Theory of Delayed Thermal Fluorescence*

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A theory of nonradiative thermal activation involved in delayed thermal fluorescence has been developed from the viewpoint of the breakdown of the Born-Oppenheimer adiabatic approximation.

The terms, delayed thermal fluorescence [1], α-phosphorescence [2], fluorescence of long duration [3], high temperature fluorescence [4], E-type delayed fluorescence [5], slow fluorescence [6], etc., refer to the fluorescence in which the excited singlet state is induced by nonradiative thermal excitation from a triplet state. Delayed thermal fluorescence has been observed in a number of dyestuffs like eosin, proflavine hydrochloride, fluorescein, etc., in deoxygenated solutions [5]. It has been found experimentally by Parker and Hatchard [5, 7] that the rate of nonradiative thermal activation, k_e, can be expressed as

$$k_e = A e^{-\Delta E'/kT}, \tag{1}$$

where A is the preexponential factor and $\Delta E'$ represents the energy difference between the singlet and triplet states involved in delayed thermal fluorescence. In this communication, we shall report the quantum mechanical derivation of Eq. (1).

In a previous paper [8], we have discussed the rate of interconversion of electronic and vibrational energy from the viewpoint of the nonstationary character of the Born-Oppenheimer adiabatic approximation. It has been shown that when the rate of vibrational relaxation is much faster than that of electronic relaxation, the transition probability of interconversion of electronic and vibrational energy is given by

$$W(b \to a) = \frac{2\pi}{\hbar} |R_i(ab)|^2 \sum_{v'} \sum_{v''} P_{v'} \left| \left\langle \theta_{av''} \left| \frac{\partial}{\partial Q_i} \right| \theta_{bv'} \right\rangle \right|^2 \delta(E_{av''} - E_{bv'}), \tag{2}$$

where $R_i(ab)$ represents the coupling matrix elements between the two electronic states, $R_i(ab) = -\hbar^2 \left\langle \Phi_a \left| \frac{\partial}{\partial Q_i} \right| \Phi_b \right\rangle$, $P_{v'}$, the Boltzmann factor, and $\theta_{av''}$ and $\theta_{bv'}$, the wave functions of nuclear motion. For simplicity, we have assumed that only one promoting mode Q_i, is responsible for inducing the radiationless transition. The nonradiative process of the relaxation of electronic energy to vibrational energy has been considerably discussed [9]. The nonradiative process in delayed thermal fluorescence involves the conversion of vibrational energy into electronic energy and hence the derivation of the transition probability of non-radiative

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thermal activation will be similar to that of nonradiative process of electronic relaxation.

By introducing the integral representation of the δ-function, it has been shown that when the changes in the normal frequencies between the two electronic states, $\omega_i'' = \omega_i'(1 - \varrho_i)$, are small, the transition probability can be expressed as [8, 10],

$$W(b \to a) = \frac{1}{\hbar^2} |C_i(ab)|^2 e^{-S} \int_{-\infty}^{\infty} dt e^{i\omega_{ab}t} \left[\frac{1}{2} \left(\coth \frac{\hbar\omega_i'}{2kT} + 1 \right) e^{i\omega_i't} + \frac{1}{2} \right.$$

$$\left. \left(\coth \frac{\hbar\omega_i'}{2kT} - 1 \right) e^{-i\omega_i't} \right] \exp \left[-\frac{1}{2} \sum_{j=1} i\varrho_j\omega_j't \coth \frac{\hbar\omega_j'}{2kT} + 2 \sum_{j=1}^{N} a_j^2 \right. \tag{3}$$

$$\left. \operatorname{csch} \frac{\hbar\omega_j'}{2kT} \cos \left(\omega_j't - \frac{i\hbar\omega_j'}{2kT} \right) \right],$$

where $\hbar\omega_{ab} = \Delta E$, $|C_i(ab)|^2 = \dfrac{\omega_i'}{4\pi\hbar^2} |R_i(ab)|^2$, $a_j = \dfrac{1}{2} \beta_j'(d_j'' - d_j')$, $\beta_j' = \dfrac{\omega_j'}{\hbar}$, and

$$S = 2 \sum_{j=1}^{N} a_j^2 \coth \frac{\hbar\omega_j'}{2kT}. \quad d_j'' - d_j' \text{ represents the change of } j\text{-th normal coordinate}$$

between the two electronic states. Several methods have been proposed to evaluate the integral in Eq. (3) [9, 10], and one of which gives [10]

$$W(b \to a) = W_+(b \to a) + W_-(b \to a), \tag{4}$$

where

$$W_+(b \to a) = \frac{2\pi}{\hbar} |C_i(ab)|^2 e^{-S} \left(\frac{1}{2} \coth \frac{\hbar\omega_i'}{2kT} + \frac{1}{2} \right) \sum_{n_1=0}^{\infty} \cdots \sum_{n_L=0}^{\infty} \sum_{m_1=0}^{\infty} \cdots \sum_{m_L=0}^{\infty}$$

