Radiationless transfer of electronic excitation during vibrational relaxation

I. Yu. Tekhver and V. V. Khizhnyakov

Institute of Physics, Estonian Academy of Sciences

(Submitted January 16, 1975)
Zh. Eksp. Teor. Fiz. **69**, 599–610 (August 1975)

We consider hot transfer (HT)—the transfer of electronic excitation in activated crystals and solutions in an unrelaxed (hot) vibrational donor state. We give calculations in the framework of: *a*) semi-classical, and *b*) quantum theory. Assuming a strong electron-phonon interaction we find the probability for HT as a function of the frequency of the excitation. We apply the results to both inter- and intra-center processes. We show that HT can serve as a cause for the Weber effect and also can explain the way the intercenter depolarization of luminescence depends on the frequency of the excitation.

PACS numbers: 71.85.Ce

1. INTRODUCTION

In condensed systems some part of the energy of an electronic excitation turns into heat. The corresponding relaxation process is, as a rule, very short: 10^{-11} to 10^{-15} s, much shorter than the lifetime of the created electronic excitation. Because of this one usually considers the subsequent electronic transitions, among which is the transfer of the electronic excitation between centers, under conditions of a thermal distribution among the vibrations. However, if the interaction energy v between centers is sufficiently large, the excitation may go over from the first center (donor) to a second one (acceptor) before the vibrational relaxation in the donor is finished.[1-3] The above-mentioned process of the transfer of electronic excitation is below called HT—hot transfer, since it proceeds in a hot (non-equilibrium) vibrational state of the donor.

We note the following important property of HT, which distinguishes it from the transfer after vibrational relaxation: in the HT mechanism there can not be an energy loss between the photo-excitation and transfer processes. HT is therefore effective when the absorption spectra of the donor and the acceptor overlap. The usual transfer, which is effective provided the luminescence spectrum of the donor and the absorption spectrum of the acceptor overlap, may in this case be absent because of a shortage of energy. An important distinguishing HT property is also the dependence of its probability on the excitation energy. This dependence gives a simple means for experimental detection and study of HT.

We shall give an estimate of what the interaction must be in order that HT be reasonably probable. We stipulate that here and below we shall deal only with incoherent HT which requires a smaller interaction energy v than the coherent HT, i.e., with the case when $t_c < \hbar/v$. (This condition means that the damping time of the phase correlation $t_c \sim (\sigma_1 + \sigma_2)^{-1}$, also called the transverse relaxation time, is smaller than the characteristic time $\hbar/v$ of the coherent HT; σ_1 and σ_2 are the half-widths of the donor and acceptor absorption bands.) The characteristic time of incoherent HT equals $\hbar^2/t_c v^2$. Its probability will thus approach unity if this time is larger than or of the order of the (longitudinal) energy relaxation time t_0. This gives the following estimate for v:

$$v \gtrsim \hbar (t_c t_0)^{-1/2}. \tag{1}$$

If we take $t_0 \gtrsim \overline{\omega}^{-1}$, $t_c \sim 0.1\, t_0$, $\overline{\omega} \sim 10^{13}$ s^{-1} ($\overline{\omega}$ is the average vibrational frequency), we have $v \sim 10^{-2}$ eV. We note that (1) does not violate the condition that the HT is incoherent, $t_c < \hbar/v$, as $t_c \le t_0$.

The estimate (1) shows that HT may play an important role in intra-center processes where the interaction of the magnitude stated here is already guaranteed by the adiabaticity operator. As an example we encounter the depolarization of the luminescence of mercury-like ions in alkali-halide crystals during vibrational relaxation, leading to a strong dependence of the degree of polarization on the excitation frequency.[4] In the case of intercenter transfer the estimate (1) imposes a limitation on the distance R between donor and acceptor. In particular, for a dipole-dipole interaction ($v \sim M_1M_2/R^3$; M_1 and M_2 the donor and acceptor electronic matrix elements) condition (1) is satisfied for distances $R \lesssim (3-5)\, l^{2/3}$ (R and l in nm), where $l = (M_1M_2/e^2)^{1/2}$ characterizes the linear dimensions of the excited states. Hence it follows that for small radius luminescence centers ($l \lesssim 0.2$ nm) in crystals and solutions HT can proceed only at distances up to 1.5 nm, and in the case of large molecules with $l \sim 2$ nm at distances up to 7 to 8 nm. For slowly relaxing molecules (centers) R can also be larger, provided there is resonance between the vibrational levels of the excited electronic states of the donor and the acceptor.

As an example of intercenter HT, where the condition (1) is satisfied at distances ~7 nm we can mention solutions of chlorophyll molecules in which Bauer and Rabinowitch[5] (see also[6]) have recently shown that energy transfer in a hot vibrational state, indeed, plays an important role. Even earlier Gueron, Eisinger, and Shulman[7] arrived at the conclusion that energy transfer processes occurred in an unrelaxed vibrational state in polynucleotides. We shall show in the present paper that hot transfer also causes the Weber effect[8]—a decrease in the probability of self-transfer in the long-wavelength side of the absorption spectrum, often observed in solutions of aromatic compounds.[1)]

Apart from the above mentioned papers[1-3,5-7] HT has also been discussed in[11,12]. General formulae describing HT were obtained. It follows from these formulae that if we neglect the dynamical correlation of the donor and the acceptor[2)] the probability for HT is determined by the overlap integral of the acceptor absorption spectrum with the total photon spectrum emitted by the donor in the vibrational relaxation process. The latter can be split into resonance scattering and hot luminescence (HL)[13] (plus interference effects between them). The possibility of such a division is caused by the difference in speed of the transverse (phase) and the longitudinal (energy) relaxations: emission after the damping of the phase correlations, but before the finish of the energy relaxation correspond to HL, while emission before the damping of the phase correlation corresponds to scattering.

