

Report on a visit to The Photon Science Institute of the University of Manchester in U.K.

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As the internship, I studied in Prof. Klaus Müller-Dethlefs' research group in The Photon Science Institute of the University of Manchester in the U.K. for two weeks, from April 25th, 2010 to May 9th, 2012.

0. Purpose

To realign the supersonic jet – laser spectrometer for the MATI spectroscopy and measure MATI spectrum of PhOH – CH₄ cluster and IR spectrum of PhOH – Ar₁ cluster by monitoring MATI signal.

1. Introduction

Photoionization generates a positive charge to neutral molecules which causes significant change of intermolecular interaction because of the induced dipole. Therefore photoionization triggers dynamics to rearrange structure. This is similar to the dynamics in condensed phase.

On the other hand, solvated cluster which consists of solute and solvent molecules and bonded by weak interactions is an ideal system to study intermolecular interactions and dynamics. In the photoionization - induced isomerization, solvated cluster changes bonding sites, so the reaction dynamics have been interested.

Our group has been studied this isomerization about Phenol – ligand cluster because phenol is the simplest molecule which has both hydrogen-bond site at the OH group and van der Waals site at the aromatic ring and rare gas is the simplest molecule and can binds to both sites. As a result of our studies, these facts were known:

1) PhOH – Ar₁ cluster

An argon atom binds above the aromatic ring of phenol (pi structure) in the S₀ state while argon is trapped at the OH group of phenol (H structure) in the D₀ state. It is because photoionization causes a pendular motion of argon atom.

2) PhOH – Ar₂ cluster

It takes pi structure in the S₀ state while only H structure is found in the D₀ state. Thus the isomerization occurs straightly without back reaction because of the IVR (Intramolecular Vibrational-energy Redistribution) at the H structure.

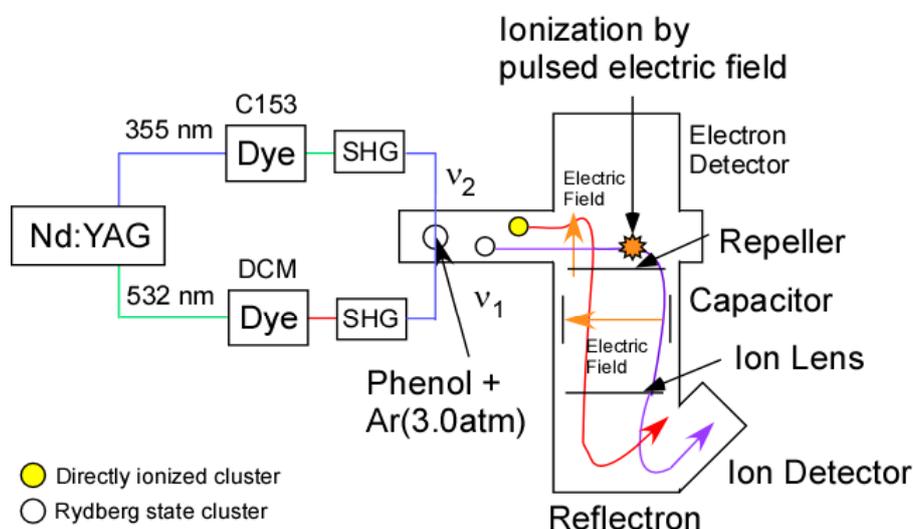
3) PhOH – (CH₄)₁ cluster

In PhOH – (CH₄)₁ cluster, no back reaction has been found although it has single ligand. It is necessary for investigating the dynamics of ionization-induced isomerization to know the structure and physical properties of molecule which has just ionized. Prof. Müller – Dethlefs' group uses Mass Analyzed Threshold Ionization (MATI) to investigate vibration for neutral and cationic molecules.

So this time I planned to measure the MATI spectrum for PhOH – (CH₄)₁ and the IR spectrum for PhOH – Ar₁ by monitoring MATI signal. Especially, the latter is expected to solve the inconsistency: the IR spectrum indicates that the argon moves while the MATI indicates the argon doesn't hold its position [1].

2. Experiment

I set up the supersonic jet – laser spectrometer for the MATI spectroscopy whose schematic diagram is shown in Fig.1.



Directly ionized cluster can't take in the ion detector because of its trajectory.

