RESEARCH ACTIVITIES III
Department of Electronic Structure

III-A Photochemical Synthesis of Exotic Atomic-Molecular Binary Clusters in Solution: π Radical -Transition Metal Alternatively Stacking (π–*d*)$_n$ Clusters

We have started the bulk synthesis of atom-molecule alternatively stacking clusters in solution. Originally, unpaired electrons are located in every atoms and molecules to induce strong interaction among *d* electrons in atoms and π electrons in molecules. Strong coupling of π and *d* electrons is shown by ab initio molecular orbital calculations of $(C_5H_5)V(C_5H_5)V(C_5H_5)V(C_5H_5)$ making inter-atomic and intermolecular distances short. Structural isomers are expected to appear for the clusters expressed by $((C_5H_5)V)_n$ and $((C_5H_5)V)_n(C_5H_5)$. One is cyclic the other is linear. For the analysis of the solid samples soluble in some specific solvents, we have developed a new mass spectrometer with a liquid jet nozzle, a rotating titanium drum for spiral adsorption of the sample on the surface, and a reflectron time-of-flight mass spectrometer situated in a separated high vacuum chamber. Thus we can mass-analyze the synthesized product directly from the solutions.

III-A-1 π Radical-Transition Metal Alternatively Stacking (π–*d*)$_n$–π Clusters: (I) $V_6(C_5H_5)_7$, a Pentagonal Ring $((C_5H_5)V)$ with a Rolling Axis Vanadocene $(C_5H_5)V(C_5H_5)$?

HINO, Kazuyuki[1]; INOKUCHI, Yoshiya; NISHI, Nobuyuki
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Photochemical treatment of the mixtures of vanadocence (bis(η–cyclopentadienyl) vanadium $((C_5H_5)V(C_5H_5))$ and tetracarbonyl (η–cyclopentadienyl) vanadium $((CO)_4V(C_5H_5))$ in dichloromethane produced the clusters with the compositions of $((C_5H_5)V)_n$ and $((C_5H_5)V)_n(C_5H_5)$ as well as $((C_5H_5)V)_n(C_5H_5)_2$. The product ratio varied with the changes of the ratio of the raw materials and the irradiation time. Addition of tricarbonyl (η–cyclopentadienyl) manganese enhanced the yields of these three kinds of clusters free from contamination of manganese in the clusters. Figure 1 shows the mass spectra of the photoproducts soluble in methanol. Starting from $((CO)_4V(C_5H_5))$, the photolysis produced vanadocene: ($m/Z = 181$) and $(C_5H_5)_2$: ($m/Z = 130$). This indicates that C_5H_5 is also dissociated by electronic excitation as well as the CO groups from the carbonyl compound. Addition of vanadocene as a raw material vanishes the signal of vanadocene but produces a new product at $m/Z = 503$. The main high mass product is found at $m/Z = 761$. This product is observed in any system with either the carbonyl compound or vanadocene. Therefore we assign this signal to $((C_5H_5)V)_6(C_5H_5)$. This compound must be much more stable than the linear polymer expressed by the same formula, since there is no reason for such a linear cluster to show specific high stability at $n = 6$. A possible structure for this cluster is shown at the upper right of Figure 1, that has a vanadocene molecule $((C_5H_5)V(C_5H_5))$ vertically inserted in a pentagonal ring $((C_5H_5)V)_5$. The pentagonal ring has 50 electrons ($4 \times 12 + 2$) distributed in the valence orbitals composed of 3*d* and 3*s* atomic orbitals of vanadium and π orbitals of cyclopentadienyl. The ring may act as a wheel rotating around the axle vanadocene. DFT calculation of this compound is now going on to check the stability of this form. The clusters are stable in alcohol solutions or in vacuum but not so stable in air.

