $n-\pi^*$ fluorescence, when this takes place.

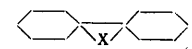
Resolution of the quasi-line structure is possible for the $n-\pi^*$ fluorescence bands, as demonstrated for the molecules of anthraquinone, anthrone, xanthone, etc. Under those conditions favouring the resolution of the vibrational structure, the $n-\pi^*$ absorption band remains structureless or shows little structure, whereas resolution of the structure is observed for the absorption bands of the higher $\pi-\pi^*$ transitions. If in a molecule the $n-\pi^*$ levels lie above the $\pi-\pi^*$ levels for a definite change in the structure of the molecule, the $\pi-\pi^*$ absorption, fluorescence, and phosphorescence bands may show a quasi-line vibrational structure ($\alpha$- and $\beta$-naphthaldehydes, $N$-methylphthalimide, and $N$-substituted derivatives of acridone provide examples of molecules with $\pi-\pi^*$ phosphorescence and a resolved structure). The close relationship between the form of the vibrational structure and the nature of the electronic transition provides new possibilities for obtaining information on this transition from the characteristic features of the structure of the band.

Dependence of the vibrational structure of the electronic bands on the three-dimensional structure. For molecules of aromatic hydrocarbons (with the same type of $\pi-\pi^*$ transitions) with a rigid structure it is possible in most instances to select conditions for distinct resolution of the structure. The introduction into these molecules of alkyl and halogeno substituents, which have little influence on the energy and nature of the $\pi-\pi^*$ transitions, may influence the form of the structure and its degree of resolution in different ways. Various examples of the spectra of halogeno-derivatives (halogenonaphthalenes, halogenoanthracenes, and halogenopyrenes) show that despite the strongly polar character of the C–halogen bond, which should lead to intensification of the interaction between the dissolved molecule and the solvent, the introduction of halogen usually is not accompanied by a marked decrease in the sharpness of the structure. Moreover, the change from pyrene to halogenopyrenes is accompanied by the same decrease in the width of the quasi-lines at 77°K as is observed for the spectra of pyrene on going from 77°K to 4°K.

The spectra of aromatic hydrocarbons (polyphenyls, diphenylpolyenes, and arylethylenes) usually consist of more diffuse bands, particularly for molecules with sterically hindered groups. For example, the electronic bands of biphenyl show a clearly defined structure, which becomes less distinct when $\alpha$-alkyl substituents are introduced. The absorption and fluorescence bands of trans-stilbene have a clearly defined structure, whereas the absorption bands of cis-stilbene are structureless, and fluorescence is not observed.

Although a non-planar structure leads to significant weakening of the $\pi$-conjugation, so that the aryl fragments of the molecule are chiefly responsible for the electronic bands, these bands nevertheless show a clearly defined structure, which is similar to that of the bands for the hydrocarbons corresponding to this fragment. A bridge with extensively weakened conjugation begins to play the part of a substituent. This picture was observed for $\beta$-binaphthyl and the cis-isomer of di-(9-anthryl)ethylene.

The introduction of bridges which fix the planar structure but do not alter the $\pi$ system leads to more distinct resolution of the structure.

In substituted aromatic compounds with an electron-donating group $-NR_2$, $-NR-$, $-OR$, $-O-$, $-SR$, or $-S-$, the unshared pair of electrons of the heteroatoms X = N, O, or S is conjugated with the $\pi$ electrons, and their electronic bands are determined by the excitation of the complete $\pi$ ($2p_z$) system of electrons. These $\pi,\pi^*$ ($2p_z$) bands have certain characteristic features, some of which are due to the incomplete conjugation of the $2p_z$ electrons of the heteroatom with the $\pi$ electrons. Kasha [139] pointed out that because of the nature of the hybridisation, the orbitals of the unshared pairs of these heteroatoms are not strictly parallel to the $p$ orbitals of the $\pi$ electrons, but may lie at an angle to them, leading to incomplete $\pi$ conjugation. To this he attributed the slightly lower values of the absorptivities $\epsilon$ of the absorption bands due to the $\pi-\pi^*$ ($2p_z$) transitions compared with those for the bands of the resolved $\pi-\pi^*$ transitions, and also the decrease in the lifetime of the phosphorescence (that is the increase in the probability of triplet–singlet conversion resulting from the fact that the $2p_z$ orbital of the heteroatom, lying at an angle to the $p$ orbitals of the $\pi$ system, as it were occupies an intermediate position between the $p$ orbitals and the $n$ orbitals which are perpendicular to the $p$ orbitals). Since these electron-donating groups can rotate relative to the C–X bond, the angle of slope of this orbital will generally be different in different electronic states. This is apparently one of the chief reasons for the lack of sharpness of the structure in the spectra of aromatic amines, alcohols, ethers, and thioethers to the extent that their bands show only a coarse structure, and not a quasi-line structure. Convincing evidence in support of this is provided by the fact that the electronic bands show a quasi-line structure when the –NR–, –O–, or –S– bridges are included in a rigid ring. Nurmukhametov and Gobov [98] demonstrated this for molecules with general formula  where X = NH (carbazole), O (diphenylene oxide or dibenzofuran), or S (diphenylene sulphide). Nurmukhametov and coworkers [7] obtained the same result for the molecules of acridan (9,10-dihydroacridine), xanthone, and $N$-substituted derivatives of acridone.

