

Report on Core-to-Core program collaboration on
MATI-monitored IR spectroscopy on $\text{PhOH}^+-\text{Ar}_1$, part II: Setup of MATI spectroscopy

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Introduction & purpose of this collaboration

In this Core-to-Core program, we aim to shed light into mechanism of the molecular recognition, which supports high selectivity of chemical reactions, e.g. in enzyme of our body, based on molecular point of view. Particularly, understanding how the intermolecular interaction changes by photo-excitation of related molecule is the central topic of this program. At present, we have been interested in mechanism of an ionization induced isomerization in Phenol- Ar_1 cluster ($\text{PhOH}-\text{Ar}_1$) as a fundamental example of molecular recognition.

The Ar atom changes the most stable interaction site upon photo-ionization of PhOH from the π cloud to tip of the OH bond according to the switching of the major intermolecular interaction form dispersion interaction to hydrogen bonding due to an effect of the created positive charge. This fact was established by Prof. O. Dopfer, who is one of collaborator of this program, by IR spectroscopy and a collision based cluster source that mainly produces the most stable conformer. The two interaction sites in the cation, π cloud and tip of the OH bond, however, are expected to be separated by a barrier of around 100 cm^{-1} height from theoretical works. Results of ZEKE/MATI spectroscopies also claim the existence of a barrier for the isomerization. It has not been clear yet whether the initially produced less stable π -bound $\text{PhOH}^+-\text{Ar}_1$ in the adiabatic ionization potential (IP_0) by photo-ionization can isomerize to the H-bound structure beyond the barrier or not. The main problem to be solved is a contradiction between IR and ZEKE/MATI spectroscopies both of which provide information about vibrational levels in the cationic state. IR spectroscopy is used to study high frequency modes like OH stretching vibration, and ZEKE/MATI spectroscopies preferentially provide information about low frequency modes. At this moment, interpretations of their results obtained for the $\text{PhOH}^+-\text{Ar}_1$ cluster are totally different. IR spectroscopy confirms the isomerization of Ar but ZEKE/MATI says the barrier is too high to isomerize from IP_0 of the π bound structure.

In order to resolve this discrepancy, we have tried to combine the two spectroscopies, MATI-monitored IR

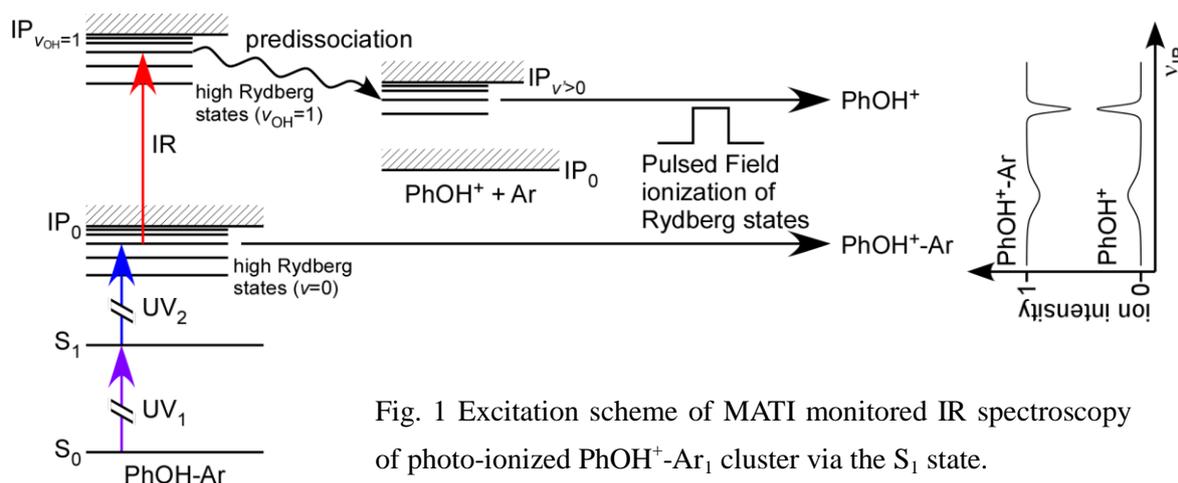


Fig. 1 Excitation scheme of MATI monitored IR spectroscopy of photo-ionized $\text{PhOH}^+-\text{Ar}_1$ cluster via the S_1 state.

spectroscopy. The excitation scheme of the spectroscopy is given in Fig. 1. By probing the MATI signal of photo-dissociation product of PhOH^+ and/or $\text{PhOH}^+-\text{Ar}_1$, which can pick up only the π bound cluster on the IP_0 , IR spectra of $\text{PhOH}^+-\text{Ar}_1$ purely on the IP_0 level would be measured.