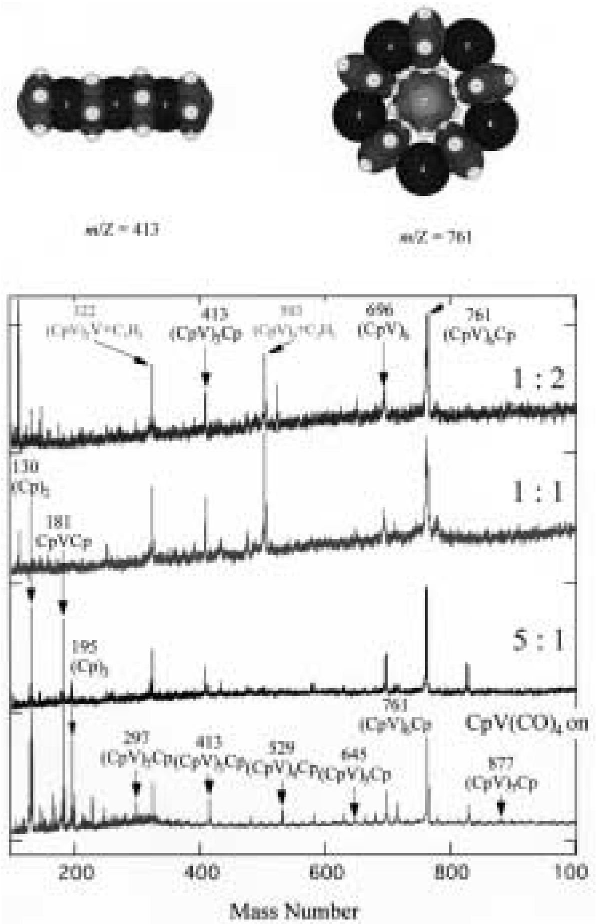

Figure 1. Mass spectra of the photoproducts from the solutions with various mixing ratio of $((CO)_4V(C_5H_5))$ to $(C_5H_5)V(C_5H_5)$.

III-A-2 Development of a New Mass Spectrometer Allowing the Injection of Solution Directly into Vacuum and the Desolvation through the Collision of Liquid Jet with Solvent Gas Flow Rebounded from a Rotating Titanium Drum for Solute Deposition

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Mass spectrometry is a very powerful method for determining mass numbers of unknown samples and getting information on molecular structures. We have developed a new mass spectrometer for non-volatile samples. Figure 1(a) shows a schematic diagram of the apparatus. It consists of a liquid beam source, a titanium drum, and a time-of-flight mass spectrometer. Non-volatile samples are dissolved in suitable solvents. Sample solutions are injected through a modified injector needle into the vacuum chamber as a liquid beam. The outer surface of the rotating titanium drum is located at 5 mm away from the exit of the needle. The liquid beam collides with gaseous shock front of the scattered solvent at the drum surface. The solvent is vaporized, and only the solute is fixed as a spiral deposit on the drum. The drum rotates at 1 rpm. The spiral solid deposit line is irradiated by the third harmonics of a Nd:YAG laser (355 nm) introduced through a hole between a sample chamber and a main chamber situated with an ion optics of the mass spectrometer. The produced ions detached from the surface are mass-analyzed by the time-of-flight mass spectrometer with a reflectron. Since the non-volatile samples are directly introduced into the spectrometer as solutions and fixed as a spiral line on the drum, we can measure the mass spectra of the non-volatile samples without exposing them to the air. Figure 1(b) represents mass spectra of polyethylene glycols used for mass calibration. Both spectra show ion signals with uniform interval of m/z = 44. This system is used for the product analysis of the synthesis of $(\pi\text{-}d)_n$ clusters.

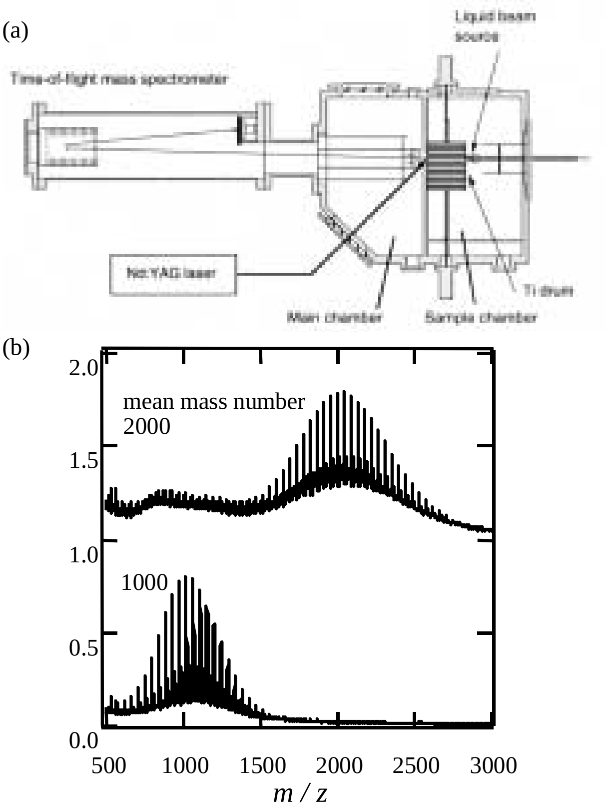

Figure 1. (a) a schematic diagram of the apparatus, (b) mass spectra of polyethylene glycol polymer samples with a mean mass number 2000 (top) and 1000(bottom).

