

Kiyokazu Fuke

Emeritus Professor, Kobe University

[Present Position]

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[Research Field]

Molecular Science, Laser Spectroscopy, Cluster Chemistry

[Date of Birth]

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Mar. 1975 Doctor of Science, University of Tokyo

(Thesis title: Electronic structures and intavalence and extravalence transitions of unsaturated organic compounds)

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[Professional Career]

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Apr. 1981 - Oct. 1988

Assistant Professor and Lecturer of Chemistry, Keio University.

Nov. 1988 - Jun 1995

Associate Professor, Institute for Molecular Science.

Jul. 1995 – Mar. 2010

Professor of Chemistry, Kobe University.

[Apr. 2004 - Mar.2005 ;

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Feb. 2012 - Mar, 2016

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[Membership]

The Chemical Society of Japan, Japan Society for Molecular Science, The Spectroscopical Society of Japan, American Chemical Society.

Research Overview

Toyota Physical and Chemical Research Institute, Kiyokazu Fuke

1 . Before 1981

In the spring of 1970, I started research as a graduate student under Prof. Saburo Nagakura in Department of Chemistry and Institute for Solid State Physics (ISSP) of Tokyo University. The research subject was the UV and VUV spectroscopies on single crystals of unsaturated organic compounds using microspectrophotometer and normal-incidence reflection spectrophotometer. The spectrometers, which were constructed by Dr. Koji Kaya, were in Nagakura's laboratory at Wako campus of Riken. We successfully elucidated the intra- and inter-molecular interaction of aromatic rings, for example, in paracyclophane derivatives¹ and in perylene crystals.

After two years of postdoctoral works in US (with Prof. M. Tamres of University Michigan and with Prof. O. Schnepp of University of Southam California), I moved to Kanazawa University to join the group of Prof. Michiya Itoh as a research associate. He kindly proposed me to start a new research project of my own. Because at that time the experimental facilities were so limited as were in the other laboratories in Japan, I decided to study the electronic relaxation processes of organic molecules in solution using the thermal lensing technique, which requires a relatively simple optical setup. Around that time, the electronic relaxation processes were one of the subjects of intensive studies. However, almost all of the studies were concerned with the observation of the photoemission from the excited states; by measuring the decay time and the yield of emission, the reactivities in the excited states were examined. The technique I had chosen is bases on the detection of transient fluctuation of the refractive index of medium, which is referred to as a thermal lens effect. The effect is induced by a local heating of the medium through a nonradiative deactivation of the excited states. This technique is enable us to carry out an extremely sensitive absorption spectroscopy. Because the response time of the refractive-index fluctuation is determined by the sound velocity in the medium, by monitoring the transient thermal lens, I expected we could attain a few ns time-resolution in a focused laser beam to study the electronic relaxation process during the chemical reactions. I invented a transient thermal-lens method to directly observe the time responses of the excited-state decay and the photoinduced reactions involving reaction intermediates. We demonstrated for the first time the application of this technique to the photochemical reactions producing a radical species, difficult to directly detect. With this method, we also succeeded to observe the singlet oxygen ($^1\text{O}_2$; $^1\Delta_g$) of an extremely low emission yield, and determined the lifetimes of $^1\text{O}_2$ in various organic solvents and elucidated its importance as a chemical intermediate.²

2. Research at Institute for Molecular Science

In the spring of 1981, I moved to Department of Chemistry, Faculty of Science and Technology, Keio University to work with Prof. Koji Kaya. He just started a new laboratory in the newly-established Department. We began constructing the setup of the pulsed supersonic jet technique combined with tunable dye lasers. The former technique, first introduced to molecular spectroscopy by R. E. Smalley in the late 1970's,³ allows us to cool the translational temperature below a few kelvin and to freeze out the rotational motion of even

medium-sized molecules such as benzene. The spectra of all such molecules could be studied without rotational congestion. Many research groups in the world started to study the visible and UV spectra of the jet-cooled molecules by using laser-induced fluorescence excitation techniques. For us, most important feature of supersonic beam was the formation of clusters of atoms and molecules. The studies of weakly bound clusters allow us to understand how the properties of atomic and molecular clusters vary as a function of size, and to examine the stepwise development of condensed phase attributes. Thus they allow us to bridge the gap between isolated molecules and condensed matter. We successfully set up a state-of-the-art supersonic beam apparatus with a pulsed supersonic nozzle and a quadrupole mass filter. The machine could be also adapted for a resonant two-photon ionization (R2PI) detection technique in addition to the ordinary fluorescence detection, so that we immediately started to study the spectrum of mass-selected clusters in the supersonic beam. We used this to probe the structure and dynamics of various molecular clusters, particularly focusing on the question of microscopic solvation process.

We also constructed a laser vaporization cluster beam apparatus, which adapted a Smalley's technique⁴, and allowed us to produce the cold atom clusters of any element in the periodic table. We initiated a series of studies on metal clusters, which are closely related with surface chemistry. In the following paragraphs, I present the brief summaries of some of pioneering works not only on jet cooled spectra of van der Waals complexes, but also on spectroscopy and reaction dynamics for the hydrogen-bonded clusters.

3. Spectroscopy on Hg-rare gas van der Waals Complexes in molecular beam

The spectroscopic profiles of the metal atoms perturbed by rare gases have been the subject of numerous investigations for many years, because they are necessary to understand the interaction potentials and to explore a lamp material. Previously the spectral studies of metal atom-rare gas complexes were possible only

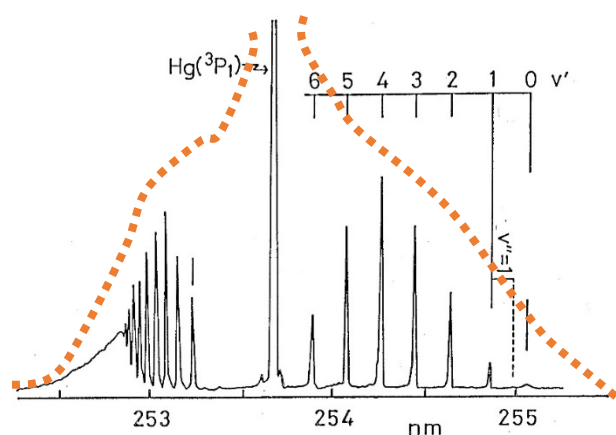


Fig. 1 (a) Fluorescence excitation spectrum of Hg-Ar complex in a supersonic jet. The intense band at 253.7 nm is due to free Hg atom (3P_1). The dotted lines shows the typical emission profile of the resonance line broadened by Ar observed in a high-temperature cell experiment.

at high temperature, and therefore the observed absorption and emission spectra were so broad for precise analysis of the electronic structures. In particular, the profile of the 253.7 nm resonance line (3P_1) of mercury atom (Hg) perturbed by rare gases had been the subject of extensive studies because of the above-mentioned importance as well as its application to the photosensitized chemical reactions. In our study, with free expansion of Hg rare-gas mixtures, the Hg-rare gas molecules with vibrational and rotational temperatures below a few kelvin are generated. Figure 1 shows the fluorescence excitation spectrum of Hg - Ar van der Waals complex, in

which the vibronic transitions to the Π - and Σ -type excited states are clearly resolved in the lower and higher

energy regions of the 3P_1 resonance line.⁵ From the analysis of the spectrum in Fig. 1 and the dispersed fluorescence spectra obtained by the excitation at each vibronic bands, we determined for the first time the precise interatomic potential functions for the ground and the Π - and Σ -type excited states. We also examined the complexes with the other rare gases and molecules such as N_2 , CO , and CH_4 , and obtained rich information on the spectroscopy and dynamics of the excited states of the van der Waals molecules. After our studies, this technique was extensively used by the other groups in the studies on the metal atom - molecule interaction and become the standard tools by replacing the conventional techniques such as high-temperature cell experiments.

