

Visiting The University of Manchester in Britain
Shinya TANAKA, M2, Laboratory of Prof. FUJII and Assoc. Prof. SAKAI
Chemical Spectroscopy Division, Chemical Resources Laboratory
Tokyo Institute of Technology

I had an opportunity to visit the Photon Science Institute of the University of Manchester as a part of the JSPS “Core to Core Program”. I worked in the laboratory of Professor K. Müller-Dethlefs during my stay for 13 days, from 6th to 18th November in 2010.

The University of Manchester

The University was founded in 2004 by merging the University of Manchester Institute of Science and Technology, which was established in 1824, and the Victoria University of Manchester, which was founded in 1851. The University of Manchester is the biggest university in Middle-England and is a centre of excellence. The University has produced as many as 25 Nobel Prize winners. Just after my arrival, it was announced that 2 professors at the University, Andre Geim and Konstantin Novosel from Russia, were to be awarded the Nobel Prize in physics for their research on graphene. The whole campus was excited by the news. Fig. 1 is Alan Turing Building at the University of Manchester.

The Photon Science Institute where I worked was established in 2005 to bring together experts from a wide range of scientific fields to foster

the development of trans- and multi-disciplinary collaborations and provide a dynamic and exciting culture for the progression of new ideas in photon science. Its broad area of research covers physics, astrology, chemistry, biology and medicine concerning with photons. The institute has currently 113 academics and is a critical site of photon related research.



Fig. 1 Alan Turing Building in the university of Manchester.

Professor K. Müller-Dethlefs & ZEKE spectroscopy

Prof. K. Müller-Dethlefs (Fig. 2) is a spectroscopist who graduated from the University of London. He is famous for the development of Pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy.



Fig. 2 Prof. K. Müller-Dethlefs.

PFI-ZEKE is a powerful spectroscopic method used to observe vibronic levels of the cationic state with high resolution. In this form of spectroscopy, high-Rydberg states of a target molecule are first excited, usually via the S₁ state. Then, the excited molecules are ionized by a pulsed electric field and electrons produced by the ionization are detected. We can observe the transitions from the S₁ state to vibrational levels of the cation by scanning the wavelength of the second laser while monitoring the electron intensity, because each vibrational level of the cation is accompanied by high Rydberg states. When the ions that are produced simultaneously with the electrons are detected, the method is called Mass Analyzed Threshold Ionization (MATI) spectroscopy. The ability to specify the spectral carrier is the key merit of MATI spectroscopy. ZEKE and MATI spectroscopies accomplish spectroscopy on cationic states with much higher resolution than traditional UV photoelectron spectroscopy. Resolution as high as 0.1 cm⁻¹ is possible, and even intermolecular vibrations of molecular clusters whose frequencies are a few tenths of a cm⁻¹ can be measured.

Phenol-Rare gas clusters

Phenol (PhOH)-rare gas clusters have been studied for a long time based on interests in their basic interactions. In addition, recently, an ionization induced isomerization reaction in which the rare gas atom moves from the aromatic ring, where it is bound in the electronic ground state S₀, to the tip of the OH group, which is the most stable binding site the cationic state D₀, is known to occur. Several spectroscopic methods have been applied to clarify the nature of the isomerization reaction. One is infrared spectroscopy on the cluster cation formed by two photon ionization of the neutral cluster, which was developed by Prof. M. Fujii, who is my supervisor. In this method, the structure of the cation is not able to change from that of the S₀ state due to the Franck-Condon principle. Thus, stabilization to the most stable structure in the cation state, that is, an ionic induced isomerization, can be observed by measuring the OH stretching vibration. The second method is IR spectroscopy on cluster cations formed by collisions between rare gas atoms and PhOH⁺ ionized by electron impact ionization. Professor O. Dopfer in Technical University of Berlin, Germany is one of the most famous Professors associated with this method. In this method, the most stable structure of a cluster cation can be formed irrespective of the neutral ground and S₁ states. Therefore, IR spectroscopy provides information of the global minimum of the D₀ state. In addition, PFI-ZEKE and MATI, which are well utilized at the K. Müller-Dethlefs lab, have been also applied. The

methods have provided contradictory results to those obtained by IR spectroscopies. Discussion about the reaction dynamics continue to this day.

