

Supporting information

for

Simulation of UV Absorption Spectra and Relaxation Dynamics of Uracil and Uracil-Water Clusters

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UV-vis spectra of DNA bases

UV-vis spectrum of uracil was measured in mQ-water at 25°C on a PG T80/T80+ spectrometer. The stock solution of uracil was prepared by dissolving 2.32 mg in water (10 mL), and this solution was then diluted twenty times. A UV-vis cell was filled with the solution of uracil (2.0 mL) and an UV-vis spectrum was taken. This solution was then diluted with water and after each dilution a spectrum was measured. Dependence of the absorbance on the base concentration was fit to linear equation and the molar absorption coefficient was determined from the slope.

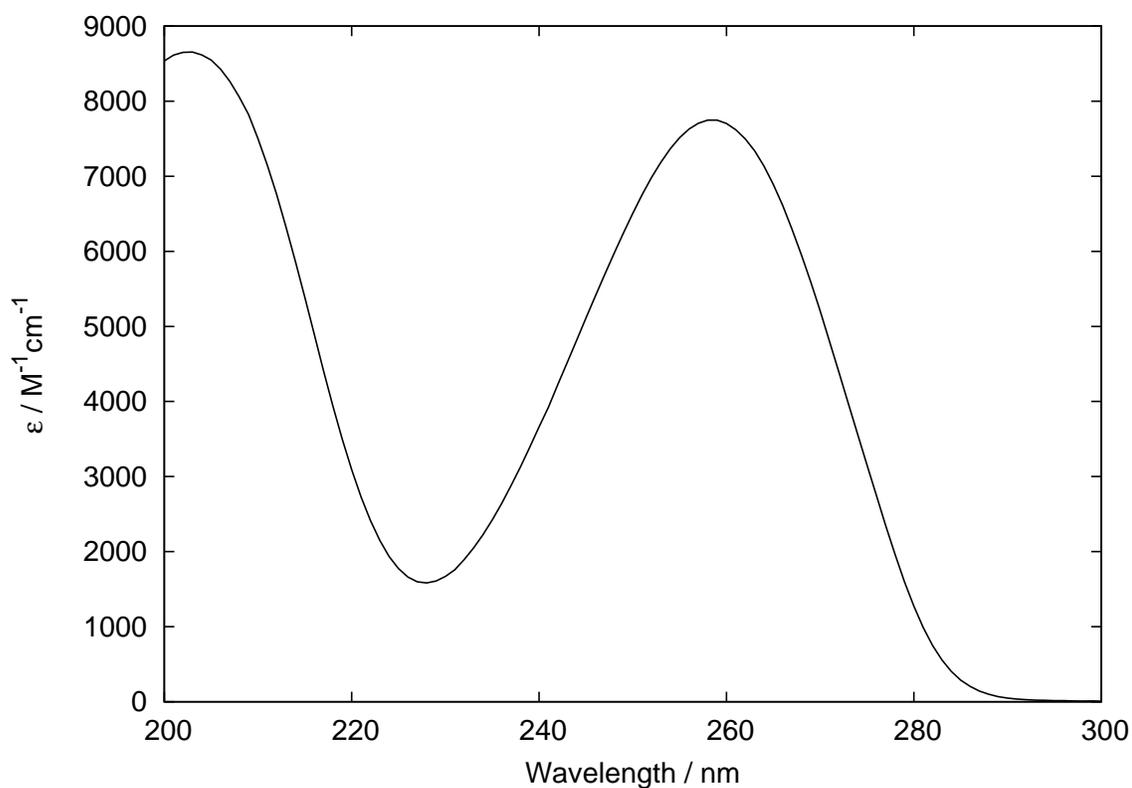


Figure S 1: Absorption spectrum of uracil in H_2O ($\epsilon_{258} = 7680 \pm 20 \text{ M}^{-1} \text{ cm}^{-1}$).

