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Duschinsky rotation effect is a simple and effective way to characterize the difference between the ground state and excited state potential energy surfaces. For complex molecules, harmonic oscillator model is still the practical way to describe the dynamics of excited states. Based on the first-order perturbation theory *à la* Fermi golden rule, the authors have applied the path integral of Gaussian type for the correlation function to derive an analytic formalism to calculate the internal conversion rate process with Duschinsky rotation effect being taken into account. The validity of their formalism is verified through comparison with previous work, both analytically for the case of neglecting Duschinsky rotation and numerically for the ethylene molecules with two-mode mixing. Their expression is derived for multimode mixing. © *2007 American Institute of Physics*.
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I. INTRODUCTION

Understanding the excited state nonradiative decay process is important for designing light-emitting molecules: the light-emitting efficiency is determined by the competition between radiative decay and the nonradiative decay.[1] This is of both fundamental and application interests. The molecular materials are usually in solid thin film form in the operating devices. In general, the luminescent efficiency in solid state is much reduced in comparison with thein solution, because the molecular aggregation usually quenches luminescence, either by Davydov splitting or intermolecular charge transfer. This is bad for light-emitting devices. In recent years, compounds such as silole derivatives,[2] cis,cis-1,2,3,4-tetra-phenylbutasiene,[3] triarylethene-based π systems,[4] etc., present extremely high luminescent efficiency in solid states as well as in other aggregate states, which present almost no luminescence in solution. This exotic photophysical behavior is termed as aggregation-induced emission (AIE).[2] Our previous studies indicated that the AIE phenomena are due to the reduction of nonradiative decay rate when going from solution phase to solid state, because the restriction of the side-phenyl ring twisting motion can greatly suppress the internal conversion (IC) process from the excited to ground state.[5,6] We found that the low-frequency modes (less than 100 cm^{-1}) are extremely important for the IC process for the silole molecules in dissipating the excited state energy

through ring twisting. A deeper understanding of AIE phenomena would be certainly helpful in designing highly luminescent organic materials.

Lin and Bersohn have proposed the formalism of interconversion between electronic and vibrational energies,[7] which results in a general theory of internal conversion.[7–14] It has been widely applied to diatomic molecules at the *ab initio* quantum chemistry level.[15,16] Both displaced harmonic oscillators and Duschinsky rotation effect (DRE) between two electronic states have been considered for small polyatomic molecules.[17,18] We note that in the AIE system, the low-frequency modes are found to play a critical role. In general, the low-frequency motions exhibit strong mode mixing effects. In DRE, it is assumed that both ground state and excited state potential energy surfaces can be described by different harmonic parabolas, where the normal modes of one electronic state can be expressed as a linear combination of all the normal modes of another parabola, namely, mode mixing. Thus, it is an effective way to take the difference between the potential energy surfaces for different electronic states. It is the primary interest of this work to develop a general analytical formalism for the internal conversion rate considering the DRE with any numbers of mode mixing.

We note that DRE has been investigated for the absorption and emission processes by many authors.[19] Recently, Ianconescu and Pollak[20] have investigated the photoexcitation cooling effects by developing a general Franck-Condon factor formula with DRE in the vibration correlation function path integral formalism. In the present work, based on the Fermi golden rule and the path integral formulation for the vibration correlation function, we derived a rate formula for

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the nonradiative process from the excited state to the ground state through vibronic coupling by considering DRE with any numbers of mode mixing. We will show both analytically and numerically that our compact formula can reproduce the previous results.

This paper is organized as follows. In Sec. II, we describe the derivation of our formalism for the rate of the nonradiative transition from the excited to ground state. And we will show that the new formalism in matrix production form can be reduced to the same formalism in literature when DRE is neglected. When DRE is considered, we will show in Sec. III that the numerical results on the internal conversion rate for ethylene molecule when only two-mode mixing is considered agree well with the previous results of Mebel *et al.*[18] Finally, in Sec. IV we summarize our results and discuss characteristic features of our new formula.

II. FORMALISM

A. The general expression of internal conversion rate constant

Based on time-dependent perturbation method and using Born-Openheimer (BO) adiabatic approximation, and following Lin *et al.*,[21] the rate constant of nonradiative transition is given by

$$W_{i \to f} = \frac{2\pi}{\hbar} \sum_{\nu} \sum_{\nu'} P_{i\nu} \left| H'_{f\nu',i\nu} + \sum_{n\mu} \frac{H'_{f\nu',n\mu} H'_{n\mu,i\nu}}{E_{i\nu} - E_{n\mu}} \right|^2 \times \delta(E_{f\nu'} - E_{i\nu}), \tag{1}$$

where the nonradiative transition process is from an initial (excited) vibronic state $|i\nu\rangle$ to the final (ground) state $|f\nu'\rangle$ and $P_{i\nu}$ denotes the Boltzmann distribution function of the initial vibronic manifold.

