Spectroscopic study
on the rearrangement of hydrogen bonds
in solvated cluster cations

Ph.D. Thesis
by
Takamasa Ikeda

Graduate School of Science
Kyushu University
2016
Contents

CHAPTER 1.
General introduction
1
1.1 General Introduction 2
1.1.1 Hydrogen bond and hydration 2
1.1.2 Laser spectroscopy in the gas phase 3
1.1.3 Current status of gas-phase spectroscopy 5
1.2 Scope of chapters 7
References to chapter 1 8

CHAPTER 2.
Methods
11
2.1 Experimental apparatus
2.1.1 Vacuum chamber 12
2.1.2 Molecular beam source 13
2.1.3 Time-of-Flight (TOF) mass spectrometer 14
2.1.4 Laser system 15
2.2 Spectroscopy
2.2.1 Resonance-enhanced two-photon ionization (R2PI) spectroscopy 17
2.2.2 Photoionization efficiency (PIE) spectroscopy 17
2.2.3 IR-dip spectroscopy 18
2.2.4 IR-UV holeburning spectroscopy 19
2.2.5 IR photodissociation (IRPD) spectroscopy 20
References for chapter 2 32

CHAPTER 3.
Structural fluctuation of hydrated benzyl alcohol cluster cations 33
3.1 Introduction 34
3.2 Experimental and computational methods 37
3.3 Results and discussion 39
3.4 Conclusion 48
References to chapter 3 57
Chapter 1.

General introduction
1.1. General introduction

1.1.1. Hydrogen bond and hydration

A hydrogen bond (H-bond) is one of the crucial intra- and intermolecular interactions to characterize many fundamental physical, chemical, and biological phenomena such as phase transitions, proton transfer reactions, and protein folding. In general, H-bonds are formed between H-bond donor and acceptor sites. The H-bond donor consists of H atom which is covalently bound to an electronegative atom, while electronegative atoms and groups having lone pairs and/or $\pi$-electrons can act as the H-bond acceptor. The physical properties of H-bonds such as interaction strength are characterized by the type of the donor and accepter sites.\textsuperscript{1–3} For example, water forms H-bonds, in which the lone pair of an oxygen atom of water accepts the H atom which is donated from the OH group of water. The strength of a single H-bond in water dimer is approximately 20 kJ/mol, which is typically classified into the H-bond having the modest strength. Actually, the strength of H-bonds extends from fairly weak (~10 kJ/mol) to significantly strong (~ 40 kJ/mol), which is larger than van der Waals forces but weaker than that of covalent bonds. The H-bonds having the modest strength such as O-H...O and N-H...O H-bonds are favorable to constructing three dimensional structures of large molecules, which shows both of stiffness and softness. This property is significant for various chemical and biological processes.

In the aqueous solutions of hydrophilic molecules, water molecules are bound to the hydrophilic solute molecules as well as the other water molecules. The layer of water molecules which is directly bound to the solute molecule is called a first hydration shell. The H-bonds between the solute and water molecules are entirely different properties from those of bulk waters such as the binding energy, preferential
motifs, and orientational flexibility. The water molecules in the first hydration shell are believed to play an essential role in various chemical and biological processes such as protein folding and biomolecular recognition.\textsuperscript{4–9} For example, in protein folding, the water molecules directly bound to amino acids retain the high-order structures (the third- and/or fourth-order structures) of the protein by fixing the relative orientation of the sub-structures formed in the early process of protein folding, which obviously shows the importance of the first hydration shell in the protein folding. Accordingly, it is highly required to reveal the local hydration structures and their dynamics at the molecular level for understanding chemical and biological processes in aqueous solutions.

1.1.2. Laser spectroscopy in the gas phase

Nowadays, the sophisticated laser spectroscopy combined with a supersonic jet expansion is one of the powerful tools to investigate the physical property and the structure of molecules and molecular clusters at the molecular level. The supersonic jet expansion was introduced in the field of the gas-phase laser spectroscopy in the late 1970’s. Up to the present, many experimental and theoretical breakthroughs have been achieved in this field. In this section, we focus on three progresses having a significant impact on the gas-phase laser spectroscopy. That is; (i) how to obtain the experimental signatures to identify the structures of molecules and molecular clusters, (ii) how to predict the favorable (stable) structures of molecules and molecular clusters, (iii) how to vaporize thermally fragile molecules such as biomolecules.

The significant progress for (i) was achieved by introducing the infrared (IR) spectroscopy in the gas phase. Vibrational spectroscopies such as IR and Raman
spectroscopy are the promising way of providing information on the structures of molecules and molecular clusters. However, the concentration of molecules and molecular clusters is so low in the molecular beam that it is difficult to obtain their IR and Raman spectra by using the direct absorption and scattering. Page et al. have introduced IR spectroscopy in the gas phase for the first time in the middle of 1980's. They measured IR spectra by monitoring the ion intensity produced by resonant two-photon ionization (R2PI), which is currently called IR-dip spectroscopy.\textsuperscript{10–12} The IR-dip spectroscopy allows us to obtain the electronic-state and isomer selective IR spectra of various molecules and molecular clusters.\textsuperscript{13,14} The emergence of tabletop tunable and powerful IR sources such as the optical parametric oscillator (OPO) system have also driven the progress of IR spectroscopy in the gas phase.\textsuperscript{15} Furthermore, the various spectroscopic techniques using the ultraviolet (UV) and IR lasers have been developed by some research groups, which has revealed the stable conformers and the potential energy landscapes of biomolecules.\textsuperscript{16–23}

The breakthrough for (ii) was achieved by the development of quantum chemical calculations. This development has been facilitated by the remarkable evolution of hardware ability of computers and the decline in the price of the hardware. Furthermore, in 1990's, the density-functional theory (DFT) calculations became popular in the field of molecular science, which reduces the computational costs of calculating the stable structures and theoretical IR spectra of molecules and molecular clusters as compared with the traditional ab initio molecular orbital calculations.\textsuperscript{24–26} The calculated IR spectra have allowed us to compare the experimental and theoretical results, which is helpful for the assignments of the complicated IR spectra of flexible molecules.
The breakthrough for (iii) was achieved by the development of the novel soft ionization techniques such as the electrospray ionization (ESI) method and the laser ablation method. In the early stage of the supersonic jet technique, the molecules were vaporized by thermal heating to obtain vapor pressure which is high enough to measure molecular spectra. However, some molecules such as amino acids and nucleic acids are frequently decomposed by thermal heating, which prevents us from measuring their spectra in the gas phase. The soft ionization techniques have been developed to introduce thermolabile molecules into vacuum, which is nowadays applied to various biomolecules such as amino acids, polypeptides and their hydrated clusters.\textsuperscript{27–31} Note that the vaporization techniques by thermal heating are also improved by applying various new materials and constructions to pulsed valves.\textsuperscript{32–34}

These improvements have been achieved synergistically. IR spectroscopy in the gas phase combined with the newly developed vaporization techniques allows us to investigate the thermolabile and/or flexible molecules. Their structures can be determined by combining the experimental IR spectra with the powerful theoretical calculations. Recently, the cold ion trap technique, which was introduced by Nolting et al. in the field of spectroscopy on biomolecules for the first time,\textsuperscript{29} is one of the current trends of the gas-phase spectroscopy. The conformations of large polypeptides and flexible biomolecules have been investigated via the cryogenically cooled ion trap technique.\textsuperscript{35–37}

1.1.3. Current status of gas-phase spectroscopy

The gas-phase laser spectroscopy has currently been applied to more "realistic" systems. As mentioned above, the larger and more flexible (bio)molecules like proteins
are the current targets of the state-of-the-art gas-phase spectroscopy. The strong and/or weak intra- and intermolecular interactions, which may determine the complicated conformations of the large molecules, can be investigated now at the molecular level. In addition, the study on the solvation effect of the large number of solvent molecules is also fascinating, though the large clusters have already been studied in the previous works.\textsuperscript{38,39} Bridging the gap between the gas phase and the condensed phase is one of the most important issues to understand more "realistic" systems at the molecular level.\textsuperscript{40–43}

Finally, we would like to describe the studies on the rearrangement of H-bonds in the gas-phase spectroscopy. The H-bonded clusters produced by the supersonic jet expansion are cooled down to extremely low temperature, which facilitates the study on the static nature of H-bonds. However, many (bio)chemical reactions proceeds at or above room temperature, in which thermal energy causes the rearrangement and/or fluctuation of H-bonds. Actually, some research groups reported the studies on H-bonds in solvated clusters having large internal energy (high temperature).\textsuperscript{44–51} The previous studies mainly reported the "one-way" rearrangement of H-bonds, which can be regarded as the relaxation process toward the stable H-bonded structures. Obviously, study on the fluctuation of the H-bonded structures, in which the H-bonded clusters isomerize among their stable H-bonded structures, is also important for understanding the rearrangement of H-bonds in aqueous solution at the molecular level. Furthermore, the potential barrier height, which is quite significant to characterize the H-bond dynamics, has never been determined experimentally in hydrated cluster cations. In this thesis, therefore, we particularly focus on the structural fluctuation and the potential barrier height for the rearrangement of H-bonds.
1.2. **Scope of chapters**

The present thesis focuses on two topics: (i) experimental observation of the structural fluctuation of H-bonds, and (ii) experimental determination of the potential barrier height for the rearrangement of H-bonds.

In chapter 2, the experimental apparatus is described in detail. Principles of the spectroscopic techniques we used in this thesis, such as resonant two-photon ionization (R2PI), photoionization efficiency (PIE), IR-dip, IR-UV hole-burning and IR photodissociation (IRPD) spectroscopy, are also explained.

In chapter 3, IR spectra of monohydrated benzyl alcohol cluster cations ([BA-(H₂O)₁]⁺) in the D₀ state are reported. We will discuss structural fluctuation in [BA-(H₂O)₁]⁺ based on the IR-dip spectra measured with the intense IR pulse.

In chapter 4, the rearrangement of H-bonds in monohydrated 5-hydroxyindole cluster cation ([5HI-(H₂O)₁]⁺) is discussed based on the IRPD spectra in the D₀ state. In addition, the potential barrier height for the rearrangement of H-bonds in [5HI-(H₂O)₁]⁺ is also presented.

In chapter 5, IRPD spectrum of 5HI-(
*tert*-butyl alcohol) (t-BuOH) 1:1 cluster cation ([5HI-(t-BuOH)₁]⁺) is reported. The difference in the rearrangement of H-bonds between [5HI-(H₂O)₁]⁺ and [5HI-(t-BuOH)₁]⁺ is discussed based on their IRPD spectra and potential barrier heights for the rearrangement of H-bonds.
References for chapter 1


(22) Garand, E.; Kamrath, M. Z.; Jordan, P. A; Wolk, A. B.; Leavitt, C. M.; McCoy, A. B.; Miller, S.
J.; Johnson, M. A. Science 2012, 335 (6069), 694–698.


6726–6735.


117 (29), 5962–5969.


2524–2529.


Chapter 2.

Methods
2.1. Experimental apparatus

2.1.1. Vacuum chamber

Figure 2.1 shows a picture of a vacuum chamber equipped with a linear time-of-flight mass spectrometer (TOF-MS). Figure 2.2 shows a picture of the whole experimental system including a vacuum chamber and lasers. The apparatus consists of three chambers; a source, ionization, and drift chambers. A source chamber was evacuated with a 10-inch diffusion pump (ANELVA, CDP-3700A, 3700 l/s (air)) backed by an oil rotary pump (ALCATEL, T2033A, 635 l/min). A water cooling baffle was mounted on the 10-inch diffusion pump in order to prevent a backflow of the oil from the diffusion pump. An ionization chamber was evacuated with a 6-inch diffusion pump (ANELVA, CDP-1200, 1200 l/s) backed by an oil rotary pumps (ALCATEL, M2015SD, 250 l/min). A drift chamber was also evacuated with a 6-inch diffusion pump (ANELVA, CDP-1200, 1200 l/s) backed by an oil rotary pumps (ALCATEL, M2015SD, 250 l/min). Both a liquid-nitrogen trap and a water cooling baffle were mounted on the 6-inch diffusion pumps for the ionization and drift chamber in order to achieve a high-vacuum condition which is appropriate for mass spectrometry.

The pressure of the vacuum chamber was monitored by an ionization gauge tube (ANELVA, UGD-1S) with a controller (Ionization chamber: ANELVA, MIG-061, Drift chamber: ANELVA, M-722HG). The background pressure of the drift chamber was maintained below ca. $2.5 \times 10^{-5}$ and ca. $5.0 \times 10^{-5}$ Pa when a pulse nozzle is operated with He and Ne as a carrier gas, respectively. In the beginning of the evacuation from an atmospheric pressure, the pressure of the source and ionization chambers was monitored by two Pirani gauge tubes (ULVAC, WP-02) with a controller (ULVAC, GP-2A).
2.1.2. Molecular beam source

A stainless steel tube was adopted to the nozzle housing of samples. The nozzle housing was rolled by a coiled heater. The applied voltage to a coiled heater was controlled to obtain adequate signal intensity. The temperature of the nozzle housing was monitored by a thermoelectric couple with a controller (Watlow, 935A). He or Ne was used for a carrier gas, whose backing pressure was controlled by a regulating valve.

The carrier gas was passed through a reservoir which contained solvent molecules. The temperature of the reservoir was controlled by a thermostat bath (AS ONE, LTB-250) from 268 K to ca. 320 K. The carrier gas containing the solvent molecules was mixed with the sample gas in the nozzle housing.

For expanding the mixture of the sample and carrier gas into the source chamber, we used the commercial pulsed valve of a single solenoid type (Parker Hannifin, Pulse Valves Series 9, 0.8 mm as an orifice diameter with a cone-type orifice shape) controlled by a commercial pulsed valve driver (Parker Hannifin, IOTA ONE). The maximum operating temperature of the commercial pulsed valve is ca. 400 K. To heat the sample above 400 K, we used a homemade heat-resistant pulsed valve whose solenoid consists of a polytetrafluoroethylene (PTFE) coated wire (Junkosha).

The gas expanded with the pulsed valve was skimmed into the ionization chamber. A commercial conical skimmer (Beam dynamics, Model 1, the diameter of the orifice is 1.5 mm) was used for generating the molecular beam. The distance between the pulse valve and the skimmer was adjusted to be ca. 20 mm in order to obtain adequate ion signal intensity. The skimmed molecular beam was ionized in the ionization chamber by the resonant two-photon ionization (R2PI) (see chapter 2.2.1)
2.1.3. Time-of-flight mass spectrometer

The cluster cations generated by R2PI were mass-selected by using a Wiley-McLaren type linear time-of-flight mass spectrometer (TOF-MS). Figure 2.3 displays the schematic diagram of TOF-MS. The ion signal was detected by micro-channel plates (MCP) (BURLE 18mm Detection) with a Z-Gap detector assembly (R. M. Jordan). The voltages applied to the MCP detector, acceleration electrodes, deflectors and a mass gate were controlled by a TOF power supply (R. M. Jordan). The voltage applied to the MCP detector was increased up to $-2.80 \text{kV}$.

In the ion-acceleration region, high positive voltages were applied to the first and second extraction grids ($+2.5 \text{kV}$ and $+2.2 \text{kV}$, respectively), whereas the final grid was held at ground potential. The distance among each grid is 15 mm. In order to guide the ions in the MCP detector efficiently, we introduced two plate-type ion deflectors which adjust the ion trajectories in the perpendicular and horizontal directions to an expansion axis. The applied voltages to the deflectors were typically between $-50$ and $+50 \text{V}$. In front of the MCP detector, a plate-type mass gate was introduced so as not to detect unnecessary species. The pulsed voltage applied to the mass gate was fixed at $200 \text{V}$, whose trigger pulse was synchronized with the time sequence of the whole experimental system.

The ion signal detected with MCP was amplified by a preamplifier (Stanford research systems, SR445A), then time-averaged by two digital oscilloscopes (LeCroy, WaveRunner 64xi and 9350A). The averaged signals were fed into a personal computer (Dell, OptiPlex 3020) to record the signal intensity of each mass channel separately.
2.1.4. Laser system

Figure 2.4 illustrates a block diagram of the laser system and detection devices for the measurement of all spectra in the present study. A single UV laser system was used for one-color R2PI (1C-R2PI) experiment, while two different UV laser systems were used for two-color R2PI (2C-R2PI) experiment. For 1C-R2PI, a frequency-doubled dye laser (Sirah Cobra Stretch and Inrad Autotracker III) pumped by the second harmonic of a Nd\textsuperscript{3+}:YAG laser (Spectra Physics INDI-40-20, 20 Hz, 50 mJ/pulse) was used as a UV source. For 2C-R2PI, the UV laser system used for 1C-R2PI was operated as an excitation UV source. A frequency-doubled dye laser (Lumonics HD-300 and BBO crystal) pumped by the second harmonic of a Nd\textsuperscript{3+}:YAG laser (Spectra Physics LAB-130, 10 Hz, 100 mJ/pulse) was used for the ionization UV source. The two UV lasers were combined collinearly with a half mirror and simultaneously focused on the molecular beam with a plano-convex quartz lens (300 mm focal length).

For the measurement of IR spectra, an optical parametric oscillator (LaserVision) pumped by an injection-seeded Nd\textsuperscript{3+}:YAG laser (Continuum Powerlite Precision II 8000, 580 mJ/pulse) was used as an IR source. The IR laser was focused on the molecular beam with a plano-convex CaF\textsubscript{2} lens (300 mm focal length). The IR laser system was triggered at 10 Hz and 5 Hz for 1C- and 2C-R2PI, respectively. The IR intensity was reduced to be ~1 mJ/pulse in the frequency region of 3300 ~ 3800 cm\textsuperscript{-1} in order to avoid unfavorable saturation of vibrational transitions. The ion signals with and without the IR pulse were stored separately to correct the artificial fluctuation of the spectral baseline.

