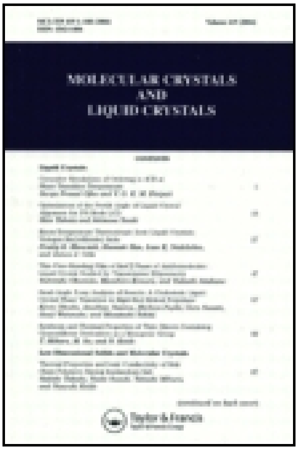

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Davydov Splitting in the Absorption Spectra of Molecular Crystals

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Davydov Splitting in the Absorption Spectra of Molecular Crystals†

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Davydov splitting of the absorption spectra of molecular crystal is considered from the standpoint of the law of conservation of the first spectrum moment. Various models of states of crystal excitations are applied to the analysis of the law:

1. Davydov one-particle model of rigid lattice,
2. Rashba two-particle model of vibron states of rigid lattice,
3. The model based on exciton–phonon and vibron–phonon interactions.

The analysis, based on exciton–phonon and vibron–phonon spectra of benzene crystals, naphthalene and anthracene crystals, shows that it is feasible to determine both values of parameters of exciton–phonon and vibron–phonon interactions and Davydov splittings in the exciton and vibron regions of spectrum.

1 INTRODUCTION. ABSORPTION SPECTRUM MOMENTS

The optical spectrum can be described by moments.[1,2] The description, complemented by the analysis of energy values of the transitions that coincide with the positions of individual bands, is actually a quantitative spectrum description. In this case two first moments are of the greatest importance, the former being the zeroth (integral intensity), and the latter being the first moment (the position of gravity centre), both are spectrum integrals. In the latter case it is of particular interest not the gravity centre itself but the difference between the gravity centres in two spectrum components, obtained by varying the polarization of incident light. Integral properties of

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these moments are expressed by the conservation laws. The conservation law of the zeroth moment states that the integral intensity of the complete crystal spectrum is equal to that of molecular spectrum. The conservation law of the first moment, however, denotes that the difference between the gravity centres in the complete crystal spectrum of the two components is Davydov splitting, that corresponds to the total resonance interaction, and also that the quantity does not depend on pattern of the coupling of electron excitation with the internal and external vibrations of the lattice. In the above mentioned interpretation the conservation laws in the molecular crystal spectra have been stated by Merrifield.[2] Actually, however, one never has perfect conditions for making an investigation into the complete crystal spectrum. We are generally concerned only with the lowest electron transition, but, as a matter of fact, even only with some part of its vibron structure. Therefore, let us consider what these integral features are in this region of spectrum and what they describe.

The problem on electron excitations of the molecular crystal is rather complicated. The excitations are described by the properties of the system of the three interplaying quasi-particles: exciton, internal and external phonons. In view of complexity of considering the problem in the general view a series of approximations has to be applied, As a consequence, one should comprehend genetic alterations of the concerned integral characteristics employing the models in succession.

As far as the intensity is concerned, the question is rather plain. The intensity of each vibron transition or their aggregates is described either by the intensity of the allowed transition in the molecular spectrum corresponding to the vibron transition or one should take into account the effect of configuration mixing[3,4] in case of the breakdown of molecular spectrum forbidence or its intensity significant change in crystal. Therefore, in what follows, Davydov splitting will be given a major attention to.

2 DAVYDOV SPLITTING AND CRYSTAL VIBRON STATE MODELS. RIGID LATTICE

Historically, it was Davydov who first developed one-particle model for a rigid lattice.[5–7] According to the model the terms of the molecule spectrum shifted due to static interactions coincided with the gravity centres of density of states of the appropriate one-particle exciton and vibron crystal states. The absorption spectrum was described by a series of δ-bands (see Figure 1) corresponding to optical transitions, the conservation law of wave vector as $\mathbf{K}_{ex} = \mathbf{q}_{pt} \approx 0$ being observed. Davydov splitting, introduced in the theory[5] as the distance between the levels with $\mathbf{K}_{ex} = 0$ are split by removing the

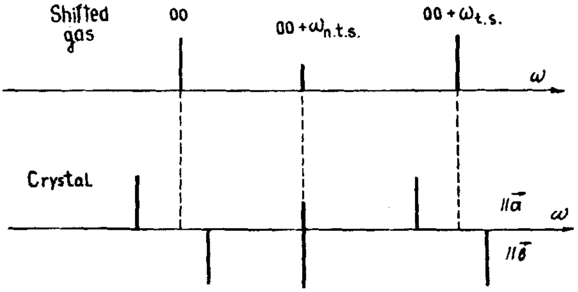

FIGURE 1 Scheme of absorption spectra of gas and crystal. One-particle approximation. Rigid lattice. Several molecules are assumed to be in the unit cell of the crystal. $\|a$ and $\|b$ correspond to the two reciprocally perpendicular directions of the incident light polarization. $\omega_{\text{n.t.s.}}$ and $\omega_{\text{t.s.}}$ are the frequencies of non- and totally symmetric internal vibrations respectively.

exchanged degeneration of exciton bands, was determined as the distance between these δ-bands. As consequence, in practice, so far Davydov splitting has been determined in most cases as the distance between the maxima of markedly polarized bands in an absorption spectrum.

McClure, however, as early as 1958 noted[8] that there might be two types of vibron configurations in the system of a weakly coupled double molecule: namely, the joint and separated ones (see in detail the review[9]). Their energies must differ by the value of energy of coupling of electron and vibration excitations. This value can be estimated as a sum of the Frank–Condon energy and change in the vibration frequency $\delta\omega$ under electron excitation. From the same point of view Rashba in 1966, suggested a dynamic model of vibron states.[10–12]

According to this model the vibron states of a molecular crystal are described as a set of coupled and dissociated states of the system of the quasi-particles: exciton and one or several internal phonons. The lattice was assumed to be rigid.