Considering the first-order perturbation, for the internal conversion transition process, Eq. (1) can be written as

$$W_{i \to f} = \frac{2\pi}{\hbar} \sum_{\nu} \sum_{\nu'} P_{i\nu} |\langle \Phi_f \Theta_{f\nu'} | H'_{BO} | \Phi_i \Theta_{i\nu} \rangle|^2 \delta(E_{f\nu'} - E_{i\nu}). \tag{2}$$

Here $|\Phi_i\rangle$ and $|\Phi_f\rangle$ are the initial and final electronic states, respectively; $|\Theta_{i\nu}\rangle$ and $|\Theta_{f\nu'}\rangle$ designate the vibrational states of the system and are expressed as the product of the wave functions of each normal mode: $|\Theta_{i\nu}\rangle = \Pi_j |\chi_{i\nu_j}\rangle$, $|\Theta_{f\nu'}\rangle = \Pi_j |\chi_{f\nu'_j}\rangle$; H'_{BO} represents the Born-Oppenheimer coupling

due to the breakdown of the adiabatic approximation which can be expressed as the following first-order term:

$$H'_{BO}|\psi_{i\nu}\rangle = -\hbar^2 \sum_l \left| \frac{\partial \Phi_i}{\partial Q_l} \right\rangle \left| \frac{\partial \Theta_{i\nu}}{\partial Q_l} \right\rangle, \tag{3}$$

where Q is the vibration normal mode coordinate.

Substituting Eq. (3) into Eq. (2), applying Condon approximation, and for simplicity assuming only one "promoting mode," the rate constant of internal conversion transition becomes

$$W_{i \to f} = \frac{2\pi}{\hbar^2} |R_l(fi)|^2 \sum_{\nu} \sum_{\nu'} P_{i\nu} \left| \left\langle \Theta_{f\nu'} \middle| \frac{\partial \Theta_{i\nu'}}{\partial Q_l} \right\rangle \right|^2 \times \delta(E_{f\nu'} - E_{i\nu}), \tag{4}$$

where

$$R_l(fi) = -\hbar^2 \langle \Phi_f | \frac{\partial}{\partial Q_l} | \Phi_i \rangle \tag{5}$$

represents the coupling between the electronic wave functions of two states. The above expressions have been given in Refs. 18 and 21.

B. Construction of the thermal cross-correlation function

The nuclear vibration motion Hamiltonians of the electronic ground and excited states are assumed to be harmonic. Thus, the ground state Hamiltonian is a collection of N normal modes,

$$H_g = \frac{1}{2} \sum_{i=1}^{N} (P_{g_i}^2 + \omega_{g_i}^2 Q_{g_i}^2), \tag{6}$$

where Q_{g_i} and P_{g_i} are the ith mass-weighted normal mode coordinate and momentum, respectively. The excited state Hamiltonian is also composed of N normal modes, but with different coordinates, momentum, and frequencies, i.e.,

$$H_e = \frac{1}{2} \sum_{i=1}^{N} (P_{e_i}^2 + \omega_{e_i}^2 Q_{e_i}^2). \tag{7}$$
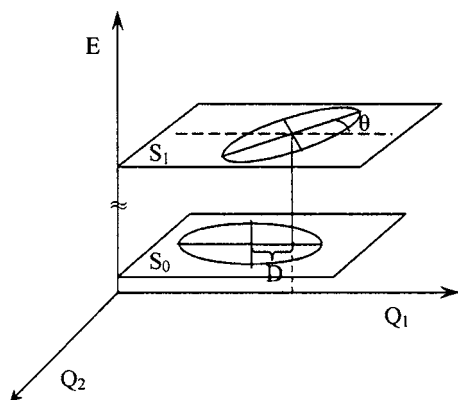
FIG. 1. Scheme of the displaced and rotational potential energy surfaces of the Duschinsky rotation effect for nonradiative decay process.

The excited state coordinates Q_{e_i} are assumed to be linear combinations of the ground state coordinates Q_{g_j}, in addition to a rigid displacement, that is,

$$Q_{e_i} = \sum_j S_{ij} Q_{g_j} + D_i, \tag{8}$$

where S is the Duschinsky[22] orthogonal rotation matrix and D represents the displacement vector between the minima of the excited state and ground state parabolas. A model for the displaced and rotational surface is presented in Fig. 1. θ represents that there is Duschinsky rotation between the ground and excited state potential energy surfaces in Fig. 1.

Equation (4) can be expressed for multimode case as

$$W_{i \to f} = \frac{2\pi}{\hbar^2} |R_l(fi)|^2 \sum_\nu \sum_{\nu'} P_{i\nu} \left| \langle \chi_{f\nu'_j} | \frac{\partial}{\partial Q_l} | \chi_{i\nu_l} \rangle \right|^2$$
$$\times \prod_j {}' |\langle \chi_{f\nu'_j} | \chi_{i\nu_j} \rangle|^2 \delta(E_{f\nu'} - E_{i\nu}), \tag{9}$$

where j indicates any mode except lth. The Boltzmann distribution function for the initial state is

$$P_{i\nu_k} = \frac{e^{-\beta E_{l\nu_k}}}{Z_{ik}}, \tag{10}$$

where $Z_{ik} = \sum_{\nu_k=0}^{\infty} e^{-\beta E_{i\nu_k}}$ is the partition function for the kth mode in the initial electronic manifold.

The delta function can be expressed as a Fourier transformation

$$\delta(E_{f\nu'} - E_{i\nu}) = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} d\tau e^{-i(E_{f\nu'} - E_{i\nu})\tau}, \tag{11}$$

where $\tau = t/\hbar$.