All laser systems were synchronized with the trigger pulses for the pulsed
valve, the oscilloscopes and the mass gate by digital delay and pulse generators (Stanford Research Systems, DG-535).
2.2. Spectroscopy

2.2.1. Resonant two-photon ionization (R2PI) spectroscopy

R2PI\(^2-4\) was used for measuring the vibronic transitions between the S\(_1\) and S\(_0\) states. When the frequency of the UV photon is resonant with a specific vibronic state in the S\(_1\) state, a molecule (or a cluster) is excited to the vibronic state (S\(_1\)-S\(_0\) transition). The excited molecule absorbs another UV photon within the lifetime of the excited vibronic state. This sequential absorption allows the excited molecule to be ionized (D\(_0\)-S\(_1\) transition). In 1C-R2PI, two photons coming from the same laser are absorbed while in 2C-R2PI, the frequency of the ionization laser (\(\nu_2\)) is different from that of the excitation laser (\(\nu_1\)). Figure 2.5 shows the schematic diagram of 2C-R2PI. In general, two UV lights were focused on the molecular beam at the same position simultaneously. The \(\nu_1\) is scanned in the frequency region where the S\(_1\)-S\(_0\) transition occurs while the \(\nu_2\) is fixed at the frequency which is large enough to ionize the molecules. If the \(\nu_1\) is resonant with the S\(_1\)-S\(_0\) transition, the excited molecule is ionized by absorbing the \(\nu_2\) photon, then the ion signal is detected on MCP. Therefore, R2PI spectra contain information on the vibronic levels of the molecule (or cluster) in the S\(_1\) state. Note that mass spectrometry can be applied to the molecular (cluster) cations, which allows us to obtain mass-selected vibronic spectra.

2.2.2. Photoionization efficiency (PIE) spectroscopy

PIE spectroscopy\(^5-9\) was used to determine the adiabatic ionization energy (IE\(_0\)) of a molecule or a cluster. Figure 2.6 shows a schematic diagram of the PIE spectroscopy. The \(\nu_1\) is fixed at the S\(_1\)-S\(_0\) origin transition of each isomer observed in R2PI spectra, while the \(\nu_2\) is scanned. When the total photon energy (h\(\nu_1\) + h\(\nu_2\)) exceeds
IE₀, the excited molecule in the S₁ state is ionized to the ionization continuum in which the vibrational states in the D₀ state are buried. Accordingly, we obtain PIE spectra by monitoring the ion signal intensity as a function of the total photon energy. The Franck-Condon factors between the S₁ and D₀ states determine the vibrational states to which the excited molecules are accessible via photoionization. The step-like increase in the ion signal intensity is observed when the Franck-Condon region covers the zero-point energy level in the D₀ state. The ionization to the vibrational excited states in the D₀ state is observed as the increase in the ion signal intensity above IE₀. On the other hand, if the Franck-Condon region is far from IE₀, the ion signal intensity does not show the step-like increase but gradual increase at the beginning of the Franck-Condon region.₈,⁹ We note that the disappearance of the step-like increase in the ion signal is also observed when the internal rotation of a methyl group consists of dense low-frequency vibrational states as is observed in the PIE spectrum of indole-(MeOH).⁷

2.2.3. IR-dip spectroscopy

IR spectroscopy is one of the powerful tools for determining the conformations and structures of molecular clusters. In the gas phase spectroscopy, however, it is difficult to detect the direct IR absorption of the molecular clusters because the density of molecular clusters per unit volume is typically below the detection limit. Accordingly, we applied the population labeling spectroscopy in order to obtain IR spectra of the molecular clusters, which is called IR-dip spectroscopy.¹⁰⁻¹³ Figure 2.7 displays a schematic diagram of IR-dip spectroscopy in the S₀ state. The v₁ is fixed at the vibronic band of a single isomer observed in R2PI spectra. The v₂ is fixed at the same frequency
as when the R2PI spectra is measured. The two UV lasers are fired simultaneously while the irradiation of the IR laser precedes the UV lasers by 20 ns. When the IR photon is resonant with the vibrational transition of the monitored isomer in the $S_0$ state, the populations of the isomer in the $S_0$ state decrease, leading to the depletion of the ion signal. Therefore, IR-dip spectrum is obtained when the ion signal intensity is monitored as a function of the frequency of the IR laser ($v_{IR}$). In the present study, the $v_{IR}$ is scanned in the frequency region of ca. 3000 ~ 3800 cm$^{-1}$. The ion intensity with and without the IR pulse was stored separately to correct the artificial fluctuation of the spectral baseline.

IR-dip spectroscopy can be also available for obtaining the IR spectrum of molecular cluster cations in the $D_0$ state.$^{14,15}$ When the $v_{IR}$ laser is irradiated after R2PI, the IR-dip spectrum of the cluster cations is obtained as the depletion of the ion signal intensity due to photodissociation. It should be noted that the internal energy of the cluster cations after the absorption of an IR photon must be larger than their binding energy to bring about photodissociation. The IR spectrum in the $D_0$ state is also obtained by monitoring the fragment ion signals, which is called the IR photodissociation (IRPD) spectroscopy (see chapter 2.2.4).

### 2.2.4. IR-UV hole-burning spectroscopy

R2PI spectrum typically contains the vibronic bands of multiple isomers. IR-UV hole-burning spectroscopy allow us to separate the vibronic bands into those of each isomer.$^{12}$ Figure 2.8 shows the schematic diagram of IR-UV hole-burning spectroscopy. The basic strategy of IR-UV hole-burning spectroscopy is similar to that of IR-dip spectroscopy. The $v_{IR}$ laser is fixed at the vibrational transition of a specific isomer, while the $v_1$ is scanned. Absorbing the $v_{IR}$ laser reduces the population of the

19
isomer in the $S_0$ state. Accordingly, the vibronic bands of the isomer disappear in IR-UV hole-burning spectrum, whereas the vibronic bands of the other isomers still remain. The remaining vibronic bands are also classified into those of the other isomers by changing $v_{IR}$.

When the $v_{IR}$ overlaps with the vibrational transitions of two or more isomers, the vibronic transitions of each isomer cannot be distinguished by IR-UV hole-burning spectroscopy. Instead of the vibrational transition, the electronic transition (in the UV region) can also be available for reducing the population of the isomers in the $S_0$ state. This method is called UV-UV hole-burning spectroscopy. In the present study, however, we did not apply it.

2.2.5. IR photodissociation (IRPD) spectroscopy

IR spectra of molecular clusters in the $D_0$ state can be obtained by applying not only IR-dip spectroscopy but IRPD spectroscopy.\cite{16,17} Figure 2.9 shows a schematic diagram of IRPD spectroscopy. The $v_1$ and $v_2$ are fixed at the vibronic band of a single isomer observed in R2PI spectra. The $v_{IR}$ laser, the frequency of which is scanned in the region of 3300 \textsuperscript{–} 3800 cm\textsuperscript{-1}, is fired after the irradiation of the UV lasers by 700 ns. When the $v_{IR}$ is resonant with a vibrational transition of the monitored isomer in the $D_0$ state, the fragment ion (the daughter ion) is observed due to the photodissociation of the cluster cations. Accordingly, IRPD spectra are obtained as the increase in the intensity of the fragment ion signal without the fluctuation of the baseline (so-called zero-background spectroscopy). The portion of the molecular beam to which the UV lasers are irradiated flows to the downstream during the delay time of 700 ns. Thus, the alignment of the UV and IR lasers was manually adjusted to obtain the maximum
intensity of the fragment ion signals.

IRPD spectrum of monohydrated clusters is obtained as the increase in the monomer ion signal. In some cases, however, the unfavorable monomer ion signals originating from UV photodissociation (UVPD) process and/or direct photoionization of the monomer also appear in the mass channel of the monomer ion. Figure 2.10 displays a schematic diagram of the method used for eliminating unfavorable monomer ion signals. In this protocol, the delay time between the UV and IR lasers is fixed at 700 ns. After irradiating the UV lasers, the cluster cations and the unfavorable monomer cations (UVPD and/or direct photoionization) are generated in the acceleration region. The cluster cations are accelerated more slowly than the monomer cations due to the difference in their own mass. After 700 ns, the monomer cations precede the cluster cations in the acceleration region. Therefore, the unfavorable monomer ion signal appears in a TOF mass spectrum prior to the signal of the monomer cation via IRPD, which allows us to separate the IRPD signal from the unfavorable monomer ion signal.
Figure 2.1. Schematic diagram of vacuum chambers.
Figure 2.2. Picture of the whole experimental system including vacuum chambers and lasers.
Figure 2.3. Schematic diagram of Wiley-McLaren type linear time-of-flight mass spectrometer (TOF-MS) with detection devices.
Figure 2.4. Brock diagram of the laser systems and detection devices.
Figure 2.5. Schematic diagram of two-color resonant two photon ionization (2C-R2PI) spectroscopy. The $\nu_1$ is scanned in the region of the $S_1$-$S_0$ transition while the $\nu_2$ is fixed at the frequency which is large enough to cause the $D_0$-$S_1$ transition. The 2C-R2PI spectrum obtained as the increase in the ion signal intensity includes information on the vibrational states in the $S_1$ state.
Figure 2.6. Schematic diagram of photoionization efficiency (PIE) spectroscopy. The $\nu_1$ was fixed at the $S_1$-$S_0$ origin transition of a specific isomer observed in R2PI spectra, while the $\nu_2$ was scanned. The adiabatic ionization energy ($IE_0$) is obtained as the step-like increase in the ion signal intensity.
Figure 2.7. Schematic diagram of IR-dip spectroscopy in the $S_0$ state. The $\nu_1$ and $\nu_2$ are fixed, while the $\nu_{IR}$ is scanned in the range of ca. 3000 ~ 3800 cm$^{-1}$. When the $\nu_{IR}$ is resonant with the vibrational transition in the $S_0$ state, the ion intensity is reduced. The IR-dip spectrum is obtained as the depletion of the ion intensity.
Figure 2.8. Schematic diagram of IR-UV hole-burning spectroscopy. The $\nu_{IR}$ is fixed at the vibrational transition of a specific isomer, while the $\nu_1$ is scanned. The vibronic bands of the isomer do not appear in the IR-UV hole-burning spectrum, whereas the vibronic bands of the other isomers still remain.
Figure 2.9. Schematic diagram of IR photodissociation (IRPD) spectroscopy. The $\nu_{\text{IR}}$ in the region of 3300-3800 cm$^{-1}$ is fired after the irradiation of the UV lasers by 700 ns. The fragment ions derived from IRPD are selectively detected as a function of the IR frequency.
Figure 2.10. Schematic diagram of the method used for eliminating unfavorable monomer ion signals derived from UVPD or photoionization of the monomer. The delay between UV and IR lasers is fixed at 700 ns. The cluster cations are accelerated more slowly than the monomer cations. IRPD signal is separated from the signal originating from UVPD and/or photoionization of monomer.
References for chapter 2.

Chapter 3.

Structural fluctuation

of hydrated benzyl alcohol cluster cations
3.1. Introduction

The hydrogen bond (H-bond) is one of the most important interactions in aqueous solutions. Many chemical and biological reactions in aqueous solutions proceed around room temperature. In general, the H-bonds in aqueous solutions frequently break and re-form repeatedly. This phenomenon is regarded as a rearrangement and/or fluctuation of the H-bonds. In particular, the dynamics of water molecules in the first solvation shell may be significantly different from those of bulk water molecules. Hydrated structures and their dynamics in the first solvation shell have attracted attention for the importance of understanding chemical and biological processes such as protein folding and molecular recognition.\textsuperscript{1–7} Since there are many bulk water molecules in aqueous solutions, it is difficult to distinguish the behavior of water molecules in the first solvation shell on the chemical and biological processes from that in bulk. Furthermore, experiments in aqueous solutions are hardly able to focus on a particular water molecule. Although theoretical approaches\textsuperscript{6–8} such as molecular dynamics (MD) simulation allow us to discuss the H-bonding dynamics at the atomic resolution, experimental approaches at the molecular level are also required for comprehending chemical and biological processes in aqueous solutions in detail.

A supersonic jet expansion combined with various spectroscopic techniques is one of the most powerful tools for the investigation of hydration structures, because the jet-cooled hydrated molecular clusters, which consist of limited number of water molecules, are free from the disturbance of the bulk water. Furthermore, the supersonic jet expansion typically simplifies the spectral pattern of the hydrated molecular clusters due to the elimination of thermal energy. This is a great advantage to determine the structure of the hydrated clusters precisely. For example, many hydrated structures of
biomolecules such as amino acids and nucleobases have been identified in the gas phase by applying the combination of IR spectroscopy in the 3 μm region and theoretical calculations.9–11

In general, the jet-cooled hydrated clusters are located at local potential energy minima. However, the hydrated clusters storing sufficient internal energy to overcome the potential energy barriers may interconvert among various potential minima, which is equivalent to the rearrangement and fluctuation of the H-bonds. Recently, resonant two-photon ionization (R2PI) has been applied to hydrated clusters to investigate the dynamics of the H-bonds in the D0 state.12–22 In some cases, cluster cations produced by R2PI store a large amount of internal energy due to their large binding energy and the large structural displacement between the S1 and D0 states. For instance, the monohydrated trans-acetanilide cluster cation ([AA-(H2O)1]+), in which a water molecule is bound to the CO group, exhibits a migration of a water molecule from the CO group to the NH group after R2PI via the S1-S0 origin.14,19,20 Similarly, in the monohydrated tryptamine cluster cation ([TRA-(H2O)1]+), a water molecule migrates from the amino group to the NH group of the indole ring after photoionization.17,18 These cluster cations, however, show no migration in the opposite direction (i.e., a water molecule does not migrate from the NH group to the CO group in [AA-(H2O)1]+ and from the NH group to the amino group in [TRA-(H2O)1]+), indicating that these cluster cations show the “one-way” rearrangement of the H-bonds.

On the other hand, the fluctuation of hydration structures has been observed experimentally in the monohydrated 2-phenylethanol cluster cation ([PEAL-(H2O)1]+), in which the “consecutive” rearrangements of H-bonds occur.22 In this case, all of [PEAL-(H2O)1]+ fluctuate among the hydration structure of [PEAL(OH)-(H2O)1]+ and
[PEAL(Free)-(H2O)1]+, where a water molecule is bound to the OH group of [PEAL]+ or not. The internal energy of [PEAL-(H2O)1]+ produced by R2PI completely exceeds the potential energy barriers among of the structural isomers, since R2PI induces a large structural displacement including the configurational change of the PEAL side chain. On the other hand, the monohydrated phenol cluster cation ([Phenol-(H2O)1]+) having no side chain does not show the rearrangement of a water molecule even after R2PI.\textsuperscript{23,24} Accordingly, the flexibility and/or the length of the side chain may affect the rearrangement of H-bonds.

Compared with PEAL, Benzyl alcohol (BA) has a shorter side chain (hydroxymethyl group). Actually, the side chain of BA is a middle length between those of phenol and PEAL. Owing to the different length of the side chain in BA, the rearrangement of H-bonds in the monohydrated BA cluster cation ([BA-(H2O)1]+) may exhibit different features from those of [Phenol-(H2O)1]+ and [PEAL-(H2O)1]+. In this chapter, we report the H-bonded structure of [BA-(H2O)1]+ in the D\textsubscript{0} state by using IR spectroscopy. IR-dip spectroscopy using high power IR laser successfully shows the structural fluctuation in [BA-(H2O)1]+.
3.2. Experimental and computational methods

The experimental setup used in this study has been described in chapter 2. A commercially available BA was purchased from Wako Pure Chem. Ind. and used without further purification. BA was introduced in a stainless steel tube without heating. The vaporized BA molecules were mixed with neon carrier gas which passed through a reservoir containing water cooled down to 278 K. A typical stagnation pressure was 2 atm. The mixture gas was expanded into a vacuum chamber by using a pulsed valve (General Valve, series 9, 0.8 mm as an orifice diameter) operated at 20 Hz. The supersonic expansion was skimmed into an ion-source chamber. The skimmed hydrated clusters were photoionized by a UV laser for mass selection. The produced ions were analyzed with a linear time-of-flight mass spectrometer for all measurements.

For the measurements of 1C-R2PI spectra, a frequency-doubled dye laser (Sirah Cobra Stretch and Inrad Autotracker III) pumped by the second harmonic of an Nd³⁺:YAG laser (Spectra Physics INDI-40-20, 20 Hz, 50 mJ/pulse) was used as the UV source. The UV light was focused on the molecular beam with a plano-convex lens (300 mm focal length). The UV laser was scanned in the frequency region of 37400-38000 cm⁻¹. For the measurements of IR spectra, an optical parametric oscillator (LaserVision) pumped by an injection-seeded Nd³⁺:YAG laser (Continuum Powerlite Precision II 8000, 5 Hz, 580 mJ/pulse) was used as an IR source. The IR energy used for the measurements of IR-dip spectra was reduced to be ~ 2 mJ/pulse at 3300 ~ 3800 cm⁻¹ in order to avoid unfavorable saturation of vibrational transitions, whereas the IR energy was increased up to ~ 10 mJ for measuring high power IR-dip spectra. The repetition rate of the UV laser was 20 Hz, whereas that of the IR laser was 10 Hz. The IR and UV lasers were spatially overlapped with one another. The ion signals with and without the
IR pulse were stored separately to correct the artificial fluctuation of the spectral baseline. For the measurement of IR spectra in the $S_0$ state, the IR laser in the frequency region of $3300 \sim 3800 \text{ cm}^{-1}$ preceded the UV laser by $\sim 20$ ns, while the UV laser was followed by the IR laser with the delay time of $\sim 20$ ns for measuring IR-dip spectra in the $D_0$ state (see chapter 2.2).

