

Electronic Supplementary Information: Excited State Proton Transfer in 1:1 Complexes of 2-(Oxazol-2-yl)-3-hydroxychromone with Water

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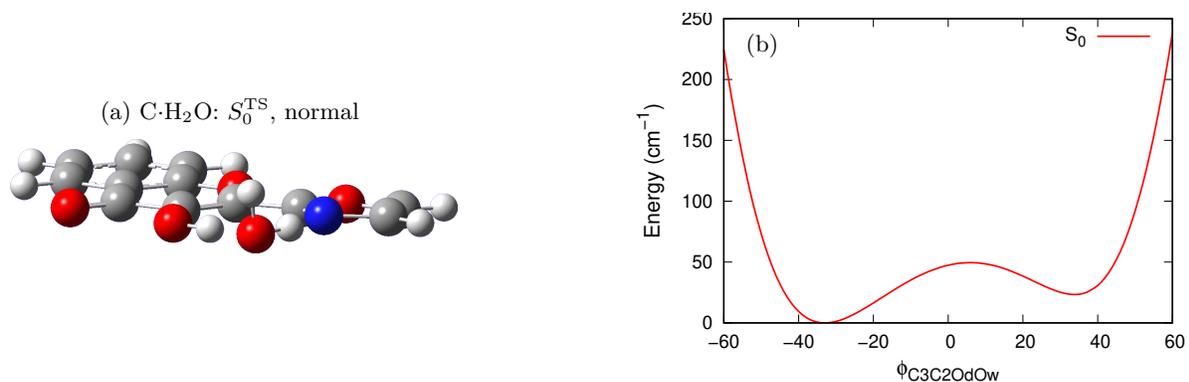


FIG. S-1. (a) Reactant-side transition state geometry on S_0 between C·H₂O[d] and [u] geometries. The latter are shown in Figure 2. (b) Relaxed S_0 scan along the $C_3C_2O_aO_w$ dihedral between C·H₂O[d] and [u] geometries. Note also that, at the optimized geometries of this scan, we find that S_1 energies show two deeper minima while S_2 shows a single minimum at a dihedral value close to 0°.

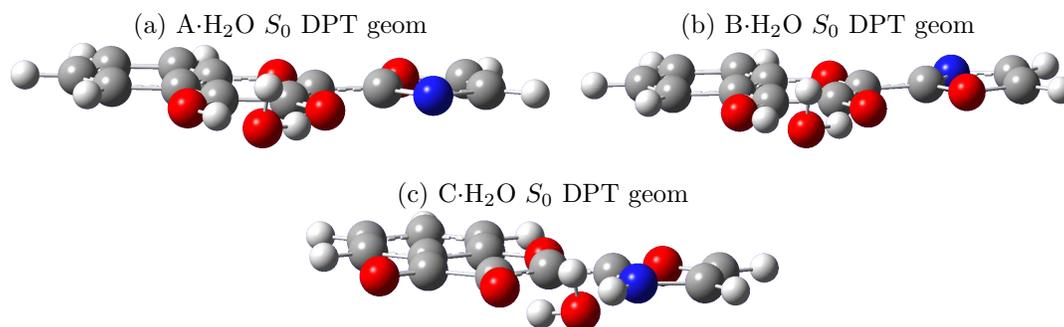


FIG. S-2. Ground state DPT minima of (a) A·H₂O, (b) B·H₂O, (c) C·H₂O. All structures were optimized at the B3LYP/cc-pVDZ level. See Table S-1 for the key geometrical parameters of these geometries.

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TABLE S-1. Key geometrical parameters of DPT forms of A·H₂O, B·H₂O and C·H₂O, optimized on S_0 . All calculations were carried out with B3LYP/cc-pVDZ. The distances are defined in Figure 1. The angles are defined as $\theta_{1dw} = \theta(\text{H}_1\text{O}_d\text{O}_w)$ and $\theta_{2wa} = \theta(\text{H}_2\text{O}_w\text{O}_a/\text{N}_a)$. Dihedrals are defined as follows: for A·H₂O and B·H₂O, $\phi_{dw} = \phi(\text{C}_1\text{C}_2\text{O}_d\text{O}_w)$, $\phi_{aw} = \phi(\text{C}_2\text{C}_1\text{O}_a\text{O}_w)$; for C·H₂O, $\phi_{dw} = \phi(\text{C}_3\text{C}_2\text{O}_d\text{O}_w)$, $\phi_{aw} = \phi(\text{C}_3\text{C}_4\text{N}_a\text{O}_w)$. All distances are in Å. All angles and dihedrals are in degrees.

Coord.	A·H ₂ O	B·H ₂ O	C·H ₂ O
r_1	1.587	1.585	1.750
r'_1	1.013	1.013	0.986
$r(\text{O}_d\text{O}_w)$	2.550	2.550	2.637
r_2	1.505	1.510	1.707
r'_2	1.039	1.037	1.047
$r(\text{O}_w\text{O}/\text{N}_a)$	2.543	2.546	2.747
r_3	0.970	0.970	0.970
r'_3	3.000	2.998	3.250
$r(\text{O}_d\text{O}_a)$	2.850	2.854	2.889
θ_{1dw}	9.0	8.744	11.5
θ_{2wa}	1.3	1.3	3.3
ϕ_{dw}	0.0	0.1	-5.2
ϕ_{aw}	-0.5	-0.2	4.8

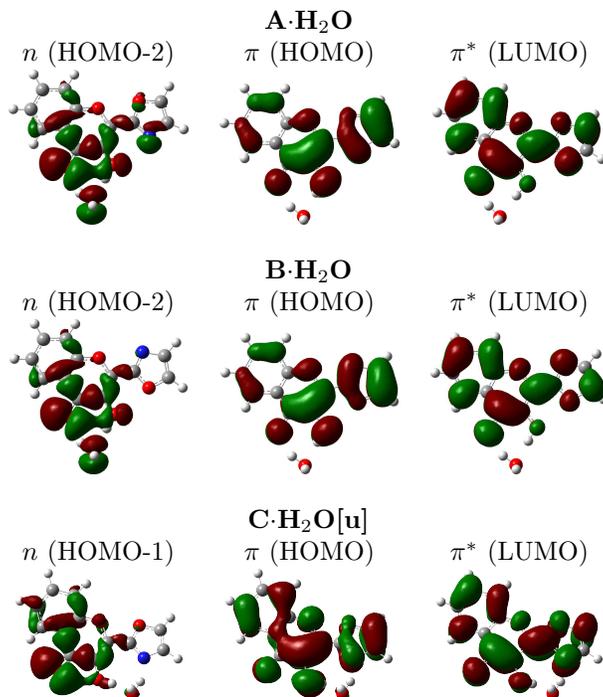


FIG. S-3. Orbitals involved in the descriptions of low-lying excited states of the OHC-water complexes. They are obtained with TDA-B3LYP/cc-pVDZ at the normal form geometries of the respective complexes.

