Enhanced Excitation Transfer during Vibrational Relaxation after Pumping and Generalized Förster's Formula

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Electron or excitation transfer can be enhanced during vibrational relaxation after optical excitation of a donor. When it occurs after vibrational relaxation with a thermal activation energy E_A, enhanced transfer during vibrational relaxation is also governed by an activation energy E_H which, however, is smaller than E_A or even vanishes. The decrement $E_A - E_H$ depends on the total energy of vibrations triggered by optical excitation, and also on their average direction relative to that of the activation barrier for transfer in the phonon-coordinate space.

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Much interest has recently been aroused in the dynamic behavior of a localized electron-phonon system occurring during vibrational relaxation (VR) after a pulse excitation. To detect this optically, we observe the hot luminescence emitted during VR, which is different from the ordinary luminescence emitted after VR, that is, for thermal equilibrium of the excited electronic state.[1-3] For this purpose, however, it is necessary to use a pulse width Δt (and an observation interval) much smaller than the time τ_v for VR, which is usually of the order of 1 psec in solids and liquids. One would need femtosecond laser techniques now being developed[4] which might, however, be premature for such application. Under steady excitation the intensity ratio of hot luminescence to ordinary luminescence in the emission spectrum is very small, being of the order of τ_v/τ_0, where τ_0 is the radiative lifetime of the excited electronic state and is at least of the order of nanoseconds in usual cases. The main purpose of the present Letter is to point out that the photoinduced electron or excitation transfer process can be a sensitive probe of the dynamic behavior of the electron-phonon system, since its rate can be greatly enhanced only during VR after a pulse excitation. The yield of the enhanced transfer occurring during VR can be large enough to be detected also under the condition of $\Delta t \gg \tau_v$.

Excitation transfer occurring after VR is called ordinary transfer, and its rate is given by the well-known Förster formula[5] as

$$k_0 = (2\pi J^2/\hbar)\int dE'\, D(E')A(E'), \tag{1}$$

where J represents the transfer integral, $D(E')$ the (ordinary) luminescence spectrum of the (energy) donor, and $A(E')$ the absorption spectrum of the (energy) acceptor, with normalization $\int D(E)dE = \int A(E)dE = 1$. In the case of electron transfer, $D(E')$ represents the energy spectrum of the outer-sphere electron of the donor while $A(E')$ represents the energy spectrum of the unoccupied level of the acceptor to which the electron is to be transferred.[6] Equation (1) is based on the "golden rule," where $D(E')$ gives the density of initial states at energy E' weighted by the occupation probability while $A(E')$ gives the density of final states for transfer at the same energy. In the following we use terminology appropriate to excitation transfer for simplicity.

Now let us assume that the donor is excited by a photon with energy E at time zero. (In the case of electron transfer, E should be regarded as the initial energy of the outer-sphere electron given at the instant of photoexcitation of the donor.) The phonon system begins to relax, interacting with the excitation, and the energy of the excitation begins to change, interacting with phonons. The distribution function of this energy E' at time t (>0) is denoted by $D(E';t;E)$ with normalization $\int D(E';t;E)dE' = 1$. Then, using the "golden rule" we can get the transfer rate at time t by[7]

$$k(t;E) = (2\pi J^2/\hbar)\int dE'\, D(E';t;E)A(E'). \tag{2}$$

Equation (2) may be called the generalized Förster formula. In fact, when t is much larger than the VR time τ_v, (2) approaches (1) since $D(E';t;E)$ approaches $D(E')$. Therefore, with the excitation-transfer rate of (2) we can detect the time-resolved emission spectrum of the donor with a window of the absorption spectrum $A(E')$ of the acceptor. The resolution of time t is limited by the inverse of the width of $A(E')$. Therefore $A(E')$ must be sufficiently broad.

