RECENT DEVELOPMENTS IN RADIATIONLESS TRANSITIONS

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Abstract – In this paper, the historical development of radiationless transitions will be briefly reviewed. The paper will then focus on the ab initio calculations of internal conversion rate constants with emphasis on the case of small polyatomic molecules where the Duschinsky effect is important. As an example, we have chosen the new expressions for singlevibronic level rate constants of radiationless transitions. This type of rate constants is important in femto-second processes.

INTRODUCTION

Radiationless transition is a very important primary process in photochemistry. It consists of internal conversion and intersystem crossing. When the electronic states involved in radiationless transitions are not very high in energy, the Born-oppenheimer approximation can be used as a basis set, and the radiationless transition can be regraded as due to the breakdown of the Born-Oppenheimer approximation.[1,2] For internal conversion, their B-O breakdown is induced by the kinetic energy operator of the nuclear motion, while for intersystem crossing this breakdown can be induced by the spin-orbit couping or vibronic spinorbit coupling.[1,2]

Recently, the experimental and theoretical investigations of femtosecond processes have attracted considerable attention. For the case in which the fs process involves a non-adiabatic transition like electronic xation, photo-induced electron transfer, photo-induced energy transfer etc, vibrational equilibrium often cannot be assumed to be completed before the fs process takes place. In this case, vibrational relaxation and the particular electronic process under consideration are competing (*i.e.*, they occur simultaneously); in this case, single-level rate constants rather than the canonical (or thermal average) rate constants of the electronic process are involved in fs processes. In this paper, new expressions of the single-vibronic level IC rate constants will be presented.

For small polyatomic molecules, the Duschinsky effect[3] is very important. The calculation of rates of transition among various electromic states in a polyatomic molecule (in both radiative and nonradiative processes) necessitates and exact evaluation of multidimensional Franck-Dondon (FC) integrals. In an electronic transition, the normal coordinates of electronic states generally undergo a displacement and/or distortion as well as a rotation. The rotation of potential surfaces results in a non-separability of the multidimensional FC integrals.[4] To treat this effect on radiationless transitions, we shall consider the internal conversion.

Recent rapid progress in *ab initio* molecular orbital calculations has made it possible to carry out the ab initio cal-

culations of spectroscopy and dynamics of molecules of reasonable size. In this paper, the *ab initio* calculation of radiationless transitions will be reported. Although general theory of radiationless transitions is well documented,[1,2,5-13] practical calculations of these rates using ab initio electronic wavefunctions and ab initio potential surfaces are still rare.[14-16]

. The preseent pape ris organized as follows, in Section 2, a general theory of IC with the Duschinsky effect will be developed and in Section 3, we shall present new expressions for single-vibronic level rate constants of IC. The application of this theory to the IC of the ethylenc molecule is presented in Section 4.

DUSCHINSKY EFFECT

The thermal average rate constant of internal conversion (IC) for the electronic transition $a \to b$ in the Condon approximation can be expressed as[1]

$$W = \frac{2\pi}{\hbar} |R_\ell(ab)|^2 \sum_v \sum_{v'} P_{av} \left| \langle \Theta_{bv'} | \frac{\partial}{\partial Q_\ell} | \Theta_{av} \rangle \right|^2 \delta(E_{av} - E_{bv'}), \quad (2\text{-}1)$$

where

$$R_\ell(ab) = -\hbar^2 \langle \Phi_b | \frac{\partial}{\partial Q_\ell} | \Phi_a \rangle. \quad (2\text{-}2)$$

Here for simplicity it is assumed that only one promoting mode Q_ℓ is reponsible for IC. Notice that

$$W = \frac{1}{\hbar^2} |R_\ell(ab)|^2 \int_{-\infty}^{\infty} dt e^{it\omega_{ba}} K_\ell(t) \overline{G}(t) \quad (2\text{-}3)$$

where

$$K_\ell(t) = \sum_v \sum_{v'} P_{av} \left| \langle \chi_{bv'_\ell}(Q'_\ell) | \frac{\partial}{\partial Q_\ell} | \chi_{av_\ell}(Q_\ell) \rangle \right|^2$$

$$\times \exp[it\{(v'_\ell + \frac{1}{2})\omega'_\ell - (v_\ell + \frac{1}{2})\omega_\ell\}], \quad (2\text{-}4)$$

and $\overline{G}(t)$ is given by

Table 1. Vibrational frequencies (cm⁻¹) of C_2H_4 in the ground and excited states.[ ]

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 CH2 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]Calculated at the CASSCF(2,11)/6-311(2+)G* level and scaled by 0.9. See Ref.32 for more detail.

$$\overline{G}(t) = \sum_v \sum_{v'} P_{av} |\langle \Theta_{bv'} | \Theta_{av} \rangle|^2 \exp\left[\frac{it}{\hbar}(E_{bv'} - E_{av})\right] \quad (2\text{-}5)$$

Here $|\langle \Theta_{bv'} | \Theta_{av} \rangle|^2$ denotes the FC factor for accepting modes.

