

Report on Visit to Université Paris-Sud 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 participated in an international collaboration with Dr. Pierre Çarçabal at the Université Paris-Sud. I also presented results of the collaboration with Dr. Çarçabal obtained by a previous visit in a Core-to-Core international symposium held in Marseille, France. I took a part in this program with Dr. Shun-ichi Ishiuchi, Mr. Woonyong Sohn. This is a report of my study in France from 4th to 18th of March, 2013.

Purpose of the visit

My purpose of this visit was to investigate hydrated clusters of biologically relevant molecules in Dr. Pierre Çarçabal's group and to make a presentation in the Core-to-Core international symposium. This was the second time that I participated in the collaborative study with Dr. Çarçabal at the Université Paris-Sud. In May last year, I visited his laboratory to learn how to produce hydrated clusters by using laser desorption technique, because we were faced to a problem that signals of clusters could not be observed at all in our machine. After the first visit, we improved our machine to observe signals derived from hydrated clusters. However, the signals were too weak to measure spectra. In order to measure spectra, much improvement is necessary, which is now in progress.

We have recently studied homophenylalanine (HPhe) in the gas phase to compare the conformational landscape with that of phenylalanine (Phe). HPhe has one more methylene group in the side chain by comparison with Phe (Fig. 1). In the next

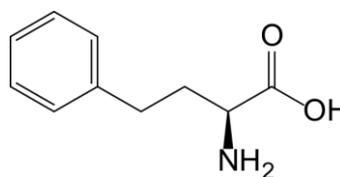


Fig.1 homophenylalanine (HPhe)

step, we aimed to investigate hydrated HPhe clusters. So we visited his laboratory in order to study HPhe-water clusters by using the machine that can measure clusters.

In addition to this study, I had an opportunity to make the presentation about hydrated tyrosine, which was the results of the collaboration with Dr. Çarçal in the previous visit, in the international symposium held in Marseille.

Experimental

We used laser desorption supersonic jet technique to measure hydrated HPhe. The experimental setup is shown in Fig. 2. A mixture of HPhe and a small amount of graphite was applied to a plate made from graphite, and it was irradiated by a fundamental of a YAG laser to vaporize the sample. The sample vapor was picked up by supersonic jet expansion of Ar gas including water vapor. The backing pressure of Ar gas was 6 bar. The supersonic jet was trimmed by a skimmer to molecular beam and it was crossed with a tunable UV laser to be ionized. The generated cations were detected by a MCP through a time of flight (TOF) mass spectrometer to measure mass-selected resonance enhanced two photon ionization (R2PI) spectra.

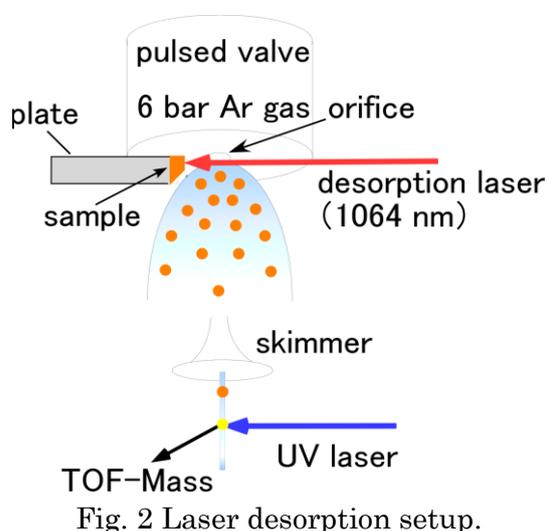


Fig. 2 Laser desorption setup.

Progress of the study

1. Measurement of R2PI spectrum of hydrated HPhe clusters

First, we measured R2PI spectrum by monitoring the mass of HPhe in the presence of water vapor in order to examine whether hydrated clusters exist or not. If hydrated clusters are generated, some bands derived from fragmentation of the water clusters frequently appear in the monomer spectrum. Actually, by comparing this R2PI spectrum with previously measured one by us without water vapor, we found some additional peaks which may be come from fragmentation of the hydrated clusters (Figure 3a), which is denoted by blue lines. So we measured mass spectrum by changing the wavelength of UV to find out mass peaks of HPhe–water

clusters, however signals derived from the clusters were not observed for some reason.

