

# CHANGE OF THE VIBRATIONAL FREQUENCY AND THE LINEAR VIBRONIC COUPLING IN MOLECULAR CRYSTALS. III. OPTICAL ABSORPTION CURVE AT EXCITON BAND IN THE ZERO-PHONON APPROXIMATION

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The expression for the absorption curve of light in molecular crystals at the exciton band, in the case of strong linear vibronic coupling and small frequency change on molecular vibration after electronic excitation, is obtained. It is shown, that a small frequency change of vibration causes no significant changes in the absorption spectrum, apart of renormalization of the pure linear vibronic coupling constant. The obtained absorption curve agrees semi-quantitatively with experimental data.

## 1. Introduction

In the first part of this series of publications [1] we have considered the simple two-level model of a molecular crystal. The lattice vibrations were ignored. We have assumed further, for simplicity, that only one vibrational mode of molecule couples effectively with the exciton motion. This model was analyzed under the assumption, that the vibronic interaction energy is greater than interactions between molecules (weak coupling case). It was shown that such a model can be well described by the zero- and one-phonon processes. The energetic changes in the exciton system [1], as well as the exciton transfer processes correlated with phonons [2] were analyzed. We have shown, that the linear vibronic coupling constant is renormalized by the frequency change, and is

$$\gamma_{\text{ren}} = \kappa Q(1 - 2\kappa) \quad (1)$$

where

$$\kappa Q = \frac{2\gamma e^{8\kappa}}{1 - e^{2\kappa}}, \quad e^{-8\kappa} = \frac{\omega_1^2}{\omega^2} \quad (2)$$

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and  $\gamma$  is the linear vibronic coupling constant,  $\omega_1, \omega$  are the frequencies of vibration of a molecule in the excited and ground electronic state, respectively.

In this paper we shall consider the absorption of light by our model of molecular crystal. We shall work only in the zero-phonon approximation, and only discuss, what changes in the absorption spectrum arise when one-phonon processes are included.

The Hamiltonian of our model is [1]:

$$H = \sum_n \left( e_0 - \frac{\gamma^2 \omega^3}{\omega_1^2} + \frac{\omega_1 - \omega}{2} \right) a_n^\dagger a_n + \omega \sum_n \left( 1 + \frac{\omega_1 - \omega}{2} a_n^\dagger a_n \right) b_n^\dagger b_n + \quad (3)$$

$$+ \sum'_{n,m} V_{nm}^0 a_n^\dagger a_m \exp [-\kappa(b_n^2 - b_n^{+2} - b_m^2 + b_m^{+2}) - \kappa \rho (b_n - b_n^+ - b_m + b_m^+)]$$

where  $e_0$  is the energy of the free, localized exciton,  $V_{nm}^0$  is the resonance-interaction electronic matrix element between the  $n$ -th and  $m$ -th molecules,  $b_n, b_n^+$  are the phonon annihilation and creation operators, respectively, and the annihilation operator of the exciton at the  $n$ -th molecule is given by

$$A_n = a_n \exp [-\kappa(b_n^2 - b_n^{+2}) - \kappa \rho (b_n - b_n^+)]. \quad (4)$$

In the zero-phonon approximation the "effective" Hamiltonian is:

$$H_{of} = \sum_n e_1 a_n^\dagger a_n + \sum'_{n,m} V_{nm} a_n^\dagger a_m + \omega \sum_n b_n^\dagger b_n \quad (5)$$

where

$$e_1 = e_0 - \frac{\gamma^2 \omega^3}{\omega_1^2} + \frac{\omega_1 - \omega}{2} (2\bar{n} + 1), \quad \bar{n} = (e^{\beta\omega} - 1)^{-1} \quad (6)$$

and  $V_{nm}$  is the renormalized resonance interaction matrix element by the Debye-Waller type factor. Its expression was given in [1]. In Eq. (5) we have ignored a small change in the energy of the phonon system, which is proportional to the average number occupation of excitons.