The last visit on May 2012, we reset optical arrangement, peripheral equipment and software of ZEKE/MATI machine in Manchester University. At that time, however, spectroscopic tests of ZEKE/MATI were not possible due to problems of the pulsed valve. This visit, we proceeded the experiment aimed to establish the MATI spectroscopy.

Progress & Results

At first, some troubles on the vacuum system were fixed. These were leaks from a regulation valve at a gas cylinder of Ar and sealing of a flange that introduces a gas inlet line. The vacuum chamber was evacuated after checking the configuration of pulsed valve holding parts and spatial alignment of the pulsed valve to skimmer of the chamber. During we waited the evacuation, which takes one night, the oscillation of dye lasers and second harmonic generations (SHG) were optimized to illuminate the $\text{PhOH}-\text{Ar}_1$ clusters in a supersonic jet. After alignment of the UV pulses, 1+1 REMPI signal of PhOH was monitored to check the reflectron mass spectrometer and the ion detection (MCP) system. Adjustment of voltages of ion deflection plates (called capacitor at the Müller-Dethlefs lab.) was critical to introduce the ions to the ion detector, which was finally settled to about ± 3 V, respectively. Production of $\text{PhOH}-\text{Ar}_1$ cluster was also confirmed using pure Ar gas (~ 2 bar) as the carrier. After that, 1+1' REMPI spectra of $\text{PhOH}-\text{Ar}_1$ were measured in order to fully optimize the jet cooling condition and to know the exact resonance wavelength. The first spectrum showed intermolecular bands with the intensities of about half of the origin band as shown in Fig. 2(a). This implied the light intensities were too high and resulted in a saturation of the origin band. This saturation has been later solved by introducing ND filters and a polarizer into the optical paths as shown in Fig. 2(b). The bandwidth of the origin was less than 1 cm^{-1} and no hot band due to β_x mode was observed beside the origin. This means the jet condition was cold enough.

To check dryness of the sample inlet system, a comparison of signal intensities of $\text{PhOH}-\text{Ar}_1$ and $\text{PhOH}-(\text{H}_2\text{O})_1$ clusters was done. After optimizing the signal of $\text{PhOH}-\text{Ar}_1$ cluster, the wavelength of the excitation laser was tuned to

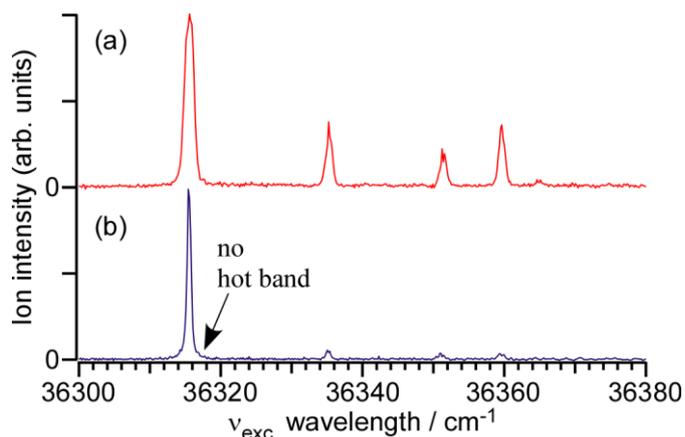


Fig. 2 1+1' REMPI spectra of $\text{PhOH}-\text{Ar}_1$ cluster recorded under (a) strong and (b) weak light intensity conditions.

