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SUPPLEMENTARY MATERIAL

for article to be Published in *J. CHEM. PHYS.***Full-dimensional ground- and excited-state potential energy surfaces and state couplings for photodissociation of thioanisole**

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S1. Symmetry of diabatic couplings along ϕ

By construction the absolute value of diabatic couplings has to be even about $\phi = n\pi/2$ along ϕ (n is an integer). To determine if the diabatic couplings themselves are even or odd, we used the plot of diabatic couplings along the C-C-S-C torsion with all other coordinates fixed at their values for the equilibrium geometry of the ground state (in which case ϕ is equal to the torsion), which is shown in Figure S1. U_{12} is even about $\phi = 0$ and 90° according to the shape of the curve and the fact that U_{12} is nonzero at the two C_s geometries with $\phi = 0$ and 90° . By the same token, U_{13} and U_{23} are odd about $\phi = 0$ and 90° according to the shape of the curves and the fact that U_{13} and U_{23} are zero at the two C_s geometries with $\phi = 0$ and 90° . (Note that U_{13} and U_{23} are not zero at $\phi = 90^\circ$ in the plot because it is an unrelaxed scan and the geometry at 90° does not have C_s symmetry.)

Such symmetries of diabatic couplings are dictated by symmetries of the corresponding diabatic wave functions. At $\phi = 0$, diabatic states 1 and 2 (DS1 and DS2) have A' symmetry while DS3 has A'' symmetry. At $\phi = 90^\circ$, DS1 and DS2 have A'' symmetry while DS3 has A' symmetry. (Such symmetries of diabatic wave functions can be seen from their dominant configurations.¹) Since ϕ behaves like an a'' mode, A' wave functions are even, and A'' wave functions are odd, about ϕ . The symmetry of coupling U_{ij} is in turn determined by the symmetry of diabatic states i and j . For instance, at $\phi = 0$, U_{13} is odd since DS1 (A') is even and DS3 (A'') is odd.

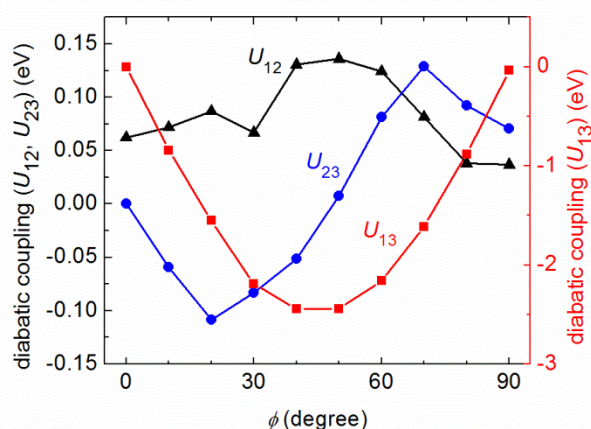


Figure S1. Diabatic couplings as a function of C-C-S-C torsion with all other coordinates fixed at their values for the equilibrium geometry of the ground state (in which case ϕ is equal to the torsion). (Note that the U_{13} curve has a different scale from U_{12} and U_{23} .)

S2 Geometric parameters of the D₀ and D₁ equilibrium geometries of thiophenoxyl radical

TABLE S1. Geometric parameters of the D₀ equilibrium geometry of thiophenoxyl radical

	APRP	M06-2X ^a
Bond lengths (Å)		
C1-C2	1.410	1.401
C2-C3	1.401	1.393
C3-C4	1.403	1.394
C4-C5	1.403	1.395
C5-C6	1.401	1.393
C6-C1	1.410	1.401
C1-S7	1.755	1.755
C-H (average)	1.090	1.090
Bond angles (deg)		
C1-C2-C3	119.7	119.7
C2-C3-C4	120.7	120.7
C3-C4-C5	119.4	119.4
C4-C5-C6	120.7	120.7
C5-C6-C1	119.6	119.7
C6-C1-C2	119.9	119.9

^a Basis set: jul-cc-pV(D+d)Z.

TABLE S2. Geometric parameters of the D₁ equilibrium geometry of thiophenoxyl radical.

	APRP	τ -HCTHhyb ^a
Bond lengths (Å)		
C1-C2	1.423	1.414
C2-C3	1.405	1.397
C3-C4	1.410	1.402
C4-C5	1.410	1.402
C5-C6	1.405	1.397
C6-C1	1.423	1.414
C1-S7	1.747	1.747
C-H (average)	1.093	1.093
Bond angles (deg)		
C1-C2-C3	119.8	119.8
C2-C3-C4	120.8	120.9
C3-C4-C5	119.3	119.2
C4-C5-C6	120.8	120.9
C5-C6-C1	119.8	119.8
C6-C1-C2	119.4	119.4

^a Basis set: jul-cc-pV(D+d)Z.