When $t \lesssim \tau_v$, where $D(E';t;E)$ represents the hot luminescence, $k(t;E)$ represents excitation transfer taking place during VR within the excited electronic state of the donor, which is called hot transfer. When $t \gg \tau_v$, where $D(E';t;E)$ represents the ordinary luminescence, $k(t;E)$ tends to the Förster ordinary-transfer rate. [When t is smaller than the phase correlation time ($\ll \tau_v$) of the localized excitation, the Rayleigh and Raman scattering are emitted.[1-3] When $D(E';t;E)$ in (2) is replaced for this case, however, (2) represents the direct excitation of the acceptor (or the direct charge-transfer excitation in the case of electron transfer) mediated by a virtual excitation of the donor, and so it cannot be regarded as excitation transfer. Moreover it can be neglected, when the exciting-photon energy is in the region of the absorption band of the donor.]

The hot-luminescence spectrum changes with time t. Therefore, if it overlaps with the absorption spectrum $A(E')$ of the acceptor to a greater extent at some t's for $t \lesssim \tau_v$ than the ordinary-luminescence spectrum does, then the rate of hot transfer becomes much larger than that of ordinary transfer. When the pulse width Δt of the exciting photon is much larger than τ_v, however, hot transfer has already terminated when observation starts. Then, the rate that we can observe is only the rate k_0 of ordinary transfer or the decay time τ_F $\{=\tau_0/[1+(k_0+k')\tau_0]\}$ of luminescence from the excited donor, where τ_0 and k' represent respectively the radiative lifetime and the nonradiative decay rate other than the k_0 under consideration. The presence of hot transfer, however, reduces the quantum yield η_F of luminescence from the value $[1+(k_0+k')\tau_0]^{-1}$ $(=\tau_F/\tau_0)$ obtained without consideration of hot transfer, and increases the yield η_R of excitation transfer from the value $k_0\tau_0/[1+(k_0+k')\tau_0]$ $(=k_0\tau_F)$, as

$$\eta_F = (1-\eta_H)\tau_F/\tau_0, \tag{3}$$

$$\eta_R = k_0\tau_F + \eta_H(1-k_0\tau_F), \tag{4}$$

where η_H represents the quantum yield of hot transfer given by

$$\eta_H = 1-\exp\left[-\int_0^{\tau_v} k(t;E)dt\right], \tag{5}$$

when $\tau_v \ll \tau_F$. In some cases η_H can even be larger than $k_0\tau_F$ in (4). When we measure either (τ_0,τ_F,η_F) or (τ_F,k_0,η_R), we can get η_H from (3) or (4). In the usual analysis, however, one considers that from measurement of only two of these three quantities we can obtain the remaining one by using the assumed relations $\eta_F=\tau_F/\tau_0$ or $\eta_R=k_0\tau_F$.

In the following we investigate in some detail a case where k_0 has a thermally activated temperature dependence with an activation energy E_A much larger than the average phonon energy $\hbar\bar{\omega}$. Such a case has often been found in solid-state physics, chemistry, and biophysics.[8] We will show in this case that overlap between $D(E';t;E)$ and $A(E')$ is surely enhanced at some t's smaller than τ_v, and moreover that the enhanced transfer can be described by η_H [or, more precisely, $\ln(1-\eta_H)$] with activation energy E_H smaller than E_A or even vanishing. When $E_A - E_H$ is large enough, η_H can be larger than $k_0\tau_F$ in (4).

