

# Transfer of electronic excitation during the course of vibrational relaxation

I. Yu. Tekhver and V. V. Khizhnyakov

Physics Institute, Estonian Academy of Sciences

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A theory is proposed for the transfer of electronic excitation, during the course of vibrational relaxation, for a donor and acceptor that interact strongly with the vibrations of the nuclei. It is shown that Weber's effect<sup>[2]</sup> is explained by this mechanism of electronic-excitation transfer.

It is usually assumed that transfer of electronic excitation in crystals and solutions occurs following vibration in the excited electronic state of the donor. The basis for this assumption is that the time of vibrational relaxation is usually very short ( $\tau_{rel} \sim 10^{-13}$  sec), as a result of which the excited donor spends an overwhelming part of the time in an equilibrium vibrational state. However, if the interaction  $v$  between the donor and acceptor is large enough ( $v \sim \hbar\tau_{rel}^{-1}$ ), then the excitation can go over to the acceptor even before the end of the vibrational relaxation, i. e., in a hot vibrational state (we denote this transfer mechanism by HT, for "hot transfer"). An estimate shows that this condition can be satisfied at a distance  $R \gtrsim nm$  (see below).

HT was recently considered by one of us in<sup>[1]</sup>. It was shown that the corresponding probability is determined by the overlap integral of the acceptor absorption spectrum with the summary spectrum of the hot luminescence and scattering of the donor. (At small  $R$ , the spectra involved in the overlap integrals should be corrected to take into account the dynamical correlation.) A feature of HT is its dependence on the excitation frequency  $\omega_0$ . In this paper we obtain this dependence, and also the value of the HT probability for donors and acceptors having broad structureless absorption bands. We shall show on the basis of the derived formulas that

Weber's effect,<sup>[2]</sup> namely the decrease in the probability of the transfer of electronic excitation in solutions of aromatic molecules when excited in the long-wave wing of the absorption spectrum, is explained by the HT.

The probability of acceptor excitation, if the intermediary is the donor excited state, is described by the formula

$$W(\omega_0) = 2\pi \sum_{i,f} n_i \left| \sum_m \frac{\langle a, f | V | d, m \rangle \langle d, m | D | 0, i \rangle}{E_i + \omega_0 - E_m + i\gamma_m/2} \right|^2 \times \delta(E_i - E_f + \omega_0), \quad (1)$$

where  $|0, i\rangle$ ,  $|d, m\rangle$ , and  $|a, f\rangle$  denote the electron-vibrational states of the system, with unexcited donor and acceptor, with excited donor and unexcited acceptor, and with unexcited donor and excited acceptor, respectively,

$$n_i = Z^{-1} e^{-E_i/kT}, \quad Z = \sum_i e^{-E_i/kT}, \quad E_i,$$

$E_i$ ,  $E_m$ , and  $E_f$  are the energies of the states  $|0, i\rangle$ ,  $|d, m\rangle$ , and  $|a, f\rangle$ ,  $\gamma_m$  is the damping constant of the state  $|d, m\rangle$ ,  $D$  is the operator of the interaction of the donor with the light, and  $\hbar = 1$ .

We use the adiabatic approximation and introduce the vibrational Hamiltonians  $H_0$ ,  $H_d$ , and  $H_a$  in the electronic states  $|0\rangle$ ,  $|d\rangle$ , and  $|a\rangle$ . Then, neglecting the dependences of  $M = \langle 0 | D | d \rangle$  and  $v = \langle d | V | a \rangle$  on the vibrational

coordinates (in this case  $\gamma_m = \gamma$  is a  $c$  number), formula (1) becomes

$$W(\omega_0) = M^2 v^2 \int_{-\infty}^{\infty} dt \int_0^{\infty} ds \int_0^{\infty} ds' \exp[-i\omega_0 t - \gamma(s + s')/2] A(t, s, s'), \quad (2)$$

where

$$A(t, s, s') = \langle e^{i s H_d} e^{i(t+s-s')H_a} e^{-i s H_d} e^{-i t H_0} \rangle, \quad (3)$$

