Dynamics of Radiationless Transitions: Effects of Displacement−Distortion−Rotation of Potential Energy Surfaces on Internal Conversion Decay Rate Constants[†,‡]

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General expressions for calculating the internal conversion decay rate constants between two adiabatic electronic states and between two diabatic electronic states are derived. The expressions include the displacements, distortions, and rotations of potential energy surfaces as well as the temperature. For illustration, internal conversion rate constants between various singlet electronic states of ethylene and between the first excited S_1 and the ground S_0 singlet electronic states of azulene are calculated.

1. Introduction

Perhaps the most convincing experimental evidence for radiationless transitions was provided by Kasha in 1950, which has been known as Kasha's rule ever since.[1] With rare exceptions, polyatomic molecular luminescence was observed only from the lowest excited electronic state of a given multiplicity, no matter which stable electronic state was excited. Fluorescence always occurred from the lowest excited singlet state and phosphorescence occurred from the lowest triplet state. Kasha discriminated between two types of radiationless transitions, the one occurring between states of the same multiplicity, which he called internal conversion, and the one occurring between states of different multiplicity, called intersystem crossing. Such processes are necessarily energy-conserving in an isolated molecule, so the electronic energy difference is converted into excess vibrational energy.

A theory that had success in at least qualitatively describing these transitions in large molecules was outlined by Robinson and Frosch[2,3] and was formulated in a somewhat different way by Hunt et al.[4] The formal theory of the intramolecular nonradiative transitions in isolated (collision-free) polyatomic molecules of sufficient size was put forward by Lin[5,6] and by Bixon and Jortner,[7] who attempted to reformulate the entire problem of radiationless transitions by being more explicit about the coupling mechanism that was responsible for the radiationless process and to establish the criteria that make an irreversible radiationless relaxation process possible. They have attributed the nonstationary character of the excited electronic states to a coupling between vibrational and electronic motion brought about by a breakdown of the Born−Oppenheimer approximation (in case of internal conversion) plus the spin−orbit coupling (in case of intersystem crossing). For a list of other contributors to the subject, the reader is referred to the book by Medvedev and Osherov.[8]

The aim of the present paper is to derive new general expressions for the internal conversion decay rate constants, which includes the effects of Franck−Condon (the displacement−distortion−rotation of harmonic potential energy surfaces), the promoting modes, and the temperature. Even though the displacements of potential energy surfaces (PESs) play a predominant role in radiationless processes, it is believed that the distortions and the rotations of these surfaces may also play a significant role.[8−11] In our derivation we have taken all three effects as well as the whole set of vibrational normal modes into account. For illustration, we calculated the internal conversion decay rate constants between various singlet electronic states of ethylene and between the S_1 and S_0 electronic states of azulene.

2. General Considerations

2.1. Static and Dynamic Aspects of Perturbations. Consider a physical system with a time-independent Hamiltonian ($\hat{H}^0$) in which the Schrodinger equation $\hat{H}^0|\varphi_j\rangle = E_j^0|\varphi_j\rangle$ can be solved exactly for the eigenstates and eigenvalues of the bound stationary states. Assume that we want to take into account an external perturbation or interactions internal to the system, initially neglected in $\hat{H}^0$. The Hamiltonian now becomes $\hat{H} = \hat{H}^0 + \hat{V}$, whose eigenstates and eigenvalues will be denoted by $|\psi_j\rangle$ and E_j, respectively. We shall assume here that the coupling (or perturbation) $\hat{V}$ is time-independent. Two aspects of $\hat{V}$ are as follows:[12] (1) $\{E_j^0\}$ are not the possible energies (the static aspect) and (2) $\{|\varphi_j\rangle\}$ are not the stationary states (the dynamic effect) of the system any more. So we are faced with two problems, first is the calculation of $\{E_j\}$ in terms of $\{E_j^0\}$ and the matrix elements of V_{ij} of $\hat{V}$, and second is the calculation of the transition rate among various unperturbed states $\{|\varphi_j\rangle\}$ in terms of the same quantities. We shall now investigate these two aspects quantitatively.

Let eq 1 be the state vector of the system at the instant t.

$$|\psi(t)\rangle = \sum_{j=1}^{n} a_j(t)|\varphi_j\rangle \qquad (1)$$

The evolution of $|\psi(t)\rangle$ in the presence of the coupling ($\hat{V}$) is given by the Schrodinger equation $i\hbar(\mathrm{d}/\mathrm{d}t)|\psi(t)\rangle = (\hat{H}^0 + \hat{V})|\psi(t)\rangle$. Projecting this equation onto the basis vectors $\{|\varphi_j\rangle\}$, we obtain eq 2 (without loss of generality we may set $V_{11} = V_{22} = ... = V_{nn} = 0$):

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}a_k(t) = \sum_{j=1}^{n}(\delta_{kj}E_j^0 + V_{kj})a_j(t) \quad k = 1, 2, ..., n \qquad (2)$$

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Let us consider a solution in the form of eq 3;

$$a_k(t) = \alpha_k \mathrm{e}^{-iEt/\hbar} \quad k = 1, 2, ..., n \tag{3}$$

where $\alpha_1, ..., \alpha_n$ are constants to be determined. Substitution of eq 3 into the system in eq 2 results in the algebraic equations of eq 4.

$$\sum_{j=1}^{n} [\delta_{kj}(E_j^0 - E) + V_{kj}]\alpha_j = 0 \quad k = 1, 2, ..., n \tag{4}$$

These equations have nontrivial (nonzero) solutions if and only if the determinant of the coefficients vanishes (eq 5).

$$\det\,[\delta_{kj}(E_j^0 - E) + V_{kj}] = 0 \quad k, j = 1, ..., n \tag{5}$$

This characteristic equation is a polynomial of degree n in the unknown E. Its roots $E_1, E_2, ..., E_n$ give the desired eigenvalues of $\hat{H}$. By substituting each eigenvalue E_j into the set of algebraic equations of eq 4 and invoking the requirement of normalization, we then obtain the elements $\alpha_{1j}, \alpha_{2j}, ..., \alpha_{nj}$ of the jth eigenvector. This procedure yields a fundamental set of solutions (eq 6).

$$\begin{pmatrix} \alpha_{1j}\mathrm{e}^{-iE_jt/\hbar} \\ \alpha_{2j}\mathrm{e}^{-iE_jt/\hbar} \\ \vdots \\ \alpha_{nj}\mathrm{e}^{-iE_jt/\hbar} \end{pmatrix} \quad j = 1, 2, ..., n \tag{6}$$

Thus the general solution to the system in eq 2 on the interval $-\infty < t < +\infty$ is eq 7.

$$a_k(t) = \sum_{j=1}^{n} c_j \alpha_{kj} \mathrm{e}^{-iE_jt/\hbar} \quad k = 1, 2, ..., n \tag{7}$$

To find the constants $c_1, c_2, ..., c_n$ we need some initial conditions. If the initial conditions are given, then these constants can be determined by solving the algebraic $n \times n$ system, resulting from substituting the conditions into general solution eq 7. Suppose the system is prepared in the state $|\varphi_s\rangle$ at time $t = 0$, we can then write eq 7 as eq 8;

$$a_k(0) = \sum_{j=1}^{n} c_j \alpha_{kj} = \delta_{ks} \quad k = 1, ..., n \tag{8}$$

which simply implies that $c_j = \alpha_{sj}^*$, $j = 1, 2, ..., n$. Combining this with eq 7 and substituting the results into eq 1 we obtain the state vector of the system as eq 9;

$$|\psi(t)\rangle = \sum_{j=1}^{n} \alpha_{sj}^* \mathrm{e}^{-iE_jt/\hbar} |\psi_j\rangle \tag{9}$$

with eq 10.

$$|\psi_j\rangle = \sum_{i=1}^{n} \alpha_{ij} |\varphi_i\rangle \tag{10}$$

Because the matrix α_{ij} is unitary, the inverse of eq 10 is eq 11.

$$|\varphi_j\rangle = \sum_{i=1}^{n} \alpha_{ji}^* |\psi_i\rangle \tag{11}$$

Likewise, the probability amplitude that the system is still in the state $|\varphi_s\rangle$ is given by eq 12;

$$a_s(t) = \sum_{j=1}^{n} |\alpha_{sj}|^2 \mathrm{e}^{-iE_jt/\hbar} \tag{12}$$

the probability amplitude of finding the system at time t in the state $|\varphi_l\rangle$, assuming it was prepared in the state $|\varphi_s\rangle$ at $t = 0$, is given by eq 13.

$$a_l(t) = \sum_{j=1}^{n} \alpha_{sj}^* \alpha_{lj} \mathrm{e}^{-iE_jt/\hbar} \tag{13}$$

