

Report on Core-to-Core program collaboration for

MATI-monitored IR spectroscopy of PhOH⁺–Ar₁, part III: Measurement of MATI-IR spectra

@ Klaus Müller-Dethlefs laboratory, Photon Science Institute, Manchester University, Manchester, England, Nov. 10th – Dec. 1st, 2013.

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Introduction and purpose of this visit

In this Core-to-Core program, we aim to shed light into the mechanism of molecular recognitions, which supports high selectivity of chemical reactions, e.g. in enzymes of our body, based on the molecular point of view. Particularly, understanding how the intermolecular interaction changes upon photo-excitation of a related molecule is a central topic of this program. At present, we have been interested in the mechanism of an ionization induced isomerization in phenol–argon₁ cluster (PhOH–Ar₁) as a fundamental example of molecular recognition.

The most stable interacting site of the Ar atom in the neutral states of PhOH–Ar₁ has been determined by a rotational band analysis of a high resolution LIF spectrum. The Ar atom binds only on the π-cloud because the dispersion interaction dominates in the neutral states. The most stable interaction site changes upon the photo-ionization of PhOH from the π cloud to the tip of the OH bond according to switching of the major intermolecular interaction form dispersion interaction to the hydrogen bonding, because induction forces due to the created positive charge enhance the hydrogen bonding ability of the OH bond. This fact was established by Prof. O. Dopfer, one of collaborators of this program, by IR spectroscopy in combination with a collision based cluster source that mainly produces the most stable isomer. ZEKE/MATI spectra of PhOH–Ar₁, which utilizes very high-*n* Rydberg states (*n* > 100) produced by photo-excitation from the neutral π-bound structure, provide structured spectra and thus imply existence of a local minimum on the π-cloud and also existence of a barrier between the two interaction sites, the π cloud and the tip of the OH bond. The height of the barrier has been estimated to be > 100 cm⁻¹ from high level *ab initio* calculations.

IR spectra of photo-ionized PhOH⁺–Ar₁, on the other hand, show features both of the π- and H-bound structures even if it is ionized to just above the adiabatic ionization energy (IE₀) with the excess energy less than 5 cm⁻¹. Picosecond time resolved IR spectroscopy on the photo-ionization process of PhOH–Ar₁ demonstrated the IR feature of the H-bound structure gradually grows after the ionization with the time constant of ~15 ps while that of the π-bound structure appears synchronizing to the ionization and a part of them then decays with a time constant similar to that of the H-bound. This observation implies that the H-bound isomer results from an isomerization from the initially prepared less stable π-bound structure. The isomerization, however, is not plausible because Ar is too heavy for tunneling through the barrier of 100 cm⁻¹ height. Therefore, finding a reason why the IR feature of the H-bound structure can be observed simultaneously in the IR spectra of photo-ionized PhOH⁺–Ar₁ and an unified explanation of results from ZEKE/MATI and IR spectroscopies is a main problem to be solved in the Core-to-Core program.

One possibility is an effect from the Rydberg electron, though it is usually assumed to be negligibly small. Another possibility is an effect of a stray field in the ionization region on the photo-ionized cation. IR

spectroscopy on PhOH–Ar₁ in the high-*n* Rydberg states (*n* > 100) would give a clue because the position of the Ar atom, which can be most sensitively probed by IR spectroscopy of the OH stretching vibration, has not been determined convincingly for the Rydberg states and effects of the stray field must be minimized to survive high Rydberg states. In order to clarify these effects, we have tried to combine MATI and IR spectroscopies to develop MATI-IR spectroscopy.

An excitation scheme of the MATI-IR spectroscopy is given in Fig. 1. High-*n* Rydberg states of PhOH–Ar₁ that converge to IE₀ are prepared by 2-color excitation via the S₁ 0⁰ level. An IR beam is irradiated to the Rydberg states 50 ns after the UV excitation. When the IR frequency is resonant on that of the OH stretching vibration, a vibrational excitation occurs and then dissociation of the Ar atom follows. Since the Rydberg electron is orbiting quite far away from the cation core and does not have interaction with the core, the dissociation results in production of high Rydberg states of PhOH. The Rydberg states then ionized by a weak pulsed field and the resultant ions detected using a TOF mass spectrometer as a MATI signal. Thus, IR absorption of the cationic core in high Rydberg states of PhOH–Ar is obtained as depletion of the MATI signal of PhOH⁺–Ar₁ and enhancement of that of PhOH⁺. The same procedure can be applied for Rydberg states converging to vibrational excited levels of the cationic core. An ion signal due to the direct ionization, which is simultaneously detected with the MATI signals, also behaves similar to the MATI signals and provides IR spectral information of photo-ionized PhOH⁺–Ar₁.