In this paper, we shall discuss the effect of the Duschinsky effect on internal conversion. Let us first consider the simplest case; that is, only modes 1 and 2 exhibit the Duschinsky effect. In this case, $\overline{G}(t)$ can be written as

$$\overline{G}(t) = G_{12}(t) \prod_{i=1}^{i \neq 1,2} G_i(t), \quad (2\text{-}6)$$

where

$$G_i(t) = \sum_{v_i} \sum_{v_i'} P_{av_i} |\langle \chi_{bv_i'}(Q_i') | \chi_{av_i}(Q_i) \rangle|^2$$

$$\exp[it\{(v_i' + \tfrac{1}{2})\omega_i' - (v_i + \tfrac{1}{2})\omega_i\}], \quad (2\text{-}7)$$

and

$$G_{12}(t) = \sum_{v_1} \sum_{v_2} \sum_{v_\alpha'} \sum_{v_\beta'} P_{av_1 v_2} |\langle \chi_{bv_\alpha'}(Q_\alpha') \chi_{bv_\beta'}(Q_\beta') | \chi_{av_1}(Q_1) \chi_{av_2}(Q_2) \rangle|^2$$

$$\times \exp[it\{(v_\alpha' + \tfrac{1}{2})\omega_\alpha' + (v_\beta' + \tfrac{1}{2})\omega_\beta' - (v_1 + \tfrac{1}{2})\omega_1 - (v_2 + \tfrac{1}{2})\omega_2\}]. \quad (2\text{-}8)$$

Using the Slater sum,[17] we obtain

$$G_{12}(t) = \frac{2\sinh\frac{\hbar\omega_1}{2kT} 2\sinh\frac{\hbar\omega_2}{2kT} \sqrt{\beta_1\beta_2\beta_\alpha'\beta_\beta'}}{\sqrt{2^4\pi^4 \sinh\lambda_1 \sinh\lambda_2 \sinh\mu_\alpha' \sinh\mu_\beta'}} \int_{-\infty}^{\infty} dQ_1 \int_{-\infty}^{\infty} d\overline{Q}_1 \int_{-\infty}^{\infty} dQ_2 \int_{-\infty}^{\infty} d\overline{Q}_2$$

$$\times \exp\left[-\frac{\beta_1}{4}\left\{(Q_1 + \overline{Q}_1)^2 \tanh\frac{\lambda_1}{2} + (Q_1 - \overline{Q}_1)^2 \coth\frac{\lambda_1}{2}\right\}\right]$$

$$\times \exp\left[-\frac{\beta_2}{4}\left\{(Q_2 + \overline{Q}_2)^2 \tanh\frac{\lambda_2}{2} + (Q_2 - \overline{Q}_2)^2 \coth\frac{\lambda_2}{2}\right\}\right]$$

$$\times \exp\left[-\frac{\beta_\alpha'}{4}\left\{(Q_\alpha' + \overline{Q}_\alpha')^2 \tanh\frac{\mu_\alpha'}{2} + (Q_\alpha' - \overline{Q}_\alpha')^2 \coth\frac{\mu_\alpha'}{2}\right\}\right]$$

Table 2. Normal modes of C_2H_4 in the ground state.[a]

Mode Sym	Q_{12} b_{2u}	Q_9 b_{3u}	Q_{11} b_{2g}	Q_4 a_u	Q_8 b_{3g}	Q_3 a_g	Q_6 b_{1u}	Q_2 a_g	Q_5 b_{1u}	Q_1 a_g	Q_7 b_{3g}	Q_{10} b_{2u}
C^1, x	.00	.27	.43	.00	.00	.00	.00	.00	.00	.00	.00	.00
y	-.13	.00	.00	.00	.43	.00	.00	.00	.00	.00	-.23	.23
z	.00	.00	.00	.00	.00	.33	.23	.59	.14	-.19	.00	.00
C^2, x	.00	.27	-.43	.00	.00	.00	.00	.00	.00	.00	.00	.00
y	-.13	.00	.00	.00	-.43	.00	.00	.00	.00	.00	.23	.23
z	.00	.00	.00	.00	.00	-.33	.23	-.59	.14	.19	.00	.00
H^1, x	.00	-.46	-.40	.50	.00	.00	.00	.00	.00	.00	.00	.00
y	.23	.00	.00	.00	-.11	-.17	.27	.23	-.42	.41	.40	-.40
z	-.43	.00	.00	.00	.38	.41	-.39	-.15	-.25	.25	.25	-.25
H^2, x	.00	-.46	-.40	-.50	.00	.00	.00	.00	.00	.00	.00	.00
y	.23	.00	.00	.00	-.11	.17	-.27	-.23	.42	-.41	.40	-.40
z	.43	.00	.00	.00	-.38	.41	-.39	-.15	-.25	.25	-.25	.25
H^3, x	.00	-.46	.40	-.50	.00	.00	.00	.00	.00	.00	.00	.00
y	.23	.00	.00	.00	.11	-.17	-.27	.23	.42	.41	-.40	-.40
z	.43	.00	.00	.00	.38	-.41	-.39	.15	-.25	-.25	.25	-.25
H^4, x	.00	-.46	.40	.50	.00	.00	.00	.00	.00	.00	.00	.00
y	.23	.00	.00	.00	.11	.17	.27	-.23	-.42	-.41	-.40	-.40
x	-.43	.00	.00	.00	-.38	-.41	-.39	.15	-.25	-.25	-.25	-.25