The nuclear momentum is

$$P_l = -i\hbar \frac{\delta}{\delta Q_l}. \tag{12}$$

Then, Eq. (9) can be expressed as

$$W_{i \to f} = \frac{1}{\hbar} |R_l(fi)|^2 \frac{1}{\prod_k Z_k} \int_{-\infty}^{\infty} d\tau \frac{1}{\hbar^2} e^{iE_{if}\tau} \rho_i(\tau, \beta) \rho_a(\tau, \beta), \tag{13}$$

where

$$\rho_l(\tau, \beta) = \sum_{\nu_l} \sum_{\nu'_l} e^{-\beta E_{i\nu_l}} |\langle \chi_{f\nu'_l} | P_l | \chi_{i\nu_l} \rangle|^2 e^{i\tau(E_{i\nu_l} - E_{f\nu'_l})}, \tag{14}$$

$$\rho_a(\tau, \beta) = \prod_{j \neq l} \sum_{\nu_j} \sum_{\nu'_j} e^{-\beta E_{i\nu_j}} |\langle \chi_{f\nu'_j} | \chi_{i\nu_j} \rangle|^2 e^{i\tau(E_{i\nu_j} - E_{f\nu'_j})}. \tag{15}$$

Inserting complete sets in the summation, we have

$$\rho_l(\tau, \beta) = \sum_{\nu_l} \sum_{\nu'_l} e^{-\beta E_{i\nu_j}} |\langle \chi_{f\nu'_l} | P_l | \chi_{i\nu_l} \rangle|^2 e^{i\tau(E_{i\nu_l} - E_{f\nu'_l})}$$
$$= \sum_{\nu_l} \sum_{\nu'_l} e^{-\beta E_{i\nu_l}} \langle \chi_{i\nu_l} | P_l e^{i\tau E_{i\nu_l}} | \chi_{f\nu'_l} \rangle$$
$$\times \langle \chi_{f\nu'_l} | P_l e^{-i\tau H'_j} | \chi_{i\nu_l} \rangle$$
$$= \sum_{\nu_l} \langle \chi_{i\nu_l} | P_l e^{-(\beta - i\tau)H'_i} P_l e^{-i\tau H'_f} | \chi_{i\nu_l} \rangle$$
$$= \text{Tr}(P_l e^{-i\tau H'_f} P_l e^{-(\beta - i\tau)H'_l})$$
$$\equiv \text{Tr}(P_l e^{-i\tau_g H'_g} P_l e^{-i\tau_e H'_e}), \tag{16}$$

where $H_i^l = \frac{1}{2}(P_{i_l}^2 + \omega_{i_l}^2 Q_{i_l}^2)$, $H_f^l = \frac{1}{2}(P_{f_l}^2 + \omega_{f_l}^2 Q_{f_l}^2)$, and $\tau_g = \tau, \tau_e = \beta/i - \tau$.

Similarly, the nuclear wave functions and the harmonic oscillator Hamiltonians excluding the promoting mode are denoted as

$$\Theta_{i\nu_j}^a = \prod_{j(\neq l)} \chi_{i\nu_j},$$

$$\Theta_{f\nu_j}^a = \prod_{j(\neq l)} \chi_{f\nu'_j},$$

$$H_i^a = \frac{1}{2} \sum_{j(\neq l)} (P_{i_j}^2 + \omega_{i_j}^2 Q_{i_j}^2),$$

$$H_f^a = \frac{1}{2} \sum_{j(\neq l)} (P_{f_j}^2 + \omega_{f_j}^2 Q_{f_j}^2).$$

Then the nuclear motion correlation function is

$$\rho_a(\tau, \beta) = \sum_{\nu_j} \sum_{\nu'_j} e^{-\beta E_{i\nu_j}} |\langle \Theta_{f\nu'_j}^a | \Theta_{i\nu_j}^a \rangle|^2 e^{i\tau(E_{i\nu_j} - E_{f\nu_j})}$$
$$= \sum_{\nu_j} \langle \Theta_{i\nu_j}^a | e^{(i\tau - \beta)H_i^a} e^{-i\tau H_f^a} | \Theta_{l\nu_j}^a \rangle$$
$$\equiv \text{Tr}(e^{-i\tau_g H_g^a} e^{-i\tau_e H_e^a}). \tag{17}$$

This is precisely the Franck-Condon factor with Duschinsky rotation for the absorption and emission processes, which have been investigated by many authors.[19] Equation (17) is the same correlation expression as in Ref. 20 by Ianconescu and Pollak. The advantages of the correlation function expression are (i) that any number of mode mixing is consid-

ered and (ii) that both Eqs. (16) and (17) are mathematically compact and can be solved easily by the path integral formalism. For specific number of mode mixings, these are fully equivalent to the previous expressions.[18,19] It should also be pointed out that the Hamiltonian in Eqs. (16) and (17) are not necessarily for harmonic oscillators. The correlation function expressions are general.