III-B States of Neutral and Ionic Molecular Associates in Solutions

States of molecular associates particularly in aqueous solutions are of great importance in understanding the role of molecules in living organisms. Our recent studies of low frequency Raman spectroscopy of binary aqueous solutions of alcohols and carboxylic acids have shown that these amphiphilic molecules form “microphases” of clusters with the same solute species (*J. Phys Chem.* **102**, 4054 (1998), *J. Phys. Chem. A* **103**, 10851 (1999)). We have extended these studies from both experimental and theoretical point of view.

III-B-1 Monomeric and Cluster States of Acetic Acid Molecules in Solutions: A Raman Spectroscopic Study

NAKABAYASHI, Takakazu; NISHI, Nobuyuki

The purpose of this study is to understand on a microscopic scale about local structures of acetic acid in the liquid and solution states. Since acetic acid has both the hydrogen donor and acceptor sites in a molecule, various kinds of associations of acetic acid molecules can be expected depending on the situation. As shown in Figure 1, acetic acid forms a cyclic dimer in the gas phase, polymer chains in the crystalline state, and the chain clusters as the fragments of the crystalline networks in the liquid state.[1)] In aqueous solution, we have recently suggested that acetic acid preferentially forms microphase aggregates in which the side-on dimer structure is an elementary unit.[2)] In other words, two microphases exist in acetic acid-water binary solutions: one is water rich phase and the other is acetic acid one. What should be discussed next is whether the acetic acid microphases exist in other solvents or not. To examine this point, we have observed Raman spectra of acetic acid in alcohols and aprotic solvents with varying mole fraction of acetic acid (χ_{AA}). Raman spectra of acetic acid in the C=O stretching region are shown in Figure 2. With the addition of water into liquid acetic acid, the C=O band broadens and shifts to a higher wavenumber, which is ascribed to the generation of the side-on dimer microphases.[2)] In alcohols, the C=O band also shifts to a higher wavenumber and the resultant peak position is the same as that observed in water. This result suggests that the side-on dimer microphases also exist in alcohols. Low-frequency Raman spectra also support the above conclusion. In dipolar aprotic solvents such as acetonitrile, however, the spectral shift was apparently different from that in protic solvents: two prominent Raman bands appear on the higher-wavenumber side of the C=O bands observed in protic solvents. Analyses of the temperature and concentration dependencies of the Raman spectra suggest the generation of monomeric acetic acid in dipolar aprotic solvents with dilution. From these results, it is concluded that the acetic acid molecules exist as the microphases in protic solvents and as the monomeric molecules in dipolar aprotic solvents as depicted in Figure 1.

References

1) T. Nakabayashi, K. Kosugi and N. Nishi, *J. Phys. Chem. A* **103**, 8595 (1999).
2) N. Nishi, T. Nakabayashi and K. Kosugi, *J. Phys. Chem. A* **103**, 10851 (1999).

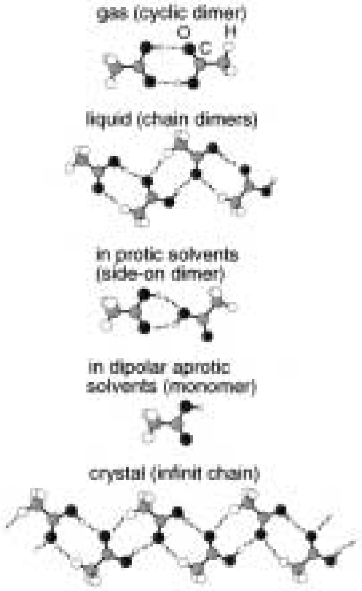

Figure 1. Structures of acetic acid clusters in various situations.

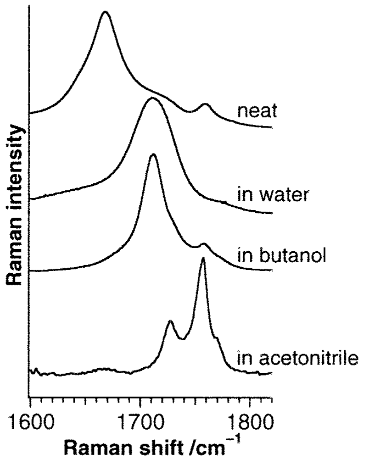

Figure 2. Raman spectra of acetic acid in the C=O stretching region (χ_{AA} = 0.015).

