

MODERN TRENDS IN QUASI-LINEAR SPECTRA STUDIES

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ABSTRACT

The data of the theoretical and experimental investigations of the luminescence and absorption spectra of different organic compounds (aromatic hydrocarbons and their derivatives, phthalocyanines and porphyrins, polyenes, etc.) in frozen polycrystal solutions are summarized and systematized.

The recent data prove that quasi-line spectra are the sets of zero-phonon lines accompanied by their vibrational repetitions when the impurity arrangement provides insignificant heterogeneous line broadening and the electron-phonon interaction is sufficiently small.

Extensive experimental data make it possible to conclude that in the organic systems under consideration such conditions may be realised by means of a matrix modification near the impurity centres.

The characteristics of quasi-line spectra (namely, the well-resolved vibrational structure and the sensitivity to internal and external perturbations) are shown to be of use in solving different problems of molecular and crystal spectroscopy.

Quasi-linear fluorescence and absorption spectra of condensed aromatic hydrocarbons were discovered more than twenty years ago¹. In the first papers devoted to the study of these spectra it was shown that they were high-resolved vibronic spectra of polyatomic organic molecules^{2,3}.

To obtain quasi-linear spectra the crystallinity of the matrix is a prerequisite. Originally the choice of solvents was limited to normal saturated hydrocarbons (*n*-paraffins), which were crystallized on freezing. Later, however, solvents of other classes were used in a number of studies. Structural spectra of each compound studied can only be obtained in a limited number of solvents.

Temperature is a significant factor in the observation of a quasi-linear spectrum. Thus, in some cases it is sufficient to decrease the temperature to 77 K (for instance, *n*-paraffin solutions of a large number of aromatic hydrocarbons) while in others it is necessary to cool the solution tested to 20 K or 4 K (for instance, chlorophyll⁴, diphenylpolyene⁵ and benzophenone⁶ solutions).

At present quasi-linear spectra of about 500 compounds have been obtained and analysed. This means that we are dealing with a reasonably common phenomenon: a phenomenon which is consistent with the standard concept which is based on the discrete system of electronic and vibrational levels, of vibronic spectra of polyatomic molecules. Therefore, the problem

of the nature of quasi-linear spectra, in particular that of the narrow bandwidth, is closely associated with the inverse problem of the nature of diffuse bands in the radiation and absorption spectra of polyatomic molecules in liquid and solid solutions. At present theoretical and experimental data make it possible to solve the problem in principle.

From the point of view of the most general concepts homogeneous or heterogeneous widening can occur. The latter is associated with statistical spreading of the positions of the electronic levels of the molecules which interact with light†.

Recently Personov⁷ has shown that it is heterogeneous widening that accounts for the diffuse radiation and absorption spectra of aromatic hydrocarbons in some *n*-paraffins and organic glasses. Homogeneous widening depends upon the coupling of the electron transition with different vibrations in the molecule-solvent system.

It is known that independently of the frequency and character of the vibrations (acoustic and optical phonons, local modes including intramolecular ones, etc.) the influence of the electron transition on vibrations manifests itself in the displacement of equilibrium positions of normal coordinates and in the changes of the normal mode frequencies^{8,9}.

Generally these mechanisms of electron-vibration coupling are known to act independently and they both determine all of the spectral parameters—spectrum width as a whole, intensity distribution and the width and contours of individual bands.

Polycrystalline solutions of complex organic compounds are, in fact,

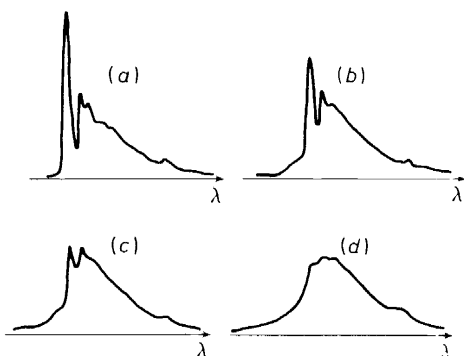


Figure 1. Temperature dependence of the zero-phonon line intensity. Fluorescence spectrum of perylene in *n*-hexane: $\lambda = 4408 \text{ \AA}$; (a) 4.2 K, (b) 20 K, (c) 28 K, (d) 40 K

a particular case of impurity-doped crystals whose long-wave absorption region is well separated from matrix absorption.