[a]Mass-weighted.

$$\times \exp\left[-\frac{\beta_\beta'}{4}\left\{(Q_\beta' + \overline{Q}_\beta')^2 \tanh\frac{\mu_\beta'}{2} + (Q_\beta' - \overline{Q}_\beta')^2 \coth\frac{\mu_\beta'}{2}\right\}\right], \quad (2\text{-}9)$$

where for example $\beta_1 = \frac{\omega_1}{\hbar}$, $\beta_\alpha' = \frac{\omega_\alpha'}{\hbar}$,,

$$\lambda_1 = it\omega_1 + \frac{\hbar\omega_1}{kt}, \quad \lambda_2 = it\omega_2 + \frac{\hbar\omega_2}{kt}, \quad \mu_\alpha' = -it\omega_\alpha', \quad \mu_\beta' = -it\omega_\beta', \quad (2\text{-}10)$$

and

$$Q_\alpha' = C_{\alpha 1}(Q_1 + \Delta Q_1) + C_{\alpha 2}(Q_2 + \Delta Q_2),$$
$$Q_\beta' = C_{\beta 1}(Q_1 + \Delta Q_1) + C_{\beta 2}(Q_2 + \Delta Q_2). \quad (2\text{-}11)$$

Notice that

$$G_{12}(t) = 4K_{12} \int_{-\infty}^{\infty} dQ_1 \int_{-\infty}^{\infty} d\overline{Q}_1 \int_{-\infty}^{\infty} dQ_2 \int_{-\infty}^{\infty} d\overline{Q}_2$$

$$\times \exp\left[-A_{11}(Q_1 + \overline{Q}_1)^2 - A_{22}(Q_2 + \overline{Q}_2)^2 - A_{12}(Q_1 + \overline{Q}_1)(Q_2 + \overline{Q}_2)\right]$$

$$\times \exp\left[-A_1(Q_1 + \overline{Q}_1) - A_2(Q_2 + \overline{Q}_2)\right]$$

$$\times \exp\left[-B_{11}(Q_1 - \overline{Q}_1)^2 - B_{22}(Q_2 - \overline{Q}_2)^2 - B_{12}(Q_1 - \overline{Q}_1)(Q_2 - \overline{Q}_2)\right]$$

$$\times \exp[-D], \quad (2\text{-}12)$$

where

$$A_{ii} = \frac{\beta_i}{4}\tanh\frac{\lambda_i}{2} + \frac{\beta_\alpha'}{4}(C_{\alpha i})^2 \tanh\frac{\mu_\alpha'}{2} + \frac{\beta_\beta'}{4}(C_{\beta i})^2 \tanh\frac{\mu_\beta'}{2}, \quad (2\text{-}13)$$

for $i = 1,2$

$$A_{12} = \frac{\beta_\alpha'}{2}C_{\alpha 1}C_{\alpha 2} \tanh\frac{\mu_\alpha'}{2} + \frac{\beta_\beta'}{2} C_{\beta 1}C_{\beta 2} \tanh\frac{\mu_\beta'}{2}, \quad (2\text{-}14)$$

$$B_{ii} = \frac{\beta_i}{4}\coth\frac{\lambda_i}{2} + \frac{\beta_\alpha'}{4}(C_{\alpha i})^2 \coth\frac{\mu_\alpha'}{2} + \frac{\beta_\beta'}{4}(C_{\beta i})^2 \coth\frac{\mu_\beta'}{2}, \quad (2\text{-}15)$$

for $i = 1,2$

$$B_{12} = \frac{\beta_\alpha'}{2}C_{\alpha 1}C_{\alpha 2} \coth\frac{\mu_\alpha'}{2} + \frac{\beta_\beta'}{2}C_{\beta 1}C_{\beta 2} \coth\frac{\mu_\beta'}{2}, \quad (2\text{-}16)$$

Table 3. Normalized Duschinsky matrices for the $^1B_{1u} \rightarrow {}^1A_g$ and $^1B_{3u}$ $\rightarrow {}^1B_{1u}$ transitions in C_2H_4

a) $^1B_{1u} \rightarrow {}^1A_g$

	Q_{a1}	Q_{a2}	Q_{a3}	Q_{a4}
Q_{b1}	0.7977	-0.1467	-0.002727	0.5780
Q_{b2}	0.08871	-0.8622	-0.3802	-0.3153
Q_{b3}	-0.1024	0.2951	-0.9156	0.2364
Q_{b4}	-0.5850	-0.3823	0.1259	0.7195

b) $^1B_{3u} \rightarrow {}^1B_{1u}$

	Q_{a1}	Q_{a2}	Q_{a3}	Q_{a4}
Q_{b1}	0.7975	-0.1314	0.02170	-0.5815
Q_{b2}	-0.1256	0.9106	0.006717	-0.3777
Q_{b3}	0.04878	0.03957	0.9909	0.1168
Q_{b4}	0.5849	0.3823	-0.125	0.7194

