Electronic Supplementary Information: Excited State Proton Transfer in 2-(Oxazol-2-yl)-3-hydroxychromone

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TABLE S-1. Ground state energies (in kcal/mol) of OHC-A, B, C and D and their populations (percentages in parentheses) estimated at 298 K. With each method, the most stable conformer defines the zero of the energy scale. In all cases, the aug-cc-pVDZ basis is used.

Method	OHC-A	OHC-B	OHC-C	OHC-D
MP2	0.906	0.0	0.354	4.503
	(12.3%)	(56.6%)	(31.1%)	(0.0%)
B3LYP	0.834	0.162	0.0	5.795
	(12.2%)	(37.9%)	(49.9%)	(0.0%)
CAM-B3LYP	1.249	0.478	0.0	6.043
	(7.7%)	(28.5%)	(63.8%)	(0.0%)
ωB97XD	1.354	0.635	0.0	6.125
	(7.0%)	(23.7%)	(69.3%)	(0.0%)

TABLE S-2. Vertical excitation energies (VEE) of OHC-A, B and C at the TDA-B3LYP, TD-B3LYP, TD-CAM-B3LYP and TD-ωB97XD with the cc-pVDZ basis. All energies are in eV. In each case, the minima are optimized on the ground state with the respective functional. The state order is preserved across calculations. TD-B3LYP yields VEE values that are slightly lower than TDA-B3LYP; the $\pi\pi^*$ states are lower by 0.1-0.2 eV while the $n\pi^*$ states are less affected. TD-CAM-B3LYP and TD-ωB97XD overestimate the energies of all states by about 0.4-0.5 eV.

Conformer	State	TDA-B3LYP	TD-B3LYP	TD-CAM-B3LYP	TD-ωB97XD
OHC-A	S_1 ($\pi\pi^*$)	3.73	3.53	4.15	4.16
	S_2 ($n\pi^*$)	3.96	3.86	4.32	4.31
	S_3 ($\pi\pi^*$)	4.28	4.19	4.69	4.70
OHC-B	S_1 ($\pi\pi^*$)	3.76	3.56	4.17	4.19
	S_2 ($n\pi^*$)	3.98	3.97	4.34	4.34
	S_3 ($\pi\pi^*$)	4.27	4.17	4.66	4.68
OHC-C	S_1 ($n\pi^*$)	3.41	3.39	3.84	3.85
	S_2 ($\pi\pi^*$)	3.82	3.60	4.19	4.20
	S_3 ($\pi\pi^*$)	4.36	4.26	4.75	4.76

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TABLE S-3. Cartesian coordinates (in Å) of the ground state minimum energy structures of OHC-A, B and C. The z compoments are abbreviated as they are zero-valued.

OHC-A $S_{0,min}$				OHC-B $S_{0,min}$				OHC-C $S_{0,min}$			
C	−0.544182	2.180273	0.0	C	−0.370917	2.190365	0.0	C	−0.436502	2.152230	0.0
N	0.094680	3.320601	0.0	N	−1.603632	2.674487	0.0	N	0.383328	3.197169	0.0
C	−2.117545	3.663903	0.0	C	−1.463754	4.032148	0.0	C	−1.740461	3.937966	0.0
C	−0.901659	4.279193	0.0	C	−0.131027	4.383517	0.0	C	−0.420044	4.309200	0.0
H	−3.147055	3.997010	0.0	H	−2.320826	4.687355	0.0	H	−2.651544	4.511327	0.0
H	−0.676969	5.339901	0.0	H	0.367240	5.338550	0.0	H	−0.007243	5.304885	0.0
C	−0.000000	0.835224	0.0	C	0.000000	0.790431	0.0	C	−0.000000	0.776991	0.0
C	1.329938	0.505417	0.0	C	1.275975	0.307099	0.0	C	1.319353	0.415386	0.0
C	1.759686	−0.896277	0.0	C	1.569983	−1.113123	0.0	C	1.697091	−1.009599	0.0
C	0.689106	−1.887795	0.0	C	0.399178	−1.983553	0.0	C	0.544484	−1.937038	0.0
C	−0.646196	−1.447623	0.0	C	−0.877956	−1.402280	0.0	C	−0.769437	−1.455862	0.0
O	−0.974976	−0.126449	0.0	O	−1.063473	−0.053406	0.0	O	−1.040652	−0.116559	0.0
O	2.974132	−1.144089	0.0	O	2.751436	−1.482031	0.0	O	2.858643	−1.385492	0.0
O	2.319738	1.411572	0.0	O	2.360696	1.129676	0.0	O	2.318489	1.305755	0.0
H	3.137703	0.870230	0.0	H	3.125944	0.519985	0.0	H	1.937476	2.214621	0.0
C	0.947282	−3.275844	0.0	C	0.505236	−3.386343	0.0	C	0.744740	−3.328637	0.0
C	−0.100296	−4.182185	0.0	C	−0.631462	−4.171341	0.0	C	−0.331284	−4.196737	0.0
C	−1.432642	−3.718099	0.0	C	−1.901597	−3.568003	0.0	C	−1.640351	−3.688449	0.0
C	−1.713428	−2.358795	0.0	C	−2.033195	−2.190392	0.0	C	−1.866298	−2.322200	0.0
H	1.986285	−3.601797	0.0	H	1.497741	−3.820290	0.0	H	1.766991	−3.686937	0.0
H	0.100857	−5.252957	0.0	H	−0.547804	−5.251507	0.0	H	−0.167860	−5.267661	0.0
H	−2.255298	−4.433520	0.0	H	−2.791598	−4.186705	0.0	H	−2.484751	−4.367950	0.0
H	−2.734745	−1.981816	0.0	H	−3.000684	−1.704299	0.0	H	−2.868350	−1.911079	0.0
O	−1.905634	2.313266	0.0	O	0.557921	3.201305	0.0	O	−1.738450	2.559183	0.0

TABLE S-4. Cartesian coordinates (in Å) of the optimal geometries on the lowest excited bright ($\pi\pi^*$) state for OHC-A, B and C in the normal form (Franck-Condon region). The z compoments are abbreviated as they are zero-valued.