4. Stepwise solvation process of phenol in small water clusters

Hydrogen bonding was recognized for a long time as being important in a wide variety of the physical and chemical phenomena, including solvation effects. Numerous valuable experimental measurements on H bonding were mostly carried out for bulk systems, for examples, by observing the absorption and fluorescence spectra in liquids, by determining the boiling and melting point changes, and with X-ray crystallographic measurements of H bonded solids. In these experimental methods, the effects of bulk solvation on the solute

system have to be convoluted with molecular aspects of the H bonding, to elucidate fully the details of the influence of the H bonds. With the advent of supersonic molecular beams, H- bonded clusters can be created with a size-selective fashion and the powerful laser-based spectroscopic techniques can be applied to the size-selected species to deconvolve the effects of the solvent from H-bonding interactions. Furthermore, the cooling of vibrational and rotational modes in the cluster considerably simplifies assignment of the optical spectra.

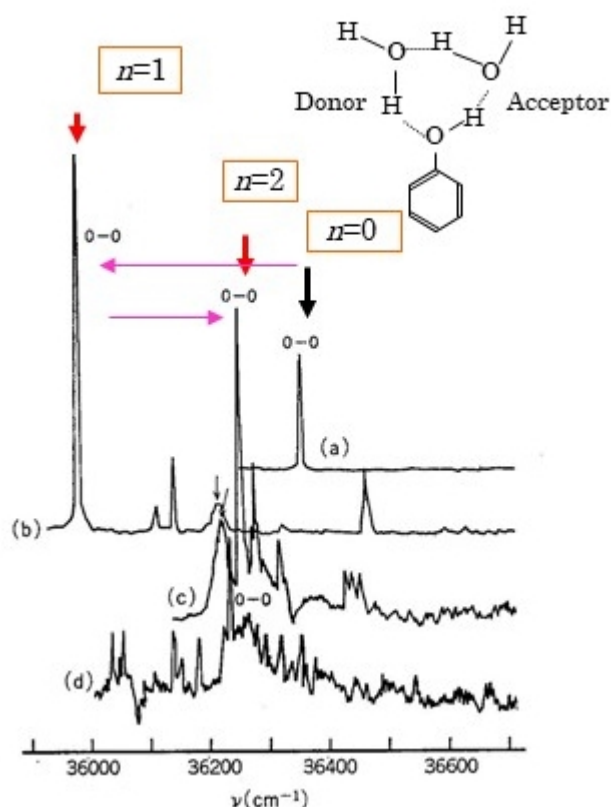


Fig. 2 MS-MPI spectra of the S_1 - S_0 transitions of phenol- $(H_2O)_n$; (a) $n=0$, (b) $n=1$, (c) $n=2$, and (d) $n=3$. The origin of phenol monomer is observed at 36352 cm^{-1} , while those of $n=1$ and $n=2$ are 35996 and 36259 cm^{-1} , respectively.

addition of the first water molecule, the 0 - 0 transition of phenol molecule is shifted to the red by 356 cm^{-1} , while the band shifts to the blue by 263 cm^{-1} by the second water molecule. On the other hand, the 0 - 0 band

From these points of view, we initiated the study for the first time on the hydration process of phenol, which is the chromophore of an important amino acid such as tyrosine. We used a mass-selected multiphoton ionization (MPI) technique to spectroscopically examine the effects of the stepwise H-bonds of water molecules to phenol. Figure 2 shows the vibronic transitions of the electronic absorption spectra of phenol $(H_2O)_n$ ($n=0$ -4) at near origin of the $S_1 - S_0$ transition.⁶ With an

of $n = 3$ shifts only slightly to the red from that of $n = 2$. From the spectral shifts, the first water molecule in phenol-(H₂O) attaches to the proton of the O—H group of phenol and phenol acts as a proton donor in the hydrogen bonding, and the second water attaches to the oxygen atom of the O—H group of the monohydrated phenol and phenol behaves as a proton acceptor to the second water. The second water also accept the proton of the first water to stabilize the system and form a cyclic structure. In these studies, we demonstrated for the first time how the spectroscopic study on microscopic solvation with hydrogen bonds is informative to mimic the solvation process in bulk solution. After these pioneer studies, the spectroscopic studies on microscopic solvation with polar molecules became one of the main subjects in the gas-phase cluster research.⁷

5. Dynamics of proton-transfer reaction in model hydrogen bonded base pairs

Proton transfer processes have received a great deal of attention by the broad scientific community due to both the fundamental interest in their behavior as well as their significance in chemical and biological processes. Hydrogen-bonded amino groups are ubiquitous in nature; the hydrogen bonds involving the amino groups play a key role in the nucleic acid base pairing in DNA and RNA; an amino group donates a hydrogen to an electronegative oxygen or nitrogen. The N—H groups of the nucleic acid bases have a complementary role in the pairing for the genetic coding in DNA and RNA. Also, the hydrogen bond strength determines the possible occurrence of proton or hydrogen transfer between donating and accepting groups, to form tautomers. Among these hydrogen bonded dimers, 7-Azaindole dimer (7-AI)₂ has been one of the most intensively studied model compound in nucleic acid base pairs. Electronic excitation of (7-AI)₂ in the UV spectral region results in excited-state double proton transfer (DPT), leading to the formation of tautomer, which emits the visible fluorescence peaking at 520 nm. The excited state double proton transfer in 7-AI dimer was first examined in early steady-state solution-phase experiments with various laser spectroscopic techniques to clarify whether this process can be of significance in mutagenesis. In solution, however, the solvation effect blurred the spectroscopic details and the reaction features of model base pairs, and as a result, the understanding of the characteristics of the proton transfer reaction was very limited. To answer the questions and to unveil the potential energy surfaces involved and the reaction dynamics progressed, the absorption and emission properties of supersonically cooled (7-AI)₂ were examined for the first time at vibrational temperature of less than a few kelvin in molecular beam. Figure 3 shows a typical fluorescence excitation spectrum of (7-AI)₂ near the origin at 32252 cm⁻¹ by monitoring the visible tautomer emission; The spectrum corresponds to the action spectrum of the proton-transfer reaction,⁸ and consists of the progressions and combinations of 98 and 120 cm⁻¹ vibrations which are assigned to the intermolecular bending and symmetric stretching vibrational modes. The bandwidth of the origin band (5 cm⁻¹) is much wider than that of monomer (2 cm⁻¹), which indicates a spectral resolution of our experimental system. The $\nu' = 1$ and $\nu' = 2$ bands of the 120 cm⁻¹ vibration exhibit the bandwidths of 10 and 30 cm⁻¹ (fwhm), from which the excited-state lifetimes are estimated to be 0.5 and 0.2 ps, respectively. The results imply that the proton transfer reaction proceed from the zero vibrational level in the first excited state through tunneling process. The spectrum also exhibits the other important features of the reaction dynamics. One of examples is a vibrational mode dependence of the reaction rate. As seen in Fig. 3, the bandwidth of the $\nu' = 1$ band of the 98-cm⁻¹ vibration is only 3 cm⁻¹, while that of the combination band with the 120 cm⁻¹ vibration at

215 cm^{-1} above the 0-0 band again increases more than twice (7 cm^{-1}), indicating the enhancement of the rate