As an example we consider a physical system that has two states whose energies are close together and very different from those of all other states of the system. If the perturbation is sufficiently weak we can calculate its effects on the two states by ignoring all the other energy levels of the system. In other words, we can confine ourselves to a two-dimensional (2D) subspace of the state space. In this case the roots of the characteristic eq 5 are given by both parts of eq 14.

$$E_1 = \frac{1}{2}(E_1^0 + E_2^0) + \frac{1}{2}\sqrt{(E_1^0 - E_2^0)^2 + 4|V_{12}|^2} \tag{14a}$$

$$E_2 = \frac{1}{2}(E_1^0 + E_2^0) - \frac{1}{2}\sqrt{(E_1^0 - E_2^0)^2 + 4|V_{12}|^2} \tag{14b}$$

Substituting E_1 and E_2 into the system given by eq 4 and making use of the normalization condition, we obtain eqs 15 and 16, respectively;[12]

$$\alpha_{11} = \cos\frac{\theta}{2}\,\mathrm{e}^{-i\phi/2} \quad \alpha_{21} = \sin\frac{\theta}{2}\,\mathrm{e}^{i\phi/2} \tag{15}$$

$$\alpha_{12} = -\sin\frac{\theta}{2}\,\mathrm{e}^{-i\phi/2} \quad \alpha_{22} = \cos\frac{\theta}{2}\,\mathrm{e}^{i\phi/2} \tag{16}$$

where $\tan\theta = 2|V_{12}|/(E_1^0 - E_2^0)$, $V_{12} = |V_{12}|\,\mathrm{e}^{-i\phi}$ with $0 \leq \theta < \pi$ and $0 \leq \phi < 2\pi$. With the initial conditions $a_1(0) = 1$, $a_2(0) = 0$, eqs 12 and 13 become eqs 17 and 18.

$$a_1(t) = \cos^2\frac{\theta}{2}\,\mathrm{e}^{-iE_1t/\hbar} + \sin^2\frac{\theta}{2}\,\mathrm{e}^{-iE_2t/\hbar} \tag{17}$$

$$a_2(t) = \sin\frac{\theta}{2}\cos\frac{\theta}{2}\,\mathrm{e}^{i\phi}(\mathrm{e}^{-iE_1t/\hbar} - \mathrm{e}^{-iE_2t/\hbar}) \tag{18}$$

The probability of finding the system at time t in the state $|\varphi_2\rangle$, assuming it was prepared in the state $|\varphi_1\rangle$ at time $t = 0$, is given by eq 19.

$$|a_2(t)|^2 = \frac{4|V_{12}|^2}{(E_1^0 - E_2^0)^2 + 4|V_{12}|^2}\sin^2\left[\sqrt{(E_1^0 - E_2^0)^2 + 4|V_{12}|^2}\,\frac{t}{2\hbar}\right] \tag{19}$$

This expression is sometimes called Rabi's formula.[12] We observe that this probability oscillates over time with a frequency of $(E_1^0 - E_2^0)/h$. Accordingly, the probability of finding the system in the state $|\varphi_1\rangle$, which is 1 at time $t = 0$, again becomes 1 at times $t = 2n\pi\hbar/(E_1 - E_2)$ with $n = 0, 1, 2, ...$ When $E_1^0 = E_2^0$, the coupling causes the system to oscillate completely from one state to the other with a frequency proportional to the coupling matrix element. This means that in a two-state system the transitions between two unperturbed states are reversible.

As a second example, we now consider a multistate system in which a single state $|\varphi_s\rangle$ couples to a large number of states $\{|\varphi_l\rangle\}$, assuming that there is no coupling in the $\{|\varphi_l\rangle\}$ manifold.

This model, which reasonably describes the irreversibility of radiationless transitions, was proposed by Wigner and Weisskopf.[21] For this model we can find approximate expressions for the expansion coefficients without carrying out Hamiltonian matrix diagonalization. We are interested in calculating the probability of the system to be found in the state $|\varphi_s\rangle$ at time t, given that it was prepared in the same state at $t = 0$. For this case, eq2 can be written as eqs 20 and 21;

$$i\hbar\frac{d}{dt}a_s(t) = \sum_l a_l(t)V_{sl}e^{-i\omega_{ls}t} \tag{20}$$

$$i\hbar\frac{d}{dt}a_l(t) = a_s(t)V_{ls}e^{i\omega_{ls}t} \tag{21}$$

where $\omega_{ls} = (E_l^0 - E_s^0)/\hbar$, and we have made the replacement $a_j(t) \rightarrow a_j(t)e^{-iE_j^0 t/\hbar}$. To solve these equations we first set $a_s(t) = e^{-iR_{ss}t/\hbar}$, then eq 21 gives eq 22.

$$a_l(t) = -V_{ls}\frac{1 - e^{-i(E_s^0 - E_l^0 + R_{ss})t/\hbar}}{E_s^0 - E_l^0 + R_{ss}} \tag{22}$$

We then substitute eq 22 into eq 20 to obtain eq 23.

$$R_{ss} = \sum_l |V_{ls}|^2\frac{1 - e^{i(E_s^0 - E_l^0 + R_{ss})t/\hbar}}{E_s^0 - E_l^0 + R_{ss}} \tag{23}$$

To proceed further, we assume that the $\{|\varphi_l\rangle\}$ manifold is sufficiently dense to allow switching from summation to integration. We thus write eq 24;

$$R_{ss} = \int |V_{ls}|^2\frac{1 - e^{i(E_s^0 - E_l^0 + R_{ss})t/\hbar}}{E_s^0 - E_l^0 + R_{ss}}\rho(E_l^0)\, dE_l^0 \tag{24}$$

where $\rho(E_l^0)$ is the density of states in the manifold $\{|\varphi_l\rangle\}$. This equation can be solved for R_{ss} by interations until R_{ss} is found to any required degree of accuarcy. As a first approximation we neglect R_{ss} in the integrand and write eq 25.

$$R_{ss} = \int |V_{ls}|^2\frac{1 - e^{i(E_s^0 - E_l^0)t/\hbar}}{E_s^0 - E_l^0}\rho(E_l^0)\, dE_l^0 \tag{25}$$

For sufficiently large t we may write $\lim_{t\to\infty}(1 - e^{i\omega_{sl}t})/\omega_{sl} = P/\omega_{sl} - i\pi\delta(\omega_{sl})$,[22] where P indicates the principal value. Therefore, we get eq 26;

$$R_{ss} = \Delta_s(E_s^0) - \frac{1}{2}i\hbar\Gamma_s(E_s^0) \tag{26}$$

where

$$\Delta_s(E_s^0) = P\int \frac{|V_{ls}|^2}{E_s^0 - E_l^0}\rho(E_l^0)\, dE_l^0 \tag{27}$$

$$\hbar\Gamma_s(E_s^0) = 2\pi|V_{ls}|^2\rho(E_s^0) = 2\pi\sum_l |V_{ls}|^2\delta(E_s^0 - E_l^0) \tag{28}$$

The real part of R_{ss} represent a correction to the energy to second order in the perturbation, whereas the imaginary part is a relaxation rate (inverse lifetime). It follows that the probability that the system is still in the state $|\varphi_s\rangle$ at time t is $P_{ss}(t) = |a_s(t)|^2 = e^{-\Gamma_s t}$, so that Γ_s is the decay rate constant. This shows that $|\varphi_s\rangle \rightarrow \{|\varphi_l\rangle\}$ transitions are now irreversible. Therefore, to have irreversible transitions and a progressive depletion of the initial state; it is essential that the initial state be coupled to a very large number of states with similar energies. It should be emphasized that eq 28 is an approximate expression for the decay rate constant.

Likewise, we may evaluate the transition probability from state $|\varphi_s\rangle$ to any arbitrary state $|\varphi_l\rangle$ in time t: $P_{sl}(t) = |a_l(t)|^2$ and the total transition probability $\sum_l P_{sl}(t)$. Using eq 22, switching from summation to integration, and neglecting the variation of the matrix elements V_{ls} and the density of states $\rho(E_l^0)$ with energy over a range $\simeq\Gamma_s$ about $E_l^0 = E_s^0$, it turns out that $\sum_l P_{sl}(t) = 1 - P_{ss}(t)$, as is required by the conservation of probability.

