

# Report on a visit to University of Paris XI 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 studied in Dr. Pierre Çarçabal group at the University of Paris XI for two weeks, from 1<sup>st</sup> to 15<sup>th</sup> December 2013. In addition, I attended to Core-to-Core international symposium held in University of Manchester on 16<sup>th</sup> December and presented results of my research. This is a report of this visit.

## 1. Purpose of the visit

In Tokyo Tech., I am investigating gas phase spectroscopy of tripeptide Ac-Gly-Trp-Pro-NH<sub>2</sub>. Previous study on a pentapeptide Gly-Trp-Pro-Pro-Val (GWPPV), which is a partial peptide of a receptor protein of plant hormone, performed in our group found that the

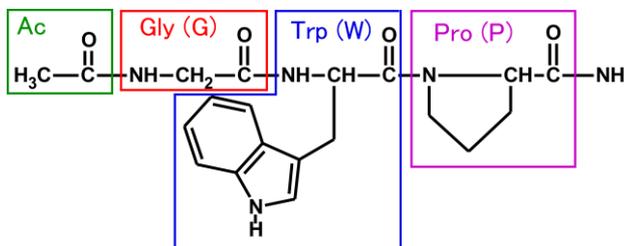


Fig. 1 Structure of Ac-Gly-Trp-Pro-NH<sub>2</sub> (GWP).

electronic spectrum of GWPPV in the gas phase shows broad absorption, implying that lifetime of the electronically excited tryptophan residue in GWPPV is quite short. On the other hand, that of Gly-Trp does not give such broad absorption.[1] Thus, other parts than GW in GWPPV should affect the tryptophan residue to reduce the lifetime of the excited state. So we took notice of tripeptide Gly-Trp-Pro (GWP) to examine whether the Pro residue reduces the lifetime of the electronically excited Trp residue. So far, I measured REMPI, UV-UV hole burning, and IR dip spectra of GWP (Fig. 1). The REMPI spectrum of GWP gives broad and sharp electronic transitions, suggesting that GWP may have several conformers and some of them have short lifetime but others have long lifetime. UV-UV hole burning spectroscopy confirmed that the broad and sharp transitions are derived from different conformers. This result clearly demonstrates that conformational difference affects the excited state dynamics and probably some specific conformations accelerate relaxation processes of electronically excited states.

Multiplicity of conformation is seen in not only flexible single molecules but also their hydrated clusters that can be regarded as a model of hydration of peptides in aqueous solutions. Thus, in this visit I planned to measure GWP–water clusters to make sure the effect of hydration on structures of peptides, because Prof. Çarçabal group excels at the investigation of biomolecule–water clusters by using laser desorption technique.

## 2. Progress of the study

### 2.1 Experimental

To produce GWP–water clusters in the gas phase, the laser desorption supersonic jet technique was used (Fig. 2). Mixture of GWP, which was synthesized by myself, and trace amount of graphite powder was applied to a graphite bar. A desorption laser (1064 nm, 5 ns, 10 Hz) was introduced on the surface to vaporize the peptide. The gaseous hot peptide molecules are cooled down by supersonic jet expansion of 5 bar Ar saturated with H<sub>2</sub>O vapor at room temperature. By three-body collisions (GWP, H<sub>2</sub>O, and Ar), the GWP–H<sub>2</sub>O clusters were produced in the expansion. The supersonic jet was trimmed by a skimmer to make a molecular beam. A tunable UV laser beam was irradiated on the molecular beam and the GWP–H<sub>2</sub>O clusters were ionized by two-photon absorption. The generated ions were detected by time-of-flight mass spectrometer (TOF-MS).