The thermally activated temperature dependence of k_0 is obtained when both $D(E')$ and $A(E')$ in (1) have a Gaussian shape (around energies E_d and E_a, respectively),[6]

$$A(E') = [(2\pi)^{1/2}\Delta_a]^{-1}\exp[-\tfrac{1}{2}(E'-E_a)^2/\Delta_a^{\,2}],$$

where $D(E')$ is obtained by replacing E_a and Δ_a with E_d and Δ_d, respectively, and their widths Δ_i for $i=a$ and d are determined by

$$\Delta_i^{\,2} = \textstyle\sum_j V_{ij}^{\,2}\coth(\tfrac{1}{2}\hbar\omega_j/k_BT),$$

where V_{ij} represents the interaction with the jth phonon with energy $\hbar\omega_j$. At high temperatures of $k_BT \gg \frac{1}{2}\hbar\bar{\omega}$, we get for $i=a$ and d

$$\Delta_i^{\,2} \simeq 2S_ik_BT,$$

with $S_i = \sum_j V_{ij}^{\,2}/\hbar\omega_j$. These equations are justified when $S_i \gg \hbar\bar{\omega}$. We get from (1)

$$k_0 = \frac{J^2}{\hbar}\left[\frac{\pi}{(S_d+S_a)k_BT'}\right]^{1/2}\exp\left(-\frac{E_A}{k_BT'}\right),$$

with

$$k_BT' = \frac{1}{2}\sum_j \frac{V_{dj}^{\,2}+V_{aj}^{\,2}}{S_d+S_a}\coth\left(\frac{\hbar\omega_j}{2k_BT}\right),$$

where T' represents the effective temperature which approaches T at high temperatures. The activation energy E_A of k_0 is given by

$$E_A = \tfrac{1}{4}(E_d-E_a)^2/(S_d+S_a). \tag{6}$$

$D(E')$ obtained above is realized when the excitation of the donor has an interaction with phonons linear in their coordinates, with a coupling constant proportional to V_{dj} for the jth phonon.[1,2,7] In this case $D(E';t;E)$ also has a Gaussian shape, given by[2,7]

$$D(E';t;E) = \frac{1}{(2\pi)^{1/2}\Delta_d(t)}\exp\left(\frac{[E'-E_d(t;E)]^2}{2\Delta_d(t)^2}\right),$$

where $E_d(t;E)$ and $\Delta_d(t)$ represent respectively the time-dependent peak energy and width of the hot luminescence, given by

$$E_d(t;E)=[1-r(t)]E_d+r(t)E,$$

$$\Delta_d(t)^2=[1-r(t)^2]\Delta_d{}^2,$$

with

$$r(t)=\frac{\sum_j(V_{dj}{}^2/\omega_j)\cos(\omega_j t)}{\sum_j V_{dj}{}^2/\omega_j}.$$

Now $r(t)$, starting from $r(0)=1$, shows a damped oscillation because of the dispersion of the ω_j's. When the width of the dispersion around $\bar{\omega}$ is denoted by $2\omega_B$, the amplitude of the damped oscillation decays with a rate of about π/ω_B, which gives the VR time τ_v of the donor. Therefore, $E_d(t;E)$, starting from $E_d(0;E)=E$, also shows a damped oscillation around E_d, while $\Delta_d(t)$, starting from $\Delta_d(0)=0$ and tending to Δ_d for $t\gg\tau_v$, becomes minimum each time $|E_d(t;E)-E_d|$ becomes maximum. The average period of these oscillations is $2\pi/\bar{\omega}$, which is of the order of 0.1 psec. Time t in these equations is determined with an uncertainty much smaller than $2\pi/\bar{\omega}$ but much larger than $2\pi\hbar/\Delta_a$.

$E_d(t;E)$ sweeps in time t approximately the energy region from E_d-E to E_d+E. Then, if the peak energy E_a of $A(E')$ is located inside this energy region, $E_d(t;E)$ crosses E_a at some t's. Even if E_a is located outside, overlap between $D(E';t;E)$ and $A(E')$ is still enhanced since $E_d(t;E)$ approaches E_a at some t's. The activation energy E_H of η_H vanishes in the former case while in the latter case it is smaller than the E_a of k_0 determined by overlap between $D(E')$ and $A(E')$. In order to obtain E_H, it is convenient to introduce

