

ELECTRON-VIBRATIONAL SPECTRA OF MOLECULES AND CRYSTALS

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CONTENTS

Introduction	484
I. Vibronic states of a molecule	484
II. Vibronic states of binary molecules and dimers	488
III. Vibronic states of molecular crystals (theory)	495
IV. Vibronic absorption spectra of aromatic crystals	504
V. Conclusion	509
Cited literature	509

INTRODUCTION

THE overwhelming majority of bands in absorption spectra of molecular crystals correspond to simultaneous occurrence, under the influence of light, of electronic and intramolecular vibrational excitations (vibronic bands). For this reason, the interpretation of the spectrum of a molecular crystal is in fact interpretation of its vibronic bands. Much experimental and theoretical material has accumulated by now, and its analysis makes it possible to formulate the main premises of the analysis of a vibronic spectrum.

The theoretical analysis of vibronic spectra is based on two models, which will be considered here in detail. In the first model (the model of coinciding configurations), the vibronic states are described by the energy spectrum of a single quasiparticle—a vibron, corresponding to wavelike propagation of a molecular vibronic excitation through the crystal. According to the second model (the general dynamic model), each vibronic state of an individual molecule in the crystal corresponds to an aggregate of bound and dissociated states of a system of quasiparticles (electronic and vibrational excitons) interacting in accordance with a definite law. The larger the number of vibrational quanta contained in the vibronic excitation of the molecule, the larger the number of corresponding quasiparticles and the more complicated the energy spectrum of such a system. The vibronic-spectrum structure predicted by the dynamic model is richer and more interesting than that of the model of coinciding configurations.

To establish the experimental laws governing the construction of vibronic spectra, the initial sections of the vibronic spectra were considered for crystals of benzene, naphthalene, and anthracene, which have been classified long ago, with respect to the properties of the electronic states, as pertaining to weak, medium, and strong resonant interactions. The difference between these crystals extends also to the vibronic spectra. On the basis of the concepts of bound and dissociated states, a connection was established between the resonant properties of electronic states and the properties of vibronic spectra. This connection has explained the variety of vibronic spectra of molecular crystals.

The properties of vibronic states of a crystal, in

either model, are most closely related with the properties of the vibronic excitations of free molecules, and are determined by the mechanism whereby the electronic and vibrational excitations interact in the molecule and by the symmetry of the vibrational states. The essence of this connection will be shown below. We therefore begin the review of vibronic states with a brief examination of the main mechanisms of electron-vibrational interaction and their influence on the vibronic spectra of a free molecule.

I. VIBRONIC STATES OF A MOLECULE

The question of the vibronic spectrum of a polyatomic molecule is very extensive and has been considered in a large number of original papers and monographs (see, for example, [1-3]). This is precisely why we shall dwell below only on the principal questions that pertain directly to the problem of interest to us. We confine ourselves also to the case of discrete molecular spectra.

In the approximation of Born and Oppenheimer^[4,5], the dependence of the total energy of the electrons on the displacement of the nuclei from the equilibrium position is that adiabatic potential which determines the vibrational motion of the nuclei and connects its properties with the properties of the electronic motion. Since the displacements are small in magnitude, the adiabatic potential can be expanded in terms of this quantity. The optical vibronic spectra of complex molecules can be interpreted well in the harmonic approximation, so that in the simplest case the dependence of the adiabatic potential on the displacement of the nuclei in the f -th electronic state is given by

$$W^f(R) = W^f(R_0^f) + \frac{1}{2} \left(\frac{\partial^2 W^f}{\partial R^2} \right)_{R=R_0^f} (R - R_0^f)^2, \quad (1)$$

where R_0^f is the equilibrium position of the nuclear configuration in the f -th electronic state, and

$$k^f = \left(\frac{\partial^2 W^f}{\partial R^2} \right)_{R=R_0^f}$$

is the force constant that characterizes the quasielastic force. In turn, $k^f = \mu (\nu^f)^2$, where μ is the reduced mass of the vibrating particles and ν^f the oscillation frequency. In complex molecules having N vibrational de-

degrees of freedom, $W^f(\mathbf{R})$ is a function of N coordinates. However, after introducing normal coordinates, relation (1) can be considered for each normal oscillation or for their aggregate.

The dependence of the force constant k^f and of the equilibrium position R_0^f on the number of the electronic state indicates that the equilibrium position of the nuclear configuration and the frequency of the normal vibrations are altered by electronic excitation of the molecule.

Let us consider the expression for the adiabatic potential in greater detail. We introduce the dimensionless displacement of the nuclei from the equilibrium position $q = R\sqrt{\mu\nu}$ (we use $\hbar = 1$ throughout) and assume that the equilibrium position of the molecule in the ground state corresponds to $q_0^0 = 0$. Then q_0^f will denote the displacement of the equilibrium position of the nuclear configuration upon excitation of the molecule to the f -th state. Under these conditions, the expressions for the adiabatic potential in the ground and f -th excited states are

$$W^0(q) = W^0(0) + \frac{1}{2} \nu^0 q^2 \quad (2a)$$

and

$$W^f(q) = W^f(q_0^f) + \frac{1}{2} \nu^f (q - q_0^f)^2. \quad (2b)$$

The expression for $W^f(q)$ is conveniently rewritten in more detailed form

$$W^f(q) = W^f(q_0^f) + \frac{1}{2} \nu^f (q_0^f)^2 - \nu^f q_0^f q + \frac{1}{2} \nu^f q^2; \quad (2c)$$

Here $W^f(q_0^f)$ corresponds to the energy of the purely electronic excitation; $\frac{1}{2} \nu^f (q_0^f)^2$ is the displacement of the minimum of the potential-energy curve as a result of the displacement of the equilibrium position following electronic excitation. This quantity is called the Franck-Condon energy, which will henceforth be designated

ϵ_{FC} . The value of the energy defined by $\Delta W^{of} = W^f(q_0^f) + \epsilon_{FC} - W^0(0)$ corresponds to the maximum transition probability in the electron-vibrational spectrum, since it corresponds to a vertical transition from the equilibrium position in the ground state. Consequently, ϵ_{FC} multiplied by two corresponds to the Stokes loss on radiation^[5,8]. The change of the interaction between the electronic and vibrational motions in the ground and f -th electronic states, according to (2a) and (2b), is determined by an electron-vibrational interaction operator of the form

$$\Delta W(q) = \nu^f q_0^f q + \frac{1}{2} \Delta \nu q^2, \quad (3a)$$

or, using the expression for ϵ_{FC} , we can rewrite the operator (3a) in the form

$$\Delta W(q) = \sqrt{2\nu^f \epsilon_{FC}} q + \frac{1}{2} \Delta \nu q^2. \quad (3b)$$

The first term of this expression characterizes the energy of distortion of the molecule as a result of the change of the equilibrium position of its nuclei following electronic excitation. It is sometimes called the distortion energy of the molecule. We shall therefore designate it ϵ_d ^[7]. The distortion energy at low temperatures ($kT < \nu^f$) determines the width of the electron vibrational spectrum. The second term is connec-

ted directly with the change of the vibration frequency. The vibration frequency defect is $\Delta \nu = \nu^f - \nu^0$.

In the harmonic approximation considered by us, the shift of the equilibrium position and the change of the vibration frequency following electronic excitation are the two principal mechanisms of the electron-vibrational interaction. The contribution that each of these mechanisms makes to the vibronic state taken separately is determined primarily by the symmetry of the oscillation. The shift of the equilibrium position following excitation of the vibronic transition with a non-fully-symmetrical (n.s.) vibration should be accompanied by a change in the symmetry of the molecule. Yet it is known that the molecule retains a symmetrical configuration for nondegenerate states upon excitation of n.s. vibrations (the Jahn-Teller effect^[3]). For this type of oscillation there is therefore no shift of the equilibrium position, and the interaction between the electronic and vibrational motions is determined only by the change of its frequency. The frequency defect is not small, and in many cases amounts to several tens of cm^{-1} (10–20% and more of the magnitudes of the vibration). Fully symmetrical (f.s.) vibrations are characterized primarily by a shift of the equilibrium position, although electronic excitation also changes their frequency. As already noted, a shift of the equilibrium position leads to a renormalization of the energy position of a purely electronic transition and determines the width of the vibronic spectrum. The latter characteristic is most closely connected with the probabilities of the vibronic transitions, which we shall consider below.

The intensity of the vibronic transition is proportional to the square of the matrix element of the dipole moment of the transition, which for transitions from the ground vibration-free state is given by

$$M_{0c,fn} = \int M_{of}(R) U^{0*}(R) X_m^f(R) dR, \quad (4)$$

$$M_{of} = \int \varphi^{0*}(r, R) M(r) \varphi^f(r, R) dr,$$

where $\{r\}$ and $\{R\}$ are the aggregates of the electronic and nuclear coordinates. Here $\varphi(r, R)$, $U(R)$, $X_m(R)$ are the wave functions of the electronic state and of the zeroth and m -th vibrations, respectively. The indices 0 and f pertain to the ground and f -th excited electronic states. The wave functions of the electron depend parametrically on the nuclear coordinates, and determine by the same token the dependence of the matrix element of the dipole moment of the electronic transition $M_{of}(R)$ on the position of the nuclei. In the adiabatic approximation, it is legitimate to expand this matrix element in terms of the small displacement of the nuclei from the equilibrium position^[9], so that

$$M_{of}(R) = M_{of}^0(R_0^0) + M_{of}^{(1)}(R_0^0)(R - R_0^0) + \dots \quad (5)$$

where R_0^0 is the equilibrium position of the nuclei in the ground state, and the coefficient $M_{of}^{(1)}(R_0^0)$ describes the effect of mixing of the wave functions of the considered electronic state with the wave functions of the other electronic states, and by the same token determines the degree to which other electronic zeroth-approximation states take part in the excitation of the f -th electronic state.

The zeroth approximation of the expansion (the Condon approximation^[5,8]) describes satisfactorily a

large number of vibronic transitions in which f.s. vibrations take part in spectra with allowed purely electronic transitions. In this case the matrix element of the dipole moment of the electronic transition is determined at the equilibrium position of the nuclei, and the total matrix element of the dipole moment of the vibronic transition is

$$M_{00, fm}^{(0)} = M_{0f}^{(0)}(R_0^0) \xi_{00, fm}, \quad (6)$$

where

$$\xi_{00, fm} = \int U^{0*}(R) X_m^f(R) dR.$$

The spectrum intensity distribution among the different vibronic transitions within a single electronic transition is determined, in accordance with this expression, by the values of the superposition integrals of the vibrational functions $\xi_{00, fm}$ (the Condon integrals) in the ground and f-th electronic states. In order for the Condon integral not to be an orthogonality integral upon variation of the vibrational quantum number m, it is necessary that the wave functions $U^0(R)$ and $X_m^f(R)$ be solutions of different equations. This condition is satisfied if electronic excitation shifts the equilibrium positions or changes the vibration frequencies of the nuclei. If the relative change of the vibration frequency is small ($\Delta\nu/\nu \ll 1$), then the intensity of the vibronic transitions, which is governed by the change of the vibration frequency, is low^[10] and consequently the principal role is played in the Condon approximation by the shift of the equilibrium position of a nuclear configuration. In this case the Condon integral takes the form

$$\xi_{00, fm} = \int U^{0*}(R - R_0^0) X_m^f(R - R_0^0) dR, \quad (6a)$$

and it differs from zero in the case of a vibronic transition with change of the vibrational quantum number^[11-14].

Vibronic transitions with participation of n.s. vibrations are forbidden in the Condon approximation and are allowed only in first order of the expansion of the electronic-transition matrix element in terms of the nuclear displacement^[9] (the Herzberg-Teller effect^[15]). In this case the total matrix element of the dipole moment of the vibronic transition is equal to

$$M_{00, fm}^{(1)} = M_{0f}^{(0)}(R_0^0) R_{00, fm}, \quad (7)$$

where

$$R_{00, fm} = \int U^{0*}(R_0^0) [R - R_0^0] \chi_m^f(R - R_0^0) dR, \quad (8)$$

and $M_{0f}^{(1)}(R_0^0)$ is the coefficient of the linear term of the expansion in (5).

Expressions (6) and (8) are the basis of the principal laws governing the construction of the vibronic molecular spectrum and connected with the different mechanisms of interaction between the electronic and vibrational motions for the two types of vibrations. Let us consider some of these laws.

1. The intensity of a vibronic transition with f.s. vibration is connected with the intensity of the purely electronic transition through the Condon integral (see (6)). To the contrary, the intensity of a vibronic transition with n.s. vibration is not determined by the intensity of this purely electronic transition, but depends, through the matrix element $M_{0f}^{(1)}(R_0^0)$, on the intensity of other symmetry-allowed electronic transitions. This circum-

stance leads to two distinguishing features of vibronic transitions with n.s. vibrations. First, the absolute intensity of such transitions is always small, since the total matrix element of the dipole moment of the transition is a quantity of first order of smallness, owing to the large energy difference between the two mixing electronic states. The oscillator strengths of vibronic transitions with n.s. vibrations, according to the experimental data, do not exceed 10^{-3} – 10^{-4} . Second, the condition that the matrix element $M_{0f}^{(1)}(R_0^0)$ differ from zero limits the number of symmetry types of the n.s. vibrations that can take part in the vibronic transition. The maximum number of symmetry types of the n.s. vibrations that are active in a given electronic state is equal to the number of symmetry types of the electronic transitions in the molecule other than the transition under consideration^[2,16].

2. An essential feature of a vibronic transition is the intensity of the multiquantum vibrational transition. Among the transitions with n.s. vibrations, the most intense, as follows from (7), are the single-quantum transitions. The transition intensity decreases sharply with increasing vibrational quantum number, like a power function of the ratio $\Delta\nu/\nu$, which, as already mentioned, is much smaller than unity. For transitions with f.s. vibrations, the intensity of their multiquantum replicas is determined in accordance with (6) by the Condon integrals, which depend primarily on the displacement of the equilibrium position of the nuclear configuration. The integral can reach large values and can determine, in contrast with the results of the frequency change, a large number of replicas. It is easy to show in the case of harmonic vibrations that the ratio of the intensity J_{fm} of a m-quantum vibronic transition with f.s. vibration to the intensity J_{f_0} of the band of the purely electronic transition is given by

$$I_m = \frac{J_{fm}}{J_{f_0}} \frac{\nu_{f_0}}{\nu_{fm}} = \frac{\gamma^{2m}}{m!} = \frac{|\xi_{00, fm}|^2}{|\xi_{00, f_0}|^2}; \quad (9)$$

here ν_{f_0} and ν_{fm} are the frequencies of the purely electronic and vibronic transitions, $\xi_{00, fm}$ and ξ_{00, f_0} are the Franck-Condon integrals for the fm-th vibronic and vibration-free electronic transitions, respectively, and γ is a quantity that plays an important role in the theory of electron-vibrational interactions; it is called the coupling constant between the electronic and vibrational motions and is expressed in terms of the distortion energy of the molecule as follows:

$$\gamma = \frac{1}{\sqrt{2}} \frac{\epsilon_d}{\nu} = \sqrt{\frac{\epsilon_{FC}}{\nu}}. \quad (10)$$

Figure 1 shows a theoretical plot^[17] of the ratio I_m against the value of γ . It is seen from the figure that the existence of a long progression of vibronic transitions calls for large values of γ . The points on the figure denote the experimental values of I_m for the series of vibronic transitions of a number of aromatic molecules. The deviations of the positions of the points from vertical are small if it is recognized that in these transitions preference was given to only one f.s. vibration, and the others were disregarded.

3. The f.s. and n.s. vibrations behave differently in compound vibronic transitions. Such transitions are produced when different numbers quanta of different f.s.

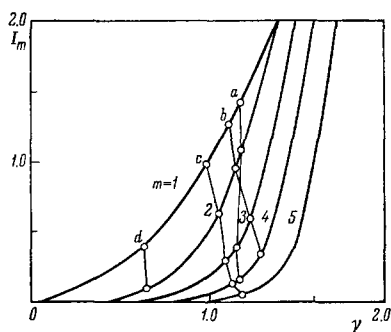


FIG. 1. Theoretical dependence of the intensity ratio $I_m = J_{fm}/J_{00}$ for $m = 1, 2, 3, 4,$ and 5 on the electron-vibrational coupling constant γ . The points denote the experimental values of I_m for the vibronic transitions of the following molecules: a—benzene, 2600Å transition (A_{1g} vibration, $\nu = 920 \text{ cm}^{-1}$); b—naphthalene, 2900Å transition (A_{1g} vibration, $\nu = 1400 \text{ cm}^{-1}$); c—anthracene, 3900Å transition (A_{1g} vibration, $\nu = 1400 \text{ cm}^{-1}$); d—naphthalene, 4200Å (triplet-triplet) transition (A_{1g} vibration, $\nu = 1400 \text{ cm}^{-1}$) [17].

vibrations are superimposed on single-quantum transitions. The compound transition in which only f.s. vibrations take part can contain in this case overtones of each of these vibrations, as well as a sum of different vibrations. In the aggregate, such vibronic transitions constitute a spectrum that proceeds from the purely vibrational transition. The distribution intensity in this spectrum is determined by the displacements of the equilibrium positions for different vibrations. Similar regularities in the intensity distributions also occur in compound vibronic transitions based on single-quantum transitions with participation of n.s. vibrations. Since this single-quantum transition always has an outstanding intensity and distinct symmetry properties in the spectrum, it plays the role of the frontal transition in the sequence of compound transitions. Naturally, the absolute intensity of the compound transitions of this sequence is small. To determine this intensity it is necessary to replace the matrix element $M_{of}^{(0)}(R_0^0)$ in (6) by the matrix element of the dipole moment of the single-quantum transition $M_{00;fm}^{(1)}(R_0^0)$ from expression (7).

Let us illustrate the general laws governing the construction of a vibronic spectrum using as an example the spectra of a number of simplest molecules, which have become classical examples of the spectroscopy of molecules and crystals.

Figure 2 shows schemes depicting the main features of vibronic spectra of several aromatic molecules (the numerical data on the vibrations are gathered in Table I); the spectra are so arranged that the intensity of the purely electronic transition increases in the downward direction. In benzene, which is the most symmetrical of all these molecules (Fig. 2a), the purely electronic transition (${}^1A_{1g} \rightarrow {}^1B_{2u}$, group D_{6h}) is symmetry-forbidden and is not observed in the spectrum. Accordingly, all the related vibronic transitions with f.s. vibrations are also forbidden. Consequently the relatively intense transitions in the spectrum of the molecule are single-quantum transitions in which two n.s. vibrations of symmetry E_{2g} take part, namely ν_2 (520 cm^{-1}) and ν_2' (1480 cm^{-1}) [9,18]. The choice of vibrations of precisely this type of symmetry is due to

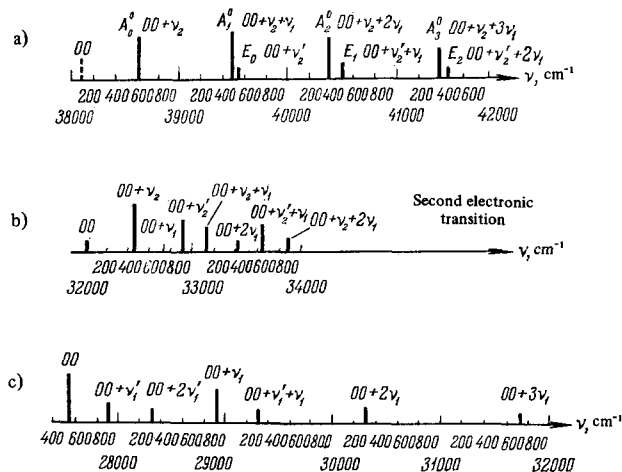


FIG. 2. Schemes of principal transitions of absorption spectra of aromatic molecules. a) Benzene [18]. The theoretical position of the pure electronic transition is $\nu = 38089 \text{ cm}^{-1}$. b) Naphthalene, position of pure electronic transition $\nu = 32020 \text{ cm}^{-1}$ [19,21]. c) Anthracene [22], frequency of purely electronic transition $\nu = 27560 \text{ cm}^{-1}$.

the fact that the nearest electronic state of symmetry E_{1u} becomes mixed with the electronic state B_{2u} under consideration in accordance with the Herzberg-Teller effect. Each of these vibronic transitions is the start of a series (A_i^0 and E_i , respectively [16]) of compound vibronic transitions with participation of a "breathing" f.s. vibration ν_1 (923 cm^{-1}). The laws governing its appearance in the spectrum point to a large displacement of the equilibrium position upon excitation of this vibration. The coupling constant, as shown in Fig. 1, is $\gamma = 1.2$. The corresponding displacement, determined from (8a), and also estimated theoretically in an independent manner, is close to 0.087 \AA [17].

