On the Nonradiative Decay of Individual Vibronic States

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A general formulation of the nonradiative decay-rate constant of initially selected vibronic states in polyatomic molecules is developed. This method includes the effects of displacements as well as distortions of the potential-energy surfaces. The rate constant is also calculated perturbatively using the cumulant expansion technique. For a comparison of the two methods, a numerical analysis is carried out.

The theory of intramolecular nonradiative transitions in an isolated molecule was put forward by Lin$^{1)}$ and by Bixon and Jortner,$^{2)}$ who derived the necessary restricting conditions for the occurrence of a nonradiative transition in an isolated molecule in the gas phase from the standpoint of a breakdown of the Born–Oppenheimer approximation.

The theoretical methods for calculating the nonradiative rate constants are usually based on the following assumptions: applicability of the Fermi golden rule; independence of the electronic matrix elements on the vibrational configuration (the Condon approximation); considering a harmonic potential-energy surface for nuclear motion;# and the occurrence of an energy equilibration in the initial vibronic manifold after excitation.

Attempts have been made to relax some of these assumptions. For instance, the effect of anharmonicity on the nonradiative rate constants was first examined by Burland and Robinson$^{3)}$ and others.$^{4-7)}$ Likewise, a non-Condon approach, originally due to Kovarskii,$^{8)}$ has been applied by Nitzan and Jortner$^{9)}$ to nonradiative transitions in molecules (see also, Refs. 10, 11, and 12). The link between these two separate approximations, that is, anharmonic potential-energy surfaces within the Condon approximation and a non-Condon scheme for the harmonic potential energy, has been made by Sobolewski.$^{14)}$

The first experiment for investigating electronic relaxation in different vibronic levels was performed by Schlag and Weyssenhoff.$^{15)}$ They studied the excess vibrational energy dependence of nonradiative decay rates in the first singlet of the 2-naphthylamine molecule from different optically selected vibronic levels in the low-pressure gas phase.

Among the first theoretical discussions concerning optical-selection studies in isolated polyatomic molecules was that offered by Brailsford and Chang,$^{16)}$ who avoided the assumption of energy equilibration in the initial vibronic manifold, and derived analytical expressions for the nonradiative decay rates of individual vibronic levels in the simple case of displaced potential surfaces (i.e., neglecting the frequency distortions). However, the crucial step in their derivation is an expansion of the vibrational overlap integrals in a power series in the equilibrium displacement of the normal modes to obtain analytical expressions for the weak-coupling limit. Heller, Freed, and Gelbart$^{17)}$ extended the theory in order to interpret some of the experimental observations concerning the emission lifetimes and quantum yields of individual vibronic levels in several organic molecules.

Recently, the dynamics of a single vibronic level and the excess vibrational energy dependence of nonradiative transition-rate constants in isolated polyatomic molecules have been active topics in both theoretical and experimental studies.$^{18-22)}$ Thus, it is of some interest to extend the formalism of relaxation theory to the treatment of an individual excited vibronic level.

In this paper we are concerned with the theoretical treatment of single-vibronic level decay processes in displaced-distorted systems, in contrast with previous treatments, which either assumed an energy equilibration in the initial vibronic states or neglected the frequency distortions which occur upon electronic transitions. In Section 1 we calculate the decay-rate constants while taking into account the equilibrium displacements as well as the frequency distortions, neglecting the Duschinsky rotations. In Section 2 we calculate the decay-rate constants perturbatively, that is, we expand the time-domain decay-rate expression in terms of cumulants. Finally, in Section 3 we discuss numerical calculations used to compare the various approximations that have been made.

#Very often it is further assumed that the vibrational-electronic interactions are linear in normal modes, neglecting the frequency changes which are due to quadratic interactions.$^{13)}$

1. Nonradiative Decay of Single Vibronic States

We consider a polyatomic molecule with two electronic states (a and b), and N vibrational degrees of freedom. The vibronic Hamiltonian of the molecule can be expressed as an adiabatic basis set $\{|a\utilde{v}''\rangle, |b\utilde{v}'\rangle\}$ (where, for instance, $\utilde{v}'$ denotes collectively the set of vibrational quantum numbers in the electronic state ## b) as follows:

$$\hat{H}=\sum_{\utilde{v}''}|a\utilde{v}''\rangle(E_a+\hat{H}_a)\langle a\utilde{v}''|+\sum_{\utilde{v}'}|b\utilde{v}'\rangle(E_b+\hat{H}_b)\langle b\utilde{v}'|$$
$$+\sum_{\utilde{v}'\utilde{v}''}(|a\utilde{v}''\rangle H_{a\utilde{v}'',\ b\utilde{v}'}\langle b\utilde{v}'|+|b\utilde{v}'\rangle H_{b\utilde{v}',\ a\utilde{v}''}\langle a\utilde{v}''|), \quad (1)$$

where $H_{a\utilde{v}'',\ b\utilde{v}'}$ are the off-diagonal matrix elements of the vibronic Hamiltonian, which induce nonradiative transitions between the adiabatic sets $\{|b\utilde{v}'\rangle\}$ and $\{|a\utilde{v}''\rangle\}$, and E_a,E_b ($\hat{H}_a$,$\hat{H}_b$) are the electronic (vibrational Hamiltonians) of states a and b, respectively.