The theory of the hot luminescence and resonance Raman scattering spectra has been developed in a number of papers (see, e.g., [13-16]). The formulae determining these spectra are, in the general case, complicated and as a consequence we shall perform the evaluation of the probability for HT analytically only for a few simple cases. One such case—the case of a strong interaction of the donor and the acceptor with the nuclear vibrations—is of considerable interest and is considered in the present paper.

2. SEMICLASSICAL THEORY OF HT. WEBER EFFECT

We consider first of all the intercenter HT at distances such that the dynamical correlation effects are unimportant (we note that these effects diminish like R^{-3} with increasing R [17]). We assume that the donor and the acceptor are characterized by a strong electron-phonon interaction and have overlapping broad structureless absorption bands with a Gaussian shape:

$$\varkappa_{1(2)}(\omega)=\mathscr{M}_{1(2)}^{2}\hbar^{-2}(2\pi\sigma_{1(2)}^{2})^{-1/2}\exp[-(\omega-\Omega_{1(2)})^{2}/2\sigma_{1(2)}^{2}]. \tag{2}$$

Here $\Omega_{1(2)}$ is the frequency at maximum, and $\sigma_{1(2)}$ is the variance of the donor (acceptor) absorption band, $\mathscr{M}_{1(2)}$ a normalizing factor which determines the donor (acceptor) electronic matrix element. In this case $t_c \sim \{\overline{\omega}/[S(2\overline{n}+1)]\}^{-1}$ and the time during which the donor energy while relaxing remains in resonance with the acceptor absorption band equals $t_0 \sim \{\overline{\omega}[S/(2\overline{n}+1)]^{1/4}\}^{-1}$ (here $S \gg 1$ are the dimensionless Stokes losses of the donor, $\overline{n} = \{\exp(\hbar\omega/kT) - 1\}^{-1}$, $\sigma_1 \sim \sigma_2 \sim \overline{\omega}\sqrt{\{S(2\overline{n}+1)\}}$; for an estimate of t_0 see below), i.e., the characteristic damping time of the phase correlations is much shorter than the time during which HT can proceed. A small part of the energy, which gives a contribution to the overlap integral for the HT probability, goes therefore to scattering; the main part of the energy is the HL itself.

It follows from what we have said that in the case considered

$$w_{\mathrm{HT}}(\omega_0)=\frac{2\pi v^2}{\gamma_0\hbar^2}\int d\omega\, I_{\mathrm{HL}^1}(\omega_0,\omega)\varkappa_2(\omega), \tag{3}$$

where $\kappa_2(\omega)$ is the acceptor absorption spectrum in which $\mathscr{M}_2^2/\hbar^2 = 1$ (such a choice of $\mathscr{M}_2$ corresponds to normalizing the area of the spectrum to unity), $I_{\mathrm{HL},1}$ is the donor HL spectrum determined by the probability that the donor emits a photon of frequency ω while it relaxes, γ_0 is the radiative damping coefficient of the excited electronic state of the donor.

We assume that after absorbing a photon the donor falls into a strongly excited vibrational state. Quantum effects are small in that state. We can therefore find the HL spectrum which interests us using the semi-classical approximation.[18] According to that approximation the electronic transition takes place with conservation of the coordinates and momenta of the nuclei (Franck-Condon principle). The frequency ω of the transition at the coordinate q is then determined by the difference in the adiabatic potentials V(q). Hence

$$I_{\mathrm{HL}}(\omega_0,\omega)=\gamma_0\int dq\,\rho(q)\delta[\omega-\hbar^{-1}V(q)], \tag{4}$$

where $\rho(q)$ is the probability that in the relaxation process following the absorption of a photon of frequency ω_0 the system reaches the coordinate q. Bearing in mind that this probability can be written in the form $\rho(q) = 1/|dq/dt|$, and using for the difference in the adiabatic potentials the linear approximation in terms of the nuclear displacement $V(q) = \hbar(\Omega_L + aq)$ we write this formula in the form

$$I_{\mathrm{HL}}(\omega_0,\omega)=\frac{\gamma_0}{a}\sum_k\left|\left(\frac{dq}{dt}\right)_{t=t_k}\right|^{-1} \tag{4a}$$

Here t_k is the solution of the equation $\omega - \Omega_L - aq(t) = 0$ with $q(0) = (\omega_0 - \Omega_L)/a \sim 2S\overline{\omega}/a$; Ω_L is the frequency at the maximum of the luminescence spectrum (see Fig. 1). Equation (4a) expresses the well-known fact that the main contribution to the spectrum comes in the semiclassical approximation from the region near the turning points where the absolute magnitude of the velocity $|dq/dt|$ is small.

