Concentration quenching of noncoherent excitation in solutions

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Delocalization of excitation in a system of disordered but uniformly distributed centers, its quenching by alien admixtures, and self-quenching by cross relaxation by pairs of identical particles are considered. It is shown that the direct transfer of excitation from an initial center to its neighbors becomes sequential and transforms into diffusion. However, quenching is seldom diffusive. As a rule, it follows a singly-acting hopping mechanism. Different theories of this mechanism are discussed and compared. The transformation from the diffusive to the hopping mechanism is described, and criteria for both are examined. Theoretical considerations are illustrated by applications to the kinetics and rates of concentration quenching of electronic, vibrational, and spin excitations in solid and liquid solutions. This is based on data on the selective and nonselective luminescence of rare-earth ions, picosecond absorption by dye molecules, and the decay of the electron spin echo signal due to hydrogen atoms in irradiated hosts.

CONTENTS

INTRODUCTION

Concentration quenching is encountered in connection with different systems such as crystals and glasses activated by luminescing impurity ions, liquid solutions of dyes, and paramagnetic solid solutions. The problem may be formulated in a very general manner in terms of the dissipation of excitation energy in the course of its migration over a system of impurity centers that exhibit resonance interaction. The transfer of excitation between identical impurity centers that are randomly but uniformly distributed in a solid or liquid medium facilitates its delivery to energy acceptors in the form of alien impurities that are effective quenchers. As the concentration of donor centers increases, the separation between them is reduced, and the interaction responsible for resonance energy transfer is enhanced. This accelerates the migration of excitation and reduces the time required to reach an acceptor to which the energy is transferred irreversibly. The net result of all this is that the excitation lifetime decreases monotonically with increasing concentration of centers that are being excited.

Electronic excitation of atoms and ions, singlet and triplet states of excited molecules, their vibrational excitations, and spin excitations in dilute solutions of paramagnet-

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ic particles all exhibit concentration quenching. Depending on the nature of the excitations, their transfer is accomplished either by long-range (multipole) or short-range (exchange) interaction between centers. As a rule, the interaction is weak enough to ensure that energy transfer between two centers may be regarded as noncoherent, i.e., as occurring with constant probability that is quadratic in the interaction. If the interaction is a given function of separation, and is different for donor-donor and donor-acceptor transfers, we have to answer two questions, namely, what is the rate at which the excitation migrates and how is quenching forced by this migration?

To answer the first question, we must consider the delocalization of excitation in a system of randomly disposed identical centers. For a long time, there was a dispute as to whether this process was equivalent to diffusion and, if this were so, what was the corresponding diffusion coefficient. It is only relatively recently that an affirmative answer has been obtained to this question, and the concentration dependence of the diffusion coefficient was determined for both multipole and exchange interactions.

However, the possibility of diffusion of excitation to large distances does not mean at all that its quenching is necessarily diffusive. The quenching zone around an acceptor may be so narrow that the excitation can enter and leave it again in a single displacement rather than in a sequence of small steps that is equivalent to continuous diffusion. It is well-known that, in this situation, the quenching of coherent excitons occurs within the limits of one free path and is characterized by the scattering cross section of the acceptor.[1] On the other hand, when one is concerned with noncoherent excitons, that undergo hopping transport over the donor system, single-step quenching is referred to as hopping quenching. Like diffusion quenching, it is characterized by an effective radius of the quenching sphere, but both the radius and the rate constant are defined in a different way. As a result, the rates of diffusive and hopping quenching have different dependence on donor concentration or, at least, a different dependence on the microparameters of excitation transfer to donors and acceptors, and this enables us to discriminate between these mechanisms.

In the ensuing review, we shall examine in detail both theoretical and experimental evidence for the hopping mechanism of quenching, which is probably the dominant effect in dilute solutions. Experimental data derive from kinetic studies of the concentration quenching of electronic, vibrational, and spin excitation in solid and liquid solutions. Such studies have become possible because of the advent of microsecond, nanosecond, and picosecond techniques.

1. PHENOMENOLOGY

The deactivation of excited states produced under the influence of radiation can be examined by either stationary or nonstationary methods. The most common among the latter are studies of decay after δ-pulse excitation. Having investigated the kinetics of excitation decay in pulse-type experiments, one can predict the nature of the decay when a continuous pump is turned off, and then calculate any sta-

tionary parameter of the process, e.g., the yield or duration of luminescence.[1-4] We shall therefore consider the problem in the following formulation: a particle D to which we shall refer as the energy donor suddenly takes up an excited state D^* at $t = 0$, and thereafter the probability $\mathcal{P}(t)$ that it will remain in that state decreases with time from 1 to 0. This process may be due to the natural decay of excitation in the interior of the center in a time τ_D, which occurs by direct radiation or by radiationless internal conversion of energy. As a rule, however, it occurs much more rapidly because of impurity quenching in which the excitation is irreversibly transferred from the donor to an acceptor A in which it is dissipated into heat or light quanta. With rare exceptions,[5] decay in the interior of the center may be regarded as exponential: $\exp(-t/\tau_D)$. On the contrary, impurity quenching is a complicated multistep process $N(t)$, the rate of which is determined by the migration of excitation over donors. In other words,

$$\mathcal{P} = \exp\left(-\frac{t}{\tau_D}\right) N(t), \qquad (1.1)$$

where $N(t)$ contains the acceptor and donor concentrations $C = [A]$ and $\rho = [D]$ as parameters.

When the donor concentration is vanishingly small, excitations vanish within the centers in which they arise. This is called static quenching. Static impurity quenching develops nonexponentially because the decay probability W depends on the proximity of acceptors, and nearest-neighbor donors decay first, whereas those that are in random isolation decay last. For moderate acceptor concentrations, the kinetics of static quenching is described by an exponential function[3,4,6,7] of c:

$$N_0(t) = \exp[-c\, Q(t)], \qquad (1.2)$$

where $Q(t)$ is a monotonically increasing function of time.

Resonance transfer of energy between donors becomes established as the donor concentration increases. This leads to the migration of excitation, which accelerates its delivery to points of effective energy sinks, i.e., donors with shortest life. This mechanism of removal of excitation readily competes with static quenching of long-lived centers, but is insignificant for short-lived centers. The process as a whole is thus seen to be complicated. Initially, short-lived centers decay statically and, at the end, long-lived centers decay by losing their excitation as a result of migration to more effective sinks:

$$N(t) = \begin{cases} N_0(t), & t \to 0, & (1.3a) \\ \exp(-ckt), & t \to \infty, & (1.3b) \end{cases}$$

where ck is the rate of the process in its stationary stage and k is a constant independent of time.

From the formal point of view, $N(t)$ satisfies the equation

$$\dot{N} = -k(t)\, cN, \qquad (1.4)$$

in which $k(t)$ decreases with time from its maximum value k_0 to the minimum value k (Fig. 1). It is only in the concluding stationary stage, in which $k(t) \to k = \text{const}$, that this equation is equivalent to the law of mass action. It is only then that quenching can be looked upon as a Markov process in which
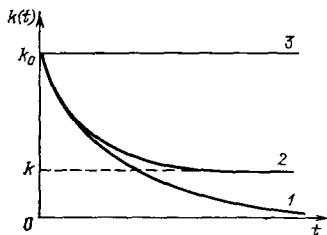
FIG. 1. Time-dependence of the instantaneous rate of quenching $ck(t)$ for different concentrations of donors responsible for static (1), migrationally accelerated (2), and kinetic (3) quenching limits.

ck is the excitation decay probability that is constant in time. However, in general (1.4) is a non-Markov process and $k(t)$ is not at all the rate "constant" of the usual equations of chemical kinetics. As the donor concentration ρ increases, the fraction of excitations lost during the static nonstationary stage of the process with $k(t) = Q(t)$ becomes increasingly smaller, whereas the fraction lost at constant rate becomes increasingly greater. At the same time, the rate constant increases monotonically with ρ and, when the process becomes entirely exponential, the rate constant reaches its upper limit k_0 which is referred to as the "kinetic" constant (Fig. 1). This is the essence of concentration quenching: it involves the accelerated loss of excitations with increasing concentration of particles being excited.

There is a number of concentration quenching mechanisms. When the migration of excitation over a disordered set of donors may be looked upon as continuous diffusion with diffusion coefficient $D(\rho)$, we have[8-11]

$$k = 4\pi R_s D. \tag{1.5}$$

The effective diffusion quenching radius R_s determines the size of the "black sphere" drawn around the acceptor and such that excitation entering it is inevitably lost. The diffusion mechanism prevails when the migration step $\lambda \simeq \rho^{-1/3}$ is small enough. When it is not, and one step is sufficient to enter the black sphere of radius R_w, we have the hopping mechanism[12-15] and

$$k = \frac{4\pi R_w^3}{3\tau}, \tag{1.6}$$

where $\bar{\tau}(\rho)$ is the mean time between hops.

The difference between these mechanisms cannot be wholly accounted for by modifying the definition of k. It is reflected in the particular increase in $k(\rho)$ with increasing donor concentration as a result of the increase in D and $1/\bar{\tau}$, respectively. This difference persists until we reach the kinetic limit k_0 of the rate constant, which is independent of the rate of migration and consequently of ρ. The kinetic limit corresponds to the "total mixing" model (also that of a continuous medium) in the terminology of the monograph by Agranovich and Galanin,[1] or the so-called "ultrafast migration," which can be either hopping or diffusion migration.[13]

Our problem in this review will be to specify more precisely the above functional relationships and the overall picture of the phenomena. In Section 2, we shall examine static quenching and establish the connection between its kinetic behavior $N_0(t)$ and the type of interaction responsible for quenching. In Section 3, we shall interpret more precisely

the mean hopping frequency $1/\bar{\tau}$ and the diffusion coefficient D as functions of donor concentration. In Section 4, we shall examine diffusion quenching and, in Section 5, hopping quenching, and will determine the functions $R_s(D)$ and $R_w(\bar{\tau})$, respectively. In Section 6, these mechanisms will be compared by considering the examples of exchange and dipole-dipole transfer. Finally, in Section 7, we shall compare theoretical predictions with experimental data drawn from optical and magnetic spectroscopy.

2. STATIC QUENCHING

The probability of quenching of a donor by an acceptor at a distance $r = |\mathbf{r}|$ from it depends on the interaction responsible for energy transfer. For multipole interactions, this probability is[1,3]

$$w = \frac{C_{DA}}{r^m}, \tag{2.1a}$$

where C_{DA} is the transfer microparameter and m is the multipolarity index equal to 6 for the dipole-dipole interaction, 8 for the dipole-quadrupole interaction, 10 for the quadrupole-quadrupole interaction, and so on. However, it sometimes happens that transfer is forbidden in all orders, for example, in triplet-triplet energy transfer. When this is so, the only interaction that remains is the exchange interaction[16]

$$w = w(R_0)\exp\left[-\frac{2(r-R_0)}{L}\right] = w_0\exp\left(-\frac{2r}{L}\right), \tag{2.1b}$$

where L is the spatial scale of overlap of the donor and acceptor wave functions, and R_0 is the distance of their closest approach. Since L is considered to be sufficiently small ($L < 1\ \text{Å}$), the preexponential power function is assumed constant. Dipole-dipole and exchange interactions may be looked upon as limiting cases corresponding to long-range and short-range interactions.

When deactivation of the donor is exclusively due to its interaction with the acceptor, the quenching kinetics for excitation produced at $t = 0$ is described by

$$n(r, t) = \exp[-w(r)t]. \tag{2.2}$$

The quantity $n(r,t)$ is the probability that the donor will be excited up to time t if a single acceptor is present at a distance r from it. In other words, after the time t, excitations survive only on donors in whose neighborhood there are no acceptors up to a distance R^*. The spherical region around the donor that is free of acceptors must increase with increasing t. Its radius is defined by

$$w(R^*)t = 1, \tag{2.3}$$

from which it is clear that it increases monotonically with time. Simplifying the picture of the phenomenon somewhat, we may suppose that all excitations have vanished within the "black sphere" of radius R^* whereas, outside this sphere, they have survived. This approximation is described by the step approximation to (2.2), where the position of the step is defined by (2.3).

The idea of black spheres is very convenient in the interpretation of results and semiquantitative estimates. In the language of this model, the function $Q(t)$ in (1.2) is none other but the volume of the black sphere. The probability that this sphere will be entered by any of the N acceptors that are

uniformly but randomly distributed in the volume V is Q/V. When there is only one acceptor, the probability that the donor remains excited is $1 - (Q/V)$. When there is a large number of donors, and they are distributed in space independently of one another, the probability that none of them will enter the black sphere is $[1 - (Q/V)]^N$. It is only in this case that the excitation will survive at time t. The probability of this event in a sufficiently large specimen is

$$N_0(t) = \lim_{V, N \to \infty} \left(1 - \frac{Qc}{N}\right)^N = \exp(-cQ), \qquad (2.3a)$$

where $c = N/V = $ inv. It is clear from this derivation of (1.2) that this formula is the solution of the many-body quenching problem in which one donor is quenched by an ensemble of acceptors in the specimen.

A more rigorous derivation of (1.2) is based on the fact that acceptors quench excitations additively, i.e., the total probability of deactivation is $W = \sum_{k=1}^{N} w_k$, where w_k is the probability of the transfer of energy to the k th acceptor. In that case,

$$N_0(t) = \langle \exp(-Wt) \rangle = \left\langle \exp\left(-\sum_{k=1}^{N} w_k t\right)\right\rangle, \qquad (2.4)$$

where the angle brackets represent averaging over all the possible distributions of acceptors around the donor. Each acceptor is distributed uniformly in space with probability $d^3 r_k / V$, and these distributions are independent if the solution is so dilute that

$$c v_0 \ll 1, \qquad (2.5)$$

where v_0 is the intrinsic volume of the acceptors. In the opposite case $(c v_0 \sim 1)$, we have alignment and at least short-range order appears. On the other hand, when (2.5) is satisfied, the set of acceptors is disordered and the probability of any of its configurations is given by the product of the single-particle probabilities $\prod_{k=1}^{N} (d^3 r_k / V)$. Since the expression that is averaged in (2.4) is also multiplicative in the acceptors, calculations are elementary and, in the limit of an infinite specimen $(N \to \infty, V \to \infty, c = $ const$)$, we again have (1.2) with

$$Q(t) = \int_{R_0}^{\infty} [1 - n(r, t)] d^3 r, \qquad (2.6)$$

where $n(r,t)$ is given by (2.2).

It is clear from (2.6) that the static quenching kinetics is different in the initial and concluding stages of the process. The latter occurs when

$$w(R_0) t = \frac{t}{t_r} \gg 1. \qquad (2.7)$$

It is described quite well by the black-sphere model. The radius of these spheres is then so large that $R^* > R_0$ and hence the volume is $Q = (4/3)\pi R^{*3}$. Using (2.1) and (2.3), we find that $R^* = (C_{DA} t)^{1/m}$ for multipole quenching and $R^* = (L/2)\ln(w_0 t)$ for exchange quenching. It is readily verified that the function $Q(t)$ estimated in this way differs from the results obtained from (2.6) for $R_0 = 0$ by a numerical factor of the order of unity.

Using the exact result in (1.2), we find that, for the multipole quenching,[7]

$$N_0(t) = \exp\left[-\frac{4\pi}{3} c\Gamma\left(1 - \frac{3}{m}\right)(C_{DA} t)^{3/m}\right]. \qquad (2.8)$$

In particular, when $m = 6$, we have the Förster "root-type" kinetics

$$N_0(t) = \exp(-\sqrt{qt}), \qquad (2.8a)$$

where $q = 16\pi^3 / 9 C_{DA} \rho^2$. If, on the other hand, we have exchange-quenching, then[4]

$$N_0(t) = \exp\left(-\frac{\pi L^3}{6} c \ln^3 w_0 t\right). \qquad (2.9)$$

Clearly, the nonstationary character of long-term static quenching kinetics is explained by the fact that there is strong quenching in the interior of the black spheres and weak quenching elsewhere, and the latter becomes even weaker as the spheres expand.

However, for times shorter than t, for which the inequality (2.7) is reversed, the black sphere is inaccessible $(R^* < R_0)$ and quenching is weak in all space. Let us expand (2.2) into a series in terms of the small parameter $w(r)t$ and evaluate (2.6) in the first order of this expansion. This readily yields (1.3b), but with a constant rate

$$k_0 = \int_{R_0}^{\infty} w(r) d^3 r. \qquad (2.10)$$

Consequently, during the initial stage of decay, which is sometimes referred to as the "ordered stage,"[17,18] the process develops exponentially. It is only for times satisfying (2.7) that it becomes "disordered" in the sense that we have the successive loss of excitations that are in increasing isolation from the acceptor environment.

It is useful to note that interaction with the nearest acceptor predominates over other interactions only for

$$c \, Q(t) \ll 1. \qquad (2.11)$$

In other words, static quenching is binary only during the initial stage when, instead of (1.2), we have

$$N_0(t) \approx 1 - cQ = 1 - N\frac{Q}{V}. \qquad (2.12)$$

The interpretation of this formula is that the "black spheres" surround the acceptors but not the donor. The quantity N_0 is then simply the probability of finding an excited donor outside these spheres, which is therefore unquenched. However, the probabilities of entering the black spheres are additive only when the spheres are separated in space. The binary description of quenching ceases to be valid when, as they expand, the black spheres eventually begin to overlap. The process does not occur only if the migration of excitations stops the expansion of the black spheres and stabilizes the rate of quenching.