As early as 1963 Rebane and Khizhnyakov¹⁰ suggested that quasi-linear spectra were optical analogues of the Mössbauer effect. This means that the spectra of the systems under study were formed by a zero-phonon line and

† Since we are dealing with the question of molecular spectra, the interaction between identical molecules, which leads to the splitting of electronic levels into the zone, is not considered here.

its vibrational replicas. The works by Rebane and Khizhnyakov stimulated experimental studies aimed at confirming the zero-phonon character of bands in quasi-linear spectra and comparing experimental data with theoretically predicted results. Such tasks required detailed studies of the dependence of bandwidth and band-shape upon temperature.

Detailed studies of the quasi-linear spectra of some aromatic hydrocarbons¹¹⁻¹⁶ allowed an unambiguous separation of the phonon sideband from the zero-phonon line at 4.2 K and the decrease of zero-phonon line intensity, which is characteristic for an increase of temperature to be shown (Figure 1). Furthermore, temperature widening and shift, typical of optical lines, were observed.

It is known that the intensity and the width of a phonon sideband are mainly determined by the first mechanism of electron-phonon interaction (equilibrium position displacement of crystal modes as a result of electron transition)^{9,17}. The temperature widening and shift of zero-phonon lines are associated with the second mechanism of electron-phonon interaction, that is, the change of crystal vibration frequencies on the electron transition in the impurity.

An analysis of the experimental data has shown that among the systems

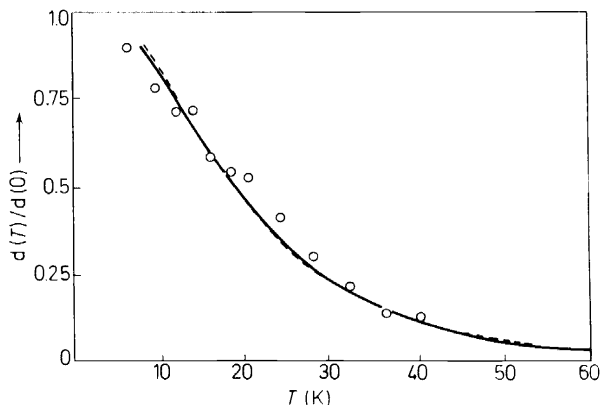


Figure 2. Temperature dependence of the Debye-Waller factor in the fluorescence spectrum band 4400–4450 Å of perylene in *n*-hexane: O, experimental data; —, calculated by means of photon state weighted density function; - - -, calculated according to the Debye approximation ($\theta = 80$ K)

tested there are cases of different strengths of electron-phonon coupling, both by the first and the second mechanisms. For instance, for 1,12-benzperylene in *n*-hexane at 4.2 K the Debye-Waller factor (which is known to be equal to the zero-phonon line integral intensity divided by the total band intensity) turned out to be 0.85. On the other hand for the perylene fluorescence spectrum in *n*-heptane the Debye-Waller factor at the same temperature has been found to be 0.23.

An analysis of phonon sideband structure made it possible to obtain the function $f(\omega)$ of phonon state weighted density and evaluate the Debye

temperature of crystals, which appeared to be 40–80 K for *n*-hexane and *n*-heptane. This function has been used to calculate the temperature dependence of the zero-phonon line intensity $I(\omega)$. The results of the measurements have turned out to be in good agreement with the theoretical predictions. The dependence $I(\omega)$, calculated according to the Debye approximation, shows that this approximation can be employed only in the temperature region below 80 K (Figure 2).

A comparison of the experimental data about the shift and width of zero-phonon lines with the theoretical formulae obtained by Krivoglaz and McCumber^{14–16} allowed the elucidation of a number of specific characteristics of quasi-linear spectra. It is known that according to Krivoglaz and McCumber the changes of crystal vibration frequencies are taken into account by perturbation theory and in the Debye approximation they can be presented in formulae permitting experimental testing. The line is of Lorentz shape. However, in all the cases tested the transformation of the line form from Gaussian at 4.2 K to Lorentzian at 75 K was observed and in a common case the contours were approximated by Voigt curves. The Gauss component practically does not depend upon temperature whereas the Lorentz component markedly increases with temperature. This means that at a low temperature the zero-phonon line width is determined by heterogeneous widening.