The t-dependence of q in the turning point region has a simple form:

$$q(t)\approx q_i[1-{}^1\!/_2\overline{\omega}^2(t-t_i)^2],\quad |t-t_i|\ll 2\pi/\overline{\omega} \tag{5}$$

($q_i \equiv q(t_i)$ is the coordinate and t_i the time when the i-th turning point is reached; we neglected in (5) the i-dependence of $\overline{\omega}$ which is unimportant in the actual range $q_0 - q_i \ll q_0$). Hence it follows, in particular, that the time during which V(q) changes by an amount $\sim\sigma \sim \overline{\omega}\sqrt{\{S(2\overline{n}+1)\}}$ is, as far as order of magnitude is concerned, larger than or equal to

$$t_0\sim\frac{1}{\overline{\omega}}\left(\frac{2\overline{n}+1}{S}\right)^{1/4}. \tag{6}$$

Substituting (5) into (4a) gives the following formula for the HL spectrum in the actual region $\omega_0 - \omega \sim \sigma$:

$$I_{\mathrm{HL}}(\omega_0,\omega)=\frac{\gamma_0}{2(S\overline{\omega}^3)^{1/2}}\sum_i\frac{(2-\delta_{i0})\theta(\omega_0-\omega-\Delta_i)}{(\omega_0-\omega-\Delta_i)^{1/2}} \tag{7}$$

($\Delta_i = a(q_0 - q_i)$, $\Delta_0 = 0$; $\delta_{i0} = 1$, if $i = 0$, $\delta_{i0} = 0$, if $i \neq 0$, $\theta(x) = 1$, if $x > 0$, $\theta(x) = 0$, if $x < 0$), where we must here sum only the contributions from those turning points for which $\Delta_i \lesssim \overline{\omega}\sqrt{S}$. (We assumed in (7) that for an excitation in the donor absorption band $\omega_0 - \Omega_L \approx 2S\overline{\omega}$, see Fig. 1.)

We note that in the case of centers with a fast vibrational relaxation we must take into account in (7) only

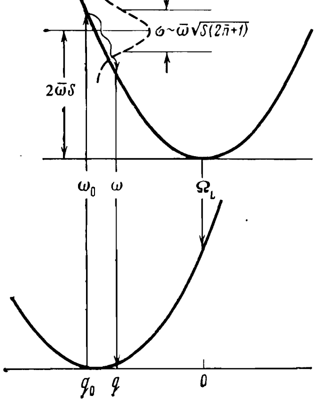

FIG. 1. Potential curves and transitions leading to hot luminescence; $\kappa(\omega_0)$: absorption spectrum.

the term i = 0 as here $\Delta_i \sim \overline{\omega}S$, i ≥ 1. In that case Eq. (7) is in the region $\omega_0 - \omega \gg \overline{\omega}$ the same as the more exact formula for the HL spectrum obtained in [12] in the framework of quantum theory. However, in those cases when there are high-frequency local vibrations it may turn out to be important to consider several terms in (7).

To find the probability for HT it remains to substitute the expression obtained for HL of the donor into Eq. (3) and use (2). We then get

$$w_{\text{HT}}(\omega_0)=\frac{v^2}{\hbar^2}\left(\frac{2\pi\sqrt{2}}{S\overline{\omega}^3\sigma_2}\right)^{1/2}\sum_i(2-\delta_{i0})T(x-\zeta_i), \tag{8}$$

where the function

$$T(x)=\frac{1}{2}\int_0^\infty\exp(-(z-x)^2)\frac{dz}{z^{1/2}} \tag{9}$$

determines the probability for HT as functions of the dimensionless excitation frequency

$$x=(\omega_0-\Omega_2)/\sigma_2\sqrt{2},\quad \zeta_i=\Delta_i/\sigma_2\sqrt{2}. \tag{10}$$

This function is shown in Figs. 2c and 3, from which can be seen that this is a strong dependence.

It is clear from Eq. (8) that taking the non-zero turning points into account is important only for the short-wavelength edge of the above-obtained x-dependence of w_{HT}. One must, however, stress that the number of turning points which must be taken into account in (8) depends strongly on the nature of the vibrational relaxation. The non-vanishing terms with $\zeta_i \sim 1$ in (8) (see Fig. 2) will be present only in those cases when there are high-frequency local vibrations. We note also that not only in those cases when there are high-frequency local vibrations, but also in those cases when they are not present, there can be deviations in the short-wavelength region of the frequency-dependence of the probability for HT from the simple dependence given by the function T(x). Indeed, if in (6) we take into account the next term in the expansion we must in (8) replace the function T(x) by the function

$$T_1(x)=\frac{1}{2}\int_0^\infty\frac{dz}{z^{1/2}}\exp(-(z-x)^2)(1+\beta z) \tag{9a}$$

($\beta = \sigma_2/2^{5/2}S\overline{\omega} \sim S^{-1/2}$) which differs appreciably from T(x) only in the region $x \gg 1$ (see Fig. 3).

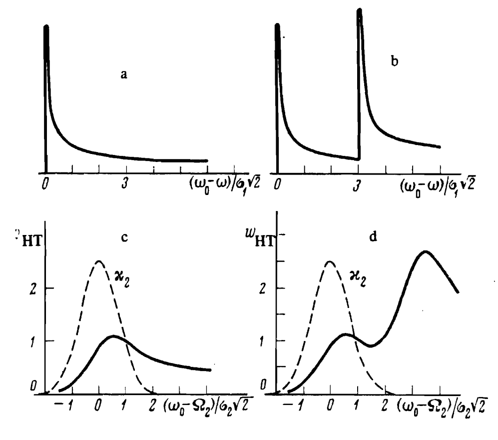

FIG. 2. a) HL spectrum in the case of fast vibrational relaxation ($\Delta_i \gg \sigma$, i ≥ 1); b) HL spectrum taking into account the turning point for which $\Delta_1 = 3\sigma/2$; c) probability for HT as function of the excitation frequency (in units $v^2(2\pi/2)^{1/2}/\hbar^2(S\overline{\omega}^3\sigma)^{1/2}$) for $\Delta_i \gg \sigma$, i ≥ 1; d) the same as c) but taking into account the turning point with $\Delta_1 = 3\sigma\sqrt{2}$. $\varkappa_2$ is the acceptor absorption spectrum.