2.2. Diagonalization of Vibronic Hamiltonian; Adiabatic and Diabatic Basic Sets. In the treatment of the radiationless processes in large molecules, one ususally neglects details concerning the rotational motion and concentrates on the dynamics of the vibrational and the electronic motions. Therefore, the vibronic Hamiltonian operator is written as $\hat{H} = \hat{T}_e(\mathbf{r}) + \hat{T}_N(\mathbf{Q}) + \hat{U}(\mathbf{r}, \mathbf{Q})$, where $\hat{T}_e$ is the electronic kinetic energy operator, $\hat{T}_N$ is the vibrational kinetic energy operator, and $\hat{U}$ is the potential energy of the entire molecule ($\mathbf{r}$ and $\mathbf{Q}$ symbolize the electronic variables and vibrational normal coordinates, respectively.); for the complete rovibronic Hamiltonian, see ref 13. The adiabatic electronic states $\{|\Phi_n\rangle\}$ are chosen so as to diagonalize the electronic Hamiltonian: $(\hat{T}_e + \hat{U})|\Phi_n\rangle = E_n(\mathbf{Q})|\Phi_n\rangle$. The full jth vibronic state $|\psi_j\rangle$ can now be expanded in terms of these adiabatic electronic states as eq 29;

$$|\psi_j\rangle = \sum_n \chi_n^{(j)}(\mathbf{Q})|\Phi_n\rangle \tag{29}$$

where the coefficients $\chi_n^{(j)}(\mathbf{Q})$ are determined by substituting this expansion into the Schrodinger equation (eq 30).

$$\hat{H}|\psi_j\rangle = \epsilon_j|\psi_j\rangle \tag{30}$$

We obtain a set of coupled nonlinear equations for the coefficients shown in eq 31;

$$\sum_n \{[\hat{T}_N + E_n(\mathbf{Q}) + \hat{\Lambda}_{nn}(\mathbf{Q}) - \epsilon_j]\delta_{mn} + (1 - \delta_{mn})\hat{\Lambda}_{mn}(\mathbf{Q})\}\chi_n^{(j)}(\mathbf{Q}) = 0 \tag{31}$$

where the nonadiabatic coupling operator $\hat{\Lambda}_{mn}(\mathbf{Q})$ is defined by eq 32;

$$\hat{\Lambda}_{mn}(\mathbf{Q}) = -\frac{\hbar^2}{2}\sum_k\left[\int d^3\mathbf{r}\Phi_m^*(\mathbf{r}, \mathbf{Q})\frac{\partial^2\Phi_n^*(\mathbf{r}, \mathbf{Q})}{\partial {Q_k}^2} + 2\int d^3\mathbf{r}\Phi_m^*(\mathbf{r}, \mathbf{Q})\frac{\partial\Phi_n^*(\mathbf{r}, \mathbf{Q})}{\partial Q_k}\frac{\partial}{\partial Q_k}\right] \tag{32}$$

with

$$\left\langle\Phi_m\left|\frac{\partial}{\partial Q_k}\right|\Phi_n\right\rangle = \frac{1}{E_n(\mathbf{Q}) - E_m(\mathbf{Q})}\left\langle\Phi_m\left|\frac{\partial\hat{U}}{\partial Q_k}\right|\Phi_n\right\rangle \tag{33}$$

Equation 35 may be proved by taking the derivative of the electronic Schrodinger equation with respect to Q_k, multiplying each side of the result by Φ_m^* ($m \neq n$), and integrating over the electronic variables.

In the adiabatic approximation of Born−Huang,[15] the dynamic off-diagonal coupling elements $\hat{\Lambda}_{mn}(\mathbf{Q})$ are neglected.

In the adiabatic approximation of Born−Oppenheimer[14] the diagonal elements $\hat{\Lambda}_{nn}(\mathbf{Q})$ are neglected as well. By these approximations, the above coupled equations become decoupled, and the expansion coefficients $\chi_n^{(j)}(\mathbf{Q})$ are interpreted as the vibrational states belonging to the adiabatic electronic state $|\Phi_n\rangle$ and the electronic energy $E_n(\mathbf{Q})$ as a PES in which the nuclei of the molecule perform their vibrational motions. This approximation is justifiable when the separation of electronic energy surfaces is large compared with typical energy spacings of the nuclear motion. Even though a large number of molecular processes can be interpreted on the basis of this approximation, there are cases in which the adiabatic approximation is no longer appropriate.

A definite prescription for finding the exact vibronic states $|\psi_j\rangle$ and the eigenvalues ϵ_j is to first make the coupled equations linear by expanding the coefficients $\chi_n^{(j)}(\mathbf{Q})$ for each electronic state $|\Phi_n\rangle$ in suitable basic sets $\{|\chi_{n\nu}\rangle\}$. The vibronic states now become eq 34;

$$|\psi_j\rangle = \sum_{n\nu} \alpha_{n\nu,j}|\Phi_n\chi_{n\nu}\rangle \tag{34}$$

in which the expansion coefficients $\alpha_{n\nu,j}$ are obtained by diagonalizing the Hamiltonian matrix. The elements of this matrix are given by eq 35;

$$H_{m\mu,n\nu} = \langle\chi_{m\mu}|[\hat{T}_\mathrm{N} + E_n(\mathbf{Q}) + \hat{\Lambda}_{nn}(\mathbf{Q})]\delta_{mn} + (1-\delta_{mn})\hat{\Lambda}_{mn}(\mathbf{Q})|\chi_{n\nu}\rangle \tag{35}$$

which suggests that the basis sets should be chosen as the solutions of the unperturbed Hamiltonian (eq 36).

$$[\hat{T}_\mathrm{N} + E_n(\mathbf{Q}) + \hat{\Lambda}_{nn}(\mathbf{Q})]|\chi_{n\nu}\rangle = \epsilon_{n\nu}^0|\chi_{n\nu}\rangle \tag{36}$$

If the electronic integrals in the nonadiabatic coupling operator $\hat{\Lambda}_{mn}(\mathbf{Q})$ are taken as constants (the Condon approximation), then for the harmonic oscillator wavefunctions as a basis set the off-diagonal elements of the Hamiltonian matrix can be reduced to the evaluation of Franck−Condon integrals. In a previous work[19] we derived general expressions for these integrals between the diplaced−distorted−rotated harmonic PESs. In a non-Condon scheme, the functional dependence of the nonadiabatic couplings is approximated by a single product of Gaussian functions over the active vibrational modes or by a linear combination of such product functions,[26,27] and the dynaminc off-diagonal elements of the Hamiltonian matrix are calculated.[26]

However, when two electronic energy surfaces closely approach or intersect each other, the nonadiabatic coupling matrix elements become large and even singular (see eq 33). In this case, it is preferable to introduce an alternative electronic representation, the so-called diabatic representation; see ref 23 and references therein. The diabatic electronic states $\{|\phi_n\rangle\}$ are defined as a unitary transformation of the adiabatic electronic states such that the electronic states become smoothly varying functions of the nuclear coordinates and the derivative coupling are sufficiently small to be neglected. The expansion of the exact vibronic states in terms of the diabatic electronic states is given by eq 37;

$$|\psi_j\rangle = \sum_n \tilde{\chi}_n^{(j)}(\mathbf{Q})|\phi_n\rangle \tag{37}$$

where the expansion coefficients $\tilde{\chi}_n^{(j)}(\mathbf{Q})$ are determined by substituting eq 37 into eq 30. We obtain, after neglecting the residual derivatives couplings, the following coupled nonlinear equations (eq 38);

$$\sum_n \{[\hat{T}_\mathrm{N} + \tilde{E}_n(\mathbf{Q}) - \epsilon_j]\delta_{mn} + (1-\delta_{mn})\tilde{\Lambda}_{mn}(\mathbf{Q})\}\tilde{\chi}_n^{(j)}(\mathbf{Q}) = 0 \tag{38}$$

where $\tilde{E}_n(\mathbf{Q}) = \tilde{\Lambda}_{nn}(\mathbf{Q})$ and diabatic coupling elements are defined by eq 39.

$$\tilde{\Lambda}_{mn}(\mathbf{Q}) = \int \mathrm{d}^3\mathbf{r}\phi_m^*(\hat{T}_\mathrm{e} + \hat{U})\phi_n \tag{39}$$

Again, to make eqs 38 linear, we expand the coefficients in terms of the suitable basis sets $\{|\tilde{\chi}_{n\nu}\rangle\}$; thereby the exact vibronic states become (eq 40);

$$|\psi_j\rangle = \sum_{n\nu} \tilde{\alpha}_{n\nu,j}|\phi_n\tilde{\chi}_{n\nu}\rangle \tag{40}$$

the Hamiltonian matrix, which is to be diagonalized, has the following matrix elements (eq 41).

$$\tilde{H}_{m\mu,n\nu} = \langle\tilde{\chi}_{m\mu}|[\hat{T}_\mathrm{N} + \tilde{E}_n(\mathbf{Q})]\delta_{mn} + (1-\delta_{mn})\tilde{\Lambda}_{mn}(\mathbf{Q})|\tilde{\chi}_{n\nu}\rangle \tag{41}$$

