Report on my visit to Université d'Aix Marseille by 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 visited the laboratory of Prof. Christophe at the Université d'Aix Marseille for two weeks, from November 3rd to November 17th, 2014.

I studied with Dr. Shun-ichi Ishiuchi, Ms. Hikari Oba and Mr. Daichi Kato who belong to the same laboratory with me.

1. Purpose of this visit

Now our laboratory is developing a new machine for ion spectroscopy that equips electrospray ionization (ESI) as the ion source. My purpose of this visit was to study and to have an experience how to handle ESI at the Université d'Aix Marseille (Fig. 1).

Fig. 1 Université d'Aix Marseille.

This time we aimed to measure photodissociation spectra of protonated adrenaline and noradrenaline using the ESI machine. Last year, photo dissociation spectra of protonated dopa and dopamine have been measured. UV spectroscopy on adrenaline and noradrenaline completes the series of measurements of protonated catecholamines to discuss their excited state dynamics.

In this report, I will focus on the principle and method of ESI because I used this machine for the first time. As for the spectroscopic results of protonated adrenaline and noradrenaline, please refer the D. Kato's report.

2. Experiments

2.1. Electrospray ionization [1]

ESI method is one of ionization methods developed in mass spectrometry. This is a powerful tool to ionize macromolecules without fragmentation i.e. to achieve "soft ionization". Fig. 2 shows the principle of ESI. The sample solution is introduced in a metallic electrospray needle. High voltage is applied between the end of the needle and opposite electrode. A liquid cone (Taylor cone) is formed in a direction toward mass spectrometer by high voltage.

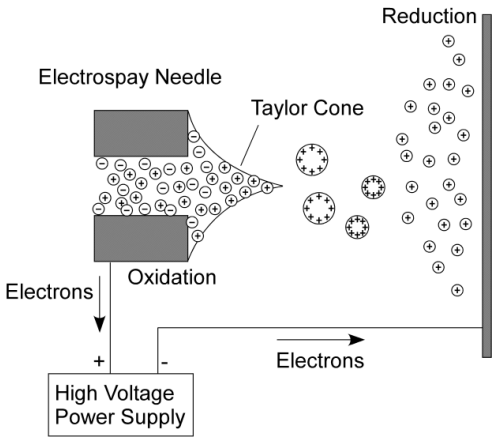

Fig. 2 Principle of ESI process.

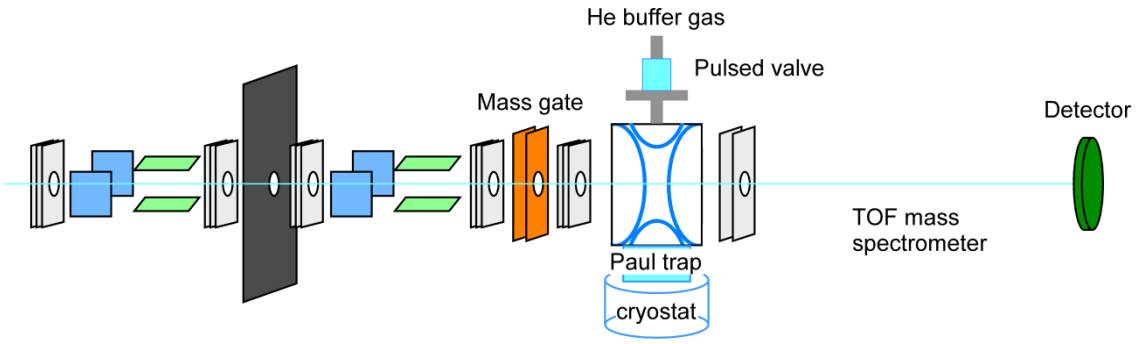

Fig. 3 Configuration of the ESI-cold ion trap spectrometer. [2]

2.2. Experimental setup

Figure 3 shows an experimental setup of ESI in the Prof. Christophe's group. Ions are generated in the ESI source. At exist of the capillary, ions are guided and accelerated by a pulsed voltage in order to produce an ion packet with duration between 500 ns and 1 μs. The ions are stored in an octopole ion trap.