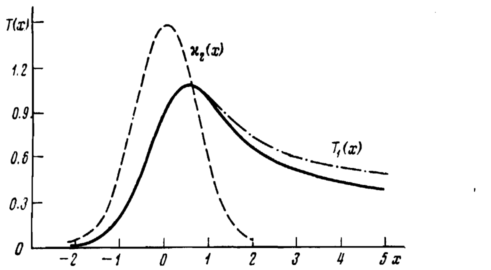

FIG. 3. The function T(x): full drawn curve (see Eq. 9)), and the function $T_1(x)$: dash-dotted curve (see Eq. (9a)), evaluated for $\beta = 0.04$ (S = 20). $\varkappa_2(x)$ is the acceptor absorption spectrum ($x = (\omega_0 - \Omega_2)/\sigma_2\sqrt{2}$).

We estimate the magnitude of w_{HT}. When the excitation is in the region of the maximum of the acceptor absorption band (x = 0) T(x) ≈ 0.9. The factor $(S\overline{\omega}^3\sigma_2)^{-1/2}$ is approximately equal to

$$t_c t_0 \sim \frac{1}{\sigma_2\overline{\omega}}\left(\frac{2\bar{n}+1}{S}\right)^{1/4}.$$

As a result we have, in accordance with the above given qualitative considerations $w_{\text{HT}} \sim t_c t_0 (v/\hbar)^2$.

A dependence of the probability for energy transfer on the excitation energy, similar to the one obtained above, was observed in 1960 by Weber [8] in solutions of aromatic molecules. It is important to emphasize that not only the spectral dependence of HT, obtained above, but also its probability agree with Weber's experimental data. Indeed, for self-transfer in the case of dipole-dipole interactions ($v = kM^2/nR^3$, n: index of refraction, $k^2 = 2/3$: orientation factor)

$$w_{\text{HT}}(x)=B\left(\frac{\gamma_0}{\sigma}\right)^2\left(\frac{c}{Rn\Omega_L}\right)^6\sum_i(2-\delta_{i0})T(x-\zeta_i),$$
$$B=\frac{9}{16}2^{3/4}\pi^{1/2}k^2S^{-1/4}(2\bar{n}+1)^{-3/4} \tag{11}$$

(we used $M^2 = 3\gamma_0\hbar^2c^3/4n\Omega_L^3$). Defining the transfer radius as the distance R_0 at which w = ½ we find for a phenol solution ($\Omega_L = 10^{15}$ s⁻¹, $\sigma = 4.5 \times 10^{13}$ s⁻¹, $\gamma_0 = 2.5 \times 10^7$ s⁻¹, n = 1.5) for excitation in the region $|x| \lesssim 1$ that $R_0 = 1.8 \pm 0.2$ nm which completely agrees with Weber's experimental estimate [8] $R_0 = 1.7$ nm.

3. QUANTUM THEORY OF HT. GENERAL FORMULAE

We take into account that when evaluating the probability for incoherent transfer we can restrict ourselves to the weak interaction approximation. We can then find the probability for incoherent HT in which we are interested from the following second order formula:

$$W(\omega_0)=\frac{2\pi}{\hbar}\sum_i z_i\sum_f\left|\sum_m\frac{\langle 2,f|H_{\text{int}}|1,m\rangle\langle 1,m|D|0,i\rangle}{E_f-E_m+i\hbar\gamma_m/2}\right|^2\delta(E_i+\hbar\omega_0-E_f) \tag{12}$$

(this formula describes the probability for the excitation of the acceptor when the donor absorbs a photon of frequency ω_0). Here $|0, i\rangle$, $|1, m\rangle$, and $|2, f\rangle$ are vibrational states of the crystal (solution) with, respectively, unexcited donor and acceptor, excited donor and unexcited acceptor, and excited acceptor and unexcited donor; E_i, E_m, and E_f are the energies of the states $|0, i\rangle$, $|1, m\rangle$, and $|2, f\rangle$; γ_m is the donor damping constant in the state $|1, m\rangle$, D is the operator of the interaction between the optical electrons in the donor and light, H_{int} is the operator of the donor-acceptor interaction, $z_i = \exp(-E_i/kT)/\sum_i\exp(-E_i/kT)$. We can rewrite Eq. (12)

in invariant form, if we use the formulae

$$\delta(x)=(2\pi)^{-1}\int_{-\infty}^{\infty}d\tau\, e^{-ix\tau},$$

$$\frac{1}{(x+i\gamma/2)(x'-i\gamma/2)}=2\int_0^{\infty}dt\int_{-t}^{t}ds\exp[i(x-x')t+i(x+x')s-\gamma t]$$

and introduce the vibrational Hamiltonians H_0, H_1, and H_2 in the electronic states $|0\rangle$, $|1\rangle$, and $|2\rangle$, respectively. We then get

