

Report on 68th Ohio State University International Symposium on Molecular Spectroscopy by JSPS Core-to-Core Program

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As part of the JSPS (Japan Society for the Promotion of Science) Core-to-Core Program, I have participated and made an oral presentation in the international symposium held at the Ohio State University (OSU) from 17th to 21st of June, 2013. It was a second experience for me to attend an international symposium. I took part in this program with Mr. Shunpei Yoshikawa who is also a member of Fujii group in Tokyo Tech. In this report, I would like to describe my presentation and impressions of the symposium briefly.

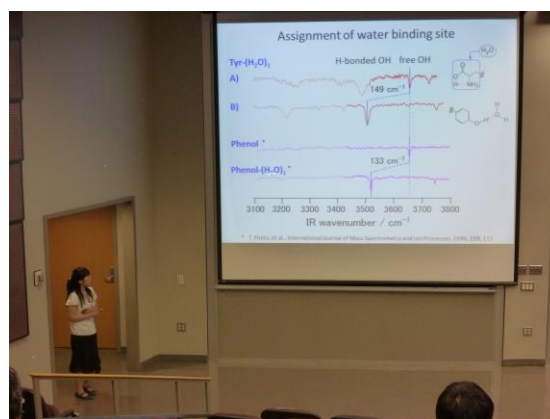


Fig.1 Presentation in the OSU international symposium

Presentation in the symposium

The OSU international symposium is held every year, and it is 68th time this year. This symposium focuses on fundamental molecular spectroscopy. Many researchers and students from across the world make only oral presentations. Unfortunately however this symposium will mark the end of an uninterrupted series of annual meetings at the OSU after this time. So I had my first and last chance to attend this symposium.

On 18th June, I gave a talk about the results of collaborative works with Dr. Pierre Çarçabal at the Université Paris-Sud 11 by the Core-to-Core Program. The title of the presentation was “Laser desorption supersonic jet spectroscopy of hydrated tyrosine”. In this presentation, I reported the cooperative effect of hydrogen bonding on tyrosine-water 1:1 clusters.

The purpose of the collaborative research was to investigate the structure of hydrated tyrosine in the gas phase by using laser desorption supersonic jet spectroscopy. Resonance enhanced 2 photon ionization (R2PI) spectrum of hydrated tyrosine has

already been reported by de Vries and co-workers, however there was no analysis on the hydrated structures. So we measured R2PI and IR spectra of tyrosine-(H₂O)₁ clusters and assigned the structures with the aid of quantum chemical calculations. As the result, we observed two isomers in which the hydrogen-bonding site of water molecule is different; one is the amino-acid chain and another is the phenolic OH group (Fig. 2). In the latter isomer, it was found that the intra-molecular hydrogen bond within the amino-acid chain (OH-N), which is far from the water molecule and cannot interact directly with each other, is strengthened by the hydration. Namely, the enhancement of hydrogen bond strength in the amino-acid chain is induced by the hydrogen bond formed between the water molecule and the phenolic OH, which is called “cooperative effect” of hydrogen bonding. The cooperative effect is usually observed in hydrogen bond networks, in this case however it is observed between two hydrogen-bonding parts separated far away from each other. According to natural bond orbital analysis, it is confirmed that the direction of dipole moment of each part is important to enhance the hydrogen bond strength in the amino-acid chain.

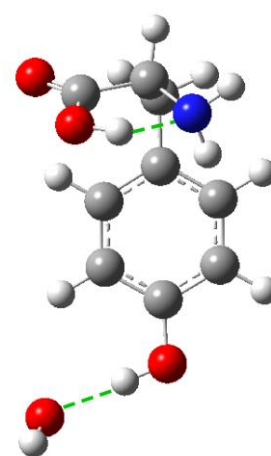


Fig. 2 Phenolic OH bound isomer of hydrated tyrosine

In the discussion time, I was asked three questions. However it was hard for me to answer on the spot, I make a list of Q&A as following.

