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

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Version of record first published: 28 Mar 2007.

To cite this article: M. Lisitsa & A. M. Yaremko (1972): The Temperature Dependence of the Absorption Bands Intensities of the Spectra of Molecular Crystals at Fermi Resonance I. The Relation of the Intensities in Maxima of the Absorption Bands, Molecular Crystals and Liquid Crystals, 18:3-4, 297-307

To link to this article: http://dx.doi.org/10.1080/15421407208083600

Molecular Crystals and Liquid Crystals. 1972. Vol. 18, pp. 297–307

Printed in Great Britain

The Temperature Dependence of the Absorption Bands Intensities of the Spectra of Molecular Crystals at Fermi Resonance

I. The Relation of the Intensities in the Maxima of the Absorption Bands

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Received July 25, 1971; *in revised form January* 25, 1972

Abstract—The influence of temperature on the components of the Fermi-doublet in molecular crystals is studied. It is shown that the presence of the resonance interaction of the energy states leads to the shape of the absorption curve different from the Lorentzian. In the case of weak exciton–phonon coupling, both the doublet components grow in intensity with the reduction of temperature, but their relative behaviour can be different from each other. In particular, an anomalous intensity distribution between the components of the doublet can take place, when the band corresponding to the overtone will be stronger than the band for oscillation of the fundamental.

1. Introduction

When studying the temperature dependence of the absorption spectra, one usually examines a single band shape which is determined by the interaction of the electron transition or the intromolecular oscillation with the lattice vibrations. Depending on the degree of this interaction, one obtains Lorentzian or Gaussian shapes, slightly distorted on account of the frequency dependence of the members determining the half-width of the band.

Much more often one can indicate in the spectrum the groups of closely situated bands with the mutual influence of the latter. Notwithstanding the close location, the separate components of the doublets and the multiplets can have different temperature dependence.† Thus, it is necessary to investigate the temperature influence upon such groups of bands to find out the characteristics of the crystal leading to the different temperature behaviour of the components mentioned. The theoretical consideration of the problem is usually made in adiabatic approximation, when the system of particles composing the crystal is divided into two sub-systems—a fast and a slow one. At zero approximation, the slow system can be considered as an immobile one, its motion to be taken into account later. The criterion for the adiabatic case is the relation $\sqrt{m/M} \ll 1$ where m and M are the masses of the particles of the slow and the fast sub-system correspondingly. This criterion takes place when the forces of the same order act between the particles of the different sub-systems and inside each sub-system (the molecule of hydrogen, the electrons in semiconductors and in metals). But if the forces in the sub-systems are essentially different, then the criterion of the adiabatic case will be the relation $\alpha\, \omega_s \ll \omega_f$, ω_s being the frequency of the slow sub-systems, ω_f that of the fast one.⁽¹⁾ The value of $\alpha < 1$ so that one should not demand a strong inequality to be held. In this latter form the criterion of adiabatic case can be applied to the molecular crystals when intramolecular vibrations are examined.

Molecular crystals are formed of particles having complicated internal structure. These particles in the lattice can be characterized by purely internal motions ($\omega_f \sim 800 \div 3500$ cm^{-1}) as well as by shifts of a molecule as a whole (a rotation, a translation) representing the lattice vibrations ($\omega_s \lesssim 100$ cm^{-1}).⁽²,³⁾ The ratio of the frequencies of intermolecular to intramolecular vibrations is $\omega_s/\omega_f \sim (3 \div 12)\, 10^{-2}$ therefore the account of the influence of the lattice upon intramolecular vibrations in adiabatic approximation will be adequate.