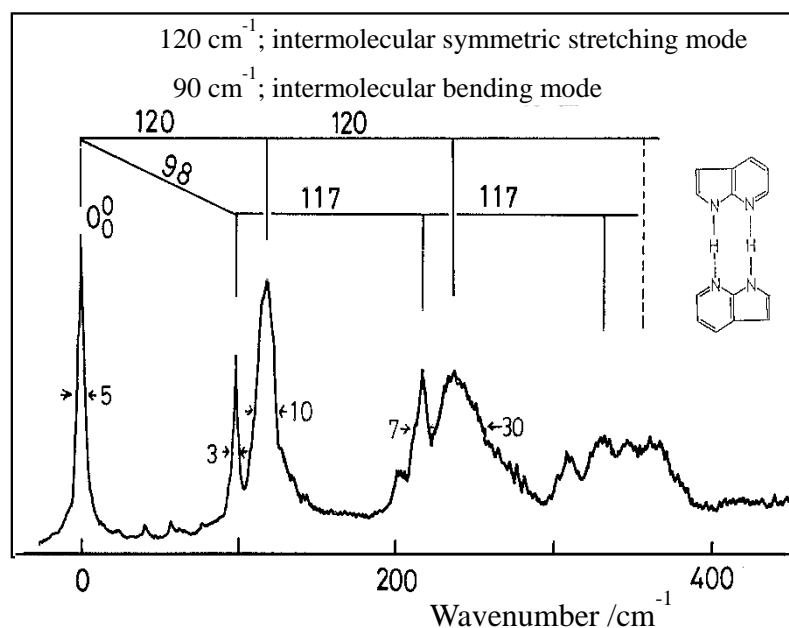


Fig. 3 Fluorescence excitation spectrum of jet-cooled 7 AI dimer obtained by monitoring visible emission of tautomer. The spectrum corresponds to the action spectrum of the DPT reaction. The numbers inserted with arrow are the bandwidths (fwhm) in cm^{-1} .

of the DPT reaction at this mode. These results clearly indicate that the 120 cm^{-1} vibration is the promoting mode of DPT reaction in the 7-AI dimer. Thus, the dynamical features of the proton-transfer reaction were elucidated for the first time. The issues on the mechanistic nature of the proton transfer in the 7-azaindole dimer have subsequently been the subjects of extremely intensive studies and explored in depth by means of theories and experiments.⁹

6. Research at Institute for Molecular Science

In the autumn of 1988, I moved to Okazaki as associate professor at Institute for Molecular Science. I had an opportunity to do some extended reading journal articles, searching for possible topics for starting the new research on the gas-phase clusters. After the recharging days in the IMS library, one of the topics I chose was the spectroscopic study on atomic clusters of semiconductor elements. The study on the physical properties of these clusters were quite limited, because the small semiconductor clusters have high ionization potentials and it was difficult to ionize by a commercial laser. I also re-recognized that the clusters containing metal ions and solvent molecules have extensively been studied for more than two decades by several research groups, to bridge the gap between the gas and condensed phases. However, these studies were mostly concerned with the thermodynamic properties with high-pressure mass spectrometry and collision induced dissociation experiments, and the structural information was based mainly on the theoretical calculations. I expected that the spectroscopic studies on the clusters consisting of metal ions with polar solvent molecules may provide us rich structural and energetic information on the stepwise solvation processes in finite clusters. Moreover, the molecular beam method coupled with the laser vaporization technique allows us to produce the solvated metal ions of any element in the periodic table and therefore, a new field of cluster chemistry could emerge. In the next paragraphs, I present the brief summaries of the photoionization studies on semiconductor clusters and some of the pioneering works on solvated metal atoms (ions) related not only to solvated electrons, but also to the redox reactions of metal ions in solvent clusters. The latter works were conducted in collaboration with Dr. Fuminori Misaizu (Tohoku University), and the theoretical groups of Dr. Suehiro Iwata (Keio University) and

7. Photoionization studies on semiconductor clusters

The physical properties of small silicon clusters have been an extremely active area of both experimental and theoretical studies because of its importance in fundamental as well as applied sciences. The motivation for the studies is to elucidate what happens to the physical and chemical properties of a bulk material as dimensions approach interatomic distances and to determine whether there are any special clusters with unique properties. Especially, information on the electronic structures is indispensable to characterize the small silicon clusters. It also becomes important after the discovery of emissive nanometer-scale silicon clusters. Studies of the electronic structures of Si_n were hampered by high values of the IPs and also by the very low volume density of

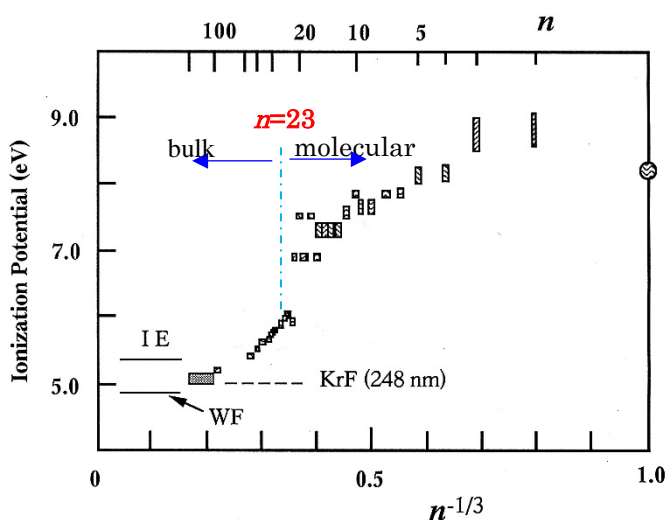


Fig. 4 Ionization potentials of Si_n , $n = 2 - 200$, plotted vs $n^{-1/3}$ and the bulk ionization energy and work function for Si(111). The solid line is the prediction of a classical conducting spherical droplet model.

silicon clusters produced in the laser vaporization source. Photoelectron spectroscopy of negatively charged clusters and the photoionization experiments of neutral clusters have been conducted to gather information on the growth of the electronic level structure of Si_n , but the clusters examined were still limited to small size.

To overcome these situations, we carried out the photoionization threshold measurements for Si_n with an unprecedentedly wide photoionization energy (5.0–8.5 eV) using an IP bracketing. A high-output vacuum ultraviolet (VUV) laser was developed as the photoionization light source in the energy above

6.42 eV (ArF excimer laser), in addition to the second harmonic of an excimer-pumped dye laser below this energy. We adopted the anti-Stokes shifting technique to generate radiation down to 146 nm, because this method may enable us to generate the highest energy output in VUV with a combination of commercial lasers. Figure 4 shows the size-dependence of IPs of Si_n , $n = 2 - 200$.¹⁰ The major maxima at the cluster sizes of 10 and 20 atoms and a large gap in IPs between $n = 20$ and 22 are found. Figure 4 shows that the IPs decrease smoothly up to 5.17 eV for the cluster size of $25 < n < 100$. For larger clusters with Si atom of $n = 100 - 200$, IPs does decrease to 5.17–4.99 eV, which are slightly higher than the bulk work function (4.85 ± 0.02 eV) determined by photoemission threshold measurements. The discrepancy of IPs between clusters and bulk were attributable to the difference in the distribution of surface states for these phases.

We also extended to the studies for Ge_n ($n = 2 - 57$) and Sn_n ($n = 2 - 41$) in the energy region of 5.0–8.8 eV.¹¹ The IPs of the clusters with fewer than 11 atoms were found to exhibit the size dependence very similar to that for Si_n including the major maximum at 10 atoms, which implies the similarity in the geometrical and electronic structures for these clusters. Based on the theoretical results in the literature, we discussed the size dependence

of IPs for small germanium and silicon clusters in relation to the compact metal-like structures. We found the remarkable difference in the size dependence of the IPs for the medium-size Si_n , Ge_n , and Sn_n clusters. Ge_n ($n > 12$) clusters were found to exhibit the large gap in IP at around 20 atoms, similar to that found for Si_n . On the other hand, the IPs of large tin clusters decrease slowly without a gap. The large IP gaps for the Si_n and Ge_n clusters were attributed to the possible existence of a structural transition, reported in the mobility measurements for the cluster ions. The IPs of semiconductor clusters were systematically determined for the first time ever, and they become the reference values to elucidate the accuracy of the theoretical calculations of the clusters for the last decades.

