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# The Theory of Sensitized Fluorescence in Solids

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In honour of Prof. Dr. Dr. h. e. P. Görlich's 70th birthday

The widely used Förster-Galanin-Dexter's (FGD) procedure of representation of the electronic excitation energy-transfer rate between donor and acceptor impurity molecules, imbedded in small concentration in molecular crystals, is discussed by the overlap, integral of their light emission and absorption spectra. It is shown that this representation is only an approximative one, therefore a correction factor to the optical spectra overlap integral is given. This correction factor depends on the distance between donor and acceptor molecules and has a longer range in the case of the interaction of the donor and acceptor electronic excitations with acoustic phonons as compared to the interaction with optical phonons. The validity conditions of the representation mentioned above are discussed in detail.

Обсуждается широко используемая процедура Фёрстера-Галанина-Декстера представления скорости передачи энергии электронного возбуждения между примесными молекулами донора и акцептора, в малой концентрации внедренных в молекулярный кристалл, с помощью интеграла перекрытия оптических спектров излучения и поглощения этих молекул. Показано, что такое представление является приближенным, и существует поправочный множитель к интегралу перекрытия. Этот поправочный множитель зависит от расстояния между молекулами донора и акцентора и имеет более дальнодействующий характер в случае взаимодействия электронных возбуждений молекул донора и акцентора с акустическими фононами, чем в случае взаимодействия с оптическими фононами.

# 1. Introduction

The FGD formula [1 to 3] for the electronic excitation energy transfer rate  $P_{DA}(R)$  between donor (D) and acceptor (A) impurity molecules imbedded in a small concentration in crystals is widely used [4] for the interpretation of numerous experiments on the study of the sensitized luminescence phenomenon in solids. The attractiveness of this formula arises from the possibility to represent  $P_{DA}$  through the overlap integral of the light emission and absorption spectra of guest molecules. In particular, the FGD formula was widely used for the calculation of the diffusion coefficient in a number of works [7 to 9]. In [5, 6] the approximate character of this representation was firstly pointed out. But the analysis made in [6] was only qualitative and practical use of the results in [6] is rather complicated. Therefore it seems important to consider the FGD procedure of the  $P_{DA}$  representation in detail and to estimate the separations R between the D and A molecules at which this representation would be a good approximation for  $P_{DA}(R)$ . It is shown below that in a more correct theory of  $P_{DA}(R)$  a correction factor to the FGD overlap integral appears, which decreases with increasing R. In the case of a sufficiently strong interaction of donor and acceptor electronic excitations with acoustic waves in molecular

crystals this correction factor may be of rather long range nature and its estimation becomes an important problem.

### 2. The Resonance Energy Transfer Rate $P_{DA}$

Let us firstly derive a general formula for  $P_{\rm DA}$  considering a molecular crystal of an arbitrary symmetry in which two impurity molecules, donor and acceptor, are placed at lattice sites, n and m, respectively. We shall assume that

a) there is one molecule in an elementary cell of the crystal;

b) the energy transfer rate  $P_{DA}$  may be calculated in the first order of the nonsteady-state perturbation theory;

c) the energy terms of electronic excited states of host molecules are higher than the corresponding terms of guest molecules and well separated from the last terms;

d) the interaction Hamiltonian of electronic excited states of guest molecules with crystal vibrations is linear in the displacements of nuclei from their equilibrium positions in the crystal.

The assumption b) may be justified if the interaction of excited states of D and A with the phonon field is sufficiently strong. Due to assumption d) the account of the polarizability of the host substance results in a renormalization of the matrix element of the Coulomb interaction  $V_{nm}$  between ground and excited states of the D and A molecules, which, according to [10], consists of replacing  $V_{nm}$  by the matrix element of an effective interaction  $V_{nm}^{eff}$ .

