Supporting Information

Adenine ultrafast photorelaxation via electron driven proton-transfer

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CONTENTS

1. Computational details

Density functional theory (TDDFT)[1] method is used to simulate the excited-state nonadiabatic dynamics of adenine tautomers in water clusters, i.e. 7h-adenine+W and 9h-adenine+W. Geometrical optimization in the ground state (S0) carried out using the density functional theory (DFT) method choosing the long-range and dispersion corrected ωB97XD functional[2,3] along with 6-31G(d,p) basis set[4] for all calculations as implemented in Gaussian09 code.[5]

For initial condition generation, Wigner distribution[6] was used in the subspace of the ground-state for both water-adenine tautomers. The absorption spectrum is simulated from the first ten excited states with 200 points for each state. A total of the 58 trajectories are simulated including twenty-nine (29) each for the 7h-adenine+W and 9h-adenine+W respectively.

Nonadiabatic trajectory dynamics between the excited states are interpreted using the fewest-switches surface hooping[7] with decoherence corrections.[8] Trajectories ran for a maximum of 300 fs or until an S1−S0 energy gap smaller than 0.15 eV is reached. Integration is done with a time step of 0.5 fs for the classical equations and a time step of 0.025 fs for the quantum equations, using interpolated quantities between classical steps. Newton-X[9] interfaced with the gaussian09 program is used for dynamics simulations within the time-dependent DFT (TDDFT) method using the long-range and dispersion corrected ωB97XD functional. Single point complete active space self-consistent field (CASSCF)[10] calculations are done for the constructed active space composed of 12 electrons in the 12 orbitals. 6-31G(d,p) basis set is chosen for CASSCF calculations as implemented in the Gaussian09 code.

2. Ground-state vertical transitions

Vertical transition state energies calculated at the ground-state (S0) optimized geometries for 7h-adenine+W and 9h-adenine+W systems (Table S1).

Table S1. Vertical excitation energies, oscillator strengths, and state characters.

Adenine Type	E (eV)	f (state)	Character
7h-adenine+W	5.13	0.214	$\pi\pi^*$
	5.67	0.076	$n_N\pi^*$
	5.71	0.008	$\pi\pi^*$
	5.97	0.007	$n_N\pi^*$
	6.05	0.000	$n_{NO}\pi^*$
	6.54	0.003	$n_O\pi^*$
	6.66	0.342	$n_N\pi^*$
	6.95	0.193	$\pi\pi^*$
	7.13	0.005	$n_N\pi^*$
	7.18	0.003	$n_O\pi^*$
9h-adenine+W	5.25	0.311	$\pi\pi^*$
	5.39	0.016	$\pi\pi^*$
	5.87	0.000	$n_N\pi^*$
	6.26	0.005	$\pi\pi^*$
	6.42	0.002	$n_N\pi^*$
	6.61	0.103	$\pi\pi^*$
	6.74	0.003	$\pi\pi^*$
	6.75	0.002	$n_{NO}\pi^*$
	6.97	0.140	$\pi\pi^*$
	7.06	0.002	$\pi\sigma^*$

3. Distribution of the deactivation mechanisms

Table 1. Distribution of the percentage of deactivation pathways for 7H-adenine+W and 9H-adenine+W. Numerical values represent the percentage of the total trajectories divided into the possible outcome of simulations. Numerical values in parenthesis taken from previously published data and bold numbers indicate present calculational results.

Tautomer	Percentage deactivation mechanism					
	EDPT	H-diss	C2	C6	R-diss	S1-state
7H isomer	**65.51**	**0**	**0** $(10)^{10}$	**0** $(02)^{10}$	0	**34.48**
9H isomer	**0** $(06)^{10}$	**0**	**72.41** $(90)^{10}$, $(42, 54)^{13}$	**10.35** $(04)^{10}$, $(21, 23)^{13}$	0	**17.24**