2. The Dielectric Constant

The losses at the propagation of the electromagnetic wave through the substance are determined by the imaginary part of the dielectric constant which obvious expression can be obtained by analogy to the paper.⁽⁴⁾ In the case of a plane electromagnetic wave, the crystal

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† The doublets, triplets etc. appearing for the reason of the presence of the Fermi resonance and of the Davydov resonance, are of particular interest.

properties can be conveniently characterized by the complex transversal tensor $\epsilon^{\perp}(\mathbf{Q},\omega)^{(5,6)}$ to be found from the relation

$$\mathbf{P}(\mathbf{r},t) = \tfrac{1}{2}\left\{\frac{\epsilon^{\perp}(\mathbf{Q},\omega)-1}{4\pi}\mathbf{E}_0 \exp\left[i(\mathbf{Qr}-\omega t)\right] + \text{c.c.}\right\} \qquad (1)$$

where $\mathbf{P}(\mathbf{r},t)$ is the specific electrical momentum, $\mathbf{E}_0$ the amplitude of the incident wave, $\mathbf{Q},\omega$ the wave vector and the frequency of the wave falling on the crystal.

The operator of interaction of the emission with the crystal in representation of secondary quantization$^{(7,4)}$ has a form

$$V(t) = -\frac{\sqrt{N}}{2\omega}\sum_{f}\{\omega^{f}(\mathbf{E}_0\mathbf{d}^{f})(a_{\mathbf{Q}}^{+f} - a^{f}_{-\mathbf{Q}})\exp(-i\omega t + \eta t) + \text{c.c.}\} \qquad (2)$$

if we confine ourselves to the long wavelength approximation. Here N is the number of molecules in the principal region for cycling (we assume that the elementary cell contains one molecule) $\eta \to +0$ is a small positive value determining the adiabaticity of application of the interaction, ω^{f} and $\mathbf{d}^{f}$ are the frequency and the dipole momentum for transition from the main into the excited state, $a_{\mathbf{Q}}^{+f}$ and $a_{\mathbf{Q}}{}^{f}$ are the operators of appearance and of disappearance of the excitations of the frequency ω^{f} and of wave vector $\mathbf{Q}(\hbar = 1)$, f is an index enumerating closely located levels. In a similar way the operator of specific electrical momentum can be written in representation of secondary quantization:

$$\mathbf{P}_{\mathbf{n}} = \frac{1}{v\sqrt{N}}\sum_{f,\mathbf{k}}\mathbf{d}^{f}(a_{\mathbf{k}}^{+f}\mathrm{e}^{-i\mathbf{kn}} + a_{\mathbf{k}}{}^{f}\mathrm{e}^{i\mathbf{kn}}) \qquad (3)$$

where v is the volume of the elementary cell, $\mathbf{k}$ the vector of the inverted lattice, $\mathbf{n}$ the number of the cell. The average value of the operator of specific electrical momentum should be found with the help of the density matrix of the system

$$\langle\mathbf{P}_{\mathbf{n}}(t)\rangle = Sp\{\rho(t)\mathbf{P}_{\mathbf{n}}\} \qquad (4)$$

where

$$\rho(t) = \rho_0 - i\int_{-\infty}^{t}\exp\{iH(\tau - t)\}[V(\tau),\rho_0]\exp\{-iH(\tau - t)\}\,\mathrm{d}\tau \qquad (5)$$

$[V,\rho_0]$ the commutator of two operators V and ρ_0, ρ_0 is the operator of the density matrix for the system of particles in absence of electromagnetic field, H the hamiltonian of the same system, $\rho(t)$

the operator of the density matrix at the moment of time t after the application of an external electromagnetic field.

When we introduce (2), (3) and (5) into (4), we get the final expression for the average value of the specific momentum. At this point, we take into account the closeness of the levels, so that in the zeroth approximation the following relations will be held.

$$[a_{\mathbf{k}}^{+f'}(0), a_{\mathbf{k}}{}^{f}(t)] \sim [a_{\mathbf{k}}^{+f}(0), a_{\mathbf{k}}{}^{f}(t)] \tag{6}$$

$$[a_{\mathbf{k}'}^{+f'}(0), a_{\mathbf{k}}^{+f}(t)] \simeq [a_{\mathbf{k}'}^{f}(0), a_{\mathbf{k}}{}^{f}(t)] = 0 \tag{6a}$$

In this approximation

$$\langle \mathbf{P}_{\mathbf{n}}(t) \rangle = -\frac{1}{2\omega v} \sum_{ff'} \omega^{f} (\mathbf{E}_0 \mathbf{d}^{f}) \mathbf{d}^{f'} \{ G_r^{ff'}(\mathbf{Q},\omega) \exp[i(\mathbf{Qn} - \omega t)] + \mathrm{c.c.} \} \tag{7}$$