Another factor leading to a decrease in the sharpness of the spectra of compounds of this type is the high sensitivity of their electronic bands to the nature of the solvent. A marked displacement of the bands is usually observed for these compounds on going from a non-polar solvent to a polar solvent. The presence of small quantities of polar impurities in n-hydrocarbon solvents is therefore sufficient for the formation, in the solution, of molecular centres with appreciable dispersion of the frequencies of the electronic transitions. A unique example of the departure from a planar structure as a result of interaction of the electrons of an unshared pair with $\pi$ electrons is provided

by benzylideneaniline, in which the $N$-phenyl ring is turned out of the plane by 60°, so that the molecule acquires the energetically most favourable spatial configuration. The introduction of an –O– bridge (the phenylbenzoxazole molecule) leads to a planar structure for the molecule, in which the $n$ electrons are now not conjugated with the $\pi$ electrons of the $N$-phenyl ring. Benzylideneaniline shows broad absorption bands and no fluorescence, whereas the absorption and fluorescence bands of 2-phenylbenzoxazole show a clearly defined quasi-line structure.

## 4. SPECTROSCOPIC-ANALYTICAL APPLICATIONS

The highly characteristic nature of quasi-line electronic spectra has found extensive application as a basis for the development of spectroscopic-analytical methods for the detection and quantitative determination of small quantities of organic substances. On the basis of the quasi-line luminescence spectra it has been possible to achieve the high sensitivity in the determination of traces of organic compounds (down to $10^{-12}$ M) which was previously attained only for inorganic compounds. The fact that the luminescence light in these spectra is collected into narrow quasi-line bands makes it possible to carry out an analysis at "noise level", that is when the luminescence of other trace materials in the same range has an intensity comparable with that of the compound being determined. The high sensitivity, the speed of the analysis, the unlimited reproducibility in a given specimen, and the fact that the specimens to be analysed do not have to satisfy special requirements make analytical methods based on Shpol'skii's spectra very effective and promising. The analytical applications have been developed chiefly for substances which exhibit fluorescence in the visible range. Shpol'skii's spectra have proved very effective for the detection and determination of carcinogenic aromatic compounds. Carcinogenic substances have been detected and their concentrations determined in atmospheric air [140,141], tobacco smoke [142], industrial products [143], and in various smoked products [144]. Work on the detection and identification of individual aromatic compounds in bitumens and petroleums has been carried out by Il'ina and coworkers [145-147], who unambiguously identified perylene, 1,12-benzperylene, coronene, and pyrene in the naphthenic–aromatic fractions of bituminous substances. Utkina [148], without preliminary chromatography, determined a number of aromatic hydrocarbons of the anthracene–phenanthrene fraction of coal tar.

A series of papers by Teplitskaya and coworkers [149-154] described the use of Shpol'skii's spectra in the analytical determination of organic substances in rocks of different origin, meteorites, and minerals. The organic substances are present in rocks in small quantities ($10^{-4}$–$10^{-1}$% [154]) and the concentration of aromatic hydrocarbons to be determined often amounts to only $10^{-7}$%. The authors cited [149-154] were able to determine organic substances in rocks even when this was impossible by other analytical methods. Teplitskaya [149] was the first to detect a number of polycyclic aromatic hydrocarbons in igneous rocks, using Shpol'skii spectra. The individual composition of the carbonaceous material in igneous rocks has been studied [151] and it has been established that calcite from the Darasun deposit contains 1,12-benzperylene, 3,4-benzpyrene, and various other unidentified aromatic compounds.

