Collisional energy transfer and quenching of electronic excitation

(singlet-singlet transfer/triplet-triplet transfer/polar quenching/spectral overlap)

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ABSTRACT The purpose of this paper has been to explore in a preliminary way the nature and mechanism of collisional energy transfer and quenching of electronic excitation. For this purpose, the Born approximation has been used, and the triplet-triplet and singlet-singlet transfer, and the triplet-triplet and singlet-singlet quenching have been studied. It has been shown theoretically that (i) the singlet-singlet transfer constants (or cross sections) are always larger than the triplet-triplet transfer constants (or cross sections) for the same system of donor and acceptor; (ii) for the singlet-singlet transfer, the observed cross section varies linearly with respect to the spectral overlap between the donor emission and the acceptor absorption; (iii) the reason that the quenching constants (or cross sections) are always smaller than the energy transfer constants (or cross sections) is due to the fact that for the quenching the vibration of the acceptor hardly participates in accepting the electronic excitation and for the energy transfer only part of the excited electron energy of the donor is converted into the energy of nuclear motion; and (iv) the polar acceptor molecules are better quenchers than nonpolar acceptor molecules.

I. Introduction

When a molecule (donor D^*) is in an excited electronic state and collides with another molecule (acceptor A) the electronic energy may transfer to the acceptor

or the electronic energy may transform into the energy of nuclear motion of A and D through collision,

For convenience, the first case will be called the energy transfer and the second will be called the quenching of electronic excitation.

Another way for energy transfer or quenching to take place will be through the formation of a long-lived collision intermediate or complex and the redistribution or transformation of the electronic energy (nonradiative process) before the donor and acceptor molecules move apart. This case involves several elementary processes and will not be discussed in this paper.

In a previous paper (1), we have treated the collisional energy transfer of electronic excitation using the Born approximation. In this paper, we investigate the collisional quenching of electronic excitation and report some results of application of the theoretical treatment of energy transfer and quenching of electronic excitation. The reason for using the Born approximation is that analytical expressions for cross sections and rate constants of energy transfer or quenching of electronic excitation can be obtained and hence can be easily used to interpret experimental data qualitatively or semiquantitatively. For quantitative agreement between theoretical and experimental results, a more elaborate meth-

od than the Born approximation is required; for energy transfer or quenching of electronic excitation of polyatomic molecules, at present it is very difficult to carry out such a task. It should be noted that the Landau-Zener type of energy transfer or quenching processes for small systems (2, 3) is not included in this investigation.

II. Energy transfer

The collisional energy transfer of electronic excitation has been discussed in the previous paper (1). Here we shall report some applications of the theoretical results given in that paper. It has been shown that for the triplet-triplet transfer, $^1A + ^3D^* \rightarrow ^3A^* + ^1D$, the electronic interaction between A and D is of exchange interaction and the rate constant of the triplet-triplet transfer can be expressed as (1, 4, 5)

$$k_{ab}^{(E)}(T) = 256\pi^3 C(e^4 L^6 / R_0^2) \sum_{v'} \sum_{v''} P_{av'} \times |\langle \oplus_{bv''} | \oplus_{av'} \rangle|^2 \bar{\omega}^2 D(E_{av'} - E_{bv''}) \quad [2-1]$$

$$\bar{\omega}^2 = |\langle \oplus_{bv''(\text{rot})} | \omega | \oplus_{av'(\text{rot})} \rangle|^2;$$

$$D(E_{av'} - E_{bv''}) = \int_0^\infty f(v) \frac{k_{bv''}}{k_{av'}} v dv \quad [2-2]$$

Here the Dexter equation for the exchange interaction (6-8) has been used,

$$V_{ba}(\mathbf{R})_E = (\omega e^2 / R_0) \exp\left(-\frac{R}{L}\right) \quad [2-3]$$

where R_0 and L are constants and ω is determined by the relative orientation between A and D .

