

Supporting Information for

Theoretical and Experimental Investigation of the Electronic Propensity Rule: A Linear Relation between Radiative and Nonradiative Decay Rates of Molecules

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1. The Hamiltonian of the electron-nuclei interacting system and the basic expressions for wave functions.

The Hamiltonian of the electron-nuclei interacting system is given as

$$H = T_e + T_n + V_n + V_{en}, \quad (\text{S1})$$

where T and V stand for kinetic energy and potential energy respectively. The subscripts indicate the electron (e) and the nucleus (n). Herein we have employed the single electron approximation, in which only one electron excitation is considered, so the interaction potential energy between electrons V_{ee} can be omitted.

In the weak electron-photon coupling limit, it is convenient to use Born-Oppenheimer adiabatic approximation to separate the electronic and nuclear motions. Then, the wave functions (Ψ) can be written as a product of electronic (ϕ) and vibrational (χ) wave functions, i.e. $\Psi_{lm}(\mathbf{r}, \mathbf{R}) = \phi_l(\mathbf{r}, \mathbf{R})\chi_{m(l)}(\mathbf{R})$. We respectively denote the electron and nuclei coordinates by \mathbf{r} and \mathbf{R} , and electronic and vibrational state quantum number by l and m . The corresponding eigen-energy for wave function is represented by E_{lm} . Here the electronic wave function ϕ_l satisfies

$$[T_e + V_{en}]\phi_l(\mathbf{r}, \mathbf{R}) = E_l(\mathbf{R})\phi_l(\mathbf{r}, \mathbf{R}), \quad (\text{S2})$$

and the vibrational wave function $\chi_{m(l)}(\mathbf{R})$ obeys

$$[T_n + W_l(\mathbf{R})]\chi_{m(l)}(\mathbf{R}) = E_{lm}\chi_{lm}(\mathbf{R}), \quad (\text{S3})$$

where $W_l(\mathbf{R})$ is the effective nuclear potential energy.¹ According to harmonic approximation, the vibrational wave function can be written as

$$\chi_{m(l)}(\mathbf{R}) = \prod_{k=1}^{3N} X_{m_k;l}(Q_{k;l}). \quad (\text{S4})$$

The quantities Q introduced above are normal coordinates, describing independent simple harmonic vibrations, and k stands for normal modes. The vibrational eigenfunction $X_{m_k;l}(Q_{k;l})$ satisfies the harmonic oscillator equation and can be specifically expressed as

$$X_{m_k;l} = N_{m_k;l} H_{m_k}(\alpha_{k;l} Q_{k;l}) \exp\left(-\frac{1}{2}\alpha_{k;l}^2 Q_{k;l}^2\right), \quad (\text{S5})$$

where $\alpha_{k;l} = (M\omega_{k;l}/\hbar)^{1/2}$ and $N_{m_k;l} = [\alpha_{k;l}/(2^{m_k} m_k! \sqrt{\pi})]^{1/2}$; $\omega_{k;l}$ is the vibration frequency; H_{m_k} is the Hermite polynomial of order m_k .

2. The radiative decay rate.¹

The interaction Hamiltonian inducing the radiative decay is written as

$$H_{rad} = -\boldsymbol{\mu} \cdot \mathbf{E}, \quad (\text{S6})$$

where $\boldsymbol{\mu} = e \sum_e \mathbf{r}_e$ is the electric dipole moment of the electrons. Under low-temperature limit, the expression of the decay rate then reads

$$k_R(i \rightarrow f) = \frac{2\pi}{\hbar} \sum_\alpha \sum_m |\langle f m; \alpha_{ph} | H_{rad} | i 0; O_{ph} \rangle|^2 \delta(E_{i0} - E_{fm} - E_\alpha^{ph}), \quad (\text{S7})$$

where O_{ph} describes the initial no photon state and α_{ph} describes the final one photon states. E_α^{ph} is the photon energy. i and f refer to the initial and final electronic states, while $m' = 0$ and m are the quantum number of the vibrational states in the initial and final electronic state respectively. Further evaluation needed is eliminating the photon state. Through the quantization of electromagnetic fields, the electric field operator can be written as

$$\mathbf{E} = \mathbf{E}^{(+)} + \mathbf{E}^{(-)}, \quad (\text{S8})$$

where

$$\mathbf{E}^{(+)} = \sum_{k\lambda} \mathbf{e}_\lambda \varepsilon_k a_{k\lambda} e^{i(\mathbf{k}\cdot\mathbf{r} - \omega_k t)}, \quad (\text{S9})$$

