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The Role of the Promoting Mode in Nonradiative Transitions in Large Molecules

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A rate expression for the intramolecular nonradiative transition where a promoting mode acts also as an accepting mode at the same time has been derived within the statistical limit. The dependence of the nonradiative transition rate on the shift of the equilibrium point of the promoting mode in the relevant electronic states, Δ_p, has been examined for two cases, i) excited $\rightsquigarrow$ ground states and ii) excited $\rightsquigarrow$ excited states, in aromatic hydrocarbons which satisfy the above condition.

In recent years, there have been many theoretical and experimental discussions[1-18] regarding the nature of the intramolecular nonradiative transitions in large molecules. Many theoretical discussions have been made of electronic relaxation processes in which vibrational modes are explicitly classified as promoting, accepting, and irrelevant modes for the nonradiative transitions: further, the promoting modes have been distinguished from the accepting modes.

The promoting modes for the internal conversions are determined from the symmetry consideration in the coupling matrix element between the relevant electronic states.[19] On the other hand, for the intersystem crossings where two kinds of perturbing operators, *i.e.*, the spin-orbit and nuclear kinetic energy operators, may act, the identification of the promoting modes is dependent on the coupling mechanism; when the zero order spin-orbit interaction does not vanish by symmetry, the rate for the intersystem crossing is irrelevent to the promoting modes, while when the higher order spin-orbit vibronic interaction has to be included, the promoting modes will play an essential role in the intersystem crossing. Various mechanisms have been proposed,[20-24] but no one has been able to uniquely identify the promoting mode for the intersystem crossing. We shall confine our investigation to the role of the promoting mode for the internal conversion of large molecules.

Considering the simple model of the non-displaced and non-distorted harmonic potential-energy surfaces for the promoting mode, Lin[1] and Freed and Jortner[7] have demonstrated the propensity rule for the promoting mode—that is, it must gain or lose one quantum of the vibrational energy in the electronic transition. The propensity rule for the promoting mode leads to the concept of an effective energy gap which differs, as a result of increase or decrease by one quantum of the vibrational energy of the promoting mode, from the electronic energy gap between the relevant electronic states. The applicability of the propensity rule is, however, restricted to the electronic relaxation between electronic states with different irreducible representations of the point groups of a molecule in the weak coupling cases. When we consider the nonradiative transitions between the electronic states with the same irreducible representation of the point group of a molecule, the propensity rule should be altered because the promoting mode will act as an accepting mode at the same time. The physical situation in this category will involve, for example, the internal conversion from the first excited singlet state ($^1A_1$) to the ground state of phenanthrene.[25,26]

A similar problem was considered by Fong and Wassam.[27] Their formalism was based on the time-correlation function proposed by Kubo.[28] They thought that the situation will be encountered in the nonradiative transition, $S_1 \rightsquigarrow T_1$, of benzene in the solid state, where the D_{6h} symmetry is retained in the first excited singlet state and where, on the other hand, the symmetry in the lowest triplet state has a lower value than D_{6h}. However, the application of the formalism of Fong and Wassam to the $S_1 \rightsquigarrow T_1$ transition of benzene in the solid state was criticized by Nitzan and Jortner[29] because the symmetry reduction in the lowest triplet state might be due to the crystal-field effect.

In the present paper, we will derive a rate expression for the nonradiative transition, considering that the promoting mode acts also as an accepting mode in the weak coupling case; the results will be compared with those of the case in which the promoting and accepting modes act independently. The present formalism will be primarily based on the treatment by Lin[1] and Englman and Jortner[6] in the framework of the weak coupling case in large molecules. The interference effect between promoting modes will be neglected. As a simple case in which there is no displacement for the promoting mode between the relevant electronic states, the expression contains the same results as those derived by Freed and Jortner.[7] The steepest-descent method will be used to determine the most probable path for the nonradiative transition (the highest frequency mode belonging to the displaced potential surfaces) and to examine the contribution of the second-highest frequency mode to the partitioning of the excess energy. Nonradiative transitions between the excited states of such aromatic hydrocarbons as naphthalene having dimensions larger than benzene will be treated, where the shift of the origin of the highest mode ($\hbar\omega_{C-H} \approx 3000\ \mathrm{cm}^{-1}$) may be considered to be smaller than that of the second-highest ($\hbar\omega_{C-C} \approx 1500\ \mathrm{cm}^{-1}$) by about one order.