Again, it seems natural that basis sets $\{|\tilde{\chi}_{m\nu}\rangle\}$ are chosen as the solutions of eq 42.

$$[\hat{T}_N + \tilde{E}_n(\mathbf{Q})]|\tilde{\chi}_{n\nu}\rangle = \tilde{\epsilon}^0{}_{n\nu}|\tilde{\chi}_{n\nu}\rangle \tag{42}$$

It is assumed that the adiabatic PESs $E_n(\mathbf{Q})$ (or their diabatic versions) are a slowly varying function of $\mathbf{Q}$. Thus, we may expand $E_n(\mathbf{Q})$ for any electronic state about a reference nuclear configuration (A possible choice for the reference configuration is the equilibrium nuclear configuration of the ground electronic state of molecule. We specify the lower state quantities by double prime and the upper state by single prime.).

$$\begin{aligned} E_n(\mathbf{Q}) &= E_n(0'') + \sum_j \kappa_j^{(n)}Q_j'' + \frac{1}{2}\sum_{ij}\eta_{ij}^{(n)}Q_i''Q_j'' + \dots \\ &= E_n(0'') + \mathbf{Q}''^T\kappa^{(n)} + \frac{1}{2}\mathbf{Q}''^T\eta^{(n)}\mathbf{Q}'' + \dots \end{aligned} \tag{43}$$

where $E_n(0'')$ is the vertical excitation energy, $\kappa_j^{(n)}$ are the first-order intrastate coupling constants, and $\eta_{ij}^{(n)}$ are the second-order intrastate coupling constants. For the ground electronic state, that is $n = g$, the linear terms vanish and $\eta_{ij}^{(g)} = \omega_i''^2\delta_{ij}$, where $\{\omega_j''\}$ are the set of the angular vibrational frequencies of the ground electronic state. To remove the linear terms for the excited electronic states and to diagonalize the symmetric matrix $\eta^{(n)}$, we may employ the orthogonal transformation (eq 44, the so-called Duschinsky transformation[16]);

$$\mathbf{Q}' = \mathbf{J}\mathbf{Q}'' + \mathbf{D} \tag{44}$$

where $\mathbf{J}$ is the Duschinsky rotation matrix, and $\mathbf{D}$ is a column vector whose components are the shift of the equilibrium nuclear configuration of the excited electronic state with respect to that of the ground electronic state. The matrix $\mathbf{J}$ is chosen such that to diagonalize the matrix $\eta^{(n)}$;

$$\mathbf{J}\eta^{(n)}\mathbf{J}^\mathrm{T} = \Lambda' = \mathrm{diag}(\omega_1'^2, \omega_2'^2, \dots, \omega_N'^2) \tag{45}$$

where “T’’ stands for the transpose of the matrix, so we obtain to the second-order of approximation (eq 46);

$$E_n(\mathbf{Q}) = E_n(0') + \frac{1}{2}\mathbf{Q}'^{T}\Lambda'\mathbf{Q}' \tag{46}$$

with $E_n(0') = E_n(0'') - (1/2)\mathbf{D}^{\mathrm{T}}\Lambda'\mathbf{D}$ and $\mathbf{D} = \Lambda'^{-1}\mathbf{J}\kappa^{(n)}$. A similar transformation may be used for any electronic excited state. By these transformations, the basic sets $\{|\chi_{n\nu}\rangle\}$ become the harmonic oscillator wavefunctions centered on the corresponding PES. If the anharmonic cubic, quartic, ... terms in eq 43 cannot be neglected, then the anharmonic oscillator wavefunctions should be used as the basic sets. It is found that anharmonicities may have significant effects on radiationless transitions in polyatomic molecules.[8,41]

3. Calculation of Internal Conversion Decay Rate Constant

Equation 28 can be adapted to a "statistical'' case of a complex molecule in which the vibrational relaxation takes place very rapidly after excitation and leads to a Boltzmann distribution over the vibrational levels of the initial electronic state. Therefore, the thermally averaged nonradiative decay rate constant $k_{\mathrm{IC}}(\Omega_{ab}, T)$ from the statistically equilibrated initial vibronic states $\{|a\alpha\rangle\}$ to the manifold of the final states $\{|b\beta\rangle\}$ is given by eq 47;

$$k_{\mathrm{IC}}(\Omega_{ab}, T) = \sum_{\alpha} \rho_{\alpha}(T)\Gamma_{a\alpha} = \frac{2\pi}{\hbar}\sum_{\alpha}\sum_{\beta} \rho_{\alpha}(T)|H_{a\alpha,b\beta}|^2\,\delta(\hbar\Omega_{ab} + E_{\alpha} - E_{\beta}) \tag{47}$$

where $\rho_a(T)$ is the Boltzmann distribution function for the initial vibronic states, Ω_{ab} is the zero−zero transition frequency, E_α and E_β are the vibrational energies (excluding the zero-point energies) of the electronic states a and b, respectively, and $H_{a\alpha,b\beta}$ are the dynamic off-diagonal elements of the Hamiltonian matrix that induce the intramolecular nonradiative transitions between electronic states a and b.

An alternative expression for eq 47 can be obtained by employing the generating function of Kubo and Toyazawa.[17,18] Inserting the integral representation of the delta function, the transition rate in eq 47 reads as eq 48;

$$k_{\mathrm{IC}}(\Omega_{ab},T) = \int_{-\infty}^{\infty} \mathrm{d}t\, \exp(i\Omega_{ab}t)G(t) \tag{48}$$

where the generating function $G(t)$ is defined by eq 49.

$$G(t) = \frac{1}{\hbar^2}\sum_{\alpha}\sum_{\beta} \rho_{\alpha}(T)|H_{a\alpha,b\beta}|^2 \exp[i(E_{\alpha} - E_{\beta})t/\hbar] \tag{49}$$

Therefore, if the generating function is available, then the transition rate calculation may be reduced to a Fourier transformation on $G(t)$. In the following we shall calculate the generating function for two separate cases: (1) the case in which the internal conversion takes place between two adiabatic and (2) the case in which it takes place between two diabatic electronic states.

3.1. Internal Conversion Between Two Adiabatic Electronic States. Neglecting the 2-fold differentiation of the electronic wavefunctions, the first term in the brackets of eq 32, and assuming that the electronic integral in the second term is independent of the vibrational variables, the simplified off-diagonal elements of the vibronic Hamiltonian matrix (eq 35) take the following form;

$$H_{a\alpha,b\beta} = \langle\chi_{\alpha}|\hat{\Lambda}_{ab}(\mathrm{Q})|\chi_{\beta}\rangle \simeq \sum_{p=1}^{N}\langle\Phi_a|\hat{P}'_p|\Phi_b\rangle_0\langle\chi_{\alpha}|\hat{P}'_p|\chi_{\beta}\rangle \tag{50}$$

where $\hat{P}'_p = -i\hbar\partial/\partial Q_p{}'$, $\langle ...\rangle_0$ means the value of the matrix elements in the vicinity of the equilibrium nuclear configuration of the initial electronic state, and χ_α and χ_β are the N-dimensional harmonic oscillator vibrational wavefunctions corresponding to the initial (a) and the final (b) adiabatic electronic states, respectively.

Introducing eq 50 into eq 49 we may write eq 51;

$$G(t) = \frac{1}{z'}\sum_{p=1}^{N}\sum_{p'=1}^{N} R_{ab}(p)R^{*}_{ab}(p') \int\int \mathrm{d}\mathbf{Q}'\,\mathrm{d}\bar{\mathbf{Q}}' \times \sum_{\beta_1=0}^{\infty}\cdots\sum_{\beta_N=0}^{\infty} \exp\Bigl(-\sum_{j=1}^{N}\lambda''_j\beta_j\Bigr)\chi_{\beta_1\cdots\beta_N}(Q''_1, ..., Q''_N)\chi_{\beta_1\cdots\beta_N}(\bar{Q}''_1, ..., \bar{Q}''_N) \times \frac{\partial}{\partial Q'_p}\frac{\partial}{\partial \bar{Q}'_{p'}}\sum_{\alpha_1=0}^{\infty}\cdots\sum_{\alpha_N=0}^{\infty} \exp\Bigl(-\sum_{j=1}^{N}\lambda'_j\alpha_j\Bigr)\chi_{\alpha_1\cdots\alpha_N}(Q'_1, ..., Q'_N)\chi_{\alpha_1\cdots\alpha_N}(\bar{Q}'_1, ..., \bar{Q}'_N) \tag{51}$$

where $R_{ab}(p) = \langle\Phi_a|\hat{P}'_p|\Phi_b\rangle_0$, $\lambda'_j = -i\omega'_jt + \hbar\omega'_j/kT$, $\lambda''_j = i\omega''_jt$, and $z' = \Pi_{j=1}^{N}(1 + n'_j)$ in which the mean occupation number n'_j is defined by eq 52.