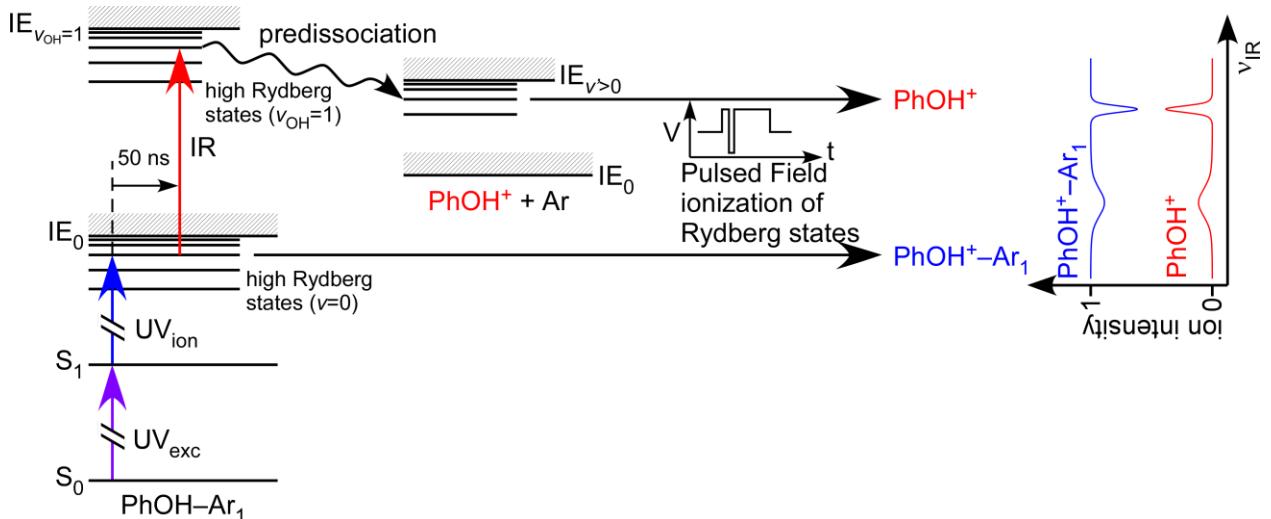


Fig. 1 Excitation scheme of MATI monitored IR spectroscopy of the photo-ionized PhOH⁺–Ar₁ cluster via the S₁ state.

In the last visit on Nov. 2013, we established MATI spectroscopy of PhOH–Ar₁. In the present visit, we setup an IR laser and measured MATI-IR spectra under several ionization conditions to investigate the mechanism of the ionization induced isomerization.

Progress and Results

In the first week, conditions of the MATI spectroscopy were fixed. Those include cleaning of a sample line to exchange the sample, alignment of UV beams, mixture gas formation, adjustment of ion optics for optimization of the MATI signal, and so on. Fig. 2 shows a 1+1' REMPI spectrum of PhOH–Ar₁, and confirms the jet expansion is well cooled down.

To check dryness of the sample system, signal intensities of PhOH–Ar₁ and PhOH–(H₂O)₁ clusters were compared. Fig. 3 shows TOF spectra obtained by tuning the excitation laser to each origin band of the cluster. After optimizing the signal of PhOH–Ar₁, the excitation laser was tuned to the resonance of PhOH–(H₂O)₁. The intensity of PhOH–(H₂O)₁ was about 1/4 of that of PhOH–Ar₁. This result shows that

the sample system was dry enough considering no drying procedure was incorporated in. In addition, intensity of the PhOH monomer is very weak. This means efficient production of PhOH–Ar and spectroscopic probe using reduced UV beams were achieved under this experimental condition. An expanded TOF spectrum also proves there was no fragmentation from higher PhOH–Ar_n clusters under this condition. This fact is important to ensure the experiment condition was clean and free from contaminations from them.

The MATI spectroscopy was carried out using Fractional Stark-State Field Ionization (FSSFI) method to minimize field effects that are expected to induce lowering of IE of vibration and rotational levels above the IE₀ level. FSSFI can also provide a high resolution MATI spectrum. The photo-ionization efficiency curve (PIE) can be recorded simultaneously. The high resolution MATI spectrum and PIE of PhOH–Ar₁ are shown in Fig. 4. A careful optimization of ion optics parameters and more importantly subtraction of a background contribution from the FSSFI signal provided nearly perfect separation of three ion peaks (direct ion, FSSFI, and conventional MATI) and gave the highest quality data ever.