For the two-particle system, vibron states of the crystal are classified as one-particle and two-particle states. If the position and the dimensions of the exciton band in the crystal energy spectrum are known, the energy region of two-particle or dissociated states can easily be found by the shift of the exciton band towards high energy region by the phonon frequency in a ground state (Figure 2). If the phonon band shows dispersion, the spectrum width of two-particle states should be corrected for this value. Depending on the energy sign of the electron-vibration coupling E_{cp}, one-particle vibron states are on the right ($E_{\text{cp}} > 0$) or left hand ($E_{\text{cp}} < 0$) of the spectrum. The conception of coupled and dissociated states was developed in a number of recent papers on the crystal vibron spectra.[13–16]

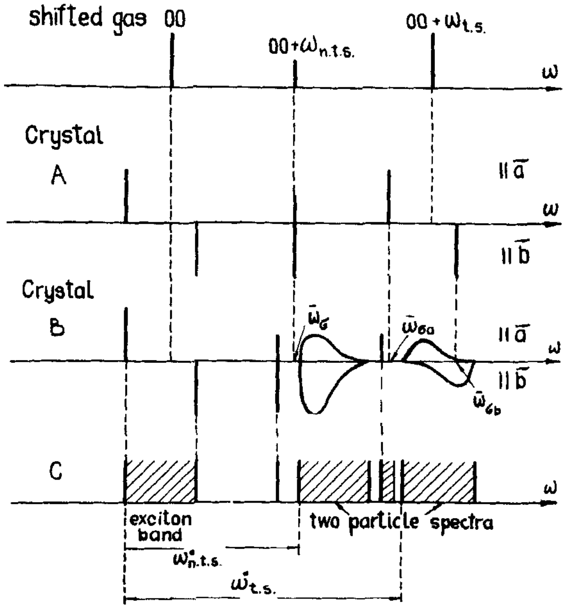

FIGURE 2 Schematic comparison between the absorption spectra of a free molecule and crystal. The lattice is rigid. (A) One-particle approximation. (B) Two-particle approximation. (C) Scheme of an energy spectrum for the case of (B). $\bar{\omega}_\sigma$, $\bar{\omega}_{\sigma_a}$ and $\bar{\omega}_{\sigma_b}$ are the centres of gravity of absorption spectra. ω^0 are vibration frequencies in ground electron state.

The crystal optical spectrum in the vibron region is represented by the two types of bands: δ-bands for the one-particle absorption and two-particle wide bands caused by the enlarged selection rule for the wave vector $\mathbf{K}_{ex} + \mathbf{K}_{ph} = \mathbf{q}_{pt} \approx 0$. The comparison with the Davydov model (Figure 2) shows that the positions of δ-peaks in the Davydov model correspond to the positions of centres of gravity of the total vibron spectrum in the Rashba model. Davydov splitting is determined as the difference in these positions ($\Delta_{\mathrm{Dav}} = \bar{\omega}_{\sigma_a} - \bar{\omega}_{\sigma_b}$, see Figure 2). The absorption may chiefly be one-particle as in the benzene crystal[9,17,18] or mixed as in the naphthalene crystal,[9,17,19] or, finally, completely two-particle as in the anthracene crystal.[9,17] The pronounced spectrum polarization is hence determined not by the type of vibron absorption but by the value of resonance interaction in this vibron state.

3 GENERAL FORMULATION OF THE PROBLEM ON EXCITON–PHONON AND VIBRON–PHONON INTERACTIONS

The current theory of vibron states has advanced one considerably towards the qualitative and quantitative interpretations of absorption spectra of molecular crystals. It enabled one to calculate theoretically the shape of the spectrum of two-particle absorption under certain ratios of parameters and as well as to determine the positions of bands of the one-particle absorption.[10,19] Also, in this theory the bands of one-particle absorption both exciton and vibron are represented as δ-bands. Whereas in practice real spectra always consist of the bands of finite width, sometimes, a rather large one. That is due to the interaction of appropriate quasi-particles, exciton and vibrons with external phonons. Naturally, this interaction must affect the shape of the two-particle spectrum.

In its general formulation, the problem on the interaction of the three types of quasi-particles has not been solved so far. Theoretically, the mostly developed is the case as expressed in the following assumptions: $\omega_{\mathrm{ph}_1} > \omega_{\mathrm{ph}_2}$; $H_{\mathrm{exph}_1} > H_{\mathrm{exph}_2} \approx H_{\mathrm{exph}_1\mathrm{ph}_2}$. The term $H_{\mathrm{ph}_1\mathrm{ph}_2}$ is small. At the same time $H_{\mathrm{ex}} \approx H_{\mathrm{exph}_1} \ll \omega_{\mathrm{ph}_1}$. Here ω_{ph_1} and ω_{ph_2} are the frequencies of internal and external phonons, respectively. H_{exph_i} describes the interaction of exciton with the i-th phonon. H_{ex} is the exciton kinetic energy. It should be noted that these particular requirements are met when we deal with a common phenomenon, namely, the vibron structure is pronounced in the crystal absorption spectrum, and the effects due to the interaction with external phonons are not too great. The wellknown spectra of benzene, naphthalene, anthracene and other crystals might be a good example to this.

A great deal of papers are devoted to the problem on the interaction of electron excitation with phonons. But the theoretical problem has been solved successfully only when the interaction of the crystal one-particle excitation (electron, exciton, vibron, etc.) with phonons was involved. Notwithstanding, the problem on the interaction of many-particle excitation states has still to be solved. To illustrate this interaction, above mentioned two-particle vibron states could be pointed out. Therefore, further the exciton crystal states will be dealt with. Thereupon, the conclusions made will be extended to the spectra of one-particle vibron absorption.

4 DAVYDOV SPLITTING IN THE CRYSTAL EXCITON SPECTRUM. REAL LATTICE

The molecular crystal absorption corresponding to the pure electron excitation of a free molecule is generally implied the region of exciton absorption. Actually, the observed absorption is the exciton-phonon one. Two problems arise when analyzing this spectrum, *i.e.*, 1) the determination of characteristics of the electron resonance interaction as such, 2) the detection of free or "phononless" excitons and the evaluation of their dynamic parameters.

Two stages of the problem should be emphasized. It is usually assumed that the occurance of sharply polarized regions of absorption in a crystal spectrum and, that is, Davydov splitting, is unambiguous testimony to exciton presence. The very Davydov splitting value Δ_{Dav} is employed in this case as an estimation of the exciton band width. But, it may be the case when the interaction with phonons is so great that the exciton state being stationary in the rigid lattice, is no longer as stationary in the real lattice. The observed absorption may thus be many-particle exciton–phonon one. As a matter of fact, Davydov splitting still describes the very electron resonance interaction. But the exciton, as a steady quasi-particle, as well as the exciton band peculiar to the exciton are absent. The ratio of the exciton kinetic energy to the part of the exciton–phonon interaction energy E_{int} inducing the steady state damping is a quantitative parameter in analyzing the real situation. The exciton kinetic energy is being the band width in the rigid lattice or the Davydov splitting value in the real spectrum. Recently, the methods have been developed to determine the E_{int} values by the computer quantitative processing of experimental spectra.[20,21]

The experimentally determined nondimensional light absorption coefficient $æ(\omega)$ expressed through the microscopic characteristics of medium, the tensor of dielectric permeability, $\varepsilon = \varepsilon' + i\varepsilon''$, has the form[7]

$$æ(\omega) = \frac{\operatorname{Im} \varepsilon(\omega)}{2\sqrt{\operatorname{Re} \varepsilon(\omega)}}. \tag{1}$$