In naphthalene vapor (Fig. 2b), a pure electronic transition (${}^1A_{1g} \rightarrow {}^1B_{2u}$, group D_{2h}), albeit very weak, is observed in the spectrum [19]. Simultaneously, equally weak vibronic transitions with participation of f.s. vibrations are observed. The transitions having the largest relative intensity in this series are those with participation of the vibration ν_1 (702 cm^{-1}), which gives a series of replicas. A considerable fraction of the oscillator strength of the spectrum in the region of the first electronic transition lies in the vibronic transitions with n.s. vibrations of symmetry B_{1g} , namely, ν_2 (438 cm^{-1}) and ν_2' (876 cm^{-1}). Their appearance in the molecule spectrum is due to the mixing of the upper electronic state B_{1u} with the electronic state B_{2u} . The vibration ν_1 develops these vibronic transitions into series. The displacement of the equilibrium position for this vibration is estimated from the values of I_m of the relative intensities of the bands in the series to be 0.070 \AA [17].

In the anthracene spectrum [22] (Fig. 2c) the pure electronic transition is allowed with a large oscillator strength. It is accompanied by intense replicas, principally with the aid of f.s. vibrations ν_1' (400 cm^{-1}) and ν_1 (1400 cm^{-1}). The summary oscillator strength of these transitions is 0.16. Naturally, alongside such strong transitions it is difficult to observe transitions with n.s. vibrations, the oscillator strengths of which, as in the preceding cases, do not exceed several thou-

Table I. Main characteristics of molecular vibrations and principal vibronic transitions of the absorption spectra of the benzene, naphthalene and anthracene molecules

Molecule	Transition	Oscillator strength	Characteristics of vibrations					Notes
			ν^0 , cm^{-1}	ν^1 , cm^{-1}	Δ_ν	m	R_0^f	
Benzene ^[18]	00	0						Initial transition of series A_1^0 [18] Initial transition of series E_1 [18] Transition series A_1^0
	$00 + \nu_1$	0	992	923	-69	1	0	
	$00 + \nu_2$	0.001	606	520	-86			
	$00 + \nu_2'$	0.001	1596	1480	-116	1	0	
	$00 + \nu_2 + m\nu_1$	0.005 *	992	923	-69	4	0.087	
Naphthalene ^[19-21]	00	0.0001						Shift of equilibrium position not determined
	$00 + m\nu_1$	0.00015	760	702	-58	2	?	
	$00 + \nu_2$	0.001	509	438	-71	1	0	
	$00 + \nu_2'$	0.001	935	911	-24	1	0	
	$00 + \nu_2 + m\nu_1$	0.0015 *	760	702	-58	3	0.070	
Anthracene ^[22]	00	0.07 **)						Shift of equilibrium position not determined
	$00 + m\nu_1$	0.08 *)	1400	1400	0	5	0.095	
	$00 + m\nu_1'$	0.01 *)	400	400	0	2	?	

*The indicated oscillator strength pertains to the entire aggregate of the compound vibronic transitions.
**The oscillator strengths were calculated in accordance with [22] at a summary oscillator strength 0.3 of the first electronic transition for three directions of light propagation.

Table II. Shifts of the equilibrium positions of the nuclei following vibronic transitions with f.s. vibrations

Molecule	Transition	Vibration frequency, cm^{-1}	Shift of equilibrium position R_0^f , Å*
Benzene	Сингл.-сингл., 2600 Å	923	0.087
Naphthalene	Singlet-singlet, 3200A Å	700	0.070
	Singlet-singlet, 2900A Å	1400	0.105
	Singlet-singlet, 2200A Å	1400	0.065
	Triplet-triplet, 4200A Å	1400	0.054
Anthracene	Singlet-singlet, 3900A	1400	0.095
	Singlet-singlet, 2500A	1400	0.060
	Triplet-triplet, 4450A	1400	0.043

*The shift of the equilibrium position R_0^f was determined from the ratio of the intensities of the vibronic bands of the corresponding transition.

andths, in the spectrum of the molecule. The "breathing" vibration ν_1 predominates in the vibronic spectrum and is characterized by a large value of the coupling constant $\gamma = 1$, and accordingly by a large shift of the equilibrium position, the magnitude of which is 0.095 \AA [17].

In spite of the fact that the spectra of the benzene and anthracene molecules are quite different, owing to the different nature of their initial bands, nonetheless a common picture, due to the f.s. vibrations, is observed in their construction. Namely, the f.s. vibrations impart a common feature to all the discrete molecular spectra, since the laws governing the development of the individual transitions in the series with the aid of the f.s. vibrations do not depend on the nature of the initial transition, but are determined by the size of the dis-

placement of the equilibrium position of the nuclear configuration. Table II lists the shifts of the equilibrium positions for the well known transitions of the benzene, naphthalene, and anthracene molecules.

II. VIBRONIC STATES OF BINARY MOLECULES AND DIMERS

1. Formulation of Problem. Classification of Types of Bonds

The interpretation of vibronic spectra of free molecules is based essentially on the separation of the electronic and nuclear motions, considered in the preceding section in accordance with the scheme of Born and Oppenheimer. Does this also obtain in the case of systems of weakly bound molecules, such as binary molecules with weak conjugate bonds, dimers, or molecular crystals? This question has been under discussion for the last 10-15 years in a number of papers and is presently the most urgent problem of molecular quantum theory and experiment. The difficulty of the problem consists in the fact that the solution of the problem of vibronic states of a system of molecules calls for simultaneous consideration of two types of interaction: intramolecular interaction between the electronic and vibrational motions, and intermolecular resonant interaction. It follows from experiment that the energies of the two interactions can be comparable, as a result of which the problem of vibronic states of a system ceases to be a problem with a single small parameter, and in this general case the separation of the electronic and nuclear motions does not take place. There exist, however, two limiting cases when one can speak of such a separation.

If the intramolecular interaction predominates, then separation of the electronic and nuclear motions, which is realized in an individual molecule, also remains in force for a system of molecules, in which connection individuality of the molecular vibronic state of the molecule in the system of molecules remains in force. The second limiting case takes place if the intermolecular resonant interaction greatly exceeds the intramolecular interaction between the electronic and vibrational motions. Under these conditions the separation of the electronic and nuclear motions is possible only for the entire system as a whole. Thus, before we proceed to solve the problem of the vibronic states of a given system, we must establish the limiting case to which it belongs and determine the necessary numerical criteria. The first to deal with this problem were Frenkel in 1931^[23] and Peierls in 1932^[24], in connection with an analysis of the interaction of electronic excitations of a crystal with the lattice vibrations. Quantitative criteria for the two limiting cases were given by Frenkel in 1936^[25] in an analysis of the free and "trapped" excitons, on the basis of a comparison of the time of displacement of the electronic excitation through the crystal (τ_{exc}) and the time of development of local deformation of the lattice in the region of the excited site (τ_{def}). For a free exciton $\tau_{exc} < \tau_{def}$, and for a "trapped" one $\tau_{exc} > \tau_{def}$. The same limiting cases were considered in 1938 by Frank and Teller^[26] in connection with a study of migration and photochemical action of the excitation energy in a crystal. In 1951, Davydov^[27,28] considered from the same point of view the question of free and localized excitons, and in 1957 Simpson and Peterson^[29] extended the qualitative aspect of the criterion to include vibronic states of a system of molecules, replacing only the relations for the characteristic times by the relation between the corresponding energies of the resonant and electron-vibrational interactions, and introducing the terms weak and strong coupling. In parallel, the concepts of strong and weak electron-phonon coupling were introduced into the microscopic theory of the solid state by solving the problems of the electron-phonon interactions (see, for example, the review^[11]). Although it might seem that one deals with the same subject in both groups of phenomena, the strong and weak coupling in the terminology of Simpson and Peterson differ significantly from the strong and weak coupling in the theory of electron-phonon interactions. In the former case the type of coupling is established by comparing the energy of the resonant interaction with the energy of the electron-phonon interaction. In the latter case, the dimensionless coupling constant γ , comparison of which with unity determines the type of coupling, is determined by the ratio of the energy of the electron-phonon interactions to the vibration energy. By way of illustration of the difference between the terminologies, we present the example of Frenkel's "trapped" exciton. From the point of view of electron-phonon interactions, it pertains to the strong coupling. But with respect to the resonant interactions this is a weak coupling. To avoid a misunderstanding in the exposition that follows, the coupling to which the classification of Simpson and Peterson pertains will be called resonant. In the most general case, the criteria for a resonant coupling can be written in the form:

- 1) Weak coupling, $E_{res} \ll E_{e,v}$,
- 2) Intermediate coupling, $E_{res} \sim E_{e,v}$,
- 3) Strong coupling, $E_{res} \gg E_{e,v}$.

Concrete expressions for E_{res} and $E_{e,v}$ will be given in the analysis of the individual problems.

The general approach to the problem of vibronic states can be used both for molecular aggregates and for molecular crystals. In binary molecules, dimers, and other molecular aggregates with a limited number of molecules, however, the interacting molecules are coupled by a point-group symmetry operation, whereas in a crystal the molecules are coupled by space-group operations. This circumstance leads to an essential difference between the concrete analysis of the different systems, and they will therefore be considered separately.

2. Vibronic States of Binary Molecules

Investigations of the vibronic states of binary molecules were made by McClure^[30,31]. By way of an example, he considered a molecule consisting of two weakly coupled benzene rings. The electronic and vibrational excitations of the entire molecule are described with good approximation by the corresponding excitations of one ring. Consequently, the electronic interaction between the rings can be regarded as a small parameter. The other energy parameters of the system are the energy of the electron-vibrational interaction, defined by McClure in terms of the defect Δ_ν of the vibration frequency of one ring, and the vibration frequency itself. Within the framework of these parameters, McClure considered qualitatively the vibronic states of a binary molecule.

The main physical advantage of the model is allowance for two types of vibronic configurations, which differ from each other by the method of placing the electronic and vibrational excitations. The first configuration (henceforth called the coinciding vibronic configuration) corresponds to a situation wherein the electronic and vibrational excitations are on a single ring of the binary molecule. In this case the vibrational motion of the molecule is determined in the f -th electronic state and is characterized by a frequency ν^f . The second type of configuration corresponds to placing the electronic and vibrational excitations on different rings. The vibrational motion occurs in the ground electronic state. Such a configuration will henceforth be called separated.

In the case of a weak resonant coupling, defined by the relation $E_{res} \ll \Delta_\nu \ll \nu$, the binary molecule has two vibronic states—bound and dissociated, corresponding to separated and coinciding vibronic configurations. The energy difference between these states is equal to the frequency defect of the vibration Δ_ν in electronic excitation of the ring (Table III)*. At an extremely small value of E_{res} , a single-photon optical transition is allowed only to the bound state. A dissociated vibronic state can be excited by two photons that produce independently electronic and vibrational excitations of the

*The description represented in Table III should be regarded as only qualitatively explaining the physical meaning of the states under consideration.

Table III. Wave functions, energies, and dipole moments of transitions for the cases of weak and strong resonant couplings in binary molecules

States	Symmetry	Wave functions	First-order energy	Dipole moments of transitions
Ground	S	$\varphi_1^0 \varphi_2^0 U_1^0 U_2^0$	0	
f-electronic	S A	$1/\sqrt{2} (\varphi_1^f \varphi_2^0 U_1^f U_2^0 \pm \varphi_1^0 \varphi_2^f U_1^0 U_2^f)$	$E^f \pm E_{res}$	$(M_1 \pm M_2)/\sqrt{2}$
Extremely weak coupling, f-electronic plus m-vibrational	S A	$1/\sqrt{2} (\varphi_1^f \varphi_2^0 U_1^f X_2^{0m} \pm \varphi_1^0 \varphi_2^f X_1^{0m} U_2^f)$	$E^f + \nu^{0m} \pm E_{res}$	$\begin{cases} 0 \\ 0 \end{cases}$
	S A	$1/\sqrt{2} (\varphi_1^f \varphi_2^0 X_1^{fm} U_2^0 \pm \varphi_1^0 \varphi_2^f U_1^{fm} X_2^m)$	$E^f + \nu^{fm} \pm E_{res}$	$\{(M_1 \pm M_2) S_{1m}/\sqrt{2}\}$
Strong coupling, f-electronic plus m-vibrational	S	$1/\sqrt{2} (\varphi_1^f \varphi_2^0 + \varphi_1^0 \varphi_2^f) (U_1^{S0} X_2^{Sm} + X_1^{Sm} U_2^{S0})$	$E^S + \nu^{Sm}$	$(M_1 + M_2) S_{1m}$
	A	$1/\sqrt{2} (\varphi_1^f \varphi_2^0 - \varphi_1^0 \varphi_2^f) (U_1^{A0} X_2^{Am} + X_1^{Am} U_2^{A0})$	$E^A + \nu^{Am}$	$(M_1 - M_2) S_{1m}$

f—f-th excited electronic state of one ring; m—m-th vibration of molecule, E_{res} —energy of resonant electronic interaction, E^f —energy of f-th electronic state of ring; M—dipole moment of f-th transition in ring; S_{1m} —Franck-Condon overlap integral for m-th quantum of oscillation in one ring. The symbols for the wave functions are given in the preceding section.

two rings. With increasing E_{res} , a single-photon transition to a dissociated vibronic state also becomes allowed, as a result of mixing of its wave functions with the wave functions of the bound state. This decreases the probability of single-photon transitions to the bound vibronic state. This property becomes most clearly manifest when $\Delta\nu \leq E_{res} \leq \nu^f$. This interval of parameter variation was called by McClure the case of intermediate resonant coupling. Thus, at not too large E_{res} , the vibronic spectrum of a binary molecule consists of a doublet of bands $E^f + \nu^f \pm E_{res}$ of bound states and a doublet of bands $E^f + \nu^0 \pm E_{res}$ of the dissociated states, located in the region of high energies, since, as a rule, $\nu^0 > \nu^f$. If $E_{res} \sim \Delta\nu$, the intensity of all four bands is approximately equal and is determined only by the orientation of the moments $M_1 + M_2$ and $M_1 - M_2$. According to McClure, when E_{res} varies from $\Delta\nu$ up to ν^f , no significant changes should occur in the intensities of the four bands.

The inequality $E_{res} > \nu^f$ was defined by McClure as the criterion of transition to strong resonant coupling. In strong coupling, the electronic excitations of the individual rings lose their individuality. The same thing also happens with the vibrational states, which are now determined under conditions of electronic excitation of both rings. The wave functions and the energies of the vibronic states are given in Table III for this limiting case. The optical spectrum should present two doublets, widely spaced owing to the large E_{res} , with the intensity of one of the components depressed in each case.

The described concepts were used by McClure to interpret the spectrum of the dibenzyl molecule^[31]. The spectrum of the crystal was used for the analysis of the molecular spectrum. It was assumed here that the collective resonant effects in the crystal are small and that its spectrum has a molecular character. For comparison, the spectrum of the toluol crystal was considered, for which the resonant effects were also assumed

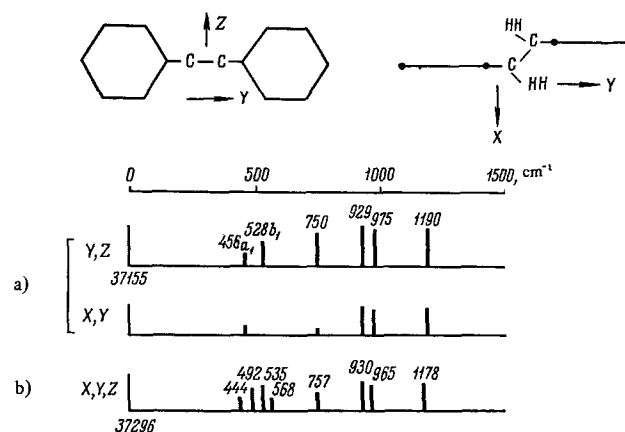


FIG. 3. Scheme of absorption spectra of crystals of toluol (a) and dibenzyl (b) in polarized light. The oscillation frequencies were calculated from the frequency of the pure electronic transition indicated on the figure at the start of the spectrum.

to be small. The spectra of both crystals, shown in Fig. 3, correspond to excitation of the optical electrons of the benzene ring under conditions when the purely electronic transition is weakly allowed and the degeneracy is lifted from the n.s. vibration of the benzene molecule, E_{res} , as a result of the lowering of the symmetry. A comparison of the spectra can reveal the changes due to the transition from the toluol molecule with its one ring to the binary molecule of dibenzyl.

The pure electronic transition of dibenzyl is represented by a single band. Since the dipole moments of both benzene rings are parallel to each other, the difference dipole moment, which determines the probability of the transition to the asymmetrical state, is equal to zero. In the region of the vibronic transition, made up of the vibrations a_1 and b_1 produced upon splitting of the benzene n.s. vibration E_{2g} , which are well pronounced

in the toluol spectrum (Fig. 3a), four absorption bands are observed. The presence of four bands of comparable intensity in place of two can be explained only as being due to the fact in addition to the excitation of the bound vibronic states, there appear in the vibronic spectrum of the dibenzyl molecule also dissociated vibronic states. A numerical analysis of the band frequencies makes it possible to determine the energy of the interaction between the rings. It equals $2E_{\text{res}} = 45 \pm 14 \text{ cm}^{-1}$ and is comparable with the values of the defects of the vibrational frequencies for both vibrations. The author took no note of the complete similarity between the spectra of toluol and dibenzyl in the region of the f.s. vibrations at 757, 930–965, and 1178 cm^{-1} . Since the frequency defects of these vibrations are of the same order as that of the vibrations a_1 and b_1 , one should in general expect a doubling of the bands in this region of the spectrum.

The notions developed by McClure for binary molecules were used also by Ron and Schnepf^[32] to analyze the spectrum of the di-paraxylol crystal.

3. Vibronic States of Dimers

The problem of the vibronic state of binary molecules is closely related to the analysis of the vibronic states of dimers,* the quantitative theory of which has been considered by many authors and has been sufficiently well developed. The general premises of the theory of vibronic states of dimers are as follows:

1. The electronic and vibrational motions of the free molecule are separated in agreement with Born and Oppenheimer.
2. The motion of the nuclei is limited to one normal vibration.
3. This vibration is harmonic.
4. The interaction between the electronic and vibrational motions in the molecule is described in terms of the displacement of the equilibrium position of the nuclear configuration.

Most authors have also assumed that the electronic and vibrational excitations are always simultaneously acting on one of the two molecules forming the dimer.

The foundation for the general theory of vibronic states of dimers was laid by Witkowsky and Moffit^[33], who derived a general equation governing the nuclear motion. Since the principal mechanism of the electron-vibrational interaction is the displacement of the equilibrium position, the energy used for this interaction of the problem is the distortion energy^[7], introduced earlier in Sec. 1. At not too high temperatures, the distortion energy is equal to the width of the electron-vibrational spectrum. Cases of weak and strong resonant couplings are defined by suitable inequalities for the energies of the resonant interaction between the molecules in the dimer and the half-width of the vibronic spectrum. The first investigations of the intermediate coupling, which is frequently realized in experimental systems, were first carried out for dimers by McRay^[34,35]. Figure 4 shows the calculated^[35] and the experimentally observed^[36] spectra of the monomer and dimer of iodide-1, 1'-diethyl-2, 2'-pyridocyanine

*By dimers is meant a pair of identical molecules coupled by Van der Waals forces.

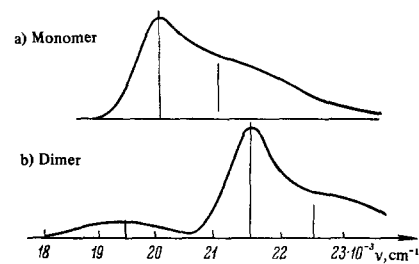


FIG. 4. a) Absorption band of monomer of pyridocyanine dye; b) absorption band of the dimer (solid curve). The vertical lines correspond to the theoretically calculated spectra.

dye. Attention is called to the difference between the intensity distributions in the absorption spectra of the monomer and dimer in the region of the pure electronic transition. We shall return to this question later. The case of intermediate coupling was considered also by Merrifield^[37], but the nondegenerate vibronic states of dimers were considered most exhaustively and in greatest detail by Fulton and Gouterman^[38,39], who presented their results in terms of two dimensionless parameters

$$\beta = \frac{E_{\text{res}}}{\nu} \quad \text{and} \quad \gamma = \left(\frac{k}{2\nu} \right)^{1/2} \Delta R. \quad (11)$$

The first parameter describes the energy of the intermolecular interaction per unit vibration energy, and the second is the coupling constant between the electronic and vibrational interactions, which is already known to us (see (10)), and characterizes the energy of the intramolecular interaction between the electronic and nuclear motions, due to the displacement ΔR of the nuclear-configuration equilibrium position following electronic excitation, and referred to unit vibration energy. The quantity $\gamma\nu$ determines the distortion energy and can be obtained from the experimental spectrum as the width of the electron-vibrational bands. The quantity γ can be determined independently from the ratio of the intensities of the vibronic and pure electronic bands in accordance with (9).

