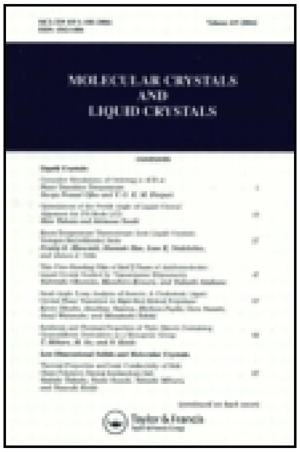


Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Combined Fermi-Davydov Resonance in Solid Solutions

M. P. Lisitsa [a] & A. M. Yaremko [a]

[a] Semiconductor Research Institute Ukrainian Academy of Sciences Kiev, U.S.S.R.

To cite this article: M. P. Lisitsa & A. M. Yaremko (1969): Combined Fermi-Davydov Resonance in Solid Solutions, Molecular Crystals, 6:3-4, 393-406

To link to this article: http://dx.doi.org/10.1080/15421407008083474

Molecular Crystals and Liquid Crystals. 1970. Vol. 6, pp. 393–406

Combined Fermi-Davydov Resonance in Solid Solutions

M. P. LISITSA and A. M. YAREMKO

Semiconductor Research Institute
Ukrainian Academy of Sciences
Kiev, U.S.S.R.

Received April, 25, 1969; *in revised form October* 13, 1969

Abstract—A combined Fermi-Davydov resonance in solid molecular solutions is considered. It is shown that migration of the energy of vibrational excitation can lead to an abnormal redistribution of intensities of the components of Fermi-doublet when higher order harmonics are dominant. The concentrational dependence of the ratio of the intensities of doublet components is investigated. At a certain value of the concentration, determined by parameters of the solvent and the dissolved substance, a sharp increase in the intensity of one of the doublet components can be observed. The basic conclusions of the theory are in agreement with the experiment.

Introduction

When Fermi resonance in an isolated molecule takes place, the intensity of the absorption band corresponding to the higher order transition can be smaller than or equal to the intensity of the band for the transition the order of which is lower by 1. Equality is valid when undisturbed levels exactly coincide.[1]

For the same quantum transitions in crystals the ratio of the intensities of the bands mentioned above can sometimes exceed unity. For example, a harmonic can be stronger than the fundamental which is in resonance with it. Such a phenomenon was observed experimentally. It was assumed[2] that such an anomaly arose because of the migration of excitation energy in a molecular lattice leading to intermolecular resonance of the Davydov type.[3] Thus, an intermixing of resonances inside and between molecules takes place.

Such a combined resonance was for the first time observed[4] and interpreted[5] for the spectra of CH_3I and CD_3I. It was shown[5] that if the intermolecular interaction was present, the Fermi-doublet could convert into a number of bands (4 in this case). In that paper the characteristic relations among the components of combined resonance were also obtained. But it did not touch on the question of the ratio of the intensities in those bands. We have considered this problem for pure crystals.[6] In the present communication a similar problem is solved for the more complicated case of solid solutions.

Energy of the System

We consider a solid solution where some of the molecules of the solvent are substituted for by molecules of the dissolved substance having accidentally degenerate states with corresponding wave functions of identical symmetry. Just this kind of state is liable to resonant interaction of the Fermi-type. Next, we assume that the solid solution constitutes a crystal the main region of which contains K cells. Each cell has σ differently orientated molecules, and N is a number of substitutions in any orientation.

If in the harmonic approximation an isolated impurity molecule could be characterized by two adjacent levels p[‡] and q, then in an anharmonic condition we get a new pair of more remote levels f and g. As experiment shows,[2] in vibrational spectra the value of the Fermi splitting for isolated molecules is often comparable with the value of the Davydov splitting for the molecular lattice (about several tens of cm^{-1}). Therefore, in zeroth approximation one can write down the following expression for the wave function of an excited impurity crystal

$$\Psi = \sum_{n\alpha f}^{N} a^{f}_{n\alpha}\, \varphi^{f}_{n\alpha} \prod_{K\lambda \neq n\alpha}^{K} \varphi^{0}_{K\lambda} \tag{1}$$

[‡] To be specific, we assume that a transition into p state gives a harmonic of lower order (basic harmonic, for example), whereas a transition into q state gives a harmonic having the order higher by 1 (for example, the first harmonic of the second normal oscillation).