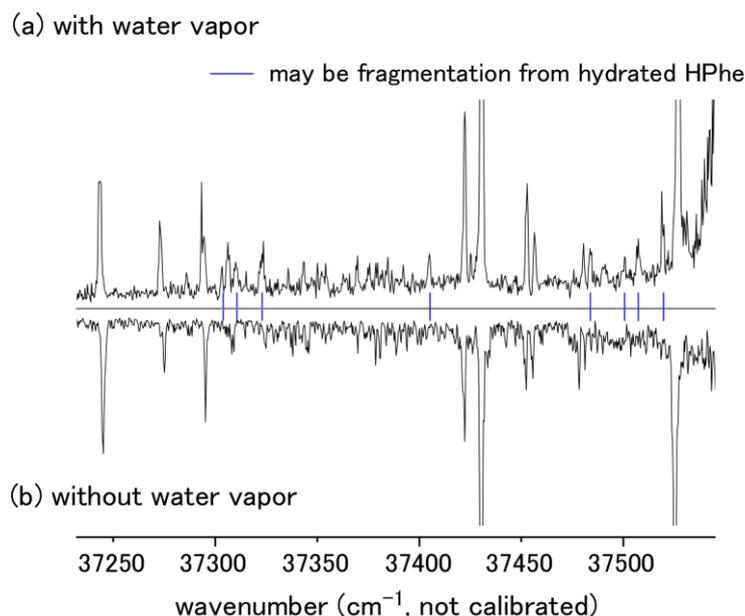


Fig.3 Comparison of R2PI spectra of HPhe measured by probing the monomer mass peak (a) with and (b) without water vapor in the sample system to examine generation of hydrated HPhe clusters. Blue lines indicate additional peaks that are thought to appear in the spectrum (a) due to fragmentation from the hydrated clusters.

2. R2PI spectrum of HPhe measured by picosecond laser

One of the possible explanations why the water clusters were not observed is that the lifetime of the S_1 state of the clusters is quite short (\sim ps). To confirm this possibility, we switched the nanosecond laser system to picosecond one. By using the picosecond UV laser (pulse width: \sim 15 ps), we measured a mass spectrum at several wavelengths. However, any signals of water clusters were not observed. Thus, the reason why the water clusters were not observed is not due to the lifetime.

En passant, we measured R2PI spectrum of HPhe monomer by using the picosecond laser in order to confirm the lifetime effect on signal intensities of each conformer. In the REMPI spectrum of HPhe measured by nanosecond laser, the signal intensities of each conformer are largely different. So there is a possibility

that some conformers which give weak bands have short lifetimes in the S_1 states. By comparing the R2PI spectrum measured by the picosecond laser with that obtained by the nanosecond laser, it was found that the picosecond spectrum is almost the same as the nanosecond one (Fig. 4). It means that the lifetime of each conformer is not much different and the difference of signal intensities of each conformer should be explained by distribution of the conformational population.

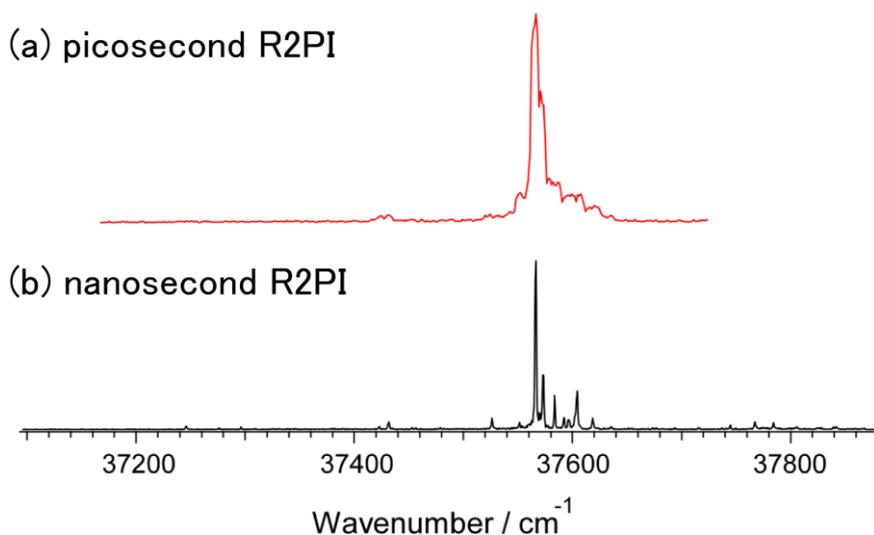


Fig.4 R2PI spectra of HPhe measured by (a) picosecond laser and (b) nanosecond laser.

3. Future plan to study hydrated HPhe

As mentioned above, any signals of hydrated HPhe were not observed though a few additional peaks that may be derived from the fragmentation of hydrated clusters were observed. In addition, it was found that the absence of the cluster signals is not due to the short lifetime in the S_1 state. So, we are considering a possibility of quite highly efficient dissociation of water clusters in the cationic states due to large excess energy. Namely, hydrated HPhe clusters would be generated but the cluster signals are not observed due to the dissociation.

As shown in Fig. 5(a), the HPhe–water clusters can be dissociated into the HPhe cation and a water molecule by the excess internal energy in the case of one-color R2PI scheme. We can resolve this problem by applying a two-color R2PI scheme to reduce the excess energy as shown in figure 5(b). This method makes it possible to

prevent the dissociation of hydrated clusters because of the smaller excess energy. So we will try the two-color experiment to examine whether R2PI spectra of HPhe–water clusters can be measured or not.