Studies on widening and displacement of zero-phonon lines reveal that a satisfactory agreement with theory has only been observed in some cases. In these the theoretical parameters are found to correlate, but in other cases the widening and shift of zero-phonon lines are not consistent with theoretical dependences, even in a low-temperature region at different values of the Debye temperature (from 50 K up to 150 K). Osad'ko¹⁷ has shown the inapplicability of the relationship in which quadratic terms in the electron-phonon coupling operator have been obtained by perturbation theory. In this paper¹⁷, the shift and widening of a zero-phonon line are calculated, taking into account an arbitrary value of that part of the electron-phonon interaction which determines the change of lattice elasticity constants as a result of electron transition in the impurity. The relationships obtained in an ultimate case¹⁷ are transformed into the formulae of Krivoglaz and McCumber. The experimental data on the shift and width of zero-phonon lines are satisfactorily consistent with the theoretically predicted relationships.

Consequently, one can conclude that the radiation and absorption spectra of polycrystal solutions have a quasi-linear character because of weak electron-phonon coupling (due to the first mechanism) of the impurity centre with the crystal lattice, provided that the heterogeneous widening, caused by statistical spreading of electronic levels of impurities, does not exceed the phonon sideband width.

In many cases the quasi-linear spectrum is complicated because of the so-called multiplet structure. Near the pure electron transition, a fine structure, sometimes having up to ten lines, is observed, which is reproduced throughout the vibronic spectrum. As early as the first stages of investigation it was suggested that the spectrum multiplicity is caused by the presence of different centres whose electron levels are shifted relative to one another.

An analysis of the experimental data on multiplet structure reveals that a number of multiplet components (the most intensive as a rule) are really associated with the difference in electron levels of the impurities. This is confirmed by the resonance coincidence of a few luminescence and absorption lines in the region of 0-0 transition, as well as by the relative displacement of the excitation spectra of different multiplet components in the fluorescence spectrum¹⁸. Considering porphyrine and phthalocyanine spectra, Korotaev^{19, 20} and Solov'ev with his co-workers²¹ independently reported reversible intensity redistribution between multiplet components at the irradiation of frozen solutions. According to these authors this phenomenon can be explained by the conversion of one centre type into another.

In a general case, the difference in centres can be caused either by the distinction in the orientation of impurity molecules or by the existence of several crystal modifications of the solvent^{22, 23}. However, all peculiarities of the multiplets cannot be explained solely by the presence of different centres. A detailed analysis of the structure of some complex multiplets^{24, 25} reveals that frequency intervals in the multiplet coincide with the frequencies of optical crystal modes.

An appearance of crystal frequencies in impurity spectra can be often observed and it is naturally explained by the interaction of electron transition in the impurity with the lattice modes. When considering such interactions the main role is usually assigned to the displacement of equilibrium positions of crystal modes at the electron transition. Therefore, the assignment of additional peaks to crystal vibrations is evident if the latter are mirror-symmetrical in fluorescence spectra and in long-wave absorption spectra, and if their intensity is temperature dependent in accordance with the Boltzmann distribution.

The difference in multiplet structure, which is often observed in the region of different electron transitions of the same molecule, can be explained both by discrepancy of electron levels and by different strengths of the electron-phonon interaction. However, there are frequent cases when multiplet structure cannot be explained within the framework of this pattern. Thus, the presence of non-resonance components in the region of pure electron transition, in the absence of mirror symmetry, in radiation and absorption spectra has been repeatedly reported^{26, 27}. This indicates that a consideration of the interactions of electron transition in the impurity with lattice optical vibrations as well as with acoustic phonons, cannot be limited by taking into account only one mechanism of electron-phonon interaction. In fact, it has been shown²⁸ that if, as a result of electron transition in the impurity, the frequencies as well as the equilibrium positions of the oscillators are changed, then even in the Condon approximation the mirror symmetry of fluorescence and long-wave absorption spectra is absent.

