

RESEARCH ACTIVITIES III

Department of Electronic Structure

III-A Synthesis and Characterization of Exotic Molecule-Based Nano-Clusters with Transition Metals : Behavior as Single Domain Magnets

Molecule-based nanoclusters with transition metals are highly important in introducing electronic and magnetic functionalities in nanoelectronic devices. In view of electronic structure of metal- π conjugate systems, $M-C_2$ molecules, where $M = \text{Fe, Co, Ni}$ etc., are expected to generate $d-\pi^*$ interaction networks on cluster $(M-C_2)_n$ formation or on solidification. The ground state of $\text{Co}-C_2$ molecule is predicted to be 4B_1 with a symmetric triangular configuration where the $4s$ and d -orbital occupation numbers are far from integer, and the energy range of the upper sextets is only 5–6 kcal/mol (A.V. Arbunzniv and M. Hendriks, *Chem Phys. Lett.* **320**, 575 (2000)). Thus this high spin molecule should be very much suitable for making molecule-based nanocluster magnets. Here we report how we have generated molecule-based $(\text{Co}-C_2)_n$ magnets. The nano-size clusters isolated in amorphous carbon matrices are demonstrated to work as room-temperature single domain magnets.

III-A-1 Magnetic Behavior of Crude CoC_2 Solid Synthesized in Acetonitrile Solution

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CoC_2 molecules are synthesized from CoCl_2 and CaC_2 in acetonitrile or benzonitrile solution. The reaction scheme is expected as follows:



This reaction occurs on the surface of the CaC_2 particles in the solutions. Thus the structure of the solid products is not homogeneous. The infrared spectrum of the raw materials indicated that the commercial CaC_2 was heavily contaminated with $\text{Ca}(\text{OH})_2$ and H_2O . The product solid was washed with water to convert CaC_2 to $\text{Ca}(\text{OH})_2$ and C_2H_2 and the residual CoCl_2 , CaCl_2 and $\text{Ca}(\text{OH})_2$ were also removed by water. The color of the final product was greenish black. The infrared spectrum of the product exhibited the doublet band at 1375 and 1475 cm^{-1} that corresponds to the doublet band of CaC_2 at 1420 and 1500 cm^{-1} . The energy dispersed X-ray emission analysis indicated that the cobalt to carbon ratio changes from particle to particle in the range of 1.5 to 2.0. The particles containing higher oxygen concentration (due to water or OH contamination) exhibited lower ratios. The evolution of $(\text{CoC}_2)_n$ clusters in these particles is thought to be blocked by the inclusion of the hydroxide or water molecules. Figure 1 shows the temperature dependence of the magnetic susceptibility of the solid CoC_2 synthesized in acetonitrile. The CoC_2 solid produced in benzonitrile solution showed much larger susceptibility and the reason is ascribed to less water contamination in benzonitrile. The inserted graph in Figure 1 shows the magnetic hysteresis curve of the product in acetonitrile. The cohesive force of the CoC_2 solid produced in benzonitrile solution was 500 Oe at 1.8 K. Thus the $\text{Co}^{++}\text{C}_2^{--}$ salt compound becomes cluster

magnets at the temperatures lower than 4.5 K. The removal of the interstitial impurity species from the solid is expected to produce crystalline magnets that works at higher temperatures.

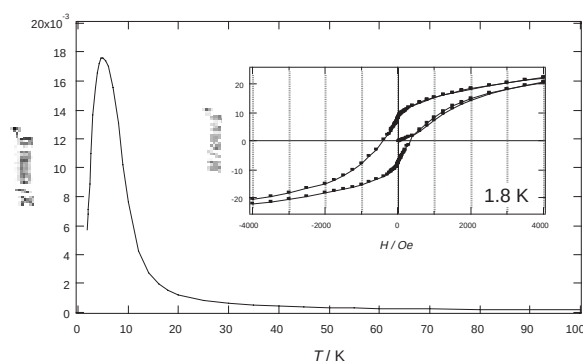


Figure 1. Temperature change of the magnetic susceptibility of CoC_2 solids synthesized from CoCl_2 and CaC_2 in acetonitrile solution.