Figures 5 and 6 show the computer-calculated absorption spectra of the dimers for different values of β and γ .* One of the most essential features of these spectra is the law governing the variation of the intensity of the set of vibronic bands for each polarization as a function of the parameters β and γ . Let us examine Fig. 5, which shows the spectra for $\gamma = 1, 0$ at different values of β . The case $\beta = 0$ corresponds to the monomer spectrum. At β different from zero, two spectra are produced, with mutually perpendicular directions of the dipole moments of the transitions. The values $\beta = 0.25$ and $\beta = 0.5$ correspond to weak resonant couplings. Each of the vibronic states of the monomer splits into several components. It is essential to call attention not to the overall band contour, but to the vertical lines which represent the square of the matrix element of the dipole transition. It is seen from the figure that whereas the electronic state splits into two

*The δ -function bands that follow from the theory are assigned a Gaussian shape with half-width $\alpha = 0.2$ in order to bring them closer to experiment.

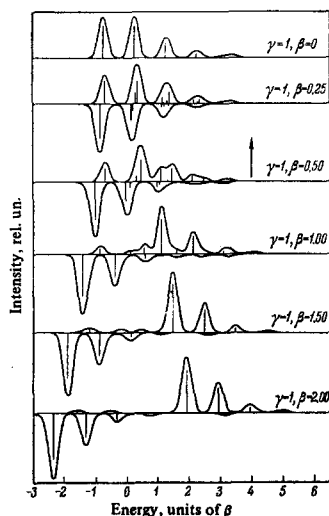


FIG. 5. Calculated absorption spectra of dimers for $\beta = 1$ and different values of β . The abscissa axis in each spectrum is the line of separation between the positive and negative band systems. The length of the arrow corresponds to 0.5 for a line spectrum and to 1 for a continuous spectrum. [39]

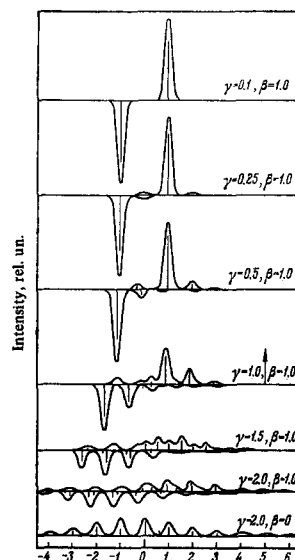


FIG. 6. Calculated absorption spectra of dimers for $\beta = 1$ and for different values of γ , and also for $\beta = 0$ and $\gamma = 2$ [39]. Abscissas—energy in units of β .

Table IV. Main types of vibronic configurations of dimers

Vibrational quantum number	Wave functions	Note
$m = 0$	$\varphi_1^f \varphi_2^0 U_1^f U_2^0$ $\varphi_1^0 \varphi_2^f U_1^0 U_2^f$	φ_1^f — molecule is excited to the f -th electronic state
$m = 1$	$\varphi_1^f \varphi_2^0 X_1^f U_2^0$ $\varphi_1^f \varphi_2^0 U_1^f X_2^0$ $\varphi_1^0 \varphi_2^f U_1^0 X_2^f$ $\varphi_1^0 \varphi_2^f X_1^0 U_2^f$	U_1^f — wave function of zero-point vibrations of molecule 1 in the f -th electronic state X_1^f — single-quantum vibrational function of molecule 1 in f -th electronic state
$m = 2$	$\varphi_1^f \varphi_2^0 X_1^f X_2^0$ $\varphi_1^f \varphi_2^0 X_1^0 X_2^f$ $\varphi_1^f \varphi_2^0 U_1^f X_2^0$ $\varphi_1^0 \varphi_2^f U_1^0 X_2^f$ $\varphi_1^0 \varphi_2^f X_1^0 X_2^f$ $\varphi_1^0 \varphi_2^f X_1^f U_2^f$	X_1^f — two-quantum vibrational function of molecule 1 in f -th electronic state

components, each vibronic state splits into $2(m + 1)$ components, where m is the vibrational quantum number. This circumstance is connected with the possibility of different allotments of the vibrational excitation to the molecules of the dimer at a fixed position of the electronic excitation, i.e., it is connected with the formation of different separated vibronic configurations. Following McClure, Fulton and Gouterman extended the notions of two types of vibronic configurations to include also the case of dimers. Table IV shows sets of such configurations for several values of m .

Let us turn now to Fig. 5. The values $\beta = 1$ and 0 correspond to the intermediate case. It is interesting to note that the intensity distributions are different in the negative and positive systems. Whereas in the negative system the distribution of the intensity follows the Franck-Condon principle, in the positive system the maximum of the intensity shifts towards the short-wave side of the spectrum, and the intensity of the pure electronic transition becomes much weaker. Since the transition to the negative system is symmetry-forbidden for

most dimers, a positive system of bands appears in the spectrum, with a curious intensity distribution. The values $\beta = 1.5$ and $\beta = 2.0$ correspond to strong resonant coupling.

Figure 6 shows the set of spectra for fixed $\beta = 1, 0$ and for a variable γ . The upper spectra correspond to the case of strong coupling; in the spectrum at $\beta = 1, 0$ and $\gamma = 1, 0$ is the limiting-one and corresponds to the intermediate case; a weak coupling is represented in the lower spectra.

In spite of the fact that the spectra depend very strongly on the values of both parameters β and γ , they have characteristics that depend only on each of these parameters. Thus, the distance between the centers of gravity of the intensity in both systems of strongly polarized vibronic bands of the dimer spectrum is equal to $2\beta \cos \theta$ for all the values of γ . It is seen from Fig. 5 that this distance increases with increasing β , and Fig. 6 shows that it is constant at different values of γ . The angle θ is made up by the directions of the dipole moments of the transitions in both molecules of the dimer.

Since in many cases $\theta = 0^\circ$ or 180° , one of the two systems of strongly polarized bands may be absent, and difficulties arise in the experimental determination of β when using only the absorption spectrum of the dimer. In this case it is convenient to use the same theorem of Fulton and Gouterman, which relates the position of the centers of gravity of the dimer and monomer spectra, namely, the distance between the values of the corresponding frequencies is equal to $\pm\beta \cos\theta$. In turn, γ determines the width of the vibronic spectrum for all values of β . This irregularity can also be traced clearly in Figs. 5 and 6. The first experimental absorption spectra of the dimers were obtained for dyes, the spectrum of one of which is shown in Fig. 4. The general character of the spectrum offers evidence that the molecules forming the dimer are parallel to each other, since the spectrum represents only one system of bands of the dimer spectrum. The attenuation of the region of the purely electronic transition and the shift of the intensity to the interior of the vibronic transitions indicate that this is a positive system of bands in the intermediate case, when the energy of the resonant interaction between the molecules and the molecule distortion energy are comparable. Dye molecules, however, are poor models for the study of vibronic states, since neither the monomer nor the dimer spectra have sharply pronounced vibrational structures. In this respect, spectra of aromatic compounds are much more convenient. In 1966, detailed investigations were made of the spectra of the dimers of anthracene^[40] and substituted anthracenes^[41], and an analysis was made of their vibronic structure. Since the regularities observed in these spectra have a character that is common to all aromatic molecules, it is advisable to stop to discuss the results of the investigation of this group of substances in greater detail.

In the spectra of monomers and sandwich dimers ($\theta = 0^\circ$) of these compounds, two electronic transitions were investigated: the first electronic transition ${}^1A_{1g} \rightarrow {}^1B_{3u}$ with the transition dipole moment oriented along the short axis of the molecule, and the second electronic transition ${}^1A_{1g} \rightarrow {}^1B_{2u}$, with the direction of the dipole moment along the long axis of the molecule. The spectra obtained are shown in Figs. 7 and 8. Since the molecules in the dimer are parallel to each other, the absorption spectra of the dimers contain only posi-

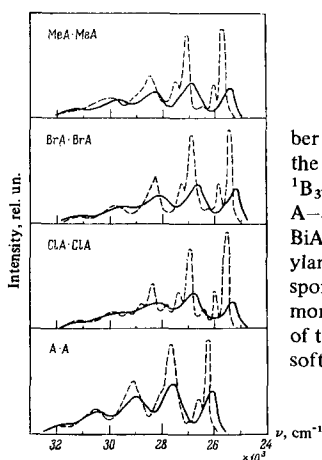


FIG. 7. Absorption spectra of a number of sandwich dimers in the region of the first electronic transition (${}^1A_{1g} \rightarrow {}^1B_{3u}$) at 77°K in methylcyclohexane. A—anthracene, ClA—9-chloroanthracene, BrA—9-bromoanthracene, MeA—9-methylanthracene. The dashed curves correspond to the absorption spectra of the monomers produced upon dissociation of the dimers when the glass becomes softened^[41].

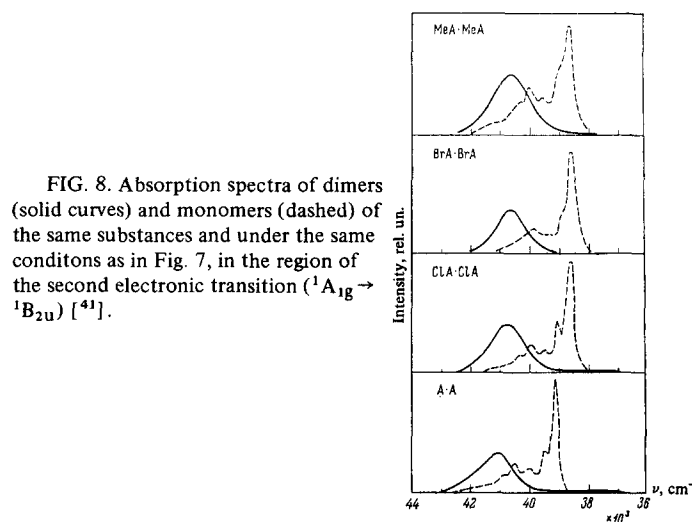


FIG. 8. Absorption spectra of dimers (solid curves) and monomers (dashed) of the same substances and under the same conditions as in Fig. 7, in the region of the second electronic transition (${}^1A_{1g} \rightarrow {}^1B_{2u}$)^[41].

tive systems of the bands. On the other hand, if the molecules are located at an angle (the authors of^[40] succeeded in obtaining dimers with the angle $\theta = 55^\circ$ between molecules), then the negative system of bands also becomes allowed, and the absorption spectrum of the dimer becomes much more complicated. The obtained spectra were analyzed by the authors on the basis of the theory of Fulton and Gouterman^[39], and the spectra were calculated theoretically in accordance with their method for the dimers of anthracene. The remaining spectra were analyzed by analogy. To establish the type of the resonant bond in the investigated dimers, it was necessary to determine the values of β and γ . Both quantities can be determined experimentally. The parameter γ determines the ratio of the intensities of the vibronic transitions to the intensity of the purely electronic transition, and can be determined by using Fig. 1. It should be remembered here that Fig. 1 is suitable only for the case when the vibronic spectrum of the molecule is developed by only one vibration. In the anthracene molecule in the region of the first electronic transition, two f.s. vibrations are active: $\nu_1 = 1400 \text{ cm}^{-1}$ and $\nu'_1 = 400 \text{ cm}^{-1}$ (see Fig. 2 and Table II). The main fraction of the oscillator strength of the vibronic spectrum goes, however, to vibronic transitions with participation of the vibration ν_1 , and therefore one can consider, with a certain degree of error, the vibronic spectrum based on this single vibration. It follows both from the analysis of the anthracene-vapor spectrum (see Table I) and from an analysis of the spectrum of its solution that $\gamma = 1$. The second electronic transition in the anthracene molecule contains only one vibration, $\nu_1 = 1400 \text{ cm}^{-1}$, and the intensity in it is mainly concentrated in the region of bands of the purely electronic transition, so that accordingly $\gamma = 0.5-0.6$.

The energy E_{res} of the resonant interaction between the molecules of the dimer can be determined on the basis of the theory of Fulton and Gouterman as the difference between the frequencies determining the positions of the centers of gravity in the spectra of the monomer and the corresponding dimer. The values of these quantities in cm^{-1} (E_{res}), referred to the vibration-quantum energy (β), are given in Tables V and VI

Table V. Comparison of the spectrum characteristics and of the constants of the intra- and intermolecular interactions in the electronic transition ${}^1A_{1g} \rightarrow {}^1B_{3u}$ of anthracene and its derivatives

Substance	Position of center of gravity of monomer spectrum, cm^{-1}	Position of center of gravity of dimer spectrum, cm^{-1}	Energy of resonant interaction, $E_{\text{res}}, \text{cm}^{-1}$	$\beta = \frac{E_{\text{res}}}{\hbar\nu}$ *	γ	Distortion energy $\epsilon_d = \gamma\hbar\nu$, cm^{-1}
Anthracene	$28\,000 \pm 50$	$28\,250 \pm 50$	250 ± 100	0.18	~ 1	1400
9-chloroanthracene	$27\,500 \pm 50$	$27\,900 \pm 50$	400 ± 100	0.29	~ 1	1400
9-bromoanthracene	$27\,100 \pm 50$	$27\,500 \pm 50$	400 ± 100	0.29	~ 1	1400
9-methylanthracene	$27\,300 \pm 50$	$27\,600 \pm 50$	300 ± 100	0.21	~ 1	1400

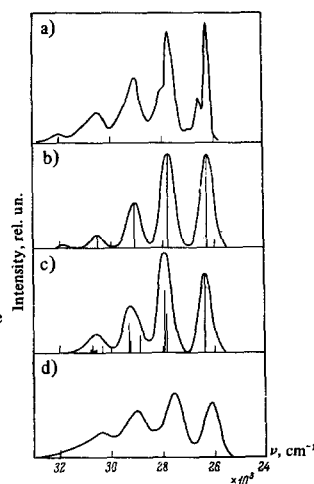
*The vibration quantum energy is $\hbar\nu = 1400 \text{ cm}^{-1}$.

Table VI. Comparison of the spectral characteristics and constants of intra- and intermolecular interaction in the electronic transition ${}^1A_{1g} \rightarrow {}^1B_{2u}$ of anthracene and its derivatives

Substance	Position of center of gravity of monomer spectrum, cm^{-1}	Position of center of gravity of dimer spectrum, cm^{-1}	Energy of resonant interaction, $E_{\text{res}}, \text{cm}^{-1}$	$\beta = \frac{E_{\text{res}}}{\hbar\nu}$	γ	Distortion energy $\epsilon_d = \gamma\hbar\nu$, cm^{-1}
Anthracene	$39\,500 \pm 50$	$41\,200 \pm 50$	1700 ± 100	1.2	0.5–0.6	700–840
9-chloroanthracene	$39\,250 \pm 50$	$40\,800 \pm 50$	1500 ± 100	1.1		
9-bromoanthracene	$40\,730 \pm 50$	$39\,350 \pm 50$	1400 ± 100	1.0		
9-methylanthracene	$39\,200 \pm 50$	$40\,350 \pm 50$	1350 ± 100	0.96		

for both transitions and for all the investigated substances. An analysis of the quantities β and γ shows that for all the investigated substances in the region of the first electronic transition there is a weak resonant coupling, based on a relatively low energy of resonant interaction relative to the distortion energy of the molecule. At the same time, for the second electronic transition the energy of the resonant interaction greatly exceeds the distortion energy, as a result of which the changes in the spectrum correspond to the case of strong resonant coupling. Figure 9 compares the experimentally observed absorption spectra of the monomer and dimer of anthracene with parameters β and γ determined experimentally and the spectra calculated by the Fulton-Gouterman theory. The agreement between both types of spectra is very good. It should be noted here that such a successful agreement between the spectra calculated in accordance with Fulton and Gouterman and the experimental spectra should be expected only for molecular aggregates whose molecule vibrational frequencies do not change when the electronic state is changed, since the Fulton-Gouterman theory does not take into account the vibration frequency defect under electronic excitation. The frequency defect governs the shares of intensity going to the coinciding and separated configurations, since it gives rise to a difference between the situations in which the vibration is applied to the electronically-excited molecule and to the molecule in the ground electronic state, since in the former case the potential energy is changed by an amount $\Delta\nu$. The Fulton-Gouterman theory pertains only to the particular case $\Delta\nu = 0$. The contribution of the intensities of the separated and coinciding configurations for anthracene can be traced in this case by means of vertical lines placed inside the envelope of the vibronic transition. It

FIG. 9. a) Absorption spectrum of anthracene monomers at 77°K in methylcyclohexane, obtained following the softening of glass containing photochemically produced dimers, whose spectrum is shown in Fig. (d); b) calculated spectrum of monomer; c) the same for the dimer [41].



is obvious that for molecules with a noticeable frequency defect, at the same values of the parameters β and γ , the intensity distribution in the experimental spectrum can differ greatly from that calculated by the Fulton-Gouterman theory.

A second limitation of the Fulton-Gouterman theory, by virtue of the assumption made, is that it is utterly unsuitable for the description of vibronic spectra with n.s. vibrations, for which the distortion energy is equal to zero.

The general laws established for vibronic spectra of dimers remain in force also for other molecular aggregates with finite numbers of molecules. In 1967, Perrin and Gouterman^[42] considered the vibronic states of a trimer comprising a trigonal system with a threefold symmetry axis. The main premises on which the calculation was based were the same as for dimers. The en-

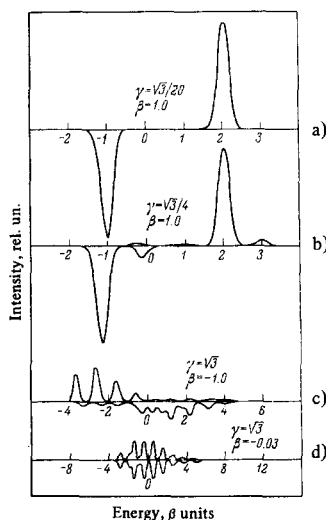


FIG. 10. Calculated absorption spectra of trimer for different values of β and γ . The half-width of the Gaussian bands is $\alpha = 0.2$.

ergy parameters in the system were the previously defined dimensionless quantities β and γ . As expected, the results turned out to be similar to those for dimers. Figure 10 shows the vibronic-absorption spectra of the chosen model of the trimer as functions of the parameters β and γ . Just as in Figs. 5 and 6, the horizontal lines separate the spectra for two mutually orthogonal directions of light polarization. Cases (a) and (b) pertain to strong resonant coupling, case (c) to intermediate coupling, and case (d) to weak coupling. The distance between the centers of gravity of the individual components of the spectrum was equal to 3β in each of the cases. The quantity γ describes the width of the spectrum. At present there are no known experimental investigations of trimers.

III. VIBRONIC STATES OF MOLECULAR CRYSTALS (THEORY)

1. Introduction. Theoretical Models

Research on the vibronic states of molecular crystals has developed independently of that on vibronic states of molecular aggregates, and its start dates back to 1948, when, owing to the work of Davydov^[23,27,28], the exciton theory of Frenkel and Peierls came into intensive use for the interpretation of spectra of molecular crystals. In the model proposed by Davydov, the vibronic states are described by a wave of intramolecular vibronic excitation that moves through the crystal under the influence of the resonant forces. It is possible to associate with this wave the quasiparticle which has recently come to be called the vibron. This model was developed by different workers^[44-49] as applied to vibronic states with vibrations of different symmetry. It made it possible to explain the general similarity of the spectra of crystals and of the free molecule, to obtain a correct quantitative description of such characteristics of the vibronic spectrum as the values of the Davydov splittings in individual transitions and their integral intensity. Because of its simplicity and clarity, the Davydov model remained until 1966 the primary basis for the interpretation of vibronic spectra of crystals (see the reviews^[50-52]), although McRay pointed out in

his first papers, as early as in 1960, the need for taking into account, when constructing the vibronic states of a crystal, the possibility of separate placement of the electronic and vibrational excitations on the molecules of the crystal, in accordance with the concepts of coinciding and separated vibronic configurations introduced by McClure^[30]. McRay reached the conclusion that in those cases when the resonant coupling is strong, the vibronic energy spectrum of the crystal comprises a broad spectral region determined by the energy of the electronic resonant interaction. The crystal states corresponding to this region are described by two quasivectors \mathbf{k} . The analysis was based on an intramolecular transition which in general has p quanta of vibration. Under these assumptions, one of the vectors, \mathbf{k}_1 , describes a wave of vibronic excitation with m quanta of vibration in the sense indicated above, and the second describes a wave of n -quantum vibrational excitation over the crystal molecules that are not electronically excited, with $m + n = p$. It is easy to see from this representation that McRay's vibronic states are in essence two-particle states. These concepts were subsequently extended by McRay to include also the case of weak resonant coupling^[54,55]. However, the perturbation theory used by them cannot be regarded as sufficiently correct,* as a result of which many important results were left unobserved. In 1966, Rashba^[56] proposed a general dynamic model of vibronic states of a crystal, according to which the exciton and the phonons† are regarded as stable quasiparticles with a definite interaction between them. Different vibronic states of the crystal are defined as bound and dissociated states of this aggregate of quasiparticles. If the crystal contains only one phonon, the bound states correspond to correlated motion of the electronic and vibrational excitations, are described by a single value of the quasimomentum, and accordingly are single-particle states. To the contrary, the associated states corresponding to independent motion of the electronic and vibrational excitations are characterized by two values of the quasimomenta and are consequently two-particle states. We see that the single-particle states in the general dynamic model have much in common with the vibronic states in the Davydov model. The difference between them lies in the fact that in the Davydov model the electronic and vibrational excitations are always on the same site, whereas in the general dynamic model in the bound state, the electronic and vibrational excitations spend only part of the time on one site, moving relative to each other in a limited region of space. We shall therefore henceforth call the Davydov model the model of coinciding configurations. The dynamic model, which uses the concepts of two types of vibronic configurations, is more general, and the spectrum resulting from it has a richer and more interesting structure than that in the model of coinciding configurations. Nonetheless, the model of coinciding configurations exerted a strong influence on the development of the ideas concerning the quantitative characteristics of vibronic states and led to

*A critical review of McRay's work can be found in [97].