OHC-A $S^{FC}_{1,min}$ ($\pi\pi^*$)				OHC-B $S^{FC}_{1,min}$ ($\pi\pi^*$)				OHC-C $S^{FC}_{2,min}$ ($\pi\pi^*$)			
C	−0.463577	2.219626	0.0	C	−0.356142	2.227824	0.0	C	−0.275483	2.201110	0.0
N	0.246321	3.334488	0.0	N	−1.568508	2.755688	0.0	N	0.661108	3.148470	0.0
C	−1.950445	3.784333	0.0	C	−1.350803	4.106556	0.0	C	−1.375120	4.061374	0.0
C	−0.687470	4.333775	0.0	C	0.003476	4.356236	0.0	C	−0.034387	4.333351	0.0
H	−2.960563	4.181404	0.0	H	−2.168328	4.824056	0.0	H	−2.278252	4.661470	0.0
H	−0.408435	5.385052	0.0	H	0.621590	5.248408	0.0	H	0.464585	5.298789	0.0
C	−0.000000	0.866097	0.0	C	0.000000	0.841546	0.0	C	0.000000	0.800963	0.0
C	1.319619	0.463327	0.0	C	1.275468	0.315359	0.0	C	1.321068	0.317947	0.0
C	1.708347	−1.005613	0.0	C	1.529155	−1.180385	0.0	C	1.613215	−1.154676	0.0
C	0.633626	−1.933839	0.0	C	0.374485	−2.004407	0.0	C	0.415437	−1.979723	0.0
C	−0.703346	−1.438493	0.0	C	−0.911330	−1.384478	0.0	C	−0.878613	−1.410238	0.0
O	−0.993687	−0.071838	0.0	O	−1.075983	0.001066	0.0	O	−1.062855	−0.027146	0.0
O	2.943926	−1.200342	0.0	O	2.745369	−1.483373	0.0	O	2.776661	−1.569315	0.0
O	2.376331	1.246508	0.0	O	2.405651	0.993262	0.0	O	2.351601	1.139309	0.0
H	3.112491	0.544424	0.0	H	3.065806	0.213699	0.0	H	2.004992	2.091011	0.0
C	0.819224	−3.354573	0.0	C	0.425156	−3.435583	0.0	C	0.497842	−3.397718	0.0
C	−0.285870	−4.203886	0.0	C	−0.753854	−4.178036	0.0	C	−0.667118	−4.182487	0.0
C	−1.587379	−3.691971	0.0	C	−2.001868	−3.545473	0.0	C	−1.927564	−3.590336	0.0
C	−1.799148	−2.284133	0.0	C	−2.080471	−2.125655	0.0	C	−2.038375	−2.171687	0.0
H	1.839143	−3.738177	0.0	H	1.404676	−3.913309	0.0	H	1.492081	−3.844241	0.0
H	−0.131052	−5.285553	0.0	H	−0.701011	−5.269393	0.0	H	−0.578511	−5.271391	0.0
H	−2.447507	−4.363008	0.0	H	−2.921320	−4.132646	0.0	H	−2.831936	−4.200304	0.0
H	−2.800869	−1.854278	0.0	H	−3.037224	−1.603265	0.0	H	−3.006152	−1.669566	0.0
O	−1.820188	2.433275	0.0	O	0.649430	3.161746	0.0	O	−1.540404	2.698111	0.0

TABLE S-5. Cartesian coordinates (in Å) of the optimal geometries on the lowest excited bright ($\pi\pi^*$) state for OHC-A, B and C in the proton-transferred (PT) form. The z components are abbreviated as they are zero-valued.

OHC-A $S^{PT}_{2,min}$ ($\pi\pi^*$)				OHC-B $S^{PT}_{2,min}$ ($\pi\pi^*$)				OHC-C $S^{PT}_{2,min}$ ($\pi\pi^*$)			
C	−2.267923	−0.158557	0.000005	C	−0.446657	2.212240	0.0	C	−0.266302	2.166208	0.0
N	−3.302194	0.648207	0.000084	N	−1.693946	2.627801	0.0	N	0.648994	3.169390	0.0
C	−3.970008	−1.492703	−0.000017	C	−1.592675	4.003646	0.0	C	−1.341103	4.085439	0.0
C	−4.393552	−0.194740	0.000056	C	−0.275762	4.362708	0.0	C	−0.019733	4.379155	0.0
H	−4.454166	−2.463601	−0.000042	H	−2.471891	4.643736	0.0	H	−2.244758	4.682949	0.0
H	−5.411346	0.188498	0.000100	H	0.270794	5.299876	0.0	H	0.494003	5.334555	0.0
C	−0.857872	0.150344	−0.000020	C	0.000000	0.840152	0.0	C	0.000000	0.794661	0.0
C	−0.282765	1.407765	−0.000010	C	1.301885	0.371950	0.0	C	1.375715	0.321340	0.0
C	1.140954	1.525719	−0.000009	C	1.541402	−1.036542	0.0	C	1.619045	−1.187786	0.0
C	1.965147	0.371227	−0.000018	C	0.459635	−1.953190	0.0	C	0.413115	−1.999288	0.0
C	1.299953	−0.884276	−0.000022	C	−0.847127	−1.392963	0.0	C	−0.881817	−1.427945	0.0
O	−0.063648	−0.973628	−0.000055	O	−1.052315	−0.043785	0.0	O	−1.072192	−0.030748	0.0
O	1.664908	2.753930	0.000000	O	2.809645	−1.455041	0.0	O	2.777333	−1.619978	0.0
O	−0.956705	2.551149	−0.000033	O	2.383711	1.142685	0.0	O	2.316997	1.135713	0.0
H	0.874691	3.344565	0.000059	H	3.331866	−0.618281	0.0	H	1.645280	2.908063	0.0
C	3.382122	0.388205	0.000005	C	0.593667	−3.364057	0.0	C	0.486176	−3.418808	0.0
C	4.094245	−0.811523	0.000026	C	−0.542617	−4.172787	0.0	C	−0.679653	−4.200070	0.0
C	3.418733	−2.038537	0.000041	C	−1.821580	−3.600265	0.0	C	−1.936741	−3.605004	0.0
C	2.014547	−2.082171	0.000014	C	−1.981494	−2.205220	0.0	C	−2.038472	−2.181809	0.0
H	3.892791	1.351109	0.000009	H	1.595538	−3.793447	0.0	H	1.478762	−3.868926	0.0
H	5.185812	−0.792491	0.000043	H	−0.433681	−5.259054	0.0	H	−0.593678	−5.289553	0.0
H	3.982038	−2.973664	0.000065	H	−2.706915	−4.239030	0.0	H	−2.844559	−4.209986	0.0
H	1.464991	−3.023811	0.000019	H	−2.964778	−1.734279	0.0	H	−3.004323	−1.675634	0.0
O	−2.604673	−1.488023	−0.000056	O	0.472037	3.220121	0.0	O	−1.504021	2.712044	0.0

