CHANGE OF THE VIBRATIONAL FREQUENCY AND THE LINEAR VIBRONIC COUPLING IN MOLECULAR CRYSTALS. II. ONE-PHONON EXCITON TRANSFER

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It is shown that in molecular crystals, in which the vibronic coupling occurs, phonon-induced exciton transfer exists. This transfer can compensate and even be superior to an increase of exciton effective mass resulting from molecular distortion, which accompanies the exciton. It depends on the linear vibronic coupling constant (or renormalized coupling constant in the case of a frequency change). An increase of vibrational frequency in the exited state of a molecule causes effective damping of such a transfer. It is suggested that this transfer of a vibronic exciton can go through scattering vibronic exciton-phonon states, which have been discussed by Philpott.

A crude numerical calculation of the probability of this transfer in the first singlet-exciton state of naphtalene crystal is given.

1. Formulation of the problem

In the first paper of this series of publications [1] it was shown that in the zero-phonon approximation, which does not take into account any correlations between the vibronic exciton and phonons, the effective mass of the exciton increases with the vibronic coupling constant. This effect decreases the probability of an exciton transfer from one molecule to another. The electronic matrix resonance interaction element is depressed by the Debye-Waller-type factor, and is

$$V_{nn'} = V_{nn'}^0 e^{-\varkappa^2\varrho^2(2\bar{n}+1)} \qquad (1)$$

where $V_{nn'}^0$ is the pure electronic matrix element of the resonance interaction between the n-th and n'-th molecule, $\varkappa^2\varrho^2$ is the square of the linear vibronic coupling constant renormalized by a frequency change, and $\bar{n}$ is the the average number of phonons [1].

It is rather evident that the exciton-phonon coupling should lead to the opening of new channels for exciton transfer processes. Such a transfer should be correlated with phonons.

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Three years ago Philpott published two papers [2, 3] in which he considered mixing between one-exciton states, and vibronic exciton-phonon correlated and scattering states. It was shown that this mixing leads, among other results, to the asymmetrical compression of the vibronic exciton band [2]. Such a compression was pointed out first by Merriefield [4]. In the reference [1] the Dyson equation for the exciton Green's function was obtained. This equation was written in the one-phonon approximation which takes into account the correlations between vibronic exciton and phonon states. It was pointed out that the asymmetrical compression of an exciton band results from the one-phonon processes which describe exciton-phonon correlations. This suggests that approximation used in [1] take into account implicitly the mixing considered by Philpott. The direct proof of this is rather difficult because of totally different mathematical formalisms used in those papers.

Although vibronic-exciton-phonon correlated and scattering states do not explicitly appear in the field-theoretical formalism used in [1], it seems that this formalism is more suitable for the considerations of the indirect exciton transfer processes. Such a transfer can be thought as going through the exciton-photon scattering states. The direct transfer described by the formula (1) does not take scattering states into account.

The one-phonon processes which describe the mixing of the exciton and scattering states are included in the mass operator, which was obtained in [1]. It reads:

$$M(E) = \frac{\varkappa^2 \varrho^2 (1-2\varkappa)}{N} \sum_{\boldsymbol{q},\sigma} \boldsymbol{L}_{\boldsymbol{q},\sigma}^* \left\{ \frac{\bar{n}+1}{E-\boldsymbol{A}-\omega} + \frac{\bar{n}}{E-\boldsymbol{A}+\omega} \right\} \boldsymbol{L}_{\boldsymbol{q},\sigma} +$$

$$+ \frac{4\varkappa^3 \varrho^2}{N} \sum_{\boldsymbol{q},\sigma} \boldsymbol{L}_{\boldsymbol{q},\sigma}^* \frac{1}{(E-\boldsymbol{A}-\omega)(E-\boldsymbol{A}+\omega)} \boldsymbol{L}_{\boldsymbol{q},\sigma} = M_1(E) + M_2(E) \tag{2}$$

where

$$(\boldsymbol{L}_{\boldsymbol{q},\sigma})_{nn'} = V_{nn'}^0 e^{-\varkappa^2 \varrho^2 (2\bar{n}+1)} (c_{\varrho\sigma}(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{f}} - c_{\varrho'\sigma}(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{f}'}), \quad n = (f, \varrho) \tag{3}$$

