EXCITON SPECTRA OF MOLECULAR CRYSTALS

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ABSTRACT

The present methods of investigation of the exciton band structures in molecular crystals, which are mainly based on the study of the interaction of excitons with isotopic impurities and intramolecular phonons, are considered. A review and an analysis of the wide range of papers on this problem are given. The results obtained so far on the exciton energy spectrum in benzene, naphthalene and anthracene are discussed.

1. Introduction

In this paper, an analysis of the present state of the theoretical and experimental investigation of the energetic spectrum of excitons in organic molecular crystals is presented. In these crystals the Frenkel excitons[1] were first discovered experimentally, and later the exciton spectra of organic molecular crystals became the subject of intensive experimental and theoretical investigations. This field has been widely developed[2], but we will only be able to discuss one of the diverse and interesting investigations that are being carried out. Nevertheless, we believe that the investigation of the energy spectrum of excitons, discussed below, is now a very important part of the problem of molecular excitons and is closely connected with many other problems in molecular spectroscopy. In order to understand the origin of this problem those classical works upon which exciton spectroscopy is founded should be studied.

Low-temperature spectroscopy of molecular crystals originated from the pioneer work of Obreimov[3] and his collaborators Prikhot'ko and Shabaldas, and also of Prinsheim and Kronenberger[4], in which the low-temperature spectra were shown to involve a great number of narrow lines. These lines are now called zero-phonon lines. However, molecular exciton spectroscopy proper appeared much later and is connected with Prikhot'ko's[5] discovery of strongly polarized bands in the spectra of crystal naphthalene. The initial part of the naphthalene electron absorption spectrum and also the scheme of arrangement of the molecules is shown in *Figure 1*. It can be seen from *Figure 1*, that in spite of the fact that the orientation of the molecules does not correspond to any of the crystallographic axes, the absorption bands (A line, B band) are polarized along the crystal axes. Therefore, they are

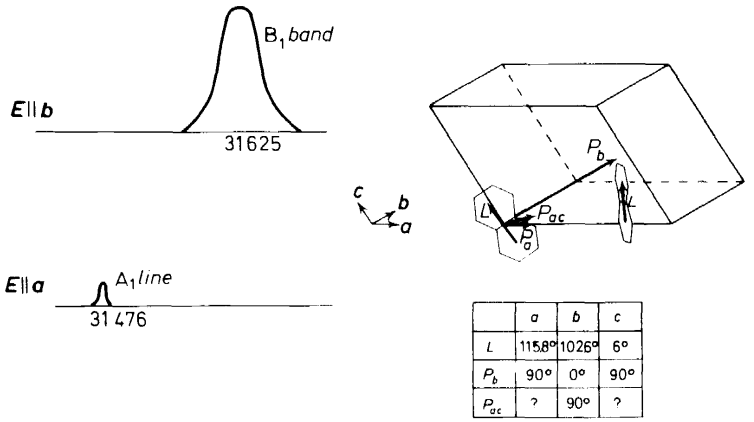

Figure 1. The first bands of the absorption spectrum of a plate of crystalline naphthalene with a developed plane *ab* at $T = 20.4$ K. The arrangement of naphthalene molecules in the primitive cell is shown schematically. The directions of intramolecular transition dipole momenta (along the long axis L of the molecule), and the directions of the dipoles P_{ac} and P_b, corresponding to the optical transitions in a crystal, are also shown.

connected with the excitation of the crystal as a whole rather than with that of individual molecules. Davydov[6] was the first to understand this fact, and he connected strongly polarized bands with the Frenkel excitons. He proposed a theory[7] which defined the direction of further investigations for a long period of time. It is from these works of Prikhot'ko and Davydov that the spectroscopy of molecular crystals later developed.

2. The BASIC PROBLEM AND APPROACHES TO ITS SOLUTION

2.1. Setting of the problem

Each electron intramolecular level is a progenitor of a certain system of exciton bands in the crystal. Optical transitions are allowed in states with zero quasi-momentum, $\boldsymbol{k} = 0$ only. Therefore every intramolecular transition corresponds to a group of absorption bands in a crystal, which are usually strongly polarized along the crystallographic axes. Such groups are known as Davydov multiplets.

The first question that naturally arises is: what kind of consistent procedure enables us to arrange separate, strongly polarized bands, in the spectrum under experimental consideration, into the Davydov multiplets and to assign them to definite intramolecular transitions? In other words, how should the genesis of the Davydov multiplets, or more generally, the *exciton band genesis*, be established?

It is easy to understand that this question, in principle, is only a certain aspect of the general problem of the investigation of the *exciton energy spectrum*—the problem of the definition of dispersion laws in exciton bands, mutual location of exciton bands, spectrum rearrangement as a result of the interaction with phonons of various types, and so on.

The investigations attempting to solve this problem have been carried out in different laboratories throughout world during the last 10–15 years, and their intensity is growing. A whole system of experimental methods has been worked out, and our understanding of exciton dynamics has reached a new level. The main aim of the present paper is to summarize the results obtained and, as far as it is possible, to evaluate the prospects.

2.2. Exciton band genesis

To elucidate some difficulties in the solution of this problem and to show the way in which it was studied, one should first consider the question of multiplet genesis.

Let us consider the naphthalene AB doublet (*Figure 1*). It is determined by two parameters—the splitting value and the polarization ratio I_A/I_B. Splitting cannot be practically calculated, but the polarization ratio can be determined simply by the inclination of the transition dipole with respect to the crystal axes. If the dipole is oriented along the long axis of the molecule (in agreement with a known symmetry of the intramolecular transition A_{1g}–B_{3u}), then we obtain $(I_A/I_B)_{theor} \approx 4$, whereas $(I_A/I_B)_{exp} \approx 10^{-2}$. And also, the widths of A and B bands differ from one another by an order of magnitude. Thus it would be easy to understand the doubts, which were held for a long time, whether it is right to combine A and B bands into one single doublet. It is very essential that in the framework of these experimental data there is no direct argument which could have solved the question in one or another direction.

The general solution to the band genesis problem has been found by investigating the spectra of crystal solutions, the molecules being of different isotopic content[8–10]: it can be directly seen from the spectra that with an increase of concentration the impurity band turns into a Davydov multiplet. The 'picture' of the naphthalene spectrum is shown in *Figure 2*. The formation of the AB doublet from the impurity absorption band of naphthalene-h_8 in naphthalene-d_8 may be directly observed†.

So, in this way, we have come to the method which is widely used in studying the band structure—the investigation of the effect of impurities on the spectrum. In general, in order to study the dynamics of some quasiparticles, one should be able to affect them by some external action. Band electrons are usually affected by magnetic or electric fields; but the effect of these fields upon the singlet molecular excitons is almost negligible. Therefore, some other ways of affecting the excitons have to be found. Up to now the study of the effect on the exciton spectra of impurities inserted into a crystal appears to be the most efficient, and so does the study of the interaction of excitons with intramolecular phonons. Both these methods will be discussed in the sections below.

2.3. Calculation of exciton bands

Together with the programme of the definition of exciton band parameters from different experimental data formulated above, an approach based on

† The anomalous polarization ratio mentioned above may be explained by the perturbation of the weak intramolecular transition in a crystal field[11].

