

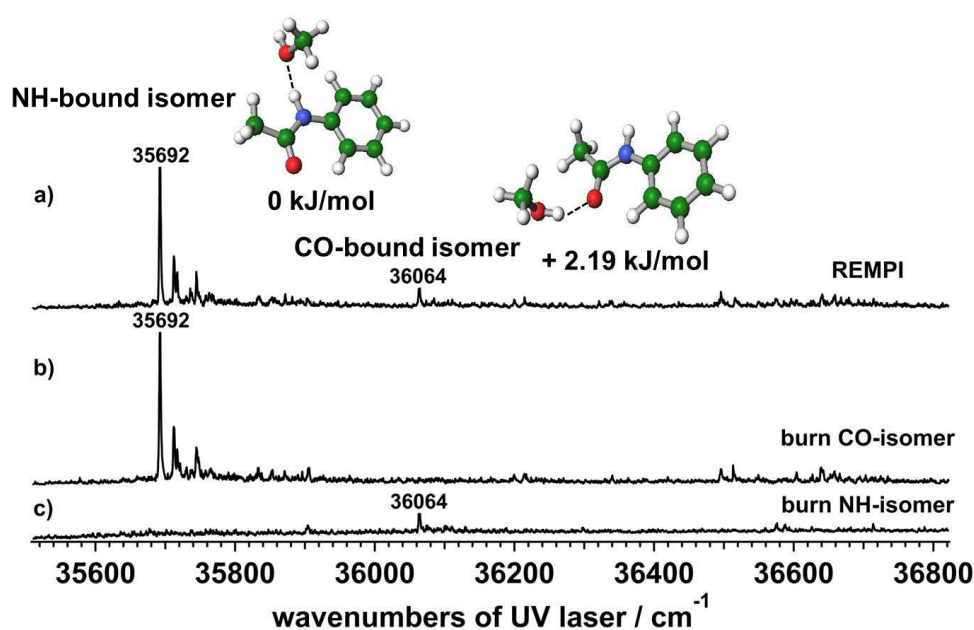
## Isomer selective investigation of solvent migration induced by photoionization around peptide linkage in Acetanilide-(methanol) 1:1 cluster

(Tokyo Institute of Technology) Martin Weiler, Mitsuhiro Miyazaki, Masaaki Fujii

**[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. Because of their peptide linkage, these biological supramolecules can either act as proton donor (by NH-group) or as proton acceptor (by CO-group). The biological environment of proteins is affected by water and the hydration has a strong effect to the structure (e.g.  $\alpha$ -helix or  $\beta$ -sheet) and reactivity. The dynamics of solvent molecules becomes important, e.g. in case of folding motion, because here the solvent molecule has to migrate and a rearrangement of the system is necessary.

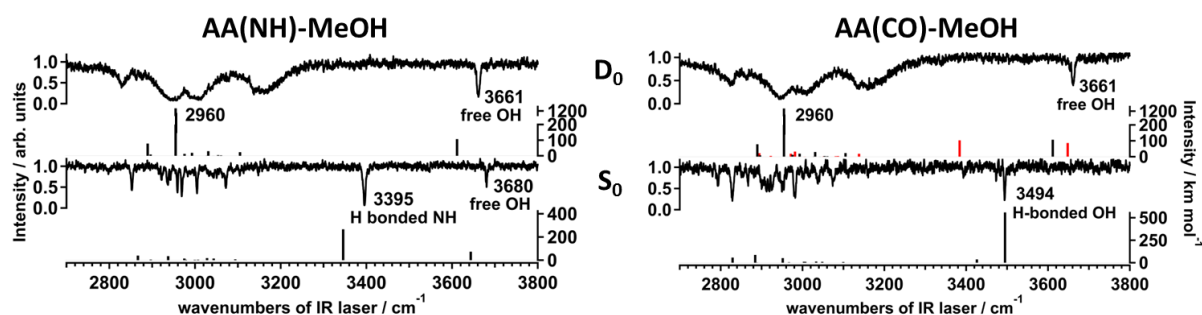
Acetanilide (AA) is one of the smallest aromatic molecules containing a peptide linkage and acts as a model substance for investigation on a molecular level. In case of the water 1:1 cluster, a rearrangement of the solvent molecule induced by photoionization is observed.<sup>[1]</sup> The solvent migrates from the CO-binding site to the NH-binding site. By applying time resolved IR spectroscopy, the migration dynamics was observed in real time and 5ps lifetime of the migration, role of intracuster vibrational redistribution (IVR) and existence of an intermediate have been revealed.<sup>[2]</sup>

In this work, we will investigate the clusters of acetanilide with methanol (AA-(MeOH)) and will discuss the effect of the solvent. We measured the R2PI and IR-UV hole burning spectra for two isomers (see Fig. 1). By applying combined IR/UV techniques a migration of the solvent is observed after ionizing the CO-binding isomer like in the AA-(H<sub>2</sub>O). Furthermore, we will compare our results with DFT calculations (M06-2X/cc-pVDZ) and to the former results of the AA-(H<sub>2</sub>O) clusters.