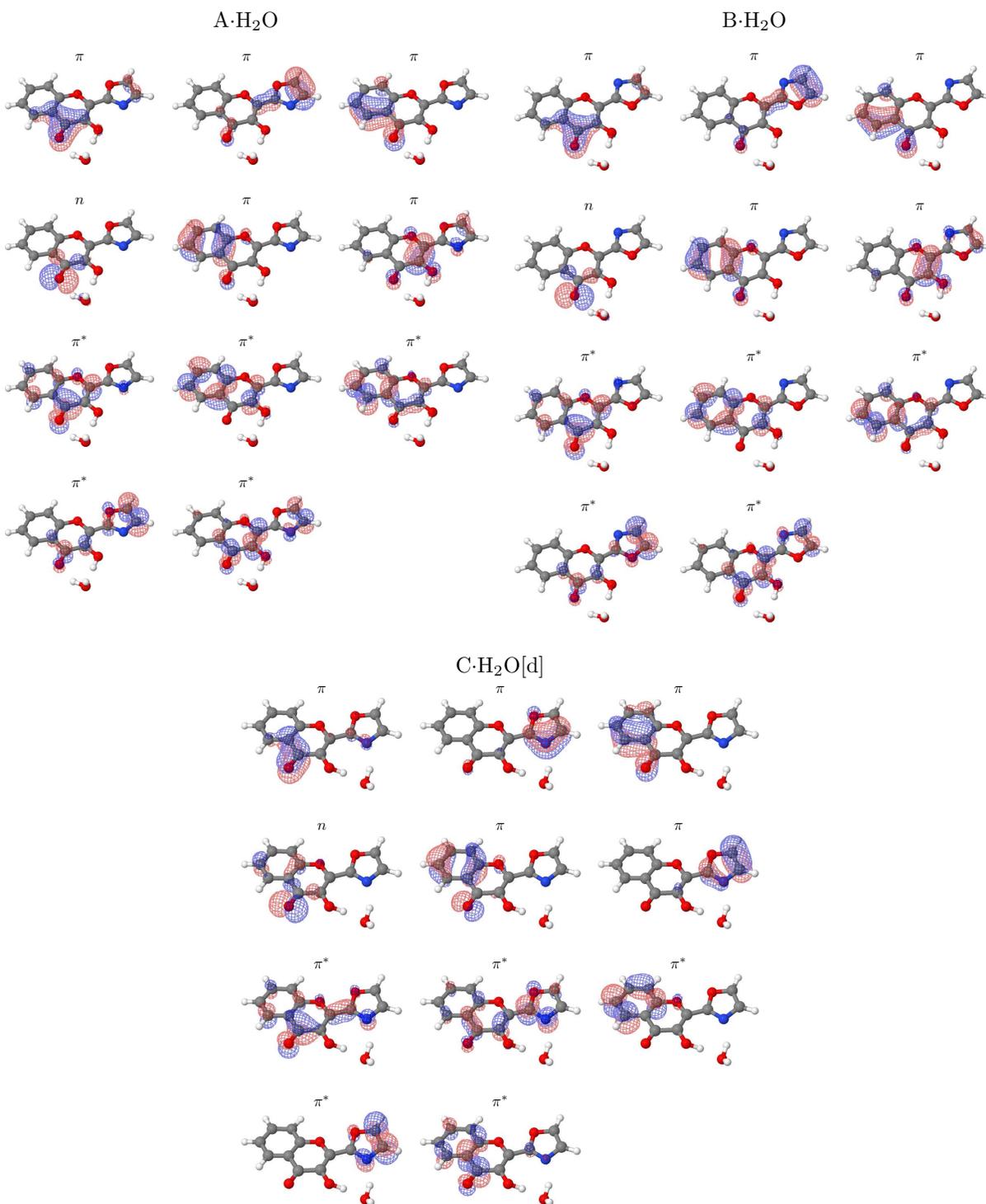


FIG. S-4. Orbitals of the (12e, 11o) active space for A·H₂O, B·H₂O and C·H₂O[d], obtained with four-state (S_0 - S_3) averaged CASSCF calculations. The orbitals for C·H₂O[u] are very similar to that of C·H₂O[d] and hence are not shown.

TABLE S-2. Vertical excitation energies and state characters of first three excited states of the three OHC-H₂O complexes obtained with XMS-CASPT2. The cc-pVDZ basis with the cc-pVDZ-JKFIt auxiliary basis was used. The geometries used are those optimized with B3LYP/cc-pVDZ. The energies compare well with excitation energies obtained with TDA-B3LYP/cc-pVDZ given in Table 2. The energies for C·H₂O[u] were not converged and are hence not shown.

A·H ₂ O		B·H ₂ O		C·H ₂ O[d]	
State	E_{ex} (eV)	State	E_{ex} (eV)	State	E_{ex} (eV)
S_1 ($\pi\pi^*$)	3.644	S_1 ($\pi\pi^*$)	3.676	S_1 ($n\pi^*$)	3.478
S_2 ($n\pi^*$)	3.839	S_2 ($n\pi^*$)	3.868	S_2 ($\pi\pi^*$)	3.994
S_3 ($\pi\pi^*$)	4.194	S_3 ($\pi\pi^*$)	4.175	S_3 ($\pi\pi^*$)	4.475

TABLE S-3. Key geometrical parameters of A·H₂O optimized in the excited states. All calculations are carried out using TDA-B3LYP/cc-pVDZ. The distances are defined in Figure 1. The angles are defined as $\theta_{1dw} = \theta(\text{H}_1\text{O}_d\text{O}_w)$ and $\theta_{2wa} = \theta(\text{H}_2\text{O}_w\text{O}_a)$. Dihedrals are defined as follows: $\phi_{dw} = \phi(\text{C}_1\text{C}_2\text{O}_d\text{O}_w)$, $\phi_{aw} = \phi(\text{C}_2\text{C}_1\text{O}_a\text{O}_w)$. All distances are in Å. All angles and dihedrals are in degrees.

