Report on Visit to the Aix Marseille Université and Symposium in the University of Manchester by JSPS Core-to-Core Program

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This is a report on collaborative study with Prof. Christophe Jouvet's group at the Aix Marseille Université and international symposium at the University of Manchester by JSPS (Japan Society for the Promotion of Science) Core-to-Core program. I participated in this program with Dr. Shun-ichi Ishiuchi, Mr. Woonyong Sohn and Mr. Takuma Aoki. We have studied at the Aix Marseille Université for a week from 24th of November to 1st of December and made a presentation in Core-to-Core international symposium on ionization induced switching in Manchester on 16th December.

Purpose of collaborative investigation in Marseille

The purpose of visit to Prof. Christophe Jouvet's group was to observe their machine of electrospray ionization (ESI). We observed it to get useful information to develop an ESI machine by ourselves. We are now in the progress phase of the development. Also, we have measured photo dissociation spectra of protonated dopa and protonated dopamine using the ESI machine.

Electrospray ionization

As its name implies, electrospray is the process of generating a fine mist of sample droplets by applying an electrical voltage across a sample. The ESI transfers large unvolatile molecules from liquid phase into the gas phase as charged isolated molecules. It is a very mild ionization method. The process of ESI is classified into three steps: (1) formation of charged droplets, (2) desolvation, (3) introduction to mass analyzer. An analyte is dissolved in a polar solvent and the solution is introduced by means of a syringe in a capillary. The application of a high electric field to the capillary accumulates ions and causes the formation of a so-called "Taylor-cone" at the surface of the capillary tip (figure 1). The solution containing the analyte breaks into droplets due to a nitrogen nebulizing gas located at the outside of the capillary. Those droplets are

enriched in ions (eg. cations in the case of positive tip). The charged droplets reduce in size by evaporation of the solvent and coulomb explosion. When the charge density at the droplet surface reaches a critical value (Rayleigh limit), a so-called coulomb explosion occurs and several even smaller droplets are formed as shown in figure 2. The process of solvent evaporation and coulomb explosions is repeated until a bare charged molecule is left without any solvent. Those molecular ions initially at atmospheric pressure are attracted by a counter electrode and pass down a pressure gradient towards the high vacuum of a mass analyzer.