The dielectric permeability is associated with the Green function $G(\omega)$ for the excitons with $\mathbf{K}_{\text{ex}} = 0$ interacting with phonons. For low-intensity transitions $\operatorname{Re} \varepsilon(\omega) = n^2 \approx$ const. This approximation is valid for benzene and naphthalene crystals. In this case, in the Condon approximation there is an unambiguous relation between $æ(\omega)$ and $G(\omega)$ in the form[7,22]

$$a(\omega) = \frac{æ(\omega)}{\int æ(\omega')\, d\omega'} = -\frac{1}{\pi} \operatorname{Im} G(\omega). \tag{2}$$

The Green function explicit form depends on the type of elementary excitation interacting with phonons. In the case of nonlocalized exciton states, it is convenient to express the Green function through the mass operator $M(\omega)$[7]

$$G(\omega) = [\omega - \omega_0 - M(\omega)]^{-1} \tag{3}$$

where ω_0 is the exciton energy for $\mathbf{K} = 0$ in the rigid lattice and

$$M(\omega) = \Delta(\omega) - i\pi\gamma(\omega). \tag{4}$$

Here $\Delta(\omega)$ describes a change in the exciton energy and $\pi\gamma(\omega)$ does its damping which are due to interaction with phonons. Thus, the value $\pi\gamma(\omega)$ is the energy of interaction which one needs to determine the quasi-stationarity of the exciton state.

From (2) and (3) the common formula is derived for the description of optical spectrum

$$a(\omega) = \frac{\gamma(\omega)}{[\omega - \omega_0 - \Delta(\omega)]^2 + \pi^2\gamma^2(\omega)}. \tag{5}$$

The feedback between $\gamma(\omega)$ and $a(\omega)$ can be suggested[21] based on the relations (2) and (4) just as it was the case with the determination of the exciton states density from the two-particle vibron absorption spectrum.[19] It can be seen that the expression for $\gamma(\omega)$ has the form

$$\gamma(\omega) = \frac{a(\omega)}{\left[\displaystyle\fint \frac{a(\omega')}{\omega - \omega'}\,\mathrm{d}\omega'\right]^2 + \pi^2 a^2(\omega)}. \tag{6}$$

If one employs only the linear term of expansion into small shifts from the equilibrium position in the operator of the exciton–phonon interaction, the functions $\Delta(\omega)$ and $\gamma(\omega)$ turn out to be correlated by the dispersion relation.

$$\Delta(\omega) = \fint \frac{\gamma(\omega')}{\omega - \omega'}\,\mathrm{d}\omega' \tag{7}$$

if the additional condition fulfilled

$$\omega_0 = \bar{\omega} = \int \omega' a(\omega')\,\mathrm{d}\omega'. \tag{8}$$

Integration in (6), (7) and (8) is performed throughout the whole region of the exciton–phonon spectrum. It should be noted that although ω_0 concides with $\bar{\omega}$ only in the linear approximation with respect to the exciton–phonon interaction, the difference of $\bar{\omega}$ in various components of the spectrum always determines the Davydov splitting value.

Thus, relation (6) enables one to determine the necessary energy characteristics of the exciton–phonon interaction E_{int} using the experimental data. We may apply expression (8) to determine the values of Davydov splitting in the rigid lattice and estimate the widths of undisturbed exciton bands through them.

Now, we apply this approach to the analysis of absorption spectra in some crystals.

5 ANALYSIS OF THE EXCITON ABSORPTION OF BENZENE, NAPHTHALENE AND ANTHRACENE CRYSTALS

Benzene Figure 3a shows the exciton absorption of benzene crystals.[21,23] The spectrum is strongly dependent on the incident light polarization. This dependence is pronounced in the initial absorption region represented by the narrow strongly polarized *a*, *b* and *c*-bands, and, more smoothed off in the short-wave wide-band region. Because of this, the *a*, *b* and *c*-bands are assumed to be referred to as the components of the Davydov triplet in a crystal.[24,25]

The values of Davydov splitting were determined from the difference of positions of their maxima. However, as seen from the figure, each of the above mentioned bands is followed by the intense wide band. Table I gives the ratios of integral intensities of wide-band absorption to the total integral intensity, α. These values, as seen from the table, are not very small, so that

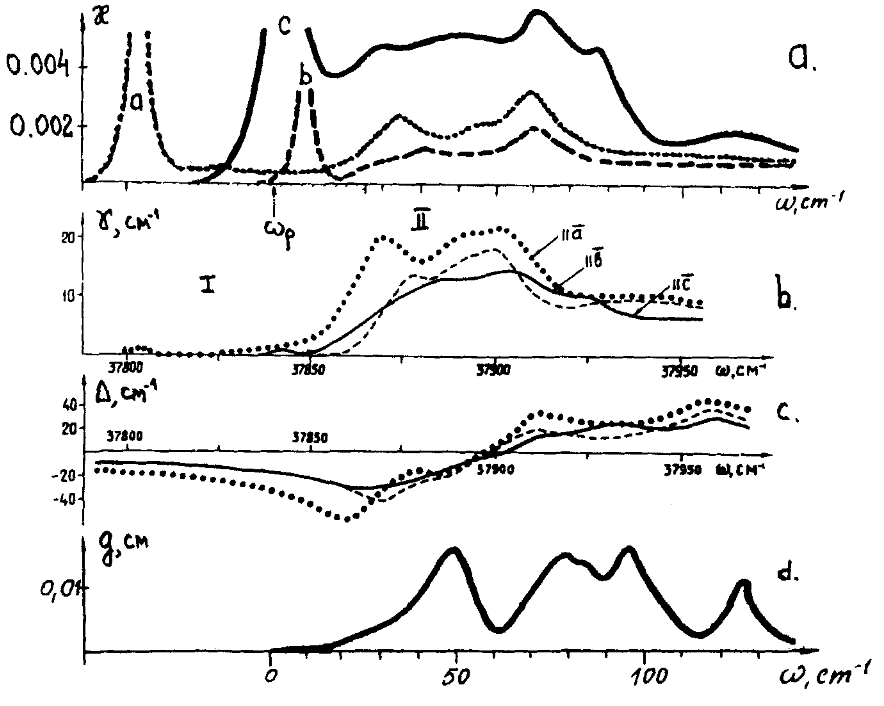

FIGURE 3 (a) The spectrum of exciton–phonon absorption of benzene crystal in polarized light, $T = 4{,}2$°K.[21] The shading region corresponds to the exciton band width. ω_p is the centre of gravity of exciton density of states.[24] (b) and (c) Calculated according to (6) and (7) functions $\gamma(\omega)$ and $\Delta(\omega)$ for the spectra of (a). Marking of the curves of (b), (c) and (a) corresponds to each other. (d) The density of phonon states of benzene crystal.[26] The beginning of reading of $g(\omega)$ is coincident with ω_p.

TABLE I

Values of Davydov splittings and relative intensities of phonon sidebands of the exciton–phonon spectrum of benzene crystal.