$$\prod_{j}^{L} \prod_{k}^{L} \frac{\left(a_j^2 \operatorname{csch} \dfrac{\hbar\omega_j'}{2kT} e^{-\frac{\hbar\omega_j'}{2kT}} \right)^{n_j} \left(a_k^2 \operatorname{csch} \dfrac{\hbar\omega_k'}{2kT} e^{-\frac{\hbar\omega_k'}{2kT}} \right)^{m_k}}{n_j! \, m_k!} \delta \left(\Delta E + \hbar\omega_i' \right.$$

$$\left. -\frac{1}{2} \sum_{j}^{L} \varrho_j\hbar\omega_j' \coth \frac{\hbar\omega_j'}{2kT} + \sum_{j}^{L} n_j\hbar\omega_j' - \sum_{k}^{L} m_k\hbar\omega_k' \right) \tag{5}$$

and

$$W_-(b \to a) = \frac{2\pi}{\hbar} |C_i(ab)|^2 e^{-S} \left(\frac{1}{2} \coth \frac{\hbar\omega_i'}{2kT} - \frac{1}{2} \right) \sum_{n_1=0}^{\infty} \cdots \sum_{n_L=0}^{\infty} \sum_{m_1=0}^{\infty} \cdots \sum_{m_L=0}^{\infty}$$

$$\prod_{j}^{L} \prod_{k}^{L} \frac{\left(a_j^2 \operatorname{csch} \dfrac{\hbar\omega_j'}{2kT} e^{\frac{\hbar\omega_j'}{2kT}} \right)^{n_j} \left(a_k^2 \operatorname{csch} \dfrac{\hbar\omega_k'}{2kT} e^{-\frac{\hbar\omega_k'}{2kT}} \right)^{m_k}}{n_j! \, m_k!} \delta \left(\Delta E - \hbar\omega_i' \right.$$

$$\left. -\frac{1}{2} \sum_{j}^{L} \varrho_j\hbar\omega_j' \coth \frac{\hbar\omega_j'}{2kT} + \sum_{j}^{L} n_j\hbar\omega_j' - \sum_{k}^{L} m_k\hbar\omega_k' \right). \tag{6}$$

L in the above equations represents the total number of normal modes involved in the nonradiative process, m_k denotes the number of vibrational quanta in the k-th normal mode of the initial electronic state due to thermal excitation, and n_j, the number of quanta in the j-th normal mode of the final electronic state. The summations over n_j, m_k in Eqs. (5) and (6) indicate that all the possible ways of converting the thermal vibrational energy of the initial electronic state into the electronic energy plus vibrational energy of the final electronic state are to be

included. Because of the factors $m_k!$ and $n_j!$ in Eqs. (5) and (6), it is not favorable for a normal mode to contribute or accept too many quanta. This implies that the normal modes with high frequencies may be favored in nonradiative thermal activation if their changes in normal coordinates are not too small [10, 11]. In the harmonic oscillator approximation used in the above derivation, for small ϱ_i's, any normal mode without any change in the normal coordinate between the two electronic states cannot contribute or accept any vibrational quanta in nonradiative thermal activation.

Following Lax [12], and Huang and Rhys [13, 14], we can write the transition probability of nonradiative thermal excitation as,

$$W_+(b \to a) = \frac{2\pi}{\hbar^2 \omega'} |C_i(ab)|^2 e^{-S} \left(\frac{1}{2} \coth \frac{\hbar \omega_i'}{2kT} + \frac{1}{2} \right) \sum_{n_1} \cdots \sum_{n_L} \sum_{m_1} \cdots \sum_{m_L} \prod_j^L \prod_k^L$$
$$\frac{\left(a_j^2 \operatorname{csch} \frac{\hbar \omega_j'}{2kT} e^{\frac{\hbar \omega_j'}{2kT}} \right)^{n_j} \left(a_k^2 \operatorname{csch} \frac{\hbar \omega_k'}{2kT} e^{-\frac{\hbar \omega_k'}{2kT}} \right)^{m_k}}{n_j! m_k!}, \tag{7}$$

where $\sum_k^L m_k \hbar \omega_k' = \Delta E + \hbar \omega_i' - \frac{1}{2} \sum_j^L \varrho_j \hbar \omega_j' \coth \frac{\hbar \omega_j'}{2kT} + \sum_j^L n_j \hbar \omega_j'$, and

$$W_-(b \to a) = \frac{2\pi}{\hbar^2 \omega'} |C_i(ab)|^2 e^{-S} \left(\frac{1}{2} \coth \frac{\hbar \omega_i'}{2kT} - \frac{1}{2} \right) \sum_{n_1} \cdots \sum_{n_L} \sum_{m_1} \cdots \sum_{m_L} \prod_j^L \prod_k^L$$
$$\frac{\left(a_j^2 \operatorname{csch} \frac{\hbar \omega_j'}{2kT} e^{\frac{\hbar \omega_j'}{2kT}} \right)^{n_j} \left(a_k^2 \operatorname{csch} \frac{\hbar \omega_k'}{2kT} e^{-\frac{\hbar \omega_k'}{2kT}} \right)^{m_k}}{n_j! m_k!}, \tag{8}$$

where $\sum_k^L m_k \hbar \omega_k' = \Delta E - \hbar \omega_i' - \frac{1}{2} \sum_j^L \varrho_j \hbar \omega_j' \coth \frac{\hbar \omega_j'}{2kT} + \sum_j^L n_j \hbar \omega_j'$. Using the relations, $\bar{n}_j = \left(e^{\frac{\hbar \omega_j'}{kT}} - 1 \right)^{-i}$, and $\sum_j^L n_j \hbar \omega_j' = \sum_k^L m_k \hbar \omega_k' - \hbar \omega_i' - \Delta E'$ where $\Delta E'$