C. Analytic solution

Define

$$\rho_l(\tau_g, \tau_e) = \mathrm{Tr}(P_l e^{-i\tau_g H_g^l} P_l e^{-i\tau_e H_e^l}). \tag{18}$$

Tracing over the excited-electronic-state coordinates, we have

$$\rho_l(\tau_g, \tau_e) = \int_{-\infty}^{\infty} d\underline{x}' \langle \underline{x}' | P_l e^{-i\tau_g H_g^l} P_l e^{-i\tau_e H_e^l} | \underline{x}' \rangle, \tag{19}$$

where the vector $\underline{x}'$ represents the excited-electronic (initial)-state normal mode coordinates Q_{e_i}. By inserting three complete sets of ground state coordinates $\underline{y}$, $\underline{z}$, and $\underline{w}$, and two complete sets of excited state coordinates $\underline{x}'$ and $\underline{y}'$, Eq. (18) can be recast as

$$\rho_l(\tau_g, \tau_e) = \int_{-\infty}^{\infty} dxdydzdwdx'dy' \langle x'|x\rangle\langle x|P_l|y\rangle\langle y|e^{-i\tau_g H_g^l}|z\rangle$$
$$\times \langle z|P_l|w\rangle\langle w|y'\rangle\langle y'|e^{-i\tau_e H_e^l}|x'\rangle. \tag{20}$$

The matrix element for the nuclear momentum is

$$\langle x|P|y\rangle = -i\hbar\frac{\partial}{\partial x}\delta(x-y). \tag{21}$$

The off-diagonal matrix element for harmonic Hamiltonian (Gaussian type[23]) is

$$\langle x|e^{-i\tau H}|y\rangle = \sqrt{\frac{a(\tau)}{2\pi i\hbar}}$$
$$\times \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}b(\tau)(x^2+y^2) - a(\tau)xy\right]\right\}, \tag{22}$$

where $a_{g(e)i}(\tau_{g(e)i}) = \omega_i/\sin(\hbar\omega_i\tau_{g(e)})$ and $b_{g(e)i}(\tau_{g(e)i}) = \omega_i/\tan(\hbar\omega_i\tau_{g(e)})$. Here, the subscripts g and e are the ground and excited state potential energy surfaces, respectively, and ω_i is the frequency of the ith normal mode in the specific manifold. The inner product between the ground and excited state coordinates is given by

$$\langle \underline{x}'|\underline{x}\rangle = \delta[\underline{x}' - (S\underline{x} + \underline{D})]. \tag{23}$$

Inserting Eqs. (21)–(23) into Eq. (20), we have

$$\rho_l(\tau_g, \tau_e) = -\hbar^2\sqrt{\frac{a_{gl}(\tau_g)}{2\pi i\hbar}}\sqrt{\frac{a_{el}(\tau_e)}{2\pi i\hbar}}\int_{-\infty}^{\infty} dxdydzdwdx'dy'\frac{\partial}{\partial x}\delta(x-y)\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}b_{gl}(\tau_g)(y^2+z^2) - a_{gl}(\tau_g)yz\right]\right\}$$
$$\times\frac{\partial}{\partial z}\delta(z-w)\delta(w-y')\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}b_{el}(\tau_e)(x'^2+y'^2) - a_{el}(\tau_e)x'y'\right]\right\}\delta(x'-x). \tag{24}$$

The δ functions and their first-order derivatives can be integrated first, leaving only twofold integrations, instead of six fold,

$$\rho_l(\tau_g, \tau_e) = -\hbar^2\sqrt{\frac{a_{gl}(\tau_g)}{2\pi i\hbar}}\sqrt{\frac{a_{el}(\tau_e)}{2\pi i\hbar}}$$
$$\times\int_{-\infty}^{\infty} dx_l dy_l S_{ll}(b_g x_l - a_g y_l)(b_e y_l' - a_e x_l')$$
$$\times\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}b_g(x_l^2+y_l^2) - a_g x_l y_l\right]\right\}$$
$$\times\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}b_e(x_l'^2+y_l'^2) - a_e x_l' y_l'\right]\right\}. \tag{25}$$

For the Hamiltonian of a collection of N independent modes, the off-diagonal matrix element can be obtained based on Eq. (22),

$$\langle \underline{x}|e^{-i\tau H}|\underline{y}\rangle = \sqrt{\frac{\det(\boldsymbol{a})}{(2\pi i\hbar)^N}}$$
$$\times\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}(\underline{x}^T\boldsymbol{b}\underline{x} + \underline{y}^T\boldsymbol{b}\underline{y}) - \underline{x}^T\boldsymbol{a}\underline{y}\right]\right\}, \tag{26}$$

where $\boldsymbol{a}$ and $\boldsymbol{b}$ are diagonal matrices with elements

$$a_i(\tau) = \omega_i/\sin(\hbar\omega_i\tau), \tag{27a}$$

$$b_i(\tau) = \omega_i/\tan(\hbar\omega_i\tau). \tag{27b}$$

Similarly, the correlation function $\rho_a(\tau_g, \tau_e) = \mathrm{Tr}(e^{-i\tau_g H_g^a} e^{-i\tau_e H_e^a})$ can be evaluated through Eqs. (23) and (26). In fact, this is precisely the Franck-Condon overlap factor for the radiative decay process.

