Effect of the kinematics of the mutual approach of particles in solutions on the transfer of energy between them

A. B. Doktorov, A. A. Kipriyanov, and A. I. Burshteǐn

Institute of Chemical Kinetics and Combustion, Siberian Department, USSR Academy of Sciences

(Submitted 31 October 1977)
Zh. Eksp. Teor. Fiz. **74**, 1184–1198 (March 1978)

The effect of the kinematics of motion of particles in solution on the transfer of energy between them, which results in the quenching of luminescence, is considered within the framework of the random walk model. An analysis of the general solution of the problem reveals the conditions under which diffusion-accelerated quenching occurs, and the conditions which involve purely hopping quenching. One other quenching mechanism is possible, besides these familiar mechanisms. This one is characterized by an unusual dependence of the quenching rate on the parameters of the problem.

PACS numbers: 32.50.+d, 33.50.−j

1. INTRODUCTION

Any reaction between dissolved particles is important only upon sufficiently close approach of the partners. If the process of their approach is described as encounter diffusion, then the problem as to how it is organized cannot be given. The diffusion description of the migration of particles is all-purpose and is always valid on a macroscopic scale. However, it has long been noted that this description can lose force upon decrease in the distance between partners to molecular dimensions.[1] In gases, where diffusion consists of a succession of free paths, the reaction begins and ends within the limits of one of them, when their length is large in comparison with the characteristic size of the reaction zone. This also happens in the condensed phase, where the migration takes place as a result of the random wandering of the particles, one step frequently turns out to be sufficient if it strongly accelerates the reaction.

In spite of the difference in the kinematics of the motion, processes which come about in a single act (run or hop) are a natural alternative to diffusion-controlled reactions. However, in spite of the fact that the theory of reactions in rarefield gases is well developed[2] and the theory of hopping processes has advanced considerably in recent years,[3,4] the limits of their applicability are outlined only intuitively. An exception is the problem of the annihilation of excitions on impurity centers.[5] It has been solved in the case of an arbitrary relation between the path length of the exciton and the quenching radius, which enables one to establish where and how the change in the quenching transfer mechanism is brought about by the diffusion.

The present research sets as its goal the solution in general fashion of the problem of quenching in the random walk model. This walk can be executed by a localized exciton in a crystal or by an excited particle migrating in a liquid medium. The quenching is due to the transfer of energy to the metastable level of an impurity center. The transfer probability increases sharply with decrease in their separation:

$$U(r)=a/r^m \tag{1.1a}$$

in the case of multipole interaction,

$$U(r)=U_0e^{-2\varkappa r} \tag{1.1b}$$

in the exchange approximation. Therefore, the mutual approach of the particles during the time of motion forces the quenching process.

The kinetics of multipole quenching has been studied in both the diffusion[6] and the hopping[3,4] variants, and it has been assumed that these exhausted all possibilities. The stationary rate of exchange quenching, accelerated diffusion[7] or hops[8] have also been studied, but the problem as to how these mechanisms are differentiated has remained unclear. In the present work, we have succeeded in answering this question in exhaustive fashion, thanks to the rigorous solution in its entirety of the problem of stationary exchange quenching. This solution is obtained within the framework of the specific random-walk model, but the basic conclusions can be formulated and substantiated in general form.

It turns out that, along with the diffusion and hopping mechanisms of quenching, a mixed mechanism is possible in which the molecule is deactivated in the first step in the quenching zone, but leaves it only after several successive steps. This situation comes about when the boundaries of the strong quenching zone are sharply defined (in comparison with its extent), which occurs in the case of exchange quenching and in interactions of high multipolarity. With increase in viscosity, the ordinary hopping quenching yields place to the mixed process, the rate of which falls off slowly and depends otherwise on the parameters of (1.1b). At the same time, for fixed viscosity, the effective quenching radius can be both greater and less than the diffusion radius, depending on which mechanism is realized. Therefore, in the interpretation of the experimental data, it is necessary to take into account their boundaries in the parameter $\varkappa\lambda$ (λ is the mean value of the hop), which are established in the present work, and to use adequate formulas.

0038-5646/78/030623-08$02.40

2. STATEMENT OF THE PROBLEM

The quenching rate constant is determined from the formula[7]

$$k=\int U(\mathbf{r})n(\mathbf{r},t)\,d\mathbf{r},\tag{2.1}$$

where n is the density of excitations at a distance $\mathbf{r}$ from the quencher at the time t. The latter quantity is obtained from the equation

$$\frac{\partial n(\mathbf{r},t)}{\partial t}=-U(\mathbf{r})n(\mathbf{r},t)-\frac{1}{\tau_0}\left[n(\mathbf{r},t)-\int f(|\mathbf{r}-\mathbf{x}|)n(\mathbf{x},t)\,d\mathbf{x}\right],\tag{2.2}$$

which differs from the generally accepted form[1,7] by a replacement of the differential operator corresponding to diffusion by the more general integral operator, which describes the random walk, as a consequence of stochastic hops. Here τ_0 is the time between successive hops and $f(|\mathbf{r}-\mathbf{x}|)$ is the conditional probability of obtaining the value $\mathbf{r}$ as a result of the hop if, before the jump, it was equal to $\mathbf{x}$, and

$$4\pi\int_0^\infty f(\xi)\xi^2d\xi=1.\tag{2.3}$$

If we neglect the characteristic size of the particles for simplicity, then f depends only on $\xi=|\mathbf{r}-\mathbf{x}|$. Moreover, we shall assume the quenching to be spherically isotropic, $U(\mathbf{r})=U(r)$, and we limit ourselves to consideration of the final quasi-stationary stage of the quenching, when $\partial n/\partial t=0$. Then the formulas (2.1) and (2.2) take the form

