Hopping Mechanism of Energy Transfer

A. I. Burshteĭn
Institute of Chemical Kinetics and Combustion, Siberian Division, USSR Academy of Sciences
Submitted September 28, 1971
Zh. Eksp. Teor. Fiz. 62, 1695–1701 (May, 1972)

An investigation is carried out on excitation decay whose probability changes suddenly and in a noncorrelated manner as a result of migration over randomly distributed centers that interact with each other more strongly than they do with the energy acceptors. It is shown that hopping migration, just as diffusion, renders the decay exponential and increases its rate, but leads to a different dependence on donor concentration and interaction parameters. The existence of an upper limit for the deactivation rate during concentration quenching is established.

THE deactivation of an excited donor impurity by energy transfer to acceptors that are stochastically distributed around it is usually effected through a direct multipole interaction between them. The kinetics of this process have been thoroughly investigated in the statistical limit, i.e., assuming that the excitation does not leave the impurity center at which it arose. It has been established, in particular, that owing to the difference between the acceptor surrounding of the different donors there is a sufficiently wide probability distribution $\varphi(w)dw$ of their deactivation. This results in a non-exponential decay of the entire aggregate of donors, which takes the following form in the case of weak dipole-dipole interaction[1]:

$$N_0 = \int_0^\infty e^{-wt}\varphi(w)dw = e^{-(\Delta t)^{1/2}}, \qquad (1)$$

where

$$\varphi(w) = \left(\frac{\Delta}{4\pi w^3}\right)^{1/2} \exp\left(-\frac{\Delta}{4w}\right), \quad \Delta = \frac{16\pi^3}{9}ac^2. \qquad (1a)$$

Here a is the interaction constant and determines the rate of deactivation by one acceptor, namely a/R^6 (R is the distance from the acceptor to the donor), and c is the density of the acceptors in the sample. Allowance for the real dimensions of the particles[2] or for the possibility of a strong interaction between them[3] makes the decay process more complicated, in that a short exponential section appears in its earlier stage. This effect, however, becomes appreciable only at very high acceptor concentrations, when the fraction of the donor-acceptor pairs that are in direct or strong contact with one another is appreciable.

The changes due to the increase of the donor concentration are much more significant. The interaction between them leads to a resonant migration of the excitation, causing the acceptor ambient of the latter to change several times during the decay process. The motion of the excitation over the system of donors places in an equal position those donors at which the deactivation is quite slow, leading in turn to exponentialization of the decay process during its final stage. The parameter of this exponential, which determines the actual rate of luminescence quenching in concentrated solid solutions, depends not only on c and a, but also on the migration rate d/r^6 of the energy over the donors (r is the distance between the donors), i.e., in final analysis on their concentration n and on the interaction force d.

A very closely related problem is encountered when spin-lattice relaxation of nuclei is accelerated by a paramagnetic impurity. This problem was investigated under the assumption that the migration of the spin excitation over the crystal can be regarded as a real diffusion, with a coefficient specified by the scale of the dipole-dipole interaction of the nuclei in terms of the period of the lattice[4,5]. The same model was calculated as applied to exciton quenching by impurities in molecular crystals[6]. Mathematically, the problem turned out to be far from simple, and a rigorous solution was obtained only for models with limited interaction[7,8]. In the case of real dipole-dipole interaction, it is possible to consider only the asymptotic form of the decay process under rather significant assumptions[9,10].

On the other hand, if the donor molecules do not form a real lattice but are stochastically distributed, then the very introduction of a diffusion coefficient (in coordinate space) becomes problematic. Such a problem is more conveniently considered from a different point of view, assuming that the excitation migration leads to random walks of w(t). This is particularly important if $a \ll d$, when the migrating donor comes close to the acceptor in a single step and abruptly rather than gradually and in many steps, and in this sense it is more similar to individual particle collisions in the gas phase than to diffusion[11]. Such a situation is impossible in nuclear resonance, since the interaction between the nuclei is certainly weaker than the interaction with the electron, but is perfectly realistic in the case of molecular and atomic excitations, in view of the resonant character of the donor-donor energy transfer.

DECAY KINETICS

There is, however, also an appreciable difference from the gas variant of the theory. In free translational motion of the particles, the interaction between them is turned on only during the collision time, since the hopping of the excitation from donor to donor nowhere interrupts the process, and only modulates its velocity. Therefore in the most general definition of the decay law

$$N(t) = \left\langle \exp\left[-\int_0^t w(t)\,dt\right]\right\rangle, \qquad (2)$$

w(t) is a random function of the time and varies

steadily, in jumps, but remains constant between the jumps, while the averaging (denoted by the angle brackets) extends over all the realizations of this random process.