Fig.1 Schematic diagram of the supersonic jet – laser spectrometer for MATI spectroscopy

The sample, here is phenol, was diluted in pure argon gas and the gas mixture was introduced to the vacuum chamber by supersonic expansion. So the phenol – argon cluster was generated. This obtained cluster was excited to the first excited state by one UV laser ν_1 and to higher Rydberg state by the other one, ν_2 . Ionic cluster ionized by lasers directly was raised by the electric field from the repeller while high-Rydberg state ones were remained to go straight because of lack of charge. The high-Rydberg cluster was ionized by the pulse electric field from the repeller. Then cluster ion was reflected by the reflectron and detected by the ion detector. Because flight time of directly ionized cluster and field-ionized cluster were different, both signals were separated. In the MATI spectroscopy, the ion signal of field-ionized cluster is measured.

But there were many problems to start experiments, so I had to solve them. The problems and solutions were listed in Table 1.

Table.1 Problems and solutions during the realignment of the supersonic jet – laser spectrometer

Problem	Solution
ν_1 laser couldn't excite molecules.	I suppressed the Amplified Spontaneous Emission (ASE).
Auto tracker didn't work.	I cut visible emission by filter.
Poppet was chipped away by touching the nozzle exit.	I changed the shape of the exit to fit with the poppet and cut the top of the poppet.
The valve didn't move freely because the surrounding metallic gas tube was too rigid.	I replaced the tube by Teflon one.
The ions weren't detected by the MCP detector symmetrically (It prevents from distinguishing parent ion from daughter one.)	I optimized the voltage of the ion capacitor by comparing the simulation.
Signals couldn't be assigned by the time of flight. (Molecular mass didn't correspond to the indicated time.)	I checked the timing of applying pulse electric field to indicate correct time of flight.
Signal from PhOH – Ar ₂ didn't appear.	I changed the wavelength of ν_2 from 605 nm to 619 nm.

At first the pulse valve didn't work, so I measured the REMPI spectrum of phenol without operating the valve. But the result of the solutions as previously explained, I could observe the REMPI signals of PhOH – Ar_n (n = 0 - 2). The condition of the measurement is summarized in Table.2.

Table.2 The condition of the REMPI measurement

	Phenol (Without operating pulse valve)	PhOH – Ar _n (n = 0 - 2) (With operating pulse valve)
ν_1 / nm	549.5 – 551.5 (scanned)	549.5 – 551.5 (scanned)
ν_2 / nm	605.0	619.0
Repeller / V	1350	1300
Capacitor / V	-1.539, 1.676	-2.861, 2.954
Ion lens / V	880	950
Reflector / V	1400	1400
Ion detector / V	-1900	-2000
Duration / μ s	-	220
Cumulated number	2	3

3. Results and Discussions

The REMPI spectra for phenol obtained with and without operation of the pulsed valve were shown in Fig. 2. In Fig.2, (a) was measured without operating the valve and (b) was measured with operating. The REMPI spectra for PhOH – Ar_n (n = 0, 1 and 2) are shown in Fig.3, (a), (b) and (c) respectively.

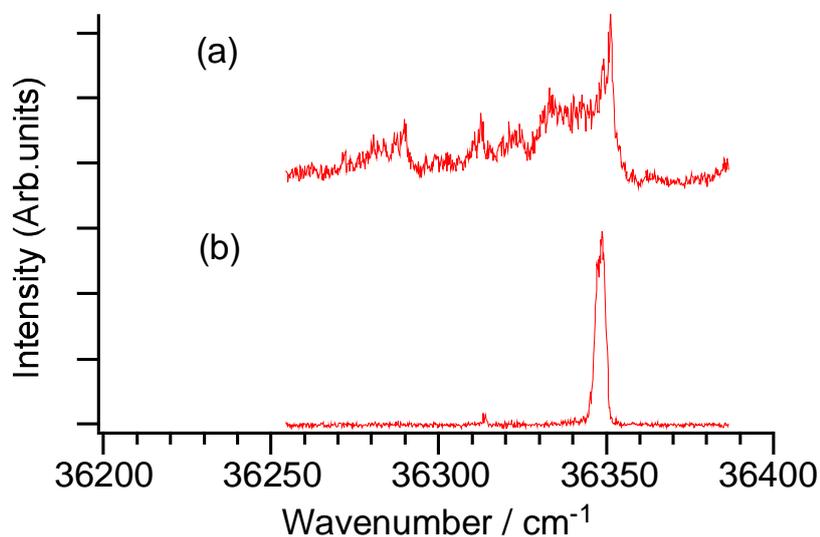


Fig.2 The REMPI spectra for phenol ((a) Without operating the valve (b) With operating)