In the second week, oscillation of an IR OPO laser (Laser Vision) was checked, and alignment to the counter propagating UV beams was built. Focusing of the IR beam was adjusted using a cylindrical lens ($f = 350$) and the UV pulses were reflected off by a Brewster angled Si plate ($t = 1$) to protect the IR system from the very strong UV_{ion} beam. The calibration and power curve of the IR laser were checked by recording an absorption spectrum of water

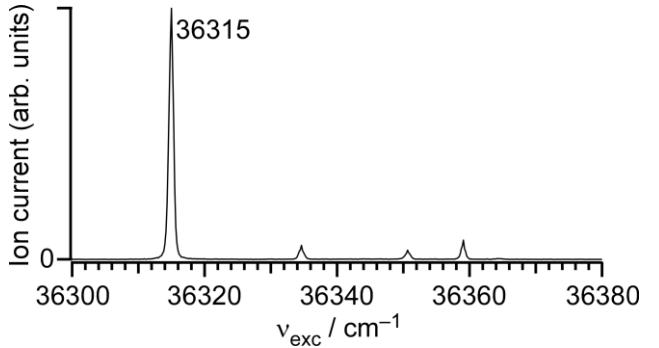


Fig. 2 1+1' REMPI spectrum of PhOH–Ar₁.

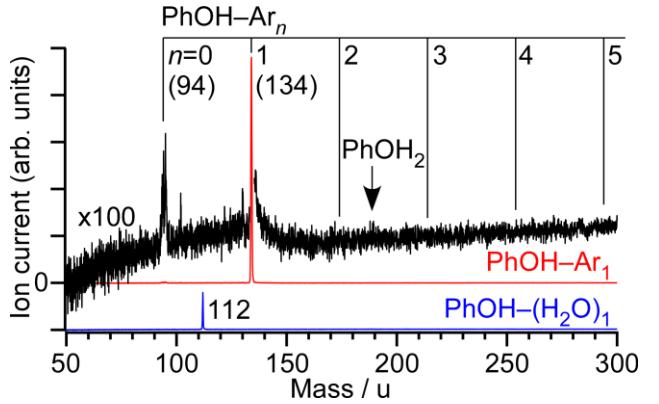


Fig. 3 Comparison of TOF mass spectra obtained by resonating the origin bands of PhOH–Ar₁ and PhOH–(H₂O)₁ clusters.

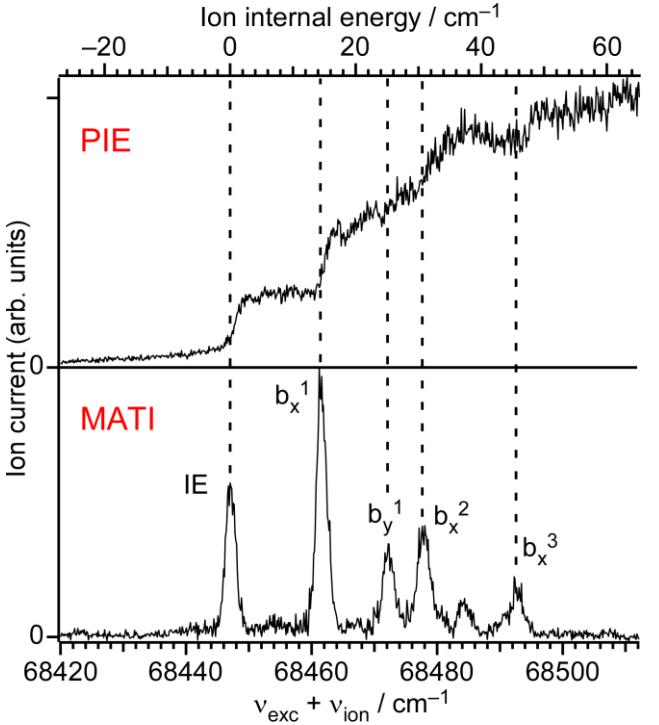


Fig. 4 High resolution MATI spectrum and PIE curve of PhOH–Ar₁ via the S₁ 0⁰ level.

vapor in the optical path. The irradiation of the IR beam could actually induce a depletion of $\text{PhOH}^+ - \text{Ar}_1$ and enhancement of the PhOH^+ fragment peaks both of which kept the peak splitting caused by the MATI separation pulse, when the IR frequency was tuned to the free OH stretching vibration as we expected. Therefore, we scanned wavelength of IR OPO to record the MATI-IR spectra while monitoring all six mass peaks (direct ion, high and low resolution MATI peaks of parent $\text{PhOH}^+ - \text{Ar}_1$ and fragment PhOH^+ , respectively).