Band polarization	$\bar{\omega}$, cm^{-1}	Δ_{Dav}, cm^{-1}	$\omega_{\max}$	$\tilde{\Delta}_{\mathrm{Dav}}$, cm^{-1}	ω_0 through (8)	α
IIa	37821		37803		37822	0,2
IIc	37861	$\Delta_{ca} = 40$	37842	$\Delta_{ca} = 39$	37859	0,34
IIb	37870	$\Delta_{ba} = 49$	37848	$\Delta_{ba} = 45$	37870	0,38

[a] $\alpha = (I_{\mathrm{ph}}/I_0 + I_{\mathrm{ph}})$, I_0 and I_{ph}—are the integral intensities of phononless bands and phonon sidebands, respectively.

the problem on the correspondence of *a*, *b* and *c*-bands to the crystal steady excitons states is to be solved. To do this, one should determine the true values of Davydov splittings in this absorption region as well as the value $\pi\gamma$.

The values of Davydov splittings in the rigid lattice were determined from the difference of centres of gravity in the observed spectra. Their values are represented in the table. The width of the crystal exciton spectra $E = 63$ cm^{-1} corresponds to these values Δ_{Dav}.

The values $\gamma(\omega)$ were calculated from expression (6). The results are given in Figure 3b. As seen from the figure, the two regions I and II with different almost by 10 times values of γ can be marked out in the dependencies $\gamma(\omega)$. Region 1 coincides with the region of *a*, *b* and *c*-absorption bands. The values γ do not exceed 1,5–2 cm^{-1}, so that $\pi\gamma \ll E$. It follows that *a*, *b* and *c*-excitons are rather steady in the benzene crystal and *a*, *b* and *c*-bands correspond to phononless transitions allowing for the interaction only with virtual phonons. Consequently, the wide-band short-wave absorption is the phonon sidebands of these bands. More detail analysis of the shape of the sidebands and their relation with the density of crystal phonon states have been given earlier.[23]

Since the asymmetry of *a*, *b* and *c*-bands is small, the distance between their maxima enables one to determine the values of Davydov splittings of the crystal exciton bands involving "dressing" effects caused by virtual phonons.[27] The values of these Davydov splittings $\tilde{\Delta}_{\mathrm{Dav}}$ are given in the table. As seen from the table, the Davydov splittings values which are determined from the centres of gravity exceed the values of splitting in the real crystal only by 5–10%. The relative contribution of the intensity of phonon sidebands to the total absorption intensity is 20–30%.

There is always some uncertainty as to the length of absorption region when determining experimentally the position of gravity centre, since the error due to weak sidebands may be considerable. We confined to the region of one-phonon transitions when determining $\bar{\omega}$ as in a more short-wave part of the spectrum the absorption level was no longer discerned from the background.

However, if the law of exciton-phonon interaction is linear (the values $\alpha \approx 0{,}3$ serve as the basis for such assumption), $\bar{\omega}$ coincides with ω_0, and we have an unambiguous relation between the functions $\Delta(\omega)$ and $\gamma(\omega)$ in the form (7). On the other hand, from (5), the relation follows

$$\omega_0 = \omega_{\max} - \Delta(\omega_{\max}) \tag{9}$$

where $\omega_{\max}$ are the frequencies of maxima of phononless bands. This expression may serve as a check upon the validity of ω_0 determining.

The calculated functions $\Delta(\omega)$ are given in Figure 3b. From the figure and the table it is well seen that the values ω_0 obtained according to (9) agree well with the determined values when calculating the first spectrum moment.

Naphthalene The crystal absorption spectrum in this region is well studied quantitatively.[28,29] It consists of three bands. From these the bands A_1 and B_1 are polarized along the orthogonal directions of the incident light at right angles to and in parallel with the *b*-axis of the crystal, respectively. As it has been shown,[30] these bands are genetically connected with the band of the pure electron transition in molecule.

In contrast to the benzene crystal, the exciton-phonon absorption involves no pronounced phonon sideband, which, at first, seems to be strange, in particular, with respect to the intense B_1-band (Figure 4). The question arises, however, to what extent the bands A_1 and B_1 may be referred to as Davydov doublet components corresponding to the excitation of one-particle exciton states.

To clear up the question, one should treat the matter as in the case of the benzene crystal. The value of Davydov splitting in the rigid lattice, estimated by the gravity centres of A_1 and B_1 bands is 153 cm^{-1}. It exceeds only by 2 cm^{-1} the value obtained as the difference of positions of maxima of these bands due to small asymmetry of the B_1-band. Hence, the exciton band width in the rigid lattice E approaches that found experimentally[19] and being $\approx$ 180–200 cm^{-1}.

The calculated according to (6) values $\gamma(\omega)$ in the *b*-component of the spectrum are shown in Figure 4. The maximum values γ for A_1 band do not exceed 0,25 cm^{-1}. As seen from the figure $\pi\gamma_B \ll E$. This inequality is valid for the A_1-band even to greater degree. Thus, the A_1 and B_1 bands correspond to the excitation of one-particle exciton states, dynamics of which got

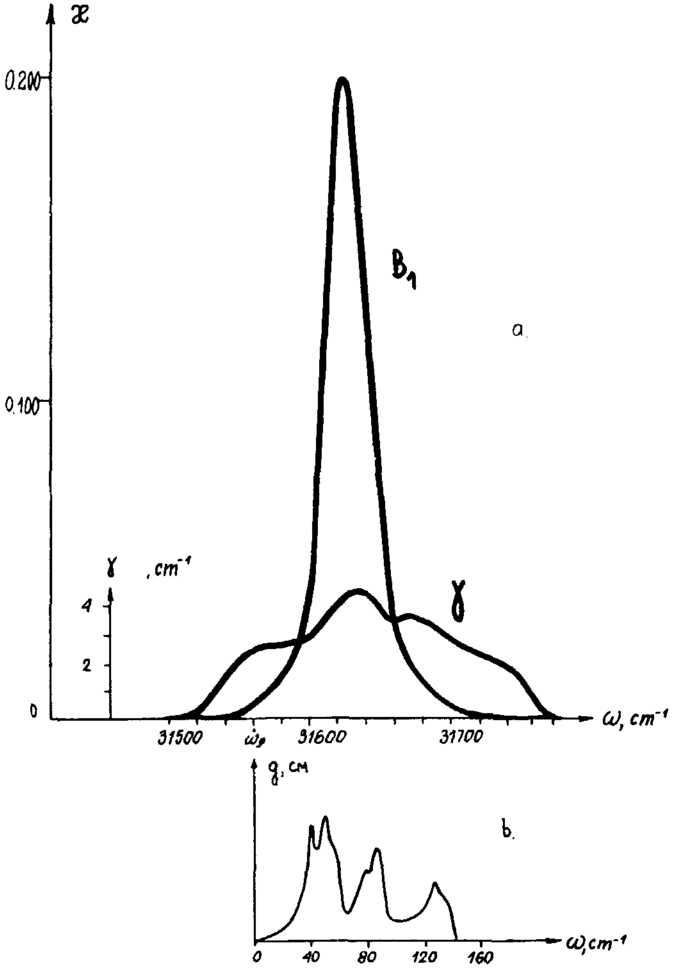

FIGURE 4 (a) The B_1-band of the exciton-phonon absorption of napthalene crystal[29] at $T = 4{,}2°K$ and the calculated function $\gamma(\omega)$. ω_ρ is the centre of gravity of the exciton band.[19] (b) Density of phonon states of naphthalene crystal.[31] The beginning of reading of $g(\omega)$ is coincident with ω_p.

a comprehensive discussion.[19,32,33] The absence of phonon sidebands of A_1 and B_1-bands points towards the weak exciton–phonon coupling.

