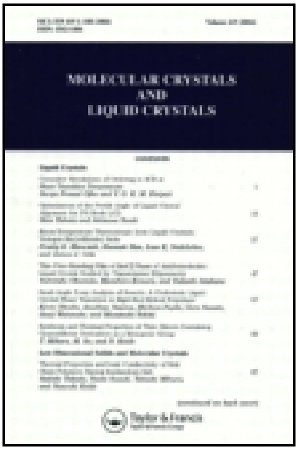
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 23 February 2013, At: 07:09
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Davydov Splitting and Fermi Resonance in Molecular Crystals

M. P. Lisitza [a] , N. E. Ralko [a] & A. M. Yaremko [a]
[a] Institute of Semiconductors, Academy of Sciences of the Ukrainian SSR, Kiev, 28, USSR

Version of record first published: 21 Mar 2007.

To cite this article: M. P. Lisitza , N. E. Ralko & A. M. Yaremko (1974): Davydov Splitting and Fermi Resonance in Molecular Crystals, Molecular Crystals and Liquid Crystals, 28:1-2, 161-166

To link to this article: http://dx.doi.org/10.1080/15421407408083160

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., Vol. 28, pp. 161-166
© Gordon and Breach Science Publishers, Ltd.
Printed in Dordrecht, Holland

Davydov Splitting and Fermi Resonance in Molecular Crystals

M.P. LISITZA, N.E. RALKO, A.M. YAREMKO

*Institute of Semiconductors,
Academy of Sciences of the
Ukrainian SSR, Kiev-28, USSR*

(*Received September 4, 1973*)

Exciton splitting in molecular crystals with several molecules in the elementary cell is considered in the Fermi resonance region. General expressions for the energy and the intensity of the bands are obtained at the arbitrary value of intramolecular state mixing. The conclusions drawn are used to analyze C_6H_5I crystal spectra, in crystals of which the weak Fermi resonance takes place.

In previous papers[1-3] the problem of exciton splittings in molecular crystals was examined in the presence of Fermi resonance. The theory of these phenomena was worked out with the assumption of strong intramolecular resonance interaction, i.e. mixing of the fundamental and the overtone (compound tone) when the intensities of the corresponding absorption bands become comparable. The conclusions drawn were experimentally confirmed by investigations of the vibrational spectrum of methyl iodide.[3-4]

However, the strong resonance conditions are not always realized, and therefore, the theoretical conclusions mentioned above are not always valid because the dipole moments of the transitions into the levels created as a result of the weak resonance interaction can differ from each other in an essential way.

In the present paper the general case of exciton splitting in molecular crystals is considered taking into account the Fermi resonance without any restrictions of the degree of intramolecular mixing of the states in resonance.

The equation of state of the crystal takes the form[†]

[†] We do not account for the complex nature of excitation which arises because of the Fermi resonance, which gives according to /5/ a correction to the transition dipole moment not exceeding 10-15%.

$$\sum_{g} (E\delta_{fg} - \omega^{fg})\, a^{g}_{\alpha} = \sum_{\beta g} M^{fg}_{\alpha\beta} (\vec{K})\, a^{g}_{\beta}$$

$$\omega^{fg} = \Delta\epsilon^{f}\delta_{fg} + D^{fg} \qquad (1)$$

Here E is the excitation energy, $M^{fg}_{\alpha\beta}(\vec{K})$ determines the resonance transmission of the excitation from the molecules of α-orientation in the f-state to the molecules of β-orientation in the g-state; $\Delta\epsilon^{f}$ is the excitation energy of the free molecule into the f-state. D^{fg} is the change of energy of interaction of one molecule with all other ones in the crystal caused by the change of the state of this molecule; a^{f}_{α} determines the probability of excitation of the α-molecule into f-state; δ_{fg} is the Kronecker's symbol; $\alpha = 1, \ldots, \sigma$, where σ is the number of molecules in the elementary cell.

