# Report on Visit to Université 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's group at the Université Paris XI for two weeks, from 9th to 22nd of May, 2012. I participated in this program with Dr. Shun-ichi Ishiuchi, Ms. Yoko Shimozomo, and Mr. Hiroya Asami. This is a report of my study and life in Paris.

## Purpose of the visit

We are investigating conformational structures of neurotransmitters, amino acids and peptides in the gas phase by using laser desorption supersonic jet technique. In the gas phase, where there are no solvent molecules, we can observe the intrinsic structure of the molecules under study, which means a structure determined only by the properties of molecules, such as their intra-molecular hydrogen bonds networks. By comparing the structures between the gas phase and solution phase, we can know the solvent effect on the structures of biomolecules. From this point of view, both molecular structures of biomolecules with and without solvent molecules are important. Prof. J. P. Simons's group at University of Oxford, where Dr. Çarçabal studied as a post doctoral researcher, investigated both the isolated and hydrated molecular structures of neurotransmitters by using laser desorption technique. We also would like to investigate the structures of hydrated biomolecules, however we are faced to a problem that cluster signals cannot be observed at all in our machine.

Recently, the equipment of the oxford group has been transferred to Orsay where Dr. Çarçabal continues the work on the spectroscopy of biomolecules and hydrated in the gas phase. This is why we have visited Dr. Çarçabal laboratory to learn how to produce hydrated clusters by using laser desorption technique. The purpose of this visit was to use the machine that can generate clusters and to decide how to improve our machine to observe cluster signals.

## Progress of the study

At first, we measured mass spectra using tyrosine as a sample in order to check the cluster generation in Dr. Çarçabal's machine (Fig. 1). We used 4 bar of Ar gas as a carrier gas. The wavelength of desorption laser was 1064 nm. The excitation laser was fixed

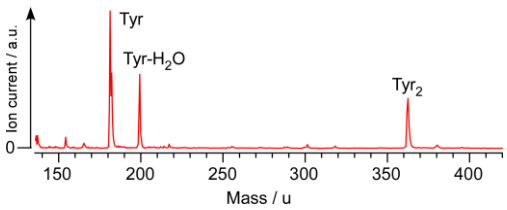



Fig. 1 Mass spectrum of tyrosine

to 282 nm, which is off resonant to both tyrosine monomer and its hydrated clusters. As shown in the figure, tyrosine monomer (at 181 u), hydrated tyrosine cluster (at 199 u) and tyrosine dimer (at 362 u) were observed. To investigate the difference between Dr. Çarçabal's machine and ours, I looked the inside of the vacuum chamber, especially around the pulsed valve and the desorption target. I could identify a number of differences with our experiments, the following being probably important for cluster generation.

(1) The shape of the desorption target
(2) The distance between the valve orifice and the desorption target
(3) The distance between the pulsed valve and the skimmer

I will discuss each topic bellow.

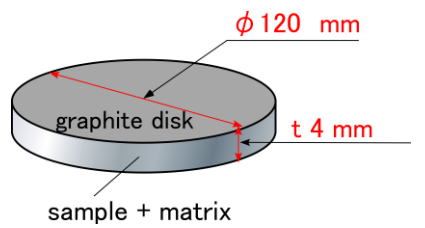
**(1) The shape of the desorption target**

The material of the desorption target is identical, which is graphite, however, the shape is different. Our target is a disk (Fig. 2a), while a linear plate is used in the Dr. Çarçabal's machine (Fig. 2b). The disk target is rotated during irradiation of the desorption laser, while the plate target is moved linearly. The most important point is difference of the shape of cross section. Our disk has a rectangle shape whose thickness is 4 mm, while the edge of the Dr. Çarçabal's plate is cut and the effective thickness is 2.5 mm. This difference is thought to affect the efficiency of cluster generation. The rectangle shape lead the cluster dissociation by collision with the edge of the disk (Fig. 3). Therefore, the efficiency of the cluster generation will be significantly improved by cutting the edge of the disk.

**(2) The distance between the orifice and the desorption target**

The distance between an orifice and a disk is important and very critical to obtain intense signal and high jet-cooling effect. The difference between ours and Çarçabal's machine

a)

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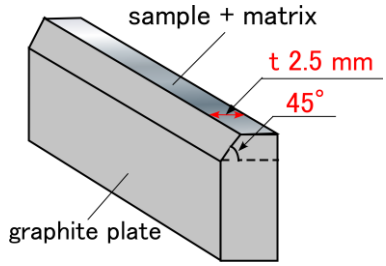



Fig. 2 Desorption targets of ours (a), Dr. Çarçabal's (b)