$$(E_{nn'} = (E-e_1)\delta_{nn'}, \tag{4}$$

$$e_1 = e_0 - \frac{\gamma^2 \omega^3}{\omega_1^2} + (2\bar{n}+1)\frac{\omega_1 - \omega}{2}, \tag{5}$$

$$(\boldsymbol{A})_{nn'} = (1-\delta_{nn'}) V_{nn'}^0 e^{-\varkappa^2 \varrho^2 (2\bar{n}+1)}, \tag{6}$$

$$\varkappa = -\frac{1}{4}\ln\frac{\omega_1}{\omega}, \tag{7}$$

$$\varkappa^2 \varrho^2 = \frac{4\gamma^2 \varkappa^2 \omega^4}{\omega_1^4 (1-e^{2\varkappa})^2}, \tag{8}$$

ω, ω_1 are the frequencies of vibrations in the ground and electronically excited state of molecule, respectively, γ is the linear vibronic coupling constant [4], e_0 is the excitation energy of a molecule contained in a molecular crystal, $\boldsymbol{q}$ is the wave vector and belongs to first Brillouin zone, $\boldsymbol{f}$ and ϱ number unit cells and positions of a molecule in a given unit cell, respectively, and σ numbers different branches of vibrations resulting from the Davydov splitting.

The operator $M_1(E)$ describes the one-phonon processes proceeding from the linear vibronic coupling and takes into account the renormalization of the coupling constant due to the frequency change. The operator $M_2(E)$ proceeds only from the quadratic vibronic coupling (*i.e.*, frequency change) and describes interactions between excitons due to virtual exchange of two phonons.

The wavefunction $\psi(n)$ describing the motion of excitons perturbed by the phonon system satisfies therefore the following "effective wave equation" [5]:

$$E\psi(n) - \sum_{n' \neq n} [V_{nn'} + M(n, n'; E)]\psi(n') = 0 \qquad (9)$$

and the exciton energy transfer between the n-th and n'-th molecules is determined by the real part of the non-diagonal term in the square bracket of (9).

Also Re $M(n, n'; E)$ describes the probability of exciton transfer of energy E between the n-th and n'-th molecule, which results from the one-phonon processes. In the following we drop the symbol Re whenever no confusion is apparent.

We shall consider further only the "effective" exciton one-phonon transfer for a given exciton band, which we define as follows:

$$M(n, n')_{\text{eff.}} = \frac{1}{\Delta E} \int_{-\Delta E/2}^{\Delta E/2} M(n, n'; E) dE \qquad (10)$$

where ΔE is the width of an exciton band, and zero of energy is taken for a centre of a band.

2. The one-phonon exciton transfer resulting from the $M_1(E)$ operator

We first consider the probability of one-phonon exciton energy transfer processes which are described by the first part of the mass operator (2), $M_1(E)$.
We can write

$$M_1(n, n'; E) = \frac{\gamma_r^2}{N} \sum_{q,\sigma} \sum_{n_1,n_2} V_{nn_1} V_{n_2 n'}[(\bar{n}+1)g(n_1, n_2; E-\omega) +$$

$$+\bar{n}g(n_1, n_2; E+\omega)][c_{\varrho\sigma}^*(q)e^{-iq \cdot f} - c_{\varrho_1\sigma}^*(q)e^{-iq \cdot f_1}] \, [c_{\varrho_2\sigma}(q)e^{iq \cdot f_2} - c_{\varrho'\sigma}(q)e^{iq \cdot f'}]$$

$$= 2\gamma_r^2 \sum_{n_1} V_{nn_1} V_{nn'}[(\bar{n}+1)g(n_1, n; E-\omega) + \bar{n}g(n_1, n; E+\omega)] -$$

$$-\gamma_r^2 \sum_{n_1} V_{nn_1} V_{n_1 n'}[(\bar{n}+1)g_0(E-\omega) + \bar{n}g_0(E+\omega)] \qquad (11)$$

where the following notations were introduced

$$g(n_1, n_2; E) = \left(\frac{1}{E-A}\right)_{n_1 n_2}, \quad g_0(E) = \left(\frac{1}{E-A}\right)_{nn}, \quad \gamma_r^2 = \varkappa^2 \varrho^2(1-2\varkappa) \qquad (12)$$

and hermitian properties of the resonance interaction matrix V were used. $g(n_1, n_2; E)$ is the zero-phonon exciton Green's function and is equal to [6, 7, 8]:

$$g(n_1, n_2; E) = \frac{1}{N} \sum_{k,\sigma} \frac{c_{\varrho_1\sigma}(k)c_{\varrho_2\sigma}(k) e^{ik \cdot (f_2 - f_1)}}{E - E_\sigma^{\text{of}}(k)} \qquad (13)$$

where $E_\sigma^{\text{of}}(\boldsymbol{k})$ is the zero-phonon energy of an exciton from the σ-th branche of a Davydov manifold with the wave-vector $\boldsymbol{k}$, and for molecular crystals with one molecule per unit cell is

$$E^{\text{of}}(\boldsymbol{k}) = e_1 + \sum_{n_1 \neq n} V_{nn_1} e^{-i\boldsymbol{k}' \cdot (n-n_1)} \tag{14}$$

where e_1 is given by Eq. (6). We put further $e_1 = 0$.
From Eqs (13) and (14) we have

$$\sum_{n_1} V_{nn_1} g(n_1, n; E \pm \omega) = (E \pm \omega) g_0(E \pm \omega) - 1 \tag{15}$$

and taking into account this last equation and the orthogonality relation

$$\frac{1}{N} \sum_{\boldsymbol{q},\sigma} c_{\varrho_1\sigma}(\boldsymbol{q}) c_{\varrho_2\sigma}^*(\boldsymbol{q}) e^{i\boldsymbol{q} \cdot (f_1-f_2)} = \delta_{\varrho_1\varrho_2} \delta_{f_1 f_2} = \delta_{n_1 n_2} \tag{16}$$

we can rewrite Eq. (11) in the following form:

$$M_1(n, n'; E) = -2\gamma_r^2 \, V_{nn'}(2\bar{n}+1) +$$
$$+ \gamma_r^2 \{(\bar{n}+1) g_0(E-\omega)[2V_{nn'}(E-\omega) - (V^2)_{nn'}] +$$
$$+ \bar{n} g_0(E+\omega)[2V_{nn'}(E+\omega) - (V^2)_{nn'}]\}, \tag{17}$$

where

$$(V^2)_{nn'} = \sum_{n_1} V_{nn_1} V_{n_1 n'}. \tag{18}$$

In order to obtain $M_1(n, n')_{\text{eff.}}$ we must know explicitly the energy dependence of the zero-phonon Green's function $\operatorname{Re} g_0(E)$. The properties of $\operatorname{Re} g_0(E)$ have been discussed by many authors [9, 10]. It is finite and positive at the upper edge, goes through zero near the band centre, and is negative at the lower edge. It can be shown that [11, 12]

$$g_0(E) = -\frac{i}{N} \sum_{\boldsymbol{k}} \int_{-\infty}^{\infty} dt\, \theta(t) e^{iEt - \Gamma t - iE(\boldsymbol{k})t + G(t)} \tag{19}$$

where $E(\boldsymbol{k})$ is the energy of a free-exciton, Γ is a positive constant which describes the damping of excitons due to their interactions with crystal vibrations, and

$$G(t) = \varkappa^2 \varrho^2 [(\bar{n}+1) e^{-i\omega t} + \bar{n} e^{i\omega t} - (2\bar{n}+1)] +$$
$$+ \varkappa^3 \varrho^2 [2\bar{n} e^{-i\omega t} + 2(\bar{n}+1) e^{i\omega t} - (2\bar{n}+1)(e^{2i\omega t} - e^{-2i\omega t})]. \tag{20}$$

As the value of the integral in (19) depends mainly on integrand values in the $t \approx 0$ region, we can put

$$G(t) = -itA - t^2 B^2 + \varkappa^2 \varrho^2, \tag{21}$$
$$A = \omega \varkappa^2 \varrho^2 (1 - 2\varkappa), \tag{21a}$$
$$B^2 = \omega A (2\bar{n}+1), \tag{21b}$$

for not too weak vibronic coupling $(\varkappa^2\varrho^2 \gg 1)$ and for energies inside the exciton band we obtain therefore

$$\operatorname{Re} g_0(E) = \frac{1}{N} \sum_k \frac{E + A - E(k)}{B^2} \left\{ 1 - \frac{[E + A - E(k)]^2}{24 B^2} \right\} \exp \left\{ - \frac{[E + A - E(k)]^2}{4 B^2} \right\} \quad (22)$$

whereas for energies outside of the exciton band we have

$$\operatorname{Re} g_0(E) = \frac{1}{N} \sum_k \frac{E + A - E(k)}{[E + A - E(k)]^2 + \Gamma^2} . \quad (23)$$