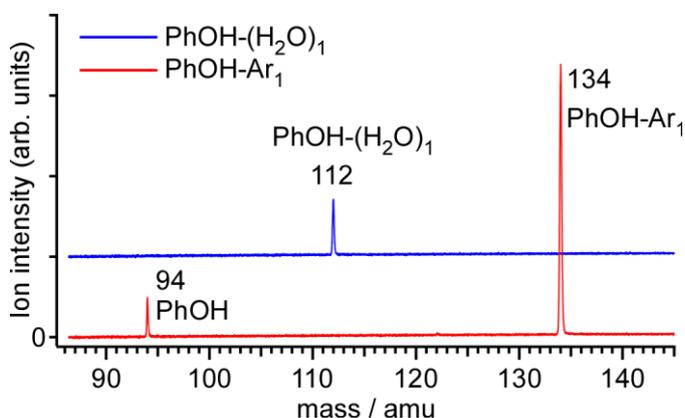


Fig. 3 Comparison of TOF mass spectra obtained by resonating $\text{PhOH}-\text{Ar}_1$ and $\text{PhOH}-(\text{H}_2\text{O})_1$.

the resonance of $\text{PhOH-(H}_2\text{O)}_1$. The intensity of $\text{PhOH-(H}_2\text{O)}_1$ was about 1/3 of PhOH-Ar_1 as can be seen in Fig. 3. This result showed that the sample system was dry enough because intensity of PhOH-Ar_1 is usually weaker than that of $\text{PhOH-(H}_2\text{O)}_1$ if no drying procedure like evacuation of the sample inlet system is equipped. Because higher clusters, PhOH-Ar_n , tend to prevent production of PhOH-Ar_1 under dried condition, the carrier gas was changed to a mixture of Ar/Ne 10% to further improve the PhOH-Ar_1 production.

MATI spectroscopy was tried as a next step. At first a low resolution (conventional) MATI spectroscopy was tested. The position of light pulses was shifted by 1/2" to the valve direction. This shift enables us to wait $\sim 20 \mu\text{s}$ from the irradiation of laser pulses until a pulsed filed ionization of remaining Rydberg clusters, which should occur at the center of the TOF electrodes.

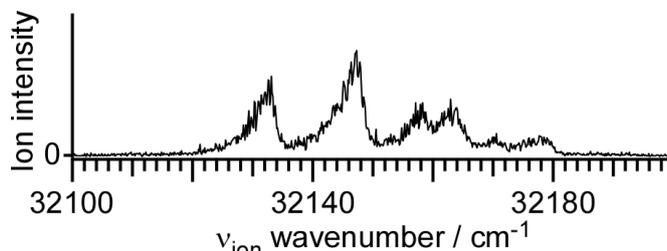


Fig. 4 Example of low resolution MATI spectrum of PhOH-Ar_1 cluster.

A separation voltage of $\sim 1 \text{ V}$, which was given by a DG535 pulse generator, was applied to the TOF electrode $\sim 300 \text{ ns}$ after shining the lasers to spatially separate the neutral threshold Rydberg clusters from directly ionized cluster ions. By scanning the wavelength of the ionization laser while monitoring the pulsed field ionized Rydberg ion, low resolution MATI spectra were obtained as shown in Fig. 4. The spectral quality was tried to optimize by changing mainly parameters of the MATI separation pulse.

To minimize the field effects, which are expected to arise lowering of IPs of vibration and/or rotational levels above the vibration less adiabatic ionization state, a high resolution MATI spectroscopy, Fractional Stark-State Field Ionization (FSSFI) method, was tried. FSSFI utilizes blue seeking states of very high Rydberg states (so called ZEKE states) that can survive

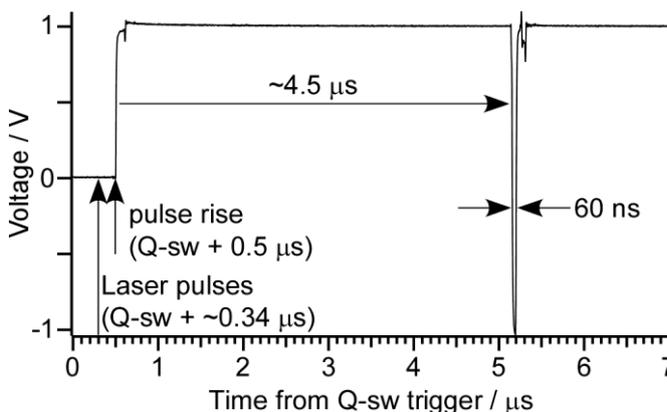


Fig. 5 Shape of the high resolution MATI separation pulse.

longer time than red seeking states under MATI separation electric field. An example of the electric field used FSSFI are depicted in Fig. 5.