8. Spectroscopic studies on solvated electron in finite-size clusters

Solvated electrons in polar solvent have been the subject of intensive studies for the last decades. Recent advances in laser spectroscopy permit one to obtain unique information on the dynamical aspects of the solvated electron, especially on the early stage of solvated-electron formation in solution. Despite these efforts, the microscopic structure and dynamics of the solvated electron in solution remain unresolved. One of the most intriguing and difficult issues may be the many-body interaction between a diffuse electron and solvent molecules. It is difficult to fully understand the solvation dynamics of the electron in polar solvent without detailed knowledge on the nature of the diffused electron. On the other hand, these issues are significantly simplified in clusters, in which the fundamental interaction in solution may be retained. The cluster study enables us a direct comparison between the experimental and theoretical results and will provide information on the intrinsic nature of the solvated electron. From this point of view, we carried out a series of pioneering

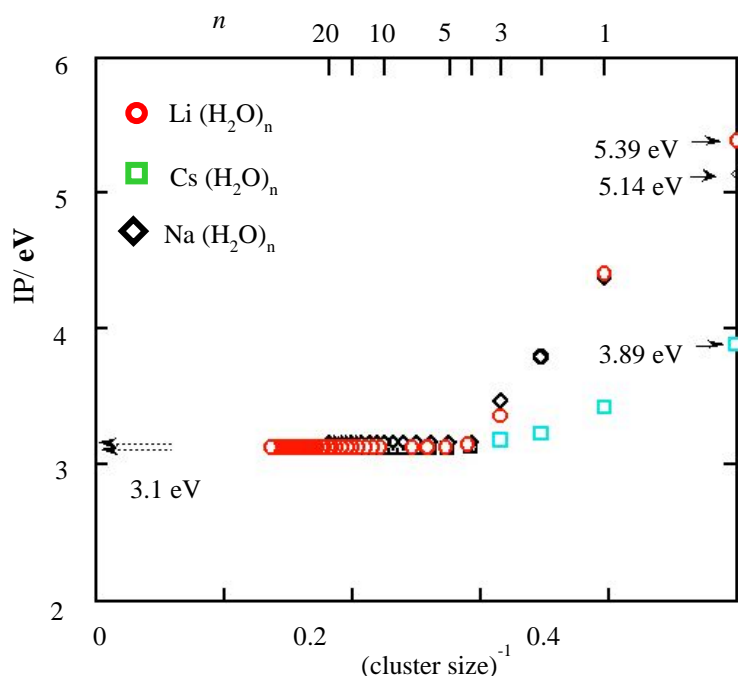


Fig. 5 Ionization potentials (IPs) of $\text{Li}(\text{H}_2\text{O})_n$ (\circ ; ref. 13), $\text{Na}(\text{H}_2\text{O})_n$ (\diamond ; ref. 12), and $\text{Cs}(\text{H}_2\text{O})_n$ (\square ; ref. 13) plotted as a function of $n^{-1/3}$. IPs of these clusters for $n \geq 4$ are $3.1 \pm 0.05 \text{ eV}$.

experiments on solvated electron in finite-size clusters using the photoionization and photoelectron spectroscopies.

The polar-solvent clusters containing neutral alkali atoms are the prototype of a dilute alkali metal solution, in which solvated electrons have been investigated extensively, and may serve as a good model for linking the microscopic properties with macroscopic ones of alkali metal-solvent systems. In these clusters, the valence electron of an alkali metal atom is expected to be transferred to a solvent cluster with sufficiently large n , and the ground state is expected to be of an ion-pair character as in the case of

bulk fluids. To find this transition, Hertel's¹² and our groups¹³ investigated the photoionization processes of the clusters consisting of alkali metal atoms of Li¹³, Na¹² and Cs¹³ with ammonia and water molecules. Figure 5 shows the size-dependence of ionization potentials (IPs) of Li(H₂O)_n, Na(H₂O)_n, and Cs(H₂O)_n. We found the rapid converge of IPs at $n = 4$ (3.2 eV), independent on the metals, to the estimated photoelectric threshold of ice. On the other hand, the IPs of metal-ammonia clusters decrease monotonously for n as large as 40; its limiting values again agree with the bulk photoelectric threshold of liquid ammonia at ca. 1.4 eV. These characteristics in IPs were analyzed in terms of the stabilization of an ion-pair state correlating with the solvated-electron state in bulk solution. Several theoretical groups have also made efforts to correlate the IP behaviors with the solvation state of alkali atoms. However, because the experimental data were limited only to the IP measurements, the microscopic solvation process of alkali-metal atoms in clusters has not yet been fully understood.

To get further insight into the electronic structure of solvated alkali atoms, we constructed a magnetic-bottle type

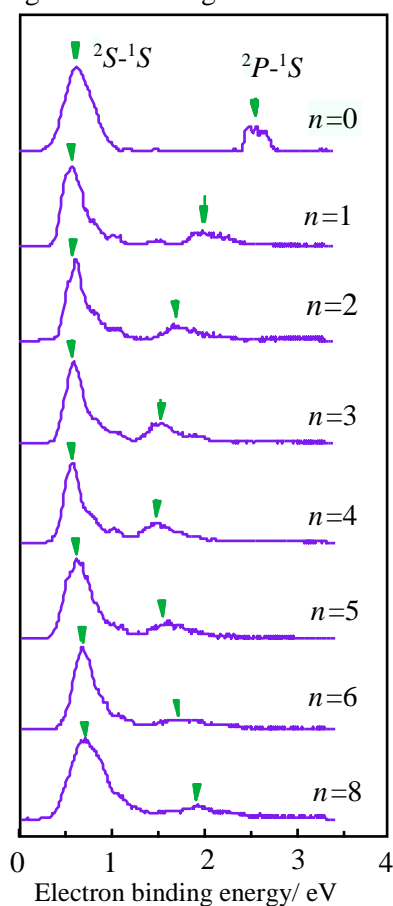


Fig. 6 Photoelectron spectra of Li⁺(D₂O)_n ($n = 0 - 10$), collected using a photodetachment energy of 3.50 eV. In order to improve the mass separation, D₂O is used instead of H₂O.

photoelectron spectrometer and studied the photoelectron spectra of the closed shell anions, M⁻(H₂O)_n and M⁻(NH₃)_n (M = Li, Na), produced by a laser vaporization technique coupled with a supersonic expansion method. Because the final states of the photoelectron transitions of the anion clusters are the ground and excited states of neutral clusters, the photoelectron spectra as a function of size provide information on how the electronic structure of alkali atom in both the neutral ground and excited states changes with the solvation number, n .

The photoelectron spectra of Na⁻(NH₃)_n and Li⁻(NH₃)_n indicate that the electronic structure of alkali atoms in ammonia clusters are extensively changed with the cluster size. Especially, in the case of Li⁻(NH₃)_n, the 3²S- and 2²P-type states of clusters were dramatically stabilized and almost become degenerate with the ground state (2²S) for $n \geq 10$.¹⁴ This trend in PES is consistent with the theoretical results that the SOMO electron density of the alkali atom is delocalized over and beyond the solvent molecules with increasing n . These findings suggest that the photoionization process of the larger clusters corresponds to the ejection of an electron over the delocalized region of solvent molecules. The observations that the Li-, Na-, and Cs-ammonia clusters have the same IP value for $n \geq 5$ support the above conclusions. The characteristics of the PES exhibit the early stage of the spontaneous ionization of the alkali-metal atom in ammonia

clusters to form the one-center (Rydberg like) ion-pair state.

