

## SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

**Action number: CA18222 (Attosecond Chemistry)**

**STSM title: Theoretical assignment of the electronic spectra of aqueous uracil and state specific analysis of solvation effects**

**STSM start and end date: 29/1/2020 to 18/2/2020**

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### PURPOSE OF THE STSM:

Due to their biological relevance, DNA nucleobases excited state dynamics is extensively examined both experimentally and theoretically<sup>[1], [2]</sup>. Understanding competing photophysical mechanisms that can lead to and prevent light-induced damage of the DNA nucleobases is of interest because of their widespread potential applications. Determination of the character of large number of the excited electronic states is a challenging problem for nucleobases and other polyatomic molecules in general. Using previously developed procedure<sup>[3]</sup> we should be able to automatically determine character of the excited electronic states of uracil both in gas phase and aqueous solution. The procedure is based on the electronic wave function analysis by calculating overlap of the hole and particle NTOs for the series of previously determined nuclear geometries. This procedure ensures information's about: theoretical assignment of the electronic spectra; state specific analysis of solvation effects; effects of vibrational averaging, temperature and solvent-induced structural changes; state specific solvent shifts for the solvent sensitive  $n\pi^*$  electronic states. Acquired data should provide more convenient insights into absorption spectra of the uracil and therefore foundation for studying photodynamics of uracil in aqueous solution and the possibility of the excited state driven N-H bond fission. Hopefully, detailed characterization of the electronic states involved in the relaxation of gas phase and aqueous uracil structures will shed new light on the active role of the environment in the excited state deactivation of nucleobases.

### DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

First, we performed ground state optimization of the uracil at MP2/aug-cc-pVDZ level of theory using resolution of identity approximation both in gas phase and in the solution (water) environment simulated with the COSMO continuum solvation model. The effect of the vibrational averaging was accounted using Wigner distribution for the harmonic oscillator thermal density. Vibrational displacements were sampled from the gas phase ground state minimum normal modes at 0 and 298 K (200 geometries each), in order to consider temperature effects. Another sampling from the gas phase ground state minimum normal modes was done using COSMO continuum model in order to reflect electrostatics influence (200 geometries). Finally, 200 geometries were sampled from the optimized COSMO ground state minimum in search for solvent induced structural changes. Subsequently, vertical excitations were calculated using ADC(2)/aug-cc-pVDZ method for each previously sampled configuration. ADC(2)/aug-cc-pVDZ vertical excitations were also computed for the reference, optimized gas phase ground state minima geometry. Using overlaps between the dominant hole and particle NTOs we determined the character of the electronic transitions for the reference geometry. For Wigner distribution generated nuclear ensembles, states of the same electronic character were diabatically mapped to the each other using the procedure described elsewhere<sup>[3]</sup>. With the results obtained we calculated absorption spectra using non-standard procedure circumventing introduction of any empirical

broadening parameters since each excited state is characterized with the mean value (and standard deviation) of excitation energy and oscillator strength. Results obtained are presented in the next chapter.

### DESCRIPTION OF THE MAIN RESULTS OBTAINED

Results regarding characterization of the excited states, their energies, oscillator strength and the influence of the solvent are compiled in the Table 1. and absorption spectra for different models is presented on Figure 1. First three ground state minima vertical transitions are  $n_1\pi_1^*$ ,  $\pi_1\pi_1^*$  and  $n_2\pi_2^*$ , respectively, dominated with a single NTO pair. These states are followed with two mixed  $n\pi^*+\pi$ Ryd states. Latter is somewhat higher in energy closely lying to the next  $n_1$ Ryd<sub>1</sub> transition dominated with a single NTO pair. Next transition is  $n_2\pi_1^*+n_1\pi_3^*$  with hole NTOs delocalized over both oxygen atoms of uracil. Last transition taken into account is another bright  $\pi_1\pi_3^*$  state which is mixed to some extent with a  $n_1$ Ryd<sub>2</sub> transition. Sampling from the Wigner distribution in the gas phase results in a comparable redshift of all examined transitions and that is on average 0.17 eV and 0.21 eV when accounting vibrational and temperature effects, respectively. Influence of the electrostatics and solvation on two strongly absorbing  $\pi\pi^*$  transitions (S<sub>2</sub> and S<sub>8</sub>) has rather similar trend and it leads to their stabilization with the respect to the reference system. S<sub>2</sub>( $\pi_1\pi_1^*$ ) state is stabilized by  $\approx 0.32$  eV while S<sub>8</sub>( $\pi_1\pi_3^*+n_1$ Ryd<sub>2</sub>) is stabilized even more,  $\approx 0.51$  eV, by solvent inclusion. On the other hand,  $n\pi^*$  transitions (S<sub>1</sub>, S<sub>3</sub> and S<sub>6</sub>) are strongly destabilized by electrostatic effects which accounts on average for 0.24 eV. This could be due to very different electron density organization upon excitation of these transition which leads to apparent blueshifts in the absorption spectra. Solution induced structural changes, however, are differently affecting  $n_1\pi_1^*$  and  $n_2\pi_2^*/n_2\pi_1^*$  transitions. In the case  $n_1\pi_1^*$  this blueshift is much larger, 0.24 eV compared to the  $n_2$  hole NTO characterized counterparts.  $n_2$  orbital is localized on the oxygen of the carbonyl group positioned in between nitrogen ring atoms and it should be less negatively charged compared to the other oxygen atom which should lead to the smaller delocalization of the electron density upon excitation and consequently smaller blueshift of the transition. Solvation effect on the transition involving contribution of the Ryd orbitals can be in either direction but mostly following similar trends as  $n\pi^*$  states with whom they tend to mix.