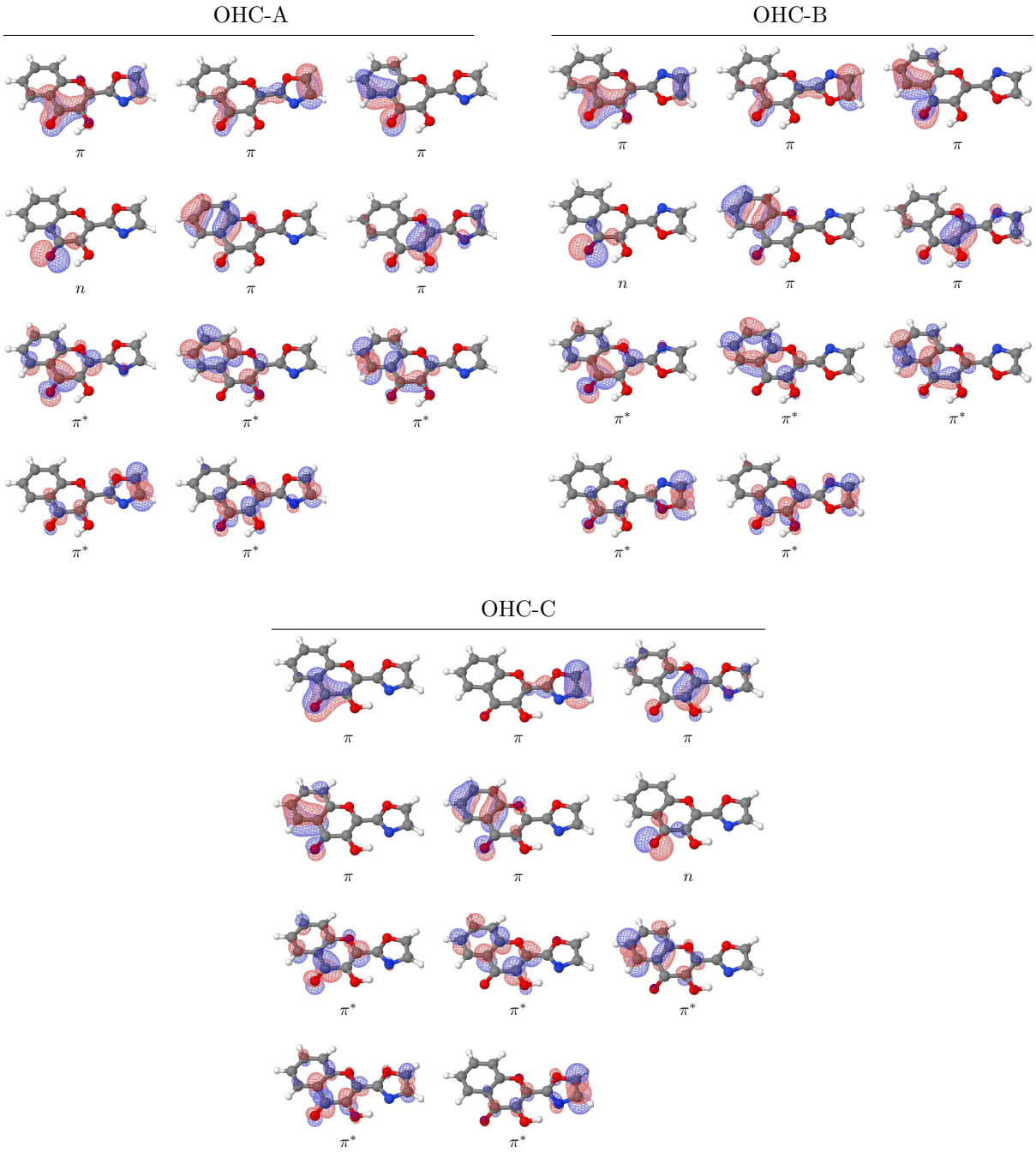

FIG. S-1. Orbitals of the CAS(12, 11) space of OHC-A, B and C used in the XMS-CASPT2 calculations

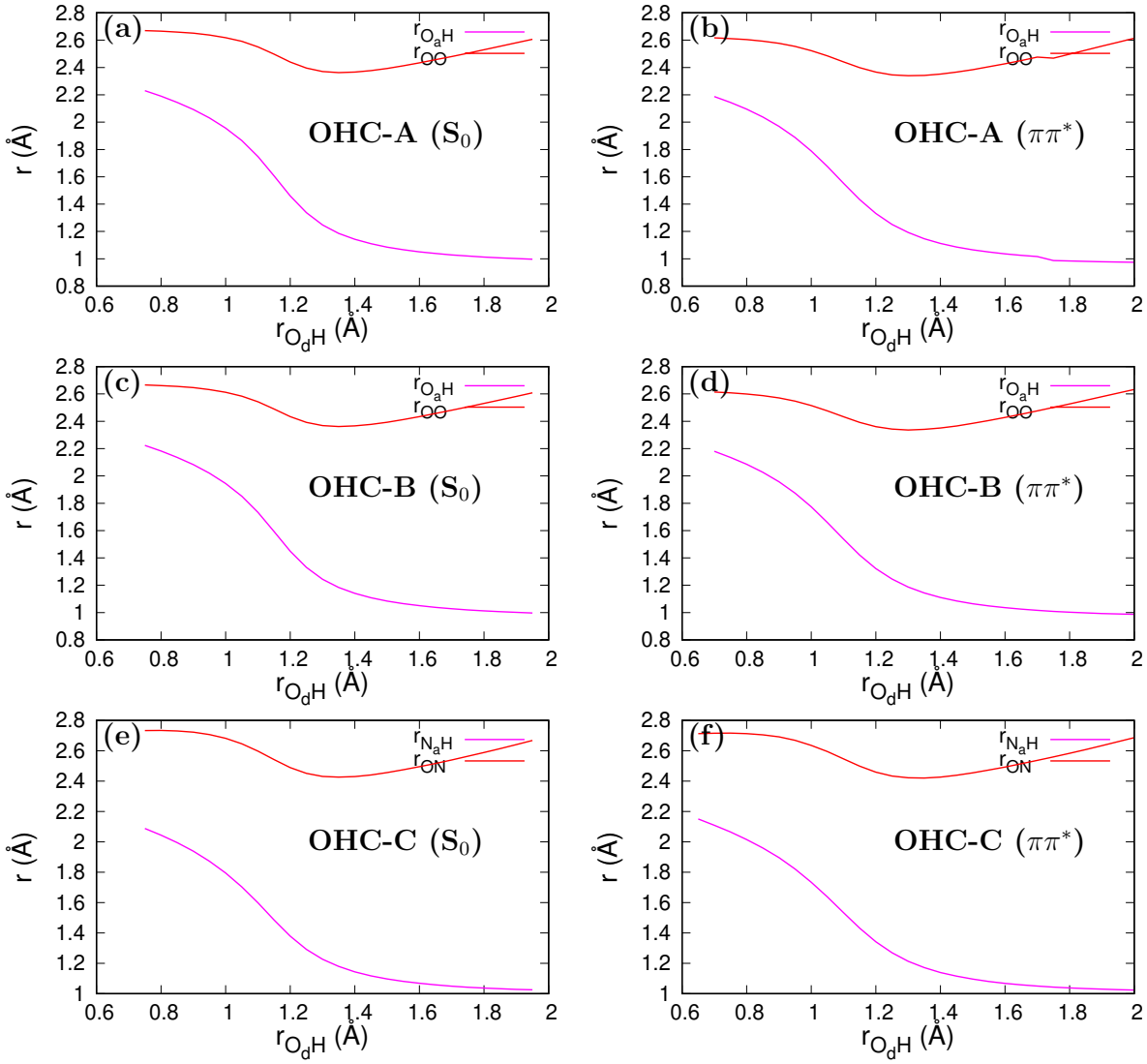

FIG. S-2. Plots of the donor-acceptor (O_d-O_a or O_d-N_a) distances and acceptor-H distance (O_a-H or N_a-H) as a function of donor-H distance (O_d-H) in the ground as well as excited-state *relaxed* scans for OHC-A, B and C. The corresponding potential profiles are shown in Figures 4 of the manuscript. The plots in the left column are for ground state optimized geometries (B3LYP/cc-pVDZ level), while those in the right column are for lowest bright state optimized geometries (TDA-B3LYP/cc-pVDZ level). It can be clearly seen that the donor-acceptor distances decrease in all cases in the barrier region of the proton transfer. The acceptor-H distances also undergo a non-linear change. Both are typical of transfers across an H-bond.