Detection of ion signal arising from these blue seeking states ionized by a short inverted pulse can pick up only ZEKE states and can exclude signal from Rydberg states with relatively larger shift of IP that construct red tail of conventional MATI peak. FSSFI MATI, thus gives symmetric spectral peaks and ambiguity of peak positions is reduced. This improvement of the peak shape can be clearly seen in Fig. 6(a) comparing low resolution MATI spectra (Fig. 6(b)). Another advantage of this technique is that low resolution MATI and photo-ionization efficiency curve (Fig. 6(c)) can be recorded simultaneously. The high resolution MATI spectra favorably compares with reported one as can be seen in Fig. 6.

In order to fully establish the FSSFI, however, three ion signals, i.e. direct ion, high & low resolution MATI ions, have to be separated in the time of flight to reduce contamination from other ion peaks. The

perfect separation of these peaks was not easy even using the well-constructed reflectron mass spectrometer. Adjustment of parameters can improve the time separation but the signal intensity was necessarily weakened. Establishing both the separation and intensity of the signal is a future challenge to achieve MATI-IR spectroscopy under ideal condition.

Finally, we carried IR OPO laser (laser vision) to beside the MATI machine and connected cooling water and electricity cables. Operation of the IR laser was not allowed at the time due to laser safety restriction, but laser equipment for MATI-IR experiment had been fully constructed.

Summary & future work

In this visit, we set up the MATI spectrometer, lasers, sample, supersonic jet and data acquisition systems, and could record REMPI and MATI (both low and high resolution) spectra of

PhOH-Ar₁ cluster. Preparation of the spectrometer for MATI-IR spectroscopy, therefore, has been almost finished. Success was made mainly due to utilization of standard normal general valve as the pulsed valve.

To improve the spectral quality, incorporation of a drying device into the sample system and improvement the MATI peaks separation of TOF by optimizing parameters are desired. In addition, reason why the pressure of the source chamber largely fluctuates should also be clarified. To carry out the MATI-IR spectroscopy, setup of the IR laser, safety construction, check of the control software and construction of IR path and so on, are necessary. These issues will be done by members of Manchester Univ. until next visit.

Acknowledgements

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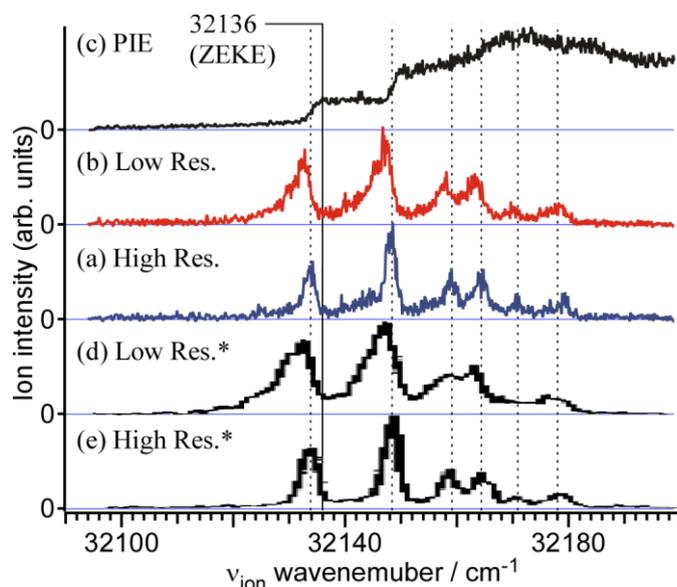


Fig. 6 Spectra obtained by FSSFI of PhOH-Ar₁, (a) high, (b) low resolution MATI spectra and (c) photo-ionization efficiency (PIE) curve. Spectra in (d) and (e) compare high and low resolution MATI spectra reported by “C. E. H. Dessent and K. Müller-Dethlefs, *Chem. Rev.* **100**, 3999 (2000)”, respectively.