3. DELOCALIZATION OF EXCITATON

Let us now consider the migration of excitation over identical donors in the total absence of acceptors. This type of migration does not reduce the excitation lifetime if the decay of all the donors in the interior of a center is the same $(\tau_D = $ inv$)$. It only facilitates spatial delocalization of excitation which, having appeared on some center, is transferred to its neighbors until it is distributed over the entire system.

The question whether this process may be looked upon as diffusion, and what is the diffusion coefficient, is relatively complicated. The uniformly but randomly distributed donors form a disordered system in which the lifetime of excitations on different centers is different, and the transition probability is correlated with the center separation (migration step). When the excitation density on the ith center is $N_i = n_i \exp(- t /\tau_\mathrm{D})$, the kinetic equations describing noncoherent migration in the balance approximation are as follows:[19]

$$\dot{n}_i = -\sum_l u_{il} n_i + \sum_l u_{li} n_l, \tag{3.1}$$

where $u_{il} = u_{li} = u(r_{il})$ is the probability of transition between donors i and l separated by the distance $r_{il} = |\mathbf{r}_i - \mathbf{r}_l|$. The equations are valid when the number of excitations is so small that encounters between them can be neglected. They describe the delocalization of excitation produced in a center over all the other centers that are not initially excited.

The mean density $n(r,t)$ of excitations per unit volume is calculated from the recipe

$$n(\mathbf{r}, t) = \left\langle \sum_i \delta (\mathbf{r}_i - \mathbf{r}) n_i \right\rangle, \tag{3.2}$$

in which the angle brackets signify averaging over all the possible dispositions of donors in space. If the excitation is initially localized at the point r', the subsequent density is given by

$$n (\mathbf{r}, t) = R (t) \delta (\mathbf{r} - \mathbf{r}') + P (\mathbf{r} - \mathbf{r}', t), \tag{3.3}$$

where $R(t)$ represents the "outflow kinetics," i.e., the departure of excitation from the center on which it was produced, and $P(\mathbf{r} - \mathbf{r}', t)$ represents its delocalization in space. It is clear that

$$1 - R (t) = \int P (r, t) \, d^3r. \tag{3.4}$$

Since in isotropic and homogeneous space everything is independent of the starting point, we have placed the origin at r' and will continue to do so.

A. Escape of excitation

Initially, outflow kinetics develops in the same way as static quenching because the escape of excitation predominates over its return. In other words, during the initial stage, the process may be looked upon as irreversible and can be described by the same expression as $N_0(t)$, namely,

$$R_0 (t) = \exp [-\rho Q (t)], \tag{3.5}$$

where $Q(t)$ is given by (2.6) and $u(r)$ must be used in (2.2) instead of $w(r)$. The outflow kinetics at this stage differs from (2.8) and (2.9) only by the definition of the parameters.

In particular, for the dipole-dipole mechanism of migration over point centers, we have

$$R_0 (t) = \exp \left(- \sqrt{\frac{6t}{\tau_0}} \right) = \int e^{-Ut} G (U) \, dU. \tag{3.6}$$

This expression reveals the significance of "static" or single-step stage of outflow of excitation. So long as the excitation is localized on the initial center, it will leave it at the rate
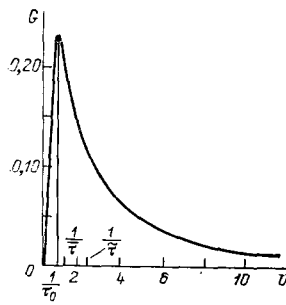
$U = \sum_l u_{il}$, which depends on the disposition around it of other unexcited donors. Some excitations leave rapidly, others more slowly, and the depletion of the entire ensemble is described by (3.6). The distribution of donors over the outflow probabilities in the case of the dipole-dipole transfer is known:[20]

$$G (U) = \sqrt{\frac{3}{2\pi\tau_0 U^3}} \exp \left(- \frac{3}{2U\tau_0} \right). \tag{3.7}$$

The quantity $1/\tau_0$ corresponds to the maximum of this probability (Fig. 2). It is given by

$$\frac{1}{\tau_0} = \frac{8\pi^3}{27} C_\mathrm{DD} \rho^2, \tag{3.8}$$

where C_DD is the donor-donor transfer microparameter that is analogous to C_DA. The probability averaged over this distribution is found to diverge, but the mean lifetime in a given center is finite and given by

$$\tilde{\tau} = \int \frac{1}{U} G (U) \, dU = \int_0^\infty R_0 (t) \, dt. \tag{3.9}$$

For the dipole-dipole transfer, $\tilde{\tau} = \tau_0/3$, whereas, for exchange transfer, $(u = u_0 \exp (- 2r/l))^{21}$

$$\tilde{\tau} = \sqrt{\pi} \, \eta^{-1/4} \exp \left(\frac{2}{3 \sqrt{\eta}} \right) u_0^{-1}, \tag{3.9a}$$

where $\eta = \pi \rho l^3/2$.

B. Effect of return

Strictly speaking, reverse transitions returning the excitation to the initial center can be neglected only when $n(r,t)$ in (2.6) is close to unity, i.e., when $U(r)t \ll 1$. This means that (3.5) describes correctly the outflow kinetics only during the ordered stage, for which $\dot{Q} = k_0$, and $R_0(t) \approx 1$. In the disordered stage, the description must be modified by allowing for the reversible nature of excitation transfer between the initial center and its partners.

The return of excitation to the initial center from its nearest-neighbor donor is the simplest to take into account.[22,23] When there are only two centers, the excitation transferred from one to the other is eventually equally distributed between them, so that its density on the initial center is given by

$$n (r, t) = \frac{1}{2} + \frac{1}{2} \exp [- 2u (r) t]. \tag{3.10}$$

The return of excitation from the nearest-neighbor center to the initial center will be exactly taken into account if we use this expression in (2.6) instead of $\exp[-u(r)t]$, and the probability that two or more centers are equally close to the latter center in dilute solutions is small. So far as more distant centers are concerned, they are, in any case, described by $n(r,t) \approx 1 - ut$, so that with reasonably good precision we find from (2.6) and (3.10) that

$$R(t) = \exp\left[-\frac{\rho}{2} \int [1 - \exp(-2ut)]\, d^3r\right]. \quad (3.11)$$

Whatever the form of $u(r)$ in this expression, the kinetics of the process will not differ from the "static" kinetics, but corrections applied to the numerical coefficients result in a considerable improvement in the agreement between theory and computer experiments.[22,23]

For example, for multipole transfer $u(r) = C_{DD}/r^n$, and

$$R(t) = \exp\left[-\frac{2\pi}{3}\, \rho\Gamma\left(1 - \frac{3}{n}\right)(2C_{DD}t)^{3/n}\right]. \quad (3.12)$$

The argument of this expression is smaller by the factor $2^{1-(3/n)}$ as compared with that obtained from (3.5) for $n = \exp(-ut)$ [cf. (2.8)]. This is the extent to which the return of excitation slows down the depletion of the initial center. There is a corresponding increase in the average time spent on this center $\bar{\tau}$. In the same way as $\tilde{\tau}$ is expressed in terms of $R_0(t)$, this average time can be expressed in terms of $R(t)$:

$$\bar{\tau} = -\int_0^\infty t\dot{R}(t)\, dt = \int_0^\infty R(t)\, dt. \quad (3.13)$$

For multipole transfer (3.12), we have

$$\frac{1}{\bar{\tau}} = \gamma_n C_{DD}\rho^{n/3}, \quad (3.13a)$$

where $\gamma_n = 6[(2\pi/3)\Gamma(1 - (3/n))]^{n/3}/n\Gamma(n/3)$. In particular, $\gamma_6 = 4\pi^3/9$, so that, in the dipole-dipole case

$$\bar{\tau} = 2\tilde{\tau} = \frac{2\tau_0}{3}. \quad (3.14a)$$

For exchange interactions,

$$\bar{\tau} = \frac{1}{2}\tilde{\tau}\left(\frac{\eta}{2}\right). \quad (3.14b)$$

Thus, the definition of $R(t)$ given by (3.11) enables us to describe not only the "ordered" but also the "disordered" stage of outflow of excitation that takes place in a nonstationary manner. Excitations leaving the initial center first transfer to the nearest neighbors, and then to more distant centers, with probability $1 - n(r,t)$. However, the more distant the donor, the more probable it is that it will receive excitation not by direct transfer from the initial center but through intermediaries (Fig. 3). This means that the "direct transfer" approximation (3.11) is limited in time, and for large values of t the dominant process is "sequential transfer" via a large number of successive transitions that effectively constitute diffusion in space.

C. Delocalization kinetics

Let us now consider the spatial distribution of excitation that has left the initial center. This can be done by sub-
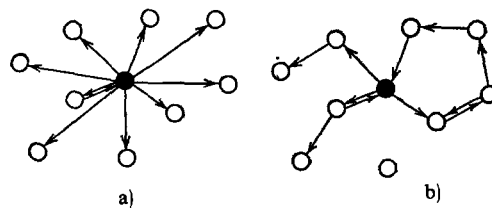

FIG. 3. Schematic diagram explaining the delocalization of excitation over donors: a—with return from nearest neighbors via (3.10), b—true sequential transfer of excitation over the system.

stituting (3.11) in (3.4) and then expanding in powers of ρ. In the approximation that is linear in donor concentration, we have

$$P(r, t) = \rho(1 - n) = \frac{1}{2}\rho\{1 - \exp[-2u(r)t]\}.$$

This is the spatial distribution of donors excited by direct transfer. It expands with time, but not in accordance with the laws of diffusion. The variance of this distribution is[24]

$$\langle r^2 \rangle = \int r^2 P(r, t)\, d^3r$$

and increases nonlinearly with time, contrary to the well-known Einstein law, and the corresponding "effective diffusion coefficient" is given by[25]

$$D(t) = \frac{1}{6}\frac{d\langle r^2 \rangle}{dt} = \frac{\rho}{6}\int r^2 u(r)\, e^{-2u(r)t}\, d^3r \quad (3.15)$$

and decreases monotonically to zero. This was first demonstrated by Sakun,[19] who found that, for dipole-dipole transfer,

$$D(t) \propto \frac{\rho C_{DD}^{5/6}}{t^{1/6}}. \quad (3.16)$$

This conclusion was subsequently extended with the aid of (3.15) to interactions of arbitrary multipolarity, and to exchange excitation transfer.[25]

Of course, direct transfer of excitation must eventually be replaced by the sequential process. This leads to the stabilization of the diffusion coefficient, and thereafter the delocalization process proceeds as in ordered systems. In fact, it has been shown[26] that the long-term asymptotic behavior of $R(t)$ is

$$R(t) \propto \left(\frac{\tilde{\tau}}{t}\right)^{3/2}. \quad (3.17)$$

Still earlier, Vugmeister[15] showed that, for large values of the time t, the density $n(r,t)$ satisfied the usual diffusion equation

$$\dot{n} = D\,\Delta n, \quad (3.18)$$

where D is independent of time. If this is so, then it is well-known that

$$n(0, t) = \frac{1}{(4\pi Dt)^{3/2}}, \text{ and } \langle r^2 \rangle = 6Dt, \quad (3.19)$$

if the excitation starts at the origin. Since, in the diffusion approximation, the density $n(r,t)$ is identified with $P(r,t)$, it is clear that $P(0,t)/\rho$ decreases with time in the same way as $R(t)$. This was to be expected because, for large t, the number of excitations that have not left the initial center is smaller

than the number that have returned after migration over the system. The net result of this is that the center ceases to be "special" in comparison with the neighboring but initially unexcited centers that have received excitation by means of migration.

D. Diffusion coefficient

All that remains is to provide an interpretation of the coefficient of diffusion of excitation over a disordered system. It is clear from physical considerations that this coefficient can be defined by

$$D = \frac{1}{6} \rho \int_\lambda^\infty r^2 u(r) \, d^3 r. \tag{3.20}$$

The only nontrivial aspect of this formula is the choice of the lower limit of integration. In an ordered crystal or other medium consisting of a continuous distribution of donors, this limit is, of course, the lattice period[27] R_0, or the distance of closest approach,[28] respectively. If this is still valid for dilute solutions, as is indeed the view of some authors,[29,30] the coefficient of diffusion should be a linear function of the donor density. However, it is clear from (3.15) and (3.16) that, in the approximation that is linear in ρ, the diffusion coefficient is not a constant. On the other hand, if the lower limit is chosen as in (3.20), then $V(\rho)$ is a nonlinear function of density because the migration step is $\lambda = (3/4\pi\rho)^{1/3}$.

As far as we know, this definition of D was first put forward in Ref. 12 well before it was firmly established that a disordered system did, in fact, have a time-independent diffusion coefficient. This coefficient was subsequently estimated in precisely the same way by other authors.[31–33] If we define it in this way, we can start with the assumption that the transfer of excitation to large distances, even though it has low probability, does facilitate the spatial propagation of excitation, whereas transitions between nearest neighbors (however frequent) are totally ineffective in this respect.

Nevertheless, some doubts persist[34] about the validity of the diffusion description of migration. It is clear from (3.15) that the basis for this is the theory that is linear in ρ. To extend its range of applicability, Vugmeĭster used the decoupling adopted in the theory of continuous random walks (Refs. 21, 35–39). He used this procedure not only to reproduce the diffusion equation (3.18), but also to show that the coefficient D in this equation can be defined in the usual way in terms of the ratio of the variance of hop length to hop time:

$$D = \frac{1}{6\tilde{\tau}} \int_0^\infty r^2 f(r) \, d^3 r. \tag{3.21}$$

The only unusual feature of this definition is the hop length distribution

$$\tilde{\rho} f(r) = \rho u(r) \int_0^\infty \exp[-u(r)\,t] \, R_0(t) \, dt, \tag{3.22}$$

used in the definition of variance. For large distances, it decreases as $u(r)$, but is finite for $r \to 0$ (Fig. 4). Since it is free from the divergence exhibited by the multipole transfer probability, an artificial cutoff procedure such as was applied in (3.20) is unnecessary here.
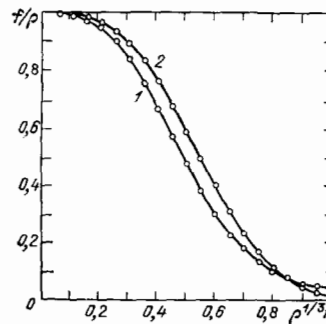
FIG. 4. Hopping length distribution for dipole-dipole transfer (1) compared with the distribution of distances to nearest neighbors (2).

Godzik and Jortner,[40] who also used continuous random-walk theory, have recently confirmed the definition and suggest that it could be corrected by taking into account the back transfer of excitation that was partially taken into account in (3.11). To achieve this, it is sufficient to replace $\tilde{\tau}$ with $\bar{\tau}$ in (3.21) and, instead of (3.22), use the distribution[40]

$$f(r) = \rho u(r) \int_0^\infty \exp[-2u(r)\,t] \, R(t) \, dt. \tag{3.23}$$

Proceeding in this way, we can readily show that

$$D = \frac{1}{\bar{\tau}} \int_0^\infty D(t) \, R(t) \, dt, \tag{3.24}$$

where $\bar{\tau}$ is defined by (3.13). It is clear that the constancy of D is ensured by averaging $D(t)$ as defined by (3.15) over the normalized distribution of times.

For the dipole-dipole migration mechanism, all three formulas (3.20), (3.21), and (3.22) yield

$$D = \alpha C_{DD} \rho^{4/3}. \tag{3.25}$$

The only difference is in the numerical value of α, which is 3.38, 3.42, and 2.72, respectively. As can be seen, the last of these is greater by the factor $2^{1/3}$ than the result calculated without taking into account the back transfer process. Similar values have been obtained by other methods.[24,41,42] They are discussed and compared in Ref. 43. According to (3.20), for interactions of arbitrary multipolarity,[33]

$$D \varpropto C_{DD} \rho^{(n-2)/3}, \tag{3.26}$$

and for exchange transfer,[25]

$$D \varpropto \frac{1}{4} u_0 \lambda l \exp\left(-\frac{2\lambda}{l}\right) \varpropto \exp\left(-\frac{\beta}{l\rho^{1/3}}\right), \tag{3.27}$$

where $\beta = 1.2$ if $\lambda = (4\pi\rho/3)^{-1/3}$. The last result is confirmed by percolation theory of hopping conductivity according to which[44] the exact value is $\beta = 1.7$.

