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 7th to 21th December 2014. I participated in this program with Junpei Shinohara. This is a report of my study.

1. Purpose of the visit

It is known that dynamics of peptides containing phenylalanine depends on their conformations [1-2]. It is also interesting to study how dynamics of peptides containing other kinds of chromophore depends on their conformations. To this end, a capped tyrosine molecule (Fig. 1) and capped GYG (Fig. 2), a model peptide containing tyrosine as the chromophore, were investigated by resonance enhanced multi-photon ionization (REMPI) and UV-UV hole burning (HB) spectroscopy. The UV-UV HB spectroscopy found that the capped tyrosine and GYG have 5 and 2 conformers, respectively [3]. For the capped tyrosine, the REMPI spectra of two conformers show broad absorption but other three do not. Thus, it was suggested that excited states dynamics of the capped tyrosine depends on its conformation. a pump-probe spectroscopy using picosecond laser is useful to investigate difference among their dynamics. In our lab, however, it is not easy to combine picosecond laser to the ablation source. And signal stability of our ablation source is not enough to measure the excited state dynamics by pump-probe spectroscopy. In Dr. Pierre Çarçabal's lab, pump-probe spectroscopy can be applied to their ablation source because the signal stability is higher than our equipment. Therefore, measurement of exited states lifetime of the capped tyrosine and GYG was planned in this visit.

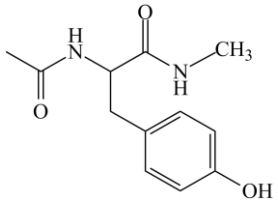

Fig. 1 Structure of capped tyrosine.

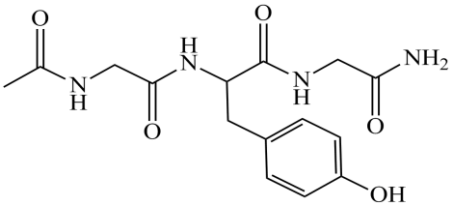

Fig. 2 Structure of capped GYG.

2. Progress of the study

In this report, I will report the experimental section. Results of the measurement will be reported by the Junpei's report. First, REMPI spectra were measured using ns pulse laser to confirm jet conditions. Next, REMPI spectra were measured by one color or two color ionization schemes using the picosecond laser. Then, the picosecond pump-probe spectroscopy was applied to the capped tyrosine and capped GYG to determine lifetime of the excited states.

Laser ablation technique

To vaporize the samples without damage, the laser ablation technique was used (Fig. 3 and Fig. 4). First, a spatula of graphite was mixed with sample (20~30 mg). This mixture was applied to a lateral face of a graphite plate. Desorption laser (1064 nm: Quantel Brilliant b) was irradiated to the surface in a vacuum chamber to vaporize the sample. The beam size of the desorption laser is about 1 cm in diameter, while the beam size was reduced to 2 mm by an aperture in the experiment. The sample vapor is collisionally cooled by pulsed Ar gas to get a supersonic jet expansion of the sample seeded in Ar, and a molecular beam was obtained through a skimmer. The Graphite plate can be moved with motors to supply fresh samples continuously. This method can keep the signal intensity for 3 hours.

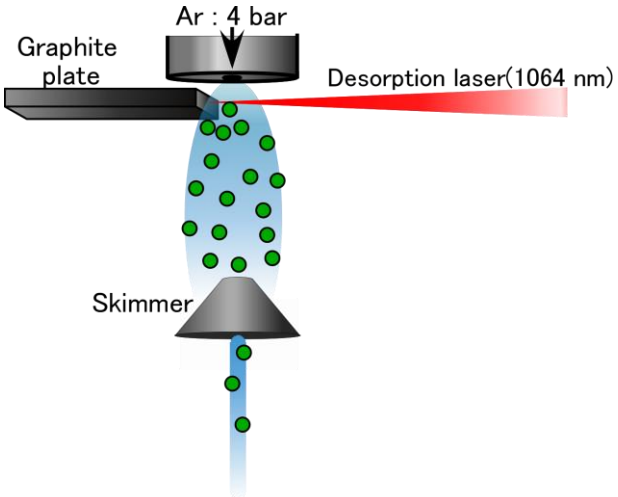

Fig. 3 Schematic of laser ablation method.

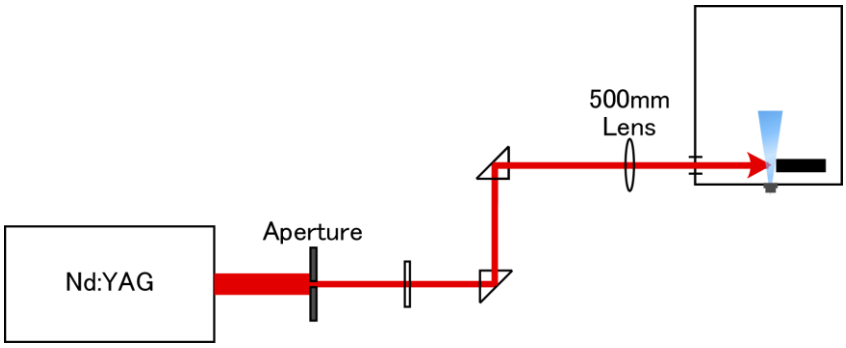

Fig. 4 Layout of the desorption laser.

