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Influence of excess energy in the cationic ground state on photoionization induced solvent migration in Acetanilide-water 1:1 cluster studied by time-resolved IR spectroscopy

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[Introduction] The interactions between molecule and solvent are manifold, e.g. dispersion forces, hydrophobic/hydrophilic interactions or hydrogen bonds can be mentioned. With regard to the importance in biological processes proteins are of great interest. The biological environment of proteins is strongly affected by water and the hydration has a strong effect on the structure (e.g. α -helix or β -sheet) and reactivity. One of the fundamental processes for growth and health of biological systems is the folding motion of proteins. This reconfiguration requires a rearrangement of the solvent molecules.

Acetanilide (AA) is one of the smallest aromatic molecules containing a peptide linkage and acts as a model substance of peptide-water interaction for mass- and isomer selective investigation on a molecular level in the gas phase. In case of the water 1:1 cluster, a rearrangement of the solvent molecule induced by photoionization is observed.^[1] In the S_0 state, the water molecule is either hydrogen-bonded to the CO or to the NH site of the peptide bond. In the cationic ground state (D_0) only the NH bound isomer is observed. By applying time resolved infrared (IR) spectroscopy, the migration dynamics was observed in real time and 5 ps lifetime of the migration, role of intracuster vibrational redistribution (IVR) and existence of an intermediate have been revealed for the first time.^[2]

In this work, we investigated the influence of excess energy in the D_0 state (by reducing stepwise from 9250 cm^{-1} to 4450 cm^{-1}) on the dynamics of the mentioned migration by applying time resolved ps-IR spectroscopy in a two color photoionization experiment.

[Experiment] The principle and setup of the ps time resolved UV-UV-IR measurements are described elsewhere^[2] and a scheme is shown in Fig.1. For investigating the dependence on the excess energy, the experiments were performed via a resonant two photon ionization (R2PI). The clusters were isomer selectively excited by using a first UV photon (UV_{exc}) and then they are ionized by using a second UV photon (UV_{ion}). By varying UV_{ion} , the excess energy in D_0 can be controlled.

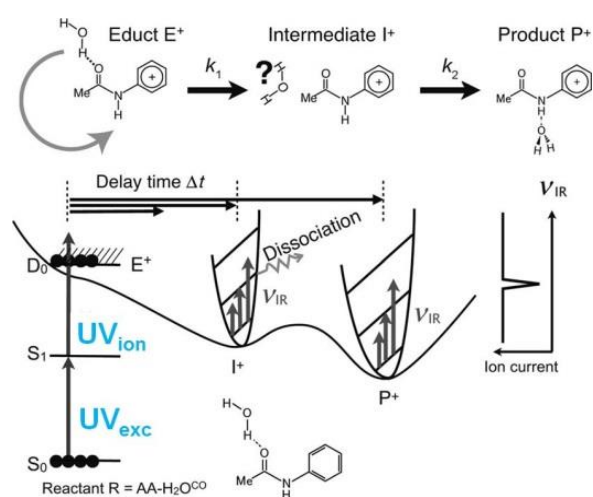


Figure 1: scheme of the setup for UV-UV-IR measurements

[Results and discussion] Fig. 2 shows the ps-R2PI spectra of AA(H₂O) recorded by using two different ionization wavelengths (320 nm in red and 330 nm in black). The transition at 35697 cm⁻¹ is assigned to the NH-bound isomer while the one at 36050 cm⁻¹ is assigned to the CO-bound isomer. By reducing the excess energy in the D₀ state the relative intensities of the clusters change significantly. For the higher excess energy, the CO-bound isomer is dominant while the NH-bound water cluster dominates at lower excess energy. This effect can be explained by different Franck-Condon-Factors of the isomers.