Anthracene In contrast to benzene and naphthalene crystals, the index of refraction for the anthracene crystal in the region of exciton absorption is great and sharply changeable. One should substitute a common expression (1) for expression (2) to calculate the parameters of the exciton–phonon interaction. In this region, the inequality $\text{æ}^2 \ll n^2$ is fulfilled for the anthracene crystal, so that instead of expression (2) may be written the following expression

$$\mathscr{C}(\omega) = \frac{\text{æ}(\omega)n(\omega)}{\int \text{æ}(\omega')n(\omega')\,\mathrm{d}\omega'} = -\frac{1}{\pi}\,\mathrm{Im}\,G(\omega). \tag{10}$$

From the expression it is clear that the curve of the crystal absorption coefficient is not directly associated with characteristics of its exciton spectrum, hence neither its maximum not its centre of gravity determine the value of Davydov splitting. To find this value, the curve $\mathscr{C}(\omega)$ should be analyzed. The difference of positions of its centres of gravity in the two spectrum components yields the value of Davydov splitting in the rigid lattice.

Figure 5 shows the curves $\mathscr{C}(\omega)$ according to the experimental data of the paper.[34] The values $\text{æ}(\omega)$ and $n(\omega)$ corresponding to them refer to the crystal on the optical contact. The difference in coefficients of thermal expansion

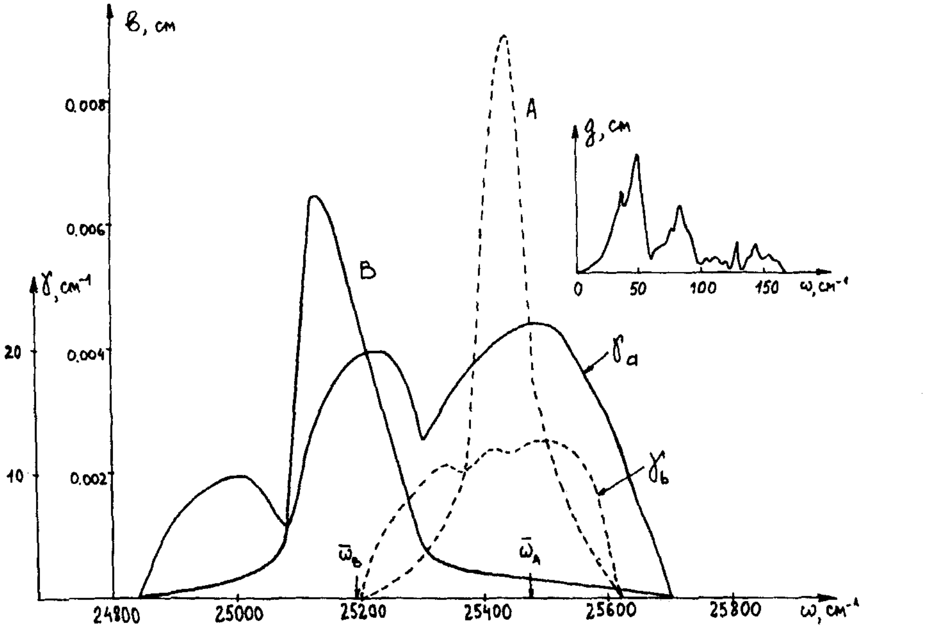

FIGURE 5 Curves of $\mathscr{C}(\omega)$ for anthracene crystal at $T = 20{,}4°\mathrm{K}$[34] in parallel with (solid line) and at right angles (dotted line) to the b-axis of a crystal polarizations of the incident light. γ_B and γ_A are calculated functions of the exciton–phonon interaction. $\bar{\omega}_B$ and $\bar{\omega}_A$ are the positions of centres of gravity of the curves $\mathscr{C}(\omega)$. $g(\omega)$ is the density of phonon states of anthracene crystal.[35]

of the crystal and a quartz plate, causes thermal stress of the crystal and broadening of absorption bands at low temperatures.[36]

The crystal refraction curves[37] independent of the optical contact stress, so far have not enabled one to detect the explicit form of the absorption curve although they have shown a number of features not revealed in the curves æ(ω). They supported the fact that absorption bands in the unstressed crystal have the widths close to those measured in the experiment for deformed crystals. The deformation effect on the curves $n(\omega)$ has not been studied. Figure 5 also gives the curves $\gamma(\omega)$ from expression (6) in which the function $\mathscr{C}(\omega)$ from (10) substituted for the function $a(\omega)$. Taking into account the stated above it should be noted that the shape of the curve $\gamma(\omega)$ may be considerably distorted by stress effects. The very values γ may also be overstated if part of the widths of the B and A absorption bands is due to deformation. In this way, we determine a certain upper limit of parameters of the exciton–phonon interaction, which may be reduced after separating the deformation effects.

Davydov splitting in the rigid lattice determined from the centres of gravity is $\Delta_{\mathrm{Dav}} = 250\ \mathrm{cm}^{-1}$ ($\bar{\omega}_B = 25190\ \mathrm{cm}^{-1}, \bar{\omega}_A = 25440\ \mathrm{cm}^{-1}$) instead of $\tilde{\Delta}_{\mathrm{Dav}} = 320\ \mathrm{cm}^{-1}$ found from the bands $\mathscr{C}(\omega)$ maxima. The values $\pi\gamma$ throughout the whole absorption region are less that Δ_{Dav} and, consequently, E since the rigid anthracene crystal Δ_{Dav} characterizes the least possible E due to linkage of the two exciton band energies on the Brillouin zone boundary.[38] But $\pi\gamma$ exceeds or is comparable with the value of frequencies of the anthracene crystal phonon spectrum[35] over a wide frequency region (the phonon frequency spectrum is shown in the top right hand corner of Figure 5). At the same time, the spectrum of rather large γ is the length $500\ \mathrm{cm}^{-1}$ which corresponds to the two and three phonon excitations. This fact indicates that the exciton state of the anthracene crystal is strongly coupled with phonons and probably, is close to polaron states.[39]

6 VIBRON ABSORPTION OF MOLECULAR CRYSTALS

Benzene From numerous transitions of the vibron spectrum of the benzene crystal, the detailed quantitative consideration of its characteristics is possible only for the M_1-transition ${}^1A_{1g} \rightarrow {}^1B_{2u} \cdot e_{2g}$ involving the non-totally symmetric vibration. The remainder of the transitions are considerably overlapped and their quantitative analysis is rather difficult.