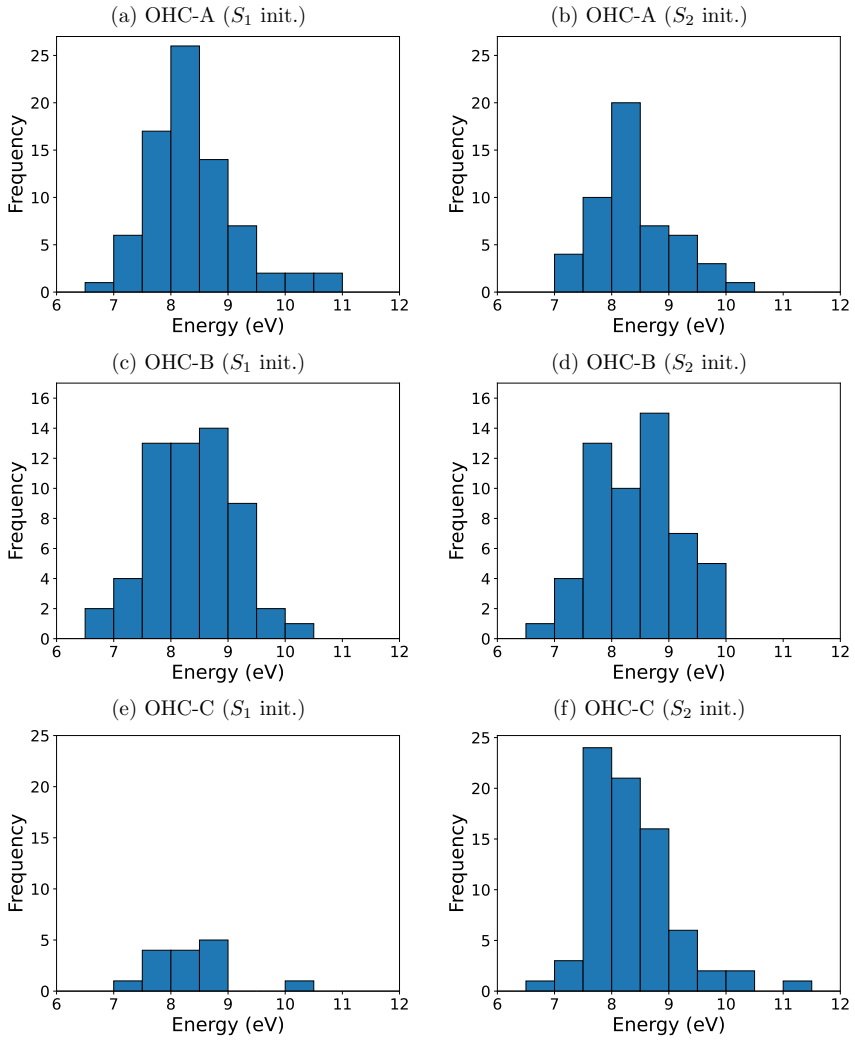

FIG. S-3. Distributions of the total energies of all propagated trajectories of OHC-A, B and C in the indicated states.

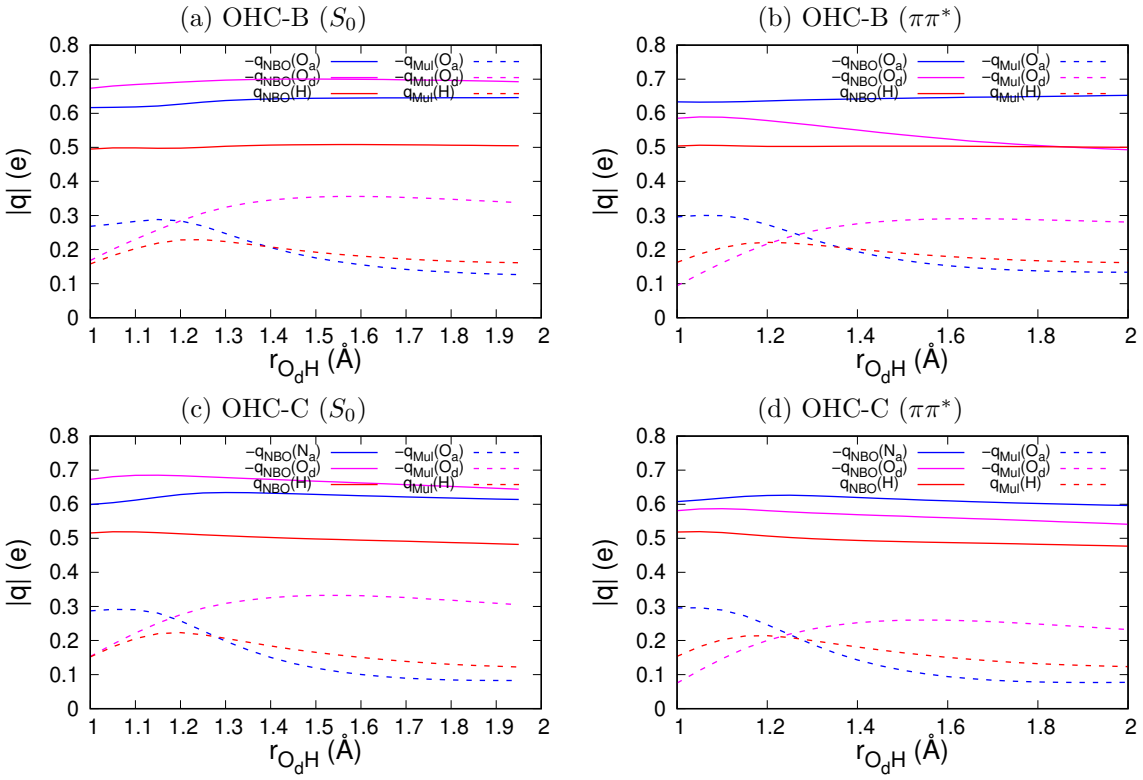

FIG. S-4. NBO (solid) and Mulliken (dashed) charges on the donor, acceptor and transferring H for (a, b) OHC-B and (c, d) OHC-C. The geometries used in each case are from relaxed r_{O_dH} scans on the (a, c) ground state and (b, d) the lowest $\pi\pi^*$ bright state; these are the same as the geometries of Figure 4 in the manuscript. Also, the state densities used in the analysis are those of the ground state in (a, c) and the lowest $\pi\pi^*$ bright state in (b, d). Only the magnitudes of the charges are plotted; of course, O and N have negative charges while that of H is positive.

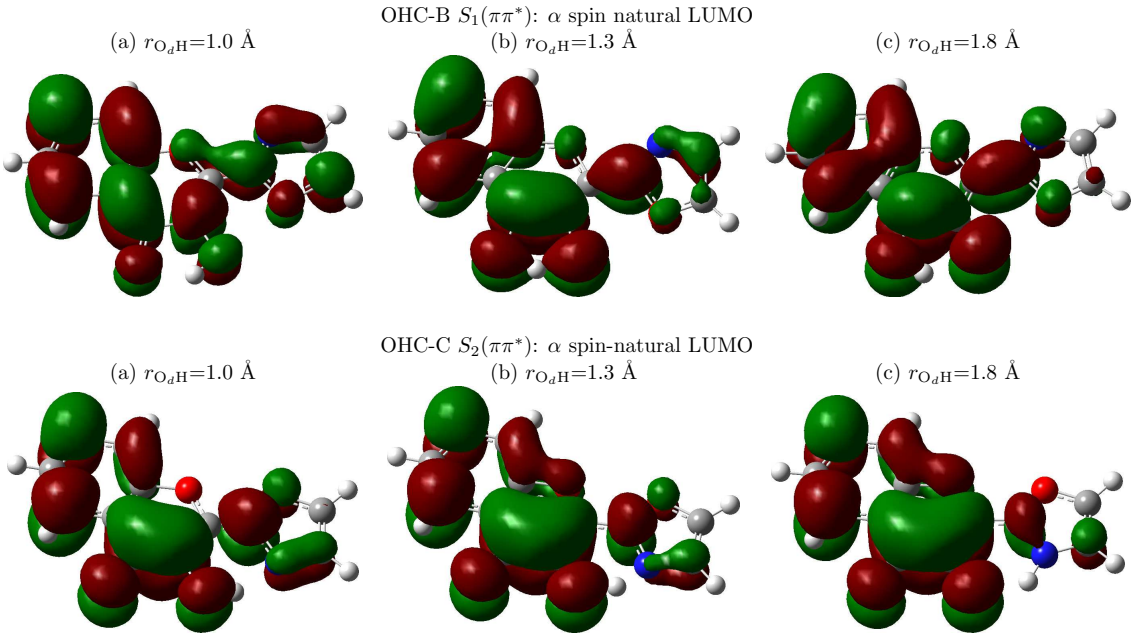

FIG. S-5. Spin natural orbitals (SNOs) obtained for OHC-B and OHC-C at selected geometries along the relaxed r_{O_dH} scan on the lowest $\pi\pi^*$ bright state (excited state transfer path; same as that in Figure 4). Shown are the spin natural α LUMOs (π^*) at these geometries.