Where $G_r^{ff'}(\mathbf{Q},\omega)$ is the Fourier-component of the delayed Green-function, which is determined by the relation

$$G_r^{ff'}(\mathbf{Q},\tau) = -i\theta(\tau) \langle [a_{\mathbf{Q}}{}^{f}(\tau), a_{\mathbf{Q}}{}^{+f_0}(0)] \rangle \tag{8}$$

Let the expression for the specific momentum to be represented as a sum of two components

$$\mathbf{P}_{\mathbf{n}}(t) = \langle \mathbf{P}_{\mathbf{n}}(t) \rangle + \tfrac{1}{2} \{ \beta_0{}^{\perp} \mathbf{E}_0 \exp[i(\mathbf{Qn} - \omega t)] + \mathrm{c.c.} \} \tag{9}$$

where the first member in the right-hand part describes the contribution into the specific momentum of the excitation of the f levels, this member is determined by the formula (7). The second member will be a smooth function of the frequency in this region, taking account of all the other excited states. Then we can easily obtain an expression for the transversal tensor of the dielectric constant

$$\epsilon_{xy} - \delta_{xy} = 4\pi\beta_{0,xy}^{\perp} - \frac{4\pi}{\omega v} \sum_{ff'} \omega^{f} d_x{}^{f} d_y^{f'} G_r^{ff'}(\mathbf{Q},\omega) \tag{10a}$$

Having confined ourselves to the frequency region $\omega \sim \omega^{f}$ and neglecting the participation of the rest of the transitions in the absorption, we get the following expression for the imaginary part of $\epsilon_{xx}^{\perp}(\mathbf{Q},\omega)$

$$\mathrm{Im}\, \epsilon_{xx}^{\perp}(\mathbf{Q},\omega) = -\frac{4\pi}{\omega v} \sum_{ff'} \omega^{f} d_x{}^{f} d_x^{f'} \,\mathrm{Im}\, G_r^{f'f}(\mathbf{Q},\omega) \tag{10b}$$

This expression determines the energy losses at propagation of the electromagnetic wave through the crystal.(4,8) It is seen from the expression that the losses depend not only on one Green-function but on a set of functions as well as on all the dipole momenta of the transitions into the levels f. When f has only one value, then the expression for $\epsilon_{xy}^{\perp}$ will coincide with that given in Ref. 4. Thus, to determine the absorption, we have to calculate the complete set of Green-functions.

3. The Green-function

The delayed Green-function is determined by the expression (8). It satisfies a certain time-dependent equation whose solution will be looked for by the method of splintering of the chains of equations.(9) At that we assume a small interaction between the lattice vibrations and the excitons caused by the excitation of intramolecular vibrations. In adiabatic approximation we can express the hamiltonian of the crystal as a sum of three terms, similarly to Ref. 10:

$$\begin{aligned} H = &\sum_{\mathbf{k},f,g} z^{fg}(\mathbf{k}) a_{\mathbf{k}}^{+f} a_{\mathbf{k}}{}^{g} + \sum_{s,\mathbf{q}} \Omega_s(\mathbf{q}) b_{s,\mathbf{q}}^{+} b_{s,\mathbf{q}} \\ &+ \frac{1}{\sqrt{N}} \sum_{\substack{\mathbf{k},\mathbf{q},s,\\ f,g}} F_s^{fg}(\mathbf{k},\mathbf{q}) a_{\mathbf{k}+\mathbf{q}}^{+f} a_{\mathbf{k}}{}^{g} (b_{s,\mathbf{q}} + b_{s,-\mathbf{q}}^{+}) \end{aligned} \tag{11}$$

where

$$z^{fg}(\mathbf{k}) = \Delta\epsilon^f \delta_{fg} + D^{fg} + \tilde{M}^{fg}(\mathbf{k}) \tag{12a}$$

$$F_s^{*fg}(\mathbf{k},\mathbf{q}) = F_s^{gf}(\mathbf{k}+\mathbf{q}, -\mathbf{q}) \tag{12b}$$

