Supporting Information

Lan *et al.* 10.1073/pnas.0801062105

SI Text

CT–S_0 Conical Intersection Geometry and g-h Vector. Tables S1 and S2 give the Cartesian coordinates of the equilibrium configuration of the S_0 state and the conical intersection, respectively. Fig. S1 *a* and *b* show the **g** (gradient difference) and **h** (derivative coupling) vectors, respectively.

Diabatic Potential-Energy Surfaces. The diabatic potential-energy surfaces, V_{11} and V_{22}, are modeled as a function of the hydrogen-transfer coordinate R and as harmonic functions of the 19 tuning coordinates $Q_{t,i}$ and the 19 coupling coordinates $Q_{c,i}$

$$V_{11} = v_{11}(R) + \sum_i \left[\frac{1}{2}\omega_{t,i}Q_{t,i}^2 + \kappa_i^{(1)}(R)Q_{t,i}\right] + \sum_j \frac{1}{2}\omega_{c,j}Q_{c,j}^2, \qquad [1]$$

$$V_{22} = v_{22}(R) + \sum_i \left[\frac{1}{2}\omega_{t,i}Q_{t,i}^2 + \kappa_i^{(2)}(R)Q_{t,i}\right] + \sum_j \frac{1}{2}\omega_{c,j}Q_{c,j}^2, \qquad [2]$$

where $\omega_{t,i}$ and $\omega_{c,i}$ are frequencies of the tuning and coupling modes, respectively.

The coupling element in the diabatic representation is approximated as a linear function of $Q_{c,i}$:

$$V_{12} = \sum_i \lambda_i Q_{c,i}. \qquad [3]$$

The coupling constants of the tuning modes are obtained as

$$\kappa_i^{(\kappa)}(R) = \sum_m \frac{\delta V_\kappa^a(R)}{\delta x_m}\frac{\delta x_m}{\delta Q_{t,i}}, \ (k = 1,2). \qquad [4]$$

The transformation between the Cartesian coordinates and the dimensionless normal coordinates, $\frac{\partial X_m}{\partial Q_{ti}}$, is given by the so-called L matrix, which can be obtained with the Gaussian package.

Analytic functions $v_{11}(R)$, $v_{22}(R)$, $\kappa_i^{(1)}(R)$ and $\kappa_i^{(2)}(R)$ are obtained by fitting the data to a fourth-order polynomial in R

$$v_{11}(R) = A_1R^4 + B_1R^3 + C_1R^2 + D_1R + E_1, \qquad [5]$$

$$v_{22}(R) = A_2R^4 + B_2R^3 + C_2R^2 + D_2R + E_2, \qquad [6]$$

$$\kappa_i^{(1)}(R) = a_i^{(1)}R^4 + b_i^{(1)}R^3 + c_i^{(1)}R^2 + d_i^{(1)}R + e_i^{(1)}, \qquad [7]$$

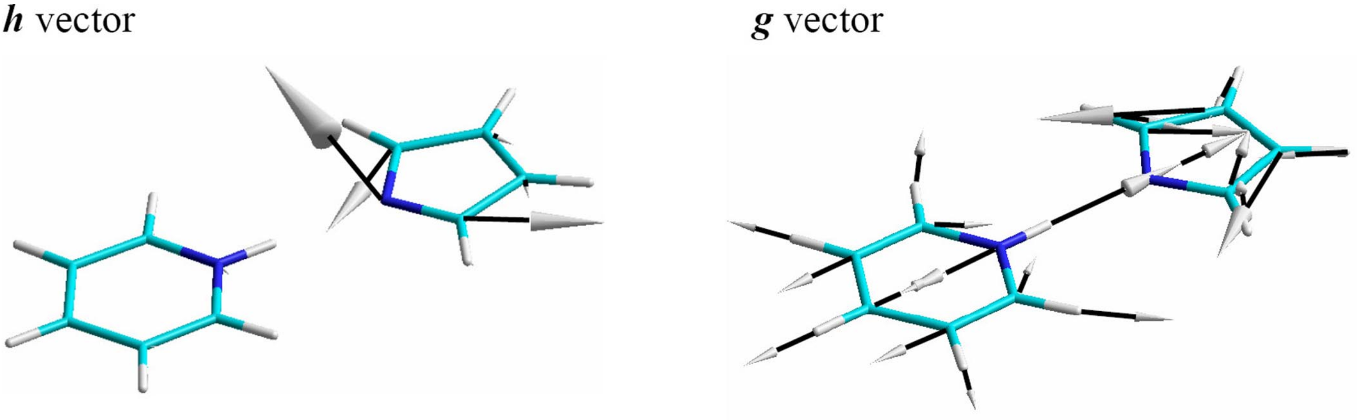
$$\kappa_i^{(2)}(R) = a_i^{(2)}R^4 + b_i^{(2)}R^3 + c_i^{(2)}R^2 + d_i^{(2)}R + e_i^{(2)}. \qquad [8]$$

