Hybrid QM/QM Simulations of Excited-State Intramolecular Proton Transfer in the Molecular Crystal 7-(2-pyridyl)-indole

Supporting Information

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Embedded Cluster Calculations

In order to quantify the effect of polarization by the crystal lattice on the photoexcited 7PyIn molecule, we have constructed a simple embedded cluster model of the photoexcited molecule within the bulk lattice. In the experimental crystal structure of 7PyIn,^{1,2} we selected a single molecule of symmetry Type I, which will henceforth be referred to as the "central molecule" (see Figure 2 in the main body of the present work for an explanation of the symmetry labels). In addition to the central molecule, we selected all sixteen molecules whose centers of mass are located within 10 Å from the center of mass of the central molecule. From now on, these molecules will be referred to as the "surrounding molecules;" their purpose is to represent the polarizing influence of the bulk lattice. The embedded cluster model, shown in Figure 1, incorporated the central molecule and the sixteen surronding molecules, while the bulk lattice beyond the selected surrounding molecules was neglected. Figure 1: The seventeen-molecule embedded cluster model utilized to study the effect of polarization on the photoexcited 7PyIn molecule. The central molecule is shown using a ball-and-stick representation.



Three single point calculations were carried out on this embedded cluster model:

Calculation 1 was designed to provide information on the distribution of charge within the embedded cluster model. Here, the entire embedded cluster was treated at the quantum-mechanical, ground state PBE0/6-31G(d,p) level of theory as implemented in Gaussian 09.³ The charges on all atoms were calculated using the Merz-Singh-Kollman^{4,5} scheme, which fits atomic charges positioned at the nuclei to reproduce the electrostatic potential at a set of points outside the van der Waals radii of atoms in the system. For reference, in Figure 2 we present the atomic charges obtained from the



Figure 2: Atomic charges obtained using the Merz-Singh-Kollman scheme for the isolated molecule of the 1-syn tautomer at the PBE0/6-31G(d,p) level.

Merz-Singh-Kollman scheme for the isolated molecule of the 1-syn tautomer at the optimal PBE0/6-31G(d,p) geometry.

Calculation 2, here the central molecule was treated using the TD-DFT method using the PBE0 exchange-correlation functional⁶ coupled with the 6-31G(d,p) basis set, while the surrounding molecules were replaced by the atomic point charges that had been obtained from the Merz-Singh-Kollman fit carried out in Calculation 1. These point charges were included in the DFT Hamiltionian, allowing the electron density of the central molecule to experience the polarizing influence of the surrounding molecules. Thus this calculation probed the polarizing influence of the surrounding molecules on the central molecule. The five lowest singlet excited states of the central molecule were calculated, as well as the electric dipole moment of the S₁ state. The calculation of the dipole moment of the S₁ state was achieved using the Density=(Check,Transition=1) keyword in Gaussian 09; note the resulting dipole moment vector describes only the charge distribution of the central molecule, and does not include the dipole moment of the surrounding system of point charges.

Calculation 3 was performed for the central molecule in the absence

of the surrounding charges, and was otherwise identical to Calculation 2. Its purpose was to enable a comparison with the previous calculation, and thereby to allow us to quantify the effects of polarization of the central molecule by the surrounding charge distribution.

Kohn-Sham orbitals obtained from Calculations 2 and 3 were compared visually. For all orbitals up to HOMO+5, the shapes were found to change only marginally for both calculations, and the ordering of the orbitals was also retained.

In Table 1 below, we compare the excitation energies of the central molecule obtained in Calculations 2 and 3. Also listed for each excitation are the highest coefficients in the CI expansion as printed by Gaussian 09. Inspection of the data in Table 1 shows that the nature of each of the lowest five singlet excited states of 7PyIn is unchanged by the presence of the point charges generated by the embedded cluster model, and that the excitation energies are affected only slightly (by up to around 0.02 eV).