$$K_{12} = \frac{\sqrt{\beta_1\beta_2\beta'_\alpha\beta'_\beta}\,\sinh\frac{\hbar\omega_1}{2kT}\sinh\frac{\hbar\omega_2}{2kT}}{\sqrt{2^4\pi^4\sinh\lambda_1\sinh\lambda_2\sinh\mu'_\alpha\sinh\mu'_\beta}}, \tag{2-17}$$

$$D = \beta'_\alpha\tanh\frac{\mu'_\alpha}{2}(C_{\alpha1}\Delta Q_1 + C_{\alpha2}\Delta Q_2)^2 \tag{2-18}$$
$$+ \beta'_\beta\tanh\frac{\mu'_\beta}{2}(C_{\beta1}\Delta Q_1 + C_{\beta2}\Delta Q_2)^2,$$

$$A_1 = \beta'_\alpha\tanh\frac{\mu'_\alpha}{2}C_{\alpha1}(C_{\alpha1}\Delta Q_1 + C_{\alpha2}\Delta Q_2)$$
$$+ \beta'_\beta\tanh\frac{\mu'_\beta}{2}C_{\beta1}(C_{\beta1}\Delta Q_1 + C_{\beta2}\Delta Q_2), \tag{2-19}$$

and

$$A_2 = \beta'_\alpha\tanh\frac{\mu'_\alpha}{2}C_{\alpha2}(C_{\alpha1}\Delta Q_1 + C_{\alpha2}\Delta Q_2)$$
$$+ \beta'_\beta\tanh\frac{\mu'_\beta}{2}C_{\beta2}(C_{\beta1}\Delta Q_1 + C_{\beta2}\Delta Q_2). \tag{2-20}$$

It follows that

$$G_{12}(t) = K_{12}\sqrt{\frac{\pi^4}{(A_{11}A_{22} - A_{12}{}^2/4)(B_{11}B_{22} - B_{12}{}^2/4)}}$$

$$\times \exp\left[\frac{A_1^2}{4A_{11}} + \frac{(A_2 - \frac{A_1A_{12}}{2A_{11}})^2}{4(A_{22} - \frac{A_{12}{}^2}{4A_{11}})} - D\right]. \tag{2-21}$$

It should be noted that $K_\ell(t)$ can be expressed as

$$K_\ell(t) = \frac{1}{2}G_\ell(t)\left[\frac{\beta_\ell\beta'_\ell}{\beta'_\ell\tanh\frac{\lambda_\ell}{2} + \beta_\ell\tanh\frac{\mu'_\ell}{2}} - \frac{\beta_\ell\beta'_\ell}{\beta'_\ell\coth\frac{\lambda_\ell}{2} + \beta_\ell\coth\frac{\mu'_\ell}{2}}\right.$$

$$\left. + \frac{2\beta_\ell^2\beta'_\ell{}^2(\Delta Q_\ell)^2}{(\beta'_\ell\coth\frac{\lambda_\ell}{2} + \beta_\ell\coth\frac{\mu'_\ell}{2})^2}\right] \tag{2-22}$$

where $G_\ell(t)$ is given by

$$G_i(t) = \frac{2_i\sinh\frac{\hbar\omega_i}{2kT}}{\sqrt{(\beta_i\tanh\frac{\lambda_i}{2} + \beta'_i\tanh\frac{\mu'_i}{2})(\beta_i\coth\frac{\lambda_i}{2} + \beta'_i\coth\frac{\mu'_i}{2})}}$$

$$\times\left(\frac{\beta_i\beta'_i}{\sinh\lambda_i\sinh\mu'_i}\right)^{\frac{1}{2}}\exp[-\frac{\beta_i\beta'_i\Delta Q_i^2}{\beta_i\coth\frac{\mu'_i}{2} + \beta'_i\coth\frac{\lambda_i}{2}}], \tag{2-23}$$

where

$$\lambda_i = it\omega_i + \frac{\hbar\omega_i}{kt}\;;\;\mu'_i = -it\omega'_i, \tag{2-24}$$

As can be seen from the above discussion, one central theoretical concept, which is yet to be tested in a rigorous manner, is that the critical role the "promoting mode" is predicted[2] to play in electronic relaxation processes. Recently, Moule and Lim[18] have shown that the inefficiency of $S_1(A_2) \rightarrow S_0(A_1)$ and $S_2(A_1) \rightarrow S_1(A_2)$ internal conversions in gaseous thiophasgene (Cl_2CS) has its most likely origin in the absence of an a_2 virbration that can vironically couple S_1 with S_0 and S_2.