E. Summary

Thus, diffusive delocalization is preceded by direct transfer which is characterized by a diffusion coefficient that is linear in the concentration, for example, that given by (3.16). It is clear that neither in the linear nor even in the quadratic (in ρ) theory[34] is it possible to establish how the transition from (3.16) to (3.25) is accomplished. When the theory is constructed by expanding into a power series in ρ,
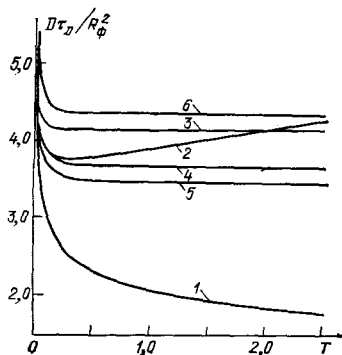
FIG. 5. Dependence of D on $T = t/\tau_D$ for $4\pi R_\phi^3 \rho/3 = 5$ in the case of dipole-dipole transfer $u = (R_\phi/r)^6/\tau_D)$. Calculations based on the linear (1) and quadratic (2) approximation, and the two-particle (3) and three-particle (4) variant of the self-consistent method[41] and the random-walk method[40] with (5) and without (6) reverse transfer of excitation.

the transition from $D(t)$ to D can be followed only by summing this series.

This problem has been solved[41] by partial summation of the series in two versions of the self-consistent method, namely, the two-particle and the three-particle versions. It is clear from Fig. 5 that both methods demonstrate the stabilization of the diffusion coefficient in time, but the second is in better agreement with both linear and quadratic approximations (Fig. 5).

Similar results are obtained in the continuous random-walk theory,[40] either with or without allowing for back-transfer in outflow kinetics. Roughly speaking, the separation boundary between direct and sequential (diffusive) delocalization coincides with the time limit of the linear theory.

More precisely, this limit (t_D) can be established by equating the derivatives $d \ln R /d \ln t$ of the opposite asymptotic forms of $R(t)$, for example, (3.12) and (3.17). This yields

$$t \gg t_D = \tilde{\tau}\left(\frac{n}{2}\right)^{n/3}. \tag{3.28}$$

When this inequality is reversed, direct transfer is replaced by diffusive transfer, by which time the initial center is practically depleted. Even for $n = 6$, we have $n = 6R(t_D) \approx \exp(-\sqrt{t_D/\tilde{\tau}}) = e^{-3} \ll 1$. This is why only the direct transfer process could be seen experimentally. It is only quite recently that it was first shown[45] that the long-term kinetics of the delocalization process is described by (3.17), i.e., the process is in fact diffusive. It has also been confirmed that the concentration dependence of the diffusion coefficient is described by (3.26) for dipole-dipole transfer.

4. DIFFUSION QUENCHING

So far, we have examined static quenching and diffusion of excitations separately. We shall now take into account the fact that diffusion can affect quenching by forcing the loss of excitations that have arisen well away from energy acceptors. It will be convenient to use (2.6) and (2.2) in order to write $k(t) = \dot{Q}(t)$ in the form

$$k(t) = \int w(r) n(r, \pi t) d^3r. \tag{4.1}$$

During the static stage of quenching, the density $n(r,t)$ is determined by

$$\dot{n} = -w(r) n, \tag{4.2}$$

which must be solved subject to the initial condition $n(r,0) = 1$. However, when resonance of excitation takes place, the function $n(r,t)$ is also influenced by migration which tends to smooth out spatial inhomogeneities that arise during the quenching process.

In particular, when migration is equivalent to diffusion, and can be described by (3.18), we have from (4.2)

$$\dot{n} = -w(r) n + D \Delta n. \tag{4.3}$$

The initial condition remains the same as before, but is augmented by the boundary condition

$$4\pi R_0^2 D \frac{dn}{dr}\Big|_{R_0} = 0. \tag{4.4}$$

The latter reflects the fact that the excitation cannot approach an acceptor to a distance less than R_0, and quenching is accomplished at the rate $w(r)$ throughout, including the point $r = R_0$. Up to a certain definite instant of time, the difference between (4.3) and (4.2) is insignificant and the process develops statically. However, the stationary distribution of excitation $n(r,\infty) = n(r)$ is eventually established around the acceptor and is a solution of the equation

$$D \Delta n = w(r) n. \tag{4.5}$$

The solution of this can then be used in (4.1) to calculate the stationary diffusion-accelerated quenching constant k.

This method of calculating the constant is a substantial advance on the phenomenological theory in which stationary quenching is assumed to be possible only when the excitation comes into contact with the "gray sphere" or radius R (Ref. 46). The quenching efficiency on the boundary of the gray sphere is introduced via the boundary condition

$$4\pi R^2 D \frac{dn}{dr}\Big|_R = k_0 n(R) \tag{4.6}$$

for the equation $D\Delta n = 0$, which differs from (4.3) in that it completely ignores distant quenching. This is equivalent to assuming that quenching is possible only within the gray sphere, i.e., in a spherical layer of thickness $\delta = R - R_0 \ll R_0$, in which it may be assumed[47] that $w = $ const. The kinetic rate constant $k_0 = w \cdot 4\pi R^2 \delta$ is a phenomenological parameter of the gray-sphere model, in which it is assumed that $w \to \infty$ and $\delta \to 0$, which ensures the instantaneous loss of excitation inside the layer. The static stage of quenching is thus not present in this model and the diffusion-accelerated quenching constant is given by

$$k = \frac{k_0 k_D}{k_0 + k_D}. \tag{4.7}$$

Energy transfer is assumed to be kinetically controlled when $k \simeq k_0 \ll k_D$. On the other hand, when the reverse condition is satisfied, the process is controlled by diffusion, and its rate is described by the constant $k \simeq k_D = 4\pi RD$. Since $R = $ const, quenching is linearly accelerated as the diffusion coefficient increases.
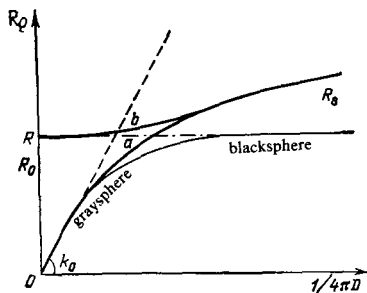
FIG. 6. Quenching of excitation by "white" (a) and "black" (b) acceptors. Lower thin line represents the gray-sphere model and the broken line the kinetic limit.

The true situation is more complicated than in the gray-sphere model. For distant quenching, the dependence of k on D is nonlinear during the diffusion-controlled stage. The effective quenching radius R_s in (1.5) itself depends on D, and the problem for the theory is to identify this relationship. This requires the solution of (4.5), which can then be used to calculate k from (4.1). It is clear from Fig. 6 that the difference between the distant-quenching and gray-sphere radii increases as diffusion slows down.

Taken together, (1.4), (4.1), and (4.3) form a closed formulation of the distant-quenching theory that is capable of describing the entire process, ranging from static to stationary diffusion quenching. After the first, unsuccessful, attempt to construct this theory,[48] three groups of authors managed to develop it simultaneously and independently.[8-10] They have, in fact, found a connection—through the formula given by (4.1)—between the macroscopic equation (1.4) describing the quenching of a donor by an ensemble of acceptors, and (4.3) which describes how a single acceptor will quench excitation distributed in its ambient space. The latter problem had already been solved,[49] but its connection with macrokinetics was established in a different way, for example, by the Wigner-Seitz cell method.[50] The validity of this reduction of the many-body problem to a binary problem subsequently became clear[51,52] and was assured by the binary character of the distant-quenching theory. It was assumed that the acceptors were sufficiently distant from one another. The condition that the spheres of radius R_s drawn around them do not overlap is

$$\frac{c \cdot 4\pi R_s^3}{3} \ll 1. \tag{4.8}$$

It is clear that this condition is more stringent than (2.11), since $R^*(t) \leqslant R_s$. It is also clear that, when it is satisfied, the fraction of excitations lost during the static stage of the process is small (it is approximately equal to $c \cdot 4\pi R_s^3/3$). Computer simulations show that, so long as this fraction does not exceed 0.1, the binary approximation provides a satisfactory description of the kinetics of the entire process.[53]

Acceptors are sometimes looked upon as gray spheres in the theory of distant quenching. This is appropriate only when long-range but weak quenching is replaced by some stronger mechanism at short distances. For example, in the case of direct contact, the dipole-dipole interaction gives way to the more effective exchange interaction. The short-

range interaction can be taken into account phenomenologically in order to keep the spatial function $w(r)$ as simple as possible. This is done simply by replacing the boundary condition (4.4) with (4.6). On the other hand, when quenching on direct contact with an acceptor is so strong that it unavoidably leads to the loss of excitation, the sphere may be regarded as black, and this corresponds to the boundary condition

$$n(R_0, t) = 0. \tag{4.9}$$

This boundary condition was used in Refs. 53 and 54 to solve the distant quenching problem. The kinetic stage is not present in this formulation of the problem, and the quenching radius is always greater than R and tends to R_s for $D \to 0$. However, below, we shall look upon acceptors as "white" in accordance with (4.4). The justification for this is that the kinetic stage is reached in the case of concentration quenching and is interpreted without introducing additional parameters.

A. Stationary quenching

To calculate the rate constant for stationary quenching, it is convenient to eliminate $w(r)$ from (4.1), using (4.5). This yields[8,55]

$$k = D \int_{R_0}^{\infty} \Delta n \cdot 4\pi r^2 \, dr = 4\pi D R_Q, \tag{4.10}$$

where

$$R_Q = \lim_{r \to \infty} r^2 \frac{dn}{dr} \tag{4.11}$$

is none other than the parameter of the asymptotic expression

$$n(r) = 1 - \frac{R_Q}{r} \quad \text{for } r \to \infty. \tag{4.12}$$

In this formulation, the problem may be solved even when the quenching of a donor by an acceptor cannot be characterized by the transition probability $w(r)$ and is described by a set of equations for the density matrix of the resonating states.[55] In this general form, the theory describes the transfer not only of energy but of polarization as well, including magnetic (spin exchange)[56,57] and electric (dephasing of molecular oscillations) polarizations.[58] Moreover, it enables us to describe the forces of electrostatic interaction between the donor and acceptor when they are charged.[59]

We are interested here in the simplest case of uncomplicated counterdiffusion of particles between which energy transfer occurs with probability $w(r)$. Quite general solutions can be obtained for this case both for multipole and exchange quenching. The solution becomes very simple in the limiting cases of kinetic (a) and diffusion (b) control:

$$R_Q \approx \begin{cases} k_0/4\pi D, & R_0 > R_s, \tag{4.13a} \\ R_s, & R_0 < R_s. \tag{4.13b} \end{cases}$$

The kinetic rate constant k_0 is defined by (2.10). As far as the effective radius R_s of the black sphere is concerned, it is given by[7,8,60,61]

$$R_s = v^{2v} \frac{\Gamma(1-v)}{\Gamma(1+v)} \left(\frac{C_{DA}}{D}\right)^v, \tag{4.14}$$

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in the case of the multipole mechanism and by[54,55]

$$R_s = \frac{L}{2} \ln \left(\frac{w_0 L^2 e^{2C}}{4D} \right), \qquad (4.15)$$

in the case of the exchange mechanism, where $v = 1/(m-2)$ and $C = 0.577$ is Euler's constant.

It is clear from these results that R_s increases monotonically as diffusion slows down (Fig. 6). On the contrary, the rate constant remains constant during the kinetic stage, but begins to fall with decreasing D as we enter the diffusion-controlled region. This result is qualitatively the same as the result obtained in the gray-sphere model (4.7). However, quantitative agreement with the latter is possible only for the short-range exchange interaction, and only within restricted limits[55,62] with $R_Q \leqslant R_0 + L$.[55,62]

B. Quenching layer

Since, in the diffusion limit, quenching occurs on the boundaries of the black sphere of radius R_s, this radius can be approximately determined from

$$\beta(R_s) = \frac{w(R_s)\,\delta^2}{D} = 1. \qquad (4.16)$$

The quantity $\beta(r)$, which is the analog of action, characterizes the quenching force at a distance r from the acceptor, and δ^2/D is the time spent by the excitation on this boundary. It is clear that quenching is weak for $r > R_s$ and strong for $r < R_s$. It is also clear that the strong-quenching region is present only so long as $R_s > R_0$, as indicated in (4.13b). When this condition is not satisfied, the region is inaccessible and quenching is weak throughout, and is therefore kinetically controlled.

Since quenching is ineffective at large distances from the black sphere, whereas in its interior there is nothing to quench, it is clear that the loss of excitation occurs largely in a spherical layer of radius R_s, where δ is a measure of its thickness. When the layer is so thin that it may be regarded as flat, $\delta^2/2D$ is the time at which it is crossed in the diffusion process. However, the quenching time is not necessarily equal to this quantity because the layer may be crossed several times and quenching may not be uniform within the layer. A physically reasonable estimate can be obtained for this quantity on the basis of indirect considerations. The point is that $\beta(R_0)$ must be equal to the intrinsic parameter β_m of the general theory, which is used to distinguish between kinetic $(\beta_m \ll 1)$ and diffusion $(\beta_m \gg 1)$ stages of quenching. Since β_m is determined to within a numerical factor, it is readily shown with the same precision that[63]

$$\delta = \begin{cases} vR_s, & (4.17a) \\ L/2 & (4.17b) \end{cases}$$

for multipole and exchange interactions, respectively. Using (2.1) and (4.17) in (4.16), and solving the resulting equation for R_s, we can readily reproduce (4.14) and (4.15) to within numerical factors where, in the multipole case, the difference decreases with increasing m.

For a high degree of multipolarity and for sufficiently small L, the layer may be looked upon as thin in the sense that $\delta \ll R_s$ and, consequently, quenching is accomplished as the layer is crossed rather than in the interior of the black
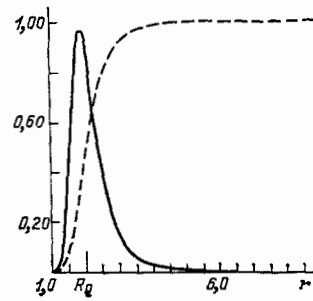

FIG. 7. Distant quenching during diffusion. Broken line shows the reduction in the current of excitations to the acceptor $(j(r)/j(\infty))$ as the acceptor is approached. Solid curve shows the distribution of excitations over the locations of their extinction. Distances are measured in units of R_0—the distance of closest approach; $m = 10$, $\beta m = 100$.

sphere. However, in the dipole-dipole interaction, the layer is so diffuse that one can accept the definition[64,33] $\delta^2 = R_s^2/3$, which identifies the quenching time with the total time spent in the interior of the sphere. The deficiency of this definition appears only for large m and for exchange quenching for which it gives an incorrect form for $R_s(L)$. The fact that excitations do not penetrate the interior of the black sphere can also be verified by direct determination of the flux $j = -4\pi r^2 (dn/dr)D$ as a function of r. This flux vanishes rapidly on the boundary of the black sphere and its derivative characterizes the distribution of excitations over the points at which they disappear. Both are shown in Fig. 7, from which it is clear that excitations vanish without succeeding in coming into direct contact with the acceptor even for moderate β_m.

The manner in which the boundary of the black sphere is crossed is of fundamental importance. The time spent in the quenching layer can be estimated as δ^2/D only when the motion through the layer may be looked upon as diffusion. When motion is accomplished by migration with a step λ, it can only be so regarded in a spatial interval δ such that

$$\delta > \lambda \approx \rho^{-1/3}. \qquad (4.18)$$

For multipole quenching, we can use this in conjunction with (4.17a), (4.14), and (3.26) to show that

$$\rho^{(n-m)/3(m-2)} < \left[\frac{z}{(m-2)^m} \right]^{1/(m-2)}, \qquad (4.19)$$

where $z = C_{DA}/C_{DD}$ is an important parameter of the theory, since it is a measure of the relative strength of irreversible and reversible energy transfer between the impurity centers. When the latter is due to interaction between donors characterized by a higher degree of multipolarity than the interaction with acceptors $(n > m)$, the diffusion mechanism prevails only for low donor concentrations for which quenching is essentially static. Diffusion-accelerated quenching at high donor concentrations is possible only in the reverse situation when quenching is of a shorter range than transfer $(m > n)$. If, on the other hand, $n = m$, it may occur for any concentration, but only if

$$z \gg 1. \qquad (4.19a)$$

Finally, for exchange quenching, we find that, according to (4.17b) and (4.18), the diffusion mechanism occurs for

$$L\rho^{1/3} > 2. \qquad (4.20)$$

C. Concentration dependence of k

Within the limits established above, the rate of diffusion-accelerated quenching depends on ρ, as follows. For multipole quenching, forced by multipole migration with diffusion coefficient given by (3.26), we have from (4.14)

$$k \simeq 4\pi R_s D \infty C_{DA}^{1/(m-2)} C_{DD}^{(m-3)/(m-2)} \rho^{(n-2)(m-3)/3(m-2)}.$$

In the important case of dipole-dipole quenching and energy transfer ($n = m = 6$), this estimate can be improved in accordance with (3.25):

$$k = 8\pi\alpha^{3/4} \frac{\Gamma(3/4)}{\Gamma(1/4)} C_{DA}^{1/4} C_{DD}^{3/4} \rho. \tag{4.21}$$

For exchange quenching and dipole-dipole diffusion,

$$k \infty 2\pi\alpha C_{DD} L \rho^{4/3} \ln \frac{w_0 L^2}{4\alpha C_{DD}\rho^{1/3}}, \tag{4.22}$$

and, when the exchange interaction is responsible for both quenching and diffusion, we find from (4.15) and (3.27) that

$$k \infty u_0 L l \exp\left(-\frac{2}{l\rho^{1/3}}\right)\left(\ln\frac{w_0 L^2 \rho^{1/3}}{u_0 l} + \frac{2}{l\rho^{1/3}}\right)\rho^{-1/3}. \tag{4.23}$$

These formulas show that dipole-dipole quenching in dipole transfer is exceptional in the sense that it is only in this case that the rate of concentration quenching increases linearly with the donor density ρ. When quenching is accomplished by interaction of higher degree of multipolarity, the function $k(\rho)$ become irrational, whereas for exchange quenching it is given by (4.22). However, it is only in the case of exchange diffusion that quenching is turned on exponentially rapidly, as in (4.23), for concentrations approaching the maximum value.