When the relative change of crystal vibration frequencies is less than the dimensionless displacement of equilibrium positions, the frequency distribution functions of phototransition intensity with the creation of the n -phonons $\Phi_n^g(\omega)$ in absorption and $\Phi_n^0(\omega)$ in radiation are completely determined by the one-phonon functions $\Phi_1^g(\omega)$ and $\Phi_1^0(\omega)$ (superscript g refers to the excited electronic state of the impurity and superscript 0 refers to the ground state). In the impurity spectrum, normal lattice modes appear which correspond

to the finite electronic state. The differences in the normal coordinate system lead to the fact that the projection of the equilibrium position displacement vector of the crystal modes on the normal coordinates may prove to be dependent upon the electronic state of the impurity. It is the difference in one-phonon functions, associated with this, that induces the disappearance of mirror symmetry.

If a relative change of the crystal mode frequencies is less than the dimensionless displacement of the equilibrium positions, then the differences in the absorption and fluorescence spectra should be largest in the case of the

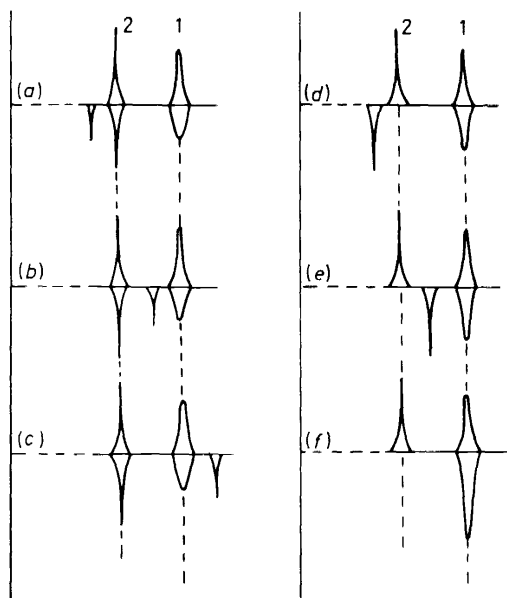


Figure 3. Differences in the vibrational structures of absorption (top) and fluorescence (bottom) spectra: 1, bands are assigned to the delocalized optical vibrations of crystal lattice; 2, bands of the local modes: (a), (b), (c) appearance of 'new' local modes; (d), (e), the shift of local mode frequency; (f), disappearance of the local mode from one of the spectra

discrete electron-phonon spectrum. In fact, the electronic state of the impurity does not influence the frequencies of delocalized crystal modes, i.e. optical phonons. Therefore, these frequencies, if they appear in the spectrum, should not be dependent upon electron transition and the relevant bands in fluorescence and long-wave absorption spectra should be located mirror-symmetrically. However, as a result of electron transition, both the frequencies and the number of local modes can be changed. Then, the structure of the absorption spectrum will be considerably different from that of the fluorescence spectrum (Figure 3). First, the appearance of 'new' local modes in one of the spectra will lead to the difference in the intensity of mirror-symmetrically located bands because of the conservation of integral spectrum intensity (Figure 3 a, b, c). Second, the frequency shift of local mode can lead

to its entry into the zone (Figure 3f), to the intensification of the band associated with delocalized optical modes and even to the disappearance of local mode from the spectrum.