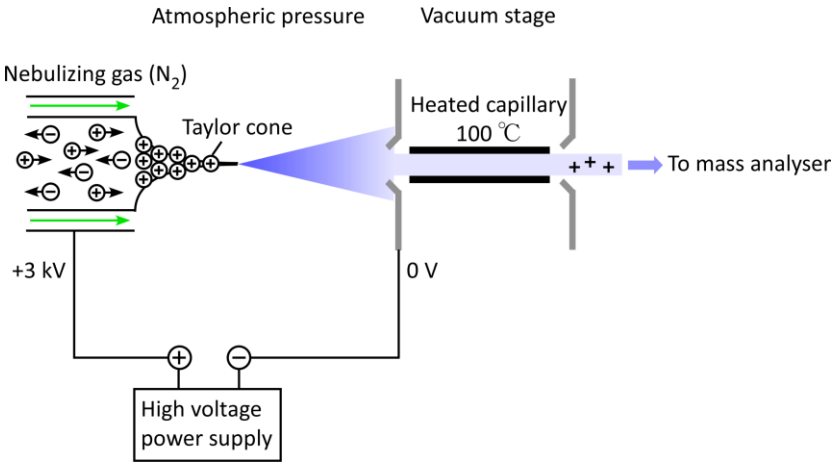


Fig.1 Schematic view of electro spray ionization

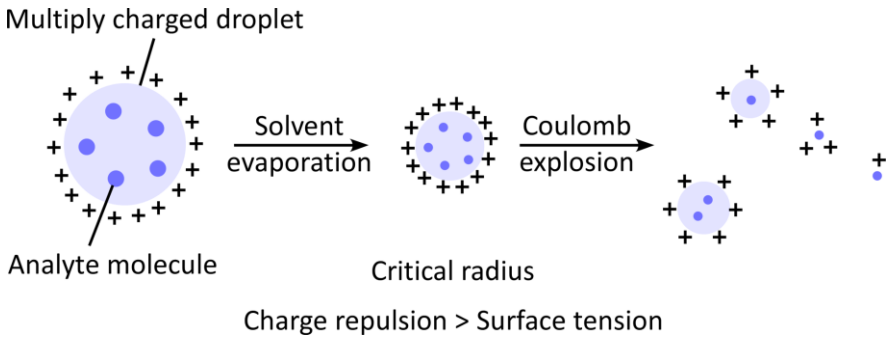


Fig. 2 Process of solvent evaporation and coulomb explosions

Experimental setup

Figure 3 shows a schematic view of the setup for ESI in the Prof. Christophe Jouvet's group. The setup consists of an ESI source, an octopole ion trap, a time of flight (TOF) mass spectrometer and a tunable UV pulsed laser. In ESI source, we produce gas phase

protonated molecules at atmospheric pressure using electrospray from solution including analyte. The ions from the electrospray source go into vacuum stage to be stored in the octople ion trap and bunched. After being released from the octopole, the ions pass through a mass gate which selects those of particular mass-to-charge ratio (m/z). Mass-selected ions go to a paul trap which is cooled to 10 K by a close cycle refrigerator. A pulsed of helium (He), introduced into the trap before the arrival of the ions, collisionally cools the ions. An ultraviolet (UV) laser pulse is sent through the trap to excite the cooled ions. Parent ions and charged fragments resulting from absorption of a UV photon are released from the trap and pass through a Time-of-Flight (TOF) which select either fragment ions (to monitor the photo fragmentation yield) or parent ions. The ion signal is detected by micro channel plate (MCP) and transferred to an oscilloscope.

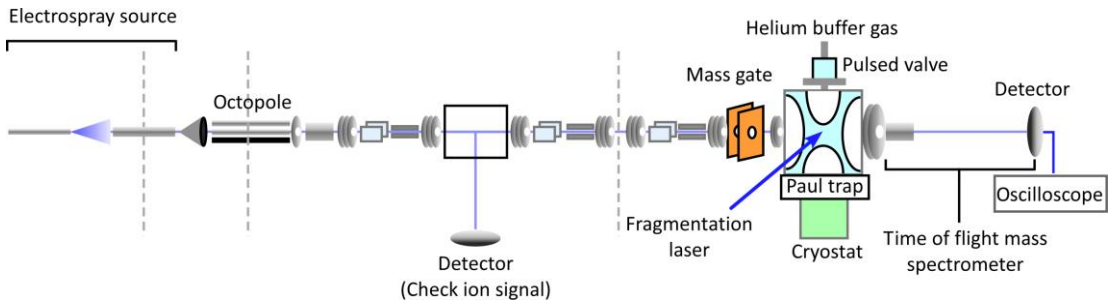


Fig.3 Experimental setup

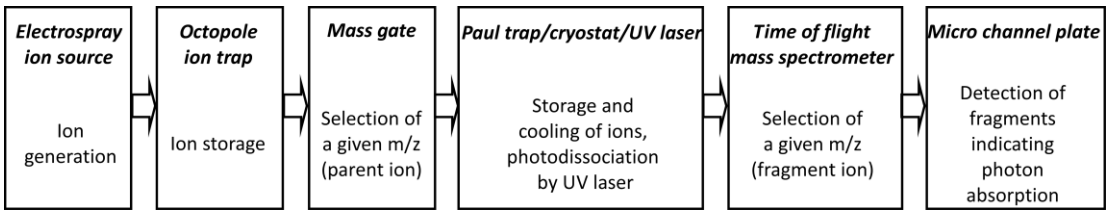


Fig.4 Sequence of event during photodissociation experiment

Results and discussion

In the ESI method, action spectra which correspond to electronic spectra of isolated molecular ions are obtained by measuring photo fragment yield by photo-induced dissociation (PID). The PID leads to observation of fragments which are different from

those obtained by collision-induced dissociation (CID). The former occurs by photon absorption, on the other hand, the latter occurs by collision with helium buffer gas. Figure 5 shows TOF spectra of protonated dopa ($dopaH^+$) and protonated dopamine ($dopamineH^+$). The PID spectra (a), (b) were measured with UV laser at 34843 cm^{-1}, on the other hand, CID spectra (c), (d) were recorded without UV laser at 1000 V collision