Eq. [2-1] should be compared with the corresponding expression for the triplet-triplet transfer in solids obtained from the Förster-Dexter theory (6-9).

$$P_{ab}(T) = \frac{2\pi}{\hbar} \cdot \frac{\bar{\omega}^2 e^4}{R_0^2} \exp\left(-\frac{2R}{L}\right) \sum_{v'} \sum_{v''} P_{av'} \times |\langle \oplus_{bv''} | \oplus_{av'} \rangle|^2 \delta(E_{av'} - E_{bv''}) \quad [2-4]$$

In other words, while the energy conservation in the solid state energy transfer is controlled by the delta function $\delta(E_{av'} - E_{bv''})$, the energy conservation in the collisional energy transfer is regulated by the translational energy of the relative translational motion through the factor $D(E_{av'} - E_{bv''})$. However, because of the difference in the scales between translational and internal energy, one may expect that the translational motion does not participate effectively in the energy transfer. This indicates that the effectiveness of the gaseous triplet-triplet transfer can also be determined by the spectral overlap between the donor emission and acceptor absorption just as is done in the solid state triplet-triplet

transfer. In this case, the absorption spectrum for the singlet-triplet transition is difficult to obtain directly; indirect methods like the O₂-induced optical absorption or electron-impact spectroscopy, etc. can be used, however. From Eqs. [2-4] and [2-1] we can see that the constants L and R_0 determined from the solid phase triplet-triplet transfer can be transferred to the collisional triplet-triplet transfer and vice versa.

For the singlet-singlet transfer, $^1A + ^1D^* \rightarrow ^1A^* + ^1D$; since the interaction between A and D consists of the Coulomb and exchange interactions, it has been shown that the bimolecular rate constant for the singlet-singlet transfer can be written as

$$k_{ab}(T) = k_{ab}^{(c)}(T) + k_{ab}^{(E)}(T) \quad [2-5]$$

where $k_{ab}^{(E)}(T)$ is exactly the same as that given in Eq. [2-1] and $k_{ab}^{(c)}$ is due to the contribution from the Coulomb interaction,

$$k_{ab}^{(c)}(T) = 64\pi^3 C \sum_{v'} \sum_{v''} P_{av'} \left| \langle \Phi_{bv''}^{(D)} | \hat{K} \cdot \mathbf{R}_{D \cdot D} | \Phi_{av'}^{(D)} \rangle \right|^2 \times \left| \langle \Phi_{bv''}^{(A)} | \hat{K} \cdot \mathbf{R}_{AA^*} | \Phi_{av'}^{(A)} \rangle \right|^2 D(E_{av'} - E_{bv''}) \quad [2-6]$$

where $\hat{K}$ represents the unit vector of $\mathbf{K}$. This should be compared with the transition probability of the singlet-singlet transfer in the solid phase (9, 10),

$$P_{ab}(T) = \frac{4\pi}{3\hbar\epsilon^2 R^6} \sum_{v'} \sum_{v''} P_{av'} \left| \langle \Phi_{bv''}^{(D)} | \mathbf{R}_{D \cdot D} | \Phi_{av'}^{(D)} \rangle \right|^2 \times \left| \langle \Phi_{bv''}^{(A)} | \mathbf{R}_{AA^*} | \Phi_{av'}^{(A)} \rangle \right|^2 \delta(E_{av'} - E_{bv''}) \quad [2-7]$$

where ϵ is the dielectric constant of the medium. Except for the factors $\hat{K} \cdot \mathbf{R}_{D \cdot D}$ and $\hat{K} \cdot \mathbf{R}_{AA^*}$, which determine the contribution of rotational motion to the energy transfer process, the similarity between Eqs. [2-6] and [2-7] is remarkable.

From Eq. [2-5] we can see that due to the fact the electronic interaction involved in the singlet-singlet transfer consists of Coulomb and exchange interactions, the rate constant of the singlet-singlet transfer consists of the contribution from the Coulombic interaction and the contribution from the exchange interaction. For the triplet-triplet transfer, the rate constant consists only of the contribution from the exchange interaction. Thus for the same set of the donor and acceptor, we may expect that the rate constant (or the corresponding cross section) of the singlet-singlet transfer will be bigger than that of the triplet-triplet transfer. This is in agreement with the experimental results of Lee *et al.* (11-13).

For the singlet-singlet transfer, the rate constant contributed from the Coulombic interaction $k_{ab}^{(c)}$ has been shown to be closely related to the transition probability of the singlet-singlet transfer in the solid phase. We may expect that $k_{ab}^{(c)}$ varies linearly with the product of the radiative rate constant of the donor and the spectral overlap J between the donor emission and acceptor absorption, and that the intercept of the straight line yields the contribution from the exchange interaction. The experimental results of Lee *et al.* (11-13) indeed demonstrate the existence of the contribution from the exchange interaction. In other words, in contrast with the singlet-singlet transfer in the solid phase in which the exchange interaction is unimportant in dilute solutions, for the collisional singlet-singlet transfer, both Coulomb and exchange interactions are significant, since the donor and acceptor may come close together during collision. From the

above discussion, we can see that an empirical equation of $Q(T) = aJ + b$, where a and b are constants, can be used to correlate the cross sections and the spectral overlap for the singlet-singlet transfer (11, 12).