## 2. Coefficient of light absorption

The general formula for the light absorption for the molecular crystal near the exciton band is given by [3, 4]:

$$\Omega \sigma(\Omega) = - \frac{4\pi d^2 \omega_f}{v} \text{Im } G(\mathbf{k} = 0, \Omega) \quad (7)$$

where  $\Omega$  is the light frequency,  $\omega_f$  is the energy difference between the ground and excited state,  $v$  is the group velocity of excitons, and  $d$  is the electronic matrix element of transition for the molecule. It has been assumed that the moment of transition does not depend on the nuclear coordinates (Condon approximation). The function  $G$  is given by

$$G(\mathbf{k} = 0, \Omega) = -i \int_{-\infty}^{\infty} dt \theta(t) e^{i\Omega t - \Gamma t} \langle [A_{\mathbf{k}=0}(t), A_{\mathbf{k}=0}^\dagger(0)] \rangle \quad (8)$$

and is the retarded Green's function of the exciton.  $\Gamma$  is the width of the exciton level, which does not result from vibronic coupling, and we can include, formally, into  $\Gamma$  all processes different from those being under consideration which cause damping of excitons, e.g., coupling with lattice phonons. In general  $\Gamma$  should depend on energy and forms the lattice-phonon's background for a given vibronic line in the absorption spectrum. Operators  $A_{\mathbf{k}}(t)$  are given by

$$\begin{aligned} A_{\mathbf{k}}(t) &= e^{iH_{\text{of}}t} A_{\mathbf{k}} e^{-iH_{\text{of}}t}, \\ A_{\mathbf{k}} &= N^{-1/2} \sum_n A_n e^{-i\mathbf{k} \cdot \mathbf{n}}. \end{aligned} \quad (9)$$

Equations (5), (7) and (8) form a base for further considerations.

We note, that the Green's function (8) can be expressed in a simple form by the Green's function

$$\tilde{G}_{nm}(t) = -i\theta(t) \langle [a_n(t), a_m^+(0)] \rangle. \quad (10)$$

Namely, taking into account Eq. (4) and the fact that the average number of excitons per site is negligibly small, we obtain

$$G(\mathbf{k} = 0, \Omega) = \int_{-\infty}^{\infty} dt e^{-i\Omega t - \Gamma t} N^{-1/2} \sum'_{n,m} \langle e^{-\varphi_n(t)} e^{\varphi_m(0)} \rangle \tilde{G}_{nm}(t) \quad (11)$$

where

$$\varphi_n(t) = \varkappa [b_n^2(t) - b_n^{+2}(t)] + \varkappa \varrho [b_n(t) - b_n^+(t)], \quad (11a)$$

$$b_n(t) = e^{iH_{\text{of}}t} b_n e^{-iH_{\text{of}}t}. \quad (11b)$$

We note, further, that

$$\tilde{G}_{nm}(t) = -\frac{i\theta(t)}{2\pi N} \sum_{\mathbf{k}} \langle [a_{\mathbf{k}}(t), a_{\mathbf{k}}^+(0)] \rangle e^{i\mathbf{k} \cdot (\mathbf{n}-\mathbf{m})} \quad (12)$$

where

$$\langle [a_{\mathbf{k}}(t), a_{\mathbf{k}}^+(0)] \rangle = e^{-iE_{\text{of}}(\mathbf{k})t} \quad (13)$$

and

$$E_{\text{of}}(\mathbf{k}) = e_1 + \sum'_{n,m} V_{nm} e^{i\mathbf{k} \cdot (\mathbf{n}-\mathbf{m})} \quad (14)$$

is the zero-phonon energy of excitons in a molecular crystal. Now, as the average  $\langle e^{-\varphi_n(t)} e^{\varphi_m(0)} \rangle$  does not depend on indexes  $n, m$  but only on the equalness or non-equalness between  $n$  and  $m$  we obtain finally

$$\begin{aligned} G(\mathbf{k} = 0, \Omega) &= -\frac{i}{2\pi} \int_{-\infty}^{\infty} dt \theta(t) e^{-i\Omega t - \Gamma t} \times \\ &\times \{ N^{-1} \sum_{\mathbf{k}} e^{-iE_{\text{of}}(\mathbf{k})t} [K(t) - k(t)] + e^{-iE_{\text{of}}(0)t} k(t) \} \end{aligned} \quad (15)$$

where

$$\begin{aligned} K(t) &= \langle e^{-\varphi(t)} e^{\varphi(0)} \rangle, \\ k(t) &= \langle e^{-\varphi(t)} \rangle \langle e^{\varphi(0)} \rangle. \end{aligned} \quad (16)$$