†By phonon branches of the spectrum are meant here and below the branches resulting from intramolecular vibrations. Intermolecular phonons will be taken into account separately.

a number of correct conclusions in the interpretation of the crystal spectra; we shall therefore consider the main premises of this model.

2. Model of Coinciding Configurations

In developing a general theory for the exciton states of a crystal, Davydov proposed that, regardless of the type of excitation, the intramolecular excitation retains in the main its individuality in the crystal, while intermolecular excitation is only a small perturbation^[27,28]. As applied to vibronic states, this assumption corresponds to the case of weak resonant coupling. Accordingly, Davydov proposed to determine the main characteristics of the energy and optical spectra of a crystal separately for each state. By using the same assumptions, Craig and Hobbs^[44] and later Bingel^[45] extended Davydov's theory to include vibronic states of a crystal. In these first papers, they considered vibronic states with participation of f.s. vibrations. Since the resonant interactions, which are in this case the principal object of the study, depend strongly on the characteristics of the optical transitions in the free molecule, the consideration of vibronic states with f.s. vibrations could not be the general case, since the optical characteristics of the vibronic transitions with participation of n.s. vibrations obey entirely different laws. This circumstance was taken into account by Craig and Walsmley^[46,49], and consequently the theoretical concepts developed by them remained until recently the most complete ones. We shall not, however, follow the Craig and Walsmley scheme in developing a theory for single-particle vibronic states, but consistently consider the properties of the vibronic states of a crystal, making use of the fundamental results of Davydov's theory and the results of Sec. 1.

According to Davydov's theory^[27,28], the value of the energy in the exciton band $\mathcal{D}^{fm}(\mathbf{k})$ of the vibronic state is determined by sums of the type

$$\mathcal{L}_{\alpha\beta}^{fm}(\mathbf{k}) = \sum_{\mathbf{n}} M_{0\beta, n\alpha}^{fm} e^{i\mathbf{k}\mathbf{n}}, \quad (12)$$

here $\alpha, \beta = 1, 2, \dots, \sigma$ indicate the position of the molecule in the unit cell, and the vector \mathbf{n} numbers the cells of the crystal*. $M_{0\beta, n\alpha}^{fm}$ is the matrix element of the resonant interaction between the molecule 0β , which is in the vibronic state fm , and the molecule $n\alpha$, which is in the ground state. The expression for $M_{0\beta, n\alpha}^{fm}$ is

$$M_{0\beta, n\alpha}^{fm} = \int X_{0\beta}^{m*} U_{n\alpha}^{0*} X_{n\alpha}^0 U_{0\beta}^0 \int \Psi_{0\beta}^{f*} \Psi_{n\alpha}^{0*} \hat{M}_{0\beta, n\alpha} \Psi_{0\beta}^f \Psi_{n\alpha}^0 d\tau, \quad (13)$$

The integration is carried out over the electronic and nuclear spaces of the molecules 0β and $n\alpha$. The interaction-energy operator \hat{M} is the sum of all the electrostatic interactions of the electrons and nuclei of one molecule with the electrons and nuclei of the other. In calculating its matrix elements in molecular crystals

*In a number of cases of practical importance, involving two molecules per unit cell (for example, monoclinic crystals of symmetry C_{2h}), each nondegenerate vibronic state of the molecule corresponds in the crystal to two bands of single-particle excitation^[28,29]. In this case

$$\mathcal{D}_{1,2}^{fm}(\mathbf{k}) = \mathcal{L}_{11}^{fm}(\mathbf{k}) \pm \mathcal{L}_{12}^{fm}(\mathbf{k})$$

for wave-vector directions perpendicular or parallel to the symmetry planes of the crystal.

one usually employs the pointlike-multipole approximation. In this approximation, the matrix element of the resonant interaction is determined by the values of the multipole moments of the optical transitions in the free molecule. In the simplest case, when the optical transition is dipole-allowed and sufficiently strong, the extent of the energy band is determined by the same parameters as the intensity of the corresponding transition in the molecular spectrum, and the problem of determining the widths of the exciton bands of the vibronic states in the energy spectrum of the crystal is analogous to the problem of the distribution of the intensities in the vibronic spectrum of the molecule.

Let us consider expression (13); we are interested only in that part of this expression which is connected with the quantitative characteristics of the optical spectrum of the molecule. As expected, the quantities $M_{0\beta, n\alpha}^{fm}$ will be determined by different expressions for vibronic states with participation of f.s. and n.s. vibrations^[44,46,49]. In the former case

$$M_{0\beta, n\alpha}^{fm} = M_{0\beta, n\alpha}^{f0(0)}(R_{00}^0) |\xi_{00, fm}|^2. \quad (14)$$

For n.s. vibrations

$$M_{0\beta, n\alpha}^{fm} = M_{0\beta, n\alpha}^{f0(1)}(R_{00}^0) |R_{00, fm}|^2. \quad (15)$$

The matrix elements $\xi_{00, fm}$ and $R_{00, fm}$ have the same meaning as in (6) and (8), namely, the additional superior index of $M_{0\beta, n\alpha}^{f0}$ indicates the order of the expansion of the matrix element of the dipole moment of the transition in powers of the nuclear displacements at which the corresponding optical transition is allowed in the free molecule (see, for example, [9]).

The sums of the resonant integrals, which determine the values of the energy in the exciton band, can now be written as follows:

$$L_{\alpha\beta}^{fm}(\mathbf{k}) = |\xi_{00, fm}|^2 \sum_{\mathbf{n}} M_{0\beta, n\alpha}^{f0(0)} e^{i\mathbf{k}\mathbf{n}}, \quad (16)$$

for vibronic states with participation of f.s. vibrations. If we recall that, in accord with (8),

$$\text{formula} \quad \frac{|\xi_{00, fm}|^2}{|\xi_{00, f0}|^2} = \frac{\gamma^{2m}}{m!},$$

then the connection between the exciton band $\mathcal{D}^{f0}(\mathbf{k})$, defined by $|\xi_{00, f0}|^2 \sum_{\mathbf{n}} M_{0\beta, n\alpha}^{f0} e^{i\mathbf{k}\mathbf{n}}$, of a purely electronic state, and the band $\mathcal{D}^{fm}(\mathbf{k})$ of the vibronic state with participation of m quanta of f.s. vibration is expressed as follows:

$$\mathcal{D}^{fm}(\mathbf{k}) = \frac{\gamma^{2m}}{m!} \mathcal{D}^{f0}(\mathbf{k}). \quad (17)$$

In turn, for vibronic states with n.s. vibrations, the sum of the resonant integrals has the following form:

$$L_{\alpha\beta}^{fm}(\mathbf{k}) = |R_{00, fm}|^2 \sum_{\mathbf{n}} M_{0\beta, n\alpha}^{f0(1)} e^{i\mathbf{k}\mathbf{n}}. \quad (18)$$

It is easy to note that the properties of the exciton bands of the vibronic states are determined by the type of vibration. Thus, exciton bands with participation of f.s. vibrations are analogous to the band of the purely electronic state. The absolute value of the energy in the vibronic band is determined by the corresponding Franck-Condon factor, and in the approximation considered there is a correlation between the dimensions of

the exciton band of the vibronic states and the oscillator strength of the corresponding molecular vibronic transition. Allowance for the second order in perturbation theory in the intermolecular interaction (the contribution of the interactions in other electronic states to the characteristics of the resonant interaction in the considered state—the Craig effect^[44-49]—does not disturb this correlation).

As to the vibronic states with n.s. vibrations, their exciton bands are not coupled with the band of the pure electronic states, and as a result of the Herzberg-Teller effect they are quantities of first order of smallness and are determined by the bands of other higher pure electronic states. This conclusion is valid only in the case when the mixing of the electronic wave functions in the Herzberg-Teller effect does not affect the ground state. This is usually always the case, since the distance from the ground electronic state to all the excited states is much larger than the distance between the nearest excited states. It is precisely this difference between the properties of the bands of vibronic exciton states with participation of f.s. and n.s. vibrations that was first pointed out by Craig and Walsmley^[48,49].

The validity of these relations is illustrated by the connection between the intensities of vibronic transitions in which vibrations of different symmetries take part and the values of the Davydov splitting in them for crystals with several molecules per unit cell. Numerous examples of this type are given in the review^[49-52].

3. General Dynamic Model

The dynamic model proposed by Rashba is a valid extension of the "many-particle" approach of solid-state theory to include vibronic excited states of molecular crystals. On the basis of the notion that the solid is a system of quasiparticles, the vibronic states are represented in the dynamic model by a system consisting of one exciton interacting with one or several phonons. It follows from the most general formulation of the problem that the vibronic states of the crystal correspond to an aggregate of dissociated and bound states describing its quasiparticles. The originator of such an approach to composite excited states of a crystal was Bethel^[57], who considered the two-magnon states of a linear crystal as bound and dissociated states of two interacting magnons. We can also consider the structure of the spectrum of electron-hole states from the same point of view. Dissociated states of this pair of quasiparticles are the basis for the band scheme of solids, and the bound states due to the electron-hole interaction are Wannier-Mott excitons^[58]. The major computational difficulties, and also the absence of interest on the part of the experimentors have caused this problem to be neglected for a long time. Some impetus was provided in 1960 by the requirement for explaining the complicated structure of the rotational-vibrational spectrum of the parahydrogen crystal^[59], which could not be explained from the traditional exciton point of view. The theory of treating the rotational-vibrational states of a crystal as bound and dissociated states of a rotational exciton and phonon was developed by Van Kranendonk in 1959–1960^[60,61], and a quantitative interpretation of the spectrum of the crystal was devel-

oped as a result. The development of a many-particle theory of composite states of a solid, which began in the early Sixties and has been developing at an accelerated rate, can be attributed to improvement of the computation techniques and especially to the introduction of field methods in solid-state theory. These include two-magnon states of three-dimensional crystals (Wortis^[62], 1963) vibronic states of molecular crystals (Rashba^[57,63], 1966 and 1968), exciton-magnon states in antiferromagnetic crystals (Laudon^[64] and Freeman and Hopfield^[65], 1968), exciton-phonon complexes (Toyozawa and Hermanson^[66], 1968), polaron-phonon complexes (Mel'nikov and Rashba^[66a], 1969, Levinson^[66b], 1970), two-phonon complexes (Cohen et al.^[66c], 1964), and multiphonon states of molecular crystals in the region of overtones of intramolecular vibrations (Agranovich^[67], 1970)*. These theoretical papers stimulated a large number of experimental investigations and uncovered new aspects of spectral properties of solids, namely, vibronic states of molecular crystals^[71-77], exciton-magnon states of antiferromagnetic crystals^[78-80], exciton-phonon complexes in a number of ionic crystals^[81-83], absorption in the region of overtones of vibrations of molecular crystals^[84].

The unified approach to the different phenomena and the possibility of carrying the quantitative calculations to their conclusion in a number of cases now make the many-particle analysis of the excited states of crystals most promising.

The generality of the approach does not, of course, exclude specific singularities of any concrete system of quasiparticles, so that the detailed theory of vibronic states differs substantially, say, from the theory of exciton-magnon interactions. A manifestation of this difference is a separate operator of the interaction between quasiparticles for each problem, and requirements imposed on this operator in connection with the conservation of the number of quasiparticles in the investigated problem. Only when this last condition is satisfied is it possible to carry out a real investigation of the complete Hamiltonian of the system and obtain a general solution in a number of cases. Rashba^[56,63] succeeded in satisfying these requirements for the construction of vibronic states, by considering for these states a dynamic model whose gist will be described below.

The Hamiltonian of excitons and phonons that do not interact with one another can be represented as the sum of two terms

$$\mathcal{H}_{00} = \sum_{n\alpha} [e^i \varphi_{n\alpha}^+ \varphi_{n\alpha} + v^0 X_{n\alpha}^+ X_{n\alpha}], \quad (19)$$

$$\mathcal{H}_{\text{pea}} = \sum_{n\alpha, m\beta} [M_{n\alpha, m\beta} \varphi_{n\alpha}^+ \varphi_{m\beta} + \mu_{n\alpha, m\beta} X_{n\alpha}^+ X_{m\beta}]; \quad (20)$$

here $\varphi_{n\alpha}^+$ and $X_{n\alpha}^+$ are respectively the operators for

*For the sake of completeness, mention should be made of a number of papers on cooperative exciton states^[68-70]. These are also many-particle states. However, unlike the paper cited above, in which the ratio of the quasiparticle interaction energy to the sum of their kinetic energies can be practically arbitrary, the theory of cooperative states, based on perturbation theory, pertains to the limiting case when the first of these quantities is much smaller than the second. This circumstance immediately leads to a loss of the bound states and therefore limits the application of the theory of^[66-70] only to problems involving two- and many-electron excited states of a crystal.

the production of an exciton and a phonon at the site α , ϵ^{\dagger} and ν^0 are the terms of electronic and vibrational excitations of the crystal, and $M_{n\alpha, m\beta}$ and $u_{n\alpha, m\beta}$ are the resonant integrals which determine the probability of transfer of the corresponding excitation from site to site. In the harmonic approximation, the exciton-phonon interaction operator is

$$\mathcal{H}_{\text{int}} = \mathcal{H}_{\text{int}}^{(1)} + \mathcal{H}_{\text{int}}^{(2)} = \sum_{n\alpha} \varphi_{n\alpha}^{\dagger} \varphi_{n\alpha} [a(X_{n\alpha}^{\dagger} + X_{n\alpha}) + b(X_{n\alpha}^{\dagger} + X_{n\alpha})^2] + H_{\text{int}}^{(2)}. \quad (21)$$

The first term in $\mathcal{H}_{\text{int}}^{(1)}$ describes the displacement of the equilibrium position of the intramolecular oscillators following electronic excitation, while the second term describes the change of the vibrational frequencies upon excitation. $\mathcal{H}_{\text{int}}^{(2)}$ includes exciton-phonon interaction terms describing different types of electron-vibrational motion through a crystal and therefore containing indices of different sites.

Owing to the practically infinite number of molecules, it is impossible to obtain a solution for the problem in general form with an interaction Hamiltonian in the form (21). Rashba^[56,62] therefore separated limiting cases that can be investigated rigorously. The simplification proposed by him was based on the fact that the main feature of phonons produced from intramolecular vibrations is the relatively large value of their average frequency ν^0 at a small value of the dispersion. In many cases of practical importance, ν^0 exceeds the width of the exciton band $\tilde{\omega}^0$. Sometimes even the strong inequality $\nu^0 \gg \tilde{\omega}^0$ is satisfied with high accuracy. When this inequality is satisfied, the transfer of an exciton from site to site proceeds with conservation of the number of phonons, since the matrix elements of all the processes connected with the change of the number of phonons enter with large energy denominators. Thus, the phonon turns out to be a stable particle, and the problem of the electron vibration spectrum of the crystal can be reduced to the dynamic problem of investigating the mutual motion of several stable quasiparticles, namely an exciton and one (or several) phonons.

Thus, assuming that $M_{n\alpha, m\beta}$, $\mu_{n\alpha, m\beta}$, and the frequency defect of the vibration, which can be commensurate, are also much smaller than the phonon frequency ν^0 , and carrying out a canonical transformation that eliminates the linear terms determining the change of the number of phonons in $\mathcal{H}_{\text{int}}^{(1)}$, Rashba^[63] obtained a dynamic Hamiltonian that permitted a rigorous investigation of the general solution:

$$\mathcal{H}_{\text{int}} = \frac{1}{\mathfrak{N}} \sum_{\substack{\mathbf{k}, \mathbf{k}_1, \mathbf{k}_2 \\ \alpha, \beta, \gamma, \delta}} U_{\alpha\beta\gamma\delta}(\mathbf{k}, \mathbf{k}_1, \mathbf{k}_2) \varphi_{\mathbf{k}_1\alpha}^{\dagger} X_{\mathbf{k}-\mathbf{k}_1\beta}^{\dagger} X_{\mathbf{k}-\mathbf{k}_2\gamma} \varphi_{\mathbf{k}_2\delta}; \quad (22)$$

Here \mathfrak{N} is the number of cells in the main region, and the indices $\alpha, \beta, \gamma, \delta$ indicate the number of the molecule in the unit cell; \mathbf{k}, \mathbf{k}_1 and \mathbf{k}_2 correspond to the quasimomenta of different motions, and the matrix $U_{\alpha\beta\gamma\delta}(\mathbf{k}, \mathbf{k}_1, \mathbf{k}_2)$ is given by

$$U(\mathbf{k}, \mathbf{k}_1, \mathbf{k}_2) = J(\mathbf{k}) + K(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}) + T(\mathbf{k}_2) + T^*(\mathbf{k}_1), \quad (22a)$$

where

$$\begin{aligned} J_{\alpha\beta\gamma\delta}(\mathbf{k}) &= J_{\alpha\gamma}(\mathbf{k}) \delta_{\alpha\beta} \delta_{\gamma\delta}, \\ K_{\alpha\beta\gamma\delta}(\mathbf{k}) &= K_{\alpha\beta}(\mathbf{k}) \delta_{\alpha\gamma} \delta_{\beta\delta}, \\ T_{\alpha\beta\gamma\delta}(\mathbf{k}) &= T_{\alpha\delta}(\mathbf{k}) \delta_{\alpha\beta} \delta_{\gamma\delta}, \\ T_{\alpha\beta\gamma\delta}^*(\mathbf{k}) &= T_{\delta\alpha}^*(\mathbf{k}) \delta_{\beta\delta} \delta_{\gamma\delta}. \end{aligned}$$

The quantities $J_{\alpha\gamma}(\mathbf{k})$ etc. are resonant sums of the type

$$J_{\alpha\gamma}(\mathbf{k}) = \sum_{n-m} J_{n\alpha, m\gamma} e^{-ik(n\alpha - m\gamma)} \text{ etc.}$$

The matrix element $J_{n\alpha, m\gamma}$ is equal to the change $\Delta\nu$ of the vibration frequency following electronic excitation when $n\alpha = m\gamma$, and is determined by the probability of simultaneous transfer of an exciton and phonon from site to site when $n\alpha \neq m\gamma$. The expression for $J_{n\alpha, m\gamma}$ is

$$J_{n\alpha, m\gamma} = \langle \varphi_{n\alpha}^{\dagger} X_{n\alpha}^{\dagger} \varphi_{m\gamma} X_{m\gamma} \hat{M} \varphi_{n\alpha} X_{n\alpha} \varphi_{m\gamma}^{\dagger} X_{m\gamma}^{\dagger} \rangle; \quad (23)$$

here \hat{M} is the operator of the intermolecular resonant interaction. It is easy to verify that the expression for $J_{n\alpha, m\gamma}$ coincides fully with expression (13) for the matrix element of the resonant interaction in the vibronic state in the model of coinciding configurations.