We assume that the molecule is prepared in some single vibronic state $|b\utilde{v}'\rangle$. The nonradiative rate constant from the single vibronic state $|b\utilde{v}'\rangle$ to the all states $\{|a\utilde{v}''\rangle\}$ is given by,[23,24)]

$$W_{\utilde{v}'}(\Delta E_{ba})=(2\pi/\hbar)\sum_{\utilde{v}''}|H_{a\utilde{v}'',\ b\utilde{v}'}|^2\ \delta(\Delta E_{ba}+E_{\utilde{v}'}-E_{\utilde{v}''}), \quad (2)$$

where $\Delta E_{ba}=E_b-E_a$ is the electronic energy gap. By introducing Kubo and Toyazawa's[25)] generating function, the last expression takes the following form:

$$W_{\utilde{v}'}(\Delta E_{ba}) = (1/\hbar^2)\int_{-\infty}^{+\infty}\mathrm{d}t\left\langle\hat{V}(0)\hat{V}(t)\right\rangle_{b\utilde{v}'}, \quad (3)$$

where $\langle\cdots\rangle_{b\utilde{v}'}$ means a quantum-mechanical average over the initial vibronic states $\{|b\utilde{v}'\rangle\}$,

$$\hat{V}(t) = \exp{(i\hat{H}_0t/\hbar)}(\hat{H}-\hat{H}_0)\ \exp{(-i\hat{H}_0t/\hbar)}, \quad (4)$$

and $\hat{H}_0$ is the adiabatic part of the Hamiltonian ($\hat{H}$). The integral of Eq. 3 can be evaluated by using the saddle-point (the steepest descent) approximation; the result is

$$W_{\utilde{v}'}(\Delta E_{ba})=(1/\hbar^2)\left\{2\pi/\left[\frac{g'_{\utilde{v}'}(t^*)^2}{g_{\utilde{v}'}(t^*)^2}-\frac{g''_{\utilde{v}'}(t^*)}{g_{\utilde{v}'}(t^*)}\right]\right\}^{\frac{1}{2}} g_{\utilde{v}'}(t^*), \quad (5)$$

where $g_{\utilde{v}'}(t)=\langle\hat{V}(0)\,\hat{V}(t)\rangle_{b\utilde{v}'}$, and the saddle-point t^* is determined by the condition

$$g'_{\utilde{v}'}(t^*) = 0. \quad (6)$$

Within the Condon approximation, e.g., $|H_{a\utilde{v}'',b\utilde{v}''}|=C|\langle\utilde{v}''|\utilde{v}'\rangle|$, (where C is the electronic factor and $\langle\utilde{v}'|\utilde{v}''\rangle$ represents the Franck–Condon integrals) Eq. 3 takes the following form:

$$W_{\utilde{v}'}(\Delta E_{ba})=(C/\hbar)^2\int_{-\infty}^{+\infty}\mathrm{d}t\ \exp{(-i\omega_{ba}t)}G_{\utilde{v}'}(t), \quad (7)$$

where $\omega_{ba}=\Delta E_{ba}/\hbar$ is the electronic-transition frequency and

$$G_{\utilde{v}'}(t) = \left\langle\exp{(i\hat{H}_at/\hbar)}\ \exp{(-i\hat{H}_bt/\hbar)}\right\rangle_{\utilde{v}'}. \quad (8)$$

If the vibrational motion can be described based on the individual oscillators, then

$$G_{\utilde{v}'}(t) = \prod_j G_{v'_j}(t). \quad (9)$$

For the case in which the potential-energy surfaces can be described harmonically, we can write

$$G_{v'_j}(t)=\sum_{v''_j}\left|\left\langle v'_j|v''_j\right\rangle\right|^2\ \exp\left\{i\omega''_jt\left(v''_j+1/2\right)-i\omega'_jt\left(v'_j+1/2\right)\right\}$$
$$=\int\int\mathrm{d}Q'_j\mathrm{d}\bar{Q}'_j\exp\left\{-\lambda'_j\left(v'_j+1/2\right)\right\}\chi_{v'_j}\left(Q'_j\right)\chi_{v'_j}\left(\bar{Q}'_j\right)$$
$$\sum_{v''_j}\exp\left\{-\lambda''_j\left(v''_j+1/2\right)\right\}\chi_{v''_j}\left(Q''_j\right)\chi_{v''_j}\left(\bar{Q}''_j\right), \quad (10)$$

where $\chi_{v_j}(Q_j)$ is the vibrational wavefunction corresponding to the *j*th normal mode with frequency ω_j, $\lambda'_j=i\omega'_jt$, and $\lambda''_j=-i\omega''_jt$. The sum in Eq. 10 can be eliminated by introducing the Mehler formula,[26)]

$$\sum_v\exp{\{-\xi(v+1/2)\}}\chi_v(Q)\chi_v(\bar{Q})=\left(\frac{2\pi}{\gamma}\sinh\xi\right)^{-1/2}$$
$$\exp\left\{-\frac{1}{4}\gamma(Q+\bar{Q})^2\tanh{(\xi/2)}-\frac{1}{4}\gamma(Q-\bar{Q})^2\coth{(\xi/2)}\right\}, \quad (11)$$

where $\gamma=\omega/\hbar$. We can then write Eq. 10 as

$$G_{v'_j}(t)=\left(\frac{2\pi}{\gamma''_j}\sinh\lambda''_j\right)^{-1/2}\exp\left\{-\lambda'_j\left(v'_j+1/2\right)\right\}$$
$$\times\int\int\mathrm{d}Q'_j\mathrm{d}\bar{Q}'_j\chi_{v'_j}\left(Q'_j\right)\chi_{v'_j}\left(\bar{Q}'_j\right)$$
$$\times\exp\left\{-\frac{1}{4}\gamma''_j\left(Q''_j+\bar{Q}''_j\right)^2\tanh\left(\lambda''_j/2\right)\right.$$
$$\left.-\frac{1}{4}\gamma''_j\left(Q''_j-\bar{Q}''_j\right)^2\coth\left(\lambda''_j/2\right)\right\}. \quad (12)$$

Substituting for the harmonic-oscillator wavefunctions, letting $d_j=Q''_j-Q'_j$ be the displacement between the upper and lower minimum potential-energy positions, and changing the variables properly, we may write Eq. 12 as follows:

$$G_{v'_j}(t)=\left\{\mathrm{e}^{-(v'_j+1/2)\lambda'_j}/2^{v'_j}\pi v'_j!\right\}\left(u_j^2-w_j^2\right)^{1/2}$$
$$\exp\left\{-z_j^2u_j^2/\left(1-u_j^2\right)\right\}$$
$$\times\int\int\mathrm{d}x_j\mathrm{d}y_jH_{v'_j}(u_jx_j+w_jy_j)H_{v'_j}(u_jx_j-w_jy_j)$$
$$\exp\left\{-(x_j-z_j)^2-y_j^2\right\}, \quad (13)$$