The dipole moments of the transitions to the levels f and g $(\vec{d}^{f}, \vec{d}^{g})$ are determined by the linear combination of the dipole moments of the fundamental $(\vec{d})$ and the overtone or the compound tone $(\vec{d}_{ov})$. Since the inequality $|\vec{d}| >> |\vec{d}_{ov}|$ is usually valid, then

$$\vec{d} = \mu_f \vec{d} \qquad (2)$$

where the coefficients μ_f are determined by the character of intramolecular resonance interaction. Taking into account the dipole-to-dipole character of interaction between the molecules, we obtain

$$M^{fg}_{\alpha\beta}(\vec{K}) = \mu_f \mu_g M_{\alpha\beta}(\vec{K}) \qquad (3)$$

Substituting (3) into (1) gives

$$\sum_{g} \mu_f^{-1} (E\delta_{fg} - \omega^{fg})\, a^{g}_{\alpha} = \sum_{\beta g} \mu_g M_{\alpha\beta}(\vec{K})\, a^{g}_{\beta} \qquad (4)$$

As the right-hand part of Eq. (4) depends on α only, we can use the designation

$$\sum_{\beta g} \mu_g M_{\alpha\beta}(K)\, a^{g}_{\beta} = b_{\alpha} \qquad (4a)$$

then after transformations similar to those made in[2,3], we have instead of (4):

$$\sum_{\beta} M_{\alpha\beta}(K)\, B^{\rho}_{\beta} = E^{\rho} B^{\rho}_{\alpha} \qquad (5)$$

$$E^{\rho} \sum_{f'f} \mu_f \Delta^{f'f}(E) = \Delta(E) \qquad (6)$$

where $\Delta^{f'f}(E)$ is an algebraic supplement to the element $R^{fg} = \mu_f^{-1}(E\delta_{fg} - \omega^{fg})$ in the determinant $\Delta(E)$,

$$B^{\rho}_{\alpha} = \frac{b^{\rho}_{\alpha}}{\sqrt{\sigma}\,|b^{\rho}_{\alpha}|}; \qquad \sum_{\alpha} |B^{\rho}_{\alpha}|^{2} = 1;$$

Here E^{ρ} is the root of Eq. (5). The roots of Eq. (6) will be denoted by indexes $\rho\lambda$ similarly to the previous papers[2,3]. The intensities of the corresponding transitions to $E^{\rho\lambda}$ levels are determined by the expression

$$D^{\rho\lambda} = |\sum_{\beta} B^{\rho}_{\beta} \vec{d}_{\beta}|^2 \frac{|\sum\limits_{f'f} \Delta^{f'f}(E^{\rho\lambda})\,\mu_f|^2}{\sum\limits_{f} |\sum\limits_{f'} \Delta^{f'f}(E^{\rho\lambda})|^2}\,; \tag{7}$$

As seen, Eqs. (6) and (7) differ from the similar expressions in[2,3] by the presence of the coefficients μ_f which also enter in the algebraic supplements $\Delta^{f'f}$. It must be noted that the transformations made enable us to separate the exciton and the intramolecular parts independently of the number of molecules σ in the elementary cell and of the crystal symmetry. It is easy to see that in the case when the coefficients μ_f are equal to each other, then we come to the previous results corresponding to the strong resonance case. Eqs. (6) and (7) take the simpler and more descriptive form when concrete cases are considered. Specifically, we shall assume below that only two states take part in the resonance, which states correspond to the fundamental and the overtone (or the compound tone), i.e. index f has only two values (f = 1,2). The number of molecules in the elementary cell remains arbitrary. Then the expressions (6) and (7) take the following form:

$$\begin{aligned} \epsilon^{\rho}_{\pm} &= \tfrac{1}{2}\,[\delta + (\mu_1^2 + \mu_2^2)\,\chi^{\rho}\,] \pm \\ &\pm \tfrac{1}{2}\sqrt{[\delta + (\mu_1^2 - \mu_2^2)\chi^{\rho}\,]^2 + 4\mu_1^2\mu_2^2\,(\chi^{\rho})^2}\;; \end{aligned} \tag{6a}$$

$$D^{\rho}_{\pm} = |\sum_{\beta} B^{\rho}_{\beta}\, \vec{d}_{\beta}|^2\; \frac{[\,(\mu_1^2 + \mu_2^2)\,\epsilon^{\rho}_{\pm} - \mu_2^2\,\delta]^2}{\mu_1^2\,(\epsilon^{\rho}_{\pm})^2 + \mu_2^2\,(\epsilon^{\rho}_{\pm} - \delta)^2}\,; \tag{7a}$$

$$\chi^{\rho} = D_o + E^{\rho}\,;$$

where δ is the distance between the intramolecular levels after the resonance. Setting $\delta \equiv 1$, we can present all energy values in δ units; D_o is the energy of molecule interaction with the rest of the crystal when its fundamental is excited, indexes '+' and '–' correspond to two values of λ. The value $\epsilon^{\rho}_{\pm}$ is connected with the solution of Eq. (6) by the relation