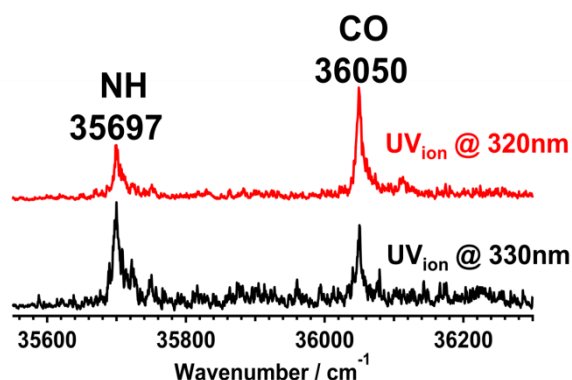


Figure 2: ps-R2PI spectra of AA(H₂O) measured by using different ionization wavelength

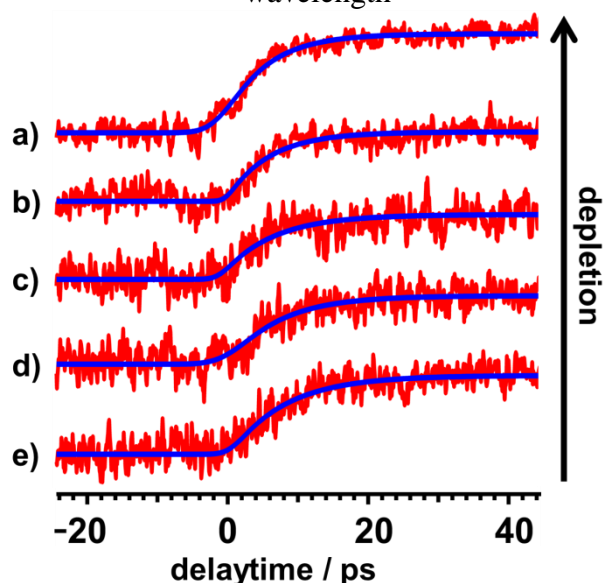


Figure 3: time evolution of H-bonded NH stretching vibration of migration product
a) 277.4 nm; b) 310 nm; c) 312 nm
d) 314 nm and e) 316 nm

To obtain information of the dynamics of the solvent migration, the time evolution of the H-bonded NH stretching vibration of the product (3185 cm⁻¹) was investigated. Fig. 3 shows the results for UV_{ion} in the range from 277.4 nm to 316 nm. This corresponds to an excess energy of about 9250 cm⁻¹ to 4842 cm⁻¹. By fitting the time evolution curves, the water migration time can be estimated. The time constant τ changes from a) $\tau = (5.8 \pm 0.3)$ ps, b) $\tau = (6.0 \pm 0.2)$ ps, c) $\tau = (6.4 \pm 0.5)$ ps, d) $\tau = (7.0 \pm 0.3)$ ps to e) $\tau = (7.7 \pm 0.4)$ ps with decreasing excess energy. This is in good agreement with the expectation. The repulsive effect in the D₀ state depends on the energy induced by photoionization.

Furthermore, we measured the time resolved IR spectra for different excess energies. These spectra are similar to the already reported results and verify the reaction pathway as well as the existence of an intermediate state. For further analysis, more sophisticated theoretical calculations (including multidimensional potential energy surface) are required.

As a conclusion, the reducing of the excess energy from about 9250 cm⁻¹ to 4842 cm⁻¹ causes a slowing down of the photoionization induced migration of the water molecule from the CO- to the NH-binding site of the AA, but the time resolved measurements of the IR spectra show that there is no significant change in the reaction pathway. The already reported existence of an intermediate state^[2] during the migration has been confirmed.

References:

- [1] K. Sakota, S. Harada, Y. Shimazaki, H. Sekiya, *J. Phys. Chem. A* **2011**, *115*, 626.
- [2] K. Tanabe, M. Schmies, A. Patzer, M. Schuetz, H. Sekiya, M. Sakai, O. Dopfer, M. Fujii, *Angew. Chem.-Int. Edit.* **2012**, *51*, 6604.