Coord	S_1 normal	S_1 DPT, ‘up’	S_1 DPT, ‘down’	S_2 DPT
r_1	1.035	1.873	1.923	1.770
r'_1	1.518	0.979	0.977	0.987
$r(\text{O}_d\text{O}_w)$	2.553	2.659	2.576	2.666
r_2	0.998	1.706	1.713	1.617
r'_2	1.674	0.994	0.992	1.011
$r(\text{O}_w\text{O}_a)$	2.596	2.690	2.703	2.627
r_3	0.970	0.970	0.971	0.970
r'_3	3.018	3.049	3.118	3.093
$r(\text{O}_d\text{O}_a)$	2.843	2.866	2.869	2.861
θ_{1dw}	0.0	15.0	18.8	10.9
θ_{2wa}	17.7	3.9	1.4	0.3
ϕ_{dw}	-0.2	-27.2	14.1	-3.2
ϕ_{aw}	0.7	25.2	-12.1	2.1

TABLE S-4. Key geometrical parameters of B-H₂O optimized in the excited states. All calculations are carried out using TDA-B3LYP/cc-pVDZ. The distances are defined in Figure 1. The angles are defined as $\theta_{1dw} = \theta(\text{H}_1\text{O}_d\text{O}_w)$ and $\theta_{2wa} = \theta(\text{H}_2\text{O}_w\text{O}_a)$. Dihedrals are defined as follows: $\phi_{dw} = \phi(\text{C}_1\text{C}_2\text{O}_d\text{O}_w)$, $\phi_{aw} = \phi(\text{C}_2\text{C}_1\text{O}_a\text{O}_w)$. All distances are in Å. All angles and dihedrals are in degrees.

Coord	S_1	S_1	S_1	S_2
	normal	DPT, 'up'	DPT, 'pl'	D PT
r_1	1.037	1.911	2.469	3.074
r'_1	1.511	0.977	0.972	0.970
$r(\text{O}_d\text{O}_w)$	2.548	2.665	2.519	2.668
r_2	1.000	1.718	1.729	1.620
r'_2	1.656	0.992	0.988	1.010
$r(\text{O}_w\text{O}_a)$	2.585	2.697	2.716	2.629
r'_3	2.998	3.048	3.015	2.717
r_3	0.970	0.970	0.975	0.987
$r(\text{O}_d\text{O}_a)$	2.846	2.828	2.850	2.864
θ_{1dw}	0.266	15.8	22.4	17.7
θ_{2wa}	17.1	4.4	1.3	0.5
ϕ_{dw}	-0.0	-32.7	-8.2	3.4
ϕ_{aw}	1.3	31.2	6.9	-2.8

TABLE S-5. Key geometrical parameters of C-H₂O optimized in the excited states. All calculations are carried out using TDA-B3LYP/cc-pVDZ. The distances are defined in Figure 1. The angles are defined as $\theta_{1dw} = \theta(\text{H}_1\text{O}_d\text{O}_w)$ and $\theta_{2wa} = \theta(\text{H}_2\text{O}_w\text{N}_a)$. Dihedrals are defined as follows: $\phi_{dw} = \phi(\text{C}_3\text{C}_2\text{O}_d\text{O}_w)$, $\phi_{aw} = \phi(\text{C}_3\text{C}_4\text{N}_a\text{O}_w)$. All distances are in Å. All angles and dihedrals are in degrees.

Coord	S_2	S_2
	normal	DPT
r_1	1.036	1.915
r'_1	1.494	0.978
$r(\text{O}_d\text{O}_w)$	2.518	2.703
r_2	0.999	1.722
r'_2	1.713	1.047
$r(\text{O}_w\text{N}_a)$	2.658	2.758
r_3	0.970	0.970
r'_3	3.118	3.278
$r(\text{O}_d\text{N}_a)$	3.270	3.846
θ_{1dw}	6.5	14.6
θ_{2wa}	15.0	3.9
ϕ_{dw}	6.9	3.6
ϕ_{aw}	1.4	1.4

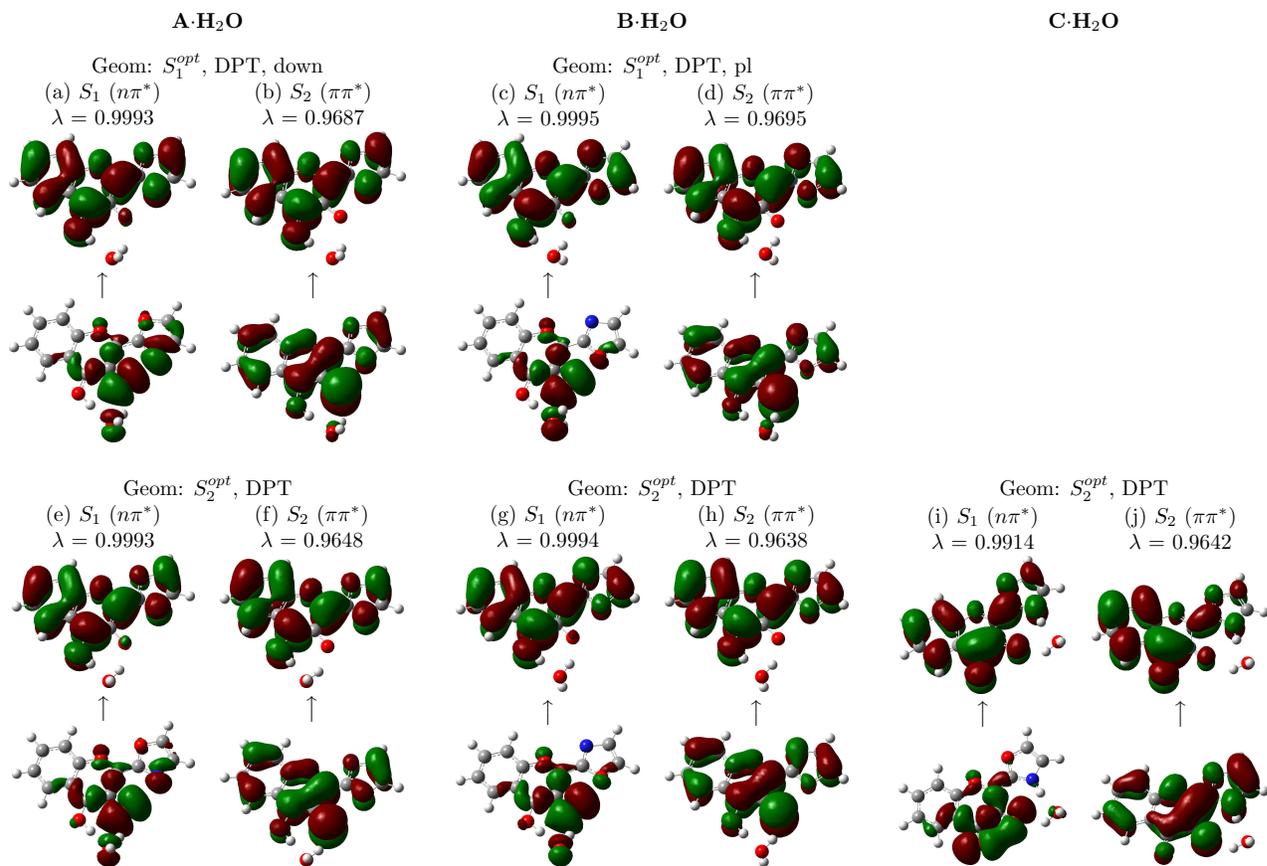


FIG. S-5. Natural transition orbitals (NTOs) at DPT geometries optimized on S_1 and S_2 . Shown are the hole-electron orbital pairs for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions at each geometry along with the corresponding occupation numbers (λ).