$$n'_j = [\exp(\hbar\omega'_j/kT) - 1]^{-1} \tag{52}$$

The summations over vibrational quantum numbers in eq 51 are calculated by making use of the multidimensional Mehler's formula (eq 53);[19,20]

$$\sum_{\alpha_1=0}^{\infty}\cdots\sum_{\alpha_N=0}^{\infty}\exp\Bigl(-\sum_{j=1}^{N}\lambda_j\alpha_j\Bigr)\chi_{\alpha_1...\alpha_N}(Q_1, ..., Q_N)\chi_{\alpha_1...\alpha_N}(\bar{Q}_1, ..., \bar{Q}_N) = \pi^{-N/2}(\det \Gamma^{-1}\mathbf{T})^{-1/2} \exp\Bigl[-\frac{1}{4}(\mathbf{Q} + \bar{\mathbf{Q}})^{\mathrm{T}}\Gamma\mathbf{A}(\mathbf{Q} + \bar{\mathbf{Q}}) - \frac{1}{4}(\mathbf{Q} - \bar{\mathbf{Q}})^{\mathrm{T}}\Gamma\mathbf{A}^{-1}(\mathbf{Q} - \bar{\mathbf{Q}})\Bigr] \tag{53}$$

where Γ is the $N \times N$ diagonal matrix of the reduced frequency $\omega_j/\hbar$, and $N \times N$ diagonal matrices $\mathbf{T}$ and $\mathbf{A}$ are defined by eqs 54 and 55, respectively.

$$T_j = 1 - \exp(-2\lambda_j) \tag{54}$$

$$A_j = \frac{1 - \exp(-\lambda_j)}{1 + \exp(-\lambda_j)} \tag{55}$$

Introducing eq 53 into eq 51 we obtain eq 56;

$$G(t) = \pi^{-N}(\det \Gamma'^{-1}\Gamma''^{-1}\mathbf{T}'\mathbf{T}'')^{-1/2}\sum_{p=1}^{N}\sum_{p'=1}^{N}R_{ab}(p)R^{*}_{ab}(p') \int\int \mathrm{d}\mathbf{Q}'\,\mathrm{d}\bar{\mathbf{Q}}' \times \exp\Bigl[-\frac{1}{4}(\mathbf{Q}'' + \bar{\mathbf{Q}}'')^{\mathrm{T}}\Gamma''\mathbf{A}''(\mathbf{Q}'' + \bar{\mathbf{Q}}'') - \frac{1}{4}(\mathbf{Q}'' - \bar{\mathbf{Q}}'')^{\mathrm{T}}\Gamma''\mathbf{A}''^{-1}(\mathbf{Q}'' - \bar{\mathbf{Q}}'')\Bigr] \times \frac{\partial}{\partial Q'_p}\frac{\partial}{\partial \bar{Q}'_{p'}} \exp\Bigl[-\frac{1}{4}(\mathbf{Q}' + \bar{\mathbf{Q}}')^{\mathrm{T}}\Gamma'\mathbf{A}'(\mathbf{Q}' + \bar{\mathbf{Q}}') - \frac{1}{4}(\mathbf{Q}' - \bar{\mathbf{Q}}')^{\mathrm{T}}\Gamma'\mathbf{A}'^{-1}(\mathbf{Q}' - \bar{\mathbf{Q}}')\Bigr] \tag{56}$$

where the $N \times N$ diagonal matrices Γ', Γ'', $\mathbf{T}'$, $\mathbf{T}''$, $\mathbf{A}'$, and $\mathbf{A}'$ are defined by $\Gamma'_j = \omega'_j/\hbar, \Gamma''_j = \omega''_j/\hbar$, and eqs 57a−d, respectively.

$$T'_j = (1 + n'_j)^2 - n'^2_j \exp(2i\omega'_j t) \tag{57a}$$

$$T''_j = 1 - \exp(-2i\omega''_j t) \tag{57b}$$

$$A'_j = \frac{(1 + n'_j) - n'_j \exp(i\omega'_j t)}{(1 + n'_j) + n'_j \exp(i\omega'_j t)} \tag{57c}$$

$$A''_j = \frac{1 - \exp(-i\omega''_j t)}{1 + \exp(-i\omega''_j t)} \tag{57d}$$

After taking the derivatives with respect to Q'_p and $\bar{Q}'_p$ we introduce the Duschinsky transformation (eq 44) into the resulting equation, and then we change variables as $\mathbf{Q}' + \bar{\mathbf{Q}}' = 2\mathbf{X}$ and $\mathbf{Q}' - \bar{\mathbf{Q}}' = 2\mathbf{Y}$ to obtain eq 58;

$$\begin{aligned} G(t) = {} & \left(\frac{2}{\pi}\right)^N (\det \Gamma'^{-1}\Gamma''^{-1}\mathbf{T}'\mathbf{T}'')^{-1/2} \exp(-\mathbf{D}^\mathrm{T}\mathbf{J}\Gamma''\mathbf{A}''\mathbf{J}^\mathrm{T}\mathbf{D}) \times \\ & \sum_{p=1}^{N}\sum_{p'=1}^{N} R_{ab}(p)R^*_{ab}(p') \int\int \mathrm{d}\mathbf{X}\,\mathrm{d}\mathbf{Y} \left\{\left[-\frac{1}{2}(\Gamma'\mathbf{A}')_{pp} + \right.\right. \\ & \left. \frac{1}{2}(\Gamma'\mathbf{A}'^{-1})_{pp}\right]\delta_{pp'} + (\Gamma'\mathbf{A}')_{pp}(\Gamma'\mathbf{A}')_{p'p'}X_pX_{p'} - \\ & (\Gamma'\mathbf{A}'^{-1})_{pp}(\Gamma'\mathbf{A}'^{-1})_{p'p'}Y_pY_{p'} - (\Gamma'\mathbf{A}')_{pp}(\Gamma'\mathbf{A}'^{-1})_{p'p'}X_pY_{p'} + \\ & \left.(\Gamma'\mathbf{A}'^{-1})_{pp}(\Gamma'\mathbf{A}')_{p'p'}Y_pX_{p'}\right\} \times \exp\,(-\mathbf{X}^\mathrm{T}\mathbf{J}\mathbf{W}_1\mathbf{J}^\mathrm{T}\mathbf{X} + \\ & 2\mathbf{X}^\mathrm{T}\mathbf{J}\Gamma''\mathbf{A}''\mathbf{J}^\mathrm{T}\mathbf{D}) \exp\,(-\mathbf{Y}^\mathrm{T}\mathbf{J}\mathbf{W}_2\mathbf{J}^\mathrm{T}\mathbf{Y}) \end{aligned} \tag{58}$$

where $N \times N$ symmetric matrices $\mathbf{W}_1$ and $\mathbf{W}_2$ are defined as eqs 59 and 60.

$$\mathbf{W}_1 = \Gamma''\mathbf{A}'' + \mathbf{J}^\mathrm{T}\Gamma'\mathbf{A}'\mathbf{J} \tag{59}$$

$$\mathbf{W}_2 = \Gamma''\mathbf{A}''^{-1} + \mathbf{J}^\mathrm{T}\Gamma'\mathbf{A}'^{-1}\mathbf{J} \tag{60}$$

The integrations over $\mathbf{X}$ and $\mathbf{Y}$ can now be carried out with the aid of the Gaussian integration formula evaluated in the appendix (eqs A5−7). The result is eq 61;

$$\begin{aligned} G(t) = {} & 2^N h(t)\,(\det \Gamma'^{-1}\Gamma''^{-1}\mathbf{T}'\mathbf{T}''\mathbf{W}_1\mathbf{W}_2)^{-1/2} \\ & \exp(-\mathbf{D}^\mathrm{T}\mathbf{W}_3{}^{-1}\mathbf{D}) \end{aligned} \tag{61}$$

with

$$h(t) = \frac{1}{2}\mathbf{R}^\dagger(-\mathbf{W}_3{}^{-1} + \mathbf{W}_4{}^{-1})\mathbf{R} + (\mathbf{R}^\dagger\mathbf{W}_3{}^{-1}\mathbf{D})(\mathbf{D}^\mathrm{T}\mathbf{W}_3{}^{-1}\mathbf{R}) \tag{62}$$

where use is made of the matrix identity $\mathbf{A}^{-1} = \mathbf{B}^{-1} + \mathbf{B}^{-1}(\mathbf{B} - \mathbf{A})\mathbf{A}^{-1}$. In this equation, $\mathbf{R}$ is the N-dimensional column vector of $\{R_p \equiv R_{ab}(p);\ p = 1, ..., N\}$, and the following $N \times N$ symmetric matrices are defined (eqs 63 and 64).

$$\mathbf{W}_3 = \Gamma'^{-1}\mathbf{A}'^{-1} + \mathbf{J}\Gamma''^{-1}\mathbf{A}''^{-1}\mathbf{J}^\mathrm{T} \tag{63}$$

$$\mathbf{W}_4 = \Gamma'^{-1}\mathbf{A}' + \mathbf{J}\Gamma''^{-1}\mathbf{A}''\mathbf{J}^\mathrm{T} \tag{64}$$

Equation 61 is our general expression for the generating function $G(t)$, which includes the effects of Franck−Condon, the promoting modes, and the temperature on the nonradiative rate constants. Notice that in the low-temperature limit $n'_j \to 0$, $T'_j \to 1$, $A'_j \to 1$, $j = 1, ..., N$.