D. Nonstationary quenching

We note in conclusion that the stationary stage of quenching does not, in general, follow immediately after the static stage. This emerges from the example of the rectangular model of a quenching layer. It corresponds to $w(r) = w = \text{const}$ for $R_0 \leqslant r \leqslant R_0 + \delta = R$ and $w(r) = 0$ elsewhere. In this model, static quenching takes the form

$$N_0(t) = \exp\{-c4\pi R_0^2\delta [1 - \exp(-wt)]\}.$$

This is experienced by only a limited number of donors occupying the quenching layer at the time of excitation. At the end of this stage, i.e., for $t \gg 1/w$, diffusion quenching develops and its rate is given by[1,11,46]

$$k(t) = k_D\left(1 + \frac{R}{\sqrt{\pi Dt}}\right). \tag{4.24}$$

It is nonstationary for $1/w < t < R^2/D\pi$ and reaches the stationary limit with $k_D = 4\pi RD$ for $t \gg R^2/\pi D$.

Exactly the same situation prevails for the extended interaction. The nonstationary stage corresponds to a change in the profile $n(r,t)$ from the initial value equal to unity in all space to the stationary level with the asymptotic form given by (4.12). In the case of exchange quenching, the static and stationary stages are actually separated from one another, and the kinetics of the entire process can be described only by solving (4.3). In principle, this is also valid for multipole quenching.[60,65] However, the more long range it becomes,

the more difficult it is to divide the process into successive stages. Replacing R in (4.24) with the effective radius of strong dipole-dipole quenching, $R_s = 0.7 (C_{DA}/D)^{1/4}$, it may be shown that[66,67]

$$k(t) = 4\pi R_s D + \frac{4\sqrt{\pi} R_s^2 \sqrt{D}}{\sqrt{t}}$$
$$= 4\pi \cdot 0.7 C_{DA}^{1/4} D^{3/4} + 2\sqrt{\frac{\pi C_{DA}}{t}}. \tag{4.25}$$

Although the diffusion coefficient has disappeared from the second term on the right, and its dependence on time and C_{DA} is quite similar to the static $\dot{Q}(t)$ obtained from (2.8) for $m = 6$, it is not right to suppose that the two are identical. We are, in fact, dealing with a fortuitous coincidence which does not occur for other values of m. Nevertheless, it is instructive in the sense that it shows that the time scale of diffusion and of static nonstationarity is the same for the dipole-dipole quenching, so that the two cannot, in principle, be separated. In the context of this paper, there is little point in considering the nonstationarity of diffusion quenching for the further reason that, as explained in the last section, diffusion is also a nonstationary process at the initial stage and must be described quite differently from that in (4.3).

5. HOPPING QUENCHING

We shall now suppose that excitation reaches the black sphere in a single hop and leaves it in precisely the same way. The radius of the sphere is then defined as the distance between the acceptor and donor over which excitation is lost in one lifetime:

$$w(R_w)\bar{\tau} = 1. \tag{5.1}$$

If both quenching and energy transfer are due to the multipole interaction, we find from (5.1) together with (2.1a) and (3.13a) that

$$R_w = \left(\frac{z}{\gamma n}\right)^{1/m} \rho^{-n/3m}. \tag{5.2}$$

Excitation reaches the interior of this sphere in a single hop (or leaves it in a single hop) if

$$\lambda > R_w, \tag{5.3}$$

or, in other words,

$$\rho^{(n-m)/3m} > \left(\frac{z}{\gamma n}\right)^{1/m}. \tag{5.4}$$

It is clear that (4.19) and (5.4) constitute opposite inequalities. This means that, for $n > m$, the diffusion mechanism operates at low donor concentrations, whereas the hopping mechanism prevails at higher concentrations. Conversely, when $n < m$, concentration quenching is at first accomplished by the hopping mechanism as ρ increases, but it subsequently relies on the diffusion mechanism. Finally, when $n < m$, the hopping mechanism prevails for any concentration provided only

$$z = \frac{C_{DA}}{C_{DD}} \ll 1. \tag{5.4a}$$

Hopping quenching differs from diffusion quenching not only by the different definition of the black-sphere radi-

us, but also by the functional dependence (1.6) of the quenching constant on this radius. The structure of this dependence is such that the quenching rate can be interpreted as follows. The excitation changes its location in hops, on average at intervals of time $\bar{\tau}$, so that the black sphere of radius R_w drawn around it covers different regions of space in succession. The total volume (per unit time) covered in this way is equal to k, and the number ck of hops that are fatal to the excitation is equal to the number of acceptors located in this volume. This is, in fact, the rate of hopping quenching that was first estimated in Refs. 12 and 13. Using (5.2) and (3.13a) in (1.6), we obtain

$$k \approx \frac{1}{3}\, 4\pi C_{DA}^{3/m}\,(\gamma_n C_{DD})^{1-(3/m)}\,\rho^{n[1-(3/m)]/3}. \tag{5.5}$$

It is clear that the dependence of k on donor concentration is, in general, irrational and can be linearized only for $n = m = 6$. In that case (and as always for $n = m$), the dependence becomes functionally indistinguishable from its diffusion analog (4.21). The only difference is in the dependence of k on the transfer microparameters C_{DA} and C_{DD}.

The hopping rates of any other variants of transfer can be calculated by analogy with (5.5). In particular, for exchange quenching accelerated by exchange excitation transfer, we have from (1.6), (3.9a), (3.14b), (5.1), and (2.1b)

$$k = \frac{\sqrt{\pi}}{3}\, u_0 L^3\, (\eta/2)^{1/4} \exp\left(-\frac{2}{3}\sqrt{\frac{2}{\eta}}\right)$$
$$\times \left\{\ln\left[\frac{\sqrt{\pi}}{2}\,\frac{w_0}{u_0}\left(\frac{2}{\eta}\right)^{1/4}\right] + \frac{2}{3}\sqrt{\frac{2}{\eta}}\right\}^3, \tag{5.6}$$

where $\eta = (\pi/2)\,\rho l^3$. This result is essentially different from its diffusion analog given by (4.23) in which $k \sim \exp[-(4\pi/\eta)^{1/3}]$. The reason for the difference is that the diffusion coefficient does not duplicate the concentration dependence of $1/\bar{\tau}$ that dominates (5.6). However, the choice of $\bar{\tau}$ as a measure of the quenching time is still largely arbitrary. For example, the authors of Ref. 68 replace $\bar{\tau}$ with τ_h defined by $R(\tau_h) = 1/e$. For multipole transfer, the quenching time introduced in this way differs from $\bar{\tau}$ only by a numerical factor. In particular, for dipole-dipole transfer, (3.12) and (3.14a) show that $\tau_h = \bar{\tau}/2 = \tilde{\tau}$. However, for the exchange interaction

$$\frac{1}{\tau_h} = 2u_0 \exp\left[-\left(\frac{6}{\eta}\right)^{1/3}\right],$$

as can be seen from the asymptotic form of $R(t)$ that is obtained from (2.9) by substituting $c \to \rho/2, w_0 \to 2u_0$ and $L \to l$. The use of τ_h instead of $\bar{\tau}$ brings the estimate of the hopping rate closer to the diffusion rate although it does not totally remove the differences between them. On the other hand, τ_h is no more rigorous than $\bar{\tau}$ because there is little to distinguish either when very approximate estimates are made. The ensuing ambiguity can be overcome only by the more rigorous theories discussed below.

A. Markov model

It is clear from the foregoing that the hopping mechanism of quenching is the natural alternative to the diffusion mechanism although the latter has for long been regarded as the only possibility. The necessity for the transition to the hopping description of the process occurring in a relatively narrow quenching zone has not as yet been finally accepted.

And yet, there are a number of fundamental arguments in favor of the hopping mechanism, the first of which was given in a previous paper.[13] It relies on the assumption of uncorrelated replacement of the acceptor environment in the course of the random walk of excitations over a disordered system. This enables us to look upon the probability of quenching, which undergoes a discontinuous change in each hop, as an uncorrelated and purely discrete Markov process $W(t)$, while the excitation density

$$N_1(t) = \left\langle \exp\left[-\int_0^t W(t')\,dt'\right]\right\rangle \tag{5.7}$$

is a functional of the Markov process. The fact that the successive values of W are uncorrelated means that the probability that the excitation will be lost on the ith donor is the sum of the probabilities of quenching by all the ambient acceptors ($W_i = \sum_k w_{ik}$), and is independent of the value of this sum on the preceding ($i - 1$th donor from which the excitation was transferred to the given donor. In other words, the probability of realization of W after a hop preceded by W' is

$$f(W', W) = G(W), \tag{5.8}$$

where $G(W)$ is the density of the equilibrium distribution of donors over the quenching probabilities and is the same as the function $G(U)$ in (3.7).

It is clear that the only uncorrelated mechanism is the hopping quenching mechanism. When migration takes place in small steps that add up to continuous diffusion, each of them produces only a slight change in W'. In order for the new value W to be realized with equal probability independently of the previous value, the migration step must be large in comparison with the radius of the black sphere drawn around the excitation. It is only in this case that the distribution of acceptors in this sphere and its immediate environment after the successive step will be completely new and in no way resembling the previous state. The average over all the possible realizations $W(t)$, indicated by the angle brackets in (5.7), has been performed[13] under these assumptions. This results in the Volterra integral equation which has frequently been used to solve similar problems in nonlinear optics,[69] spectroscopy,[70,71,72] and chemical kinetics:[73]

$$N(t) = N_0(t)\,e^{-t/\tau_0} + \frac{1}{\tau_0}\int_0^t N_0(t-t')\,e^{-(t-t')/\tau_0}N(t')\,dt'. \tag{5.9}$$

The function $N_0(t)$ describes the static kinetics (2.4) and is the kernel of this equation, whereas τ_0^{-1} is the frequency of hops that constitute the Poisson process in the Markov theory. The form of the kernel is specific for each of the problems enumerated above, but the properties of the solution are common to them all: static kinetics develops first, and the final stage is exponential, as in (1.3).

When the rate of static quenching is q, as in (2.8a), the migration process is slow so long as $q\tau_0 \gg 1$, and fast otherwise. For slow migration, quenching essentially ends on the

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static stage and the excitation that still remains vanishes at the rate τ_0^{-1}, leaving the unfavorable acceptor-depleted region in a single hop.[13] On the other hand, when migration is fast, most of the excitations decay in accordance with (1.3b) with the constant[13]

$$k = \frac{1}{\tau_0^2} \int_0^\infty Q(t)\, e^{-t/\tau_0}\, dt = \int_0^\infty \dot{Q}(t)\, e^{-t/\tau_0}\, \frac{dt}{\tau_0}, \qquad (5.10)$$

where $Q(t)$ is defined in (2.6). Using this definition, we have[74,75]

$$k = \int_{R_0}^\infty w(r)\, d^3r \cdot [1 + w(r)\,\tau_0]^{-1}.' \qquad (5.11)$$

B. Concentration dependence of k

The estimate of the hopping rate of quenching based on the black-sphere model can readily be justified by this formula. Having determined the radius of the spheres from the relation $w(R_w)\tau_0 = 1$, we can use the rectangular approximation to the integrand in (5.11), assuming that it is equal to $1/\tau_0$ for $R_0 < r < R_w$ and zero elsewhere. If we neglect R_0, this way of estimating k immediately takes us to a formula that is identical with (1.6) provided only $\bar{\tau}$ is replaced with τ_0.

Direct evaluation of the integral in (5.11) with $R_0 = 0$ improves only the numerical coefficient in k. In the case of dipole quenching, this yields

$$k = \frac{\pi}{2} \cdot \frac{4\pi R_w^3}{3\tau_0} = \pi \left(\frac{2\pi}{3} \right)^{5/2} \rho\, \sqrt{C_{DA}C_{DD}}, \qquad (5.12)$$

where $R_w = (C_{DA}\tau_0)^{1/6}$. However, when R_0 is not neglected, the increase in $1/\tau_0$ unavoidably leads to the situation where R_w becomes less than R_0 and the correction term in the denominator of (5.11) can be neglected. In this situation, which was originally referred to as "supermigration,"[13] we again obtain (2.10) which sets the upper, kinetic, limit on the rate of quenching. The transition from the migration-accelerated to the kinetic stage in the dipole-dipole interaction is described by

$$k = \frac{\pi}{2} \cdot \frac{4\pi R^3 w}{3\tau_0} \left[1 - \frac{2}{\pi} \arctan\left(\frac{R_0}{R_w} \right)^3 \right], \qquad (5.12a)$$

which, in the general case, is obtained[23] from (5.11).

In exchange quenching accelerated by hopping, the estimate of k based on the black-sphere model of radius $R_w = (L/2)\ln w_0\tau_0$ gives practically the same result as direct calculation[76]

$$k = \frac{\pi L^3 \ln^3 (w_0\tau_0)}{6\tau_0}. \qquad (5.13)$$

When excitation transfer is due to the dipole-dipole interaction, we can use (3.8) for τ_0, so that the dependence of the constant on ρ is almost quadratic rather than linear as in (5.12). In principle, this enables us to identify not only the interaction responsible for quenching, but also its mechanism. According to (4.22), $k \sim \rho^{4/3}$ for exchange quenching in the diffusion process, whereas for the hopping mechanism the function $k(\rho)$ is shown by (5.13) and (3.8) to be nearly quadratic. This type of dependence has been found for quenching by erbium in phosphate and borate glasses[77,78] and may be evidence for hopping exchange quenching en-
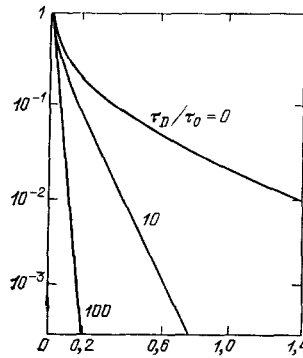

FIG. 8. Survival probability $\mathscr{P} = \exp\{ - t/\tau_D \} N(t)$ for different values of the ratio[80] τ_D/τ_0.

hanced by dipole-dipole transfer. If, on the other hand, not only quenching but also the transfer of excitation is of the exchange type, the parameter τ_0 in (5.13) must be replaced with $\bar{\tau}$ from (3.9a) or, better still, with $\bar{\tau}$ from (3.14b). The result of this will be that $k(\rho)$ will become an exponentially rising function, as in (4.23), i.e., quenching will suddenly set in at the critical concentration given by[68] $\eta_c = (\pi/2)\rho_c l^3 = 1$. A similar situation obtains in the case of capture by a trap of a hopping electron executing migration over impurity centers.[79]

C. Quenching kinetics

We now turn to hopping quenching kinetics. The solution of (5.9) has been determined by numerical methods,[80] so that it has been possible to follow how, as $1/\tau_0$ increases, the quasistatic dipole quenching transforms into hopping-accelerated quasiexponential quenching (Fig. 8). The latter can be described analytically at all times, ranging from the nonstationary to the stationary stage.[74] As a result, the kinetic description of concentration quenching can be improved, both at the beginning and at the end of the process. For multipole quenching,[74]

$$N(t) = \begin{cases} \exp\{ -(q/t)^{3/m}[1 + (t/\tau_0)] \} & \text{for } t \ll \tau_0, \quad (5.14a) \\ \exp(-\delta c - kct) & \text{for } t \gg \tau_0. \quad (5.14b) \end{cases}$$

Comparison with (1.3) shows that the initial, quasistatic, stage of the process is modified only slightly, and the fraction of particles disappearing at this stage, $1 - e^{-\delta c} \approx \delta c$, is small. For multipole quenching, it is given by

$$\delta c = \left(1 - \frac{3}{m} \right) (q\tau_0)^{3/m}\, \Gamma\left(\frac{3}{m} + 1 \right) \approx \frac{4\pi R_w^3 c}{3},$$

and if both quenching and transfer are of the dipole-dipole type, we find, using (3.8), that

$$\delta c = \sqrt{\frac{3\pi z}{8}}\, \frac{c}{\rho}, \qquad (5.15)$$

where $\sqrt{zc}/\rho \approx \sqrt{q\tau_0} \ll 1$, since migration is assumed to be fast.