M06-2X$^{25}$/aug-cc-pVTZ calculations were performed to obtain the stable structures, stabilization energies, harmonic vibrational frequencies and IR intensities. The calculated harmonic vibrational frequencies in the $S_0$ and $D_0$ states were scaled by 0.9459. The basis set superposition error was corrected by a counterpoise method. All quantum chemical calculations were performed by GAUSSIAN 09 program package.$^{26}$ The computations were carried out using the computer facilities at Research Institute for Information Technology, Kyushu University.
3.3. Results and discussions

Figure 3.1a shows the 1C-R2PI spectrum of the jet-cooled BA monomer. In the previous study, the vibronic band at 37528 cm\(^{-1}\) was assigned to the origin transition of BA.\(^{27-33}\) Furthermore, three vibronic bands at 37579 (32528 + 51), 37625 (32528 + 97) and 37650 (32528 + 122) cm\(^{-1}\) in Figure 3.1a were also assigned to the vibronic transitions of a single conformer observed at 37582 cm\(^{-1}\) on the basis of isotope shift.\(^{27}\) Although the configuration of the side chain in BA has been debated, the origin band at 37528 cm\(^{-1}\) was assigned to that of the gauche-cis conformer.\(^{29-33}\) The 1C-R2PI spectra of the jet-cooled hydrated BA clusters obtained by monitoring at [BA-(H\(_2\)O)\(_1\)]\(^+\) and [BA-(H\(_2\)O)\(_2\)]\(^+\) mass channels are shown in Figure 3.1b, c, respectively. A prominent band at 37583 cm\(^{-1}\) was previously assigned to the origin transition of BA-(H\(_2\)O)\(_1\) where a water molecule forms a bridge between the OH group and the \(\pi\)-ring of the BA moiety.\(^{28,29,32}\) In addition, the band at 37605 (37583 + 22) cm\(^{-1}\) was also assigned to the vibronic transition of BA-(H\(_2\)O)\(_1\) observed at 37583 cm\(^{-1}\).\(^{28,29,32}\) In the R2PI spectrum obtained by monitoring the [BA-(H\(_2\)O)\(_2\)]\(^+\) mass channel, however, the origin band of BA-(H\(_2\)O)\(_2\) does not appear (Figure 3.1c). This result is consistent with the previous study.\(^{28}\) The disappearance of the band at 37529 cm\(^{-1}\) in Figure 3.1c indicates that a single water molecule completely dissociates from BA-(H\(_2\)O)\(_2\) after R2PI via the origin transition of BA-(H\(_2\)O)\(_2\). The vibronic band at 37684 cm\(^{-1}\) in Figure 3.1c was also assigned to the origin transition of BA-(H\(_2\)O)\(_4\) in the previous study.\(^{28}\)

In order to confirm the assignment of each origin transition in Figure 3.1b, we performed IR-dip spectroscopy for BA-(H\(_2\)O)\(_1\) and BA-(H\(_2\)O)\(_2\). Figure 3.2a, b show the
IR-dip spectra obtained by probing the origin band at 37583 and 37529 cm\(^{-1}\), respectively. The stick spectra in Figure 3.2a, b are the theoretical IR spectra of BA-(H\(_2\)O)\(_1\) and BA-(H\(_2\)O)\(_2\), respectively. The calculated stable structures of BA-(H\(_2\)O)\(_1\) and BA-(H\(_2\)O)\(_2\) are also shown in Figure 3.3a, b. In Figure 3.2a, three vibrational bands are observed at 3727 (free OH stretch), 3616 (\(\pi\)-bonded OH stretch) and 3562 cm\(^{-1}\) (H-bonded OH stretch), which are in good agreement with the previous assignments based on the IR spectroscopy.\(^{29,32}\) We have confirmed that the IR-dip spectrum obtained by probing at 37605 cm\(^{-1}\) is completely identical to the IR-dip spectra shown in Figure 3.2a. The IR-dip spectrum in Figure 3.2b shows four prominent bands. They can be assigned to a free OH stretch (3724 cm\(^{-1}\)), a \(\pi\)-bonded OH stretch (3597 cm\(^{-1}\)) and two H-bonded OH stretches (3504 and 3464 cm\(^{-1}\)) based on the theoretical prediction. These assignments are consistent with the previous result obtained by measuring the fluorescence detected IR (FDIR) spectroscopy.\(^{29}\)

The experimental protocol of the IR-dip spectroscopy we used does not provide the IR spectrum of the bare [BA]\(^+\). Therefore, we performed an Ar-tagging technique. Figure 3.4a displays the IR-dip spectrum of [BA-(Ar)\(_1\)]\(^+\) in the D\(_0\) state, which was measured to obtain information on the free OH stretching vibration of the bare [BA]\(^+\). [BA-(Ar)\(_1\)]\(^+\) was produced by the fragmentation of Ar atoms after R2PI of the neutral BA-(Ar)\(_n\). In general, the vibrational frequency of the OH group to which an Ar atom is bound is red-shifted from that of [BA]\(^+\). For example, the H-bonded OH stretching vibration of [Phenol-(Ar)\(_2\)]\(^+\), where an Ar atom is bound to the OH group in the [Phenol]\(^+\) moiety, is red-shifted by \(~200\) cm\(^{-1}\) from the free OH stretching vibration of the bare phenol in the S\(_0\) state (3657 cm\(^{-1}\)).\(^{34-37}\) In Figure 3.4a, the observed vibrational band at 3666 cm\(^{-1}\) is slightly blue-shifted from that of the bare BA in the S\(_0\) state.
suggesting that the Ar atom is not bound to the OH group but the π-ring in the [BA]+ moiety. Accordingly, the vibrational band at 3666 cm\(^{-1}\) in Figure 3.4a corresponds to the free OH stretching vibration of [BA]+.

Figure 3.4b shows the IR-dip spectrum of [BA-(H\(_2\)O)\(_1\)]\(^+\) in the D\(_0\) state produced by R2PI via the origin transition of BA-(H\(_2\)O)\(_1\) at 37583 cm\(^{-1}\). In Figure 3.4b, four prominent transitions are observed at 3724, 3666, 3641 and 3354 cm\(^{-1}\). The vibrational bands at 3641 and 3724 cm\(^{-1}\) appear at typical frequencies of the \(\nu_1\) and \(\nu_3\) vibrations of the water molecule in hydrated clusters. An intense and broad vibrational band centered at 3354 cm\(^{-1}\) is readily assigned to the H-bonded OH stretching vibration. Furthermore, the frequency of the vibrational band at 3666 cm\(^{-1}\) is completely identical to that of the free OH stretching vibration of [BA-(Ar)\(_1\)]\(^+\) (Figure 3.4a), allowing us to assign it to the free OH stretching vibration of [BA]+. Figure 3.4c displays the IR-dip spectrum of [BA-(H\(_2\)O)\(_2\)]\(^+\) produced by R2PI via the origin transition of BA-(H\(_2\)O)\(_2\) at 37528 cm\(^{-1}\). Each vibrational transition in Figure 3.4c is essentially the same as that in Figure 3.4b, indicating that the structure of [BA-(H\(_2\)O)\(_1\)]\(^+\) in Figure 3.4c is identical with that in Figure 3.4b.

Figure 3.4d displays the theoretical IR spectrum of [BA(OH)-(H\(_2\)O)\(_1\)]\(^+\) where a water molecule is bound to the OH group of the [BA]+ moiety. The calculated stable structure of [BA(OH)-(H\(_2\)O)\(_1\)]\(^+\) is shown in Figure 3.5a. In [BA(OH)-(H\(_2\)O)\(_1\)]\(^+\), there is no OH-π interaction between the water molecule and the π-ring of [BA]+ in contradiction to BA-(H\(_2\)O)\(_1\) in the S\(_0\) state. Furthermore, the configuration of the side chain of the [BA]+ moiety is not gauche cis but planar. The theoretical calculation predicts that [BA(OH)-(H\(_2\)O)\(_1\)]\(^+\) has three vibrational bands in the frequency region of the OH stretching vibration; the \(\nu_1\) and \(\nu_3\) vibrations of the water molecule and the
H-bonded OH stretching vibration of the [BA]+ moiety. These three vibrations are observed in Figure 3.4b, c. However, the free OH stretching vibration of the [BA]+ moiety is simultaneously observed at 3666 cm\(^{-1}\) in Figure 3.4b, c, which cannot be explained by the vibrational transitions of [BA(OH)-(H\(_2\)O)\(_1\)]\(^+\). This observation suggests that [BA-(H\(_2\)O)\(_1\)]\(^+\) having the free OH group of the [BA]+ moiety, denoted as [BA(Free)-(H\(_2\)O)\(_1\)]\(^+\), also contributes to the IR-dip spectrum in Figure 3.4b, c.

Theoretical calculations predict that [BA(Free)-(H\(_2\)O)\(_1\)]\(^+\) has several stable isomers where a water molecule is bound to the CH group or the \(\pi\)-ring of the [BA]+ moiety. These stable structures are shown in Figure 3.5b-g. Figure 3.4e shows the theoretical IR spectrum of [BA(CH1)-(H\(_2\)O)\(_1\)]\(^+\) as a representative structure of [BA(Free)-(H\(_2\)O)\(_1\)]\(^+\). [BA(CH1)-(H\(_2\)O)\(_1\)]\(^+\) has three vibrational bands in the free OH stretching region. In particular, the free OH stretching vibration of the [BA]+ moiety is predicted to be observed between the \(\nu_1\) and \(\nu_3\) vibrations of the water molecule. This prediction is consistent with the experimental spectra (Figure 3.4b, c). The other stable isomers of [BA(Free)-(H\(_2\)O)\(_1\)]\(^+\) have also similar vibrational bands to those of [BA(CH1)-(H\(_2\)O)\(_1\)]\(^+\) (Figure 3.6b-g). Accordingly, the vibrational band at 3666 cm\(^{-1}\) can be assigned to the free OH stretching vibration of the [BA]+ moiety in [BA(Free)-(H\(_2\)O)\(_1\)]\(^+\), meaning that the IR-dip spectra of [BA-(H\(_2\)O)\(_1\)]\(^+\) in Figure 3.4b,c consist of the superposition of the vibrational bands of [BA(OH)-(H\(_2\)O)\(_1\)]\(^+\) and [BA(Free)-(H\(_2\)O)\(_1\)]\(^+\).

The uppermost panel of Figure 3.6 shows the IR-dip spectrum of [BA-(H\(_2\)O)\(_1\)]\(^+\) in the frequency region of the CH and OH stretching vibrations (2600 ~ 3800 cm\(^{-1}\)). The theoretical IR spectra of [BA(Free)-(H\(_2\)O)\(_1\)]\(^+\) are also shown in 3.6b-g. In Figure 3.6b-g, the vibrational pattern of the CH stretching vibrations of [BA(\(\pi\))-(H\(_2\)O)\(_1\)]\(^+\), where a
water molecule is bound to the π-ring of [BA]+, at ~2700 cm⁻¹ is slightly different from those the other isomers. Unfortunately, however, the CH stretching vibration(s) of [BA-(H₂O)₁]⁺ is too broad to distinguish [BA(π)-(H₂O)₁]⁺ from [BA(CH)-(H₂O)₁]⁺. Moreover, the vibrational patterns of [BA-(H₂O)₁]⁺ in the free OH stretching region are also very similar to each other (Figure 3.6b-g), and the relative stabilization energies of [BA(Free)-(H₂O)₁]⁺ are hardly different from each other (within 450 cm⁻¹). Unfortunately, we cannot determine which isomer(s) contributes to the IR-dip spectrum (the uppermost panel of Figure 3.6) at the present stage.

In Figure 3.4b, the initial structure of [BA-(H₂O)₁]⁺ in the D₀ state just after photoionization via the S₁⁻S₀ origin band of BA-(H₂O)₁ is similar to the stable geometry in the S₁ state, because the vertical transition preferentially occurs. Although the theoretical calculation of BA-(H₂O)₁ in the S₁ state has not been performed, the stable structure of BA-(H₂O)₁ in the S₁ state is expected to be similar to that in the S₀ state (Figure 3.3a). However, such a H-bonded motif in Figure 3.3a is unstable in the D₀ state, because the positively charged π-ring of [BA]+ repels the partially positive H atom of the water molecule. This leads to the large structural displacement of the stable structures in the S₁ and D₀ states. Accordingly, the Franck-Condon region between the S₁ and D₀ states of BA-(H₂O)₁ is expected to be broad up to the higher vibrational energy levels of [BA-(H₂O)₁]⁺. In particular, [BA-(H₂O)₁]⁺ with internal energy larger than the potential barrier heights of potential energy minima may isomerize between [BA(OH)-(H₂O)₁]⁺ and [BA(Free)-(H₂O)₁]⁺. This consideration is consistent with the fact that the IR-dip spectra of [BA-(H₂O)₁]⁺ in Figure 3.4b,c consist of the superposition of the vibrational bands of [BA(OH)-(H₂O)₁]⁺ and [BA(Free)-(H₂O)₁]⁺. Therefore, we conclude that [BA-(H₂O)₁]⁺ produced by photoionization undergoes isomerization
between [BA(OH)-(H₂O)₁]⁺ and [BA(Free)-(H₂O)₁]⁺.

For completeness, we discuss how the isomerization rate affects the coexistence of [BA(OH)-(H₂O)₁]⁺ and [BA(Free)-(H₂O)₁]⁺ after photoionization. We consider three cases. First, the isomerization rate is extremely slower than the delay time between the UV and IR pulses (20 ns). In this case, the initially populated hydration structure after photoionization does not isomerize to the other isomers, meaning that we never observe the sign of [BA(OH)-(H₂O)₁]⁺ and [BA(Free)-(H₂O)₁]⁺ in the IR-dip spectrum. This scenario is obviously inconsistent with the experimental finding. Accordingly, the first case can be ruled out. Second, the isomerization rate is much faster than the delay time. In this case, the isomerization between [BA(OH)-(H₂O)₁]⁺ and [BA(Free)-(H₂O)₁]⁺ occurs frequently in both directions. This scenario is consistent with the coexistence of [BA(OH)-(H₂O)₁]⁺ and [BA(Free)-(H₂O)₁]⁺ in the IR-dip spectrum. Note that in this scenario, the fluctuation of the hydration structures in [BA-(H₂O)₁]⁺ actually occurs. Third, the isomerization rate is comparable to the delay time. In this case, a part of the initially populated isomer isomerizes to the other isomers but the other part of it does not isomerize during the delay time. This scenario is also consistent with the experimental finding. In order to investigate the appreciate scenario, we performed the IR-dip spectroscopy using the higher IR pulse energy.

Figure 3.7 shows the IR-dip spectra of [BA-(H₂O)₁]⁺ produced by R2PI via the origin transition of (a) BA-(H₂O)₁ and (b) BA-(H₂O)₂. The IR pulse energy in Figure 3.7a was increased to be ~ 8 mJ/pulse at the H-bonded and the free OH stretching bands. The IR pulse energy in Figure 3.7b was also increased to be ~ 8 mJ/pulse at the H-bonded OH stretching band while ~ 10 mJ/pulse at the free OH stretching band. The
observed vibrational bands in Figure 3.7a, b are essentially the same as those in Figure 3.4b, c. Note that in Figure 3.7a, b, the H-bonded OH stretching band centered at 3354 cm\(^{-1}\) shows a significantly broad feature due to the saturation of the band (so-called saturation broadening). The vertical axis of Figure 3.7a,b indicates the depletion ratio of [BA-(H\(_2\)O\(_1\))]\(^+\). The depletion reaching at 100 % means that all of [BA-(H\(_2\)O\(_1\))]\(^+\) in a molecular beam completely dissociate by absorbing the IR photon. In both of Figure 3.7a and b, the H-bonded OH stretching band shows 100 % depletion. Here, we should remind that [BA(Free)-(H\(_2\)O\(_1\))]\(^+\) does not absorb the IR photon having the frequency of the H-bonded OH stretching band. In the second scenario (the isomerization rate is significantly large), [BA(Free)-(H\(_2\)O\(_1\))]\(^+\) can isomerize to [BA(OH)-(H\(_2\)O\(_1\))]\(^+\) during the IR pulse duration (ca. 8 ns), then [BA(OH)-(H\(_2\)O\(_1\))]\(^+\) absorbs the IR photon and photodissociation occurs. Accordingly, this scenario can explain the observation of the 100 % depletion at the H-bonded OH stretching band (Figure 3.7a, b). On the other hand, in the third scenario (the isomerization rate is comparable to the delay time), [BA(Free)-(H\(_2\)O\(_1\))]\(^+\) cannot completely isomerize to [BA(OH)-(H\(_2\)O\(_1\))]\(^+\) during the IR pulse duration, meaning that [BA(Free)-(H\(_2\)O\(_1\))]\(^+\) remains in the molecular beam, and it contributes to the ion signal of [BA-(H\(_2\)O\(_1\))]\(^+\). Therefore, the third scenario cannot explain the 100 % depletion observed at the H-bonded OH stretching band. Based on these consideration, we conclude that the isomerization between [BA(OH)-(H\(_2\)O\(_1\))]\(^+\) and [BA(Free)-(H\(_2\)O\(_1\))]\(^+\) occurs frequently in both directions. That is, the fluctuation of the hydration structures occurs in [BA-(H\(_2\)O\(_1\))]\(^+\).

The structural fluctuation in [BA-(H\(_2\)O\(_1\))]\(^+\) would cause 100 % depletion at the free OH stretching band. However, it does not show the 100 % depletion in Figure 3.7 (3666 cm\(^{-1}\)). This contradiction implies that some of [BA-(H\(_2\)O\(_1\))]\(^+\) are trapped in the
potential well of \([\text{BA(OH)}-(\text{H}_2\text{O})_1]^+\) after photoionization. As mentioned above, the internal energy distribution of \([\text{BA}-(\text{H}_2\text{O})_1]^+\) may be broad in a wide energy range. \([\text{BA}-(\text{H}_2\text{O})_1]^+\) having the internal energy which is smaller than the potential barrier height is trapped in the potential well of \([\text{BA(OH)}-(\text{H}_2\text{O})_1]^+\). It does not isomerize to \([\text{BA}-(\text{free})-(\text{H}_2\text{O})_1]^+\). Note that \([\text{BA(OH)}-(\text{H}_2\text{O})_1]^+\) trapped in the well does not absorb an IR photon having the frequency of the free OH stretching band. Therefore, \([\text{BA(OH)}-(\text{H}_2\text{O})_1]^+\) below the barrier remains in the molecular beam, leading to the depletion of less than 100%. On the other hand, \([\text{BA}-(\text{H}_2\text{O})_1]^+\) having the sufficient internal energy exceeding the potential barrier can fluctuate between \([\text{BA(OH)}-(\text{H}_2\text{O})_1]^+\) and \([\text{BA(Free)}-(\text{H}_2\text{O})_1]^+\). Accordingly, \([\text{BA}-(\text{H}_2\text{O})_1]^+\) produced by photoionization via the origin transitions of \([\text{BA}-(\text{H}_2\text{O})_1]^+\) and \([\text{BA}-(\text{H}_2\text{O})_2]^+\) can be regarded as the mixture of “frozen” (trapped in the potential well) and “melted” (structurally fluctuated) clusters.

The spectral features in Figure 3.7b are essentially the same as those in Figure 3.7a except for the depletion ratio at the free OH stretching band (3666 cm\(^{-1}\)). In Figure 3.7a, the intensity of the free OH stretching band is very similar to that of \(\nu_1\). However, its intensity in Figure 3.7b is obviously weaker than that of \(\nu_1\). This trend is also observed in Figure 3.4b, c. \([\text{BA}-(\text{H}_2\text{O})_1]^+\) in Figure 3.7b is produced by the dissociation of a water molecule from \([\text{BA}-(\text{H}_2\text{O})_2]^+\). Therefore, the evaporative cooling may reduce the amount of the internal energy in \([\text{BA}-(\text{H}_2\text{O})_1]^+\) in Figure 3.7b. The smaller depletion ratio in Figure 3.7b suggests that the structural fluctuation of \([\text{BA}-(\text{H}_2\text{O})_1]^+\) is suppressed by the evaporate cooling.