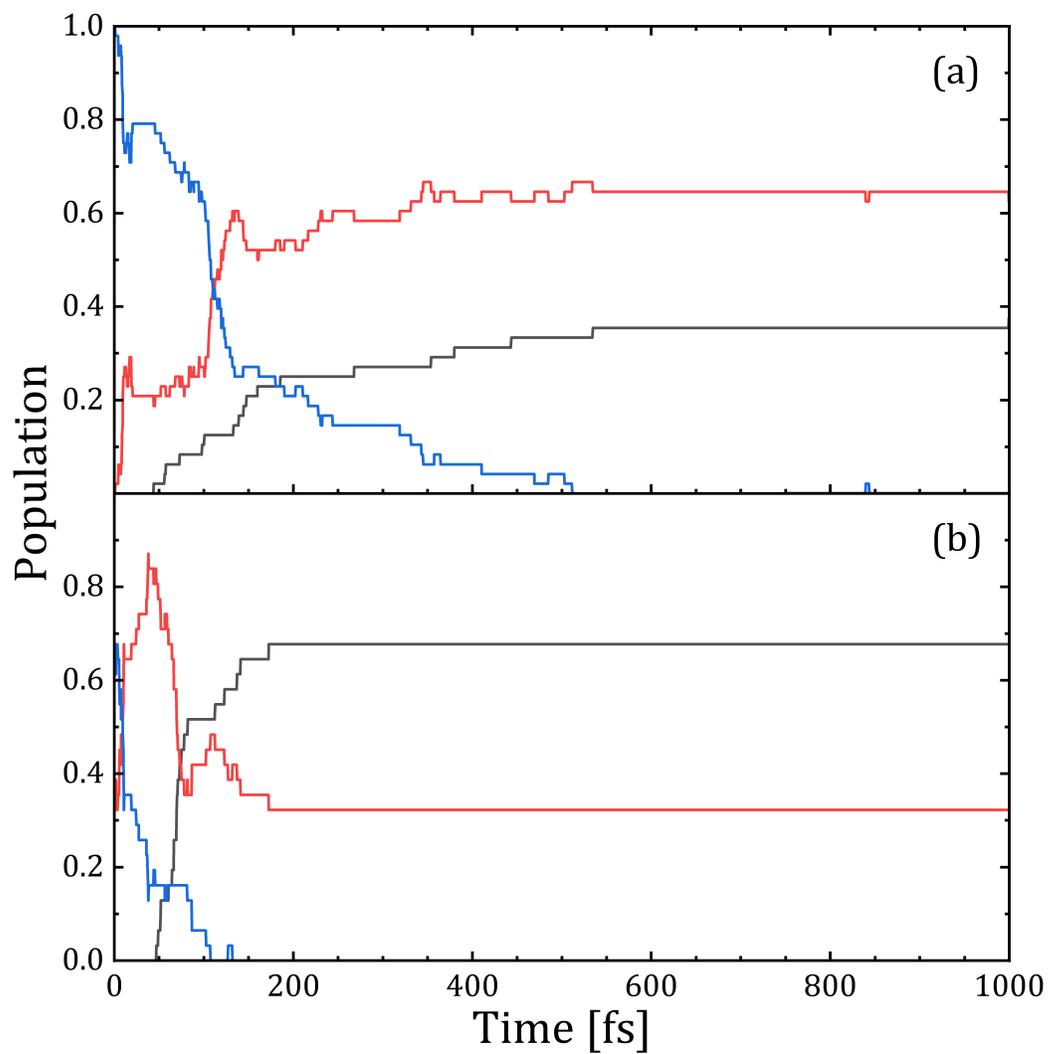


Figure S 2: Average population of the ground state, S_0 (black) and the two lowest excited states S_1 (red) and S_2 (blue) for (a) uracil and (b) $U(H_2O)_6$.