##The lower states quantities are labeled by a double prime and those of the upper states by a single prime.

where

$$u_j=\left\{1+\left(\gamma_j''/\gamma_j'\right)\tanh\left(\lambda_j''/2\right)\right\}^{-\frac{1}{2}}, \tag{14a}$$

$$w_j=\left\{1+\left(\gamma_j''/\gamma_j'\right)\coth\left(\lambda_j''/2\right)\right\}^{-\frac{1}{2}}, \tag{14b}$$

$$z_j=-u_jd_j\left(\gamma_j''/\gamma_j'\right)\tanh\left(\lambda_j''/2\right), \tag{14c}$$

and $H_n(x)$ represents the nth-order Hermite polynomials. We now make use of the following identities:[27,28)]

$$H_n(x_1+x_2)H_n(x_1-x_2)=(-2)^{-n}\sum_{\lambda=0}(-1)^{\lambda}\{n!/\lambda!(n-\lambda)!\}$$
$$H_{2\lambda}\left(\sqrt{2}x_1\right)H_{2n-2\lambda}\left(\sqrt{2}x_2\right)H_{2n-2\lambda}\left(\sqrt{2}x_2\right) \tag{15a}$$

$$\times\int_{-\infty}^{+\infty}\mathrm{d}x\mathrm{e}^{-(x-y)^2}H_n(ax)$$
$$=\pi^{1/2}\left(1-a^2\right)^{n/2}H_n\left\{ay/\left(1-a^2\right)^{1/2}\right\}, \tag{15b}$$

$$H_{2n}(x)=(-1)^n2^{2n}n!L_n^{-1/2}\left(x^2\right), \tag{15c}$$

where $L_n^{\alpha}(x)$ represents the associated Laguerre polynomials, to carry out the integrations in Eq. 13 to obtain

$$G_{v_j'}(t)=$$
$$G_{0j}\mathrm{e}^{-v_j'\lambda_j'}\sum_{k=0}A_j^kB_j^{v_j'-k}(t)L_{v_j'-k}^{-1/2}(0)L_k^{-1/2}\left\{-C_j^2(t)/2A_j(t)\right\} \tag{16}$$

as a general expression for the single vibronic-state time-correlation function for the displaced and/or distorted harmonic-oscillator system. Here,

$$G_{0j}=\left\{f_j^{1/2}\mathrm{e}^{\lambda_j'(a_j-1)/2}/\left(1-b_j^2\mathrm{e}^{2a_j\lambda_j'}\right)^{1/2}\right\}$$
$$\times\exp\left\{-2a_jS_j'\left(1-\mathrm{e}^{a_j\lambda_j'}\right)/(1+a_j)\left(1+b_j\mathrm{e}^{a_j\lambda_j'}\right)\right\}, \tag{17a}$$

$$A_j(t)=\left(b_j+\mathrm{e}^{a_j\lambda_j'}\right)/\left(1+b_j\mathrm{e}^{a_j\lambda_j'}\right), \tag{17b}$$

$$B_j(t)=\left(-b_j+\mathrm{e}^{a_j\lambda_j'}\right)/\left(1-b_j\mathrm{e}^{a_j\lambda_j'}\right), \tag{17c}$$

$$C_j(t)=\left\{2a_j\sqrt{2S_j'}/(1+a_j)\right\}\left(1-\mathrm{e}^{a_j\lambda_j'}\right)/\left(1+b_j\mathrm{e}^{a_j\lambda_j'}\right), \tag{17d}$$

with

$$f_j=4a_j/(1+a_j)^2,a_j=\omega_j''/\omega_j'$$
$$b_j=(1-a_j)/(1+a_j),S_j'=1/2\gamma_j'd_j^2. \tag{18}$$

At this point we should emphasize that Eq. 16 along with Eq. 9 represent the time-domain nonradiative rate expression from a particular vibronic state $|b\underset{\sim}{v}'\rangle$ to all vibronic states $\{|a\underset{\sim}{v}''\rangle\}$, in contrast with the previous expressions, which only apply at thermal equilibrium.[1,2)] It should also be noted that for computational purposes expression in much easier to handle than that used in the previous work.[29)]

Equation 16 can be adapted to the statistical case of a polyatomic molecule, where the vibrational relaxation proceeds very rapidly after excitation, leading to a Boltzmann distribution over the initial vibrational state. To make this adaptation we take the canonical average, $G_j(t)=\sum_{v_j'}P_{v_j'}G_{v_j'}(t)$, (where $P_{v_j'}$ is the Boltzmann factor) by employing the generating function for the associated Laguerre polynomials,

$$\exp\{xz/(z-1)\}/(1-z)^{\alpha+1}=\sum_{n=0}L_n^{\alpha}(x)z^n, \tag{19}$$

which leads to the same time-domain expression as that used for the canonically averaged rate constants.[31)]

Now, let us consider the following two limiting cases:

(i) Displaced Oscillator: For this case $a_j=1$, $b_j=0$, $f_j=1$, and Eq. 16 reduces to

$$G_{v_j'}(t)=$$
$$\exp\left\{-S_j'\left(1-\mathrm{e}^{i\omega_j't}\right)\right\}L_{v_j'}\left\{-S_j'\left(\mathrm{e}^{i\omega_j't/2}-\mathrm{e}^{-i\omega_j't/2}\right)^2\right\}, \tag{20}$$

where $L_n(x)$ is the nth-order Laguerre polynomial. For the weak-coupling case, we may write

$$L_n(x)=\mathrm{e}^{\ln\{1+L_n(x)-1\}}=\mathrm{e}^{\left\{-nx-\frac{1}{4}n(n+1)x^2+0\left(x^3\right)\right\}}.$$

Thus,

$$G_{v_j'}(t)=\exp\left\{-S_j'\left(2v_j'+1\right)-\frac{3}{2}S_j'^2v_j'\left(v_j'+1\right)\right.$$
$$+S_j'\left[\left(v_j'+1\right)\mathrm{e}^{i\omega_j't}+v_j'\mathrm{e}^{-i\omega_j't}\right]$$
$$\left.+S_j'^2v_j'\left(v_j'+1\right)\left[2\cos\left(\omega_j't\right)-\frac{1}{2}\cos\left(2\omega_j't\right)\right]+0\left(S_j'^3\right)\right\}. \tag{21}$$

which is just Eq. III-4 of Ref. 16 for the displaced-oscillator system in the weak-coupling limit.