We found that all of \([\text{PEAL}-(\text{H}_2\text{O})_1]^+\) produced by photoionization via the origin transition of \([\text{PEAL}-(\text{H}_2\text{O})_1]\) fluctuate between \([\text{PEAL(OH)}-(\text{H}_2\text{O})_1]^+\) and \([\text{PEAL(Free)}-(\text{H}_2\text{O})_1]^+\) while a certain amount of \([\text{BA}-(\text{H}_2\text{O})_1]^+\) is trapped in the
potential well. The length of a side chain is the dominant structural difference between PEAL and BA. Hence, it may be assumed that the rearrangement of H-bonds after photoionization of BA-(H₂O)₁ is suppressed by the shorter side chain than the PEAL side chain. The total amount of the internal energy after photoionization and the potential barrier heights among each isomer may be dependent on the length of the side chain. Unfortunately, however, the effect of the side chain length on the H-bond dynamics after photoionization cannot be discussed quantitatively at the present stage.

It should be noted that two-color R2PI experiment might allow us to obtain the information on the energy dependence of the structural fluctuation since the internal energy of [BA-(H₂O)₁]⁺ can be reduced by tuning the ionization UV laser. However, it is difficult to obtain the precise values of the internal energy and the potential barrier height for [BA-(H₂O)₁]⁺ even when the two-color R2PI experiment is applied to BA-(H₂O)₁, because the adiabatic ionization energy, which is crucial information to determine the internal energy and the potential barrier height precisely, cannot be determined due to the large geometry change induced by photoionization. Accordingly, for further investigation on the energy dependence of structural fluctuation, it is necessary to find the H-bonded cluster cations which show the structural fluctuation and whose adiabatic ionization energy is determined experimentally.
3.4. Conclusion

In summary, we have investigated the H-bonded structure and the dynamics of [BA-(H₂O)₁]+ in the D₀ states by R2PI and IR-dip spectroscopy. [BA-(H₂O)₁]+ was produced by photoionization via the origin transition of BA-(H₂O)₁ and BA-(H₂O)₂. After photoionization, we found that the IR-dip spectra of [BA-(H₂O)₁]+ consist of the superposition of the vibrational bands of [BA(OH)-(H₂O)₁]+ and [BA(Free)-(H₂O)₁]+, in which a water molecule is bound to the OH group of [BA]+ or not. Furthermore, the IR-dip spectra of [BA-(H₂O)₁]+ measured with higher IR pulse energy show 100% depletion at the H-bonded OH stretching band, indicating that the structural fluctuation among [BA(OH)-(H₂O)₁]+ and [BA(Free)-(H₂O)₁]+ occurs in the D₀ state. On the other hand, the free OH stretching band does not show 100% depletion. This observation suggests that [BA-(H₂O)₁]+ having the internal energy which is smaller than the potential barrier height is trapped in the potential well of [BA(OH)-(H₂O)₁]+. When [BA-(H₂O)₁]+ is generated by photoionization of BA-(H₂O)₂, the evaporative cooling caused by photodissociation of a water molecule immediately after photoionization reduces the internal energy of [BA-(H₂O)₁]+. This leads to the increase in the population of [BA-(H₂O)₁]+ which is trapped in the potential well of [BA(OH)-(H₂O)₁]+. In this case, the depletion ratio of the free OH stretching band becomes smaller than that of [BA-(H₂O)₁]+ generated from BA-(H₂O)₁.
Figure 3.1. 1C-R2PI spectra obtained by monitoring the mass channel of (a) BA$^+$, (b) [BA-(H$_2$O)$_1$]$^+$ and (c) [BA-(H$_2$O)$_2$]$^+$.
Figure 3.2. IR-dip spectra of (a) BA-(H₂O)₁ and (b) BA-(H₂O)₂ in the S₀ state obtained by probing the vibronic bands at 37583 cm⁻¹ and 37529 cm⁻¹ in Figure 3.1, respectively. The stick spectra correspond to the theoretical IR spectra of the calculated stable isomers obtained at the M06-2X/aug-cc-pVTZ level of theory. The harmonic frequencies were scaled by 0.9459.
Figure 3.3. Calculated stable structures of (a) BA-(H$_2$O)$_1$ and (b) BA-(H$_2$O)$_2$ in the S$_0$ state, respectively, obtained at the M06-2X/aug-cc-pVTZ level of theory.
Figure 3.4. IR-dip spectra of (a) [BA-Ar1]+ and (b,c) [BA-(H2O)1]+ in the D0 state. [BA-(H2O)1]+ is produced by R2PI via the vibronic bands at (b) 37583 cm⁻¹ and (c) 37529 cm⁻¹ in Figure 3.1, respectively. The theoretical IR spectra of (d) [BA(OH)-(H2O)1]+ and (e) [BA(Free)-(H2O)1]+ are obtained at the M06-2X/aug-cc-pVTZ level of theory. The intensity of the IR bands marked by asterisks is multiplied by a factor of five to the calculated values. The harmonic frequencies were scaled by 0.9459.
Figure 3.5. Calculated structures of (a) [BA(OH)-(H₂O)₁]⁺ and (b-g) [BA(Free)-(H₂O)₁]⁺ in the D₀ state obtained at the M06-2X/aug-cc-pVTZ level of theory. Relative stabilization energies are given in the wavenumber units. The zero-point vibrational energy and basis set superposition error are corrected for all values.
Figure 3.5. (d-g)

(d) $[\text{BA(CH}_2\text{)-(H}_2\text{O)}_1]^+$

(e) $[\text{BA(CH}_3\text{)-(H}_2\text{O)}_1]^+$

(f) $[\text{BA(CH}_4\text{)-(H}_2\text{O)}_1]^+$

(g) $[\text{BA(CH}_5\text{)-(H}_2\text{O)}_1]^+$

(+ 1279 cm$^{-1}$)  (+ 1614 cm$^{-1}$)

(+ 1420 cm$^{-1}$)  (+ 1322 cm$^{-1}$)
Figure 3.6. (Exp.) IR-dip spectrum of [BA-(H2O)1]+ in the D₀ state measured in 2600 ~ 3800 cm⁻¹. [BA-(H2O)1]+ is produced by R2PI via the origin transition of BA-(H2O)₁. (a-g) the theoretical IR spectra of [BA-(H2O)₁]+ shown in Figure 3.5. The predicted bands at around 2800 cm⁻¹ correspond to the symmetrical stretching vibration of the CH₂ group of the α-carbon in [BA]+ moiety.
Figure 3.7. IR-dip spectra of $[\text{BA-(H}_2\text{O)}_1]^+$ produced by R2PI via the origin transition of (a) $\text{BA-(H}_2\text{O)}_1$ and (b) $\text{BA-(H}_2\text{O)}_2$ with higher IR pulse energy. The IR energy in Figure 3.7a is increased to $\sim 8$ mJ/pulse at the H-bonded OH stretching band and the free OH stretching band. The IR energy in Figure 3.7b is also increased to $\sim 8$ mJ/pulse at the H-bonded stretching OH band, while $\sim 10$ mJ/pulse at the free OH stretching band.
References for chapter 3


Chapter 4.

Experimental determination of the energy threshold for the rearrangement of a water molecule in monohydrated 5-hydroxyindole cluster cations

Reproduced in part with permission from *Journal of Physical Chemistry A*, in press.

Unpublished work copyright 2016 American Chemical Society.
4.1. Introduction

Many chemical and biological processes proceed in aqueous solutions. Hydrophilic molecules in aqueous solutions typically form hydrogen bonds (H-bonds) with water molecules. The hydration shell around the hydrophilic molecules is believed to play an essential role in various chemical and biological processes such as proton transport, protein folding and biomolecular recognition.\textsuperscript{1–6} Water molecules in the first hydration shell may have a particularly significant impact on these processes. Thus, understanding the local hydration structures and their dynamics is mandatory for comprehending chemical and biological processes in aqueous solutions at the molecular level.

Hydrated clusters produced in a supersonic jet expansion in the gas phase represent ideal systems for investigating local hydration structures in complex H-bonded networks. The jet-cooled technique combined with mass spectrometry facilitates simplification of the spectral pattern of the hydrated clusters by eliminating the thermal energy and the disturbance of the bulk water, which is highly beneficial for spectral analysis. Sophisticated laser spectroscopy has been applied to various jet-cooled hydrated clusters to identify the characteristic features of H-bonds. IR spectroscopy in the 3 μm region aided by theoretical calculations allows us to determine the stable structures of the hydrated clusters.\textsuperscript{7–11} Detailed structural information on the hydrated clusters has contributed to the understanding of preferential H-bond motifs.

The thermal energy in aqueous solutions may cause the H-bonds between the solute and water molecules to break and re-form repeatedly, resulting in rearrangement and/or fluctuation of the H-bonds. The reactivity of chemical and biological species and the efficiency of such reactions in aqueous solutions may be affected by the
rearrangement and fluctuation of the H-bonds. Accordingly, molecular level evaluation of the rearrangement and fluctuation of the H-bonds provides valuable information for understanding chemical and biological reactions in aqueous solutions in more detail. In contrast, the elimination of thermal energy in jet-cooled hydrated clusters isolates the clusters in each potential well, leading to “frozen” H-bonded structures. The hydrated clusters that store sufficient internal energy to overcome the potential energy barriers may interconvert among various potential energy minima, which is equivalent to the rearrangement and fluctuation of the H-bonds.

Resonant two-photon ionization (R2PI) has been applied to H-bonded clusters to investigate rearrangement of the H-bond in the D_0 state, since a large amount of internal energy can be stored in the H-bonded cluster cations owing to their large binding energy and the large structural displacement between the S_1 and D_0 states. Moreover, sharp vibronic transitions of the H-bonded clusters, leading to selective ionization of each isomer, can be recorded in the R2PI spectra, which is advantageous for identifying the initial H-bonded structures and triggering rearrangement of the H-bonds in the D_0 state. For example, monohydrated trans-acetanilide ([AA-(H_2O)_1]^+) and trans-formanilide ([FA-(H_2O)_1]^+) cluster cations exhibit migration of a water molecule from the CO group to the NH group after R2PI via the S_1-S_0 origin of the CO isomer, where a water molecule is bound to the CO group. Picosecond time-resolved spectroscopy has successfully been applied to monitoring migration of water in [AA-(H_2O)_1]^+ to obtain information on the time scale of H-bond rearrangement. In chapter 3, we introduced the structural fluctuation in monohydrated benzyl alcohol cluster cation ([BA-(H_2O)_1]^+) produced by R2PI. Recently, two groups reported a structural change in the S_0 state of (H_2O)_n and
phenol-(H$_2$O)$_2$, although reduction of the stagnation pressure was used to warm the clusters instead of applying R2PI.\textsuperscript{23,24}

The potential barrier height separating two potential minima of hydrated clusters is one of the most important factors for characterizing the rearrangement of H-bonds. However, experimental studies on the determination of the potential barrier height remain limited. Clarkson \textit{et al.} successfully measured the energy thresholds for the isomerization of water between two preferential H-bonding sites (the CO and NH groups) of FA-(H$_2$O)$_1$ in the S$_0$ state via stimulated emission pumping-population transfer spectroscopy.\textsuperscript{25} Two-color R2PI (2C-R2PI) is also useful for determining the potential barrier heights because the internal energy of cluster cations produced by 2C-R2PI can be controlled by changing the frequency of an ionization laser, although the Franck-Condon region of the cluster cations restricts the range of their internal energy that can be changed.

5-hydroxyindole (5HI), which is the chromophore of serotonin, has two preferential H-bonding sites for attachment of water, i.e., the OH group and the NH group. Therefore, in the gas phase, 5HI-(H$_2$O)$_1$ is expected to have two structural isomers where a water molecule is bound to the OH group or the NH group of the 5HI moiety. In this chapter, we investigate the H-bonded structures of 5HI-(H$_2$O)$_1$ in the S$_0$ and D$_0$ states by using IR spectroscopy. Photoionization efficiency (PIE) and isomerization threshold measurements are successfully applied to [5HI-(H$_2$O)$_1$]$^+$. We report the first experimental observation of rearrangements of a water molecule in [5HI-(H$_2$O)$_1$]$^+$ and the upper limit of the potential barrier height for the rearrangement in the gas phase.
4.2. Experimental and computational methods

The experimental setup used in this study has been described in chapter 2. A commercially available 5HI was purchased from Wako Pure Chem. Ind. and used without further purification. 5HI introduced in a stainless steel tube was heated to around 393 K by a coiled heater. The vaporized 5HI molecules were mixed with helium carrier gas passed through the reservoir containing water cooled down to 268 K. A typical stagnation pressure was 2 atm. The mixture gas was expanded into a vacuum chamber by using a pulsed valve (General Valve, series 9, 0.8 mm as an orifice diameter) operated at 10 Hz. The supersonic expansion was skimmed into an ion-source chamber. The skimmed hydrated clusters were photoionized by UV lasers for mass selection. The produced ions were analyzed with a linear time-of-flight mass spectrometer for all measurements below.

For the 2C-R2PI spectra, a frequency-doubled dye laser (Sirah Cobra Stretch and Inrad Autotracker III) pumped by the second harmonic of a Nd\(^{3+}\):YAG laser (Spectra Physics INDI-40-20, 20 Hz, 50 mJ/pulse), and a frequency-doubled dye laser (Lumonics HD-300 and BBO crystal) pumped by the second harmonic of a Nd\(^{3+}\):YAG laser (Spectra Physics LAB-130, 10 Hz, 100 mJ/pulse) were used as the excitation (\(v_1\)) and ionization (\(v_2\)) UV sources, respectively. Two UV lights were combined collinearly with a half mirror and simultaneously focused on the molecular beam with a plano-convex lens (300 mm focal length). The \(v_1\) laser was tuned in the region of 32200 ~ 33000 cm\(^{-1}\), while the \(v_2\) laser was fixed at 31000 cm\(^{-1}\). For measuring PIE spectra, the \(v_1\) laser was fixed at the S\(_1\)-S\(_0\) origin of each isomer while the \(v_2\) laser was scanned in the region of 24800 ~ 26000 cm\(^{-1}\). For the measurement of IR spectra, an optical parametric oscillator (LaserVision) pumped by an injection-seeded Nd\(^{3+}\):YAG laser (Continuum Powerlite Precision II 8000, 5 Hz, 580 mJ/pulse) was used as an IR source. The IR energy was reduced to be ~ 1
mJ/pulse at 3300 ~ 3800 cm⁻¹ in order to avoid unfavorable saturation of vibrational transitions. The repetition rate of the v₂ laser was 10 Hz, whereas that of the IR laser was 5 Hz.

For the measurement of the IR spectra in the S₀ state, the IR laser in the region of 3300 ~ 3800 cm⁻¹ preceded the UV laser by ~ 20 ns. The IR and UV lasers were spatially overlapped with one another. When an IR photon was resonant with a vibrational transition of the isomer monitored ([5HI-(H₂O)₁]⁺), the ion intensity of [5HI-(H₂O)₁]⁺ was reduced. Therefore, IR-dip spectra were obtained as the depletion of [5HI-(H₂O)₁]⁺. The ion signals with and without the IR pulse were stored separately to correct the artificial fluctuation of the spectral baseline. For measuring the IR spectra in the D₀ state, the IR laser was irradiated after the production of [5HI-(H₂O)₁]⁺ by 2C-R2PI. The delay time between the v₂ and IR pulses was 700 ns. When an IR photon was resonant with a vibrational transition of [5HI-(H₂O)₁]⁺, photodissociation of [5HI-(H₂O)₁]⁺ to 5HI monomer cations ([5HI]⁺) occurred. As a result, IR photodissociation (IRPD) spectra were obtained as an enhancement of the [5HI]⁺ intensity. We note that the signals from the daughter ions ([5HI]⁺) were completely separated on the flight time from the [5HI]⁺ signals generated by unfavorable multi photon processes of the v₁ and/or v₂ lasers only.

M06-2X²⁶/aug-cc-pVDZ calculations were performed to obtain the stable structures, stabilization energies, harmonic vibrational frequencies and IR intensities. The calculated harmonic vibrational frequencies in the S₀ and D₀ states were scaled by 0.9424. The basis set superposition error was corrected by a counterpoise method. All quantum chemical calculations were performed by GAUSSIAN 09 program package.²⁷ The computations were carried out using the computer facilities at Research Institute for Information Technology, Kyushu University.
4.3. Results and discussions

Figure 4.1a, b show the 2C-R2PI spectra of 5HI and 5HI-(H_2O)_1, respectively. The frequency of the v_2 laser was fixed at 31000 cm\(^{-1}\). Figure 4.1a shows two prominent bands at 32674 and 32905 cm\(^{-1}\), which were assigned to the origin transitions of the syn- and anti-conformers of 5HI (syn-5HI and anti-5HI) in previous studies.\(^{28-30}\) Note that the OH group of 5HI points to the NH group in the pyrrole ring of 5HI in syn-5HI, whereas in anti-5HI the OH group points in the opposite direction.\(^{30}\) Figure 4.1b shows four peaks at 32291, 32489, 32552, and 32785 cm\(^{-1}\), which can be assigned to the vibronic bands of 5HI-(H_2O)_1.

Figure 4.2a and 4.3a show the IR-dip spectra of syn- and anti-5HI in the S_0 state, obtained by probing the origin bands at 32674 and 32905 cm\(^{-1}\). Figure 4.2a shows two prominent vibrational bands at 3526 and 3665 cm\(^{-1}\), which can be assigned to the free NH and OH stretching vibrations (free \(v_{\text{NH}}\) and \(v_{\text{OH}}\), respectively. In Figure 4.3a, the free \(v_{\text{NH}}\) band was observed at the same position as in Figure 4.2a, whereas the free \(v_{\text{OH}}\) band observed at 3659 cm\(^{-1}\) was red-shifted by 6 cm\(^{-1}\) relative to that in Figure 4.2a.