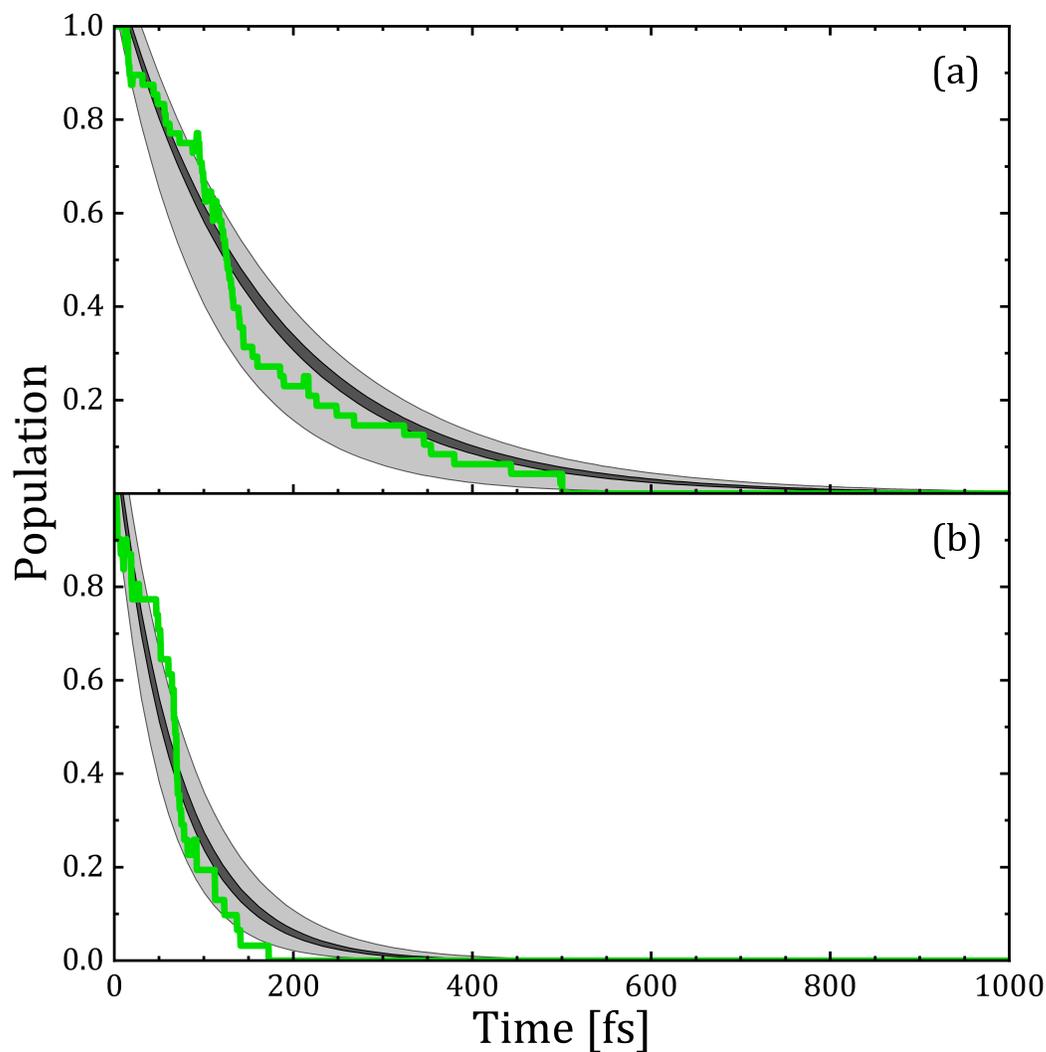


Figure S 3: Average population of the diabatic $\pi_1\pi_1^*$ state (green) as obtained using 5000 randomly selected structures from the original set of (a) 48 trajectories of U and (b) 31 trajectories of $U(\text{H}_2\text{O})_6$ with replacement. The gray areas represent the 95 % confidence interval (dark gray) yielding lifetimes of 161 ± 6 fs for U and 76 ± 3 fs for $U(\text{H}_2\text{O})_6$ and the 95 % prediction interval (light gray) with error margins of ± 40 fs for U and ± 18 fs for $U(\text{H}_2\text{O})_6$.