and the members of the sum (11) will be the operators of excitons, phonons and of exciton–phonon interaction correspondingly; $\Delta\epsilon^f$ is the energy of excitation of a free molecule into f state, D^{fg} and $\tilde{M}^{fg}$ describe the resonant energy transfer among the molecules of the crystal†, δ_{fg} is the Kronecker's symbol, $\mathbf{q}$ the vector of the inverted lattice, s enumerates the branches of lattice vibrations, $b_{s,\mathbf{q}}^{+}$ and $b_{s,\mathbf{q}}$ are the operators of appearance and disappearance of phonons of the type $s,\mathbf{q}$, $\Omega_s(\mathbf{q})$ are the frequencies of lattice vibrations. When composing the chains of the equations for the Green-function, we shall need the derivatives of the operators of appearance and of disappearance entering the equation (11). We have

$$i\partial_t a_{\mathbf{k}}{}^{f} = \sum_{g'} z^{fg'}(\mathbf{k}) a_{\mathbf{k}}{}^{g'} + \frac{1}{\sqrt{N}} \sum_{g',s',\mathbf{q}'} F_{s'}^{*g'f}(\mathbf{k},\mathbf{q}') a_{\mathbf{k}+\mathbf{q}'}^{g'} (b_{s',-\mathbf{q}'} + b_{s',\mathbf{q}'}^{+}) \tag{13a}$$

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† More complete description is given in Ref. 11.

$$i\partial_t a_{\mathbf{k}}^{+f} = -\sum_{f'} z^{f'f}(\mathbf{k})a_{\mathbf{k}}^{+f'} - \frac{1}{\sqrt{N}}\sum_{f',g',s'} F_s^{f'f}(\mathbf{k},\mathbf{q}')a_{\mathbf{k}+\mathbf{q}'}^{+f'}(b_{s',\mathbf{q}'} + b_{s',-\mathbf{q}'}) \tag{13b}$$

$$i\partial_t b_{s,\mathbf{q}} = \Omega_s(\mathbf{q})b_{s,\mathbf{q}} + \frac{1}{\sqrt{N}}\sum_{f',g',\mathbf{k}'} F_s^{f'g'}(\mathbf{k}',-\mathbf{q})a_{\mathbf{k}'-\mathbf{q}}^{+f'}a_{\mathbf{k}'}^{g'} \tag{13c}$$

$$i\partial_t b_{s,\mathbf{q}}^{+} = -\Omega_s(\mathbf{q})b_{s,\mathbf{q}}^{+} - \frac{1}{\sqrt{N}}\sum_{f',g',\mathbf{k}'} F_s^{f'g'}(\mathbf{k}',\mathbf{q})a_{\mathbf{k}+\mathbf{q}}^{+f'}a_{\mathbf{k}'}^{g'} \tag{13d}$$

We write the time-dependent equation for the Green-function

$$i\partial_t G_r^{ff_0}(\mathbf{k},t) = \delta(t)\delta_{ff_0} - i\theta(t)\langle[i\partial_t a_{\mathbf{k}}{}^f(t), a_{\mathbf{k}}^{+f_0}(0)]\rangle \tag{14}$$

Having introduced (13a) into (14), we get the equation including the Green-function of the higher order

$$P_{1s'}^{g'f_0}(\mathbf{k}+\mathbf{q}',\mathbf{k}) = -i\theta(t)\langle[a_{\mathbf{k}'+\mathbf{s}'}^{g'}b_{s',\mathbf{q}'};\, a_{\mathbf{k}}^{+f_0}]\rangle \tag{15a}$$

$$P_{2s'}^{g'f_0}(\mathbf{k}+\mathbf{q}',\mathbf{k}) = -i\theta(t)\langle[a_{\mathbf{k}+\mathbf{q}'}^{g'}b_{s',-\mathbf{q}'};\, a_{\mathbf{k}}^{+f_0}(0)]\rangle \tag{15b}$$

