

# Report on a visit to the Photon Science Institute of the University of Manchester in U. K. through the JSPS Core to Core Program

**Katsuya KIKUCHI**  
**Department of Electronic Chemistry,**  
**The Interdisciplinary Graduate School of Science and Engineering,**  
**Tokyo Institute of Technology**

As part of the JSPS Core to Core program, I studied in Prof. Klaus Müller-Dethlefs' research group in The Photon Science Institute of Manchester University in the U. K. for two weeks, from October 14<sup>th</sup>, 2010 to October 28<sup>th</sup>, 2010. This is report of my stay.

## Research

### (a) Research theme

Photoionization reactions, give neutral molecules electric charge. This charge generates an induced dipole in surrounding solvent molecules. Thus the photoionization reaction changes the molecular interactions around the ionized molecule and substantially influences intermolecular structure. This has lead to solvent reorientation dynamics being studied

Although photoionization has often been applied to study molecular clusters, there are few examples studies of photoionization dynamics with a change of structure. Typical molecular interactions within a molecular cluster are van der Waals forces and vibronic interactions (hydrogen bond).

Phenol (PhOH) is the simplest molecule which possesses both a van der Waals site at the  $\pi$  electron cloud of the aromatic ring and

a hydrogen bond site at the OH group. In addition, the simplest molecule possessing both sites is a rare gas. Therefore, our research group has studied the photoionization dynamics of PhOH-rare gas clusters.

The PhOH-Ar (1:1) cluster of the neutral ground state has a  $\pi$  type structure with Ar bound to aromatic ring. However in the cation state, isomers exist in both this  $\pi$  type structure but also in an H type structure, where Ar is bound to the OH site. PhOH-Ar (1:2) clusters in the cation state only exist in the H type structure. So it is clear for these clusters,  $\pi \rightarrow$ H isomerization occurs with a yield of 100%.

However, in the PhOH-CH<sub>4</sub> cluster which it is not a rare gas cluster, but is bonded through a comparatively weak intermolecular force, the PhOH-CH<sub>4</sub> (1:1) cluster in the cation state only exists as an H type structure. In fact,  $\pi \rightarrow$ H isomerization occurs with 100% yield in the (1:1) cluster. This indicates that back reaction does not occur because the surplus energy in the cluster is distributed to the internal rotation mode of the CH<sub>4</sub> molecule after  $\pi \rightarrow$ H isomerization.

The Müller-Dethlefs research group

established a technique of measuring molecular vibration in cation states after ionization known as MATI (Mass Analyzed Threshold Ionization) spectroscopy and has studied many molecular cluster cations. Therefore, we measured MATI spectra of the PhOH-CH<sub>4</sub> (1:1) cluster to get information about the initial structure of the cluster after ionization.

### (b) Experiment

At first, we measured the MATI spectrum of the PhOH-CH<sub>4</sub> (1:1) cluster via the S<sub>1</sub> origin. In MATI spectroscopy, the molecule is excited to a vibronic state by  $\nu_1$  of a UV laser and this is further excited to a high Rydberg state, near the Ionization Potential (IP), by  $\nu_2$  of a UV laser.

This high Rydberg state is electrically neutral but high *n* Rydberg electron is bound very weakly. Thus this molecule is ionized easily by an electric field of a few V/cm. For this reason, high Rydberg states can be selectively-detected relative to any cations by synchronization of mass detection a weak electric field pulse, and so vibrational spectroscopy of low vibrational modes of cation state can be achieved.

At this time, it is need to distinguish between a direct ionization cation and an electric ionization cation. By the application an electric field pulse of around 1-2 V for 10-20  $\mu$ s applied immediately after the laser pulse (Fig. 1), a direct ionization cation can be separated spatially because the high Rydberg state is neutral and a direct ionization cation has positive charge.

After that, the high Rydberg molecule is ionized by a 1 kV pulse electric field applied for 5  $\mu$ s and this pulsed electric ionization cation is detected by TOF-MS (Time of Flight Mass Spectrometer). At the same time, a direct ionization cation is detected by TOF-MS but both are detected at different arrival times, so that they are separated spatially. MATI spectra are measured by monitoring the pulse field ionization signal and PIE (Photoionization Efficiency) spectra are measured by monitoring the direct ionization signal.