Table 1. Mean values and standard deviations of electronic excitation energies (eV) and oscillator strength (in parenthesis) of uracil. Electronic transitions below 6.57 eV ( $\approx 190$  nm) are included. Dominant NTO pairs for the electronic transitions at the reference geometries ( $E_{ref}$ ) are indicated. The effect of vibrational averaging ( $E_0^{gas}$ ), temperature ( $E_{298}^{gas}$ ), electrostatics ( $E_{298}^{COSMO}$ ) and solvent induced structural changes ( $E_{298}^{solution}$ ) on the mean excitations are analyzed.

State	NTOs	$E_{ref}$	$E_0^{gas}$	$E_{298}^{gas}$	$E_{298}^{COSMO}$	$E_{298}^{solution}$
S <sub>1</sub>	$n_1\pi_1^*$	4.52 (0.000)	4.37±0.38 (0.001±0.005)	4.29±0.38 (0.003±0.009)	4.84±0.32 (0.023±0.033)	4.75±0.35 (0.017±0.027)
S <sub>2</sub>	$\pi_1\pi_1^*$	5.18 (0.205)	5.03±0.27 (0.184±0.038)	4.97±0.27 (0.178±0.040)	4.89±0.27 (0.211±0.041)	4.84±0.31 (0.220±0.039)
S <sub>3</sub>	$n_2\pi_2^*$	5.82 (0.001)	5.61±0.37 (0.006±0.009)	5.56±0.37 (0.009±0.015)	5.99±0.33 (0.023±0.030)	5.85±0.35 (0.019±0.025)
S <sub>4</sub>	$n_2\pi_2^*+n_1$ Ryd <sub>1</sub>	5.83 (0.003)	5.70±0.22 (0.010±0.011)	5.68±0.23 (0.012±0.013)	6.12±0.18 (0.043±0.035)	6.13±0.18 (0.047±0.039)
S <sub>5</sub>	$\pi_1$ Ryd <sub>1</sub> + $n_2\pi_2^*$	6.03 (0.028)	5.88±0.39 (0.036±0.034)	5.83±0.36 (0.035±0.031)	6.09±0.35 (0.084±0.063)	5.98±0.37 (0.076±0.063)
S <sub>6</sub>	$n_1$ Ryd <sub>1</sub>	6.18 (0.030)	6.00±0.29 (0.024±0.020)	5.98±0.29 (0.023±0.017)	6.62±0.21 (0.045±0.048)	6.51±0.21 (0.043±0.041)
S <sub>7</sub>	$n_2\pi_1^*+n_1\pi_3^*$	6.37 (0.001)	6.19±0.39 (0.012±0.015)	6.16±0.39 (0.017±0.020)	6.60±0.33 (0.033±0.039)	6.47±0.36 (0.026±0.031)
S <sub>8</sub>	$\pi_1\pi_3^*+n_1$ Ryd <sub>2</sub>	6.57 (0.148)	6.38±0.30 (0.106±0.053)	6.32±0.29 (0.099±0.045)	6.07±0.31 (0.157±0.055)	6.05±0.33 (0.162±0.059)