$= \Delta E - \frac{1}{2} \sum_j^L \varrho_j \hbar \omega_j' \coth \frac{\hbar \omega_j'}{2kT}$, Eq. (7) becomes

$$W_+(b \to a) = \frac{2\pi}{\hbar^2 \omega'} |C_i(ab)|^2 e^{-S} \bar{n}_j e^{-\Delta E'/kT} \sum_{n_1} \cdots \sum_{n_L} \sum_{m_1} \cdots \sum_{m_L} \prod_j^L \prod_k^L$$
$$\frac{(2a_j^2 \bar{n}_j)^{n_j} \left(2\bar{n}_k a_k e^{\frac{\hbar \omega_k'}{kT}} \right)^{m_k}}{n_j! m_k!}, \tag{9}$$

where ω' represents the average normal frequency of intermolecular modes. Similarly,

$$W_-(b \to a) = \frac{2\pi}{\hbar^2 \omega'} |C_i(ab)|^2 e^{-S} \bar{n}_i e^{\frac{\hbar \omega_i'}{kT}} e^{-\Delta E'/kT} \sum_{n_1} \cdots \sum_{n_L} \sum_{m_1} \cdots \sum_{m_L} \prod_j^L \prod_k^L$$
$$\frac{(2a_j^2 \bar{n}_j)^{n_j} \left(2\bar{n}_k a_k^2 e^{\frac{\hbar \omega_k'}{kT}} \right)^{m_k}}{n_j! m_k!}. \tag{10}$$

Both $W_+(b \to a)$ and $W_-(b \to a)$ are zero at $T = 0$. When temperature is not very high, $\bar{n}_j$ is smaller than unity and $\bar{n}_j e^{\frac{\hbar\omega_j'}{kT}}$ approaches unity. Thus $W_-(b \to a)$ is larger than $W_+(b \to a)$, and the terms of $n_j = 0$ will be dominating. In this case, we have

$$W(b \to a) = \frac{2\pi}{\hbar^2 \omega'} |C_i(ab)|^2 e^{-S} e^{-\frac{\Delta E'}{kT}} \sum_{m_1} \cdots \sum_{m_L} \prod_k^L \frac{(2a_k^2)^{m_k}}{m_k!} . \tag{11}$$

Comparing Eq. (11) with Eq. (1) we obtain $A = \frac{2\pi}{\hbar^2 \omega'} |C_i(ab)|^2 e^{-S} \sum_{m_1} \cdots \sum_{m_L} \prod_k^L \frac{(2a_k^2)^{m_k}}{m_k!}$. The summations over m_k in Eq. (11) imply that all the possible ways of converting vibrational energy into electronic energy should be included, each way being weighted by the Franck-Condon factor, $e^{-S} \prod_k^L \frac{(2a_k^2)^{m_k}}{m_k!}$. As is well known in electronic relaxation, one can correlate the energy gap between the two electronic states with the Franck-Condon factor, and because of the Franck-Condon factor one may expect the isotope substitution to have some effect on the rate of non-radiative thermal activation.

In practice one may find it useful to have a semiempirical expression for the rate of nonradiative thermal excitation. For this purpose we introduce the average quantities for all the normal modes involved in Eq. (3). It follows

$$W(b \to a) = \frac{2\pi}{\hbar^2 \bar{\omega}} |C_i(ab)|^2 e^{-S} e^{-\frac{\Delta E'}{kT}} \frac{(2L\bar{a}^2)^m}{m!} \left[1 + e^{-\frac{\hbar\bar{\omega}}{kT}} \left\{ (m+1) \right. \right.$$
$$\left. \left. + \frac{(2L\bar{a}^2)^2}{m+1} + \frac{(2L\bar{a}^2)^2}{(m+1)(m+2)} \right\} + \cdots \right], \tag{12}$$

where $m\hbar\bar{\omega} = \Delta E' - \hbar\bar{\omega}$. The second term in Eq. (12) represents the correction term. In concluding the discussion, it should be noted that as in the cases of electronic relaxation, and resonance energy transfer, the transition probability of nonradiative thermal activation can be written as a product of two parts; one is electronic and the other, nuclear. While the former determines the mechanism of nonradiative processes, the latter determines the population and distribution of vibrational quanta, and hence it determines the dependence of the rate of non-radiative processes on temperature, isotope substitution, and the energy gap between the two electronic states. It is apparent that the above derivation can also be applied to thermal ionization.

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