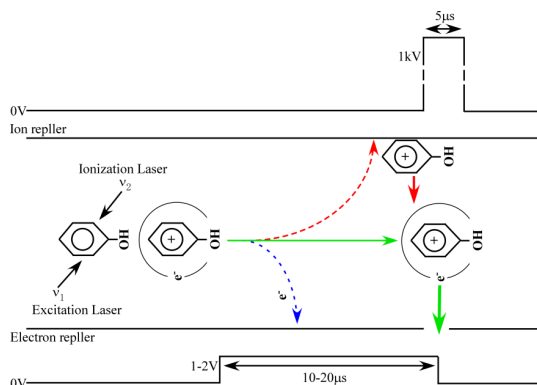


Fig. 1 The principle of MATI spectroscopy

Figure 2 shows (a) the PIE spectrum and (b) the MATI spectrum of PhOH<sup>+</sup>-CH<sub>4</sub> (1:1) cluster monitored by the mass of PhOH<sup>+</sup>-CH<sub>4</sub> (1:1) cluster, and (c) the Dissociation MATI spectrum monitored by the mass of PhOH<sup>+</sup> monomer (detected PhOH<sup>+</sup> after dissociation of PhOH<sup>+</sup>-CH<sub>4</sub>). All spectra were measured three times and added. To measure them, Ar (5 atm) and CH<sub>4</sub> (1 atm) mixed gas was used.

The PIE and MATI spectra in figure 2(a) and 2(b) were able to be measured with good S/N ratio.

In the PIE spectrum in figure 2(a), the first

step occurs at a total photon energy of  $\sim 68320\text{ cm}^{-1}$  and is assigned to the ionization threshold ( $IP_0$ ) of the  $\text{PhOH}^+\text{-CH}_4$  (1:1) cluster. In the MATI spectrum in figure 2(b), a strong and broad band with some fine structure, which is attributed to a progression of an intermolecular vibration with  $10\text{ cm}^{-1}$ , was observed around  $IP_0$ . In addition, no intramolecular vibration of  $\text{PhOH}^+\text{-CH}_4$  (1:1) cluster is detected in figure 2(b), implying that dissociation occurs in the very low energy range above  $IP_0$ .

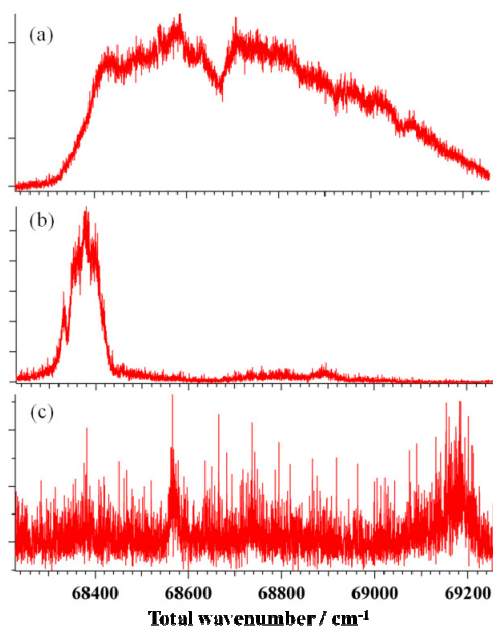


Fig. 2 (a) PIE, (b) MATI, and (c) Dissociation MATI spectra of  $\text{PhOH-CH}_4$  (1:1) cluster obtained via the  $S_1$  origin. ((a) and (b) were measured by monitoring the mass of  $\text{PhOH}^+\text{-CH}_4$  (1:1) cluster, while (c) was measured by monitoring the mass of  $\text{PhOH}^+$  monomer)

On the other hand, the dissociation MATI spectrum monitored at the mass of the  $\text{PhOH}^+$  monomer in figure 2(c) contains no

strong signal. Some weak signals at 68570, 68740, and 69180  $\text{cm}^{-1}$  were observed. It is very likely that these bands were contaminated by  $\text{PhOH-Ar}_n$  clusters because these bands increased in intensity when preparation of  $\text{PhOH-CH}_4$  (1:1) clusters was stopped by interrupting the supply of methane gas. To avoid contamination by  $\text{PhOH-Ar}_n$  clusters, we must use Ne as the buffer gas in future work.

Next, to examine the details of any orientational change of the cationic state, we measured MATI spectra via each vibronic band of the  $S_1$  state. Through vibronic state excitation, it is possible to discuss the structural changes that occur from different kinds of intermolecular vibration from the spectral intensity meaning that more detailed structural analysis is possible.

Figure 3 shows the two-color REMPI (Resonance Enhanced Multi-Photon Ionization) spectrum of the  $\text{PhOH-CH}_4$  (1:1) cluster ( $\nu_2 = 32249\text{ cm}^{-1}$ ).

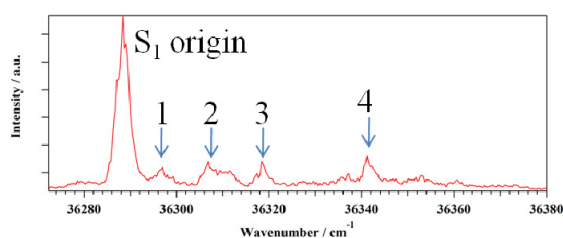


Fig. 3 The REMPI spectrum of  $\text{PhOH-CH}_4$  (1:1) cluster

The band at  $36288\text{ cm}^{-1}$  is the  $S_1$  origin. The four bands [ $36297$  (origin +  $9\text{ cm}^{-1}$ ),  $36307$  (origin +  $19\text{ cm}^{-1}$ ),  $36319$  (origin +  $31\text{ cm}^{-1}$ ),  $36341$  (origin +  $53\text{ cm}^{-1}$ )] may be assigned to vibronic bands. The band of lowest

wavenumber [36297 (origin + 9)  $\text{cm}^{-1}$ , No.1 in Fig.3] is tentatively assigned to the internal rotation of  $\text{CH}_4$  and another bands are the intermolecular bending and stretching vibrations.

