CHANGE OF THE VIBRATIONAL FREQUENCY AND THE LINEAR VIBRONIC COUPLING IN MOLECULAR CRYSTALS. I

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It is shown that a small decrease in vibrational frequency in the excited state of molecule intensifies all energy changes in the exciton system resulting from arbitrary linear vibronic coupling, what is the case for most organic crystals. The situation is reversed in the case of a small increase in vibrational frequency. The temperature dependence of the probability of exciton transfer, without any correlation with phonons, is given. Also expressions for the center of gravity of the exciton optical transition band and its width are obtained.

1. Introduction

A vibrational structure of Frenkel excitons in molecular crystals results from the coupling of the motion of nuclei with an exciton. It is well known that the potential energy for vibrations changes from one electronic state to another. This change of potential energy leads to vibronic coupling. In the last few years there have been many studies dealing with the spectral consequences resulting from such coupling [1–8]. An excellent review of this problem in dimeric systems is given in Ref. [9]. However, only in a few works [6,7] has the change of the vibrational frequency after excitation, *i. e.*, quadratic vibronic coupling, been investigated. In others, only the change of the equilibrium configuration of the excited molecule has been taken into account (linear vibronic coupling). The quadratic vibronic coupling in dimeric systems has been investigated in Refs [10, 11].

As is known, the linear vibronic coupling leads to the reduction of the matrix elements of the electronic resonance interaction between molecules. In the case of dimeric systems this is expressed by the multiplication of the electronic matrix elements by the Franck-Condon integrals [2,9] (weak coupling case), and in the case of molecular crystals by the Debye-Waller-type factor, being the multiplier of the electronic matrix elements. The latter factor, in fact, is similar to the Huang-Rhys factor [12] in the theory of multiphonon processes on F-centers in ionic crystals.

Other effects resulting from the linear vibronic coupling are the asymmetrical compression of the exciton band [3,7] resulting from the one-phonon processes, the uniform shift

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of the whole exciton band towards the lower energies [7], and the dynamical interaction between excitons, which is attractive, provided that the vibrational quantum coupled to the exciton is larger than the unperturbed exciton bandwidth [13].

The square width of the exciton line in an optical transition increases proportionally with the linear coupling constant and with temperature [8, 14]. Moreover the intensity of the pure exciton line decreases rapidly with an increase of coupling constant and temperature. The shape of the vibrational structure of the exciton transition depends on the ratio of vibronic coupling parameter and the electronic resonance interaction. In the strong coupling case [15] it consists of several very sharp lines, whereas in the weak coupling case it is similar to the isolated molecule spectrum. These predictions are in good qualitative agreement with experimental data [16]. For dimeric system the full experimental verification of the theory is given in Ref. [17].

In molecular crystals the change of the equilibrium configuration of a molecule is usually greater than the vibrational frequency changes after excitation, and this was the reason why the quadratic term, in normal vibrational coordinates, of the interaction Hamiltonian between excitons and intramolecular vibrations is neglected. In Ref. [7] it was shown, however, that the vibrational frequency change $\Delta\omega = \omega_1 - \omega$ (ω_1 and ω are the frequencies in the exited and ground states, respectively) may increase or decrease the red-shift of the whole exciton band which results from the linear vibronic coupling. The direction of this change depends on sgn $\Delta\omega$.

In this study we investigate more systematically all energy changes in the exciton system produced by the frequency change in the case of arbitrary linear vibronic coupling. In Section II the Hamiltonian of our problem is transformed into a more convenient form, which diagonalize Hamiltonians of crystal sites. In Section III the Dyson equation for the exciton subsystem including zero-and one-phonon processes is obtained. Zero- and one--phonon processes are defined in such way, that in our approximation the motion of an exciton from one molecule to another is correlated only with one phonon or none at all. Inside a given molecule all multiphonon processes may occur. A brief discussion is given in Section IV. Finally, the formulae for the center of gravity and width of the exciton optical transition band are given in Section V. These formulae are applicable for the weak coupling theory of molecular crystals.

2. Hamiltonian of the system

We assume for simplicity that an exciton couples with only one intramolecular vibration. This assumption does not change our final results. We neglect the lattice vibrations and dispersion of intramolecular phonons. Furthermore, we assume the two-level model of the crystal, *i. e.*, the ground state and only one electronically excited state of the molecule are taken into account (thus configuration interaction effects are neglected [18]). The potential energy for the vibration which couples with the exciton is, for the ground state of the n-th molecule,

$$E_0(Q_n) = \tfrac{1}{2}\omega^2 Q_n^2 \qquad\qquad (2.1a)$$

and for the excited state,

$$E_1(Q_n) = \varepsilon_0 + lQ_n + \tfrac{1}{2}\omega_1^2 Q_n^2 \qquad (2.1b)$$

where ω_1 and ω are the frequencies of vibration in the excited and ground state, respectively, Q_n is the normal coordinate of vibration, l is the relative change in the equilibrium configuration of the molecule, and ε_0 is the "vertical" electronic excitation energy which consists of the electronic excitation energy in the isolated molecule and the energy of van der Waals interaction between molecules. The subscript n labels the unit cells of the crystal and the position of the molecule in a given unit cell. We assume that the harmonic approximation holds for the vibrations under consideration. Under these assumptions the Hamiltonian of the exciton-phonon system, written in the second quantization language, has the following form [3, 7, 13]:

$$H = \sum_n \varepsilon_0 A_n^+ A_n + \sum_n \omega B_n^+ B_n + {\sum_{n,m}}' V_{n,m}^0 A_n^+ A_m +$$
$$+ \sum_n A_n^+ A_n [\alpha(B_n^+ + B_n) + \beta(B_n^+ + B_n)^2] \qquad (2.2)$$

where

$$\alpha = \gamma\omega$$

$$\beta = \frac{\omega_1^2 - \omega^2}{4\omega} \qquad (2.3)$$

γ is the linear coupling constant [13], A_n^+ and A_n are the creation and annihilation operators of the exciton on the n-th molecule, respectively, and B_n^+ and B_n are the phonon operators. $V_{n,m}^0$ is the electronic element of the resonance interaction between the n-th and m-th molecules.

In order to transform (2.2) into a more convenient form for subsequent investigations we perform the canonical transformation which diagonalizes the site Hamiltonians. The non-diagonal term will be therefore proportional to the electronic matrix element $V_{n,m}^0$ and we shall treat it as perturbation, $i.$ $e.$ we shall consider weak coupling theory of molecular crystals. We put

$$A_n = e^{\varkappa S} a_n e^{-\varkappa S}, \quad B_n = e^{\varkappa S} b_n e^{-\varkappa S} \qquad (2.4)$$

where

$$S = \sum_n a_n^+ a_n \left[(b_n^2 - b_n^{+2}) + \varrho(b_n - b_n^+) \right] \qquad (2.5)$$

$\varkappa$ and ϱ are to be determined. Taking into account the idempotent character of $a_n^+ a_n$ we obtain from (2.4) and (2.5)

$$B_n = -\frac{\varrho}{2} a_n^+ a_n (1 - e^{2\varkappa}) + b_n [1 + a_n^+ a_n (\operatorname{ch} 2\varkappa - 1)] +$$
$$+ b_n^+ a_n^+ a_n \operatorname{sh} 2\varkappa \qquad (2.6)$$

and

$$A_n = a_n \exp\left[-\varkappa(b_n^2 - b_n^{+2}) - \varkappa\varrho(b_n - b_n^+) \right]. \qquad (2.7)$$

Putting

$$e^{-8\varkappa} = 1 + \frac{4\beta}{\omega} \equiv 1 + c, \quad c = \frac{\omega_1^2 - \omega^2}{\omega^2} \tag{2.8a}$$

$$\varrho = -\frac{2\gamma}{1-(1-c)(1+c)^{-1/4}} = -\frac{2\gamma}{(1+c)(1-e^{2\varkappa})}, \tag{2.8b}$$

we obtain

$$H = \sum_n \left[\varepsilon_0 - \frac{\gamma^2\omega}{1+c} + \frac{\omega}{2}(\sqrt{1+c}-1) \right] a_n^+ a^n +$$

$$+ \omega \sum_n [1 + (\sqrt{1+c}-1)\, a_n^+ a_n]\, b_n^+ b_n +$$

$$+ \sum_{n,m}{}' V_{n,m}^0 a_n^+ a_m \exp\left[\varkappa(b_n^2 - b_n^{+2} - b_m + b_m^{+2}) + \varkappa\varrho(b_n - b_n^+ - b_m + b_m^+)\right] \tag{2.9}$$

or going from the operators b_n^+ and b_n to the operators P_n and Q_n (momentum and vibrational coordinate of the n-th molecule)

$$H = \sum_n \tilde{\varepsilon}_0 a_n^+ a_n + \frac{1}{2} \sum_n (P_n^2 + \omega^2 Q_n^2) + \frac{(1+c)^{1/2}-1}{2} \sum_n a_n^+ a_n (P_n^2 + \omega^2 Q_n^2) +$$

$$+ \sum_{n,m}{}' V_{n,m}^0 a_n^+ a_m \exp\left[2i\varkappa(P_n Q_n - P_m Q_m) + i\varkappa\varrho'(P_n - P_m)\right] \tag{2.10}$$

where

$$\tilde{\varepsilon}_0 = \varepsilon_0 - \frac{\gamma^2\omega^3}{\omega_1^2} + \frac{\omega_1 - \omega}{2} \tag{2.11a}$$

$$\varrho' = \left(\frac{2}{\omega}\right)^{1/2} \varrho. \tag{2.11b}$$

The Hamiltonian (2.10) is the starting point for further considerations.