The summation in (1) is made only for the impurity (active) molecules, while multiplication refers to the whole crystal; $\varphi_{n\alpha}^{f}$ represents a wave function of an isolated molecule situated in the n cell with an orientation α in the f excited state; $a_{n\alpha}^{f}$ are coefficients in the expression of Ψ function as a series in molecular functions. The wave function of the unexcited state has upper index " 0".

The wave function of the basis state of the crystal is

$$\Psi^0 = \prod_{m\beta}^{K} \varphi_{m\beta}^{0} \tag{2}$$

and the Hamiltonian of the system is

$$H = \sum_{s\nu}^{K} H_{s\nu} + \tfrac{1}{2} \sum_{s\nu \neq r\delta}^{K} V_{s\nu, r\delta} \tag{3}$$

where $H_{s\nu}$ is a Hamiltonian of an isolated molecule, $V_{s\nu,r\delta}$ the operator of the energy of interaction of molecules $s\nu$ and $r\delta$.

A solution of the Schrodinger equation gives for the excitation energy of the crystal

$$E = \sum_{n\alpha f}^{N} a_{n\alpha}^{*f} a_{n\alpha}^{f} \Delta\epsilon_{n\alpha}^{f} + \sum_{n\alpha fg}^{N} a_{n\alpha}^{*f} a_{n\alpha}^{g} \mathscr{D}_{n\alpha}^{fg} + \sum_{\substack{n\alpha \neq m\beta \\ fg}}^{N} a_{n\alpha}^{*f} a_{m\beta}^{g} M_{n\alpha,m\beta}^{f\,g} \tag{4}$$

where $\Delta\epsilon_{n\alpha}^{f}$ is an energy of excitation of isolated $n\alpha$ molecule into f state. Since all the active molecules are identical $\Delta\epsilon_{n\alpha}^{f} \equiv \Delta\epsilon^{f}$ does not depend upon indexes n and α; $M_{n\alpha,m\beta}^{fg}$ is a resonance term describing a transfer of excitation from molecule $n\alpha$ to molecule $m\beta$, the latter being in a g state which might be different from f. For $f = g$, $M_{n\alpha,m\beta}^{ff} = M_{n\alpha,m\beta}^{f}$ is the usual Davydov's resonance term.

$$\mathscr{D}_{n\alpha}^{fg} = \sum_{s\nu \neq n\alpha}^{K} \left[\int \varphi_{n\alpha}^{*f} \varphi_{s\nu}^{*0} V_{n\alpha,s\nu} \varphi_{n\alpha}^{g} \varphi_{s\nu}^{0} d\tau - \delta_{fg} \int \varphi_{n\alpha}^{*0} \varphi_{s\nu}^{*0} V_{n\alpha,s\nu} \varphi_{n\alpha}^{0} \varphi_{s\nu}^{0} d\tau\right] \tag{5}$$

which characterizes a change of energy of interaction between all the molecules in the crystal and $n\alpha$ caused by excitation of $n\alpha$ molecule; $\mathscr{D}_{n\alpha}^{fg}$ includes summation over the whole crystal, so it also does not depend upon $n\alpha$; i.e. $\mathscr{D}^{fg}_{n\alpha} \equiv \mathscr{D}^{fg}$. If the indexes f and g coincide, $\mathscr{D}^{ff} \equiv \mathscr{D}^{f}$ and we have a matrix element usual for the theory of molecular crystals.

Expression (4) was obtained for random distribution of impurity molecules in the cells of the basic lattice. The only condition was a uniform (at an average) distribution of active molecules. Besides, a normalizing condition was imposed upon the amplitudes:

$$\sum_{n\alpha f}^{N} a^{f}_{*n\alpha} a^{f}_{n\alpha} = 1 \tag{6}$$

The determination of coefficients $a^{f}_{n\alpha}$ from Eq. (4) is a rather difficult problem, so we shall use a simpler model assuming that impurity molecules form a sublattice points of which coincide with some points of the basic lattice. The distance between them we shall consider as a parameter, which can take various values. Thus we have two matching lattices with different translational vectors. A periodicity allows some simplification of (4).