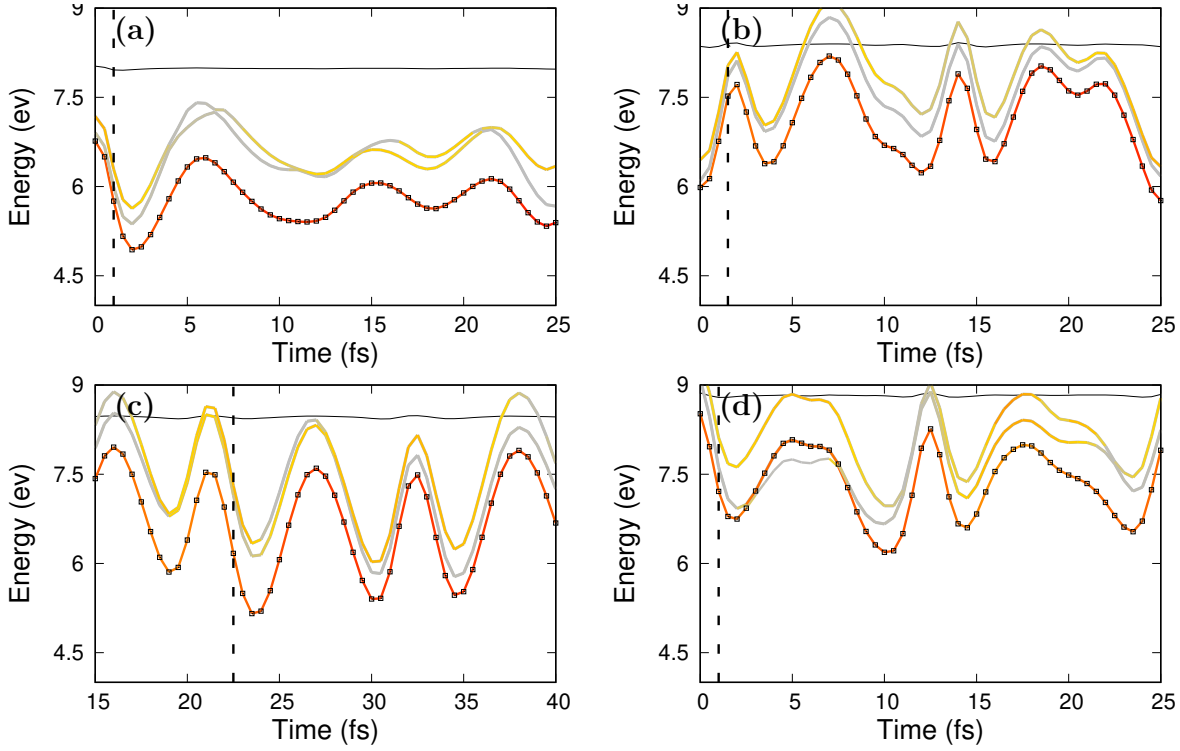

FIG. S-6. Plots of the energies of S_1-S_3 for the four OHC-A trajectories initialized on S_1 where a potential energy change between successive points exceeding the default 0.7 eV per-step threshold was seen. The dashed vertical line indicates the time location of the potential energy excess change, which occur at (a) 1 fs, (b) 1.5 fs, (c) 22.5 fs and (d) 1 fs. The black horizontal line indicates the total energy of the trajectory. Except for (a), other total energy lines have vertical offsets of (b) -2 eV, (c) -1 eV and (d) -2 eV so that they appears within the plotted energy range.

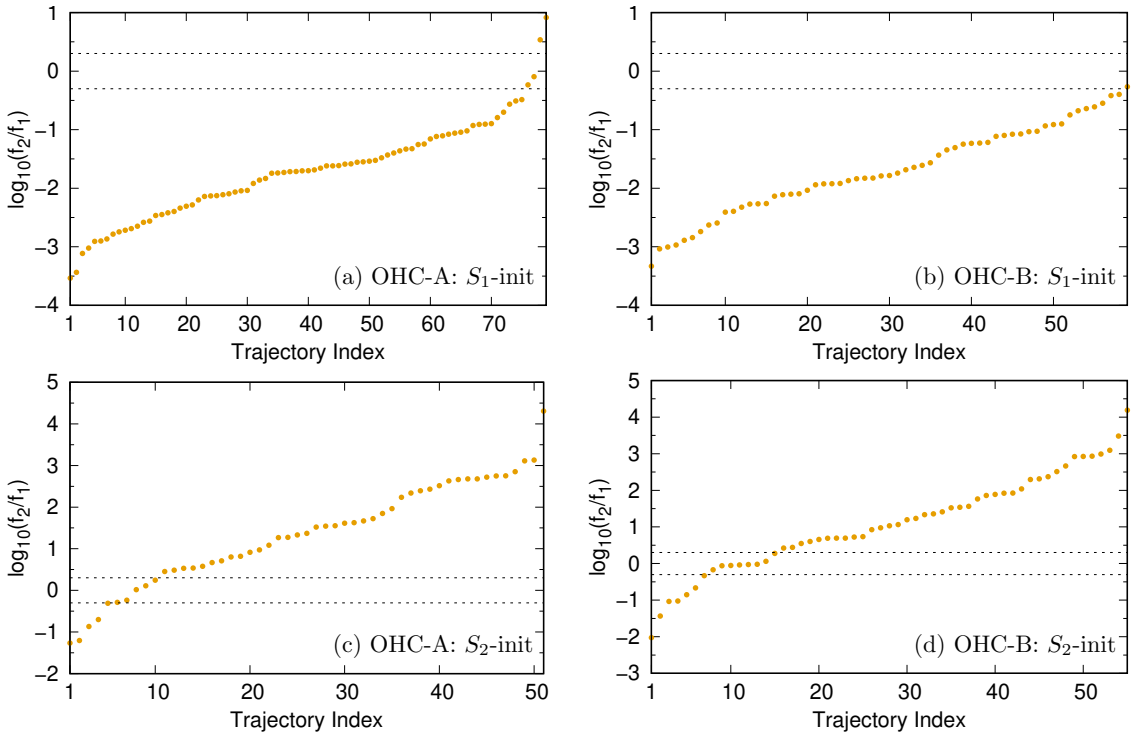

FIG. S-7. Ratio of oscillators strengths $\log_{10}(f_2/f_1)$ of all the initial conditions of (a, c) OHC-A and (b, d) OHC-B placed on (a, b) S_1 and (c, d) S_2 . Values below zero indicate that S_1 is brighter than S_2, while those above indicate the opposite. The dashed lines indicate f_2/f_1 being 1/2 (lower line) or 2 (upper line). Note that for the purpose of this plot, the initial conditions are sorted as per increasing values of f_2/f_1.