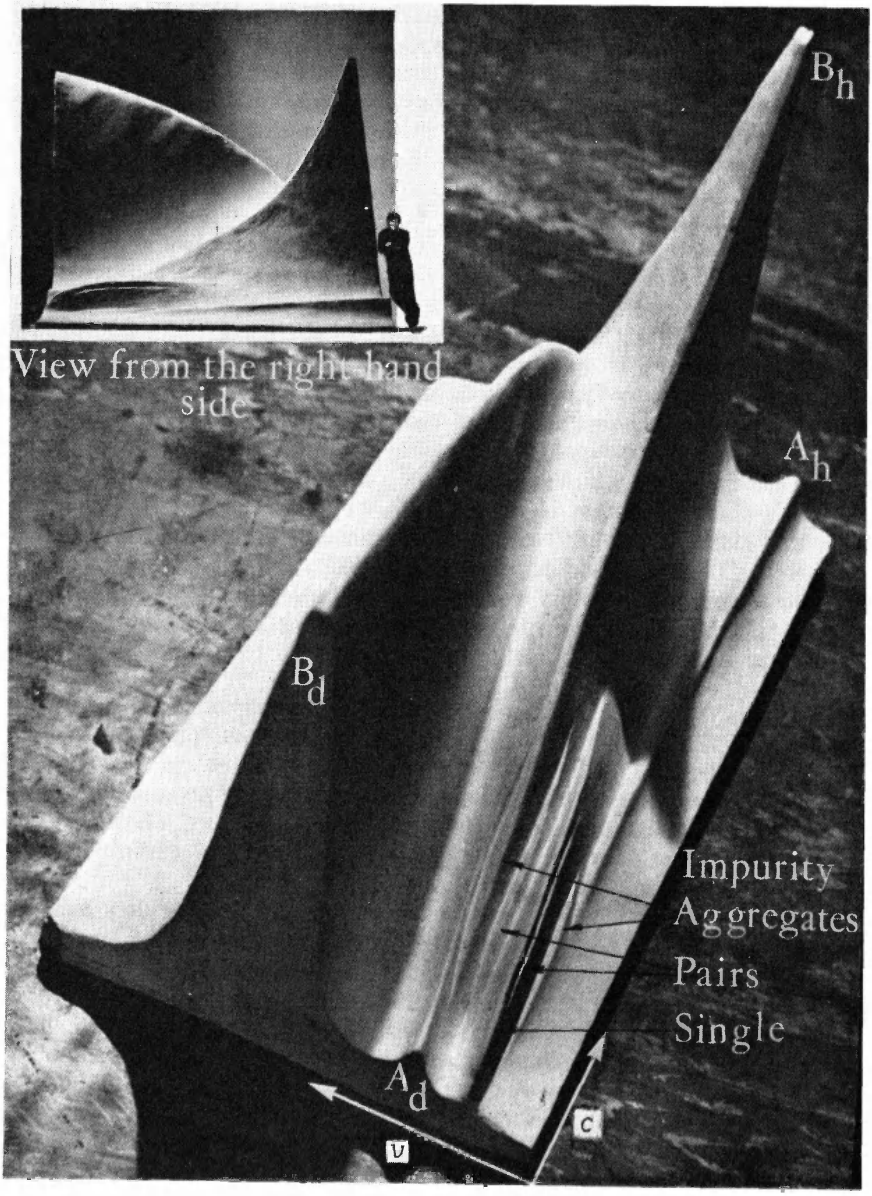

Figure 2. 'Panorama' of the crystalline solutions of naphthalenes-h_8 and -d_8 which shows the transformation of the impurity band of naphthalene-h_8 into the AB doublet[67]. In the insert the view from the right is shown

the attempts to calculate the exciton spectra *ab initio* is also possible. But the simple enumeration of those mechanisms *per se* which have been considered by many authors, and which, undoubtedly, are essential to some

extent (resonance interaction of the molecules including the highest multipoles[12, 13], mixing with other excited states[14], and the account of states with charge transfer[15]), from our point of view indicates the fact that attempts to define the energy spectra from first principles are almost hopeless at the present state of such calculations. For instance, multipole expansions converge very slowly, since the expansion parameter (the ratio of the molecule size to intermolecular separation) is of the order of unity, while for the neighbouring molecules the case is additionally complicated by the necessity to take account of the spatial dispersion of the dielectric constant. So it seems quite natural that up to now no satisfactory results have been achieved in such calculations.

It seems to us that there are more prospects in a half-empirical approach when a simplified form of the exciton Hamiltonian is taken, including a number of parameters which should be determined from the experiment. In such an approach the numerical calculations remain of great importance, but their role has changed: they should serve for the elucidation of the predominant mechanisms which define the Hamiltonian parameter values obtained experimentally. The understanding of these mechanisms in its turn enables one to choose an optimum form for the model Hamiltonians. Such a combined programme is, apparently, practicable, but also rather difficult.

In a general case, the Frenkel exciton Hamiltonian may be written as a matrix

$$\hat{H} = |M_{n\alpha, m\beta}| \tag{1}$$

consisting of elements $M_{n\alpha, m\beta}$ which correspond to the excitation transfer between the sites $n\alpha$ and $m\beta$; n, m numerate the cells, and α, β the sub-lattices with translationally independent molecules. At large $(n - m)$, the resonance dipole–dipole interaction dominates. However, it is usually not very large numerically, since in the majority of cases weak electron transitions are under investigation. For this reason in the interaction of neighbouring molecules the rapidly decreasing no-dipole interactions predominate. They often provide

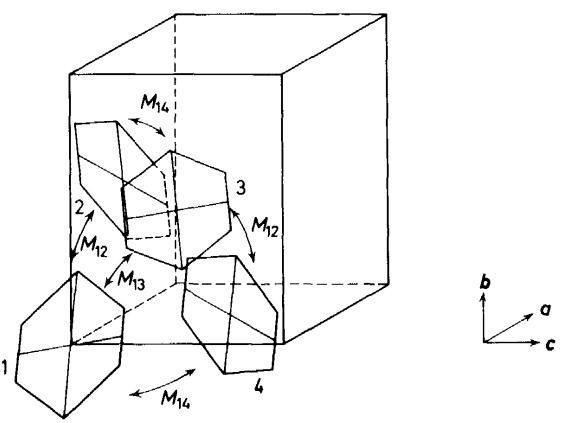

Figure 3. The position of translationally non-equivalent molecules in the primitive cell of benzene P_{bca} is shown. M_{ij} are the matrix elements of the pair interaction for the nearest neighbours

the main contribution to the width of the exciton bands. Therefore, as a rule, one takes the model Hamiltonians in the form which corresponds to retention of the interaction with a limited number of neighbours only (the so-called 'restricted Frenkel model').

For instance, in the benzene lattice (four molecules in a cell, *Figure 3*) there are three different types of nearest neighbours. Retaining the interaction with them only, we get the following formula for the dispersion law in four exciton bands:

$$\varepsilon(\boldsymbol{k}) = 4\{b_2 M_{12} \cos(k_a a/2) \cos(k_b b/2) + b_3 M_{13} \cos(k_b b/2) \cos(k_c c/2) + b_4 M_{14} \cos(k_a a/2) \cos(k_c c/2)\}, \quad (2)$$

i.e. the spectrum is defined by the values of three parameters M_{12}, M_{13} and M_{14}. Four sets of b_i corresponding to different bands are defined by the conditions $b_i = \pm 1$, $b_2 b_3 b_4 = 1$.

In the naphthalene lattice (two molecules in a cell, see *Figure 1*) the interaction with the nearest neighbours is also dominating; they belong to different sub-lattices. The spectrum in the lowest approximation is, therefore, defined by only one parameter:

$$\varepsilon(\boldsymbol{k}) = \pm 4 M_{12} \cos(k_a a/2) \cos(k_b b/2) \quad (3)$$

In this approximation, both of the resulting bands are two dimensional (in the cleavage plane $\{ab\}$).

2.4. Information contained in Davydov multiplets

The absorption bands of the Davydov multiplet correspond to the electron transitions from the crystal ground state with frequencies $\omega_\mu = \varepsilon_\mu(\boldsymbol{k} = 0)$, where subscript μ numerates the exciton bands. The absorption spectrum per single primitive cell is determined by the conductivity tensor:

$$\sigma(\omega) = -\frac{1}{\pi} \sum_\mu \hat{\boldsymbol{P}_\mu \boldsymbol{P}_\mu} \operatorname{Im} G_\mu(\omega, \boldsymbol{k} = 0), \qquad \omega = \omega + i0 \quad (4)$$

where $G_\mu(\omega, \boldsymbol{k}) = [\omega - \varepsilon_\mu(\boldsymbol{k})]^{-1}$ is the electronic Green function of the ideal crystal, and $\hat{\boldsymbol{P}_\mu \boldsymbol{P}_\mu}$ diada constructed on the transition dipole momenta in the cell.

Using the separation of absorption bands inside the multiplet one can find some parameters of the restricted Frenkel model. For instance, in the benzene crystal spectrum the multiplet consists of three bands: $\omega_a = 37803\ \mathrm{cm}^{-1}$, $\omega_b = 37847\ \mathrm{cm}^{-1}$ and $\omega_c = 37839\ \mathrm{cm}^{-1}$, corresponding to the allowed transitions to the $\boldsymbol{k} = 0$ points of the three exciton bands (the transition to the fourth band is forbidden). From these data, using the position of the original electronic term found independently† $\omega_0 = 37839\ \mathrm{cm}^{-1}$, we obtain[16]:

$$M_{12} = -1.0\ \mathrm{cm}^{-1}, \qquad M_{13} = 4.5\ \mathrm{cm}^{-1}, \qquad M_{14} = 3.5\ \mathrm{cm}^{-1}$$

† In the case when in a separate vibronic transition the single particle absorption with a small exciton band width predominates (see below), the position of the term may be defined by subtracting the energy of the vibration quantum from the energy of this vibronic transition. The extrapolation of the position of the electronic or vibronic impurity absorption band in an isotopic solvent, that takes into account the quasi-resonance interaction of guest and host molecules, may be used as another method for the definition of the term (see also below).