The transformation matrix $\mathbf{J}$ entangles the normal coordinates belonging to the same symmetry species so that matrix $\mathbf{J}$ and all related matrices $\mathbf{W}_1$, $\mathbf{W}_2$, $\mathbf{W}_3$, and $\mathbf{W}_4$ (along with their inverses) are in block diagonal forms. Each block corresponds to a particular symmetry species, and its dimension is equal to the number of the vibrational modes that belong to that particular irreducible representation. Therefore, the expression for $G(t)$ may be factored out as eq 65;

$$\begin{aligned} G(t) = {} & 2^N h(t)\,\Pi_j\,[(\det \Gamma'^{-1}\Gamma''^{-1}\mathbf{T}'\mathbf{T}''\mathbf{W}_1\mathbf{W}_2)^{-1/2} \\ & \exp(-\mathbf{D}^\mathrm{T}\mathbf{W}_3{}^{-1}\mathbf{D})]_{\Gamma_j} \end{aligned} \tag{65}$$

with

$$\begin{aligned} h(t) = {} & \sum_j \left[\frac{1}{2}\mathbf{R}^\dagger(-\mathbf{W}_3{}^{-1} + \mathbf{W}_4{}^{-1})\mathbf{R}\right]_{\Gamma_j} + \\ & \sum_{ij} (\mathbf{R}^\dagger\mathbf{W}_3{}^{-1}\mathbf{D})_{\Gamma_i}(\mathbf{D}^T\mathbf{W}_3{}^{-1}\mathbf{R})_{\Gamma_j} \end{aligned} \tag{66}$$

where Γ_j refers to a particular symmetry species, and the matrices are now the blocks due to that particular species. The vibrational normal modes are classified into two group: (1) the promoting modes, which are capable of performing the nonradiative transitions, and (2) the accepting modes, which act as sinks for the electronic energy. If the electronic states a and b belong to the same irreducible representation, then the promoting modes belong to the totally symmetric representation, and if the electronic states belong to two different irreducible representations, then the promoting modes are nontotally symmetric. For the nontotally symmetric mode Q_j, $D_j = 0$, and for the accepting mode Q_j, $R_j = 0$.

3.2. Internal Conversion Between Two Diabatic Electronic States. For this case, the dynamic off-diagonal elements of the Hamiltonian matrix (eq 41) have the form given by eq 67;

$$\tilde{H}_{a\alpha,b\beta} = \langle\tilde{\chi}_\alpha|\tilde{\Lambda}_{ab}(\mathbf{Q})|\tilde{\chi}_\beta\rangle \simeq \sum_{p=1}^{N}\left(\frac{\partial\tilde{\Lambda}_{ab}(\mathbf{Q})}{\partial Q'_p}\right)_0 \langle\tilde{\chi}_\alpha|Q'_p|\tilde{\chi}_\beta\rangle \tag{67}$$

where we have taken a linear expansion for $\tilde{\Lambda}_{ab}(\mathbf{Q})$ about the equilibrium configuration of the initial diabatic electronic state, assuming the electronic states belong to different irreducible representation. In eq 67, $\tilde{\chi}_\alpha$ and $\tilde{\chi}_\beta$ are the diabatic N-dimensional harmonic oscillator vibrational wavefunctions corresponding to the initial (a) and the final (b) diabatic electronic states, respectively.

A calculation parallel to that of the adiabatic case leads to the following expression for the generating function;

$$\begin{aligned} \tilde{G}(t) = {} & 2^N\,\tilde{h}(t)\,(\det \Gamma'^{-1}\Gamma''^{-1}\mathbf{T}'\mathbf{T}''\mathbf{W}_1\mathbf{W}_2)^{-1/2} \\ & \exp(-\mathbf{D}^\mathrm{T}\mathbf{W}_3{}^{-1}\mathbf{D}) \end{aligned} \tag{68}$$

where

$$\begin{aligned} \tilde{h}(t) = {} & \frac{1}{2}\tilde{\mathbf{R}}^\dagger\mathbf{J}(-\mathbf{W}_2{}^{-1} + \mathbf{W}_1{}^{-1})\mathbf{J}^\mathrm{T}\tilde{\mathbf{R}} + \\ & (\tilde{\mathbf{R}}^\dagger\mathbf{J}\mathbf{W}_1{}^{-1}\Gamma''\mathbf{A}''\mathbf{J}^\mathrm{T}\mathbf{D})(\mathbf{D}^\mathrm{T}\mathbf{J}\Gamma''\mathbf{A}''\mathbf{W}_1{}^{-1}\mathbf{J}^\mathrm{T}\tilde{\mathbf{R}}) \end{aligned} \tag{69}$$

with $\tilde{R}_p = (1/\hbar)(\partial\tilde{\Lambda}_{ab}(\mathbf{Q})/\partial Q'_p)_0$. All matrices ($\mathbf{\Gamma}'$, $\mathbf{\Gamma}''$, $\mathbf{T}'$, $\mathbf{T}''$, $\mathbf{W}_1$, $\mathbf{W}_2$, and $\mathbf{W}_3$) in these equations have the same definitions

TABLE 1: Calculated Vibrational Frequencies (cm^{-1}) of Ethylene in the Ground and Excited Electronic States[a]

	assignment	^1A_g	$^1B_{1u}$	$^1B_{3u}$	$^1B_{1g}$	$^1B_{2g}$	2^1A_g
a_g	ν_1 CH str	2979	2828	2970	2964	2956	3002
a_g	ν_2 CC str	1580	1398	1508	1536	1527	1532
a_g	ν_3 CH_2 scis	1286	1227	1227	1234	1192	1234
a_u	ν_4 CH_2 twist	977	855	502	883	507	333
b_{1u}	ν_5 CH str	2960	2798	2947	2980	2950	2994
b_{1u}	ν_6 CH_2 scis	1435	1274	1417	1438	1421	1433
b_{3g}	ν_7 CH str	3032	2840	3093	3065	3040	3099
b_{3g}	ν_8 CCH bend	1205	908	1207	1190	1178	1212
b_{3u}	ν_9 CH_2 wag	860	666	985	1097	999	856
b_{2u}	ν_{10} CH str	3059	2841	3065	3088	3090	3114
b_{2g}	ν_{11} CH_2 wag	813	915	1090	1159	1098	1113
b_{2u}	ν_{12} CCH bend	795	655	796	884	799	816

[a] Reference 28.

TABLE 2: Normalized Duschinsky Matrix for the a_1 Modes of $^1B_{1u}$ and ^1A_g in Ethylene[a]

	Q''_1	Q''_2	Q''_3	Q''_4
Q'_1	0.7977	−0.1467	−0.0027	0.5780
Q'_2	0.0887	−0.8622	−0.3802	−0.3153
Q'_3	−0.1024	0.2951	−0.9156	0.2364
Q'_4	−0.585	−0.3822	0.1259	0.7195

[a] References 29 and 30.

TABLE 3: Energy Gap, Haung-Rhys Factors, and Vibronic Coupling Constants Between Various Singlet Electronic States of Ethylene[a]

	$^1B_{1g}$−$^1B_{3u}$	$^1B_{2g}$−$^1B_{3u}$	2^1A_g−$^1B_{3u}$	$^1B_{1u}$−^1A_g
ω_{ab} (2π cm^{-1})	6151	5391	8837	43945
S_1	0.006	0.033	0.242	7.258
S_2	0.044	0.007	0.020	4.647
S_3	0.049	0.081	0.051	1.514
S_4	0.577	0.350	1.813	21.038
$\langle \Phi_a \vert \partial/\partial Q'_P \vert \Phi_b \rangle$ (a.u.)	0.2134 (Q'_{10}) 0.1129 (Q'_{12})	0.0589 (Q'_5) 0.2619 (Q'_6)	0.1276 (Q'_9)	0.0038 (Q'_5) 0.0723 (Q'_6)

[a] References 29 and 30.

as in the adiabatic case, except that the diabatic, rather than adiabatic, vibrational frequencies have to be used in the related equations.