$\mathbf{E}^{(+)}$ is the positive frequency part and the negative frequency part $\mathbf{E}^{(-)} = (\mathbf{E}^{(+)})^\dagger$. \mathbf{k} and λ describe the wave vector and polarization of the photon separately. $a_{\mathbf{k}\lambda}$ is the photon annihilation operator. The amplitude $\varepsilon_{\mathbf{k}} = i \sqrt{\frac{2\pi\hbar c k}{\Omega_{ph}}}$, where Ω_{ph} is the quantization volume for the photons. The polarization vector \mathbf{e}_λ satisfy

$$\sum_{\lambda=1,2} e_{\lambda a} e_{\lambda b} = \delta_{ab} - \frac{k_a k_b}{k^2}, \quad (\text{S10})$$

where δ_{ab} is the Kronecker delta; a, b stands for Cartesian coordinate. Substituting the electric field expression into eq S7 yields

$$k_R(i \rightarrow f) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}\lambda} \frac{2\pi\hbar c k}{\Omega_{ph}} \times \sum_{ab,m} \langle \mu_a \rangle \langle \mu_b^* \rangle e_{\lambda a} e_{\lambda b} \delta(E_{i0} - E_{fm} - \hbar c k), \quad (\text{S11})$$

where $\langle \boldsymbol{\mu} \rangle = \langle f m | \boldsymbol{\mu} | i 0 \rangle$. Ω_{ph} can be chosen large at will, therefore we replace $\sum_{\mathbf{k}}$ by $\frac{\Omega_{ph}}{(2\pi)^3} \int d\Omega_{\mathbf{k}} \int k^2 d\mathbf{k}$. Using eq S10 and $\int_{4\pi} d\Omega_{\mathbf{k}} (\delta_{ab} - \frac{k_a k_b}{k^2}) = \frac{8\pi}{3}$, we finally obtain

$$k_R(i \rightarrow f) = \frac{4}{3\hbar^4 c^3} \sum_m |\langle f m | \boldsymbol{\mu} | i 0 \rangle|^2 (E_{i0} - E_{fm})^3, \quad (\text{S12})$$

where $|\langle \boldsymbol{\mu} \rangle|^2 = \sum_a |\langle \mu_a \rangle|^2$. Note that in the absence of vibrations eq S12 boils down to the well-known spontaneous emission rate $\frac{4k_0^3 |\langle \boldsymbol{\mu} \rangle|^2}{3\hbar}$, where $k_0 = \frac{\omega_0}{c}$ and ω_0 is the transition frequency.

Using Born-Oppenheimer adiabatic approximation and harmonic oscillator approximation, eq S12 turns to

$$k_R(i \rightarrow f) = \frac{4}{3\hbar^4 c^3} \sum_{\{m_k\}} |\langle \phi_f | \boldsymbol{\mu} | \phi_i \rangle|^2 (\prod_k F(f m_k; i 0_k)) (E_{i0_k} - E_{f m_k})^3, \quad (\text{S13})$$

The Franck-Condon factor is defined by

$$F(f m_k; i m'_k) = |\langle X_{m_k f} | X_{m'_k i} \rangle|^2 = \left| \int dQ_k X_{m_k f}(Q_k) X_{m'_k i}(Q_k) \right|^2. \quad (\text{S14})$$

This factor measures the degree of vibrational overlap of the initial and final states. For displaced and undistorted oscillators, when $m' = 0$ the Franck-Condon factor can be reduced to²

$$F(f m_k; i 0_k) = e^{-S_k} \frac{(S_k)^{m_k}}{m_k!}. \quad (\text{S15})$$

$S_k = \frac{\Delta_k^2}{2}$ is the Huang-Rhys factor defined to measure the electron-phonon coupling strength and Δ_k is the dimensionless displacement in the potential energy curves. According to eq S15, the Franck-Condon factor $F(f m_k; i 0_k)$ is maximum when