III-B-2 Comparison of the Theoretical Models for Calculating Acetic Acid Clusters in Aqueous Solution

NAKABAYASHI, Takakazu; SATO, Hirofumi; HIRATA, Fumio; NISHI, Nobuyuki

There has been tremendous progress in the theories for calculating molecular properties in solutions. In the present study, we have applied the SCRF and the RISM-SCF methods to clarify the electronic structures of acetic acid clusters in aqueous solution. In the SCRF method, the solute occupies a cavity surrounded by the dielectric continuous solvent. A solute dipole and/or multipole will induce a reaction field, which in turn will act to stabilize the solute. We applied the simplest SCRF model that makes use of a spherical cavity and considers only the solute dipole. The RISM-SCF method is an ab initio self-consistent field method combined with an extended version of the reference interaction site method. The advantage of the RISM-SCF method is to maintain the molecular aspects of solvents and thus to describe local interactions such as hydrogen bonds. Table 1 shows the calculated binding energies of acetic acid dimers (the linear dimer structure is depicted in Figure 1). In the gas phase, the cyclic dimer is the most stable among acetic acid dimers. Force calculations for the cyclic and side-on dimers confirm convergence to the minima on the energy surface, while the linear dimer is optimized to be a saddle point. In aqueous solution, owing to the stabilization in the side-on dimer, the energy difference between the cyclic and side-on dimers is calculated to be reduced by the RISM-SCF method; 3.0 kcal/mol in the solution compared with 8.1 kcal/mol in the gas phase. Decomposition of the solvation energy indicates that the hydration around the free carbonyl oxygen is of great importance for lowering the total energy of the side-on dimer. Marked stabilization is also obtained in the linear dimer. Not only solvation around the free carbonyl oxygen but also the increase in the O–H··O=C hydrogen bond contributes the stabilization in the linear dimer, although the free hydroxyl group has only a minor effect on the solvation energy. From the RISM-SCF results, the cyclic and linear dimer structures as well as the side-on dimer one are suggested in aqueous solution, although force calculations under the RISM-SCF model are needed to discuss whether the linear dimer is at the energy minimum in aqueous solution or not. In the case of the SCRF method, the binding energies in aqueous solution for the cyclic, side-on and linear dimers are calculated to be –12.86, –6.79, and –6.05 kcal/mol, respectively. This result indicates that, within the limits of the electrostatic interactions at the dipole level, the cyclic dimer is fairly stable even in aqueous solution. The SCRF model predicts that the energy difference between the side-on and linear dimers remains almost unchanged on going from the gas phase to aqueous solution, which is also different from the RISM-SCF result.

Figure 1. Chemical structure of the linear dimer.

	Gas	Solution	
		RISM	SCRF
Cyclic	–14.37	–1.32	–12.86
Side-on	–6.25	1.68	–6.79
Linear	–5.55	0.32	–6.05

Table 1. Binding Energies (in kcal/mol) of Acetic Acid Dimers in Gaseous phase and Aqueous Solution at the HF/DZP Level.

III-C Ultrafast Dynamics and Structural Changes of Excited Cation Radicals in Solution

Dynamic behavior and structural change of ion molecules generated in liquid solution, particularly in the presence of electron donor or acceptor species, are of great interest in relation to the formation of complexes as reaction intermediates. As an initiating stage, we have studied photogeneration of aromatic radical cations in polar solvents for understanding ion stabilization and destabilization processes in solution.

III-C-1 First Observation of the Formation Process of a Solvated Aromatic Cation Radical in Polar Solvents: A Two-Photon Pumped Femtosecond Time-Resolved Absorption Study

KAMO, Satoshi[1]; NAKABAYASHI, Takakazu; WATANABE, Kazuo; SAKURAGI, Hirochika[1]; NISHI, Nobuyuki
([1]Univ. Tsukuba and IMS)