The matrix element $K_{n\alpha, m\beta}$ is determined by the probability that an exciton and a phonon located at different sites will exchange places, and thus characterizes the exchange-resonant interaction. The expression for the $K_{n\alpha, m\beta}$ is

$$K_{n\alpha, m\beta} = \langle \varphi_{n\alpha}^{\dagger} X_{n\alpha}^{\dagger} \varphi_{m\beta} X_{m\beta}^{\dagger} \hat{M} \varphi_{n\alpha} X_{n\alpha}^{\dagger} \varphi_{m\beta}^{\dagger} X_{m\beta} \rangle. \quad (24)$$

The matrix elements $T_{n\alpha, m\delta}$ and $T_{n\delta, m\alpha}^*$ determine the influence of the phonon on the probability of exciton displacement, and describe the decay of a coinciding vibronic configuration ($T_{n\alpha, m\delta}$) and coincidence of a separated configuration ($T_{n\delta, m\alpha}^*$). They correspond to the following integrals:

$$\begin{aligned} T_{n\alpha, m\delta} &= \langle \varphi_{n\alpha}^{\dagger} X_{n\alpha}^{\dagger} \varphi_{m\delta} X_{m\delta} \hat{M} \varphi_{n\alpha} X_{n\alpha}^{\dagger} \varphi_{m\delta}^{\dagger} X_{m\delta} \rangle, \\ T_{n\delta, m\alpha}^* &= \langle \varphi_{n\delta} X_{n\delta}^{\dagger} \varphi_{m\alpha} X_{m\alpha} \hat{M} \varphi_{n\delta}^{\dagger} X_{n\delta} \varphi_{m\alpha} X_{m\alpha}^{\dagger} \rangle. \end{aligned} \quad (25)$$

In the derivation of (22a) it was assumed that the motion of the phonon can be neglected, corresponding to the case $M_{n\alpha, m\beta} \gg \mu_{n\alpha, m\beta}$. In most cases of practical importance this condition is rigorously satisfied. Thus, in the dynamic model of vibronic states there exist different effective-interaction mechanisms. The simplest of them is connected with a decrease of the vibrational frequency upon excitation of a molecule, and corresponds to "contact" attraction of the exciton and phonon (the integral $J_{n\alpha, n\alpha}$). The quantity $\Delta\nu$ plays the role of the potential energy, and this interaction is the only local interaction that follows from $\mathcal{H}_{\text{int}}^{(1)}$ in (21). The remaining exciton-phonon interactions are essentially nonlocal and are determined by the simultaneous displacement of the exciton and phonon in the coincident configuration ($J_{\alpha\gamma}(\mathbf{k})$), by interchange of positions of an exciton and a phonon ($K_{\alpha\beta}(\mathbf{k})$), and by the decay and coincidence of vibronic configurations ($T_{\alpha\delta}(\mathbf{k})$ and $T_{\delta\alpha}^*(\mathbf{k})$). These nonlocal interactions are the consequence of the shift of the equilibrium of the nuclear configuration following electron excitation and therefore play the principal role for f.s. vibrations. For n.s. vibrations, to the contrary, the principal role is assumed by the "contact" interaction term. In accordance with the difference in the vibration symmetry, different relations are realized between $J_{n\alpha, m\gamma}$, $K_{n\alpha, m\beta}$, $T_{n\alpha, m\delta}$, and $M_{n\alpha, m\beta}$. For f.s. vibrations

$$J_{n\alpha, m\beta} = K_{n\alpha, m\beta} = -T_{n\alpha, m\beta} = \gamma^2 M_{n\alpha, m\beta}^{(0)} e^{-\gamma^2} \quad (26)$$

(see expression (17)*); here γ is the intramolecular coupling constant, $M_{n\alpha, m\beta}^{f_0(0)}$ is the matrix element of the total electronic resonant interaction, and the factor $\exp(-\gamma^2)$ reflects renormalization, "dressing," of the electronic resonant integral, due to the interaction with the virtual phonons. For n.s. vibrations we have in accord with (15)

$$J_{n\alpha, m\beta} = K_{n\alpha, m\beta} = \frac{|R_{00, f_1}|^2}{|\xi_{00, f_0}|^2} M_{n\alpha, m\beta}^{f_0(1)}, \quad (27)$$

$$|K_{n\alpha, m\beta}| \gg |T_{n\alpha, m\beta}|;$$

here $M_{n\alpha, m\beta}^{f_0(1)}$ stands for the resonant interactions in the upper excited states and enters in (27) with a large energy denominator.

The total dynamic Hamiltonian of a system in a vibronic excited state is a sum of the operators \mathcal{H}_{00} (in the form (19)), \mathcal{H}_{res} (in the form (20)), and \mathcal{H}_{int} (in the form (22)). Thus, the problem of vibronic interactions in a system with an infinite number of particles has been reduced to a problem of two stable quasiparticles with definite effective interaction between them.

Such a problem is best investigated by quantum field theory methods, introducing the Green's function of the system. Using the clear-cut physical meaning of the Green's function, Rashba^[56, 63] succeeded in analyzing the problem of exciton-phonon interactions in a crystal in general form, and solved it rigorously in a number of cases.

The Green's function for a problem containing an exciton interacting with a phonon is described by the usual two-particle function

$$\tilde{F}_{n_1\sigma_1, n_2\sigma_2, n_3\sigma_3, n_4\sigma_4}(t-t') = -i \langle P \varphi_{n_1\sigma_1}(t) X_{n_2\sigma_2}(t) \varphi_{n_3\sigma_3}^+(t') X_{n_4\sigma_4}^+(t') \rangle \quad (28)$$

and is the amplitude of the probability that if, at the instant t , the molecule $n_1\sigma_1$ was electronically excited in the system and the molecule $n_2\sigma_2$ was in the vibrational state, the state of the system at the instant t' will coincide with the state obtained for the same system by shifting the electronic excitation to the molecule $n_3\sigma_3$ and the vibrational excitation to $n_4\sigma_4$. Thus, the function \tilde{F} describes propagation of two excitations through the crystal. The indices n_i indicate the number of the cell, and σ_i number the molecules in the cell.

The energy spectrum of the system described by the function \tilde{F} contains, at any energy of interaction between the exciton and the phonon, a region of the energies of two-particle states constituting, neglecting small corrections, the eigenvalues of the operator $\mathcal{H}_{00} + \mathcal{H}_{\text{res}}$ in expressions (19) and (20). The center of gravity of this region corresponds to the sum of the electronic and vibrational terms $\epsilon^f + \nu^0$ of the crystal, and its width is determined by the sum of the widths of the exciton and phonon bands $\tilde{\nu}^{f_0}$ and $\tilde{\mu}$.

But the large set of functions \tilde{F} also includes functions of the type

$$F_{n\alpha, m\beta}(t-t') = -i \langle P \varphi_{n\alpha}(t) X_{n\alpha}(t) \varphi_{m\beta}^+(t') X_{m\beta}^+(t') \rangle, \quad (29)$$

which describe the propagation of the electron-vibrational excitation as a unit through the crystal. Just like the complete function \tilde{F} , such a function corresponds to

*The quantities $J_{n\alpha, m\beta}$ and $K_{n\alpha, m\beta}$ are equal to each other only if the absorption and luminescence spectra have symmetry, which in the general case may be violated^[85, 86]. They can readily be calculated, however, on the basis of the properties of molecular spectra.

the region of two-particle states in the energy region $\epsilon^f + \nu^0$, and poles outside this spectrum. These poles denote the presence in the system of interacting particles of a bound state corresponding to a new quasiparticle—a vibron. The energy corresponding to the pole can be interpreted as the vibron energy. The existence of a pole depends critically on the energy of the exciton-phonon interaction. The optical properties of the crystal are described completely by the function F . This is connected with the fact that in the Heitler-London approximation the optical properties of a crystal are determined by the optical excitation of one molecule. Consequently we shall henceforth refer, in the analysis of the vibronic spectra, to the function $F_{n\alpha, m\beta}$.

Returning to the analysis of the dynamic Hamiltonian, we note that even with the simplified excited-phonon interaction operator in the form (22a) its investigation in general form is still quite complicated. We shall therefore use the dependence of the terms contained in \mathcal{H}_{int} on the symmetrical properties of the phonons, and consider vibronic states for the f.s. and n.s. phonons separately.

4. Vibronic Spectra of a Crystal with Non-fully-symmetrical Intramolecular Vibrations

The main simplifying assumption used in the analysis of the vibronic spectrum with an n.s. phonon is that the term $J_{n\alpha, n\alpha} = \Delta_\nu$ predominates in the operator of the exciton-phonon interaction \mathcal{H}_{int} in the form (22a). All the remaining terms do not exceed several cm^{-1} owing to relations (27), which follow from the intramolecular Herzberg-Teller effect^[15], and can be omitted in comparison with Δ_ν , which amounts to several times ten cm^{-1} . Neglect of these terms means neglecting all the effects connected with the displacement of the phonon either alone or in conjunction with the exciton. Under these conditions, the problem of vibronic states reduces to a problem with a local potential. The vibrating molecule is transformed into a "trap" for the exciton with a potential-well depth Δ_ν . In most known examples, $\Delta_\nu < 0$, and therefore the coincidence of the exciton and phonon on the same site is accompanied by a gain in the potential energy. Qualitatively, this singularity of vibronic states with n.s. vibration was pointed out by Nieman and Robinson^[87] on the basis of a study of the electronic spectra of impurity systems. When reduced to a problem with local interaction, the problem of the vibronic spectrum of a crystal with n.s. vibration can be solved exactly.

The retarded exciton-phonon Green's function (its Fourier transform) is described in this case by the relation

$$F(\nu) = \frac{G(\nu - \nu^0)}{1 - \Delta_\nu G(\nu - \nu^0)}; \quad (30)$$

here $G(\nu - \nu^0)$ is the Green's function of the unperturbed exciton state^[56]. In accordance with (30), the energy spectrum of two-particle vibronic states is the exciton band shifted in frequency by an amount equal to the vibration frequency ν^0 in the ground state. Outside this band, under the condition

$$1 - \Delta_\nu G(\nu - \nu^0) = 0 \quad (31)$$

there can exist bands of single-particle states. It is

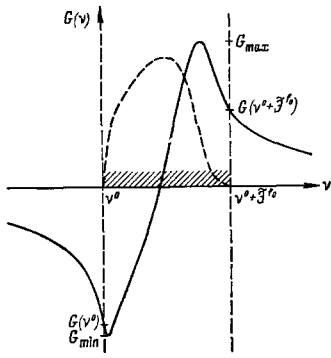


FIG. 11. Green's function $G(\nu)$ calculated on the basis of relation (30) using $\rho(\nu)$ as represented by the dashed curve.

well known from the theory of impurity electronic states^[88-91] that in three-dimensional crystals Eq. (31) does not have an isolated solution at all values of Δ_ν . Figure 11 shows a typical form of the real part of the function $G(\nu)$ for a bell-shaped spectral distribution of the density of states in the exciton spectrum $\rho(\nu)$. The maximum and minimum of the function $G(\nu)$ correspond to $(\Delta_{\max})^{-1}$ and $(\Delta_{\min})^{-1}$, respectively. At $\Delta_\nu < \Delta_{\max}$ or $\Delta_\nu > \Delta_{\min}$, Eq. (31) has no solution. The values of $G(\nu_0)$ and $G(\tilde{\nu}^{f_0} + \nu^0)$ determine Δ_{cr}^- and Δ_{cr}^+ , respectively, which are limiting for the existence of a real single-particle state outside the interval $(\nu^0, \tilde{\nu}^{f_0} + \nu^0)$. When $\Delta_{\max} < \Delta_\nu < \Delta_{\text{cr}}^+$ or $\Delta_{\min} > \Delta_\nu > \Delta_{\text{cr}}^-$, one can speak of the existence of virtual single-particle vibronic states. Notice should be taken here of the patent inadequacy of the coinciding-configurations model, according to which the bound vibronic state is assumed to exist at all times.

The absorption spectrum of the crystal is determined by the imaginary part of the function $F(\nu)$. At $\Delta_\nu < \Delta_{\text{cr}}^+$ and $\Delta_\nu > \Delta_{\text{cr}}^-$ it consists of two parts. The first part corresponds to a δ -like band of single-particle absorption and is described by the relation

$$\sigma(\nu) = \frac{r}{\Delta_\nu^2} \frac{\delta(\nu - \bar{\nu}_0)}{|G'(\nu - \bar{\nu}_0)|}, \quad (32)$$

where $\bar{\nu}_0$ is the position of the single-particle band; here $\sigma(\nu)$ is the conductivity tensor of the crystal and r is the oscillator strength of the intramolecular transition. The two-particle absorption band has a spectral distribution in the region $(\nu^0, \tilde{\nu}^{f_0} + \nu^0)$ that is given by the formula

$$\sigma(\nu) = \frac{r\rho(\nu)}{|1 - \Delta_\nu \text{Re} G(\nu)|^2 + \pi^2 \Delta_\nu^2 \rho(\nu)^2}, \quad (33)$$

where

$$G(\nu) = \int_0^{\tilde{\nu}^{f_0}} \frac{\rho(\nu')}{\nu - \nu' + i\delta} d\nu', \quad \delta \rightarrow 0^+.$$

The reference point is the red boundary of the exciton band, shifted by ν^0 . The integral intensity of the single-particle absorption, I_1 , is equal to

$$I_1 = r|a|^2 = r \left[\Delta_\nu^2 \frac{dG}{d\nu} \Big|_{\nu=\bar{\nu}_0} \right]^{-1}; \quad (34)$$

here $|a|^2$ is the square of the modulus of the wave function of the exciton at the site at which the vibrating molecule is located. The integral intensity I_2 of the two-particle absorption is equal to $I_2 = r(1 - |a|^2)$. Thus, the ratio of I_1 and I_2 is

$$\frac{I_1}{I_2} = \frac{|a|^2}{1 - |a|^2}. \quad (35)$$

At a fixed width of the exciton band and a fixed distribution of the density of states in the band, the value of

$|a|^2$ depends strongly on Δ_ν , and changes from 1 to 0 with variation of this parameter.

Expressions (31) and (34) are perfectly analogous to the expressions in the electronic theory of an impurity crystal with isotopic impurity, if Δ_ν is replaced by the difference of the electronic terms of the impurity molecules and of the host matter, and $|a|^2$ is taken to mean the square of the amplitude of the wave function of the exciton at the impurity site^[76, 89, 92]. Thus, the single-particle band, as well as the impurity level, will be repelled from the boundary of the spectrum of the two-particle states at small values of $|\Delta_\nu|$, in accord with (31). At the same time, it is possible to introduce for single-particle vibronic states, in analogy with impurity states, the concept of the radius of the states in accordance with the quantity $|a|^2$. If $|a|^2 = 1$, then the electronic excitation is on the vibrating (impurity) molecule and the corresponding single-particle vibronic (impurity) state is a small-radius state. The equality $|a|^2 = 1$ is satisfied when $|\Delta_\nu| \gtrsim \tilde{\nu}^{f_0}$. When $|a|^2 < 1$, the electronic excitation spends some of the time on molecules that are neighbors of the vibrating (impurity) molecule, and the corresponding state is characterized by a large radius. To satisfy this inequality it is necessary to have $|\Delta_\nu| \sim |\Delta_{\text{cr}}|$. When $\Delta_\nu < \Delta_{\text{cr}}^+$ and $\Delta_\nu > \Delta_{\text{cr}}^-$, the vibronic single-particle band (impurity level) is not splitt off from the continuous spectrum. Let us examine the general form of vibronic absorption spectra of a molecular crystal with n.s. vibration in three cases, which exhaust in practice all the possible situations in crystal.

1. The energy spectrum of the crystal contains no single-particle states. In this case there is observed in the interval $(\nu^0, \tilde{\nu}^{f_0} + \nu^0)$ a broad absorption band satisfying the selection rule

$$\mathbf{k}_{\text{exc}} + \mathbf{k}_{\text{phon}} = \mathbf{q}_{\text{phot}}. \quad (36)$$

The spectral distribution of the intensities in this band obeys relation (33). The integral absorption intensity is equal to the total oscillator strength of the intramolecular transition.

2. The energy spectrum of the crystal contains single-particle states, but such that $|a|^2 < 1$. The absorption spectrum of the crystal should reveal two absorption bands. The single-particle band is located in the region $\nu \sim \bar{\nu}_0$ corresponding to a pole of the function (27) at a given Δ_ν . The optical transition causing this band satisfies the selection rule

$$\mathbf{k}_{\text{vibr}} = \mathbf{q}_{\text{phot}}. \quad (37)$$

The frequency ν is shifted relative to $\bar{\nu}_0$ to the extent that the level with $\mathbf{k} = \mathbf{q}$ is shifted in the single-particle vibronic band relative to its center of gravity. The two-particle absorption band is described by (33), and its integral intensity in oscillator-strength units is equal to $1 - |a|^2$.

3. $|a|^2 \sim 1$ for single-particle states. The vibronic single-particle states are small-radius states. The absorption spectrum should contain only a single-particle band. In this limiting case, the optical spectrum has the properties that follow from the coinciding-configuration model.

If the crystal contains several molecules per unit cell, then the polarization properties of the spectrum

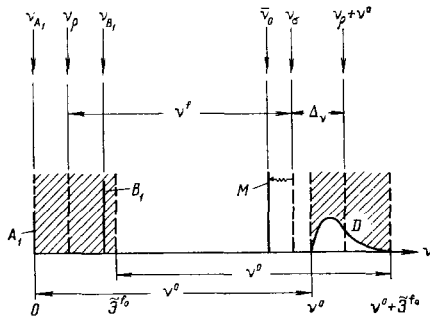


FIG. 12. Absorption spectrum of monoclinic crystal with two molecules per unit cell in the regions of pure electronic and vibronic transitions with participation of n.s. vibration. ν^f —crystal vibration frequency in the f -th excited state.

become important. Let us consider the most widespread case of a monoclinic crystal with two molecules per unit cell. The optical spectrum of such a crystal is shown schematically in Fig. 12. When constructing the optical spectrum in the region of the vibronic transition, the case of a single-particle state of large radius was selected.

The pure electronic transition is represented by two sharply polarized bands A_1 and B_1 located in different components of the spectrum with corresponding transitions to the points $\mathbf{k}_{\text{exc}} = \mathbf{q}_{\text{phot}}$ of two exciton bands. Both exciton bands are in contact in \mathbf{k} -space at the boundary of the Brillouin zone for all vectors \mathbf{k} perpendicular to the monoclinic axis \mathbf{b} , which is a two-fold screw symmetry axis^[93]. As a result, both bands are represented in the figure by a continuous energy spectrum. The frequency ν_ρ denotes the crystal electronic-excitation term serving as the center of gravity of the exciton spectrum.

The shaded region in the vibronic region of the spectrum was obtained by shifting the exciton spectrum by an amount equal to the vibration frequency in the ground electronic state, ν^0 , and represents the spectrum of the two-particle states. If the condition $|a|^2 < 1$ is chosen, the single-particle state band exists and is located to the left ($\Delta_\nu < 0$) of the two-particle spectrum. It is shifted away from the position of the term of the coinciding vibronic configuration ν_σ , as shown by the wavy arrow. In the case of crystal absorption, two absorption bands appear in the two principal components of the spectrum: the M band of the single-particle spectrum and the D band of the two-particle spectrum. The polarization properties of both bands are in accord with the oriented-gas model. The squares of the amplitudes $|a|^2$ are equal in both components of the spectrum, so that the ratio of the total intensities of the M and D bands in both components satisfies relation (35). The shapes of the M and D bands are described by relations (32) and (33).

In the limiting case of large $|\Delta_\nu|$, only the M band remains in the absorption spectrum. On the other hand, if $|\Delta_\nu| < |\Delta_{\text{cr}}|$, only the D band will be observed in the absorption spectrum. Thus, the foregoing description shows how closely interrelated are the characteristics of the exciton and vibronic spectra in the case of n.s. phonons. An important role is played in the analysis of this connection, and also in the quantitative interpretation of the vibronic absorption spectra, by a number of integral relations derived in the dynamic theory.

1. The total intensity of absorption in the M and D bands is equal to the total oscillator strength of the vibronic absorption in the crystal. As a result we have, in oscillator-strength units,

$$\int_0^{\infty} \sigma(\nu) d\nu = 1. \quad (38)$$

At the same time, the polarization ratios in the M and D bands are determined by the oriented-gas model.

The center of gravity of the vibronic absorption

$$\nu_\sigma = \int_0^{\infty} \nu' \sigma(\nu') d\nu' \quad (39)$$

(the σ region of integration includes the M and D bands) coincides with the term of the coinciding vibronic configuration in the crystal, defined by

$$\nu_\sigma = \nu_\rho + \nu^0 + \Delta_\nu, \quad (40)$$

where ν_ρ is the center of gravity of the density of states of the exciton spectrum. Relation (38) is the conservation law for the zeroth moment of the absorption bands, while relations (39) and (40) establish the connection between the first moments of the curves $\sigma(\nu)$ and $\rho(\nu - \nu^0)$. Supplementing these conservation laws is also the equality of the second moments of the curves $\sigma(\nu)$ and $\rho(\nu)$ ^[76]:

$$\int_0^{\infty} (\nu' - \nu_\sigma)^2 \sigma(\nu') d\nu' = \int_0^{\infty} (\nu' - \nu_\sigma)^2 \rho(\nu') d\nu'. \quad (41)$$

Relations (38)–(41) make it possible to indicate qualitatively the changes occurring in the shape of the D band when Δ_ν varies and at a known value of ν_ρ . Besides expression (33), which connects the spectral distribution in the two-particle absorption band with the distribution of the density of states, it is possible to establish an inverse relation with which to determine ρ_ν from the known $\sigma(\nu)$ dependence^[76]. This is possible only for n.s. phonons, since it is essentially connected with the fact that, in accordance with (30), the functions $F(\nu)$ and $G(\nu - \nu^0)$ are defined perfectly symmetrically, apart from the sign preceding Δ_ν . By virtue of this, we obtain for $\rho(\nu - \nu^0)$ a formula analogous to (33)

$$\rho(\nu - \nu^0) = \frac{\sigma(\nu)}{[1 + \Delta_\nu \text{Re} F(\nu)]^2 + [\pi \Delta_\nu \sigma(\nu)]^2}; \quad (42)$$

here

$$F(\nu) = \int_0^{\infty} \frac{\sigma(\nu')}{\nu - \nu' + i\delta} d\nu', \quad \delta \rightarrow 0^+.$$

The integration extends over the region of the M and D bands.

Formula (42) thus makes it possible to reconstruct the density of states in the exciton band from the spectral distribution in the vibronic D band. This method of determining $\rho(\nu)$ has a fundamental advantage over other existing methods^[94], since it makes it possible to use experimental data at arbitrarily low temperature, when the band structure becomes most distinct.