$$-U(r)n(r)-\frac{1}{\tau_0}\left(n(r)-4\pi\int_0^\infty f(r,x)n(x)x^2dx\right)=0,\tag{2.4a}$$

$$k=4\pi\int_0^\infty U(r)n(r)r^2dr,\quad n(\infty)=1,\tag{2.4b}$$

and, by definition,

$$f(r,x)=(4\pi)^{-1}\int f(|\mathbf{r}-\mathbf{x}|)\sin\theta\,d\theta\,d\varphi,$$

where $\mathbf{r}=\{r,\theta,\varphi\}$ and $\mathbf{x}=\{x,\theta',\varphi'\}$. Taking it into consideration that the result of integration should not depend on the orientation of $\mathbf{x}$, we assume $\theta'=\varphi'=0$. Then

$$f(r,x)=\frac{1}{2}\int_0^\pi f([r^2+x^2-2xr\cos\theta]^{1/2})\sin\theta\,d\theta$$

$$=\frac{1}{2xr}\int_{|r-x|}^{r+x}f(\xi)\xi d\xi=\frac{1}{8\pi xr}[\Phi(|r-x|)-\Phi(r+x)].\tag{2.5}$$

Here we introduce the function

$$\Phi(z)=4\pi\int_z^\infty f(\xi)\xi d\xi,\qquad \int_0^\infty\Phi(z)dz=1.\tag{2.5a}$$

Calculating the latter integral by parts, with account of (2.3), we can easily establish the fact that Φ is actually normalized to unity and the function $f(r,x)$ is normalized in both its arguments:

$$4\pi\int_0^\infty f(r,x)r^2dr=4\pi\int_0^\infty f(r,x)x^2dx=1,\tag{2.6}$$

thanks to which the integral representation of n in (2.4a) leaves it constant if $U\equiv 0$.

We shall show that, both in the problem of the diffusion-accelerated quenching[7] and in this more general case, the constant of the rate of quasi-stationary quenching is determined as a whole by the asymptotic behavior of $n(r)$ as $r\to\infty$. For this, we transform formula (2.4b) with the help of Eq. (2.4a) and the properties of the function $f(r,x)$ into the following equivalent formula:

$$k=\frac{16\pi^2}{\tau_0}\int_0^\infty r^2dr\int_0^\infty x^2dx f(r,x)[n(x)-n(r)].$$

In view of the symmetry of $f(r,x)$ relative to the permutation of its arguments, the obtained expression changes sign when the order of integration is interchanged. However, it is obvious that $k\neq 0$ and consequently, such an interchange for the given improper integral is incorrect and the integral should be regarded as the limit of the expression

$$k=\frac{16\pi^2}{\tau_0}\lim_{R\to\infty}\int_0^R r^2dr\int_R^\infty x^2dx f(r,x)[n(x)-n(r)].\tag{2.7}$$

Here we have taken it into account that the multiple integral in finite limits from O to R, which admits of interchange of the order of integration, is identically equal to zero. The expression (2.7) has the meaning of the total flux of excitations to the quencher through a sphere of radius R. Since $f(r,x)$ differs from zero only at $|r-x|\leq\lambda$, where λ is the mean scale of the jump, the, as $x\to\infty$ in (2.7), $r\to\infty$. Thus, the quenching rate constant is actually determined by the asymptotic behavior of $n(r)$.

Taking it into account that as $r\to\infty$ both $U(r)$ and $\Phi(r+x)$ in Eq. (2.4a) vanish, we obtain the result that the $n(r)$ has the asymptotic form

$$n(r)\sim 1-R_Q/r,\tag{2.8}$$

where R_Q is the asymptotic coefficient. Substituting this expression in (2.7), carrying out the change of integration variables $z=x-r$ and $y=R-r$, and taking the limit as $R\to\infty$, we get

$$k=\frac{2\pi R_Q}{\tau_0}\int_0^\infty dy\int_y^\infty z\Phi(z)dz=\frac{2\pi R_Q}{\tau_0}\int_0^\infty z^2\Phi(z)dz=4\pi DR_Q.\tag{2.9}$$

Here $D=\lambda^2/6\tau_0$ is the diffusion coefficient, and

$$\lambda^2=3\int_0^\infty z^2\Phi(z)dz=4\pi\int_0^\infty\xi^4f(\xi)d\xi\tag{2.10}$$

is the mean square value of the hop length.

Thus, the determination of the constant k in terms of the asymptotic coefficient R_Q turns out to be the same as in the diffusion-accelerated quenching.[7] This is connected with the fact that in the remote approach to the quencher, the motion of the excitations via stochastic hops can always be regarded as diffuse.

3. MODEL PROBLEM

The direct solution of Eq. (2.4a) becomes possible only after specification of its kernel. However, the kernel cannot be determined in more detail than in (2.5), because of the general physical considerations. Thus, there is a certain freedom of choice in the function $\Phi(z)$. We use this to solve the problem analytically. For this purpose, we set

$$\Phi(z)=\frac{1}{\lambda_0}\exp\left(-\frac{z}{\lambda_0}\right). \tag{3.1}$$

Then the corresponding distribution over the hop lengths takes the form

$$dw=4\pi f(\xi)\xi^2 d\xi=\lambda_0^{-2}\xi e^{-\xi/\lambda_0}d\xi.$$

The parameter λ_0 has the meaning of the most probable hop length, since its mean square value is

$$\lambda^2=\lambda_0^{-2}\int\limits_0^\infty \xi^3 d\xi e^{-\xi/\lambda_0}=6\lambda_0^2. \tag{3.2}$$

The choice of Φ in the form (3.1) is useful in that, in the case of such a definition, the function $f(r,x)$, introduced in (2.5), becomes the regular solution of the equation

$$\Delta_r f(r,x)=\lambda_0^{-2}f(r,x)-(4\pi\lambda_0^2 rx)^{-1}\delta(r-x),$$

where Δ_r is the Laplacian, acting on the variable r. Expressing the function $f(r,x)$ in this equation, and substituting it in (2.4a), we can transform the obtained integral equation to a differential equation. In fact, interchanging the integration over x and the differentiation with respect to r in it and again making use of Eq. (2.4a), we get

$$\frac{\lambda_0^2}{\tau_0}\frac{d^2}{dr^2}r\eta(r)-\frac{U(r)}{1+U(r)\tau_0}r\eta(r)=0. \tag{3.3}$$

Here, we have introduced a new function

$$\eta(r)=n(r)[1+U(r)\tau_0], \tag{3.4}$$

in place of n, satisfying the condition of boundedness at $r=0$ and the condition $\eta(\infty)=n(\infty)=1$.