Multiple-photoionization of aromatic compounds has been studied extensively in view of its importance in photochemical and photobiological primary processes. Photoionization in condensed phase is considered to be characterized by the production of a solvent-separated electron-cation ion pair. In polar solvents, the resultant charges can be stabilized by the polarization of the solvent and then solvated free cation radicals are produced efficiently. However, direct observations of the formation of the solvated free ion are still lacking. In order to clarify the details of multiple-photoionization process, therefore, we first observed the ultrafast dynamics of the naphthalene cation radical by using two-color two-photon pumped femtosecond time-resolved absorption spectrometer. The neutral naphthalene molecules were excited to the S_1 state by the first pump photon at 267 nm. After 100 ps, the S_1 molecules were excited by the second pump photon at 400 nm through the $S_n \leftarrow S_1$ absorption, producing the naphthalene cation radical. The absorption changes induced by the two-color two-photon pump pulses were probed by a white light continuum with the time resolution of ≈300 fs. Figure 1A shows the transient absorption spectra of naphthalene in ethyl acetate in the delay time of 600 fs–24 ps from the second pump pulse. The transient absorption observed at 600 fs exhibits two broad peaks around 660 and 710 nm. This absorption signal decreases in several picoseconds and the new absorption with peaks around 660 and 690 nm appears at 15 and 24 ps. The spectral profile of the latter absorption changes from a broad one to a sharp one as seen in Figure 1B, indicating that the absorption appeared at 15 and 24 ps arises from the vibrationally hot solvated naphthalene cation radical. The absorption observed at 600 fs is ascribable to its precursor. Almost the same spectral changes are observed in acetonitrile in Figure 2A, although the absorption signal at 600 fs is ≈1.8 times larger in acetonitrile than in ethyl acetate. This suggests that the yield of the solvated cation radical is determined within 600 fs. As shown in Figures 1B and 2B, the peak intensity in acetonitrile rises with a time constant of tens of picoseconds, while that in ethyl acetate remains almost unchanged. This result appears to be consistent with the picosecond Raman study (in the next subsection) suggesting that the Raman intensity change in acetonitrile arises from the fluctuation of the solvation structure due to vibrational relaxation.

III-C-2 Vibrational Relaxation Process of Solvated Aromatic Cation Radicals in Polar Solvents: A Two-Photon Pumped Picosecond Time-Resolved Raman Study

NAKABAYASHI, Takakazu; KAMO, Satoshi[1]; SAKURAGI, Hirochika[1]; NISHI, Nobuyuki
([1]Univ. Tsukuba and IMS)

Time-resolved Raman spectroscopy is already well recognized as a powerful technique for studying the structure and dynamics of short lived species in solution. To our knowledge, however, no one has reported picosecond Raman spectra of aromatic cation radicals, primarily because of the difficulty in obtaining two color picosecond pulses with sufficient pulse energies. Recently, we have constructed a two independently tunable Raman spectrometer with the time resolution of 3 ps. By using this system, we have first measured picosecond Raman spectra of aromatic cation radicals (biphenyl, trans-stilbene and naphthalene) in polar solvents. The results for biphenyl in ethyl acetate and acetonitrile are shown in Figure 1. Resonance Raman bands due to the S_1 state and cation radical of biphenyl are observed in this figure. The laser power dependencies confirm that the cation radical is produced through a two photon process. The frequencies of cation bands as well as their bandwidths change with the delay time in both the solvents. Immediately after biphotonic ionization, vibrationally excited cation radicals should be generated because of a large amount of excess vibrational energy. Thus the spectral changes can be ascribed to vibrational relaxation of the cation radical toward a thermal equilibrium with solvents. The time constant of the positional change of the 1610 cm^{-1} cation band is estimated to be 17 ps in acetonitrile and 13 ps in ethyl acetate. The obtained constants are roughly the same as those of other neutral aromatic molecules reported so far, although the interactions between the cation radical and surrounding solvents can be expected to be large. This result therefore supports the very rapid cooling model that the ultrafast energy transfer to the nearest solvent shell first occurs and then the energy flow into the bulk solvent follows in tens of picoseconds. As shown in Figures 1A and 2A, both the Raman intensities arising from the S_1 and cation species show an instrumental-limited rise (< 3 ps) in weak polar solvents such as ethyl acetate. On the other hand, in highly polar solvents such as acetonitrile, the Raman intensities arising from the cation radical rise in tens of picoseconds, and reach their maxima at ≈40 ps (Figures 1B and 2B). Since the picosecond intensity rise only occurs in highly polar solvents forming strong solvent-solute interactions and its time constant is roughly the same as that of vibrational relaxation, it is conceivable that the energy transfer to solvents disturbs the solvation structure, which causes the intensity change in the cation Raman bands.