At first, MATI-IR spectrum was recorded at the IE_0 level (Fig. 5). Both traces show only a sharp and strong peak at 3537 cm^{-1} , just matching with that of the bare PhOH^+ and no other absorption is seen at all. This means the high Rydberg states converging to the IE_0 level do not isomerize and only the “ π -bound” structure exists at the IE_0 level. This observation is consistent with results of ZEKE/MATI spectroscopy and also theoretical works that predict a barrier for the isomerization. In order to estimate height of the barrier, MATI-IR spectra at various intermolecular vibration levels were measured. A comparison of MATI-IR spectra shown in Fig. 6 clearly illustrates that excitation of any intermolecular modes can induce the isomerization even from the b_x^1 level with only 15 cm^{-1} excess energy. This implies the barrier height is quite low though it contradicts the observation of sharp intermolecular levels in ZEKE/MATI spectra up to at least 50 cm^{-1} and theoretical predictions.

To study the energy dependence more precisely, next, IR spectra of $\text{PhOH}^+ - \text{Ar}_1$ were recorded around IE_0 probing the direct ion signal that causes the PIE curve, because when the ionization is off-resonance with the IE_0 level the MATI signal disappears. This probe does not detect the structure of the Rydberg states of $\text{PhOH}^+ - \text{Ar}_1$ but the $\text{PhOH}^+ - \text{Ar}_1$ cation directly ionized by the excitation. The results shown in Fig. 7 are again surprising. The relative intensity of the free and the H-bonded OH stretching totally inverted, the free OH dominates above IE_0 but the H-bonded OH does below IE_0 , and at IE_0 both look to be averaged. This observation means $\text{PhOH}^+ - \text{Ar}_1$ cations produced at the IE_0 level contain both the π -bound and the H-bound isomers in spite of the corresponding high Rydberg states consist of only the π -bound structure as demonstrated by the MATI-IR spectrum shown in Fig. 5. Another point is the ionization

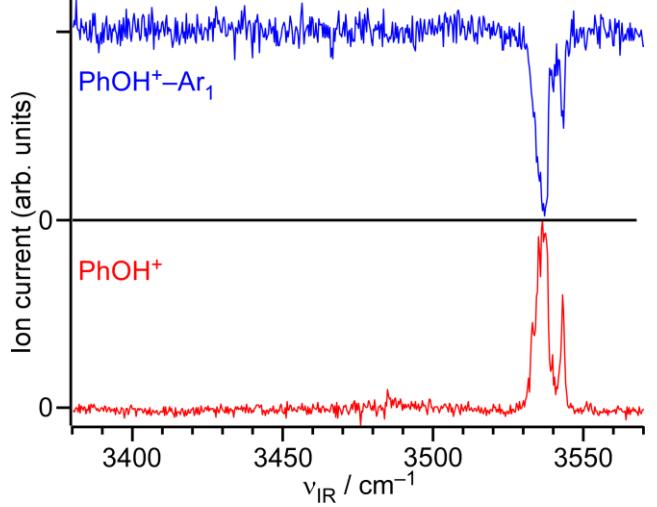


Fig. 5 MATI-IR spectrum of $\text{PhOH}^+ - \text{Ar}_1$ at the IE_0 level monitored in the parent and fragment channels.

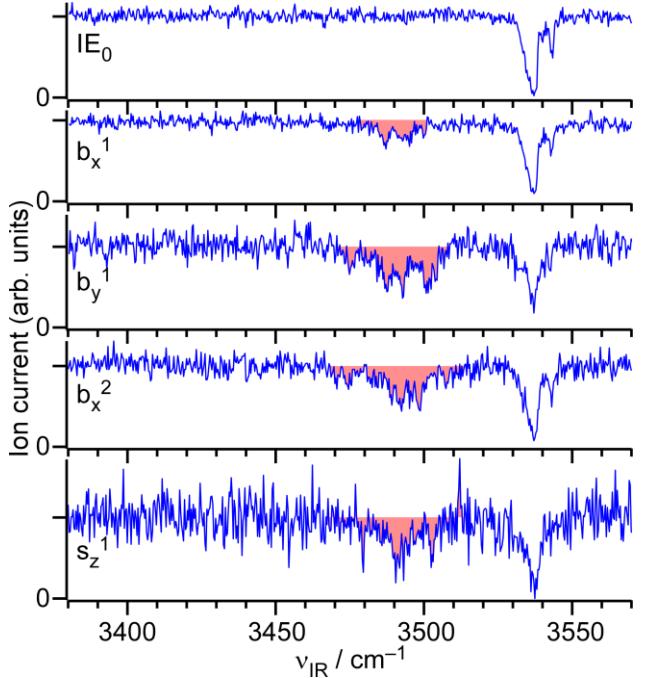


Fig. 6 Comparison of MATI-IR spectrum of $\text{PhOH}^+ - \text{Ar}_1$ at various intermolecular vibration levels in the cation monitored in the parent channel.