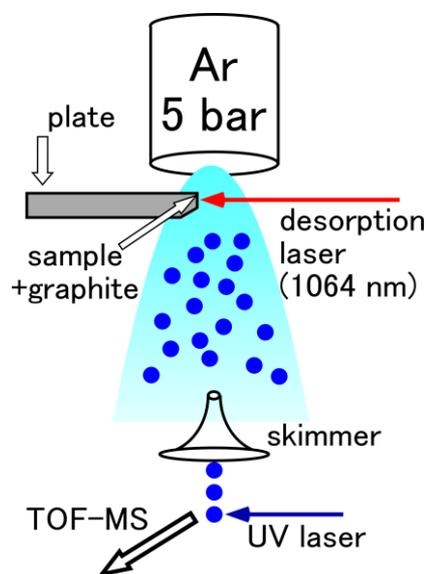


Fig. 2 Schematic of the laser desorption supersonic jet technique.

### 2.2 Results and discussion

First of all, I measured a mass spectrum of GWP–water clusters to make sure cluster generation (Fig. 3). The wavelength of the ionization UV laser was fixed at 287.6 nm. As can be seen in the figure, higher clusters (up to 1:4) and GWP dimer are observed with the highest intensity on the GWP–H<sub>2</sub>O (1:1) cluster.

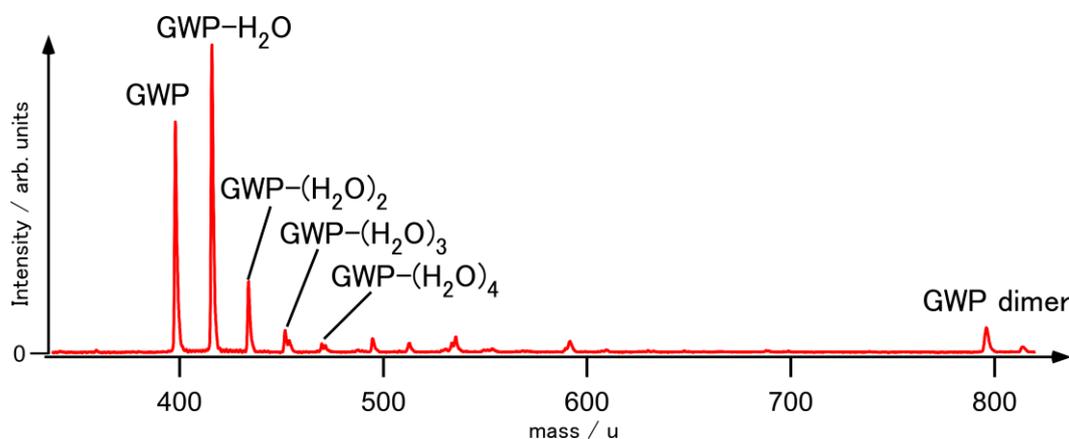


Fig. 3 Laser ablation mass spectrum of GWP expanded with water vapor.

Then, I measured REMPI spectrum by monitoring mass peak of GWP–water cluster (1:1) cluster (Fig. 4). In the figure, a REMPI spectrum of the GWP monomer measured in Tokyo Tech. is also shown for a comparison. As can be seen in the figure, GWP–water (1:1) cluster shows only broad absorption. Structures observed at 34800–35100  $\text{cm}^{-1}$  is duo to power fluctuation of the UV laser. Though it is difficult to determine the 0-0 electronic transition energy exactly, the rise of the absorption is similar to that of GWP monomer, which is at  $\sim 34600 \text{ cm}^{-1}$ . In the case of indole–water 1:1 cluster, the 0-0 electronic transition appears at 35109  $\text{cm}^{-1}$  red-shifted by 132  $\text{cm}^{-1}$  from that of the monomer.[2] In the indole–water 1:1 cluster, the water molecule binds to the NH group of indole, and the hydrogen bond causes the large red shift of the electronic transition. Thus, it be expected that the GWP-H<sub>2</sub>O (1:1) cluster does not form the hydrogen bond between the indole NH group and the water molecule.