For the three-mode case, we find

$$G_{123}(t) = K_{123}$$

$$\times\sqrt{\frac{\pi^3}{a_{33}(A_{11}A_{22} - A_{12}{}^2/4)}}\sqrt{\frac{\pi^3}{b_{33}(B_{11}B_{22} + B_{12}{}^2/4)}}$$

$$\times\exp\left[-D + \frac{A_1^2}{4A_{11}} + \frac{(A_2 - A_1A_{12}/2A_{11})^2}{4(A_{22} - A_{12}{}^2/4A_{11})} + \frac{a_3^2}{4a_{33}}\right], \tag{2-25}$$

where

$$a_{33} = (A_{33} - \frac{A_{13}{}^2}{4A_{11}}) - \frac{(A_{23} - \frac{A_{12}A_{13}}{2A_{11}})^2}{4(A_{22} - \frac{A_{12}{}^2}{4A_{11}})}, \tag{2-26}$$

$$a_3 = (A_3 - \frac{A_{13}A_1}{2A_{11}}) - \frac{(A_2 - \frac{A_{12}A_1}{2A_{11}})(A_{23} - \frac{A_{12}A_{13}}{2A_{11}})}{2(A_{22} - \frac{A_{12}{}^2}{4A_{11}})}, \tag{2-27}$$

$$b_{33} = (B_{33} - \frac{B_{13}{}^2}{4B_{11}}) - \frac{(B_{23} - \frac{B_{12}B_{13}}{2B_{11}})^2}{2(B_{22} - \frac{B_{12}{}^2}{4B_{11}})}, \tag{2-28}$$

and

$$K_{123} = \frac{\sqrt{\beta_1\beta_2\beta_3\beta'_\alpha\beta'_\beta\beta'_\gamma}\,\sinh\frac{\hbar\omega_1}{2kT}\sinh\frac{\hbar\omega_2}{2kT}\sinh\frac{\hbar\omega_3}{2kT}}{\sqrt{2^6\pi^6\sinh\lambda_1\sinh\lambda_2\sinh\lambda_3\sinh\mu'_\alpha\sinh\mu'_\beta\sinh\mu'_\gamma}}. \tag{2-29}$$

Similarly for the four-mode case, we have

$$G_{1234}(t) = K_{1234}$$

$$\times\sqrt{\frac{\pi^4}{(A_{11}A_{22} - \frac{A_{12}{}^2}{4})(a_{33}a_{44} - \frac{a_{34}{}^2}{4})}}\sqrt{\frac{\pi^4}{(B_{11}B_{22} - \frac{B_{12}{}^2}{4})(b_{33}b_{44} - \frac{b_{34}{}^2}{4})}}$$

$$\times\exp\left[-D + \frac{A_1^2}{4A_{11}} + \frac{(A_2 - \frac{A_{12}A_1}{2A_{11}})^2}{4(A_{22} - \frac{A_{12}{}^2}{4A_{11}})} + \frac{a_3^2}{4a_{33}} + \frac{(a_4 - \frac{a_{34}a_3}{2a_{33}})^2}{4(a_{44} - \frac{a_{34}{}^2}{4a_{33}})}\right], \tag{2-30}$$

Table 4. Vibronic coupling and the rates of internal conversion between various singlet states of C_2H_4.

	$^1B_{1g} \rightarrow {}^1B_{3u}$	$^1B_{2g} \rightarrow {}^1B_{3u}$	$2^1A_g \rightarrow {}^1B_{3u}$	$^1B_{3u} \rightarrow {}^1B_{1u}$	$^1B_{1u} \rightarrow {}^1A_g$
$\omega_{ba}{}^{(a)}$	6151	5391	8837	13243	43945
$\omega_i{}^{(a)}$	3076(ω_a10)	2948(ω_{a5})	918(ω_{b9})	993(ω_{a11})	2877(ω_{a5})
	839(ω_a12)	1419(ω_{a6})			1353(ω_{a6})
$\Delta Q_{a1}{}^{(b)}$	0.010	0.025	0.072	0.414	0.416
$\Delta Q_{a2}{}^{(b)}$	0.025	0.006	0.013	0.443	0.469
$\Delta Q_{a3}{}^{(b)}$	0.028	0.029	0.029	0.224	0.286
$\Delta Q_{a4}{}^{(b)}$	0.106	0.058	0.304	0.953	1.273
$< \Phi a \left\| \frac{\partial}{\partial Q_i} \right\| \Phi_b >^{(c)}$	0.2134(Q_{a10})	0.0589(Q_{a5})	0.1276(Q_{a9})	0.0080(Q_{a11})	0.0038(Q_{a11})
	0.1129(Q_{a12})	0.2619(Q_{a6})			0.0723(Q_{a6})
$W_{b \rightarrow a}(T=0)^{(d)}$	1.09 ×10^{11}(Q_{a10})	2.97 ×10^{10}(Q_{a5})	4.72 ×109(Q_{a9})	1.08 ×107(Q_{a11})	7.39 ×106(Q_{a5})
	1.64 ×10^8(Q_{a10})	4.09 ×10^{10}(Q_{a6})			1.26 ×109(Q_{a6})

(a) In the units of $2\pi cm^{-1}$.   (b) In $\mathring{A} \cdot amu^{1/2}$.
(c) In atomic units.   (d) In s^{-1}.