Therefore, the product of the correlation functions may be integrated over x and y and expressed as

$$\rho_{\text{tot}}(\tau_g,\tau_e) = \rho_l(\tau_g,\tau_e)\rho_a(\tau_g,\tau_e) = \sqrt{\frac{\det(\boldsymbol{a}_g)\det(\boldsymbol{a}_e)}{(2\pi i\hbar)^{2N}}} \int_{-\infty}^{\infty} dx_i dy_i S_{ll}(\boldsymbol{b}_g x_l - \boldsymbol{a}_g y_l)(\boldsymbol{b}_e y_l' - \boldsymbol{a}_e x_l')$$

$$\times \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\boldsymbol{b}_g(x_l^2 + y_l^2) - \boldsymbol{a}_g x_l y_l\right]\right\} \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\boldsymbol{b}_e(x_l'^2 + y_l'^2) - \boldsymbol{a}_e x_l' y_l'\right]\right\}$$

$$\times \int_{-\infty}^{\infty} dx_1 \cdots dx_N \int dy_2 \cdots dy_N \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}(\underline{x}^T\boldsymbol{b}_g\underline{x} + \underline{y}^T\boldsymbol{b}_g\underline{y}) - \underline{x}^T\boldsymbol{a}_g\underline{y}\right]\right\}$$

$$\times \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}(\underline{x}'^T\boldsymbol{b}_e\underline{x}' + \underline{y}'^T\boldsymbol{b}_e\underline{y}') - \underline{x}'^T\boldsymbol{a}_e\underline{y}'\right]\right\} \quad (x_N \neq x_l, y_N \neq y_l), \tag{28}$$

where the lth normal mode is assumed as the promoting mode; $\boldsymbol{a}_g$, $\boldsymbol{b}_g$, and $\boldsymbol{a}_e$, $\boldsymbol{b}_e$ are defined as in Eq. (27) for the ground and excited states, respectively; $\underline{x}'$ and $\underline{y}'$ represent $(Sx+D)$ and $(Sy+D)$, respectively, according to Eq. (23).

In order to simplify the above formula, we further define the following matrices:

$$A(\tau_g,\tau_e) = a_g(\tau_g) + S^T a_e(\tau_e)S,$$

$$B(\tau_g,\tau_e) = b_g(\tau_g) + S^T b_e(\tau_e)S,$$

$$E(\tau_e) = b_e(\tau_e) - a_e(\tau_e),$$

$$G(\tau_g) = b_g(\tau_g) - a_g(\tau_g).$$

And Eq. (28) can be recast into a matrix product form

$$\rho_{\text{tot}}(\tau_g,\tau_e) = \sqrt{\frac{\det(a_g)\det(a_e)}{(2\pi i\hbar)^{2N}}} \int_{-\infty}^{+\infty} d\underline{x}d\underline{y} S_{ll}(b_{gl}x_l - a_{gl}\dot{y}_l)[b_{el}S_l^T\underline{y} - a_{el}S_l^T\underline{x} + (b_{el} - a_{el})D_l]$$

$$\times \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}(\underline{x}^T B\underline{x} + \underline{y}^T B\underline{y}) - \underline{x}^T A\underline{y} + \underline{D}^T ES(\underline{x} + \underline{y}) + \underline{D}^T E\underline{D}\right]\right\}, \tag{29}$$

where S_l^T denotes the lth row of the S matrix, a vector now.

This is a typical Gaussian integration problem with linear and quadratic prefactors. It can be solved through the first and second order derivatives of the Gaussian integral. We define a new argument $z=(x,y)$ as well as several new auxiliary vectors and matrices with doubled dimensionality $(2N\times 2N)$,

$$\underline{H} = \begin{pmatrix} & & & 0 & & & \\ & & & \cdot & & & \\ & & & \cdot & & & \\ & & & \cdot & & & \\ & & b_{gl}b_{el}D_l - b_{gl}a_{el}D_l & & & \\ & & 0 & & & \\ & & \cdot & & & \\ & & 0 & & & \\ & & a_{gl}a_{el}D_l - a_{gl}b_{el}D_l & & & \\ & & 0 & & & \\ & & \cdot & & & \\ & & \cdot & & & \\ & & \cdot & & & \end{pmatrix}_{2N}, \quad \underline{G} = \begin{pmatrix} 0 & 0 \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ -a_{el}b_{gl}S_l^T & b_{gl}b_{el}S_l^T \\ 0 & 0 \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ 0 & 0 \\ \cdot & \cdot \\ \cdot & \cdot \\ a_{gl}a_{el}S_l^T & -a_{gl}b_{el}S_l^T \\ 0 & 0 \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \end{pmatrix}_{2N\times 2N},$$

$$K = \begin{pmatrix} B & -A \\ -A & B \end{pmatrix},$$

$$F = (D^T ES, D^T ES)_{2N}, \quad \text{and} \quad \underline{z}^T = (\underline{x}^T, \underline{y}^T).$$

Then, Eq. (29) is now recast into a simple form of

$$\rho_{\text{tot}}(\tau_g, \tau_e) = \sqrt{\frac{\det(a_g)\det(a_e)}{(2\pi i\hbar)^{2N}}} \int_{-\infty}^{+\infty} d\underline{z} S_{ll}(\underline{z}^T G\underline{z} + \underline{H}^T \underline{z})$$

$$\times \exp\left\{ \frac{i}{\hbar} \left[\frac{1}{2} \underline{z}^T K \underline{z} + F^T \underline{z} + \underline{D}^T E\underline{D} \right] \right\}. \quad (30)$$

Using the Guassian integration formula, it is straightforward to obtain

$$\rho_{\text{tot}}(\tau_g, \tau_e) = \sqrt{\frac{\det(a_g)\det(a_e)}{\det K}} S_{ll}\{-i\hbar[(\text{Tr}(GK^{-1})\ ]$$

$$+ H^T K^{-1} F - (K^{-1} F)^T G(K^{-1} F)\}$$

$$\times \exp\left\{ \frac{i}{\hbar} \left[-\frac{1}{2} F^T K^{-1} F + \underline{D}^T E\underline{D} \right] \right\}. \quad (31)$$