As for the alkali atom-water clusters, we had also examined the PESs of closed shell ions Li⁻(H₂O)_n and Na⁻(H₂O)_n. Because of the large difference in the geometrical structures of the anion and neutral states for Na⁻

(H₂O)_n, we could not obtain information on the electronic structure of the neutral clusters. On the other hand, the anomalous red-shift of the Li (²S) – Li⁺(¹S) - type transition was found in the PES of Li⁺(H₂O)_n for $n \leq 4$, and as shown in Fig. 6, for $n \geq 5$ the spectral shift together with the sudden increase of the bandwidth were observed.¹⁵ The large solvation energy of the neutral clusters, compared with the corresponding energy of the anion clusters, was ascribed to the increase in ionic character resulting from the spontaneous ion pair formation, Li⁺ -- (H₂O)_n⁻. Through these studies, we could experimentally demonstrate for the first time the early stage of solvated-electron formation from alkali atoms in small ammonia and water clusters.

9. Spectroscopic studies on solvation processes of alkaline-earth metal ion in water clusters

The redox reaction process of metal ions related to the solvated-electron formation has been one of the central issues in solution chemistry, and has a long history in inorganic chemistry. In most of the previous studies, the molecular level of analysis for solvation of the atomic ions had to be guessed from the properties of bulk solvation, and therefore, the solvation process was not fully elucidated. Advances in molecular beam techniques allow us to create size-controlled hydrated metal ion clusters. Thus the solute-solvent interaction can be controlled, and the laser-based gas phase spectroscopic techniques can be applied to examine in details the effects of solvation on metal ions, and to follow its induced reactions with solvent. Moreover, because the clusters are much simpler than the bulk solution systems, further clarification becomes possible by performing the direct theoretical calculations of the target systems. We carried out for the first time the spectroscopic studies to reveal the electronic structures, geometrical structures, and oxidation reactions of hydrated monovalent metal ions, Mg⁺(H₂O)_n and Ca⁺(H₂O)_n, produced by multiple collisions between the laser-vaporized atomic ions and the water clusters. With a series of papers, we successfully developed a new field of the gas-phase metal-ion chemistry in finite size clusters.¹⁶

(1) Spectroscopy on hydrated metal ions: Geometries and electronic structures

Hydrated metal ions such as Mg⁺(H₂O)_n was synthesized by expanding the laser-vaporized alkaline-earth metal ions with a method with a water vapor seeded in high pressure He. A reflection-type time-of-flight (TOF) mass spectrometer was utilized to examine the photodissociation products as well as the dissociation spectrum of mass-selected cluster ions. During the photodissociation process of Mg⁺(H₂O)_n, not only the evaporation of one or more water molecules (1) but also the photoinduced chemical reaction to produce hydrated MgOH⁺ ions (2) are found as follows;

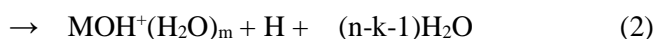
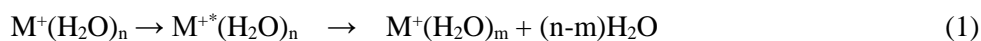


Figure 7 shows photodissociation spectra of Mg⁺(H₂O)_n, $n=1-5$, obtained by taking the total yield of fragment ions as a function of photolysis wavelength.¹⁸ The spectrum of $n=1$ consists of an intense band at 30500 cm⁻¹ with a weak shoulder at 28300 cm⁻¹, and another band at 38500 cm⁻¹, which locate close to a Mg⁺ resonance line. These bands were assigned to the transitions to ²B₁(p π_x), ²B₂(p π_y), and ²A₁(pσ), respectively. For $n=2$, a new overlapped band at 30500 cm⁻¹ was observed in addition to the band at 25000 cm⁻¹. The dissociation

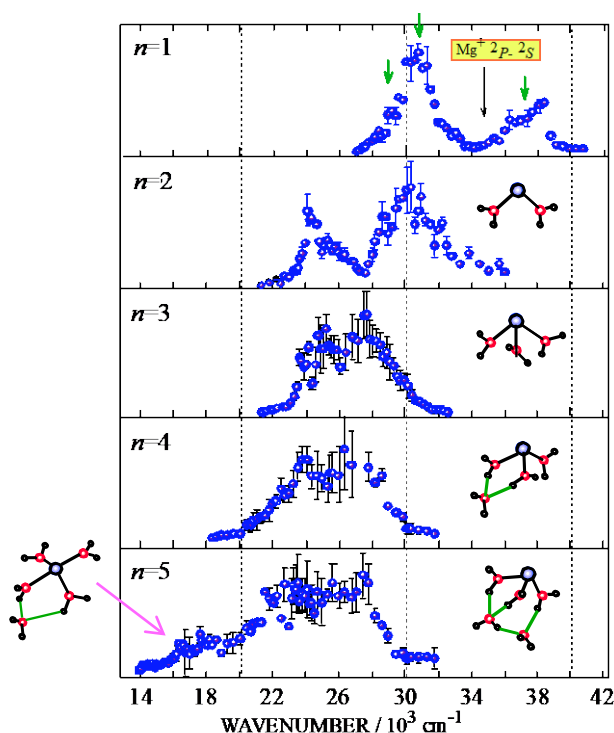


Fig. 7 Photodissociation spectra of $\text{Mg}^+(\text{H}_2\text{O})_n$ with $n = 1$ to $n = 5$. These are obtained by taking into account the total yield of the fragment ions. The intensities of the spectra are normalized at their peak positions. The calculated most stable structures cited from ref. 16 are inserted for each size.

spectrum for $n = 3$ consists of two main bands and exhibits the smallest band width; the higher-energy band is observed at about 28500 cm^{-1} which is shifted by ca. 2000 cm^{-1} from that for $n = 2$. However, the lower energy peak does not shift appreciably by addition of the third water molecule. Small redshifts of these bands from those for $n = 3$ were observed for $n = 4$ and 5 , and a weak shoulder appears at ca. 17000 cm^{-1} for $n = 5$. The spectra were well reproduced by the ab initio CI calculations. In Fig. 7, the calculated most stable structures are also inserted.¹⁷ The spectra for this entire series of clusters show significant redshift relative to the atomic resonance lines of Mg^+ near 35700 cm^{-1} and exhibit the stepwise shell formation around the Mg^+ ion showing the clear evolution of solvation shell closing at $n=3$. Based on the theoretical calculations, the new band observed in the lowest energy region for $n=5$ was assigned to a $(4 + 1)$ isomer in which four water molecules coordinate directly to Mg^+ from the same side and

the 5th water molecule locates in the second hydration shell. The rapid decrease of the transition energy by increasing the coordination number may imply the progress in oxidation of the metal ion further. In the spectra of $\text{Ca}^+(\text{H}_2\text{O})_n$, similar and much more profound shifts were observed.¹⁹ From these series of works, the relationship between the hydration structure and the oxidation process was elucidated for the first time.

(2) Size dependence of oxidation reactions of metal ions in water clusters.