The Hamiltonian of the system may be written in the following form:

$$H = \Delta_{\mathbf{n}} B_{\mathbf{n}}^{+} B_{\mathbf{n}} + \Delta_{\mathbf{m}} B_{\mathbf{m}}^{+} B_{\mathbf{m}} + V^{\text{eff}} \left( B_{\mathbf{n}}^{+} B_{\mathbf{m}} + B_{\mathbf{m}}^{+} B_{\mathbf{n}} \right) +$$

$$+ \sum_{\mathbf{x}} \hbar \omega_{\mathbf{x}} b_{\mathbf{x}}^{+} b_{\mathbf{x}} + B_{\mathbf{n}}^{+} B_{\mathbf{n}} \sum_{\mathbf{x}} \hbar \omega_{\mathbf{x}} \left( V_{\mathbf{x}}^{*}(\mathbf{n}) \ b_{\mathbf{x}} + V(\mathbf{n}) \ b_{\mathbf{x}}^{+} \right)^{(1)} +$$

$$+ B_{\mathbf{m}}^{+} B_{\mathbf{m}} \sum_{\mathbf{x}} \hbar \omega_{\mathbf{x}} \left( V_{\mathbf{x}}^{*}(\mathbf{m}) \ b_{\mathbf{x}} + V(\mathbf{m}) \ b_{\mathbf{x}}^{+} \right) , \qquad (1)$$

where  $B_l^+$  and  $B_l$  are Bose operators representing the creation and annihilation of an excited state of the molecule at lattice site l (l = n, m),  $b_x^+$  and  $b_x$  are analogous operators for the  $\varkappa$ -th phonon with the energy  $\hbar\omega_{\varkappa}$ ,  $\mathcal{A}_n$  and  $\mathcal{A}_n$  are the energies of electronic excitations of the isolated D and A molecules, respectively,  $V_{\varkappa}(l)$  is the electron-phonon interaction matrix element;  $\varkappa = q, s$ , where q is the phonon wave vector, s is the phonon mode number.

To calculate  $P_{DA}$  it is useful to introduce a "polaron" representation making the following unitary transformation  $\tilde{H} = e^{\hat{S}\hat{H}-\hat{S}}$ , where  $\hat{S} = B_n^+ B_n \hat{S}_n + B_m^+ B_m \hat{S}_m$ ,  $\hat{S}_I = \sum_{x} [b_x^+ V_x(l) - b_x V_x^*(l)]$ . Omitting the terms of the direct interaction between the excited D and A molecules, which are unimportant for the present consideration, one obtains

$$\tilde{H} = \hat{H}_0 + \hat{V}_{nm} + \hat{V}_{mn} \,,$$

where

$$\hat{H}_{0} = \left( \Delta_{n} - \sum_{\varkappa} |V_{\varkappa}(n)|^{2} \right) B_{n}^{+} B_{n} + \left( \Delta_{m} - \sum_{\varkappa} |V_{\varkappa}(m)|^{2} \right) + \sum_{\varkappa} \hbar \omega_{\varkappa} b_{\varkappa}^{+} b_{\varkappa}; \qquad (2)$$
$$\hat{V}_{nm} = V_{nm}^{\text{eff}} e^{\hat{S}_{n}} B_{n}^{+} B_{m} e^{-\hat{S}_{m}}.$$

In the first order of the nonsteady-state perturbation theory the rate  $P_{DA}$  is

$$P_{\rm DA} = \frac{2\pi}{\hbar} \sum_{l,l'} \varrho(E_l) \langle l| \ \hat{V}_{nm} \ |l' \rangle \langle l'| \ \hat{V}_{mn} \ |l\rangle \ \delta(E_l - E_{l'}) , \qquad (3)$$

where  $\rho(E_l)$  is the density matrix,  $|l\rangle$  and  $E_l$  are the eigenvector and eigenvalue of the Hamiltonian  $\hat{H}_0$ , respectively.

Using (2) and (3) one may write

$$P_{\rm DA} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \langle V_{nm}(t) | V_{nm}(0) \rangle , \qquad (4)$$

where

$$V_{nm}(t) = e^{i \hat{H}_{o} t/\hbar} V_{nm} e^{-i \hat{H}_{o} t/\hbar}$$

Further assuming that only one electronic excitation exists in the system considered, one finds

$$P_{\rm DA} = \frac{|V_{nm}^{\rm eff}|^2}{\hbar^2} \int_{-\infty}^{\infty} dt \, e^{i\,\Omega t} \left\langle e^{\hat{S}_{n}(t)} \, e^{-\hat{S}_{m}(t)} \, e^{\hat{S}_{m}(0)} \, e^{-\hat{S}_{n}(0)} \right\rangle, \tag{5}$$

where

$$\hbar\Omega = (\Delta_{\mathbf{n}} - \Delta_{\mathbf{m}}) + \sum_{\mathbf{x}} \hbar\omega_{\mathbf{x}} (|V_{\mathbf{x}}(\mathbf{m})|^2 - |V_{\mathbf{x}}(\mathbf{n})|^2)$$

is the difference between the electronic excitation energies of donor and acceptor molecules in the crystal.