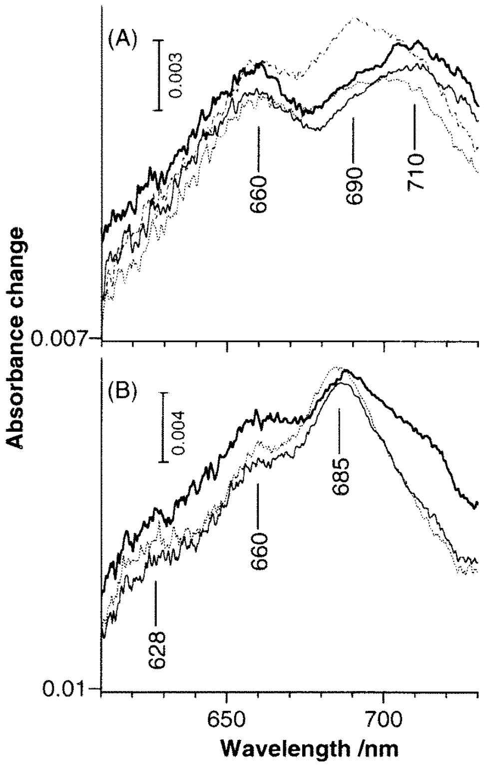

Figure 1. Transient absorption spectra of naphthalene in acetonitrile. (A) Thick-solid line, 600 fs; thin-solid line, 2 ps; dotted line, 15 ps; dash-dotted line, 24 ps. (B) Thick-solid line, 35 ps; thin-solid line, 65 ps; dotted line, 145 ps.

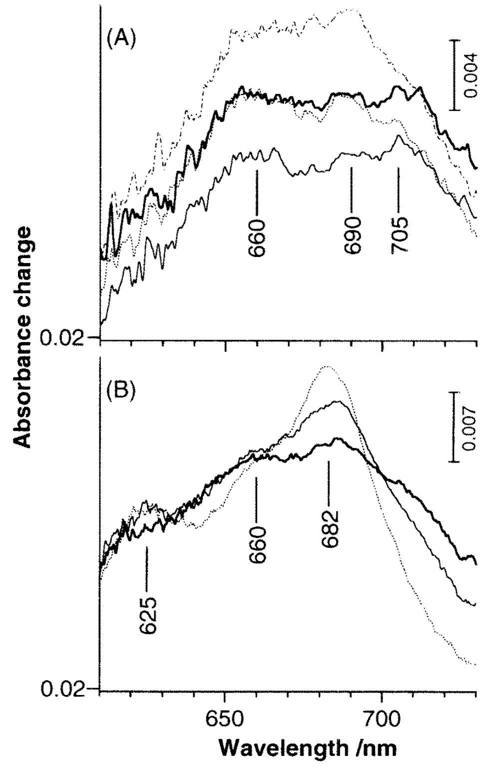

Figure 2. Transient absorption spectra of naphthalene in ethyl acetate. (A) Thick-solid line, 600 fs; thin-solid line, 2 ps; dotted line, 15 ps; dash-dotted line, 24 ps. (B) Thick-solid line, 35 ps; thin-solid line, 65 ps; dotted line, 145 ps.

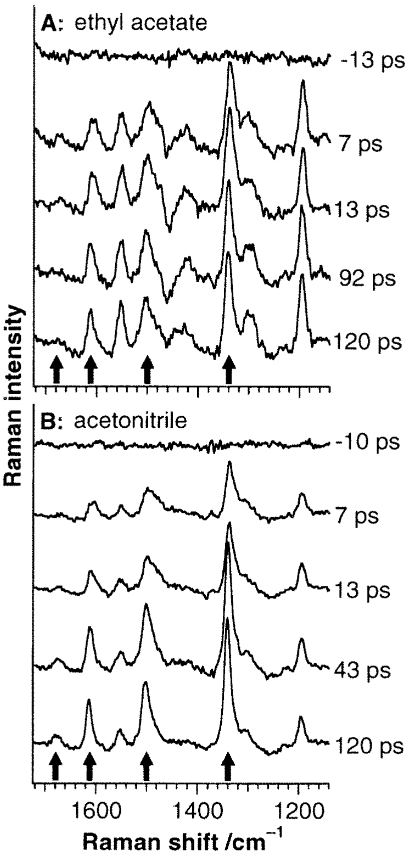

Figure 1. Picosecond time-resolved Raman spectra of biphenyl. Arrows indicates Raman bands due to the cation radical of biphenyl. Pump: 262 nm, probe: 633 nm. The Raman bands of the solvents are subtracted.