In the reference [8] the experimental curve of $\operatorname{Re} g_o(E)$ for the first singlet-exciton band in naphthalene crystal is given. Such curves can be obtained from the measurements of the dispersion of the crystal dielectric constant [13][1].
One can see that the $\operatorname{Re} g_0(E)$ can be well approximated by the following formula:

$$\operatorname{Re} g_0(E) = aE \left(1 - \frac{cE^2}{6} \right) e^{-cE^2} \quad (24a)$$

for $E \in (-\varDelta E/2,\ \varDelta E/2)$ and

$$\operatorname{Re} g_0(E) = \frac{\alpha E}{E^2 + \beta} \quad (24b)$$

for $E \in (-\infty,\ -\varDelta E/2)$ or $(\varDelta E/2, \to \infty)$.

These formulae are in accordance with (22) and (23). The van Hove's singularities which appear in the density of state function, and therefore also in $\operatorname{Re} g_o(E)$ [14] are not essential for our calculations because of our definition of the "effective" transfer probability (see Eq. (10)). We can now find values of $a,\ c,\ \alpha,\ \beta$ parameters from the following conditions:
a) values of extrema and their positions should be equal to the experimental ones,
b) values of $\operatorname{Re} g_0(E)$ at band edges should be also equal to the experimental ones.
For the first singlet-exciton band in the naphthalene crystal we obtain

$$\operatorname{Re} g_0(E) = \begin{cases} \dfrac{0.8773\,x}{x^2 - 37.14} & x < -10.5 \\[2mm] 0.0407\,x(1 - 0.0016\,x^2)e^{-0.0094x^2} & -10.5 \leqslant x < 0 \\[1mm] 0.0451\,x(1 - 0.0016\,x^2)e^{-0.0094x^2} & 0 < x \leqslant 10.5 \\[2mm] \dfrac{0.961\,x}{x^2 - 37.14} & x > 10.5 \end{cases} \quad (25)$$

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[1] The function $g_0(E)$ can be also obtained from the density of states function, by the relation

$$\operatorname{Re} g_0(E) = P \int \frac{\varrho(E')dE'}{E - E'}$$

where $\varrho(E')$ can be estimated from the band-to-band optical transitions [22].

where $x = E/10$, and E is given in reciprocal centimeters. The comparison between Re $g_0(E)$ values obtained from the formulae (25) and from experiment is given in Table I. We see that the reproduction of experimental data is quite accurate. We can therefore take the formulae (24a, b) for further calculations.

TABLE I

x	Re $g_0(E)$	exp. data	x	Re $g_0(E)$	exp. data
−100	−0.0088	−0.010	0	0.0000	0.0000
−50	−0.0178	−0.019	2	0.0866	0.084
−30	−0.0305	−0.032	4	0.1542	0.156
−20	−0.0483	−0.052	6	0.1820	0.180
−10.5	−0.1261	−0.120	7	0.1840	0.184
−9	−0.1494	−0.148	8	0.1779	0.180
−8	−0.1605	−0.160	9	0.1655	0.164
−7	−0.1660	−0.166	10.5	0.1380	0.132
−6	−0.1643	−0.160	20	0.0530	0.052
−4	−0.1392	−0.130	30	0.0334	0.032
−2	−0.0782	−0.076	50	0.0195	0.02
0	0.0000	0.000	100	0.0096	0.01

Approximations leading to the mass-operator (2) are good enough for the case of strong vibronic coupling, or, equivalently, for the weak-coupling theory of molecular crystals. In such cases, the quantum of vibration coupled to the exciton is greater than the exciton bandwidth ΔE, therefore in Eq. (17) all arguments of $g_0(E)$ lie outside of the exciton band, so only Eq. (24b) is needed. In future we assume that Re $g_0(E)$ is an odd function. For naphthalene this assumption introduces an error of about 10%. We have done this assumption in order to simplify the next formulae, and because we do not lose anything physically important.