Inserting expression (15) into the equation (7) we obtain the following formula for the light absorption coefficient:

$$\begin{aligned} \Omega\sigma(\Omega) &= \frac{2d^2\omega_f}{v} \left\{ N^{-1} \sum_{\mathbf{k}} \operatorname{Re} \int_{-\infty}^{\infty} dt \theta(t) e^{-i\Omega t - \Gamma t - iE_{\text{of}}(\mathbf{k})t} \times \right. \\ &\quad \left. \times [K(t) - k(t)] + \operatorname{Re} \int_{-\infty}^{\infty} dt \theta(t) e^{-i\Omega t - \Gamma t - iE_{\text{of}}(0)t} k(t) \right\}. \end{aligned} \quad (17)$$

We see therefore, that we must now calculate the following averages

$$\begin{aligned} &\langle e^{-\kappa\varrho A(t) - \kappa B(t)} e^{\kappa\varrho A(0) + \kappa B(0)} \rangle \\ &\langle e^{-\kappa\varrho A(t) - \kappa B(t)} \rangle \langle e^{\kappa\varrho A(0) + \kappa B(0)} \rangle \end{aligned} \quad (18)$$

where

$$\begin{aligned} A(t) &= b e^{-i\omega t} - b^+ e^{i\omega t}, \\ B(t) &= b^2 e^{-2i\omega t} - b^{+2} e^{2i\omega t}. \end{aligned} \quad (18a)$$

The calculation of these averages can be performed by the method similar to that given in [3] with the help of Weyl-type theorem, or by the cumulant method [5].

We can see from Eq. (2) that for frequency changes of less than 10%, which is the case for most molecular crystals, is of the order 0.01, also all terms proportional to  $\kappa^n$  can be neglected in comparison with terms proportional to  $(\kappa\varrho)^n$ . If we do this, we obtain

$$\begin{aligned} K(t) &= \exp \{ \kappa^2 \varrho^2 [(\bar{n} + 1) e^{-i\omega t} + \bar{n} e^{i\omega t} - (2\bar{n} + 1)] \}, \\ k(t) &= \exp [ -\kappa^2 \varrho^2 (2\bar{n} + 1) ]. \end{aligned} \quad (19)$$

Inserting (19) into (17) we can see that  $\sigma(\Omega)$  satisfies the following sum law

$$\int_0^{\infty} d\Omega \sigma(\Omega) = \frac{4\pi d^2 \omega_f}{v} \quad (20)$$

as it should.

The vibration, which effectively couples with the exciton motion for aromatic crystals is usually C—C stretching vibration of energy about 1300—1400  $\text{cm}^{-1}$ . So for not too high temperatures we can insert in Eq. (19) ( $\bar{n} = 0$ , and after integration in (17) over time we obtain finally:

$$\begin{aligned} \Omega\sigma(\Omega) &= \frac{2d^2\omega_f}{v} e^{-\kappa^2\varrho^2} \frac{\Gamma}{[(\Omega - E_{\text{of}}(0))^2 + \Gamma^2]} + \\ &+ \frac{2d^2\omega_f}{vN} e^{-\kappa^2\varrho^2} \sum_{\mathbf{k}} \sum_{m \neq 0} \frac{(\kappa\varrho)^{2m}}{m!} \frac{\Gamma}{[(\Omega - E_{\text{of}}(\mathbf{k}) - \omega m)^2 + \Gamma^2]} + 0(\kappa^3\varrho^2). \end{aligned} \quad (21)$$

### 3. Discussion

The first term in Eq. (21) describes the zero-phonon transition, *i.e.*, the transition without change in the vibrational state of the molecule. We see that all other peaks in the absorption spectrum are spread out over the whole exciton band, and they should be thicker than the zero-phonon line if only the exciton band is not too narrow, especially on lower temperatures. This conclusion is in agreement with experiment (see, for instance [6, 7, 8]).