$X_{m_k f}$ is a nodeless solution, i.e. $m_k = 0$. This implies that corresponding radiative transition is governed by the 0-0 transition, in which the Franck-Condon factor is estimated as 1. In this case, eq S13 can be simplified to

$$k_R(i \rightarrow f) \simeq \frac{4}{3\hbar^4 c^3} |\langle \phi_f | e \sum_e \mathbf{r}_e | \phi_i \rangle|^2 \Delta E^3. \quad (\text{S16})$$

Using Condon approximation, i.e., $\langle \phi_f(\mathbf{r}, \mathbf{R}) | \boldsymbol{\mu} | \phi_i(\mathbf{r}, \mathbf{R}) \rangle_e$ is independent of \mathbf{R} , the electronic coupling element in eq S16 equals to

$$J = \langle \phi_f(\mathbf{r}, \mathbf{R}^0) | \boldsymbol{\mu} | \phi_i(\mathbf{r}, \mathbf{R}^0) \rangle_e, \quad (\text{S17})$$

where \mathbf{R}^0 denotes suitably chosen equilibrium position of the ions. Then we have

$$k_R(i \rightarrow f) \simeq \frac{4|J|^2}{3\hbar^4 c^3} \Delta E^3. \quad (\text{S18})$$

3. The nonradiative decay rate.¹

To describe the nonradiative transition between different electronic states, we introduce the non-adiabatic operator (ΔH) which contains the nuclear vibrational energy. When we apply the Hamiltonian H to $\Psi = \phi\chi$, we obtain $H_0\psi_{lm} = E_{lm}\psi_{lm}$, where H_0 is the zeroth-order adiabatic part given by $H_0 = H - \Delta H$. The perturbation operator ΔH is responsible for inducing the nonradiative transition, depicting the effect of nuclear coordinate shifts on the electronic wave function:

$$\Delta H \phi_l \chi_{m(l)} = - \sum_{an} \frac{\hbar^2}{M_n} \left(\frac{\partial}{\partial R_{an}} \phi_l(\mathbf{r}, \mathbf{R}) \right) \left(\frac{\partial}{\partial R_{an}} \chi_{m(l)}(\mathbf{R}) \right). \quad (\text{S19})$$

Here a depicts Cartesian coordinate component, M_n is the mass of nucleus n , and R_{an} is the coordinate component of the nucleus n . ΔH here is reserved to the first order. In the normal coordinate representation, ΔH can be expressed as:

$$\Delta H \phi_l \chi_{m_k} = - \sum_k \frac{\hbar^2}{M} \left(\frac{\partial}{\partial Q_k} \phi_l \right) \left(\frac{\partial}{\partial Q_k} \chi_{m_k} \right), \quad (\text{S20})$$

where M is the geometric mean of nuclear masses. A typical level spacing of the final states d is used to estimate the density of final states, replacing the δ function in the Fermi golden-rule. The δ function in Fermi golden-rule can be approximated as $\sum_m \delta(E_{i0} - E_{fm}) = \rho_E = \frac{G}{d}$, where ρ_E is the density of final vibrational states and G

is the number of vibration states in the energy region $|E_{i0} - E_{fm}| \leq \frac{1}{2}d$. The nonradiative decay rate then turns to

$$k_{NR}(i \rightarrow f) = \frac{2\pi\hbar^3\eta}{dM^2} \sum_k \left(\left| J_{if}^k \left\langle X_{m_{kf}} \left| \frac{\partial}{\partial Q_k} \right| X_{0_{ki}} \right\rangle \prod_{k' \neq k} \left\langle X_{m_{k'f}} \left| X_{0_{k'i}} \right\rangle \right|^2 \right), \quad (\text{S21})$$

where η is the correction factor for the non-Condon effect and the electronic part of k_{NR} in Condon approximation is defined as

$$J_{if}^k = \left\langle \phi_f \left| \frac{\partial}{\partial Q_k} \right| \phi_i \right\rangle_e. \quad (\text{S22})$$

It is extremely inconvenient to calculate the sum of all normal modes k . Assuming that the dominant contribution to the transition comes from a few maximum frequency modes with zero values of Huang-Rhys factor as promoting modes, promoting modes k_p and accepting modes k_a are employed for simplicity. Promoting modes with the largest J_{if}^k have the main contribution to k_{NR} and the remaining accepting modes take up the energy difference $\Delta E - \hbar\omega_{k_p}$, where $\Delta E = E_i - E_f$ is the energy gap and ω_{k_p} is the vibration frequency of the promoting mode. For any promoting mode, energy conservation law preserves, which reads $\Delta E = \hbar\omega_{k_p} + m_a\hbar\omega_{k_a}$. $m_a = \sum_{k_a \neq k_p} m_{k_a}$ counts the total vibration quanta of all accepting modes.