By means of Shpol'skii's spectra, it has been possible for the first time to identify the individual organic substances present in meteorites; before this, it was considered an achievement to determine even the group composition of the organic material in meteorites. Teplitskaya and coworkers [152] identified a number of individual compounds—anthracene, 3,4-benzpyrene, 1,12-benzperylene, and coronene—in extracts obtained from meteorites—carbonaceous chondrites. The authors cited [152] also observed a similarity in the compositions of the polycyclic aromatic hydrocarbons in the organic material from carbonaceous chondrites, rocks, and minerals of endogenic origin.

Interesting results were obtained by Teplitskaya and coworkers [153] in a study of the spectra of the mineral hackmanite, which exhibits phototropic properties. Some specimens of hackmanite show a pink-red colour, which becomes paler under the influence of daylight. This colour is restored in the dark or under the influence of ultraviolet light. The luminescence spectrum associated with the red colour centres of hackmanite shows a structure at 77°K similar to the structure of the spectra of thioindigoids. On this basis, these authors [153] put forward the new suggestion that the colour centres in this instance are organic sulphur-containing compounds. The presence of aromatic compounds was established from the quasi-line spectra in extracts of organic substances from hackmanite.

Shpol'skii's method has also been used as a basis for the development of quantitative methods of spectrochemical analysis. Personov and Teplitskaya [155] developed a method for the quantitative determination of small quantities of perylene and 1,12-benzperylene from their quasi-line fluorescence spectra, and achieved a high sensitivity (down to $10^{-11}$ g ml$^{-1}$) with an accuracy of 10–20%. Quantitative methods for the determination of the strongly carcinogenic 3,4-benzpyrene from the quasi-line spectra were described by Muel and Lacroix [156], Dikun [157], Personov [158], and Khesina [159]. Photoelectric recording [156,158,159] or photographic recording [157] were used. Muel and Lacroix determined the concentration by the method of additions, and Personov used the method of internal standards; the latter achieved a sensitivity of $10^{-9}$ M with an accuracy of 7–15%.

---o0o---

Extensive possibilities are provided by Shpol'skii's spectra in photochemical studies. Personov [52] observed the photochemical transformation of perylene in chloroform under the influence of daylight. The product of the photoreaction, tentatively regarded as a chloro-substituted perylene, gave a quasi-line fluorescence spectrum in hexane solution at 77°K, displaced towards lower frequencies by ~ 400 cm$^{-1}$.

Gobov and coworkers [89] showed that ultraviolet irradiation of a solution of di-$\alpha$-naphthylethylene produces a photoproduct for which the quasi-line structure of the fluorescence and phosphorescence spectra indicated the presence of naphthyl nuclei in the molecular structure. Later, Nurmukhametov and Grishina [160] proved unambiguously that these spectra are due to the hydrocarbon picene, produced by the photocyclohydrogenation of di-$\alpha$-naphthylethylene.

Intensive studies are now being made of the widely encountered reaction of photochemical cyclisation (photocyclodehydrogenation), by means of which polycyclic condensed hydrocarbons are formed from arylethylenes (for example phenanthrene from stilbene), the corresponding substituted polycyclic hydrocarbons are obtained from substituted arylethylenes, $N$-heteroaromatic polycyclic compounds are obtained from the $N$-heteroanalogues of arylethylenes, etc. The photocyclisation products are characterised by a more rigid molecular structure, and

hence by electronic bands with a clearly defined vibrational structure. The use of Shpol'skii's spectra to study these reactions opens up the possibility of ready, rapid, and unambiguous identification of the photocyclisation products and the possibility of studying the kinetics of the reaction by spectroscopic methods. Nurmukhametov and Grishina[161] unambiguously established from the quasi-line spectra the formation of chrysene from $\alpha$-naphthylphenylethylene, 3,4-benzphenanthrene from $\beta$-naphthylphenylethylene, and 1,12-benzperylene from di-$\beta$-naphthylethylene.

The application of Shpol'skii's method to the detection and identification of aromatic radicals appears attractive. Grajcar and Leach[63] used the characteristic structure of the fluorescence spectrum in the region of 4600 Å to establish the formation of the benzyl radical when a solution of toluene in methylcyclohexane + 3-methylbutane (2 : 3), frozen at 77°K, was irradiated by light with wavelength 2537 Å ($\lambda_{Hg}$). Mileshina and coworkers[65] observed the production of green luminescence during the photolysis of diphenylketen in hexane at 77°K. On the basis of an analysis of the quasi-line spectrum of this luminescence, together with electron paramagnetic resonance data, it was shown that the biradical of diphenylmethylene is formed from diphenylketen.