Since $U(r)\to 0$ more rapidly than r^{-3} as $r\to\infty$ (which is necessary for the existence of a finite quenching rate constant), $\eta(r)$ according to (3.4) has the same asymptotic form (2.8) as $n(r)$. For this reason, the quenching rate constant is determined by a formula identical to (2.9):

$$k=4\pi\frac{\lambda_0^2}{\tau_0}R_Q=4\pi\frac{\lambda_0^2}{\tau_0}\lim_{r\to\infty}r^2\frac{d}{dr}\eta(r). \tag{3.5}$$

We solve Eq. (3.3) in the case of exchange mechanism of transfer of the energy, when U is given by Eq. (1.1b). Substituting it in (3.3), we obtain an equation which has already been encountered in the theory of diffusion-accelerated quenching,[7] albeit in a somewhat different form. Copying its solution from Ref. 7, we obtain, after suitable rearrangement of the parameters,

$$k=4\pi\frac{\lambda_0^2}{\tau_0}(2\varkappa)^{-1}\left[\ln\gamma^2 z+2\psi(\nu)+\frac{1}{\nu}+2\pi\Lambda(z,\nu)\,\mathrm{ctg}\,\pi\nu\right], \tag{3.6a}$$

where

$$\Lambda(z,\nu)=\frac{F(\nu,\nu,1+2\nu;-1/z)}{F(\nu,\nu,1+2\nu;-1/z)-e^{2i\pi\nu}\Phi(\nu,\nu,1+2\nu;-1/z)} \tag{3.6b}$$

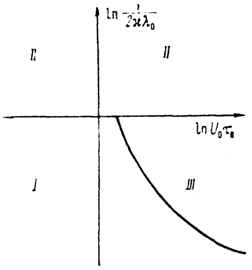

FIG. 1. Regions corresponding to various quenching mechanisms: I—jump, II—diffusion, III—mixed.

$F(\nu,\nu,1+2\nu;=1/z)$ and $\Phi(\nu,\nu,1+2\nu,-1/z)$ are the hypergeometric functions of the first and second kind, $\psi(\nu)$ is the Euler psi function, $\gamma=e^C$ (C = Euler's constant).

The obtained two-parameter solution is completely general. The parameter $z=U_0\tau_0$ characterizes the depth of the course of the process during the time that the excitation remains at the point where the quenching is maximal. The quenching will be strong or weak, depending on the value of this parameter. So far as the parameter $\nu=1/2\varkappa\lambda_0$ is concerned, it correlates the spatial scale of the change in the quenching probability with the hop length and at the same time distinguishes the situations according to the method of crossing of the quenching zone. Depending on this, we shall in what follows, designate the quenching process as diffusion, hopping, or mixed. Figure 1 shows the boundaries of the situations, both according to the sign of the quenching force and also according to the mechanism. We shall consider each of these in turn.

4. DIFFUSION QUENCHING

It is obvious that diffusion quenching should occur at small values of the hop length. Actually, as shown in Appendix A, at

$$\nu\gg 1,\ \text{i.e., at}\quad \lambda_0\ll 1/2\varkappa \tag{4.1}$$

the general solution (3.6) reduces to the well-known result of diffusion quenching[7]

$$k=4\pi D\frac{1}{2\varkappa}\left[\ln\gamma^2\beta_m+2\frac{K_0(2\beta_m^{1/2})}{I_0(2\beta_m^{1/2})}\right], \tag{4.2}$$

where $I_0(x)$ and $K_0(x)$ are the modified Bessel functions, $D=\lambda_0^2/\tau_0$ is the diffusion coefficient, and $\beta_m=\nu_z^2=U_0/4\varkappa^2 D$ is a parameter which characterizes the effectiveness of the diffusion quenching. At $\beta_m\ll 1$, the diffusion quenching is weak and its constant

$$k=\pi U_0/\varkappa^3 \tag{4.3}$$

does not depend on the diffusion rate; this corresponds to the so-called kinetic stage. On the other hand, at $\beta_m \gg 1$, the quenching becomes strong, i.e.,

$$k=4\pi DR_S,\quad R_S=\frac{1}{2\varkappa}\ln\beta_m=\frac{1}{2\varkappa}\ln\frac{U_0}{4\varkappa^2 D}, \tag{4.4}$$

which corresponds to diffusion control. As was shown in Ref. 7, R_S has the meaning of the radius of the sphere of strong quenching, falling into which surely leads to annihilation of the excitation. Here the total extinction of the excitation already occurs on the boundary of this sphere in a layer of thickness $1/2\varkappa$ (in the following we shall call this the quenching layer). Therefore R_s is determined by the equality

$$U(R_s)/4\varkappa^2 D=1, \tag{4.5}$$

where $1/4\varkappa^2 D$ has the meaning of the time of crossing of the quenching layer. Upon satisfaction of (4.1), this time becomes much longer than τ_0, thanks to which the diffusion damping becomes strong long before $z=U_0\tau_0$ becomes equal to unity.