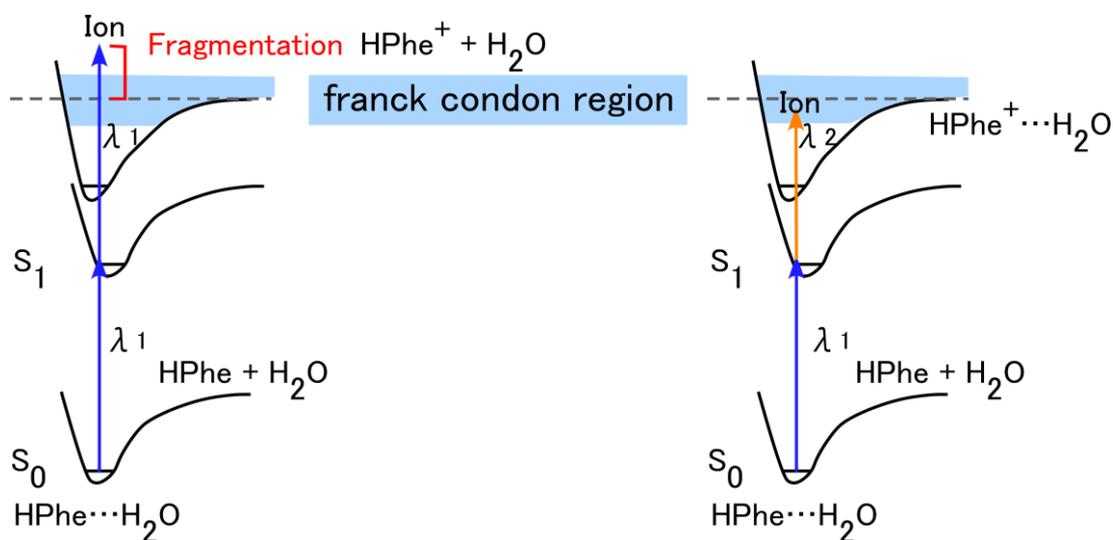


Fig. 5 (a) One-color ($\lambda_1+\lambda_1$) and (b) two-color ($\lambda_1+\lambda_2$) scheme of the resonant 2 photon ionization.

Core-to-core symposium in Marseille

On 15th March, the Core-to-Core international symposium on ionization induced switching was held in Marseille. I gave a talk about hydrated tyrosine in the gas phase which is the results of the corroborative study with Dr. Çarçal in the previous visit. We measured R2PI and IR spectra of tyrosine-water 1:1 clusters to assign the structures by comparing with quantum chemical calculations. In this study, we found a curious phenomenon of the cooperative effect of the hydrogen bond. The cooperative effect is that the formation of a hydrogen bond does affect other hydrogen bond strength. In general, the cooperative effects are observed in hydrogen bond networks. In the tyrosine–water cluster, we however found that the cooperative effect obviously exists between a hydrogen bond of phenolic OH–water and that of the amino-acid group despite the long distance between them. According to a result of theoretical calculations, it was found that the configuration of the partial dipole moment of each part is important to change the strength of the cooperative effect.

It was the first time for me to have a presentation in English abroad, so it was a challenge for me. I realized that it was necessary to learn molecular science more and to improve my English speaking in order to answer to questions. Anyway it was quite nice opportunity for me to learn a lot of things.

Visiting Prof. Christophe Jouvét's group

On 18th March, I visited Prof. Christophe Jouvét's group at the Aix-Marseille Université to see their laboratory. At that time, I introduced my research project to members of his group. My project is to study the conformation of peptide which mimics the binding site of β_2 -adrenergic receptor in the gas phase. In this study, it is necessary to synthesize peptides by myself because many kinds of isotopomers are necessary to assign the IR spectra and they are too expensive to order specially. I learned how to synthesize peptides and actually synthesized 5-residue peptide which is a partial peptide of the adrenergic receptor. Prof. Christophe Jouvét and his wife, Prof. Claude Dedonder, showed an interest in the peptide synthesis, so I explained them how to synthesize peptides.

Conclusion and acknowledgment

We measured R2PI spectrum of HPhe by using the picosecond laser. It was confirmed that the life time of each conformer does not affect the signal intensity. We consider that dissociation due to the excess energy in the cationic state could be the reason why no signal of hydrated HPhe clusters was observed in the R2PI spectrum. We will try the two-color experiment to check whether the signal of the clusters can be observed or not. I would like to express my appreciation to Dr. Pierre Çarçabal, Dr. Shun-ichi Ishiuchi, Mr. Woonyong Sohn, Prof. Christophe Jouvét, and Prof. Masaaki Fujii who gave me such a nice opportunity.