A detailed analysis of the intensity distribution of multiplet components

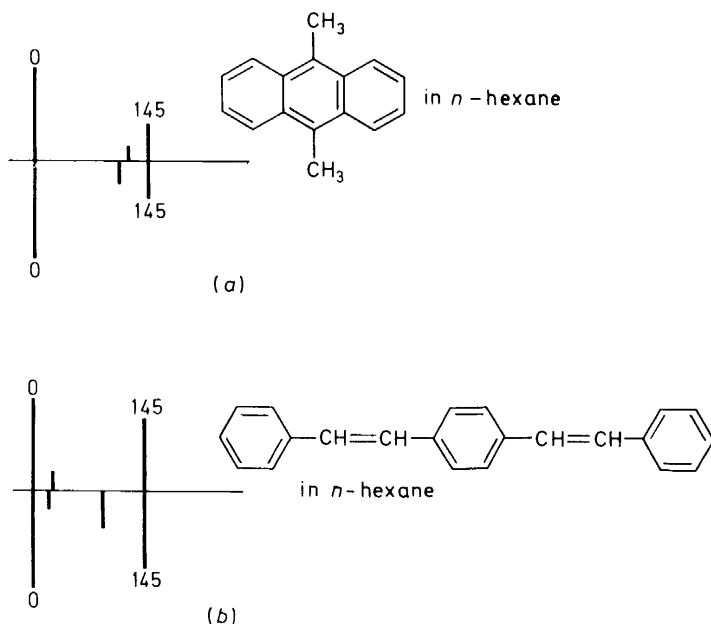


Figure 4. Part of the multiplet structure from the absorption (bottom) and fluorescence (top) spectra of (a) 9,10-dimethylantracene in *n*-hexane, (b) *p*-distyrylbenzene in *n*-hexane: temperature 4.2 K; (0 ± 145) cm⁻¹ bands are assigned to crystal optical modes

presents a number of experimental difficulties; however, a frequency analysis of some complex multiplets can serve as a qualitative confirmation of the validity of the theoretical results considered above (Figure 4).

Up to now we have discussed the problems mainly associated with the structure of vibronic bands (including the 0-0 band). Since quasi-linear spectra are well-resolved vibronic molecular spectra, they can serve as a source of information on intramolecular electron-vibration interactions as well as on electron-phonon interactions in an impurity crystal. The former interactions are the coupling of electron transitions in impurity molecules with the intramolecular vibrations. It is evident that with respect to the whole impurity crystal these vibrations are local and that the mechanisms of the electron-vibration interaction are not different from those of the electron-phonon interaction. However, it is the locality of these vibrations that results in the fact that the spectrum structure of each compound has individual characteristics.

The studies on quasi-linear spectra of individual compounds allowed not only the precise position of the electron energy levels and the values of the

vibration frequencies in the ground and excited electronic states to be determined, but also a number of regularities reflecting the connection between molecular composition, and sometimes the details of its structure, with fluorescence and absorption spectra to be elucidated. These problems have been discussed in a number of reviews^{29,30} and will not be dealt with here. We shall consider the possibility of using quasi-linear spectra for solving some quite general problems of electron spectroscopy of polyatomic molecules. For reliable interpretation of the spectra of complex molecules it is important to elucidate the applicability of one or another theoretical approximation. In this respect the quasi-linear spectra present extremely suitable objects for investigation since owing to an insignificant bandwidth it is possible to reliably separate the vibrational frequency progression and to compare the vibration frequencies in the ground and excited electronic states. In a large number of studies, it has been possible to show an unambiguous relationship between the vibrations active in fluorescence and absorption spectra. As a rule, changes of totally symmetric vibration frequencies are insignificant. This means that an analysis of such spectra can be limited to a consideration of only the first mechanism of the electron-vibration interaction, i.e. the changes in the equilibrium values of the appropriate normal coordinates at electron transition, whereas the change of force constants can be neglected. In this case, according to the Condon approximation, the intensity distribution in the progression of totally symmetric vibration is known to be determined by one parameter³¹ and the law of mirror symmetry of fluorescence and long-wave absorption spectra should be fulfilled. This does occur in the spectra of some aromatic hydrocarbons (anthracene, naphthacene, anthanthrene, etc.).

An analysis of a sufficiently large number of the spectra of aromatic hydrocarbons demonstrates that the Condon approximation can be applied to the interpretation of the spectra of the first electron transition, when characterized by high intensity and sufficiently separated from the rest of the transitions. When the electron transition is allowed, but is rather weak, the disappearance of mirror symmetry in the spectra is frequently observed^{23,33} (Figure 5). In this case the absence of symmetry cannot be explained by the change of the system of molecular normal coordinates at electron transition, as it has been previously explained for multiplets. In fact it has already been noted that totally symmetric vibration frequencies are changed insignificantly and the analysis of the spectra shows that deviation from the spectral symmetry is associated with the difference in intensity distribution in progression only of the totally symmetrical vibrations. It is clear that in this case the disappearance of symmetry is caused by the dependence of the electron wave functions upon the nuclear coordinates, that is, by the inapplicability of the Condon approximation. In previous studies it has been shown^{34,35} that electron wave function dependence on totally symmetric normal nuclear coordinates, according to the Herzberg-Teller theory, should result in non-mirror symmetry of the absorption and fluorescence spectra (the Herzberg-Teller effect for totally symmetric vibrations)³⁶. In order to describe these spectra it is necessary to introduce a second parameter (non-Condonian one) which will take into account the effect of electron transitions on the intensity distribution in the spectrum