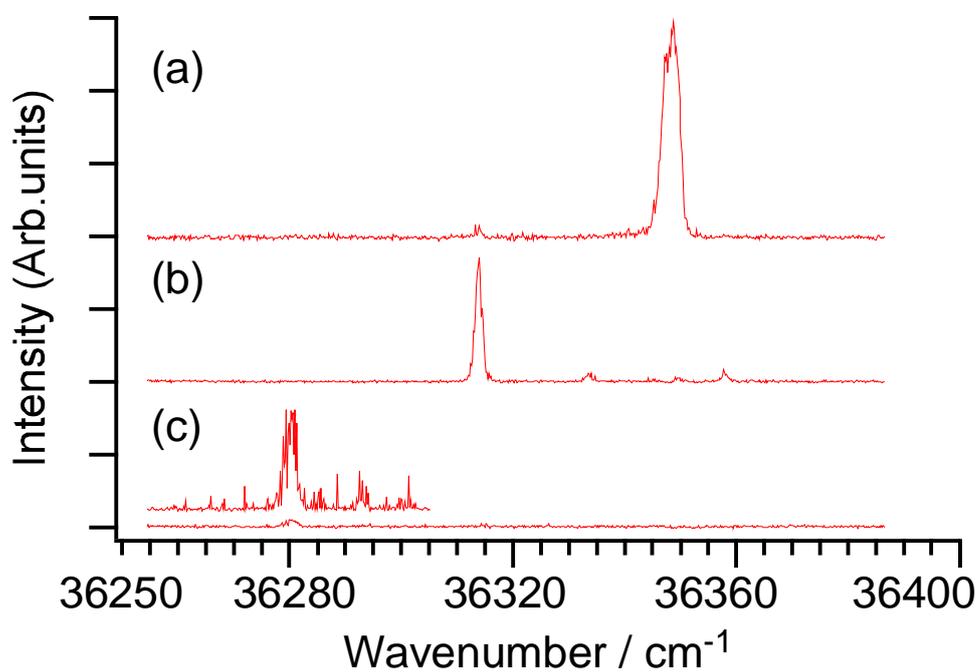


Fig.3 The REMPI spectra for PhOH – Ar_n ((a) n = 0 (b) n = 1 (c) n = 2)

As shown in Fig.2 (b), the origin band of phenol is observed at 36349 cm^{-1} , which is same as previous report [2]. On the other hand, as shown in (a), the origin band is observed at 36351 cm^{-1} when the valve was stopped, but this spectral feature means that the sample is at room temperature. It is reasonable if the spectrum was obtained from the phenol vapor.

The origin band of $\text{PhOH} - \text{Ar}_1$ is observed at 36314 cm^{-1} as shown In Fig.3 (b), which is also same as previous report [2]. For $\text{PhOH} - \text{Ar}_2$ shown in (c), only one peak was observed though this cluster has two isomers. The intense peak at 36281 cm^{-1} corresponds to the (1|1) cluster where two argons bind to both surfaces of phenol respectively. The other isomer, (2|0) isomer in which both argon atoms solvated in one side wasn't found in this condition.

I succeeded to measure REMPI spectra for $\text{PhOH} - \text{Ar}_n$ ($n = 0 - 2$) clusters, but had no time to realign the apparatus for MATI spectroscopy. For MATI measurement in the next step, the laser paths must be shifted to upper stream of the jet to separate the ion signal due to the field – ionization of high Rydberg states from directly ionized signal.

4. About the life

In the first day I arrived in Manchester via the Heathrow Airport. I had to wait to pass the immigration and wait over one hour because of huge amount of people. It was the first my surprise in the UK. (This problem was reported in BBC news!)

From the second day I went to the Manchester University and worked with Prof. Müller-Dethlefs' group. During the two weeks, I could study the principle of MATI spectroscopy and apparatus. Furthermore, I knew the high attitude of security in the university. For example, I had to sign many terms about security in the security lecture and stop laser when I went out even though it was just a moment.

I felt a few impressive features of Manchester. First, the weather tended to be rainy and cold. But I saw many young people wore T – shirt in spite of such a cold weather, I was very surprised. Second, I noticed the multiethnic society. I saw many non-European people. In fact the cafeteria of the university reflects it, so I didn't get bored. Third, Of course, Manchester United is famous in this city. I went to the museum attached to the stadium of Manchester United and attended to the stadium tour, and I felt the long history of football in Manchester. As mentioned above, I was able to experience not only the laboratory activities but also touch British culture. All the moments in the two weeks were fresh and stimulating, and I thank the Core to core program for giving me such experience.

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

5. References

- [1] M. Miyazaki, S. Tanaka, S. Ishiuchi, O. Dopfer, M. Fujii, Chem. Phys. Lett., **513** (2011) 208-211
- [2] S. Ishiuchi, M. Miyazaki, M. Sakai, M. Fujii, M. Schmies, O. Dopfer, Chem. Chem. Phys., **13** (2011) 2409–2416