The calculation of the integral in (5) offers no difficulty (see, for example, Appendix in [11]). One obtains

$$P_{\rm DA} = \frac{|V_{\rm nm}^{\rm eff}|^2}{\hbar^2} \int_{-\infty}^{\infty} {\rm e}^{i\,\Omega t + g_{\rm nm}(t)}, \qquad (6)$$

where

$$g_{\mathbf{nm}}(t) := \sum_{\mathbf{x}} |V_{\mathbf{x}}(\mathbf{n}) - V_{\mathbf{x}}(\mathbf{m})|^2 \,\xi_{\mathbf{x}}(t)\,; \tag{7}$$

$$\xi_{\mathbf{x}}(t) = -\frac{\cosh\left(\frac{\hbar\omega_{\mathbf{x}}}{2kT} + i\omega_{\mathbf{x}}t\right)}{\sinh\left(\frac{\hbar\omega_{\mathbf{x}}}{2kT}\right)} - \operatorname{etgh}\left(\frac{\hbar\omega_{\mathbf{x}}}{2kT}\right).$$
(8)

# 3. The Approximation of the Resonance Energy Transfer Rate P<sub>DA</sub> by an Overlap Integral of the Light Absorption and Emission Spectra of Impurity Molecules

Let us return from "the polaron" representation to the initial one in (5):

$$P_{\mathrm{DA}} = \frac{|V_{\mathbf{nm}}^{\mathrm{eff}}|^2}{\hbar^2} \int_{-\infty}^{\infty} \mathrm{d}t \left\langle B_{\mathbf{n}}^{+}(t) \; B_{\mathbf{m}}(t) \; B_{\mathbf{m}}^{+}(0) \; B_{\mathbf{n}}(0) \right\rangle \,. \tag{9}$$

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If now the two-particle correlation function in (9) is approximately presented as a product of the one-particle correlation functions as follows:

$$\langle B_{\mathbf{n}}^{+}(t) \ B_{\mathbf{m}}(t) \ B_{\mathbf{m}}^{+}(0) \ B_{\mathbf{n}}(0) \rangle \approx \langle B_{\mathbf{n}}^{+}(t) \ B_{\mathbf{n}}(0) \rangle \langle B_{\mathbf{m}}(t) \ B_{\mathbf{m}}^{+}(0) \rangle$$
(10)

and the Fourier components of these one-particle correlation functions are introduced,

$$G_{\boldsymbol{m}}(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{iEt/\hbar} \langle B_{\boldsymbol{m}}(t) \ B_{\boldsymbol{m}}^{+}(0) \rangle \, \mathrm{d}t ,$$

$$g_{\boldsymbol{n}}(-E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{iEt/\hbar} \langle B_{\boldsymbol{n}}^{+}(t) \ B_{\boldsymbol{n}}(0) \rangle \, \mathrm{d}t ,$$
(11)

one easily obtains  $P_{DA}$  in the form of

$$\tilde{P}_{\mathrm{DA}} = \frac{2\pi |V_{\mathbf{nm}}^{\mathrm{eff}}|^2}{\hbar} \int_{-\infty}^{\infty} \mathrm{d}E G_{\mathbf{m}}(E) g_{\mathbf{n}}(E) .$$
(12)

The functions  $G_m(E)$  and  $g_n(E)$  describe the optical absorption and luminescence spectra of molecules m and n, respectively. Indeed, in case of dipole optical transitions in the guest molecule the rate  $w_m(E)$  of the absorption of a photon with energy E (for the sake of simplicity the refractive index is assumed to be independent of the energy E in the frequency range of interest) is

$$W_{\boldsymbol{m}}(E) = \frac{(2\pi)^2 E}{3\hbar V} |\boldsymbol{P}_{\boldsymbol{m}}^{\text{eff}}|^2 G_{\boldsymbol{m}}(E) , \qquad (13)$$

where V is the crystal volume,  $P_m^{\text{eff}}$  is the effective dipole transition moment of an acceptor molecule from its ground state to the excited one found by taking into account the polarizability of the host substance.

The spontaneous emission rate  $A_n(E)$  of a photon with an energy lying in the interval E, E + dE is equal to

$$A_{n}(E) = \frac{4E^{3}}{3\hbar^{4}c_{0}^{3}} |P_{n}^{\text{eff}}|^{2} g_{n}(E), \qquad (14)$$

where  $P_n^{\text{eff}}$  is the corresponding effective dipole transition moment of the donor molecule,  $c_0$  is the light velocity in the crystal.