Figure 4.2b, c show the IR-dip spectra of 5HI-(H_2O)_1 in the S_0 state, obtained by probing the vibronic bands at 32291 and 32552 cm\(^{-1}\) in Figure 4.1b, respectively. Figure 4.3b, c also display the IR-dip spectra of 5HI-(H_2O)_1 in the S_0 state, obtained by probing the vibronic bands at 32489 and 32785 cm\(^{-1}\) in Figure 4.1b, respectively. The stick spectra in Figure 4.2b, c and 4.3b, c are the theoretical IR spectra. The calculated stable structures of 5HI-(H_2O)_1 are also indicated in Figure 4.4a-d respectively. In Figure 4.4a, b, a water molecule is bound to the OH group or the NH group of syn-5HI, whereas a water molecule is bound to the OH group or the NH group of anti-5HI in Figure 4.4c, d, respectively. We readily classify the four IR-dip spectra in Figure 4.2b, c and 4.3b, c into two groups; i.e.,
the spectral structures in Figure 4.2b and 4.3b are very similar to each other whereas the spectra in Figure 4.2c and 4.3c have similar spectral patterns, which are different from those in Figure 4.2b and 4.3b.

The vibrational bands observed at 3526 cm\(^{-1}\) in Figure 4.2b and 4.3b are assigned to the free \(v_{\text{NH}}\) vibration, as also observed in Figure 4.2a and 4.3a. In addition, compared with the theoretical IR spectra, the vibrational bands observed at 3545 and 3538 cm\(^{-1}\) in Figure 4.2b and 4.3b are assigned to the vibration of the H-bonded OH group. Accordingly, the IR-dip spectra in Figure 4.2b and 4.3b can be assigned to 5HI(OH)-(H\(_2\)O)\(_1\). We note that the peak of the H-bonded \(v_{\text{OH}}\) vibration in Figure 4.3b is slightly red-shifted by 7 cm\(^{-1}\) relative to that in Figure 4.2b. The theoretical IR spectra of \(\text{syn-}\) and \(\text{anti-5HI(OH)-(H}_2\text{O)}\_1\) presented in Figure 4.2b and 4.3b predict similar red shifts for the H-bonded \(v_{\text{OH}}\) vibrations. Furthermore, the relative intensity of the vibronic bands observed at 32291 and 32489 cm\(^{-1}\) in Figure 4.1b is similar to that of the origin bands of \(\text{syn-}\) and \(\text{anti-5HI}\) in Figure 4.1a. Therefore, we assigned the IR-dip spectra in Figure 4.2b and 4.3b to \(\text{syn-}\) and \(\text{anti-5HI(OH)-(H}_2\text{O)}\_1\), respectively.

Figure 4.2c and 4.3c show vibrational bands at 3666 and 3659 cm\(^{-1}\), respectively, the frequencies of which are essentially the same as those of the free \(v_{\text{OH}}\) vibrations of \(\text{syn-}\) and \(\text{anti-5HI}\) shown in Figure 4.2a and 4.3a, respectively. Moreover, based on comparison of the experimental and theoretical IR spectra, the vibrational bands observed at 3434 and 3438 cm\(^{-1}\) in Figure 4.2c and 4.3c can be assigned to the H-bonded \(v_{\text{NH}}\) vibrations, indicating that the IR-dip spectra in Figure 4.2c and 4.3c can be assigned to 5HI(NH)-(H\(_2\)O)\(_1\). Further, the relative intensity of the vibronic bands at 32552 and 32785 cm\(^{-1}\) is similar to that of the origin bands of \(\text{syn-}\) and \(\text{anti-5HI}\) in Figure 4.1a. Therefore,
we assigned the IR-dip spectra in Figure 4.2c and 4.3c to syn- and anti-5HI(NH)-(H2O)1, respectively.

The vibronic bands marked with asterisks in Figure 4.1b may be assigned to the intermolecular vibrations of each isomer. We measured IR-UV hole-burning spectra shown in Figure 4.5. The IR laser was fixed at (a) 3545 cm\(^{-1}\), (b) 3538 cm\(^{-1}\), and (c) 3438 cm\(^{-1}\), corresponding to the H-bonded \(v_{OH}\) of syn-5HI(OH)-(H2O)\(_1\) and anti-5HI(OH)-(H2O)\(_1\), and the H-bonded \(v_{NH}\) of 5HI(NH)-(H2O)\(_1\), respectively. We note that Figure 4.5c includes both transition of syn- and anti-5HI(NH)-(H2O)\(_1\) since the H-bonded \(v_{NH}\) almost overlaps in Figure 4.2c and 4.3c. The vibronic feature at 32443 (32291 + 152) in Figure 4.5a and 32642 (32489 + 153) cm\(^{-1}\) in Figure 4.5b are readily assigned to the vibronic band of syn- and anti-5HI(OH)-(H2O)\(_1\), respectively. Furthermore, compared with the R2PI spectrum of 2-naphthol-(H2O)\(_1\), the vibronic bands at 32443 (32291 + 152) and 32642 (32489 + 153) cm\(^{-1}\) may be assigned to the intermolecular stretching vibration of syn- and anti-5HI(OH)-(H2O)\(_1\), respectively.\(^{31}\) In addition, the vibronic feature at 32809 cm\(^{-1}\) (32785 + 24) in Figure 4.5c is assigned to that of anti-5HI(NH)-(H2O)\(_1\), the frequency of which is similar to the intermolecular bending vibration of indole-(H2O)\(_1\).\(^{32,33}\) In the following text, we focus our attention on the anti-5HI-(H2O)\(_1\) conformer which is hereafter denoted as 5HI-(H2O)\(_1\), because the signal arising from the syn-5HI-(H2O)\(_1\) conformer is too weak to obtain IRPD spectra with an appropriate signal-to-noise ratio.

In order to obtain information on the free \(v_{NH}\) and \(v_{OH}\) of [5HI]\(^{+}\) in the D\(_0\) state, we performed the Ar-tagging technique since the IR spectrum of [5HI]\(^{+}\) in the D\(_0\) state cannot be directly measured in our experiment. Figure 4.6 shows the IRPD spectra corresponding to (a) [anti-5H-(Ar)\(_1\)]\(^{+}\) and (b) [syn-5HI-(Ar)\(_1\)]\(^{+}\). These [5HI-(Ar)\(_1\)]\(^{+}\) were
generated by the fragmentation from the neutral precursors of 5HI-(Ar)_n by
photoionization. In [5HI-(Ar)_1]^+, an Ar atom can be bound to not only the OH or NH
group but the π-ring of [5HI]^+. In the case of [anti-5HI-(Ar)_1]^+ shown in Figure 4.6a, two
vibrational transitions are observed at 3457 cm\(^{-1}\) and 3582 cm\(^{-1}\), which are in good
agreement with the free \(v_{\text{NH}}\) band of [Indole-(Ar)]^+ (3454 cm\(^{-1}\)) and the free \(v_{\text{OH}}\) of
[Naphthol-(Ar)]^+ (3580 cm\(^{-1}\)), respectively.\(^{34-37}\) Hence, these observed bands are assigned
to the free \(v_{\text{NH}}\) and \(v_{\text{OH}}\) of [5HI]^+. In Figure 4.6b, the spectral features are quite similar to
that in Figure 4.6a. Therefore, we cannot identify which is anti- or syn-5HI monomer
cation in the \(D_0\) state by measuring the IRPD spectra in the region of the free stretching
vibration only. The theoretical IR spectra of anti- and syn-5HI in Figure 4.6 are also
consistent with experimental results.

Figure 4.7 displays the IRPD spectra of [5HI-(H\(_2\)O)]^+ in the \(D_0\) state in the
frequency region of the free \(v_{\text{NH}}\) and \(v_{\text{OH}}\) vibrations. As shown in Figure 4.7a, b,
[5HI-(H\(_2\)O)_1]^+ was produced by R2PI via the origin transitions of 5HI(OH)-(H\(_2\)O)_1 and
5HI(NH)-(H\(_2\)O)_1, respectively. The stick spectra in Figure 4.7c, d correspond to the
theoretical IR spectra of [5HI(OH)-(H\(_2\)O)_1]^+ and [5HI(NH)-(H\(_2\)O)_1]^+, the stable structures
of which are displayed in Figure 4.8a, b, respectively. From Figure 4.7c, d, both
[5HI(OH)-(H\(_2\)O)_1]^+ and [5HI(NH)-(H\(_2\)O)_1]^+ are predicted to have three vibrational
transitions corresponding to the \(v_1\) and \(v_3\) vibrations of a water molecule and the free X-H
\((X = O \text{ or } N)\) stretching vibration of the [5HI]^+ moiety. However, Figure 4.7a, b, show
four vibrational transitions. Furthermore, the observed vibrational frequencies in Figure
4.7a, b are very similar to each other. The two vibrational transitions at 3634 and 3715
\( \text{cm}^{-1}\) in Figure 4.7a are assigned to the \(v_1\) and \(v_3\) vibrations of the water molecule,
respectively. Likewise, the vibrational bands at 3633 and 3713 \( \text{cm}^{-1}\) in Figure 4.7b are
assigned to the $\nu_1$ and $\nu_3$ vibrations of the water molecule. Based on the theoretical prediction in Figure 4.7c, the lowest frequency bands at 3465 and 3463 cm$^{-1}$ in Figure 4.7a, b can be assigned to the free $\nu_{\text{NH}}$ vibrations of the [5HI]$^+$ moiety, the frequencies of which are similar to that of [5HI]$^+$ in Figure 4.6. In addition, vibrational bands are observed at 3590 and 3589 cm$^{-1}$ in Figure 4.7a, b, although the intensity of the band in Figure 4.7a is much weaker than that in Figure 4.7b. Based on comparison with the theoretical IR spectrum in Figure 4.7d, we assigned these bands to the free $\nu_{\text{OH}}$ vibrations of the [5HI]$^+$ moiety, the frequencies of which are also similar to that of [5HI]$^+$ in Figure 4.6.

The initial H-bonded structures in the $D_0$ state just after photoionization are expected to be [5HI(OH)-(H$_2$O)$_1$]$^+$ and [5HI(NH)-(H$_2$O)$_1$]$^+$, respectively, given that the vertical transition via the $S_1$-$S_0$ origin bands of 5HI(OH)-(H$_2$O)$_1$ and 5HI(NH)-(H$_2$O)$_1$ occurs preferentially. Accordingly, the $\nu_1$, $\nu_3$, and free $\nu_{\text{NH}}$ bands in Figure 4.7a can be attributed to [5HI(OH)-(H$_2$O)$_1$]$^+$ whereas the $\nu_1$, $\nu_3$, and free $\nu_{\text{OH}}$ bands in Figure 4.7b are attributed to [5HI(NH)-(H$_2$O)$_1$]$^+$. However, the appearance of the free $\nu_{\text{NH}}$ band (3463 cm$^{-1}$) in Figure 4.7b cannot be attributed to [5HI(NH)-(H$_2$O)$_1$]$^+$. Similarly, the appearance of the free $\nu_{\text{OH}}$ band (3590 cm$^{-1}$) in Figure 4.7a cannot be accounted for as arising from [5HI(OH)-(H$_2$O)$_1$]$^+$, although the intensity is fairly weak. These observations demonstrate that the IRPD spectra in Figure 4.7a, b consist of the superposition of the vibrational transitions of [5HI(OH)-(H$_2$O)$_1$]$^+$ and [5HI(NH)-(H$_2$O)$_1$]$^+$. That is, the vibrational bands at 3590 and 3463 cm$^{-1}$ in Figure 4.7a, b are attributed to the free $\nu_{\text{OH}}$ and the free $\nu_{\text{NH}}$ vibrations of [5HI(NH)-(H$_2$O)$_1$]$^+$ and [5HI(OH)-(H$_2$O)$_1$]$^+$, respectively.

As mentioned above, the vertical ionization of 5HI(OH)-(H$_2$O)$_1$ provides [5HI(OH)-(H$_2$O)$_1$]$^+$ immediately after photoionization. However, the free $\nu_{\text{OH}}$ vibration
of [5HI(NH)-(H2O)]+ is evident in Figure 4.7a, implying that [5HI(OH)-(H2O)]+ isomerizes to [5HI(NH)-(H2O)]+ in the D0 state. The appearance of the free vNH vibration in Figure 4.7b is also explained by the isomerization of [5HI(NH)-(H2O)]+ to [5HI(OH)-(H2O)]+ in the D0 state. Therefore, it has been found that [5HI-(H2O)]+ undergoes rearrangement of the H-bond after photoionization.

For completeness, we note that the IRPD spectra in Figure 4.7a, b may arise from other isomers having free NH and OH groups, such as [5HI(CH)-(H2O)]+ shown in Figure 4.8c-f and [5HI(π)-(H2O)]+ shown in Figure 4.8g, h, where a water molecule is bound to the CH group or the π-ring of the [5HI]+ moiety, respectively. However, the vibrational bands of the H-bonded OH and NH groups are apparent in the IRPD spectra in the frequency region of 2800-3200 cm⁻¹ (see Figure 4.9). Moreover, the computed relative stabilization energies of [5HI(CH)-(H2O)]+ and [5HI(π)-(H2O)]+ are around +3000 cm⁻¹ from those of [5HI(OH)-(H2O)]+ and [5HI(NH)-(H2O)]+. Although the existence of [5HI(CH)-(H2O)]+ and/or [5HI(π)-(H2O)]+ cannot be ruled out, the majority of the vibrational bands in Figure 4.7a, b can be attributed to those of [5HI(OH)-(H2O)]+ and [5HI(NH)-(H2O)]+.

Figure 4.10a, b show PIE spectra of 5HI(OH)-(H2O)1 and 5HI(NH)-(H2O)1, respectively. Both of the PIE spectra in Figure 4.10a, b clearly show step-like increases in the ion signals at 57387 and 58200 cm⁻¹. In addition, no step-like increases in the ion signals were observed below 57387 and 58200 cm⁻¹ in Figure 4.10a, b, respectively. Accordingly, we concluded that the step-like thresholds at 57387 and 58200 cm⁻¹ correspond to the adiabatic ionization energies of 5HI(OH)-(H2O)1 (IE₀^{OH}) and 5HI(NH)-(H2O)1 (IE₀^{NH}). Based on the DFT calculations, the second step around IE₀^{OH} + 206 cm⁻¹ in Figure 4.10a and IE₀^{NH} + 180 cm⁻¹ in Figure 4.10b may correspond to the
intermolecular stretching vibration of [5HI(OH)-(H2O)1]+ and [5HI(NH)-(H2O)1]+ in the D0 state, respectively. We note that the frequency of the second step (180 cm\(^{-1}\)) in Figure 4.10b is similar to the vibrational frequency of the intermolecular stretching mode of [indole-(H2O)]\(^+\) in the D0 state (PIE: 179 cm\(^{-1}\), mass analyzed threshold ionization spectroscopy: 189 cm\(^{-1}\)).\(^{32,33}\)

By determining \(IE_0^{OH}\) and \(IE_0^{NH}\) from Figure 4.10, the potential barrier height \(E_b\) along the isomerization coordinate of [5HI-(H2O)1]+ in the D0 state could be measured. We applied the protocol in Figure 4.11 to measure \(E_b\). In this protocol, the origin band of 5HI(NH)-(H2O)1 is excited by \(v_1\), then \(v_2\) is scanned across \(E_b\). The internal energy of [5HI(NH)-(H2O)1]+ in the D0 state is calculated as: \((hv_1 + hv_2) - IE_0^{NH}\). If the internal energy of [5HI(NH)-(H2O)1]+ is larger than \(E_b\), the isomerization of [5HI(NH)-(H2O)1]+ to [5HI(OH)-(H2O)1]+ proceeds. Subsequently, [5HI(OH)-(H2O)1]+ absorbs an IR photon, the frequency of which is fixed at 3463 cm\(^{-1}\) (the free \(v_{OH}\) vibration of [5HI(OH)-(H2O)1]+), which leads to photodissociation of [5HI(OH)-(H2O)1]+ to [5HI]+.

Accordingly, the intensity of the daughter ion ([5HI]+) signal begins to increase once the internal energy of [5HI(NH)-(H2O)1]+ exceeds \(E_b\). We note that according to Figure 4.11, the isomerization must proceed during the delay time between \(v_2\) and \(v_{IR}\) (700 ns) to observe the increase in the intensity of the daughter ion signal. Based on Figure 4.11, therefore, we can determine the upper limit of \(E_b\) by monitoring the intensity of the daughter ion signal as a function of the internal energy of [5HI(NH)-(H2O)1]+. In principle, the potential barrier for isomerization of [5HI(OH)-(H2O)1]+ to [5HI(NH)-(H2O)1]+ would be determined in the same manner. However, the band intensity of the free \(v_{OH}\) vibration of [5HI(NH)-(H2O)1]+ is too weak to determine the potential barrier height (Figure 4.7a).
Figure 4.12 shows the intensity of the daughter ion signal as a function of the internal energy of [5HI(NH)-(H2O)1]+. A gradual increase in the intensity of the daughter ion signal was observed. Fitting the baseline and the increase in the ion signal to two linear plots allows us to determine the upper limit of $E_b$ for isomerization of [5HI(NH)-(H2O)1]+ to [5HI(OH)-(H2O)1]+ ($E_b^{NH}$) as $2127 \pm 30$ cm$^{-1}$. To the best of our knowledge, this is the first experimental observation of the isomerization threshold for hydrated cluster cations. Furthermore, the intensity of the daughter ion signal plateaus above ca. 3000 cm$^{-1}$ in Figure 4.12, suggesting that the total photon energy ($h\nu_1 + h\nu_2$) exceeds the Franck-Condon region of [5HI(NH)-(H2O)1]+ around $I_{E_0^{NH}} + 3000$ cm$^{-1}$. Note that the PIE curve of 5HI(NH)-(H2O)1 also plateaus over $I_{E_0^{NH}} + 3000$ cm$^{-1}$ (see Figure 4.13).