The vibron absorption spectrum in the region of the M_1-transition ($\omega^0_{\mathrm{ph}_1} = 606\ \mathrm{cm}^{-1}$, $\delta\omega = -86\ \mathrm{cm}^{-1}$) contains the narrow M_1-band and the wide-band phonon sideband from its short-wave side (Figure 6a). As it was shown earlier,[18] the two-particle vibron absorption must occur in the region

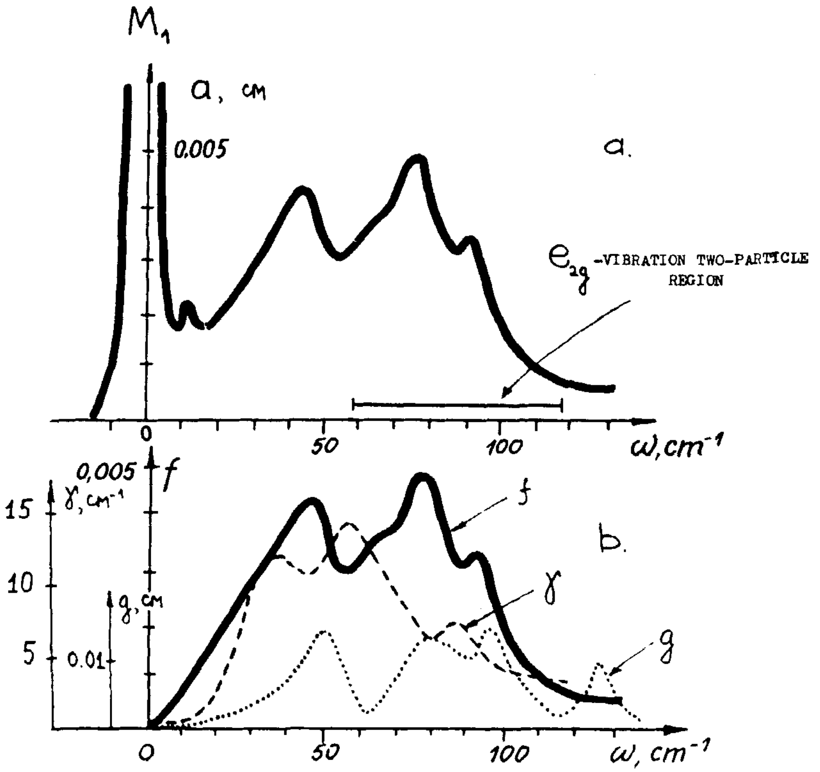

FIGURE 6 (a) Vibron–phonon absorption of benzene crystal in the M_1-transition $^1A_{1g} \rightarrow {}^1B_{2u}\,e_{2g}$ region[18] at $T = 4{,}2°\mathrm{K}$. $\omega = 38355\ \mathrm{cm}^{-1}$ corresponds to the zeroth maximum frequency of the M_1-band. (b) Calculated functions of $\gamma(\omega)$, the probability of the one-phonon vibron–phonon absorption $f(\omega)$ and the density of phonon states of the benzene crystal.[26]

indicated in Figure 6a. But, the experimentally measured value of its integral intensity accounts for only 2% of the intensity of absorption in the vibron region and may hence be disregarded. Thus, the vibron absorption in the transition discussed is due to the excitation of the one-particle vibron states and external phonons. The intensity of the vibron-phonon transition is 50% of the total absorption intensity.

Figure 6b illustrates the calculated function $\gamma(\omega)$ in the absorption region according to (6). The centres of gravity of the vibron–phonon absorption at all polarizations of the incident light with a precision of $\pm 2\ \mathrm{cm}^{-1}$ are at $\bar{\omega} = 38378\ \mathrm{cm}^{-1}$. Davydov splitting is in this way absent in this transition. This fact as well as the same shape of the vibron–phonon spectrum in different components evidence the vibron one-particle band being narrow.

This is also supported by a complete similarity of this spectrum and the vibron–phonon spectrum of benzene-d_6 impurity molecules in the benzene-d_0 crystal.[40] In this case, a criterion for the coupling of the crystal vibron excitation with phonons is the ratio between the value of $\pi\gamma$ and an average phonon frequency $\langle\omega_{\mathrm{ph}_2}\rangle$ due to local character of the crystal vibron excitation.

The narrowness of the one-particle vibron band enables one to apply the approach developed for local states[7,20] to the analysis of vibron–phonon spectrum. In this case, the Green function in expression (2) is represented as an integral form. The probability of the one-phonon transition $f(\omega)$ can be calculated from the experimental spectrum.[20] This function is shown in Figure 6b. The comparison of the calculated function with spectral distribution in the phonon sideband allows one to comprehend the one-phonon transition contribution to the phonon sideband. As seen from the comparison of Figure 6a and 6b actually the function $f(\omega)$ is completely coincident with the phonon sideband. Thus, the vibron–phonon transitions are, in principle, one-phonon transitions even though the value of the parameters α and $\pi\gamma$ are considerable.

Figure 7 gives the spectrum of the vibron–phonon absorption in the region of the K_2-transition ${}^1A_{1g} \rightarrow {}^1B_{2u}a_{1g}$ with the totally symmetric vibration ($\omega^0_{\mathrm{ph}_1} = 990\ \mathrm{cm}^{-1}$, $\delta\omega = -70\ \mathrm{cm}^{-1}$). From the qualitative analysis[17,41] it is clear that the vibron absorption practically in this transition is a completely one-particle absorption. And it is represented as in the exciton region, by the triplet of sharply polarized a, b and c-bands having the distances between them $\tilde{\Delta}_{ac} = 43\ \mathrm{cm}^{-1}$, $\tilde{\Delta}_{ab} = 51\ \mathrm{cm}^{-1}$ and $\tilde{\Delta}_{cb} = 8\ \mathrm{cm}^{-1}$. Each band is accompanied by the wide-band absorption in the short-wave region similar to the exciton–phonon absorption (see Figure 7). The integral intensity of this absorption is, on the average, 30% of the total absorption intensity. The band with $\omega = 38829\ \mathrm{cm}^{-1}$ shown in Figure 7b is not associated with the vibron transition discussed. Thus, the structure similarity of phonon sidebands and the proximity of the value of their relative intensities in exciton and vibron absorption, allow one to conclude that the vibron K_2-state is also rather steady with respect to the interaction with external phonons. The above mentioned values of the distances between the maxima of phononless bands correspond to the values of Davydov vibron splittings in the "dressed" lattice. Unfortunately, the superposition of absorption from other vibron transitions does not allow one to detect the positions of centres of gravity in separate spectrum components, and consequently, the values of the rigid lattice Davydov vibron splitting. This superposition is revealed in the a and b spectrum components even in a greater degree than it can be seen in Figure 7. Nevertheless, on the basis that the relative intensity of vibron–phonon and exciton–phonon sidebands are similar, one should expect, however, that the