mechanism when the system is excited below IE_0 . The π -bound structure should not be ionized at this energy because here is below the adiabatic IE, though the trace A in Fig. 7 shows a weak depletion due to the free OH stretching vibration at 3537 cm^{-1} . In addition, photo-ionization of the H-bound isomer might be unlikely because Franck-Condon overlap between structures of the π -bound in the S_1 state and the H-bound in the D_0 state seems to be negligibly small due to large structural difference between them. That is, ion signals should not be observed at position A. The PIE curve, however, always provides a broad tail even below IE_0 . Usually such tail is ascribed to ionization of lower Rydberg states. But if that is true, it is hard to rationalize the large isomerization probability resulting from the trace A, because the Rydberg states have the π -bound structure.

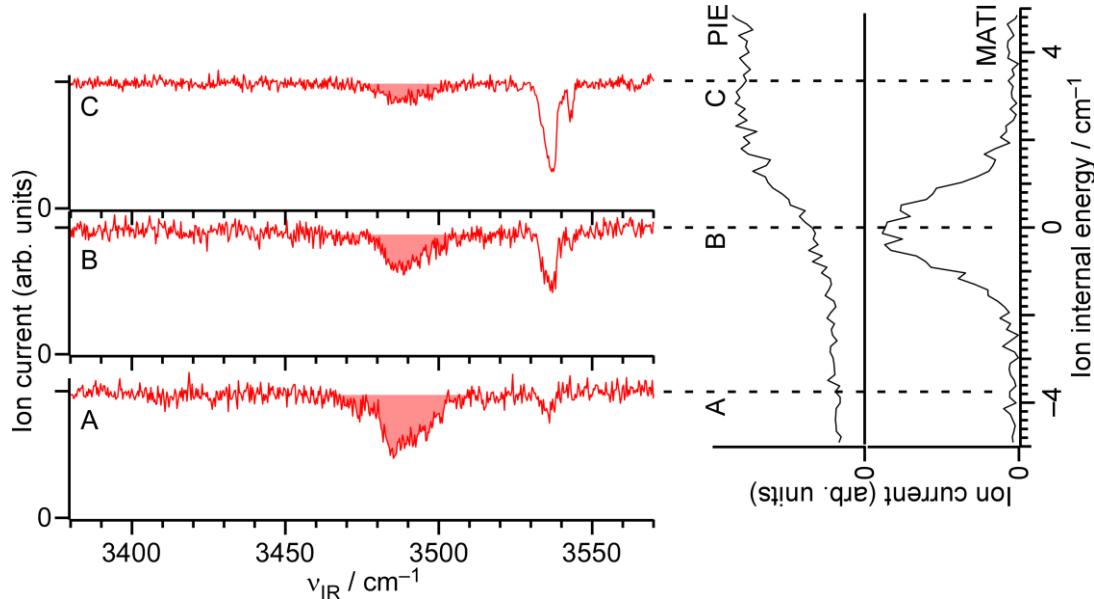


Fig. 7 IR spectra of $\text{PhOH}^+ - \text{Ar}_1$ obtained by monitoring the direct ion signal around the IE_0 level. Corresponding excitation positions are indicated on MATI and PIE traces shown right by dashed lines.

Summary and future work

In this visit, we have achieved development a new IR spectroscopy, MATI-IR spectroscopy, to investigate the mechanism of ionization induced isomerization reaction in $\text{PhOH}-\text{Ar}_1$. The MATI-IR spectrum obtained at the IE_0 level shows only the free OH stretching vibration and thus definitely proves the vibration-less level of the π -bound cation does not isomerize to the H-bound structure. Other experimental findings, isomerization from the b_x^1 level and dominance the H-bound structure below IE_0 , are quite new, however, seem to conflict to those of ZEKE/MATI and theoretical works. At this stage, we have no good idea to consistently reconcile all the things. Clarification of these phenomena is a next important target of this collaboration.

Acknowledgements

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