Supposing that there are only several promoting modes designated by p , the nonradiative decay rate can be written as

$$k_{NR} \simeq \frac{2\pi\hbar^3\eta}{dM^2} \sum_{k_p=1}^p \left(\left| J_{if}^{k_p} \left\langle X_{m_{k_p f}} \left| \frac{\partial}{\partial Q_{k_p}} \right| X_{0_{k_p i}} \right\rangle \prod_{k_a \neq k_p} \left\langle X_{m_{k_a f}} \left| X_{0_{k_a i}} \right\rangle \right|^2 \right), \quad (\text{S23})$$

According to the properties of Hermite polynomials in vibrational eigen-functions X_{m_k} (eq S5), the cross-products appearing in eq S23 vanish. Then k_{NR} turns to

$$k_{NR} = \frac{2\pi\hbar^3\eta}{dM^2} \sum_{k_p=1}^p \left| J_{if}^{k_p} \right|^2 \left| \left\langle X_{m_{k_p f}} \left| \frac{\partial}{\partial Q_{k_p}} \right| X_{0_{k_p i}} \right\rangle \right|^2 \prod_{k_a \neq k_p} F(f m_{k_a}; i 0_{k_a}). \quad (\text{S24})$$

According to eqs S5, the squared matrix element about the promoting mode in electronic part can be written as:

$$\left| \left\langle X_{m_{k_p} f} \left| \frac{\partial}{\partial Q_{k_p}} X_{0_{k_p} i} \right. \right\rangle \right|^2 = \frac{M\omega_{k_p}}{2\hbar} \frac{(m_{k_p} - S_{k_p})^2 e^{-S_{k_p}} S_{k_p}^{m_{k_p}}}{S_{k_p} m_{k_p}!}. \quad (\text{S25})$$

For promoting modes with $S_{k_p} = 0$, the matrix element eq S25 will vanish unless $m_{k_p} = 1$, which indicates each promoting mode consumes only 1 phonon. Then the

squared matrix element $\left| \left\langle X_{m_{k_p} f} \left| \left(\frac{\partial}{\partial Q_{k_p}} \right) X_{0_{k_p} i} \right. \right\rangle \right|^2$ reduces to $\frac{M\omega_{k_p}}{2\hbar}$. Thus, eq S24 is

simplified to

$$k_{NR} = \frac{\pi\hbar^2\eta}{Md} \sum_{k_p=1}^p |J_{if}^{k_p}|^2 \omega_{k_p} \prod_{k_a \neq k_p} F(f m_{k_a}; i 0_{k_a}). \quad (\text{S26})$$

It should be noted that, unlike the other sections, in this section (SI-3) the subscript a refers specifically to the accepting modes.

4. The comparison between the energy gap law in our paper and that proposed by Jortner *et al.*³

Through a multinomial expansion $\frac{(\sum_k S_k)^m}{m!} = \sum_{m_k [\sum_k m_k = m]} \prod_k \frac{S_k^{m_k}}{m_k!}$ and eqs S14, S15, we find

$$k_{NR} = \frac{\pi\eta\hbar^2}{Md} \left(\sum_{k_p=1}^p |J_{if}^{k_p}|^2 \omega_{k_p} \frac{S^m e^{-S}}{m!} \right). \quad (\text{S27})$$

One uses Stirling's approximation $m! = m^m \sqrt{2\pi m} e^{-m}$ to obtain¹

$$k_{NR} = \sqrt{\frac{\pi}{2m_a}} \frac{\eta\hbar}{Md} \left(\sum_{k_p=1}^p |J_{if}^{k_p}|^2 \omega_k \right) e^{-S} e^{-m_a \gamma_a}. \quad (\text{S28})$$