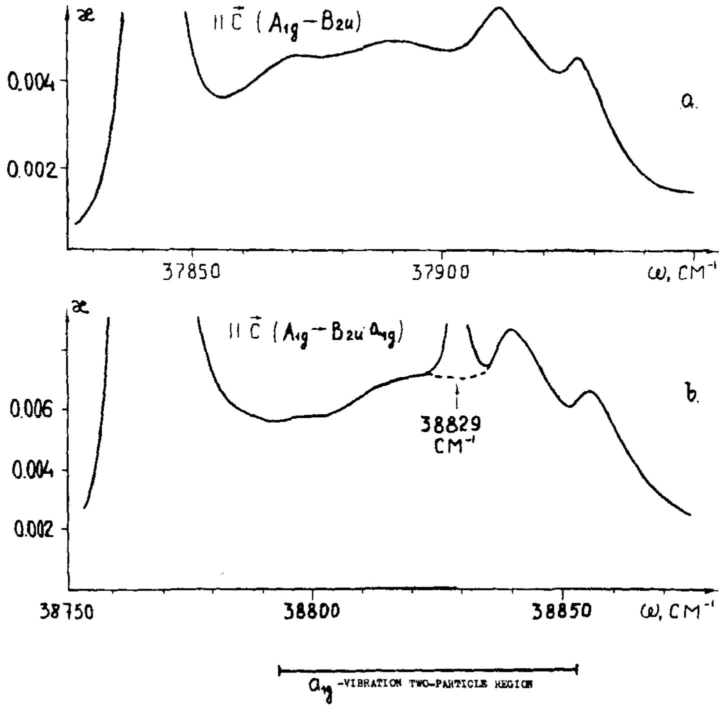

FIGURE 7 Comparison of benzene crystal absorption spectra in the exciton (a) and vibron $^1A_{1g} \to {}^1B_{2u}a_{1g}$ (b) transitions region;[41] $T = 4{,}2°K$. The light is polarized along the c-axis of a crystal.

values of Davydov vibron splitting in the rigid lattice, as in the case of exciton states, exceed the values measured with respect to maxima positions by 5–10%.

Naphthalene In contrast to the benzene crystal, the two-particle absorption plays a great part in the vibron spectrum of the naphthalene crystal absorption.[17,19] This fact is no bar to the determining of the Davydov splitting value if the total absorption associated with one intramolecular vibron transition is well pronounced. However, it involves difficulties for making a thorough analysis of the vibron–phonon spectrum.

The first vibron transition $^1A_{1g} \to {}^1B_{2u}b_{3g}$ involves the excitation of non-totally symmetric vibration. Therefore, the positions of centres of gravity in different spectrum components must coinside both for the sum of one-particle and two-particle absorptions in the rigid lattice[9] and if external phonons in both types of vibron absorption are considered. It has been shown above on the example of the vibron–phonon spectrum of benzene crystal.

The observed spectrum of the naphthalene crystal absorption in this region (Figure 8) is complicated. It contains the phononless M_1-band of the one-particle vibron absorption and a wide short-wave length D_1-band. This band is represented as a sum of the phonon sideband of the M_1-band, the two-particle band,[19] and, as well as the dissociated absorption due to the excitation of the totally symmetric vibration with $\omega^0_{\mathrm{ph}_1} = 512\ \mathrm{cm}^{-1}$. Nevertheless,

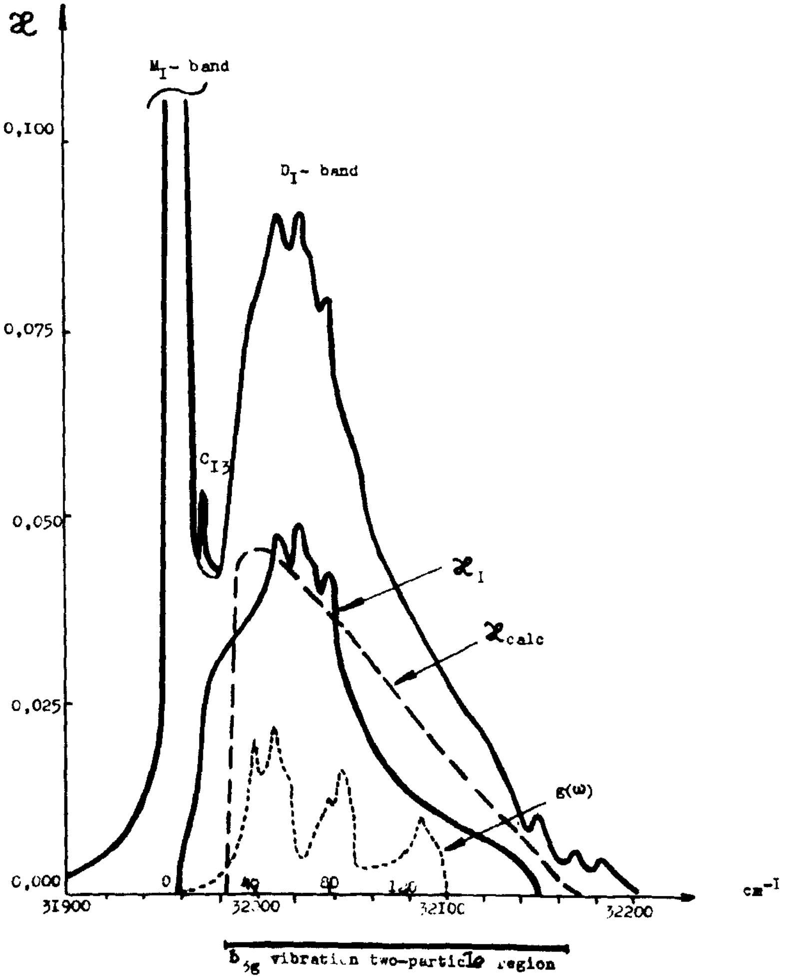

FIGURE 8 The vibron–phonon absorption of naphthalene crystal in the M_1-transition region ${}^1A_{1g} \rightarrow {}^1B_{2u}b_{3g}$, $T = 4{,}2°\mathrm{K}$.[29] The light is polarized along the b-axis of a crystal. $æ_{\mathrm{calc}}$ is the calculated two-particle absorption band.[19] $g(\omega)$ is the density of crystal phonon states.[31] C_{13} corresponds to C^{13} impurity absorption. The beginning of reading of $æ_1(\omega)$ and $g(\omega)$ corresponds to the maximum position of the M_1-band ($\omega = 31958\ \mathrm{cm}^{-1}$).

the centres of gravity in the *a* and *b* spectrum components coincide, Davydov splitting being absent.