where

$$a_{44} = (A_{44} - \frac{A_{14}{}^2}{4A_{11}}) - \frac{(A_{24} - \frac{A_{12}A_{14}}{2A_{11}})^2}{4(A_{22} - A_{12}{}^2/4A_{11})}, \qquad (2\text{-}31)$$

$$a4 = (A_4 - \frac{A_{14}A_1}{2A_{11}}) - \frac{(A_2 - \frac{A_{12}A_1}{2A_{11}})(A_{24} - \frac{A_{12}A_{14}}{2A_{11}})}{2(A_{22} - A_{12}{}^2/4A_{11})}, \qquad (2\text{-}32)$$

$$a_{34} = (A_{34} - \frac{A_{13}A_{14}}{2A_{11}}) - \frac{(A_{23} - \frac{A_{12}A_{13}}{2A_{11}})(A_{24} - \frac{A_{12}A_{14}}{2A_{11}})}{2(A_{22} - \frac{A_{12}{}^2}{4A_{11}})}, \qquad (2\text{-}33)$$

$$b_{34} = (B_{34} - \frac{B_{13}B_{14}}{2B_{11}}) - \frac{(B_{23} - \frac{B_{12}B_{13}}{2B_{11}})(B_{24} - \frac{B_{12}B_{14}}{2B_{11}})}{2(B_{22} - \frac{B_{12}{}^2}{4B_{11}})}, \qquad (2\text{-}34)$$

$$b_{44} = (B_{44} - \frac{B_{14}{}^2}{4B_{11}}) - \frac{(B_{24} - \frac{B_{12}B_{14}}{2B_{11}})^2}{4(B_{22} - \frac{B_{12}{}^2}{4B_{11}})}, \qquad (2\text{-}35)$$

and

$$K_{1234} = \frac{\sqrt{\beta_1\beta_2\beta_3\beta_4\beta'_\alpha\beta'_\beta\beta'_\gamma\beta'_\delta} \sinh\frac{\hbar\omega_1}{2kT}\sinh\frac{\hbar\omega_2}{2kT}\sinh\frac{\hbar\omega_3}{2kT}\sinh\frac{\hbar\omega_4}{2kT}}{\sqrt{2^8\pi^8 \sinh\lambda_1 \sinh\lambda_2 \sinh\lambda_3 \sinh\lambda_4 \sinh\mu'_\alpha \sinh\mu'_\beta \sinh\mu'_\gamma \sinh\mu'_\delta}}, \qquad (2\text{-}36)$$

SINGLE-VIBRONIC LEVEL RATE CONSTANT

Here we shall consider the evaluation of single-vibronic level IC rate constant which can be expressed as

$$W_{av} = \frac{2\pi}{\hbar}|R_i(ab)|^2 \left(\frac{\omega_i}{2\hbar}\right) \Sigma_{v'} |\langle \Theta_{bv'} | \Theta_{av} \rangle|^2 \delta(E_{bv'} + \hbar\omega_i - E_{av}) \quad (3\text{-}1)$$

Here the Franck-Condon factor $|\langle \Theta_{bv} | \Theta_{av} \rangle|^2$ does not contain the contribution from the promoting mode Q_i. Notice that W_{av} can be written as

$$W_{av} = \frac{1}{\hbar^2}|R_i(ab)|^2 \left(\frac{\omega_i}{2\hbar}\right) \int_{-\infty}^{\infty} dt e^{it\omega'_{ba}} \prod_{\ell}' G_{v_\ell}(t) \quad (3\text{-}2)$$

where $\omega'_{ba} = \frac{1}{\hbar}(E_b + \hbar\omega_i - E_a)$, and

$$G_{v_\ell}(t) = \sum_{v_\ell} \sum_{v'_\ell} |\langle X_{bv'_\ell} | X_{av_\ell} \rangle|^2 \exp\left[it\left\{\left(v'_\ell + \frac{1}{2}\right)\omega_\ell - \left(v_\ell + \frac{1}{2}\right)\omega'_\ell\right\}\right] \quad (3\text{-}3)$$

It can be shown that $G_{v\ell}(t)$ can be expressed as (see Appendix)

$$\frac{G_{v_\ell}(t)}{G_{0_\ell}(t)} = \sum_{m_\ell=0}^{v_\ell} \frac{v_\ell! e^{-it(v_\ell - m_\ell)\omega'_\ell}}{2^{v_\ell - m_\ell} \cdot m_\ell! [(v_\ell - m_\ell)!]^2} H_{v_\ell - m_\ell}\left[\sqrt{\frac{S_\ell}{2}}(e^{it\omega_\ell} - 1)\right]^2 \quad (3\text{-}4)$$

where

$$G_{0_\ell}(t) = \exp\left[-S_\ell\left(1 - e^{it\omega_\ell}\right)\right] \quad (3\text{-}5)$$

and $S_\ell = \frac{\omega_\ell}{2\hbar}\Delta Q_\ell^2$. In Eq. (3-5), $Hn(z)$ denotes the Hermite polynomial.