We can give a universal form to the criterion of diffusion quenching (4.1) if we establish the thickness of the quenching layer δ in the general case. For a quenching probability that is monotonically falling with increase in r, it can be estimated as the distance from the boundary of the quenching sphere, at which $U(r)$ falls off by a factor of e. Using (1.1), it is not difficult to prove that

$$\delta=R_s(e^{1/m}-1)\approx R_s/m \tag{4.6a}$$

for multipole interaction and

$$\delta=1/2\varkappa \tag{4.6b}$$

for the exchange interaction, while the radius of the quenching sphere is determined by the relation

$$U(R_s)\delta^2/D=1, \tag{4.7}$$

which is a natural generalization of (4.5). As is seen from these formulas, the thickness of the quenching layer is always less than the radius of the quenching sphere, even in the case of dipole-dipole interaction, when m is minimal and equal to 6. But no matter how narrow the layer, in the case of diffusion quenching several steps would be required to effect its crossing. This is easily proved if we take it into account that the equation (3.3) goes over into the ordinary equation of diffusion-accelerated quenching (Eqs. (3.1) from Ref. 7), when $U(r)\tau_0\ll 1$. It is important only that this equation keep valid until $r\approx R_s$. The character of the motion in the interior of the sphere of strong quenching no longer has significance, because the excitation does not reach that region. Therefore, the actual criterion for diffusion description of the process is the inequality

$$U(R_s)\tau_0\ll 1 \quad\text{or}\quad \frac{\lambda^2}{\delta^2}U(R_s)\frac{\delta^2}{D}\ll 1. \tag{4.8}$$

Using (4.7) in it, we find the desired relation

$$\lambda\ll\delta, \tag{4.9}$$

which generalizes (4.1) to the case of arbitrary dependence of $U(r)$. Although these considerations allow us to establish the boundary of diffusion quenching only in the case in which it is strong, this is quite sufficient. In kinetic control, the character of the motion is not important at all, because nothing depends on it.

For exchange interaction, the criterion (4.9) is the final one, since the thickness δ is a constant quantity. On the other hand, in the case of multipole quenching both the layer thickness and its radius depend on λ, and therefore the limit on the hop length

$$\lambda\ll R_s(\lambda)/m \tag{4.10}$$

introduced in (4.9), is not explicit. Using (4.6a), (4.7) and (1.1a), it is not difficult to establish the fact that

$$R_s=\left(\frac{a}{m^2D}\right)^{1/(m-2)}=\left(\frac{6\tau_0 a}{m^2\lambda^2}\right)^{1/(m-2)}. \tag{4.11}$$

With the help of this relation, we get from (4.10)

$$\lambda\ll(a\tau_0)^{1/m}/m=R_W/m, \tag{4.12}$$

where $R_W=(a\tau_0)^{1/m}$, as is shown in the next section, is the radius of the sphere of strong multipole quenching, in the hopping variant of the theory, and is the analog of R_s.

The conditions (4.9) and (4.12) are valid for any distribution of hop lengths. It is only important that the mean hop length λ remain small in comparison with the layer thickness δ, which the diffusion flow of excitations, directed toward the quencher, is exhausted. Writing this relation in the form

$$dj/dr\approx j/r\ll j/\lambda,$$

it is not difficult to see that it is the upper bound of the value of the second derivative of n with respect to the first. This makes valid the expansion $n(r+x)$ in (2.4a) in a Taylor series in the vicinity of the point r, which converts the integral operator into a differential one. Retaining only the first non-vanishing term in it, we get for all $r\gg\lambda$ (where $\Phi(r+x)\approx 0$), with account of (2.5),

$$-\frac{1}{\tau_0}\left[n(r)-4\pi\int_0^\infty x^2 f(r,x)n(x)\,dx\right]$$

$$\approx\frac{1}{2r\tau_0}\int_0^\infty dx\,\Phi(x)\{r[n(r-x)+n(r+x)-2n(r)]+x[n(r+x)-n(r-x)]\}$$

$$\approx\frac{\lambda^2}{6\tau_0}\left[\frac{d^2n}{dr^2}-\frac{2}{r}\frac{dn}{dr}\right]=D\frac{1}{r}\frac{d^2}{dr^2}rn(r)=D\Delta n,$$

where the diffusion coefficient is expressed in the usual fashion in terms of λ^2, which is defined in (2.10).

There have been attempts to improve the diffusion description of the reaction by keeping subsequent terms of the expansion, in particular, the third derivative of n.[9] However, the correction is umimportant on the boundaries of applicability of diffusion quenching of such type and insufficient beyond them. When the inequalities (4.9) or (4.12) are applied, all the terms of the expension become important and, in order to obtain a simple description of the process, it is necessary to approach it from another side.

5. HOPPING QUENCHING

As an alternative to the above, we consider first the case in which $\nu\to 0$. Expanding the general solution (3.6) in this parameter, with accuracy to terms of first order (Appendix B), we find

$$k=\frac{\pi}{\varkappa^3\tau_0}\begin{cases} q(z), & z\leqslant 1, \quad (5.1a)\\ q(1/z)+{}^1\!/_6\ln^3 z+{}^1\!/_6\pi^2\ln z, & z\geqslant 1, \quad (5.1b)\end{cases}$$

where

$$q(\alpha)=-\sum_{n=1}^{\infty}\frac{(-\alpha)^n}{n^3}.$$

The expression (5.1), represented in the form (Appendix B)

$$k=\frac{4\pi}{\tau_0}\int_0^{\infty}\frac{ze^{-2\varkappa r}}{1+ze^{-2\varkappa r}}r^2\,dr, \tag{5.2}$$

is easily identified with the result pertaining to the hopping mechanism of exchange quenching.[8] Although this result was obtained in Ref. 8 for migration of the excitation over equivalently located donors, when the hop length changes by a discrete amount, this result remains in force, as is now seen, even in the case in which this distribution is continuous. The parameter z in this case, as also in the previous, characterizes the effectiveness of the quenching, in absolute fashion, without relation to the quantity ν, i.e., the result (4.3) referring to the kinetic stage of the quench, is reproduced here in every case in which

$$U_0\tau_0=z\ll 1. \tag{5.3}$$

The coincidence of the results with the conditions of superfast migration was expected, inasmuch as the reaction constant should not depend on the migration velocity in this case, but rather on the methods of this realization.