**Fig. 1:** R2PI spectrum of AA-MeOH in the region from 35500-36800  $\text{cm}^{-1}$  and the structures of the assigned NH-bound and CO-bound isomers and their relative stabilities a). The IR-UV hole burning spectrum of the NH-isomer is shown in b) and the one of the CO-isomers in c)

**[Results]** Fig. 1a shows the  $S_1$ - $S_0$  R2PI spectrum of AA-MeOH. From the analogy to AA- $H_2O$ , the band systems at around  $35692\text{ cm}^{-1}$  and  $36064\text{ cm}^{-1}$ , are tentatively assigned to NH-bound and CO-bound isomers of AA-MeOH cluster, respectively. An experimental proof is given by measuring the IR-UV hole burning spectra of both isomers. The IR laser is fixed at  $3494\text{ cm}^{-1}$  (H-bound OH stretching vibration of CO-isomer) and the UV laser is scanned. The resulting UV excitation spectrum of the NH-isomer is shown in Fig. 1b. The UV excitation spectrum of the CO-isomer is measured in the same way by fixing the IR laser to  $3395\text{ cm}^{-1}$  (H-bound NH stretching vibration of NH-isomer). The structures are also shown in Fig. 1. The observed relative intensities of the species are confirmed by the calculations. The AA(CO)-MeOH is  $2.19\text{ kJ/mol}$  less stable than the AA(NH)-MeOH species. Furthermore, the assignments are immediately confirmed by the IR dip spectroscopy that gives the IR transitions in the  $S_0$  state.



**Fig. 2:** IR/R2PI spectra of AA(NH)-MeOH (left) and AA(CO)-MeOH (right) in the  $S_0$ - (lower traces) and  $D_0$  state (upper traces) and the related calculated stick spectra. For the  $D_0$  state of the AA(CO)-MeOH isomer, the stick spectrum of the assigned solvent migrated AA(NH)-MeOH is shown in black and the stick spectrum of the last optimized structure for the AA(CO)-MeOH in red. The free NH stretching vibration of the monomer in the  $S_0$  state is observed at  $3472\text{ cm}^{-1}$ .

The IR spectrum of the NH-bound isomer in the  $S_0$  state is shown in Fig. 2 (left side). The transition at  $3395\text{ cm}^{-1}$  is assigned to the H-bonded NH stretching vibration, the transition at  $3680\text{ cm}^{-1}$  to the free OH stretching vibration of the MeOH. The corresponding transitions in the AA(NH)- $H_2O$  are observed at  $3417$ ,  $3644$  and  $3743\text{ cm}^{-1}$ . The IR spectrum of the CO-isomer in the electronic ground state is shown in Fig. 2 (right side). The transition at  $3494\text{ cm}^{-1}$  is assigned to the H-bonded OH stretching vibration. The same vibration in AA(CO)- $H_2O$  is observed at  $3492\text{ cm}^{-1}$ . A very weak transition is observed at  $3473\text{ cm}^{-1}$  and can be assigned to the free NH stretching vibration ( $3472\text{ cm}^{-1}$  in the AA monomer). From both measured IR spectra, the assignments of NH- and CO-bound isomers are confirmed.

The IR spectra in the  $D_0$  state for both ionized species are shown in Fig. 2 in the upper traces. No significant differences are observed. The transitions at  $2960\text{ cm}^{-1}$  are assigned to the H-bonded NH stretching vibration of the AA(NH)-MeOH isomer and the transition at  $3661\text{ cm}^{-1}$  to the free OH stretching vibration of the MeOH. This assignment is also valid for the AA(CO)-MeOH isomer. The existence of the same structure in the  $D_0$  state can be explained by isomerization, the solvent molecule migrates from CO to NH binding site after ionization.

In the presentation, we will discuss the IR spectra for both isomers after electronic excitation and photoionization with regard to the structural dynamics induced by the photoionization and will compare the results for methanol with water.

- [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.