The first term of (2.10) describes the free exciton localised on the n-th molecule. We see that its energy is renormalized. It is a potential well of depth $-\gamma^2\omega^3/\omega_1^2 + (\omega_1-\omega)/2$. This gives the temperature independent red-shift of the whole exciton band. For $c < 0$ this shift is larger than in the case of pure linear vibronic coupling. The adverse situation occurs for $c > 0$. This result is in agreement with Ref. [7]. This potential well results from the molecular distortion which accompanies the exciton. The greater the energy of vibration in the excited state is, the smaller the effective distortion accompanying the exciton. The third term of (2.10), in the approximation which includes only zero- and one-phonon processes, gives an additional correction to the potential well, $\bar{n}(\omega_1-\omega)$ ($\bar{n}$ is the average number of phonons), making the shift of the whole exciton band temperature-dependent. We see that the resulting shift for $\gamma = 0$ is $\frac{1}{2}(2\bar{n}+1)(\omega_1-\omega)$, what for $c \ll 1$ gives the same value as that obtained in Ref. [7] after disregarding two-phonon processes.

As γ is usually greater than c in molecular crystals, in further considerations we completely disregard two-phonon processes, and we shall look for the influence of the frequency change on zero- and one-phonon processes only.

3. Derivation of the Dyson equation for the exciton subsystem

We shall deal with the Hamiltonian (2.10) by the method of retarded time-dependent thermodynamic Green's functions, defined by the following expression [19]:

$$G_{AB}(t-t') = \langle\langle A(t)|\beta(t')\rangle\rangle \equiv -i\Theta(t-t')\langle[A(t), B(t')]\rangle \qquad (3.1)$$

$$A(t) = e^{-iHt}Ae^{iHt} \qquad (3.1a)$$

where $\langle\ldots\rangle$ means averaging over the equilibrium density matrix of the system with Hamiltonian H, and $A(t)$ and $B(t')$ are the arbitrary operators in the Heisenberg picture.

Such Green's functions satisfy the following equation of motion

$$E\langle\langle A|B\rangle\rangle_E = \frac{1}{2\pi}\langle[A, B]\rangle + \langle\langle[A, H]|B\rangle\rangle_E \qquad (3.2)$$

where

$$\langle\langle A|B\rangle\rangle_E = \frac{1}{2\pi}\int\limits_{-\infty}^{+\infty}e^{iE(t-t')}G_{AB}(t-t'). \qquad (3.2a)$$

We shall investigate further the exciton subsystem. The phonon subsystem is weakly perturbed by the interactions with excitons, as its perturbation is proportional to the average number of excitons f, and as usually $\varepsilon_0 \gg kT$ at room temperatures, we have $f \ll 1$. So we neglect henceforth the renormalization of phonon frequencies and in all formulae we shall average the phonon operators over the free-phonon Hamiltonian (second term in Eq. (2.10)).

We shall seek the Dyson equation for the Green's function $G^{n,m} = \langle\langle a_n|a_m^+\rangle\rangle_E$, as its poles give the elementary excitations of the exciton subsystem [19]. Its equation of motion reads:

$$E\langle\langle a_n|a_m^+\rangle\rangle_E = \frac{1}{2\pi}\delta_{n,m} + \frac{(1+c)^{1/2}-1}{2}\langle\langle a_n(P_n^2+\omega^2Q_n^2)|a_m^+\rangle\rangle_E + \check{\varepsilon}_0\langle\langle a_n|a_m^+\rangle\rangle_E +$$

$$+ \sum_{n_1\neq n}V_{nn_1}^0\langle\langle a_{n_1}\exp[2i\varkappa(P_nQ_n-P_{n_1}Q_{n_1})+i\varkappa\varrho'(P_n-P_{n_1})]|a_m^+\rangle\rangle_E. \qquad (3.3)$$

Regarding only zero- and one-phonon processes we decouple the higher order Green's functions which have emerged in Eq. (3.3) in a similar way as in the theory of anharmonic crystals [20]. We put:

$$\langle\langle a_n(P_n^2+\omega^2Q_n^2)|a_m^+\rangle\rangle = \langle P_n^2+\omega^2Q_n^2\rangle\langle\langle a_n|a_m^+\rangle\rangle_E, \qquad (3.4a)$$

$$\langle\langle a_{n_1}\exp[2i\varkappa(P_nQ_n-P_{n_1}Q_{n_1})+i\varkappa\varrho'(P_n-P_{n_1})]|a_m^+\rangle\rangle_E \qquad (3.4b)$$

$$\approx \langle D_{nn_1}\rangle\langle\langle a_{n_1}|a_m^+\rangle\rangle_E + i\varkappa\varrho'\langle D_{nn_1}\rangle\langle\langle a_{n_1}(P_n-P_{n_1})|a_m^+\rangle\rangle_E,$$

where

$$\langle D_{nn_1}\rangle = \langle\exp[2i\varkappa(P_nQ_n-P_{n_1}Q_{n_1})+i\varkappa\varrho'(P_n-P_{n_1})]\rangle \qquad (3.4c)$$

and averaging is carried over the ensemble of harmonic oscillators. Inserting (3.4a) to (3.4c) into equation (3.3) we obtain