D. Correlation of quenching probabilities

We now return to the restrictions on the generality of the foregoing theory. They ensue from the fact that the fluctuations in quenching probability are regarded as a Markov process and are uncorrelated. Strictly speaking, this is not

the case even when the donors form a spatially ordered structure and are located at the sites of some extended crystal lattice. There is, in fact, a finite probability that an excitation migrating over this quasilattice will return to the center on which it has already resided, and will do so more than once. Consequently, the quenching probability corresponding to this center is encountered more frequently than was assumed in equilibrium statistics, and (5.8) loses its validity. However, an attempt to validate the theory[75] has shown that its conclusions remain in force when τ_0 in (5.11) is replaced with

$$\tilde{\tau} = \int_0^\infty R(t)\, dt.$$

This result was subsequently confirmed in Ref. 81. When excitation is delocalized in a regular lattice, its kinetics differs from the exponential (Markov) kinetics only by the long-term diffusional asymptotic behavior that includes the return of the excitation to the original center.

As an example, the authors of Ref. 75 and 81 examined a process with known kinetics along the entire time axis.[35] This process occurs when the excitation can be transferred only to neighboring sites in a simple cubic lattice. For this process, $\tilde{\tau} = 1.5\tau_0$. More generally,

$$\tilde{\tau} = \xi \tau_0, \tag{5.16}$$

where ξ is the mean number of returns to the original center. When transfer is due to the multipole interaction, transitions to arbitrarily distant centers become possible. The coefficient ξ then depends on the structure of the lattice and on the multipole order m. The scale of this factor may be judged from the data taken from Ref. 82 and listed in Table I. The last row corresponds to transitions between only the nearest sites and may be looked upon as corresponding to the exchange interaction. It is clear that the correction due to the return effect is small and decreases as the interaction becomes more extended.

E. Allowance for the random disposition of donors

The correction due to the random migration of excitation over a disordered system is more important and more difficult to introduce. The rigorous approach to this problem must start with equations generalizing (3.1) with allowance for the quenching of excitation by acceptors:

$$\dot{n}_i = -\sum_l u_{il} n_i + \sum_l u_{li} n_l - \sum_k w_{ik} n_i. \tag{5.17}$$

The main difficulty is that the solution of these equations must be averaged over the random distribution of both acceptors and donors. As we have seen, this cannot be done rigorously even in the absence of quenching. Attempts to

TABLE I.

Lattice	Simple cubic	BCC	FCC
$m = 6$	$\xi = 1{,}266$	1,214	1,211
8	1,404	1,307	1,299
10	1,464	1,342	1,328
∞	1,517	1,393	1,345

solve these problems have had to rely on certain assumptions that cannot always be controlled and are difficult to compare.

Several different approaches have been proposed in which account was taken of the difference between hopping quenching in a disordered system of donors and the process described above that develops in the "equivalent" regular structure. The first of these attempts[19] was a theory that was linear in the donor concentration ρ. However, both the excitation quenching kinetics and the delocalization discussed in Section 3 are described by the linear theory only on the initial nonstationary stage of the process. For this stage of dipole-dipole quenching, it is found[19] that (5.14a) is replaced with

$$N(t) = \exp\left[-V\overline{qt}\left(1 + \frac{9}{4\pi} V\sqrt{\frac{3t}{2\tau_0}}\right)\right]$$
$$= \exp\left[-c\left(\frac{4\pi}{3}V\sqrt{\pi C_{DA}t} + 2\pi^2\rho\, V\sqrt{C_{DA}C_{DD}}\, t\right)\right]. \tag{5.18}$$

As before, the correction to the static term is small because $t \ll \tau_0$, but its functional dependence on time is different from that in (5.14a). Purely fortuitously, this time dependence is linear, and the corresponding proportionality coefficient differs from the constant in (5.12) only by a numerical factor. It is therefore sometimes identified with the latter, but this is quite incorrect. It has been shown[19] that, when the quenching multipolarity is different, the correction term becomes an irrational function of time, so that it has nothing in common with the exponential asymptotic behavior of quenching for times $t \gg \tau_0$.

The last possibility was examined by Zusman,[14] who showed that that stationary density of excitations on donors surrounding an acceptor was equal to the ratio of their depletion times in the presence and absence of quenching:

$$n(r_n) = \langle (W_n + \sum_{n'} u_{nn'})^{-1}\rangle \langle (\sum_{n'} u_{nn'})^{-1}\rangle^{-1}.$$

By taking the average over a random distribution of donors, and using the results given by (4.1), he found that

$$k = \frac{1}{\tilde{\tau}} \int_0^\infty \dot{Q}(t) R_0(t)\, dt = -\frac{1}{\tilde{\tau}} \int_0^\infty Q(t) \dot{R}_0(t)\, dt. \tag{5.19}$$

This formula is a natural generalization of the definition of k given by (5.10). It has not received its due recognition because, in the appendix to Ref. 14, Zusman reported a result of doubtful validity, which claimed to describe quenching kinetics along the entire time axis. The correction to the static term in the nonstationary stage of quenching deduced from Zusman's result differs both in magnitude and sign from that given by (5.18).

In view of this, it is significant that (5.19) has been confirmed independently by Vugmeĭster.[15] He obtained an equation that was a natural generalization of (5.9) to the case of a non-Markov outflow process:

$$N(t) = N_0(t) R_0(t) - \int_0^t N_0(t-t') \dot{R}_0(t-t') N(t')\, dt'. \tag{5.20}$$

This equation has recently been deduced in a different way in Ref. 83. The only assumption made was that both the acceptor and the donor environment was subject to uncorrelated

variation in the course of the random-walk migration. The original Vugmeĭster papers on magnetic resonance were confined to the spin, i.e., the dipole-dipole interaction when, according to (2.8a) and (3.6), (3.9),

$$N_0 = \exp(-V\overline{qt}), \quad \text{a} \quad R_0 = \exp\left(-\sqrt{\frac{2t}{\tilde{\tau}}}\right). \quad (5.21)$$

From (5.20) we then obtain the following expression for the rate of hopping quenching:

$$\overline{W} = ck = \sqrt{\frac{q}{2\tilde{\tau}}} \approx \frac{8\pi^3}{9} V \overline{C_{DA}C_{DD}}\,\rho c. \quad (5.22)$$

Precisely the same result is obtained from (5.19) when (5.21) is used in it.

These results can be improved somewhat by taking into account the advantages of partial inclusion of the return of excitation to the original center. This correction is desirable because the outflow of excitation is a reversible and, consequently, a correlated process. When the centers lie close to one another, the corresponding probabilities U are not very different and repeat more frequently than predicted by statistics. To take this into account in (5.20), it is sufficient to replace[84] $R_0(t)$ with $R(t)$. This yields

$$N(t) = N_0(t)\, R(t) - \int_0^t N_0(t-t')\, \dot{R}(t-t')\, N(t')\, dt'. \quad (5.23)$$

Correspondingly, in (5.19) we must replace R_0 with R, and $\tilde{\tau}$ with $\overline{\tau}$:

$$k = -\frac{1}{\tilde{\tau}} \int_0^\infty Q(t)\, \dot{R}(t)\, dt = \frac{\overline{Q}}{\tilde{\tau}}. \quad (5.24)$$

It is precisely in this way, using intuitive ideas, that the quenching constant was estimated in the original variant of the theory:[12] it was obtained in terms of the mean excitation quenching efficiency $\overline{Q}$ on a donor, divided by the mean time $\tilde{\tau}$ spent on the donor. From (3.12) and (5.24) we find that

$$k = \frac{8\pi^3 V\overline{C_{DA}C_{DD}}\,\rho}{9\sqrt{2}}. \quad (5.25)$$

The numerical difference between this and (5.12) is wholly due to the fact that the migration was assumed in (5.10) to be a Markov process with $\overline{\tau} \equiv \tau_0$ and $R = \exp(-t/\tau_0)$ whereas, in reality, the process is not of the Markov type and the time distribution $\dot{R}(t)$ obtained from (3.12) is nonexponential.

Since quenching is a non-Markov process only in the hopping limit, it has sometimes been assumed that this can be ignored in the interests of a unified description of the hopping and diffusion mechanisms.[15,85] Judging by the results obtained on this basis,[85] we find that the data can be described by using the pseudo-Markov outflow function $\widetilde{R}_0 = \exp(-t/\tilde{\tau})$, in place of R_0 in (5.19). It is clear from Table II that this produces an increase in the rate constant by

the factor $\sqrt{\pi/2}$. The hopping quenching constant calculated by Huber[33,86] is greater by the same factor as compared with (5.25). This agreement is not fortuitous: Huber's recipe for calculating k is the same as (5.24) in which, however, we have to use $\overline{R} = \exp(-t/\tilde{\tau})$. When this is done, we obtain (5.10) which corresponds to the equivalent ordered lattice of donors, but with outflow time $\tilde{\tau}$ instead of τ_0. Evidently, the "average t-matrix" method used by Huber transforms quenching into a Markov process. It is therefore not surprising that its temporal evolution is in better agreement with the exact solution for ordered systems than with the solution for disordered systems.[87] According to Table II, the neglect of the return of excitation produces a greater increase in the final result than the non-Markov nature of the process. By a happy accident, the very first estimate of the quenching constant (5.12) obtained in Refs. 12 and 13 is the closest to the standard value adopted here. Other Markov estimates, listed in the last two columns, are obtained from it by a simple replacement of τ_0 with $\tilde{\tau}$ and $\overline{\tau}$, respectively.

6. SEPARATION OF QUENCHING MECHANISMS AND STAGES

Comparison of the inequalities given by (4.18) and (5.3) shows that the diffusion and hopping quenching regions are not, in general, in contact with one another. They are separated by a gap in which

$$\delta < \lambda < R_w. \quad (6.1)$$

To describe quenching occurring in this region, and the continuous transition through it between the diffusion and hopping mechanisms, we must adopt a more general approach to the problem. It must be considered as a problem involving a random walk of excitation around the acceptor that produces distant quenching. The stationary Markov formulation of this problem is given by the equation[63,85]

$$-\frac{n(r)}{\tau_0} + \frac{1}{\tau_0} \int f(|\mathbf{r} - \mathbf{r}'|)\, n(r')\, d^3r' = w(r)\, n(r). \quad (6.2)$$

This differs from (4.5) in the same way as the Einstein-Smoluchowski equation differs from the diffusion equation. Because of this generalization, we can proceed either to the diffusion or the hopping limit in this equation.

A. Exchange quenching

It is also possible to solve (6.2) in a general form by taking the kernel in the special form

$$f(r, r') = \frac{\Phi(|r - r'|) - \Phi(r + r')}{8\pi rr'}. \quad (6.3)$$

The kernel chosen in Ref. 63 was

$$\Phi(x) = \frac{\exp(-x/\lambda_0)}{\lambda_0}. \quad (6.4)$$

TABLE II.

Formula	(5.12)	(5.25)	(5.19)		
Numerical factor	$\sqrt{\dfrac{\pi}{3}}$	1	$\sqrt{2}$	$\sqrt{\pi}$	$\sqrt{\dfrac{\pi}{2}}$
Reference	12, 13	84	14, 15	85	33, 86

Strictly speaking, it corresponds to hopping migration of a solvated electron but, in the present context, it is looked upon as a model that has an exact analytic solution. The only parameter of this model is the root mean square hopping length

$$\lambda^2 = 3 \int_0^\infty x^2 \Phi(x)\, dx = 6\lambda_0^2, \qquad (6.5)$$

which also appears in a natural manner in the expression for the diffusion coefficient:

$$D = \frac{\lambda^2}{6\tau_0} = \frac{\lambda_0^2}{\tau_0}. \qquad (6.6)$$

Since the hopping length distribution is exponential, it models only the exchange process which, according to (3.22), is characterized by this behavior for large r.

It was established in Ref. 63 that the general solution of the problem is, as before,

$$k = 4\pi D R_Q, \qquad (6.7)$$

where D is given by (6.6) and R_0 is the parameter in the asymptotic solution (4.12) satisfying (6.2). This solution was found in Ref. 63 for exchange quenching of the form given by (2.1b), neglecting the intrinsic volume of the particles, i.e., for $R_0 = 0$. This enables us to distinguish between mechanisms of distant quenching of triplet excitations migrating over the continuum.

Direct calculations confirm that (4.15) remains in force in the region of diffusion quenching ($L/2 \gg \lambda_0$). In the opposite situation, ($L/2 \ll \lambda_0$), we have

$$R_Q = R_w - \lambda_0 \, \text{th} \, \frac{R_w}{\lambda_0}, \qquad (6.8)$$

where $R_w = L \ln(w_0\tau_0)/2$ is the hopping radius of the black sphere in exchange quenching. In the hopping quenching region ($R_w \ll \lambda_0$), the hyperbolic function in (6.8) can be expanded into a series in the small argument, and this yields

$$R_Q = \frac{R_w^3}{3\lambda_0^2}.$$

Substitution of this together with (6.6) in (6.7) brings us back to (5.13), which describes hopping quenching in the case of exchange interaction. If, on the other hand, $R_w \gg \lambda_0$, we find from (6.8) that

$$R_Q = R_w - \lambda_0. \qquad (6.9)$$

This is the effective quenching radius in the intermediate region defined by (6.1):$L/2 \ll \lambda_0 \ll R_w$. Since this is practically identical with R_w, one is tempted to estimate the rate constant in the intermediate region in the black-sphere approximation, assuming that $k = 4\pi R_w D$. This construction provides us with a basis for considering the quenching mechanism as "mixed," since R_w is the hopping parameter and D the diffusion parameter. This terminology was proposed for the further reason that, in the region defined by (6.1), the black sphere is entered by the excitation in a single hop, whereas the region is crossed (reached) as a result of many hops, which constitute continuous diffusion.

However, closer examination reveals that the black sphere idea is only of heuristic value and of little significance as a computational procedure.[88] Although the error which it
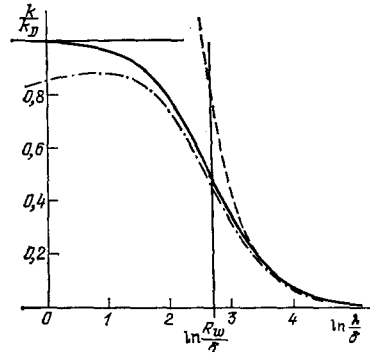

FIG. 9. Transition from diffusion to hopping quenching with increasing λ_0 at constant τ_0. Solid curve—R_Q, broken curve—R_w, dot-dash curve (6.8) (all in units of R_s). $R_w/\delta = 15$.

introduces into the calculated effective quenching radius is small, the error is greater than the difference between the diffusion and hopping estimates of the black-sphere radius in this region:

$$R_w - R_Q = \lambda_0 > \lambda_0 \, \frac{L \ln (2\lambda_0/L)}{\lambda_0} = R_w - R_s.$$

It follows from these relationships that $R_w > R_s > R_Q$ in the intermediate region, since the neglect of λ_0 in (6.9) leads to an illusory increase in the rate constant as compared with the diffusion rate constant, whereas in actual fact there should be a reduction. In other words, as we pass from the diffusion region to the intermediate region, the ratio $k/k_D = R_Q/R_s$ does not increase with increasing λ_0 (as is shown in Fig. 3 of Ref. 63) but, instead, decreases monotonically although very slowly (Fig. 9). Moreover, the difference between the diffusion and mixed mechanisms does not generally vanish[62] when contact quenching is established, i.e., when it occurs in the immediate neighborhood of the acceptor, in a thin layer of thickness $\delta \ll R_s - R_0$. The intermediate region is then absent altogether and diffusion quenching goes over directly into hopping quenching.

B. Dipole quenching

In dipole-dipole distant quenching, the intermediate region is narrower than in exchange quenching. Although the change in the rate constant in this region is not very large, it is very important to know by how much it does change if we wish to solve the inverse problem, namely, determine z from the measured k. The general solution of (6.2) for dipole quenching accelerated by dipole transfer[85] is therefore valuable from this point of view. This solution employs $\tilde{\tau}$ instead of τ_0 and the kernel (3.22) which, after substitution of (3.6) and evaluation of the integral with respect to time, assumes the form

$$f(x) = \rho \left\{ 1 - \frac{1}{2} a\pi \exp \left(\frac{\pi a^2}{4} \right) \left[1 - \Phi \left(\sqrt{\frac{\pi a^2}{4}} \right) \right] \right\}, \qquad (6.10)$$

where $a = 4\pi \rho x^3/3 = (x/\lambda)^3$ and $x = |r - r'|$. Figure 4 shows this distribution over the hopping length. It is a universal function of the single parameter x/λ and, in this, it resembles the nearest-neighbor distribution, but has a somewhat different form. However, the solution of (6.2) with this
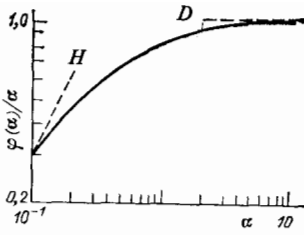
FIG. 10. Rate constant for dipole quenching forced by dipole excitation transfer as a function of $\alpha = \frac{1}{2}(C_{DA}/C_{DD})^{1/4}$. Broken line shows the behavior of this quantity in regions where hopping (H) and diffusion (D) approximations are valid.

kernel can only be accomplished by numerical methods. The result[85] is shown in Fig. 10 which plots $\varphi(\alpha)/\alpha = k/k_D$, i.e., the same quantity as Fig. 9, against $\alpha \approx z^{1/4}/2$. It is clear that the estimates of k obtained in the diffusion and hopping limits are asymptotic values obtained for the general solution as $z \to \infty$ and $z \to 0$, respectively, as is indeed indicated by their respective validity criteria given by (4.19a) and (5.4a). We do not know *a priori* how strong these inequalities are because this depends on the numerical coefficients in (4.19) and (5.4), which are not known exactly. Figure 10 throws some light on this question. It is clear from this figure that k can be calculated to within about 10% from the asymptotic formulas (4.21) and (5.12), using τ_0 instead of $\bar\tau$, and this can be done everywhere with the exception of the intermediate region defined by

$$0{,}2 < \alpha < 2 \quad \text{or} \quad 3 \cdot 10^{-2} < z < 3 \cdot 10^2. \quad (6.11)$$

Since the rate constant changes across this region by only an order of magnitude, it is clear that it must be measured with high precision in order to enable us to use this type of graph as a way of determining the value of z for which quenching occurs.