Issues at Manchester

In this visit, we aimed to measure MATI spectra of PhOH-CH₄ (1:1) at the Müller-Dethlefs lab in order to get insight into the dynamics of CH₄ after ionization (Fig. 3). This idea originate from the fact that PhOH-Ar (1:1) and -Ar (1:2) show completely different behavior in the isomerization reaction. The IR spectrum of PhOH-Ar (1:1) has two OH stretching vibration bands ascribed to two species, isomerized and none isomerized species. On the other hand, PhOH-Ar (1:2) clusters show only OH stretching of the isomerized species. At present, the reason for the difference has been explained by their IVR processes. In a PhOH-Ar (1:2) cluster, one Ar atom moves to the tip of the OH group and the other Ar atom remains on the aromatic ring. The intermolecular vibrations of Ar atoms on the aromatic ring can act as a heat bath that accepts and dissipates the excess energy released by isomerization, and the reverse reaction from OH to π is prohibited. The existence of such bath modes in the 1:2 clusters is the key factor of the difference between 1:1 and 1:2 clusters.

CH₄ is a spherical molecule like Ar, but the PhOH-CH₄ (1:1) cluster, has three additional internal rotation modes associated with the internal rotation of CH₄. It has been confirmed that only the H-bonded OH str. is observed after photo-ionization of PhOH-CH₄. This is just the

same behavior as PhOH-Ar (1:2) despite involving only a 1:1 cluster.

IVR to the three additional modes is expected to be the reason for the lack of the back reaction. We thought other information on the intermolecular modes obtained by MATI would give as a clue about the dynamics of the isomerization and IVR processes.



Fig. 3 Apparatus used for MATI spectroscopy.

Experimental

(a) Resonance Enhanced Multiphoton Ionization (REMPI) spectroscopy.

This method is used to measure $S_1 \leftarrow S_0$ electronic transitions by detecting ions resulting from a multi-photon absorption. Because the ionization probability is drastically enhanced by the resonance effect, ions can be produced only when the wavelength of the laser resonates on vibronic levels. Thus, the electronic transitions of molecules are measured as enhancements of the monitored ion signal. REMPI spectroscopy is a very sensitive technique and can be applied to the spectroscopy of gas-phase clusters. In this experiment, the REMPI spectrum of PhOH-CH₄ (1:1) was measured to obtain information about intermolecular modes in the S_1 state and to

check the experimental conditions.

(b) MATI spectroscopy (Fig. 4)

MATI spectroscopy is a high-resolution spectroscopic technique used to observe vibronic states of a cation. In MATI spectroscopy, some molecules are excited to high Rydberg states accompanied by others which are excited to particular vibrational levels of the cationic state, via a vibronic level of the S_1 state, using two UV lasers. Immediately after laser irradiation, Rydberg states and the cations produced by direct ionization upon 2-photon absorption are mixed. An electric field is applied to spatially separate the cations from the Rydberg species. A short time later, a strong electric field is applied to ionize the Rydberg molecules and the resultant ions are introduced into a TOF together with the ions directly ionized by 2-photon absorption. Thus, the TOF spectrum shows two mass peaks originating from the two processes. As the long-lived Rydberg states only exist just below vibrational levels of the cationic state, transitions to vibrational levels of the cationic state can be observed by scanning the UV2 while monitoring the intensity of the Rydberg mass peak.

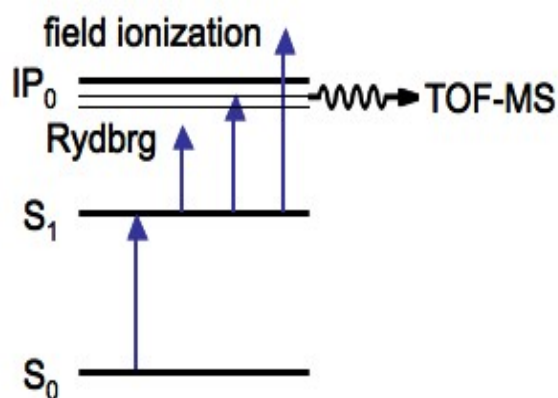


Fig. 4 Excitation scheme of MATI spectroscopy.

