Report on visit Université Paris Sub 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's group at the Université Paris XI for two weeks, 7th to 20th of December, 2014. This is a report of my study in Paris.

1. Purpose of this visit

We are investigating the relationship between excited state dynamics and conformation of isolated peptides containing a tyrosine chromophore capped by two amide groups such as *N*-acetyl-tyrosine-methyl amide (capped Tyr) and *N*-acetyl-glycyl-tyrosyl-glycine-amide (GYG, Fig. 1) in the gas phase by using laser desorption jet technique. In our laboratory, we measured electronic spectra of them and identified five conformers for capped Tyr and two conformers for GYG using resonance enhanced multiple photo ionization (REMPI) and UV-UV hole burning (HB) spectroscopy. In addition, we assigned the structures of these conformers tentatively by applying IR dip spectroscopy and quantum chemical calculation. From these results, the conformers of capped Tyr could be classified to three groups according to the structual similalities. One forms an intermolecular C5 structure. Here, "C" and "5" mean a cyclic hydrogen bond structure and number of atoms included in the cyclic hydrogen bond, respectively (Fig. 1). Other groups are C7 and non-hydrogen bond structures. In each group, probably there are two conformers whose peptide chain structure is common but the orientation of phenolic OH was different. In contrast, conformers of GYG both have intermolecular C5, C7 and C10 hydrogen bonds in common but the back bone structures are different. The electronic spectra of two isomers with the C5 structure of capped Tyr exhibits band broadening, which implies short lifetimes, while those of GYG show only sharp bands. These observation implies the lifetime strongly depends on conformaion around the tyrosine chromophore. So, as the next step, we intended to get information about the lifetime of excited state of each conformer so as to discuss the excited

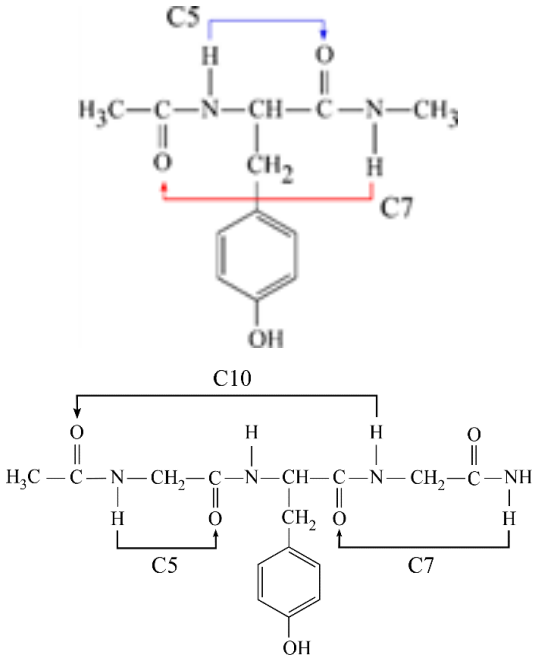

Fig. 1 Structure of capped Tyr (top) and GYG (bottom)

state dynamics quantitatively. However, in our laboratory it is difficult to carry out lifetime measurement of peptides in picosecond time domain for some reason. Dr. Pierre Çarçabal's group at the Université Paris XI has a picosecond laser system that can measure lifetime of biomolecules with laser desorption technique. Thus, I decided to visit his laboratory to measure lifetime of capped Tyr and GYG.

2. Progress of this study

2.1 Picosecond REMPI spectrum

First, we measured the picosecond REMPI of capped Tyr and GYG using the laser desorption supersonic jet technique to confirm whether REMPI spectrum recorded by picosecond laser reproduces the spectral features observed by nanosecond laser. The REMPI spectra obtained by nanosecond laser (red) and picosecond laser (blue) are shown in Fig. 2 with the structures of capped Tyr. In the nanosecond spectrum, we can find five conformers 1–5 (by the UV-UV HB experiment). The picosecond REMPI spectrum roughly reproduces the nanosecond REMPI, though conformer 3 is not observed.