A similar procedure can be applied to (15a) and (15b) to get the Green-function containing four operators. They will have more complicated form than that in case of one level, since the indexes f, f_0 to etc. will appear characterizing the excited state of a molecule. To get the temperature dependence of the Fermi-doublets, it will be enough to close the chain of equation at this stage. It is convenient then to use the Fourier-components to get a system of algebraic equations for the Green-functions;

$$\sum_{g'}[\omega\delta_{fg'} - z^{fg'}(\mathbf{k})]G_r^{g'f_0}(\mathbf{k},\omega) = \delta_{ff_0}$$
$$+\frac{1}{\sqrt{N}}\sum_{g',s',\mathbf{q}'} F_{s'}^{*g'f'}(\mathbf{k},\mathbf{q}')[P_{1s'}^{g'f_0}(\mathbf{k},\mathbf{q}',\omega) + P_{2s'}^{g'f_0}(\mathbf{k},\mathbf{q}',\omega)] \tag{16a}$$

$$\sum_{f'}\{[\omega + \Omega_{s'}(\mathbf{q}')]\delta_{f'g'} - z^{g'f'}(\mathbf{k}+\mathbf{q}')\}P_{1s'}^{f'f_0}(\mathbf{k},\mathbf{q}',\omega)$$
$$= \frac{1}{\sqrt{N}}\sum_{f'} \nu_{s',\mathbf{q}'}F_{s'}^{g'f'}(\mathbf{k},\mathbf{q}')G_r^{f'f_0}(\mathbf{k},\omega). \tag{16b}$$

$$\sum_{f'}\{[\omega - \Omega_{s'}(\mathbf{q}')]\delta_{f'g'} - z^{g'f'}(\mathbf{k}+\mathbf{q}')\}P_{2s'}^{f'f_0}(\mathbf{k},\mathbf{q}',\omega)$$
$$= \frac{1}{\sqrt{N}}\sum_{f'} (1 + \nu_{s',\mathbf{q}'})F_{s'}^{g'f'}(\mathbf{k},\mathbf{q}')G_r^{f'f_0}(\mathbf{k},\omega) \tag{16c}$$

Here $\nu_{s',\mathbf{q}'}$ is the average occupation number for phonons. The equations (16) are obtained in assumption that the occupation numbers of excitons are small: $n_{\mathbf{k}} \ll \nu_{s,\mathbf{q}}$. From the expressions (16b) and (16c) we determine P_1 and P_2. To do this, we introduce the notations

$$z^{g'f'}_{1,\pm}(\mathbf{k}+\mathbf{q}',\omega) = [\omega \pm \Omega_{s'}(\mathbf{q}')]\delta_{g'f'} - z^{g'f'}(\mathbf{k}+\mathbf{q}') \tag{17a}$$

$$\Delta_{1,\pm}(\mathbf{k}+\mathbf{q}',\omega) = \det \| \, z^{g'f'}_{1,\pm}(\mathbf{k}+\mathbf{q}',\omega) \, \| \tag{17b}$$

$$\nu^{-}_{s',\mathbf{q}'} = \nu_{s',\mathbf{q}'}\,; \;\; \nu^{+}_{s',\mathbf{q}'} = 1 + \nu_{s',\mathbf{q}'}\,; \tag{17c}$$

Having determined $\Delta^{g'f'}_{1,\pm}(\mathbf{k}+\mathbf{q}',\omega)$ as an algebraic complement in the determinant $\Delta_{1,\pm}(\mathbf{k}+\mathbf{q}',\omega)$ to the element $z^{g'f'}_{1,\pm}(\mathbf{k}+\mathbf{q}',\omega)$ we get

$$P^{g'f_0}_{i,s'}(\mathbf{k},\mathbf{q}',\omega) = \frac{\nu^{\mp}_{s',\mathbf{q}'}}{\sqrt{N}} \sum_{f_1,f'} \frac{\Delta^{f_1g'}_{1,\pm}(\mathbf{k}+\mathbf{q}',\omega)}{\Delta_{1,\pm}(\mathbf{k}+\mathbf{q}',\omega)} F^{f_1f'}_{s}(\mathbf{k},\mathbf{q}') G^{f'f_0}_{r}(\mathbf{k},\omega) \tag{18}$$

Here $i = 1,2$, index "I" to be taken with an upper sign.