$$W(\omega_0)=\frac{2\mathscr{M}^2}{\hbar^2}\int_0^{\infty}dt\int_{-\infty}^{\infty}d\tau\int_{-t}^{t}ds\exp(-i\omega_0\tau-\gamma t)A(t,\tau,s), \tag{13}$$

$$A(t,\tau,s)=\frac{v^2}{\hbar^2}\langle\exp[i(t-s)H_1/\hbar]\exp[i(\tau+2s)H_2/\hbar] \times\exp[-i(t+s)H_1/\hbar]\exp[-i\tau H_0/\hbar]\rangle_0, \tag{14}$$

where $\mathscr{M}=\langle 1|D|0\rangle=(\mathbf{E}\cdot\mathbf{M})$ ($\mathbf{E}$ is the electrical field strength of the light), $v=\langle 2|H_{\text{int}}|1\rangle$, $\langle\ldots\rangle=Z_0^{-1}$ $=Z_0^{-1}\operatorname{Tr}\{\exp(-H_0/kT)\}$, $Z_0=\operatorname{Tr}\{\exp(-H_0/kT)\}$. We neglected in (13) the dependence of $\mathscr{M}$ and v on the vibrational coordinates. In that case $\gamma_m=\gamma=\text{const}$. We note that for transitions which are allowed in the dipole approximation the Condon approximation $\mathscr{M}=\text{const}$ is well satisfied. The approximation v = const may turn out to be inadequate at small distances between the donor and the acceptor. It has been shown in[12], however, that in the case of a strong electron-phonon interaction taking into account the dependence of v on the vibrational coordinates leads in first approximation simply to replacing v^2 by $\langle v^2\rangle_1$ in (14), where

$$\langle\ldots\rangle_1=Z_1^{-1}\operatorname{Sp}[\exp(-H_1/kT)\ldots],\quad Z_1=\operatorname{Sp}[\exp(-H_1/kT)].$$

We must then also replace γ by

$$\bar\gamma=Z_1^{-1}\sum_m\gamma_m\exp(-E_m/kT).$$

One can give the following physical interpretation of the integration variables τ and s occurring in Eq. (13): τ describes the phase difference in the excited donor state after absorption of the photon, and s the phase difference in the excited acceptor state after the transfer of the excitation. The variable t also has a simple physical meaning: it describes the time the excitation stays at the donor.[11] Thus, the correlator $A(t,\tau,s)$ considered as function of τ and s describes the phase (transverse) relaxation in the excited states of the donor and the acceptor, while its dependence on t corresponds to the longitudinal (energy) relaxation of the donor. From what has been stated an important conclusion follows for the division of the normal and the hot transfer: HT corresponds to the integration in (13) in the small time region $t\ll\gamma^{-1}$, and the normal transfer to integration in the long time region $t\gtrsim\gamma^{-1}$.

We can easily check that this last conclusion is valid if we bear in mind that in the long time region $t\gtrsim\gamma^{-1}$ we can use for the correlation function $A(t,\tau,s)$ its asymptotic value as $t\to\infty$ which is equal to$^{3)}$

$$A(\infty,\tau,s)=\frac{v^2}{\hbar^2}\left\langle\exp\left[\frac{i}{\hbar}\tau H_1\right]\exp\left[-\frac{i}{\hbar}\tau H_0\right]\right\rangle_0 \times\left\langle\exp\left[\frac{i}{\hbar}(\tau+2s)H_2\right]\exp\left[-\frac{i}{\hbar}(\tau+2s)H_1\right]\right\rangle_1. \tag{15}$$

Substitution of (15) into (13) gives the following formula:

$$W_0(\omega_0)=\varkappa_1(\omega_0)w_0, \tag{16}$$

$$\varkappa_1(\omega_0)=\frac{\mathscr{M}^2}{2\pi\hbar^2}\int_{-\infty}^{\infty}d\tau\exp(-i\omega_0\tau)\left\langle\exp\left(\frac{i}{\hbar}\tau H_1\right)\exp\left(-\frac{i}{\hbar}\tau H_0\right)\right\rangle_0,$$

$$w_0=\frac{v^2}{2\pi\gamma}\int_{-\infty}^{\infty}d\tau'\left\langle\exp\left(\frac{i}{\hbar}\tau' H_2\right)\exp\left(-\frac{i}{\hbar}\tau' H_1\right)\right\rangle_1 =(Z_1\gamma)^{-1}\sum_{m,f}\exp\left(-\frac{E_m}{kT}\right)|\langle f|H_{\text{int}}|m\rangle|^2\delta(E_i-E_f), \tag{17}$$

where w_0 is the probability for the transfer of the electronic excitation. The formula for w_0 obtained here is the same as the original formula in Förster's theory for the transfer after vibrational relaxation in the donor.[19] This also demonstrates the conclusion that the normal transfer corresponds to integrating in (13) over the region of long times t. In the general case, however, we must take into account the region of both long and short times t.