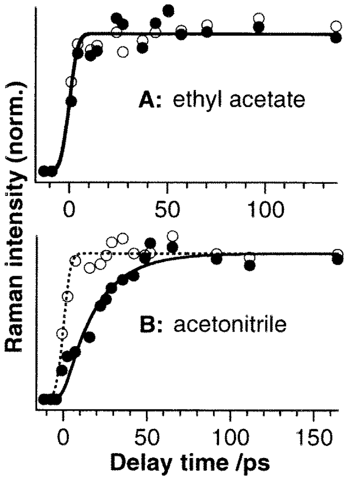

Figure 2. Plot of the transient Raman intensities against the delay time. Blank circles, S_1 (1195 cm^{-1}); filled circles, cation (1340 cm^{-1}).

III-D Spectroscopic and Dynamical Studies on Charge Delocalization and Charge Transfer in Aromatic Molecular Cluster Ions

Electron deficiency of aromatic molecular cations can attract electron rich groups or atoms exhibiting charge resonance(CR) interaction between similar molecules or charge transfer (CT) interaction with electron donor molecules. Here we show intersting cases of benzene cation complexes and clusters.

III-D-1 Photodissociation Spectroscopy of Benzene Cluster Ions in Ultraviolet and Infrared Regions. Static and Dynamic Behavior of Positive Charge in Cluster Ions

INOKUCHI, Yoshiya; NISHI, Nobuyuki

[*J. Chem. Phys.* submitted]

Photodissociation spectroscopy is applied to benzene cluster ions in ultraviolet and infrared regions. In the ultraviolet photodissociation spectrum of $(C_6H_6)_3^+$, a characteristic broad band emerges at 255 nm. This band is assigned to a $\pi^* \leftarrow \pi$ transition of a solvent benzene molecule that exists in the trimer. On the basis of the ultraviolet and the previous near-infrared spectra, we confirm a dimer ion core structure of $(C_6H_6)_3^+$; there are a dimer ion core and the solvent benzene molecule in $(C_6H_6)_3^+$. Figure 1 shows infrared photodissociation spectra of $(C_6H_6)_n^+$ (n = 3–5) (open circles). The spectra clearly show a sharp band at 3066 cm^{-1}. The band is attributed to a C–H stretching vibration of the dimer ion core. The infrared spectra can be reproduced by combining the C–H stretching bands of the dimer ion core and the solvent benzene molecules. The infrared photodissociation spectra of mixed benzene trimer ions with one or two benzene-d_6 molecules demonstrate that there is no correlation between the excited dimer ion core site in the trimer and the photofragment dimer ion species. This implies that a dimer ion core switching, in other words, a charge hopping occurs in photoexcited vibrational states prior to the dissociation. The charge hopping in cluster ions is thought to be a simple example of the charge transportation in condensed phases.

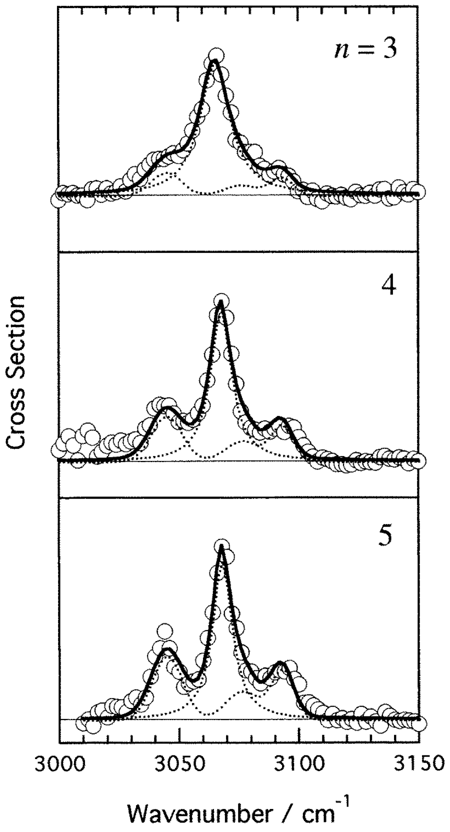

Figure 1. Infrared photodissociation spectra of $(C_6H_6)_n^+$ (n = 3–5).