The situation is different in the case of strong interaction, when the inequality (5.3) is applied. In such a case, we get from (5.1b)

$$k=\frac{4\pi}{3\tau_0}R_W{}^3,\quad R_W=\frac{1}{2\varkappa}\ln z=\frac{1}{2\varkappa}\ln U_0\tau_0, \tag{5.4}$$

where R_W has the meaning of the radius of the sphere, hops into which annihilate the excitation. This radius is the analog of R_S in (4.4), but is determined by the relation

$$U(R_W)\tau_0=1, \tag{5.5}$$

differing essentially from (4.5). Upon substitution of (1.1a) in it, we obtain just that value of R_W which figured in (4.12) as the radius of the sphere of strong jump quenching in the case of multipole transfer of energy.

Analysis of the expansion of (3.6) in a series in ν under the conditions of strong hopping quenching ($z\gg 1$) shows that it is admissible only upon satisfaction of the inequality

$$\nu\ln z\ll 1, \tag{5.6}$$

which is equivalent to the requirement

$$\lambda_0\gg R_W. \tag{5.7}$$

It is not difficult to recognize here the ordinary criterion of applicability of the hopping quenching mechanism.[3,4] The physical meaning of it is that the particle carrying the excitation falls into the quenching sphere and gives it up in a single hop.

The obtained results are easily extended to quenching of an arbitrary type. At large λ_0 the second term in (3.3) is small in comparison with the first and it can be neglected in the zeroth approximation. The evident solution in this case, which satisfies the condition at infinity, is

$$\eta(r)=1\quad\text{or}\quad n(r)=1/[1+U(r)\tau_0]. \tag{5.8}$$

Using this in the determination of the rate constant (2.4b), we find

$$k=4\pi\int_0^{\infty}\frac{U(r)}{1+U(r)\tau_0}r^2\,dr. \tag{5.9}$$

This result is the direct generalization of (5.2) for arbitrary $U(r)$. In strong exchange interactions, the fraction under the integral, as a function of r, is close to a right triangle with height $1/\tau_0$ and base R_W, the latter determined by the condition (5.5). Therefore, the constant (5.4) is simply the volume of a sphere of radius R_W, multiplied by the frequency of falling into it. In multipole interaction, this function is not so close to a right triangle, and therefore, the result should be found by direct integration of (5.9) with account of (1.1a). The satisfaction of it is not a necessity, since the prescription (5.9) is identical to that used earlier for these same purposes (see Ref. 3).

The model representation of the distribution function over hop lengths, used in the derivation of (3.3), in no way limits the generality of the results. They also follow directly from (2.4) if it is taken into account that $n(x)$ rapidly reaches its asymptotic value, equal to unity, beyond the limits of the quenching sphere (at $x>R_W$). Therefore, if λ, which characterizes the width of the function $f(r,x)$, in accord with (5.7), significantly exceeds the radius of the quenching sphere R_W, then the principal contribution to the integral (2.4a) is made by the region lying outside it, where $n\approx 1$. Taking this into account, and also the condition of stationarity of (2.6), we can set

$$4\pi\int_0^{\infty}x^2f(r,x)n(x)\,dx\approx 4\pi\int_0^{\infty}x^2f(r,x)\,dx\approx 1, \tag{5.10}$$

after which the solution (2.4a) transforms into (5.8), and (5.9) follows from (2.4b).

It must be noted that $n(x)$, which is determined in (5.8), in the zeroth approximation in $\nu=1/2\varkappa\lambda$, does not agree entirely with the asymptotic behavior of this quantity established in (2.8). The term R_Q/r is absent in it. This term, as has been pointed out, is connected with the diffusion character of the motion in the remote approach to quenching. This is explained by the fact that the first term in (2.4a) falls off at $r\to\infty$ more rapidly than $1/r$. It is therefore evident that the next term in the expansion in (5.10) is responsible for the term R_Q/r in $n(r)$ as $r\to\infty$. This is quite natural, since, according to (2.19), $R_Q\sim O(1/\lambda^2)$ as $\lambda\to\infty$. The absence of this correction to (5.8) roughens the asymptotic behavior of n. Nevertheless, the use of such a function in (2.4b) does not distort the result, thanks to the presence of the cutoff factor $U(r)$ under the integral sign; it reveals its inadequacy only in the use of the formula (2.9) as a rule for the calculation of k.

In this connection, it is appropriate to note that the effective quenching radius (it is also the asymptotic coefficient) R_Q can be identified with the radius of strong quenching, except that it is of the diffusion type. It actually follows from the formal similarity of (2.9) and (4.4) that

$$R_Q=R_s \quad \text{at} \quad \beta_m \gg 1. \tag{5.11}$$

But, if we compare (2.9) and (5.4), it then turns out that

$$R_Q=2R_W\left(\frac{R_W}{\lambda}\right)^2=\frac{R_W}{3}\left(\frac{R_W}{\lambda_0}\right)^2 \quad \text{at} \quad z\gg 1. \tag{5.12}$$

In view of the inequality (5.7), R_Q in hopping quenching is much smaller than R_W. Determined experimentally as the ratio $k/4\tau D$, this quantity can also turn out to be smaller than the molecular size, which is typical of the kinetic stage of the reaction, but will increase with increase in the viscosity, which is characteristic for the diffusion stage in the ordinary sense of this word. A combination of these conflicting properties simply indicates that we are dealing with hopping control of the reaction.