The number $m_a = \sum_{k_a} m_{k_a}$ counts the vibration quanta of accepting modes. Under the weak coupling limit, i. e. $S = \sum_k S_k \leq 1$, we have

$$\begin{cases} k_{NR} = \sqrt{\frac{\pi}{2m_a}} \frac{\eta\hbar}{Md} \left(\sum_{k_p=1}^p |J_{if}^{k_p}|^2 \omega_k \right) e^{-\gamma_a m_a} \\ \gamma_a = \ln \left(\frac{m_a}{S} \right) - 1. \end{cases} \quad (\text{S29})$$

Moreover, the energy gap law proposed by Jortner *et al.* is given by³

$$\begin{cases} W = \frac{\sqrt{2\pi}}{\hbar\sqrt{\hbar\omega_M \Delta E}} C^2 e^{-\gamma_b \left(\frac{\Delta E}{\hbar\omega_M} \right)} \\ \gamma_b = \log \left(\frac{\Delta E}{de_M} \right) - 1, \end{cases} \quad (\text{S30})$$

where $de_M = \frac{1}{2} \sum_M \hbar \omega_M \Delta_M^2$ and

$$C = \sum_{k_p=1}^p J_{if}^{k_p} \left\langle X_{m_{k_p}f} \left| \frac{\partial}{\partial Q_{k_p}} \right| X_{0_{k_p}i} \right\rangle. \quad (\text{S31})$$

Based on the promoting and accepting modes assumption in the weak coupling limit under low temperature, both eq S29 and eq S30 are derived from the Fermi golden-rule in adiabatic approximation:

$$k(i0 \rightarrow fm) = \frac{2\pi}{\hbar} \sum_m \left| \langle \phi_f | H | \phi_i \rangle \left\langle \prod_k X_{m_{k}f}(Q_k) | H | \prod_{k'} X_{0_{k'}i}(Q_{k'}) \right\rangle \right|^2 \delta(E_{i0} - E_{fm_k}). \quad (\text{S32})$$

There is consensus that in the weak coupling case the nonradiative decay is dominated by the highest frequency modes ω_M .^{2,3} Therefore, it is obviously that $m_a \propto \frac{\Delta E}{\hbar \omega_M}$ and $S \propto \frac{de_M}{\hbar \omega_M}$, giving the comparative relations listed in Table S1.

Table S1. Comparison of eq S29 and eq S30 with their initial equation: Fermi golden-rule.

Fermi golden-rule ($\Delta H \rightarrow \frac{\partial}{\partial Q_k}$)	Equation S29 by Schuurmans <i>et al.</i> ¹	Equation S30 by Jortner <i>et al.</i> ³
$\langle \phi_f H \phi_i \rangle$	J_{if}^k	J_{if}^k
$\left\langle X_{m_{k}f} \left \left(\frac{\partial}{\partial Q_k} \right) X_{0_{k}i} \right\rangle$	$\frac{M \omega_k}{2\hbar}$	$\left\langle X_{m_{k}f} \left \left(\frac{\partial}{\partial Q_k} \right) X_{0_{k}i} \right\rangle$
$F(fm_k; im'_k)$	$\frac{e^{-\gamma_a m_a}}{\sqrt{m}}$ $m_a \propto \frac{\Delta E}{\hbar \omega_M}$	$\frac{e^{-\gamma_b \left(\frac{\Delta E}{\hbar \omega_M} \right)}}{\sqrt{\Delta E}}$ $\gamma_b \propto \gamma_a$
$\delta(E_{i0} - E_{fm_k})$	The δ function is approximated by the typical density of the final states ($\frac{1}{d}$).	The δ function is eliminated by the generating function method.

Obviously, eq S29 and eq S30 are basically the same, while eq S30 has a wider range of applications.^{2,3} Practically, the above two formulas can be written to a rougher form according to the experimental experience where k_{NR} has an exponential trend

with respect to the energy gap ΔE . The Frank-Condon factor can be directly approximated by a semi-empirical exponential function, i. e.

$$k_{NR} = \frac{\pi\eta\hbar^2}{Md} \left(\sum_{k_p=1}^p |J_{if}^{k_p}|^2 \omega_{k_p} \right) \exp(\gamma(\Delta E + \delta E)). \quad (\text{S33})$$

γ and δE are the coefficients in the exponent, which can be obtained by experimental fitting.¹

5. The detailed derivation of eqs 6, 7 and 9 in the main text.

(a) The well-known velocity form of the electronic coupling element in the radiative decay rate.