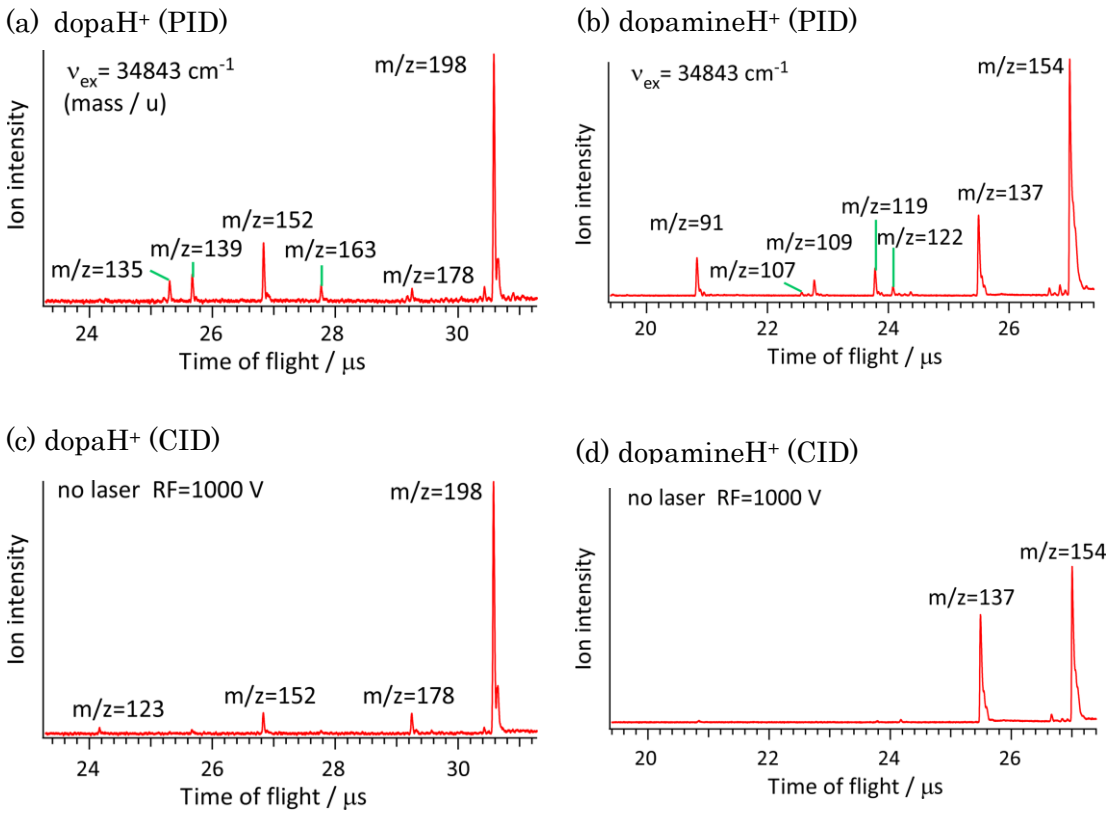


Fig. 5 Time-of-flight spectra observed in photo-induced dissociation: (a) protonated dopa, (b) protonated dopamine and time-of-flight spectra observed in collision-induced dissociation: (c) protonated dopa, (d) protonated dopamine.

energy. As shown in the TOF spectra, fragment species are different between PID and CID. For instance, regarding dopa, the fragment (m=123 u) was only observed in the CID spectrum, which means the fragment was generated by collision with buffer gas.

We have measured PID spectra of protonated catechol amine neurotransmitters by measuring the intensity of fragment and parent ions. The PID spectra of $dopaH^+$ were obtained by monitoring the five fragment channels with m=135, 139, 152, 163 and 197 u as shown in figure 6. The depletion spectrum of the parent ion (m=198 u) is also

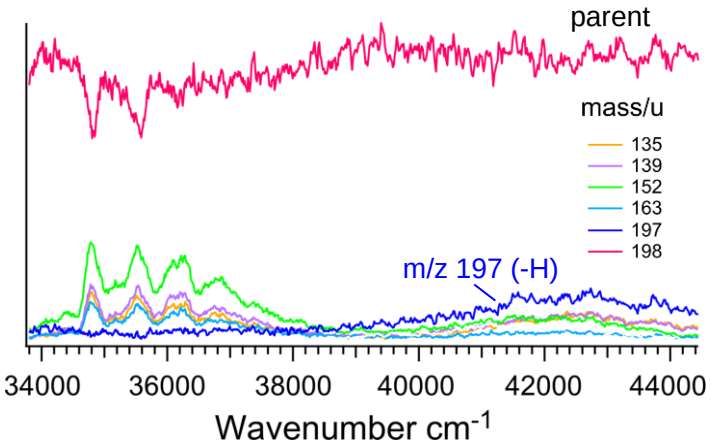


Fig. 6 Photo-induced dissociation spectrum of protonated dopa.