6. MIXED QUENCHING MECHANISM

Figure 1 enables us to see how and where the change in mechanisms with increase in λ (decrease in ν) takes place. At $z \ll 1$, strong quenching gives way to weak, remaining diffusive in character. The replacement of the diffusion mechanism by the jump that takes place after this (at $\nu \approx 1$) is imperceptible since the quenching rate does not depend on the motion in the kinetic stage. If $z > 1$, then the quenching is strong for all ν and the situation is much more complicated.

First of all, it is necessary to take into account the difference between the criteria (4.1) and (5.6). The first of these limits from below the range of diffusion quenching, while the second establishes the upper bound of ν for the jump. These n limits do not abut one another, as a consequence of which there is space between the limiting cases considered for the intermediate situation (see Fig. 1):

$$1/\ln z \ll \nu \ll 1 \quad \text{or} \quad 1/2\varkappa \ll \lambda_0 \ll R_W. \tag{6.1}$$

In the case of multipole quenching we can assess the change in the situation in terms of Fig. 2. On it is shown the change with increase in λ of the radii of the quenching spheres, with which we must compare the hop length in order to make the choice between the mechanisms. In this case, the intermediate region is

$$R_W/m \ll \lambda \ll R_W, \tag{6.2}$$

which has a large extent only for large m, and in the dipole case it degenerates into a comparatively narrow band that separates the diffusion and the hopping quenchings.

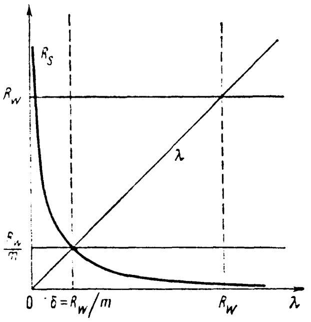

FIG. 2. Behavior of effective radii R_W and R_S upon change in hopping scale λ for multipole quenching.

In order to decide on how the exchange quenching exists in the intermediate region, it is necessary to expand (3.6) under the condition $1/\ln z \ll 1$ (Appendix B), which gives

$$k=4\pi\lambda_0^2 R_W/\tau_0=4\pi D R_W. \tag{6.3}$$

This result is new. Such a combination of the parameters of the problem in the determination of the rate of the process has never been encountered previously. The rate constant is expressed linearly in terms of the radius of the band of strong quenching, both in diffusion quenching (but the radius is determined by the equation (5.5)) and in the hopping mechanism. It is just this which furnishes the basis for calling the mechanism a mixed one.

However, the situation can be considered in another aspect; in the cross section $\nu = \text{const} \ll 1$ we can assume that we are dealing simply with a new quenching stage, which is controlled by the migrations. Increase in z in this cross section corresponds to a slowing of the diffusion (increase in the viscosity of the medium). The kinetic stage at $z \ll 1$ gives way to hopping, but ends as a mixed stage, in which the latter two can be described by the single expression

$$k=4\pi\frac{\lambda_0^2}{\tau_0}R_W\left(1-\frac{\lambda_0}{R_W}\operatorname{th}\frac{R_W}{\lambda_0}\right), \tag{6.4}$$

which is obtained from (3.6) at $\nu \ll 1$ and $\ln z \gg 1$, but arbitrary $\nu \ln z$. (Appendix B). It is obvious that it will be necessary to deal with the mixed state, as a rule, in the change of viscosity over wide ranges. This conclusion is valid in relation to arbitrary short-range types of quenching, including quenching of high multipolarity. It is necessary to keep it in mind also in the calculations of quenching as a consequence of migration of the excitation through donors in solid and viscous solutions. In this case, the frequency of migration is determined by the concentrations of the activator n_0, according to the formula[3,8]

$$\frac{1}{\tau_0}=\frac{8\pi^3}{27}dn_0^2, \tag{6.5}$$

where d is the constant of dipole-dipole interaction between the particles of the activator. For this reason, R_W turns out to be dependent on n_0[8]:

$$R_W = \frac{1}{2\varkappa} \ln \frac{27U_0}{8\pi^3 dn_0^2}. \qquad (6.6)$$

However, the rate constant, which is determined by R_W in (6.3), is different from the hopping variant of the theory developed in Ref. 8. An entirely different concentration dependence is characteristic of it:

$$k = \frac{17\pi^4}{27\varkappa} dn_0^{4/3} \ln \frac{27U_0}{8\pi^3 dn_0^2}, \qquad (6.7)$$

which can be used for the identification of the mechanism.

7. CONCLUSION

The stationary quenching rate constant, when it is controlled by migrations, can always be represented in the form

$$k = v/\tau,$$

where v has the meaning of the volume of the quenching sphere, and τ is its duration in it. The table indicates how all these quantities are determined in the case of the various quenching mechanisms considered above. In the hopping and mixed mechanisms, the volumes of the quenching sphere is identical. On the contrary, the expression for the time of stay in the sphere is of the same structure in the diffusion and mixed mechanisms, since in both these cases the crossing of this sphere is accomplished by several hops, as is clear from the criteria of applicability.