Also in Eq. (17) we shall put

$$\text{Re } g_0(E) = \frac{\alpha E}{E^2 + \beta}. \tag{26}$$

In order to connect the α and β parameters with any physical quantities, we note that in the effective mass approximation we can write for $E + A = e \gg k_o^2/2m_{\text{eff}}$.

$$\text{Re } g_0(k) \sim \int_0^{k_0} \frac{(e - k^2/2m_{\text{eff.}})k^2 dk}{(e - k^2/2m_{\text{eff.}})^2 + \Gamma^2} - \Gamma^2 \int_0^{k_0} \frac{k^2 dk}{(e - k^2/2m_{\text{eff.}})^3} \tag{27}$$

where $k_o^2/2m_{\text{eff}} = \Delta E$, or

$$\text{Re } g_0(k) \sim \frac{2(2\Delta E m_{\text{eff.}})^{3/2}}{3E} - \frac{\Gamma^2(2\Delta E m_{\text{eff.}})^{5/2}}{3E^3}. \tag{27a}$$

Putting

$$\Delta E = \frac{\hbar^2 \pi^2}{2|m_{\text{eff.}}|b^2} \tag{28}$$

which holds in the effective mass approximation (b is the lattice constant), we obtain by comparing (27a) and (26)

$$\alpha \sim 1/b^3, \quad \beta \sim \Gamma^2/b^3. \tag{29}$$

Also values of the zero-phonon exciton Green's function outside of the band depend mainly on the geometrical structure of the crystal, whereas its derivative at the edges depends on the damping of exciton states by the lattice vibrations. We note that β should increase with temperature.

Insertion of Eqs (26) and (17) into Eq. (10) leads after some manipulations to the following result:

$$M_1(n, n'_{\text{eff.}}) = 2\gamma r_r^2 V_{nn'}(2\bar{n}+1)(10\alpha - 1) +$$

$$+ \frac{100\alpha\sqrt{|\beta|}\,\gamma_r^2 V_{nn'}}{\Delta E} \ln \frac{\omega^2 - \Delta E^2/4 - 100\beta + 10\Delta E\sqrt{|\beta|}}{\omega^2 - \Delta E^2/4 - 100\beta - 10\Delta E\sqrt{|\beta|}} -$$

$$- \gamma_r^2(V^2)_{nn'} \frac{\alpha}{2\sqrt{|\beta|}} \ln \frac{100\beta + \omega^2 + \Delta E^2/4 + \Delta E\omega}{100\beta + \omega^2 + \Delta E^2/4 - \Delta E\omega}. \tag{30}$$

For the naphthalene crystal first singlet exciton band parameters, which (assuming odd property of the Re $g_0(E)$) are $\alpha = 0.916$, $\beta = -37.14$, $\Delta E = 210$ cm^{-1}, $\omega = 1400$ cm^{-1} (we have taken for the ω the frequency of vibrations which couple effectively to the exciton in all aromatic hydrocarbon crystals [15]), we obtain

$$M_1(n, n')^{\text{naph.}}_{\text{eff.}} = 16.6\ \gamma_2^r(2\bar{n}+1)V_{nn'} - 0.28 \times 10^{-4}\gamma_r^2(V^2)_{nn'}. \tag{31}$$

We see that the second term in (30) and (31), which diminishes the one-phonon exciton transfer is five order smaller than the first, providing that the values of $V_{nn'}$ and $(V^2)_{nn'}$ are comparable. For small distances $|\boldsymbol{n}-\boldsymbol{n}'|$ we can safely assume that $(V^2)_{nn'} < 10^3 V_{nn'}$ and this term is indeed negligible. However, the situation for large values of $|\boldsymbol{n}-\boldsymbol{n}'|$ requires some clarification. We must namely verify the asymptotical behaviour of $(V^2)_{nn'}$ for large $|\boldsymbol{n}-\boldsymbol{n}'|$. Assuming that the interaction is of the dipol-dipol type, we have $V_{nn'} \sim \varphi/R^3$, where $R = |\boldsymbol{n}-\boldsymbol{n}'|/b$ (b is the lattice unit), and φ is proportional to the oscillator strength for the transition from the ground state to the excited one, being under considerations. We evaluate $(V^2)_{nn'}$ substituting the summation over n_1 by integration over the total crystal volume except for the neighbourhoods of the n-th and n'-th molecules (see Fig. 1). This gives

$$(V^2)_{nn'} \sim \varphi^2 \int_\Omega \frac{d\boldsymbol{r}}{r^3(\boldsymbol{r}-\boldsymbol{R})^3} = 2\pi\varphi^2 \left[\frac{1}{R} - \frac{1}{R^2} + \frac{\ln(1+R)}{R^3} \right]. \tag{32}$$