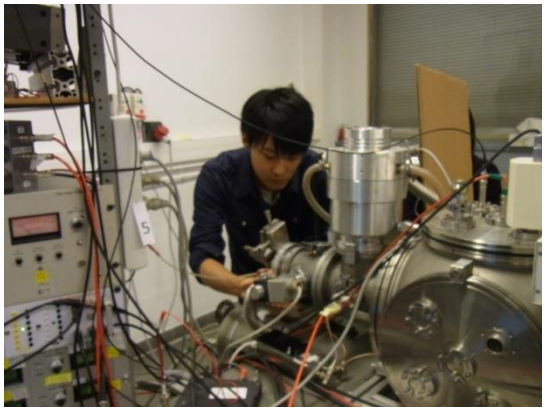

Fig. 4 Setting the sample solution and handling the ESI needle.

A mass gate is placed at the entrance of a Paul trap and is able to select a species of a given m/z. A liquid helium cryostat is mounted on the Paul trap to cool down the trapped ions. The temperature of the cold trap is monitored by two sensors. The first sensor T_1 is located on the cryostat head on which the trap is mounted and the second sensor T_2 is on the top of the Paul trap. Generally, the temperature reached are T_1 = 14 K and T_2 = 40 K.

Helium gas is introduced in the trap using a pulsed valve triggered 1–2 ms before the entrance of ions into the trap. The valve is opened for 150 μs. Before the photodissociation laser is triggered, the ions are trapped several tens of milliseconds to equilibrate the ion temperature with the buffer gas. Parent and fragment ions produced by the UV laser are analyzed by a time-of-flight (TOF) mass spectrometer. Photo-fragmentation spectra are obtained by recording the fragment signal of cations by a micro channel plates as a function of laser wavelength with a digitizing storage oscilloscope interfaced to PC.

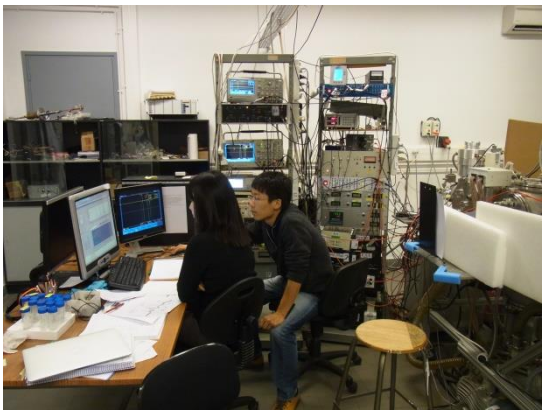

Fig. 5 Operating the ESI machine.

2.3. Preparation of the sample

We brought adrenaline and noradrenaline from our laboratory and prepared sample solutions of them in Marseille. At first, we dissolved 4 mg sample in a 25 mL 1:1 solution of water and ethanol. And the pH of the sample solution was adjusted by adding 3 drops of acetic acid, and then it was diluted 10 times to set ESI.

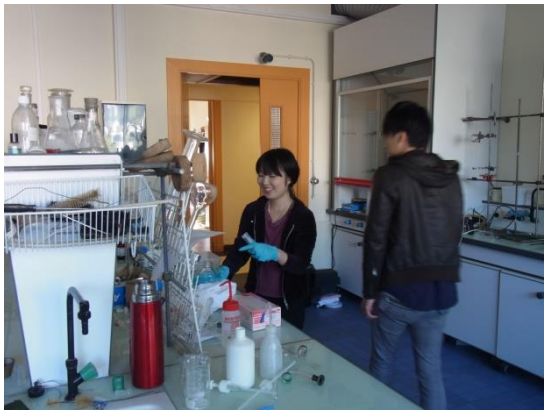

Fig. 6 Preparing the sample solution.

3. About my stay in Marseille

I had to communicate with members of the Prof. Christophe's group in English. This was a very good chance for me to improve my English skill.

In holidays, I walked around the Vieux-Port station and Aix-en-Provence. I was moved by these cityscapes because this visit is my first foreign travel. In addition, Prof. Christophe invited us to a dinner and I enjoyed eating French cuisine.

4. Conclusion and acknowledgments

First, I obtained the opportunity of studying the principle and method of ESI. Second, we measured the photodissociation spectra of adrenaline and noradrenaline and performed UV-UV HB spectroscopy.

Finally, I would like to express my thanks to Prof. Christophe Jouvet, Prof. Claude Dedonder, Dr. Géraldine Feraud and Prof. M. Fujii.

5. References

[1] J. V. Iribarne and B. A. Thomson, *J. Chem. Phys.* **64**, 2287 (1976).

[2] F. Géraldine et al., *Phys. Chem. Lett.* **5**, 1236 (2014).