The existence of three different mechanisms of strong quenching creates the problem of choice among them, on which the interpretation of the experimental data depends critically. If the diffusion coefficient is known along with the rate constant, then this enables us to calculate $R_Q = k/4\pi D$, but this is not to be identified with the diffusion radius R_S, as has been done up to now. As is seen from Fig. 3, the found quantity can be larger or smaller than its asymptotic value, which it achieves in the diffusion limit ($\lambda \to 0$). The mechanism can be identified only by studying the dependences of R_Q on λ and τ_0, which is different in all cases. If $\lambda \approx$ const, then it is relatively simple to distinguish the hopping mechanism from the others according to its dependence $R_Q \propto \ln^2 D$ (for the others $R_Q \propto \ln D$). The wider the range of change of the diffusion coefficient, the more reliable will be this choice. By varying the pressure on the liquid over wide limits, we can significantly change the diffusion rate, without changing the composition of the solution. For purity of such an experiment, it is desirable to control the coefficient of encounter diffusion directly by the given luminescence. This is possible, for example, if, in addition to the phosphorescence of the triplet state of the donor, its fluorescence in the dipole-dipole transition is also recorded.[6,7] Knowing the quenching rate of the triplet and the diffusion rate, we can readily identify the mechanism. The realization of such an experiment would allow us to extract information on the scale of the hops, i.e., on the methods of organization of the diffusion in the liquid phase.

TABLE I.

Quenching	k	v	τ	Region of applicability
Diffusion	$4\pi DR_S$	$^4/_3\pi R_S^3$	$R_S^2/3D$	$\lambda \ll \delta$
Mixed	$4\pi DR_W$	$^4/_3\pi R_W^3$	$R^2_W/3D$	$\delta \ll \lambda \ll R_W$
Hopping	$4\pi R_W^3/3\tau_0$	$^4/_3\pi R_W^3$	τ_0	$R_W \ll \lambda$

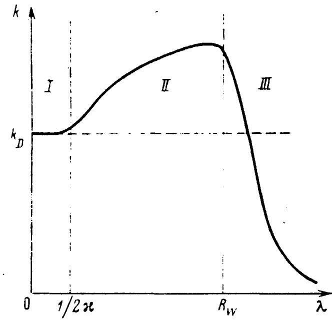

FIG. 3. Behavior of the quenching rate constant in a change in the hopping scale ($k_D = 4\pi DR_S$ is the value of the rate constant calculated from the formula for diffusion accelerated quenching; regions I, II and III correspond to diffusion, mixed and hopping quenching mechanisms).

APPENDIX A

To determine the formulas (4.2), we express (3.6b) only in terms of the hypergeometric function of the first kind:

$$\Lambda(z,\nu) = \left[1 - \frac{\Gamma^2(-\nu)\Gamma(2\nu)}{\Gamma^2(\nu)\Gamma(-2\nu)} z^{2\nu} \frac{F(-\nu,-\nu,1-2\nu;-1/z)}{F(\nu,\nu,1+2\nu;-1/z)}\right]^{-1}, \qquad (A.1)$$

where $\Gamma(\nu)$ is the Euler gamma function. We now take it into account that as $\nu \to \infty$ and $\beta_m = z\nu^2 =$ const, $z \to 0$. Carrying out such a transition for the analytic continuation of the hypergeometric series[10]

$$F\left(\nu,\nu,1+2\nu;-\frac{1}{z}\right) = \frac{2\Gamma(2\nu)}{\Gamma^2(\nu)} z^{\nu} \sum_{n=0}^{\infty} \frac{(\nu)_n(-\nu)_n(-z)^n}{(n!)^2}[h_n - \ln z], \qquad (A.2)$$

where

$$h_n = 2\psi(1+n) - \psi(n-\nu) - \psi(n+\nu) + \pi \operatorname{ctg} \pi(1+\nu),$$
$$(\nu)_n = \nu(\nu+1)\ldots(\nu+n-1),$$

and using the asymptotic expansion

$$\psi(\nu) \sim \ln\nu - \frac{1}{2\nu} - \frac{1}{12\nu^2} + O\left(\frac{1}{\nu^3}\right), \qquad (A.3)$$

we get

$$F\left(\nu,\nu,1+2\nu;-\frac{1}{z}\right) \sim \frac{4\Gamma(2\nu)}{\Gamma^2(\nu)} z^{\nu}\left[K_0(2\beta_m^{1/2}) + O\left(\frac{\beta_m^{3/2}}{\nu^2}\right)\right],$$
$$\times F\left(-\nu,-\nu,1-2\nu;-\frac{1}{z}\right) \sim \frac{4\Gamma(-2\nu)}{\Gamma^2(-\nu)} z^{-\nu}\left[K_0(2\beta_m^{1/2}) \right. \qquad (A.4)$$
$$\left. \times\left(1+O\left(\frac{\beta_m^{3/2}}{\nu^2}\right)\right) - \pi I_0(2\beta_m^{1/2}) \operatorname{ctg}\pi\nu \left(1+O\left(\frac{\beta_m}{\nu^2}\right)\right)\right]$$

Substituting (A.4) in (A.1), (A.1) in (3.6a) with account of (A.3), we obtain the expression (4.2), and the discarded terms are small under the condition $\nu^2 \gg \max(1, \beta_m^{3/2})$. At $\beta_m \lesssim 1$, the obtained condition is identical with (4.1), but at $\beta_m \gg 1$ it is more rigorous. The latter circumstance, however, does not change the general criterion for the diffusion description (4.1), since at $\beta_m \gg 1$, the expansion of the functions in (3.6) can be carried out subject to the solitary condition $\nu \gg 1$, if we use the integral representation F[11]:

$$F\left(\nu, \nu\ 1+2\nu; -\frac{1}{z}\right) = \frac{2\Gamma(2\nu)}{\Gamma^2(\nu)} \int_0^1 r^{\nu-1}(1-r)^\nu \left(1+\frac{x}{z}\right)^{-\nu} dx$$

and the formula

$$2\pi\Lambda(z,\nu)\operatorname{ctg}\pi\nu = \frac{\Gamma^2(\nu)F(\nu,\nu,1+2\nu;-1/z)}{2\Gamma(2\nu)z^\nu F(-\nu,\nu,1;-z)} \tag{A.5}$$