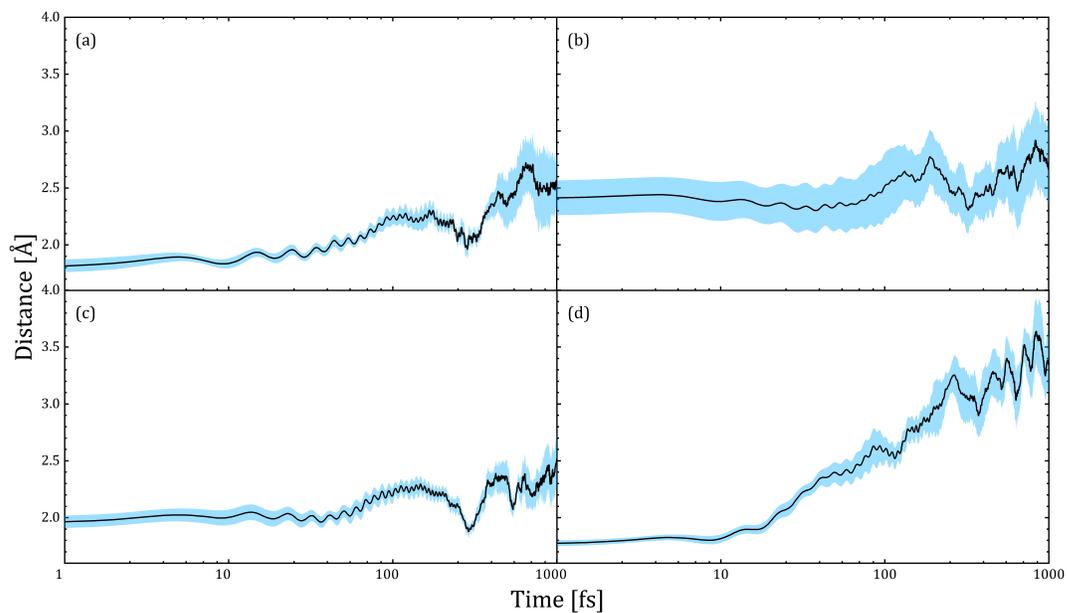


Figure S 4: Time evolution of the hydrogen bond distances in $U(H_2O)_6$ averaged over trajectories that remained in the $S_1(n_1\pi_1^*)$ state at the end of the simulation. The black curves indicate the mean value of the (a) $N1-H1\cdots OH_2$ (b) $N3-H3\cdots OH_2$ (c) $C2=O7\cdots HOH$ (d) $C4=O8\cdots HOH$ distances. The blue shaded areas indicate the margin of error (90% confidence interval).

Table S 1: Comparison of geometrical parameters (in Angstroms and degrees) of U as obtained with MP2/aug-cc-pVDZ and with BLYP-D3/DZVP-GTH.

	MP2	BLYP
N1-C2	1.39	1.42
C2-N3	1.39	1.41
N3-C4	1.41	1.44
C4-C5	1.46	1.47
N1-H1	1.01	1.02
N3-H3	1.02	1.02
C4-O8	1.23	1.24
C2-O7	1.23	1.24
C5-C6	1.37	1.37
C2-N1-H1	115.1	114.9
N3-C2-O7	124.1	124.5
C4-N3-H3	116.2	116.2
C5-C4-O8	126.1	126.4

Table S 2: SCS-ADC(2)/aug-cc-pVDZ excitation energies (in eV) and oscillator strengths (in parentheses) of U computed at the MP2/aug-cc-pVDZ optimized ground-state geometry (E^{ref}) and at the BLYP-D3/DZVP-GTHD3 optimized ground-state geometry (E^{BLYP}). Transitions below 6.85 eV (180 nm) are included. Dominant NTO pairs contributing to the transitions are specified.

S	E^{ref}	NTOs	E^{BLYP}
S ₁	4.88 (0.000)	$n_1\pi_1^*$	4.67 (0.000)
S ₂	5.36 (0.223)	$\pi_1\pi_1^*$	5.19 (0.221)
S ₃	6.01 (0.004)	$\pi_1\text{Ryd}_1$	6.01 (0.004)
S ₄	6.19 (0.000)	$n_2\pi_2^*$	5.94 (0.000)
S ₅	6.42 (0.048)	$\pi_2\pi_1^*$	6.19 (0.052)
S ₆	6.74 (0.038)	$n_1\text{Ryd}_1$	6.72 (0.022)
S ₇	6.85 (0.208)	$\pi_1\pi_2^* + n_1\text{Ryd}_2$	6.66 (0.231)