REFERENCES


1. E. V. Shpol'skii, A. A. Il'ina, and L. A. Klimova, Dokl. Akad. Nauk SSSR, 17, 235 (1952).
3. D. N. Shigorin, N. A. Shcheglova, R. N. Nurmukhametov, and N. S. Dokunikhin, Dokl. Akad. Nauk SSSR, 120, 1242 (1958).
3. R. I. Personov and O. M. Korotaev, "Trudy Vtoroi Mezhvuzovskoi Konferentsii Pedinstitutov po Radiofizike i Spektroskopii" (Proceedings of the Second Inter-university Conference of Pedagogic Institutes on Radiophysics and Spectroscopy), 1967, p. 71.
4. E. V. Shpol'skii, Uspekhi Fiz. Nauk, 71, 215 (1960).
5. R. N. Nurmukhametov, D. N. Shigorin, and Yu. I. Kozlov, Izv. Akad. Nauk SSSR, Ser. Fiz., 27, 686 (1963).
6. D. N. Shigorin, N. V. Volkova, A. K. Piskunov, and A. N. Gurevich, Optika i Spektrosk., 12, 657 (1962).
7. R. N. Nurmukhametov, D. N. Shigorin, L. A. Mileshina, and G. A. Ozerova, Zhur. Fiz. Khim., 40, 2206 (1966) [Russ. J. Phys. Chem., No. 9 (1966)].
8. H. Sponer, Y. Kanda, and L. Blackwall, Spectrochim. acta, 16, 1135 (1960).
9. Y. Kanda and R. Shimada, Spectrochim. acta, 17, 7 (1961).
10. Y. Kanda and R. Shimada, Spectrochim. acta, 17, 1268 (1961).
11. G. D. Sheremet'ev and M. M. Val'dman, Izv. Akad. Nauk SSSR, Ser. Fiz., 27, 693 (1963).
12. R. N. Nurmukhametov and E. G. Popova, Fiz. Problemy Spektrosk., 1, 216 (1962).
13. R. N. Nurmukhametov, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, Moscow, 1962.
14. T. N. Bolotnikova, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, Moscow, 1958.
15. T. N. Bolotnikova, Optika i Spektrosk., 7, 44, 217 (1959).
16. T. N. Bolotnikova, Izv. Akad. Nauk SSSR, Ser. Fiz., 24, 620 (1960).
17. R. N. Nurmukhametov, E. G. Popova, and N. S. Dokunikhin, Optika i Spektrosk., 9, 593 (1960); 11, 134 (1961).
18. G. V. Tsitsishvili and M. K. Charkviani, Dokl. Akad. Nauk SSSR, 167, 139 (1966).
19. N. A. Fenina, Optika i Spektrosk., 20, 768 (1966).
20. G. V. Gobov and T. N. Bolotnikova, in collected papers "Optika i Spektroskopiya, I, Lyuminestsentsiya" (Collected Papers on Optics and Spectroscopy, I, Luminescence), 1963, p. 36.
21. G. V. Gobov, Optika i Spektrosk., 15, 362 (1963).
22. R. N. Nurmukhametov, G. V. Gobov, and L. N. Pushkina, Zhur. Fiz. Khim., 41, 1553 (1967) [Russ. J. Phys. Chem., No. 7 (1967)].
23. R. N. Nurmukhametov, L. A. Mileshina, L. Ya. Malkes, and L. V. Shubina, Optika i Spektrosk., 20, 36, 970 (1966).
24. E. V. Shpol'skii and L. A. Klimova, Optika i Spektrosk., 7, 852 (1961).
25. R. N. Nurmukhametov and D. N. Shigorin, Zhur. Fiz. Khim., 35, 72 (1961) [Russ. J. Phys. Chem., No. 1 (1961)].
26. G. M. Svishchev, Optika i Spektrosk., 18, 614 (1965); Izv. Akad. Nauk SSSR, Ser. Fiz., 27, 696 (1963).
27. E. V. Shpol'skii, Uspekhi Fiz. Nauk, 68, 51 (1959).
28. E. V. Shpol'skii, Uspekhi Fiz. Nauk, 77, 321 (1962).
29. E. V. Shpol'skii, Uspekhi Fiz. Nauk, 80, 255 (1963).
30. E. V. Shpol'skii, Priroda, No. 10, 27; No. 11, 6 (1965).
31. Cl. Courpron, R. Lochet, Y. Meyer, and A. Rousset, Compt. rend., 250, 3095 (1960).
32. Y. Kanda and R. Shimada, Spectrochim. acta, 17, 7 (1961).
33. L. Pesteil, Compt. rend., 250, 497 (1960).
34. V. I. Mikhailenko, P. A. Teplyakov, V. V. Trusov, and V. M. Martynenko, Optika i Spektrosk., 20, 58 (1966).
35. I. B. Livshits and R. I. Personov, Zhur. Prikl. Spektrosk., 7, 400 (1967).
36. V. M. Vatul'ov, Ukrain. Fiz. Zhur., 7, 37 (1962).
37. T. N. Bolotnikova, L. A. Klimova, G. N. Nersesova, and L. F. Utkina, Optika i Spektrosk., 21, 420 (1966).
38. R. M. Hochstrasser and M. Robin, J. Chem. Phys., 45, 2270 (1966).
39. P. A. Teplakov, Optika i Spektrosk., 15, 645 (1963).
40. L. Pesteil and M. Rabaud, J. Chem. Phys. et physchem. biol., 59, 167 (1962).
41. V. I. Mikhailenko, Author's Summary of Candidate's Thesis, Higher Nautical School, Odessa, 1967.
42. E. V. Shpol'skii and E. A. Girdzhiyauskaite, Optika i Spektrosk., 4, 620 (1958).
43. L. A. Klimova, Optika i Spektrosk., 15, 344 (1963).
44. E. V. Shpol'skii, L. A. Klimova, and R. I. Personov, Optika i Spektrosk., 13, 341 (1962).
45. E. V. Shpol'skii and L. A. Klimova, Optika i Spektrosk., 13, 174 (1962).
46. M. K. Charkviani, Author's Summary of Candidate's Thesis, Tbilisi State University, Tbilisi, 1968.
47. A. Ya. Khesina, Optika i Spektrosk., 10, 607 (1961).
48. E. V. Shpol'skii and A. A. Klimova, Fiz. Problemy Spektrosk., 1, 209 (1962).
49. L. A. Klimova, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, Moscow, 1963.
50. R. I. Personov, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, Moscow, 1963.
51. E. V. Shpol'skii and R. I. Personov, Optika i Spektrosk., 8, 328 (1960).
52. R. I. Personov, Izv. Akad. Nauk SSSR, Ser. Fiz., 24, 620 (1960).