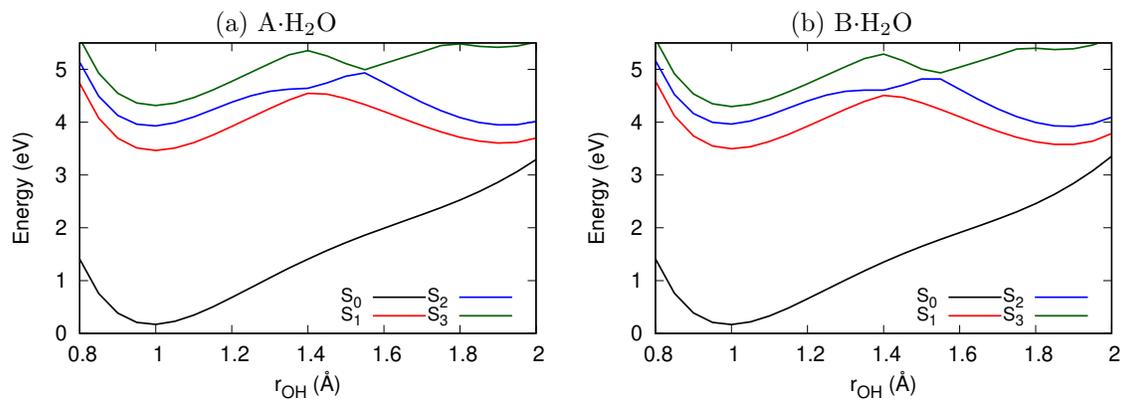


FIG. S-6. Potential energy profiles (unrelaxed scans) along r_2 ($\equiv r(O_w H_2)$) for (a) A·H₂O and (b) B·H₂O. All other geometrical parameters are fixed at their values for the respective S_1 normal form minima.

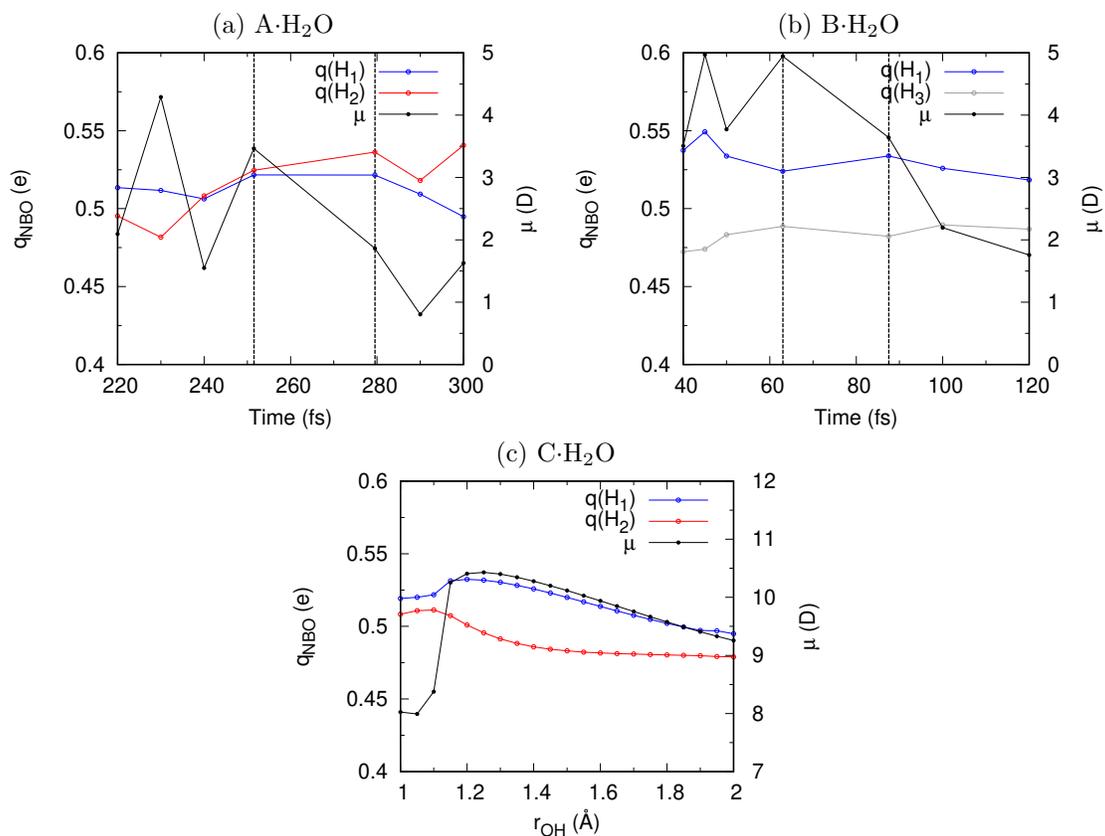


FIG. S-7. (a, b) NBO charges on the transferring H atoms and the molecular dipole moment for A·H₂O and B·H₂O at geometries sampled around the DPT events from donor-first DPT trajectories shown in Figures 7 and 8, respectively. The quantities are computed using the electronic density of the active state at that time point in the simulations. The dashed vertical lines mark the transfer events. (c) NBO charges on the transferring H atoms and the molecular dipole moment for C·H₂O, computed using the S_2 electronic density, along the relaxed DPT path on S_2 along $r_2 \equiv r(\text{O}_w\text{H}_2)$ shown in Figure 6. All computations are at the TDA-B3LYP/cc-pVDZ level.