The external intermolecular phonons were completely excluded from the foregoing reasoning. Actually, however, the theoretically-predicted^[56] shape of the bands of single- and two-particle absorption in real crystals will be distorted. Acoustical phonons broaden the absorption bands (transforming, for example, δ -function peaks of single-particle absorption into curves of the Lorentz or Gauss type). Optical phonons, in conjunction

with single-particle transitions, can yield an additional structure of the spectrum in the high-energy region. Consequently, phonon replicas of single-particle bands can appear in the region of the two-particle energy spectrum in a real absorption spectrum. In addition, the true structure of the two-particle absorption can also be distorted by external phonons. Since it is impossible at present to take the influence of the phonons into account theoretically, it is necessary in the analysis of the real spectrum of a crystal to search for experimental ways of separating the exciton-phonon spectrum from the spectrum of the two-particle states. This is a complicated problem and must be solved individually for each crystal.

Included among the problems with a contact interaction potential of two quasiparticles are the already mentioned problems concerning the vibrational-rotational spectrum (the role of Δ_ν is played by the change of the rotational frequency following vibrational excitation of the molecule)^[60,61] and problems concerning two-quantum vibration spectra (the role of Δ_ν is played by the change of the molecule vibration frequency following two-quantum excitation as a result of anharmonicity)^[67]. The results obtained for the energy spectra of these systems, and the laws governing the distribution of the total intensity in the optical spectra, are similar in many respects to the results for vibronic states with n.s. phonons.

5. Vibronic Spectra of a Crystal with Fully Symmetrical Intramolecular Vibration

For fully symmetrical vibrations, the principal role in the exciton-phonon interaction is played by the non-local interaction described by the terms $J_{\alpha\gamma}(\mathbf{k})$, $K_{\alpha\beta}(\mathbf{k})$, $T_{\alpha\delta}(\mathbf{k})$ and $T_{\delta\alpha}^*(\mathbf{k})$ in the Hamiltonian \mathcal{H}_{int} (22a)^[56,63]. The role of these terms increases with increasing intramolecular electron-vibrational coupling constant γ , i.e., with increasing ratio of the intensity of the vibronic replica to the intensity of the purely electronic transition. This regularity reflects the value of the shift of the equilibrium position of the nuclear configuration following electronic excitation in electron-vibrational interaction. Although this mechanism of interaction with f.s. vibrations is predominant for most vibrations, many molecules have f.s. vibrations for which there is practically no shift of the equilibrium position of the nuclei (for example, the 750 cm^{-1} vibration in toluol^[66], 610 cm^{-1} in phenanthrene^[66], etc.). Such vibrations are as a rule genetically related to the n.s. vibrations in more symmetrical molecules, with respect to which the present molecules are derivatives (these molecules can be regarded as derivatives of benzene and naphthalene). Such f.v. vibrations in the vibronic spectrum of a crystal should be regarded in the same manner as n.s. vibrations, and all the deductions and laws of the preceding section remain in force for them. We shall discuss below those f.s. vibrations for which the shift of the equilibrium position of the nuclear configuration is appreciable.

The energy spectrum of the system is determined from the equation for the poles of the Green's function F , which has the following form for a crystal with one molecule per unit cell^[56]

$$F^0(\mathbf{k}, \omega) = \frac{1}{N} \sum_{\mathbf{k}_1} \frac{1}{\omega - \vartheta(\mathbf{k}_1) - \mu(\mathbf{k} - \mathbf{k}_1) - \Sigma(\mathbf{k}, \omega)}. \quad (43)$$

Here N is the number of crystal cells and $\Sigma(\mathbf{k}, \omega)$ is the complete irreducible self-energy part and represents a sum made up of the quantities $J_{\alpha\gamma}(\mathbf{k})$, $K_{\alpha\beta}(\mathbf{k})$, etc.

Unlike the case with n.s. phonon that was considered above, in this case knowledge of the density of states in the exciton band is no longer sufficient for the solution of (43), and it is necessary to have information on the dispersion laws for the excitons and phonons and on the dispersion relations of the energy of the nonlocal exciton-phonon interaction ($J_{\alpha\gamma}(\mathbf{k})$, $K_{\alpha\beta}(\mathbf{k})$, etc.). From the point of view of theory, the most complicated is the exchange-resonant interaction $K_{\alpha\beta}(\mathbf{k})$, which does not make it possible to obtain an explicit solution of the problem in the general case. This solution can be obtained only for some simple models, which will be discussed somewhat later.

In spite of the difficulty in obtaining a general solution, some properties of vibronic spectra with f.s. phonons can be deduced also on the basis of Eq. (43). At fixed \mathbf{k} , the roots of (43) will occupy an energy interval defined by the sum $\vartheta(\mathbf{k}) + \mu(\mathbf{k} - \mathbf{k}_1)$. In this part of the spectrum, the exciton and phonon are not bound to each other, and therefore it corresponds to the spectrum of two-particle states. The center of gravity of this spectrum is determined, just as in the case with n.s. phonons, by the sum of terms $\epsilon^f + \nu^0$. On the other hand, nothing can be said concerning the existence of isolated roots outside the region of the two-particle states without solving (43).

In a crystal with two molecules per cell, the function F is transformed into^[56]

$$\hat{F}(\omega) = \sum_{\lambda} F_{\lambda}(\omega) \mathbf{k}_{\lambda}^f \mathbf{k}_{\lambda}^{f*}, \quad \lambda = 1, 2; \quad (44)$$

here \mathbf{k}_{λ}^f are the matrix elements of the quasimomentum for the intramolecular vibronic transition. The vectors \mathbf{k}_{λ}^f are oriented along the symmetry elements of the crystal. Accordingly, a system of independent equations, in which all terms have the index λ , is obtained for the determination of the poles of the function $\hat{F}(\omega)$. The general form of the equations is much more complicated than (43). Each isolated root of this system corresponds to a narrow absorption band (and, in the energy spectrum, to a single-particle vibronic band) with a polarization determined by the corresponding \mathbf{k}_{λ}^f . It should be noted that, inasmuch as the equations for different values of λ can differ greatly (as in the case of probabilities for transferring vibrational excitations comparable with the probability of transferring the electronic excitation), some of them may not have any isolated roots at all. Therefore the electron-vibrational multiplets can be incomplete, unlike the electronic Davydov multiplet^[27,28] in which the number of bands is determined exclusively by the number of molecules per unit cell and by the selection rules. In this respect, the results of the dynamic model differ significantly from the coinciding configuration model, according to which the multiplets of the vibronic transitions with f.s. vibrations are completely analogous to the electronic multiplets, and differ from them only in the magnitude of the Davydov splitting.

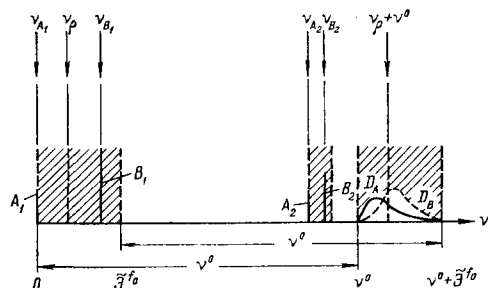


FIG. 13. Scheme showing the absorption spectrum of a monoclinic crystal with two molecules per unit cell in the region of purely electronic and vibronic transitions with participation of f.s. vibration.

The independence of the formation of the absorption spectrum in the two components of the spectrum leads to a strong difference between the spectra at different polarizations of the light. This difference is manifest in the fact that the number of single-particle bands, the shape of the two-particle bands, the distribution of the intensities among the single- and two-particle bands (the values of $|a|^2$) should all be different in the two components of the spectrum.

As a result, the polarization relations of the separately-taken single-particle or two-particle bands will not satisfy the oriented-gas model, in contrast to the case with n.s. phonon. The oriented-gas model will be satisfied only for the total absorption over the components. The indicated properties of the vibronic spectrum do not depend on the possibility of solving Eq. (43), and are a reflection of only the general properties of these equations. On the basis of the foregoing, the spectrum of the vibronic absorption of the crystal with f.s. phonon can be described by the scheme represented in Fig. 13. The region $(0, \tilde{\nu}^{f_0})$ corresponds to two contiguous exciton bands, optical transitions to which are allowed at the point $\mathbf{k}_{exc} = \mathbf{k}_{phot}$ and are represented by the bands A_1 and B_1 . In the vibronic region, the interval $(\nu^0, \tilde{\nu}^{f_0} + \nu^0)$ corresponds to a two-particle spectrum. The D_A and D_B bands correspond to two-particle bands in two components of the spectrum. The A_2 and B_2 bands are sharply polarized bands of single-particle absorption. Owing to the non-equivalence under the conditions of splitting of two single-particle bands, the produced summary spectrum of the single-particle states is narrower than the spectrum predicted in the model of coinciding configurations.

Among the common properties of the vibronic spectrum is also the definition of the center of gravity of the summary vibronic absorption. According to^[63], the center of gravity of vibronic absorption with f.s. phonon is defined by

$$\nu_G = \nu_p + \nu^0 + \Delta_\nu + J_{\alpha\beta}(\mathbf{q}). \quad (45)$$

For crystals with two molecules per unit cell we have

$$J_{\alpha\beta}(\mathbf{q}) = \mathcal{L}_{11}^{f_1}(\mathbf{q}) \pm \mathcal{L}_{12}^{f_1}(\mathbf{q}),$$

where $\mathcal{L}_{11}^{f_1}(\mathbf{q})$ and $\mathcal{L}_{12}^{f_1}(\mathbf{q})$ have the meaning of the resonant sums in the model of coinciding configurations (see (12a)). Thus, the centers of gravity ν_G differ in the two

*A similar statement was made by Merrifield with respect to the total vibronic spectrum, without the condition for the conservation of the number of phonons. [96]

components of the spectrum, and the difference between them is equal to $2|\mathcal{L}_{12}^{f_1}(\mathbf{q})|$,* i.e., it coincides with the Davydov splitting of the vibronic transition in the coinciding-configuration model. This circumstance leaves a unique imprint on the form of the absorption spectrum of the crystal. On the basis of Fig. 13 we can visualize the absorption spectrum in limiting cases. If $|a|^2 \approx 0$ in both components, the absorption spectrum consists of two-particle absorption bands D_A and D_B , whose centers of gravity are separated by a distance equal to the Davydov splitting. If $|a|^2 \approx 1$ in both components the main absorption intensity is concentrated in the A_2 and B_2 bands of the single-particle absorption, the distance between which coincides with the Davydov splitting. In both cases this quantity is equal to $\gamma^2(\nu_{B_1} - \nu_{A_1})$. The different cases will be illustrated below in the analysis of the experimental spectra of a number of crystals.

Rashba succeeded in obtaining an exact solution of the problem only for some simple models. Worthy of special attention is the particular case $\gamma^2 = 1$. In this case the absorption spectrum consists of several δ -function bands with frequencies $\epsilon^{\dagger} + \nu^0 + J_\lambda$. This result is valid both when the absorption bands are outside the region of the two-particle states and in the cases when they fall within this region. The physical reason for this is that when $\gamma^2 = 1$ the matrix element of the decay of the coinciding configuration is equal to zero. Therefore the coinciding configuration produced following the optical transition does not decay into an exciton and a phonon even when this decay is energywise possible, and forms a metastable ("quasi-single-particle") state. A deviation from $\gamma^2 = 1$ leads to a rapid broadening of such bands.

For a linear chain in the nearest-neighbor-interaction model it is possible to obtain an exact solution of the problem in a large range of variation of the parameters^[63]. It is shown at the same time that, depending on their values, the shape and width of the two-particle band are radically altered and under certain conditions it can have several maxima. In turn, the picture of the single-particle states is also more complicated. In many cases they correspond to several branches. It must be assumed that, without doubt, some of these singularities remain also in a three-dimensional crystal. We note in conclusion that unlike the case with n.s. phonon, the problem of occurrence of an exciton with f.s. phonon is much more difficult to investigate, but physically the picture is much more interesting and richer.

The presence of the criterion $\tilde{\nu}^{f_0} \ll \nu^0$ limits the applicability of the dynamic model to cases of weak ($\tilde{\nu}^{f_0} < \Delta_\nu \ll \nu^0$) and intermediate ($\Delta_\nu < \tilde{\nu}^{f_0} \ll \nu^0$) resonant couplings. For this interval of values of $\tilde{\nu}^{f_0}$, the conclusions drawn above concerning the general character of the energy spectrum are rigorously correct. If the inequality $\tilde{\nu}^{f_0} \ll \nu^0$ is violated, then the matrix U loses the structure determined by (22a), and becomes a general-type function of \mathbf{k}_1 and \mathbf{k}_2 . To determine its explicit form it is necessary to sum a perturbation-theory series. If the series converges, the problem retains a dynamic character, and all the conclusions given above are applicable to it. The series remains convergent so long as the exciton remains a stable particle and cannot decay into an exciton-phonon pair. This

Table VII. Main configurations of vibronic states of a crystal

Vibrational quantum number	Wave functions*	Type of configuration	Composition of configuration	ΔE **)	Corresponding exciton states of crystal
$p=0$	$\varphi_1^f U_1^f \cdot \prod_{i \neq 1}^N \varphi_i^0 U_i^0$	Coinciding	Purely electronic excitation of molecule I		Single-particle (electronic exciton)
$p=1$	$\varphi_1^f \varphi_2^0 \times \prod_{i \neq 1, 2}^N \varphi_i^0 U_i^0$	Coinciding Separated	Vibronic single-quantum excitation of molecule I Purely electronic excitation of molecule I and vibrational excitation of molecule II***	Δ_v	Single-particle (vibronic exciton) Two-particle (electronic and vibrational excitons)
$p=2$ ****)	$\varphi_1^f \varphi_2^0 \varphi_3^0 \times \prod_{i \neq 1, 2, 3}^N \varphi_i^0 U_i^0$	Coinciding Separated » » » »	Vibronic two-quantum excitation of molecule I Vibronic single-quantum excitation of molecule I and vibrational excitation of molecule II The same, but with participation of molecule III Purely electronic excitation of molecule I and two-quantum vibrational excitation of molecule III The same, but with participation of molecule II Purely electronic excitation of molecule I and vibrational single-quantum excitations of molecules I and III	Δ_{v_1} *****) or Δ_{v_2} Δ_{v_1} or Δ_{v_2} $2\Delta_v$ or $\Delta_{v_1} + \Delta_{v_2}$ $2\Delta_v$ or $\Delta_{v_1} + \Delta_{v_2}$ $2\Delta_v$ or $\Delta_{v_1} + \Delta_{v_2}$	Single-particle vibronic exciton state Two-particle (vibronic and vibrational excitons) ditto Two-particle (electronic and vibrational excitons) ditto Three-particle (pure electronic and two vibrational excitons)

*The notation is the same as in Table IV.

** ΔE is the difference between the energies of the separated and coinciding configurations of the corresponding molecular states.

***The number of configurations of this type at a fixed position of the pure electronic excitation is $N-1$, where N is the number of molecules in the crystal.

**** $m = 2$ represents arbitrarily two types of vibronic states: with participation of two quanta of the same vibration, as well as a sum of two different quanta.

***** Δ_{v_1} and Δ_{v_2} pertain to different vibrations, and in this case the described configuration characterizes two different vibronic excitations.

condition is also satisfied for the less rigorous relation $\nu^0 > \tilde{\nu}^0 e^{-\gamma^2}$, where the factor $\exp(-\gamma^2)$ takes into account the polarizing action of the phonons. When $\nu^0 < \tilde{\nu}^0 e^{-\gamma^2}$, the exciton and phonon cease to be stable quasiparticles. The foregoing description of the spectrum does not apply to this case of extremely strong resonant coupling.

The complex and rich structure of the vibronic spectrum, which follows from the dynamic model, is observed experimentally in spectra of molecular crystals. An analysis of the spectra of three typical crystals that differ in the magnitudes of their resonant interactions will be given in the next section.

In concluding the review of the theory of vibronic states, let us stop to discuss the problem of complicated vibronic excitations with a large number of phonons. It is easy to conclude that in this case the picture will be extremely complicated. This can be seen already from the extent to which the set of different vibronic configurations increases and becomes more complicated with increasing number of different placements of the electronic and vibrational excitations on the crystal molecules. Table VII lists by way of an example the vibronic configurations corresponding to the quantum numbers $p = 0, 1$, and 2 . The last column of the table indicates the possible exciton states of the crystal. The total number of configurations is equal to $2(p+1)$, and only one of them is coinciding and responsible for optical absorption in the corresponding transition.

The first attempt to construct a theory of multiphonon vibronic states is due to McRay^[34]. His theory, however, contained two serious limitations. First, it was based on perturbation theory and therefore could not be correctly applied to vibronic states. Second, out of the large set $(2p+1)$ of separated configurations, only one

was taken into account, described by vibronic excitation with m phonons of one molecule and n -phonon excitation of the other ($n+m=p$). Philpott has recently attempted to solve this problem^[37]. However, while overcoming the first difficulty in McRay's theory with the aid of the variational and field methods, he retained completely its representations concerning the construction of separated configurations. There is still no theory of vibronic states in which account is taken of the entire variety of the vibronic configurations for the multiphonon vibronic state.

IV. VIBRONIC ABSORPTION SPECTRA OF AROMATIC CRYSTALS

1. Introduction

The picture of the absorption spectrum of a crystal in the case when the energies of the intramolecular and resonant interactions are comparable is very complicated and shows little similarity to the spectrum of the free molecule. The "molecularity" of the spectrum, which was frequently mentioned earlier, consists only in a very general correspondence of the individual transitions in the spectra of the crystal and of the free molecule. In light of the foregoing notions concerning bound and dissociated vibronic excitations, the difference between the spectrum of the crystal and the spectrum of the free molecule finds an explanation. The change of the structure (nature) of the spectrum changes also our approach to its analysis. Whereas in the analysis of the molecular spectrum the main problem was to establish the type of vibration participating in the vibronic transition, and to determine its frequency in the excited state as the difference between the frequencies of the pure electronic and vibronic transitions, in the analysis of the

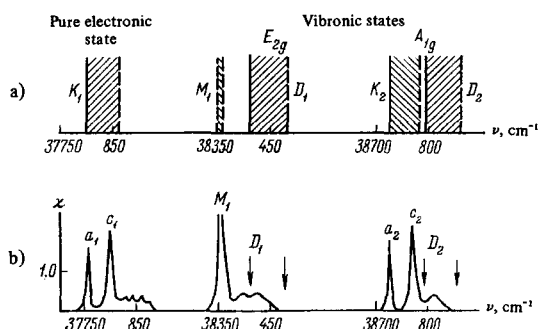


FIG. 14. Diagram of energy spectrum (a) and absorption spectrum (b) of benzene crystal for light normally incident on the ac plane of the crystal [101^b] ($T = 20^\circ\text{K}$).

spectrum of a crystal the problems become much more complicated. The question of the classification of the vibronic bands, i.e., their separation into single- and two-particle bands, becomes predominant. On the other hand, to determine the characteristic energy parameters, for example, the vibration frequency, it is now necessary to carry out quantitative measurements of the absorption spectra and to determine their centers of gravity in the set of bands pertaining to the given vibronic transition.

The identification of concrete bands of the absorption spectrum of a crystal with a given vibronic excitation can be carried out by comparing its energy and optical spectra. For reasons given at the end of the preceding chapter, we confine ourselves for the time being, in the analysis of the experimental spectra, to vibronic states with one phonon. If the positions and dimensions of the electronic and vibrational exciton bands and the values of the vibration frequencies in the ground state are known, one can construct the energy spectrum of the two-particle excitations. By comparing this spectrum with the optical-absorption spectrum and bearing in mind that single-particle states can exist only outside the region of the two-particle excitation spectrum^[58,63], we can separate the observed single-particle absorption from the two-particle one.

2. Benzene

The exciton spectrum of the energies of the benzene crystal in the electronic state is represented by a continuous energy interval $\sim 60\text{ cm}^{-1}$ wide^[98,99]. The red boundary of the crystal corresponds to the position of the maximum of the a-band of the exciton doublet of the purely electronic transition^[100]. For f.s. and n.s. g-type crystal vibrations, the widths of the exciton bands amount to 1 cm^{-1} for the A_{1g} vibration^[101a] and approximately 10 cm^{-1} for the E_{2g} vibration^[73].

The energy spectrum of the two-particle excitations in the region of the first vibronic transition of the benzene crystal (Fig. 14a) is represented by the continuous spectrum D_1 . Its width is equal to the sum of the widths of the vibrational and electronic exciton bands, and the red boundary is separated from the red boundary of the pure exciton band by an amount equal to the E_{2g} vibration in the ground state (606 cm^{-1})*. In the region of the

*Such a treatment of the vibronic state does not take into account the splitting of the molecular doubly-degenerate vibronic state E_{2g} in the crystal field; the maximum of this splitting is estimated at 9 cm^{-1} .