Nanosecond laser

Fundamental of Nd:YAG laser (Quantel YG981E) was used as the pump laser (Fig. 5) of dye laser (Quantel TDL: rhodamine574). UV was obtained by second harmonic generation of the

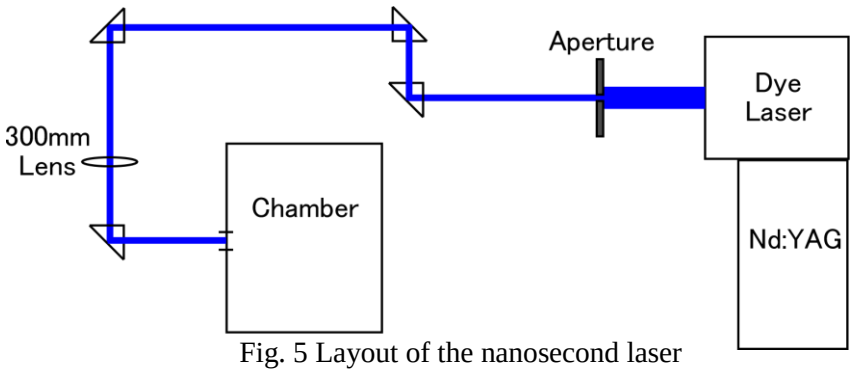

Fig. 5 Layout of the nanosecond laser

output of the dye laser. Initial beam size is 1 cm while it was reduced to 4 mm by an aperture. The UV was introduced to the vacuum chamber after passing through a 300 mm focusing lens.

Picosecond laser

First, a laser pulse (1064 nm) was generated with picosecond YAG laser (EKSPLA PL2241C-10-TH) (Fig. 6). The output was split into 2 beams in ratio 4:6, and the third harmonics were generated. These pulses were use as pumps of OPG (EKSPLA PG401), and after passing through OPA, picosecond UV pulses were finally obtained by second harmonic generation of the signal output of these OPA. These UV pulses were used as the excitation and ionization pulses for the pump-probe measurement. The excitation laser was focused on the molecular beam by a 1030 mm focusing lens, while the ionization laser was focused by a 720 mm focusing lens after passing through a delay line. The delay stage was controlled by Newport Universal Motion Controller/Driver (Model ESP 300). By controlling the delay time, excited states lifetime was measured.

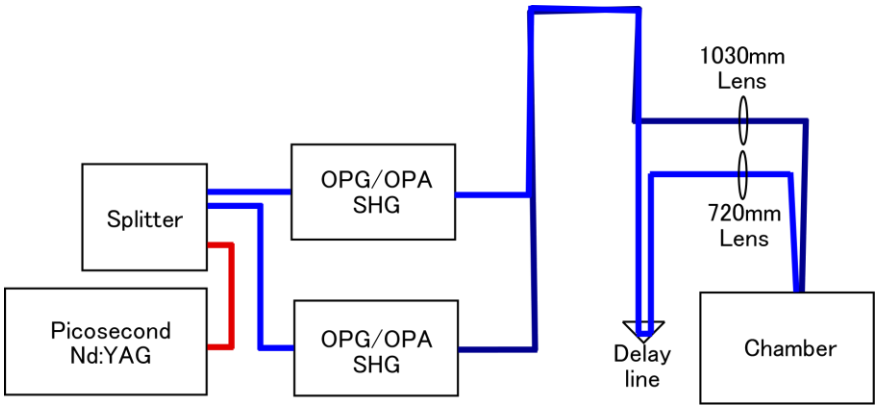

Fig. 6 Layout of the picosecond laser

3. Conclusion and acknowledgment

By using the setup, the excited state lifetimes of the capped tyrosine and capped GYG were measured. Lifetimes of the capped tyrosine and capped GYG are about 1 nanosecond irrespective of broadness of the REMPI spectra. Therefore, it was concluded that lifetime do not depend on their conformation in the tyrosine chromophore. Overlap of a lot of vibronic bands is suggested as a reason for the broadening of the REMPI spectra instead.

Finally, this visit was very valuable opportunity for me, and I had a very happy time. I would like to express my appreciation to Prof. Pierre Çarçabal, Dr. Shun-ichi Ishiuchi, Prof. Makoto Sakai, Prof. Masaaki Fujii, and everyone involved this program.

References

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