53. M. M. Val'dman, Optika i Spektrosk., 19, 531 (1965).
54. V. A. Butlar and D. M. Grebenshchikov, "Trudy Pervoi Mezhvuzovskoi Konferentsii Pedinstitutov po Radiofizike i Spektroskopii" (Proceedings of the First Inter-university Conference of Pedagogic Institutes on Radiophysics and Spectroscopy), Moscow, 1965, p. 24.
55. Z. Ruziewcz, Acta phys. polon., 28, 389 (1965).
56. M. M. Val'dman and G.D.Sheremet'ev, "Trudy Fizicheskogo i Matematicheskogo Fakul'teta Chelyabinskogo Pedinstituta" (Proceedings of the Physics and Mathematics Faculty of Chelyabinsk Pedagogic Institute, Vol. 2, 1964.
57. R. N. Nurmukhametov and G. V. Gobov, Optika i Spektrosk., 13, 676 (1962).
58. V. V. Trusov and P. A. Teplyakov, Optika i Spektrosk., 16, 52 (1964).
59. L. Pesteil, P. Pesteil, and F. Laurent, Canad. J. Chem., 42, 2601 (1964).
60. M. M. Val'dman, Candidate's Thesis, Lenin Moscow Pedagogic Institute, Moscow, 1964.
61. Z. Ruziewicz, Optika i Spektrosk., 15, 357 (1963).
62. R. N. Nurmukhametov, Uspekhi Khim., 35, 1129 (1966) [Russ. Chem. Rev., No. 7 (1966)].
63. L.Grajcar and S. Leach, Compt. rend., 252, 1014 (1961).
64. Y. Ripoche, Spectrochim. acta, 23A, 1003 (1967).
65. L. A. Mileshina, R. N. Nurmukhametov, D. N. Shigorin, and Sh. Nadzhmutdinov, Dokl. Akad. Nauk SSSR, 182, 386 (1968).
66. O. P. Kharitonova, Optika i Spektrosk., 21, 51, 166 (1966).
67. P. P. Dikun, Voprosy Onkologii, 7, No. 10, 64 (1961).
68. P. P. Dikun, Voprosy Onkologii, 6, No. 11, 75 (1960).
69. N. A. Fenina, Zhur. Prikl. Spektrosk., 6, 216 (1967).
70. L. F. Utkina, "Trudy Komissii po Spektroskopii Akademii Nauk SSSR" (Proceedings of the Committee on Spectroscopy, Academy of Sciences, USSR), Vol. 1, Part 1, Izd. Akad. Nauk SSSR, Moscow, 1964, p. 626.
71. L. F. Utkina, Izv. Akad. Nauk SSSR, Ser. Fiz., 29, 1410 (1965).
72. L. F. Utkina, see Ref. 3, p. 99.
73. M. Kasha, Disc. Faraday Soc., 9, 14 (1950).
74. M. A. El-Sayed, J. Chem. Phys., 38, 2834 (1963).
75. R. N. Nurmukhametov, V. G. Plotnikov, and D. N. Shigorin, Zhur. Fiz. Khim., 40, 1154 (1966) [Russ. J. Phys. Chem., No. 5 (1966)].
76. R. N. Nurmukhametov, Uspekhi Khim., 36, 1629 (1967) [Russ. Chem. Rev., No. 9 (1967)].
77. Kh. I. Mamedov and R. Z. Laipanov, Optika i Spektrosk., 20, 505 (1966).
78. Kh. I. Mamedov and R. Z. Laipanov, Zhur. Prikl. Spektrosk., 9, 475 (1968).
79. Z. Ruziewicz, Zesz. naukowe politechniki Wrocławskiej, Chemia, 14, 1 (1966).
80. Z. Ruziewicz, Proc. Intern. Confer. o Luminescence, Budapest, 1968.
81. M. A. El-Sayed (private communication).
82. T. N. Bolotnikova and G. V. Gobov, Izv. Akad. Nauk SSSR, Ser. Fiz., 27, 683 (1963).
83. G. V. Gobov, Izv. Akad. Nauk SSSR, Ser. Fiz., 27, 11 (1963).
84. G. V. Gobov, Candidate's Thesis, Moscow State Pedagogic Institute, Moscow, 1964.
85. K. Hausser, H. Kuhn, and E. Kuhn, Ztschr. Phys. Chem., 29, 417 (1935).