obtained from (A.1) by use of the properties of hypergeometric functions. Actually, carrying out the asymptotic estimate of $F(\nu;\nu;1+2\nu;-1/z)$ by the saddle-point method:

$$F(\nu,\nu,1+2\nu;-1/z) \sim \frac{2\Gamma(2\nu)}{\Gamma^2(\nu)}\left(\frac{\pi}{\nu}\right)^{1/2}\left(\frac{1+z}{z}\right)^{1/4} \times \left(\frac{z}{1+2z+2[z(1+z)]^{1/2}}\right)^\nu \left\{1+O\left(\max\left(\frac{1}{\nu},\frac{1}{\beta_m^{1/2}}\right)\right)\right\} \tag{A.6}$$

and using (see Ref. 10)

$$F(-\nu,\nu,1;-z) \sim \frac{1}{2(\pi\nu)^{1/2}}\left(\frac{1+z}{z}\right)^{1/4}(1+2z+2[z(1+z)]^{1/2})^\nu\left[1+O\left(\frac{1}{\nu}\right)\right]$$

we establish the fact that these estimates are correct under the conditions $\beta_m \gg 1, \nu \gg 1$. Using them in (A.6), and (A.6) and (A.3) in (3.6), we obtain the result (4.4), which is just a special case of (4.2), corresponding to strong diffusion quenching $\beta_m \gg 1$. Thus, the result (4.2) is valid for any value of β_m if only the condition (4.1) is satisfied.

APPENDIX B

To obtain Eq. (5.1a), we must use the expression (A.5), substituting (A.2) in it. Further, using the representation $F(-\nu,\nu,1,-z)$, in the form of a series, and the asymptotic formula (as $\nu \to 0$)

$$\psi(\nu) \sim C - \frac{1}{\nu} + \frac{\pi^2}{6}\nu - \zeta(3)\nu^2 + \frac{\pi^4}{90}\nu^3 + O(\nu^4) \tag{B.1}$$

(where $\zeta(x)$ is the Riemann zeta function), under the condition $\nu \ll 1$, we get the desired result.

To obtain (5.1b), we must use the expression (A.1) and, for the function F entering into it, a representation in the form of a series. Further, using the expansion $z^{2\nu} = e^{2\nu \ln z}$ under the condition $\nu \ln z \ll 1$, and expanding the remaining function under the condition $\nu \ll 1$, we obtain the desired result.

The identity of the result (5.1a) with (5.2) is established by reduction of the integral (5.2) to the table[11] by the change of variable $y = 2xr$. Calculation of (5.2) at $z \geqslant 1$ is performed by dividing it into two integrals (after the variable change $y = 2\varkappa r$):

$$k = \frac{\pi}{\varkappa^3\tau_0}\left(\frac{1}{2}\int_0^{\ln z}\frac{y^2\,dy}{1+e^y/z} + \frac{z}{2}\int_{\ln z}^{\infty}\frac{y^2e^{-y}}{1+ze^{-y}}dy\right), \tag{B.2}$$

in each of which the integrand is represented in the form of the sum of an infinite geometric progression. Integrating term by term, we obtain (5.1b).

To obtain the result (6.4), which covers the region of the mixed and strong jump quenching, we may use the same expanded functions as in obtaining (5.1), but now take it into account that we do not expand the function $z^{2\nu} = \exp(2\nu \ln z)$, since $\nu \ln z$ is not small in the general case. The expression (6.3) follows from (6.4) at $\nu \ln z \gg 1$.

[1] N. N. Tunitskiĭ, Diffuziya i sluchaĭnye protsessy (Diffusion and Random Processes) Nauka, 1970.

[2] E. E. Nikitin, Teoriya élementarnykh atomno-molekularnykh protessov v gazakh (Theory of Elementary Atomic-molecular Processes in Gases) Khimiya, 1970.

[3] M. V. Artamonova, Ch. M. Briskina, A. I. Burshteĭn, L. D. Zusman and A. G. Skleznev, Zh. Eksp. Teor. Fiz. **62**, 863 (1972) [Sov. Phys.-JETP **35**, 457 (1972)] A. I. Burshteĭn, Zh. Eksp. Teor. **62**, 1965 (1972) [Sov. Phys.-JETP **35**, 882 (1972)].

[4] L. D. Zusman, Optika i spektr. **36**, 497 (1974) [Opt. and Spectrosc. **36**, 287 (1974)] B. E. Vugmeister, Fiz. Tverd. Tela **18**, 819 (1976) [Sov. Phys.-Solid State **18**, 469 (1976)].

[5] V. M. Agranovich, Teoriya eksitonov (Theory of Excitons) Nauka, 1968.

[6] N. N. Tunitskiĭ, Kh. S. Bagdasar'yan, Optika i epektrosk. **15**, 100 (1963) [Optics and Spectrosc. **15**, 50 (1963)].

[7] A. B. Doktorov and A. Burshteĭn, Zh. Eksp. Teor. Fiz. **68**, 1349 (1975) [Sov. Phys.-JETP **41**, 671 (1975)].

[8] A. I. Burshteĭn and L. D. Zusman, Optika i spekstrosk. **38**, 1020 (1975) [Optics and Spectrosc. **38**, 588 (1975)].

[9] G. T. Evans and M. Fixman, J. Phys. Chem. **80**, 1544 (1976).

[10] I. S. Gradshteĭn and I. M. Ryzhik, Tables of Integrals, Sums, Series and Derivatives, (VEB Deutscher Verlag, Berlin, 1963).

[11] G. Korn and T. Korn, Mathematical Handbook for Scientists and Engineers 2nd Ed. McGraw-Hill, N.Y., 1968.

Translated by R. T. Beyer