Because of translational symmetry, $a^{f}_{n\alpha}$ can be chosen as

$$a^{f}_{n\alpha} = \frac{1}{\sqrt{N}} a^{f}_{\alpha} e^{i\mathbf{t}\mathbf{n}} \tag{7}$$

where N has its former value; $\mathbf{t}$ is a wave vector satisfying the usual periodicity condition $t_i = 2\pi g_i / N_i B_i$: B_i is a component of the translational vector of the sublattice; factor g_i determines one of the states in the energy band.

Using expressions (7) and (4) we get

$$E = \sum_{\alpha f g} \omega^{fg} a^{*f}_{\alpha} a^{g}_{\alpha} + \sum_{\alpha\beta, fg} M^{fg}_{\alpha\beta}(\mathbf{t}) a^{*f}_{\alpha} a^{g}_{\beta} \tag{8}$$

where

$$\omega^{fg} = \Delta\epsilon^{f} \delta_{fg} + \mathscr{D}^{fg} \tag{9}$$

$$M^{fg}_{\alpha\beta}(\mathbf{t}) = \sum_{m \neq n}^{N} M^{f\,g}_{n\alpha, m\beta} e^{i\mathbf{t}(\mathbf{m}-\mathbf{n})} \tag{10}$$

We shall be interested only in small $\mathbf{t}$-values, so all exponents in (10) can be considered as unity. Then $M^{fg}_{\alpha\beta}(\mathbf{t})$ will represent a sum of resonant terms of energy transfer from molecule $n\alpha$ to all the other molecules of the crystal. We consider one of these terms. In the dipole approximation

$$M^{fg}_{n\alpha,m\beta} = \frac{1}{R_m^3}\left\{(\mathbf{d}_\alpha^f\mathbf{d}_\beta^g) - 3(\mathbf{d}_\alpha^f\mathbf{e}_m)(\mathbf{d}_\beta\mathbf{e}_m)\right\} \tag{11}$$

where R_m is a distance between $n\alpha$ and $m\beta$ molecules; $\mathbf{e}_m$ is a unit vector directed along the line connecting these molecules; $\mathbf{d}_\alpha^f$, $\mathbf{d}_\beta^g$ are the dipole moments of isolated $n\alpha$ and $m\beta$ molecules correspondingly. If the active molecules are separated by $\mathscr{L}$ lattice constants of the basic lattice, then

$$R_m = \mathscr{L}r_m \tag{12}$$

where r_m is a parameter of basic lattice which does not depend upon $\mathscr{L}$.

Introduction of (12) into (11) gives

$$M^{fg}_{n\alpha,m\beta} = \frac{1}{\mathscr{L}^3 r_m^3}\left\{(\mathbf{d}_\alpha^f\mathbf{d}_\beta^g) - 3(\mathbf{d}_\alpha^f\mathbf{e}_m)(\mathbf{d}_\beta^g\mathbf{e}_m)\right\} \tag{13}$$

$1/\mathscr{L}^3 = C$ is the concentration of active molecules in the crystal. The rest of the expression (13) characterizes an interaction between the molecules number $n\alpha$ and $m\beta$ in a new lattice, the parameters of which are independent of concentration.

Factor C will appear in all terms of the sum (10), therefore

$$M^{fg}_{\alpha\beta}(\mathbf{t}) = CM^{\sim fg}_{\alpha\beta}(\mathbf{t}) \tag{14}$$

where $M^{\sim fg}_{\alpha\beta}(\mathbf{t})$ could be considered as a constant value independent of concentration " C".

Introducing (14) into (8) and varying the result in a_α^{*f} with a condition (6) taken into account we obtain a system of uniform algebraic equations

$$Ea_\alpha^f = \sum_{\beta g} a_\beta^g \mathscr{L}^{fg}_{\alpha\beta}(\mathbf{t}) \tag{15}$$

where

$$\mathscr{L}^{fg}_{\alpha\beta}(\mathbf{t}) = \omega^{fg}\delta_{\alpha\beta} + CM^{\sim fg}_{\alpha\beta}(\mathbf{t}) \tag{16}$$

determines an excitation spectrum of crystal and intensities of absorption bands. For $f = g$ and $C = 1$ the expression in (16) coincides with that usually employed in the theory of molecular crystals.