Theory

The nonradiative transition rate from an electronic state, s, to a lower electronic state, t, with a quasicontinuum vibronic manifold is given by the time-dependent perturbation theory as:

$$W(s \rightsquigarrow t) = \frac{2\pi}{\hbar}\sum_{lm} P_{sl}|\langle tm|V|sl\rangle|^2\delta(E_{tm}-E_{sl}) \qquad (1)$$

where l and m refer to vibrational states belonging to s and t electronic states respectively and where E_{sl} and E_{tm} refer to the energies of the initial and final states respectively. P_{sl} is the Boltzmann weighting factor for the initial vibronic states:

$$P_{\mathrm{sl}} = \exp(-\beta E_{\mathrm{sl}}) / \sum_{\mathrm{l}} \exp(-\beta E_{\mathrm{sl}}) \tag{2}$$

where $\beta = 1/k_{\mathrm{B}}T$.

There has been a fair amount of discussion concerning the choice of the zero-order basis set for describing the nonradiative transition in an isolated molecule.[30-35] We shall take Born-Oppenheimer states as the zero-order set in the present treatment. In the adiabatic representation, the electronic wave function, Φ_{s}, and the vibrational wave function, Ξ_{sl}, satisfy the following equations:

$$H_0(r, Q)\Phi_{\mathrm{s}}(r, Q) = E_{\mathrm{s}}(Q)\Phi_{\mathrm{s}}(r, Q), \tag{3}$$

and:

$$[T(Q) + E_{\mathrm{s}}(Q)]\Xi_{\mathrm{sl}}(Q) = E_{\mathrm{sl}}\Xi_{\mathrm{sl}}(Q) \tag{4}$$

where

$$H_0(r, Q) = T(r) + U(r, Q), \tag{5}$$

and where r and Q denote the coordinate of the electrons and the vibrational coordinates respectively. $T(r)$, $T(Q)$, and $U(r,Q)$ denote the kinetic energy of the electrons, the kinetic energy of the nuclei, and the electrostatic potential energy respectively. The adiabatic wave function, $\Psi_{\mathrm{sl}}(r,Q)$, is given by the product of the electronic wavefunction, $\Phi_{\mathrm{s}}(r,Q)$, and the vibrational wave function, $\Xi_{\mathrm{sl}}(Q)$:

$$\Psi_{\mathrm{sl}}(r, Q) = \Phi_{\mathrm{s}}(r, Q)\Xi_{\mathrm{sl}}(Q). \tag{6}$$

The perturbation, V, for the nonradiative transition is the nuclear kinetic energy, $T(Q)$. Then, the matrix element in Eq. (1) can be expressed in the following way:

$$\begin{aligned}\langle \mathrm{tm}|V|\mathrm{sl}\rangle = \\ &-\hbar^2 \sum_{\mathrm{p}} \frac{1}{M_{\mathrm{p}}} \left\langle \Phi_{\mathrm{t}}(r, Q)\Xi_{\mathrm{tm}}(Q) \middle| \frac{\partial \Phi_{\mathrm{s}}(r, Q)}{\partial Q_{\mathrm{p}}} \frac{\partial}{\partial Q_{\mathrm{p}}} \Xi_{\mathrm{sl}}(Q) \right\rangle \\ &-\frac{\hbar^2}{2} \sum_{\mathrm{p}} \frac{1}{M_{\mathrm{p}}} \left\langle \Phi_{\mathrm{t}}(r, Q)\Xi_{\mathrm{tm}}(Q) \middle| \frac{\partial^2 \Phi_{\mathrm{s}}(r, Q)}{\partial Q_{\mathrm{p}}^2} \Xi_{\mathrm{sl}}(Q) \right\rangle\end{aligned} \tag{7}$$

where the subscript, p, denotes the promoting mode which induces the nonradiative transition between relevant electronic states. We assume the potential energy surfaces to be harmonic and displaced.