In the naphthalene crystal spectrum the doublet width is approximately $150\,\mathrm{cm}^{-1}$, and then, according to equation 3, $|M_{12}| \approx 19\,\mathrm{cm}^{-1}$ (in this approximation the electronic term is in the centre of the doublet).

From the absorption intensities in the bands of a multiplet one can obtain the transition dipole momenta, and using them estimate the matrix elements of the dipole–dipole interactions in the crystal. The position of the most short-wave band in the low-temperature luminescence spectrum of a pure crystal may be used to find the bottom of the exciton band. The last method is especially convenient when the band bottom is at $\boldsymbol{k} = 0$ and thus the corresponding transitions in a luminescence spectrum are allowed and may be observed up to $T \to 0\,\mathrm{K}$.

Thus, in the structure of the multiplets of the crystal absorption spectra, as well as in the luminescence bands corresponding to inverse transitions, quite definite though rather incomplete information is contained. Even in the naphthalene crystal spectrum, where one may succeed in defining the only parameter of the restricted Frenkel model, it is not possible to check the validity of the result obtained in the framework of these experimental data.

3. METHODS OF THE DENSITY OF STATES DETERMINATION

In this section we consider the phenomena related to the solution of a restricted problem—to find the density of states in the exciton spectrum without finding the dispersion law.

3.1. Isotopic impurity spectra

Isotopically substituted molecules (in practice they are usually deuterated) form the simplest type of defects in crystals. The experiment indicates that the approximation, in which all matrix elements $M_{n\alpha,\,m\beta}$ are supposed to be equal to those in the ideal crystal, while the isotopic shift of the electronic level Δ is the same as that in the vapour, is fairly satisfactory. Then the contribution to the conductivity tensor, which describes the impurity absorption per one guest molecule, is defined by the formula analogous to the above expression 4 for the pure crystal[17]:

$$\sigma_{\mathrm{imp}}(\omega) = -\frac{1}{\pi\sigma_c}\sum_{\mu}\widehat{\boldsymbol{P}_\mu\boldsymbol{P}_\mu}G_\mu^2(\omega, \boldsymbol{k}=0)\,[\mathrm{Im}\;T(\omega)], \tag{5}$$

where the scattering amplitude

$$T(\omega) = \frac{\Delta}{1-\Delta F(\omega)}, \quad F(\omega) = \frac{v}{\sigma_c(2\pi)^3}\sum_{\mu}\int\frac{\mathrm{d}^3\boldsymbol{k}}{\omega-\varepsilon_\mu(\boldsymbol{k})} = \int\frac{\rho(\varepsilon)}{\omega-\varepsilon}\,\mathrm{d}\varepsilon. \tag{6}$$

Here v is the volume of the primitive cell, σ_c is the number of molecules in it and $\rho(\varepsilon)$ is the normalized density of states in the exciton energy spectrum.

Starting from some $\Delta = \Delta_{\mathrm{cr}}$, the amplitude $T(\omega)$ has an isolated pole ω_i:

$$\Delta F(\omega_i) = 1 \tag{7}$$

corresponding to the impurity level. The impurity absorption in the spectrum component corresponding to the dipole $\boldsymbol{P}_\mu$ is:

$$\sigma^{\mu}_{\text{imp}}(\omega) = \frac{\boldsymbol{P}^2_\mu}{\sigma_c} \frac{G^2_\mu(\omega)}{|\mathrm{d}F/\mathrm{d}\omega_i|} \delta(\omega - \omega_i), \qquad G_\mu(\omega) \equiv G_\mu(\omega, \boldsymbol{k} = 0) \tag{8}$$

whereas the polarization ratio is:

$$P_{\mu/\nu} = \frac{\sigma^{\mu}_{\text{imp}}}{\sigma^{\nu}_{\text{imp}}} = \frac{\boldsymbol{P}^2_\mu}{\boldsymbol{P}^2_\nu} \frac{G^2_\mu(\omega_i)}{G^2_\nu(\omega_i)} \tag{9}$$

When the impurity level approaches the edge of the exciton spectrum, the absorption intensity undergoes gigantic changes (Rashba effect). Indeed, provided the distance up to the spectrum edge is denoted by $\bar{\omega}$, then $|\mathrm{d}F/\mathrm{d}\omega| \propto \bar{\omega}^{-\frac{1}{2}}$ whilst $G^2_\mu \propto \bar{\omega}^{-2}$ or $G^2_\mu \to$ *constant* depending on whether the μ-component of the exciton multiplet coincides with this edge of the exciton spectrum or not. Then $\sigma^{\mu}_{\text{imp}} \propto \bar{\omega}^{-\frac{3}{2}}$ or $\sigma^{\mu}_{\text{imp}} \propto \bar{\omega}^{\frac{1}{2}}$, respectively (the flaming up or the dying out of the band). Therefore, the polarization ratio changes simultaneously as $\bar{\omega}^2$.

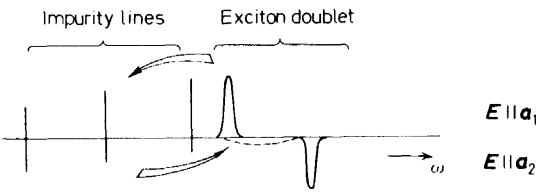

Figure 4. Redistribution of the oscillator strength in the absorption spectrum when the impurity level approaches the exciton band edge. Impurity induced absorption within the exciton band is shown by the dashed line

This effect† is caused by a formation of large radius states in which the excitation covers a considerable region around the impurity centre. With this, the impurity transition oscillator strength is taken from the intrinsic absorption, or, on the contrary, the oscillator strength of the guest molecule may be consumed for collective excitations (*Figure 4*). The progressive delocalization of the exciton at $\bar{\omega} \to 0$ is connected with the simultaneous decrease of the excitation amplitude square of the guest molecule:

$$\psi^2_{\text{imp}} = \mathrm{d}\omega_i/\mathrm{d}\Delta = |\mathrm{d}F^{-1}(\omega_i)/\mathrm{d}\omega_i|^{-1} \tag{10}$$

which may be directly seen in the electronic-vibrational impurity luminescence[20]. It should be noted that both these effects are based upon the same mechanism, but they have quite different scales: a noticeable change of ψ^2_{imp} is observed in the narrow vicinity of the exciton band only, whereas the changes of intensity due to the factor $G^2_\mu(\omega)$ in equation 8 arises at large

† This effect is rather general and is manifested for the centres of arbitrary type. Some limitations arise due only to the discontinuity in the band at $\boldsymbol{k} = 0$[18,19].

distances (of the order of bandwidth)†. Therefore, the polarization ratio is the quantity in which the exciton effects in impurity spectra are most significantly displayed.

The impurities also produce continuous induced absorption in the whole region where $\rho(\varepsilon) \neq 0$ (Sugakov[21], Sommer and Jortner[22]). This absorption may be described by formula 5 with

$$-\frac{1}{\pi}\operatorname{Im} T(\omega) = \frac{\Delta^2 \rho(\omega)}{[1 - \Delta F_R(\omega)]^2 + [\pi \Delta \rho(\omega)]^2} \tag{11}$$

where $F_R(\omega)$ is a real part of $F(\omega)$.

In large organic molecules with a great number of atoms a successive deuteration allows one to obtain a series of systems with closely located levels, so that Δ may be changed with a short step. The appearance of such a quasi-continuous parameter, that governs the spectrum, is very favourable towards further experimentation.

(*A*) The study of the strong dependence of $P_{\mu/\nu}$ on ω_i directly indicates the presence of exciton effects. In naphthalene, for instance, $P_{a/b}$ changes by a factor of almost 20 when $\bar{\omega}$ changes by 37 cm^{-1}.

(*B*) Since the stationary impurity levels arise only outside the exciton spectrum, and observing the limits inside which they exist, we may define the extent of the exciton energy spectrum. The uncertainty caused by the existence of quasi-local levels and by broadening of local level due to interaction with lattice phonons may be eliminated by measuring the band intensities and by their comparison with equation 8. So, in the work of Broude *et al.*[23], the lower edge of the exciton spectrum in naphthalene was found and this happened to coincide with the A band.

(*C*) According to equations 6, 8 and 11 all the parameters of the impurity absorption are defined solely by the function $F(\omega)$, which in its turn is expressed through the density of states $\rho(\omega)$. Therefore, by measuring $F(\omega)$, we may, in principle, deduce $\rho(\omega)$. But since formula 6 is an integral equation of the first kind with respect to function $\rho(\omega)$, the expected accuracy is low. That is why this method is used in combination with other methods[13,22,24–26]; the results are given in Section 3.4.