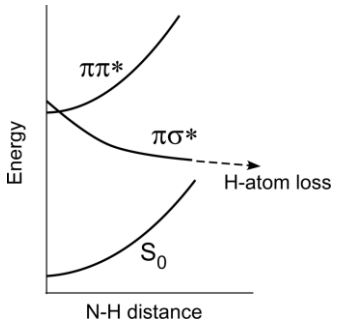


Fig. 7 Electronic states along the amino group N-H dissociation coordinate.

shown in the figure. The m=152 u ion is the dominant fragment and generated by elimination of COOH+H.The other losses of fragment ions are presented in table 1 of supplemental.

In the PID spectrum of dopaH^+, the first origin transition at 34783 cm^{-1} occurs 317 cm^{-1} to the red of that of the neutral species [1]. At larger excitation energies, observation of hydrogen atoms can be attributed to the existence of a higher πσ* excited state dissociative along the N-H coordinate (figure 7). It is supposed that dopaH^+ is stabilized through the intramolecular NH- π interaction. Following UV excitation, the π electron transfer to the protonated amino group and induced fragmentation with the loss of a hydrogen atom. On the other hand, the observed conformer of neutral dopa corresponds to establishment of OH-N hydrogen bond between OH and NH_2 groups. The OH-N hydrogen bond is replaced by an interaction between the protonated amino group and the π electron cloud of benzene ring.

We have also measured the PID spectra of dopamineH^+ monitoring eight fragment ions (m=65, 91, 107, 109, 119, 122, 137, 153 u) and parent ions (m=154 u) as shown in figure 8. The m=137 u ion is the dominant fragment and generated by elimination of NH_3 group. The other losses of fragments are shown in Table 2 of supplemental. The feature of PID spectra is similar as those of dopaH^+. The origin band was observed at 34843 cm^{-1} and hydrogen atom is lost at larger energy region which indicates observation of πσ* transition.

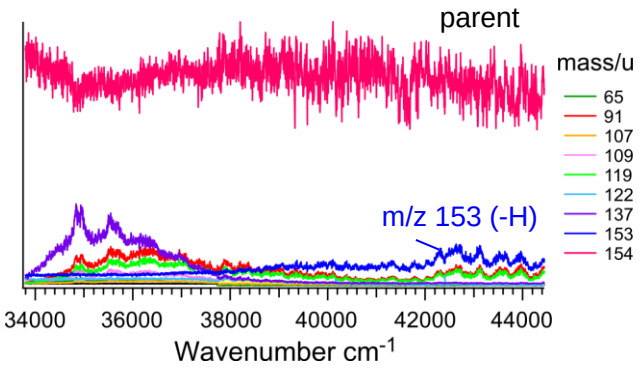


Fig. 8 Photo-induced dissociation spectrum of protonated dopamine.

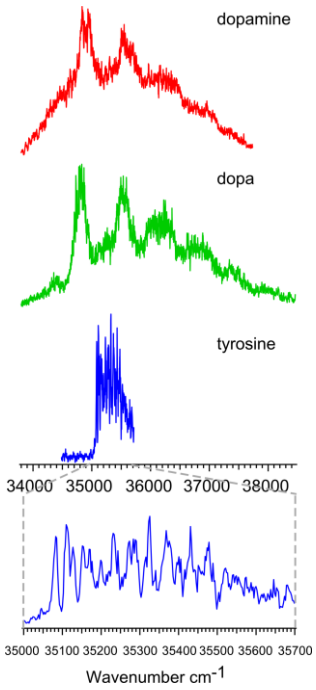


Fig. 9 Comparison of photo-induced dissociation spectra: dopamine, dopa and tyrosine from the top.