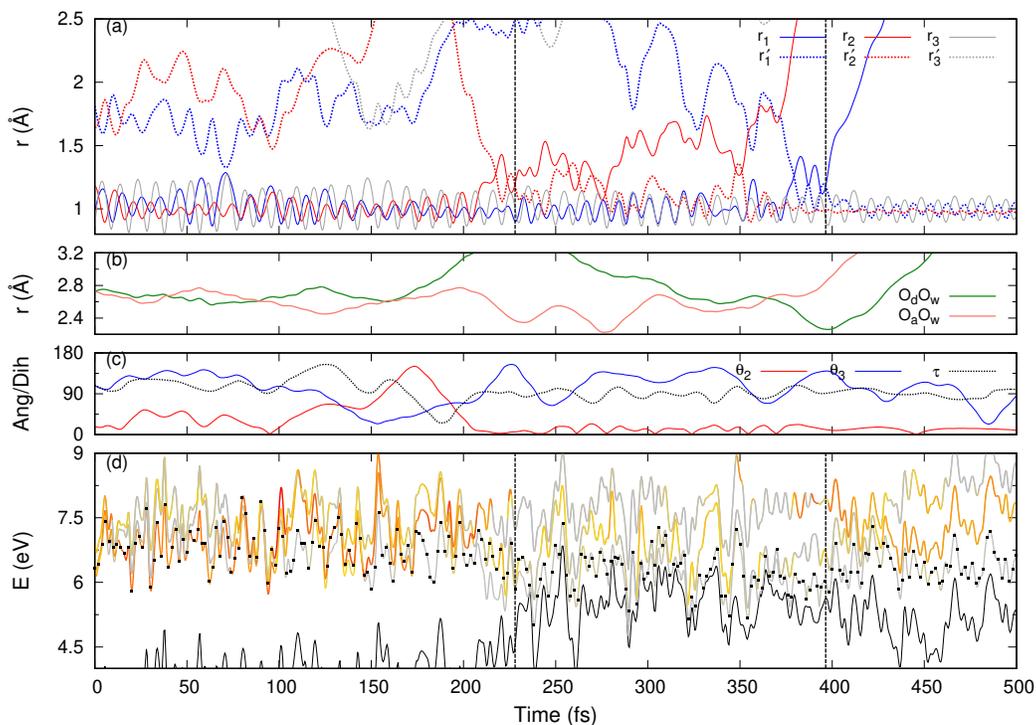


FIG. S-8. Representative trajectory showing acceptor-first DPT in A·H₂O. (a) Key OH distances; see Figure 1. The two black dashed vertical lines indicate the PT times. (b) O_dO_w and O_aO_w distances. (c) $\theta_2 \equiv \theta(O_aO_wH_2)$, $\theta_3 \equiv \theta(O_aO_wH_3)$. τ is the angle between vectors $\vec{r}_{O_wO_a}$ and $\vec{r}_{O_wH_3} \times \vec{r}_{O_wH_2}$; see text. (d) Evolution of the energies of S_1 - S_3 . The line colours indicates the oscillator strength red (bright, $\mathcal{O}(0.1)$), yellow (intermediate, $\mathcal{O}(0.01)$) and gray (dark, $\mathcal{O}(0.001)$) or lower). The black squares indicates the active state. The thin black line is the ground state.

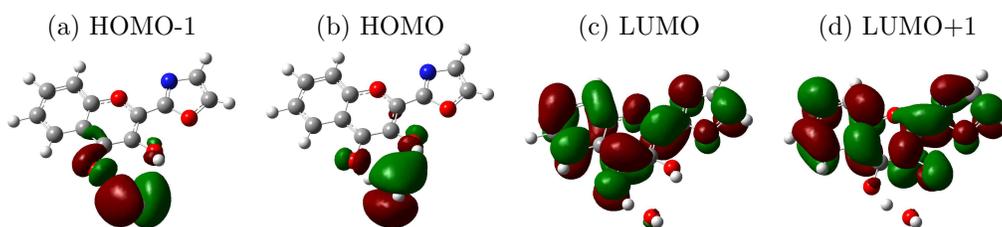


FIG. S-9. Key MOs for the acceptor-first DPT B·H₂O trajectory shown in Figure 11 in the region between the two PTs, for the geometry at 200 fs.

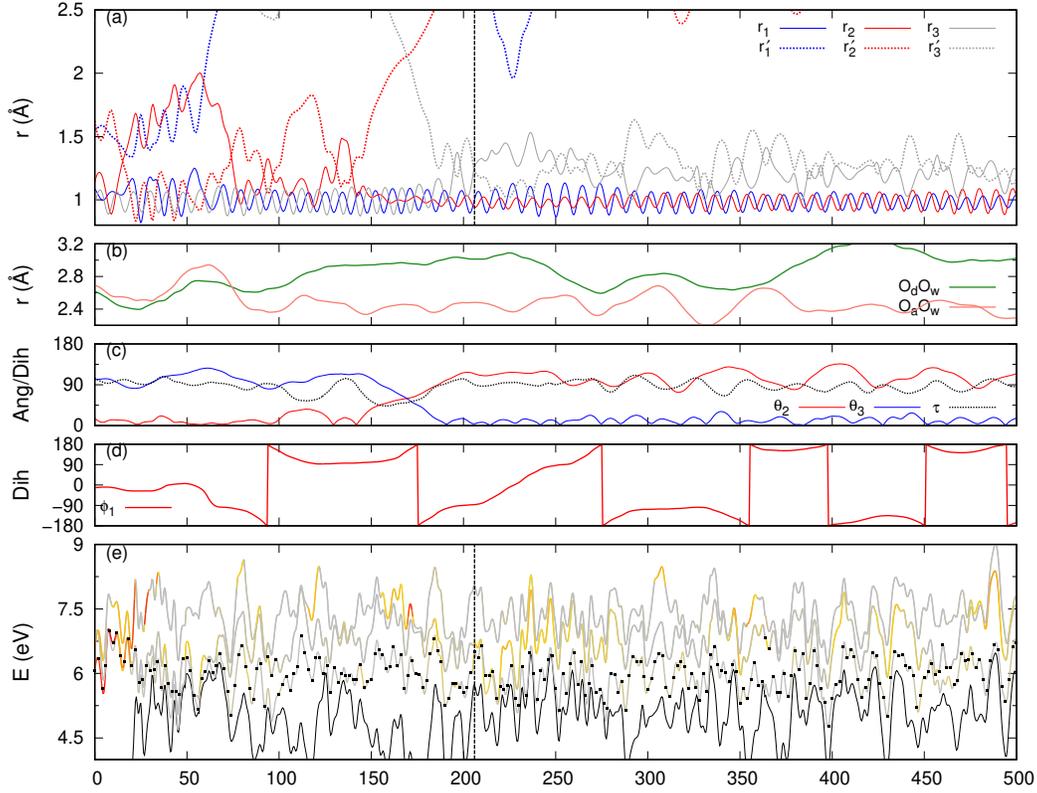


FIG. S-10. Representative trajectory showing SPT for $B \cdot H_2O$. (a) Key OH distances; see Figure 1. The black dashed vertical line indicate the PT time. (b) O_dO_w and O_aO_w distances. (c) $\theta_2 \equiv \theta(O_aO_wH_2)$, $\theta_3 \equiv \theta(O_aO_wH_3)$. τ is the angle between vectors $\vec{r}_{O_wO_a}$ and $\vec{r}_{O_wH_3} \times \vec{r}_{O_wH_2}$; see text. (d) The evolution of the OH torsion $\phi_1 = \phi(C_1C_2O_dH_1)$. (e) Evolution of the energies of S_1 - S_3 . The line colours indicates the oscillator strength red (bright, $\mathcal{O}(0.1)$), yellow (intermediate, $\mathcal{O}(0.01)$) and gray (dark, $\mathcal{O}(0.001)$ or lower). The black squares indicates the active state. The thin black line is the ground state.