$\langle \dots \rangle = Z^{-1} \text{Tr}[\exp(-H_0/kT) \dots]$ . If we take into account only the changes in the equilibrium positions of the nuclei in the electronic transitions in the donor and acceptor [in this case we have  $H_d = \omega_d + \exp(\nabla_d)H_0 \times \exp(-\nabla_d)$  and  $H_a = \omega_a + \exp(\nabla_a)H_0 \exp(-\nabla_a)$ , where  $\omega_{d(a)}$  is the frequency of the purely electronic transitions of the donor ( $d$ ) or acceptor ( $a$ ) and  $\nabla_{d(a)}$  is the linear shift operator], and confining ourselves to the pair-correlation approximation, then

$$A(t, s, s') = \exp[g_d(t) + \bar{g}_d(t + s - s') + \bar{g}_d(-s) + \bar{g}_d(s') - \bar{g}_d(t + s) - \bar{g}_d(t - s') + \bar{g}_d(t + s - s')] \exp[i(\omega_a - \omega_d)(t + s - s') + i\omega_d t], \quad (4)$$

where  $\bar{g}_i = g_i - g_{ad}$ ,  $g_i(t) = \langle \nabla_i^2 \rangle - \langle \nabla_i \nabla_i(t) \rangle$  ( $i = a, d$ ) determines the logarithm of the Fourier transform of the absorption spectrum of the donor or acceptor;  $g_{ad}(t) = \langle \nabla_a \nabla_d \rangle - \langle \nabla_a \nabla_d(t) \rangle$  takes into account the dynamical correlation between them ( $g_{ad} \sim R^{-3}$ ,  $R \rightarrow \infty$ ).

We change over in (2) to the variables  $\tau = (s + s')/2$  and  $z = s - s'$ , and recognize that  $\tau$  determines the time of stay of the excitation on the donor.<sup>[1]</sup> The integration in the region of large  $\tau \gg \gamma^{-1} \gg \tau_{rel}$  therefore corresponds to taking into account the transfer of excitation after the vibrational relaxation while integration in the region of small  $\tau \leq \tau_{rel}$  takes the HT into account (this is proved in<sup>[1]</sup>). We are interested here only in HT. In the case of donors and acceptors with large Stokes losses  $P$ , having broad structureless bands, this enables us to use the expansions  $g_i(x) = \sum_{l=0}^{\infty} (ix)^l \mu_{li}/l!$  and  $\bar{g}_i(x) = \sum_{l=0}^{\infty} (ix)^l \bar{\mu}_{li}/l!$  ( $i = a, d$ ) and to confine ourselves to the first three non-vanishing terms. Here  $\bar{\mu}_{li} = \mu_{li} + \mu_{l,ad}$  and  $\mu_{li}$  is the semi-invariant of  $l$ th order of the absorption band of the donor ( $i = d$ ) or of the acceptor ( $i = a$ ). In order of magnitude we have  $\mu_l \sim \omega_v P \theta$ , where  $\omega_v$  is the average oscillation frequency,  $\theta = 2\bar{n} + 1$  for even  $l$ ,  $\theta = 1$  for odd  $l$ , and  $\bar{n} = [\exp(\omega_v/kT) - 1]^{-1}$ . The actual values of  $\tau$  ( $\sim \omega_v^{-1} P^{-1/4}$ ) are much larger than the actual values of  $z$  ( $\sim \omega_v^{-1} P^{-1/2}$ ). We can therefore replace the integration limits  $\pm 2\tau$  of the integral with respect to  $z$  by  $\pm \infty$ . This yields

$$W(\omega_0) = \kappa_d(\omega_0) v^2 \sqrt{2\pi} \sqrt{2/\bar{\mu}_{3d}} \sigma T(x), \quad (5)$$

where

$$\kappa_d(\omega_0) = M^2 (2\pi/\mu_{2d})^{1/2} \exp[-(\omega_0 - \omega_d)^2 / 2\mu_{2d}] \quad (6)$$

is the donor absorption spectrum,  $\sigma^2 = \mu_{2a} - \mu_{2d} \alpha^2$ ,  $\alpha = \mu_{2,da}/\mu_{2d}$ ,  $\bar{\omega}_i = \omega_i + \omega_{1i}$  is the frequency of the maximum of the absorption band of the donor ( $i = d$ ) or of the acceptor ( $i = a$ ),  $x = [\omega_0(1 - \alpha) - \omega_a + \omega_d \alpha] / \sqrt{2}\sigma$  is the dimensionless excitation frequency, and

$$T(x) = \int_0^{\infty} dy e^{-(y^2 - x)^2} \quad (7)$$

It follows from the obtained formula that the HT actually depends strongly on the excitation frequency. If its probability  $w(\omega_0)$  is normalized to  $\kappa_d(\omega_0)$ , then this dependence is determined by the function  $T(x)$ .