For simplicity one can take into account only the dipole-dipole interaction between the guest molecules averaged over all possible directions of vectors  $\boldsymbol{P}_{\boldsymbol{m}}^{\text{eff}}$  and  $\boldsymbol{P}_{\boldsymbol{n}}^{\text{eff}}$ . Then the expression for  $V_{\boldsymbol{n}\boldsymbol{m}}^{\text{eff}}$  becomes  $V_{\boldsymbol{n}\boldsymbol{m}}^{\text{eff}} = \frac{2}{3} |\boldsymbol{P}_{\boldsymbol{n}}^{\text{eff}}|^2 \cdot |\boldsymbol{P}_{\boldsymbol{m}}^{\text{eff}}|/|\boldsymbol{n}-\boldsymbol{m}|^6$ (see [10]). Introducing the normalized spectral distributions  $f_{\mathrm{D}}(E)$  and  $F_{\mathrm{A}}(E)$  as  $A_{\boldsymbol{n}}(E) = (1/\tau_{\mathrm{D}}) f_{\mathrm{D}}(E)$  and  $W_{\boldsymbol{m}}(E) = (c_0 Q_{\mathrm{A}}/V) F_{\mathrm{A}}(E)$ , where  $\tau_{\mathrm{D}}$  is the radiative life-time of the donor molecule,  $Q_{\mathrm{A}}$  is the total light absorption cross-section of the activator molecule, one obtains the known result [2] of the FGD theory

$$\tilde{P}_{\rm DA} = \frac{3\hbar^4 c_0^4 Q_{\rm A}}{4\pi |n - m|^6 \tau_{\rm D}} \int \frac{f_{\rm D}(E) F_{\rm A}(E)}{E^4} \, \mathrm{d}E \;. \tag{15}$$

It is interesting to note that taking into account the normalization equations

$$\int g_n(E) dE = 1, \quad \int G_m(E) dE = 1 \tag{16}$$

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one may write expression (12) in a more general form

$$\tilde{P}_{\mathrm{DA}} = \frac{2\pi |V_{nm}^{\mathrm{eff}}|^2}{\hbar} \frac{\int \frac{W_m(E) A_n(E)}{E^4} \mathrm{d}E}{\left(\int \frac{W_m(E)}{E} \mathrm{d}E\right) \left(\int \frac{A_n(E)}{E^3} \mathrm{d}E\right)}.$$
(17)

The last expression for  $\tilde{P}_{DA}$  is valid, in principle, at an arbitrary distance between guest molecules including the small distances at which the dipoledipole interaction may be a crude approximation of the real interaction. But a poor knowledge of  $V_{nm}^{\text{eff}}$  at small distances makes (17) of little value.

Let us now discuss the approximations made when obtaining (10). For this purpose let us use the formulae for  $G_m(E)$  and  $g_n(E)$ , known from the theory of light absorption and emission spectra of impurity centres (see, for example [12])

$$G_{\boldsymbol{m}}(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i(E-\tilde{\boldsymbol{\Delta}}_{\boldsymbol{m}})t/\hbar + g_{\boldsymbol{m}}(t)} dt , \ g_{\boldsymbol{n}}(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-i(E-\tilde{\boldsymbol{\Delta}}_{\boldsymbol{n}})t/\hbar + g_{\boldsymbol{n}}(t)} dt , \ (18)$$

where  $\tilde{\Delta}_{l}$  and  $g_{l}(t)$  (l = m, n) are

$$\tilde{\mathcal{A}}_{\boldsymbol{l}} = \mathcal{A}_{\boldsymbol{l}} - \sum_{\boldsymbol{x}} \hbar \omega_{\boldsymbol{x}} |V_{\boldsymbol{x}}(\boldsymbol{l})|^2 , \qquad g_{\boldsymbol{l}}(t) = \sum_{\boldsymbol{x}} |V_{\boldsymbol{x}}(\boldsymbol{l})|^2 \, \xi_{\boldsymbol{x}}(t) . \tag{19}$$

Substituting (18) into (12) and integrating over E one obtains the following expressions for  $P_{DA}$ :

$$\tilde{P}_{\mathrm{DA}} = \frac{|V_{\mathrm{nm}}^{\mathrm{eff}}|^2}{\hbar^2} \int_{-\infty}^{\infty} \mathrm{e}^{i\Omega t + g_{\mathrm{n}}(t) + g_{\mathrm{m}}(t)}, \qquad (20)$$

where  $\hbar \Omega = \tilde{\varDelta}_n - \tilde{\varDelta}_m$ .