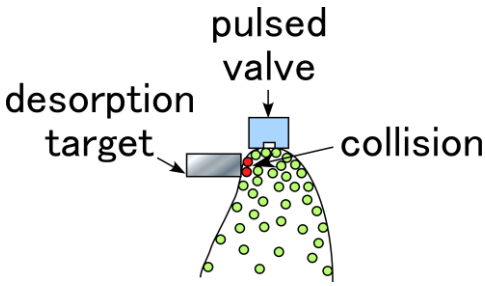



Fig. 3 Collision with the edge of the disk

is shown in Fig. 4. In our system, we fix the distance to 0.5 mm by adjusting a micrometer before pumping the vacuum chamber. In other words, we must open the chamber to adjust the distance. The distance was roughly optimized by comparing the signal intensity and jet-cooling effect in each distance. On the other hand in Dr. Çarçabal's machine it is possible to change the distance from the outside of the vacuum chamber. Thus, the distance can be optimized by monitoring the signal intensity. This function is extremely important to optimize the detection of the cluster signal because the best distance depends on the cluster size. The short distance (maybe ~ 0.5 mm) is suitable for monomer, while slightly longer distance is better for clusters. This dependency can be rationalized by the efficiency to pick up desorbed molecules into the supersonic jet and dissociation of the clusters by collision with the desorption target. To pick up the desorbed molecules into the supersonic jet efficiently, the desorption target should be close to the orifice, however, if the distance is too short, the collision between the molecules in the supersonic jet and the desorption target may take place, which leads to dissociation of clusters.

**(3) The distance between the pulsed valve and the skimmer**

The other difference is the distance between the pulsed valve and the skimmer. The distance is 10 cm in the Çarçabal's machine, while it is 2 cm in

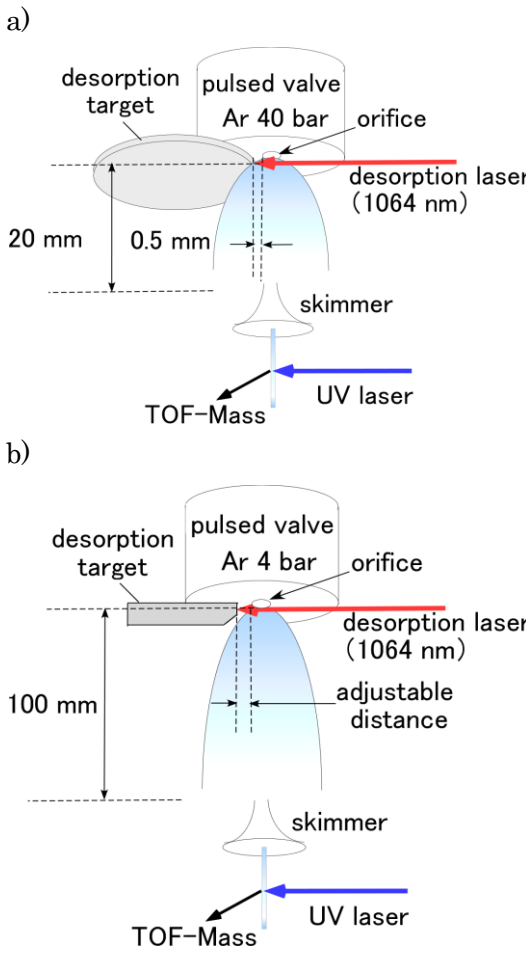



Fig.4 Machines in our (a) and Çarçabal's (b) group

our setup (Fig. 4). This distance generally affects the jet-cooling effect, however I expect that the distance probably does not affect the cluster generation seriously, because cluster signals can be observed by using normal supersonic jet technique in our setup.

**How our setup should be improved**

Based on the differences between Çarçabal's machine and ours, I would like to discuss how to improve our machine to detect cluster signal. First I suppose that cutting the edge of the disk will have a beneficial effect. I will improve the disk as showing in Fig.5. Cutting the edge of the disk will keep clusters from destroying.

In addition, the distance between the orifice and the disk should be adjustable from outside of the chamber with monitoring the cluster signal. In our setup the disk is mounted on a motor which is placed on a movable linear slide (Fig. 6a). The motor block can be moved by a micrometer and the distance between the orifice and the disk is adjustable. In order to move the motor block from outside of the chamber, we designed a system in which a ball plunger for a spindle of the

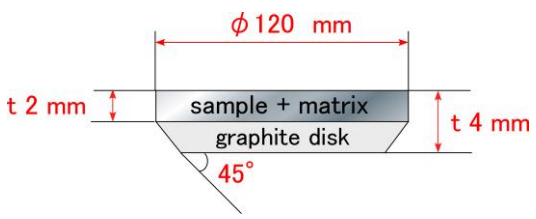
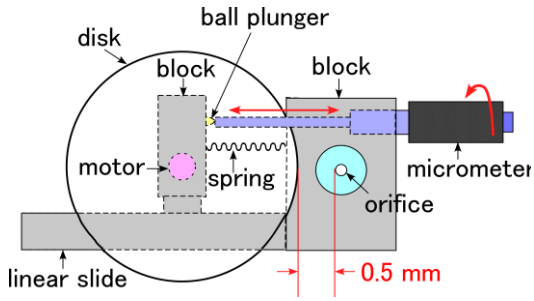