Applying the saddle-point method to Eq. (3-3) yields

$$\frac{W_{av}}{W_{a0}} = \prod_{\ell}' G_{v_\ell}(t^*) \quad (3\text{-}6)$$

where

$$W_{a0} = \frac{1}{\hbar^2}|R_i(ab)|^2 \left(\frac{\omega_i}{2\hbar}\right) \int_{-\infty}^{\infty} dt \exp\left[it\omega'_{ba} - \Sigma_\ell S_\ell(1 - it\omega_\ell)\right] \quad (3\text{-}7)$$

and t* denotes the saddle-point value of t determined by

$$\omega_{ab} = \omega_i + \sum_\ell ' S_\ell \omega_\ell e^{it^*\omega_\ell} \tag{3-8}$$

DISCUSSION

From the previous section, we can see that in order to calculate the IC rate constants for polyatomic systems, it is necessary to determine vibronic coupling between the electronic states, which constitutes the electronic part of the IC rate constant. *Ab initio* calculations of vibronic coupling in the application to symmetry-forbidden vibronic spectra of formoldehyde[14-16 19-21] and benzene[22-24] are well known. Recently, we have shown how to calculate vibronic coupling for polyatomic moecules using modern quantum chemical programs and applied this approach to the calculations of the vibronic coupling among the singlet excited π-π* states, Rydberg π-$3s$ and $\pi 3p$ states and the ground electronic state of C_2H_4. These results will be used in this paper for the calculation of IC rate constants of C_2H_4. Some preliminary results have been reported.[25]

Radiationless transitions in ethylene are of significant interest to experimentalists and theorists because of their relevance to the photochemical behavior and photodissociation dynamics of this molecule.[26-30] We have investigated vibronic coupling between various singlet excited states and the ground state of C_2H_5 by ab initio calculations.[31] Table I shows the CASSCF-calculated vibrational frequencies of six singlet electronic states of C_2H_4, including the ground state (^1A_g) and the excited valence π-π*($^1B_{1u}$) state and Rydberg π-$3s(^1B_{3u})$, π-$3p_y(^1B_{1g})$, π-$3p_z(^1B_{2g})$ and $\pi=3p_x(2^1A_g)$ states.[32]

Normal modes of the ground state are presented in Table 2. The normal modes for the Rydberg states, ($^1B_{3u}$), ($^1B_{1g}$), ($^1B_{2g}$) and (2^1A_g) are similar to those of the ground state; virtually there is no mixing between the normal modes. The π-π* state has the equilibrium geometry of D_{2d} symmetry with CH_2 groups twisted by 90° with respect to each other[32]. This results in heavy mixing of four normal modes Q-$Q4$ with respect to the ground state normal modes. These four mixed modes found in the π-π* state belong to the a irreducible representation of the D_2 point group, common to the ground state (D_{2h}) and the π-π* state (D_{2d}) minima. Quantitatively, the mixing between these Q_1-Q_4 is characterized by the Duschinsky matrix. The normailized Duschinsky matrices are shown in Table 3.

Table 4 contains the energy gaps (ω_{ba}) between variou states, the promoting mode frequencies (ω_ℓ), displacements of the normal modes ΔQ_{a1}- ΔQ_{a4} calculated from the optimized geometries, and vibronic couplings $\langle \Phi_a|\partial/\partial Q_i| \Phi_b\rangle$ for IC transitions. Here the suffices a and b denote the final state and the initial state of IC, respectively. Notice that

$$\left\langle \Phi_a \left| \frac{\partial}{\partial Q_i} \right| \Phi_b \right\rangle = \frac{\left\langle \Phi_a \left| \frac{\partial V}{\partial Q_i} \right| \Phi_b \right\rangle}{E_b - E_a} \tag{4-1}$$

For the computations of vibronic coupling, we have used MRCI/ANO(2+) wave functions and the transition matrix elements between various states over the one-electron electric field operator at the atomic centers calculated using the MOLPRO-96 program.

Table 4 also lists the calculated IC rate constants for $^1B_{1g}$ $\rightarrow^1B_{3u}$, $^1B_{2g}\rightarrow^1B_{3u}$, $2^1B_g\rightarrow B_{3u}$, $^1B_{3u}\rightarrow^1B_{1u}$ and $^1B_{1u}\rightarrow^1A_g$. As can be seen from Table 4, the IC for $^1B1g\rightarrow^1B_{3u}$, $^1B_{2g}\rightarrow^1B_{3u}$ and $^1B_{1u}\rightarrow^1A_g$ can be induced by more than one promoting mode.

In concluding this paper, it should be noted that in this paper we have reported the general expressions for single-vibronic level rate constants for radiationless transitions. These expressions arc useful not only for collision-free molecules but also for the case in which femto-second non-adiabatic transitions are involved and vibrational relaxation is not much faster that the rate of non-adiabatic transition. In this paper we have also shown how one can perform ab initio calculations of IC rate constants by using C_2H_4 as an example.