$$E_P=\tfrac{1}{4}(E-E_d)^2/S_d\,, \tag{7}$$

$$g=\left(\frac{\Delta_d{}^2}{\Delta_d{}^2+\Delta_a{}^2}\right)^{1/2}s\simeq\left(\frac{S_d}{S_d+S_a}\right)^{1/2}s, \tag{8}$$

where s is the sign of $(E_d-E_a)/(E-E_d)$ and $|g|<1$. Then we get from (2)

$$k(t;E)=(J^2/\hbar)\{(S_d+S_a)k_BT'[1-g^2r(t)^2]/\pi\}^{-1/2}\exp[-E_A(t;E)/k_BT'], \tag{9}$$

with

$$E_A(t;E)=[(E_A)^{1/2}+gr(t)(E_P)^{1/2}]^2/[1-g^2r(t)^2].$$

We define E_H by $\ln(1-\eta_H)\propto\exp(-E_H/k_BT')$. Then, from (5), E_H is given by the minimum value of $E_A(t;E)$ obtained under $|r(t)|\leqslant 1$. Thus we get

$$E_H=\begin{cases}E_A-E_P, & \text{for } E_P<g^2E_A,\\ [(E_A)^{1/2}-|g|(E_P)^{1/2}]^2/(1-g^2), & \text{for } g^2E_A<E_P<E_A/g^2,\\ 0, & \text{for } E_P>E_A/g^2.\end{cases} \tag{10}$$

E_H decreases continuously, starting from E_A, with increasing E_P.

It is possible to reinterpret the results obtained above in terms of the configuration coordinates Q_d and Q_a of phonons which describe respectively the optical properties of the donor and the acceptor. The adiabatic potentials associated with the ground and the excited states are respectively written as $W_{ig}=Q_i{}^2/4S_i$ and $W_{ie}=(Q_i-2S_i)^2/4S_i+E_i\pm S_i$ with $i=d$ and the plus sign in $\pm S_i$ for the donor and with $i=a$ and the minus sign for the acceptor, where Q_i was chosen to have a dimension of energy for convenience.[7] We introduce new coordinates by $Q\equiv Q_d-Q_a-2S_d$ and

$$Q'\equiv(S_a/S_d)^{1/2}(Q_d-2S_d)+(S_d/S_a)^{1/2}Q_a.$$

The optical excitation of the donor occurs at $\{Q_d=E_d+2S_d-E,\ Q_a=0\}$, where $W_{de}-W_{dg}=E$, that is, at the point P, $\{Q=-(E-E_d),\ Q'=-(S_a/S_d)^{1/2}(E-E_d)\}$. After the excitation, we get the adiabatic potential $W_{de}+W_{ag}$, which is rewritten as

$$W(Q,Q')=\tfrac{1}{4}(Q^2+Q'^2)/(S_d+S_a)+E_d+S_d,$$

and the phonon system relaxes into $\{Q=0,\ Q'=0\}$ which is called point O. The excitation transfer occurs at $\{Q=E_d-E_a,\ Q'=0\}$ for $W_{de}+W_{ag}=W_{dg}+W_{ae}$, which is called point R. The energy difference of $W(Q,Q')$ between points R and O gives E_A of (6), while that between P and O gives E_P of (7). The direction cosine between vectors PO and OR gives g of (8). Thus E_P represents the energy dissipated by VR of the donor from P to O, during which excitation transfer is greatly enhanced. Therefore E_P can be called the phonon-kick energy, while g describes the direction PO of the phonon kick. Moreover $1-|g|$ describes a misfit between PO and OR in which direction excitation transfer occurs. As will be shown elsewhere, $E_P + E_A(t;E)$ equals the minimum value E_m of the total energy of the phonon system measured from the relaxed point O obtained under the condition that the value of the reaction coordinate Q reaches $E_d - E_a$ at time t when that of the energy-accepting coordinate Q_d was $E_d + 2S_d - E$ at time zero. (Here, the minimum energy on the start line $Q_d = E_d + 2S_d - E$ is obtained at point P with energy E_P, while that on the goal line $Q = E_d - E_a$ is obtained at point R with energy E_A.) It is essential in this statement that even if we fix coordinates Q and/or Q_d the phonon system has many degrees of freedom other than Q and Q_d since Q and Q_d are a linear combination of many normal-mode coordinates. Energy E_P is supplied by the optical excitation of the donor, while $E_A(t;E)$ must be supplied by thermal fluctuations of the phonon system itself occurring within the ground electronic state at a temperature T. This is the origin of the exponential factor appearing in (9). Since E_m must satisfy $E_m \geq E_A$, the minimum value E_H of $E_A(t;E)$ should satisfy $E_H \geq E_A - E_P$, as in (10).