86. V. L. Levshin and Kh. I. Mamedov, Optika i Spektrosk., 12, 593 (1962).
87. N. N. Malykhina and M. T. Shpak, Optika i Spektrosk., 14, 829 (1963).
88. R. H. Dyck and D. S. McClure, J. Chem. Phys., 36, 2326 (1962).
89. G. V. Gobov, R. N. Nurmukhametov, and L. L. Nagornaya, Zhur. Fiz. Khim., 38, 1142 (1964) [Russ. J. Phys. Chem., No. 5 (1964)].
90. A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1957.
91. R. N. Nurmukhametov, O. S. Chepigo, and O. P. Shvaika, Zhur. Fiz. Khim., 39, 2951 (1965) [Russ. J. Phys. Chem., No. 12 (1965)].
92. T. S. Zhuravleva, R. N. Nurmukhametov, Yu. I. Kozlov, and D. N. Shigorin, Optika i Spektrosk., 22, 898 (1967).
93. G. Tsitsishvili, G. D. Bagratishvili, M. K. Charkviani, and G. G. Oniashvili, Soobshch. Akad. Nauk Gruz. SSR, 34, 331 (1964).
94. P. Bossignano, C. Cogrossi, and M. Gandino, Spectrochim. acta, 19, 1885 (1963).
95. G. V. Gobov and R. N. Nurmukhametov, Zhur. Fiz. Khim., 41, 2330 (1967) [Russ. J. Phys. Chem., No. 9 (1967)].
96. R. N. Nurmukhametov, G. V. Gobov, and L. N. Pushkina, Zhur. Fiz. Khim., 43, 57 (1969) [Russ. J. Phys. Chem., No. 1 (1969)].
97. V. L. Ermolaev, Optika i Spektrosk., 11, 492 (1961).
98. R. N. Nurmukhametov and G. V. Gobov, Optika i Spektrosk., 18, 227 (1965).
99. P. F. Teplyakov and V. A. Trusov, Optika i Spektrosk., 18, 63 (1965).
100. P. F. Teplyakov and V. A. Trusov, Optika i Spektrosk., 16, 52 (1964).
101. P. Longin, Compt. rend., 251, 2499 (1960).
102. E. Dorr, Ztschr. Electrochem., 61, 950 (1957).
103. V. L. Ermolaev, Optika i Spektrosk., 1, 523 (1956).
104. D. N. Shigorin, N. A. Shcheglova, and N. S. Dokunikhin, Dokl. Akad. Nauk SSSR, 137, 1416 (1961).
105. R. N. Nurmukhametov, Optika i Spektrosk., 23, 389 (1967).
106. N. A. Shcheglova, D. N. Shigorin, T. S. Ryabchikova, N. S. Dokunikhin, and Z. Z. Moiseeva, Zhur. Fiz. Khim., 37, 371 (1963) [Russ. J. Phys. Chem., No. 2 1963)].
107. N. A. Shcheglova, D. N. Shigorin, and N. S. Dokunikhin, Zhur. Fiz. Khim., 40, 1048 (1966) [Russ. J. Phys. Chem., No. 5 (1966)].
108. N. A. Shcheglova, D. N. Shigorin, and N. S. Dokunikhin, Zhur. Fiz. Khim., 36, 1938 (1962) [Russ. J. Phys. Chem., No. 9 (1962)].
109. N. A. Shcheglova, D. N. Shigorin, and N. S. Dokunikhin, Zhur. Fiz. Khim., 38, 1963 (1964) [Russ. J. Phys. Chem., No. 8 (1964)].
110. N. A. Shcheglova and N. S. Dokunikhin, Zhur. Phys. Khim., 38, 1261 (1964) [Russ. J. Phys. Chem., No. 5 (1964)].
111. T. M. Ivanova, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, Moscow, 1965.
112. R. N. Nurmukhametov, L. A. Mileshina, and D. N. Shigorin, Optika i Spektrosk., 22, 740 (1967).
113. B. S. Neporent and A. I. Inyushin, Dokl. Akad. Nauk SSSR, 98, 197 (1954).
114. L. F. Gladchenko, L. G. Pikulik, and I. L. Belozarevich, Optika i Spektrosk., 17, 209 (1964).
115. L. G. Pikulik and L. F. Gladchenko, Izv. Akad. Nauk SSSR, Ser. Fiz., 27, 758 (1963).