Band Intensities

The Intensity of an absorption band for dipole transitions is determined by the squared absolute value of the dipole moment of the corresponding transition. When a crystal is excited into state of energy E_τ (index τ will denote the roots of determinant of the system (15), the corresponding amplitudes will be $a_\alpha^f(\tau)$) this moment is equal to

$$\mathbf{d}(\tau) = \langle \Psi'(\tau) \mathbf{d} \Psi^0 \rangle \tag{17}$$

where

$$\mathbf{d} = \sum_{s\nu}^{K} \mathbf{d}_{s\nu} \tag{18}$$

$\mathbf{d}_{s\nu}$ is a dipole moment of $s\nu$ molecule. After the introduction of (1), (2), (7) and (18) into (17), we get

$$\mathbf{d}(\tau) = \sum_{\alpha f} \sqrt{N} a_\alpha^{*f}(\tau) \mathbf{d}_\alpha^f \tag{19}$$

where

$$\mathbf{d}_\alpha^f = \int \varphi_{n\alpha}^{*f} \mathbf{d}_{n\alpha} \varphi_{n\alpha}^0 d\tau$$

is a dipole moment of transition of $n\alpha$ molecule from a basic state into an excited one, namely f. Expression (19) was obtained under the assumption $\mathbf{t} \rightarrow 0$, i.e. for the case of long wave length.

We shall use the expression in (15) to determine the coefficients $a_\alpha^f(\tau)$ supposing that a molecule contains only two adjacent levels f and g, whereas a unit cell of the crystal contains only two molecules with different orientation. Thus we get a system of four uniform algebraic equations which has no general solution. Therefore it will be relevant to restrict ourselves to a consideration of some particular cases.

The separation between the f and g levels in an isolated molecule is determined by the value of the Fermi interaction V^F.

The splitting of the non-degenerate f level (or g level) associated with different orientations of the molecules within the unit cell is determined by the value of the intermoleculer interaction V^D. Let us consider the cases when $V^F \gg V^D$.

A. An overlapping of the wave functions corresponding to f and g states is much smaller than that of the wave functions corresponding to the Davydov components arising as a result of splitting of f and g states (i.e. $|a^f_\alpha|, |a^f_\beta| \gg |a^g_\alpha|, |a^g_\beta|$ for fixed f). Then we can omit the summation upon g in equations (15) and (6). So we have

$$Ea^f_\alpha = \sum_\beta a^f_\beta \mathscr{L}^f_{\alpha\beta}(\mathbf{t}) \tag{20}$$

$$\sum_\alpha a^{*f}_\alpha a^f_\alpha = 1 \tag{21}$$

For these conditions also instead of

$$|\mathbf{d}(\tau)|^2 = N|\sum_{\alpha f} a^{*f}_\alpha(\tau)\mathbf{d}^f_\alpha|^2 \tag{22}$$

the following expression will be valid for the squared absolute value of the dipole moment

$$|\mathbf{d}^f(\tau)|^2 = N|\sum_\alpha a^{*f}_\alpha(\tau)\mathbf{d}^f_\alpha|^2 \tag{22'}$$

Joint solution of the systems (20) and (21) gives the expressions for excitation energy of the crystal and for quantities $a^f_\alpha(\tau)$:

$$E^f_\pm = \tfrac{1}{2}(\mathscr{L}^f_{11} + \mathscr{L}^f_{22}) \pm \tfrac{1}{2}\sqrt{(\mathscr{L}^f_{11} - \mathscr{L}^f_{22})^2 + 4|\mathscr{L}^f_{12}|^2} \tag{23}$$

$$\begin{cases} a^f_1(+) = \cos\dfrac{\theta^f}{2} \\ a^f_2(+) = \sin\dfrac{\theta^f}{2} \end{cases} \quad \begin{cases} a^f_1(-) = -\sin\dfrac{\theta^f}{2} \\ a^f_2(-) = \cos\dfrac{\theta^f}{2} \end{cases} \tag{24}$$

where $a^f_\alpha(+)$ and $a^f_\alpha(-)$ refer to energies E^f_+ and E^f_- correspondingly; the value of θ^f has to be determined from the relation

$$tg\theta^f = \frac{2\mathscr{L}^f_{12}}{\mathscr{L}^f_{11} - \mathscr{L}^f_{22}} \tag{25}$$

Expressions for the second Fermi-component are similar. To obtain them it is enough to substitute index g in expressions (23)–(25) for index f.