$$(E-\varepsilon_1)\,\langle\langle a_n|a_m^+\rangle\rangle_E = \frac{1}{2\pi}\,\delta_{n,m} + \sum_{n_1\neq n} V_{n,n_1}^0\,\langle D_{nn_1}\rangle\,[\langle\langle a_{n_1}|a_m^+\rangle\rangle +$$

$$+ i\varkappa\varrho'\,\langle\langle a_{n_1}(P_n-P_{n_1})|a_m^+\rangle\rangle_E], \tag{3.5}$$

where

$$\varepsilon_1 = \varepsilon_0 - \frac{\gamma^2\omega^3}{\omega_1^2} + (2\bar{n}+1)\,\frac{\omega_1-\omega}{2} \tag{3.5a}$$

$$\bar{n} = (\exp\beta\,\omega-1)^{-1}. \tag{3.b}$$

The last term in (3.5) describes the transfer of exciton energy in a crystal with the inclusion of zero- and one-phonon processes. We see that the matrix elements of the resonance interaction $V_{n,n_1}^{0]}$ are renormalized by the factor $\langle D_{n,n_1}\rangle$ which we shall hereafter call the Debye-Waller factor (it is similar to the Huang–Rhys parameter in the theory of F-centers in ionic crystals). This renormalized matrix element gives us the probability of transfer of an exciton from one molecule to another without any explicit correlation with a phonon.

In order to obtain the closed chain of equations for Green functions we write the equation of motion for the function $\langle\langle a_n P_{n_1}|a_m^+\rangle\rangle_E$:

$$(E-\varepsilon_1)\,\langle\langle a_n P_{n_1}|a_m^+\rangle\rangle_E = \frac{\delta_{n,m}}{2\pi}\,\langle P_{n_1}\rangle - i\omega^2\,\langle\langle a_n Q_{n_1}|a_m^+\rangle\rangle_E -$$

$$-i\omega^2\,\frac{(1+c)^{1/2}-1}{2}\,\langle\langle a_{n_1}^+ a_n a_n Q_{n_1}|a_m^+\rangle\rangle_E +$$

$$+\sum_{n_2\neq n} V_{n;n_2}^0\langle\langle a_{n_2} D_{n_1 n_2} P_{n_1}|a_m^+\rangle\rangle -$$

$$-2\varkappa\sum_{n_2\neq n} V_{nn_2}^0\{\langle\langle a_n a_{n_1}^+ a_{n_2} D_{n_1 n_2} P_{n_1}|a_m^+\rangle\rangle_E - \langle\langle a_n a_{n_2}^+ a_{n_1} D_{n_2 n_1} P_{n_1}|a_m^+\rangle\rangle\}. \tag{3.6}$$

According to Refs [19] and [20] we may put

$$\langle\langle a_{n_1}^+ a_{n_1} a_n Q_{n_1}|a_m^+\rangle\rangle_E \approx \langle a_{n_1}^+ a_{n_1}\rangle\langle\langle a_n Q_{n_1}|a_m^+\rangle\rangle_E + \langle a_n^+ a_n\rangle\langle\langle a_{n_1} Q_{n_1}|a_m^+\rangle\rangle_E \approx 0 \tag{3.7a}$$

as $\langle a_n^+ a_n\rangle\ll 1$,

$$\langle\langle a_n a_{n_1}^+ a_{n_2} D_{n_1 n_2} P_{n_1}|a_m^+\rangle\rangle_E \simeq \delta_{nn_1}\langle\langle a_{n_2} D_{n_1 n_2} P_{n_1}|a_m^+\rangle\rangle_E$$

$$= \delta_{nn_1} i\varkappa\varrho'\langle D_{n_1 n_2}\rangle\langle(P_n-P_{n_2})P_{n_1}\rangle\langle\langle a_{n_2}|a_m^+\rangle\rangle_E. \tag{3.7b}$$

In Eq. (3.7b) only zero-phonon processes were included, as this terms is multiplied in Eq. (3.6) by $\varkappa\ll 1$ ($\varkappa$ is of order of magnitude smaller than c, see below).
We have also

$$\langle\langle a_n a_{n_2}^+ a_{n_1} D_{n_2 n_1} P_{n_1}|a_m^+\rangle\rangle_E \approx i\varkappa\varrho'\,\delta_{nn_2}\langle D_{nn_1}\rangle\langle(P_n-P_{n_1})P_{n_1}\rangle\langle\langle a_{n_1}|a_m^+\rangle\rangle_E, \tag{3.7c}$$

$$\langle\langle a_{n_2} D_{nn_2} P_{n_1}|a_m^+\rangle\rangle_E \approx \langle D_{nn_2}\rangle\times$$

$$\times[\langle\langle a_{n_2} P_{n_1}|a_m^+\rangle\rangle_E + i\varkappa\varrho'\langle(P_n-P_{n_2})P_{n_1}\rangle\langle\langle a_{n_2}|a_m^+\rangle\rangle_E]. \tag{3.7d}$$