Figure 4.14 displays the energy diagram of 5HI-(H2O)1 in the $S_0$ and $D_0$ states. $I_{E_0^{NH}}$, $I_{E_0^{OH}}$, and $E_b^{NH}$ in Figure 4.14 were determined experimentally. The difference in the stabilization energies of 5HI(OH)-(H2O)1 and 5HI(NH)-(H2O)1 in the $S_0$ state ($\Delta E_{neutral}$) was obtained from theoretical calculations at the M06-2X/aug-cc-pVDZ level of theory. The difference in the stabilization energies of [5HI(OH)-(H2O)1]+ and [5HI(NH)-(H2O)1]+ in the $D_0$ state ($\Delta E_{cation}$) was calculated as: $(I_{E_0^{NH}} + \Delta E_{neutral}) - I_{E_0^{OH}}$. Note that $\Delta E_{cation}$ in Figure 4.14 (989 cm$^{-1}$) is similar to that in Figure 4.8b (1296 cm$^{-1}$). The upper limit of the potential barrier height for isomerization of [5HI(OH)-(H2O)1]+ to [5HI(NH)-(H2O)1]+ ($E_b^{OH}$) was also calculated from the sum of $E_b^{NH}$ and $\Delta E_{cation}$ (3116 cm$^{-1}$). In the PIE measurement, we tried to determine the binding energy of [5HI(NH)-(H2O)1]+ by monitoring the appearance of the daughter ion ([5HI]+). However, no daughter ion signals were detected, even when $h\nu_1 + h\nu_2$ increased to $I_{E_0^{NH}} + 5000$ cm$^{-1}$, which is consistent with the upper limit of the Franck-Condon...
region \((IE_0^{NH} + 3000 \text{ cm}^{-1})\) in Figure 4.12 and 4.13. Accordingly, we show the theoretical binding energies of \([5\text{HI(OH)}-(\text{H}_2\text{O})_1]^+ (BE^{OH})\) and \([5\text{HI(NH)}-(\text{H}_2\text{O})_1]^+ (BE^{NH})\) in Figure 4.14.

\([5\text{HI(NH)}-(\text{H}_2\text{O})_1]^+\), having an internal energy from \(E_b^{NH}\) to \(E_b^{NH} + 3000 \text{ cm}^{-1}\), isomerizes to \([5\text{HI(OH)}-(\text{H}_2\text{O})_1]^+\). Even after this isomerization, the total amount of energy in \([5\text{HI(OH)}-(\text{H}_2\text{O})_1]^+\) is conserved because it is isolated in vacuum. Accordingly, the internal energy of \([5\text{HI(OH)}-(\text{H}_2\text{O})_1]^+\) is large enough to overcome the potential barrier in the opposite direction. In principle, therefore, \([5\text{HI(OH)}-(\text{H}_2\text{O})_1]^+\) may also isomerize to \([5\text{HI(NH)}-(\text{H}_2\text{O})_1]^+\). We note that the initially excited vibrational states of \([5\text{HI(NH)}-(\text{H}_2\text{O})_1]^+\), having large Franck-Condon factors between \(S_1\) and \(D_0\), are unknown. However, intracluster vibrational energy redistribution (IVR) may be necessary for storing the vibrational energy in the isomerization coordinate for the forward isomerization to proceed. Similarly, IVR followed by the backward isomerization may occur. Based on these considerations, above \(E_b^{NH}\), \([5\text{HI-(H}_2\text{O})_1]^+\) may undergo structural fluctuation between \([5\text{HI(OH)}-(\text{H}_2\text{O})_1]^+\) and \([5\text{HI(NH)}-(\text{H}_2\text{O})_1]^+\), that is, in principle, the water molecule fluctuates between the two preferential H-bonding sites. We note that in practice, however, the backward isomerization of \([5\text{HI(OH)}-(\text{H}_2\text{O})_1]^+\) to \([5\text{HI(NH)}-(\text{H}_2\text{O})_1]^+\) is not observed within the delay time between \(v_2\) and \(v_{IR}\) (700 ns) when the backward isomerization is much slower than the delay time. In such a situation, the water molecule does not fluctuate within 700 ns. Unfortunately, we do not have any information on the time scale of the isomerization in both directions. Accordingly, at the present stage, we cannot conclude whether or not the water molecule in \([5\text{HI-(H}_2\text{O})_1]^+\) above \(E_b^{NH}\), fluctuates within the time window of our experiment (700 ns).
4.4. Conclusion

In summary, we have investigated the H-bonded structures of 5HI-(H₂O)₁ in the S₀ and D₀ states to explore the H-bond rearrangements of [5HI-(H₂O)₁]⁺. In the S₀ state, we identified two structural isomers of 5HI(NH)-(H₂O)₁ and 5HI(OH)-(H₂O)₁, in which a water molecule is bound to the NH and OH groups of 5HI, respectively. In the D₀ state, we found that the IRPD spectra of [5HI-(H₂O)₁]⁺ produced via the origin transition of 5HI(NH)-(H₂O)₁ and 5HI(OH)-(H₂O)₁ consist of the superposition of the vibrational bands of [5HI(NH)-(H₂O)₁]⁺ and [5HI(OH)-(H₂O)₁]⁺, indicating that the structural isomerization of [5HI(NH)-(H₂O)₁]⁺ to [5HI(OH)-(H₂O)₁]⁺ (and of [5HI(OH)-(H₂O)₁]⁺ to [5HI(NH)-(H₂O)₁]⁺) occurs in the D₀ state when 5HI(NH)-(H₂O)₁ (5HI(OH)-(H₂O)₁) is ionized. This means that the rearrangements of the water in [5HI-(H₂O)₁]⁺ occur in both directions. A step-like increase in the ion intensity was observed in the PIE spectra, facilitating determination of the \( IE₀ \) values of 5HI(NH)-(H₂O)₁ (58200 cm⁻¹) and 5HI(OH)-(H₂O)₁ (57387 cm⁻¹). Furthermore, the potential barrier height for the isomerization of [5HI(NH)-(H₂O)₁]⁺ to [5HI(OH)-(H₂O)₁]⁺ was determined to be 2127 ± 30 cm⁻¹. If the isomerization in both directions is sufficiently faster than the delay time between \( ν₂ \) and \( ν_{IR} \) (700 ns), above the potential barrier, [5HI-(H₂O)₁]⁺ may undergo the forward and backward isomerizations between [5HI(OH)-(H₂O)₁]⁺ and [5HI(NH)-(H₂O)₁]⁺, meaning that the water molecule fluctuates between the two preferential H-bonding sites.
Figure 4.1. 2C-R2PI spectra of (a) 5HI and (b) 5HI-(H₂O)₁. The ν₂ laser was fixed at 31000 cm⁻¹. Asterisks in (b) indicate the progression of each isomer.
Figure 4.2. IR-dip spectra of (a) syn-5HI in the S₀ state. (b,c) IR-dip spectra obtained by probing the vibronic bands at 32291 and 32552 cm⁻¹ in Figure 4.1b, respectively. The stick spectra correspond to the theoretical IR spectra obtained at the M06-2X/aug-cc-pVDZ level of theory. The harmonic frequencies were scaled by 0.9424.
Figure 4.3. IR-dip spectra of (a) anti-5HI in the $S_0$ state. (b,c) IR-dip spectra obtained by probing the vibronic bands at 32489 and 32785 cm$^{-1}$ in Figure 4.1b, respectively. The stick spectra correspond to the theoretical IR spectra obtained at the M06-2X/aug-cc-pVDZ level of theory. The harmonic frequencies were scaled by 0.9424.
Figure 4.4. Calculated stable structures of (a) syn-5HI(OH)-(H₂O)₁, (b) syn-5HI(NH)-(H₂O)₁, (c) anti-5HI(OH)-(H₂O)₁ and (d) anti-5HI(NH)-(H₂O)₁ in the S₀ state, respectively, obtained at the M06-2X/aug-cc-pVDZ level of theory. Relative stabilization energies are given in wavenumber units. The zero-point vibrational energy and basis set superposition error are corrected for all values.
Figure 4.5. IR-UV hole-burning spectra obtained by fixing the frequency of IR laser at (a) 3545 cm⁻¹, (b) 3538 cm⁻¹ and (c) 3438 cm⁻¹. R2PI spectrum in figure 4.1b is shown in the bottom.
Figure 4.6. IRPD spectra of (a) \([anti-5HI-(Ar)_{1}]^+\) and (b) \([syn-5HI-(Ar)_{1}]^+\), where an Ar atom is bound to the \(\pi\)-ring of \([5HI]^+\). The stick spectra correspond to the theoretical IR spectra of \([anti-5HI]^+\) and \([syn-5HI]^+\) obtained by the M06-2X/aug-cc-pVDZ level of theory. The insets indicate the stable structures of each monomer cation.
Figure 4.7. IRPD spectra of $[\text{HI}-(\text{H}_2\text{O})_1]^+$ produced by R2PI via the origin transitions of (a) $5\text{HI(OH)}-(\text{H}_2\text{O})_1$ and (b) $5\text{HI(NH)}-(\text{H}_2\text{O})_1$. Theoretical IR spectra of (c) $[\text{HI(OH)}-(\text{H}_2\text{O})_1]^+$ and (d) $[\text{HI(NH)}-(\text{H}_2\text{O})_1]^+$ obtained at the M06-2X/aug-cc-pVDZ level of theory. The harmonic frequencies were scaled by 0.9424.
Figure 4.8. Calculated structures of (a) [5HI(OH)-(H₂O)₁]+, (b) [5HI(NH)-(H₂O)₁]+, (c-f) [5HI(CH)-(H₂O)₁]+ and (g,h) [5HI(π)-(H₂O)₁]+ in the D₀ state, obtained at the M06-2X/aug-cc-pVDZ level of theory. Relative stabilization energies are given in wavenumber units. The zero-point vibrational energy and basis set superposition error are corrected for all values.
Figure 4.8. (c-h)
Figure 4.9. IRPD spectra of [5HI-(H_2O)_1]^+ produced by R2PI via the origin of (a) 5HI(OH)-(H_2O)_1 and (b) 5HI(NH)-(H_2O)_1, in the region of 2800~3800 cm\(^{-1}\). Broad features around 2800~3400 cm\(^{-1}\) are typically attributed to the H-bonded \(v_{OH}\) and \(v_{NH}\) transitions, which may slightly saturate because of their strong transition intensities.
Figure 4.10. PIE spectra of (a) $5\text{HI(OH)}-(\text{H}_2\text{O})_1$ and (b) $5\text{HI(NH)}-(\text{H}_2\text{O})_1$ obtained via the origin transition of each isomer. The inset arrows indicate the field-corrected $IE_0$ values of each isomer.
Figure 4.11. Schematic diagram of protocol for measuring the isomerization threshold. The \( \nu_1 \) laser is fixed at the origin of 5HI(NH)-(H\(_2\)O)\(_1\) while the \( \nu_2 \) laser is scanned across \( E_b^{NH} \). The \( \nu_{IR} \) laser is fixed at 3463 cm\(^{-1}\) corresponding to the free \( \nu_{NH} \) band of [5HI(OH)-(H\(_2\)O)\(_1\)]\(^+\). See the text for more details..
Figure 4.12. Measurement of energy threshold for isomerization of $[5\text{HI(NH)}-(\text{H}_2\text{O})_1]^+$ to $[5\text{HI(OH)}-(\text{H}_2\text{O})_1]^+$, based on Figure 4.11. The delay time between $v_2$ and $v_{\text{IR}}$ was 700 ns. The IR laser was fixed at 3463 cm$^{-1}$, corresponding to the free $v_{\text{NH}}$ band of $[5\text{HI(OH)}-(\text{H}_2\text{O})_1]^+$. The horizontal axis indicates the internal energy of $[5\text{HI(NH)}-(\text{H}_2\text{O})_1]^+$ obtained from the difference between ($h v_1 + h v_2$) and $I E_0^{NH}$. The inset arrow shows the upper limit of the isomerization threshold from $I E_0^{NH}$, denoted as $E_b^{NH}$. 
Figure 4.13. PIE spectrum of 5HI(NH)-(H₂O)₁ measured up to \((IE_0^{NH} + 3300)\) cm⁻¹.
Figure 4.14. Energy diagram for $5\text{HI(OH)-(H}_2\text{O)}_1$ and $5\text{HI(NH)-(H}_2\text{O)}_1$ in the $S_0$ and $D_0$ states. The solid-black arrows display the experimental $I E_0$ values. The dashed-gray arrows show the theoretical binding energy of each isomer in $D_0$ ($BE^{OH}$ and $BE^{NH}$), and the difference in the theoretical binding energy of each isomer in $S_0$ ($\Delta E_{\text{neutral}}$) calculated at the M06-2X/aug-cc-pVDZ level of theory. The solid-gray arrow was obtained from $(IE_0^{NH} + \Delta E_{\text{neutral}}) - IE_0^{OH}$. The regions marked by gray slashes demonstrate the Franck-Condon region. All values are indicated in wavenumber units.
References to chapter 4


Chapter 5.

Elevation of the energy threshold for isomerization in 5-hydroxyindole-tert-butyl alcohol cluster cations

Reproduced in part with permission from Journal of Physical Chemistry A, submitted for publication.

Unpublished work copyright 2016 American Chemical Society.
5.1. Introduction

The solvation structure is one of the most dominant factors to characterize various chemical and biological processes.\textsuperscript{1,2} In particular, the molecular interactions between a solute and solvent molecules in the first solvation shell have been considered to affect these processes significantly. Various H-bonding interactions have been investigated by using the gas-phase spectroscopy with a supersonic jet expansion.\textsuperscript{3–5} Jet-cooled solvated clusters allow us to investigate the stable structures of H-bonds at the molecular level, since the supersonic jet expansion can eliminate the thermal fluctuation of the solvation structures. However, many chemical and biological processes undergo at (or above) room temperature, in which the thermal fluctuation of solvation structures plays an important role.\textsuperscript{6–8} Therefore, spectroscopic studies on the solvation dynamics such as the rearrangement of H-bonds are highly required so as to reveal its influence on the chemical and biological processes at the molecular level.

The rearrangement of H-bonds in several H-bonded cluster cations has been observed in the D\textsubscript{0} state by using the gas-phase spectroscopy.\textsuperscript{9–19} In these studies, the rearrangement is initiated by resonant two-photon ionization (R2PI). R2PI has a great advantage of identifying the initial H-bonded structures and triggering the rearrangement of the H-bonds in the D\textsubscript{0} state. In chapter 4, we described spectroscopic study on the rearrangement of the H-bonds in monohydrated 5-hydroxyindole cluster cation ([5HI-(H\textsubscript{2}O)\textsubscript{1}]\textsuperscript{+}). We successfully determined the potential barrier height for the isomerization of [5HI(NH)-(H\textsubscript{2}O)\textsubscript{1}]\textsuperscript{+} to [5HI(OH)-(H\textsubscript{2}O)\textsubscript{1}]\textsuperscript{+}. To the best of the knowledge, this is the first report on the determination of the isomerization threshold for hydrated cluster cations experimentally.

It has been well established that the potential barrier along the reaction
coordinate is one of the most important factors to determine the reaction dynamics. The potential barrier height for the rearrangement of H-bonds may also characterize the solvation dynamics, because the rearrangement can be regarded as a chemical reaction. Different kind of solvent molecules may have a different impact on the potential barrier height owing to the difference in the intermolecular interactions. The various intermolecular interactions between a solute and solvents such as methanol, ethanol, NH3, CH4 and rare gases have also been investigated in solvated clusters extensively.20–27 In particular, alcohol molecules are the typical protic solvents having a hydroxyl group like water. Furthermore, the branching pattern of alkyl groups in the alcohols has a significant effect on the chemical and physical properties such as proton affinity (PA) and bulkiness, which may affect the potential barrier height for the rearrangement of H-bonds.28–30

A tert-butyl alcohol (t-BuOH) is the simplest tertiary alcohol which has the largest PA and bulkiness among water, primary alcohol, secondary alcohol and tertiary alcohol due to the inductive (+ I) effect of the substituted methyl group.29 Accordingly, the rearrangement of H-bonds in [5HI-(t-BuOH)1]+ is expected to change drastically as compared with that of [5HI-(H2O)1]+. In this chapter, we investigate the solvation structures of 5HI-(t-BuOH)1 in the S0 and D0 states by using UV and IR spectroscopy in the gas phase. The difference in the H-bond rearrangement of [5HI-(t-BuOH)1]+ and [5HI-(H2O)1]+ is discussed.
5.2. Experimental and computational methods

The experimental setup used in this study has been described in chapter 2. A commercially available 5HI was purchased from Wako Pure Chem. Ind. and used without further purification. 5HI introduced in a stainless steel tube was heated to around 393 K by a coiled heater. The vaporized 5HI molecules were mixed with helium carrier gas passed through the reservoir containing t-BuOH cooled down to 278 K. A typical stagnation pressure was 2 atm. The mixture gas was expanded into a vacuum chamber by using a pulsed valve (General Valve, series 9, 0.8 mm as an orifice diameter) operated at 10 Hz. The supersonic jet expansion was skimmed into an ion-source chamber. The skimmed solvated clusters were photoionized by UV lasers for mass selection. The produced ions were analyzed with a linear time-of-flight mass spectrometer for all measurements below.

The laser setup and the measurement of UV and IR spectra are described in chapter 4. For the 2C-R2PI spectra, the $v_1$ laser was scanned in the frequency region of $32200 \sim 33000 \text{ cm}^{-1}$, while the $v_2$ laser was fixed at $31000 \text{ cm}^{-1}$. For measuring PIE spectra, the $v_1$ laser was fixed at the $S_1-S_0$ origin of each isomer while the $v_2$ laser was scanned in the frequency region of $23500 \sim 25500 \text{ cm}^{-1}$. For all measurements of IR spectra, the IR energy was reduced to be $\sim 1 \text{ mJ/pulse at } 3300 \sim 3800 \text{ cm}^{-1}$ in order to avoid unfavorable saturation of vibrational transitions. The repetition rate of the $v_2$ laser was 10 Hz, whereas that of the IR laser was 5 Hz. The IR and UV lasers were spatially overlapped with one another. The ion signals with and without the IR pulse were stored separately to correct the artificial fluctuation of the spectral baseline. For the IR-dip spectra in the $S_0$ state, the IR laser in the frequency region of $3300 \sim 3800 \text{ cm}^{-1}$ preceded the UV laser by $\sim 20 \text{ ns}$. For measuring IRPD spectra in the $D_0$ state, the IR laser was
irradiated at 700 ns after the production of [5HI-(H2O)1]+ by 2C-R2PI. We note that the signals from the daughter ions ([5HI]+) were completely separated on the flight time from the [5HI]+ signals generated by unfavorable multi-photon processes of the ν1 and/or ν2 lasers only.