(*D*) Special attention should be paid to formula 11, for the induced absorption, which contains $\rho(\omega)$ directly. Thus, from a purely theoretical point of view this formula is the best one to use to deduce $\rho(\omega)$. However, it is a complicated problem to single out the weak impurity absorption in the background of the intrinsic exciton absorption assisted by lattice phonon emission and it has not yet been solved. The first attempt was made with benzene[27]. Also the concentration region for which formula 11 is valid, and the sensitivity of this method (according to Ref. 28 it is low) have not been clarified.

The situation is reviewed in Refs. 29–31.

3.2. Vibronic absorption spectra: non-totally symmetric phonons

There is a deep analogy between the isotopic impurity centres and the

† From the mathematical point of view this difference arises due to the fact that one effect is determined by the amplitude of the ψ-function at the lattice site where the guest molecule is inserted, while another effect is determined by the ψ-function amplitude at zero momentum.

system of exciton plus the non-totally symmetric intramolecular phonon (NTS-phonon). It is based on the following:

(*i*) the intramolecular interaction of the electronic excitation with non-totally symmetric vibration mainly amounts to a reduction of the vibration frequency (by Δ_v),

(*ii*) matrix elements of electronic transitions are almost independent of the vibrational quantum numbers,

(*iii*) intramolecular phonon bands are narrow, and the joint transfer of exciton and NTS-phonon has a very small probability[12].

Therefore, if Δ_v is large enough, exciton and phonon bound states should arise (Nieman and Robinson[32], Rashba[33]), which almost coincide with the exciton state in the vicinity of the isotopic centre.

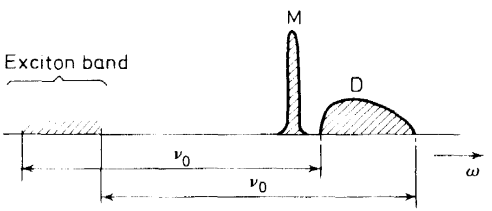

Figure 5. The scheme of the vibronic absorption spectrum. M is a single-particle band (bound state of the system exciton + phonon). D is a two-particle band (dissociated states of this system), ν_0 is the vibrational frequency of the unexcited molecule

The general features of the energy spectrum of the system are shown in *Figure 5*: M band, corresponding to the bound states (single-particle spectrum branch), is followed by the D band, corresponding to the dissociated states of the exciton + NTS-phonon pair (i.e. the two-particle states).

The vibronic absorption intensity is defined by the two-particle exciton–phonon Green function[30, 33]:

$$\sigma(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathscr{G}(\omega), \qquad \mathscr{G}(\omega) \equiv \mathscr{G}(\omega, \boldsymbol{k} = 0), \tag{12}$$

which is connected with $F(\omega)$ by a simple relation:

$$\mathscr{G}^{-1}(\omega) = F^{-1}(\omega) - \Delta_v. \tag{13}$$

From equations 12 and 13, and taking into account equation 10, we obtain:

$$\sigma_M(\omega) = \psi_M^2 \delta(\omega - \omega_M), \quad \psi_M^2 = \left|\mathrm{d}F^{-1}(\omega_M)/\mathrm{d}\omega_M\right|^{-1} \tag{14}$$

for the M band intensity and a formula similar to equation 11 for the intensity distribution in the D band.

Since equation 13 is symmetric relative to $\mathscr{G}$ and F, we may immediately write the reversion formula:

$$\rho(\omega) = \frac{\sigma(\omega)}{\left(1 + \Delta_v \int \frac{\sigma(\omega')}{\omega - \omega'}\,\mathrm{d}\omega'\right)^2 + (\pi\Delta_v\sigma(\omega))^2} \tag{15}$$

which directly expresses $\rho(\omega)$ through the vibronic absorption; the integration in equation 15 covers both M and D bands. One hopes that this simple formula will be efficient in deducing $\rho(\omega)$ from the experimental data.

The naphthalene spectrum[34] is shown in *Figure 6*. It has been interpreted[35] as consisting of the M band with the D band following it. We shall consider it again below.

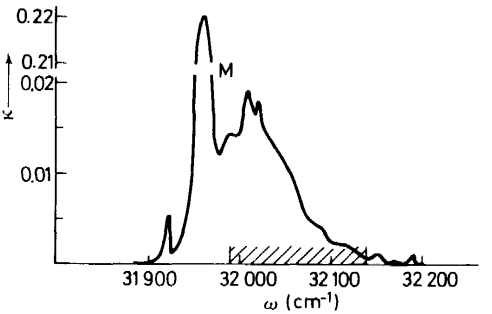

Figure 6. The absorption spectrum of the naphthalene crystal in the region of the vibronic transition with non-totally symmetric vibration 438 cm^{-1} according to Ref. 34. M is the single-particle absorption band. The region in which the two-particle absorption (D band) has to be disposed is shown by shading

In the presence of thermal NTS-phonons in a lattice, electron transitions which retain the number of phonons may also occur. These transitions are quite similar to those in isotopic centres, and namely, to the transitions to a discrete level of the system exciton + phonon and to the continuum[36]. The latter are described by equation 11 and, in principle, they also allow the determination of $\rho(\omega)$; the advantages in comparison with impurity induced absorption involve the possibility of using the thermo-absorption technique. These spectra have not yet been investigated.

3.3. Band-to-band transitions

Rashba[37] showed that $\rho(\omega)$ can also be extracted from the other group of vibronic spectra which are known as band-to-band transitions (or 'hot band spectroscopy'). The scheme of these transitions is shown in *Figure 7*. Here, the exciton and phonon are not present in the crystal simultaneously (for example, for the process of photon absorption, the phonon is in the initial state and the exciton in the final one) in contrast to the spectra discussed in Section 3.2. Therefore, in principle, the spectra are very simple and the exciton–phonon interaction only enters into the factor defining the full probability of transition, without affecting its spectral distribution.

The spectral distribution of the absorption in the Heitler–London approximation is determined by the reduced density of state function in the exciton and phonon bands $\rho_{ex\text{-}ph}(\omega)$ and by the Plank phonon distribution[37]. However, inasmuch as for intramolecular phonons the phonon band widths are usually small, it may be assumed that $\rho_{ex\text{-}ph}(\omega) \approx \rho(\omega)$ and the population

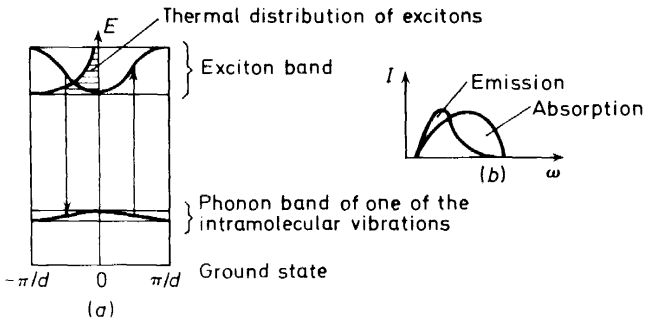

Figure 7(*a*). The band-to-band transition scheme. (*b*) Corresponding absorption and emisssion spectra

numbers $\bar{n}_{ph}$ within the phonon band are constant. Then the absorption spectrum directly reproduces $\rho(\omega)$:

$$I_{abs}(\omega) \propto \rho(\omega) \tag{16}$$

This equally holds for totally and non-totally symmetrical vibrations.

If band excitons manage to be thermalized before the light emission occurs, then the fluorescence spectrum corresponding to opposite transitions is also completely determined by the density of states in the exciton band:

$$I_{em}(\omega) \propto \rho(\omega) \exp(-\omega/T). \tag{17}$$

Thus, absorption and emission spectra can both be used for the determination of $\rho(\omega)$. The main shortcoming of this procedure is that it is necessary to carry out the measurements at rather high temperatures ($\bar{n}_{ph}$, in absorption, should not be too small and the excitons, in emission, should be distributed over the whole exciton band). This gives rise to a large contribution from lattice phonons and complicates the interpretation. Finding ways to decrease the temperature by refining the measurement technique is therefore of paramount importance (see, for example, Ref. 38).

3.4. Density of states in benzene, naphthalene and anthracene

Band-to-band transitions have been observed by a number of authors[39] but the first thorough measurements of these spectra and their systematic treatment to deduce $\rho(\omega)$ as applied to benzene and naphthalene were carried out by Colson *et al.*[40]. *Figure 8* illustrates $\rho(\omega)$ found by them for benzene and, for a comparison, adjacent to it is shown the fluorescence spectrum at 20.4 K by which $\rho(\omega)$ was determined according to Section 3.3. It can be seen from *Figure 8* that the values of $\rho(\omega)$ determined at 20 K and 27 K are almost the same. This indicates the reliability of the data. Experimental data of Dolganov and Sheka[27] on the position and intensity of impurity absorption bands (cf. Section 3.1) in deuterobenzene solutions with different degrees of deuteration are also in good agreement with these $\rho(\omega)$ values.