Finally, the nonradiative transition rate is obtained as

$$W_{i \to f} = \frac{1}{\hbar} |R_l(fi)|^2 \frac{1}{\prod_k Z_{ik}} \int_{-\infty}^{\infty} d\tau e^{-i\Delta E\tau} \frac{1}{\hbar^2} \rho_{\text{tot}}(\tau, \beta). \quad (32)$$

Equations (31) and (32) are compact but complicated. To verify the validity of the above formalism, we took the simplest case, namely, when DRE is neglected, where the analytical expression can be found in Ref. 21. Under the same approximation, namely, (i) neglecting the Duschinsky rotation, $S_{ij} = \delta_{ij}$, (ii) assuming zero displacement for the promoting mode, $D_l = 0$, and (iii) at low temperature $\hbar\omega_l/kT \gg 1$, the correlation function part of Eq. (32) is found to be

$$\rho_{\text{tot}}(t, \beta) = \frac{\hbar\omega_l}{2} \exp\left[i\omega_l t - \sum_j HR_j\{(2\bar{n}_j + 1) - \bar{n}_j e^{it\omega_i} \right.$$

$$\left. - (\bar{n}_j + 1) e^{-it\omega_j}\} \right]. \quad (33)$$

Here, the HR_j denotes the Huang-Rhys factor for the jth mode $HR_j = D_j^2 \omega_j/2\hbar$, and the thermally averaged number of phonons for the jth mode is $\bar{n}_j = (e^{\hbar\omega_j\beta} - 1)^{-1}$. Therefore, the rate constant for the internal conversion transition is recast into

$$W_{i \to f} = \frac{1}{\hbar^2} \left(\frac{\omega_l}{2\hbar} |R_l(fi)|^2 \right) \int_{-\infty}^{\infty} dt \exp\left[i(\omega_{fi} t + \omega_i t) \right.$$

$$\left. - \sum_j HR_j\{(2\bar{n}_j + 1) - \bar{n}_j e^{-it\omega_j} - (\bar{n}_j + 1) e^{it\omega_j}\} \right], \quad (34)$$

which is exactly the same as in Ref. 21. Thus, for the simplest case, our formalism is proved to be correct. It is very difficult to verify analytically our formalism when DRE is considered due to the complexity of algebra. However, this can be done numerically to compare with previous results, as

will be shown in Sec. III. Before that, we will describe the implementation of the electronic coupling prefactor.

D. Electronic coupling term

So far, by employing the path integral formalism, we have derived the analytical solution for the nuclear part of the internal conversion rate. The electronic coupling prefactor involves the transition between initial and final states of the momentum of nuclear motion. Based on the lowest order perturbation theory, $R_l(fi)$ is determined by the vibronic coupling and is given by[17]

$$\langle \Phi_f | \frac{\partial}{\partial Q_{fl}} | \Phi_i \rangle = \frac{\langle \Phi_f^0 | \partial V/\partial Q_{fl} | \Phi_i^0 \rangle}{E(\Phi_f^0) - E(\Phi_i^0)}, \quad (35)$$

where V denotes the Coulomb interaction potential between the electrons and nucleus, and Q_{fl} is the promoting mode which couples the electronic states Φ_f and Φ_i. The derivative with respect to the promoting mode is calculated at the equilibrium geometry of the electronic ground state. The vibronic coupling can be calculated as

$$\langle \Phi_f^0 | \frac{\partial V}{\partial Q_{fl}} | \Phi_i^0 \rangle = \sum_\sigma^{\text{atoms}} Z_\sigma e^2 \sum_j L_{\sigma l}^j W_\sigma^j(fi), \quad (36)$$

where $j = x, y, z$, and

$$L_{\sigma l}^j = \frac{\partial R_\sigma^j}{\partial Q_{fl}} \quad (37)$$

and

$$W_\sigma^j(fi) = \langle \Phi_f^0 | \sum_\alpha^{\text{electrons}} \frac{r_\alpha^j - R_\sigma^j}{|\mathbf{r}_\alpha - \mathbf{R}_\sigma|^3} | \Phi_i^0 \rangle. \quad (38)$$

Here R_σ^j and r_α^j are the Cartesian coordinates of the nucleus σ and the electron α, respectively, and $\sum_\alpha^{\text{electrons}} (r_\alpha^j - R_\sigma^j)/|\vec{r}_\alpha - \vec{R}_\sigma|^3$ is the jth component of the electric field operator for the nucleus σ.

$$O_\sigma = \sum_\alpha^{\text{electrons}} \frac{\mathbf{r}_\alpha - \mathbf{R}_\sigma}{|\mathbf{r}_\alpha - \mathbf{R}_\sigma|^3}. \quad (39)$$

When expanded in the atomic orbital basis,

$$\langle \mu | O_\sigma | \nu \rangle = \langle \mu | \frac{\mathbf{r} - \mathbf{R}_\sigma}{|\mathbf{r} - \mathbf{R}_\sigma|^3} | \nu \rangle$$

$$= \int_{-\infty}^{+\infty} \phi_\mu(\mathbf{r} - \mathbf{R}_\mu) \frac{\mathbf{r} - \mathbf{R}_\sigma}{|\mathbf{r} - \mathbf{R}_\sigma|^3} \phi_\nu(\mathbf{r} - \mathbf{R}_\nu) d\mathbf{r}$$

$$= \int_{-\infty}^{+\infty} \phi_\mu(\mathbf{r}') \frac{\mathbf{r}' + \mathbf{R}_\mu - \mathbf{R}_\sigma}{|\mathbf{r}' + \mathbf{R}_\mu - \mathbf{R}_\sigma|^3}$$

$$\times \phi_\nu(\mathbf{r}' + \mathbf{R}_\mu - \mathbf{R}_\nu) d\mathbf{r}',$$

where ϕ_μ and ϕ_ν are atomic basis functions.