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Appendix

Notice that

$$G_{v_\ell}(t) = \sum_{v'_\ell} \left| \langle X_{bv'_\ell} | X_{av_\ell} \rangle \right|^2 e^{it\left\{\left(v'_\ell + \frac{1}{2}\right)\omega_\ell - \left(v_\ell + \frac{1}{2}\right)\omega_\ell\right\}}$$

$$= e^{-\lambda_\ell\left(v_\ell + \frac{1}{2}\right)} \sum_{v'_\ell} e^{-\mu'_\ell\left(v'_\ell + \frac{1}{2}\right)} \left| \langle X_{bv'_\ell} | X_{av_\ell} \rangle \right|^2 \qquad (A\text{-}1)$$

Applying the Slater sum, we obtain

$$G_{v_\ell}(t) = e^{-\lambda_\ell\left(v_\ell + \frac{1}{2}\right)} \frac{\sqrt{\beta_\ell}}{(2\pi\sinh\mu'_\ell)^{1/2}} \int_{-\infty}^{\infty} \int dQ_\ell d\overline{Q}_\ell X_{av_\ell}(Q_\ell) \times$$

$$X_{av_\ell}(\overline{Q}_\ell)\exp\left[-\frac{\beta_\ell}{4}\left\{(Q'_\ell + \overline{Q}'_\ell)^2 \tanh\frac{\mu'_\ell}{2} + (Q'_\ell - \overline{Q}'_\ell)^2 \coth\frac{\mu'_\ell}{2}\right\}\right]$$

$$(A\text{-}2)$$

where $\lambda_\ell=it\omega_\ell$ and $\mu'_\ell=-it\omega_\ell$. Using the contour integral representation for $H_n(z)$

$$H_n(z) = (-1)^n \frac{n!}{2\pi i} \oint \frac{e^{-x^2-2xz}}{x^{n+1}} dx \qquad (A\text{-}3)$$

we find

$$G_{v_\ell}(t) = \frac{\sqrt{\beta_\ell}\, e^{-\lambda_\ell\left(v_\ell + \frac{1}{2}\right)}}{(2\pi\sinh\mu'_\ell)^{1/2}} N_{v_\ell}^2 \left(\frac{v_\ell!}{2\pi i}\right)^2 \oint \frac{e^{-x_1^2}}{x_1^{v_\ell+1}} dx_1 \times$$

$$\oint \frac{e^{-x_2^2}}{x_2^{v_\ell+1}} dx_2 \int_{-\infty}^{\infty} \int dQ_\ell d\overline{Q}_\ell \exp\left[-\frac{\beta_\ell}{4}\left\{(Q_\ell + \overline{Q}_\ell)^2 + (Q_\ell - \overline{Q}_\ell)^2 + \right.\right.$$

$$\left.\left. (Q'_\ell + \overline{Q}'_\ell)^2 \tanh\frac{\mu'_\ell}{2} + (Q'_\ell - \overline{Q}'_\ell)^2 \coth\frac{\mu'_\ell}{2}\right\} - 2\sqrt{\beta_\ell}(x_1 Q_\ell + x_2 \overline{Q}_\ell)\right]$$

$$(A\text{-}4)$$

Performing the integrations with respect to Q_ℓ and $\overline{Q}_\ell$ yields

$$G_{v_\ell}(t) = \frac{K_{v_\ell}}{2} \oint \frac{e^{-x_1^2}}{x_1^{v_\ell+1}} dx_1 \oint \frac{e^{-x_2^2}}{x_2^{v_\ell+1}} dx_2 \sqrt{\frac{4\pi}{\beta_\ell\left(1+\coth\frac{\mu'_\ell}{2}\right)}} \times$$

$$\sqrt{\frac{4\pi}{\beta_\ell\left(1+\tanh\frac{\mu'_\ell}{2}\right)}} \exp\left[-\beta_\ell\Delta Q_\ell^2 \tan\frac{\mu'_\ell}{2} + \frac{\left(x_1 + x_2\sqrt{\beta_\ell}\Delta Q_\ell \tanh\frac{\mu'_\ell}{2}\right)^2}{\left(1+\tanh\frac{\mu'_\ell}{2}\right)} + \right.$$

$$\left. \frac{(x_1 - x_2)^2}{\left(1+\coth\frac{\mu'_\ell}{2}\right)}\right]$$

$$(A\text{-}5)$$

where

$$H_{v_i - m_i}\left[\frac{\sqrt{\beta_i}\Delta Q_i}{2}\left(e^{it\omega_i}-1\right)\right]^2 \qquad (A\text{-}6)$$

and N_{v_ℓ} denotes the normalization constant.

It follows that

$$G_{av_i}(t) = e^{-iv_i t\omega_i} \cdot S_i\left(1-e^{it\omega_i}\right) \sum_{m_i=0}^{v_i} \frac{e^{im_i it\omega_i} v_i!}{2^{v_i-m_i} m_i! [(v_i - m_i)!]^2} \times$$

$$H_{v_i - m_i}\left[\frac{\sqrt{\beta_i}\Delta Q_i}{2}\left(e^{it\omega_i}-1\right)\right]^2 \qquad (A\text{-}7)$$

or

$$G_{a0_i}(t) = e^{-S_i\left(1-e^{it\omega_i}\right)} \qquad (A\text{-}8)$$

and

$$\frac{G_{av_i}(t)}{G_{a0_i}(t)} = e^{-itv_i\omega_i} \sum_{m_i=0}^{v_i} \frac{e^{itm_i\omega} v_i!}{2^{v_i-m_i} m_i! [(v_i - m_i)!]^2} \times$$

$$H_{v_i - m_i}\left[\sqrt{\frac{S_i}{2}}\left(e^{it\omega_i}-1\right)\right]^2 \qquad (A\text{-}9)$$