For the triplet-singlet transfer or singlet-triplet transfer, the process is spin-forbidden, but can be induced by the inclusion of the spin-orbit coupling to borrow the strength of transition from singlet-singlet and triplet-triplet transfers. The rate constant in this case can be expressed as that given by Eq. [2-5].

III. Quenching of electronic excitation

A. Triplet-Triplet Quenching. Let us first consider the triplet-triplet quenching $^3A + ^3D^* \rightarrow ^3A + ^1D$. In this case, the electronic interaction between A and D , $V_{ba}(\mathbf{R})_E$ is of exchange interaction. For example, if we use

$$\begin{aligned} {}^3\Phi_a &= \frac{1}{2} \left(\left| X_{D_1}^+ X_{D_1}^- \dots X_{D_n}^+ X_{D_n}^- X_{A_1}^+ X_{A_1}^- \dots X_{A_m}^+ X_{A_m}^- \right| \right. \\ &\quad + \left| X_{D_1}^+ X_{D_1}^- \dots X_{D_n}^+ X_{D_n}^- X_{A_1}^+ X_{A_1}^- \dots X_{A_m}^+ X_{A_{m+1}}^+ \right| \\ &\quad - \left| X_{D_1}^+ X_{D_1}^- \dots X_{D_n}^+ X_{D_{n+1}}^+ X_{A_1}^+ X_{A_1}^- \dots X_{A_m}^+ X_{A_{m+1}}^- \right| \\ &\quad \left. - \left| X_{D_1}^+ X_{D_1}^- \dots X_{D_n}^+ X_{D_{n+1}}^+ X_{A_1}^+ X_{A_1}^- \dots X_{A_m}^+ X_{A_{m+1}}^+ \right| \right) \end{aligned} \quad [3-1]$$

and

$$\begin{aligned} {}^3\Phi_b &= \left| X_{D_1}^+ X_{D_1}^- \dots X_{D_n}^+ X_{D_n}^- X_{A_1}^+ X_{A_1}^- \dots X_{A_m}^+ X_{A_{m+1}}^+ \right| \end{aligned} \quad [3-2]$$

where X_{D_n} and X_{A_m} represent the molecular orbitals, then the electronic interaction between A and D can be expressed as

$$\begin{aligned} V_{ba}(\mathbf{R})_E &= \left\langle X_{D_n} X_{A_m} \left| \frac{e^2}{r_{12}} \right| X_{A_m} X_{D_{n+1}} \right\rangle \\ &\quad + \left\langle X_{D_n} X_{A_{m+1}} \left| \frac{e^2}{r_{12}} \right| X_{A_{m+1}} X_{D_{n+1}} \right\rangle \end{aligned} \quad [3-3]$$

the exchange interaction. Thus, if we use the Dexter relation for $V_{ba}(\mathbf{R})_E$, then the differential cross section can easily be evaluated as

$$\begin{aligned} \sigma_{av',bv''}^{(E)}(\theta) &= C \frac{k_{bv''}}{k_{av'}} \cdot \frac{64\pi^2 e^4 L^6}{R_0^2} \cdot \frac{1}{(1 + L^2 K^2)^4} \\ &\quad \times |\langle \Phi_{bv''} | \omega | \Phi_{av'} \rangle|^2 \end{aligned} \quad [3-4]$$

It follows that

$$\begin{aligned} Q_{av',bv''}^{(E)} &= \frac{64\pi^3 C}{3k_{av'}^2} \cdot \frac{e^4 L^4}{R_0^2} \left[\frac{1}{(1 + L^2 K_{\min}^2)^3} \right. \\ &\quad \left. - \frac{1}{(1 + L^2 K_{\max}^2)^3} \right] |\langle \Phi_{bv''} | \omega | \Phi_{av'} \rangle|^2 \end{aligned} \quad [3-5]$$

which for $L^2 K_{\min}^2 \ll 1$ becomes

$$Q_{av',bv''}^{(E)} = 256\pi^3 C \frac{k_{bv''}}{k_{av'}} \cdot \frac{e^4 L^6}{R_0^2} |\langle \Phi_{bv''} | \omega | \Phi_{av'} \rangle|^2 \quad [3-6]$$