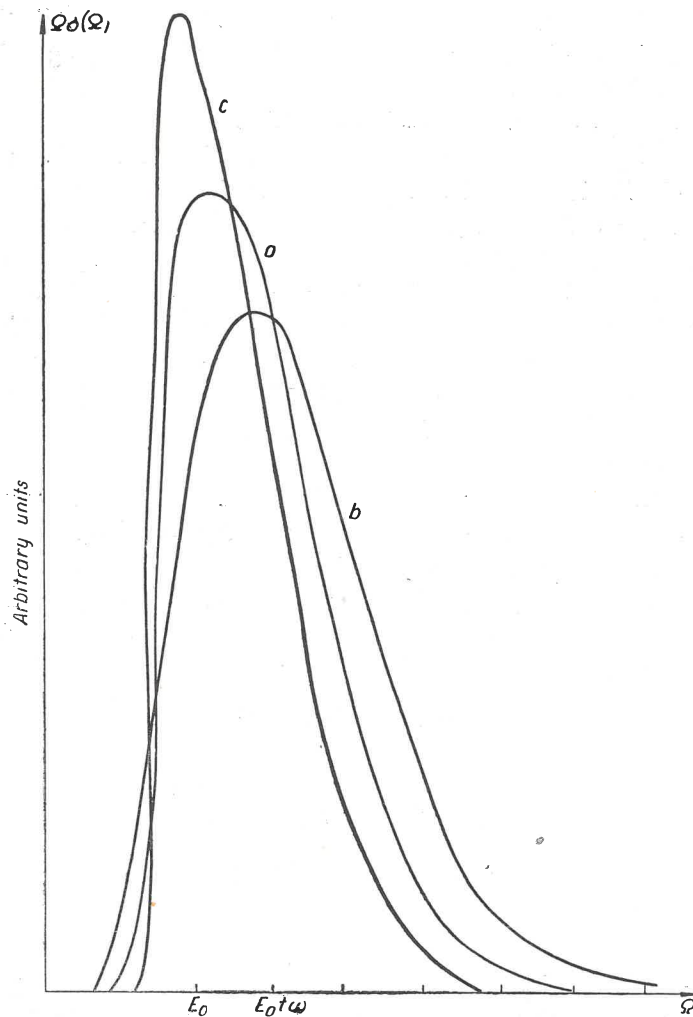


Fig. 1

The spreading of these lines results from the fact, that in the photon absorption process three particles participate: photon, exciton and phonon. This permits the creation of excitons with different quasi-momenta in the whole exciton band. It should be noted that this effect is less explicit than a similar effect in the absorption of light by an optical centre in ionic

crystal, because the zero-phonon line in a molecular crystal spreads over the lattice-phonon back-ground.

The ratio of intensities of the  $n$ -th vibrational line and the zero-phonon line is:

$$\frac{\sigma(\Omega_n^*)}{\sigma(\Omega_0)} = \frac{\Omega_n(\kappa\rho)^{2n}}{\Omega_0 n!}. \quad (22)$$

We see that the formula (22) is similar to that obtained by McCoy and Ross [9], apart of renormalization of the linear vibronic coupling constant. This renormalization can cause remarkable changes in the distribution of intensities in the vibronic progression of a given transition. Figure 1 shows the envelopes of absorption spectrum for three cases: a)  $\gamma^2 = 1$ ,  $\omega_1 = \omega$ ; b)  $\gamma^2 = 1$ ,  $\omega_1 = 0.9\omega$ ; c)  $\gamma^2 = 1$ ,  $\omega_1 = 1.1\omega$ .