To gain more insight into the effect of hydration structure on the oxidation reaction of metal ions, we examined the reactions of the alkaline-earth metal ions M^+ ($= \text{Mg}^+, \text{Ca}^+$) with the $(\text{H}_2\text{O})_m$ and $(\text{D}_2\text{O})_m$ clusters using a simple cross beam apparatus. Figure 8a shows a typical time of flight (TOF) mass spectrum of the nascent cluster ions produced by the collision of the Mg^+ ions with water clusters.²⁰ Both $\text{Mg}^+(\text{H}_2\text{O})_n$ and $\text{MgOH}^+(\text{H}_2\text{O})_{n-1}$ ions were produced by the reactions as follows,

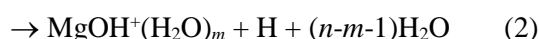
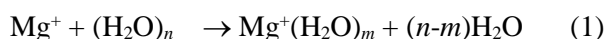


Figure 8b shows the relative abundances of $\text{Mg}^+(\text{H}_2\text{O})_n$ and $\text{MgOH}^+(\text{H}_2\text{O})_{n-1}$ determined from the mass spectrum. These cluster ions are produced with characteristic size distribution: For $1 \leq n \leq 5$ and $n \geq 15$, the $\text{Mg}^+(\text{H}_2\text{O})_n$ ions are dominantly produced. In contrast, $\text{MgOH}^+(\text{H}_2\text{O})_{n-1}$ are exclusively observed for $6 \leq n \leq 14$. The results indicate that the product ions switch rapidly at two critical cluster sizes such as $n=5$ and 15 .

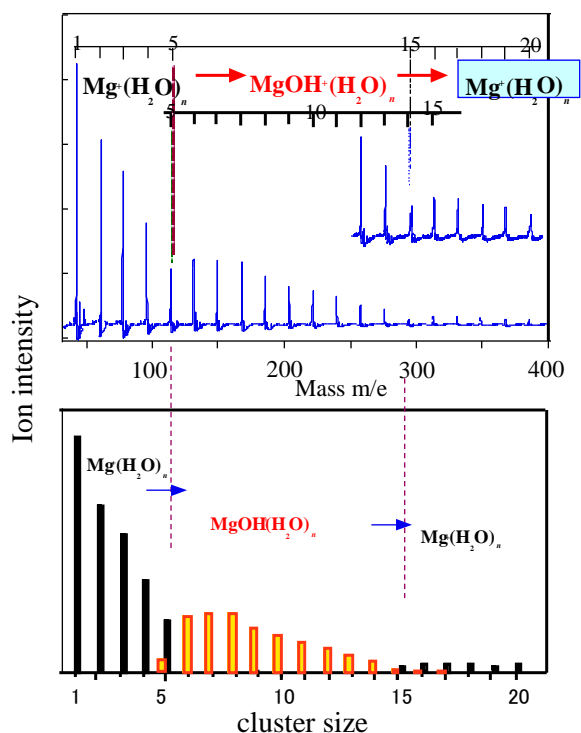


Fig. 8 (a) TOF mass spectrum of the product ions for the reaction of Mg^+ with water clusters in the cluster source. (b) Relative abundances of the product ions for the $\text{Mg}^+ - (\text{H}_2\text{O})_n$ reactions. The bars in the figures correspond to $\text{Mg}^+(\text{H}_2\text{O})_n$ (filled) and $\text{MgOH}^+(\text{H}_2\text{O})_n$ (open), respectively. The products switch at two cluster sizes; $n = 5$ and $n = 15$.

Based on these results as well as the results on the successive calculated hydration energies of MgOH^+ , the origin of the first product switching for $n \sim 5$ was ascribed to the difference in the successive hydration energies of M^+ and MOH^+ ; the product, $\text{MOH}^+(\text{H}_2\text{O})_{n-1} + \text{H}$ lowers much faster in energy than $\text{M}^+(\text{H}_2\text{O})_n$ as the cluster size increase, and it becomes the ground state of the system for $n \sim 5$.

As for the second product switching for $n \sim 15$, the origin is not self-evident. We proposed two possible mechanisms such as the participation of the Rydberg-type ion pair state $\text{M}^{2+}(\text{H}_2\text{O})_n^-$ and the formation of the new reaction product such as $\text{MgOH} \cdot \text{H}_3\text{O}^+(\text{H}_2\text{O})_{n-2}$. The former mechanism is based on the results for the photodissociation spectra of $\text{Ca}^+(\text{H}_2\text{O})_n$ and is an interesting candidate in relation to the solvation process of metal ion in bulk water. The latter mechanism stems from the chemical analogy. At present, the former mechanism is considered to be much plausible to understand the switching; however we could not rule out the latter mechanism within the present experimental data. The present study was the

first experimental work which unveil the microscopic solvation dynamics of metal ions accompanying the redox reactions in the gas phase clusters.²¹

10. Stability and solvation process of hypervalent radical in small clusters; NH_4

NH_4 is a typical hypervalent Rydberg radical, which is isoelectronic with an alkali atom, and readily formed through an attachment of hydrogen atom to ammonia molecule. This radical is also produced through the recombination of an electron with RNH_3^+ ion, which is ubiquitous in solution, and considered to be an important intermediate in many reactions including the reactions observed in biological systems. In order to elucidate the dissolved state in solution and its role in the reaction as an intermediate, we examined the ionization potentials (IP), absorption spectra, and the dynamics of the formation processes of $\text{NH}_4(\text{NH}_3)_n$ clusters. The radical clusters were produced through the photodissociation of ammonia clusters, using the nanosecond and femtosecond pump-to-probe experiments. From these studies, we clarified for the first time the stability and electronic structure of NH_4 in ammonia clusters. It was found that the isolated NH_4 dissociates into $\text{NH}_3 + \text{H}$ with a lifetime of 13 ps and it is substantially stabilized in ammonia clusters; the lifetimes of $\text{NH}_4(\text{NH}_3)_n$ increase to longer than 3 μs for $n > 1$.²² To clarify the mechanism of the stabilization, we determined the IP of these clusters. Combining the IPs for small clusters with the literature values of the successive binding energies for $\text{NH}_4^+(\text{NH}_3)_n$,

we estimated the binding energies of the ammoniated radicals. For $\text{NH}_4(\text{NH}_3)$, the binding energy was estimated to be 0.34 eV, which is much larger than the dissociation energy of ammonia dimer (< 0.12 eV). Thus, the extensive stabilization of NH_4 in the clusters was found to be due to the large solvation energy of this radical comparing with the binding energy of NH_3 itself.

Figure 9 shows the results of IPs determined for n up to 35, which are plotted as a function of $(n+1)^{-1/3}$ by assuming a spherical droplet model.²³ In this figure, the previously-determined IPs of $\text{Cs}(\text{NH}_3)_n$ are also plotted