For illustration, the dependences of $\kappa_i^{(1)}(R)$ and $\kappa_i^{(2)}(R)$ on R are shown in Fig. S2*a* for the mode ν_{27} ($\omega_{27} = 0.13683$ eV). The two-dimensional diabatic potential energy surfaces of the S_0 and CT states as function R and Q_{27} are shown in Fig. S2*b*.

The diabatic coupling strengths λ_i are obtained by projecting the nonadiabatic coupling vector (**h**) onto the $Q_{c,i}$.

The parameters of the 39-dimensional potential-energy surfaces are available from the authors upon request.

Spectral-Density Functions. The discrete spectral densities and corresponding continuous functions for the S_0 and CT states are shown in Fig. S3 *a* and *b*, respectively.


h vector

g vector

Fig. S1. The **g** and **h** vectors for the CT ($^1\pi\pi^*$)–S_0 conical intersection.

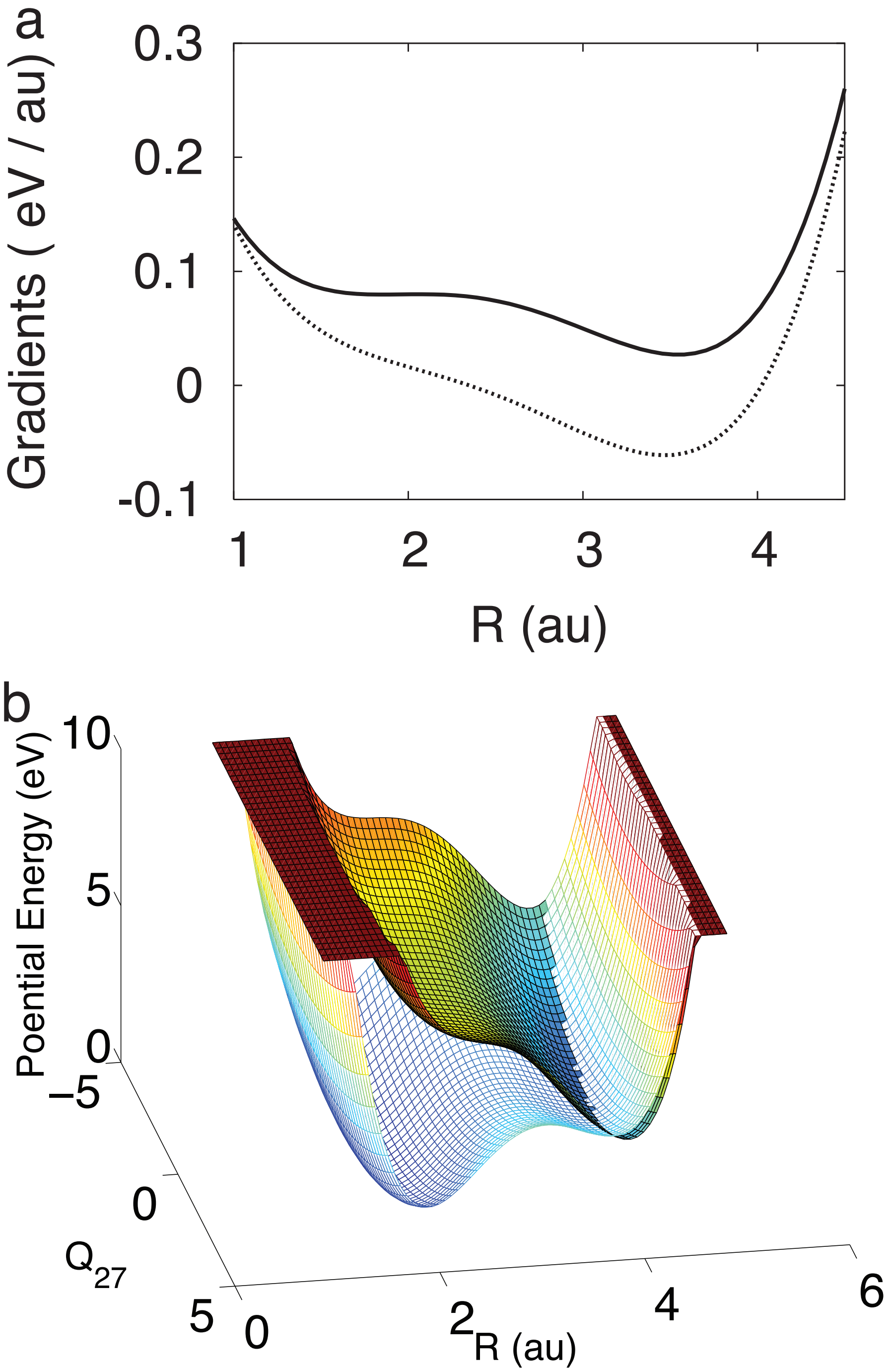


Fig. S2. Intrastate coupling strength and potential-energy surfaces for one typical tuning coordinate. (*a*) The intrastate coupling strengths for mode ν_{27} as functions of *R*: full line: $\kappa^{(1)}_{27}$ and the dashed line: $\kappa^{(2)}_{27}$. (*b*) Two-dimensional diabatic potential-energy surfaces of the S_0 and CT ($^1\pi\pi^*$) states as function *R* and Q_{27}.