of the first electron transition³⁵. The value of this parameter with only a linear term in the expansion of the electronic Hamiltonian in normal nuclear coordinates is determined by the relative intensity of the neighbouring transitions, by the distance between the electronic levels and by the strength of the vibronic perturbation (matrix element of the normal coordinate derivative of an electronic Hamiltonian). A comparison of intensities and energies of different electron transitions, carried out in a large number of aromatic hydrocarbons, shows that in many cases in order

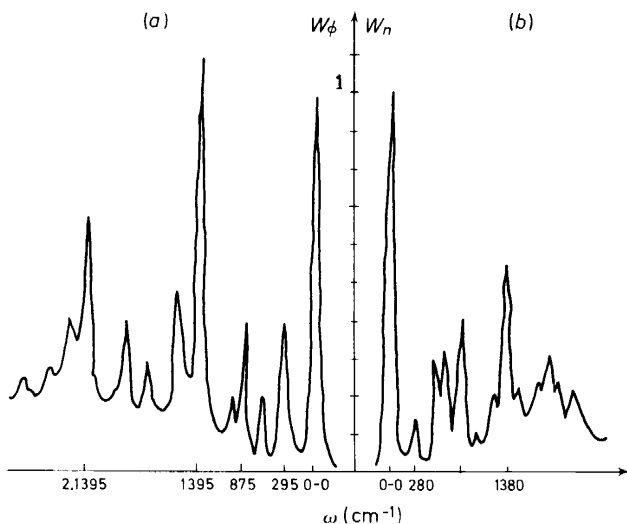


Figure 5. The mirror symmetry breakdown in the normalized absorption and fluorescence spectra of chrysene in *n*-heptane (77 K): (a) fluorescence, (b) absorption: (0-0) bands are 27 850 cm^{-1} ; 1380 (1395) cm^{-1} is the frequency of the dominant totally symmetric vibration in the spectra

to interpret the vibrational structure in fluorescence and long-wave absorption spectra (the region of the first electron transition) it is impossible to confine the consideration only to the influence of the adjacent transition³⁷. The non-Condonian parameter can be determined by the observed intensity distribution in the spectra. This parameter together with the data on the relative intensity and the position of the perturbing transition can be used to estimate the matrix elements of the vibronic perturbation. The evaluation of the matrix elements has been carried out for the spectra of some aromatic hydrocarbons³⁸. The matrix elements of vibronic perturbation are of the order of several hundred cm^{-1} , the applicability criteria of the perturbation theory being fulfilled. In analysing the observed spectra, the symmetry of the electronic state and the directions of the dipole moments of the electron transitions have been taken into account^{37, 38}.

It can be concluded from the above that quasi-linear spectra are extremely suitable for the study of different types of electron-vibration interactions. Electron-phonon interaction with acoustic phonons determines the inten-

sity and form of the phonon sideband (the first mechanism) and the temperature shifts and widening of the zero-phonon lines (the second mechanism). Electron-phonon interaction with crystal optical modes determines the fine-band structure, in particular, some peculiarities of the multiplet structure (the first and the second mechanisms). The interaction of electron transition with high-frequency intramolecular vibrations by the first mechanism and vibronic interactions, determine the energy distribution in the spectrum as a whole.

At all stages of the investigation of quasi-linear spectra much attention has been paid to the determination of how impurity fixation into crystals provides such an insignificant heterogeneous widening of the bands. Crystallographic studies of such systems are impossible, first of all because of the impurity concentrations being too low. The initial concentration of the solution at room temperature seldom exceeds 10^{-2} mol l⁻¹. Since most of the compounds tested are slightly soluble even in fluid paraffins, the impurity arrangement into the polycrystal solvent matrix can occur in different ways, i.e. as matrix-isolated molecules, segregations, microcrystals. This leads to the fact that the observed fluorescence and absorption spectra of frozen polycrystalline solutions are considerably dependent upon concentration, freezing rate, presence of additional impurities in the solution, etc. The effects of all these factors on the spectra have been studied in a large number of papers³⁹⁻⁴⁵. The results obtained make it possible to divide the frozen solutions with quasi-linear fluorescence and absorption spectra into two groups.