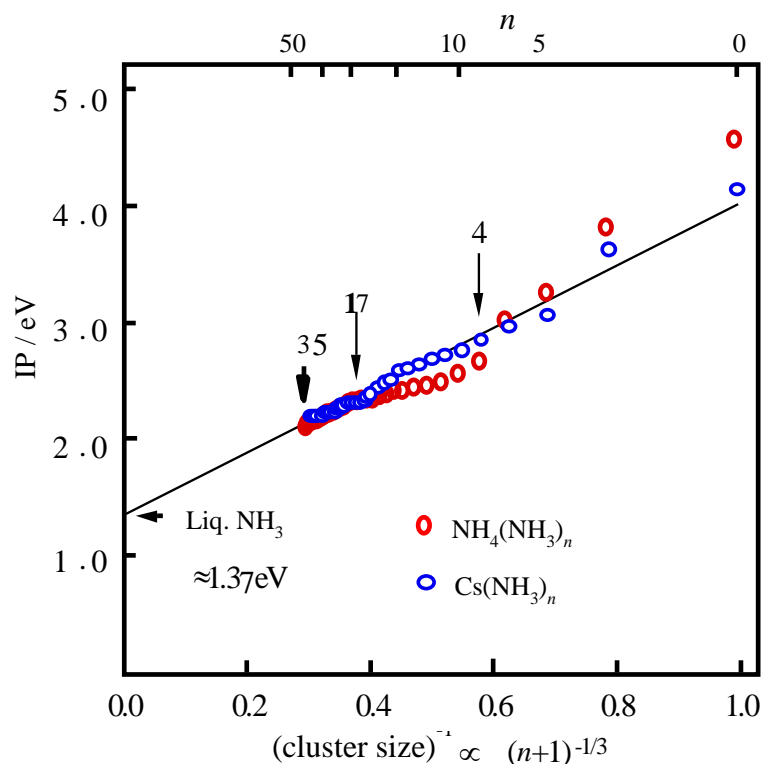


Fig. 9 Ionization potentials of $\text{NH}_4(\text{NH}_3)_n$ ($n = 0 - 35$) plotted vs $(n+1)^{-1/3}$. The IPs of $\text{Cs}(\text{NH}_3)_n$ (ref. 13) are plotted for comparison. The result of the least-squares fitting for $n = 15-35$ (straight line) gives an extrapolated value as 1.37 eV, which agrees with the photoemission threshold of liq. NH_3 .

for comparison. The IPs of $\text{NH}_4(\text{NH}_3)_n$ decrease rapidly from $n=3$ to 4 and then decrease further gradually as the cluster size increase. The rapid decrease in IPs from $n=3$ to 7 was ascribed to the large stabilization of the ionic state with respect to the neutral ground state by clustering. The observations, that the trend in IPs changes at $n \sim 17$ as seen in Fig. 9 and the IPs for larger clusters decrease almost linearly with decreasing $(n+1)^{-1/3}$, were explained by the filling of the second solvent shell in analogy with the case of $\text{NH}_4^+(\text{NH}_3)_n$; in the latter clusters, the second solvent shell is known to be closed with ca. 20 ammonia molecules. Although the feature of IPs for the small $\text{NH}_4(\text{NH}_3)_n$ clusters is slightly different from that for

$\text{Cs}(\text{NH}_3)_n$, the trends in IPs for the large clusters are quite similar as seen in Fig. 9; these systems give the same limiting value as ca. 1.4 eV. In the separate work, we also measured the electronic absorption spectra of the 3p - 3s-type transitions of $\text{NH}_4(\text{NH}_3)_n$ ($n = 1-8$).²⁴ The results show a drastic decrease of the excitation energy for $n \leq 4$ and no appreciable change for $n \geq 5$. These changes in the transition energies are very similar to those of the $^2\text{P} - ^2\text{S}$ energy separations in the PES of $\text{Na}^+(\text{NH}_3)_n$.¹⁴ From the large spectral change as well as the above similar size dependence in IPs, we concluded that the NH_4 radical is spontaneously ionized in relatively small ammonia clusters and possibly in water clusters as well. These findings on the solvation state of NH_4 might be true for the ammonium radicals created in the widespread reactions of biological systems.

11. Research at Kobe University

In the summer of 1995 just after the earthquake, I moved to Kobe as professor in the chemistry department

at Kobe University. I shipped all apparatus constructed at IMS to Kobe and rebuilt them to establish the new laboratory. Since we had just started the photoelectron works at IMS, we continued the studies on the photoelectron spectroscopy of negatively-charged alkali atoms (and its clusters) solvated with ammonia and water molecules. We also extended the photoionization study of silicon clusters to Ge_n and Sn_n . After a few years of intensive research, I conceived a new project to use an electrospray ionization (ESI) source in the photodissociation spectroscopy. At that time, this technique was limited only to be used in an ion mobility measurement of gas-phase proteins by M. F. Jarrold, except for the basic mass spectroscopy. With the ESI source in the photodissociation apparatus I expected we could start a new laser spectroscopy on any biological molecular ions such as peptides and proteins. The first photodissociation apparatus with the ESI source we developed was a tandem mass spectrometer with an octapole ion beam guide, where the laser beam is introduced to interact with the ions.²⁴ We could study biological molecules at room temperature. To carry out a temperature dependent experiment, we also developed the machine adopting a temperature-variable 22-pole ion trap so that we could cool the ions down to 20 K.²⁵

During these studies, I have also been strongly felt the importance of a new method to detect magnetic resonance for the gas phase ions. On one day I read a paper on ion cyclotron resonance (ICR) mass spectroscopy and found its close similarity to a Fourier transform NMR spectroscopy. This finding inspired me to design a new apparatus, in which an ICR cell is placed in tandem with a NMR cell in a bore of superconductive magnet so that NMR can be detected for mass selected ions. Since the ICR technique is well developed and commercially available, I spent many hours to calculate ion trajectories for establishing the mechanism of the NMR detection of the trapped ions in a Penning-trap-type cell. After several trials, I conceived the mechanism such as a Stern-Gerlach type experiment in the magnet, which is described in paragraph 13. In the next paragraphs, I present the pioneering works on the spectroscopy of solvated biological molecules using the ESI-photodissociation apparatus and the study on the gas-phase NMR spectroscopy.

12. Spectroscopies on hydrated biological clusters: Structures and energetics.

The interaction of water with peptides and with proteins is of central importance in understanding biological systems. The clusters composed of water and these biological molecules are the good target systems for the modeling, and the laser-based gas phase spectroscopic techniques can be applied to examine in details the effects of solvation on these solutes. The gas phase spectroscopic measurements of clusters, at various degrees of aqueous solvation, give information on the energetics and structures that are primarily caused by the intra- and inter molecule H-bonds. But, because these materials are nonvolatile and it is difficult to prepare their hydrated clusters, the spectroscopic study of the biological molecular systems had been very limited. To overcome the difficulty, we developed for the first time a photodissociation spectrometer with an electrospray ionization source for biological molecules. Using this apparatus, we investigated the reactions and structures of biological molecules, for example, hemine (the heme group of hemoglobin), and its solvated clusters.²⁴ We also examined the photoinduced reactions of multiply-charged cytochrome c ions, which was initiated by the electronic excitation of heme group. By following the metastable decay processes of hydrated TrpH^+ , the binding energies of the hydration were estimated.

Structures of polypeptides are one of the important factors in the characterization of physical and chemical properties of biological molecules. There are many conformers which may coexist in the experimental beams. They are at local minima in the potential energy landscape, and conformational fluctuations possibly play important roles in various functions of biological molecules. To examine microscopic aspects of structural fluctuations and reactivities of clusters containing biological molecules, it is necessary to perform spectroscopic measurements of gas-phase clusters at various temperatures. However, the experimental studies on the gas-phase clusters with a well-defined temperature or at least under controlled temperatures had been limited because of difficulties in confining gas-phase clusters under controlling temperatures. To perform a spectroscopic study of gas-phase cluster ions as a function of temperature, we constructed a photodissociation spectrometer containing the temperature-controlled multipole ion trap and a spray ionization source, and studied the structure and reactivity of cold protonated peptides.