III-A-2 Electron Microscope and EXAFS Study of Matrix Embedded $(\text{Co}-C_2)_n$ Nano-Cluster Magnets

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$(\text{Co}-C_2)_n$ nanoparticles are synthesized from CH_2Cl_2 solution of $\text{Co}_4(\text{CO})_{12}$ by heating up to 210 °C in a closed vessel. The cluster particles are embedded in amorphous carbon. Transmission electron microscope (TEM) observation of the particles provides a size distribution with an average size of 12 nm. Figure 1-a shows a TEM image of a relatively large nanocluster embedded in the matrix. Although most of the nanoparticles exhibited the single array of the lattice stripes (just like a single nanocrystals) as seen in the expanded image c, the upper part of this particle shows disor-

dered, thereby, three dimensional “step” structure around the border region between the upper and the middle parts (expanded image b). The image of the step area reminds us a structure similar to NaCl type crystals. The image of the matrix in the expanded view c shows an amorphous structure in contrast to the ordered structure of the particle. Figure 1-b displays the electron energy loss spectra of the nanoparticles (a) and the matrix (b) observed with an electron beam size of 2.5 nm. The bottom frame shows that the Co-L bands at 781 and 796 eV are seen for the nanoparticle but the matrix does not show any signals of Co component. The shape of the matrix C-K band is characteristic of amorphous carbon, while the spectral feature of the nanoparticle exhibits the enhanced π^* resonance at 285 eV and the low energy shift of the σ^* resonance, characteristic of unsaturated (sp or sp^2) carbon bonds. The intensity ratio of the C-K bands provides a ratio of cobalt to carbon to be 1 : 2. The ratio and the presence of the π^* resonance band indicates that the cluster is $(\text{Co}^{2+}\text{C}_2^{2-})_n$. The observed salt type structure image similar to that of a $\text{Ca}^{2+}\text{C}_2^{2-}$ crystal is in accord with this assignment. The radial structure function (RSF) obtained by Fourier transformation of extended X-ray absorption fine structure (EXAFS) provided the strongest Co–C peak at 2.08 Å and the two Co–Co peaks at 3.18 Å and 3.9(± 0.2) Å. These structural parameters are also in good agreement with the salt type structure for the $(\text{Co}^{2+}\text{C}_2^{2-})_n$ clusters, although the every Co and C_2 in the cluster is bonded with $d-\pi^*$ valence bond networks.

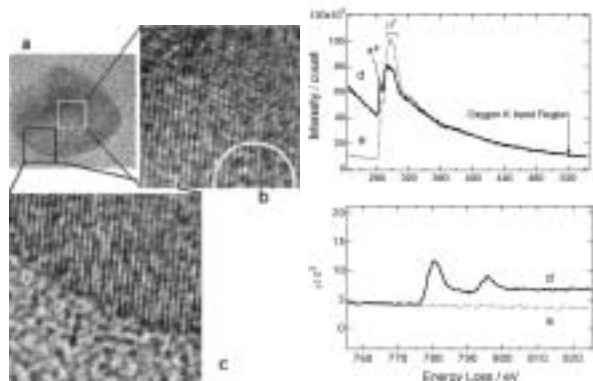


Figure 1. left: A TEM image of a relatively large particle in the matrix. The upper part was scraped off by the slicing knife of the microtome cutting machine exhibiting the disordered steps (image b). ($5 \times 5 \text{ nm}^2$) Image c shows the structural contrast of the nanoparticle with that of the amorphous carbon matrix. ($6 \times 6 \text{ nm}^2$)

Right: Electron energy loss spectra of the nanoparticle (of which image is shown on the left, spectrum d) and the matrix (spectrum e).

III-A-3 Magnetic Behavior of Matrix Embedded $(\text{Co}-\text{C}_2)_n$ Nano-Clusters as Single Domain Room-Temperature Magnets

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Magnetic properties of the $(\text{Co}-\text{C}_2)_n$ nanoparticles embedded in the amorphous carbon matrix were mea-

sured with a SQUID magnetometer (Quantum Design MPMS-7S). Figure 1 shows the temperature change of the magnetic susceptibility under the zero-field cooling (ZFC) condition and the field cooling (FC) at 10 Oe external field. The susceptibility decreases with decreasing temperature from 300 K to 20 K at zero field suggesting that the particles are interacting and prone to align antiparallel to each other, while under the field cooling condition it increases with decreasing temperature. This means that the 10 Oe external field aligns the magnetic moments of the particles along the field direction. The two curves behaves just oppositely, and the average values are nearly temperature independent. The hysteresis shows that the saturation magnetization and the residual magnetization increases at lower temperatures while the cohesive force decreases at lower temperature. This behavior is in accord with the theoretical expectation for single domain magnets which exhibit cohesive force in inverse proportional to the saturation magnetization (S. Chikazumi, *Physics of ferromagnetism*, Shokabo, Vol II, 269 (1984)).