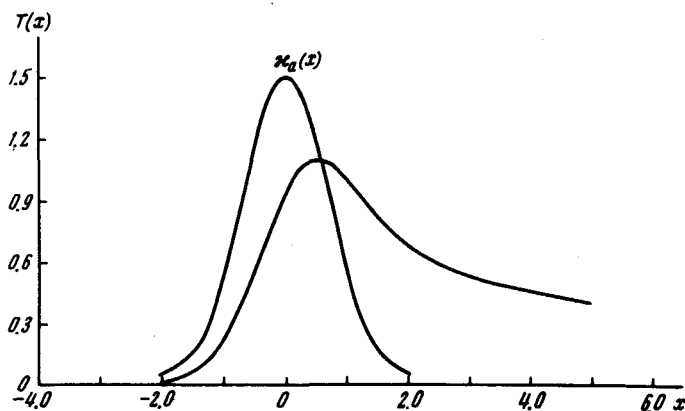
It is seen from the figure that the HT probability has a maximum at the frequency  $x = x_0 = 0.5$ , which lies on the short-wave side of the maximum of the acceptor absorption band. The decrease of the HT probability when the frequency  $x$  shifts into the "red" side of  $x_0$  explains the Weber effect. The decrease of the HT probability when  $x$  shifts to the "blue" side of  $x_0$ , insofar as we know, has never been noted in the literature, although its manifestation can be seen in Weber's experimental data.<sup>[2]</sup>

The causes of the noted effects are the following: 1) The larger the excitation frequency  $\omega_0$ , the larger the nonequilibrium vibrational energy and the vibrational relaxation time; therefore the later the HT. 2) If  $\omega_0$  differs appreciably from  $\bar{\omega}_a$ , then, in accordance with the Franck-Condon principle, the electronic transition in the acceptor during HT can occur only if the vibrational configurations deviate strongly from equilibrium. Such transitions have low probability, and this leads to the second effect.

Let us estimate the relative probability of the HT. If  $\omega_0 = \omega_a \pm \sigma$ , then for homotransfer in the case of dipole-dipole interaction ( $v = kM^2/n^2R^3$ , where  $n$  is the refractive index, and  $k^2 = 2/3$  is the orientation factor), and neglecting the dynamical correlation ( $\alpha = 0$ ), we have  $w \approx (0.75 \pm 0.45)[P(2\bar{n} + 1)^3]^{1/4} (\gamma_0/\sigma)^2 (c/Rn\omega_L)^6$ , where  $\gamma_0$  is the radiative damping constant and  $\omega_L$  is the frequency of the maximum of the luminescence spectrum (we took into account the fact that  $M^2 = 3\gamma_0 c^3 / 4\omega_L^2 n$ ). Defining the transfer radius as the distance  $R$  at which  $w = 1/2$ , we obtain for a phenol solution ( $\omega_L \approx 10^{15} \text{ sec}^{-1}$ ,  $\sigma = 4.5 \times 10^{13} \text{ sec}^{-1}$ ,  $\gamma_0 = 2.4 \times 10^7 \text{ sec}^{-1}$ ,  $P(2\bar{n} + 1)^3 = 5$ ,  $n = 1.5$ ) the value  $R = 1.8 \pm 0.2 \text{ nm}$ , which agrees with the experimental estimate  $R = 1.7 \text{ nm}$ .<sup>[2]</sup>

The obtained formula are valid also for intracenter transfer of electronic excitation. In particular, they explain the dependence of the intracenter depolarization of the luminescence centers such as  $\text{KCl:Ti}^+$  during the time of vibrational relaxation, on the excitation frequency, as observed in<sup>[3]</sup>.

We note in conclusion that D.S. Fork (see<sup>[4]</sup>) observed a dependence of the rate of photosynthesis on the ex-



Dependence of the relative probability  $T(x)$  of the transfer of electronic excitation during the course of vibrational relaxation on the dimensionless exciting frequency  $x = [\omega_0(1 - \alpha) - \omega_a + \alpha\omega_d] / \sqrt{2}\sigma$ ;  $\kappa_d(x)$  is the acceptor absorption spectrum.

citation frequency, similar to the dependence of  $T(x)$  on  $x$  (see the figure), in the red part of the spectrum (using simultaneously the additional green illumination needed to ensure the second photochemical reaction). We can propose on this basis that the energy migration in the photosynthetic unit proceeds via the HT mechanism.

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touched upon in the article.

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<sup>1</sup>V. V. Hizhnyakov, Phys. stat. Sol. (b) **51**, K117 (1972); V. V. Khizhnyakov, Energy Transfer in the Theory of Resonant Secondary Emission of Impurity Centers, Preprint FAI-11, Tartu, 1972.

<sup>2</sup>G. Weber. Biochem, J. **75**, 335 (1960).

<sup>3</sup>A. Fukuda *et al.*, J. Phys. Chem. Solids **28**, 1763 (1967).

<sup>4</sup>O. Heath, Photosynthesis (Russ. transl.), Mir, 1972, p. 264.