We see therefore that the asymptotical behaviour of $(V^2)_{nn'}$ is $1/R$ and it can be much larger at large distances than $V_{nn'}$ whose asymptotical behaviour is $1/R^3$. From Eq. (31) we obtain that the second term becomes dominant in the naphthalene crystal for distances which satisfy the following inequality

$$R > 100\sqrt{30/\pi\varphi}. \tag{33}$$

For strong transitions $\varphi \approx 1$ and one-phonon exciton transfer dissapears for distances larger than 300 lattice units[2]. However, for such distances, which are much greater than the mean free path of exciton due to their scattering with lattice phonons, the validity of our formalism and our approximations is open to question. In reference [16] a computation
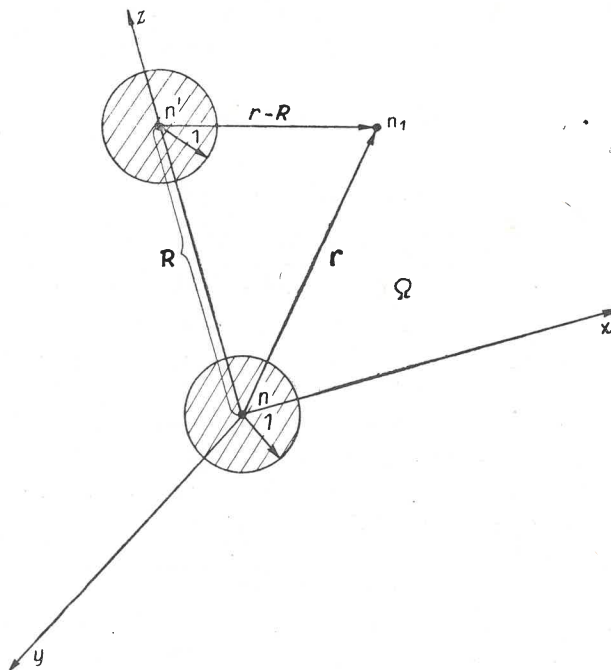

Fig. 1

is shown of the mean free path of excitons in the anthracene crystal, due to their interactions with acoustical and optical lattice phonons. It was shown that in the temperature 4°K this distance is about 40 lattice units. For such distances the second term in (31) is still very small, and in the region, in which our approximations hold, it can be neglected, so we have

$$M_1(n, n')_{\text{eff.}} = 2\gamma_r^2 V_{nn'}(2\overline{n}+1)(10\alpha-1). \tag{34}$$

We note that (34) does not indicate any oscillatory behaviour, which was obtained by Takeno [7]. We must remark, however, that the decoupling procedure used by Takeno in order to close the chain of equations for Green's function is applicable only for weak vibronic coupling or a large exciton bandwidth. Apart from this, such oscillatory behaviour was obtained for very large distances, where that formalism is also open for criticism.

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[2] One must remember that the total transition probability is given by the square of the expression in the square bracket in Eq. (9), so the negative value of $M_1(n, n')_{\text{eff.}}$ means that the one-phonon processes give an additional damping of energy transfer at very large distances.

3. The one-phonon exciton tranfer resulting from the $M_2(E)$ operator

Now, we can go to the investigation of the one-phonon exciton-transfer processes, which are described by the second part of the mass operator (2). With the help of Eqs (12), (15) and (16) we can write

$$M_2(n, n'; E) = \frac{4\varkappa^3\varrho^2\omega}{N} \sum_{q,\sigma} \sum_{n_1 n_2 n_3} V_{nn_1} V_{n_3 n'} \cdot g(n_1, n_2; E-\omega) \times$$

$$\times g(n_2, n_3; E+\omega)[c_{\varrho\sigma}(q)e^{-iq\cdot f} - c_{\varrho_1\sigma}(q)e^{-iq\cdot f_1}] \times$$

$$\times [c^*_{\varrho_3\sigma}(q)e^{iq\cdot f_3} - c^*_{\varrho'\sigma}(q)e^{iq\cdot f'}]$$

$$= 4\varkappa^3\varrho^2\omega[\sum_{n_1}\{V_{nn'}[(E-\omega)g(n, n_1; E-\omega) - \delta_{nn'}]g(n_1, n; E+\omega) +$$

$$+ V_{nn'}[(E+\omega)g(n', n_1; E+\omega) - \delta_{n'n_1}]g(n_1, n'; E-\omega)\} -$$

$$- \sum_{n_1 n_2} V_{nn_1}V_{n_1 n'}g(n_1 n_2; E-\omega)g(n_2, n_1; E+\omega). \tag{35}$$