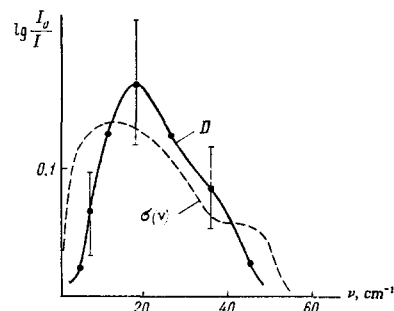


FIG. 15. Bands of two-particle absorption of benzene crystal in the region of the transitions ${}^1A_{1g} \rightarrow {}^1B_{2u}E_{2g}$ [74]. D—experimental band. The vertical bars represent experimental errors. $\sigma(\nu)$ —calculated band.

second vibronic state, the spectrum of the two-particle excitations D_2 is located 900 cm^{-1} away from the pure electronic exciton spectrum.

A comparison of the energy spectra and the optical absorption (Fig. 14b) in the region of these transitions shows that the main absorption, which consists of the M_1 , a_2 , and c_2 bands, lies outside the region of the energy spectrum of the dissociated states, and therefore corresponds to excitation of single-particle states. The corresponding exciton bands are shown in Fig. 14a on the left side of the spectra of the two-particle states. Only in a relatively small part of the spectrum, marked by the vertical arrows in the figure, can one seek two-particle absorption. It must be borne in mind here, however, that a large fraction of the considered edge absorption is apparently made up of satellites of the corresponding single-particle bands, due to the participation of intermolecular phonons. This follows from the activity of such phonons in the region of the pure electronic transition and from the similarity of the picture of the spectrum in the region of the pure electronic transition and in the region of the vibronic transitions. To establish the magnitude and form of the two-particle absorption it is therefore necessary first to determine the form of the exciton-phonon spectrum. This could be done so far only for the first vibronic transition with n.s. vibration^[74]. Use was made of the fact that the properties of the single-particle vibronic absorption are identical with the properties of the local vibronic absorption of an isotopic impurity center, in connection with which the exciton and impurity absorptions differ only in intensity. Consequently, the exciton-phonon structure of the spectrum was determined from the phonon spectrum of the vibronic absorption in the same transition of an admixture of benzene- d_6 molecules in a benzene- d_0 crystal. After subtracting the impurity spectrum from the spectrum of the benzene- d_0 crystal and suitably recalculating the concentrations, the result was the spectrum of the two-particle absorption of the benzene- d_0 crystal shown in Fig. 15. Its summary intensity is 5% of the M_1 -band intensity, corresponding to $|a|^2 = 0.95$. Within the framework of the Rashba theory^[56], a quantitative comparison was made of the theory with experiment on the basis of relations (33), using the density of states curve obtained for the benzene crystal by Colson et al.^[99]. The value obtained for the position of the M_1 band was $\bar{\nu}_0 = 38\,356\text{ cm}^{-1}$ ($\nu_{\text{exp. av}} = 38\,355\text{ cm}^{-1}$); the calculated value of $|a|^2$ is 0.98.

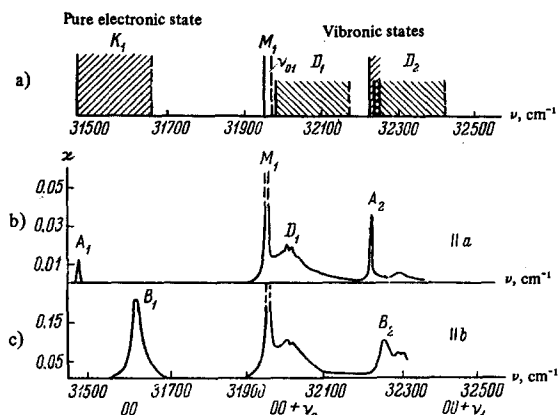


FIG. 16. Energy spectrum (a) and absorption spectrum of naphthalene crystal in polarized light with the light incident normal to the *ab* plane of the crystal (b and c) [¹⁰⁵] ($T = 20^\circ\text{K}$). ν_{01} —vibronic coinciding configuration term determining the center of gravity of the absorption ν_σ .

These quantities agree well with the experimental data. The situation is worse with the form of the D band. Figure 15 shows the theoretical curve calculated in accordance with (33) for $\Delta_\nu = -86 \text{ cm}^{-1}$ [⁹⁸]. Its area differs by a factor of 2 from that of the experimental curve, and the two have different shapes. This difference may be due to a large number of factors, which are discussed in detail in [⁷⁴]. No such analysis has been carried out so far in the region of the f.s. vibration.

It is seen from the foregoing analysis that in both vibronic transitions the two-particle absorption constitutes a small fraction of the intensity of the single-particle absorption. Consequently, both vibronic states of the benzene crystal are "small-radius" states and pertain to the case of weak resonant coupling. These results agree with the fact that in both cases the vibration frequency defects (-86 and -70 cm^{-1} , respectively) exceed the summary width of the two-particle spectrum.

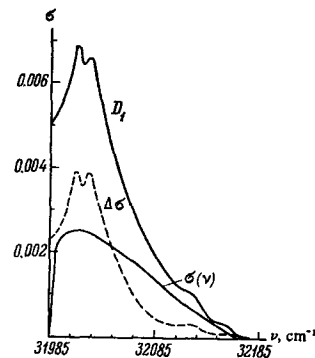
3. Naphthalene

The electronic exciton energy spectrum of the naphthalene crystal is continuous in an interval of width $180\text{--}200 \text{ cm}^{-1}$ [^{99,75}]. Its red boundary coincides with the position of the maximum of the A_1 band of the pure electronic transition.[¹⁰²] The widths of the vibrational exciton bands do not exceed several cm^{-1} [¹⁰³].

In Fig. 16a, D_1 and D_2 denote the continuous spectra of two-particle excitations of the first and second vibronic states. The distances between the red boundaries of these spectra and the pure electronic spectrum are equal to the frequencies of the B_{1g} and A_{1g} vibrations in the ground state (509 and 760 cm^{-1} , respectively). The lengths of both spectra are determined with high accuracy only by the width of the pure electronic spectrum.

a) The state $00 + B_{1g}$. The interaction between the electronic and vibrational motions in this vibronic state is characterized by a vibration-frequency defect amounting to $\Delta_\nu = -86 \text{ cm}^{-1}$ [¹⁰⁴]. There is no shift of the equilibrium position of the nuclear configuration. The vibronic absorption in this region is represented by two bands (M_1 and D_1)[¹⁰⁵]. The first lies on the long-wave side of

FIG. 17. Absorption band D_1 of naphthalene crystal in the region of two-particle states of the vibronic transition ${}^1A_{1g} \rightarrow {}^1B_{2u}B_{1g}$, and the calculated $\sigma(\nu)$ curve of two-particle absorption. The $\Delta\sigma$ curve represents the difference between the curves of D_1 and $\sigma(\nu)$ [76].



the energy region of the two-particle excitations and corresponds therefore to transitions to the single-particle vibronic-state band. The position of its maximum determines the position of the M_1 band of the single-particle excitations in the energy spectrum. The D_1 band coincides in position and length with the region of the spectrum of the two-particle excitations. The M_1 and D_1 bands are weakly polarized, and the polarization ratios of the intensities in both components of the spectrum are the same for them, while the summary intensities of these bands are practically equal. On the basis of these properties, the D_1 band was interpreted[^{71,72}] as a two-particle absorption band. Recently, however, it was possible to determine the density of states in the exciton band of the naphthalene crystal, making it possible to interpret quantitatively, with best agreement, a large number of various experimental results[⁷⁶]. On the basis of this function, using relations (33) of the preceding section, a quantitative interpretation was obtained for the vibronic absorption of the naphthalene crystal in the region of the M_1 and D_1 bands[⁷⁶]. It was established that the calculated value of the center of gravity of the M_1 band coincides exactly with the experimental one, but the shape of the two-particle absorption does not coincide with the D_1 band and has the form shown in Fig. 17. Its intensity is only 60% of the absorption in the D_1 band ($|a|^2 = 0.75$). It was concluded that the presence of excess absorption in the D_1 band, shown by the dashed curve in Fig. 17, is connected with other absorption mechanisms, chief among which is apparently one due to the interaction with the external phonons. No independent determination of the exciton-phonon spectrum of the naphthalene crystal, similar to that for benzene, has as yet been made.

b) The state $00 + A_{1g}$. According to the picture of the molecular spectrum (see Fig. 2b and Table I), the intramolecular interaction between the electronic and vibrational motions in this state is characterized by a vibration-frequency defect $\Delta_\nu = -58 \text{ cm}^{-1}$ and by a noticeable shift of the equilibrium position. In the energy spectrum of the crystal, the vibronic state is represented primarily by the interval D_2 of two-particle excitations. In the optical spectrum of the crystal there are observed two sharply polarized absorption regions with complex structure. A comparison of the absorption region with the region of the energy spectrum shows that the principal part of the absorption, which includes the entire spectrum in the b-component and a broad band in the a-component, lies in the frequency region corresponding to excitation of two-particle states. Thus, in spite of

the fact that the structure of the crystal absorption in the region of K_2 transition is similar to the absorption structure in the region of the pure electronic K_1 transition, the bands A_2 and B_2 differ in nature. Out of the entire vibronic spectrum in this region, only the A_2 band corresponds to excitation of single-particle states. The sharp absorption polarization is a consequence of the fact that the Davydov splitting is sufficiently large in this transition. At the present time it is difficult to indicate its exact value, since the lack of quantitative measurements of the absorption in the entire region of the spectrum in the b-component does not make it possible to determine its center of gravity. The distance 30 cm^{-1} between the bands A_2 and B_2 , which has been heretofore regarded as the Davydov splitting, is certainly too low.

The absorption spectrum in the region under consideration is incomplete compared with the scheme shown in Fig. 13. The spectrum does not contain the b component of the single-particle states. It must apparently be assumed that, owing to the proximity of the second band of the single-particle states to the boundary of the continuous spectrum, the split-off condition is not satisfied for it, and consequently this state is fully dissociated.

c) Naphthalene crystal subjected to tension. An ultrathin naphthalene crystal ($d < 0.1\ \mu$) placed in optical contact with a quartz plate and cooled to 20°K is in a state of elastic tension, as a result of which the intermolecular distances increase. Naturally, this decreases the integrals of the resonant interaction, leading to a narrowing of the exciton band of the pure electronic state^[106]. As shown by a number of experiments, the intramolecular characteristics of the naphthalene remain unchanged in this case^[106-109]. Figure 17a shows the continuous exciton energy spectrum of the pure electronic state under the following assumptions: 1) the width of the spectrum of the deformed crystal is smaller than that of the free sample in the same ratio as the values of the Davydov splittings of the bands of the pure electronic transitions of both crystals; 2) the A_1 band of the pure electronic transition corresponds as before to

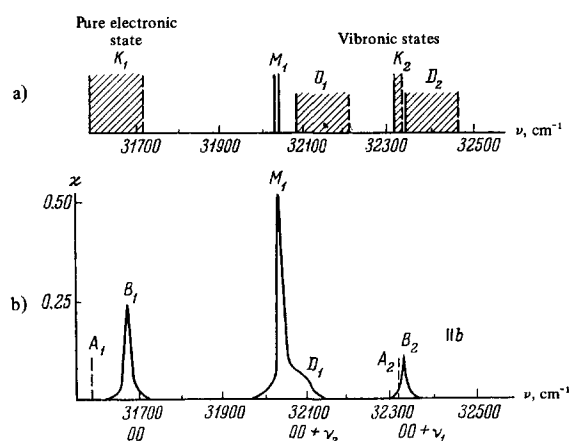


FIG. 18. Energy spectrum (a) and absorption spectrum (b) of a deformed naphthalene crystal with the polarization of the incident light directed along the b axis of the crystal^[107] ($T = 20^\circ\text{K}$, $d = 0.1\ \mu$). The dashed lines in Fig. b indicate the positions of the bands A_1 and A_2 of the spectrum in the a component.

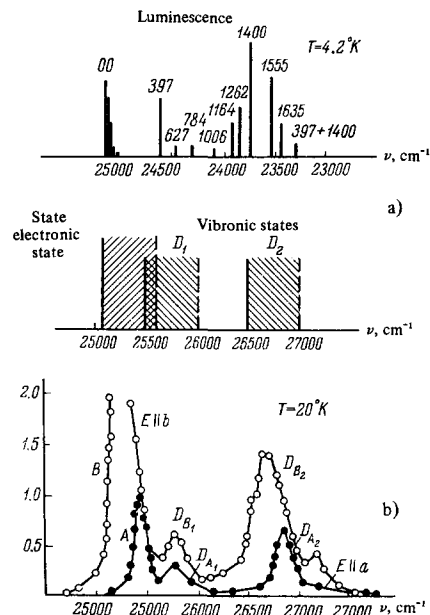


FIG. 19. Spectra of exciton luminescence (a) and absorption (b) of an anthracene crystal with light incident normal to the ab plane of the crystal^[117] ($T = 20^\circ\text{K}$, $d = 0.075\ \mu$).

the bottom of the lowest exciton band. A decrease of the width of the exciton spectrum, and accordingly of the energy spectrum of the two-particle excitations, by 80 cm^{-1} , decreases the radius of the single-particle vibronic states. This enhances the single-particle absorption in the vibronic transitions. Figure 18b shows the absorption curve of a deformed naphthalene crystal in the b-component of the spectrum^[107]. An analysis of the optical spectrum shows that the bulk of the absorption is concentrated in both vibronic states outside the energy region of the dissociated states. The fraction of the two-particle absorption in the region of the M_1 transition is decreased thereby to 8%, and its properties become analogous to the vibronic transitions of the benzene crystal. In the region of the second transition, the B_2 band as well as the A_2 band are now located outside the region of the D_2 spectrum, and correspond to transitions to single-particle-state bands. Attention is called to the strong narrowing of the absorption spectrum in the b component, owing to the change in the nature of the B_2 band and to the decrease of the intensity of the short-wave two-particle absorption.

4. Anthracene

The absorption spectrum of the crystal (Fig. 19b) begins with two strongly polarized B and A bands, which correspond to transitions into two electronic exciton bands formed in the crystal from the nondegenerate molecular level ${}^1B_{3u}$. The vibronic spectrum, like the spectrum of the molecule, is constructed only with participation of f.s. vibrations, thus explaining the similarity of the absorption structures in all the transitions. Attention is called to the large bandwidth and the relative simplicity of the absorption spectrum. For comparison, the upper part of Fig. 19 shows the exciton-luminescence spectrum of the crystal at 4°K ^[110]. Out of the ten vibrations that appear in the luminescence spectrum in a region extending over 1600 cm^{-1} , only the most

intense vibronic transitions, with participations of the vibrations $\nu'_1 = 400 \text{ cm}^{-1}$ and $\nu_1 = 1400 \text{ cm}^{-1}$, appear in the absorption spectrum in the form of individual bands. In comparing the two different spectra, it is necessary to explain the following principal differences: 1) why are the bands of the pure electronic transitions so broad, and 2) why are the bands of the vibronic transitions broad, while the vibronic absorption spectrum itself is structurally poorer than the luminescence spectrum. Since the bands of the exciton-luminescence spectrum are narrow, the interaction of the excitons with the acoustic phonons and the widths of the bands of the latter are not the main cause of the broadening of the bands and of the absorption spectrum. A second general cause of the broadening of the absorption spectrum bands might be the temperature stretching of the ultrathin crystal placed in contact with the quartz plate^[106]. Owing to the exceedingly strong absorption of the anthracene crystal, its absorption is investigated in very thin crystals ($d < 0.1 \mu$), at which the tension effect might be substantial. However, investigations of the reflection of thick anthracene crystals^[111] have confirmed that unstressed samples also have absorption bands of large width. Under these conditions, it is natural to attribute the observed widths to broad exciton bands of the pure electronic state.

Davydov and Myasnikov^[112-115] calculated theoretically the dispersion and shape of the absorption bands in pure electronic transitions for molecular crystals with a broad exciton band in weak exciton-phonon interaction. The model of the exciton-band structure was taken to be the exciton spectrum calculated for an infinite anthracene crystal^[116]. The calculations have shown that broadening of the absorption bands as a result of acoustic phonons is quite likely. On the basis of careful measurements of the dispersion and reflection curves in the region of the pure electronic transition^[117], good qualitative agreement was obtained between the experimental and the theoretical results. It was established that the widths of the B and A bands are due to the opening up of the exciton bands as a result of interaction with acoustic phonons. Optical phonons, as shown by measurements of the reflection spectra, are less pronounced and play a smaller role.

Experimental investigations have made it possible to limit the dimensions of the pure electronic exciton bands only on the low-energy side. The red boundary of the spectrum is determined by the frontal band of the excited-luminescence spectrum at 4°K and corresponds to a frequency $\omega = 25 \cdot 10^3 \text{ cm}^{-1}$ ^[110]. Just as for the naphthalene crystal, the two exciton bands of the crystal come in contact on the boundary of the Brillouin zone^[93], as a result of which both bands form a continuous spectrum. The short-wave boundary of this spectrum is unknown. However, the value of the Davydov splitting (215 cm^{-1}) under these conditions gives the minimum dimension of the width of the total spectrum. At the same time, there are grounds for assuming that actually the total width of the exciton spectrum exceeds this value, since according to theoretical calculations^[116] the value of the Davydov splitting is smaller than the total width of the bands. No great error will apparently be incurred if a value 500 cm^{-1} is assumed for this quantity, as was done in^[117].

The vibrational exciton bands of f.s. vibrations ν'_1 and ν_1 in the anthracene crystal are narrow, and their widths do not exceed $3-5 \text{ cm}^{-1}$, as can be determined from the absence of Davydov splitting of these states in the low-temperature spectra of Raman scattering of the crystal^[103].

The two-particle spectra of vibronic states with participation of the vibrations ν'_1 and ν_1 (see Fig. 19a) were obtained by shifting the pure electronic spectrum by an amount equal to the vibration frequencies in the ground state. Like the spectrum of the pure electronic state, they are bounded only on the long-wave side. A comparison of the energy and optical spectra in the region of the vibronic transitions shows that the observed vibronic absorption in both transitions lies inside the energy interval of the two-particle excitations. Thus, we encounter in the anthracene crystal a situation wherein the optical spectrum of the crystal does not have single-particle vibronic absorption bands, meaning the absence of corresponding states in the energy spectrum. The absorption structure agrees well with the picture of the vibronic absorption with participation of f.s. vibrations that was predicted for this limiting case^[93]. The absorption spectrum is represented by the broad D_B and D_A bands of two-particle absorption, and the distance between their centers of gravity agrees well quantitatively with the value of the Davydov splitting as estimated from the splitting of the pure electronic transition, with correction for the ratio of the intensities of these transitions. The anthracene crystal is very interesting in connection with this circumstance since its spectrum demonstrates how difficult it is to establish the characteristics of the spectrum from its external form. Thus the D_{B_2} and D_{A_2} bands of the second vibronic transitions form a doublet of strongly polarized bands outwardly similar to the doublet of bands of the pure electronic transition, so that their interpretation as bands of single-particle absorption was previously subject to no doubt. The vibronic states of the anthracene molecules in the first electronic excited state are characterized by the absence of a change in the vibration frequency (within $3-5 \text{ cm}^{-1}$)^[118-120]. Their appearance in the spectrum is due only to the shifts of the equilibrium positions of the nuclear configuration following electronic excitation. Under these conditions, the vibrational and electronic excitons can be connected only because of the energy of the nonlocal interaction, different terms of which depend on γ^2 . For all the f.s. vibrations of anthracene, with the exception of ν_1 , we have $\gamma^2 \ll 1$, and consequently the binding energy should be small. As a result, the single-particle vibronic states turn out to be fully dissociated. Only for the vibronic transition with the vibration ν_1 do we have $\gamma^2 = 0.9$ ^[121]. Under these conditions there can exist metastable quasi-single-particle states within the energy spectrum of the two-particle states^[93]. One must therefore assume that the relative simplicity of the absorption spectrum of the crystal, compared with the luminescence spectrum, is due precisely to these circumstances. The absorption of the anthracene crystal, even in the minima between the main bands, is exceedingly strong. Apparently, it is due to broad-band absorption caused by excitation of two-particle states of the vibrations of $627, 784, 1006, 1164, 1262 \text{ cm}^{-1}$, etc.

Owing to the close values of the vibration frequencies and the large width of the energy spectrum, broad bands of individual transitions overlap, forming a continuous absorption background. The only vibronic transitions that stand out against this background are those whose intensity is comparable with the intensity of the bands of the electronic-transition frequencies.

Now that it has been demonstrated that the vibronic bands differ in their character from the bands of the pure electronic transition, the question is why they are so similar. The half-widths of the most intense $B-DB_2$ bands differ only by a factor 1.5, although it might seem that this difference could be larger, since the energy spectrum of the two-particle excitations is broad and the width of the DB_2 band is due to its opening up as a result of the interaction with the vibrational exciton. It is possible that the similarity of the bands in these transitions is due to the fact that under conditions when γ^2 is close to unity the decay of the coinciding configuration produced upon absorption of the photon becomes difficult^[63]. Under these circumstances, the vibronic state belongs to the two-particle spectrum, but the optical properties of the absorption are quasi-single-particle. In the general case the absorption band should in this case become much narrower. The reason for its broadening, just as for bands of the pure electronic transition, may be the interaction with external phonons. The observed shapes of the DB_2 and DA_2 bands are more readily connected with the simultaneous action of two factors: 1) the influence of the exciton-phonon interaction on the quasi-single-particle absorption, and 2) the fact that the decay of the coinciding configuration is not completely forbidden, unlike the case when $\gamma^2 = 1$, and with participation of the vibrational exciton in the opening up of the exciton spectrum. The final answer to this question calls for additional experimental and theoretical research.