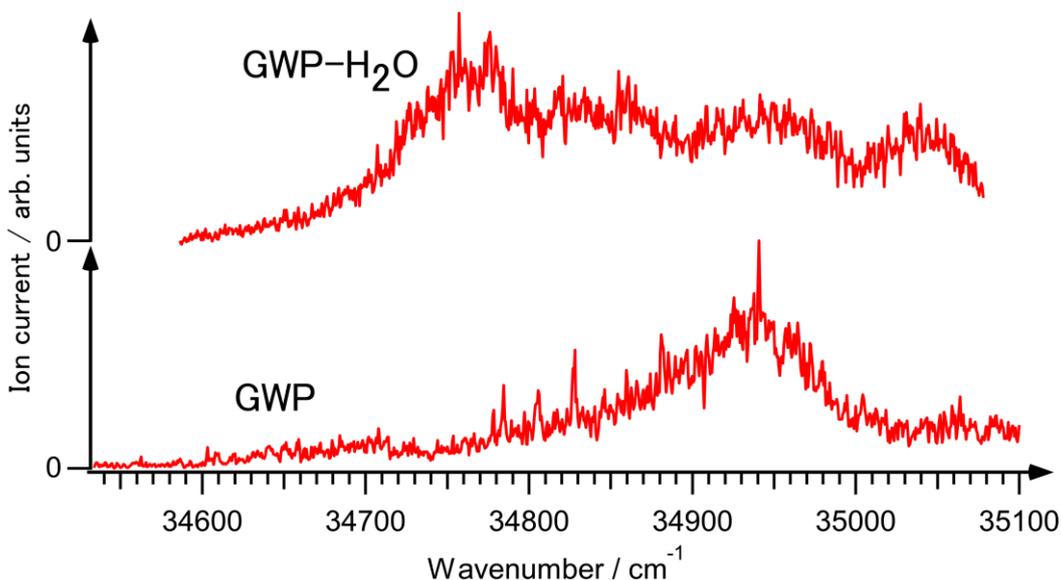


Fig. 4 REMPI spectra of GWP monomer and GWP-water cluster.

To obtain the structural information and confirm the above expectation, I measured an IR dip spectrum by monitoring the electronic transition of GWP-water (1:1) at 34789  $\text{cm}^{-1}$ . The observed spectrum is shown in Fig. 5 with those of monomer measured in Tokyo Tech. for a comparison. The blue-most band observed at 3714  $\text{cm}^{-1}$  is assigned to a free OH stretch of H<sub>2</sub>O. The bands observed at 3525, 3476, 3453, 3331, and 3296  $\text{cm}^{-1}$  are tentatively assigned to NH<sub>ind</sub>, NH<sub>2</sub><sup>anti</sup>, NH<sub>Gly</sub>, NH<sub>Trp</sub> and NH<sub>2</sub><sup>sym</sup>, respectively, based on their frequencies. An intense band observed at 3380  $\text{cm}^{-1}$  is assigned to a hydrogen-bonded OH stretch of H<sub>2</sub>O. This frequency is lower than that of free OH symmetric stretch,  $\nu_1$ . It may suggest that the strength of the hydrogen bond between the peptide and water molecule is enhanced by structural optimization that becomes possible due to flexibility of the peptide.

To analyze the observed spectrum, theoretical IR spectra of several possible conformations are necessary. To search the possible structures, I applied classical force field calculation to the