Unfortunately, in the naphthalene crystal, the accuracy in defining $\rho(\omega)$

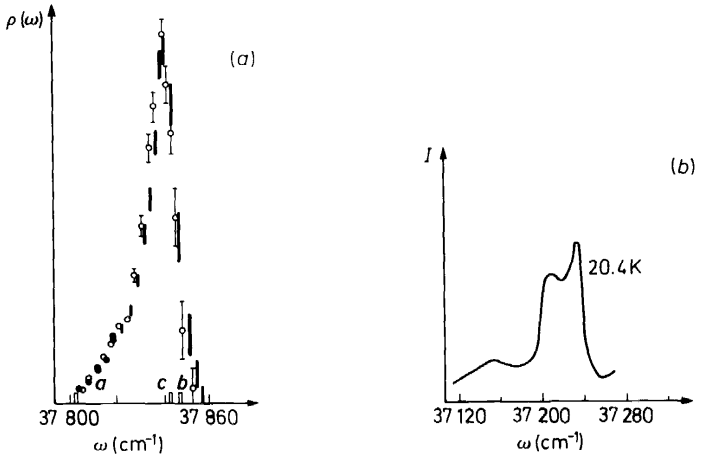

Figure 8(*a*). The density of states in the exciton energy spectrum of crystalline benzene as determined from the band-to-band fluorescence spectrum at 20.4 K (dark vertical bars) and at 27 K (open circles). The Davydov multiplet components are also designated[40].
(*b*) The 0–'606 cm^{-1}' fluorescence band used for determining $\rho(\omega)$[40]

turns out to be far lower because the wider exciton band (150 cm^{-1} compared to 60 cm^{-1}) forces one to use the fluorescence spectra at higher temperatures (77 K) at which the absorption bands become diffused because of lattice phonons. *Figure* 9 shows the experimental fluorescence and absorption spectra and the $\rho(\omega)$ curve obtained from them by a special procedure of excluding the contribution of lattice phonons[40] which, unfortunately, is not unambiguous.

A search for $\rho(\omega)$, providing optimal descriptions of a wide complex of experimental data on the spectra of the pure naphthalene crystal and appropriate isotopic solutions, has been carried out by Rabin'kina *et al.*[25]. The

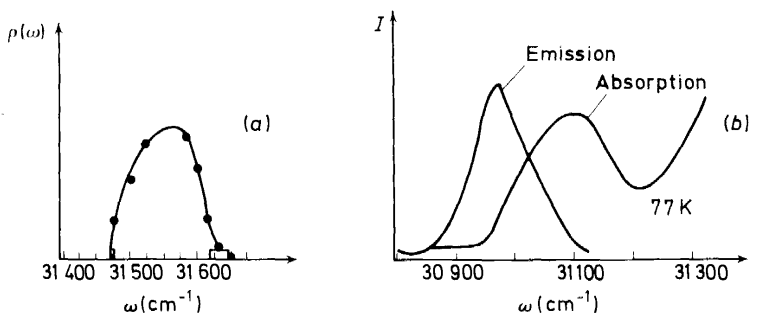

Figure 9. (*a*) The density of states in the naphthalene crystal exciton bands found from the band-to-band absorption and fluorescence spectra[40].
(*b*) The spectra of the band-to-band absorption and emission, with the 509 cm^{-1} vibration involved, used for determining $\rho(\omega)$[40]

data are summarized in *Figure 10*. These $\rho(\omega)$ data[25] are, in general, in agreement with previous data[40], however, the difference is quite marked. An excellent agreement for the positions of all the known impurity absorption bands as well as the M absorption band and impurity vibronic absorption bands has been achieved. The agreement for ψ^2_{imp} is not as good but the discrepancies are within the limits of experimental error. The sharper rise of $\rho(\omega)$

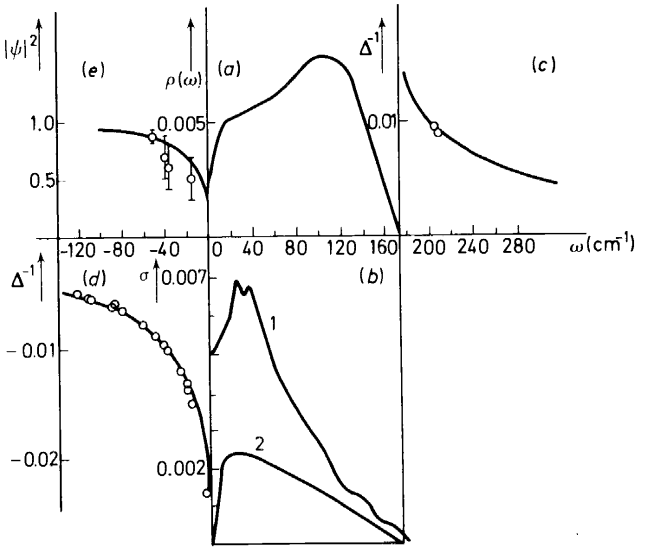

Figure 10. The summary of experimental data on the naphthalene spectra and the curve $\rho(\omega)$, determined from the condition of the best fitting of these data to the theory[25]: (*a*) The density of states curve. (*b*) The absorption spectrum in the region corresponding to the D band of the phonon 509 cm^{-1}; 1. the experimental data[34]; 2. the calculated spectrum of the two-particle absorption. (*c*) and (*d*) The position of impurity absorption bands with $\Delta > 0$ and $\Delta < 0$, respectively; o—experimental, curves—theoretical. (*e*) The excitation amplitudes for impurities with $\Delta < 0$; o—experimental, curves— theoretical

on the left edge (compared to the data of Colson *et al.*[40]) can just improve the agreement between the theoretical and the experimental data[40] for the band-to-band fluorescence. The single serious discrepancy between theory and experiment occurs in the D absorption band region of the spectrum where theory accounts for only 50 per cent of the total absorption. The rest is thought to be of another origin[25] (the contribution of the lattice phonons and of the 512 cm^{-1} vibration). A large contribution by the latter absorption is especially disappointing since it is this contribution which makes the direct extracting of $\rho(\omega)$ from the D absorption band (according to equation 15) impossible.

A comparison of the two sets of data[25, 40] shows that it is likely that the general form of the curve $\rho(\omega)$ in naphthalene has now been reliably determined. Some questions, however, need elucidation. For example, the

establishment of the positions of the van Hove singularities is advisable. Also, the origin of the tail of the density of states behind the B absorption band has not been established though it is most likely due to the lattice phonon effect.

Figure 11 illustrates the anthracene crystal fluorescence spectra in the band-to-band transition region (obtained by Broude and Tartakovskii) and the density of states in the exciton band found from these spectra. The treatment is even more complicated for anthracene since several vibronic transitions with different molecular vibrations are superimposed in the region investigated and the exciton band width is considerably larger than in naphthalene.

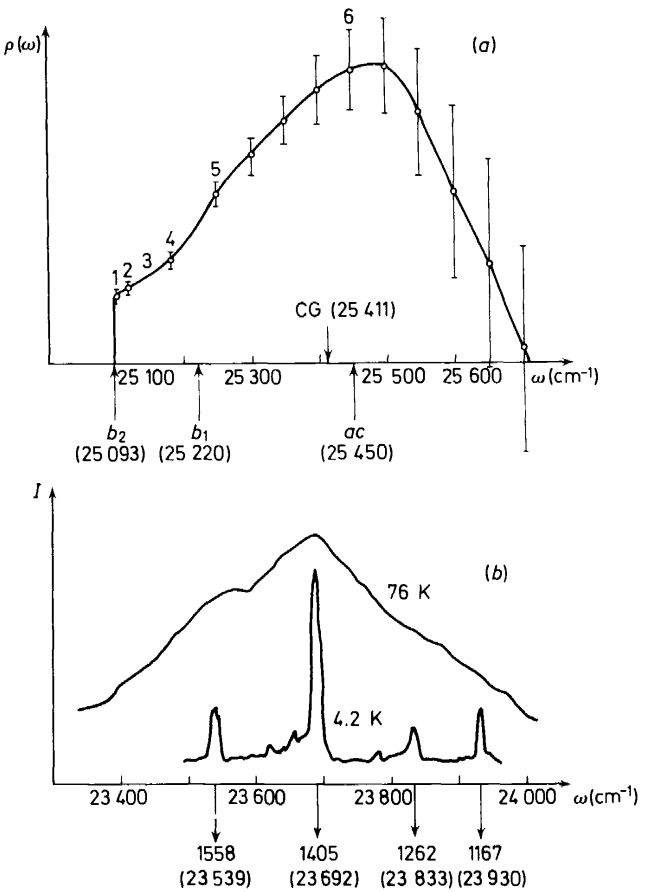

Figure 11. (*a*) The density of states in the anthracene crystal exciton spectrum obtained from an analysis of the band-to-band fluorescence spectrum (Broude and Tartakovskii). The points at which the curves, obtained from the spectra at different temperatures, were matched are marked: 1, 4.2–19.5 K; 2, 19.5–3.5 K; 3, 35–79 K; 4, 79–150 K; 5, 150–200 K; 6, 200–250 K. CG is the centre of gravity of the density of states curve.