For a single-mode system in which the molecule is initially in the lowest vibrational state, the rate expression becomes

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left(2\pi/\omega_j'\right)\mathrm{e}^{-S_j'}S_j'^{N_j}/N_j!, \tag{22}$$

where $N_j=\omega_{ba}/\omega_j'$.

(ii) Distorted Oscillator: For this case $S_j'=0$ and Eq. 16 reduces to

$$G_{v_j'}(t)=G_{0j}^{dt}\mathrm{e}^{-v_j'\lambda_j'}\sum_{k=0}A_j^kB_j^{v_j'-k}(t)L_k^{-1/2}(0)L_{v_j'-k}(0), \tag{23}$$

where $=G_{0j}^{dt}$ is obtained from Eq. 17a by setting $S_j{}'=0$. Again, for the single-mode case and an initially vibrationless molecule we obtain

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left(2\pi/2\omega_j''\right)\left\{4a_j/(1+a_j)^2\right\}^{1/2}$$
$$\times\{(1-a_j)/2(1+a_j)\}^{N_j}N_j/\{(N_j/2)!\}^2, \tag{24}$$

where $N_j=\{\omega_{ba}+\omega_j'(1-a_j)/2\}/\omega_j''$.

Applying the saddle-point approximation to Eq. 16 yields

$$W_{\underset{\sim}{v}'}(\Delta E_{ba})=(C/\hbar)^2\left\{2\pi/\sum_j\omega_j'^2a_j^2\left[\frac{f_jS_j'x_j(1-b_jx_j)}{(1+b_jx_j)^3}\right.\right.$$

$$+\frac{2(2v_j'+1)b_j^2x_j^2}{\left(1-b_j^2x_j^2\right)^2}-\frac{v_j'b_jx_j}{(1+b_jx_j)^2}$$
$$\left.\left.+\frac{1}{\omega_j'^2a_j^2}\left(\frac{R_{v_j'}'(t^*)^2}{R_{v_j'}(t^*)^2}-\frac{R_{v_j'}''(t^*)}{R_{v_j'}(t^*)}\right)\right]\right\}$$
$$\times\exp\left\{-\left[\omega_{ba}+\sum_j\omega_j'\left(2v_j'+1-a_j\right)/2\right]it^*\right\}$$
$$\prod_j\frac{f_j^{1/2}R_{v_j'}(t^*)}{\left(1-b_j^2x_j^2\right)^{v_j'+1/2}(1+b_jx_j)^{v_j'}}$$
$$\exp\left\{-2a_jS_j'(1-x_j)/(1-a_j)(1+b_jx_j)\right\}, \quad (25)$$

where $x_j=\exp\left(ia_j\omega_j't^*\right)$, and

$$R_{v_j'}(t)=\left\{\left(1-b_j^2\mathrm{e}^{2ia_j\omega_j't}\right)\left(1+b_j\mathrm{e}^{ia_j\omega_j't}\right)\right\}^{v_j'}$$
$$\times\sum_{k=0}A_j^k(t)B_j^{v_j'-k}(t)L_{v_j'-k}^{-1/2}(0)L_k^{-1/2}\left\{-C_j^2(t)/2A_j(t)\right\}, \quad (26)$$

with

$$\omega_{ba}+\sum_j\omega_j'\left(2v_j'+1-a_j\right)/2=$$
$$\sum_j\omega_j'a_j\left\{\frac{f_jS_j'x_j}{(1+b_jx_j)^2}+\frac{(2v_j'+1)b_j^2x_j^2}{\left(1-b_j^2x_j^2\right)}\right.$$
$$\left.-\frac{v_j'b_jx_j}{(1+b_jx_j)}+\frac{1}{i\omega_j'a_j}\left(\frac{R_{v_j'}'(t^*)}{R_{v_j'}(t^*)}\right)\right\}. \quad (27)$$

For the single displaced-mode case, Eq. 25 reduces to

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left(2\pi/\omega_j'\right)S_j'^{N_j}\mathrm{e}^{-S_j'}/\sqrt{2\pi N_j}N_j^{-N_j}\mathrm{e}^{-N_j}, \quad (28\mathrm{a})$$

where $N_j=\omega_{ba}/\omega_j'$; for the single distorted mode it reduces to

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left(2\pi/2\omega_j''\right)\left\{4a_j/(1+a_j)^2\right\}^{1/2}$$
$$\times\{(1-a_j)/(1+a_j)\}^{N_j}(1+1/N_j)^{N_j/2}/\sqrt{\pi N_j}, \quad (28\mathrm{b})$$

where $N_j=\{\omega_{ba}+\omega_j'(1-a_j)/2\}/\omega_j''$.

Using the Stirling approximation, $n!\approx\sqrt{2\pi n}\,n^n\mathrm{e}^{-n}$, which is in error by less than 2% for $n>4$, it is seen that for large values of the energy gap (ω_{ba}) Eqs. 28a and 28b reduce to Eqs. 22 and 24, respectively.

Equations 28a and 28b may be brought into the energy gap law. The results are

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left\{2\pi/\omega_{ba}\omega_j'\right\}^{1/2}\mathrm{e}^{-S_j'}$$
$$\times\exp\left\{-\frac{\omega_{ba}}{\omega_j'}\left[\ln\left(\omega_{ba}/\omega_j'S_j'\mathrm{e}\right)\right]\right\}, \quad (29\mathrm{a})$$

and

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left\{\pi\mathrm{e}f_j/\Omega_{ba}\omega_j''\right\}^{\frac{1}{2}}\exp\left\{-\frac{\Omega_{ba}}{\omega_j''}\ln(-b_j)\right\}, \quad (29\mathrm{b})$$

respectively, where $\Omega_{ba}=\omega_{ba}+\omega_j'(1-a_j)/2$ is the 0–0 energy gap, e is the base of the natural logarithm, and it is assumed that for large x, $(1+1/x)^x\approx\mathrm{e}$. We notice that the energy dependence of the rate is mainly through ω_{ba}/ω_j' (for the displaced oscillator) or Ω_{ba}/ω_j'' (for the distorted oscillator) in the exponential.