Problems of this type are encountered in the theory of the broadening of spectral lines[12]. Our problem also reduces formally to them if the factor −1 in (2) is replaced by i. From the stochastic point of view, the closest to our problem is that of the Doppler broadening of a spectrum, in which the line shift is a Markov random variable similar to w(t). The analogy becomes complete if it is recognized that the actual modulation of the decay process is effected only by hops with the same, most probable, migration rate, since smaller rates are immaterial, and larger ones do not lead to noticeable spatial displacements, and consequently do not change the acceptor ambient around the donor.

The most probable migration rate, as seen from (1a), is

$$1/\tau_0 = \Delta/6 = (2\pi/3)^3 dn^2, \tag{3}$$

if the interaction between the donors is of the dipole-dipole type. Hops with such a rate occur over a distance

$$r_0 = (d\tau_0)^{1/6} > (a\tau_0)^{1/6} = R_w, \tag{4}$$

where R_W is the radius of the spherical region around the acceptor which is the zone of the strong interaction, within which the particles are as a rule deactivated before they leave (Fig. 1). The inequality (4) is a reformulation of the assumption concerning the relative strength of the interaction of the excited molecules with the acceptor and the donor, namely $d \gg a$. Its sign indicates that under these assumptions the excitation can jumpwise leave the zone of the strong interaction or, to the contrary, fall into it from the periphery[1)]. In other words, each jump can change the strong interaction into a weak one and vice-versa. It is therefore natural to expect no connection whatever between the successively realized values of w (a Markov process without correlation). In this case it follows directly from the general theory of sudden modulation[12,13] that

$$N(\tau) = N_0(\tau)e^{-\tau/\tau_0} + \frac{1}{\tau_0}\int_0^\tau N_0(\tau - t)e^{-(\tau-t)/\tau_0}N(t)\,dt. \tag{5}$$

The kernel of this equation is the static-decay characteristic defined in (1), in which one can introduce if necessary all the aforementioned corrections. Its solution includes the quasistatic limit as a particular case and, in addition, contains the information of interest to us concerning the decay under conditions of strong excitation migration.

Substituting (1) in (5) and changing over to the dimensionless time $t = \tau/\tau_0$, we obtain

$$N(t) = \exp\{-q\sqrt{t} - t\} + \int_0^t \exp\{-q\sqrt{(t-t')} - (t-t')\}N(t')\,dt', \tag{6}$$

from which we see immediately that the boundary between the quasistatic and semi-exponential decays is the parameter value $q = \sqrt{\Delta\tau_0}$, although at both $q \gg 1$ and $q \ll 1$ there exist both exponential and non-exponential sections separated by a time boundary $t = t_b$. To verify this, let us consider the two limiting cases separately.

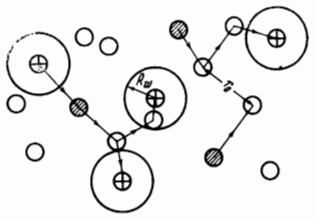

FIG. 1. Transfer via migration from excited donors (●) through unexcited ones (○) to acceptors (⊕).

LIMITING SITUATIONS

In the quasistatic limit ($q \gg 1$), the solution can be obtained by successive approximations if the free term of (6) is regarded as the zeroth approximation. In the first approximation we obtain

$$N(t) = e^{-t}[e^{-q\sqrt{t}} + I(t)], \tag{7}$$

where

$$I(t) = \frac{t}{2T}\int_{-T}^{+T} \exp[-\sqrt{T+t'} - \sqrt{T-t'}]\,dt', \quad T = \frac{q^2 t}{2}; \tag{7a}$$

I(t) first increases linearly with time, but it reaches the asymptotic limit already at $T \gg 1$, and then

$$N = \exp[-q\sqrt{t} - t](1 + 4q^{-2} + \ldots), \; t > 2/q^2. \tag{8}$$

The time boundary between the purely statistical decay (1) and the exponential asymptotic behavior observed in (8) is given by the formula $t_b = q^2$, i.e.,

$$\tau_b = 16\pi^3 ac^2\tau_0^2/9. \tag{9}$$

When $\tau > \tau_b$, the decay proceeds at an excitation migration rate $1/\tau_0$.

