Report on our visit to Technische Universität Berlin

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We visited Technische Universität Berlin (Fig. 1) to advance collaborative research with Prof. Otto Dopfer. Keisuke and Kyota stayed in Berlin for a week (Nov. 14-20, 2022) and two weeks (Nov. 14-27, 2022), respectively. This is a brief report of our activities during the stay.

Fig. 1 Technische Universität Berlin.

1. Purpose of the visit

We have collaborative research with Prof. Dopfer on hydration-induced protonation site switching of *p*-aminobenzoic acid (PABA). PABA can be protonated to the carboxy (O-) and the amino (N-) groups, and two kinds of protomers (O- and N-protomer, respectively) have been found (Fig. 2). The O-protomer is stable in the gas phase, while the N-protomer is stable in solution of polar solvents. E. Williams' group reported that hydration by six water molecules to O-protomer induces the proton switching to N-protomer. However, their IR spectra in 3 μm range show broad bands due to H-bonded OH/NH, leaving room for doubt about the number of water molecules required for proton switching. In the collaborative research, we applied the mid-IR spectroscopy, which is less sensitive to broadening by H-bonding, and found that the hydration by five water molecules is enough to induce the O- to N- proton switching. We already submitted a manuscript to Physical Chemistry Chemical Physics (PCCP) of Royal Society of Chemistry before the travel. During the stay in Germany, we aimed to revise the manuscript following reviewers' comments and to discuss the mechanism of the protonation site switching.

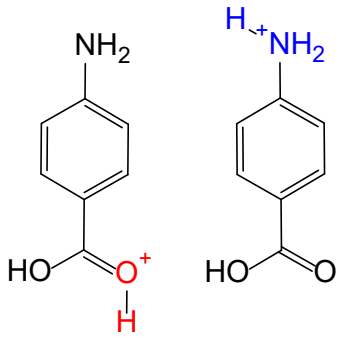

Fig. 2 Molecular structures of O- and N-protomers of $PABAH^+$.

2. Progress of the research

1) Revision of the paper

We revised our manuscript following the reviewer's comments during the stay. We were

able to make a reasonable reply to the reviewers' comments by face-to-face communication with Prof. Dopfer. The manuscript was accepted in PCCP in Dec. 6, 2022 as an open access paper (DOI: https://doi.org/10.1039/D2CP04497H).

2) Proton transfer mechanism underlying the protonation site switching

Isotope labelling is a powerful tool to reveal the proton transfer mechanism behind the hydration-induced protomer switching. We were able to selectively deuterate water in the hydrated clusters without deuteration of the PABA molecule. This allows to determine the origin of the proton transferred from O→N proton switching. We measured the IR spectra of the deuterated clusters before the travel. We discussed the mechanism of the proton transfer based on the IR spectra with Prof. Dopfer.

Keisuke made a presentation entitled "Probing proton transfer mechanism by cryogenic ion trap IR spectroscopy" in lab seminar on Nov. 17, 2022. Several students from the Dopfer Lab. asked him a couple of questions regarding the critical points of the research. This session has helped to deepen our understanding for the proton transfer mechanisms. Based on the session and discussion, we have started to write a second paper on the proton transfer mechanisms.

3) Improvement of the laser system in Berlin

During the discussion with Prof. Otto, we found that the IR laser system in Berlin can be updated to that in Japan. The IR range in 1300–1800 cm^{-1} was generated by difference frequency generation in $AgGaSe_2$ (AGS) pumped by near-IR (~1600 nm) and IR (~3000 nm) light. However, this limits the laser fluence of the generated IR light due to the low damage threshold of the AGS crystal to the pump light, hampering to measure a well-resolved IR spectrum with a high S/N ratio. We were able to double the laser fluence by introducing a new crystal, $ZnGeP_2$, with a higher damage threshold. This enables to measure an IR spectrum with a better S/N ratio.

3. Conclusion and acknowledgments

We have revised our first paper on the hydrated clusters of $PABAH^+$. We also discussed the mechanism of the proton transfer reaction and started writing a second paper on it. The stay of one/two week(s) in Berlin was a valuable experience for us. We would like to express our gratitude to Prof. Otto Dopfer and the members of the laboratory, and special thanks for the financial support by the JSPS Core-to-Core program.