Since our ultimate purpose is for relatively large molecule, we then employ the zero differential overlap approximation to evaluate the integration,

$$\langle\mu|O_\sigma|\nu\rangle = \int_{-\infty}^{+\infty} \phi_\mu(\mathbf{r}')\frac{\mathbf{r}'+\mathbf{R}_\mu-\mathbf{R}_\sigma}{|\mathbf{r}'+\mathbf{R}_\mu-\mathbf{R}_\sigma|^3}\phi_\nu(\mathbf{r}')d\mathbf{r}'. \quad (40)$$

For $\vec{R}_\mu=\vec{R}_\sigma$, Eq. (40) can be simplified as

$$\langle\mu|O_\sigma|\nu\rangle = \int_{-\infty}^{+\infty} \phi_\mu(\mathbf{r}')\frac{\mathbf{r}'}{|\mathbf{r}'|^3}\phi_\nu(\mathbf{r}')d\mathbf{r}'. \quad (41)$$

For $\mathbf{R}_\mu \neq \mathbf{R}_\sigma$, we assume $\mathbf{r}' \ll \mathbf{R}_\mu - \mathbf{R}_\sigma$. Then Eq. (40) becomes

$$\langle\mu|O_\sigma|\nu\rangle = \left(\frac{1}{|\mathbf{R}_\mu-\mathbf{R}_\sigma|^2}+\frac{-2\mathbf{R}_\mu}{|\mathbf{R}_\mu-\mathbf{R}_\sigma|^3}\right)\delta_{\mu\nu}$$
$$+\frac{-2}{|\mathbf{R}_\mu-\mathbf{R}_\sigma|^3}\int_{-\infty}^{+\infty}\phi_\mu(\mathbf{r}')\mathbf{r}'\phi_\nu(\mathbf{r}')d\mathbf{r}'. \quad (42)$$

Equations (41) and (42) combined with Eqs. (35)–(38) are the practical equations to evaluate the electronic coupling. Namely, $W_\sigma^j(fi)$ can be computed as the transition matrix element over the one-electron electric field operator at the atomic center σ. Our implementation of the above coupling term is carried out in the framework of semiempirical ZINDO level[24] with multireference determinant configuration interaction level for the electronic excited state.

III. RESULTS AND DISCUSSION FOR ETHYLENE MOLECULE

We take ethylene molecule as an example to show how our new formalism works. The internal conversion rate constant of ethylene $^1B_{1u}\rightarrow{}^1A_g$ with DRE has been discussed extensively by Mebel et al.,[18] where IC formalisms for cases with two-mode, three-mode, and four-mode mixings have been derived, respectively. In this section, to further check the validity of our new formalism, we take the case of two-mode mixing (Q_1 and Q_4) and two different promoting modes, Q_5 and Q_6, respectively, for comparison with Mebel et al. We adopted the optimized geometries, frequencies, and normal modes of the ground and first excited states, Duschinsky rotation matrix, and electronic coupling constant associated with the promoting mode given in Refs. 17 and 18.

The nuclear part time-dependent function $F(t)$ of the internal conversion rate constant of the radiationless transition (at $T=273.25$ K) is depicted in Fig. 2. The solid line represents the case without DRE, and the dashed line for the case with DRE. As we can see the dashed curve decays more rapidly to zero than the solid one, which suggests that the Duschinsky rotation accelerates the decay process from the first excited (S_1) to ground electronic state (S_0) in ethylene. Figure 3 shows the calculated temperature dependence of the internal conversion rate constants of the nonradiative transition $S_1 \rightarrow S_0$ of ethylene with and without the Duschinsky rotation effect for promoting mode being Q_5. In Fig. 4, we depicted the internal conversion rates as function of temperature from 0 to 1500 K, for two cases: the fifth (Q_5) and the sixth (Q_6) as promoting mode, respectively. The available results from Mebel et al. (Fig. 8 of Ref. 18) are also dis-
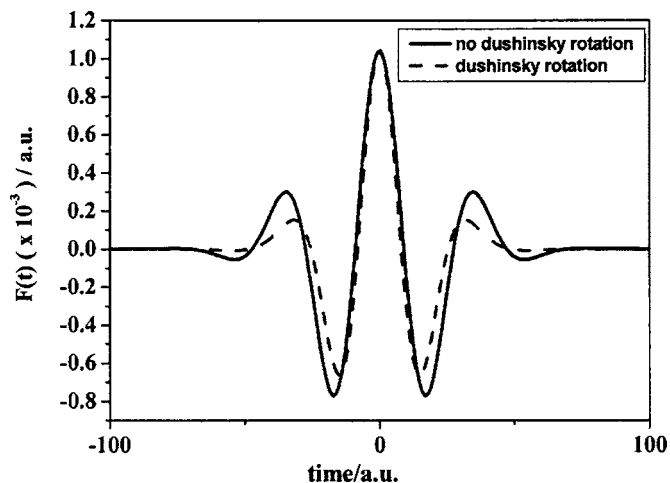

FIG. 2. Time-dependent total correlation functions for the ethylene case.

played in the same figure. It is found that our results are in full agreement with previous theoretical values.[18] This further rationalizes the validity of our formula.