The following features are characteristic of the solutions of the first group: Quasi-linear spectra are observed starting from the lowest concentrations. As the concentration increases the diffuse bands are found to superimpose the quasi-linear spectra; these diffuse bands are then transformed into a spectrum of the crystal of impurity. The intensity of the quasi-lines decreases on slow freezing of the solutions; the excitation spectra of fluorescence are different in different centres; the excitation spectra of sensitized fluorescence coincide with diffuse absorption spectra. All these data allow the quasi-linear spectrum to be considered as belonging to matrix-isolated molecules, and wider bands—to molecular aggregates. Such concentration behaviour of spectra is characteristic, first, of systems with comparable linear size of impurity molecules and solvent molecules (benzene-cyclohexane; anthracene-heptane, phenanthrene-hexane, etc.). Evidently, in these cases it is easy for the impurity to substitute solvent molecules in the lattice. Second, the spectra of diluted solutions of aromatic hydrocarbons with flat branched molecules in low-molecular paraffins (3,4-benzpyrene in cyclohexane, *n*-hexane, etc.) are of a quasi-linear nature. This can be explained by an orienting effect of such molecules on relatively small-sized solvent molecules. In this connection it becomes clear why the most complex structures of multiplets are characteristic of large low-symmetrical molecules⁴⁶.

In the intermediate case the concentration behaviour of solution spectra is quite different (the second group of solutions). When the concentrations are low the spectrum consists of diffuse bands and with an increase of concentration the spectrum becomes a quasi-linear one. The latter is often

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accompanied by an appearance of spectral bands of aggregates and micro-crystals. Evidently in such solutions an increase of the concentration causes an increase of the extent of orderliness of impurity molecules relative to solvent molecules, thus leading to a decrease of heterogeneous widening.

The assignment of quasi-linear spectra to isolated molecules is confirmed once more by the structural characteristic of fluorescence excitation and by the absence of electron excitation energy transfer from these centres.

The decrease of heterogeneous band widening as a result of a concentration increase is associated with the 'alignment' effect of the solvent crystal

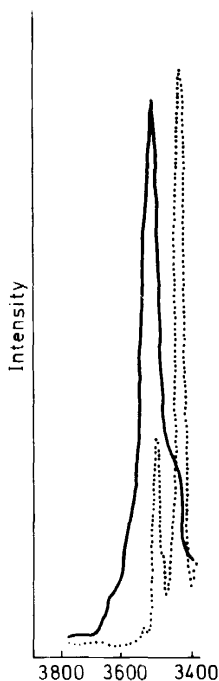


Figure 6. The shift of the original band in the quasi-linear fluorescence excitation spectra of coronene in *n*-heptane as a result of matrix rearrangement due to the addition of $10^{-2} \text{ mol l}^{-1}$ of naphthalene into the solution. The fluorescence spectrum of naphthalene is of a quasi-linear nature at the concentration used

lattice near the impurity molecules. Since the size of the impurity molecules is comparatively small, their local concentration should be high and this is provided by non-equilibrium conditions of solvent crystallization. Such a rearrangement of the matrix affects the position and multiplicity of the quasi-linear spectrum of the second component added to the solution in small amounts⁴⁷ (Figure 6). The effect of the impurity on the matrix structure has been independently confirmed by the observation of the shift of the phase transition point in a crystal solvent⁴⁷. The shift has been observed at the introduction of impurity which has a quasi-linear spectrum only at higher concentrations (e.g. 1,12-benzperylene in cyclohexane).

In conclusion it should be pointed out that the comparative simplicity of the method of quasi-linear spectra, and the strict individuality and high sensitivity of the spectra to various external perturbations of different kinds make it possible to use them for solving a number of problems confronting molecular spectroscopy. The discussion of these important problems is beyond the scope of this paper.

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