III-D-2 Charge Transfer Complex of Benzene Cation Vertically Coordinated with Acetic Acid

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[*J. Chem. Phys.* in press]

The non-bonding orbital on the oxygen atom of carboxyl group can take a role of strong electron donor for a cationic molecule. Benzene cation is a good electron acceptor molecule as a counter-part of the acetic acid. We have measured vibrational and electronic spectra of acetic acid-benzene cation complexes through ion-trap photodissociation spectroscopy. Ab initio molecular orbital calculation at CASSCF(7,7)/6-31G** level for the analysis of the electronic spectrum and at B3LYP/6-31G** level for the vibrational spectrum demonstrated that there are two or three isomers: charge transfer complex with an acetic acid sitting on a carbon atom of the benzene cation vertically to the ring (vertical isomer V), and in-plane complexes with a cis- or trans- acetic acid hydrogen-bonded to one or two hydrogen atom(s) of the benzene C-H groups (horizontal isomers H). The charge transfer complex shows very broad bands due to charge transfer electronic transitions in near infrared and visible region as seen in Figure 1, where one can see the optimized structure of the vertical complex and the intermolecular bonding and anti-bonding molecular orbitals involved in the electronic transitions. One can see the negative charge in the acetic acid is transferred to the benzene on the electronic transition indicated by V_2.

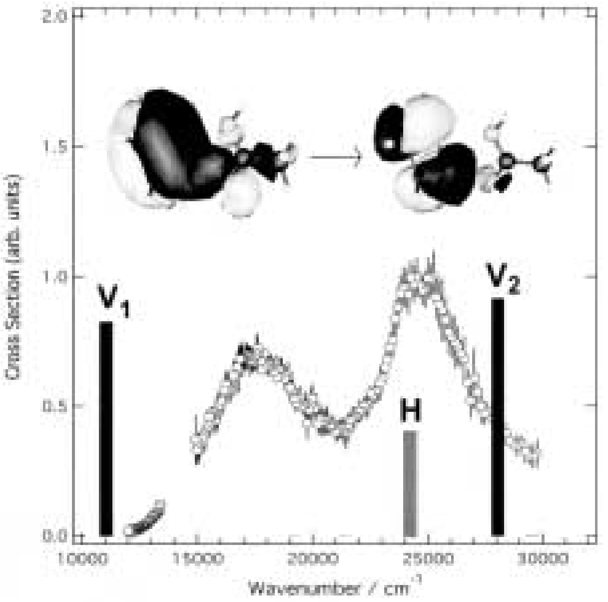

Figure 1. Observed photodissociation spectrum of $(CH_3\text{-}COOH)(C_6H_6)^+$ and the transition energies and oscillator strengths calculated by the MCQDPT method.

III-D-3 Vibrational and Electronic Spectra of (Benzene-Benzyl Alcohol)$^+$; Predominance of Charge Resonance Interaction over Hydrogen-Bonding Interaction

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([1]Kyushu Univ.)

[*Chem. Phys. Lett.* **321**, 406 (2000)]

Vibrational and electronic spectra of the benzene-benzyl alcohol hetero-dimer ion are measured by photodissociation spectroscopy. The vibrational spectrum shows a prominent band at 3662 ± 3 cm^{-1}, which is assigned to the stretching vibration of the OH group free from intermolecular perturbations. The electronic spectrum shows a broad band around 950 nm, which arises from a charge resonance interaction between the aromatic rings. These results suggest that the ion has a sandwich-like structure suitable for the resonance interaction, without the hydrogen bond between the OH group of benzyl alcohol and the - electrons of benzene.

III-D-4 Electronic and Vibrational Spectra of Aniline-Benzene Hetero-Dimer and Aniline Homo-Dimer Ions

OHASHI, Kazuhiko[1]; INOKUCHI, Yoshiya; IZUTSU, Hironobu[1]; HINO, Kazuyuki[1]; YAMAMOTO, Norifumi[1]; NISHI, Nobuyuki; SEKIYA, Hiroshi[1]
([1]Kyushu Univ.)

[*Chem. Phys. Lett.* **323**, 43 (2000)]

Structures of (aniline-benzene)$^+$ and (aniline)$_2^+$ are re-investigated by electronic spectroscopy in the near-infrared region and vibrational spectroscopy in the NH stretching region. The spectra of (aniline-benzene)$^+$ indicate a structure including a hydrogen bond between an NH bond of the ionic aniline and the -electrons of the neutral benzene. Two isomers are suggested for (aniline)$_2^+$ in which an NH bond of the ionic aniline forms different types of hydrogen bond with the neutral aniline: one with the -electrons of the aromatic ring and the other with the lone pair of the nitrogen atom.