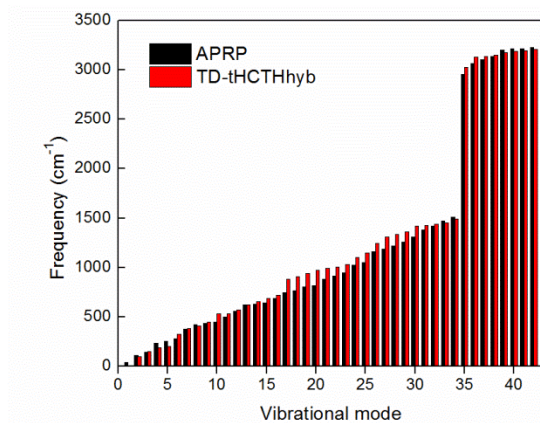
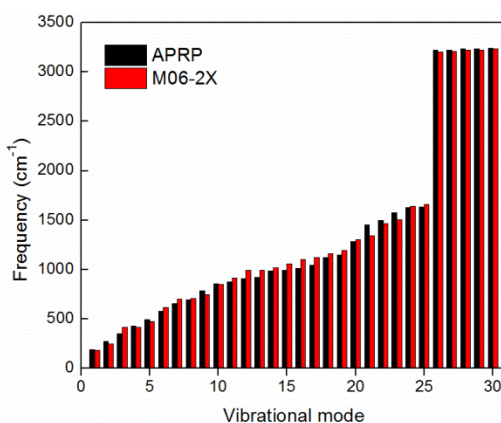
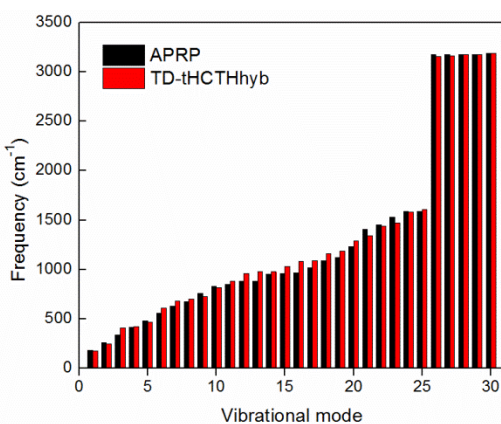
S3. Frequencies for S_1 of thioanisole and D_0 and D_1 of thiophenoxylTop: S_1 of thioanisole.Middle: D_0 of thiophenoxyl.Bottom: D_1 of thiophenoxyl.

Figure S2. Frequencies of equilibrium geometries computed by APRP, DFT with M06-2X, and TDDFT with τ -HCTHhyb.

S4. Proof of eq. (28) in the main text

Here we give a simple proof of eq. (28) in the text,

$$\frac{\partial V_i}{\partial x_\alpha} = \sum_j \sum_k C_{ji} \frac{\partial U_{jk}}{\partial x_\alpha} C_{ki} \quad (28)$$

where the (diagonal) adiabatic potential matrix \mathbf{V} and the diabatic potential matrix \mathbf{U} is related by eq. (27) in the text

$$V_i = \sum_j \sum_k C_{ji} U_{jk} C_{ki} \quad (27)$$

which is, in matrix notation, $\mathbf{V} = \mathbf{C}^T \mathbf{U} \mathbf{C}$. This, according to the orthogonality of \mathbf{C} , implies

$$\begin{aligned} \mathbf{U} \mathbf{C} &= \mathbf{C} \mathbf{V} \Rightarrow \sum_k U_{jk} C_{ki} = \sum_k C_{jk} V_k \delta_{ki} = C_{ji} V_i \\ \mathbf{C}^T \mathbf{U} &= \mathbf{V} \mathbf{C}^T \Rightarrow \sum_j C_{ji} U_{jk} = \sum_j V_i \delta_{ij} C_{kj} = C_{ki} V_i \end{aligned}$$

where δ is the Kronecker delta function.

To prove eq. (28), we start by applying the chain rule of differentiation on eq. (27)

$$\frac{\partial V_i}{\partial x_\alpha} = \sum_j \sum_k \frac{\partial C_{ji}}{\partial x_\alpha} U_{jk} C_{ki} + \sum_j \sum_k C_{ji} U_{jk} \frac{\partial C_{ki}}{\partial x_\alpha} + \sum_j \sum_k C_{ji} \frac{\partial U_{jk}}{\partial x_\alpha} C_{ki}$$

and we will prove that the sum of the first two terms on the right-hand side is zero.

The first term on the right-hand side is

$$\sum_j \sum_k \frac{\partial C_{ji}}{\partial x_\alpha} U_{jk} C_{ki} = \sum_j \frac{\partial C_{ji}}{\partial x_\alpha} \sum_k U_{jk} C_{ki} = \sum_j \frac{\partial C_{ji}}{\partial x_\alpha} C_{ji} V_i$$

The second term on the right-hand side is

$$\sum_j \sum_k C_{ji} U_{jk} \frac{\partial C_{ki}}{\partial x_\alpha} = \sum_k \frac{\partial C_{ki}}{\partial x_\alpha} \sum_j C_{ji} U_{jk} = \sum_k \frac{\partial C_{ki}}{\partial x_\alpha} C_{ki} V_i$$

Therefore the sum of the two terms above is

$$\begin{aligned} &\sum_j \sum_k \frac{\partial C_{ji}}{\partial x_\alpha} U_{jk} C_{ki} + \sum_j \sum_k C_{ji} U_{jk} \frac{\partial C_{ki}}{\partial x_\alpha} = \sum_j \frac{\partial C_{ji}}{\partial x_\alpha} C_{ji} V_i + \sum_k \frac{\partial C_{ki}}{\partial x_\alpha} C_{ki} V_i \\ &= V_i \frac{\partial}{\partial x_\alpha} \sum_j C_{ji} C_{ji} = V_i \frac{\partial}{\partial x_\alpha} 1 = 0 \end{aligned}$$

from which eq. (28) follows.

Additional References

¹ S. L. Li, X. Xu, C. E. Hoyer, and D. G. Truhlar, *J. Phys. Chem. Lett.* **6**, 3352 (2015).