The theoretical curve shown in the figure must also be highly accurate because the reliability of the solution of the inverse problem depends upon it. On the other hand, we have seen that, in the present state of the theory, even its asymptotic behavior is known only to within factors of the order of unity.

In view of this, the most widely used method of identifying the quenching mechanism is to test it for self-consistency. The static quenching kinetics is examined in the limit of slow migration (low donor concentration and high acceptor concentration) and the quantity C_{DA} is determined. The rate constant k is then measured in the diametrically opposite situation (fast migration) and, knowing C_{DA}, the quantity C_{DD} is calculated from the asymptotic formula corresponding to the diffusion or hopping mechanism. If the value of C_{DD} obtained in this way corresponds to the validity criterion for this formula ($C_{DD} \ll C_{DA}$ for the diffusion mechanism and $C_{DD} \gg C_{DA}$ for the hopping mechanism), the method used to process the data is self-consistent. An alternative quenching mechanism has to be chosen when this is not so.

C. Kinetic limit

In some cases, these mechanisms can be distinguished phenomenologically. We refer here to solid solutions in which all the lattice sites are occupied by donors up to the limiting concentration ρ_0 corresponding to their ordered disposition. The situation prevailing in the LaF_3–NdF_3 system investigated in Ref. 89 is of this type. The authors of Ref. 89 conclude that the kinetic quenching-rate limit can be reached only for the hopping mechanism whereas, for the diffusion mechanism, the rate should increase without saturation for $\rho \leqslant \rho_0$.

The validity of this conclusion can be justified on the basis of asymptotic estimates of the constants. It is convenient to introduce the following generalized concentrations:

$$\tilde c = \frac{4}{3}\pi \sqrt{\overline{C_{DA}}}\, c, \quad \tilde\rho = \frac{4}{3}\pi \sqrt{\overline{C_{DD}}}\,\rho, \quad (6.12)$$

in terms of which the rates of static dipole quenching $(q = \pi\tilde c^2)$ and delocalization $(1/\tau_0 = \pi\tilde\rho^2/6)$ can be universally expressed. The kinetic rate constant deduced from (5.12a) for $R_0 \gg R_w$ depends on $\bar\rho_0 = \sqrt{C_{DD}}/R_0^3$, if we suppose that $\rho_0 = (4\pi R_0^3/3)^{-1}$, so that

$$\overline{W}_0 = ck_0 = \sqrt{\tilde z\,\tilde c\,\tilde\rho_0}. \quad (6.13)$$

The diffusion quenching rate with the constant given by (4.21) has the form

$$\overline{W}_D = \frac{0{,}5\alpha^{3/4}\tilde c\,\tilde\rho}{z^{1/4}}, \quad (6.14)$$

whereas the hopping rate with the constant given by (5.12) is independent of z:

$$\overline{W}_J = 1{,}1\tilde c\,\tilde\rho. \quad (6.15)$$

It is now necessary to establish a common measure for the quenching rate so as to be able to determine how it varies between the static and kinetic stages. This is usually taken to be the "stationary quenching probability" W_s defined by

$$\frac{1}{W_s} = \int_0^\infty N(t)\,dt. \quad (6.16)$$

It was first introduced in Ref. 90 and has since been widely used to characterize nonexponentially developing processes,[1,3,91] such as, for example, static quenching. When quenching occurs well in advance of intracenter decay of the excitation, the stationary probability determines the luminescence yield:

$$\eta = \frac{1}{1 + W_s\tau_D} \approx \frac{1}{W_s\tau_D} \ll 1.$$

Setting $N(t) = N_0(t)$, we can readily show that, for static dipole quenching,

$$W_s = \frac{q}{2} = \frac{\pi\tilde c^2}{2}, \quad (6.17)$$

whereas, on the migration-accelerated stage of hopping quenching, we have, according to (5.14b) and (5.15)

$$W_s \approx ck(1 + \delta c) \approx \tilde c\,\tilde\rho\left(1 + \frac{\sqrt{\frac{3\pi}{8}}\,\tilde c}{\tilde\rho}\right) = \tilde c\,\tilde\rho + \sqrt{\frac{3\pi}{8}}\,\tilde c^2.$$

$$(6.18)$$

The second term in parentheses is a measure of the fraction of particles in the interior of the black spheres at the instant of excitation of the system, which decay, without leaving
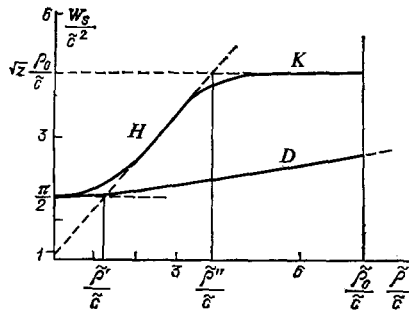
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FIG. 11. W_s as a function of $\tilde\rho$ for $\tilde c = $ const for the diffusion (D) and hopping (H) variant of the theory. Broken lines show asymptotic estimates of the quenching rate. K shows the kinetic limit.
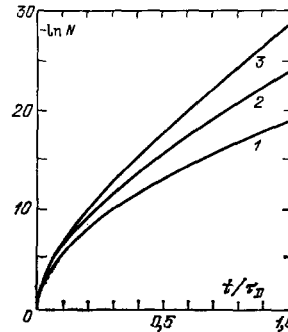

FIG. 12. Concentration quenching kinetics for $z = 1.6 \times 10^4$ (1), 1 (2), and 6.3×10^{-3} (3). Calculated in the three-particle approximation.[93]

them, during the so-called "instantaneous" or quasistatic quenching stage.[1]

A rough estimate for the separation boundary between static and hopping quenching can be established by equating the two rates given by (6.17) and (6.18). This yields

$$\tilde\rho' = \frac{\pi\tilde c}{2}. \tag{6.19}$$

This concentration is much smaller than $\bar\rho_0$ because, right from the outset, we adopted the condition $\tilde c \ll \bar\rho_0$, (2.5), which ensures disorder in the distribution of acceptors. The separation boundary between hopping and kinetic quenching can be established in a similar way, i.e., by equating (6.18) and (6.13). The result is

$$\tilde\rho'' = \sqrt{z}\,\rho_0. \tag{6.20}$$

The result obtained in precisely the same way for the diffusion mechanism turns out to lie outside the interval $(0, \bar\rho_0)$. The maximum diffusion rate, reached for $\bar\rho = \bar\rho_0$, is $\alpha^{3/4}\tilde c\rho_0 / 2z^{1/4}$. Figure 11 illustrates these results by showing $W_s(\tilde\rho)$ for the diffusion and hopping mechanisms of quenching. Since the kinetic limit of the quenching rate cannot be reached in the case of diffusion, it is clear that the hopping mechanism is more likely when the limit is detected.

D. Quasistatic quenching

As a rule, the Laplace transform of the quenching kinetics

$$\tilde N(s) = \int_0^\infty N(t)\,e^{-st}\,dt$$

is more readily evaluated than the kinetics itself. This can then be used to obtain a more realistic idea about the function $W_s = (\tilde\rho) = 1/\tilde N(0)$. It turns out that migration produces an appreciable acceleration of quenching even for $\bar\rho < \rho'$.

---

[1]We note in this connection that an empirical formula for W_s was put forward in Ref. 92. It appears to provide the best approximation to the computer simulations of hopping quenching performed in that paper. In particular, it follows from this formula that all the theoretical estimates of the rate of this process are too high by a substantial factor. However, this conclusion and the approximation upon which it is based do not inspire confidence. The approximation does not provide a qualitatively correct description of the concentration dependence of instantaneous quenching, since it gives it as a linear function of $\tilde c$ rather than the quadratic function of (6.18).

This is confirmed by direct calculations of the process kinetics for $\bar\rho = \tilde c$, which was performed in Ref. 93 by partial summation of the series in the so-called three-particle approximation. It is clear from Fig. 12 that the quenching process develops nonexponentially for a considerable time, and is forced by migration to a lesser extent as z increases.

This is in qualitative agreement with expectations based on (6.14) and (6.15), but quantitative comparisons with these expressions are invalid because they hold for $\bar\rho \gg \tilde c$. It follows that the extent to which the partial summation method agrees with Markov or non-Markov theories of concentration quenching is still an open question. However, it is noted in Ref. 93 that the results are independent of z in the two-particle approximation, i.e., they do not distinguish between the hopping and diffusion quenching. Worse than that, the static quenching kinetics $N_0(t)$ is not reproduced in the two-particle approximation and, even in the three-particle approximation, it provides a satisfactory description of only the initial stage (Fig. 13). Judging by these results and by Fig. 5, partial summation methods cannot be regarded as any better than model-based theories of the phenomenon.

7. SELF-QUENCHING

In some systems, concentration quenching occurs even in the absence of acceptors. It occurs in the course of cross relaxation which ensures that the excitation is shared between two interacting donors. It is clear that this process is possible only whenever the donor energy spectrum contains
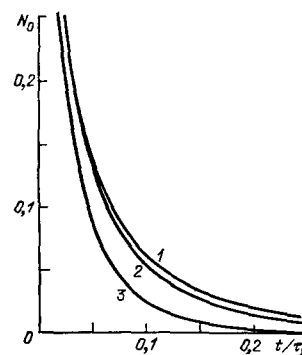

FIG. 13. Static quenching kinetics for[93] $\tilde c\sqrt{\tau_D} = 5$. 1—Förster (exact) solution, 2—three-particle approximation, 3—two-particle approximation.
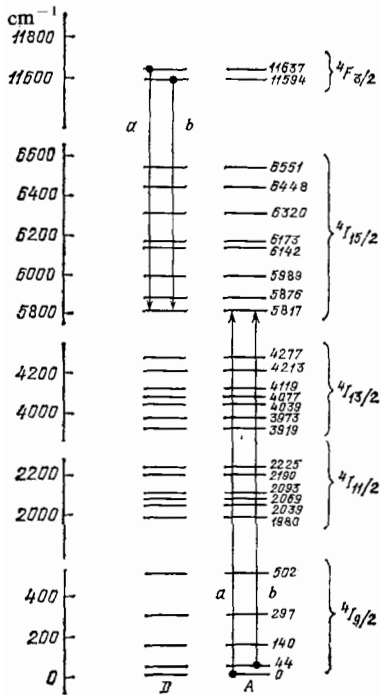
FIG. 14. Resonance cross-relaxation in Nd^{3+}, proceeding from the excited Stark sublevel of the donor (a) or acceptor (b) (Ref. 89).

an intermediate level lying roughly half-way between the ground and the excited states.

The spectrum of one of the rare-earth activators, namely, the ion Nd^{3+}, is precisely of this type. Cross relaxation can occur along two channels in this case. The most important is the resonance channel. It starts from one of the excited Stark sublevels of the ground or luminescing states (Fig. 14), so that

$$C_{DA}(T) \propto \exp\left(-\frac{\Delta E}{T}\right). \tag{7.1}$$

Cross relaxation occurring in the second channel excites the ion from the $^4I_{9/2}$ ground state to the $^4I_{15/2}$ excited state via the high-frequency transition of the partner from $^4F_{3/2}$ to $^4I_{13/2}$. It does not depend on T (C_{DA} = const) but is a highly exothermal process accompanied by the release of a large number of phonons into the lattice. This means that, by virtue of the Frank-Condon principle, the second channel is much less effective than the first, and can be ignored at high temperatures. This is the situation at least in LaF_3–NdF_3 crystals above 120 K, where the second channel predominates over the first[89] only for $T < 45$ K. The activation energy in (7.1) is a minimum at such low temperatures and is equal to 40 cm^{-1}, which corresponds to the gap between the lowest Stark components of the ground and luminescing states. For $T > 45$ K, the activation energy ΔE increases with temperature because the population of the higher-lying Stark components of the ground state accelerates the resonance cross relaxation. At room and higher temperatures, ΔE approaches[12] 300 cm^{-1}.

Another example of self-quenching in a liquid solution is the cross relaxation of vibrationally excited molecules, investigated by picosecond spectroscopy in Ref. 94. As a result
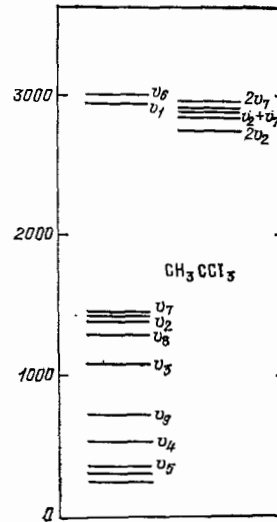

FIG. 15. Frequencies of normal vibrations of the CH_3CCl_3 molecule and some of the overtones and combination modes (in cm^{-1}).[94]

of intramolecular conversion, the initially excited symmetric stretching mode of the CH_3 group very rapidly transfers energy to overtones of low-frequency vibrations of the molecule that are in resonance with it, so that the energy is eventually equally distributed among them (Fig. 15). At least one of the overtones, namely, the doubly excited vibration v_7, can then experience cross relaxation in which it is replaced by two single-quantum excitations of the two molecules D and D' that interact via the dipole–dipole mechanism:[94]

$$2v_7 (D) \rightarrow v_7 (D) + v_7 (D'). \tag{7.2}$$
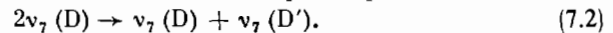
Molecular diffusion in liquids is usually too slow to accelerate the dipole-dipole quenching process. There is also direct evidence that (7.2) is a reaction due to energy transfer: its rate is a quadratic function of the concentration ρ of the molecules.[94] At the same time, it is not a static process because it develops exponentially in time rather than in accordance with the Förster law (2.3a). The alternative explanation[94] is that the self-quenching process (7.2) is forced by resonance migration of single-quantum excitation.

A. Difficulties of the continuous random walk theory

Resonance excitation transfer is also found to occur in neodymium. It has therefore been assumed right from the outset[12] that it is responsible for the exponentialization and acceleration of the self-quenching process. However, it was considered self-evident that the rate of this process could be found from the formula $\overline{W} = ck$ by assuming that

$$c \equiv \rho. \tag{7.3}$$

It is only recently that it has become clear that this is not obvious and, generally speaking, self-quenching is not a special case of quenching, as would appear at first sight.[84] Even if the total cross-relaxation probability W and the total outflow probability U vary with time in an uncorrelated manner, which was assumed in the derivation of (5.20) in Refs. 15 and 83, they are, nevertheless, strictly correlated in self-quenching in any time section of the process. For example,

when quenching and transfer are due to interactions of the same multipolarity, it is obvious that

$$\frac{W}{U} = \frac{C_{DA}}{C_{DD}} = z = \text{const},\qquad(7.4)$$

whatever the specific environment of the excited molecule. When it is such that the quenching rate is higher, the rate of outflow is higher by a comparable factor. This means that, whatever the center on which the excitation happens to reside during resonance migration, it is always quenched on it to the same degree, i.e., $W\bar{T} = W/U = z$. When $z \ll 1$, strong quenching does not occur anywhere and the rate of quenching can be found by simply multiplying z by the mean hopping frequency $1/\tilde{\tau}$. Using (3.8), we find that, for dipole quenching,

$$\overline{W} = \frac{z}{\tilde{\tau}} = \frac{3z}{\tau_0} = \frac{8\pi^3 C_{DA}\rho^2}{9}.\qquad(7.5)$$

In contrast to what can be obtained from (5.22) with the aid of (7.3), this rate is independent of C_{DD}, since we appear to be dealing with the kinetic limit. This generality is explained by the fact that, for $z \ll 1$, self-quenching is considered weak in both the migrationally-accelerated and kinetic stages.

The same conclusion is arrived at when one introduces the kinetic equation for self-quenching on the basis of the assumptions usually employed in the theory of continuous random walks.[15,83] The specificity of self-quenching is merely that, instead of two independent averages being evaluated over the acceptor and donor configurations, which lead to the product $N_0(t)R_0(t)$ in (5.20), the averaging of quenching and outflow must be performed simultaneously over the single distribution present in the single-component system of centers. The resulting equation is different from (5.20), and its solution for $z \ll 1$ decays exponentially at the rate indicated by[84] (7.5).