In order to extract some physical information from this last equation we must do some approximations. We neglect in Eq. (35) these terms which contain the function $g(n_1, n_2; E\pm\omega)$ for $n_1 \neq n_2$. For this we give the following reason. In weak coupling theory we have usually $\omega > \Delta E$, and therefore $E \pm \omega$ lies outside the exciton band. It has been shown in reference [17] that $g(n_1, n_2; E)$ decreases exponentially outside of a band with increasing $|n_1 - n_2|$ distance. We therefore conclude that the main contribution to Eq. (35) is given by terms with $g_0(E\pm\omega)$. Thus we have

$$M_2(n, n'; E) \cong 8\varkappa^3\varrho^2\omega E V_{nn'}g_0(E-\omega)g_0(E+\omega) -$$

$$- 4\varkappa^3\varrho^2\omega V_{nn'}[g_0(E-\omega) + g_0(E+\omega)] -$$

$$- 4\varkappa^3\varrho^2\omega(V^2)_{nn'}g_0(E-\omega)g_0(E+\omega). \tag{36}$$

Insertion of the formula (26) into Eq. (36) leads immediately to the evaluation of $M_2(n, n')_{\text{eff}}$. One can then conclude that the second and third terms of Eq. (36) are negligible in comparison with the first term (for naphthalene crystal first singlet-exciton band they give 0.5% and 0.005% of the total value of $M_2(n, n')_{\text{eff}}$, respectively). We have therefore

$$M_2(n, n'_{\text{eff.}}) = \frac{200\,\alpha^3\varkappa^3\varrho^2 V_{nn'}(4\omega^2+\beta)}{\Delta E \sqrt{|\beta|}} \ln \frac{(\Delta E/2 - \sqrt{|\beta|})^2 - \omega^2}{(\Delta E/2 - \sqrt{|\beta|})^2 + \omega^2} \tag{37}$$

which for the naphthalene crystal is $\sim 10^3 \varkappa^3\varrho^2 V_{nn'}$.

We can thus observe that one-phonon exciton energy transfer is very sensitive to small frequency changes. In the case, where the vibrational frequency in electronically excited state of the molecule is somewhat smaller than that in the ground state, we obtain the supplementary mechanisms which increase the phonon-assisted exciton energy transfer. Such a situation usually occurs in molecular crystals.

However, a small increase of vibrational frequency in the excited state can cause an almost total damping of the one-phonon exciton transfer. From Eqs (37) and (34) it is easy to

point out, that for $\omega \gg \varDelta E$, such a transfer dissapears for $\omega_1 > 1.05\,\omega$. We must remember, however, that formula (2) is correct only for small frequency changes ($|\varkappa| \ll 1$), and we can say nothing about larger frequency changes.

4. Discussion

We can conclude that the linear vibronic coupling, apart from the compression of the exciton band by the Debye-Waller type factor, leads also to one-phonon exciton transfer processes. Mathematically, this is possible because of non-zero values of the exciton Green's function outside of the band, at energies where another vibrational replication of exciton band exists. The exciton-phonon coupling can therefore cause a virtual removing of an exciton to another vibrational state, opening in such a way new channels of energy transport.

Physically, it can be thought, that the vibronic exciton dissociate into scattering states which are, for pure linear vibronic coupling, degenerate with the exciton states [2, 3]. One exciton state is reproduced later on another molecule. The quadratic vibronic coupling can essentially modify the one-phonon exciton transfer probability (apart of the renormalization of the linear vibronic coupling constant). One-exciton states are no longer degenerate with the scattering states, and in the case of frequency decrease after electronic excitation, lie below the two-particle scattering states. This favourizes vibronic exciton states and unreversible dissociation into scattering states is less probable. The situation is somewhat similar here to that which occurs at resonance interaction between two impurity centres in molecular crystals which have energies below the exciton band [18, 19]. An opposite situation arises in the case of frequency increase after electronic excitation. Vibronic-exciton states lie now on top of the scattering states band, and therefore are less stable. This should lead to the decrease of the phonon assisted transfer probability, which goes through scattering states, and, indeed, we have shown that (see also [20]).