Insertion of equations (3.7a) to (3.7d) into equation (3.6) gives

$$(E-\varepsilon_1) \langle\langle a_n P_{n_1}|a_m^+\rangle\rangle_E = \frac{\delta_{n,m}}{2\pi} \langle P_{n_1}\rangle -i\omega^2 \langle\langle a_n Q_{n_1}|a_m^+\rangle\rangle_E +$$

$$+ \sum_{n_2 \neq n} V_{nn_2}^0 \langle D_{nn_2}\rangle [\langle\langle a_{n_2} P_{n_1}|a_m^+\rangle\rangle_E + i\varkappa\varrho' \langle(P_n-P_{n_2})P_{n_1}\rangle \langle\langle a_{n_2}|a_m^+\rangle\rangle_E] -$$

$$-2i\varkappa^2\varrho' \sum_{n_2 \neq n} (\delta_{nn_1}-\delta_{n_1 n_2}) V_{nn_2}^0 \langle D_{nn_2}\rangle\langle(P_n-P_{n_2})P_{n_1}^-\rangle \langle\langle a_{n_2}|a_m^+\rangle\rangle. \tag{3.8}$$

Analogously we obtain the equation of motion for the Green's function $\langle\langle a_n Q_{n_1}|a_m^+\rangle\rangle_E$:

$$(E-\varepsilon_1) \langle\langle a_n Q_{n_1}|a_m^+\rangle\rangle_E = \frac{\delta_{n,m}}{2\pi} \langle Q_{n_1}\rangle +i \langle\langle a_n P_{n_1}|a_m^+\rangle\rangle_E +$$

$$+ \sum_{n_2 \neq n} V_{nn_2}^0 \langle D_{nn_2}\rangle [\langle\langle a_{n_2} Q_{n_1}|a_m^+\rangle\rangle_E + i\varkappa\varrho'\langle(P_n-P_{n_2})Q_{n_1}\rangle\langle\langle a_{n_2}|a_m^+\rangle\rangle_E] -$$

$$-2i\varkappa^2\varrho' \sum_{n_2 \neq n} (\delta_{nn_1}-\delta_{n_1 n_2}) V_{nn_2}^0 \langle D_{nn_2}\rangle\langle(P_n-P_{n_2})Q_{n_1}^-\rangle\langle\langle a_{n_2}|a_m^+\rangle\rangle_E -$$

$$-\varkappa\varrho' \sum_{n_2 \neq n} (\delta_{nn_1}-\delta_{n_1 n_2}) V_{nn_2}\langle D_{nn_2}\rangle \langle\langle a_{n_2}^-|a_m^+\rangle\rangle_E. \tag{3.9}$$

The equations (3.5), (3.8) and (3.9) form a closed set from which the Dyson equation for $\langle\langle a_n|a_m^+\rangle\rangle_E$ can be derived. In order to resolve this set of equations we go to the momentum representation of vibrations. We define

$$Q_{\sigma q} = N^{-1/2} \sum_{f,\varrho} c_{\varrho\sigma}^*(q)e^{-iq\cdot f}Q_{f\varrho}$$

$$P_{\sigma q} = N^{-1/2} \sum_{f,\varrho} c_{\varrho\sigma}^*(q)e^{-iq\cdot f}P_{f\varrho} \tag{3.10}$$

where $(f, \varrho) \equiv n$, f labels the position of the unit cell and ϱ labels the position of a molecule in a given unit cell, q is the quasi-momentum of the phonon, and σ labels the branches of vibrations in the crystal. Introducing the following matrices:

$$(E)_{m,n} = (E-\varepsilon_1)\delta_{nm},$$

$$(A)_{nm} = (1-\delta_{nm})V_{nm}^0\langle D_{nm}\rangle,$$

$$(L(q\sigma))_{nn_2} = V_{nn_2}^0\langle D_{nn_2}\rangle[c_{\varrho\sigma}(q)e^{iqf}-c_{\varrho_2\sigma}(q)e^{iqf_2}],$$

$$(G)_{nm} = \langle\langle a_n|a_m^+\rangle\rangle_E,$$

$$(G_{\sigma q})_{nm} = \langle\langle a_n P_{\sigma q}|a_m^+\rangle\rangle_E,$$

$$(\tilde{G}_{\sigma q})_{nm} = \langle\langle a_n Q_{\sigma q}|a_m^+\rangle\rangle_E, \tag{3.11}$$

and inserting the following relations which hold in the harmonic approximation

$$\langle P\rangle = \langle Q\rangle = 0,$$

$$\langle P^2\rangle = \frac{\omega}{2}(2\bar{n}+1), \quad \langle PQ\rangle = -\frac{i}{2}, \tag{3.12}$$

we obtain

$$(E-A)\,G = \frac{1}{2\pi} + i\varkappa\varrho'N^{-\frac{1}{2}}\sum_{\boldsymbol{q}\sigma} L^*(\boldsymbol{q}\sigma)\,G_{\sigma\boldsymbol{q}}, \tag{3.13a}$$