By comparison of (6) and (20) one can see that the approximation (10) consists of neglecting the "interference" factor in (6)

$$\gamma(t) = \exp\left\{-2\operatorname{Re}\sum_{\mathbf{x}} V_{\mathbf{x}}^{*}(n) V_{\mathbf{x}}(m) \xi_{\mathbf{x}}(t)\right\}.$$
(21)

Such neglect may be valid only at large distances between the molecules D and A, when (n - m) is much larger than the lattice constant a. Actually  $V_{\mathbf{x}}(l) \sim e^{i\mathbf{q}\cdot \mathbf{i}}$  and at  $(n - m) \gg a$  the "interference" factor mentioned, above is close to unity because the factor  $\exp(i\mathbf{q}(n - m))$  rapidly oscillates. But at  $(n - m) \approx a$  the situation may be different.

For an accurate determination of the critical distance  $R_c$  at which (6) may be well approximated by (20) one needs detailed information about  $V_{\mathbf{x}}(\mathbf{l})$ . This information is very poor at present. The approximation  $V_{\mathbf{x}}(\mathbf{l}) \sim \omega_{\mathbf{x}}^{-1/2}$  is generally accepted (see the detailed discussion in [14], p. 184). Below the validity of (20) will be discussed in the latter approximation.

Let us write (6) in the following form:

$$P_{\mathrm{DA}} = \frac{|V_{\mathbf{nm}}^{\mathrm{off}}|^2}{\hbar^2} \int_{-\infty}^{\infty} \gamma(t) \,\mathrm{e}^{i\,\Omega t + g_{\mathbf{n}}(t) + g_{\mathbf{m}}(t)} \,\mathrm{d}t \tag{22}$$

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and expand the sum  $i\Omega t + g_n(t) + g_m(t)$  in a Taylor series near  $t = t_0$ , where  $t_0$  is the extremum (maximum) point determined from the following equation:

$$\Omega = \sum_{\mathbf{x}} \left\{ |V_{\mathbf{x}}(\mathbf{n})|^2 + |V_{\mathbf{x}}(\mathbf{m})|^2 \right\} \omega_{\mathbf{x}} - -\frac{\sin \left(\frac{\hbar \omega_{\mathbf{x}}}{2kT} + i\omega_{\mathbf{x}}t_0\right)}{\sinh \left(\frac{\hbar \omega_{\mathbf{x}}}{2kT}\right)}$$
(23)

If  $\gamma(t) = \gamma(t_0)$  in (22) is taken approximately, one finds that  $P_{DA} = \gamma(t_0) \tilde{P}_{DA}$ , where  $\gamma(t_0)$  is a correction factor for FGD formula (15) being equal to

$$\gamma(t_0) = \exp\left[-2\sum_{\mathbf{x}} |V_{\mathbf{x}}(n)| |V_{\mathbf{x}}(m)| \cos\left(q(n-m)\right)\xi(t_0)\right].$$
(24)

Further treatment of  $\gamma(t_0)$  will be carried out separately for the electron-acoustic phonon and electron-optical phonon interactions.

#### **3.1** Acoustic phonons

Let  $|V_{\mathbf{x}}(\mathbf{l})|$  be of the form

$$\left| V_{\mathbf{x}}(\boldsymbol{l}) \right| = \sqrt{\frac{\overline{A(\boldsymbol{l})}}{N\omega_{\mathbf{x}}}}, \qquad (25)$$

where  $\Lambda(l)$  is a constant independent of  $\varkappa$ , N is the total number of elementary cells in the crystal. The unknown value of  $\Lambda(l)$  may be determined from the emission (absorption) line shape of the impurity molecule. Assuming in case of sufficiently strong electron-phonon interaction this shape to be Gaussian [14], the value of  $\Lambda(l)$  may be expressed through the line half-width  $\Gamma(l)$  as follows:

$$A(\mathbf{l}) = - - \frac{\Gamma^2(\mathbf{l})}{24 (\ln 2) \omega_{\mathbf{D}} \int_0^{-1} x^3 \, \mathrm{d}x \, \mathrm{ctgh}\left(\frac{\hbar\omega_{\mathbf{D}}}{2kT} x\right)}$$
(26)