(*b*) The fluorescence spectra at 4.2 K and 76 K in the region covering the vibronic transition used

Therefore, it was necessary to use the fluorescence spectra measured in a wide temperature region to preliminarily divide the whole spectrum into the separate bands and only then to carry out the exclusion of the lattice phonon contribution.

The curve of the density of state function obtained (*Figure 11*) spreads over approximately 600 cm^{-1}. The point $\boldsymbol{k} = 0$ for the upper exciton band (25450 cm^{-1}—*a*-component of the Davydov multiplet) turns out to be substantially below the exciton band top. As for the point $\boldsymbol{k} = 0$ for the lower band (*b*-component of the multiplet) then, according to the same data on the crystal absorption spectra[41], its position is 25220 cm^{-1}, which fits the point by approximately 120 cm^{-1} above the low-energy end of the density of state curve. However, the actual shape of the appropriate exciton B absorption band is highly asymmetric with the narrow intense peak 25093 cm^{-1} in the vicinity of its long-wave edge[42]. If the data are accepted, the point $\boldsymbol{k} = 0$ turns out to be near the band bottom. Further thorough measurements of crystal absorption spectra, which are rather labour-consuming tasks because of the extremely high absorption coefficient (up to 10^5 cm^{-1}), must attempt to assign the energetical position of the point $\boldsymbol{k} = 0$ in the lowest exciton band. The fact that, because of the high oscillator strength, the discontinuity in the exciton band at $\boldsymbol{k} = 0$ must be approximately 100 cm^{-1} should also be taken into account.

4. METHODS OF DETERMINATION OF THE ENERGY SPECTRUM

Methods which can be or have already been applied to determining the separate matrix elements $M_{n\alpha, m\beta}$ and, through them, the dispersion laws $\varepsilon(\boldsymbol{k})$ in exciton bands, are considered below.

4.1. Complex impurity centres

Inasmuch as the isotopic impurity spectra are defined solely by $\rho(\omega)$ (cf. Section 3.1), they are especially simple but contain only limited information. When passing to more complex centres alongside of $F(\omega)$ (see equation 6), other integrals over the exciton band arise and hence the possibility of obtaining extra information is presented. In principle, the calculations are not difficult and can be performed on the standard scheme[43] for the centres with arbitrary structure. Nevertheless, if the aim is the extracting of $\varepsilon(\boldsymbol{k})$, it is advisable to use only the centres which introduce no, or only a few, additional parameters into the theory. Two types of such centres have been investigated.

A. Aggregate isotopic centres

The aggregates of closely placed isotopic impurities (two, three or more) have the simplest structure. The energy levels of impurity pairs for various configurations are expressed by integrals:

$$F_{\alpha\beta}(\boldsymbol{n} - \boldsymbol{m}, \omega) = \frac{v}{(2\pi)^3} \sum_{\mu} \int \frac{\exp\{i\boldsymbol{k}(\boldsymbol{n}_\alpha - \boldsymbol{m}_\beta)\}}{\omega - \varepsilon_\mu(\boldsymbol{k})} B_\alpha(\mu\boldsymbol{k}) B^*_\beta(\mu\boldsymbol{k})\, \mathrm{d}^3\boldsymbol{k}, \quad (18)$$

where $B_\alpha(\mu\boldsymbol{k})$ are the usual exciton wave amplitudes, and $\boldsymbol{n}_\alpha$, $\boldsymbol{m}_\beta$ the impurity

molecule coordinates. The situation is especially simple at $|\Delta| \gg |\varepsilon_\mu(\boldsymbol{k})|$. In this case $F_{\alpha\beta}(\boldsymbol{n}-\boldsymbol{m},\ \omega) \propto M_{\boldsymbol{n}\alpha,\,\boldsymbol{m}\beta}$, which simply means that the quasi-resonance interaction with the host molecules can be neglected and only the interaction between the guest molecules inside the pair has to be taken into account. Then $M_{\boldsymbol{n}\alpha,\,\boldsymbol{m}\beta}$ is found directly from the spectrum of the pair $(\boldsymbol{n}\alpha, \boldsymbol{m}\beta)$. This method was suggested by Hanson[44].

When Δ and ε_μ are comparable the spectrum is determined by the integrals $F_{\alpha\beta}$ which, apart from ε_μ, contain the phase factors $B_\alpha(\mu\boldsymbol{k})$. However, if we restrict ourselves to the interaction with several close neighbours the $B_\alpha(\mu\boldsymbol{k})$ factors usually do not depend upon $\boldsymbol{k}$ and are easily calculated; and then the $F_{\alpha\beta}$ integrals are determined by the functions $\varepsilon_\mu(\boldsymbol{k})$. In a more general case $F_{\alpha\beta}$ are equally dependent on $\varepsilon_\mu(\boldsymbol{k})$ and $B_\alpha(\mu\boldsymbol{k})$. Therefore, it is convenient to choose some number of coefficients M_{ij} rather than the functions $\varepsilon_\mu(\boldsymbol{k})$ as values to be determined directly from the experiment. Inasmuch as both $\varepsilon_\mu(\boldsymbol{k})$ and $B_\alpha(\mu\boldsymbol{k})$ are expressed through M_{ij}, these coefficients can be determined from the known $F_{\alpha\beta}$. M_{ij}, in their turn, determine the dispersion law. That is to say. in this sense, we shall state in what follows that $F_{\alpha\beta}$ allow us to deduce the dispersion law.

B. Defect centres

In a number of crystals resonantly coinciding 'defect' bands[45] corresponding to the exciton binding in the vicinity of host molecules deformed by the lattice defect of some kind are observed in the edge absorption and luminiscence spectra. The anomalous polarization ratio for these absorption bands allowed one to assume[46] that they correspond to the exciton bound states strongly exhibiting quasi-resonance interactions (similarly to Section 3.1). The first defect centre, the nature of which has been definitely ascertained, is the thionaphthalene and thionaphthene is considered, one can see that they markedly Pröpstl and Wolf[48]). The calculation of some models of defect centres has been performed by Sugakov[49] and Osad'ko[50] and the analysis of the experimental data for a number of systems based on benzene and naphthalene (Ostapenko, Sugakov and Shpak[51–53]) supported the validity of the model.

Inasmuch as one impurity molecule can simultaneously deform some neighbouring host molecules, some unknown parameters, namely the values of shift of the electronic level Δ for these host molecules, can in principle enter into the formulae for impurity spectra expressed in terms of the integrals $F_{\alpha\beta}$ (equation 18). It is obvious that under such conditions the interpretation becomes extremely difficult. However, if such a typical pair of molecules as naphthalene and thionaphthalene is considered, one can see that they markedly differ from one another, but locally and just in the half where the thionaphthene molecule has a sulphur atom. Therefore, it is hoped that only one host molecule, the position of which can be determined from crystallographic data, will be markedly 'crumpled'. If this is the case, it may be possible to measure the different $F_{\alpha\beta}(\boldsymbol{n}-\boldsymbol{m},\omega)$ by using the impurities with properly oriented heteroatoms or radicals.

The experimental data on the electron and vibron 'defect' levels produced in naphthalene by thionaphthene, indole and benzofuran has been treated[52, 53] under the assumption that only one nearest translationally non-equivalent molecule is deformed. $F(\omega)$, found experimentally[54] by the

isotopic impurity spectra, was used in these calculations and the function $F_{12}(\omega)$ for the neighbouring translationally non-equivalent molecules was calculated under the assumption that only M_{12} is different from zero. It turned out that it was possible to fit all the data by proper choice of the unique parameter Δ. Thus, the general model of defect centres can be assumed to be well founded and the spectra of these centres made it possible to support $\rho(\omega)$ and M_{12} for naphthalene determined in the other ways. However, it is not yet clear how much the discrepancies between the theory and experiment are associated with the deformation of other host molecules, which are among the nearest neighbours of the guest molecule. This still restricts the prospects of finding different $F_{\alpha\beta}(\boldsymbol{n} - \boldsymbol{m}, \omega)$ from such experiments.