$$(E-A)\,G_{\sigma\boldsymbol{q}} = -i\omega^2\,G_{\sigma\boldsymbol{q}} + i\varkappa\varrho'\frac{\omega}{2}(2\bar{n}+1)(1-2\varkappa)N^{-\frac{1}{2}}L(\boldsymbol{q}\sigma)\,G, \tag{3.13b}$$

$$(E-A)\,G_{\sigma\boldsymbol{q}} = iG_{\sigma\boldsymbol{q}} + \frac{1}{2}\varkappa\varrho'(1-2\varkappa)\,N^{-\frac{1}{2}}L(\boldsymbol{q}\sigma)\,G - \varkappa\varrho'N^{-\frac{1}{2}}L(\boldsymbol{q}\sigma)\,G. \tag{3.13c}$$

Resolving the set of equations (3.13a) to (3.13c) we finally obtain the following integral equation for $\boldsymbol{G}$:

$$(E-A)\,G = \frac{1}{2\pi} + \frac{(\varkappa\varrho')^2\omega}{2N}\sum_{\boldsymbol{q}\sigma} L^*(\boldsymbol{q}\sigma)\left\{(1-2\varkappa)\left[\frac{\bar{n}+1}{E-A-\omega} + \frac{\bar{n}}{E-A+\omega}\right] + \right.$$

$$\left. + \frac{4\omega\varkappa}{(E-A-\omega)(E-A+\omega)}\right\}L(\boldsymbol{q}\sigma)\,G \tag{3.14}$$

which is the Dyson equation of our problem.

Equation (3.14) can be written in the form

$$G = G_0 + 2\pi G_0 MG \tag{3.15a}$$

$$G_0 = \frac{1}{2\pi}\frac{1}{E-A} \tag{3.15b}$$

where G_0 is the Green's function of excitons "dressed" in the zero-phonon processes of interactions, and M is the mass operator describing the one-phonon processes. This operator includes the interactions between excitons with virtual exchange of one and two phonons, and the transfer of exciton correlated with one phonon. The solution of equation (3.15a) is:

$$G = \frac{1}{2\pi}\frac{1}{E-A-M} \tag{3.16}$$

and the poles of $\boldsymbol{G}$ give the renormalized energies of excitons if only the damping resulting from Im $\boldsymbol{M}(E)$ is small, i.e. Im $\boldsymbol{M}(E) \ll$ Re $\boldsymbol{M}(E)$.

The equation (3.14) in the limit $\varkappa \to 0$ goes into the equation which had been obtained by Walasek [8].

4. Discussion

If we go for simplicity to the crystal with one molecule per unit cell, we then obtain from Eq. (3.16) the following expression for the real part of the exciton energy:

$$\varepsilon_k = \varepsilon_{k0} + \text{Re } M_k(\varepsilon_k), \tag{4.1}$$

where

$$\varepsilon_{k0} = \varepsilon_0 - \frac{\gamma^2\omega^3}{\omega_1^2} + \frac{(\omega_1-\omega)\,(2\bar{n}+1)}{2} + \sum_{n\neq m} V_{nm}e^{-ik(n-m)},$$

$$V_{nm} = V_{nm}^0\,\langle D_{nm}\rangle, \tag{4.2}$$

$$\mathrm{Re}\,M_k(\varepsilon_k) = (\varkappa\varrho)^2\,\frac{\Omega}{(2\pi)^3}\,(1-2\varkappa)\,P\left[\int_B \frac{(\bar{n}+1)\,(\varepsilon_{k-q,0}-\varepsilon_{k,0})^2}{\varepsilon_k-\varepsilon_{k-q,0}-\omega}\,d^3q + \right.$$

$$\left. + \int_B \frac{\bar{n}(\varepsilon_{k-q,0}-\varepsilon_{k,0})^2}{\varepsilon_k-\varepsilon_{k-q,0}+\omega}\,d^3q\right] +$$

$$+ 4\omega(\varkappa\varrho)^2\,\frac{\Omega}{(2\pi)^3}\,P\int_{V_B} \frac{(\varepsilon_{k-q,0}-\varepsilon_{k,0})^2}{(\varepsilon_k-\varepsilon_{k-q,0}-\omega)\,(\varepsilon_k-\varepsilon_{k-q,0}+\omega)}\,d^3q. \tag{4.3}$$

Here Ω is the volume of the unit cell, P is the symbol of the principal value, and V_B is the volume of the first Brillouin zone. The expressions (4.1) to (4.3) can be easily investigated in the case of a linear crystal with nearest-neibours interactions[1]. The equation (4.2) gives us the "dressed into zero-phonon processes" exciton band, which is red-shifted, its width being symmetrically reduced by the Debye–Waller factor $\langle D\rangle$. So the effective mass of an exciton is increased and temperature dependent. We shall see below that it increases with temperature ,*i.e.*, the higher the temperature, the bigger the cloud of phonons accompanying the exciton.