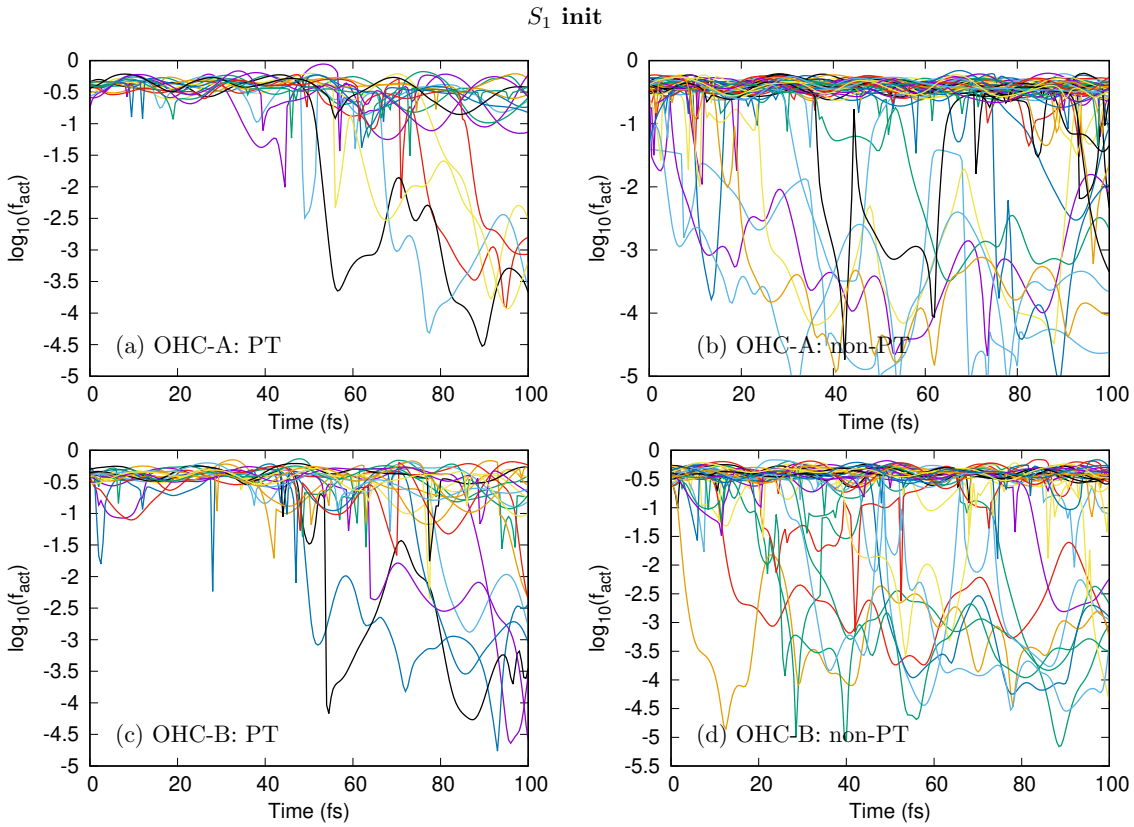

FIG. S-8. Oscillator strengths of the active states as a function of time for all (a, c) PT and (b, d) non-PT trajectories of (a, b) OHC-A and (c, d) OHC-B initialized on S_1. Each line corresponds to a single trajectory.

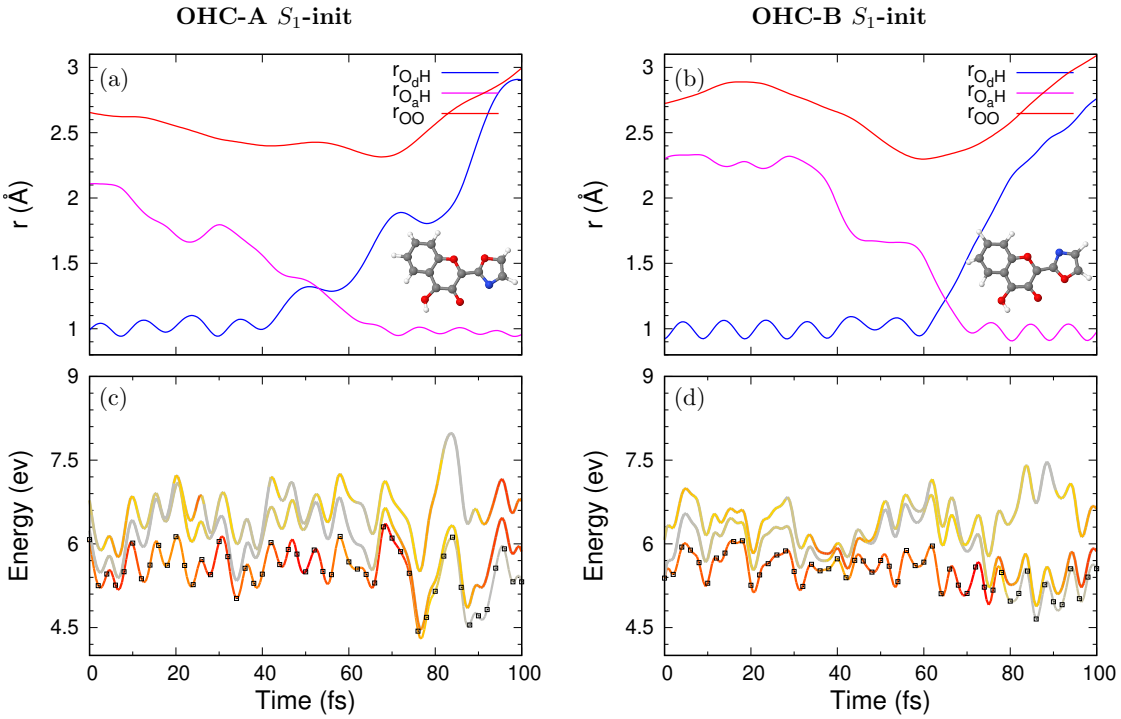

FIG. S-9. Additional trajectories showing proton transfer in (a, c) OHC-A and (b, d) OHC-B initiated on S_1. (a, b): Key distances for a representative PT trajectory each for OHC-A and B. (c, d): S_1-S_3 energies (eV) for the same trajectories. The line colours indicate the oscillator strength red (bright, $\mathcal{O}(0.1)$), yellow (intermediate, $\mathcal{O}(0.01)$ and gray (dark, $\mathcal{O}(0.001)$ or lower). The vertical dashed lines indicate the time points where a state hop occurs. **Note that** these trajectories are complementary to those in Figure 5 (a-d) of the manuscript, wherein the trajectories reached the bright S_2 state at the end of the simulation time. In the plots for the sample trajectories shown here, the molecule remains in S_1 throughout, both before and after PT. However, S_1 becomes the dark state sometime after PT.