4. QUANTUM EVALUATION OF HT TAKING DYNAMICAL CORRELATION INTO ACCOUNT

Below we shall obtain a formula for the correlation function $A(t,\tau,s)$ valid for all regions in which t, τ, and s can change in a model in which we take into account only the change in the nuclear equilibrium positions under electronic transitions in the donor and the acceptor. In that model

$$H_i=\exp(\nabla_i)H_0\exp(-\nabla_i)+\hbar\Omega_{0i},\quad i=1,2, \tag{18}$$

$$H_0=\frac{\hbar}{2}\sum_j\omega_j\left(-\frac{\partial^2}{\partial\xi_j^2}+\xi_j^2\right). \tag{19}$$

Here ξ_j and ω_j are the dimensionless coordinate and frequency of the j-th normal vibration, Ω_{0i} is the frequency of the purely electronic transition in the donor (i = 1) or the acceptor (i = 2), $\exp\nabla_i$ is the unitary shift operator, where

$$\nabla_i=\sum_j\xi_{0j}^{(i)}\frac{\partial}{\partial\xi_j}, \tag{20}$$

$\xi_{0j}^{(i)}$ is the change in the equilibrium position of the j-th oscillator for an electronic transition in a donor (i = 1) or in an acceptor (i = 2).

In the model considered the correlation function $A(t,\tau,s)$ can be written in the following simple form:

$$A(t,\tau,s)=\frac{v^2}{\hbar^2}\langle Pe^L\rangle_0=\frac{v^2}{\hbar^2}\exp\left\{\langle L\rangle_0+\frac{1}{2}\langle P(L-\langle L\rangle_0)^2\rangle_0\right\}, \tag{21}$$

where

$$L=i\Omega_{02}\tau+2i(\Omega_{02}-\Omega_{01})s+\nabla_1-\nabla_1(t-s)+\nabla_2(t-s) -\nabla_2(t+\tau+s)+\nabla_1(t+\tau+s)-\nabla_1(\tau), \tag{22}$$

P is the ordering operator which arranges the operators ∇_1, $\nabla_i(t-s)$, $\nabla_i(t+\tau+s)$, and $\nabla_1(\tau)$ from the left to the right in the given order (i = 1, 2). We used in (21) the fact that L is a linear operator and used the Bloch-De Dominicis pair correlator theorem.[20]

Substituting (22) into (21) we get

$$A(t,\tau,s)=v^2\hbar^{-2}\exp\{i\Omega_{02}\tau+2i(\Omega_{02}-\Omega_{01})s+g_1(\tau) +\bar g_1(\tau+2s)+\bar g_2(\tau+2s)+\bar G(t,\tau,s)\}, \tag{23}$$

where $g_i\equiv g_{ii}$, $\bar g_i=g_i-g_{12}$,

$$\begin{gathered} g_{ii'}(x)=\langle\nabla_i(\nabla_{i'}-\nabla_{i'}(x))\rangle_0 \\ =\sum_j\xi_{0j}^{(i)}\xi_{0j}^{(i')}[(\bar n_j+1)(\exp(i\omega_j x)-1)+\bar n_j(\exp(-i\omega_j x)-1)]; \\ G(t,\tau,s)=\bar g_1(t-s)+\bar g_1(-t-s)-\bar g_1(t+\tau+s)-\bar g_1(\tau-t-s), \\ \bar n_j=[\exp(\hbar\omega_j/kT)-1]^{-1}. \end{gathered} \tag{24}$$

The function $g_{12}(x)$ describes the effect of the dynamical correlation of the donor and the acceptor, which decreases at large distances R as $g_{12}(x)\propto R^{-3}$. However, at small distances R and in particular in intracenter processes $g_{12} \sim g_1(x)$, i.e., this effect may be large (see also below).

Equation (23) is exact in the harmonic approximation. However, it can also be used for weakly anharmonic oscillations. The anharmonicity effects are then contained in anharmonic corrections to the average values $\langle \nabla_i \nabla_{i'} \rangle$ and to the correlation functions $g_{ii'}(x)$. Equation (23) is applicable for any interaction force between the optical electrons of the donor and the acceptor and the oscillations. We are here only interested in the case of a strong interaction ($S_i = \sum_j \xi_{0j}^{(i)2} \gg 1$) and fast vibrational relaxation when we can use the expansion

$$g_{ii'}(x) = \sum_l \mu_{ii'}^{(l)} \frac{(ix)^l}{l!}, \tag{25}$$

where

$$\mu_{ii'}^{(l)} = \sum_j \xi_{0j}^{(i)} \xi_{0j}^{(i')} [1+\bar{n}_j(1+(-1)^l)] \omega_j^l.$$

We note that $\mu_i^{(l)} \equiv \mu_{ii}^{(l)}$ are semi-invariants of the donor (i = 1) and acceptor (i = 2) absorption bands. In particular, $\mu_1^{(2)} = \sigma_1^2$ and $\mu_2^{(2)} = \sigma_2^2$. As to order of magnitude

$$\mu_i^{(2k+1)} \sim S_i \bar{\omega}_i^{2k+1}, \quad \mu_i^{(2k)} \sim S_i \bar{\omega}_i^{2k} (2\bar{n}_i+1),$$

$$2\bar{n}_i+1 = \sum_j (2\bar{n}_j+1) \xi_{0j}^{(i)^2} / S_i \geqslant 1.$$

Substituting (25) into (23) and taking into account terms up to and including third order we get

$$A(t, \tau, s) = v^2 \hbar^{-2} \exp\{i\Omega_1 \tau + i(\bar{\Omega}_2 - \bar{\Omega}_1) y - \mu_1^{(2)} \tau^2/2 + \mu_2^{(2)} \tau y - (\bar{\mu}_1^{(2)} + \bar{\mu}_2^{(2)}) y^2/2 + i\bar{\mu}_1^{(3)} y t^2\}, \tag{26}$$