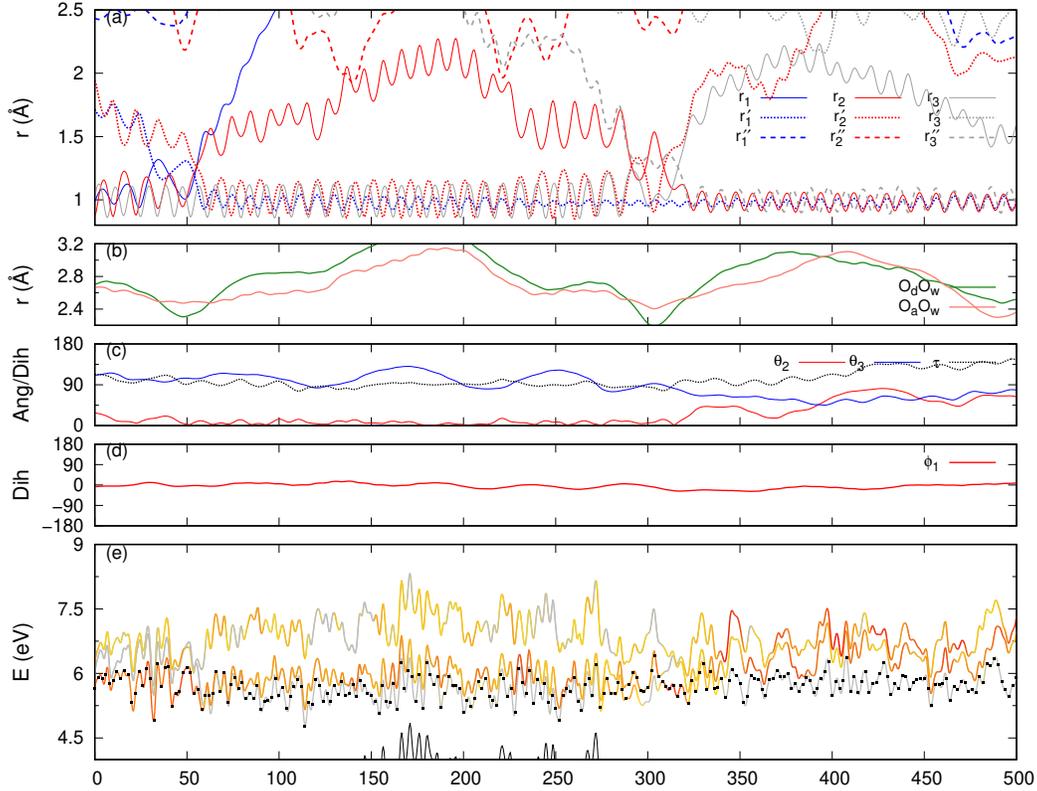


FIG. S-11. A non-PT B·H₂O trajectory showing reverse ESIntraPT around 325 fs after (donor-first) DPT around 50 fs. (a) Key OH distances; see Figure 1. (b) O_dO_w and O_aO_w distances. (c) $\theta_2 \equiv \theta(O_aO_wH_2)$, $\theta_3 \equiv \theta(O_aO_wH_3)$. τ is the angle between vectors $\vec{r}_{O_wO_a}$ and $\vec{r}_{O_wH_3} \times \vec{r}_{O_wH_2}$; see text. (d) The evolution of the OH torsion $\phi_1 = \phi(C_1C_2O_dH_1)$. (e) Evolution of the energies of S_1 - S_3 . The line colours indicates the oscillator strength red (bright, $\mathcal{O}(0.1)$), yellow (intermediate, $\mathcal{O}(0.01)$) and gray (dark, $\mathcal{O}(0.001)$ or lower). The black squares indicates the active state. The thin black line is the ground state.

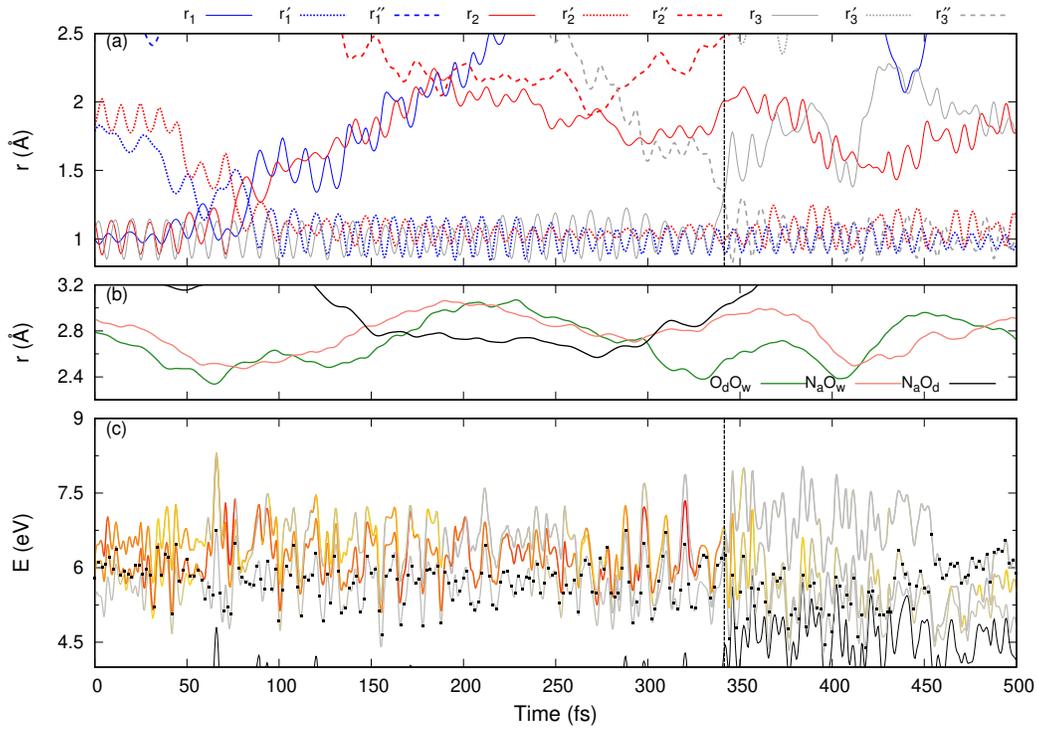


FIG. S-12. An $C\cdot H_2O[u]$ trajectory that first shows DPT around 75 fs but a water H atom returns to the donor oxygen around 350 fs [marked by the dashed black line in panel (a)]. (a) Key OH/NH distances; see Figure 1. (b) O_dO_w , N_aO_w and N_aO_d distances. (c) Evolution of the energies of S_1 - S_3 . The line colours indicates the oscillator strength red (bright, $\mathcal{O}(0.1)$), yellow (intermediate, $\mathcal{O}(0.01)$) and gray (dark, $\mathcal{O}(0.001)$ or lower). The black squares indicates the active state. The thin black line is the ground state.