Now, we note, that the mass operator $M_1(E)$ gives, apart of the asymmetrical compression of the exciton band, the renormalization energy of excitons which results from their interactions *via* virtual exchange of phonons. Twenty years ago, Fröhlich, in one of the first theoretical papers on the theory of superconductivity [21] had investigated the influence of diagonal terms in the Hamiltonian, which result from the electron-electron interaction *via* phonon, on the stability of the normal state of electrons in a metal. He had found, that renormalization of electronic energies proceeding from such interactions makes the normal state unstable, and forms in the momentum space an energy gap. Of course, in such a state the mobility of electrons increases.

A similar situation occurs also in our paper. We have also investigated only the diagonal terms (one-particle Green's function). We note further, that the operator $M_2(E)$ gives also a renormalization of exciton energy resulting from exciton-exciton interactions with virtual exchange of two phonons. This interaction is attractive for $\varkappa > 0(\omega_1 < \omega)$ and repulsive for $\varkappa < 0(\omega_1 > \omega)$. Only in the first case we have obtained an increase in the exciton energy transfer probability. Similarly, the repulsive forces between electrons make electron condensation in momentum space more difficult.

We have investigated in this paper a very crude model of a molecular crystal. The

situation in real molecular crystals is of course much more complicated. In spite of this, the existence of phonon-assisted exciton energy transfer processes in real molecular crystals seems to be undoubtful. The same mechanism should be active also in polymers. In future, it will be very interesting to examinate on a simple model, if they can play any role in the energy transfer in biochemical reactions?

Our investigations must be considered as pure qualitative ones, and they form a step towards the understanding of Frenkel exciton energy transfer processes.

The Author is deeply indebted to Professor A. Witkowski for reading the manuscript and critical remarks.

REFERENCES

[1] M. Z. Zgierski, *Acta Phys. Polon.*, **A37**, 833 (1970).
[2] M. R. Philpott, *J. Chem. Phys.*, **47**, 2534 (1967).
[3] M. R. Philpott, *J. Chem. Phys.*, **47**, 4437 (1967).
[4] R. E. Merriefield, *J. Chem. Phys.*, **40**, 445 (1964).
[5] V. L. Bonch-Bruevich, S. V. Tyablikov, in *Green-Function Methods in Statistical Mechanics*, North Holland Publ. Co., Amsterdam 1962.
[6] S. Takeno, *J. Chem. Phys.*, **44**, 853 (1966).
[7] S. Takeno, *J. Chem. Phys.*, **46**, 2481 (1967).
[8] B. S. Sommer, J. Jortner, *J. Chem. Phys.*, **50**, 187 (1969).
[9] Yu. A. Izumov, *Advan. Phys.*, **14**, 569 (1965).
[10] J. Callaway, A. J. Hughers, *Phys. Rev.*, **128**, 139 (1962).
[11] M. Z. Zgierski, unpublished results.
[12] A. S. Davydov, *Teoria Molekularnykh Eksitonov*, Nauka, Moscow 1968 (in Russian).
[13] A. S. Davydov, *Uspekhi Fiz. Nauk*, **82**, 393 (1964) (in Russian).
[14] L. Van Hove, *Phys. Rev.*, **89**, 1189 (1953).
[15] E. A. Chandross, J. Ferguson, E. G. McRae, *J. Chem. Phys.*, **45**, 3546 (1966), J. Ferguson, *J. Chem. Phys.*, **44**, 2677 (1966).
[16] K. Iguchi, *J. Chem. Phys.*, **47**, 3611 (1967).
[17] G. F. Koster, J. C. Slater, *Phys. Rev.*, **96**, 1208 (1954).
[18] M. A. Kozhushner, *Zh. Eksper. Teor. Fiz.*, **56**, 1940 (1969).
[19] V. M. Agranovich, N. E. Kamenogradskij, Yu. V. Konobieev, *Fiz. Tverdogo Tela*, **11**, 1445 (1969), N. E. Kamenogradskij, Yu. V. Konobieev, *Phys. Status. Solidi*, **37**, 29 (1970).
[20] M. R. Philpott, *J. Chem. Phys.*, **51**, 2616 (1970).
[21] H. Fröhlich, *Phys. Rev.*, **79**, 845 (1950).
[22] S. D. Colson, D. M. Hanson, R. Kopelman, G. W. Robinson, J. *Chem. Phys.*, **48**, 2215 (1968).