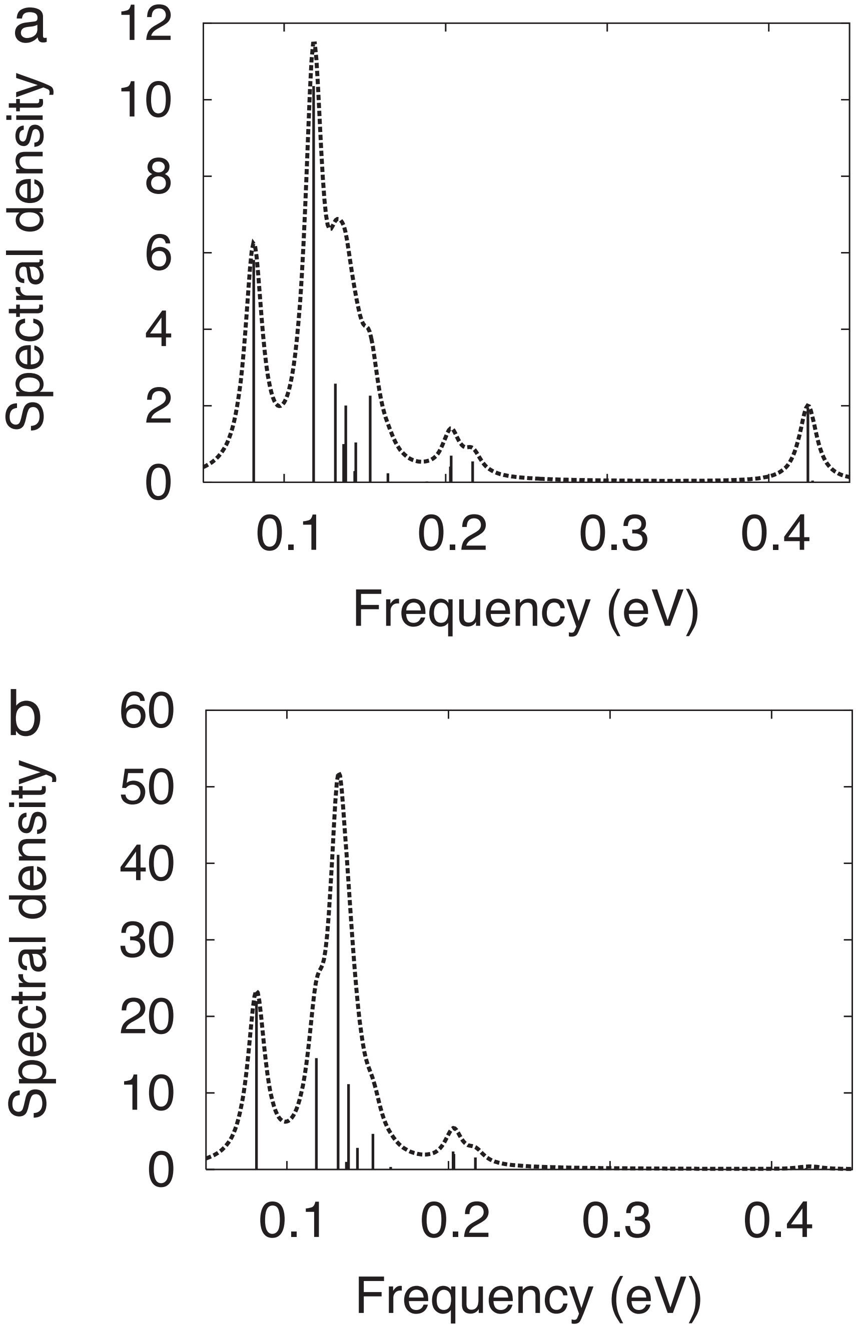


Fig. S3. The spectral density functions for the ground S_0 state (*a*) and the CT ($^1\pi\pi^*$) state (*b*). The sticks give the discrete spectral density. The envelope has been obtained by convolution with a Lorentz function of 13 meV full-width half-maximum.

Table S1. Cartesian coordinates of the ground-state equilibrium geometry of the pyridine-pyrrole system at the CASSCF level.

Atoms	*x*, Å	*y*, Å	*z*, Å
C	−2.385012	2.604117	0.000000
N	−0.198534	1.929364	0.000000
C	0.830327	2.826294	0.000000
C	0.302197	4.093008	0.000000
C	−1.118929	3.950483	0.000000
H	−2.318032	2.079937	0.000000
H	1.848870	2.497866	0.000000
H	0.858582	5.008617	0.000000
H	−1.846051	4.737372	0.000000
C	0.415573	−4.055235	0.000000
C	−0.848478	−3.469111	0.000000
C	−0.938623	−2.077932	0.000000
N	0.126715	−1.276273	0.000000
C	1.334141	−1.841698	0.000000
C	1.532040	−3.221661	0.000000
H	0.526691	−5.124215	0.000000