M06-2X³¹/aug-cc-pVDZ calculations were performed to obtain the stable structures, stabilization energies, harmonic vibrational frequencies and IR intensities. The calculated harmonic vibrational frequencies in the S₀ and D₀ states were scaled by 0.9424. The basis set superposition error was corrected by a counterpoise method. All quantum chemical calculations were performed by GAUSSIAN 09 program package. The computations were carried out using the computer facilities at Research Institute for Information Technology, Kyushu University.
5.3. Results and discussions

Figure 5.1 shows 2C-R2PI spectra of (a) 5HI, (b) 5HI-(H2O)1 and (c) 5HI-(t-BuOH)1, respectively. The frequency of the ν2 laser was fixed at 31000 cm\(^{-1}\). Figure 5.1a and 5.1b are identical to Figure 4.1a and 4.1b, respectively. In Figure 5.1c, three vibronic bands are observed at 32258, 32433 and 32669 cm\(^{-1}\), which can be assigned to the origin bands of 5HI-(t-BuOH)1.

Figure 5.2 displays IR-dip spectra of 5HI-(t-BuOH)1 in the S\(_0\) state, obtained by probing the vibronic bands at (a) 32258, (b) 32433 and (c) 32669 cm\(^{-1}\), respectively. The stick spectra in Figure 5.2 are the theoretical IR spectra of 5HI-(t-BuOH)1. Their calculated stable structures are shown in Figure 5.3 with the relative stabilization energy. In Figure 5.3a, a t-BuOH molecule is bound to syn-5HI, while it is bound to anti-5HI in Figure 5.3b, c. From theoretical prediction, the IR intensities of the H-bonded OH and NH stretching vibrations (H-bonded ν\(_{OH}\) and ν\(_{NH}\)) are much stronger than that of the free ν\(_{OH}\) and ν\(_{NH}\). The spectral features of Figure 5.2a and 5.2b are very similar to each other, while the spectral pattern of Figure 5.2c is totally different from those of Figure 5.2a, b. The vibrational transitions at 3525 cm\(^{-1}\) in Figure 5.2a, b is the same as the free ν\(_{NH}\) of syn- and anti-5HI (Figure 4.2a and 4.3a). In addition, the H-bonded ν\(_{OH}\) vibrations are observed at 3426 cm\(^{-1}\) and 3415 cm\(^{-1}\) in Figure 5.2a, b, respectively. The vibrational bands at 3631 cm\(^{-1}\) in Figure 5.2a, b are also attributed to the free ν\(_{OH}\) of t-BuOH. Therefore, the IR-dip spectra in Figure 5.2a, b can be assigned to 5HI(OH)-(t-BuOH)\(_1\), where a t-BuOH molecule is bound to the OH group of 5HI. The H-bonded ν\(_{OH}\) in Figure 5.2b is slightly red-shifted by 11 cm\(^{-1}\) from that in Figure 5.2a, which is well reproduced by theoretical IR spectra of syn- and anti-5HI(OH)-(t-BuOH)\(_1\). Furthermore, the relative intensity of the vibronic bands observed at 32258 and 32433 cm\(^{-1}\) is in good agreement.
with that of syn-and anti-5HI monomers. Accordingly, the IR-dip spectra in Figure 5.2a, b are assigned to syn- and anti-5HI(OH)-(t-BuOH)$_1$, respectively. In Figure 5.2a, an unassigned transition at 3556 cm$^{-1}$ marked by an asterisk may be a combination band such as the H-bonded $v_{OH}$ and the intermolecular stretching vibration whose frequency is calculated to be 135 cm$^{-1}$. In Figure 5.2c, the free $v_{NH}$ band completely disappears whereas the vibrational transition corresponding to the free $v_{OH}$ of anti-5HI is observed at 3660 cm$^{-1}$. The vibrational transition at 3640 cm$^{-1}$ is assigned to the free $v_{OH}$ of t-BuOH. In addition, the H-bonded $v_{NH}$ is observed at 3376 cm$^{-1}$. Therefore, the IR-dip spectrum in Figure 5.2c is assigned to anti-5HI(NH)-(t-BuOH)$_1$, where a t-BuOH molecule is bound to the NH group of 5HI.

In Figure 5.1c, several unassigned vibronic bands still remain, and some of them may correspond to the vibronic transitions of syn-5HI(NH)-(t-BuOH)$_1$. To assign the vibronic bands in Figure 5.1c, we performed IR-UV hole-burning spectroscopy. Figure 5.4 shows the IR-UV hole-burning spectrum obtained by the irradiation of IR laser, the frequency of which was fixed at 3415 cm$^{-1}$ corresponding to the H-bonded $v_{OH}$ of anti-5HI(OH)-(t-BuOH)$_1$. In the IR-UV hole-burning spectrum, the vibronic bands are observed at 32448, 32461, 32571 and 32864 cm$^{-1}$ as well as the origin band at 32433 cm$^{-1}$, which can be assigned to the vibronic transitions of anti-5HI(OH)-(t-BuOH)$_1$.

According to the relative intensities of anti-5HI(NH)-(t-BuOH)$_1$ and anti-5HI(OH)-(t-BuOH)$_1$, the origin of syn-5HI(NH)-(t-BuOH)$_1$ may also be weaker than that of syn-5HI(OH)-(t-BuOH)$_1$. In addition, based on the frequencies of the origin bands of anti-5HI(NH)-(t-BuOH)$_1$ and anti-5HI(OH)-(t-BuOH)$_1$, the origin band of syn-5HI(NH)-(t-BuOH)$_1$ is expected to be observed in the frequency region of 32400~32500 cm$^{-1}$. However, the IR-UV hole-burning spectrum (Figure 5.4) has revealed...
that the vibronic bands having weak intensity in the region are attributed to those of *anti*-5HI(OH)-(t-BuOH)$_1$. Accordingly, we conclude that the intensity of the origin band of *syn*-5HI(NH)-(t-BuOH)$_1$ is too small to be detected in Figure 5.1c (Figure 5.4) in our experimental conditions. In the following paragraph, we focus our attention on the *anti*-5HI-(t-BuOH)$_1$ conformer which is hereafter denoted as 5HI-(t-BuOH)$_1$ owing to the same reason as the case of 5HI-(H$_2$O)$_1$.

In Figure 5.3, the stable structures of 5HI-(t-BuOH)$_1$, in which t-BuOH is a single conformation, are displayed as representative ones. However, the other types of t-BuOH conformations are also stable in 5HI-(t-BuOH)$_1$. Figure 5.5 depicts three possible conformations of t-BuOH in 5HI(OH)-(t-BuOH)$_1$ and 5HI(NH)-(t-BuOH)$_1$. In 5HI(OH)-(t-BuOH)$_1$, an *anti* conformation (OH(anti)), where the OH group of the t-BuOH points to the opposite direction of the NH group in 5HI, is more stable than a *syn* conformation (OH(syn)) where the OH group of the t-BuOH points to the NH group, and a *center* conformation (OH(center)) where the OH group of the t-BuOH points toward the NH group. On the other hand, in *anti*-5HI(NH)-(t-BuOH)$_1$, the center conformation (NH(center)) is slightly stable than the anti (NH(anti)) and syn (NH(syn)) conformations. Unfortunately, the conformation of t-BuOH in 5HI-(t-BuOH)$_1$ cannot be determined by the IR-dip spectra in Figure 5.2 since the different conformations of t-BuOH hardly affect the calculated IR frequencies of $v_{OH}$ and $v_{NH}$ of 5HI-(t-BuOH)$_1$. We have no further discussion on the conformations of t-BuOH in the following text, but we note that the difference in the relative stabilization energy of 5HI-(t-BuOH)$_1$ having the different conformations of t-BuOH is subtle. Therefore, all of the conformations shown in Figure 5.5 may be possible in our experimental conditions.

Figure 5.6 shows IRPD spectra of [5HI-(t-BuOH)$_1$]$^+$ in the D$_0$ state in the
frequency region of the free $v_{OH}$ and $v_{NH}$. $[5\text{HI}-(\text{t-BuOH})_1]^+$ is produced by R2PI via the origin transitions of (a) 5HI(OH)-(t-BuOH)$_1$ and (b) 5HI(NH)-(t-BuOH)$_1$. The stick spectra shown in Figure 5.6c and 5.6d correspond to the theoretical IR spectra of [5HI(OH)-(t-BuOH)$_1]^+$ and [5HI(NH)-(t-BuOH)$_1]^+$, the stable structures of which are displayed in Figure 5.7a, b, respectively. The vibrational bands at 3465 and 3464 cm$^{-1}$ in Figure 5.6a, b can be assigned to the free $v_{NH}$ band of the [5HI]$^+$ moiety since the frequencies of these bands are essentially the same as that of the free $v_{NH}$ band of [5HI(OH)-(H$_2$O)$_1]^+$ (Figure 4.7). In addition, the vibrational band at 3590 cm$^{-1}$ in Figure 5.5b is assigned to the free $v_{OH}$ band of the [5HI]$^+$ moiety, the frequency of which is the same as that of the free $v_{OH}$ band of [5HI(NH)-(H$_2$O)$_1]^+$. The vibrational bands at 3623 cm$^{-1}$ in Figure 5.6a, b is assigned to the free $v_{OH}$ band of t-BuOH.

The theoretical calculations in Figure 5.6c, d predict observation of two free stretching vibrations (the free $v_{OH}$ and/or $v_{NH}$) in this frequency region. Comparing with the theoretical IR spectra, Figure 5.6a is assigned to [5HI(OH)-(t-BuOH)$_1]^+$. However, Figure 5.6b clearly shows three vibrational bands, which is not consistent with the theoretical predictions. This observation cannot be explained by the existence of only [5HI(OH)-(t-BuOH)$_1]^+$ or [5HI(NH)-(t-BuOH)$_1]^+$. In Figure 5.6b, [5HI-(t-BuOH)$_1]^+$ was generated via the $S_1$-$S_0$ origin transition of 5HI(NH)-(t-BuOH)$_1$. Hence, [5HI-(t-BuOH)$_1]^+$ immediately after photoionization is expected to be [5HI(NH)-(t-BuOH)$_1]^+$ because the vertical transition from the $S_1$ state preferentially occurs. However, the free $v_{NH}$ band in Figure 5.6b is not attributed to [5HI(NH)-(t-BuOH)$_1]^+$ but [5HI(OH)-(t-BuOH)$_1]^+$. Therefore, the IRPD spectrum in Figure 5.6b consists of the superposition of the vibrational bands of [5HI(OH)-(t-BuOH)$_1]^+$ and [5HI(NH)-(t-BuOH)$_1]^+$. Note that [5HI(OH)-(t-BuOH)$_1]^+$ is
not generated directly by photoionization via the origin transition of 5HI(NH)-(t-BuOH)\textsubscript{1}. Accordingly, the IRPD spectrum in Figure 5.6b provides an evidence that [5HI(NH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} isomerizes to [5HI(OH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} in the D\textsubscript{0} state. That is, the rearrangement of the H-bond occurs in the direction of [5HI(NH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} to [5HI(OH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} after photoionization.

In contrast to Figure 5.6b, the free $\nu_{OH}$ band is not observed in Figure 5.6a when [5HI-(t-BuOH)\textsubscript{1}]\textsuperscript{+} is produced by photoionization via the origin of 5HI(OH)-(t-BuOH)\textsubscript{1}. All of the vibrational bands in Figure 5.6a are attributed to [5HI(OH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+}. This observation indicates that the isomerization of [5HI(OH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} to [5HI(NH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} does not occur after photoionization via the origin of 5HI(OH)-(t-BuOH)\textsubscript{1}. Furthermore, the intensity of the free $\nu_{NH}$ band in Figure 5.6b is weaker than that in Figure 4.7b. Thus, the isomerization (the arrangement of the H-bond) dynamics and the potential energy surface of [5HI-(t-BuOH)\textsubscript{1}]\textsuperscript{+} is different from those of [5HI-(H\textsubscript{2}O)\textsubscript{1}]\textsuperscript{+}.

The vibrational bands in Figure 5.6b would also be assigned to those of the other isomers having both the free $\nu_{OH}$ and $\nu_{NH}$ bands, such as [5HI(CH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} and [5HI(\pi)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} (Figure 5.7c, d), where a t-BuOH molecule is bound to the CH group or the \pi-ring of the [5HI\textsuperscript{+}] moiety. However, the calculated relative stabilization energy of these isomers are much higher than those of [5HI(OH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} and [5HI(NH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} (ca. + 4200 – 5000 cm\textsuperscript{-1}). Thus, as is the case of [5HI-(H\textsubscript{2}O)\textsubscript{1}]\textsuperscript{+}, the majority of the vibrational bands in Figure 5.6b can be attributed to those of [5HI(OH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} and [5HI(NH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} although the existence of [5HI(CH)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} and/or [5HI(\pi)-(t-BuOH)\textsubscript{1}]\textsuperscript{+} isomer cannot be ruled out.

Figure 5.8a, b display photoionization efficiency (PIE) spectra of
5HI(OH)-(t-BuOH)$_1$ and 5HI(NH)-(t-BuOH)$_1$, respectively. In contrast to the case of 5HI-(H$_2$O)$_1$, the PIE spectra in Figure 5.8 do not show the step-like but gradual increase in the intensity of the ion signals. Accordingly, the baseline and the gradual increase in the ion signal are fit with two linear lines to determine the upper limit of the adiabatic ionization energy ($I_E^0$). The $I_E^0$ of 5HI(OH)-(t-BuOH)$_1$ and 5HI(NH)-(t-BuOH)$_1$ ($I_{OH}^0$ and $I_{NH}^0$) are determined to be 56626 and 57533 cm$^{-1}$. In this case, the internal rotation of methyl groups and/or the change in the conformation of t-BuOH may contribute to the gradual increase in the ion intensity although the calculated stable structures of [5HI(OH)-(t-BuOH)$_1$]$^+$ and [5HI(NH)-(t-BuOH)$_1$]$^+$ in the D$_0$ state (Figure 5.7) do not seem to be so different from those of 5HI(OH)-(t-BuOH)$_1$ and 5HI(NH)-(t-BuOH)$_1$ in the S$_0$ state (Figure 5.3). Note that the calculated $I_{OH}^0$ and $I_{NH}^0$ values by DFT calculations are 56039 cm$^{-1}$ and 57590 cm$^{-1}$, respectively, which are in good agreement with the experimental values.

Based on the determination of $I_{OH}^0$ and $I_{NH}^0$, we measured the isomerization threshold for [5HI-(t-BuOH)$_1$]$^+$ in the D$_0$ state by applying the same scheme shown in Figure 4.11. The internal energy of [5HI(NH)-(t-BuOH)$_1$]$^+$ in the D$_0$ state is calculated as: $(h
u_1 + h
u_2) - I_{NH}^0$. The frequency of IR photon is fixed at 3464 cm$^{-1}$ (the free $v_{NH}$ vibration of [5HI(OH)-(t-BuOH)$_1$]$^+$), which leads to photodissociation of [5HI(OH)-(t-BuOH)$_1$]$^+$ to [5HI]$^+$. Based on Figure 4.11, the upper limit of the potential barrier height ($E_b$) can be determined by monitoring the intensity of the daughter ion ([5HI]$^+$) signal as a function of the internal energy of [5HI(NH)-(t-BuOH)$_1$]$^+$. Note that in Figure 5.6a, the opposite isomerization of [5HI(OH)-(t-BuOH)$_1$]$^+$ to [5HI(NH)-(t-BuOH)$_1$]$^+$ has not been observed by photoionization via the origin transition of 5HI(OH)-(t-BuOH)$_1$. Therefore, we measured only the isomerization threshold of
[5HI(NH)-(t-BuOH)]^+ to [5HI(OH)-(t-BuOH)]^+.

Figure 5.9 displays the intensity of the daughter ion signal as a function of the internal energy of [5HI(NH)-(t-BuOH)]^+. The intensity of the daughter ion gradually increases in Figure 5.9. The upper limit of \( E_b \) for isomerization of [5HI(NH)-(t-BuOH)]^+ to [5HI(OH)-(t-BuOH)]^+ (\( E_b^{NH} \)) is determined to be 3362 ± 30 cm\(^{-1}\) by fitting the baseline and the increase in the ion signal to two linear lines. The value of \( E_b^{NH} \) for [5HI-(t-BuOH)]^+ is approximately 1200 cm\(^{-1}\) higher than that for [5HI-(H\(_2\)O)]^+ (2127 ± 30 cm\(^{-1}\)), indicating that the rearrangement of the water molecule starts at lower internal energy than that of the t-BuOH molecule. The disappearance of the backward isomerization of [5HI(OH)-(t-BuOH)]^+ to [5HI(NH)-(t-BuOH)]^+ is consistent with the elevation of \( E_b \). In the case of photoionization via the origin transition of 5HI(OH)-(t-BuOH), the rearrangement may not proceed since the internal energy of [5HI(OH)-(t-BuOH)]^+ is not sufficient to exceed the potential barrier height. Furthermore, the fact that the relative intensity of the free \( \nu_{NH} \) band in Figure 5.6b is weaker than that in Figure 4.7b may be explained by the decrease in the relative population of [5HI-(t-BuOH)]^+ having the sufficient internal energy to exceed the potential barrier.

Figure 5.10 displays the energy diagram of 5HI-(t-BuOH)\(_1\) in the S\(_0\) and D\(_0\) states. \( IE_0^{NH}\), \( IE_0^{OH}\), and \( E_b^{NH}\) in Figure 5.10 were determined experimentally. The difference in the stabilization energies of 5HI(OH)-(t-BuOH)\(_1\) and 5HI(NH)-(t-BuOH)\(_1\) in the S\(_0\) state (\( \Delta E_{neutral} \)) was obtained from theoretical calculations at the M06-2X/aug-cc-pVDZ level of theory, while the difference in the stabilization energies of [5HI(OH)-(t-BuOH)]^+ and [5HI(NH)-(t-BuOH)]^+ in the D\(_0\) state (\( \Delta E_{cation} \)) was calculated as: \((IE_0^{NH} + \Delta E_{neutral}) - IE_0^{OH}\). Note that \( \Delta E_{cation} \) in Figure 5.10 (1316 cm\(^{-1}\)) is similar to that in
Figure 5.7b (1940 cm\(^{-1}\)). The upper limit of the potential barrier height for isomerization of \([5\text{HI(OH)}-(t\text{-BuOH})_1]^+\) to \([5\text{HI(NH)}-(t\text{-BuOH})_1]^+\) \(E_b^{\text{OH}}\) was also calculated from the sum of \(E_b^{\text{NH}}\) and \(\Delta E_{\text{cation}}\) (4678 cm\(^{-1}\)). Theoretical binding energies of \([5\text{HI(OH)}-(t\text{-BuOH})_1]^+\) \(BE^{\text{OH}}\) and \([5\text{HI(NH)}-(t\text{-BuOH})_1]^+\) \(BE^{\text{NH}}\) are also shown in Figure 5.10.