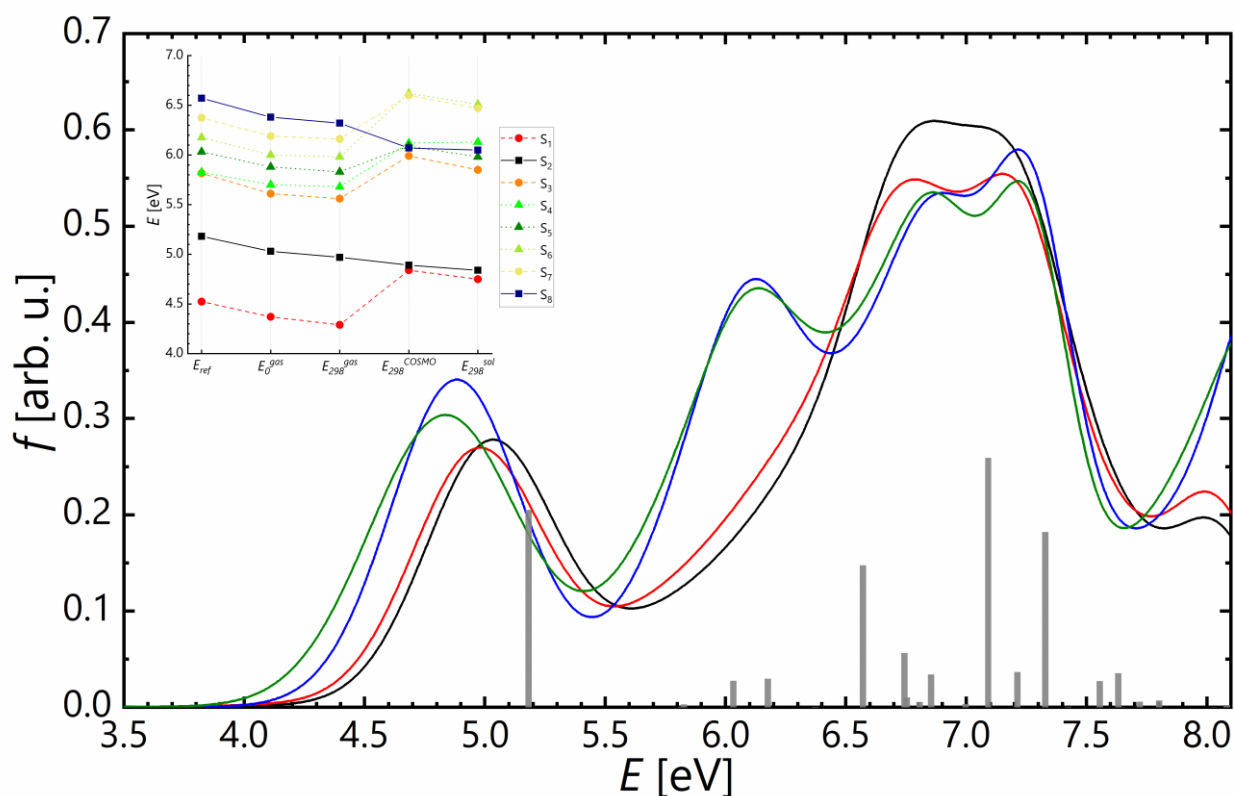


Figure 1. Total effect of solvation on the computed UV absorption spectra for uracil. Gas phase spectra at 0 K (black) and 298 K (red), spectra with electrostatic COSMO environmental effect (blue) and COSMO solution/optimized COSMO ground state geometries (green). Vertical bars represent reference geometry vertical excitation energies. Inset represents influence of the solvation on the energy of the selected excited states.

#### FUTURE COLLABORATIONS (if applicable)

We think that applied approach should provide a good description of the absorption spectra of uracil and meaningful state specific analysis. Regarding latter, we desire to develop strategy to account effects of the hydrogen bonded water molecules to the uracil and similar molecules. Hydrogen bonding could significantly affect geometries in such systems and electronic transitions through solvent specific collective electric field. On the other hand, it remains to be seen whether this research could help us resolving the mechanisms governing nonradiative decay in both gas phase and for the aqueous uracil. For this purposes nonadiabatic dynamics calculations in the gas phase and in the water environment are up and running.

#### References:

- [1] Sobolewski, A. L.; Domcke, W. Molecular mechanisms of the Photostability of Life. *Phys. Chem. Chem. Phys.* 2010, 12, 4897.
- [2] Markovitsi D.; Sage, E.; Lewis, F. D.; Davies, J. Interaction of UV Radiation with DNA, *Photochem. Photobiol. Sci. – themed issue* 2013, 12, 1256.
- [3] Sapunar, M.; Domcke, W.; Došlić, N. UV Absorption Spectra of DNA Bases in the 350 – 190 nm Range: Assignment and State Specific Analysis of Solvation Effects, *Phys. Chem. Chem. Phys.* 2019, 21, 22782.