Using (18) and (16a), we can get the equation for the Fourier-components of the Green-function of the system

$$\sum_{f'} B^{ff'}(\mathbf{k},\omega) G^{f'f_0}_{r}(\mathbf{k},\omega) = \delta_{ff_0} \tag{19}$$

where

$$B^{ff'}(\mathbf{k},\omega) = \omega\delta_{ff'} - z^{ff'}(\mathbf{k}) - M^{ff'}(\mathbf{k},\omega). \tag{20a}$$

$$M^{ff'}(\mathbf{k},\omega) = M^{ff'}_{+}(\mathbf{k},\omega) + M^{ff'}_{-}(\mathbf{k},\omega) \tag{21a}$$

$$M^{ff'}_{\pm}(\mathbf{k},\omega) = \frac{1}{N} \sum_{s',f_1,g',\mathbf{q}'} \nu_{s'\mathbf{q}'} F^{*g'f}_{s'}(\mathbf{k},\mathbf{q}') F^{f_1f'}_{s}(\mathbf{k},\mathbf{q}') \frac{\Delta^{f_1g'}_{1,\pm}(\mathbf{k}+\mathbf{q}',\omega)}{\Delta_{1,\pm}(\mathbf{k}+\mathbf{q}',\omega)} \tag{21b}$$

The solution of equation (19) will be the function

$$G^{f'f_0}_{r}(\mathbf{k},\omega) = \frac{\Delta^{f_0f'}(\mathbf{k},\omega)}{\Delta(\mathbf{k},\omega)}\,; \tag{22}$$

Here as well as before

$$\Delta(\mathbf{k},\omega) = \det \| \, B^{ff'}(\mathbf{k},\omega) \, \| \tag{20b}$$

and $\Delta^{f_0f'}(\mathbf{k},\omega)$ an algebraic complement to the element $B^{f_0f'}$ of the determinant $\Delta(\mathbf{k},\omega)$. Having introduced (22) into (10b) we get a final expression for the imaginary part of the dielectric constant. This expression in itself will be general enough. Therefore, to explain the changes caused by the presence of a group of close levels, we consider a special case of Fermi-resonance.

4. The Fermi Resonance

We assume that there are the main tone and the overtone (or the composed tone) interacting. The index can have in this case only two values, and the expressions for the Green-function and for the imaginary part of the dielectric constant will be simplified.

We represent the mass operator as a sum of two terms

$$M^{ff'}(\mathbf{k},\omega) = R^{ff'}(\mathbf{k},\omega) + i\Gamma^{ff'}(\mathbf{k},\omega) \tag{23}$$

where $R^{ff'}(\mathbf{k},\omega)$ and $\Gamma^{ff'}(\mathbf{k},\omega)$ are its real and imaginary parts correspondingly. The determinant of the system (20b) after the introduction of (23) and (20a) in it has a form

$$\Delta(\mathbf{k},\omega) = \mathrm{A}_1(\mathbf{k},\omega) - iA_2(\mathbf{k},\omega) \tag{24}$$

where

$$\begin{aligned} A_1(\mathbf{k},\omega) &= \omega^2 - \omega[z^{11}(\mathbf{k},\omega) + z^{22}(\mathbf{k},\omega)] + z^{11}(\mathbf{k},\omega)\,z^{22}(\mathbf{k},\omega) \\ &\quad - z^{12}(\mathbf{k},\omega)\,z^{21}(\mathbf{k},\omega) - \Gamma^{11}(\mathbf{k},\omega)\Gamma^{22}(\mathbf{k},\omega) + \Gamma^{12}(\mathbf{k},\omega)\Gamma^{21}(\mathbf{k},\omega) \end{aligned} \tag{25a}$$

$$\begin{aligned} A_2(\mathbf{k},\omega) &= [\omega - z^{11}(\mathbf{k},\omega)]\Gamma^{22}(\mathbf{k},\omega) + [\omega - z^{22}(\mathbf{k},\omega)\Gamma^{11}(\mathbf{k},\omega) \\ &\quad + z^{12}(\mathbf{k},\omega)\Gamma^{21}(\mathbf{k},\omega) + z^{21}(\mathbf{k},\omega)\Gamma^{12}(\mathbf{k},\omega) \end{aligned} \tag{26a}$$

$$z^{fg}(\mathbf{k},\omega) = z^{fg}(\mathbf{k}) + R^{fg}(\mathbf{k},\omega) \tag{27}$$