We denote the Hamiltonian corresponding to the electronic wave function as H_0^e , i.e. $H_0^e \phi_l = (T_e + V(\mathbf{r}, \mathbf{R})) \phi_l = E_l \phi_l$. The derivation employs the commutability between $\sum_e \mathbf{r}_e$ and $V(\mathbf{r}, \mathbf{R})$, and then we have

$$\begin{aligned} [H_0^e, \sum_e \mathbf{r}_e] \phi_l &= [T_e + V(\mathbf{r}, \mathbf{R}), \sum_e \mathbf{r}_e] \phi_l = [T_e, \sum_e \mathbf{r}_e] \phi_l = \\ &= \left[-\frac{\hbar^2}{2m_e} \sum_{ae'} \frac{\partial^2}{\partial r_{ae'}^2}, \sum_e \mathbf{r}_e \right] \phi_l = \frac{\hbar^2}{2m_e} \left(\sum_{a,e,e'} r_e \frac{\partial^2}{\partial r_{ae'}^2} \phi_l - \sum_{a,e,e'} \frac{\partial^2}{\partial r_{ae'}^2} r_e \phi_l \right) = \\ &= \frac{\hbar^2}{2m_e} \left(\sum_{a,e,e'} r_e \frac{\partial^2}{\partial r_{ae'}^2} \phi_l - \sum_{ae'} \frac{\partial}{\partial r_{ae'}} \phi_l - \sum_{a,e,e'} \frac{\partial}{\partial r_{ae'}} \left(r_e \frac{\partial}{\partial r_{ae'}} \phi_l \right) \right) = \\ &= \frac{\hbar^2}{2m_e} \left(\sum_{a,e,e'} r_e \frac{\partial^2}{\partial r_{ae'}^2} \phi_l - 2 \sum_{ae'} \frac{\partial}{\partial r_{ae'}} \phi_l - \sum_{a,e,e'} r_e \frac{\partial^2}{\partial r_{ae'}^2} \phi_l \right) = -\frac{\hbar^2}{m_e} \sum_{ae} \frac{\partial}{\partial r_{ae}} \phi_l \end{aligned}$$

That is

$$[H_0^e, \sum_e \mathbf{r}_e] \phi_l = -\frac{\hbar^2}{m_e} \sum_e \nabla_{r_e} \phi_l. \quad (\text{S34})$$

Using $\phi_l(\mathbf{r}, \mathbf{R}) = \left(\frac{1}{E_l}\right) H_0^e \phi_l(\mathbf{r}, \mathbf{R})$ and eq S34, we have

$$\begin{aligned} \langle \phi_f | \sum_e \mathbf{r}_e | \phi_i \rangle_e &= \frac{1}{E_i} \langle \phi_f | \sum_e \mathbf{r}_e H_0^e \phi_i \rangle_e = \frac{1}{E_i} \langle \phi_f | \left(H_0^e \sum_e \mathbf{r}_e + \frac{\hbar^2}{m_e} \sum_e \nabla_{r_e} \right) | \phi_i \rangle_e = \\ &= \frac{E_f}{E_i} \langle \phi_f | \sum_e \mathbf{r}_e | \phi_i \rangle_e + \frac{\hbar^2}{m_e E_i} \langle \phi_f | \sum_e \nabla_{r_e} | \phi_i \rangle_e. \end{aligned}$$

Defining $\Delta E = E_i - E_f$, after organization the above formula can be reduced to

$$\langle \phi_f | \sum_e \mathbf{r}_e | \phi_i \rangle_e = \frac{\hbar^2}{m_e \Delta E} \langle \phi_f | \sum_e \nabla_{r_e} | \phi_i \rangle_e, \quad (\text{S35})$$

which is called as the velocity form.

(b) The acceleration form of the electronic coupling element in the radiative decay rate.