In the present treatment, Eq. (1) will be evaluated within the so-called Condon approximation, which is based on the assumption that the first derivative of the initial electronic state varies slowly with the nuclear coordinates. We assume that the nonradiative transition is induced by a promoting mode, q_{p}.[36] We utilize the time-integral representation of the δ-function in Eq. (1). Performing the summation over the vibrational quanta, m_i and l_i, for the i-th mode in Eq. (1) by the aid of the Slater sum rule, and integrating Eq. (1) over the normal coordinates, we obtain:

$$W(\mathrm{s} \rightsquigarrow \mathrm{t}) = \omega_{\mathrm{p}}^2 |V_{\mathrm{st}}{}^{\mathrm{p}}|^2 \int_{-\infty}^{\infty} \mathrm{d}t \exp\left[-\frac{\mathrm{i}\Delta Et}{\hbar}\right] \Lambda_{\mathrm{p}} \prod_i^{\mathrm{N}'} \Omega_i \tag{8}$$

where:

$$V_{\mathrm{st}}{}^{\mathrm{p}} = \frac{\left\langle \Phi_{\mathrm{t}} \middle| \left(\frac{\partial U}{\partial q_{\mathrm{p}}}\right) \middle| \Phi_{\mathrm{s}} \right\rangle}{\Delta E_{\mathrm{st}}} \tag{9}$$

$$\begin{aligned}\Omega_i = \exp\Bigl[&-\frac{2n_i+1}{2}\Delta_i^2 + \frac{n_i+1}{2}\Delta_i^2 \exp(i\omega_i t) \\ &+ \frac{n_i}{2}\Delta_i^2 \exp(-i\omega_i t)\Bigr]\end{aligned} \tag{10}$$

and:

$$\begin{aligned}\Lambda_{\mathrm{p}} = \frac{\Omega_{\mathrm{p}}}{2}\Bigl[&(n_{\mathrm{p}}+1)\exp(i\omega_{\mathrm{p}}t) + n_{\mathrm{p}}\exp(-i\omega_{\mathrm{p}}t) \\ &+ \frac{\Delta_{\mathrm{p}}^2}{2}\{2n_{\mathrm{p}}+1-(n_{\mathrm{p}}+1)\exp(i\omega_{\mathrm{p}}t) - n_{\mathrm{p}}\exp(-i\omega_{\mathrm{p}}t)\}^2\Bigr]\end{aligned} \tag{11}$$

ΔE_{st} in Eq. (9) is the virtual energy-separation between zero-order electronic states, s and t. The n_i notation, in Eqs. (10) and (11) represents the average number of the excited vibrations with the frequency of ω_i at thermal equilibrium: that is,

$$n_i = [\exp(\beta\hbar\omega_i) - 1]^{-1} \tag{12}$$

and $\Delta_i = (\mu_i\omega_i/\hbar)^{1/2}(Q_i{}^{\mathrm{t}(0)} - Q_i{}^{\mathrm{s}(0)})$, the reduced displacement of the equilibrium position of the i-th normal coordinate in the two electronic states. In deriving Eq. (8), the Herzberg-Teller expansion was utilized in order to obtain the approximate adiabatic electronic wave functions. The prime in Eq. (8) means the exclusion of the promoting mode in the Ω_i product. The inclusion of the Ω_{p} appearing in Λ_{p} in the Ω_i product leads to the following equation:

$$\begin{aligned}&W(\mathrm{s} \rightsquigarrow \mathrm{t}) \\ &= \frac{\omega_{\mathrm{p}}^2}{2}|V_{\mathrm{st}}{}^{\mathrm{p}}|^2 \exp(-\eta) \int_{-\infty}^{\infty} \mathrm{d}t\Bigl[(n_{\mathrm{p}}+1)\exp(i\omega_{\mathrm{p}}t) \\ &\quad + n_{\mathrm{p}}\exp(-i\omega_{\mathrm{p}}t) + \frac{\Delta_{\mathrm{p}}^2}{2}\{2n_{\mathrm{p}}+1-(n_{\mathrm{p}}+1)\exp(i\omega_{\mathrm{p}}t) \\ &\quad - n_{\mathrm{p}}\exp(-i\omega_{\mathrm{p}}t)\}^2\Bigr] \exp\left[-\frac{i\Delta Et}{\hbar} + \eta_+(t) + \eta_-(t)\right]\end{aligned} \tag{13}$$