From the expression (25a) the resonant absorption frequencies can be found. For their determination at zero approximation, one can take the value of Γ^{fg} and R^{fg} included in (25a) at a certain value of $\omega = \bar{\omega}$ from the absorption region.† In this case $A_1(\mathbf{k},\omega)$ will turn into a quadratic triplex in relation to the frequency

$$A_1(\mathbf{k},\omega) = (\omega - \omega_-)(\omega - \omega_+) \tag{25b}$$

where ω_- and ω_+ are the roots of the equation

$$A_1(\mathbf{k},\omega) = 0 \tag{25c}$$

If now we introduce (25b), (26a), (24), (23), (21a) and (22) into (10b), we shall get an expression for the imaginary part of the dielectric constant

$$\operatorname{Im}\epsilon_{xx}^{\perp}(\mathbf{k},\omega) = -\frac{4\pi}{v\omega}\frac{F(d_x,\omega,\mathbf{k})}{(\omega-\omega_-)^2(\omega-\omega_+)^2 + A_2{}^2(\mathbf{k},\omega)} \tag{10c}$$

where $F(d_x,\omega,\mathbf{k})$ is the function appearing in the numerator of (10b) after the substitutions indicated.

The expression (10c) determines the shape of the absorption curve in case of closely located molecular levels. It differs from the Lorentzian one, since in its denominator an expression is present

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† For the more accurate determination, one should take into account the first derivatives of these functions as well.

leading to the appearance of two sharp peaks in the absorption curve at the frequencies ω_{+}. It can be easily seen from (10c) that at $\omega < \omega_{-}$ and $\omega > \omega_{+}$ (here $\omega_{-} < \omega_{+}$) both participants of the first term in the denominator vary with the frequency in one direction. Therefore when we approach the resonant frequencies from the outside of the interval $[\omega_{-},\omega_{+}]$ a sharper increase of the absorption should be observed than that for the Lorentzian curve. At the same time inside the interval $[\omega_{-},\omega_{+}]$ both the factors vary in different directions which lead to the weaker change of the absorption with the frequency than that for the Lorentzian shape. So, we get a curve with the sharp boundaries and a small saddle between the maxima.

Such a frequency dependence will be observed when the half-width of the absorption curve is comparable to the distance between the maxima of the components, i.e. $|\Gamma(\mathbf{k},\omega)| \sim \omega_{+} - \omega_{-}$. But when $|\Gamma(\mathbf{k},\omega)| \ll \omega_{+} - \omega_{-}$, than at variation of frequency ω around ω_{-} (or ω_{+}) within the limits of the bandwidth, the second factor in (10c) $(\omega - \omega_{+,(-)})$ will be practically constant so that the absorption curve will be transformed into two Lorenzian curves.

At analyses of (10c) we so far neglected the frequency dependence of $F(d_x,\omega,\mathbf{k})$ and $A_2(\mathbf{k},\omega)$. Now we note that their junction with the mass operator of the system will cause an additional specialities in the structure of the absorption curve. This problem will be considered in a second part of the paper.

From the expression (10c) one can get the temperature dependence of the absorption. It is convenient for this purpose to consider the behaviour of the maximum of each component with the variation of temperature. For the sake of simplicity we take the case of an exact Fermi-resonance† when the relation $|\mathbf{d}^{f}| = |\mathbf{d}^{f'}| = d/\sqrt{2}$ is held (d being the dipole momentum of the transition before the resonance, corresponding to the main tone$^{(12)}$) and M^{fg} does not depend upon the indexes f and g (see Sec. 2). Taking also into account that $\omega^{f} \gg |\omega^{f} - \omega^{f'}|$ we have

$$A_2(\mathbf{k},\omega) = [2\omega - z^{11}(\mathbf{k},\omega) - z^{22}(\mathbf{k},\omega) + 2\,z^{12}(\mathbf{k},\omega)]\Gamma(\mathbf{k},\omega) \qquad (26\text{b})$$

$$F(d_x,\mathbf{k},\omega) = \frac{d^2}{2}\,\frac{\omega^{f} A_2{}^{2}(\mathbf{k},\omega)}{\Gamma(\mathbf{k},\omega)} \qquad (28)$$