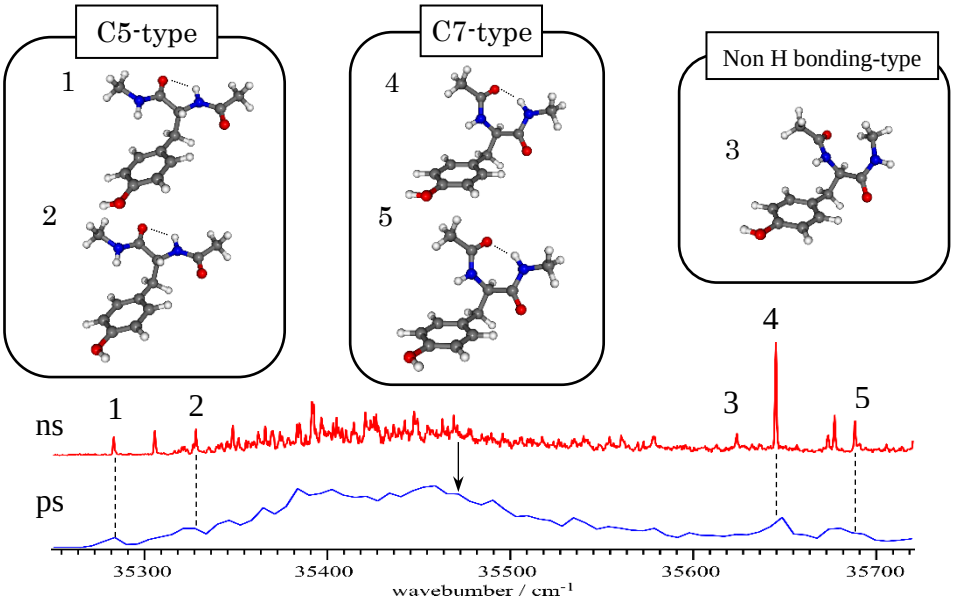

Fig. 2 REMPI spectra and structures of capped Tyr

The REMPI spectra of GYG (red: nanosecond, blue: picosecond) and two structures are shown in Fig. 3. Two conformers were named "conformer A" and "conformer B". The picosecond REMPI spectrum reproduces that obtained by nanosecond laser. In picosecond REMPI spectrum, intensity of the origin band of conformer A is weaker, but it was strong enough to measure the lifetime.

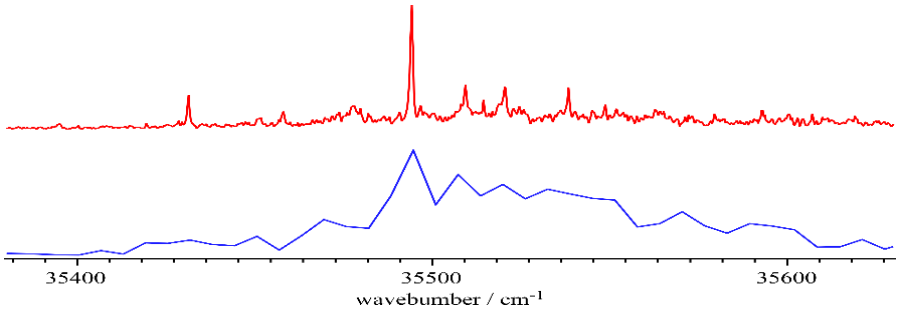

Fig. 3 REMPI spectra and structures of GYG

2.2 Pump-probe experiment

To measure the lifetime of the S_1 state, we applied UV-UV pump-probe experiment based on the picosecond REMPI spectra. Fig. 4 shows the scheme of UV-UV pump-probe experiment using the picosecond laser system. To excite a conformer of the S_0 state to that of the S_1 excited state, wavelength of the pump laser was fixed to the origin band of each conformer (shown by dot lines in Fig. 2 and 3). To ionize the conformer of S_1 excited state, wavelength of the probe laser was fixed to 280 nm. Two color ion signal was monitored by scanning delay time (Δt) between the pump and probe laser in order to obtain the time profile.

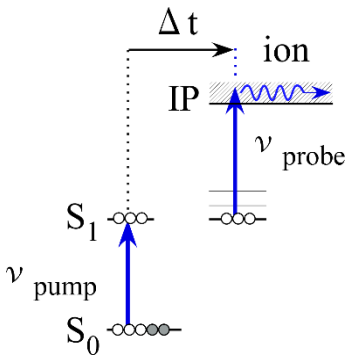

Fig. 4 Pump-probe experiment scheme

Fig. 5 shows time profiles of capped Tyr. Each time profile can be fitted by single-exponential functions. The lifetimes of C5 conformers are 1.3 ns and those of C7 conformers are 1.0 and 2.8 ns. Thus, significant difference in lifetimes among the conformers is not observed. Not only the sharp peaks but also broad absorption was pumped to investigate the reason for the broadness. The broad absorption around 35473 cm^{-1} was monitored (see an arrow in Fig. 2). In this case, the lifetime was about 1 ns. Therefore, the lifetimes of C5