Using Eq. [3-5] for $Q_{av',bv''}^{(E)}$, we can calculate the rate constant for the triplet-triplet quenching as

$$k_{ab}^{(E)}(T) = \frac{64\pi^3 C}{3} \cdot \frac{e^4 L^4}{R_0^2} \sum_{v'} \sum_{v''} P_{av'} |\langle \Theta_{bv''} | \omega | \Theta_{av'} \rangle|^2 \times \int_0^\infty \frac{f(v)}{k_{av'}^2} \left[\frac{1}{(1 + L^2 K_{\min}^2)^3} - \frac{1}{(1 + L^2 K_{\max}^2)^3} \right] v dv \quad [3-7]$$

which for $K_{\max}^2 L^2 \ll 1$ reduces to

$$k_{ab}^{(E)}(T) = 256\pi^3 C \frac{e^4 L^6}{R_0^2} \sum_{v'} \sum_{v''} P_{av'} \times |\langle \Theta_{bv''} | \omega | \Theta_{av'} \rangle|^2 D(E_{av'} - E_{bv''}) \quad [3-8]$$

or

$$k_{ab}^{(E)}(T) = 256\pi^3 C \frac{e^4 L^6}{R_0^2} \sum_{v'} \sum_{v''} P_{av'}^{(D)} \times |\langle \Theta_{bv''}^{(D)} | \Theta_{av'}^{(D)} \rangle|^2 \bar{\omega}^2 D(E_{av'} - E_{bv''}) \quad [3-9]$$

Eq. [3-4] implies that the vibrational motion of the acceptor molecule does not participate in the quenching of electronic excitation, and the amount of excited electronic energy that becomes rotational energy is determined by the factor $\bar{\omega}^2 = |\langle \Theta_{bv''}^{(\text{rot})} | \omega | \Theta_{av'}^{(\text{rot})} \rangle|^2$. In other words, most of the excited electronic energy has to be converted into the vibrational energy of the donor molecule. Comparing the Franck-Condon factor in Eq. [3-4] with that in Eq. [2-1], and noticing that in Eq. [2-1] the Franck-Condon factor $\langle \Theta_{bv''} | \Theta_{av'} \rangle = \langle \Theta_{bv''}^{(D)} | \Theta_{av'}^{(D)} \rangle \langle \Theta_{bv''}^{(A)} | \Theta_{av'}^{(A)} \rangle$, we can see that the quenching rate constant (or cross section) will be smaller than the energy transfer rate constant (or cross section). Physically, this is due to the fact that in the energy transfer, the vibration of both donor and acceptor participates in accepting the electronic excitation, whereas in the quenching process only the vibration of the donor participates in accepting the excited electronic energy; furthermore, in the energy transfer process, only part of the electronic excitation is transformed into the energy of nuclear motion, whereas in the quenching process the whole portion of electronic excitation becomes the energy of nuclear motion.

For example, if we use

$$\Phi_a = \frac{1}{\sqrt{2}} \times \left(|X_{D_1}^+ X_{D_1}^- \dots X_{D_n}^+ X_{D_n}^- X_{A_1}^+ X_{A_1}^- \dots X_{A_m}^+ X_{A_m}^-| + |X_{D_1}^+ X_{D_1}^- \dots X_{D_{n+1}}^+ X_{D_{n+1}}^- X_{A_1}^+ X_{A_1}^- \dots X_{A_m}^+ X_{A_{m+1}}^-| \right) \quad [3-10]$$

and

$$\Phi_b = |X_{D_1}^+ X_{D_1}^- \dots X_{D_n}^+ X_{D_n}^- X_{A_1}^+ X_{A_1}^- \dots X_{A_m}^+ X_{A_m}^-| \quad [3-11]$$

then it follows that $V_{ba}(\mathbf{R}) = V_{ba}(\mathbf{R})_C + V_{ba}(\mathbf{R})_E$, where

$$V_{ba}(\mathbf{R})_C = \sqrt{2} \left[\langle X_{D_n} | - \sum_{\alpha} \frac{Z_{\alpha} e^2}{r_{A\alpha}} | X_{D_{n+1}} \rangle + 2 \sum_{j=1}^m \langle X_{A_j} X_{D_n} | \frac{e^2}{r_{12}} | X_{A_j} X_{D_{n+1}} \rangle \right] \quad [3-12]$$

and

$$V_{ba}(\mathbf{R})_E = - \sqrt{2} \sum_{j=1}^m \langle X_{A_j} X_{D_n} | \frac{e^2}{r_{12}} | X_{D_{n+1}} X_{A_j} \rangle \quad [3-13]$$

The first term in Eq. [3-12] represents the Coulomb interaction between nuclei of the acceptor molecule and electrons of the donor molecules.