We also measured the Mass Analyzed Threshold Ionization (MATI) spectra of  $\text{PhOH}^+\text{-CH}_4$  (1:1) cluster via 0-0 and these vibronic bands in  $S_1$ . We succeeded in the measurement of MATI the spectra via all vibronic bands. All spectra in figure 4 show a strong and broad band with structure around  $\text{IP}_0$ , but band positions and shapes are a little bit different.

For the detailed analysis, we will perform theoretical calculations such as the structure optimization of the cation, normal vibrational calculations and a Frank-Condon analysis. Following that, by comparison of the results of the experiments with the calculations, we would like to examine the assignment of the vibrational modes and the orientational changes.

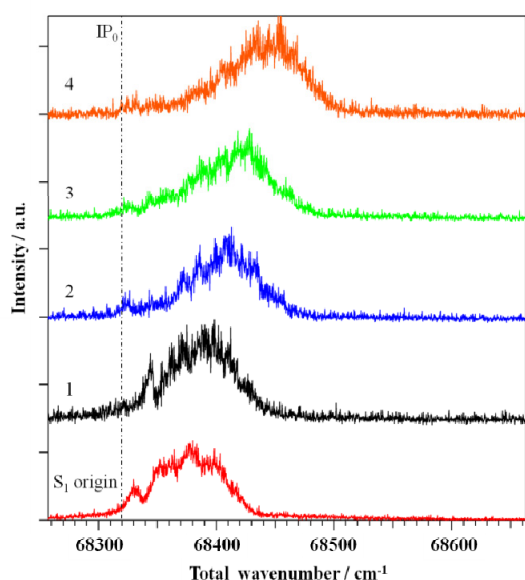


Fig. 4 MATI spectra of  $\text{PhOH-CH}_4$  (1:1) cluster obtained by exciting some vibronic bands. The numbers on the left of the each spectrum indicate the band indices, which correspond to those in the REMPI spectrum of Fig. 3.

### Life in U. K.

The first day, I arrived at Manchester Airport in the middle of the night and I went to the hotel by taxi. I took a taxi for the first time in a foreign country, unlike my mental image of taxi drivers being very careful drivers, it was very striking for me to be driven at breakneck speed to a hotel with my taxi overtaking other cars. Thanks to the taxi, I reached the hotel almost immediately and was able to take an adequate rest.

The next day, I went to the University of Manchester, overwhelmed by the campus which was full of nature. I learned the basic technique of the experiment in the Photon Science Institute. During Health and safety inductions, I had the experience to sign my name dozens of items. This experience is not considered in Japan.

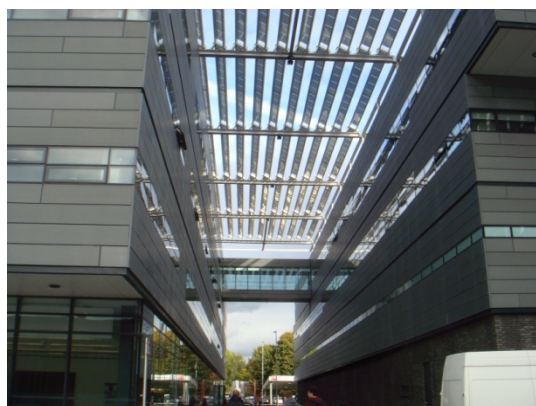


Fig. 5 The Photon Science Institute.

In terms of the weather, it was basically colder than Japan but I was able to live comfortably by wearing a little bit heavier clothes. However, as it often began to rain suddenly, I always carried folding umbrellas. I was surprised that British people didn't use umbrellas even if it rained and wore less clothing even if it was cold. Especially, I was really astonished that I saw people who drank beer like water with short sleeves in front of the bar on a very cold night.

During my stay, I watched Manchester United football match. Manchester United is one of the most famous football teams in the world. I enjoyed watching a "real football match". The people supporting the away side reached fever pitch and I heard the cheering for the away team more greatly than that for home team.



Fig. 6 Watching a football game.

As mentioned above, thanks to this program, I was able to experience not only experiments on PhOH-CH<sub>4</sub> (1:1) clusters but also British culture by staying in the U. K. and watching football matches. This stay in the U. K. gave me an irreplaceable two weeks.

Finally, I would like to express my deep appreciation to Prof. K. Müller-Dethlefs in Manchester University and Prof. M. Fujii in Tokyo Institute of Technology and all the staff who assisted with this program.