4.2. Vibronic spectra

In Section 3.2 it was shown that vibronic spectra are similar to those of impurity centres. This analogy also extends to vibronic impurity states, the spectrum also being expressed in terms of the integrals $F_{\alpha\beta}$ (see equation 18).

A. Impurity spectra: non-totally symmetric phonons

Figure 12 illustrates two possible situations in the impurity vibronic absorption: the non-totally symmetric phonon (NTS-phonon) originates either on the guest molecule or on the host one[33, 35]. In the first case, the

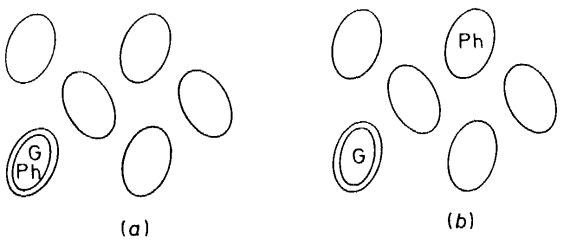

Figure 12. The two possible situations in the impurity vibronic absorption. (*a*) The NTS-phonon originates on the guest molecule. (*b*) The NTS-phonon originates on one of the host molecules; G—impurity, Ph—phonon

perturbing potential on the guest molecule is equal to $\Delta + \Delta_v$ and the usual impurity M absorption band arises (denoted by M'). Such absorption bands are described according to Section 3.2. They are well studied and have already been used in determining $\rho(\omega)$[25]. In the second case the two-centre problem arises with the potential Δ on the guest molecule, and Δ_v on the vibrationally excited host molecule. If phonon transfer is slow, the whole succession of absorption bands must arise (M'' absorption bands), their frequencies being determined by the relative positions of the guest and phonon in exactly the same manner as in the case of aggregate centres (Section 4.1).

At present the absorption bands which can be interpreted as M'' absorption bands corresponding to the guest and phonon sitting on the neighbouring interchange-equivalent molecules have been found in the spectra of naphthalene-d_8 doped by naphthalene-h_8, naphthalene-α d_1 and naphthalene-β

d_1[55, 56]. Similar absorption bands have also recently been found in the defect spectra of thionaphthene in naphthalene[56, 57].

In both cases the treatment of the experimental data has been performed in exactly the same manner as was described above for defect centres, and quite a satisfactory agreement between the theory and experiment has been achieved. The spectra exhibit a well-resolved structure and their theory involves no unknown parameters. Therefore, it may be possible to use them for the energy spectrum determination, though such attempts have not been made so far.

B. Totally symmetric phonons

The bandwidths of totally symmetric (TS) phonons are as small as those of non-totally symmetric phonons. However, their behaviour is entirely different when the electronic exciton is simultaneously present in the crystal. Inasmuch as the non-orthogonality integrals of vibrational functions, corresponding to the ground and electronically excited states of the molecule, for TS-vibrations are large and sometimes approach unity, the probabilities of transferring the vibronic and electronic excitations are comparable in value. This produces a substantially specific character of the vibronic spectra with TS-phonons. The exciton and TS-phonon interaction Hamiltonian suggested by Rashba[58] has the form:

$$H_{\text{int}} = \gamma^2 \sum_{n\alpha,\, m\beta} M_{n\alpha,\, m\beta} a^+_{n\alpha} a_{m\beta} \{ b^+_{n\alpha} b_{m\beta} + b^+_{m\beta} b_{n\alpha} - b^+_{n\alpha} b_{n\alpha} - b^+_{m\beta} b_{m\beta} \} \quad (19)$$

Here a and b are exciton and phonon operators and γ is the intramolecular constant of the electron–phonon coupling. This Hamiltonian may be obtained when the phonon frequency is much larger than the exciton bandwidth. Inasmuch as H_{int} preserves the number of phonons, the problem is purely dynamic, i.e. one of the behaviour of two interacting particles. It is of interest to note that H_{int} is determined by the same parameters M_{ij} as the exciton band and involves no unknown parameters. The first term in H_{int} describes the simultaneous exciton and phonon transfer, the second term their exchange of places and the third term the phonon effect on the exciton transfer (*Figure 13*). Because of the complicated structure of H_{int} the spectrum is determined by the quantities $F_{\alpha\beta}$ even in the perfect crystal. Therefore, the result can be written in the explicit form only within the framework of the Frenkel restricted

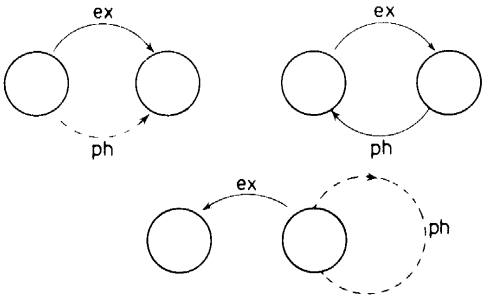

Figure 13. The processes corresponding to separate terms in H_{int} (equation 19) for TS-phonons

model. It should be pointed out that together with the volume integrals of the type $F^{R}_{q\beta}$, the integrals over the isoenergetic surfaces, generalizing $\rho(\omega)$, also enter into the formulae, which generalize equation 11 in describing the two-particle absorption. This must be of importance in the treatment of experimental data.

The theory of vibronic spectra with TS-phonons was developed by Philpott[59]; the linear chains in different aspects were considered recently[60]; and the qualitative analysis of experimental data was performed by Sheka[61] but their quantitative analysis has not been performed yet. The relationship with other problems on quasi-particle complexes was discussed by Levinson and Rashba[62].

4.3. Energy spectrum of benzene and naphthalene

The set of three parameters M_{ij} entering the dispersion law (equation 2) of excitons in benzene has already been cited in Section 2.4:

$$M_{12} = -1.0\,\mathrm{cm}^{-1}; \qquad M_{13} = 4.5\,\mathrm{cm}^{-1}; \qquad M_{14} = 3.5\,\mathrm{cm}^{-1}$$

This set was suggested by Broude[16] on the basis of the analysis of the Davydov's multiplet structure. Colson *et al.*[40] have determined these parameters in quite a different way: they found the parameter values giving optimal agreement with the density of states data (*Figure 8*). They obtained:

$$M_{12} = -1{\cdot}55\,\mathrm{cm}^{-1}, \qquad M_{13} = 3.93\,\mathrm{cm}^{-1}, \qquad M_{14} = 3.28\,\mathrm{cm}^{-1}$$

The deviations in the values of these parameters within $0.5\,\mathrm{cm}^{-1}$ has little effect on the shape of $\rho(\omega)$. A comparison of these sets shows that they agree between each other within a given accuracy, and hence the first set must be in agreement with the experimental $\rho(\omega)$. It is also supported by the coincidence of position of the original term ω_0 used[16] with that obtained from the experimental curve.

Thus, both sets of parameters agree between each other. It is difficult now to give preference to any of them but both define similar laws of dispersion. *Figure 14* illustrates the dispersion laws patterned according to the first set.

The naphthalene energy spectrum is more complicated. Hanson[44] has made an attempt to separate out the absorption bands corresponding to the

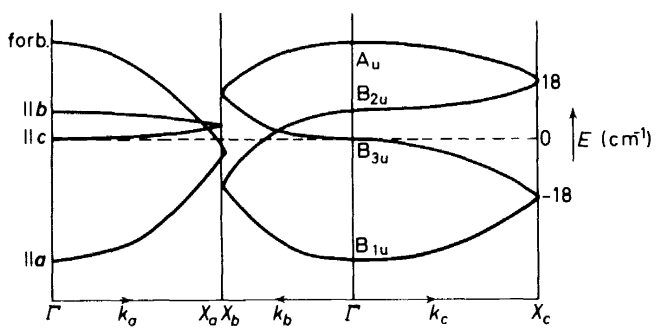

Figure 14. The exciton dispersion law in benzene constructed according to the data of Broude[16]

naphthalene-h_8 molecule pairs in naphthalene-d_8, and determine M from them for the several nearest neighbours. A number of absorption bands of the impurity spectrum, taken with a record resolution ($\sim 0.1\ cm^{-1}$), have been assigned to six types of pairs shown in *Figure 15* (two interchange-equivalent and four translation-equivalent pairs). The strongest interaction has been found for the closest interchange-equivalent molecules ($M_{12} = 18.3\ cm^{-1}$), the other values were between 3 and $8\ cm^{-1}$.