Research progress

The first day I got a guide on computer setting, and also attended a lecture on laser safety. After that, the majority of my time was spent on the experiment. I optimized laser alignment, sample condition and so on. The characteristic feature of the K. Müller-Dethlefs lab. was the ability to heat PhOH up to 60 °C to obtain a high vapor pressure. The TOF-MS was used in the reflectron mode. This is because of cellulosic species, irrespective of the measurement, to be damped by adjusting the voltage of reflection electrodes. First, we optimized the optical alignment, reflectron, and voltages while checking the REMPI spectrum of the PhOH monomer. Then I tried to observe the MATI signal via the S_1 origin. But only a very weak signal was observed under the same conditions as REMPI. Therefore, we optimized various settings such as the timing of the pulsed electric field and the reflectron voltage to increase the signal intensity. Finally we were able to measure the MATI spectrum of PhOH-CH₄ (Fig. 5).

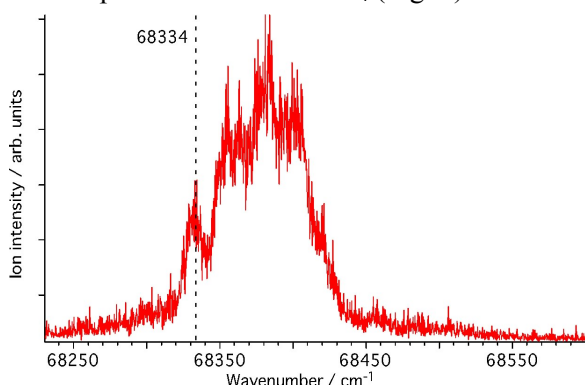


Fig. 5 MATI spectrum of PhOH-CH₄

On the last day of my stay, we were invited to the home of Prof. K. Müller-Dethlefs. I reported the successful confirmation of the MATI

spectrum of PhOH-CH₄ via the S₁ origin. In addition, we discussed the experimental plan for the next group. We decided to measure MATI spectra via different inter molecular modes in the S₁ State of PhOH-CH₄.

Symposium

I attended the 60th anniversary Symposium of Prof. K. Müller-Dethlefs. At the beginning Prof. Wolfgang Ketterle gave a speech about Bose-Einstein-condensation. He won the Nobel Prize for realizing the phenomenon with Na atom. Prof. Richard N. Zare who is famous for his studies on reaction dynamics presented a presentation about the analysis of isotope ratios using cavity ring down spectroscopy. The origin of matter can be traced by the precise determination of the isotope ratio achieved by CRDS. The lecture of Prof. K. Müller-Dethlefs was about his recent research theme on Rydberg plasma utilizing jet-cooled NO molecule. In addition many other researchers who were famous in Physics and Chemistry such as Daniel Newmark and Karl Kleinermanns also gave interesting talks to celebrate his 60th birthday.

Looking back

As for my experiment, I could achieve a beneficial result even though my stay was just 2 weeks. I measured the MATI spectrum of PhOH-CH₄ as I had planned. The experimental results themselves were not sufficient to discuss details about the isomerization of CH₄. However, I was able to set up the apparatus so that the next group can measure better spectra. As for my

daily life, I struggled to communicate in English. I keenly realize the importance of training in English conversation.

Acknowledgment

I would like to thank JSPS for providing me such a valuable opportunity. I am most grateful to Prof. Müller-Dethlefs at the University of Manchester for accepting me and cooperating with me in many ways. Thanks to Prof. K. Müller-Dethlefs and all other people who showed me such warm hospitality. I really enjoyed my stay at Manchester. Finally I would like to express my thanks Prof. Masaaki Fujii at the Chemical Resources Laboratory, Tokyo Institute of Technology, for giving me full support to realize this visit to the University of Manchester.