Having introduced (24) into (19), we obtain values of the dipole moment for transitions into states $E^{f,g}_{+,-}$ namely

$$\begin{aligned} \mathbf{d}^{f,g}(+) &= \sqrt{N}\left(\cos\frac{\theta^{f,g}}{2}\,\mathbf{d}_1^{f,g} + \sin\frac{\theta^{f,g}}{2}\,\mathbf{d}_2^{f,g}\right) \\ \mathbf{d}^{f,g}(-) &= \sqrt{N}\left(-\sin\frac{\theta^{f,g}}{2}\,\mathbf{d}_1^{f,g} + \cos\frac{\theta^{f,g}}{2}\,\mathbf{d}_2^{f,g}\right) \end{aligned} \tag{26}$$

The choice of index (f or g) depends upon the origin of the level from the Fermi-doublet with Davydov splitting. If we take into account that $|\mathbf{d}_1^f| = |\mathbf{d}_2^f|$ then after an introduction of (24) into (22′) we obtain

$$\begin{aligned} |\mathbf{d}^{f,g}(+)|^2 &= N|\mathbf{d}^{f,g}|^2(1 + \cos\nu\sin\theta^{f,g}) \\ |\mathbf{d}^{f,g}(-)|^2 &= N|\mathbf{d}^{f,g}(1 - \cos\nu\sin\theta^{f,g}) \end{aligned} \tag{27}$$

ν here is the angle between the dipole moments of molecules of different orientation.

It is worth recalling that f and g levels result from p and q levels separated because of influence of anharmonicity. When exact resonance is present

$$\begin{aligned} \mathbf{d}^f &= \frac{1}{\sqrt{2}}\left(\mathbf{d}^p + \mathbf{d}^q\right) \\ \mathbf{d}^g &= \frac{1}{\sqrt{2}}\left(\mathbf{d}^p - \mathbf{d}^q\right) \end{aligned} \tag{28}$$

where $\mathbf{d}^p$ and $\mathbf{d}^q$ are dipole moments of transition of molecule from basic state into p and q states. In our case $|\mathbf{d}^p| \gg |\mathbf{d}^q|$ therefore $\mathbf{d}^f \cong \mathbf{d}^g$. Then it follows from Eq. (26) that for values θ^f and θ^g approaching one another, dipole moments $\mathbf{d}^f(+)$ and $\mathbf{d}^g(+)$ will have almost the same polarization as well as $\mathbf{d}^f(-)$ and $\mathbf{d}^g(-)$ whereas $\mathbf{d}^f(+)$ and $\mathbf{d}^f(-)$ will be normal to each other. Thus two couples of bands mutually orthogonal will be present in the absorption spectrum. If some transitions are forbidden, the spectrum will have less components.

Now we consider the ratio of intensities of bands with the same polarization. It will be

$$f_{\pm} = \frac{1 \pm \sin\theta^{f}\cos\nu}{1 \pm \sin\theta^{g}\cos\nu}; \tag{29}$$

A couple of bands corresponding to " + " sign will be polarised normally to that corresponding to " − ".

Formula (29) shows that for $\theta^f \pm \theta^g$ either $f_+ > 1$ or $f_- > 1$. This means that for one of the polarizations a component resulting from a harmonic of higher order will have greater intensity than another component. The surplus can not be essential since θ^f and θ^g are not very different. In cases when $\theta^f \gg \theta^g$, or when opposite unequality is true, the bands of identical polarization can not be distinguished.

From (16) and (25) an independence of θ^f upon concentration follows, i.e. the ratio of interest will be constant for all concentrations of impurity molecules (Fig. 1).

B. Now we turn to an opposite case, when ($|a_{\alpha}^{f}|$, $|a_{\alpha}^{g}| \gg |a_{\beta}^{f}|$, $|a_{\beta}^{g}|$ for fixed f). Under this condition the picture will be different, since an overlapping of the wave functions corresponding to the Fermi-components will be much stronger than that for the Davydov's components. Taking this into account, we can omit the summation upon β in equations (15), (6) and (22). The corresponding equations will have the forms

$$Ea_{\alpha}^{f} = \sum_{g} \mathscr{L}_{\alpha\alpha}^{fg}(\mathbf{t})a_{\alpha}^{g} \tag{30}$$

$$\sum_{g} a^{*g}_{\alpha} a_{\alpha}^{g} = 1 \tag{31}$$

$$|\mathbf{d}(\tau)|^2 = N \left| \sum_{f} a_{\alpha}^{*f}(\tau)\mathbf{d}_{\alpha}^{f} \right|^2 \tag{32}$$