To obtain an idea of the opposite situation ($q \ll 1$), it is simplest to use the standard method of solving Volterra equations with difference kernels. This enables us to obtain a general solution (see (6)) in the form of an inverse Laplace transform

$$N = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{L(p)\exp(pt)}{1 - L(p)}\,dp, \tag{10}$$

in which L(p) is the Laplace transform of the kernel of the equation and is equal to

$$L(p) = \int_0^\infty N_0(t)e^{-(1+p)t}\,dt = \frac{1}{1+p}\left\{1 - \frac{1}{2}\sqrt{\frac{\pi q^2}{1+p}}\,e^{q^2/4(1+p)} \times\left[1 - \Phi\left(\frac{q}{2\sqrt{1+p}}\right)\right]\right\}$$

for $N_0(t)$ as defined in (1). When $q \ll 1$ this expression becomes much simpler and enables us to separate from (10) the exponential asymptotic form

$$N(\tau) = e^{-k\tau} \tag{11}$$

with the parameter

$$k = \frac{q\sqrt{\pi}}{2\tau_0}\left[1 - \frac{q}{2}\left(\frac{2}{\sqrt{\pi}} - \frac{\sqrt{\pi}}{2}\right) + \frac{q^2}{8}\left(\frac{5\pi}{4} - 1\right) - \ldots\right]. \tag{11a}$$

The principal term in k can be represented in the form

[1)] When $d \ll a$ the inequality (4) is reversed and the excitation overcomes the zone of strong interaction, executing many small steps. This causes a strong correlation between the successive values of w and physically brings the hopping model closer to the diffusion model, the only difference being, incidentally, that the diffusion goes over the impurity band (over randomly scattered donors).

$$k=\sqrt{\frac{\pi\Delta}{4\tau_0}}=\frac{2\pi^2}{3}\sqrt{\frac{a}{\tau_0}}c=\frac{\pi}{2}\frac{cv_w}{\tau_0},\quad v_w=\frac{4}{3}\pi R_w^3 \qquad (12)$$

and has a simple physical meaning: it is equal to the number of acceptors that fall into the strong-interaction zone around the migrating donor per unit time, i.e., after $1/\tau_0$ jumps. Apart from a numerical factor, it coincides with the estimate given in[11] for this quantity. The remaining terms in k are corrections that are nonlinear in the concentration.

From the formal point of view, it is very interesting to compare the exponential-decay parameters obtained for different kernels of (5). It turns out that in the first approximation

$$k=\frac{1}{\tau_0^2}\int_0^\infty Q(t)e^{-t/\tau_0}dt=\begin{cases}\Delta^2\tau_0 & (13a)\\ \Delta & (13b)\\ \sqrt{\pi\Delta/4\tau_0} & (13c)\end{cases}\quad\text{for } N_0(t)=e^{-Q(t)}=\begin{cases}e^{-\Delta^2\tau^2/2} & (13a)\\ e^{-\Delta\tau} & (13b)\\ e^{-\sqrt{\Delta\tau}} & (13c)\end{cases}$$

when the condition $\Delta\tau_0 \ll 1$, which is common to all cases, is satisfied. If we resort to the already mentioned analogy with the theory of spectral line shapes, then $N(\tau)$ take on the meaning of correlation functions of $\exp[i\int_0^\tau \Delta\omega dt]$, and their Fourier expansions give the shapes of the observed spectra. In the static case, this shape is given by the spectrum $N_0(\tau)$, but in the limit under consideration ($\Delta\tau_0 \ll 1$) we are dealing with a rapid frequency exchange, which transforms the static contour into a Lorentz contour of width k. The case (13a) corresponds to a Gaussian shape of the static spectrum, (13b) to a Lorentz shape, and (13c) is even sharper than the Lorentz shape and is typical of static spectra of gases[12]. This difference between the shapes explains also the different response to frequency exchange. The Gaussian spectrum becomes narrower by the motion, the Lorentz shape does not become deformed at all, and in the third case a broadening of the center takes place, perfectly similar to impact broadening of gas lines.

The emphasized difference is important also for the understanding of the physical nature of the mechanisms of self-quenching of luminescence. It is easy to see that the square-root dependence of $N_0(\tau)$ has a time derivative that diverges at zero, thereby distinguishing it radically from all other kernels considered in (13). This singularity corresponds to the fact that in a sample with diverging interaction, of the type a/R^n, there are always donors in which the excitation vanishes at an arbitrarily fast rate. The migration of the excitation over the sample accelerates its decay only because it provides access to these donors (energy sinks). The higher the migration frequency, the faster is the excitation transferred to the place where it is destroyed, and the more effective the self-quenching. It is not at all obligatory that the quenching at the sinks be caused by the acceptor impurity. The decay probability and its dispersion can have an arbitrary origin. All that matters is that the difference between the lifetime of the various donors be appreciable and that the static decay be less steep than the exponential one.