The \(E_b\) value for \([5\text{HI-(t-BuOH)}_1]^+\) is elevated as compared with that for \([5\text{HI-(H}_2\text{O)}_1]^+\) (Figure 4.14). The difference in the stabilization energy between the reactant and the transition states may cause the difference in \(E_b\) for \([5\text{HI-(t-BuOH)}_1]^+\) and \([5\text{HI-(H}_2\text{O)}_1]^+\). In the reactant state (i.e., \([5\text{HI(NH)}-(t\text{-BuOH})_1]^+\) and \([5\text{HI(NH)}-(H\text{}_2\text{O})_1]^+\)), these isomers form the stable H-bond in which the solvent molecule (t-BuOH or H\(_2\)O) acts as a proton acceptor. It has been well established that the proton affinity of t-BuOH is larger than that of H\(_2\)O.\(^{28-30}\) Thus, the H-bond strength of \([5\text{HI(NH)}-(t\text{-BuOH})_1]^+\) becomes larger than that of \([5\text{HI(NH)}-(H\text{}_2\text{O})_1]^+\). Actually, the \(BE^{\text{NH}}\) value of \([5\text{HI(NH)}-(t\text{-BuOH})_1]^+\) (5641 cm\(^{-1}\)) is larger than that of \([5\text{HI(NH)}-(H\text{}_2\text{O})_1]^+\) (4035 cm\(^{-1}\)). That is, t-BuOH stabilizes the stable structure ([5HI(NH)-(t-BuOH)]\(^+\)) to a larger extent than H\(_2\)O owing to its larger proton affinity. In the transition state, however, the H-bond between 5HI\(^+\) and the solvent (t-BuOH or H\(_2\)O) is expected to dissociate in part. Accordingly, the difference in the proton affinity of t-BuOH and H\(_2\)O has a little impact on the stabilization energy of \([5\text{HI-(t-BuOH)}_1]^+\) and \([5\text{HI-(H}_2\text{O)}_1]^+\) in the transition state. That is, the stabilization energies of \([5\text{HI-(t-BuOH)}_1]^+\) and \([5\text{HI-(H}_2\text{O)}_1]^+\) in the transition state may be similar to each other. In fact, the difference in the stabilization energy of the CH isomer of \([5\text{HI-(t-BuOH)}_1]^+\) and \([5\text{HI-(H}_2\text{O)}_1]^+\), which have the weaker H-bond, is around 1000 cm\(^{-1}\), while those of their OH and NH isomers are more than 2200 and 1600 cm\(^{-1}\), respectively. Therefore,
[5HI(NH)-(t-BuOH)]^+, which is more stable than [5HI(NH)-(H2O)]^+, has the higher potential barrier height, because the transition state of [5HI-(t-BuOH)]^+ and [5HI-(H2O)]^+ is stabilized from the energy level of 5HI^+ + solvent to a similar extent (see Figure 5.11). Thus, we anticipate that the elevation of \( E_b \) for [5HI(NH)-(t-BuOH)]^+ is explained by the stabilization of [5HI(NH)-(t-BuOH)]^+ to a larger extent than that of [5HI(NH)-(H2O)]^+, which is associated with the increase in the proton affinity of t-BuOH as compared with water. We note that the van der Waals interaction also contributes to the stabilization energy, but its effect may be insufficient.
5.4. Conclusion

In summary, we have investigated the H-bonded structures of 5HI-(t-BuOH)$_1$ in the S$_0$ and D$_0$ states to explore the difference in the H-bond rearrangement between [5HI-(H$_2$O)$_1$]$^+$ and [5HI-(t-BuOH)$_1$]$^+$. In the S$_0$ state, we observed two structural isomers of 5HI(NH)-(t-BuOH)$_1$ and 5HI(OH)-(t-BuOH)$_1$, in which a t-BuOH molecule is bound to the NH and OH groups of 5HI, respectively. The IRPD spectrum of [5HI-(t-BuOH)$_1$]$^+$ produced via the origin transition of 5HI(NH)-(t-BuOH)$_1$ consists of the superposition of the vibrational bands of [5HI(NH)-(t-BuOH)$_1$]$^+$ and [5HI(OH)-(t-BuOH)$_1$]$^+$, indicating that the isomerization of [5HI(NH)-(t-BuOH)$_1$]$^+$ to [5HI(OH)-(t-BuOH)$_1$]$^+$ occurs in the D$_0$ state when 5HI(NH)-(t-BuOH)$_1$ is ionized. On the other hand, [5HI-(t-BuOH)$_1$]$^+$ produced via the origin transition of 5HI(OH)-(t-BuOH)$_1$ provides the IRPD spectrum of [5HI(OH)-(t-BuOH)$_1$]$^+$. This is completely different from the case of [5HI-(H$_2$O)$_1$]$^+$ in which the rearrangement of the water occurs in both directions. In the PIE spectra, the values of upper limits of $IE_0$ 5HI(NH)-(t-BuOH)$_1$ (57533 cm$^{-1}$) and 5HI(OH)-(t-BuOH)$_1$ (56626 cm$^{-1}$) are obtained by fitting the baseline and the gradual increase in the ion signal to two linear lines. Furthermore, the potential barrier height for the isomerization of [5HI(NH)-(t-BuOH)$_1$]$^+$ to [5HI(OH)-(t-BuOH)$_1$]$^+$ was determined to be 3362 ± 30 cm$^{-1}$, which is approximately 1200 cm$^{-1}$ higher than that of [5HI-(H$_2$O)$_1$]$^+$ (2127 ± 30 cm$^{-1}$). The elevation of the potential barrier height in [5HI-(t-BuOH)$_1$]$^+$ may be caused by the stabilization of the OH and NH isomers of [5HI-(t-BuOH)$_1$]$^+$ to a larger extent than that of [5HI-(H$_2$O)$_1$]$^+$ due to the larger proton affinity of t-BuOH than that of H$_2$O.
Figure 5.1. 2C-R2PI spectra of (a) 5HI, (b) 5HI-(H$_2$O)$_1$ and 5HI-(t-BuOH)$_1$. The frequency of the Ionization-UV laser was fixed at 31000 cm$^{-1}$. Asterisks in (b) and (c) indicate the progression of anti-5HI(OH)-(t-BuOH)$_1$. 
Figure 5.2. IR-dip spectra in the S\textsubscript{0} state obtained by probing the vibronic bands at (a) 32258, (b) 32433 and (c) 32699 cm\textsuperscript{-1} in Figure 5.1c, respectively. The stick spectra correspond to the theoretical IR spectra obtained at the M06-2X/aug-cc-pVDZ level of theory. The harmonic frequencies were scaled by 0.9424. The intensity of the free $\nu_{\text{OH}}$ and $\nu_{\text{NH}}$ shown in Figure 5.2 are multiplied by a factor of five to the calculated value.
Figure 5.3. Calculated stable structures of (a) *syn*-5HI(OH)-(t-BuOH)$_1$, (b) *anti*-5HI(OH)-(t-BuOH)$_1$ and (c) *anti*-5HI(NH)-(t-BuOH)$_1$ in the $S_0$ state, respectively, obtained at the M06-2X/aug-cc-pVDZ level of theory. The right-hand side of the figure shows each lateral view of an aromatic plane, while the right-hand side shows the structures seen from the yellow arrows in the left. Relative stabilization energies are given in units of wavenumber. The zero-point vibrational energy and basis set superposition error are corrected for all values.
Figure 5.4. IR-UV hole-burning spectrum obtained by fixing the frequency of the IR laser at 3415 cm$^{-1}$. R2PI spectrum in Figure 5.1c is shown in the bottom.
Figure 5.5. The possible conformation of a t-BuOH molecule in anti-5H(0H)-(t-BuOH)$_1$ and anti-5H(NH)-(t-BuOH)$_1$ with the relative energy obtained by DFT calculations. The methyl groups in a t-BuOH molecule are simplified by the gray circles.
Figure 5.6. IRPD spectra of \([5\text{HI-(t-BuOH)}_1]^+\) produced by R2PI via the origin transitions of (a) \([5\text{HI(OH)-(t-BuOH)}_1]^+\) and (b) \([5\text{HI(NH)-(t-BuOH)}_1]^+\). Theoretical IR spectra of (c) \([5\text{HI(OH)-(t-BuOH)}_1]^+\) and (d) \([5\text{HI(NH)-(t-BuOH)}_1]^+\) obtained at the M06-2X/aug-cc-pVDZ level of theory. The harmonic frequencies were scaled by 0.9424.
Figure 5.7. Calculated stable structures of (a) $[5\text{HI(OH)}-(t\text{-BuOH})_1]^+$, (b) $[5\text{HI(NH)}-(t\text{-BuOH})_1]^+$, (c) $[5\text{HI(CH)}-(t\text{-BuOH})_1]^+$ and $[5\text{HI(\pi)}-(t\text{-BuOH})_1]^+$ in the $D_0$ state, obtained at the M06-2X/aug-cc-pVDZ level of theory. The right-hand side of the figure shows each lateral view of an aromatic plane, while the right-hand side shows the structures seen from the yellow arrow in the left. Relative stabilization energies are given in wavenumber units. The zero-point vibrational energy and basis set superposition error are corrected for all values.
(c) [5HI(CH)-(t-BuOH)\(_1\)]^+ (+ 4122 cm\(^{-1}\))

(d) [5HI(\(\pi\))-(t-BuOH)\(_1\)]^+ (+ 4600 cm\(^{-1}\))
Figure 5.8. PIE spectra of (a) 5HI(OH)-(t-BuOH)$_1$ and (b) 5HI(NH)-(t-BuOH)$_1$ obtained via the origin transition of each isomer. The inset arrows indicate the field-corrected $I_E^0$ values of each isomer.
Figure 5.9. Measurement of energy threshold for isomerization of \([5\text{HI(NH)-(t-BuOH)}]_1^+\) to \([5\text{HI(OH)-(t-BuOH)}]_1^+\), based on Figure 4.11. The delay time between \(v_2\) and \(v_{\text{IR}}\) was 700 ns. The IR laser was fixed at 3464 cm\(^{-1}\), corresponding to the free \(v_{\text{NH}}\) band of \([5\text{HI(OH)-(t-BuOH)}]_1^+\). The horizontal axis indicates the internal energy of \([5\text{HI(NH)-(t-BuOH)}]_1^+\) obtained from the difference between \((h\nu_1 + h\nu_2)\) and \(IE_0^{NH}\). The inset arrow shows the upper limit of the isomerization threshold from \(IE_0^{NH}\), denoted as \(E_b^{NH}\).
Figure 5.10. Energy diagram for 5HI(OH)-(t-BuOH)$_1$ and 5HI(NH)-(t-BuOH)$_1$ in the S$_0$ and D$_0$ states. The solid-black arrows display the experimental $IE_0$ values. The dashed-gray arrows show the theoretical binding energy of each isomer in D$_0$ ($BE^{OH}$ and $BE^{NH}$), and the difference in the theoretical binding energy of each isomer in S$_0$ ($\Delta E_{neutral}$) calculated at the M06-2X/aug-cc-pVDZ level of theory. The solid-gray arrow was obtained from ($IE_0^{NH} + \Delta E_{neutral}$) - $IE_0^{OH}$. All values are indicated in wavenumber units.
Figure 5.11. Schematic diagram of the stabilization of the H-bonded isomers (OH and NH) and the transition state. The elevation of $E_b$ is caused by the larger stabilization of the H-bonded isomers than that of the transition state. See the text for more details.
References for chapter 5


Chapter 6.

Concluding remarks
6.1. Concluding remarks

Solvated cluster cations are one of the ideal systems to investigate the rearrangement of a solvent molecule and the fluctuation of the hydration structures at the molecular scale. Sophisticated laser spectroscopy applying to the solvated cluster cations allows us to understand where a solvent molecule comes from, where a solvent molecule moves to, and when the cluster cations show the rearrangement and/or fluctuation of H-bonds. Some research groups reported the studies on photoionization-induced solvation dynamics in solvated clusters. In particular, ionization-induced $\pi$-H site switching reactions in phenol-(rare gas) clusters have been well investigated by IR-dip spectroscopy in nanosecond and picosecond time domains.\textsuperscript{1-6} These spectroscopic studies have provided various experimental details of the site switching reactions (e.g. the reaction rates and the potential energy diagrams of [phenol-(rare gas)]$^+$).

Hydrated clusters, which have a strong H-bond and whose water molecule have the larger degree of freedom than those of rare gases, are ideal model systems to investigate the elementary processes of the rearrangement and/or fluctuation of H-bonds in aqueous solutions at the molecular level. Some hydrated clusters show the rearrangement of H-bond induced by photoionization, and the reaction rates were revealed by picosecond time-resolved spectroscopy.\textsuperscript{7-15} However, the potential barrier heights for the rearrangement processes, which are important physical quantities to understand the energetic details of the photoionization-induced rearrangements of H-bond, have never been determined experimentally due to the lack of the precisely determined experimental values of the adiabatic ionization energy ($I_E_0$). Furthermore, the previous studies do not report the fluctuation of the H-bonded structures but the
"one-way" rearrangement of H-bonds. Therefore, in this thesis, we explored the solvation dynamics of [BA-(H_2O)_1]^+, [5HI-(H_2O)_1]^+, and [5HI-(t-BuOH)_1]^+ experimentally to reveal the fundamental characteristics of the fluctuation of hydrated structures.

In [BA-(H_2O)_1]^+, we succeeded in experimental observation of the fluctuation of the hydrated structures among [BA(OH)-(H_2O)_1]^+ and [BA(Free)-(H_2O)_1]^+ in the D_0 state, which is similar to the rearrangement of H-bonds in aqueous solutions. However, the potential barrier height of the structural fluctuation in [BA-(H_2O)_1]^+ cannot be determined at the present stage.

In [5HI-(H_2O)_1]^+, the structural isomerization of [5HI(NH)-(H_2O)_1]^+ to [5HI(OH)-(H_2O)_1]^+ was successfully observed. We note that the backward isomerization ([5HI(OH)-(H_2O)_1]^+ to [5HI(NH)-(H_2O)_1]^+) also occurs. Furthermore, the potential barrier height for the isomerization of [5HI(NH)-(H_2O)_1]^+ to [5HI(OH)-(H_2O)_1]^+ (E_{bNH}^N) was determined to be 2127 ± 30 cm\(^{-1}\). Since the total amount of the internal energy in [5HI-(H_2O)_1]^+ is conserved in vacuum, above the potential barrier, the water molecule in [5HI-(H_2O)_1]^+ may fluctuate between the two preferential H-bonding sites of [5HI(OH)-(H_2O)_1]^+ and [5HI(NH)-(H_2O)_1]^+.

In [5HI-(t-BuOH)_1]^+, the structural isomerization of [5HI(NH)-(t-BuOH)_1]^+ to [5HI(OH)-(t-BuOH)_1]^+ was observed after photoionization via the origin transition of 5HI(NH)-(t-BuOH)_1. Furthermore, based on the upper limit of the IE_0 values, the lower limit of the potential barrier height for the E_{bNH}^N of [5HI-(t-BuOH)_1]^+ was determined to be 3362 ± 30 cm\(^{-1}\), which is approximately 1200 cm\(^{-1}\) higher than that for [5HI-(H_2O)_1]^+ (2127 ± 30 cm\(^{-1}\)). The elevation of the E_{bNH}^N may be caused by the increase in the binding energy of the OH and NH isomers of [5HI-(t-BuOH)_1]^+ due to
the larger proton affinity of t-BuOH than that of H$_2$O.

The most remarkable achievement in the thesis is the experimental determination of the potential barrier height for the rearrangement of a water in [5HI-(H$_2$O)$_1$]$^+$. This is the first experimental report on the determination of the potential barrier height for the rearrangement of H-bonds in hydrated cluster cations, indicating that the rearrangement of a water in [5HI-(H$_2$O)$_1$]$^+$ has a great advantage for investigating the detailed solvation dynamics in terms of the forward and backward reaction rates and internal energy. For example, applying the time-resolved IR spectra by using 2C-R2PI for 5HI-(H$_2$O)$_1$ would allow us to investigate the internal energy dependence of the rearrangement. Furthermore, theoretical studies such as molecular dynamics (MD) simulations may provide the information on the reaction coordinates and the intermediate structures of [5HI-(H$_2$O)$_1$]$^+$ as well as the internal energy dependence of the rearrangement. Thus, [5HI-(H$_2$O)$_1$]$^+$ is one of the ideal systems to reveal the detailed rearrangement process of a single water molecule at the molecular level. In addition, the elevation of potential barrier height of [5HI-(t-BuOH)$_1$]$^+$ as compared with that of [5HI-(H$_2$O)$_1$]$^+$ may be a typical phenomenon which reflects the different nature of solvent molecules. The elevation of the potential barrier height in solvated 5HI cluster cations should also be investigated systematically for the various types of solvent molecules. Finally, we hope that this thesis contributes to the progress of the study of the H-bond dynamics in H-bonded clusters as well as in various solutions.
References for chapter 6


Chem. Phys. 2015, 17 (44), 29969–29977.
Acknowledgements

All works in the present thesis were accomplished at Kyushu University in collaboration with Prof. Hiroshi Sekiya, and financially supported by Grants-in-Aid for JSPS fellows (13J02937), Scientific Research C (25410022), Scientific Research B (26288010), and Scientific Research on Innovative Area (26104527).

I would like to appreciate Dr. Hiroshi Sekiya (Professor, Kyushu University) for giving the great research environment, encouragements and discussions. I am grateful to Dr. Kazuhiko Ohashi (Associated Professor, Kyushu University) for helpful comments and advices. I wish to deeply acknowledge Dr. Kenji Sakota (Assistant Professor, Kyushu University) for such extensive discussions and valuable advices for my life. I would also like to thank Dr. Masaaki Fujii (Professor, Tokyo Institute of Technology) and Dr. Mitsuhiko Miyazaki (Assistant Professor, Tokyo Institute of Technology) for meaningful discussions on the H-bonding dynamics in 5HI-(H2O)$_1$. I acknowledge all graduated and present members of the laboratory of structural chemistry in Kyushu University. Finally, I gratefully thank my parent and family for their long-term encouragements and financial supports.

Takamasa Ikeda

Fukuoka, Japan
January, 2016