The formula (22) is in a good agreement with experiment. For instance, we obtain a good intensity distribution from Eq. (22) for the first singlet exciton band in anthracene crystal if we put  $\kappa^2\rho^2 = 0.7$  (see [7]). This value is smaller than the distortion parameter in the anthracene dimer, which is needed to fit the theory with experimental data [10], and may suggest that the frequency of vibration in the excited state of molecule contained in crystal is somewhat greater than that in the ground state, however, this difference can also be caused by the dependence of the electronic wavefunction on the molecule position coordinates resulting from molecular interactions, which leads to the temperature dependence of the coupling constant [11]. This effect is actually observed in the anthracene crystal, especially in the lowest triplet exciton state [12].

The formula (22) also provides a good fit to the experimental data for the benzene crystal first singlet transition ( $38000 \text{ cm}^{-1}$ ), if we put  $\kappa^2\rho^2 = 1$  [13].

We calculate now the envelope of the absorption spectrum near the extremum. We follow the method shown by Davydov in the analysis of the multiphonon processes [3]. We note that the main contribution to the integral (17) comes from the region  $t \approx 0$ . We can therefore put (with accuracy to  $\kappa^3\rho^2$ )

$$G(t) - \kappa^2\rho^2 = -itA - t^2B \quad (23)$$

where

$$G(t) = \ln K(t), \quad A = \omega\kappa^2\rho^2(1-2\kappa),$$

$$B^2 = \omega^2\kappa^2\rho^2(1-2\kappa)(2\bar{n}+1),$$

and, if  $B^2 \geq \omega^2$  then

$$\Omega\sigma \text{ rez. } (\Omega) = \frac{d^2\omega_f\Gamma\sqrt{\pi}}{vNB} \sum_{\mathbf{k}} \left\{ 1 + \frac{\Gamma[E_{\text{of}}(\mathbf{k}) + A - \Omega]}{4\sqrt{\pi}B^3} \right\} \exp \left\{ -\frac{[E_{\text{of}}(\mathbf{k}) + A - \Omega]^2}{4B^2} \right\}. \quad (24)$$

We see the envelope of the absorption spectrum possesses asymmetrical gaussian form of the width

$$A = 2B \ln 2 = 2v\kappa\rho\omega(1-\kappa) \ln 2 (2\bar{n}+1)^{1/2} \quad (25)$$

and which asymmetry increases with  $\kappa$ .

The asymmetry is greater for  $\omega_1 > \omega$  than that for  $\omega_1 < \omega$ . The formula (25) is in agreement with that obtained in [1] apart of terms proportional to  $\varkappa^2$  which are neglected here. The centre of gravity is situated at  $\Omega = E(0) + A$ , which is also in agreement with [1] if we put  $\bar{n} = 0$  and  $\varkappa = (\omega^2 - \omega_1^2)/8\omega^2$ .

If we take into account Eqs (6) and (14) we can conclude that the centre of gravity of the absorption spectrum depends on temperature if only  $\omega_1 \neq \omega$ . This temperature dependence for larger vibrational quanta is, of course, negligible in room temperatures, however, the same effect should be caused by the small lattice quanta. Indeed, a temperature dependence of the centre of gravity was observed for the benzene crystal first singlet exciton Davydov manifold [14]. Its centre of gravity moves towards lower energies as the temperature raises, which shows that the "effective" phonon frequency coupled with the exciton is lower in the excited state. If this is true, then because of the Debye-Waller factor which multiplies all resonance electronic interaction elements [1], the splittings between Davydov's components decrease with the increase of temperature, and this is also observed [14].

The formula for the light absorption by the molecular crystal near the exciton band is, of course, true only for narrow exciton bands, which is the result of the zero-phonon approximation. The inclusion of one-phonon processes leads to the changes in the  $\mathbf{k}$ -dependence of the exciton energies in (21) and to the replacing of  $\Gamma$  by  $\Gamma + \text{Im } M(\Omega)$ , where  $M(\Omega)$  is the imaginary part of the one-phonon mass operator [1] for the exciton system. This can modify remarkably the form of vibronic lines, and especially broads the lines in the higher-energy part of the spectrum [15], however, the sequence of peaks should remain unchanged. The formula (21) is in agreement with that obtained by the similar method in [16], however, authors of that paper have not taken into account the possibility of the frequency change after excitation.

For the exciton bands which the width of band is comparable to vibronic interaction energy, also the one-phonon approximation is insufficient.

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