We compared the PID spectra of protonated catecholamine neurotransmitters with that of tyrosine ($TyrH^+$) as shown in figure 9. The transition energies of protonated catecholamine neurotransmitters are different from that of $TyrH^+$ due to different chromophore. The former has catechol OHs and the latter has a phenol OH. Also the PID spectra of $dopaH^+$ and $dopamineH^+$ show broader bands, while $tyrH^+$ shows sharper ones. It is expected that lifetimes of excited states of protonated catecholamine neurotransmitters might be much shorter than that of $TyrH^+$. Jouvet and coworkers measured the lifetimes of electronically excited protonated tryptophan ($TrpH^+$) and Tyr H^+. They confirmed that the broad and sharp lines observed in the electronic spectra of Trp H^+ and Tyr H^+ correspond to very short (380 fs for $TrpH^+$) and intermediate (22.3 ps for $TyrH^+$) lifetimes of the $\pi\pi^*$ photoexcited state, respectively [2]. In the similar way, it is assumed that the life time of $\pi\pi^*$ state of $dopaH^+$ and $dopamineH^+$ are shorter than $TyrH^+$, which causes the broadness of electronic spectra of protonated catechol amine neurotransmitter.

International symposium in Manchester

We attended Core-to-Core international symposium on ionization induced switching in Manchester on 16th December. I made a poster presentation about results of cooperative study with Dr. Pierre Çarçabal in Orsay, France. We have been investigating the

structure of 5 residue peptide (Ac-Ser-Ile-Val-Ser-Phe-NHMe: capped-SIVSF) which is related to ligand-binding site of adrenaline receptor by laser desorption supersonic jet spectroscopy. We synthesized the peptide and measured resonance enhanced multi-photon ionization (REMPI) spectrum corresponding to electronic spectrum and infrared (IR) spectra. We also conducted quantum chemical calculations to obtain theoretical IR spectra. As the result, the structure of the peptide was tentatively assigned by comparing between experimental and computational results.

In the previous work, we have investigated the structure of similar peptide which has different terminals (NH_2-SIVSF-NH_2: uncapped-SIVSF). So we compared the results between capped and uncapped-SIVSF. It was found that the number of conformers increased by capping both terminals. Also capping terminals affects the structure of the main chain. Further investigation on the structure of capped-SIVSF is now in progress

Conclusion and acknowledgment

We observed the ESI machine to get information to develop our machine. The PID spectra of the isolated protonated catecholamine neurotransmitters: dopa and dopamine have been measured. By comparing with PID spectrum of $TyrH^+$, it is expected that the life time of $\pi\pi^*$ state of $dopaH^+$ and $dopamineH^+$ are shorter than that of $TyrH^+$.

Finally, I would like to express my appreciation to Prof. Christophe Jouvet, Dr. Claude Dedonder-Lardeux, Dr. Géraldine Féraud and Prof. Masaaki Fujii who gave me this opportunity and all of the people who were involved in this program. I also would like to express my thanks to financial supports by JSPS Core-to-Core Program.

Reference

[1] Ishiuchi, S.-i.; Mitsuda, H.; Asakawa, T.; Miyazaki, M.; Fujii, M. *Physical Chemistry Chemical Physics* **2011**, *13*, 7812.

[2] Kang, H.; Jouvet, C.; Dedonder-Lardeux, C.; Martrenchard, S.; Gregoire, G.; Desfrancois, C.; Schermann, J. P.; Barat, M.; Fayeton, J. A. *Physical Chemistry Chemical Physics* **2005**, *7*, 394.

Supplemental

Table 1　Photofragments of protonated dopa

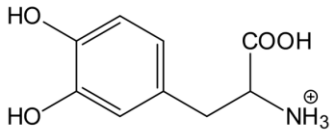
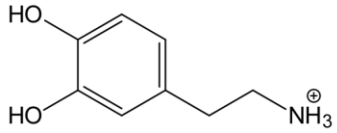
parent		photofragments	
198	dopaH$^+$ 	135	COOH-OH-H
		139	COOH-CH-H
		152	COOH-H
		163	2OH-H
		197	H

Table 2　Photofragments of protonated dopamine

parent		photofragments	
154	dopamineH$^+$ 	65	benzene-CH_2
		91	NH_3-$2CH_2$-OH-H
		107	NH_2-CH_2-OH
		109	$2CH_2$-NH_3
		119	2OH-H
		122	NH_3-CH_2-H
		137	NH_3
		153	H