116. R. N. Nurmukhametov, I. L. Belaits, and D. N. Shigorin, Zhur. Fiz. Khim., 41, 1928 (1967) [Russ. J. Phys. Chem., No. 8, (1967)].
117. D. N. Shigorin, R. N. Nurmukhametov, and Yu. I. Kozlov, Optika i Spektrosk., 12, 659 (1962).
118. R. N. Nurmukhametov, D. N. Shigorin, and N. S. Dokunikhin, Zhur. Fiz. Khim., 34, 2055 (1960) [Russ. J. Phys. Chem., No. 9 (1960)].
119. R. N. Nurmukhametov, D. N. Shigorin, and N. S. Dokunikhin, Izv. Akad. Nauk SSSR, Ser. Fiz., 24, 728 (1960).
120. F. F. Litvin and R. I. Personov, Dokl. Akad. Nauk SSSR, 136, 798 (1960).
121. R. I. Personov, Optika i Spektrosk., 15, 61 (1963).
122. S. F. Shkirman and K. N. Solov'ev, Izv. Akad. Nauk SSSR, Ser. Fiz., 29, 1378 (1965).
123. A. N. Sevchenko, K. N. Solov'ev, S. F. Shkirman, and M. V. Sarzhevskaya, Dokl. Akad. Nauk SSSR, 153, 1391 (1963).
124. R. N. Nurmukhametov, Yu. I. Kozlov, D. N. Shigorin, and V. A. Puchkov, Optika i Spektrosk., 11, 606 (1961).
125. R. N. Nurmukhametov, D. N. Shigorin, Yu. I. Kozlov, and V. A. Puchkov, in collected papers "Fizicheskie Problemy Spektroskopii" (Collected Papers on Physical Problems in Spectroscopy), Izd. Akad. Nauk SSSR, Moscow, 1963.
126. R. N. Nurmukhametov, Yu. I. Kozlov, D. N. Shigorin, and V. A. Puchkov, Dokl. Akad. Nauk SSSR, 143, 1145 (1962).
127. Yu. I. Kozlov, D. N. Shigorin, R. N. Nurmukhametov, and V. A. Puchkov, Zhur. Fiz. Khim., 37, 2432 (1963) [Russ. J. Phys. Chem., No. 11 (1963)].
128. D. M. Grebenshchikov and V. V. Solodunov, see Ref. 54, p. 20.
129. T. M. Naumova and T. N. Bolotnikova, Optika i Spektrosk., 23, 384 (1967).
130. H. Zimmerman and N. Yoop, Ztschr. Electrochem., 64, 1215 (1960).
131. H. Zimmerman and N. Yoop, Ztschr. Electrochem., 65, 61 (1961).
132. H. Zimmerman and N. Yoop, Ztschr. Electrochem., 65, 66 (1961).
133. H. Zimmerman and N. Yoop, Ztschr. Electrochem., 65, 138 (1961).
134. H. Zimmerman and N. Yoop, Ztschr. Electrochem., 66, 342 (1962).
135. N. Mentzel and H. Zimmerman, Ber. Bunsen, Ges. phys. chem., 67, 582 (1963).
136. H. Gropper and F. Dörr, Ber. Bunsen, Ges. phys. chem., 67, 46 (1963).
137. F. Dörr and H. Gropper, Ber. Bunsen, Ges. phys. chem., 67, 193 (1963).
138. R. Müller and F. Dörr, Ztschr. Electrochem., 63, 1150 (1959).
139. M. Kasha, see Ref. 80, p. 000.