where

$$\eta = \eta_+(0) + \eta_-(0) = \sum_i \left(n_i + \frac{1}{2}\right)\Delta_i^2 \tag{14}$$

$$\eta_+(t) = \frac{1}{2}\sum_i (n_i+1)\Delta_i^2 \exp(i\omega_i t) \tag{15}$$

and

$$\eta_-(t) = \frac{1}{2}\sum_i n_i\Delta_i^2 \exp(-i\omega_i t) \tag{16}$$

We have derived the rate expression for the nonradiative transition using the harmonic displaced potential-surface model in the form of the Fourier transformation. Let us, for the sake of simplicity, consider the nonradiative transitions within the low-temperature limit; then we have

$$\begin{aligned}&W(\mathrm{s} \rightsquigarrow \mathrm{t}) \\ &= \frac{\omega_{\mathrm{p}}^2}{2}|V_{\mathrm{st}}{}^{\mathrm{p}}|^2 \exp\left(-\sum_i \frac{\Delta_i^2}{2}\right) \int_{-\infty}^{\infty} \mathrm{d}t\Bigl[\exp\Bigl\{-\frac{i(\Delta E - \hbar\omega_{\mathrm{p}})t}{\hbar} \\ &\quad + \sum_i \frac{\Delta_i^2}{2}\exp(i\omega_i t)\Bigr\} + \frac{\Delta_{\mathrm{p}}^2}{2}\{1-\exp(i\omega_{\mathrm{p}}t)\}^2 \\ &\quad \times \exp\Bigl\{-\frac{i\Delta Et}{\hbar} + \sum_i \frac{\Delta_i^2}{2}\exp(i\omega_i t)\Bigr\}\Bigr]\end{aligned} \tag{17}$$

We are interested in the nonradiative transitions of large molecules within the statistical limit. The time integration of the nonradiative transition rate in Eq. (13) can be carried out by the steepest-descent method, which has frequently been applied to the evaluation of the nonradiative transition rates in large molecules on the assumption that the highest frequency mode with the displaced potential acts as an accepting mode. The modes with the displaced potential surface between relevant electronic states in the case of the weak coupling of large molecules such as aromatic hydrocarbons are identified as follows: (1) totally symmetric C–H stretching modes, and (2) totally symmetric C–C skeletal stretching modes. The other vibrational modes do not lead to the shifts of the adiabatic potentials when the vibronic coupling, such as the Jahn-Teller coupling and the pseudo-Jahn-Teller coupling, may be neglected. This assumption may be justified in benzene, which has a relatively low second-high frequency mode (the C–C skeletal stretching mode with $\sim 1000\ \mathrm{cm}^{-1}$) compared with the highest frequency mode (the C–H stretching mode with $\sim 3000\ \mathrm{cm}^{-1}$), and in the case of the nonradiative transitions between the excited and ground states of other aromatic hydrocarbons, where the reduced displacements of the accepting modes are considered to be of the same order. In this case, we have $\exp(i\omega_{\mathrm{C-H}}t) = X^3$ if $X = \exp(i\omega_{\mathrm{C-C}}t)$ and the coefficients of X and X^3 are of the same order in the time integration of the nonradiative transition rate; therefore the highest frequency terms, $\exp(i\omega_{\mathrm{C-H}}t)$, makes the main contribution to the determination of the saddle point. However, this assumption may lead to a drastic error in evaluating the rates of the nonradiative transitions between the excited states of the aromatic hydrocarbons larger than benzene, where the frequency of the highest-frequency mode remains constant ($3000\ \mathrm{cm}^{-1}$); on the other hand, that of the next highest frequency mode increases (the C–C stretching: $\sim 1500\ \mathrm{cm}^{-1}$) compared with that of benzene, and the reduced displacement of the latter may be considered to be larger than that of the former by about one order. From the above point of view, we shall use the steepest-descent method, taking into account the fact that both the C–H stretching ($3000\ \mathrm{cm}^{-1}$) and C–C stretching ($1500\ \mathrm{cm}^{-1}$) modes act as accepting modes. Utilizing the steepest-descent method, we obtain this final expression for $W(\mathrm{s} \rightsquigarrow \mathrm{t})$ at low temperature:

$$W(\mathrm{s} \rightsquigarrow \mathrm{t}) = \frac{\omega_{\mathrm{p}}^2}{2} |V_{\mathrm{st}}{}^{\mathrm{p}}|^2 \exp\left(-\sum_i \frac{\Delta_i{}^2}{2}\right)\left[(1-\Delta_{\mathrm{p}}{}^2) I(\hbar\omega_{\mathrm{p}}) + \frac{\Delta_{\mathrm{p}}{}^2}{2}\{I(0) + I(2\hbar\omega_{\mathrm{p}})\}\right] \tag{18}$$

where

$$I(\varepsilon) = \hbar(2\pi)^{1/2} \times \exp\left\{-\frac{(\Delta E-\varepsilon)}{\hbar\omega_{\mathrm{p}}} \log \mathrm{A}(\varepsilon) + \frac{\Delta_{\mathrm{H}}{}^2}{2} A^2(\varepsilon) + \frac{\Delta_{\mathrm{p}}{}^2}{2} A(\varepsilon)\right\} \times \left\{2(\hbar\omega_{\mathrm{p}})^2 \Delta_{\mathrm{H}}{}^2 A^2(\varepsilon) + \frac{1}{2}(\hbar\omega_{\mathrm{p}})^2 \Delta_{\mathrm{p}}{}^2 A(\varepsilon)\right\}^{-1/2} \tag{19}$$

and where

$$A(\varepsilon) = \frac{\Delta_{\mathrm{p}}{}^2}{4\Delta_{\mathrm{H}}{}^2}\left[-1 + \left\{1 + \frac{16\Delta_{\mathrm{H}}{}^4(\Delta E-\varepsilon)}{\hbar\omega_{\mathrm{p}}\Delta_{\mathrm{p}}{}^4}\right\}^{1/2}\right] \tag{20}$$

The Δ_{p} and Δ_{H} which appear in Eqs. (18), (19), and (20) denote the reduced displacements of the C–C stretching mode with the ω_{p} frequency and the C–H stretching mode with the ω_{H} frequency respectively.

Discussion

Assuming that the promoting mode is independent of the accepting modes, Englman and Jortner[6)] and Freed and Jortner[7)] have derived the rate expression for the nonradiative transitions in large molecules using the displaced potential-surface model for the accepting modes. Their results imply that in the case of weak coupling, the nonradiative decay is characterized by the exponential dependence on the effective gap, $\Delta E-\hbar\omega_{\mathrm{p}}$, in the low-temperature range (energy-gap law). It should be noted that Eq. (18) reduces to the expression derived by Freed and Jortner when there is no displacement for the promoting mode. Equation (18) reveals that, when $\Delta_{\mathrm{p}} \neq 0$, the nonradiative decay occurs through Processes 1, 2, and 3, whose energy gaps are ΔE, $\Delta E-\hbar\omega_{\mathrm{p}}$, and $\Delta E-2\hbar\omega_{\mathrm{p}}$ respectively.

Considering the simple model systems for the nonradiative transitions, we have examined the dependence of the nonradiative transition rate, $W(\mathrm{s} \rightsquigarrow \mathrm{t})$, on the reduced displacement for the promoting mode, Δ_{p}, in the low-temperature range. Regrettably, the exact electronic wave function is not known at present, so we cannot obtain a reliable value of $V_{\mathrm{st}}{}^{\mathrm{p}}$ by direct computation. We will instead calculate the $R = W(\Delta_{\mathrm{p}} \neq 0)/W(\Delta_{\mathrm{p}} = 0)$ ratio, since by using it $V_{\mathrm{st}}{}^{\mathrm{p}}$ need not be determined. The present information concerning the potential surfaces of aromatic hydrocarbons is insufficient for us to determine the magnitude of displacement required to evaluate the nonradiative transition rates, but at least it can be seen that the modes with the nonvanishing reduced displacements belong to the totally symmetric C–C skeletal stretching and the totally symmetric C–H stretching modes in the case of weak coupling, the magnitudes of the reduced displacements for the C–C stretching modes being of the same order between any electronic states considered. Recently, we proposed a semi-empirical method for evaluating the reduced displacements of the skeletal stretching modes in aromatic hydrocarbons; we found that the magnitudes of the reduced displacements for the C–C stretching modes are of the same order between any π–π^* electronic states considered.[37)] For the reduced displacements of the C–H stretching modes in aromatic hydrocarbons, we expect the Δ_{H} between π–π^* excited states to be smaller than the Δ_{H} between π–π^* excited and ground states, as the change in the C–H bonds is considered to be smaller between π–π^* excited states, especially when lower π–π^* excited states are involved. In fact, Burland and Robinson[3)] have reported that the Δ_{H} between the first excited-singlet and the lowest-triplet states in benzene is smaller by about one order than the Δ_{H} between the first excited singlet and ground states. In the absence of more detailed information concerning the value of Δ_{H} for other molecular systems, we suppose that the Δ_{H} between the excited states is also smaller