In order to evaluate $\langle D\rangle$, we assume that $|\varkappa|\ll 1$ $(|c|\sim 10|\varkappa|)$ and neglect terms which are proportional to $\varkappa^n$, $n\geqslant 2$. We have

$$\langle D\rangle = \langle e^{2i\varkappa(P_1Q_1-P_2Q_2)+i\varkappa\varrho^1(P_1-P_2)}\rangle \equiv \langle e^{\alpha(A+B)}\rangle$$

where

$$\alpha = i\varkappa\varrho', \quad A = P_1-P_2,$$

$$B = \frac{2}{\varrho'}\,(P_1Q_1-P_2Q_2).$$

The average $\langle\exp\alpha A\rangle$ in the harmonic approximation can be easily calculated and is

$$\langle e^{i\varkappa\varrho'(P_1-P_2)}\rangle = e^{-\varkappa^2\varrho^2(2\bar{n}+1)}. \tag{4.4}$$

We shall now show that the first correction to (4.4) is of order of magnitude $\varkappa^2$. We put

$$e^{\alpha(A+B)} = e^{\alpha A}V(\alpha)$$

$$V(\alpha) = 1 + \int_0^\alpha dx\,B(x) + \int_0^\alpha dx_2\int_0^{x_2} dx_1\,B(x_2)\,B(x_1) + \dots$$

$$B(x) = e^{-xA}Be^{xA} = \frac{2}{\varrho'}\,(P_1Q_1-P_2Q_2) + \frac{2ix}{\varrho'}\,(P_1+P_2). \tag{4.5}$$

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[1] Excitons in linear crystals can be treated as fermions [21] but the Dyson equation obtained by us for the case of three-dimensional crystals, in which excitons were treated as bosons, is also valid for the one-dimensional case.

Thus, the correction proportional to $\varkappa$ is the average of the type

$$\left\langle \int\limits_0^\alpha dx e^{\alpha A} B(x)\right\rangle$$

and in the harmonic approximation it vanishes.

Thus, we have

$$\langle D\rangle = \langle e^{i\varkappa\varrho'(P_1-P_3)}\rangle + O(\varkappa^2). \tag{4.6}$$

From Eqs (2.8a) and (2.8b) we obtain

$$\varkappa^2\varrho^2 = \gamma^2\left[1-\frac{9}{4}\,c\left(1-\frac{15}{8}\,c\right)\right] + O(c^3),$$

$$\varkappa = -\frac{1}{8}\,c + \frac{c^2}{16} + O(c^3),$$

$$\varkappa\varrho = \gamma\left[1-\frac{9}{8}\,c\left(1-\frac{11}{8}\,c\right)\right] + O(c^3), \tag{4.7}$$

and finally

$$\langle D\rangle = \langle D_0\rangle\left[1+\frac{9}{4}\,\gamma^2(2\bar{n}+1)c\left(1-\frac{15}{8}\,c\right) + \frac{81}{32}\,\gamma^4(2\bar{n}+1)^2 c^2 + O(c^3)\right]$$

$$\langle D_0\rangle = \exp\left[-\gamma^2(2\bar{n}+1)\right] \tag{4.8}$$

(we keep terms with c^2 as $|c| \sim 10|\varkappa|$). $\langle D_0\rangle$ is the expression for the Debye–Waller factor obtained by Walasek. This expression gives us the temperature dependence of the probability of exciton transition from one molecule to another, and its inverse is proportional to the effective mass of an exciton "dressed into zero-phonon processes". We see that for $c > 0$ $(\omega_1 > \omega)$ the reduction of the pure electronic transition matrix element by the zero-phonon processes is smaller than in the case of pure linear vibronic coupling. That is to say that an increase of the vibrational frequency after electronic excitation of the molecule brings about a decrease of the effective phonon cloud which accompanies the exciton. The adverse situation arises for a decrease of vibrational frequency $(c < 0)$. We see that the direction of this change is the same as for the red-shift of the whole exciton band.

The first term of Re $M_k(\varepsilon_k)$ in Eq. (4.3) describes the asymmetric compression of the exciton band resulting from the one-phonon processes [3, 7]. Again, this compression is larger for $c < 0$, and smaller for $c > 0$, so the influence of the frequency change on the one-phonon processes is of the same kind as in the case of the zero-phonon ones. This term also contains the contribution to the renormalization energy of excitons which originates from the exciton-exciton interaction *via* phonon. This interaction is attractive for all excitons as long as the vibrational quantum coupled with the exciton is larger than the unperturbed exciton bandwidth. As our formulation is applicable for the weak coupling theory of molecular crystals this last requirement is fullfilled.

The last term in Eq. (4.3) gives a small renormalization of the exciton energy and the additional shift of the whole exciton band towards the longer wavelengths for $c < 0$ and

a blue-shift for $c > 0$. This renormalization originates from the exciton-exciton interactions with the virtual exchange of two phonons. This interaction is again attractive if the frequency of vibration in the excited state of the molecule is smaller than in the ground state. Thus the attractive forces between excitons are stronger for $c < 0$.

