# TRANSFER OF ENERGY BY VIRTUAL EXCITATION OF MOLECULES OF THE MEDIUM

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## Abstract

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# TRANSFER OF ENERGY BY VIRTUAL EXCITATION OF MOLECULES OF THE MEDIUM

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In the theory of processes of radiationless energy transfer from donor molecules to acceptor molecules, the solvent is usually considered as an isotropic inert medium. The exchange-resonance and inductive-resonance mechanisms of energy transfer are usually considered. In the exchange-resonance mechanism, energy transfer takes place when the electronic wave functions of the donor and acceptor overlap; in the inductive-resonance mechanism, it takes place by multipole interaction between the donor and acceptor molecules. The influence of the medium was taken into account by introducing the corresponding dielectric permittivity ($^{1}$).

If the matrix elements of the dipole moment for the transition from the ground to the excited state of the donor and acceptor are nonzero, then the interaction Hamiltonian will be dipole–dipole,

$$H_1 \sim 1/R^3, \tag{1}$$

where $R$ is the distance between the donor and acceptor molecules. In this case the probability of excitation transfer is

$$W_{d-d} \sim 1/R^6. \tag{2}$$

Such a mechanism of inductive-resonance energy transfer was considered in works ($^{2-4}$).

However, if the absorption band of the molecules of the medium is close to the excitation energy of the donor and acceptor, then interaction between them through virtual excitations of the levels of the molecules of the medium is possible. Let us consider such a mechanism of energy transfer qualitatively. Owing to the resonance interaction of the molecules of the medium, instead of the excited level of a single molecule there arises an exciton band of width $\Delta E_0$. If the edge of this band is close to the excitation energy of the donor, then for a time $\tau \simeq \hbar/\Delta E$ the excited state of the donor can create virtual excitons ($\Delta E$ is the effective difference between the excitation energies of the donor and of the molecules of the medium). If during this time the exciton manages to reach the acceptor, then energy transfer may occur. The velocity $v$ of motion of the exciton is the greater, the wider the exciton band. The distance over which energy can effectively be transferred is

$$R \simeq \tau v \sim \Delta E_0/\Delta E. \tag{3}$$

Thus, for such a mechanism of energy transfer to operate, $\Delta E$ must be small and the width of the exciton band large.

Let us proceed to a quantitative calculation of the probability of energy transfer. We shall not take into account the direct interaction between donor and acceptor with a Hamiltonian of type (1). Then, in second-order perturbation theory, for the probability of energy transfer per unit time from donor to acceptor $W$, we have:

$$W = \frac{2\pi}{\hbar}\left|\sum_k \frac{\langle \psi_{d0}\psi_{a1}\psi_0|\hat{H}_{a-c-c}|\psi_k\psi_{a0}\psi_{d0}\rangle\langle\psi_{d0}\psi_{a0}\psi_k|\hat{H}_{d-c}|\psi_0\psi_{a0}\psi_{d1}\rangle}{E - E_0 - \Delta E(k)}\right|^2. \tag{4}$$

Here $\psi_{d0}, \psi_{a0}$ are the wave functions of the unexcited states of the donor and acceptor molecules; $\psi_{d1}, \psi_{a1}$ are the same for the excited states; $\psi_0$ and $\psi_k$ are the wave functions of the ground and excited $k$-th states of the medium; $k$ is the number of the level in the exciton band; $E$ is the excitation energy of the donor in the medium; $E_0$ is the energy corresponding to the center of the exciton band; $\Delta E(k)$ is the energy of the $k$-th level in the band, measured from the center of the band; $\hat{H}_{d-c}$ and $\hat{H}_{a-c}$ are the Hamiltonians of the interaction with the medium molecules of the excited donor and acceptor molecules, respectively. For a concrete calculation let us consider a one-dimensional system, for example a polymer chain. In this case, with good accuracy one may assume that both the donor molecule and the acceptor molecule interact only with the nearest units of the polymer. Then $\psi_k$ is the wave function of a Frenkel exciton

$$\psi_k = \frac{1}{\sqrt{N}}\sum_j e^{ikR_j}\psi_{1j}, \tag{5}$$

where $N$ is the number of units in the polymer chain; $\psi_{1j}$ is the wave function of the excited state of the $j$-th unit. Taking into account the interaction only of neighboring molecule-units, for $\Delta E(k)$ we obtain (5)

$$\Delta E(k) = \Delta E_0 \cos kd. \tag{6}$$

Here $d$ is the period of the chain.

Substituting (5) and (6) into (4) and passing from summation to integration, we obtain:

$$W = \frac{2\pi}{\hbar} \left| \langle \psi_{a1}\psi_0 | \hat{H}_{a-c} | \psi_{1j}\psi_{a0} \rangle \right|^2 \times$$

$$\times \left| \langle \psi_{d1}\psi_0 | \hat{H}_{d-c} | \psi_{1i}\psi_{d0} \rangle \right|^2 \frac{e^{-\alpha l}}{(\Delta E)^2 - (\Delta E_0)^2} = A \frac{1}{(\Delta E)^2 - (\Delta E_0)^2} e^{-\alpha l}, \qquad (7)$$

where $\Delta E = |E - E_0|$, $l = (R_j - R_i)/d$ is the distance between donor and acceptor in chain periods;

$$\alpha = 2 \ln \left( \frac{1 - \sqrt{1 - (\Delta E_0/\Delta E)^2}}{\Delta E_0/\Delta E} \right).$$

The most interesting case is that in which $\Delta E_0/\Delta E$ is close to unity, i.e., when the level of the donor molecule is very close to the exciton band of the polymer. As is seen from (7), $W$ decreases very slowly with increasing $l$. Introducing

$$\delta = 1 - \Delta E_0/\Delta E \qquad (8)$$

and assuming $\delta \ll 1$, we obtain

$$W = A \frac{1}{2(\Delta E)^2 \delta} e^{-2\sqrt{2\delta}\, l}. \qquad (9)$$

For sufficiently small $\delta$, the probability of energy transfer according to (9) may turn out to be much greater than the probability $W_{d-d}$, calculated with allowance only for the direct dipole-dipole interaction. If the interaction between the impurity molecules and the polymer is of approximately the same order as the interaction between the polymer units, then for the ratio $W/W_{d-d}$ we obtain

$$\frac{W}{W_{d-d}} \simeq \frac{1}{\delta} l^6 e^{-2\sqrt{2\delta}\, l}. \qquad (10)$$

Let us note that the decisive factor determining the efficiency of such a mechanism of energy transfer is: 1) the closeness of the excitation energies of the impurity molecules and the medium; 2) strong interaction between the molecules of the medium. The structural ordering of the medium merely makes it possible to calculate $W$ exactly; however, the qualitative character of the dependence of

$W$ on distance and on the structure of the energy spectrum should remain the same as in the presence of long-range order.

In paper ($^6$) the question of energy transfer between impurity molecules in a polymer chain was considered for the case $\Delta E_0/\Delta E \ll 1$, and it was obtained that

$$W \sim 1/l^4,$$

which contradicts (7). The erroneousness of this result is connected with the fact that the structure of the exciton band near the band minimum is incorrectly extended to the entire band.

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*Note: Figure translations are in progress. See original paper for figures.*