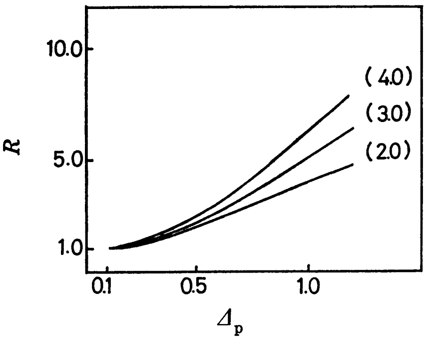

Fig. 1. Variation of R as a function of Δ_p in the excited $\rightsquigarrow$ ground state nonradiative transition. Numbers in parentheses denote the energy gap, ΔE in eV.

by one order than the Δ_H between excited and ground states in the present calculations. For the present models, two cases will be examined: i) excited $\rightsquigarrow$ ground states, and ii) excited $\rightsquigarrow$ excited states.

i) *Excited* $\rightsquigarrow$ *Ground States.* From the analysis of the absorption spectra of aromatic hydrocarbons, Byrne *et al.*[38] have concluded that the values of Δ_H are in the range of 0.18—0.42 and that Δ_H is independent of the dimensions of the molecules. For the present calculations, the value of $\Delta_H=0.3$ will be taken. In Fig. 1, R is plotted as a function of Δ_p in the range of 0.1—1.2. Figure 1 shows that the ratio, R, of the nonradiative transition between the excited and ground states within the statistical limit increases only by a factor of 2 in the vicinity of $\Delta_p=0.5$. Using the steepest-descent condition, $\partial F(t)/\partial(it)|_{it=\tau}=0$, where $F(t)$ and $it=\tau$ are the exponent in the time integration of the nonradiative transition rate and the saddle point obtained respectively, we can then determine the partitioning of the excess electronic energy into the vibrational modes involved. Considering the nonradiative transition, whose energy gap is 24000 cm^{-1} and whose reduced displacement Δ_p is 0.5, 90% of the excess energy goes into the C–H stretching mode through Process 2 with $\Delta E-\hbar\omega_p$. From the above results it seems that the existence of an effective accepting mode (the C–H stretching mode) will be enough to explain the characteristics of nonradiative transition rates when the Δ_p and Δ_H are of the same order. In this case, the ratio, R, of the nonradiative transition rates in the low-temperature limit is expressed as a function of Δ_p as following:

$$R = K\Delta_p^2 + 1,$$

where

$$K = \frac{1}{2}\left(1-\frac{\hbar\omega_p}{\Delta E}\right)^{1/2}(\zeta\Delta E)^{-\frac{\Delta E}{\hbar\omega_H}}\{\zeta(\Delta E-\hbar\omega_p)\}^{\frac{\Delta E-\hbar\omega_p}{\hbar\omega_H}}$$
$$\times \exp\left(\frac{\hbar\omega_p}{\hbar\omega_H}\right)+\frac{1}{2}\left(\frac{\Delta E-\hbar\omega_p}{\Delta E-2\hbar\omega_p}\right)^{1/2}$$
$$\times \{\zeta(\Delta E-2\hbar\omega_p)\}^{-\frac{\Delta E-2\hbar\omega_p}{\hbar\omega_H}}\{\zeta(\Delta E-\hbar\omega_p)\}^{\frac{\Delta E-\hbar\omega_p}{\hbar\omega_H}}$$
$$\times \exp\left(-\frac{\hbar\omega_p}{\hbar\omega_H}\right)-1. \tag{21}$$