2. Cumulant Expansion of $G_{\underset{\sim}{v}'}(t)$

The cumulant expansion method has been applied to calculated the band-shape functions[30)] and the electron-transfer rate constants.[31)] It has been shown that to the second order of the cumulants we have

$$G_{\underset{\sim}{v}'}(t)=\exp\left\{(i/\hbar)\left\langle\hat{H}_a-\hat{H}_b\right\rangle_{\underset{\sim}{v}'}t\right.$$
$$\left.+(i/\hbar)^2\int_0^t\mathrm{d}t'(t-t')\left\langle\hat{U}(0)\hat{U}(t')\right\rangle_{\underset{\sim}{v}'}\right\}, \quad (30)$$

where $\hat{U}=(\hat{H}_a-\hat{H}_b)-\langle\hat{H}_a-\hat{H}_b\rangle_{\underset{\sim}{v}'}$,

and

$$\hat{U}(t)=\exp\left(i\hat{H}_bt/\hbar\right)\hat{U}(0)\exp\left(-i\hat{H}_bt/\hbar\right). \quad (31)$$

In a short-time approximation, Eq. 30 immediately leads to the following expression for the nonradiative rate constant:

$$W_{v'}(\Delta E_{ba})=(C/\hbar)\left(2\pi\hbar^2/\left\langle\hat{U}^2\right\rangle_{\underset{\sim}{v}'}\right)^{1/2}$$
$$\times\exp\left\{-\left(-\Delta E_{ba}+\left\langle\hat{H}_a-\hat{H}_b\right\rangle_{\underset{\sim}{v}'}\right)^2/2\left\langle\hat{U}^2\right\rangle_{\underset{\sim}{v}'}\right\}, \quad (32)$$

where

$$\left\langle\hat{U}^2\right\rangle_{\underset{\sim}{v}'}=\left\langle\left(\hat{H}_a-\hat{H}_b\right)^2\right\rangle_{\underset{\sim}{v}'}-\left\langle\left(\hat{H}_a-\hat{H}_b\right)\right\rangle_{\underset{\sim}{v}'}^2. \quad (33)$$

Applying the saddle-point approximation, Eq. 5 can be written in terms of the cumulants as follows:

$$W_{\underset{\sim}{v}'}(\Delta E_{ba})=(C/\hbar)^2\left\{2\pi\hbar^2/\left\langle\hat{U}(0)\hat{U}(t^*)\right\rangle_{\underset{\sim}{v}'}\right\}^{1/2}$$
$$\exp\left\{(i/\hbar)\left(-\Delta E_{ba}+\left\langle\hat{H}_a-\hat{H}_b\right\rangle_{\underset{\sim}{v}'}\right)t^*\right.$$
$$\left.+(i/\hbar)^2\int_0^{t^*}\mathrm{d}t(t^*-t)\left\langle\hat{U}(0)\hat{U}(t)\right\rangle_{\underset{\sim}{v}'}\right\}, \quad (34)$$

where the saddle-point t^* is determined by

$$-\Delta E_{ba}+\left\langle\hat{H}_a-\hat{H}_b\right\rangle_{\underset{\sim}{v}'}=-(i/\hbar)\int_0^{t^*}\mathrm{d}t\left\langle\hat{U}(0)\hat{U}(t)\right\rangle_{\underset{\sim}{v}'} \quad (35)$$

To evaluate the cumulant $\langle\hat{U}(0)\,\hat{U}(t)\rangle_{\underset{\sim}{v}'}$ we may make use of the following well-known identities:

$$\langle n|Q|m\rangle=(2\gamma)^{-1/2}\left\{m^{1/2}\delta_{n,m-1}+(m+1)^{1/2}\delta_{n,m+1}\right\} \quad (36\mathrm{a})$$

and

$$\langle n|Q^2|m\rangle=(2\gamma)^{-1}\left\{[m(m-1)]^{1/2}\delta_{n,m-2}\right.$$
$$\left.+(2m+1)\delta_{n,m}+[(m+1)(m+2)]^{1/2}\delta_{n,m+2}\right\}. \quad (36\mathrm{b})$$

The results are

$$\left\langle \hat{H}_a-\hat{H}_b\right\rangle_{\underset{\sim}{v}'}=\sum_j\left\{\alpha_j\left(2v_j'+1\right)+a_j^2S_j'\right\}\left(\hbar\omega_j'\right) \tag{37}$$

and

$$\left\langle \hat{U}(0)\hat{U}(t)\right\rangle_{\underset{\sim}{v}'}=\sum_j\left\{a_j^4S_j'\left[\left(v_j'+1\right)\mathrm{e}^{i\omega_j't}+v_j'\mathrm{e}^{-i\omega_j't}\right]\right.$$
$$\left.+\alpha_j^2\left[\left(v_j'+1\right)\left(v_j'+2\right)\mathrm{e}^{2i\omega_j't}+v_j'\left(v_j'-1\right)\mathrm{e}^{-2i\omega_j't}\right]\right\}\left(\hbar\omega_j'\right)^2, \tag{38}$$

where $\alpha_j=(a_j{}^2-1)/4$. Substituting these results in Eq. 30, we obtain

$$G_{\underset{\sim}{v}'}(t)=\exp\left\{\sum_j\left[-a_j^4S_j'\left(2v_j'+1\right)-\frac{1}{2}\alpha_j^2\left(v_j'^2+v_j'+1\right)\right]\right\}$$
$$\times\exp\left(\sum_j\left\{\delta_j\left(i\omega_j't\right)+a_j^4S_j'\left[\left(v_j'+1\right)\mathrm{e}^{i\omega_j't}+v_j'\mathrm{e}^{-i\omega_j't}\right]\right.\right.$$
$$\left.\left.+\frac{1}{4}\alpha_j^2\left[\left(v_j'+1\right)\left(v_j'+2\right)\mathrm{e}^{2i\omega_j't}+v_j'\left(v_j'-1\right)\mathrm{e}^{-2i\omega_j't}\right]\right\}\right), \tag{39}$$

where

$$\delta_j=a_j^2\left(1-a_j^2\right)S_j'+\alpha_j\left(1-\alpha_j\right)\left(2v_j'+1\right). \tag{40}$$