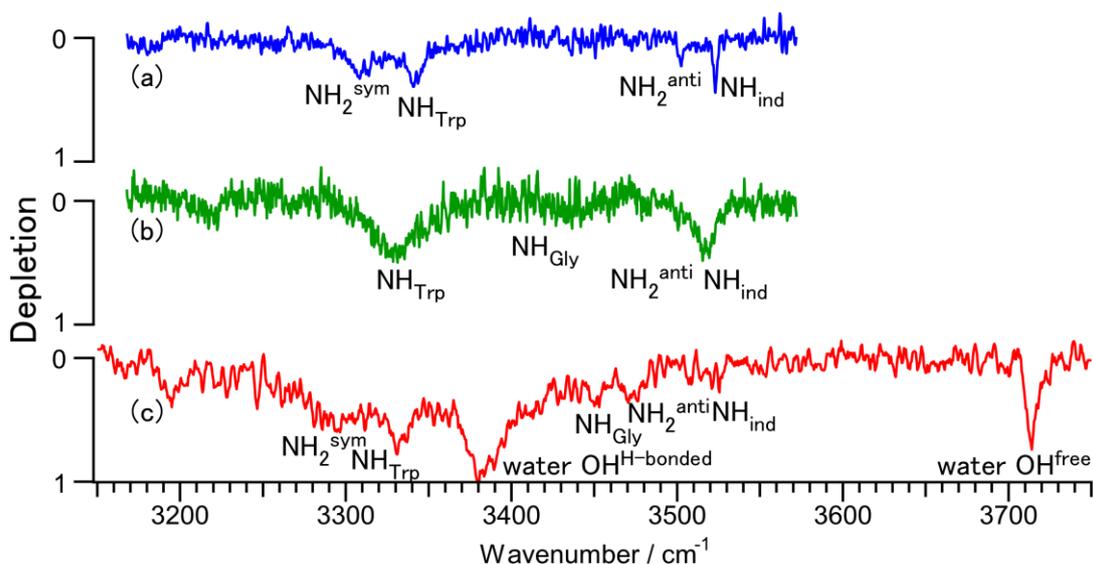


Fig. 5 IR dip spectra of GWP monomer probed at (a)  $34953\text{ cm}^{-1}$  and (b)  $34904\text{ cm}^{-1}$ , and (c) GWP–water cluster probed at  $34789\text{ cm}^{-1}$ .

GWP–water cluster by using MacroModel Table 1 Assignment of the IR spectrum of the package. The calculation provided over GWP–water cluster.

thousand conformations. From these, I searched conformers that can be expected from the experimental result, and finally picked up 20 candidates of possible conformer responsible for the experimentally observed. By using them as initial structures, I will carry out quantum chemical calculations to assign the structures of the GWP–water cluster in Tokyo Tech.

band [ $\text{cm}^{-1}$ ]	assignment
3714	$\nu_3$ of $\text{H}_2\text{O}$
3525	NH stretching (indole ring)
3476	anti- $\text{NH}_2$
3453	NH stretching (Gly)
3380	$\nu_1$ of $\text{H}_2\text{O}$
3331	NH stretching (Trp)

### 3. Core-to-Core international symposium in University of Manchester

On 16<sup>th</sup> December, I attended the 8<sup>th</sup> symposium “Core-to-Core International Symposium on Ionization Induced Switching” and presented my research on the excited state dynamics of tripeptide Ac-Gly-Trp-Pro- $\text{NH}_2$ .

It was discussed how to choose basis functions in the quantum chemical calculations. I was pointed out that if the result of calculation is not match well another basis function should be used. Influence of hydrogen-bond pattern on stability of folding structure of peptides was also discussed. It was the first time for me to have a presentation in an international symposium. So, it was very worthwhile challenge and good experience for me to discuss meaningfully.

In this symposium, many researchers who are investigating gas phase spectroscopy gave presentations. Especially, I was attracted the research about structural study of indole and

methylindole clusters and its cations by IR spectroscopy in the gas phase. I am also investigating about structural study. So, it was good opportunity to know new topics and to obtain meaningful knowledge.

#### **4. Conclusion and acknowledgment**

I succeeded in measuring REMPI and IR dip spectra of the GWP–water cluster. It was confirmed that the lifetime of the GWP–water cluster in the electronically excited state is short, similar to that of (one of the conformer of) the GWP monomer. In addition, the hydrogen bond structure between the water molecule and the peptide was predicted from the observed spectra. The structure of the GWP–water cluster will be assigned near future by comparing the observed IR spectrum with theoretical ones of several possible conformers obtained by quantum chemical calculations.

I would like to express my appreciation to Prof. Pierre Çarçabal, Dr. Shun-ichi Ishiuchi, Mr. Woon Yong Sohn, Ms. Hikari Oba, Prof. Masaaki Fujii, and everyone involved this program.

#### **References**

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- [2] J. R. Carney and T. S. Zwier, *J. Phys. Chem. A* **103**, 9943 (1999).