In view of the commutability of T_e with ∇_{r_e} , we obtain

$$\begin{aligned}
[\sum_e \nabla_{r_e}, H_0^e] \phi_l &= [\sum_e \nabla_{r_e}, V(\mathbf{r}, \mathbf{R})] \phi_l \\
&= \sum_e \nabla_{r_e} (V(\mathbf{r}, \mathbf{R}) \phi_l) - V(\mathbf{r}, \mathbf{R}) \sum_e \nabla_{r_e} \phi_l \\
&= (\sum_e \nabla_{r_e} V(\mathbf{r}, \mathbf{R})) \phi_l.
\end{aligned} \tag{S36}$$

Similarly using $\phi_l(\mathbf{r}, \mathbf{R}) = (\frac{1}{E_l}) H_0^e \phi_l(\mathbf{r}, \mathbf{R})$ and eq S36 gives

$$\langle \phi_f | \sum_e \nabla_{r_e} | \phi_i \rangle_e = \frac{1}{\Delta E} \langle \phi_f | \sum_e \nabla_{r_e} V(\mathbf{r}, \mathbf{R}) | \phi_i \rangle_e, \tag{S37}$$

which is called as the acceleration form.

(c) The acceleration form of the electronic coupling element in the non-radiative decay rate.

Correspondingly, the nonradiative decay rate can also be transformed into the equivalent acceleration form. In view of the commutability of T_e with ∇_{R_n} , we obtain an important relation

$$\begin{aligned}
[\sum_n \nabla_{R_n}, H_0^e] \phi_l &= [\sum_n \nabla_{R_n}, V(\mathbf{r}, \mathbf{R})] \phi_l \\
&= \sum_n \nabla_{R_n} (V(\mathbf{r}, \mathbf{R}) \phi_l) - V(\mathbf{r}, \mathbf{R}) \sum_n \nabla_{R_n} \phi_l \\
&= (\sum_n \nabla_{R_n} V(\mathbf{r}, \mathbf{R})) \phi_l + V(\mathbf{r}, \mathbf{R}) \sum_n \nabla_{R_n} \phi_l - V(\mathbf{r}, \mathbf{R}) \sum_n \nabla_{R_n} \phi_l \\
&= (\sum_n \nabla_{R_n} V(\mathbf{r}, \mathbf{R})) \phi_l.
\end{aligned} \tag{S38}$$

Employing $\phi_l(\mathbf{r}, \mathbf{R}) = (\frac{1}{E_l}) H_0^e \phi_l(\mathbf{r}, \mathbf{R})$ and eq S38, we obtain the acceleration form for the nonradiative decay rate:

$$\langle \phi_f | \sum_n \nabla_{R_n} | \phi_i \rangle_e = \frac{1}{\Delta E} \langle \phi_f | \sum_n \nabla_{R_n} V(\mathbf{r}, \mathbf{R}) | \phi_i \rangle_e. \tag{S39}$$

6. The potential energy curves and coordinate transformation relations.

As mentioned above, the vibrational wave function $\chi_{m(l)}(\mathbf{R})$ satisfies the Schrödinger equation

$$\left[-\sum_a \sum_{n=1}^N \frac{\hbar^2}{2M_n} \frac{\partial^2}{\partial R_{an}^2} + W_l(\{R_{an}\}) \right] \chi_{m(l)}(\{R_{an}\}) = E_{lm(l)} \chi_{m(l)}(\{R_{an}\}), \tag{S40}$$

where a depicts Cartesian coordinate component. Expand $W_l(\{R_{an}\})$ into a Taylor series according to

$$W_l(\mathbf{R}) = W_l(\mathbf{R}_l^0) + \frac{1}{2} \sum_{\nu, \lambda=1}^{3N} C_{\nu\lambda}^l u_{\nu;l} u_{\lambda;l}, \tag{S41}$$

where $u_{\nu;l} = R_n - R_{\nu;l}^0$. It is common to introduce the harmonic approximation in

computing vibrational wave functions, therefore we introduce two successive transformations:

$$u_{\nu;l} = \sqrt{\frac{M}{M_{\nu}}} \bar{u}_{\nu;l}, \quad (\text{S42})$$

and

$$\bar{u}_{\lambda;l} = \sum_{\rho=1}^{3N} A_{\lambda\rho}^l Q_{\rho,l}. \quad (\text{S43})$$