Furthermore, we depicted in Fig. 3 the case with all the modes mixing. This is straightforwardly done with our formalism. It should be noted that the Duschinsky rotation matrix for the ethylene case from Ref. 18 is such that only two-mode mixing is important. Thus, the final results for the temperature dependence as well as the internal conversion rate are close to the case of two-mode mixing. However, our recent investigation on other molecular systems which show interesting light-emitting behaviors does show a strong Duschinsky mixing and it is imperative to include many-mode mixings into consideration. In fact, we found that in such cases, there is no way to select two or a few modes mixing from a large Duschinsky matrix. Most importantly, the correlation function formalism itself is nontrivial. It provides a facile framework for further developments, for instance, one can do cumulant expansion to include the anharmonicity effects perturbatively based on our present formalism, which is in progress in our group. Indeed, Wang and Thoss showed that the correlation function formalism
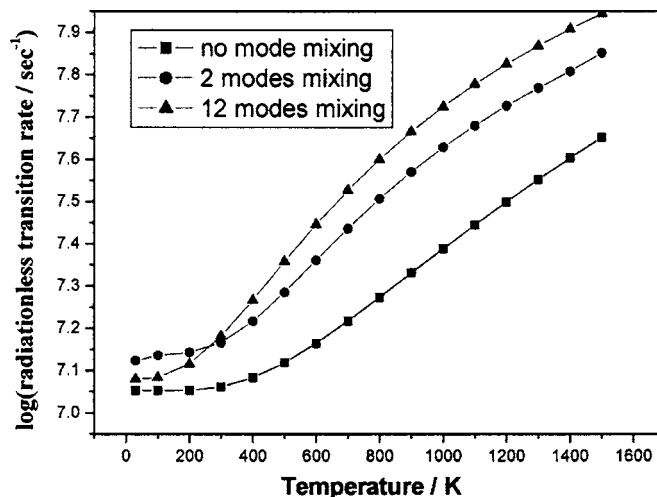

FIG. 3. Temperature dependence of internal conversion rate constants of the radiationless transition from the first excited to ground state in ethylene.
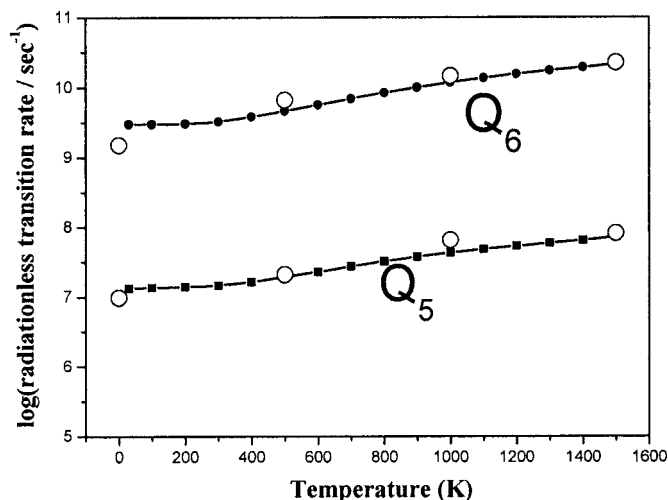
FIG. 4. Internal conversion rate of $^1B_{1u}$ to ^1A_g state as a function of temperature for ethylene molecule with one promoting mode, Q_5 and Q_6, respectively. The open circles represent the results from Ref. 18. The Duschinsky rotation is only considered for two-mode mixing (Q_1 and Q_4).

when coupled with multilayer multiconfiguration can treat quantum dynamics for complex molecules.[25] Pollak and He[26] employed the correlation function formalism for absorption and emission and have found new effects such as excited state cooling, even though the absorption and emission theory was well documented.[26] This indicates the robustness of the correlation function formalism.

IV. CONCLUSION AND DISCUSSION

In this work, we have presented a new approach to derive the nonradiative decay rate from the excited to the ground state through vibronic coupling with the Duschinsky effect. The validity of this formalism is verified through two benchmark comparisons. Namely, in the case without DRE, our formula can be shown analytically to be equivalent to the previous analytical formula, and in the case of Duschinsky rotation with two-mode mixing for the internal conversion process from $^1B_{1u} \rightarrow {}^1A_g$ transition for ethylene, the numerical results from our formalism are also in agreement with Mebel *et al.*[18]

In summary, by employing the path integral for the vibration correlation function, in the framework of the nonradiative decay theory of Lin *et al.*, we have derived an analytical expression which is valid for Duschinsky rotation containing any number of modes mixing in one compact form. Most importantly, the correlation function formalism in the present work provides a facile framework for application to large conjugated molecules, which will be addressed in future work. The anharmonicity effects can be further formulated in the present approach, which is in progress.

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