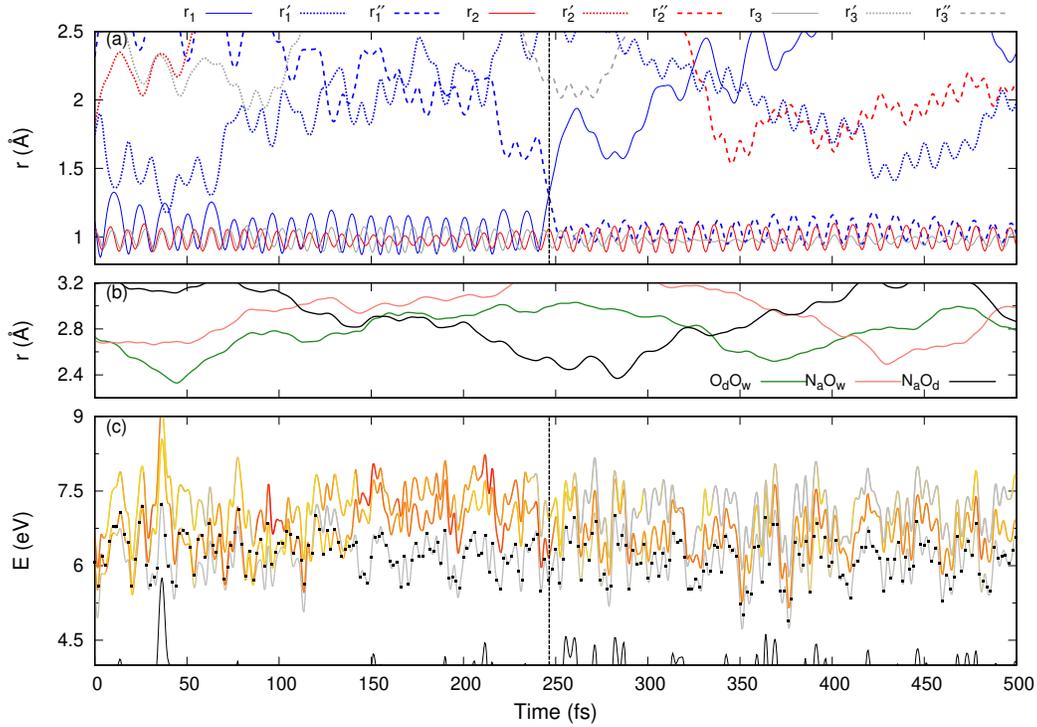


FIG. S-13. An C-H₂O[d] trajectory that shows ESIntraPT. (a) Key OH/NH distances; see Figure 1. The black dashed vertical line shows the PT time. (b) O_dO_w , N_aO_w and N_aO_d distances. (c) Evolution of the energies of S_1 - S_3 . The line colours indicates the oscillator strength red (bright, $\mathcal{O}(0.1)$), yellow (intermediate, $\mathcal{O}(0.01)$) and gray (dark, $\mathcal{O}(0.001)$ or lower). The black squares indicates the active state. The thin black line is the ground state.

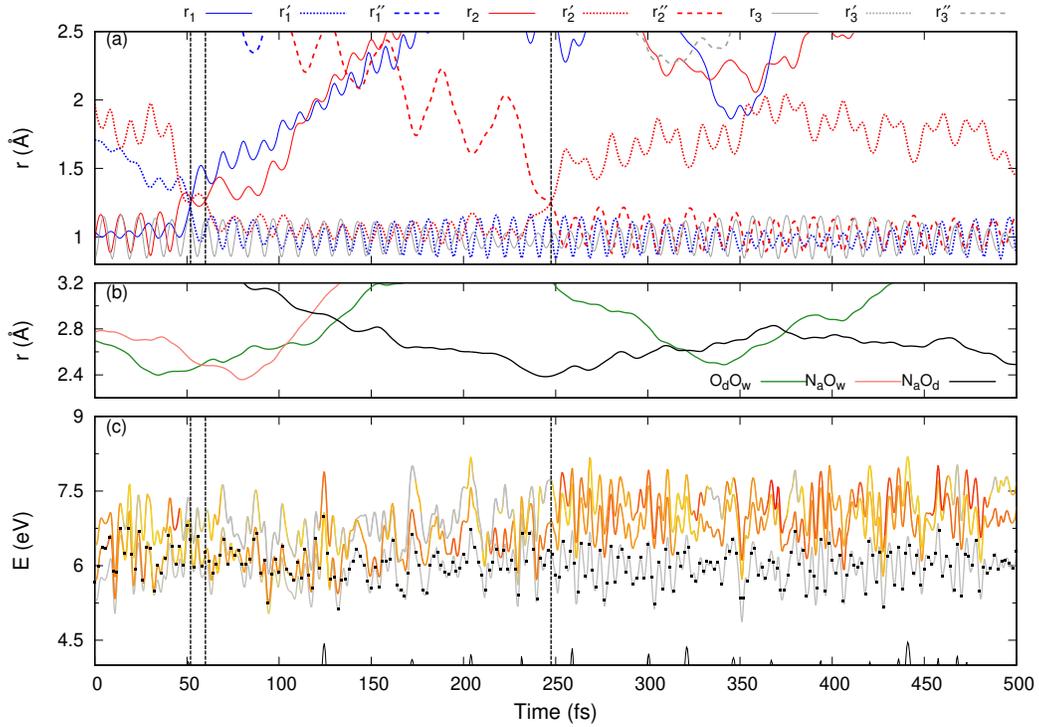


FIG. S-14. A non-PT C·H₂O[u] trajectory that first shows early DPT marked by vertical dashed lines around 50 fs, followed by reverse ESIntraPT. (a) Key OH/NH distances; see Figure 1. The black dashed vertical line shows the PT time. (b) O_dO_w , N_aO_w and N_aO_d distances. (c) Evolution of the energies of S_1 - S_3 . The line colours indicates the oscillator strength red (bright, $\mathcal{O}(0.1)$), yellow (intermediate, $\mathcal{O}(0.01)$) and gray (dark, $\mathcal{O}(0.001)$ or lower). The black squares indicates the active state. The thin black line is the ground state.

TABLE S-6. Number of trajectories for each OHC-water complex where regions showing an energy gap ΔE_{10} between S_1 and S_0 of under 0.1 eV are found. The notation n/m indicates n trajectories out of m of a given type that show such low gaps. Note that these include cases where the gap becomes negative as well; this occurs in nearly all of the n trajectories in a given type with the exception of 0-2 of them.