When obtaining (26) the Debye phonon spectrum  $\omega_{\mathbf{x}} = c |\mathbf{q}|$  is used where c is the sound velocity;  $\omega_{\mathbf{D}}$  is the Debye frequency. In an actual case  $T > \theta_{\mathbf{D}}/2$ 

$$\operatorname{ctgh}\left(\frac{\hbar\omega_{\mathrm{D}}}{2kT}x\right) \approx \frac{2kT}{\hbar\omega_{\mathrm{D}}x}, \quad (\theta_{\mathrm{D}} = \hbar\omega_{\mathrm{D}}/k)$$

and (26) reduces to

$$\Lambda(\boldsymbol{l}) = \frac{I^{\boldsymbol{2}}(\boldsymbol{l})}{16(\ln 2)\omega_{\mathrm{D}}} \frac{\theta_{\mathrm{D}}}{T}.$$
(27)

Now the condition of  $\gamma(t_0)$  being close to unity can be formulated. Substituting (25) into (24) and taking into account (27) one finds that  $\gamma(t_0) \approx 1$ , if

$$F\left(\frac{|\boldsymbol{n}-\boldsymbol{m}|}{a}, \boldsymbol{Z}_{0}\right) \equiv -\frac{3}{4\ln 2} \cdot \frac{3}{\sqrt[6]{6\pi^{2}}} \frac{a}{|\boldsymbol{n}-\boldsymbol{m}|} \times \left| \int_{0}^{1} \mathrm{d}x \frac{\mathrm{e}^{\boldsymbol{x}\boldsymbol{Z}_{0}} - 1}{x} \sin\left(\sqrt[8]{6\pi^{2}} \frac{|\boldsymbol{n}-\boldsymbol{m}|}{a} x\right) \right| \ll \frac{\omega_{\mathrm{D}}^{2}}{\overline{\Gamma(\boldsymbol{n})}} = \eta \;. \tag{28}$$

In inequality (28)  $Z_0$  is the root of the equation which results from (22)

$$\eta_{1} \equiv \frac{\Omega\omega_{\rm D}}{\Gamma^{2}(n) + \Gamma^{2}(m)} = \frac{3}{16\ln 2} \frac{\theta_{\rm D}}{T} \left\{ 2 \frac{\cosh Z_{\rm 0}}{Z_{\rm 0}} \left( \frac{T}{\theta_{\rm D}} - \frac{1}{Z_{\rm 0}} \right) + \\ + \sinh Z_{\rm 0} \left( \frac{1}{Z_{\rm 0}} - \frac{2}{Z_{\rm 0}^{2}} \left( \frac{T}{\theta_{\rm D}} - \frac{1}{Z_{\rm 0}} \right) \right) \right\}.$$
(29)

As it follows from (29) the value  $Z_0$  depends on two parameters  $\eta_1$  and  $T/\theta_D$ . The function  $F\left(\frac{|n-m|}{a}, \frac{T}{\theta_D}, Z_0\right)$  computed at  $\eta_1 = 0.05$  and  $T/\theta_D = 3$  is

shown in Fig. 1. At  $|\boldsymbol{n} - \boldsymbol{m}|/a > 1$  the function F rapidly oscillates and decreases with increasing  $|\boldsymbol{n} - \boldsymbol{m}|/a$ . The solid curve shown in Fig. 1 describes the dependence on  $|\boldsymbol{n} - \boldsymbol{m}|$  of the maxima of F and corresponds to the law  $F \sim \left(\frac{a}{|\boldsymbol{n} - \boldsymbol{m}|}\right)^2$  that differs from  $F \sim \left(\frac{a}{|\boldsymbol{n} - \boldsymbol{m}|}\right)^3$  obtained in [7]. The behaviour of F at other values of  $\eta_1$  and  $T/\theta_D$  is similar. Therefore,  $F\left(\frac{|\boldsymbol{n} - \boldsymbol{m}|}{a}, \frac{T}{\theta_D}, Z_0\right) < A(\eta_1, T/\theta_D) \cdot \left(\frac{a}{|\boldsymbol{n} - \boldsymbol{m}|}\right)^2$ , and instead of (28) one has  $|\boldsymbol{n} - \boldsymbol{m}| \gg a \left[\sqrt{\frac{A(\eta_1, T/\theta_D)}{n}}\right].$  (30)