Joint solution of (30) and (31) gives the excitation energy of the crystal $E_{\pm}^{\alpha}$ as well as the amplitudes $a_{\alpha}^{f}(\tau)$

$$E_{\pm}^{\alpha} = \tfrac{1}{2}(\mathscr{L}_{\alpha\alpha}^{ff} + \mathscr{L}_{\alpha\alpha}^{gg}) \pm \tfrac{1}{2}\sqrt{(\mathscr{L}_{\alpha\alpha}^{ff} - \mathscr{L}_{\alpha\alpha}^{gg})^2 + 4\,|\mathscr{L}_{\alpha\alpha}^{fg}|^2} \tag{33}$$

$$\begin{cases} a_\alpha^f(+) = \cos\dfrac{\theta^\alpha}{2} \\ a_\alpha^g(+) = \sin\dfrac{\theta^\alpha}{2} \end{cases} \qquad \begin{cases} a_\alpha^f(-) = -\sin\dfrac{\theta^\alpha}{2} \\ a_\alpha^g(-) = \cos\dfrac{\theta^\alpha}{2} \end{cases} \tag{34}$$

where $\mathscr{L}$ runs through the values 1, 2 corresponding to the number of molecules in a unit cell. The value of θ^α will be given by the relation

$$tg\theta^\alpha = \frac{2\mathscr{L}_{\alpha\alpha}^{fg}}{\mathscr{L}_{\alpha\alpha}^{ff} - \mathscr{L}_{\alpha\alpha}^{gg}} \tag{35}$$

Introduction of (34) into (19), where summation upon α is omitted, gives values of the dipole moments of the transitions into states with energy $E_\pm^\alpha$:

$$\begin{aligned} \mathbf{d}^\alpha(+) &= \sqrt{N}\left(\cos\frac{\theta^\alpha}{2}\mathbf{d}_\alpha^f + \sin\frac{\theta^\alpha}{2}\mathbf{d}_\alpha^g\right) \\ \mathbf{d}^\alpha(-) &= \sqrt{N}\left(-\sin\frac{\theta^\alpha}{2}\mathbf{d}_\alpha^f + \cos\frac{\theta^\alpha}{2}\mathbf{d}_\alpha^g\right) \end{aligned} \tag{36}$$

It is seen from (36) that $\mathbf{d}^\alpha(+)$ and $\mathbf{d}^\alpha(-)$ have the same polarization ($\mathbf{d}_\alpha^f \simeq \mathbf{d}_\alpha^g$) for any θ^α determined by Eq. (35). But they can be different in absolute values. Having substituted β for α in (33–36), we obtain values corresponding to molecules of another orientation. Polariaztion of the bands in case β will differ by an angle ν from polarization of the bands α. In accordance with (32) and (36) we have

$$\begin{aligned} |\mathbf{d}^\alpha(+)|^2 &= N|\mathbf{d}_\alpha^f|^2(1 + \sin\theta^\alpha) \\ |\mathbf{d}^\alpha(-)|^2 &= N|\mathbf{d}_\alpha^f|^2(1 - \sin\theta^\alpha) \end{aligned} \tag{37}$$

The ratio of intensities for bands with the same polarization will be

$$f^{\alpha,\beta} = \frac{\sqrt{1 + tg^2\theta^{\alpha,\beta}} + tg\theta^{\alpha,\beta}}{\sqrt{1 + tg^2\theta^{\alpha,\beta}} - tg\theta^{\alpha,\beta}} \tag{38}$$

where a choice of indexes α or β depends upon the orientation of the molecules for which the ratio of band intensities is considered.

If we introduce (16) into (35), we get the expression for $tg\theta^{\alpha}$

$$tg\theta^{\alpha} = \frac{2(\mathscr{D}^{fg} + CM^{\sim fg}_{\alpha\alpha})}{[(\Delta\epsilon^{f} + \mathscr{D}^{ff}) - (\Delta\epsilon^{g} + \mathscr{D}^{gg})] + C(M^{\sim ff}_{\alpha\alpha} - M^{\sim gg}_{\alpha\alpha})} \qquad (35')$$

In this case the value of $f^{\alpha,\beta}$ depends upon the concentration in a rather complicated way. Assigning some definite values to the parameters in (35′) we can obtain different forms for this dependence.