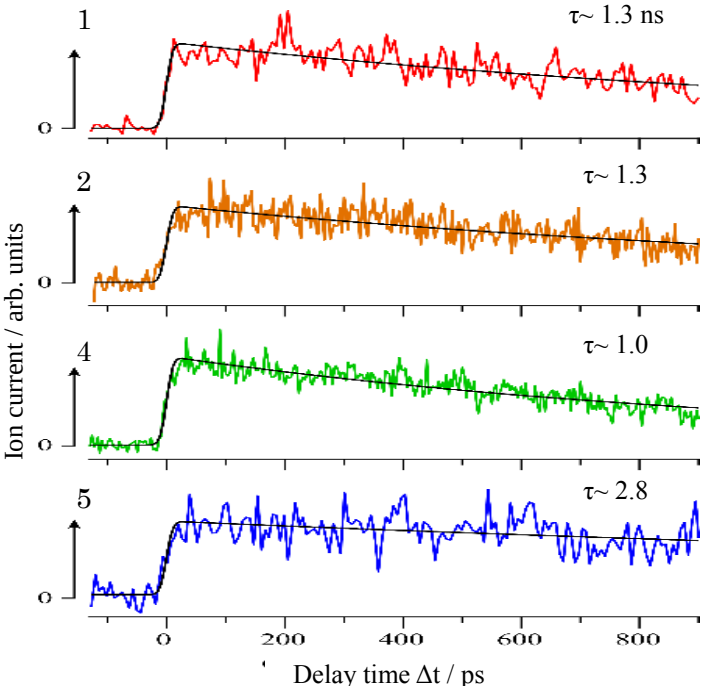

Fig. 5 Time profiles of capped Tyr

conformers are similar to those of C7 conformers.

Fig. 6 shows time profiles of GYG. The lifetimes of conformer A and B, which have different back bone structures, are both about 1 ns.

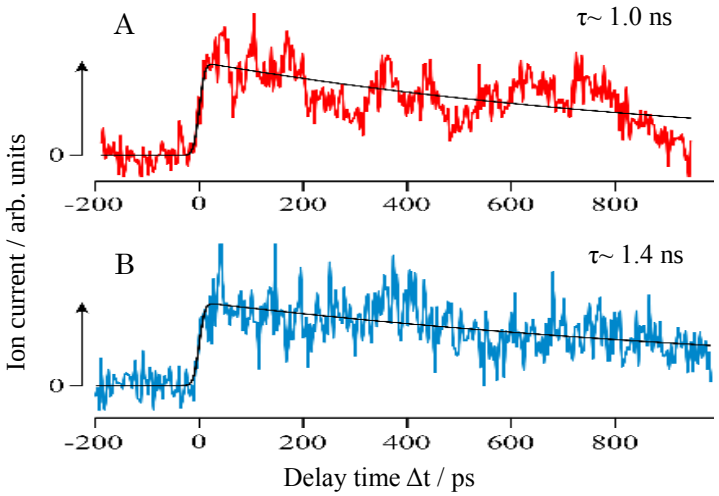

Fig. 6 Time profiles of GYG

Discussion about structure and lifetime

From the result of this experiment, I discuss the relationship of structure and lifetime. In capped Tyr, the lifetime of each conformer is almost the same. Thus, it is expected that conformational dependence of the lifetime of capped Tyr does not exist. In addition, the lifetimes of the GYG conformers are almost the same though they have different back bone structures. Therefore, peptide chain structures may not have any effects on the lifetime. The chromophore of capped Tyr and GYG was *p*-cresol (Fig. 7) whose lifetime is 1.7 ns [1]. Because the lifetime of these peptides are very close to that of *p*-cresol, the lifetimes of these peptides may be determined mainly by the lifetime of the chromophore itself.

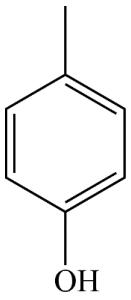

Fig. 7 Structure of *p*-cresol

Conclusion and acknowledgments

We confirmed that picosecond REMPI spectra match with those by nanosecond laser, and carried out pump-probe experiments to measure the lifetimes of capped Tyr and GYG. Based on the spectra, the time profile of each conformer was obtained. From the fitting by the single-exponential function, it was found that the lifetime of each conformer is about 1ns. Thus, it is expected that lifetimes of peptides containing a Tyr only reflect nature of the chromophore. To make sure generality of this observation, measurements of peptides with different protecting and terminal groups will be needed.

Finally, I would like to express my appreciation and thanks to Dr. Pierre Çarçabal, Dr. Shun-ichi, Prof. Makoto Sakai, Prof. Masaaki Fujii, and everyone involved in this program.

Reference

[1] G. A. Pino, et al., *J. Chem. Phys.* **133**, 124313 (2010).