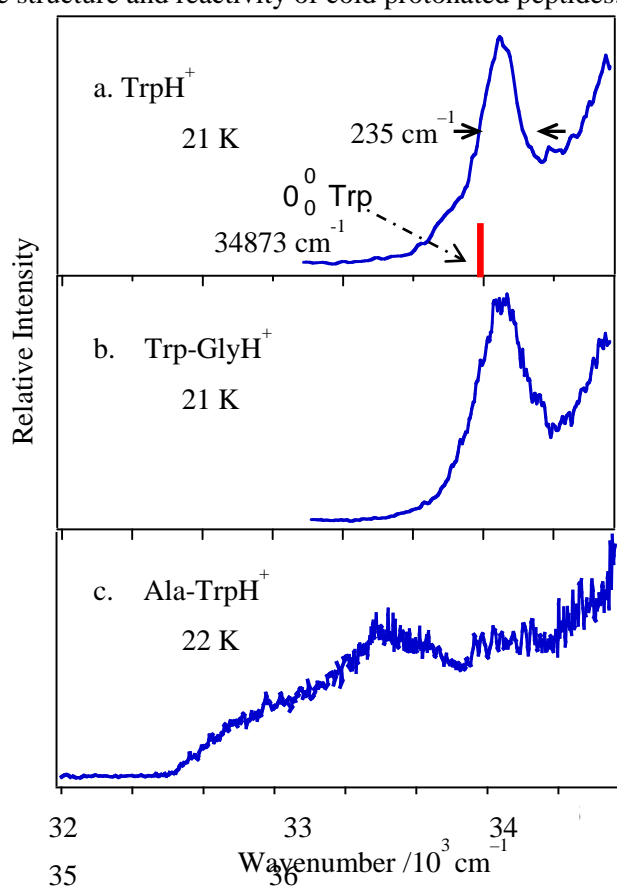


Fig. 10 UV photodissociation spectra of (a) TrpH⁺, (b) Trp-GlyH⁺, and (c) Ala-TrpH⁺. The peak at 35100 cm⁻¹ is the S₁-S₀ band origin of TrpH⁺ broaden due to a rapid photodissociation reaction in the S₁ state.

Figure 10a shows the UV photodissociation spectrum of TrpH⁺ at 21 K obtained by monitoring the fragment ion m/z 188 as a function of excitation energy.²⁵ The broad band at 35100 cm⁻¹ is attributed to the S₁-S₀ band origin of TrpH⁺. The absorption of TrpH⁺ is in the same energy range as the S₁-S₀ transition of neutral Trp (red bar). The result shows that the protonation does not affect the electronic structure. Figure 10b shows a UV photodissociation spectrum of Trp-GlyH⁺ at 21 K obtained by monitoring the fragment ion m/z 245. The spectral feature of Trp-GlyH⁺ is very similar to that of TrpH⁺. Based on the theoretical calculations, the distance between the NH₃⁺ group and the indole ring is rather long in TrpH⁺ and Trp-GlyH⁺, because of the geometrical constraint for a C_α-C_β bond. Fig. 10c is the photodissociation spectrum of Ala-TrpH⁺ at 22 K obtained by monitoring the fragment ion m/z 205. The broad band shifts to the red by ~2000 cm⁻¹ with respect to the S₁-S₀ origin of TrpH⁺ and Trp-GlyH⁺. The theoretical calculations show that the NH₃⁺ group in the most stable Ala-TrpH⁺

conformer is close to the π cloud of indole. Thus, the significant red shift in the UV spectrum of Ala-TrpH⁺ was related to the structure in which the NH₃⁺ group interacts strongly with the π cloud of indole. We also examined for the first time the temperature effect on the UV spectrum of Ala-TrpH⁺ and observed the thermally-induced conformational change.

13. Development of gas-phase NMR spectroscopy

Nuclear magnetic resonance (NMR) technique is widely used for the physical and chemical analysis of various materials in liquid and solid phases. Although it has been well established for analyzing materials in

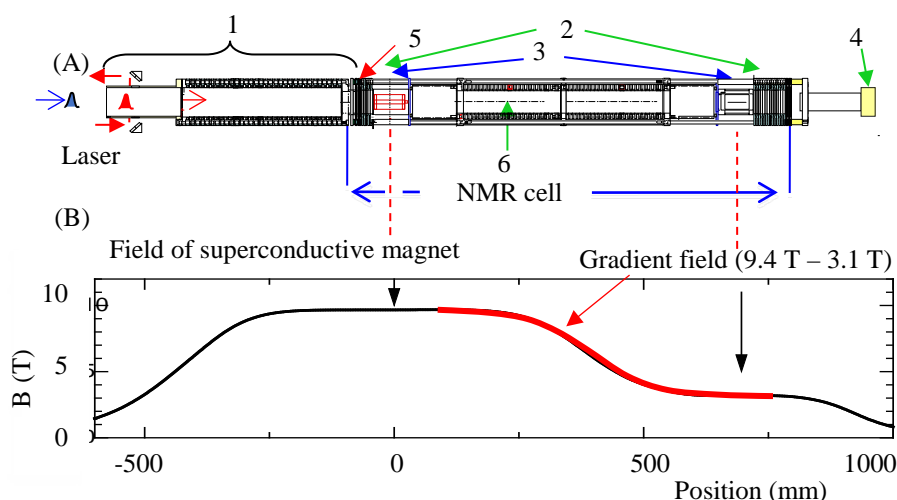


Fig. 11 Schematic of gas-phase NMR apparatus:
 1. Ion source with traveling potential well (TPW) decelerator.
 2. Front and back gates. 3. 9 T and 3 T Rf coils. 4. MCP
 5. Mesh electrodes for velocity selection
 6. velocity dispersion compensator.

condensed phase, an inherent problem of condensed phase NMR is its low sensitivity. Hence limitations come from the requirements of a large amount of sample and, also, the required purification sometimes limits the analysis. In contrast, mass spectrometric techniques can often overcome these problems, and various types of mass spectroscopic techniques have been

developed and are widely used in broad research fields because of their extremely high sensitivity and excellent selectivity. However, mass spectrometry essentially only gives information on the mass number, and for further chemical information computer simulations are often required. Under these circumstances, a new extension of NMR technique to gas-phase molecular ions becomes increasingly important for both fundamental and applied sciences.

In order to overcome the above problem for the structural analysis of mass-selected ions, we proposed a new method of magnetic resonance acceleration (and/or deceleration) to detect NMR signals of trapped ions in a high magnetic field. This method is a new extension to mass-selected ions of the Rabi technique²⁶ for neutrals. We designed and constructed the apparatus on the basis of the present method as shown in Fig. 11. The NMR cell was installed in superconductive magnet with the strong magnetic field gradient and works as a Penning-type trap. To facilitate the detection of a weak NMR signal, the cell consists of two trapping electrodes and two RF coils at both ends in order to confine the mass-selected ions in magnetic field and allow multiple magnetic interactions by resonantly flipping a nuclear spin synchronized with a shuttle motion of ion packet.²⁷

We also developed the formation and manipulation techniques for cold ions, which are the key to facilitate the detection of a weak NMR signal for the gas phase ions. We examined the deceleration and bunching of the ion packet generated by the photoionization of the supersonically cooled TMA(trimethylamine) using a TPW decelerator invented by ourselves. Ion packets with a center velocity of less than 150 m/s are generated. To cool down the ion packets, we developed a slicing technique using the mesh electrodes. By cutting out the bunched ion packet, we can reduce the velocity distribution width to 3.9 m/s FWHM, which corresponds to the temperature of 33 mK.²⁸ The ion packet is further cooled down below 1 mK using a newly developed technique

such as a velocity dispersion compensation. These results on the basic performance of the present apparatus suggest that the first NMR signal for polyatomic ions will be detected in near future.

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- (1) "Electronic Spectra and Electronic Structures of (2,2)-Paracyclophane and Related Compounds", S. Iwata, K. Fuke, M. Sasaki, S. Nagakura, T. Otsubo, and S. Misumi, *J. Molecular Spectroscopy*, **46**, 1 - 15 (1973).
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