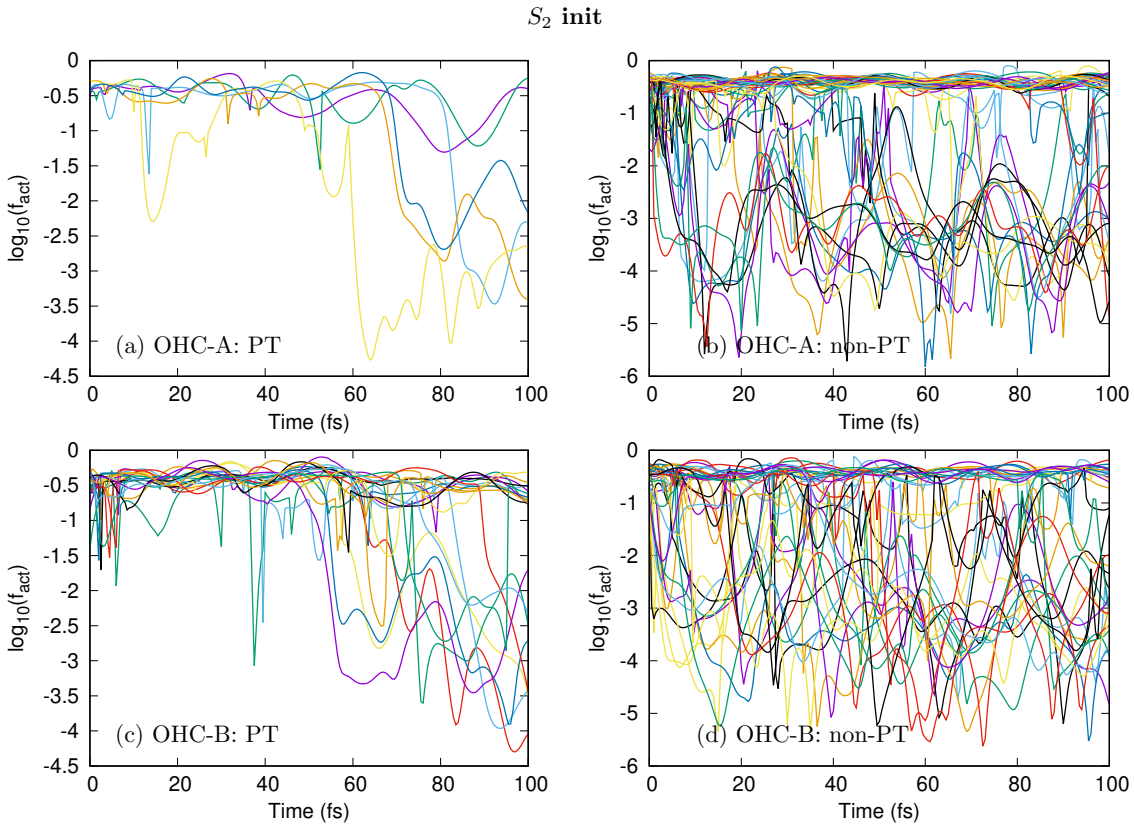

FIG. S-10. Oscillator strengths of the active states as a function of time for all (a, c) PT and (b, d) non-PT trajectories of (a, b) OHC-A and (c, d) OHC-B initialized on S_2. Each line corresponds to a single trajectory.

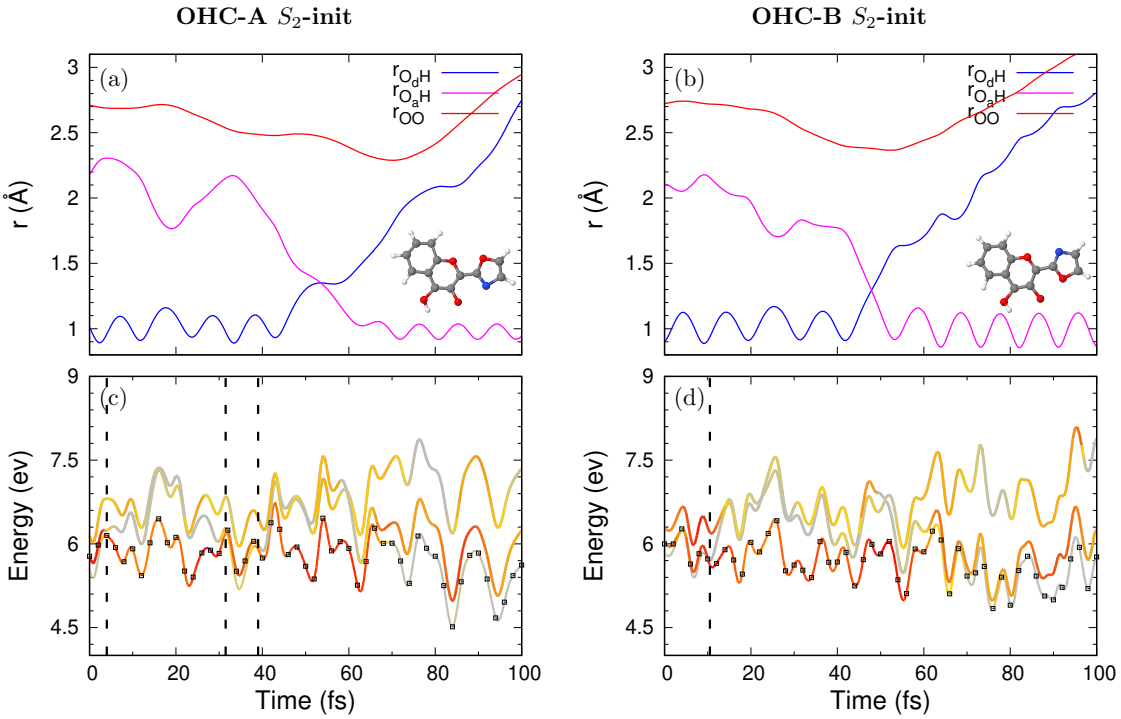

FIG. S-11. Additional trajectories showing proton transfer in (a, c) OHC-A and (b, d) OHC-B initiated on S_2. (a, b): Key distances for a representative PT trajectory each for OHC-A and B. (c, d): S_1-S_3 energies (eV) for the same trajectories. The line colours indicate the oscillator strength red (bright, $\mathcal{O}(0.1)$), yellow (intermediate, $\mathcal{O}(0.01)$ and gray (dark, $\mathcal{O}(0.001)$ or lower). The vertical dashed lines indicate the time points where a state hop occurs. **Note that** these trajectories are complementary to those in Figure 6 (a-d) of the manuscript, wherein the trajectories reached the bright S_2 state at the end of the simulation time. In the plots shown here, the trajectories instead are in the dark S_1 state within some time after PT and remain in this state until the end of the simulation.

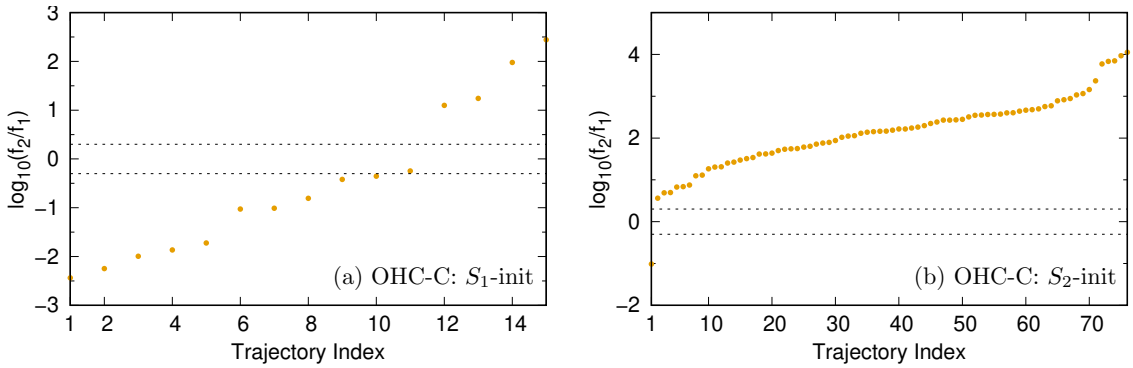

FIG. S-12. Ratio of oscillators strengths $\log_{10}(f_2/f_1)$ of all the initial conditions of OHC-C placed on (a) S_1 and (b) S_2. Values below zero indicate that S_1 is brighter than S_2, while those above indicate the opposite. The dashed lines indicate f_2/f_1 being 1/2 (lower line) or 2 (upper line). Note that for the purpose of this plot, the initial conditions are sorted as per increasing values of f_2/f_1.