If the molecule is initially vibrationless (i.e., $v_j'=0$), Eq. 39 for the single-mode case reduces to the following form:

$$G_0(t)=\exp\left\{\left(-a_j^4S_j'-\frac{1}{2}\alpha_j^2\right)+\delta_j\left(i\omega_j't\right)\right\}$$
$$\times\sum_{m_j}\left\{\left(a_j^4S_j'\right)^{m_j}/m_j!\right\}\mathrm{e}^{im_j\omega_j't}\sum_{k_j}\left\{\left(\alpha_j^2/2\right)^{k_j}/k_j!\right\}\mathrm{e}^{2ik_j\omega_j't}. \tag{41}$$

In this case $W_0(\Delta E_{ba})$ is given be

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left(2\pi/\omega_j'\right)\exp\left(-a_j^4S_j'-\frac{1}{2}\alpha_j^2\right)$$
$$\times\sum_{m_j}\left(a_j^4S_j'\right)^{N_j-2m_j}\left(\alpha_j^2/2\right)^{m_j}/m_j!(N_j-2m_j)!, \tag{42}$$

where $N_j=\{\omega_{ba}-[a_j{}^2(1-a_j{}^2)S_j'+\alpha_j(1-\alpha_j)]\}/\omega_j'$. In particular, for the displaced oscillator

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left(2\pi/\omega_j'\right)\mathrm{e}^{-S_j'}S_j'^{N_j}/N_j!, \tag{43a}$$

and for the distorted oscillator

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left(2\pi/2\omega_j'\right)\mathrm{e}^{-\alpha_j^2}\left(\alpha_j^2/2\right)^{N_j/2}/(N_j/2)!. \tag{43b}$$

By introducing Eqs. 37 and 38 into Eq. 34 we obtain the following expression for the rate constant within the cumulant-saddle-point approximation:

$$W_{\underset{\sim}{v}'}(\Delta E_{ba})=(C/\hbar)^2\left\{2\pi/\sum_j\omega_j'^2\left(a_j^4S_j'\left[\left(v_j'+1\right)x_j+v_j'x_j^{-1}\right]\right.\right.$$
$$\left.\left.+\alpha_j^2\left[\left(v_j'+1\right)\left(v_j'+2\right)x_j^2+v_j'\left(v_j'-1\right)x_j^{-2}\right]\right)\right\}^{1/2}$$
$$\times\exp\left\{-\sum_j\left[a_j^4S_j'\left(2v_j'+1\right)+\frac{1}{2}\alpha_j^2\left(v_j'^2+v_j'+1\right)\right]\right\}$$
$$\times\exp\left\{-it^*\left(\omega_{ba}-\sum_j\delta_j\omega_j'\right)+\sum_j\left(a_j^4S_j'\left[\left(v_j'+1\right)x_j+v_j'x_j^{-1}\right]\right.\right.$$
$$\left.\left.+\frac{1}{4}\alpha_j^2\left[\left(v_j'+1\right)\left(v_j'+2\right)x_j^2+v_j'\left(v_j'-1\right)x_j^{-2}\right]\right)\right\}, \tag{44}$$

where $x_j=\exp\left(i\omega_j't^*\right)$, and

$$\omega_{ba}-\sum_j\delta_j\omega_j'=\sum_ja_j^4S_j'\omega_j'\left[\left(v_j'+1\right)x_j-v_j'x_j^{-1}\right]$$
$$+1/2\sum_j\alpha_j^2\omega_j'\left[\left(v_j'+1\right)\left(v_j'+2\right)x_j^2-v_j'\left(v_j'-1\right)x_j^{-2}\right]. \tag{45}$$

For a single-mode and initially vibrationless molecule (e.g., $v_j'=0$), Eq. 44 becomes

$$W_0(\Delta E_{ba})=$$
$$(C/\hbar)^2\left(1/\omega_j'\right)\left\{2\pi/\left(a_j^4S_j'+2\alpha_j^2x_j\right)\right\}^{1/2}x_j^{-(N_j+1/2)}$$
$$\exp\left\{-a_j^4S_j'-\frac{1}{2}\alpha_j^2+a_j^4S_j'x_j+\frac{1}{2}\alpha_j^2x_j^2\right\}, \tag{46}$$

where x_j is now given by

$$x_j=\left\{-a_j^4S_j'+\left(a_j^8S_j'^2+4\alpha_j^2N_j\right)^{1/2}\right\}/2\alpha_j^2, \tag{47}$$

and $N_j=(\omega_{ba}-S_j\omega_j')/\omega_j{}'$. For displaced and distorted oscillators, Eq. 46 reduces to

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left(2\pi/\omega_j'\right)S_j'^{N_j}\mathrm{e}^{-S_j'}/\left\{\sqrt{2\pi N_j}N_j^{N_j}\mathrm{e}^{-N_j}\right\} \tag{48a}$$

and

$$W_0(\Delta E_{ba})=(C/\hbar)^2\left(2\pi/2\omega_j'\right)\left(\alpha_j^2/2\right)^{N_j/2}\mathrm{e}^{-\alpha_j^2/2}$$
$$/\left\{\sqrt{\pi N_j}(N_j/2)^{N_j/2}\mathrm{e}^{-N_j/2}\right\}, \tag{48b}$$

respectively. Equations 48a and 48b should be compared with Eqs. 43a and 43b, respectively. These equations are related to each other by the Stirling approximation. Again, similar to Eqs. 29a and 29b, Eqs. 48a and 48b may be brought into the energy-gap law.