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† Before the resonance is achieved, the levels of the overtone and of the main tone coincide.

and then the absorption in the maximum of the band is determined by the expression

$$\operatorname{Im} \epsilon_{xx}^{\perp}(\mathbf{k},\omega) = -\frac{2\pi d^2}{\nu\Gamma(\mathbf{k},\omega_{\pm})} \tag{10d}$$

We assume that the interaction of intramolecular vibrations takes place only with the optical phonons, with one certain branch predominantly. Neglecting the dispersion of the phonon's branch and using (21a), (21b) and (23), we can write

$$\Gamma(\mathbf{k},\omega_{\pm}) = \nu_0 a_{\pm} + b_{\pm}\,; \tag{29}$$

where

$$\nu_0 = \left[\exp\frac{\Omega}{kT} - 1\right]^{-1} \tag{30}$$

Ω_- is a frequency of phonons, $a_{\pm}$ and $b_{\pm}$ the coefficients independent of the temperature, which can be obtained from the mass operator (21a), (21b) with the substitution of $\omega = \omega_{\pm}$. It is seen from the expressions (10d), (29) and (30) that variation of the doublet components with the temperature depends on the values of $a_{\pm}, b_{\pm}$ and may be different. It is of interest to consider several cases for different correlation of these parameters:

(a) $a_- \sim a_+$; $b_- \sim b_+$ passing from ω_- over to ω_+ we observe no change of the coefficients, so that both components have the same behaviour (curve 1 of Fig. 1).

(b) $a_- < a_+$; $b_- \sim b_+$ the component corresponding to ω_+ will display the sharper decrease with an increase of the temperature, although at $T \to 0$ both components are approximately equal (curves 1 and 4 of Fig. 1).

(c) $a_- > a_+$; $b_- < b_+$ at lower temperatures the component ω_- will have higher intensity, at higher ω_+ (Fig. 1, curves 3 and 4 or 3 and 2). In this case we observe a transition from the normal intensity distribution in the Fermi-doublet to the abnormal one.

(d) $a_- < a_+$; $b_- < b_+$ the intensity of the component ω_- is always higher (curves 1 and 3 in Fig. 1).

The theoretical conclusions obtained allow us to explain in the qualitative features of the temperature dependence of the spectra of molecular crystals at presence of the resonant interaction of the oscillations. The more detailed comparison of the theory to the experiment will be made in a separate communication.

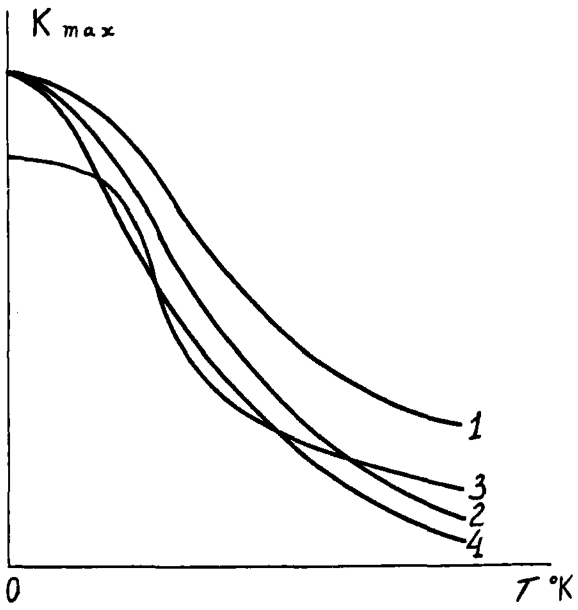

Figure 1. Theoretical temperature dependences of the intensities in the maxima of the components of Fermi-doublet ω_- and ω_+ at different values of parameters $a_\pm$, $b_\pm$.

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