$$\epsilon^{\rho}_{\pm} = E^{\rho}_{\pm} - \omega^{22} + \mu_2^2\,D_o\,;$$

Eqs. (5), (6a), and (7a) completely determine the character of the exciton spectrum of the crystal, i.e. the position, polarization and intensity of the bands in the presence of Fermi resonance. The general conclusions about the peculiarities of the spectrum remain the same as those in[2,3], but the distribution of the intensities and the position of the maxima depend upon the coefficients μ_1 and μ_2. Formulas (6a) and (7a) can be rewritten in more convenient form:

$$\epsilon^{\rho}_{\pm} = \frac{1}{2} + G_{\pm}(\chi^{\rho}, \mu_1, \mu_2); \tag{6b}$$

$$D^{\rho}_{\pm} = |\sum_{\beta} B^{\rho}_{\beta} \vec{d}_{\beta}|^2 F(\epsilon^{\rho}_{\pm}, \mu_1, \mu_2); \tag{7b}$$

Functions $G_{\pm}(\chi, \mu_1, \mu_2)$ for the values of $\mu_2 = 1/2, \mu_1 = \sqrt{3}/2$ (the intensities of the corresponding transitions differ by a factor of 3)^2 are shown in Figure 1. Each of these functions $G_+(\chi)$ and $G_-(\chi)$ has two asymptotic lines: a horizontal $G = -\frac{1}{2} \cdot \frac{\mu_1^2 - \mu_2^2}{\mu_1^2 + \mu_2^2}$, and an inclined $G = (\mu_1^2 + \mu_2^2)\chi + \frac{1}{2}\frac{(\mu_1^2 - \mu_2^2)}{(\mu_1^2 + \mu_2^2)}$, the functions are different dependence on the value of χ, as it is seen from Figure 1a.

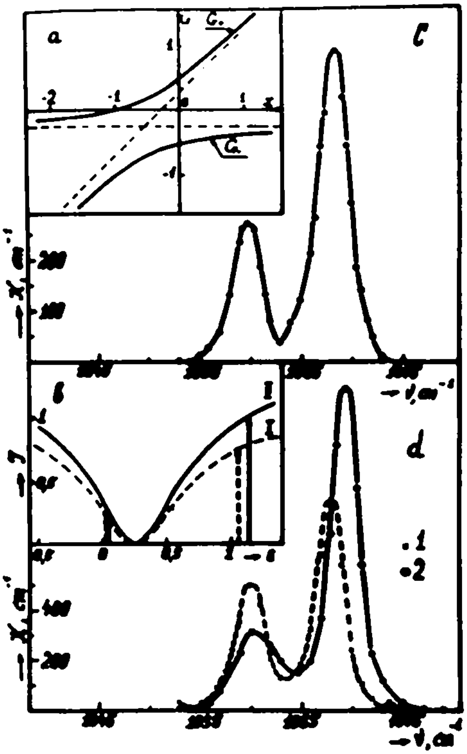


FIGURE 1. Absorption of iodo-benzene in the region of the Fermi-Davydov quartet: (a) Functions $G_{\pm}(\chi)$ determining the position of the quartet components in relation to the point $\epsilon = \frac{1}{2}$. (b) Theoretical distribution of the intensities in the case of a superposition of the exciton splitting and the weak Fermi resonance. (c) Absorption spectrum in a natural light, T = −180°C. (d) Absorption spectra in the polarized light; 1 and 2 correspond to orthogonal polarization of the incident light (T = −180°C).

---

[2] For the case of the Fermi resonance, $\mu_1^2 + \mu_2^2 = 1$.

The function $F(\epsilon, \mu_1, \mu_2)$ for the same values of μ_1 and μ_2 is presented by curve I in Figure 1b. Unlike the case of strong resonance, the minimum of this function does not coincide with the point $\epsilon = 1/2$, being removed from it to the side of $\epsilon = 0$. The shift of the minima from the point $\epsilon = 1/2$ is larger, the larger the difference between μ_1 and μ_2.

The theoretical conclusions obtained were used for the analysis of the experimental results for iodo-benzene which is apparently characterized by weak intramolecular resonance[7] in the region of 1050-1100 cm^{-1}. The evidence for this is, on the one hand, an essential difference between the intensities of the doublet in the liquid phase, and, on the other hand, a small Fermi splitting (~8 cm^{-1}) and, consequently, a small anharmonicity constant.