A specific feature of the hopping mechanism is the difference between the decay rates on its exponential section in the limiting situations under consideration. Both in the diffusion and in the impact variant of the theory, the structure of the exponential parameter does not change with changing q, and only the boundary between the static and exponential sections shifts. This uncovers a possibility of a clear-cut identification of the mechanism by direct comparison of the asymptotic form of the decay at small and large donor concentrations. In the former case, the rate of quenching should be quadratic in n, as follows from (3), whereas in the latter, according to (3) and (12), this dependence becomes linear:

$$k=\pi(2\pi/3)^{3/2}cn\sqrt{ad}. \qquad (14)$$

The aggregate of the results (1), (3), and (14) leaves also a possibility for self-control. A study of the quasistatic decay as a function of the donor and acceptor concentrations make it possible in principle to determine both parameters of the theory, a and d, after which no leeway remains in formula (14) not only with respect to the concentration dependence, but also with respect to the absolute magnitude. Valuable additional information is contained also in the temperature dependences of Δ, $1/\tau_0$, and k, which can appear in this parameters only via a(T) and d(T). A comparison of the temperature dependences may contribute not only to identification of the mechanism[11], but also to a clarification of the nature of the elementary transport act.

ULTRAFAST MIGRATION

Caution must be exercised, however, when the concentration of the donors is increased, since the anomalies of $N_0(\tau)$, which occur at the very start of the decay, becomes significant at a very high migration rate. These deviations from (1), as already noted, are due to strong or limited interaction between the donor and the acceptor. The existence of an upper limit for the transition probability eliminates the divergence of $dN_0/d\tau$ as $\tau = 0$, and by the same token limits the growth of the quenching rate with increasing $1/\tau_0$. This follows formally from the fact that the non-exponential kinetics of the type (1) gives way to the exponential law[3], namely, at times $\tau < w_S(R_0)^{-1}$ we have

$$N_0(\tau)=\exp(-k_m\tau), \qquad (15)$$

with[14]

$$k_m=4\pi c\int_{R_0}^\infty w_s(R)R^2dR,\quad w_s=w_m\frac{R_m^6}{R_m^6+R^6},\ w_mR_m^6=a. \qquad (15a)$$

Therefore, when $\tau_0 \ll w_S(R_0)^{-1}$, i.e., when

$$n\gg\left(\frac{3}{2\pi}\right)^{3/2}\left(\frac{w_s(R_0)}{d}\right)^{1/2}, \qquad (16)$$

it is precisely (15) that should be retained in (5) as the kernel. The equation then reduces to a differential one and has a rigorous solution that coincides exactly with (15). Thus, the parameter (15a) is indeed the maximum possible quenching rate under the conditions of the fastest migration

$$k_m=\frac{\pi}{2}cw_mv_m\left[1-\frac{2}{\pi}\operatorname{arctg}\frac{v_0}{v_m}\right];$$

$$v_0=\frac{4}{3}\pi R_0^3,\ v_m=\frac{4}{3}\pi R_m^3=\frac{4}{3}\pi\sqrt{\frac{a}{w_m}}.$$

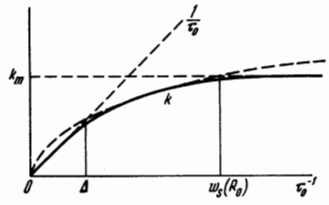

FIG. 2. Asymptotic exponential decay parameters vs. hopping frequency.

Decay of the entire aggregate of donors at such a rate is possible in the static case only at exceedingly high acceptor concentrations: $c \sim v_m^{-1}$ or $c \sim v_0^{-1}$, which ensure the presence of at least one acceptor near each donor. On the other hand, if migration does take place, then such a decay can be realized at any acceptor concentration, via rapid energy transfer to the optimal sink, i.e., at an increase corresponding to (16) in the sample donor density.

Thus, the existence of extremely large decay probabilities leads to saturation of the rate constant with acceleration of the migration (Fig. 2). This phenomenon was noted also within the framework of the diffusion model of migration[15]. It is explained physically by the fact that the limiting stage of the process in the case of very fast motion of the excitation is the leakage of energy into the lattice. It is the rate of this process which governs the limiting values:

$$k_m = \begin{cases} {}^2/_3\pi^2 c\sqrt{a w_m} & \text{for } w_m < a/R_0^6 \\ {}^2/_3\pi^2 ca/R_0^3 & \text{for } w_m > a/R_0^6 \end{cases}$$

Naturally, they do not depend on d or n, but differ in the degree to which the donor-acceptor interaction constant a(T) is raised in these expressions.

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Translated by J. G. Adashko
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