K is independent of Δ_p, since $\zeta=\left(\sum_i\frac{\hbar\omega_i\Delta_i^2}{2}\right)^{-1}$ includes the parameters of the C–H stretching mode only. The role of the promoting mode is only to reduce the excess energy by zero, one, and two quanta of vibrations for Processes 1, 2, and 3 respectively.

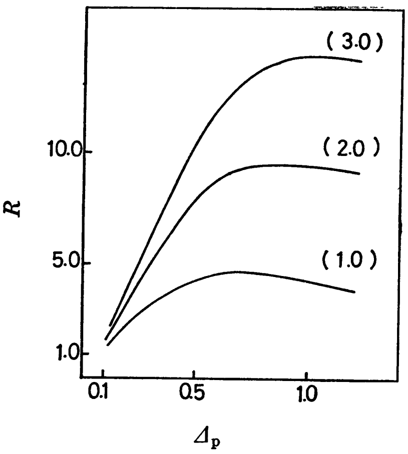

Fig. 2. Variation of R as a function of Δ_p in the excited $\rightsquigarrow$ excited state nonradiative transition.

ii) *Excited* $\rightsquigarrow$ *Excited States.* As has been stated above, we suppose that the Δ_H between lower π–π^* excited states is smaller by one order than the Δ_H between the excited and ground states. A variation in Δ_H by a numerical factor does not contribute significantly to the present results. Then, for the sake of simplicity, the $\Delta_H=3\times10^{-2}$ value is taken regardless of the relevant π–π^* excited states. Figure 2 indicates that the ratio of the nonradiative transition rates increases from a factor of 3 to one order in the Δ_p range of 0.3—0.5; this may be considered to be a case of weak coupling, and the magnitude of the ratio may be dependent on the energy gap. Let us consider the distribution of the excess electronic energy into the vibrational modes. The distribution is strongly dependent on the Δ_p: a rough estimation shows that, contrary to the nonradiative transition to the ground state, 60, 70, and 90% of the excess energy, $\Delta E=$ 16000 cm^{-1}, go into the C–C stretching modes through Process 2 when $\Delta_p=0.3$, 0.5, and 0.8 respectively. The promoting mode may, then, act as the accepting mode in this case. This fact also indicates that we cannot exclude the second-highest frequency mode with a displaced potential from the accepting modes when we study the nature of the nonradiative transition between excited states in such large molecules as aromatic hydrocarbons.

Fong and Wassam[27] suggested that, as a consequence of the removal of the zero displacement for the promoting modes, the most important point is the effective diminution of the energy gap by the $\Delta v=2$ process in the event of a small configuration change corresponding to a case of weak coupling. The present result obtained by numerical analysis indicates that the above suggestion by Fong and Wassam is justified in the case of nonradiative transitions between excited states in the aromatic hydrocarbons.

In the present treatment we have derived the nonradiative transition rate, neglecting the interference effect between promoting modes. As has been stated by Freed and Jortner[7], the interference effect can be expected between two modes, p and p′, if the following conditions are satisfied: $\Delta_{\mathrm{p}} \neq 0$, $\Delta_{\mathrm{p}'} \neq 0$, $V_{\mathrm{st}}{}^{\mathrm{p}} \neq 0$ and $V_{\mathrm{st}}{}^{\mathrm{p}'} \neq 0$. In a subsequent paper, the interference effect between promoting modes will be described in detail.