The band $æ_{calc}$ in Figure 8 is the two-particle absorption spectrum in this region calculated disregarding the phonon effects upon this band.[19] As it has been pointed out above, it is not feasible now to allow for this effect in the many-particle absorption band. After subtracting $æ_{calc}$ from D_1 the band $æ_1$ was found.

Since the structure of this band in the initial region is similar to that of the density of phonon spectrum states, it might be assumed that the principle part of it is the phonon-side-band of the M_1-band. Presumably, the short-wave length side the band $æ_1$ involves some additional absorption due to the internal phonon with $\omega^0_{ph_1} = 512\,\mathrm{cm}^{-1}$. This uncertainty as to the $æ_1$ band origin does not allow one to fit to it the curves $\gamma(\omega)$ or $f(\omega)$ as the characteristics of the vibron–phonon interaction in this region.

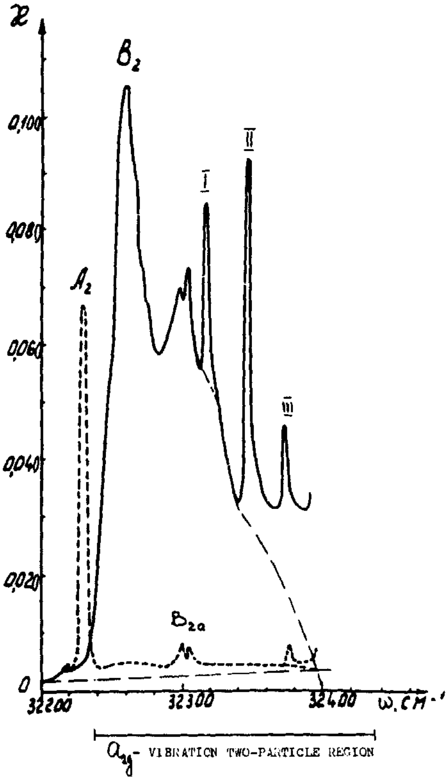

FIGURE 9 The vibron–phonon absorption of naphthalene crystal in the K_2-transition region ${}^1A_{1g} \rightarrow {}^1B_{2u}a_{1g}$, $T = 4{,}2°\mathrm{K}$.[29] Solid and dotted curves correspond to the incident light polarization along and at right angles to the *b*-axis of a crystal respectively.

The crystal absorption spectrum in the second transition region with the totally symmetric internal phonon ($\omega^0_{\mathrm{ph}_1} = 702\ \mathrm{cm}^{-1}$, $\delta\omega = -58\ \mathrm{cm}^{-1}$) is even more complicated as to the problem of Davydov splitting values determining. Unfortunately, the vibron absorption connected with this transition (Figure 9) is difficult to reveal. In the analyzed spectrum region, the bands I and II are associated with the excitation of the one-particle vibron states with the vibrations $\mathscr{C}_{2g}$ but the band III is associated with the vibration $\mathscr{C}_{1g}$.[29] The A_2-band corresponds to the one-particle vibron absorption in the transition considered. In the spectrum b-component, except for the above I–III bands, the whole vibron absorption is the two-particle vibron absorption of the transition $00 + a_g$.[17] But, the band in the total spectrum, corresponding to it, can be detected rather roughly. Therefore, one should give up the determination of Davydov splitting in this transition.

Anthracene The vibron absorption of anthracene crystal is completely two-particle.[17] A well observed similarity of the structure of vibron and exciton spectra[34] is indicative of pronounced values of the vibron resonance interaction. The experimentally determined characteristics of this interaction in this case might be only the value of Davydov vibron splittings in the rigid lattice. This value corresponds to the distances between the centres of gravity of stated above $\mathscr{C}(\omega)$ vibron bands observed in various spectrum components. The problem of correct separation of various vibron transition bands hinders this determination of Davydov splitting. On the other hand, the absence of the theory of interaction of external phonons with two-particle vibron states prevents so far from pointing the methods of quantitative analysis of such absorption.

7 CONCLUSION

The complexity and multiplicity of exciton–phonon and vibron–phonon absorption spectra are the main reasons for the fact that today the tendency for individual approach prevails in the spectrum analysis of each new object in the spectroscopy of molecular crystals. A substantial advance on has been observed recently as a result of rather comprehensive ideas on vibron spectra pointing the ways of analyzing the crystal vibron spectra from a common point of view. The similar solution is expected for the problem of exciton–phonon and vibron–phonon interactions. Despite the great difficulties of this problem, experimental and theoretical data are enough to complete this paper with a scheme of the real crystal spectrum (Figure 10). The scheme illustrates genetic ties between the already known model approximations and a final result. This genetic tie consists in reducing the number of δ-peaks as the

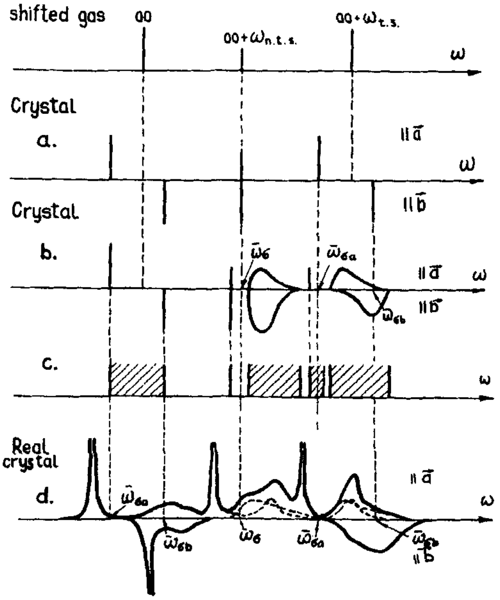

FIGURE 10 Schematic comparison between the absorption spectra of a free molecule and crystal. (a), (b) and (c)—see captions to Figures 1 and 2. (d) Many-particle model of vibron-states. Real crystal.

model becomes complicated. These are replaced by the bands and absorption regions of noticeable width. In many cases, the position of δ-peaks of one model corresponds to the position of centres of gravity in the next model. The most clear now is the region of exciton–phonon absorption. Despite the fact that we are unable now to calculate a priori its main parameters as $\gamma(\omega)$ and $f(\omega)$, we already know how to determine them from the experimental data. This enables one to hope for their stimulating effects on theory development. The picture of vibron–phonon absorption is more complicated. This is due primarily to the existance of many-particle absorption bands. Therefore, the problem of theoretical consideration of such type of interactions with external phonons seems to be one of today.

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