As a conclusion to our considerations we shall give an analysis of the limiting cases (A and B) described above. For convenience we introduce the following notation:

$$a^{fg} = (\Delta\epsilon^{f} + \mathscr{D}^{ff}) - (\Delta\epsilon^{g} + \mathscr{D}^{gg}) \qquad (39)$$

$$b^{fg}_{\alpha\alpha} = M^{\sim ff}_{\alpha\alpha} - M^{\sim gg}_{\alpha\alpha} \qquad (40)$$

The results of the analysis are presented in Figs. 1 and 2. It is evident from Fig. 1 (case A) that for one of the possible polarizations the intensity of the band corresponding to the higher order harmonic is greater than for another band. It is characteristic that for both cases the ratio of the intensities does not depend upon the concentration of the active molecules.

In the second limiting case (B) the corresponding dependences are more diverse. It follows from the theory of the spectra of

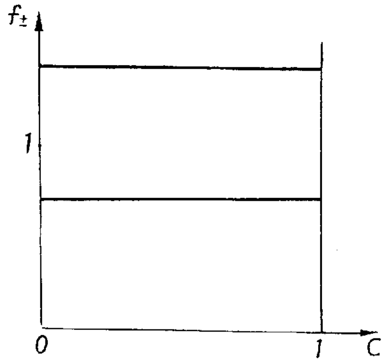
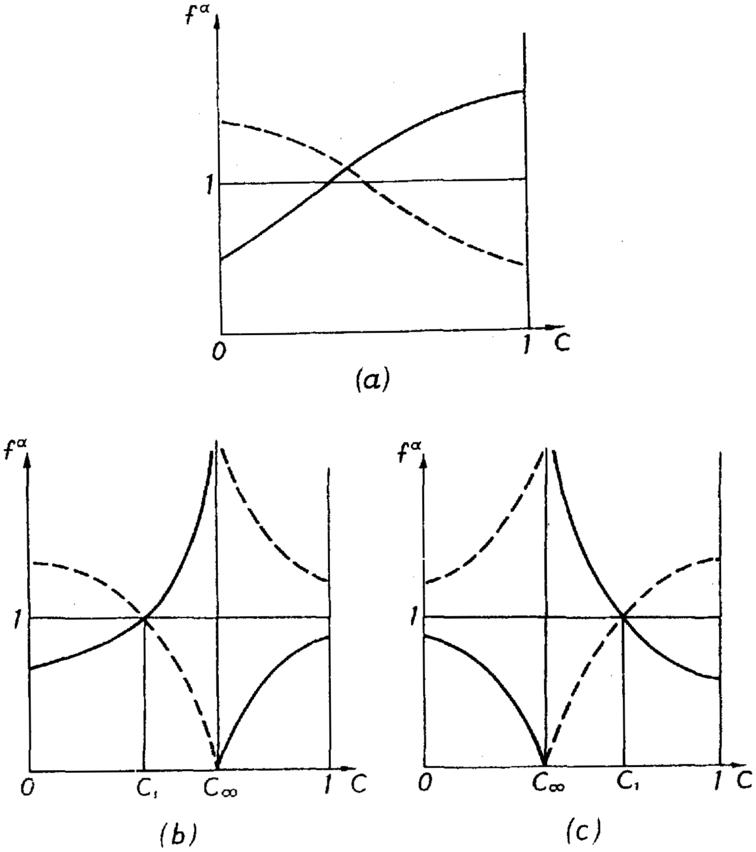


Figure 1. Concentration dependence of the intensity ratios of split components (case A).

pure molecular crystals that $\mathscr{D}^{f} < 0$. We assume that a similar inequality is valid for impurity lattices of the same type, i.e. $\mathscr{D}^{fg} < 0$. We also assume that $M^{\sim fg}_{\alpha\alpha} > 0$, $M^{\sim ft}_{\alpha\alpha} > 0$, $|\mathscr{D}^{fg}| < |M^{\sim fg}_{\alpha\alpha}|$ and that a^{fg} and $b^{fg}_{\alpha\alpha}$ can have either the same or the opposite sign. As a result we obtain several variants; Fig. 2 shows the main ones.