No intentional determination of η_H from experiments has been done yet. But the presence of η_H can be inferred from observations[9] that the excitation (or electron) transfer rate depends on the exciting-photon energy. In fact, in (4) only η_H depends on it through E_P given by (7). Moreover, when the thermal-equilibrium rate k_0 has an activation energy E_A, the present work shows that η_H rises steeply as the activation energy E_H of η_H decreases with the increase of E_P as in (10), although η_H becomes saturated after E_H vanishes when E_P exceeds a certain critical value given by E_A/g^2. Since $E_A(t;E)$, whose minimum value is E_H, is determined by dynamic trajectories of the phonon system from points P to R during VR after optical excitation, an experimental determination of E_H, if performed, will shed light on the dynamic behavior and fluctuations of a nonthermal-equilibrium phonon system. As a theory of chemical reactions in such a system, we have the Rice-Ramsberger-Kassel-Marcus theory,[10] which regards reactions as occurring after complete randomization of the excess vibrational energy E_P among various modes of a small molecule. This statistical theory gives an E_P dependence of E_H different from that given by the present dynamical theory, since E_H of (10) depends explicitly on the direction of the phonon kick. This fact has also been pointed out in connection with recombination-enhanced defect reactions,[11] where electron-hole nonradiative recombination at deep-level defects in semiconductors greatly enhances various reactions such as production and movement of defects.

The generalized Förster formula based on the "golden rule" is justified only in the nonadiabatic limit where because of small J transitions are rare even at an instant when the phonon system passes through point R.[7] Reinterpretation of the activation energy E_H of (10), given in the paragraph below (10), from the standpoint of energy minimization, however, does not depend on whether a transition at point R is rare or not. Therefore, applicability of (10) is not limited only to the nonadiabatic limit. (Remember that differences between this limit and the opposite adiabatic one manifest themselves essentially only in the preexponential factor of a rate, not in its activation energy.[7])

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[1] V. Hizhnyakov and I. Tehver, Phys. Status Solidi 21, 755 (1967).

[2] Y. Toyozawa, J. Phys. Soc. Jpn. 41, 400 (1976); Y. Toyozawa, A. Kotani, and A. Sumi, J. Phys. Soc. Jpn. 42, 1495 (1977).

[3] T. Takagahara, E. Hanamura, and R. Kubo, J. Phys. Soc. Jpn. 44, 728, 742 (1978).

[4] *Picosecond Phenomena III*, edited by K. B. Eisenthal *et al.* (Springer, Berlin, 1982).

[5] Th. Förster, Ann. Phys. (Leipzig) 2, 55 (1948).

[6] J. J. Hopfield, Proc. Natl. Acad. Sci. U.S.A. 71, 3640 (1974).

[7] H. Sumi, J. Phys. Soc. Jpn. 49, 1701 (1980), and 51, 1745 (1982).

[8] *Tunneling in Biological Systems*, edited by B. Chance *et al.* (Academic, New York, 1979).

[9] A. H. Zewail, in Ref. 4, p. 184.

[10] See, for example, P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley, London, 1972).

[11] H. Sumi, Physica (Utrecht) 117&118B, 197 (1983).