The function  $A(\eta_1, T/\theta_D)$  computed at  $T/\theta_D = 0.77$  and 3 is shown in Fig. 2. If the values  $\eta = \frac{\omega_D^2}{\overline{\Gamma(n)} \cdot \overline{\Gamma(m)}}$  and  $\eta_1 = \frac{\Omega \omega_D}{\Gamma^2(n) + \overline{\Gamma^2(m)}}$  are known from any



Fig. 1. The function  $F\left(\frac{|n - m|}{a}\right)$  at  $\eta_1 = 0.05$  and  $T/\theta_D = 3$ . The full line corresponds to  $F\left(\frac{|n - m|}{a}\right) \approx \left(\frac{a}{|n - m|}\right)^2$ 

Fig. 2. The function  $A(\eta_1)$ . The upper and lower curves correspond to  $T/\theta_D = 3$  and  $T/\theta_D = 0.77$ , respectively

experiment, one can determine from Fig. 2 the distance  $R_c = |\boldsymbol{n} - \boldsymbol{m}|_c$ , beginning from which the correction factor  $\gamma(t_0)$  is unity in practice. Then if  $R_c < R_0$ , where  $R_0$  is the characteristic radius of resonance transfer determined by (15), the approximation of  $P_{\rm DA}$  with the help of the overlap integral of luminescence and absorption spectra in (15) is good. In the opposite case the correction factor may be large and the use of the FGD formula may be misleading in some cases. For example, if

$$\Gamma(\mathbf{n}) = \Gamma(\mathbf{m}) = 1500 \text{ cm}^{-1}, \quad \Omega = 7500 \text{ cm}^{-1}, \quad \omega_{\mathrm{D}} = 70 \text{ cm}^{-1}, \quad (30 \text{ a})$$

the values  $\eta$  and  $\eta_1$  are equal to  $\approx 2 \times 10^{-3}$  and  $10^{-1}$ , respectively. Determining from Fig. 2  $A(\eta_1, T/\theta_D) = 10^{-2}$  and substituting these values of  $A(\eta_1, T/\theta_D)$ and  $\eta$  into (30) one obtains  $R_c \approx 2a < R_0$ . The typical value of  $R_0$  is ten lattice parameters or more. Variation of the parameters does not change the result of the inequality  $R_c < R_0$ . It seems that one should be especially careful when using  $\tilde{P}_{DA}$  (15) for calculating the host luminescence decay law in a binary solid solution, in which the exciton diffusion coefficient is sufficiently large ( $\sqrt{D\tau_D} \gg R_0$ ), and, therefore, in the electronic excitation transfer from host molecules to acceptor ones the largest contribution is from the excitons which may migrate close to an acceptor molecule [15]. Therefore in this case the approximation  $\tilde{P}_{DA}$  (15) is valid only if  $R_c < a$  and not if  $R_c < R_0$ .

### 3.2 Optical phonons

In the case of electron-optical phonon interaction using (25) one obtains the exponent in (24) being proportional to  $\delta(n-m)$  and thus  $\gamma(t_0) = 1$ . But if one takes into account the dependence of  $V_{\mathbf{x}}(l)$  on q, the |n - m| dependence of  $\gamma(t_0)$  may be long-range. The simplest anisotropic expression for  $V_{\mathbf{x}}(l)$  which may be proposed is of the form

$$|V(l)| = \sqrt{\frac{\overline{A(l)}}{N\omega_0}} \frac{(\underline{A} \cdot \underline{q})}{|\underline{q}|}, \qquad (31)$$

where A is some vector of unit length. The value of A(l) may be expressed in terms of the luminescence (absorption) line half width  $\Gamma(l)$  as follows:

$$\Lambda(l) = \frac{3}{8\ln 2} - \frac{\Gamma^2(l)}{\omega_0 \operatorname{ctgh}\left(\frac{\theta_0}{2T}\right)},\tag{32}$$

where  $\omega_0$  is the frequency of optical phonons ( $\theta_0 = \hbar \omega_0/k$ ). Substituting (31) into (24) and taking into account (32) we find that the correction factor  $\gamma(t_0) \approx 1$ , if

$$\tilde{F}\left(\frac{|\boldsymbol{n}-\boldsymbol{m}|}{a}, \frac{T}{\theta_{0}}, \tilde{Z}_{0}\right) \equiv \frac{3}{\ln 2} \left(\frac{\cosh\left(\frac{\theta_{0}}{2T} + \tilde{Z}_{0}\right)}{\cosh\left(\frac{\theta_{0}}{2T}\right)} - 1\right) \times \frac{1}{N} \sum_{\boldsymbol{q}} \frac{(\boldsymbol{A} \cdot \boldsymbol{q})^{2}}{|\boldsymbol{q}|^{2}} e^{i\boldsymbol{q}(\boldsymbol{n}-\boldsymbol{m})} \ll \frac{\omega_{0}^{2}}{\Gamma(\boldsymbol{n}) \cdot \overline{\Gamma}(\boldsymbol{m})} \equiv \tilde{\eta}.$$
(33)