3. Summary and Numerical Analysis

In this communication we have developed a quantum-mechanical formulation for the single vibronic-level decay-rate constants. The assumption of energy equilibration in the initial vibronic manifold has been avoided in this theory. We have explicitly included modifications of both the vibrational frequencies and the coordinates in our calculations. The derivations were made exactly, resulting in Eq. 16, and perturbatively (using the second-order cumulant expansion), resulting in Eq. 39. The saddle-point approximation has been applied to both Eqs. 16 and 39, resulting in Eqs. 25 and 44, respectively. We call these four expressions exact, exact-saddle, cumulant, and cumulant-saddle expressions for the decay-rate constants, respectively.

A nonradiative transition is a transition from the vibronic state $|b\underset{\sim}{v}'\rangle$ to the vibronic state $|a\underset{\sim}{v}''\rangle$, where $E_{b\underset{\sim}{v}'}=E_{a\underset{\sim}{v}''}$. Consider the case in which the potential energy surfaces of the two electronic state undergo an intersection in order to meet this requirement. At the crossing point we may write

$$1/2\sum_j \omega_j''^2\left(Q_j'+d_j\right)^2=\Delta E_{ba}+1/2\sum_j \omega_j'^2 Q_j'^2. \qquad (49)$$

The minimum crossing point on the initial potential-energy surface subjected to restriction Eq. 49 may be obtained by using the Lagrange-multiplier method. The result is

$$Q_j'=\lambda d_j a_j^2/\left[(1+\lambda)-\lambda a_j^2\right], \qquad (50)$$

where λ is the Lagrange multiplier. Inserting this expression into Eq. 49 yields

$$\omega_{ba}=\sum_j \omega_j'' S_j''\left[(1+\lambda)^2-\lambda^2 a_j^2\right]/\left[(1+\lambda)-\lambda a_j^2\right], \qquad (51)$$

from which we can determine λ and the position of the minimum energy. It follows that

$$\varepsilon_c=\omega_{ba}+\sum_j \omega_j'' S_j'' a_j^2\lambda^2/\left[(1+\lambda)-\lambda a_j^2\right], \qquad (52)$$

where ε_c is the minimum energy.

For a single displaced-distorted mode Eq. 52 reduces to

$$\varepsilon_c=\omega_{ba}+\left[S''\omega''/\left(1-a^2\right)^2\right]\left\{a-\left[1-\omega_{ba}\left(1-a^2\right)/S''\omega''\right]^{1/2}\right\}^2, \qquad (53)$$

which gives the following inequalities:

$$a\geq\left(\frac{\omega_{ba}/\omega''-S''}{\omega_{ba}/\omega''}\right)^{1/2} \quad \text{or} \quad a\geq\left(\frac{\omega_{ba}/\omega'}{\omega_{ba}/\omega'+S'}\right)^{1/2}, \qquad (54)$$

in order that ε_c to be a real quantity. Our calculations show that the transition-rate constant drops rapidly if the above inequalities do not hold among the parameters.

The rate constant is modulated by a number of parameters, including the excess vibrational energy, the electronic energy gap, and nuclear factors (encompassing the displacements and/or distortions of the potential energy surfaces). For a numerical comparison, various approximations have been made, and to demonstrate how these parameters affect the rate constant we have performed numerical calculations for a single-mode system. The results are displayed in Figs. 1