4. Application

In this section we shall apply eqs 61, 62, and 48 to calculate the internal conversion rate constants for two real molecular systems: ethylene and azulene.

The method of steepest descent, also called the saddle point method,[24] has been successfully applied for the approximate evaluation of integrals of the type appearing in eq 48.[8,25] The method is based on the observation that the major contribution from the integrand in integral $\int_{-\infty}^{\infty} dt \exp[f(t)]$ comes from the vicinity of the point t_s (called the saddle point) where $f(t)$ is maximum [$f'(t_s) = 0$]. We have made use of this method to evaluate the integral in eq 48.

The ethylene molecule has 12 vibrational modes that, in the ground electronic state, are distributed among the irreducible representations (of D_{2h} point group) as $3a_g + 2b_{3g} + b_{2g} + a_u + 2b_{1u} + 2b_{2u} + b_{3u}$ (with z-axis along the C−C bond). Table 1 shows the complete active space self-consistent field (CASSCF) calculated vibrational frequencies of the ground (^1A_g), the excited valence $\pi - \pi^*$ ($^1B_{1u}$), and four Rydberg $\pi - 3s(^1B_{3u})$, $\pi - 3p_y(^1B_{1g})$, $\pi - 3p_z(^1B_{2g})$, and $\pi - 3p_x(^1A_g)$ states.[28] There is no vibrational mode mixing upon excitation from the ground to the Rydberg states; however, a heavy mixing of four vibrational modes occurs upon excitation to the $\pi - \pi^*$ ($^1B_{1u}$) electronic state. The $\pi - \pi^*$ state has D_{2d} symmetry, and these four modes belong to the a irreducible representation of the D_2 point group, a subgroup of D_{2h} and D_2.[28] Table 2 displays the related normalized Duschinsky matrix for these four totally symmetric modes.[29,30] Table 3 contains the electronic energy gap between the various states, the Haung-Rhys coupling constants, $S_j = \omega'_j D_j^2/2\hbar$, corresponding to the four totally symmetic modes, and the vibronic coupling constants between the various singlet electronic states of ethylene.[29,30] Finally, Table 4 presents the calculated internal conversion decay rate constants for various nonradiative electonic transitions, along with the promoting modes that induce these transitions in this molecule. We have calculated the rates for three cases: displaced, displaced−distorted, and displaced−distorted−rotated models, taking all 12 modes into the calculations. For the displaced model, the geometic averages of the vibrational frequencies ω'_j and ω''_j, that is $(\omega'_j\omega''_j)^{1/2}$, are used. The calculated rates of the $^1B_{1g} \rightsquigarrow {}^1B_{3u}$, $^1B_{2g} \rightsquigarrow {}^1B_{3u}$, and $2^1A_g \rightsquigarrow {}^1B_{3u}$ internal conversions for the displaced model completely agree with those of refs 28 and 30; however, there is some difference between the rate of $^1B_{1u} \rightsquigarrow {}^1A_g$ internal conversion calculated here with that of refs 28 and 30. This difference is because we used the vibrational frequencies corresponding to each electronic state in our displaced−distored−rotated model, rather than the geometric averages, as used in refs 28 and 30.

Now we consider the azulene molecule. Because of the large number of organic molecules known to obey Kasha's rule[1] (fluorescence is only observed from S_1 and phosphorescence from T_1), claims of "anomalous'' emission from the S_2, S_3, etc., and the T_2, T_3, etc. electronic states should be viewed with suspicion. However, well-documented cases of $S_2 \rightarrow S_1$ fluorescence are found for azulene and its derivatives.[31−34] This emission is attributed to the relatively large S_2−S_1 energy gap, which slows down the normally very rapid rate of $S_2 \rightsquigarrow S_1$ internal conversion by decreasing the Franck−Condon factors.

Azulene has 48 vibrational modes that, in the ground electronic state, are distributed among the irreducible representations (of C_{2v} point group) as $17a_1 + 6a_2 + 9b_1 + 16b_2$. Table 5 shows the experimental vibrational frequencies of 12 a_1 modes and the calculated vibrational frequencies of 5 b_2 modes in the ground S_0 and excited S_1 electronic states, which are taken into account in the calculation of the rate constant of the $S_1 \rightsquigarrow S_0$ internal conversion of azulene in the present work. Table 6 displays the Duschinsky matrices of a_1 and b_2 modes between S_0 and S_1 electronic states; notice that the a_1 modes ν_1, ν_6, ν_7 remain unrotated from S_0 to S_1. The electronic energy gap, Huang−Rhys factors, $S_j = \omega'_j D_j^2/2\hbar$, corresponding to the totally symmetric modes a_1, and the vibronic coupling constants between S_1 and S_0 electronic states are shown in Table 7. Finally, Table 8 presents the experimental and the calculated rate constants of the $S_1 \rightsquigarrow S_0$ internal conversion of azulene. It is worth mentioning that the rate constants are computed by making use of *Mathematica* programs.[42]

The extremely weak $S_1 \rightarrow S_0$ fluorescence of azulene[35] indicates that the competing nonradiative deactivation is most effective and essentially represents an internal conversion with a rate constant of $k_{IC} = 5 \times 10^{11}$ s^{-1}.[35] The rate of $S_1 \rightsquigarrow T_1$ intersystem crossing ($\simeq 6 \times 10^6$ s^{-1})[43] is about 5 orders of magnitude smaller than the rate of the corresponding internal conversion process. Therefore, the internal conversion should be a more important deactivation channel as compared with the intersystem crossing.

Gustav and Storch[37] have also calculated the rate constant for the $S_1 \rightsquigarrow S_0$ (as well as for $S_2 \rightsquigarrow S_1$ and $S_2 \rightsquigarrow S_0$) internal

TABLE 4: Rates of Internal Conversion between Various Singlet Electronic States of Ethylene

k_{IC} $(T = 0)$ (s^{-1})	$^1B_{1g} \rightsquigarrow {}^1B_{3u}$	$^1B_{2g} \rightsquigarrow {}^1B_{3u}$	$2^1A_g \rightsquigarrow {}^1B_{3u}$	$^1B_{1u} \rightsquigarrow {}^1A_g$
displaced	$1.09 \times 10^{11}(Q'_{10})$ $1.64 \times 10^{8}(Q'_{12})$	$2.97 \times 10^{10}(Q'_5)$ $4.09 \times 10^{10}(Q'_6)$	$4.72 \times 10^{9}(Q'_9)$	$7.49 \times 10^{7}(Q'_5)$ $1.48 \times 10^{10}(Q'_6)$
displaced−distorted	$4.65 \times 10^{10}(Q'_{10})$ $9.23 \times 10^{7}(Q'_{12})$	$3.05 \times 10^{10}(Q'_5)$ $4.44 \times 10^{10}(Q'_6)$	$8.70 \times 10^{9}(Q'_9)$	$3.39 \times 10^{7}(Q'_5)$ $7.04 \times 10^{9}(Q'_6)$
displaced−distorted−rotated				$1.81 \times 10^{7}(Q'_5)$ $3.67 \times 10^{9}(Q'_6)$

TABLE 5: Experimental Vibrational Frequencies (cm^{-1}) of a_1 Modes and Calculated Vibrational Frequencies of b_2 Modes in the Ground S_0 and Excited S_1 Electronic States of Azulene[a]

mode symmetry		S_0	S_1
a_1	ν_1	406	384
a_1	ν_2	679	662
a_1	ν_3	825	857
a_1	ν_4	900	900
a_1	ν_5	942	912
a_1	ν_6	1058	1062
a_1	ν_7	1212	1213
a_1	ν_8	1260	1193
a_1	ν_9	1400	1388
a_1	ν_{10}	1443	1447
a_1	ν_{11}	1538[b]	1543
a_1	ν_{12}	1585[b]	1557
b_2	ν_{13}	1621	1627
b_2	ν_{14}	1481	1498
b_2	ν_{15}	1442	1448
b_2	ν_{16}	1525	1427
b_2	ν_{17}	1400	1349

[a] References 36 and 39. [b] These two modes were represented by Page and co-workers[38] by one effective mode of frequency at 1562 cm^{-1}.