In inequality (33)  $\tilde{Z}_0$  is the root of the following equation resulting from (22):

$$\tilde{\eta}_{1} \equiv \frac{\Omega \omega_{0}}{I^{\frac{1}{2}}(n) + I^{\frac{1}{2}}(m)} = \frac{1}{8 \ln 2} \frac{\sinh\left(\frac{\theta_{0}}{2T} + \tilde{Z}_{0}\right)}{\cosh\left(\frac{\theta_{0}}{2T}\right)}.$$
(34)

By calculating the sum on the left hand-side of (33) one finds that  $\tilde{F} \sim \left(\frac{a}{|n-m|}\right)^3$ 

being in an agreement with the result obtained in [6]. Expressions (31) to (34) may be used for finding the condition of  $\gamma(t_0)$  being close to unity through the experimental parameters of the emission and absorption spectra. Then determining the value  $\tilde{Z}_0$  from (34) and averaging over all possible mutual orientations of the A and n - m vectors one can obtain the following inequality:

$$|\boldsymbol{n} - \boldsymbol{m}| \gg a \left( \frac{3}{10\pi (\ln 2)\tilde{\eta}} \frac{\cosh\left(\ln\left[\alpha + \sqrt{1 + \alpha^2}\right]\right)}{\cosh\left(\frac{\theta_0}{2T}\right)} \right)^{1/3}$$
$$\alpha = 8 (\ln 2) \tilde{\eta}_1 \cosh\left(\frac{\theta_0}{2T}\right).$$

If  $\tilde{\eta} = \omega^2 / \Gamma(n) \Gamma(m)$  and  $\tilde{\eta}_1 = \Omega \omega_0 / (\Gamma^2(n) + \Gamma^2(m))$  are available from any experiment one can determine from (35) the distance  $\tilde{R}_c = |n - m|_c$ , beginning from which the correction factor  $\gamma(t_0)$  may be disregarded.

It is interesting to compare the critical distance  $R_c$  (30) and  $\tilde{R}_c$  (35) at the same parameters  $\Gamma(n)$ ,  $\Gamma(m)$ ,  $\Omega$ , and T. Using the parameters (30a) and T = = 300 °K it is easy to prove that  $\tilde{R}_c$  slightly decreases from  $\tilde{R}_c \approx 4a$  to  $\tilde{R}_c \approx 3a$  with increasing  $\omega_0$  from 70 to 700 cm<sup>-1</sup> and, therefore,  $\tilde{R}_c \sim R_c < R_0 \approx 10a$ .

In conclusion it should be pointed out that in case when the donor and acceptor molecules interact with different phonon branches the correction factor  $\gamma(t_0)$  is equal to unity  $\gamma(t_0) = 1$  at an arbitrary distance |n - m|.

## 4. Conclusions

In the present paper the correction factor to the overlap integral in optical spectra is calculated for both cases of interaction of donor and acceptor electronic excitations with acoustic and optical phonons. From the analysis of the electronic excitation energy transfer rate made above it follows that the above-mentioned correction factor  $\gamma(t_0) = \exp\left[\left(\frac{R_c}{|n-m|}\right)^n\right]$  is important at distances of some lattice constants  $(R_c \approx 2a \text{ to } 4a)$ . These values of  $R_c$  are small as compared to the actual values of the characteristic transfer radius  $R_0$ , which, as a rule, is close to  $R_0 = 10a$ . Therefore the conclusion made in [6] of a very important role of this correction factor in the FGD theory seems to be an overestimation for usual experimental situations.

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However, the use of the FGD formula in the sensitized luminescence theory in binary solid solutions for

- a) calculation of the diffusion coefficient,
- b) calculation of the transfer efficiency from a host substance to acceptor molecules when the diffusion coefficient is sufficiently large  $(\sqrt{D\tau_{\rm D}} \gg R_0)$  may lead to significant uncertainties.

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