Fig. 2a corresponds to the cases: (1) $a^{fg} > 0$, $b^{fg}_{\alpha\alpha} \lesseqgtr 0 \, |a^{fg}| > |b^{fg}_{\alpha\alpha}|$ (solid line); (2) $a^{fg} < 0$, $b^{fg}_{\alpha\alpha} \gtrless 0$, $|a^{fg}| > |b^{fg}_{\alpha\alpha}|$ (dashed



(a)

(b)

(c)

Figure 2. Concentration dependence of the intensity ratio of split components (case B).

line). In both cases a concentration exists for which the intensities of the bands with the same polarization are equal. In both cases the intensities of the doublet components change monotonically with the concentration. Depending on the parameters indicated above, the ratio of the components either increases or decreases with increasing concentration.

If conditions $a^{fg} > 0$, $b^{fg}_{\alpha\alpha} < 0$, $|a^{fg}| < |b^{fg}_{\alpha\alpha}|$ are obeyed, we obtain the dependences shown in Fig. 2b, c (solid lines). The existence of two possibilities results from different numerical values of the parameters in formula (35′). It can be seen that for the case represented by Fig. 2b, $C_1 < C_\infty$, whereas for the case (Fig. 2c) $C_1 > C_\infty$. For concentration C_1 the ratio of intensities is equal to 1 (a numerator of expression (35′) is equal to zero). At concentration C_∞ (the denominator in (35′) is equal to zero) a very sharp change of the ratio of the intensities is observed, reminiscent of the behaviour of the dispersion of the refractive index in a resonance region when no losses are taken into account.

The dashed lines is Figs. 2b and c, represent the results for conditions $a^{fg} < 0$, $b^{fg}_{\alpha\alpha} > 0$, $|a^{fg}| < |b^{fg}_{\alpha\alpha}|$. They are similar to the former curves in general behaviour, but now the ratio of the intensities at $C = 0$ exceeds 1, whereas in the previous case it was less than 1.

Apparently some other possibilities could be discussed, however they would not give anything principly new in comparison with those already considered.

We have also left beyond our consideration the intermediate cases taking place at $|a^f_\alpha|$, $|a^f_\beta| \sim |a^g_\alpha|$, $|a^g_\beta|$; $V^F \gtrsim V^D$. Still, we can expect in these cases an anomaly in the distribution of the intensities of Fermi doublets caused by intermolecular resonance of the Davydov type.

It is interesting at this stage to make a comparison of the conclusions drawn with experimental results[5,7] where the combined resonance was studied. It follows from these papers that their results are close to case (A) of the present communication.

It is evident from Fig. 1 of reference (5) that the ratio of the component intensities of the combined resonance in CH_3I agrees well with formulae (29, 16) (as well as with the results of reference (6)). From the same figure and from Fig. 1 of reference (7) it follows that a change of the concentration of CH_3I causes a change of the positions and intensities of the bands of the quartet, as it should according to formulae (16, 23, 29).

Thus, there is good agreement between the reported experiments and the present communication which may be taken as an experimental confirmation of the theory; this agreement is also an additional argument in favor of the interpretation proposed in reference (5).

Acknowledgement

The authors are very much indebted to A. S. Davydov and his collaborators for a detailed discussion of the results presented here and for their critical remarks.

REFERENCES

1. Herzberg, G., *Infrared and Raman spectra of poljatomic molecules*, Van Nostrand Company, New York (1945).
2. Lisitsa, M. P., Striszevsky, V. L. and Halimonova, I. N., *Dokl. Acad. Sci. USSR*, Phys. ser. **145**, 1262 (1962).
3. Davydov, A. S., *Theory of molecular exitons* (translated by M. Kasha and M. Oppenheimer) McGraw-Hill Book Company, New York (1962).
4. Dows, D. A., *J. Chem. Phys.* **29**, 484 (1958).
5. Kopelman, R., *J. Chem. Phys.* **44**, 3547 (1966).
6. Lisitsa, M. P. and Yaremko, A. M., *Opt. Spectr.* **25**, 864 (1968).
7. Verderame, F. D. and Nixon, E. R., *J. Chem. Phys.* **45**, 3476 (1966).