Fig.5 Design of desorption target

a)

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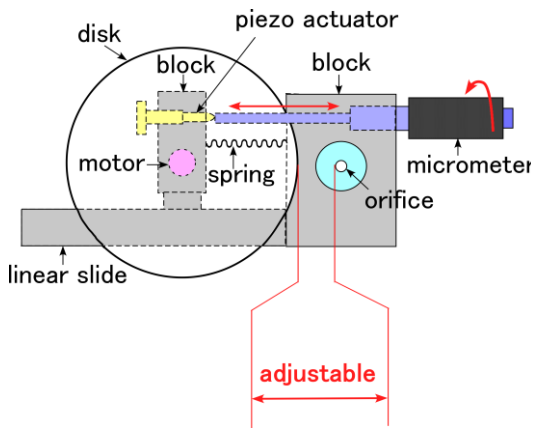


Fig.6 Before (a) and after (b) of micrometers

micrometer is replaced by piezo actuator (Fig. 6b). In this system, the motor block can be moved by not only the micrometer but also the piezo actuator which can be electrically controlled from outside of the vacuum chamber. Since the stroke of a piezo actuator is quite small, we can fine-tune the position of the motor block by the piezo actuator. With this system, the micrometer is also necessary for initial rough adjustment.

**Communication in French and English**

I studied French for a year when I was an undergraduate. So I could guess how to read French. I tried speaking French when I bought a piece of bread and cake. I was very happy to be able to communicate in French. I love France, because the town is very beautiful and fashionable. I was fascinated by France. I would like to study abroad in France from next year. I start to study French to realize my dream after I came back to Japan.

I had an image that French do not speak English, but I was surprised that most French were able to communicate in English. I talked to a "garçon" in English when I ordered my menu in café or restaurant and go shopping. Most of clerks were able to take my order in English, and understand what I meant. Both Japanese and French are not native speakers of English, but we could understand what other person meant. I realized that English skill is important for communicating with not only native speakers but also non native speakers like French. I would like to improve my English and French skill and spread my interpretation of the world.

**Life of the laboratory**

I went to the Université Paris Sud XI by a train from the hotel where I stayed. It took about an hour to go to the Université Paris from the hotel. The Université Paris is located in a suburb of Paris, so there is abundant nature in the campus. I arrived at the laboratory at 10 a.m. every day, and started experiments soon. First day I checked the inside of a vacuum chamber, and I had the lecture about the experimental set up. I was a beginner of supersonic jet spectroscopy, so it was hard to understand the experiments at first. But I gradually understood the experiments by asking questions to Dr. Çarçabal and Dr. Ishiuchi.

I participated in a group seminar in which Dr. Ishiuchi, Ms.Shimozono and Mr. Asami talked about their recent results. I studied their researches and how to express technical terms in English.

I visited two laboratories. In one of them, advanced mass spectrometry which coincidentally detects neutral and ion fragments due to photo induced dissociation were investigated. I was impressed by the huge machine.

**Life in Paris on holidays**

Dr. Çarçabal and his wife invited Japanese members to a famous cake shop in Paris on a holiday. The cake shop is popular, so we waited to be seated. I felt the cake was sweeter than the Japanese one. We walked around the Louvre museum. His wife explained about buildings and the history.

I went to the Palace and Park of Versailles with Japanese members. I

walked around the garden and saw a fountain show. The garden was much larger than I had expected, and I was very impressed. I like the garden, especially I love the detached palaces of Marie Antoinette. I took many photos in Palace and Park of Versailles. I was very happy to have an opportunity to go there.

The last day I went to the Çarçabal's laboratory, he and his wife invited Japanese members to dinner. We ate French dinner. We talked about job hunting, university entrance exam in Japan. But it was difficult to explain accurately in English. I would like to get better my English to be able to explain about Japan to foreigner.

**Conclusion and acknowledgment**

I achieved the purpose of studying the machine that can generate clusters. I found the three differences between Çarçabal's and our machine. I studied how to improve our machine to increase the cluster generation.

Finally, I would like to express my appreciation to Dr. Pierre Çarçabal, Dr. Shun-ichi Ishiuchi, Ms. Yoko Shimozomo, Mr. Hiroya Asami and Prof. Masaaki Fujii, who gave me this opportunity.