	All	DPT		SPT	non-PT
		Donor-first	Acc.-first		
A·H ₂ O	26/50	0/8	6/9	11/12	9/21
B·H ₂ O	22/50	0/8	4/6	11/13	7/23
C·H ₂ O[u]	3/50	0/8	-	1/3	2/39

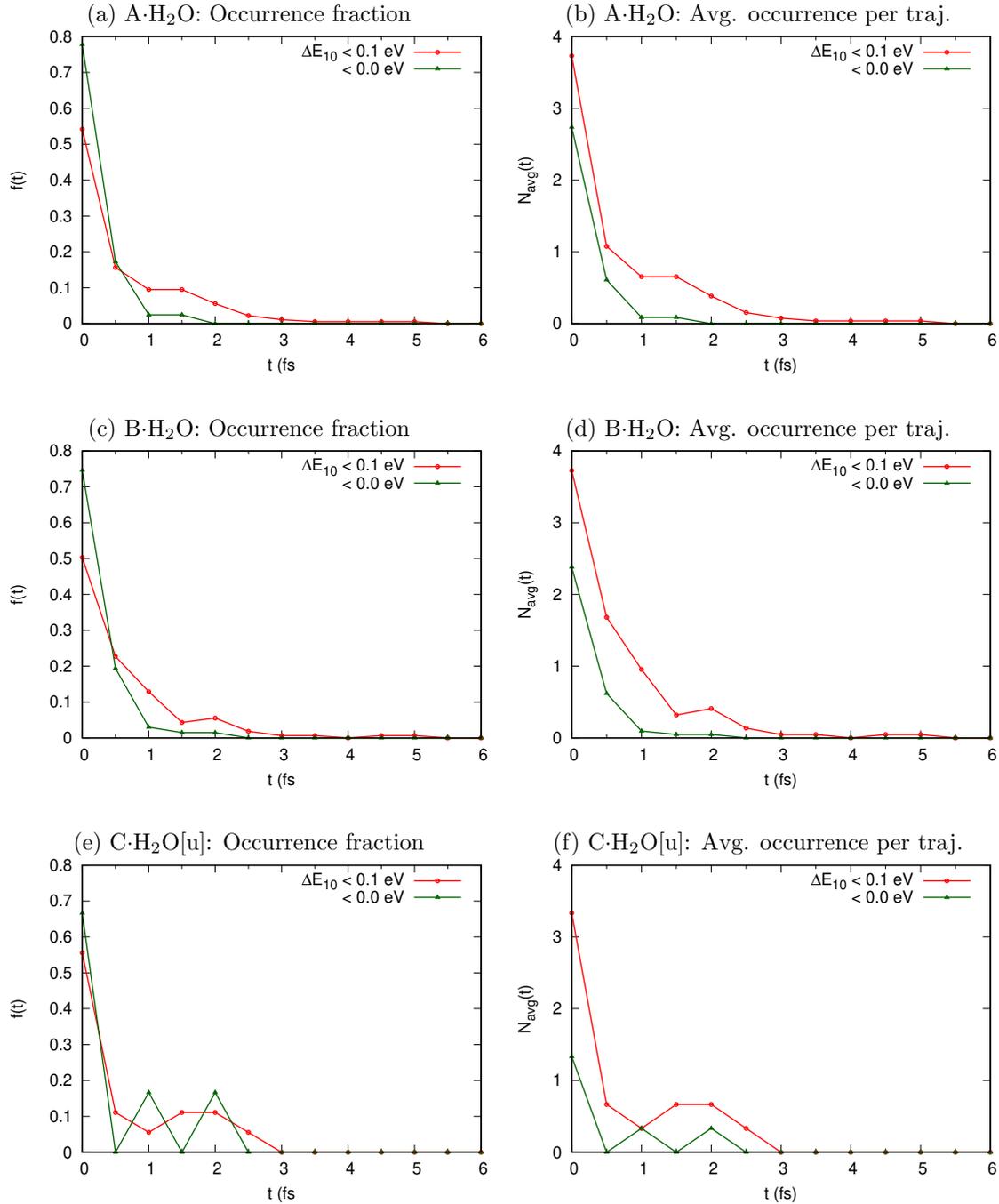


FIG. S-15. (a, c, e) Occurrence fractions $f(t)$ of various *contiguous* time durations t spent by the trajectories in regions showing $\Delta E_{10} < 0.1$ eV (including negative values) and $\Delta E_{10} < 0.0$ eV. (b, d, f) Average frequency of occurrence per trajectory $N_{avg}(t)$ of regions of various *contiguous* time durations, counting only those trajectories that show issues. In both sets of plots, $t = 0$ fs means single point excursions below the threshold while 0.5 fs means two successive points below the threshold, etc. See text for details.

TABLE S-7. Analysis of statistical reliability of the trajectory classification. For each of A·H₂O and B·H₂O, from a serially ordered set of $N_{tot} = 50$ trajectories, $N_{sample} = 25$ random subsets of trajectories of size $N_{sub} = 30$ are sampled. This is akin to obtaining N_{sub} unique random integers out of N_{tot} unique integers. The numbers of trajectories in the four categories (donor-first and acceptor-first DPT, SPT and non-PT) are obtained for each subset. Statistical analysis of this data, i.e. average number (N_k) and standard derivation (σ_k) over N_{sample} subsets and same numbers as percentage values (N_k/N_{sub} and σ_k/N_{sub}) are given. Results from two independent rounds (round 1 and 2) of such sampling are shown. The similarity of the percentage values for the original (ref) data and sub-sampled data indicated reasonable statistical reliability of the classification.

k	A·H ₂ O					
	Ref		Round 1		Round 2	
	N_k	%	$N_k \pm \sigma_k$	%	$N_k \pm \sigma_k$	%
Donor-first DPT	8	16%	4.7±1.3	15.7±4.5	4.8±1.4	15.9±4.7
Acc.-first DPT	9	18%	5.1±1.1	17.1±3.6	5.8±1.4	19.5±4.7
SPT	12	24%	7.3±1.4	24.4±4.6	6.9±1.6	22.9±5.4
non-PT	21	42%	12.8±1.6	42.8±5.2	12.5±1.7	41.7±5.5

k	B·H ₂ O					
	Ref		Round 1		Round 2	
	N_k	%	$N_k \pm \sigma_k$	%	$N_k \pm \sigma_k$	%
Donor-first DPT	8	16%	4.8±1.3	15.9±4.5	4.8±1.2	16.1±3.9
Acc.-first DPT	6	12%	3.7±1.0	12.3±3.2	3.3±1.3	11.1±4.3
SPT	13	26%	7.7±1.2	25.7±4.0	7.8±1.5	26.1±4.9
non-PT	23	46%	13.8±1.4	46.1±4.7	14.0±1.8	46.7±6.1