In order to further explore the effect of polarization on the central molecule, in Table 2 we compare the dipole moments of the S_1 state of the central molecule obtained from Calculations 2 and 3. It can be seen from Table 2 that the dipole moment of the molecule is altered by the presence of the surrounding point charges, but to only a small extent, which indicates that the central molecule in the S_1 state is only weakly polarized by the point charges.

	State	ΔE , eV ^{<i>a</i>}	Largest coefficients in the CI expansion b		
Calculation 2	S_1	3.9984	$51 \to 52: 0.69228$		
	S_2	4.2346	$50 \to 52: 0.66540$		
			$51 \rightarrow 53: -0.16676$		
			$51 \to 55 : 0.13490$		
	S ₃	4.4620	$50 \to 52: 0.16058$		
			$51 \to 53: 0.67380$		
	S_4	4.8903	$\begin{array}{l} 49 \rightarrow 52: \ -0.10339 \\ 50 \rightarrow 53: \ 0.68598 \end{array}$		
	S_5	4.9625	$\begin{array}{l} 48 \rightarrow 52: \ 0.65691 \\ \\ 48 \rightarrow 53: \ 0.14428 \\ \\ 49 \rightarrow 52: \ -0.17008 \end{array}$		
Calculation 3	S_1	4.0152	$51 \to 52: 0.69180$		
	S_2	4.2545	$50 \to 52: 0.66075$		
			$51 \to 53$: -0.18120		
			$51 \to 55: 0.14035$		
	S_3	4.4689	$50 \rightarrow 52 : 0.17435$ $51 \rightarrow 53 : 0.66974$ $48 \rightarrow 52 : 0.11993$		
	S_4	4.9082			
			$49 \to 52: -0.12162$		
			$50 \to 53: 0.67424$		
	S_5	4.9419	$48 \rightarrow 52: 0.64769$		
			$\begin{array}{l} 48 \rightarrow 53: \ 0.14081 \\ 49 \rightarrow 52: \ -0.15729 \\ 50 \rightarrow 53: \ -0.14647 \end{array}$		

Table 1: Excitation energies of the central molecule, obtained in the presence (Calculation 2) and in the absence (Calculation 3) of surrounding point charges.

 $^a~\Delta E$ is the energy of the respective excited state, relative to the ground state.

 b The Kohn-Sham orbitals are numbered according to their eigenvalues, with 51 and 52 corresponding to the HOMO and the LUMO, respectively.

Table 2: Electric dipole moment of the central molecule, obtained in the presence (Calculation 2) and in the absence (Calculation 3) of surrounding point charges.

	$ \mathbf{p} , \mathrm{D}^{a}$	p_x , D	p_y , D	p_z , D ^b
Calculation 2	5.6977	-4.1656	-1.0859	3.7326
Calculation 3	5.7871	-4.2769	-1.0576	3.7523

 a $|{\bf p}|$ is the magnitude of the dipole moment of the central molecule, in units of Debye (1 D = 3.33564×10^{-30} C \times m)

 b p_{x} , p_{y} and p_{z} are the projections of the dipole moment vector onto the Cartesian axes; see Figure 1 for the orientation of the embedded cluster model relative to the coordinate system.

In summary, single-point calculations carried out within the embedded cluster model, whereby the point charges on a set of molecules around the photoexcited 7PyIn molecule are included in the DFT Hamiltionian, suggest that the photoexcited molecule is not strongly polarized by the surrounding lattice. Although the embedded cluster model provides only an approximation of the true polarizing influence of the bulk lattice, since it contains a finite number of molecules whose centers of mass are located within a certain radius of the center of mass of the photoexcited molecule, and hence it cannot account for long-range polarization effects, we believe that it does allow for a semi-quantitative characterization of the importance of polarization effects in the photochemical reaction of crystalline 7PyIn. We therefore conclude that the polarization of the photoexcited molecule by the surrounding lattice is of minor importance in the description of the potential energy surface, and that the neglect of this effect, implicit in the subtractive QM/QM scheme, is a justifiable approximation that does not introduce significant error into the simulation results.

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