References

1) S. H. Lin, *J. Chem. Phys.*, **44**, 3759 (1966).
2) M. Bixon and J. Jortner, *ibid.*, **48**, 715 (1968).
3) D. M. Burland and G. W. Robinson, *ibid.*, **51**, 4548 (1969).
4) B. Sharf and R. Silbey, *Chem. Phys. Lett.*, **4**, 423 (1969).
5) B. Sharf and R. Silbey, *ibid.*, **4**, 561 (1970).
6) R. Englman and J. Jortner, *Mol. Phys.*, **18**, 145 (1970).
7) K. F. Freed and J. Jortner, *J. Chem. Phys.*, **52**, 6272 (1970).
8) S. Fischer, *ibid.*, **53**, 3195 (1970).
9) A. Nitzan and J. Jortner, *ibid.*, **55**, 1355 (1971).
10) A. Nitzan and J. Jortner, *ibid.*, **56**, 2076 (1972).
11) B. Katz and M. Brith, B. Sharf, and J. Jortner, *ibid.*, **52**, 88 (1970).
12) C. S. Parmenter and M. W. Schuyler, *ibid.*, **52**, 5366 (1970).
13) C. S. Parmenter and M. W. Schuyler, *Chem. Phys. Lett.*, **6**, 339 (1970).
14) W. R. Ware, B. K. Selinger, C. S. Parmenter, and M. W. Schuyler, *ibid.*, **6**, 342 (1970).
15) J. L. Richard and S. A. Rice, *ibid.*, **9**, 444 (1971).
16) J. P. Byrne and I. G. Ross, *Aust. J. Chem.*, **24**, 1107 (1971).
17) K. G. Spears and S. A. Rice, *J. Chem. Phys.*, **55**, 5561 (1971).
18) R. Scheps, D. Florida, and S. A. Rice, *ibid.*, **56**, 295 (1972).
19) It is true that the zero-order molecular eigenstates represented by the Born-Oppenheimer adiabatic basis cannot be specified in terms of the symmetry classification (A. Nitzan and J. Jortner, *Mol. Phys.*, **24**, 109 (1972)). Then, strictly speaking, the classification of the vibrational modes into the promoting and accepting modes will be invalid in the adiabatic basis. However, it seems reasonable to consider the symmetry restriction in the coupling matrix element between the electronic states in the weak coupling case where the harmonic approximation may be applicable to the multidimensional potential surfaces.
20) M. A. El-Sayed, *J. Chem. Phys.*, **38**, 2834 (1963).
21) B. R. Henry and W. Seibrand, *ibid.*, **54**, 1072 (1971).
22) V. Lawetz, G. Orlandi, and W. Siebrand, *ibid.*, **56**, 4058 (1972).
23) T. Azumi, *Chem. Phys. Lett.*, **17**, 211 (1973).
24) B. Shaif, *ibid.*, **19**, 351 (1973).
25) D. P. Craig and R. D. Gorden, *Proc. Roy. Soc.* (*London*), **A288**, 69 (1965).
26) R. M. Hochstrasser and G. J. Small, *J. Chem. Phys.*, **35**, 2270 (1966).
27) F. K. Fong and W. A. Wassam, *ibid.*, **58**, 2667 (1973).
28) R. Kubo, *J. Phys. Soc. Japan*, **12**, 570 (1957).
29) A. Nitzan and J. Jortner, *J. Chem. Phys.*, **58**, 2669 (1973).
30) D. M. Burland and G. W. Robinson, *Proc. Nat. Acad. Sci. U.S.* **66**, 257 (1970).
31) G. Orlandi and W. Siebrand, *Chem. Phys. Lett.*, **8**, 473 (1971).
32) B. Sharf and R. Silbey, *ibid.*, **9**, 125 (1971).
33) K. F. Freed and W. M. Gelbart, *ibid.*, **10**, 187 (1971).
34) A. Nitzan and J. Jortner, *ibid.*, **11**, 458 (1971).
35) B. Sharf, *ibid.*, **14**, 315 (1972).
36) The small letter q denotes dimensionless normal coordinate. The relation between the dimensionless normal coordinate and normal coordinate is given by $q=(\mu\omega/\hbar^{1/2}(Q^{s}-Q^{s(0)})$, where μ and $Q^{s(0)}$ are the reduced mass and the equilibrium position of the s-th electronic state, respectively.
37) Y. Fujimura and T. Nakajima, *Chem. Phys. Lett.*, **14**, 108 (1972).
38) J. P. Byrne, E. F. McCoy, and I. G. Ross, *Aust. J. Chem.*, **18**, 1859 (1965).