TABLE 6: Normalized Duschinsky Matrices for the a_1 and b_2 Modes of S_0 and S_1 Electronic States of Azulene

a_1 Modes[a,b]

	Q''_2	Q''_3	Q''_4	Q''_5	Q''_8	Q''_9	Q''_{10}	Q''_{11}	Q''_{12}
Q'_2	0.995	−0.085							
Q'_3	0.081	0.992		−0.058					
Q'_4			0.992	−0.110					
Q'_5		0.057	0.107	0.991					
Q'_8					0.987	0.109	0.053	0.053	0.072
Q'_9					−0.099	0.942	−0.298	0.093	0.071
Q'_{10}					−0.101	0.236	0.909	0.297	0.135
Q'_{11}						−0.061	−0.126	0.742	−0.653
Q'_{12}					0.051	−0.197	−0.254	0.598	0.737

b_2 Modes[c,d]

	Q''_{13}	Q''_{14}	Q''_{15}	Q''_{16}	Q''_{17}
Q'_{13}	0.72	−0.53	−0.38	−0.22	0.22
Q'_{14}		0.67	−0.63	0.45	
Q'_{15}	0.52		0.49	0.72	0.41
Q'_{16}	0.34	−0.25	−0.22	0.48	−0.6
Q'_{17}		−0.2	−0.39		

[a] Reference 36. [b] Only off-diagonal elements larger than 0.05 are listed. [c] Reference 39. [d] Only off-diagonal elements larger than 0.2 are listed.

conversion of azulene, considering only three (nontotally symmetric) promoting and three (totally symmetric) accepting vibrational modes of azulene in a displaced-oscillator model, and obtained $k_{IC}(S_1 \rightsquigarrow S_0) = 1.2 \times 10^{10}\ s^{-1}$. However, the present calculations show that more vibrational modes are involved in the process, and it obtains results (Table 8) that are very close (especially from the displaced−distorted model) to the experimental value. Also, it is notable that the distortions of vibrational modes cause an increase, whereas the rotations cause a decrease, in the internal conversion rate constant and that the promoting modes are more effective in decreasing the rate than the accepting modes.

TABLE 7: Energy Gap, Haung-Rhys Factors, and Vibronic Coupling Constants for the S_1−S_0 in Azulene

ω_{ab} $(2\pi\ cm^{-1})$[a]	14260
S_1[b]	0.146
S_2	0.251
S_3	0.794
S_4	0.133
S_5	0?
S_6	0?
S_7	0?
S_8	0.214
S_9	0.527
S_{10}	0?
S_{12}[c]	0.588
$\langle \Phi_a \vert \partial/\partial Q'_P \vert \Phi_b \rangle$ (a.u.)[a]	$4.905(Q'_{15})$ $3.961(Q'_{17})$

[a] Reference 37. [b] References 36 and 38. [c] This is the combined displacement for the 1557 and 1543 cm^{-1} modes.

TABLE 8: Rate of the $S_1 \rightsquigarrow S_0$ Internal Conversion of Azulene

k_{IC} $(T = 0)$ (s^{-1})	$S_1 \rightsquigarrow S_0$
experimental	5×10^{11}[a] $\geq 10^{10}$[b]
displaced	3.33×10^{11}
displaced−distorted	5.15×10^{11}
displaced−distorted, only promoting modes rotated	1.00×10^{11}
displaced−distorted, only accepting modes rotated	3.71×10^{11}
displaced−distorted−rotated	6.81×10^{10}

[a] Reference 35. [b] Reference 40.

5. Summary

We have derived general expressions for calculating the internal conversion decay rate constants between two adiabatic electronic states (eqs 61−62) and between two diabatic electronic states (eqs 68−69). The expressions include the displacements, distortions, and rotations of PESs, as well as the temperature. Our expression for the internal conversion between two adiabatic electronic states may be considered as a generalization of that derived in ref 30, because the restrictions on the number of promoting modes and the temperature have been relaxed in the present work; besides, making use of matrix algebra has led to more manageable expressions for the computational purposes.

For illustration, the internal conversion rate constants between the various singlet electronic states of ethylene and between S_1 and S_0 electronic states of azulene have been calculated.

Appendix

Consider the following integral (A1);

$$I = \int_{-\infty}^{\infty} d\mathbf{x}\, x_k x_l \exp(-\mathbf{x}^T\mathbf{p}\mathbf{x} + 2\mathbf{x}^T\mathbf{q}) \qquad (A1)$$

where $d\mathbf{x} = \Pi_{j=1}^{N} dx_j$, $\mathbf{x}$ and $\mathbf{q}$ are N-dimensional vectors, and $\mathbf{p}$ is a $N \times N$ symmetric matrix. By the linear transformation $\mathbf{y} = \mathbf{x} - \mathbf{p}^{-1}\mathbf{q}$ the integral can be written as eq A2.

$$I = \exp(\mathbf{q}^{\mathrm{T}}\mathbf{p}^{-1}\mathbf{q}) \int_{-\infty}^{\infty} \mathrm{d}\mathbf{y}(\mathbf{y}+\mathbf{p}^{-1}\mathbf{q})_k(\mathbf{y}+\mathbf{p}^{-1}\mathbf{q})_l \exp(-\mathbf{y}^{\mathrm{T}}\mathbf{p}\mathbf{y}) \tag{A2}$$

By the unitary transformation $\mathbf{y} = \boldsymbol{\theta}\mathbf{u}$, where $\boldsymbol{\theta}$ is chosen to yield the diagonal matrix $\boldsymbol{\lambda}$:$\boldsymbol{\theta}^{\mathrm{T}}\mathbf{p}\boldsymbol{\theta} = \boldsymbol{\lambda}$, it becomes eq A3.

$$I = \exp(\mathbf{q}^{\mathrm{T}}\mathbf{p}^{-1}\mathbf{q}) \times \int_{-\infty}^{\infty} \mathrm{d}\mathbf{u}[\sum_{j=1}^{N}\theta_{kj}u_j + (\mathbf{p}^{-1}\mathbf{q})_k][\sum_{j=1}^{N}\theta_{lj}u_j + (\mathbf{p}^{-1}\mathbf{q})_l] \exp(-\mathbf{u}^{\mathrm{T}}\boldsymbol{\lambda}\mathbf{u}) \tag{A3}$$

Notice that det $\boldsymbol{\theta} = 1$. Integrals over the odd integrands vanish and we obtain eq A4.

$$I = \exp(\mathbf{q}^{\mathrm{T}}\mathbf{p}^{-1}\mathbf{q}) \int_{-\infty}^{\infty} \mathrm{d}\mathbf{u}[\sum_{j=1}^{N}\theta_{kj}\theta_{lj}{u_j}^2 + (\mathbf{p}^{-1}\mathbf{q})_k(\mathbf{p}^{-1}\mathbf{q})_l] \exp(-\sum_{j=1}^{N}\lambda_j{u_j}^2) = \exp(\mathbf{q}^{\mathrm{T}}\mathbf{p}^{-1}\mathbf{q})\left[\frac{1}{2}\sum_{j=1}^{N}\frac{\theta_{kj}\theta_{lj}}{\lambda_j} + (\mathbf{p}^{-1}\mathbf{q})_k(\mathbf{p}^{-1}\mathbf{q})_l\right]\left(\frac{\pi^N}{\lambda_1 \dots \lambda_N}\right)^{1/2} \tag{A4}$$

Finally, we get eq A5.

$$I = \left[\frac{1}{2}(\mathbf{p}^{-1})_{kl} + (\mathbf{p}^{-1}\mathbf{q})_k(\mathbf{p}^{-1}\mathbf{q})_l\right]\left(\frac{\pi^N}{\det \mathbf{p}}\right)^{1/2} \exp(\mathbf{q}^{\mathrm{T}}\mathbf{p}^{-1}\mathbf{q}) \tag{A5}$$

Accordingly, we get eqs A6−7.

$$\int_{-\infty}^{\infty} \mathrm{d}\mathbf{x}x_k \exp(-\mathbf{x}^{\mathrm{T}}\mathbf{p}\mathbf{x} + 2\mathbf{x}^{\mathrm{T}}\mathbf{q}) = (\mathbf{p}^{-1}\mathbf{q})_k\left(\frac{\pi^N}{\det \mathbf{p}}\right)^{1/2} \exp(\mathbf{q}^{\mathrm{T}}\mathbf{p}^{-1}\mathbf{q}) \tag{A6}$$

$$\int_{-\infty}^{\infty} \mathrm{d}\mathbf{x} \exp(-\mathbf{x}^{\mathrm{T}}\mathbf{p}\mathbf{x} + 2\mathbf{x}^{\mathrm{T}}\mathbf{q}) = \left(\frac{\pi^N}{\det \mathbf{p}}\right)^{1/2} \exp(\mathbf{q}^{\mathrm{T}}\mathbf{p}^{-1}\mathbf{q}) \tag{A7}$$

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