The quantities $Q_{\rho,l}$ introduced above are the normal coordinates, describing independent simple harmonic vibrations. Through the coordinate transformation, the effective potential energy surface $W_l(\mathbf{R})$ is transformed into the sum of the potential energy of classical harmonic oscillators. Substituting the above two transformation relations into eq S40, one obtains¹

$$\left(\sum_{\rho=1}^{3N} H_{\rho}^l\right) \chi_{m(l)} = \left(E_{lm(l)} - W_l(\mathbf{R}_l^0)\right) \chi_{m(l)}, \quad (\text{S44})$$

where

$$H_{\rho}^l = \frac{1}{2M} \frac{\partial^2}{\partial Q_{\rho,l}^2} + \frac{1}{2} c_{\rho;l} Q_{\rho,l}^2, \quad (\text{S45})$$

and

$$c_{\rho;l} = (A_{\nu\rho}^l)^{-1} \sum_{\lambda} C_{\nu\lambda}^l \frac{M}{\sqrt{M_{\nu}M_{\lambda}}} A_{\lambda\rho}^l \quad (\text{S46})$$

Equation S44 is the Schrödinger equation for simple harmonic vibration. Therefore, the coordinate transformation relations between Q_k and R_{an} are given by

$$R_{an} - R_{an}^0 = \sqrt{\frac{M}{M_n}} \sum_{k=1}^{3N} A_{an;k} Q_k. \quad (\text{S47})$$

$A_{an;k}$ is the coordinate transformation matrix element. Employing the chain rule for derivation of compound functions, for an arbitrary composite function f we have

$$\frac{\partial f}{\partial Q_k} = \sum_{an} \sqrt{\frac{M}{M_n}} A_{an;k} \frac{\partial f}{\partial R_{an}}. \quad (\text{S48})$$

7. The evaluation of E_{an}^{new} .

The electronic interaction term defined by $E_{an}(\mathbf{R}) = \left\langle \phi_f \left| \frac{\partial V(\mathbf{r}, \mathbf{R})}{\partial R_{an}} \right| \phi_i \right\rangle_e$ will change to $E_{an}^{new}(\mathbf{R})$ with the new potential energy $V^{new}(\mathbf{r}, \mathbf{R}) = V(\mathbf{r}, \mathbf{R}) + \Delta V(\mathbf{r}, \mathbf{R})$. Through the relationship between gradient operator ∇_{R_n} and partial derivative operator $\frac{\partial}{\partial R_{an}}$:

$$\nabla_{R_n}(\Delta V(\mathbf{r}, \mathbf{R})) = \sum_{an} \left(\frac{\partial(\Delta V(\mathbf{r}, \mathbf{R}))}{\partial R_{an}} \right) \mathbf{n}_{an}, \quad (\text{S49})$$

and $\langle \phi_f | \sum_n \nabla_{R_n}(\Delta V(\mathbf{r}, \mathbf{R})) | \phi_i \rangle \propto \langle \phi_f | \sum_{an} (\alpha V(\mathbf{r}, \mathbf{R}) \mathbf{n}_{an}) | \phi_i \rangle$ (eq 17 in main text),

we have

$$\frac{\partial V^{new}(\mathbf{r}, \mathbf{R})}{\partial R_{an}} = \frac{\partial V(\mathbf{r}, \mathbf{R})}{\partial R_{an}} + \frac{\partial(\Delta V(\mathbf{r}, \mathbf{R}))}{\partial R_{an}} = \frac{\partial V(\mathbf{r}, \mathbf{R})}{\partial R_{an}} + \alpha V(\mathbf{r}, \mathbf{R}). \quad (\text{S50})$$

Correspondingly the new electronic interaction term is

$$\begin{aligned} E_{an}^{new}(\mathbf{R}) &= \left\langle \phi_f \left| \frac{\partial V^{new}(\mathbf{r}, \mathbf{R})}{\partial R_{an}} \right| \phi_i \right\rangle_e \\ &= \left\langle \phi_f \left| \frac{\partial V(\mathbf{r}, \mathbf{R})}{\partial R_{an}} \right| \phi_i \right\rangle_e + \langle \phi_f | \alpha V(\mathbf{r}, \mathbf{R}) | \phi_i \rangle_e \\ &= E_{an}(\mathbf{R}) + \langle \phi_f | \alpha V(\mathbf{r}, \mathbf{R}) | \phi_i \rangle_e. \end{aligned} \quad (\text{S51})$$

Please note that SI-1, SI-2, SI-3 and SI-6 are all cited from ref 1 below. For further details, please refer to ref 1.

Reference

- (1) Schuurmans, M. F. H.; van Dijk, J. M. F. On Radiative and Non-Radiative Decay Times in the Weak Coupling Limit. *Physica B & C* **1984**, *123*, 131-155.
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