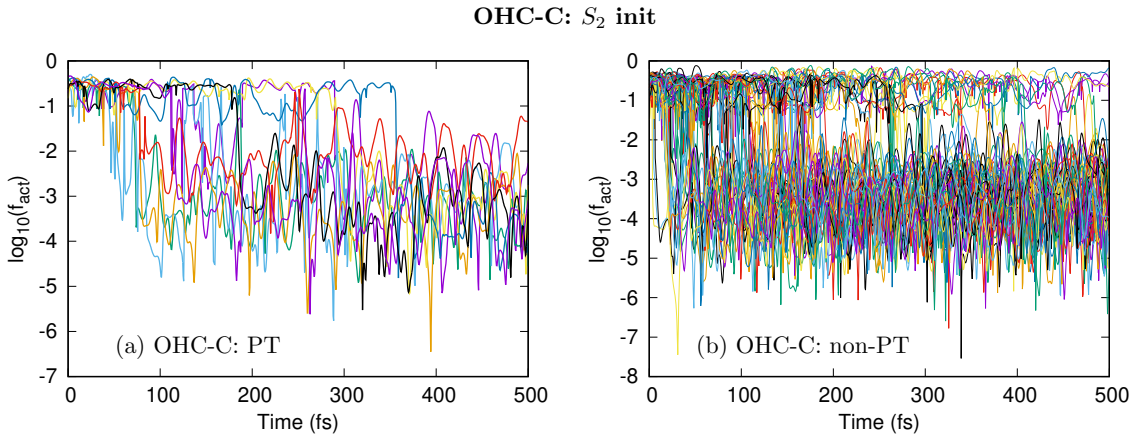

FIG. S-13. Oscillator strengths of the active states as a function of time for all (a) PT and (b) non-PT trajectories of OHC-C initialized on S_2. Each line corresponds to a single trajectory.

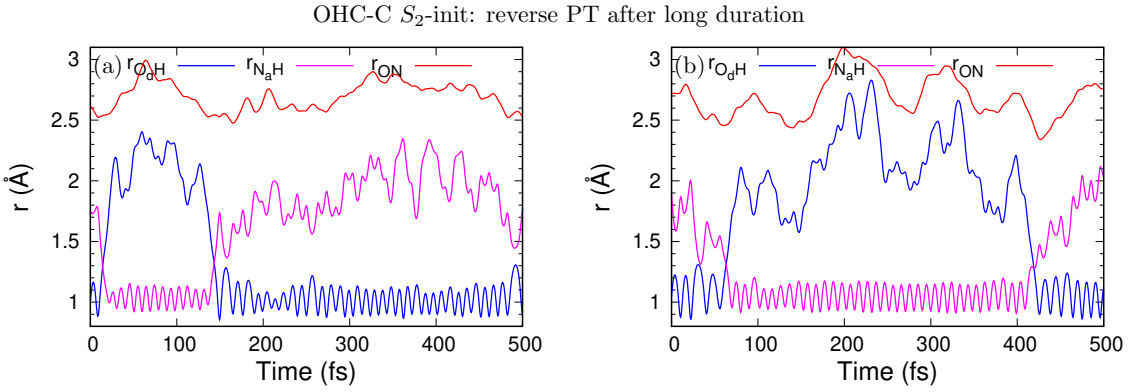

FIG. S-14. Plots of key distances for two trajectories initiated on S_2 in OHC-C that underwent proton transfer, resided in the PT region for a long duration (∼80 fs and ∼300 fs), but returned to the normal form during the simulation time.

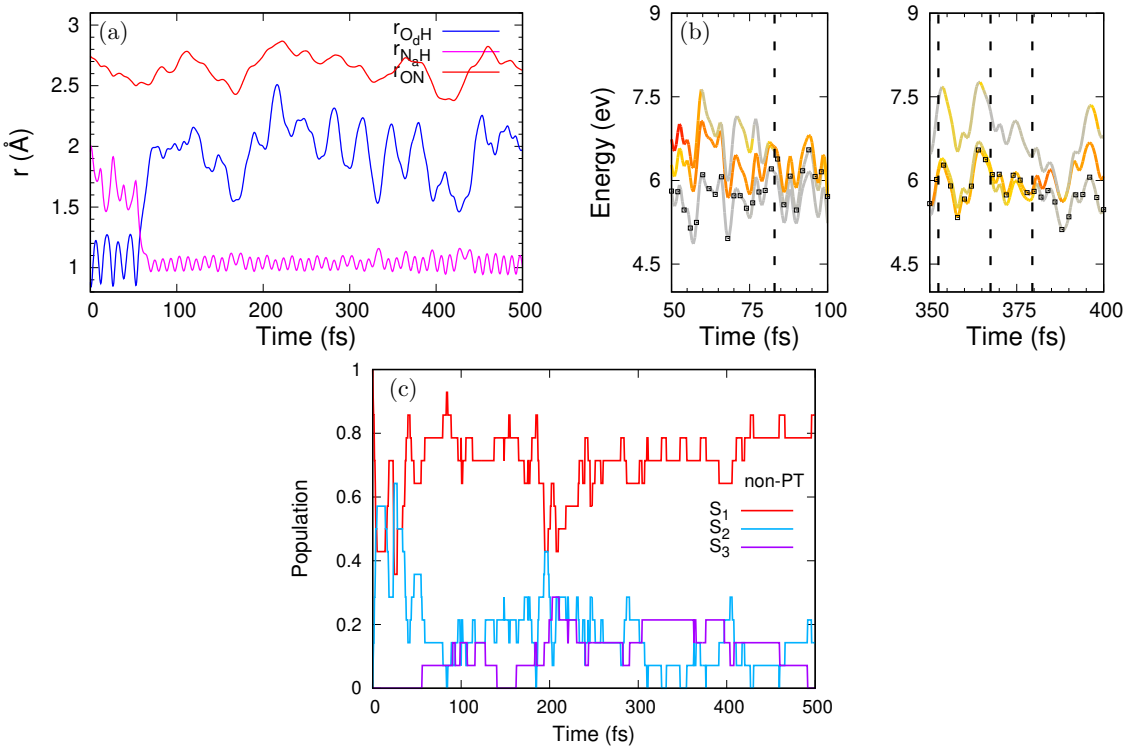

FIG. S-15. Dynamics of OHC-C initialized on S_1. (a) Key distances for the sole PT trajectory. (b) S_1-S_3 energies (eV) for this trajectory. The line colours indicates the oscillator strength red (bright, $\mathcal{O}(0.1)$), yellow (intermediate, $\mathcal{O}(0.01)$ and gray (dark, $\mathcal{O}(0.001)$ or lower). The open square shows the active state. The vertical dashed lines indicate the time points where a state hop occurs. The left panel shows the PT time window of the PT event (57.5 fs) which occurs on S_1. At later times, hops to other states are seen before finally reaching a dark state. (c) Population of states from the sample of the non-PT trajectories.