Quantum-classical effective-modes dynamics of the $\pi\pi^* \rightarrow n\pi^*$ decay in 9H-adenine. A quadratic vibronic coupling model. Supporting Information

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A. Quadratic Vibronic Coupling Hamiltonian for wave packet propagation

In order to define the Hamiltonian for the quantum wave packet propagations, we adopt a fully QVC model for the intra-state diabatic potentials (W_1 and W_2) , and a linear approximation for the diabatic coupling (W_{12}). In this work, we adopted an approach denoted

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'adiabatic' in the recent literature, meaning that the point of expansion is the minimum of the PES.

In the following, dimensionless normal coordinates (Q_j) will be used. These are related to the usual mass-weighted coordinates ($Q_j^{(MW)}$) by the transformation: $Q_j = \sqrt{\omega_j/\hbar} Q_j^{(MW)}$, where ω_j is the corresponding frequency.

In our approach, we compute the minimum energy $E_{\min}^{(\alpha)}$ and the normal modes ($\mathbf{Q}^\alpha$) of the excited state α. The Hamiltonian for the excited state is

$$\mathcal{H}_\alpha = E_{\min}^{(\alpha)} + \frac{\hbar}{2} \mathbf{P}^{(\alpha)^T} \omega_\alpha \mathbf{P}^{(\alpha)} + \frac{\hbar}{2} \mathbf{Q}^{(\alpha)^T} \omega_\alpha \mathbf{Q}^{(\alpha)} \ , \tag{1}$$

where the matrix ω_α collects the frequencies of the excited state.

In order to derive the expressions for the Hamiltonians in term of the normal modes of the ground state, we employ Duschinsky transformation among mass-weighted normal modes,

$$\omega^{-\frac{1}{2}} \mathbf{Q} = \mathbb{J}_\alpha \omega_\alpha^{-\frac{1}{2}} \mathbf{Q}^{(\alpha)} + \omega^{-\frac{1}{2}} \mathbf{K}_\alpha \ , \tag{2}$$

where ω is the diagonal matrix of the frequencies of the ground state, $\mathbb{J}_\alpha$ is the orthogonal Duschinsky matrix, and $\mathbf{K}_\alpha$ is a vector representing the displacement along the ground state normal modes to reach the excited state minimum. A similar transformation must be performed among momenta, to preserve the canonical commutation rules,

$$\omega^{\frac{1}{2}} \mathbf{P} = \mathbb{J}_\alpha \omega_\alpha^{\frac{1}{2}} \mathbf{P}^{(\alpha)} \ . \tag{3}$$

Now the final expression of the intra-state Hamiltonian is easily derived,

$$\mathcal{H}_\alpha = E_{\min}^{(\alpha)} + \frac{\hbar}{2} \mathbf{P}^T \omega \mathbf{P} + \frac{1}{2} \mathbf{Q}^T \mathbb{B}_\alpha \mathbf{Q} - \mathbf{\Lambda}_\alpha^T \mathbf{Q} + \frac{1}{2} \mathbf{K}_\alpha{}^T \mathbb{B}_\alpha \mathbf{K}_\alpha \ , \tag{4}$$

where the matrix $\mathbb{B}_\alpha$ is defined as $\mathbb{B}_\alpha = \hbar \omega^{-\frac{1}{2}} \mathbb{J}_\alpha \omega_\alpha^2 \mathbb{J}_\alpha^T \omega^{-\frac{1}{2}}$ and $\mathbf{\Lambda}_\alpha = \mathbb{B}_\alpha \mathbf{K}_\alpha$.