B. Allowance for the return of excitation

However, this method of analysis and derivation, which considers the outflow on a par with quenching as an irreversible process, can be criticized on a number of grounds. Even when the particle configuration surrounding the excitation, defined by the set of relative coordinates $\{r_i\}$, changes in an uncorrelated manner after each hop of the excitation, this does not mean that the average time $\bar{T}$ spent in the center is $1/U$. The maximum contribution to $U = \sum_i u(r_i)$ is provided by the center closest to the excited center, but it is precisely from this center that the excitation frequently returns to the original center before it finally leaves the pair. This substantially increases the time $\bar{t}$ and enhances quenching in pairs for which $W\bar{t} \gg 1 \gg W/U$. According to the recipe proposed in Ref. 22, this can be taken into account by introducing the replacement

$$\exp\left(-Ut\right) = \prod_i \exp\left[-u(r_i)\,t\right] \to \prod_i n(r_i,\,t),$$

where $n(r_i,t)$ is defined by (3.10). Leaving the derivation unaltered in all other respects, we readily obtain[84]

$$N(t) = F(t) - \int_0^t \Phi(t - t')\,N(t')\,dt',\qquad(7.6)$$

where

$$F(t) = \left\langle \exp\left(-Wt\right)\prod_i n(r_i,\,t)\right\rangle,\qquad(7.7a)$$

$$\Phi(t) = \left\langle \exp\left(-Wt\right)\frac{d}{dt}\prod_i n(r_i,\,t)\right\rangle,\qquad(7.7b)$$

and the angle brackets represent averaging over the randomly distributed surrounding particles.

For quenching by alien impurities, the averages over W and $\{r_i\}$ are independent and are performed in the usual way with the consequence that we again obtain (5.23) after the substitution of the results in (7.6). If, on the other hand, we are concerned with self-quenching, we find that $W = \sum_i w(r_i)$ depends on the same coordinates as $n(r_i,t)$, so that a different equation is obtained, namely,

$$N(t) = N_0\left(\frac{\rho}{2},\ t\right) R\left(t\left(1 + \frac{z}{2}\right)\right)$$
$$- \int_0^t \dot{R}\left((t - t')\left(1 + \frac{z}{2}\right)\right) N_0\left(\frac{\rho}{2},\ t - t'\right) N\,dt'.\qquad(7.8)$$

When $z \ll 1$, this equation differs from (5.23) only by the fact that $N_0(c,t)$ has been replaced with $N_0(\rho/2,t)$, so that its quasiexponential solution decays at the rate

$$\overline{W} = -\frac{\rho}{2\tilde{\tau}} \int Q(t)\,\dot{R}(t)\,dt.\qquad(7.9)$$

Using (2.6) and (3.12), we obtain the following result for self-quenching:[84]

$$\overline{W} = \begin{cases} k_0\rho = \left(\dfrac{4\pi}{3}\right)^2 C_{DA}\rho_0\rho, & \rho \gg \rho'', \qquad(7.10a) \\[2ex] \dfrac{4\pi^3}{9\sqrt{2}}\sqrt{C_{DA}C_{DD}}\,\rho^2, & \rho \ll \rho''. \qquad(7.10b) \end{cases}$$

The same result can be obtained from the corresponding formulas for ordinary quenching if, instead of (7.3), we use $c = \rho/2$. However, it is not altogether clear whether this has any advantages as compared with (7.3). Even if we allow for the return of excitation, we take into account only quenching at the original center, and this occurs at the same rate whatever the localization of excitation in the interacting pair.

C. Quenching pairs

From this point of view, it would be more rigorous to consider a pair of closely spaced impurities as a single quenching center to which excitation migrates over single centers, experiencing practically no cross-relaxation upon them.[95] This picture of the phenomenon corresponds to an initial Markov representation with the equivalent lattice augmented by the concept of a quenching pair. Of course, this is meaningful only when the concentration c of such pairs is small in comparison with the total concentration ρ of the impurities. This condition must be verified even when the system is so diluted that the formation of clusters of three or more particles has a low probability.

We shall refer to the quenching pair as a two-particle cluster in which quenching is strong in the sense that (5.1) is satisfied. In other words, acceptors will be pairs in which the separation between the particles is $r \leqslant R_W$. This definition is

essentially different from that used in Ref. 96 if the acceptors are taken to be particles at the distance R_0 of closest approach. The probability that a black sphere of radius R_w drawn around one center is entered by another center is $\rho 4\pi R_w^3/3$, and the number of such pairs per unit volume is

$$c = \frac{1}{2}\rho^2 \cdot \frac{4\pi R_w^3}{3} = \rho \sqrt{\frac{z}{\pi}} \; ; \tag{7.11}$$

where R_w is defined as in (5.2) with $n = m = 6$ and we have also noted the fact that each particle is taken into account twice when probabilities are simply added. It is clear that the number of quenching pairs is quite small precisely when $z \ll 1$, from which inequality the results given by (7.10) are seen to stem.

We may now estimate the rate of migrationally-accelerated quenching, assuming that it occurs only when excitation reaches a quenching pair in the course of a random walk over the equivalent lattice. Since the pairs are part of the lattice, the transfer of energy to them proceeds at precisely the same rate as to single centers: $C_{DA} = C_{DD}$. The concentration of the latter is $\rho - 2c$, and the probability of hitting a pair is obviously $p = c/(\rho - c) \approx c/\rho$. Multiplying it by the hopping frequency $1/\bar{\tau}$, we obtain a very approximate estimate for the rate of quenching

$$\overline{W} = \frac{p}{\tau} \approx \frac{c}{\rho\bar{\tau}} \cdot \tag{7.12}$$

This is the same as the estimate made in Ref. 97, where the migrationally-accelerated quenching of electronic excitation of rhodamine 6G in a glycerin solution was brought about by dimers of the same dye. The only difference was that the dimerized molecules are stable complexes bound together by an interaction, and their concentration is $c = K_T\rho^2$ (K_T is the monomer-type equilibrium constant). In contrast to (7.11), it increases quadratically with ρ and this leads to the cubic function $\overline{W}(\rho)$ observed experimentally.[97]

If, on the other hand, we substitute (7.11) and (3.14a) in (7.12), we obtain

$$\overline{W} = \frac{4\pi^{5/2}}{9}\sqrt{C_{DA}C_{DD}}\,\rho^2. \tag{7.13}$$

This result is smaller by a factor of only $\sqrt{\pi/2}$ as compared with (7.10b), and by a factor of $\sqrt{2/3}$ obtained elsewhere[95] by a somewhat different method. These differences are not unexpected because the estimate of the concentration of quenching pairs was, to some extent, arbitrary.

Strictly speaking, the expression given by (7.12) is valid only to within a numerical factor. The theory of continuous random walks gives a more rigorous expression than (7.12) for the rate of quenching corresponding to $z = C_{DA}/C_{DD} = 1$. Assuming that the number of hops per unit time is $1/\bar{\tau}$, the theory takes into account the self-crossing of trajectories with the result that some of the centers are visited by an excitation more than once. Repeated visitations have no effect on an excitation, and it is only a hop to a new center that can be the last with probability p. We must therefore take into account not all the hops $1/\bar{\tau}$ but only the fraction $a/\bar{\tau}$ that takes the excitation to new centers:[98]

$$\overline{W} = \frac{ap}{\tau} \cdot \tag{7.14}$$

In ordered structures, $a = 1/\xi$ is very sensitive to the geometry of the "equivalent" lattice (see Table I). However, computer experiments have enabled us to determine a for disordered structures:[99] $a \simeq 1/2$ for the dipole-dipole interaction. Equation (7.12) then turns out to be fortuitously exact, since $\bar{\bar{\tau}} = 2\bar{\tau}$ according to (3.14a). We note that the rate of quenching at $z = 1$, calculated from (7.14), is smaller by a factor of only $\sqrt{2}$ as compared with the extrapolation to this point of equation (5.25) which refers to hopping quenching.

D. Static self-quenching

When $z \gg 1$, the isolation of quenching pairs from a random ensemble of centers becomes meaningless, and the situation must be judged in the light of (7.8) transformed to

$$N = N_0(t) - \frac{1}{z}\int_0^t \dot{N}_0(t-t')\,N(t')\,dt'. \tag{7.15}$$

Solving this by iteration, we find in the first approximation that

$$N = N_0(t) = \exp\left(-\sqrt{\frac{16\pi^3 C_{DA}\rho^2 t}{9}}\right). \tag{7.16}$$

In contrast to (7.15), this result is valid independently of whether the environment varies in an uncorrelated manner. It corresponds to static self-quenching which alone remains when resonance excitation transfer is turned off. It sets the lower limit for the rate of the process as $C_{DD} \to 0$ (Fig. 16).

It is clear that the hopping and diffusion mechanisms are not the alternatives in self-quenching. We have either migrationally-accelerated self-quenching $(z \ll 1)$ or static quenching $(z \gg 1)$. The former includes the kinetic stage of the process that is attained at moderate concentrations. The latter, on the other hand, persists at all concentrations (except the very highest) that approach close packing. When $\rho \approx \rho_0$, static quenching must be described by the more general formula put forward in Refs. 19 and 100. It describes the transition from the nonexponential kinetics (7.16) to the strictly exponential decay in a crystal containing a continuous distribution of the activator in which disorder in the disposition of the particles has been totally eradicated. The kinetics of the quenching process in the region of the transition from the disordered to the ordered system of centers was examined in detail with the aid of this formula in Ref. 101.
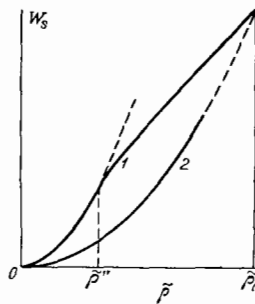

FIG 16. Stationary probability of self-quenching: accelerated by migration (1) and static (2).

8. EXPERIMENTAL CONFIRMATION OF THE THEORY

When experimental data are interpreted, it is very important to make the correct choice between the diffusion and hopping quenching mechanisms. The solution of this problem depends on which particular type of quenching—exchange or multipole—prevails in the system. For exchange quenching, the diffusion mechanism is very unlikely because (4.20) is not satisfied in a dilute set of donors. If, on the other hand, both quenching and energy transfer are of the dipole-dipole type, everything is determined by the ratio $C_{DA}/C_{DD} = z$ which, in principle, can be either large or small, depending on the particular activator and quencher. There is even evidence that the inequality $z \lessgtr 1$ can change sign within a particular temperature range, thus demonstrating the transition from diffusion to hopping quenching.[102]

A. Interatomic excitation transfer

However, as a rule, when the diffusion mechanism is given preference, this is only because the hopping mechanism is not considered as an alternative and the results are not checked for self-consistency.[31,103] This approach can be used readily to extend the diffusion description even to the self-quenching of neodymium[32] despite the fact that the hopping mechanism is not an alternative in this case. However, in the first papers devoted to concentration quenching of neodymium in crystals and silicate glasses,[12,104] measurements of the rates of static and migrationally-accelerated processes were used to determine the constants C_{DA} and C_{DD} and to demonstrate that they satisfied the hopping quenching criterion (5.4a): $C_{DD} \gg C_{DA}$. At the same time, it became clear that the activation energy of the quenching constant which, by virtue of (5.25) and (7.1), is equal to $\Delta E/2$, was in good agreement with the splitting of the Stark components of the ground and excited states.[12,89]

It was shown subsequently that C_{DA} could be determined using not only the disordered (Förster) stage of static quenching, but also the earlier, though shorter, ordered stage.[17,18,89,104] During this stage, the process develops exponentially at the rate ρk_0, the constant for which is given by (2.10). In addition to these two static stages, a study was also made in these papers of the concluding migrationally-accelerated stage that occurred exponentially. When $\ln \ln N$ is plotted against $\ln t$, the initial and concluding exponential stages are represented by straight lines of unit slope, but the intervening disordered stage of dipole-dipole quenching, which is nonstationary in time, has a slope of one-half (Fig. 17). The constants C_{DA} found for these two stages of static quenching are usually in good agreement with one another when R_0 is determined from crystallographic data.[17,18] The reverse formulation of the problem is also valid: R_0 can be determined from the kinetic rate constant if C_{DA} has been found from the kinetics of the disordered static quenching. It is precisely in this way that the distance of closest approach of luminescing impurities and quenching centers has been established in glasses for the dipole-quadrupole interaction between them.[105]

When static quenching is investigated with a view to determining C_{DA}, it is desirable to have systems with a high
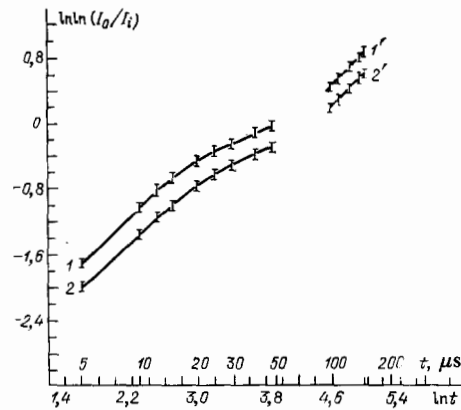

FIG. 17. Relative luminescence intensity $N = I_1/I_0$ (I_0 corresponds to infinitely diluted solution) as a function of time t since the instant of excitation.[104] Recorded at $T = 4.2$ K for two concentrations of Nd^{3+} in $YAlO_3$: 2.5 (1) and 1.8 (2) at.%. Primed numbers show the concluding exponential stage (for the same concentrations).

concentration of acceptors $(\tilde{c} > \tilde{\rho})$. Hopping quenching, on the other hand, must be investigated in systems in which the number of donors is greater than that of acceptors $(\tilde{\rho} > \tilde{c})$. By taking all these data together, we can find C_{DD} from (5.25) if the quenching process is of the hopping type. This method has been used to determine $C_{DA}(T)$ and $C_{DD}(T)$ for LaF_3–NdF_3 crystals over a broad temperature range.[89] It has therefore become possible to provide a microscopic interpretation of the temperature dependence $C_{DD}(T)$ in terms of homogeneous and inhomogeneous broadening of lines due to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition over which migration in Nd_3^+ takes place.[89] It has also been established[89] that the kinetic limit of quenching, for which the rate on the concluding stage is comparable with the initial rate, is reached for activator concentrations $\rho > 5$ at.%, and the region of static disordered quenching is then totally excluded. This corresponds to the exponential development of the process along the entire time axis with the maximum possible quenching rate ck_0.

In two-component crystals of the form[106] $La_{1-x-y} Nd_x Ln_y P_5O_{14}$, where the energy donor is Nd and the acceptors (Ln) are Tb or Eu, we can follow the transition from hopping quenching to the kinetic limit as $x = \rho/\rho_0$ is increased (Fig. 18). This transition can be described semiquantitatively by (5.12a), but a more accurate expression has also been used.[106] The latter was obtained by replacing the integral over space in (5.11) by the lattice sum over the specific crystal structure. It is clear from Fig. 18 that this results in excellent agreement between theory and experiment. Moreover, the very fact that the kinetic limit is reached can be regarded as clear evidence for the hopping quenching mechanism. This is also indicated by the ratio of C_{DA} to C_{DD}, which turns out to be[106] 0.09 for the pair Nd-Tb and $z = 0.05$ for the pair Nd-Eu.

The existence of the kinetic limit predicted in Ref. 13 is important not only from the standpoint of the hopping mechanism, but also because it ensures that higher activator concentrations do not enhance quenching. This opens up a way for a significant improvement in the parameters of active media exhibiting this property. It is also valid for self-
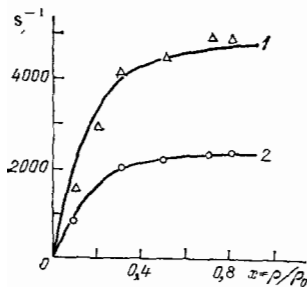
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FIG. 18. Rate of hopping quenching as a function of relative donor concentration $x = \rho/\rho_0$ during the quenching of Nd^{3+} ions by impurity centers: Tb (1) and Eu (2) [Ref. 106]. The points are experimental and the solid curves theoretical.
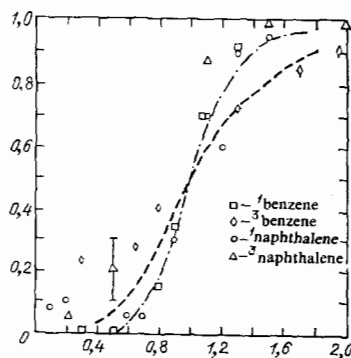

FIG. 19. Luminescence yield of acceptors as a function of donor concentration. Broken curve corresponds to $r = 4$ and the dot-dash curve to $r = 7$ [Ref. 68].

quenching because losses in the kinetic limit are lower than in the migrationally-accelerated stage, and increase linearly rather than quadratically with density (see Fig. 16). These considerations provide us with a basis for systematic searches for media with anomalously low concentration quenching of luminescence.[107-110] The theory of hopping quenching is used not only to determine transfer constants from kinetic data, but also to determine the optimum concentrations of active particles in solid-state lasers.[111] The decay kinetics of donor luminescence can be used to judge the evolution in time of the excited state of the acceptor, and the kinetics of sensitized luminescence depends on this process.[112,113] Systematic exploitation of the sensitization effect has resulted in an increase in the efficiency of existing solid-state lasers by a substantial factor.[114,115]

B. Molecular transfer of excitation

The intermolecular transfer of electronic excitation has been investigated to a lesser extent than interatomic transfer. There have been individual studies of the kinetics of static quenching of triplets[116,118] that were unrelated to concentration quenching. As a rule, the latter is investigated by stationary methods and information about it is obtained from the concentration dependence of the luminescence yield[3]

$$\eta = \frac{1}{1 + W_s \tau_D} = \frac{1}{\tau_D} \int_0^\infty N(t)\, e^{-t/\tau_D}\, dt. \qquad (8.1)$$

This expression is essentially a definition of W_s that is more general than that given by (6.16) because it is valid for any $W_s \tau_D \gtrless$. In particular, if follows from it that, in the migrationally-accelerated stage for which $N(t) = \exp(-\overline{W}t)$ along the entire time axis, we have $W_s \approx \overline{W}$. The fraction of excitations transferred to acceptors is then

$$P = 1 - \eta = \frac{\overline{W}\tau_D}{1 + \overline{W}\tau_D}. \qquad (8.2)$$

In solid molecular solutions, it is frequently the case that both donors ("traps") and acceptors ("supertraps") of excitation can luminesce, and do so with the same yield if there is no energy transfer between them. Equation (8.2) then provides us with a measure of the ratio of the luminescence intensity I_A due to acceptors to the total intensity due to all impurities: $1 - \eta = I_A/(I_D + I_A)$. At least, this is the situation in crystals of deuterated naphthalene[119,120] or benzene.[120,121] The excitation traps in these crystals are proton-

ated molecules whose concentration does not exceed a few percent. The supertraps whose impurity levels lie lower, and whose concentrations are lower still, are β-methly naphthalene (in naphthalene) and pyrazine (in benzene). The transfer from traps to supertraps of both singlet and triplet excitation was investigated in both these systems, whereas the transfer of triplet excitation from protonated molecules to their dimers was studied in phenazine crystals.[122] In all these cases, as soon as a certain specific trap concentration was reached, the luminescence stopped and was replaced by luminescence by supertraps which grew rapidly and reached the same level despite the fact that their concentration was lower by several orders of magnitude (Fig. 19).