4. TDDFT benchmarking using CASSCF calculations

In our TDDFT dynamics calculations, we chose the 0.15 eV energy gap to be considered as the CI point connecting the S1 state to the ground state. At the CI point, the TDDFT method may produce results that will not be the actual intersection geometry, which may lead to the artifact water-adenine EDPT pathway. In pursuance of a realistic intersection picture, the complete active space self-consistent field (CASSCF) method was used to cross-check the TDDFT dynamics results. Single-point CASSCF calculations were done using the selected trajectory (see Figure 4 in the manuscript) went to the S1-S0 intersection via EDPT reaction. The CASSCF S1-S0 energy gaps at several points along the trajectory computed. CASSCF gap values exceeding the gap values in the majority of the points along with TDDFT dynamics instantaneous gap trajectory (SI-Figure 1). At one point around 40 fs, the CASSCF gap is below the TDDFT trajectory values, which may cause by the hydrogen fluctuation at this point. However, for the intersection geometry, where the TDDFT gap value was 0.13 eV, CASSCF predicts a 0.27 eV energy gap which is close enough to be considered as the conical intersection. Overall, CASSCF calculation agrees to the TDDFT dynamics gap trajectory with an overestimation and, in close conformity to the TDDFT gap at intersection geometry.
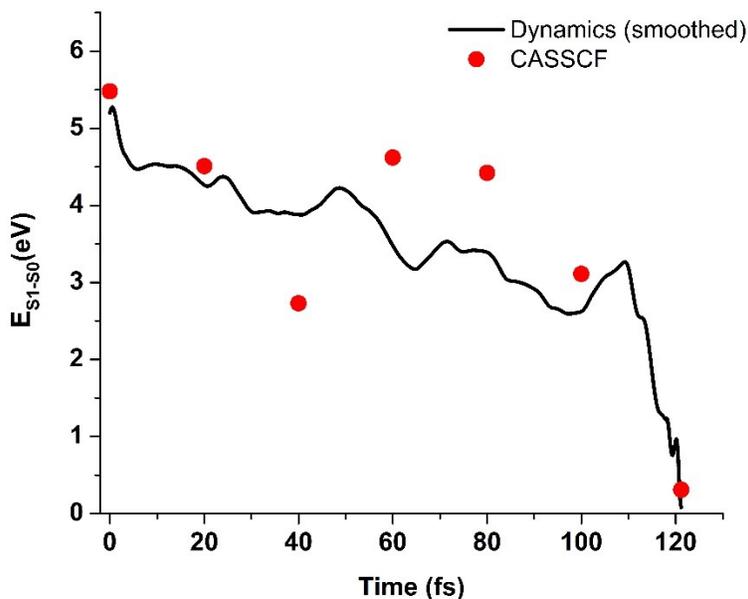
SI-Figure 1. The TDDFT dynamics energy gap trajectory and CASSCF single-point calculations at several points along the TDDFT trajectory.

5. Relaxed scan result

We constructed the minimum-energy reaction path for electron-driven proton-transfer (EDPT) from water to adenine as a relaxed scan. The driving coordinate for the reaction path is the OH bond stretching coordinate R_{OH} of the OH group of H_2O involved in the hydrogen-bonding with adenine (for $R_{OH} \approx 1.0$ Å, the H atom is covalently bonded to the oxygen atom of water, while for $R_{OH} \sim 2.0$Å, the hydrogen atom is covalently bonded to the nitrogen (N1-atom in this case of adenine). We have constructed this relaxed scan for the electronic ground state of the complex as well as for the lowest excited electronic state (SI-Figure 2).
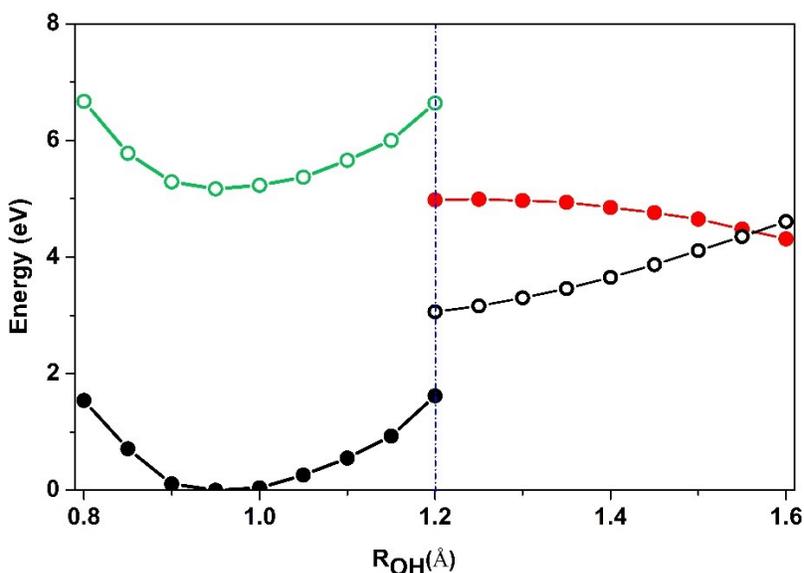
SI-Figure 2. Relaxed scan of the energy profiles of the electronic ground state and the lowest excited states of the 7h-adenine+W along minimum-energy paths for H atom transfer from water to 7h-adenine. Full circles indicate that the reaction path has been optimized in this state. Open circles represent the single point energies of electronic states calculated for geometries optimized in a different electronic state. The dashed vertical line separates the reaction path optimized in the S0 state (left) from the reaction path optimized in the lowest charge-transfer state (right). Black: S0 state; blue: locally excited 1ππ* states, red: charge-transfer state.

The energy profiles of the electronic ground state and the relevant excited electronic states along these reaction paths are shown in SI-Figure 2. For clarity, we present the energy profiles for the

reaction path optimized in the electronic ground state for $R_{OH} < 1.2$ Å and the energy profiles for the reaction path optimized in the $1\pi\pi^*$ state of charge-transfer character for $R_{OH} > 1.2$ Å. The left part of SI-Figure 2 reveals no influential force for proton-transfer in the locally excited-state of adenine in the 7h-adenine+W cluster since the excited-state energy profile is parallel to the PE function of the electronic ground-state. On the other hand, the right part tells that the lowest charge-transfer state is stabilized when the geometry is optimized in this state. Electron along with the proton transfer occurred indicating the true crossing (existence of a conical intersection). However, at R_{OH}=1.2 and afterward, the energy of the charge transfer state is below the Frank-Condon point at the optimized ground-state indicating the barrierless reaction. This is also found in a previous relaxed scan by Chaiwongwattana et al.[11] several studies by Wu et al.[12,13] where they show the barrierless EDPT reaction possibility in adenine ultrafast decay.

6. Additional references

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