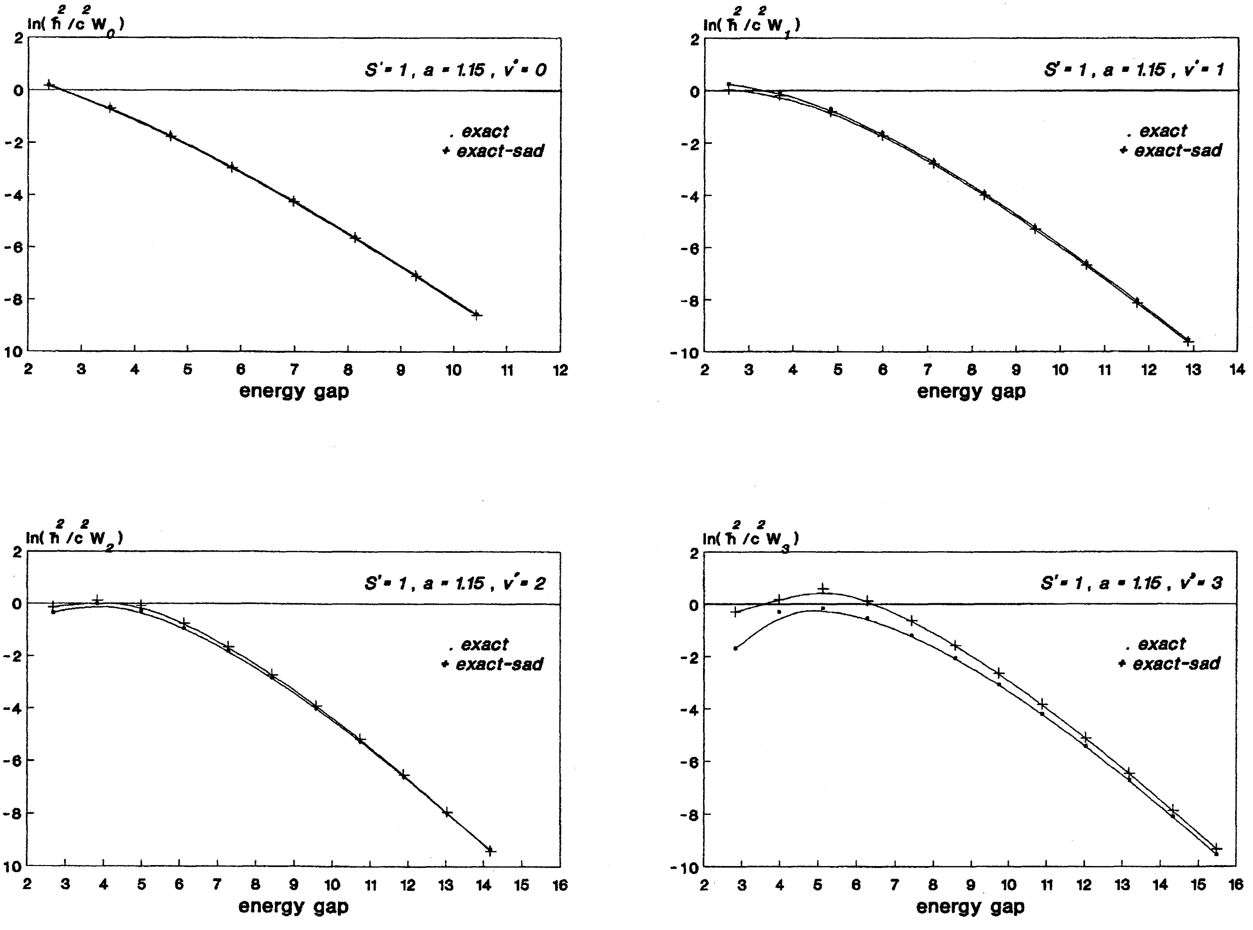

Fig. 1. Plots of $\ln\left(\frac{\hbar^2}{c^2}W_{v'}\right)$ versus electronic energy gap ω_{ba}/ω' for $v'=0,1,2,3$. The parameters used are $S''=1$, $a=\omega''/\omega'=1.15$.

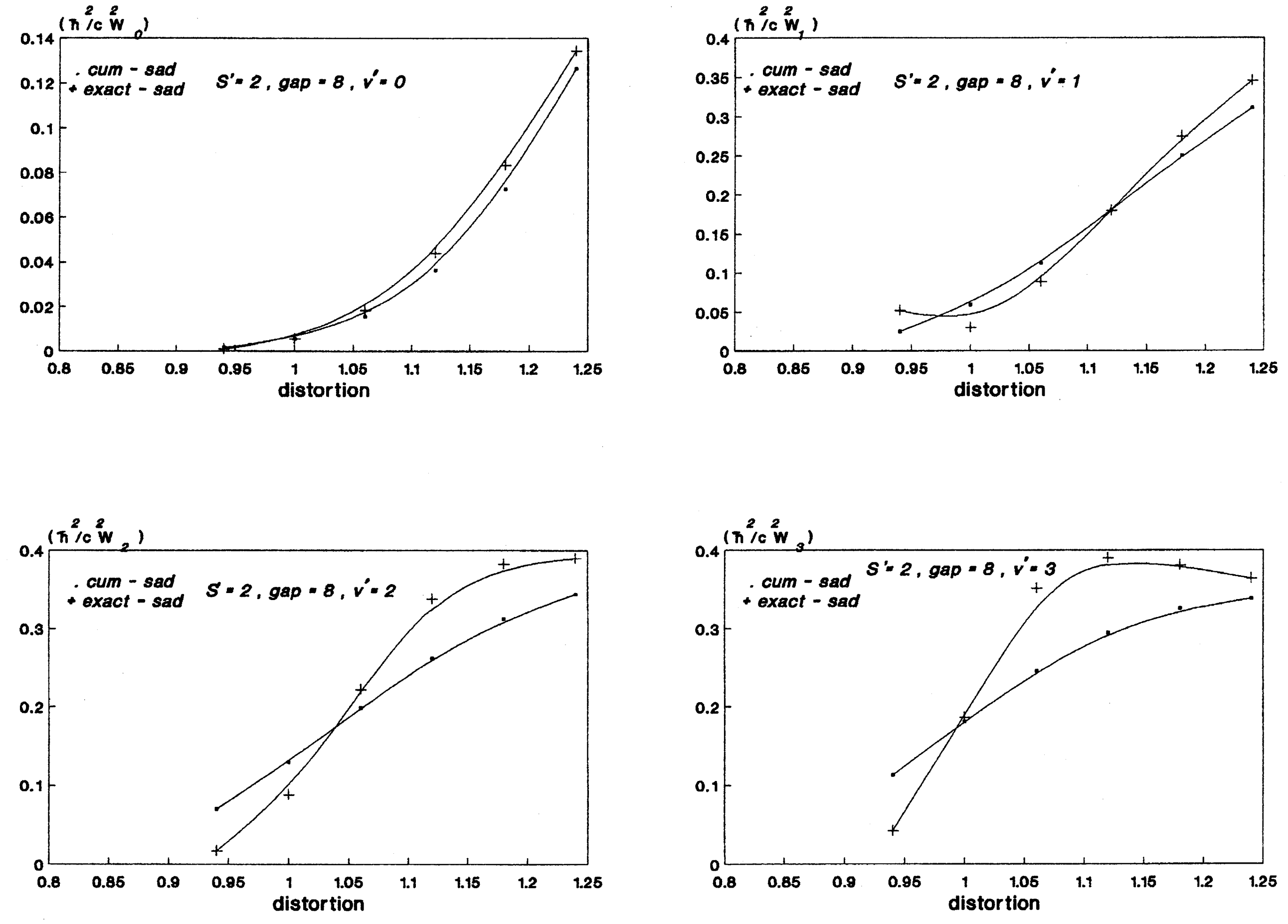

Fig. 2. Plots of $\frac{\hbar^2}{c^2} W_{v'}$ versus the distortion $a=\omega''/\omega'$ for $v'=0,1,2,3$. The parameters used are $S'=2$, electronic energy gap $\omega_{ba}/\omega'=8$.

and 2

In Fig. 1 we compare the exact rate-constant expression with its saddle-point approximated form by plotting $\ln(\frac{\hbar^2}{c^2} W_{v'})$ versus the electronic energy (ω_{ba}/ω') for $v'=0,1,2,3$. In Fig. 2 we compare the exact-saddle and the cumulant-saddle expressions by displaying $(\frac{\hbar^2}{c^2} W_{v'})$ versus the distortion, $a=\omega''/\omega'$, for the same vibrational quantum numbers, $v'=0,1,2,3$.

An examination of Figs. 1 and 2 results in the following observations: —Even for relatively large values of the modifications between the two electronic states, the agreement among the various approximations is quite satisfactory. —The distortion of the potential-energy surfaces may make an important contribution to the rate constant. —The effect of excess vibrational energy on the rate constant is significant in the displaced-distorted harmonic-oscillator system.

It is important to notice that the general theory of nonradiative transitions developed in this paper should be applicable to electron transfer (ET) and other electronic processes.

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