These data have been interpreted semiquantitatively[68] as the result of hopping quenching of excitation by supertraps in the course of the random walk of the excitation over these traps. The rate of hopping quenching was estimated from the formula

$$\overline{W} = \frac{1 - N_0(\tau_h)}{\tau_h} \approx \frac{cQ(\tau_h)}{\tau_h} = ck. \qquad (8.3)$$

This approximate estimate is in obvious agreement with (5.24) if one supposes that the time distribution has the form $\delta(t - \tau_h)$. We have already noted in Section 5 that the use of τ_h instead of $\overline{\tau}$ in multipole quenching affects only the numerical factor and not the functional form of $k(\rho)$. When $n = m$, this functional form is shown by (5.5) to be

$$k \approx C_{DA}^{3/n} C_{DD}^{1-(3/n)} \rho^{(n/3)-1}. \qquad (8.4)$$

The same form of $k(\rho)$ is obtained from (4.20) for diffusion quenching. It remains practically the same even if we suppose that the diffusion quenching length is unaltered—an assumption that is sometimes introduced[123] in very approximate estimates of k. As far as experimental data are concerned, they can be satisfactorily explained if $k \sim \rho^r$ and $4 < r < 7$ (Fig. 19). To achieve agreement with theory, it was assumed in Ref. 68 that $n = 14$, which corresponds to the octupole–octupole interaction.

The data can be explained with equal success if one assumes that both transfer and quenching are of exchange type. Although the dependence on ρ in (5.6) is not of the power type, it can explain the rapid variation in η near the critical concentration $\rho_{1/2}$ given by $\eta(\rho_{1/2}) = 1/2$. We note,

however, that the use of τ_h instead of $\bar{\tau}$ in this case produces a functional change in $k(\rho)$ to the extent that three-dimensional migration is replaced by two-dimensional migration which is regarded in Ref. 68 as an alternative and in Ref. 124 as the only possibility.

The yield was calculated from the general formula (8.1) in Ref. 124 by taking the Laplace transform of the excitation quenching kinetics for an excitation migrating over traps distributed randomly on a plane. We have already shown that, for the hopping quenching mechanism, this estimate of η has no advantages as compared with the simple formula given by (8.2) and used for the same purpose in Ref. 68. Moreover, the results obtained in these two papers are identical despite the fact that the two-particle method of summation used in Ref. 124 to calculate $N(t)$ is far from perfect. On the other hand, it is instructive to note that, when this method is applied to a finite-range interaction, it leads to a more rapid transition near the critical concentration $\rho_{1/2}$ than that observed experimentally. This is interpreted in Ref. 124 as an argument *against* the percolation theory which ignores long-range effects characteristic of multipole transfer.[124,125] It has recently become clear that the percolation interpretation of the phenomenon[126,127] in the case of the transfer of singlet excitation in naphthalene is, at best, satisfactory at very low temperatures (1.8 K), whereas the hopping theory is to be preferred[128] even at 4 K (it is incorrectly referred to as the "diffusion theory" in Ref. 128).

Inhomogeneous broadening of impurity levels, which can be due to the same interaction as excitation transfer,[129] is very important at low temperatures. Spatial transfer is then accompanied by a change in energy and therefore proceeds at a different rate in forward and reverse directions. This may give rise to the localization of a fraction of the interactions on clusterized traps producing an energy "pocket" which prevents them from reaching the supertraps. At least this is the way in which the authors of Ref. 130 explain the reduction with increasing concentration in the fraction of triplet excitations reaching supertraps under laser excitation of phosphorescence in naphthalene. However, the subsequent increase in concentration of traps facilitates the introduction of a large number of clusters into the conjugated chain, and the yield of phosphorescence from β-methyl naphthalene is partially restored.[130] To examine this phenomenon in greater detail, we must investigate the kinetics of the process as in Ref. 131, and study the energy (frequency) migration in pure form (in binary systems without supertraps) under coherent excitation of luminescence. It was shown in Ref. 132 that this can be accomplished in triplet-triplet transfer to the same extent as in interatomic transfer.[23]

C. Transfer of spin excitation

Longitudinal spin relaxation in an external magnetic field, which can be investigated by the method of electron spin resonance, is none other than dissipation of spin excitation by the transfer of the energy of a Zeeman quantum to the ambient medium.[133] In this case, we are concerned with excess excitations as compared with their equilibrium concentration which, at normal temperatures, is equal to half the total concentration of particles. Hence the attainment of equilibrium occurs twice as fast, i.e., at the rate $1/T_1 = 2\tau_D$ in the case of spin-lattice relaxation and $2w$ when the excitation is quenched by spin exchange with a rapidly-relaxing paramagnetic impurity.

Spin excitations produced on the hydrogen atom (donor) are quenched by paramagnetic ions of many metals, including Cu^{2+}, Mn^{2+}, Fe^{2+}, Ce^{2+}, Co^{2+}, and Ni^{2+}, the longitudinal relaxation of which ranges from 3×10^8 to $6 \times 10^{12} s^{-1}$, respectively. The kinetics of static quenching of spin excitation by these ions in glassy water solutions of sulfuric acid was investigated by the electron spin echo method in Ref. 134. The theory of the method (stimulated echo) shows that the quenching kinetics is described by $N(t) = 1 - (V/V_0)$, where $V(t)$ is the signal amplitude at time t and V_0 is its stationary value.[135,136] Since the transfer of spin excitation is accomplished by the magnetic dipole-dipole interaction, the kinetics of disordered static quenching should be of the Förster "square-root" type, and this is confirmed by experimental data obtained for all the ions that were investigated.

A very important point established experimentally in Ref. 134 is that, even in the absence of quenching ions, the longitudinal spin relaxation of hydrogen atoms proceeds nonexponentially in accordance with the "square-root law." This also occurs for hydrogen atoms stabilized in fused quartz.[137] The phenomenon is explained by the dispersion of the spin-lattice relaxation times. It is also observed in the luminescence of neodymium[12] and chromium[5] in glasses. On the other hand, if the static quenching kinetics can be described by the square-root nonstationarity then, whatever its origin, the migration of excitation over donors should accelerate the process, transforming it into an exponential process.

This was, in fact, established experimentally in Ref. 138. The migration of spin excitation over hydrogen atoms was accomplished by the flip-flop process due to magnetic dipole-dipole interaction between them. Its frequency $1/\tau_0$ is an increasing quadratic function of the concentration of hydrogen atoms, and the rate of hopping quenching increases linearly in accordance with (5.25). Figure 20 illus-
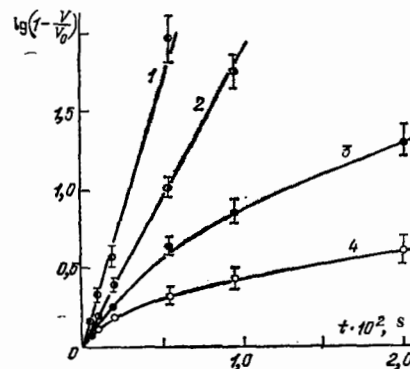

FIG. 20. Transition from hopping to static quenching of spin excitation of hydrogen atoms in frozen water solutions of sulfuric acid with decreasing concentration of hydrogen atoms:[138] $z(cm^{-3}) = 4.4 \cdot 10^{18}$ (1), $2.6 \cdot 10^{18}$ (2), $1.5 \cdot 10^{18}$ (3) and $2 \cdot 10^{17}$ (4).

trates the exponentialization of the quenching kinetics as ρ increases, which is identical with the theoretical prediction (Fig. 8). In one respect, this experiment may be preferred to the luminescence experiment: since spin excitation does not exhibit natural decay, the function that is measured directly is $N(t)$ and not $T(t)$. This means that the kinetics of concentration quenching of hydrogen can be investigated, without any complication, both in sulfuric acid and in quartz, and hence we can verify that its rate is directly proportional[138] to $\rho = [H]$. ESR studies performed immediately after the early papers[12,13] are impeccable from the kinetic point of view. The frequency of the flip-flop process obtained as a result of these studies agrees with experiment not only in the dependence on ρ, but also in the correlation with the width of the ESR spectrum components of the hydrogen atom. These studies have acted as a stimulus to the subsequent development of the theory of hopping quenching in magnetic resonance.[15,85]

D. Transfer of vibrational excitation

The quenching kinetics of vibrationally excited CH_3CCl_3 molecules (Fig. 15) is found to be a two-stage process. The brief stage of activation by the picosecond pulse is followed by the development of first static quenching and then concentration quenching, which is exponential in time.

Since static quenching continues for a short time, its kinetics is practically impossible to investigate, but the separation between this stage and the asymptotic exponential behavior can be set quite clearly: $t_s = 5 \cdot 10^{-12}$ s (Ref. 94). This information can be used to determine C_{DD} if t_s is defined as the point at which the rates of static and hopping quenching become equal[94] (Fig. 1):

$$\rho \dot{Q}(t_s) = \overline{W}. \tag{8.5}$$

Using Q from (2.8) and $\overline{W}$ from (7.10b), we find that for dipole-dipole quenching,

$$t_s = \frac{9}{2\pi^3 C_{DD}\rho^2}, \tag{8.6}$$

which, for $\rho = 2 \cdot 10^{21}$ cm^{-3}, gives

$$C_{DD} = 8 \cdot 10^{-33} \text{ cm}^6/\text{s}. \tag{8.7}$$

Because of an accidental numerical error, the result reported in Ref. 94 is very similar to this despite the fact that the rate of quenching rather than of self-quenching was used in (8.5).

As soon as C_{DD} is known, the cross-relaxation constant C_{DA} can be found from the concentration dependence of the rate of hopping quenching $\overline{W}$. This dependence can be written analytically in the form

$$\ln \overline{W} = 2\ln \rho - \ln A. \tag{8.8}$$

Its slope confirms the square-root type dependence of the rate of quenching (7.10b) on the concentration of the molecules, and the constant

$$A = \frac{9\sqrt{2}}{4\pi^3 \sqrt{C_{DA}C_{DD}}}, \tag{8.9}$$

turns out to be $2 \cdot 10^{32}$ s/cm^3 which, together with (8.7), gives

$$C_{DA} = 3 \cdot 10^{-35} \text{ cm}^6/\text{s}. \tag{8.10}$$

TABLE III.

Rate	$2\sqrt{\dfrac{\pi}{3}}$	1,72	1	$\sqrt{\dfrac{2}{\pi}}$
Reference	95	139	84	(7.14)

Hence, it follows that $z = 0.004$ is a low enough value to ensure that hopping quenching will take place.[95]

We note that the precise value of the numerical coefficient in (8.9) is, as usual, not known. If we take it to be equal to unity, the other methods of estimating the self-quenching rate differ by the factors shown in Table III. Apart from those considered above, the table lists two further rates obtained simultaneously, but independently, in Refs. 95 and 139. Both these papers use the idea of quenching pairs, but in a different way. The early result of quenching theory, given by (5.12), is reproduced in Ref. 95. It had previously been used to calculate the self-quenching rate.

This estimate of the rate turns out to be the highest, but differs from the lowest by a factor of about two. In addition, the magnitude of C_{DD}, but not that of C_{DA}, depends on this uncertainty.

9. LIMITATIONS OF THE THEORY

Two important limitations of the above theory must be mentioned once again in conclusion. They are: spatial isotropy of the system and the balance approximation.

Departure from spatial isotropy may occur in different ways. In some systems, impurity centers can aggregate into dimers or clusters, and this violates spatial uniformity and randomness of their disposition, which was assumed in all derivations of (1.2). Further information about the problem and the ways in which it is solved for static and diffusion-accelerated quenching can be found in recent papers.[53,140,141] A totally different anisotropy is found in systems of randomly distributed centers when they are coupled by the dipole-dipole interaction, but the relative orientations of their dipole moments are not random. The ensuing correction to the kinetics of static quenching is unimportant so long as the acceptor concentration is low,[142] but its contribution increases as the acceptors are packed into a regular lattice.[143]

Migration of excitation contributes additional anisotropy if it occurs largely over planes or particular crystallographic directions. This type of anisotropy is usually well taken into account by reducing the dimensionality of the space down to two or even one. The kinetics of static quenching in any of these situations can be determined, at least in principle, as in the three-dimensional case.[144] The coefficients of diffusion over disordered systems of different dimensionality can also be determined in a unified way.[42] A fundamental difference is encountered only for diffusion-accelerated quenching which, as we know, proceeds in a totally nonstationary manner in spaces of lower dimensionality.[53] This result is, of course, reproduced in the case of diffusion over impurity centers.[145] In contrast, long-term kinetics is always exponential in the theory of hopping quenching, and its rate

is defined in the same way in spaces of any dimensionality. The only difference is encountered for the concentration dependence of the rate constant that follows from these definitions.[68] It is, however, important to recall that transition to a space of lower dimensionality does not always reflect the true situation in an anisotropic crystal. Even when excitation migrates only over a plane, quenching is accomplished by acceptors that are uniformly distributed in three-dimensional space. Spaces of fractional dimensionality are sometimes employed[125,126] to take this into account.

The above theories are also basically limited by the balance approximation, in which, right from the outset, concentration quenching is looked upon as a random process, controlled by the transfer and quenching probabilities u and w. In reality, one must start with the Hamiltonian for the interaction between identical and different impurities, and examine the conditions under which excitation transfer may be looked upon as a noncoherent and quenching as a stochastic process. Luckily, this problem has frequently been examined in its own right and is now considered to be practically solved. The probabilistic description of static quenching has finally been completed in Ref. 146. The quenching probabilities are constant in time and additive when phase relaxation in the transfer channel (γ) proceeds sufficiently rapidly.[146,3] The ability of natural decay of excitation to dephase the transfer process is very restricted, and need not be taken into account.[147,148] As far as γ is concerned, it must be greater than the dipole-dipole or exchange interaction between impurities which, in dilute solutions, is on average sufficiently small.

However, the situation may alter radically with increasing donor concentration and, especially, when donors are closely packed in glass or crystal. In molecular crystals such as naphthalene and anthracene, interaction between neighboring molecules is usually greater than γ and the motion of the exciton is coherent.

In principle, we can also have the reverse situation in which the exciton moves noncoherently but so rapidly that its interaction with the quenching impurity does not succeed in turning into a stochastic process. A special theory has been developed for this case and can be used to take into account the dynamics of the quenching process modulated by diffusion[55] or random walks of excitation.[58]

CONCLUSION

To summarize, we must note that the last decade has seen substantial progress in the understanding and description of processes developing in impurity systems after excitation. The static quenching kinetics has been investigated in all its stages and under arbitrary interaction. It has been shown both theoretically and experimentally that the migration of excitation over a disordered system eventually transforms into diffusion, and this despite the fact that migration-accelerated quenching is usually of the hopping rather than the diffusion type. The hopping mechanism of quenching has become accepted relatively recently and provides the correct description of the dependence of the rate of the process on transfer microparameters and its saturation with in-

creasing activator concentration (kinetic limit). In its present state, the theory describes not only stationary quenching, but also its development in time after a delta-function excitation. It can be used to calculate the yield and kinetics of sensitized luminescence.

In writing this review, the author has benefited greatly from direct contact and correspondence with the authors of practically all the theoretical papers cited above, and is particularly indebted to those of them who have supplied him with preprints and original diagrams from these papers.

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