Using Eq. [3-12], we find (1)

$$V_{ba}^{(c)} = \frac{4\sqrt{2}\pi e^2}{K^2} \left[- \sum_{\alpha} Z_{\alpha} \exp(-i\mathbf{K} \cdot \mathbf{r}_{A\alpha}) \langle X_{D_n} | \exp(i\mathbf{K} \cdot \mathbf{r}_{D_i}) | X_{D_{n+1}} \rangle + 2 \sum_{j=1}^m \langle X_{A_j} | \exp(-i\mathbf{K} \cdot \mathbf{r}_{A_2}) | X_{A_j} \rangle \langle X_{D_n} | \exp(i\mathbf{K} \cdot \mathbf{r}_{D_1}) | X_{D_{n+1}} \rangle \right] \quad [3-14]$$

Another case of quenching of electronic excitation, ${}^3A + {}^1D^* \rightarrow {}^3A + {}^3D$, is also of the exchange interaction and can be discussed similarly.

B. Singlet-Singlet Quenching. Next we discuss the singlet-singlet quenching ${}^1A + {}^1D^* \rightarrow {}^1A + {}^1D$. In this case, the electronic interaction between A and D consists of Coulombic and exchange interactions. The contribution from the exchange interaction to the singlet-singlet quenching is similar to that of the triplet-triplet quenching. Thus, we have to consider only the contribution of the Coulombic interaction to the singlet-singlet quenching.

Using Eq. [3-14], we obtain (1)

$$\sigma_{av',bv''}^{(c)}(\theta) = C \frac{k_{bv''}}{k_{av'}} \cdot \frac{32\pi^2 e^4}{K^4} |\langle \Theta_{bv''}^{(D)} | \langle X_{D_n} | e^{i\mathbf{K} \cdot \mathbf{r}_{D_i}} | X_{D_{n+1}} \rangle | \times \langle \Theta_{av'}^{(D)} |^2 \left[\langle \Theta_{bv''}^{(A)} | - \sum_{\alpha} Z_{\alpha} e^{-i\mathbf{K} \cdot \mathbf{r}_{A\alpha}} + 2 \sum_{j=1}^m \langle X_{A_j} | e^{-i\mathbf{K} \cdot \mathbf{r}_{A_j}} | X_{A_j} \rangle | \Theta_{av'}^{(A)} \rangle \right]^2 \quad [3-15]$$

or approximately

$$\sigma_{av',bv''}^{(c)}(\theta) = C \frac{k_{bv''}}{k_{av'}} \cdot \frac{16\pi^2}{K^4} |\langle \Theta_{bv''}^{(D)} | \mathbf{K} \cdot \mathbf{R}_{D^*D} | \Theta_{av'}^{(D)} \rangle|^2 \times |\langle \Theta_{av'}^{(A)} | \mathbf{K} \cdot \boldsymbol{\mu}_A | \Theta_{av'}^{(A)} \rangle|^2 \quad [3-15A]$$

where $\boldsymbol{\mu}_A$ represents the dipole moment of the acceptor molecule at a particular nuclear configuration. It follows

$$Q_{av',bv''}^{(c)} = 64\pi^3 C \frac{k_{bv''}}{k_{av'}} |\langle \Theta_{bv''}^{(D)} | \mathbf{K} \cdot \mathbf{R}_{D^*D} | \Theta_{av'}^{(D)} \rangle|^2 \times |\langle \Theta_{av'}^{(A)} | \mathbf{K} \cdot \boldsymbol{\mu}_A | \Theta_{av'}^{(A)} \rangle|^2 \quad [3-16]$$

and the corresponding rate constant is given by

$$k_{ab}^{(c)}(T) = 64\pi^3 C \sum_{v'} \sum_{v''} P_{av'} |\langle \Theta_{bv''}^{(D)} | \mathbf{K} \cdot \mathbf{R}_{D^*D} | \Theta_{av'}^{(D)} \rangle|^2 \times |\langle \Theta_{av'}^{(A)} | \mathbf{K} \cdot \boldsymbol{\mu}_A | \Theta_{av'}^{(A)} \rangle|^2 D(E_{av'} - E_{bv''}) \quad [3-17]$$