In spite of the fact that the unit cell of iodo-benzene contains 8 molecules[8], group theory analysis shows that each non-degenerate intramolecular vibration in the infra-red absorption spectra must be split into three Davydov's components polarized in three orthogonal directions corresponding to the crystallographic axes $\vec{a}, \vec{b}, \vec{c}$.[3] Therefore, one should expect to find six polarized bands in the region of the Fermi doublet. In addition, it is necessary to take into account that the single crystal grown in thin cell, apparently, has a tendency to grow in the shape of a flake normal to one of the crystallographic axes, which is confirmed by the data of reference[9] and by our results obtained when we studied the Davydov-splitting in chloro-benzene[10]. Hence, we expect to find again only four bands instead of six in the spectrum of iodo-benzene crystal, the bands being polarized in pairs in orthogonal directions.

For the experimental exposition of the multiplet structure in the region of the Fermi resonance, the investigation of the infra-red absorption of iodo-benzene crystal in polarized light was made. Single crystals were obtained by slow freezing of the liquid layer in the NaCl cell placed in a liquid nitrogen cryostat. As a polarizer, the polarizing grate on a polyethylene substrate was used. The transmission spectra were recorded by spectrometer UR-10. The spectral width of the slit in the region of 1000 cm^{-1} was 2.3 $cm.^{-1}$

The structure of the spectrum in natural light (Figure 1c) does not differ from that observed earlier[7]. Measurements in polarized light permit the observation of the two doublets of bands with the orthogonal polarization. If the exciton splitting for one of the Fermi components is 1.5 cm^{-1}, then for the other it apparently does not exceed 0.5 cm^{-1} (i.e. is smaller than the error of the apparatus), so that the relative shift of this band is not observed when the polarization of the incident light is changed.

Peculiarities of the exciton spectrum found experimentally in the Fermi re-

---

[3] These conslusions can be easily obtained if we draw the correlation diagram, taking into account the facts that the space group of the crystal is $D_2^{14}\ h'^{8'}$, the group of the site symmetry is $C_1\ ^{9'}$, and the symmetry of the molecule of iodobenzene is $C_{2\nu}$.

sonance region can be qualitatively explained on the basis of the theory developed above. Indeed, the position of the bands with the same polarization is determined by the functions G_+ (χ) and G_- (χ) taken at the point $\chi^\rho = D_0 + E^\rho$ (Figure 1a). In the case considered, the exciton splitting ($\lesssim$ 1.5 cm^{-1}) is small in comparison with the Fermi one (~ 8-9 cm^{-1}), so the position of the exciton bands is determined by the behaviour of the functions G_+ and G_- in the vicinity of the point x = O. Their derivatives at the point mentioned are correspondingly: G_+' $(O) = \mu_1^2$, G_-' $(O) = \mu_2^2$. Therefore, when the inequality $\mu_2^1 > \mu_2^2$ is valid, the function G_- is almost horizontal while the function G_+ sharply increases. This will lead to the situation where the exciton splitting in one pair from the quartet of Fermi-exciton bands will be essentially bigger than in the other pair of bands. Just this is observed in the spectrum of solid iodobenzene (Figure 1b). The distribution of the intensities in such a quartet calculated from the theory is illustrated by Figure 1b. Because of the difference between μ_1 and μ_2, one of the Davydov's doublets essentially exceeds the other one by intensity, in distinction from the case of strong resonance. It is easy to see that the intensity distribution in the quartet of iodo-benzene investigated also agrees qualitatively with that theoretically predicted for the case of a weak intramolecular resonance.

References

1. M.P. Lisitza, A.M. Yaremko, *J. Mol. Cryst. and Liq. Cryst.*, 6, 393, 1970.
2. M.P. Lisitza, N.E. Ralko, A.M. Yaremko, *Phys. Lett.*, 40A, 329, 1972.
3. M.P. Lisitza, A.M. Yaremko, N.E. Ralko, *Opt. i spectr.* 35, 1104, 1973.
4. R. Kopelman, *J. Chem. Phys.*, 44, 3547, 1966.
5. V.M. Agranovitch, I.I. Lalov. *Fiz. Tverdogo Tela*, 13, 1033, 1971.
6. G. Herzberg. *Vibrational and Rotational Spectra of Polyatomic Molecules*. D. Van Nostrand, New York, 1966.
7. M.P. Lisitsa, V.L. Strizhevski, I.N. Khalimonova. *Dokl. Akad. Nauk USSR*, 145, 1262. 1962.
8. P.E. Henshaw, *Acta Crystallogr.*, 14, 1080, 1961.
9. G.V.Klimusheva, A.F. Prichodko, G.M. Soroka, *Opt. i spectr.*, 25, 367, 1968.
10. M.P. Lisitsa, N.E. Ralko, A.M. Yaremko, *Ukr. Fiz. Zhurn.* 19, 335, 1974.