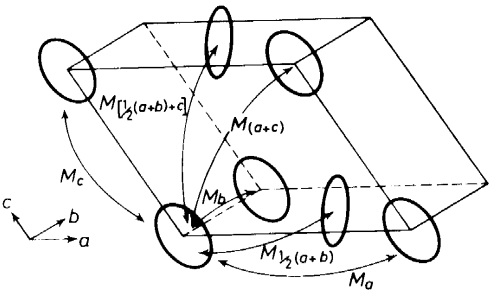

Figure 15. The six types of pair centres in the naphthalene crystal used for the treatment of experimental data on the naphthalene-h_8 impurity spectrum in naphthalene-d_8[44]

The main shortcomings of this interpretation are due to (*i*) the ambiguity involved in the assignment of absorption bands with the definite guest configurations, and (*ii*) the quasi-resonance interactions, which are rather large in naphthalene, were neglected. Hong and Kopelman[26] have attempted a consistent treatment of the data[44] within the framework of the Frenkel restricted model. The application of this model is justified since the contribution of long range dipole–dipole interactions estimated from the oscillator strength of the B absorption band ($f_B \approx 2 \times 10^{-3}$)[63] yields $\sim 2\ cm^{-1}$. However, this method has not led to an unambiguous assignment either; the three sets of M_{ij} describe Hanson's results[44] on impurity pairs and the results of Colson *et al.*[40] on the form of the density of states function with approximately equal accuracy. In all the sets $M_{12} = 18\ cm^{-1}$ and the other M_{ij} are within 1 to $9\ cm^{-1}$ and completely different in the three sets, none of them agreeing with those given by Hanson.

Thus, unfortunately, the analysis of pair spectra, though undoubtedly promising, has yielded no real result as yet. Of course, this method has additional possibilities, namely, the measurement of intensities and polarization ratios, which may give rise to additional criteria for the correct assignment. However, some radical changes are required in the experiment (the application of uniaxial deformations, employing layer structures, etc.) to allow the qualitative criteria to be used for reliable absorption band assignment. Other spectra which can be used in determining the band structure still yield a satisfactory agreement in their analysis, within experimental error, when $\rho(\omega)$ and M_{12} are used exclusively (as described in Sections 4.1B and 4.2A).

So, in conclusion, for the naphthalene crystal we can give only the density of states found by the two methods[25] and, for a comparison, the density of states calculated from the set of parameters which are preferred by the authors of that study[26] (*Figure 16*).

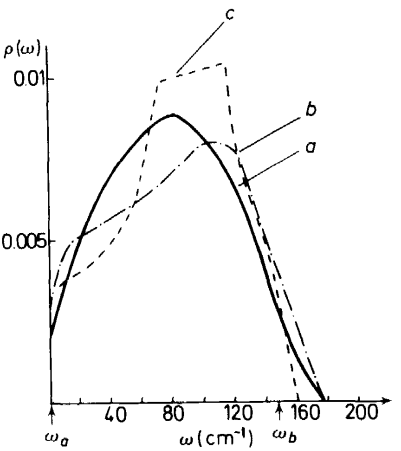

Figure 16. The density of states in the exciton bands of naphthalene: *a*, according to Ref. 40; *b*, according to Ref. 25; *c*, according to Ref. 26 (the first set of parameters M_{ij})

5. CONCLUSION

The whole complex of methods of exciton band structure analysis has been discussed above. Most of the methods have already been applied and the others can, in principle, be used in the near future. A summary scheme demonstrating the possibilities of these methods is represented in *Figure 17*. Among the methods enabling one to determine $\varepsilon(\boldsymbol{k})$ are those in which the measured values cannot be expressed in the terms of the density of states $\rho(\omega)$.

The application of these methods has greatly advanced our knowledge since 1960 when the exciton energy spectrum structure was almost unknown. However, the results obtained up to now are rather modest. This is primarily due to the fact that in all the methods applied, some mean values over the spectrum have been measured and hence the sensitivity is low. If it had turned out to be possible to investigate the scattering of any kind of particles on excitons or with the creation of excitons by analogy with the neutron spectroscopy of phonons (for example, the Raman scattering of x-rays with exciton formation has been discussed[64]), the problem would have been solved. It is only important that the momentum transfer be of the order of the Brillouin one and that the resolution be sufficiently high. Here the whole question rests on experimental possibilities and, unfortunately, we know of no optimistic prospects for such kinds of experiments for the near future.

Therefore, one should refine the existing methods for the time being and develop some new ones, even if they give only a partial solution of the

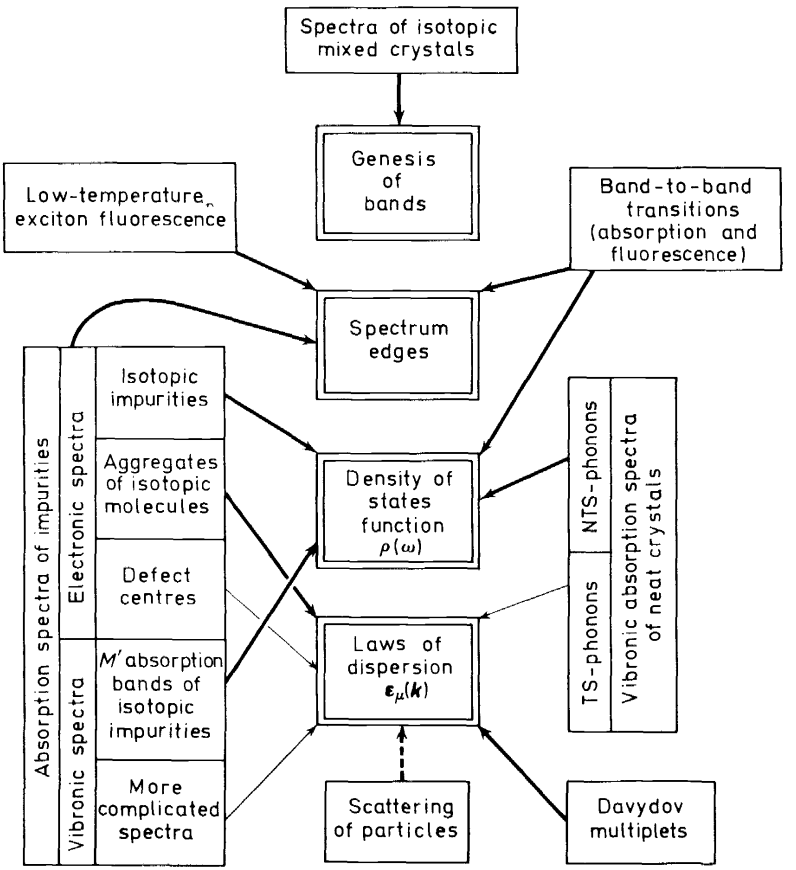

Figure 17. The exciton band parameters and the main experimental methods by which they may be determined. In the central column containing the exciton band parameters—the 'Spectrum edges', 'Density of states function' and 'Laws of dispersion'—the bulk of information on the spectrum is progressively growing. Therefore, finding each parameter makes it possible to automatically determine all the previous ones. The heavy arrows indicate the methods which have already been used for determining the above parameters with different efficiency, and the thin arrows indicate the methods which can be used in the near future. The dashed line indicates the group of methods on particle scattering, the prospect of application of which is extremely tempting but, unfortunately, is very vague as yet

problem. In this connection the fact that the great potential of modulation spectroscopy[65], as applied to molecular excitons, has not been employed attracts attention. Meanwhile, the measurement of frequency derivatives (for example, in the D absorption bands) could help in finding the van Hove singularities. This would be rather significant for the determination of M_{ij}. The investigation of thermo-absorption might also be effective. An investigation of super-thin monocrystal layers (~ 10 atomic layers) might be of great

interest since, because of the quantization of the normal component of $\boldsymbol{k}$, one could directly measure $\varepsilon(\boldsymbol{k})$ in a number of discrete points.

There is one more aspect of the problem which makes the determination of exciton spectra difficult both from the practical and principle point of view. This is the interaction of excitons with lattice phonons. This interaction is not as weak as one would like it to be and it has already caused many a problem in a number of experiments on the determination of band structure[25,40]. These difficulties can be partly circumvented by low temperatures. Up to now, the coupling constants with different groups of lattice phonons are almost unknown and thus it is difficult to estimate the phonon attenuation of excitons. If this turns out to be considerable, for example in the upper part of the exciton spectrum, the very problem of the determination of the exciton spectrum must be significantly changed. It is clear that the problem of electron–phonon interactions is the next requiring attention, and so it is gratifying that the experimental investigations in this field have become more active lately[66].

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