where

$$y = \tau + 2s, \quad \Omega_i = \Omega_{0i} + \mu_i^{(1)}, \quad \bar{\Omega}_i = \Omega_{0i} + \bar{\mu}_i^{(1)},$$

$$\bar{\mu}_i^{(l)} = \mu_i^{(l)} - \mu_{12}^{(l)}.$$

It follows from Eq. (26) that the actual values of the phase relaxation times τ and s (i.e., the values which lie in the region which contributes the main part to the integral (13)) are, indeed, as to order of magnitude, equal to $t_c \sim (\mu_1^{(2)})^{-1/2} \sim (\bar{\omega}_1^2 S_1(2\bar{n}_1 + 1))^{-1/2}$ and the actual value of the time t during which HT occurs is, as to order of magnitude, in agreement with (6) equal to $t_0 \sim (\bar{\mu}_1^{(3)} \tau_c)^{-1/2} \sim (\bar{\omega}_1^4 S_1/(2\bar{n}_1 + 1))^{-1/4}$ (as noted, it determines the time during which the energy of the donor is in resonance with the acceptor absorption band).

As the actual values of t in (13) are much larger than the actual values of |s| we can in the integral over s change the integration limits ±t to ±∞. As a result the integrals over τ and s are elementary and we get

$$W(\omega_0) = \varkappa_1(\omega_0) w_{\mathrm{HT}}(\omega_0), \tag{27}$$

where

$$w_{\mathrm{HT}}(\omega_0) = \frac{v^2}{\hbar^2} \left(\frac{2^{3/2}\pi}{\bar{\sigma}\bar{\mu}^{(3)}} \right)^{1/2} T(\bar{x}) \tag{28}$$

is the probability for HT, $\sigma = (\mu_2^{(2)} - \mu_1^{(2)} \alpha_2^2)^{1/2}$, $\bar{\mu}^{(3)} = \mu_1^{(3)}(1 - \alpha_3)$, $\alpha_l = \mu_{12}^{(l)}/\mu_1^{(l)}$,

$$\bar{x} = [(\omega_0 - \Omega_1)(1 - \alpha_2) + \bar{\Omega}_1 - \bar{\Omega}_2]/\bar{\sigma}\sqrt{2}.$$

If we neglect the dynamical correlation (its measure is in this model indicated by the parameters α_l) Eq. (28) is the same as Eq. (8), obtained earlier (in which for centers characterized by fast vibrational relaxation we must take into account only the term with i = 0).

5. INTRACENTER HT

The dynamical correlation effects are particularly important in intracenter processes. To check this we consider as an example HT between components of a T_{1u} state of a cubic center. In the approximation which is linear in the nuclear displacements the electron-phonon interaction matrix has in this state the form

$$V = \begin{pmatrix} aQ_1 + b(Q_2 - Q_3/\sqrt{3}) & cQ_6 & cQ_5 \\ cQ_6 & aQ_1 - b(Q_2 + Q_3/\sqrt{3}) & cQ_4 \\ cQ_5 & cQ_4 & aQ_1 + 2bQ_3/\sqrt{3} \end{pmatrix}, \tag{29}$$

where the Q_i are the symmetrized displacements of the A_{1g} (i = 1), E_g (i = 2, 3), and T_{2g} (i = 4, 5, 6) representations; a, b, and c are the electron-phonon interaction constants (we have used in (29) as basis the |x⟩, |y⟩, and |z⟩ states which transform as the x, y, and z components of a polar vector). We assume that c ≪ b. In such a case we can consider the effect of the T_{2g} vibrations using perturbation theory in terms of transfer of the excitation between the |x⟩, |y⟩, and |z⟩ states. The probability for HT between these states will then be given by Eq. (28) in which

$$v^2 = c^2 \langle Q_4^2 \rangle_0, \quad \bar{\sigma}^2 = 2b^2 \langle Q_2^2 \rangle_0 (1 + \alpha_2)/\hbar^2,$$
$$\bar{\mu}^{(3)} = 2b^2/\hbar. \tag{30}$$

We note that in the case considered

$$\alpha_2 = \frac{3a^2 \langle Q_1^2 \rangle_0 - 2b^2 \langle Q_2^2 \rangle_0}{3a^2 \langle Q_1^2 \rangle_0 + 4b^2 \langle Q_2^2 \rangle_0}$$
$$\alpha_3 = \frac{3a^2 - 2b^2}{3a^2 + 4b^2}, \tag{31}$$

i.e., α_2 and α_3 can be appreciably different from zero. If we recognize that quantitatively the dynamical correlation effects can be characterized by the ratio $1/(1 - \alpha_l)$, these effects can in the given case, indeed, be arbitrarily large.

The transitions considered between components of a degenerate state lead to a dependence of the degree of polarization of the luminescence on the excitation frequency. In particular, in the case of A-luminescence of KCl–Tl⁺ type centers when excited by light polarized along the C_4 axis this dependence will be given by the formula[21]

$$P(\omega_0) = \frac{1 - 3w_{\mathrm{HT}}(\omega_0)}{3(1 - w_{\mathrm{HT}}(\omega_0) - w_0)}, \tag{32}$$

where $w_0 = w_0(T)$ takes into account |x⟩ → |y⟩ transitions after relaxation. The obtained dependence of the degree of polarization on the excitation frequency is shown in Fig. 4. A similar dependence is observed experimentally (see [4]).