140. L. M. Shabad and P. P. Dikun, "Zagryaznenie Atmosfernogo Vozdukha Kantserogennym Veshchestvom" (Contamination of the Atmosphere with Carcinogenic Substances), Medgiz. Moscow, 1959.
141. O. L. Donetskaya and P. P. Dikun, Gigiena i Sanitariya, No. 7, 101 (1964).
142. P. P. Dikun and S. G. Chushkin, Voprosy Onkologii, 5, 34 (1959).
143. P. P. Dikun, "Doklady na VI Soveshchanii po Lyuminestsentsii" (Papers Presented at the 6th Conference on Luminescence), Leningrad, 1958.
144. P. P. Dikun, Voprosy Pitaniya, 24, 31 (1965).
145. A. A. Il'ina and R. I. Personov, Geokhimiya, 963 (1962).
146. A. A. Il'ina and R. I. Personov, "Trudy Vsesoyuznogo Neftyanogo Nauchno-issledovatel'skogo Geologorazvedochnogo Instituta" (Proceedings of the All Union Petroleum Scientific Research and Geological Prospecting Institute), No. 27, Leningrad, 1960, p. 217.
147. T. A. Alekseeva, "Trudy Vsesoyuznogo Neftyanogo Nauchno-issledovatel'skogo Geologorazvedochnogo Instituta" (Proceedings of the All Union Petroleum Scientific Research and Geological Prospecting Institute), No. 33, Leningrad, 1960.
148. L. F. Utkina, see Ref. 54, p. 53.
149. T. A. Teplitskaya, see Ref. 54, p. 66.
150. V. N. Florovskaya, R. B. Zezin, A. I. Ovchinnikova, Yu. I. Pikovskii, and T. A. Teplitskaya, "Diagnostika Organicheskikh Veshchestv" (The Diagnostics of Organic Substances), Izd. Nauka, 1968.
151. V. N. Florovskaya, T. A. Teplitskaya, and Yu. I. Pikovskii, Zhur. Prikl. Spectrosk., 3, 162 (1965).
152. V. N. Florovskaya, G. P. Vdovykin, T. A. Teplitskaya, and R. B. Zezin, Meteoritika, 26, 169 (1965).
153. V. N. Florovskaya, T. A. Teplitskaya, R. B. Zezin, and L. I. Ovchinnikova, Dokl. Akad. Nauk SSSR, 163, 450 (1965).
154. V. N. Florovskaya, T. A. Teplitskaya, and R. I. Personov, Geokhimiya, 538 (1965).
155. R. I. Personov and T. A. Teplitskaya, Zhur. Anal. Khim., 20, 1125 (1965).
156. B. Muel and G. Lacroix, Bull. soc. chim. France, 2139 (1960).
157. P. P. Dikun, Voprosy Onkologii, 7, 42 (1961).
158. R. N. Personov, Zhur. Anal. Khim., 17, 506 (1962).
159. A. Ya. Khesina, "Doklady na XIII Soveshchanii po Lyuminestsentsii" (Papers Presented at the 13th Conference on Luminescence), Khar'kov, 1964.
160. R. N. Nurmukhametov and G. I. Grishina, Zhur. Fiz. Khim., (in the press).
161. R. N. Nurmukhametov and G. I. Grishina, Zhur. Fiz. Khim., (in the press).

Karpov Physicochemical
Institute, Moscow