1. *Did we take into account the effect of change of charge distribution in π -cloud on the enhancement of hydrogen bond strength in the amino-acid site ?*

We considered the effect of charge distribution in π -cloud due to hydration. However we could not find out a significant difference between the monomer and hydrated clusters.

2. *For the most stable conformer of tyrosine in the supersonic jet, the conformation of amino-acid group is different from that of glycine in the liquid phase. Did we compare the conformation of tyrosine with that of glycine by microwave spectroscopy ?*

This was the thing what I did not consider, so I checked the conformation of glycine by

microwave spectroscopy. For the most stable conformer of glycine by microwave spectroscopy, the NH₂ group forms a bifurcated intermolecular hydrogen bond with the C=O group.[1] This is in contrast to the observed most stable conformer of tyrosine in the supersonic jet which forms intermolecular hydrogen bond between the carboxyl OH group and the nitrogen of NH₂ group.

3. Did we confirm the electron density distribution of nitrogen atom which forms hydrogen bond with the carboxyl OH group according to the result of NBO analysis ?

We checked the electron density distribution of the nitrogen atom, however, we could not find out a significant difference.

Impressions of the symposium

In the symposium, the lectures were given with a series of sessions, and I mainly attended lectures on infrared/Raman and electronic spectroscopy. In particular, I had an interest in talks about peptides by Prof. Zwier group in the Purdue University. They gave talks on the conformation of γ -peptides in the gas phase, which differ from α -peptides by incorporating two additional carbon atoms between amide groups. I took an interest in the specific structure of γ -peptides, so I followed up the talks by reading a paper. In methyl-capped γ -tripeptides, a hydrogen-bonded cyclic structure unprecedented in other capped α -tripeptides and β -tripeptides was observed.[2] All three amide groups form hydrogen bonds. This is an attractive example that the flexibility and separation between amide groups in the γ -peptides backbone lead to a new structure which is tightly folded. They assessed the nonbonded interactions among observed conformers by using pair interaction energy decomposition analysis based on the fragment molecular orbital method (FMO-PIEDA). This is a method to characterize relative strengths of nonbonded energy components for cutting a large molecule into fragments and then breaking the total energy into nonbonded and through-bond contributions. FMO-PIEDA analysis shows that a combination of three weaker (more distorted) amide-amide hydrogen-bonds in the hydrogen-bonded cycle results in stronger noncovalent interactions because of cooperative effects of three of them.

In the conference, I also took an opportunity to learn English oral expressions for scientific presentation. I realized that I did not know oral expressions well when I made a manuscript for the presentation. There were many native speakers in the meeting, so

it was quite good chance to study correct and natural expressions. I took a note when I heard some phrases that I thought it would be useful to presentations. I would like to use some expressions that I learned there in the future.

In my presentation, I felt that I needed more effort to study molecular science to understand and answer questions properly, however, I was happy that I had the opportunity to give a talk in the international symposium.

Acknowledgment

I would like to express my thanks to Prof. Masaaki Fujii who gave me such a nice opportunity, Dr. Shun-ichi Ishiuchi and Dr. Pierre Çarçabal who gave me helpful advises to prepare my presentation, Mr. Shunpei Yoshikawa who attended the international symposium together, and all of the people who are involve in the JSPS Core-to-Core program. I would like to also appreciate the financial supports by the JSPS Core-to-Core program.

References

- [1] F. J. Lovas, Y. Kawashima, J. -U. Grabow, R. D. Suenram, G. T. Fraser, and E. Hirota, *Astrophys. J.*, 455 (1995) L201-L204.
- [2] W.H.J. III, E.G. Buchanan, C.W. Müller, J.C. Dean, D. Kosenkov, L.V. Slipchenko, L. Guo, A.G. Reidenbach, S.H. Gellman and T.S. Zwier, *J. Phys. Chem. A*, 115 (2011) 13783-13798.



Fig.3 In front of the OSU University