V. CONCLUSION

The absorption spectra described and analyzed above for the three crystals are a splendid illustration of the dependence of the form of the vibronic spectrum of a crystal on the type of the resonant coupling. In the first transitions considered, the benzene crystal is an example of weak coupling, the naphthalene crystal an example of intermediate coupling close to weak, and the anthracene crystal an example of intermediate coupling close to strong. It is important that outwardly, the simplest picture is that of the vibronic spectra of benzene and anthracene crystals, although in the former case the absorption corresponds almost entirely to excitation of only single-particle states, and in the latter to excitation of only two-particle states. The picture of the vibronic spectrum of the naphthalene crystal is more complicated and reveals mixed absorption.

The dependence on the type of resonant coupling is characteristic not only of pure crystals, but also takes place in impurity vibronic spectra. The role of the resonant energy is played in this case by the energy of the electronic interaction of the impurity molecule with the solvent molecules. The physical basis for the dependence is the fact that the vibronic states of the impurity system in the region of the impurity spectrum are also

represented by a set of bound and dissociated states^[56,72]. The optical spectrum is determined by the energy ratio of the inter- and intramolecular interactions and, for a wide variation of this parameter, ranges from the usual local absorption to the fully dissociated one, in analogy with the situation illustrated in the spectra of the three pure crystals. The closest to pure crystals is the picture of vibronic absorption in isotopic-impurity crystals. A strong change of the impurity spectrum with changing type of resonant coupling was accordingly observed in the spectra of deuterobenzenes^[73] and deuteronaphthalenes^[75].

It should be noted in conclusion that the approach to the analysis of the vibronic spectrum of the crystal from the point of view of bound and dissociated states yields extensive new information on the exciton properties of these systems, but the realization of this possibility makes many demands on the experimenter. The first is the need for obtaining a detailed quantitative description of the experimental absorption spectrum. The second pertains to independent investigations of the exciton-phonon interactions. The question of separating the effects due to interaction with external phonons has possibly never been as acute in the entire history of the interpretation of molecular-crystal spectra. When these two conditions are met, the interpretation of vibronic spectra with n.s. vibrations can be carried through to conclusion, and this may yield new data on the pure exciton spectrum. As to a quantitative interpretation of vibronic states with f.s. vibrations, there is added to it a third requirement, namely the determination of the dispersion relations of the resonant interactions. It can be assumed that this way offers promise of comparing theory with experiment to find "fitting" parameters with aid of which it will be possible, one hopes, to determine successfully the dispersion laws of exciton states.

Note added in proof (see page 503). Vibronic states with f.s. vibrations for a one-dimensional crystal were recently investigated in detail also by Davydov and Serikov^[122]. They calculated numerically the form of the absorption spectrum of such a crystal for a large set of values of the parameters γ and Δ_p . Particular attention was paid to quasi-single-particle vibronic states at $\gamma^2 = 1$. The structure of the two-particle absorption spectrum at $\gamma^2 < 1$ and $\Delta_p \sim 0$ is attributed to the existence of unstable, metastable single-particle vibronic states.

¹ M. A. El'yashevich, *Atomnaya i molekulyarnaya Spektroskopiya (Atomic and Molecular Spectroscopy)*, Fizmatgiz, 1962.

² H. Sponner and E. Teller, *Rev. Mod. Phys.* **13**, 76 (1941).

³ L. D. Landau and E. M. Lifshitz, *Kvantovaya mekhanika (Quantum Mechanics)*, Ch. 13, Fizmatgiz, 1963 [Addison-Wesley, 1965].

⁴ M. Born and R. Oppenheimer, *Ann. d. Phys.* **84**, 457 (1927); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Ch. 4, Sec. 14, Oxford, 1954.

⁵ K. K. Rebane, *Elementarnaya teoriya kolebatel'noy struktury spektrov primesnykh tsentrov kristallov (Elementary Theory of Vibrational Structure of Spectra of Impurity Centers of Crystals)*, Nauka, 1968.

⁶ D. I. Blokhintsev, *Kvantovaya mekhanika (Quantum Mechanics)*, Sec. 47, Fizmatgiz, 1963.

⁷ R. E. Merrifield, *J. Chem. Phys.* **40**, 445 (1964).

- ⁸ M. Lax, *J. Chem. Phys.* **20**, 1752 (1952).
- ⁹ A. C. Albrecht, *J. Chem. Phys.* **33**, 156 (1960).
- ¹⁰ R. Kubo, *Phys. Rev.* **86**, 929 (1952).
- ¹¹ S. I. Pekar, *Usp. Fiz. Nauk* **50**, 197 (1953).
- ¹² S. I. Pekar, *Zh. Eksp. Teor. Fiz.* **20**, 510 (1950).
- ¹³ S. I. Pekar and M. A. Krivoglaz, *Trudy, IF AN UkrSSR* **4**, 37 (1953).
- ¹⁴ Yu. E. Perlin, *Usp. Fiz. Nauk* **80**, 553 (1963) [*Sov. Phys.-Uspekhi* **6**, 542 (1964)].
- ¹⁵ G. Herzberg and E. Teller, *Zs. phys. Chem.* **B21**, 410 (1933).
- ¹⁶ V. L. Broude, A. F. Prikhot'ko, et al., *Spektry pogloshcheniya molekulyarnykh kristallov (Absorption Spectra of Molecular Crystals)*, Vol. 1, Naukova dumka, 1965.
- ¹⁷ E. F. McCoy and F. G. Ross, *Austr. J. Chem.* **15**, 573 (1962).
- ¹⁸ H. Sponner et al., *J. Chem. Phys.* **7**, 207 (1939).
- ¹⁹ D. P. Craig et al., *Phil. Trans. Roy. Soc. (L)* **A253**, 543 (1961).
- ²⁰ J. M. Hollas, *J. Mol. Spectr.* **9**, 138 (1962).
- ²¹ D. E. Freeman, *J. Mol. Spectr.* **6**, 305 (1961).
- ²² O. P. Kharitonova, *Opt. Spektrosk.* **5**, 29 (1958).
- ²³ J. I. Frenkel, *Phys. Rev.* **37**, 17, 1276 (1931).
- ²⁴ R. Peierls, *Ann. d. Phys.* **13**, 905 (1932).
- ²⁵ J. I. Frenkel, *Zh. Eksp. Teor. Fiz.* **6**, 647 (1936).
- ²⁶ J. Frank and E. Teller, *J. Chem. Phys.* **6**, 861 (1938).
- ²⁷ A. S. Davydov, *Teoriya pogloshcheniya sveta v molekulyarnykh kristallov (Theory of Light Absorption in Molecular Crystals)*, *Trudy IF AN UkrSSR*, 1951, Sec. 17.
- ²⁸ A. S. Davydov, *Usp. Fiz. Nauk* **82**, 393 (1964) [*Sov. Phys.-Uspekhi* **7**, 145 (1964)].
- ²⁹ W. T. Simpson and D. L. Peterson, *J. Chem. Phys.* **26**, 588 (1957).
- ³⁰ D. S. McClure, *Canad. J. Chem.* **36**, 59 (1958).
- ³¹ R. E. Coffman and D. S. McClure, *C. Journ. Chem.* **36**, 48 (1958).
- ³² A. Ron and O. Shnepp, *J. Chem. Phys.* **37**, 2540 (1962).
- ³³ A. Witkowsky and W. Moffit, *J. Chem. Phys.* **33**, 872 (1960).
- ³⁴ E. G. McRay, *Austr. J. Chem.* **14**, 329 (1960).
- ³⁵ E. G. McRay, *Austr. J. Chem.* **14**, 344 (1960).
- ³⁶ G. L. Levinson, W. T. Simpson and W. Curtis, *J. Amer. Chem. Soc.* **79**, 4314 (1957).
- ³⁷ R. E. Merrifield, *Radiat. Res.* **20**, 154 (1963).
- ³⁸ R. L. Fulton and M. Gouterman, *J. Chem. Phys.* **35**, 1059 (1961).
- ³⁹ R. L. Fulton and M. Gouterman, *J. Chem. Phys.* **41**, 2280 (1964).
- ⁴⁰ E. A. Chandross, G. Ferguson and E. G. McRay, *J. Chem. Phys.* **45**, 3546 (1966).
- ⁴¹ E. A. Chandross and G. Ferguson, *J. Chem. Phys.* **45**, 3554 (1966).
- ⁴² M. H. Perrin and M. Gouterman, *J. Chem. Phys.* **46**, 1019 (1967).
- ⁴³ A. S. Davydov, *Zh. Eksp. Teor. Fiz.* **18**, 219 (1948).
- ⁴⁴ D. P. Craig and P. C. Hobbins, *J. Chem. Soc. (L)*, 539 (1955).
- ⁴⁵ W. A. Bingel, *Canad. J. Phys.* **37**, 680 (1959).
- ⁴⁶ M. Kasha, *Radiat. Res.* **20**, 55 (1963).
- ⁴⁷ R. E. Merrifield, *J. Chem. Phys.* **36**, 2519 (1962).
- ⁴⁸ D. P. Craig and S. H. Walmsley, *Mol. Phys.* **4**, 133 (1961).
- ⁴⁹ D. P. Craig and S. H. Walmsley, *Physics and Chemistry of the Organic Solid State*, v. 1, New York, 1963.
- ⁵⁰ O. Shnepp, *Ann. Rev. Phys. Chem.* **14**, 35 (1963).
- ⁵¹ R. M. Hochstrasser, *Ann. Rev. Phys. Chem.* **17**, 457 (1966).
- ⁵² T. N. Misra, *Rev. Pure Appl. Chem.* **15**, 39 (1965).
- ⁵³ E. G. McRay, *Austr. J. Chem.* **14**, 354 (1960).
- ⁵⁴ E. G. McRay, *Austr. J. Chem.* **16**, 295 (1963).
- ⁵⁵ E. G. McRay, *Austr. J. Chem.* **16**, 315 (1963).
- ⁵⁶ É. I. Rashba, *Zh. Eksp. Teor. Fiz.* **50**, 1064 (1966) [*Sov. Phys.-JETP* **23**, 708 (1966)].
- ⁵⁷ H. Bethe, *Zs. Phys.* **71**, 205 (1931). See also A. I. Akhiezer, V. G. Bar'yakhtar and S. V. Peletminskiĭ, *Spinovye volny (Spin Waves)*, Fizmatgiz, 1967, p. 185.
- ⁵⁸ G. H. Wannier and N. F. Mott, *Phys. Rev.* **52**, 191 (1937); N. F. Mott, *Trans. Far. Soc.* **34**, pt 3, 500 (1938).
- ⁵⁹ H. P. Gush, W. F. J. Hare, E. J. Allin and H. L. Welsh, *Canad. J. Phys.* **38**, 176 (1960).
- ⁶⁰ J. Van Kranendonk, *Physica* **25**, 1080 (1959).
- ⁶¹ J. Van Kranendonk, *Canad. J. Phys.* **38**, 240 (1960).
- ⁶² M. Wortis, *Phys. Rev.* **132**, 85 (1963).
- ⁶³ É. I. Rashba, *Zh. Eksp. Teor. Fiz.* **54**, 542 (1968) [*Sov. Phys.-JETP* **27**, 292 (1968)].
- ⁶⁴ R. Loudon, *Adv. Phys.* **17**, 243 (1968).
- ⁶⁵ S. Freeman and J. J. Hopfield, *Phys. Rev. Lett.* **21**, 910 (1968).
- ⁶⁶ Y. Toyozawa and J. Hermanson, *Phys. Rev. Lett.* **21**, 1637 (1968).
- ^{66a} V. I. Mel'nikov and É. I. Rashba, *ZhETF Pis. Red.* **10**, 95 (1969) [*JETP Lett.* **10**, 60 (1969)].
- ^{66b} I. B. Levinson, *ibid.* **12**, 496 (1970) [**12**, 347 (1970)].
- ^{66c} M. Cohen and J. Ruvald, *Phys. Rev. Lett.* **23**, 1378 (1969).
- ⁶⁷ V. M. Agranovich, *Fiz. Tverd. Tela* **12**, 562 (1970) [*Sov. Phys.-Solid State* **12**, 430 (1970)].
- ⁶⁸ G. V. Kventsel', *ibid.* **8**, 1819 (1966) [**8**, 1445 (1967)].
- ⁶⁹ J. Jortner and S. Rice, *J. Chem. Phys.* **44**, 3364 (1966).
- ⁷⁰ D. P. Crock and S. A. Rice, *J. Chem. Phys.* **49**, 4345 (1968).
- ⁷¹ V. L. Broude, É. I. Rashba, and E. F. Sheka, *ZhETF Pis. Red.* **3**, 429 (1966) [*JETP Lett.* **3**, 281 (1966)].
- ⁷² V. L. Broude, E. I. Rashba and E. F. Sheka, *Phys. Stat. Sol.* **19**, 395 (1967).
- ⁷³ V. K. Dolganov and E. F. Sheka, *Fiz. Tverd. Tela* **11**, 2427 (1969) [*Sov. Phys.-Solid State* **11**, 1962 (1970)].
- ⁷⁴ V. K. Dolganov and E. F. Sheka, *ibid.* **12**, 1479 (1970) [**12**, 1160 (1970)].
- ⁷⁵ E. F. Sheka and I. P. Terenetskaya, *ibid.* **12**, 720 (1970) [**12**, 558 (1970)].
- ⁷⁶ N. V. Rabin'kina, É. I. Rashba and E. F. Sheka, *ibid.* **12**, 3569 (1970) [**12**, 2898 (1971)].
- ⁷⁷ E. F. Sheka, *Opt. Spektrosk.* **29**, 275 (1970).
- ⁷⁸ D. S. McClure, *Excitons, Magnons and Phonons in Molecular Crystals*, Beirut, Lebanon, 15-18 Jan. 1968. Ed. M. Zalahn, London, Cambridge, 1968, p. 135.
- ⁷⁹ V. V. Eremenko and A. I. Belyaeva, *Usp. Fiz. Nauk* **98**, 27 (1969) [*Sov. Phys.-Uspekhi* **12**, 320 (1969)].
- ⁸⁰ R. S. Metzger, M. Y. Chen, D. S. McClure and M. Lowe-Pariseau, *Phys. Rev. Lett.* **21**, 913 (1968).
- ⁸¹ W. J. Liang and A. D. Yoffe, *Phys. Rev. Lett.* **20**, 59 (1968).

- ⁸² W. C. Walker, D. M. Roessler and E. Loh, *Phys. Rev. Lett.* **20**, 847 (1968).
- ⁸³ H. Kanzaki and S. Sakuragi, *J. Phys. Soc. Jap.* **24**, 1184 (1968).
- ⁸⁴ A. F. Ron and D. F. Hornig, *J. Chem. Phys.* **39**, 1129 (1963).
- ⁸⁵ D. P. Craig and C. I. Small, *J. Chem. Phys.* **50**, 3827 (1969).
- ⁸⁶ I. S. Osad'ko, *Fiz. Tverd. Tela* **12**, 2123 (1970) [*Sov. Phys.-Solid State* **12**, 1686 (1971)].
- ⁸⁷ G. Nieman and G. W. Robinson, *J. Chem. Phys.* **39**, 1298 (1963).
- ⁸⁸ I. M. Lifshitz, *Usp. Fiz. Nauk* **83**, 617 (1964) [*Sov. Phys.-Uspekhi* **7**, 549 (1965)].
- ⁸⁹ É. I. Rashba, *Opt. Spektrosk.* **2**, 568 (1957).
- ⁹⁰ É. I. Rashba, *Fiz. Tverd. Tela* **4**, 3301 (1962) [*Sov. Phys.-Solid State* **4**, 2417 (1963)].
- ⁹¹ B.-Sh. Sommer and J. Jortner, *J. Chem. Phys.* **50**, 187 (1969).
- ⁹² V. L. Broude, A. I. Vlasenko, É. I. Rashba, and E. F. Sheka, *Fiz. Tverd. Tela* **7**, 2094 (1965) [*Sov. Phys.-Solid State* **7**, 1686 (1966)].
- ⁹³ C. Herring, *Fiz. Phys. Rev.* **52**, 361 (1937) (see also H. Jones, *Theory of Brillouin Zones and Electronic States in Crystals*, Interscience, 1960, Ch. 4).
- ⁹⁴ E. F. Sheka, *Opt. Spektrosk.* **29**, 78 (1970).
- ⁹⁵ V. L. Broude and M. I. Onoprienko, *ibid.* **8**, 815 (1960).
- ⁹⁶ R. E. Merrifield, *J. Chem. Phys.* **48**, 3693 (1968).
- ⁹⁷ M. R. Philpott, *J. Chem. Phys.* **47**, 2534, 4437 (1967); **51**, 2619 (1969).
- ⁹⁸ V. L. Broude, *Trudy IFTT AN SSSR*, No. 2, 1969.
- ⁹⁹ S. D. Colson, D. M. Hanson, R. Koppelman and G. W. Robinson, *J. Chem. Phys.* **48**, 2215 (1968).
- ¹⁰⁰ V. N. Vatulev, M. T. Shpak and N. I. Sheremet, *Materialy XV soveshchaniya po spektroskopii (Proc. 15th Conf. on Spectroscopy)*, Vol. 3, 468 (1963); *Opt. Spektrosk.* **16**, 577 (1964).
- ^{101a} A. R. Gee and G. W. Robinson, *J. Chem. Phys.* **46**, 2847 (1967).
- ^{101b} S. M. Kochubeĭ, *Prikl. spektrosk.* **7**, 74 (1967).
- ¹⁰² M. T. Shpak and E. F. Sheka, *Opt. spektrosk.* **8**, 66 (1960).
- ¹⁰³ M. Suzuki, T. Yokoyama and M. Ito, *Spectr. Acta* **24A**, 1091 (1968).
- ¹⁰⁴ E. F. Sheka, *Fiz. Tverd. Tela* **12**, 1167 (1970) [*Sov. Phys.-Solid State* **12**, 911 (1970)].
- ¹⁰⁵ M. S. Soskin, *Ukr. fiz. zh.* **7**, 180, 635 (1962).
- ¹⁰⁶ V. L. Broude and A. K. Tomashchik, *ibid.* **9**, 39 (1964).
- ¹⁰⁷ A. F. Prihot'ko, M. S. Soskin and A. K. Tomashchik, *Opt. Spektrosk.* **16**, 615 (1964).
- ¹⁰⁸ V. L. Broude, *ibid.* **24**, 475 (1968).
- ¹⁰⁹ V. A. Lisovenko and M. T. Shpak, *Fiz. Tverd. Tela* **9**, 356 (1967) [*Sov. Phys.-Solid State* **9**, 271 (1967)].
- ¹¹⁰ M. T. Shpak and N. I. Sheremet, *Opt. spektrosk.* **14**, 816 (1963); **17**, 694 (1964).
- ¹¹¹ S. V. Marisova, *ibid.* **22**, 566 (1967); *Ukr. fiz. zh.* **12**, 521 (1967).
- ¹¹² A. S. Davydov and É. N. Myasnikov, *Dokl. Akad. Nauk SSSR* **171**, 1069 (1966) [*Sov. Phys.-Dokl.* **11**, 1073 (1967)].
- ¹¹³ A. S. Davydov, *Phys. Stat. Sol.* **20**, 143 (1967).
- ¹¹⁴ A. S. Davydov and É. N. Myasnikov, *ibid.* **20**, 153 (1967).
- ¹¹⁵ É. N. Myasnikov, *Ukr. fiz. zh.* **12**, No. 9 (1967).
- ¹¹⁶ A. S. Davydov and E. F. Sheka, *Phys. Stat. Sol.* **11**, 877 (1965).
- ¹¹⁷ M. S. Brodin, S. V. Marisova and S. A. Shturkhet-skaya, *Ukr. fiz. zh.* **13**, 353 (1968).
- ¹¹⁸ V. N. Vatulev, *ibid.* **5**, 20 (1960).
- ¹¹⁹ T. N. Bolotnikova, L. A. Klimova, G. N. Nersesova, and L. F. Utkina, *Opt. spektrosk.* **21**, 420 (1966).
- ¹²⁰ L. F. Utkina, *Candidate's dissertation*, MGPI, Moscow, 1966.
- ¹²¹ M. S. Brodin and S. V. Marisova, *Opt. spektrosk.* **10**, 473 (1961); **19**, 235 (1965).
- ¹²² A. S. Davydov and A. A. Serikov, *Phys. Stat. Sol.* **42**, 603 (1970); **44**, 127 (1971).

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