Hence the condensation of excitons proposed by Blatt *et al.* [22] seems to be doubtful. We think that this kind of condensation may be produced by the strong repulsion (of a kinematical nature) between excitons under conditions of high exciton concentration, which may be achieved by laser light (*cf.* [23]).

We conclude that a small decrease in the vibrational frequency after electronic excitation of molecules forming a molecular crystal leads to the intensification of all energetic changes in the Frenkel exciton system. A small increase in the vibrational frequency leads to opposite changes.

5. Integral properties of the exciton optical trasition band

It is worthwhile to calculate such integral properties of the exciton optical transition band as its center of gravity and width. To do this we must calculate the first and second moments of transition. In the case of the linear vibronic coupling the center of gravity of the optical transition is located at the energy of the free exciton with zero momentum, and its width is proportional to the coupling constant and increases with temperature [14].

We want to see how these conclusions are altered by the quadratic vibronic coupling.

We consider the absorption of light in a thin crystal, such that we can neglect the retardation effect. Then the absorption coefficient $\mu(E)$ is given by the spectral density of the Green's function of the exciton subsystem [24]. In dipole approximation we have

$$\mu(E) = c \sum_{\lambda,\lambda'} (\boldsymbol{\mu}_{ge}\boldsymbol{e}_\lambda)(\boldsymbol{\mu}_{ge}\boldsymbol{e}_{\lambda'}) \int_{-\infty}^{+\infty} \langle A_q(t)A_q^+(0)\rangle e^{iEt}dt \tag{5.1}$$

where $\boldsymbol{\mu}_{ge}$ is the dipole transition moment between the ground and the excited state under consideration, $\boldsymbol{e}_\lambda$ is the vector of light polarization, $\boldsymbol{q}$ is the momentum of the absorbed light, and c is a constant. As $|\boldsymbol{q}| \ll 1$, we henceforth assume $\boldsymbol{q} = 0$.

The first and the second moments of the transition are defined as follows:

$$M_1 = \int_{-\infty}^{+\infty} E\mu(E)dE$$

$$M_2 = \int_{-\infty}^{+\infty} E^2\mu(E)dE. \tag{5.2}$$

Inserting Eqs (5.1) into (5.2) we obtain (we neglect the multiplicative factor which is of no interest to us)

$$M_1 = \int_{-\infty}^{+\infty} dE \int_{-\infty}^{+\infty} dt Ee^{iEt}\langle A_{q=0}(t)A_{q=0}^+(0)\rangle$$

$$= -i\left[\frac{d}{dt}\langle A_q(t)A_{q=0}^+(0)\rangle\right]_{t=0} = \langle[A_{q=0}, H]A_{q=0}^+\rangle \tag{5.3}$$

and similarly

$$M_2 = \langle [[A_{q=0}, H], H] A_{q=0}^+ \rangle \tag{5.3b}$$

H is the Hamiltonian of the exciton-phonon system. If we want to calculate (5.3a) and (5.3b) in the zero-phonon approximation for the weak coupling theory of molecular crystals we must insert into these expressions the equations (2.7) and use the Hamiltonian given by Eq. (2.9). After some algebraic computations we obtain:

$$\bar{E} = M_1 = \varepsilon_1 + \varkappa^2 \varrho^2 \omega + \sum_n V_{n,0}^0 + \frac{\omega_1^2 - \omega^2}{4\omega} (2\bar{n}+1) + O(c^2), \tag{5.4a}$$

$$\overline{(\Delta E)^2} = M_2 - M_1^2 = \varkappa^2 \varrho^2 \omega (1-2\varkappa)(2\bar{n}+1) + \frac{(\omega_1^2 - \omega^2)^2}{8\omega^2} (2\bar{n}+1)^2 + O(c^3) \tag{5.4b}$$

where ε_1 is given by Eq. (3.5a), and $\bar{n}$ is the average number of phonons coupled to an exciton.

We see that the center of gravity of the exciton optical transition is no longer located at the energy of the free, zero-momentum exciton, but in the case of the decrease in the vibrational frequency after electronic excitation of the molecule, it is red-shifted and temperature dependent. We see also, that the linear coupling constant γ is now renormalized in the same way as in the equation (4.3). This renormalization does not occur in the strong-coupling theory of molecular crystals [25]. So, in the case of a small decrease in the vibrational frequency in the excited state, the estimation of the linear vibronic coupling parameter, i.e., the distortion of molecule, from the width of the exciton optical transition band may lead to an overestimated value.

The breakdown of the $T^{1/2}$ dependence of the width in the high temperature limit and the temperature dependence of the center of gravity should give us information of the existence of the quadratic vibronic coupling.

Formulae (5.4a) and (5.4b) go for $\omega_1 = \omega$ into the formulae which have been obtained by Merriefield [14].

The problem of the detailed structure of the exciton optical transition band and the problem of the influence of the one-phonon processes on the exciton transition probabilities will be treated in the future studies.

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