Now we notice that $\boldsymbol{\mu}_A$ is a function of normal coordinates,

$$\boldsymbol{\mu}_A = \boldsymbol{\mu}_A^0 + \sum_i \left(\frac{\partial \boldsymbol{\mu}_A}{\partial Q_i} \right)_0 Q_i + \dots \quad [3-18]$$

Using Eq. [3-18], Eq. [3-17] can be written as

$$k_{ab}^{(c)}(T) = k_{ab}^{(c)}(T)_0 + \sum_i k_{ab}^{(c)}(T)_i \quad [3-19]$$

where

$$k_{ab}^{(c)}(T)_0 = 64\pi^3 C \sum_{\nu'} \sum_{\nu''} P_{\nu'\nu''} \left| \langle \Theta_{b\nu''}^{(D)} | \mathbf{K} \cdot \mathbf{R}_{D^*D} | \Theta_{a\nu'}^{(D)} \rangle \right|^2 \\ \times \left| \langle \Theta_{a\nu''}^{(A)} | \mathbf{K} \cdot \boldsymbol{\mu}_A | \Theta_{a\nu'}^{(A)} \rangle \right|^2 D(E_{a\nu'} - E_{b\nu''}) \quad [3-20]$$

and

$$k_{ab}^{(c)}(T)_i = 64\pi^3 C \sum_{\nu'} \sum_{\nu''} P_{\nu'\nu''} \left| \langle \Theta_{b\nu''}^{(D)} | \mathbf{K} \cdot \mathbf{R}_{D^*D} | \Theta_{a\nu'}^{(D)} \rangle \right|^2 \\ \times \left| \left\langle \Theta_{a\nu''}^{(A)} \left| \mathbf{K} \cdot \left(\frac{\partial \boldsymbol{\mu}_A}{\partial Q_i} \right)_0 Q_i \right| \Theta_{a\nu'}^{(A)} \right\rangle \right|^2 D(E_{a\nu'} - E_{b\nu''}) \quad [3-21]$$

From Eqs. [3-19]–[3-21], we can see that for polar acceptor molecules, the quenching can take place without the participation of the vibrational motion of the acceptor in accepting the electronic excitation, (compare Eq. [3-20]), i.e., it is like the intermolecularly induced radiationless transition, and the quenching can also take place with the participation of the infrared active modes of the acceptor (compare Eq. [3-21]). The infrared active modes to the first order approximation can accept only one vibrational quantum in the quenching process.

For nonpolar acceptor molecules, μ_A^0 vanishes and the quenching takes place only through the first order terms in Eq. [3-18] with the participation of the infrared active modes in accepting the excited electronic energy. Thus we may expect that in most cases, polar molecules are more efficient in quenching the electronic excitation than nonpolar molecules. It should be noted that the dipole moment derivatives $(\partial \mu_A / \partial Q_i)_0$ can be determined from the intensity of infrared spectra. In other words, the quenching process is closely related to the dipole moment and infrared intensity of the acceptor molecule and the radiative rate constant of the donor. Eq. [3-19] implies that except for a small portion of excited electronic energy that is being converted into the vibrational, rotational, and translational energy of the acceptor, most of excited electronic energy is converted into the energy of nuclear motion of the donor molecule, and thus the singlet-singlet quenching constants (or cross sections) are smaller than the singlet-singlet transfer constants (or cross sections).

For small polar acceptor and small donor molecules, $k_{ab}^{(c)}(T)_i$ might be significant in comparison with $k_{ab}^{(c)}(T)_0$

in this case the smallness of $(\partial \mu_A / \partial Q_i)_0$ in Eq. [3-21] compared with μ_A^0 in Eq. [3-20] may be compensated by the Franck-Condon factors of the donor in Eqs. [3-21] and [3-20], because in Eq. [3-21] the donor accepts less excited electronic energy.

It should be noted that the above treatment for the singlet-singlet quenching (compare Eqs. [3-15]–[3-21]) can only be applied to polyatomic acceptor molecules and polar diatomic acceptor molecules.

For nonpolar acceptor diatomic molecules and atoms, the dipole moment μ_A in the above results should be replaced by the quadrupole moment or polarizability of the acceptor. The nature of the quenching of the excited singlet donor by the triplet (or other paramagnetic) quencher is fundamentally the same as that by the singlet quencher and will not be discussed here.

It is well known that the lifetimes of forbidden transitions in the liquid phase are sensitive to the effect of solvents (14–16). The shortening of these lifetimes in liquid solutions may be attributed to the quenching of the excited electronic state by solvent molecules and may be treated by using the theoretical approach developed in this paper.

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