The authors are grateful to K. K. Rebane, D. L.

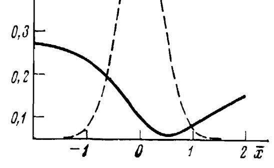

FIG. 4. The polarization P of luminescence as function of the dimensionless excitation frequency $\bar{x} = (\omega_0 - \Omega)(1 - \alpha_2)/\bar{\sigma}\sqrt{2}$ for the following values of the parameters: $\alpha_2 = 0.5$; $w_0 = 0.25$; $w_{\mathrm{HT}}(\omega_0) = 0.25\,T(x)$; $\kappa(x)$ is the absorption spectrum.

Dexter, and R. S. Knox for discussions of the problems of HT theory.

---

[1] In a number of papers (see, e.g., [9]) the assumption has been expressed that the effect observed by Weber is caused by the emission of dimers. However, a number of the regularities observed by Weber, such as the independence of the luminescence quantum yield of the excitation energy, can not be explained by the emission of dimers or of other associates (see [10] for a more detailed discussion of this problem).

[2] The dynamical correlation takes into account that the vibrations of the environments of the donor and of the acceptor are not independent. For that reason the nuclear displacements occurring in the energy transfer theory when the excitation changes from the donor to the acceptor do not reduce to a sum of independent nuclear displacements for the electronic transitions in the donor and in the acceptor.

[3] To find $A(\infty, \tau, s)$ we must bear in mind that $\langle \exp(itH_1/\hbar)\, a \exp(-itH_1/\hbar)\, b\rangle_1 \to \langle a\rangle_1 \langle b\rangle_1$, when $t \to \infty$. We note that $A(\infty, \tau, s)$ determines the value of the correlation function after the relaxation.

---

[1] D. L. Dexter, Phys. stat. sol. (b) **51**, 571 (1972).

[2] V. V. Hishnyakov, Phys. stat. sol. (b) **51**, K 117 (1972).

[3] I. Yu. Tekhver and V. V. Khizhnyakov, ZhETF Pis. Red. **19**, 338 (1974) [JETP Lett. 19, 191 (1974)].

[4] A. Fukuda, S. Makishima, T. Maruchi, and R. Onaka, J. Phys. Chem. Sol. **28**, 1768 (1967).

[5] R. K. Bauer and E. Rabinowitch, Migration of Electronic Energy between Chlorophyll Molecules in Viscous Solutions, Preprint No. 162, Institute of Physics, N. Copernicus University, Torun, 1971.

[6] R. K. Bauer, L. Szalay, and E. Tombasz, Biophys. J. **12**, 731 (1972).

[7] M. Gueron, J. Eisinger, and R. Shulman, J. Chem. Phys. **47**, 4077 (1967).

[8] G. Weber, Biochem. J. 75, 335 (1960).

[9] V. A. Luchin, Proc. XI European Conf. Molec. Spectrosc., Contrib. No. 29, Tallinn, 1973.

[10] J. Eisinger, A. A. Lamola, J. W. Longworth, and W. B. Gratzer, Nature **226**, 113 (1970).

[11] V. V. Khizhnyakov, Peredacha energii v teorii rezonansnogo vtorichnogo svecheniya primesnykh tsentrov (Energy transfer in the theory of resonance secondary emission of impurity centers) Preprint FAI-11, Tartu, 1972.

[12] V. V. Hishnyakov and I. J. Tehver, Radiationless Transfer of Electronic Excitation During Vibrational Relaxation, Preprint FI-31, Tartu, 1974.

[13] V. Hizhnyakov, K. Rebane, and I. Tehver, Light Scattering Spectra of Solids, Ed. G. B. Wright, Springer Verlag New York, 1969, p. 513; V. Hizhnyakov and I. Tehver, Phys. stat. sol. **39**, 67 (1970).

[14] I. Tekhver and V. Khizhnyakov, Izv. Akad. Nauk Estonian SSR, Seriya fiz. mat. i tekhn. nauk **15**, 9 (1966); V. Hizhnyakov and I. Tehver, Phys. stat. sol. **21**, 755 (1967).

[15] K. Poiker and E. D. Trifonov, Fiz. Tverd. Tela **10**, 1705 (1968) [Sov. Phys.-Solid State **10**, 1346 (1968)]; Phys. stat. sol. **30**, 479 (1968).

[16] V. Hizhnyakov and I. Tehver, Light Scattering in Solids, Ed. M. Balkanski, Flammarion, Paris, 1971, p. 57; Physics of Impurity Centers in Crystals, Ed. G. S. Zavt, Tallinn, 1972, p. 607.

[17] M. A. Kozhushner, Fiz. Tverd. Tela **13**, 2601 (1971) [Sov. Phys.-Solid State **13**, 2183 (1972)].

[18] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

[19] Th. Förster, Ann. Physik **2**, 55 (1948).

[20] C. Bloch and C. De Dominicis, Nucl. Phys. **7**, 459 (1958).

[21] V. V. Khizhnyakov, Adiabaticheskie poverkhnosti i kharakteristiki izlucheniya primesnykh tsentrov v dvumya opticheskimi elektronami (Adiabatic Surfaces and Characteristics of the Radiation of Impurity Centers with Two Optical Electrons) Preprint FI-36, Tartu, 1975.

Translated by D. ter Haar
64