H	−1.741503	−4.065983	0.000000
H	−1.897711	−1.592420	0.000000
H	2.172892	−1.169334	0.000000
H	2.528732	−3.622108	0.000000
H	−0.098797	0.935324	0.000000

Table S2. Cartesian coordinates of the minimum of the CT–S_0 conical intersection seam at the CASSCF level.

Atoms	*x*, Å	*y*, Å	*z*, Å
C	−1.341586	2.574648	0.000000
N	−0.190227	1.880509	0.000000
C	0.794567	2.795696	0.000000
C	0.263848	4.146684	0.000000
C	−1.098783	4.005669	0.000000
H	−2.293560	2.067723	0.000000
H	1.830194	2.494546	0.000000
H	0.835440	5.057343	0.000000
H	−1.844835	4.779890	0.000000
C	0.402478	−3.967147	0.000000
C	−0.875840	−3.355783	0.000000
C	−0.988913	−1.993904	0.000000
N	0.124447	−1.195237	0.000000
C	1.374323	−1.756914	0.000000
C	1.533892	−3.114144	0.000000
H	0.508910	−5.028647	0.000000
H	−1.767626	−3.948203	0.000000
H	−1.929299	−1.492255	0.000000
H	2.196329	−1.078466	0.000000
H	2.525509	−3.517828	0.000000
H	0.025808	−0.207749	0.000000