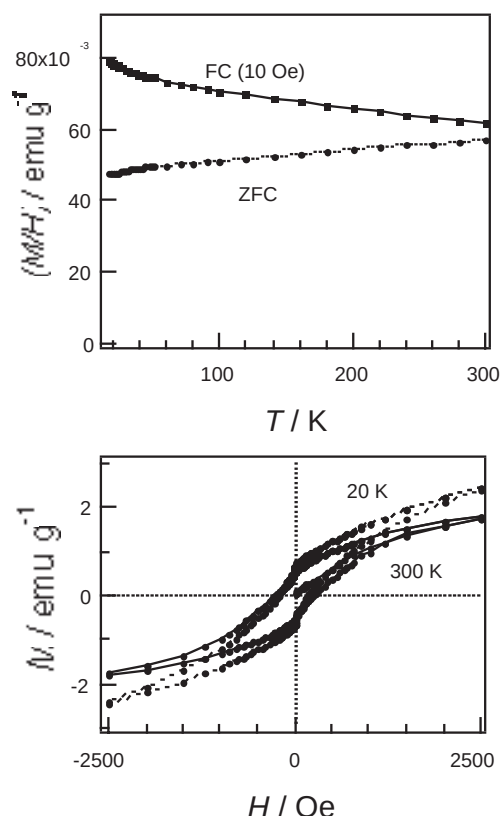


Figure 1. top: Temperature change of magnetic susceptibility of the matrix embedded $(\text{Co}-\text{C}_2)_n$ nano-clusters measured under the zero-field cooling condition (ZFC) and the field cooling (FC) condition. bottom: magnetic hysteresis curves at 300 K (solid curve) and 20 K (dotted curve).

III-A-4 Construction of Vacuum Apparatus for Mass-Resolved Spectroscopies of Non-Volatile Solid Samples

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In order to apply mass-resolved spectroscopic methods to non-volatile samples, we need to vaporize them in a vacuum apparatus. In particular, for the samples prone to be damaged by water or oxygen, it is necessary to introduce them into the vacuum apparatus without being exposed by the air. Recently, we have constructed a new apparatus for mass-resolved spectroscopies of non-volatile (and non-metallic) solid samples. Figure 1 shows a schematic diagram of the apparatus. It consists of a liquid beam source, a titanium rotating drum, and a time-of-flight mass spectrometer. Non-volatile samples are dissolved in some volatile solvents. The solutions are injected through a modified injector needle into the vacuum chamber as a liquid beam. The surface of the rotating titanium drum is located at 5 mm away from the exit of the needle. The solvent is vaporized, and only the solute species are fixed on the drum. The solid sample on the drum is laser-desorbed by the third harmonics of a Nd:YAG laser (355 nm) introduced through a hole between a sample chamber and a main chamber. The gaseous sample is ionized by three types of ionization technique: matrix-assisted laser desorption-ionization (MALDI), electron impact (EI), and resonance-enhanced multiphoton ionization (REMPI). The produced ions are mass-analyzed by the time-of-flight mass spectrometer. Since the non-volatile samples are directly introduced into the spectrometer as solutions and fixed on

the drum, the samples do not contact with the air. We can obtain excitation spectra of the samples by scanning the wavelength of the ionization laser. Photodissociation spectra of the sample ions can be measured by the introduction of a dissociation laser into the drift region of the spectrometer.

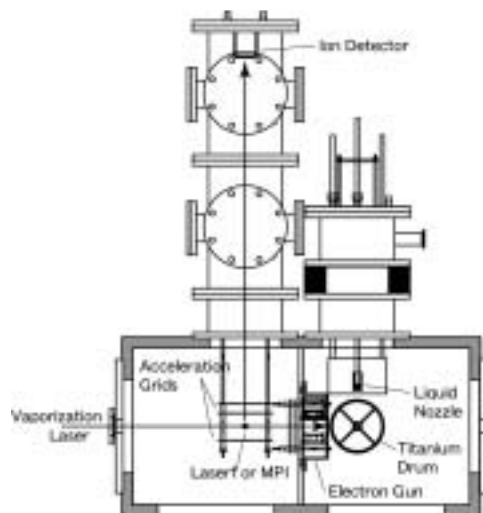


Figure 1. Schematic diagram of a time-of-flight mass spectrometer for solid samples.

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. We found that any ideally mixed state cannot be seen in protic-protic mixtures such as water-alcohol, water-acetic acid, and alcohol-acetic acid systems on the molecular level at solute molar fractions (χ_A) higher than 0.001. In such a system, solute-solute association is highly favored resulting in microscopic phase separation. Here we demonstrate that aprotic solvent such as acetonitrile can produce ideally mixed state(s) for acetic acid.

III-B-1 States of Molecular Associates in Binary Mixtures of Acetic Acid with Protic and Aprotic Polar Solvents: A Raman Spectroscopic Study

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[*J. Phys. Chem. A* **106**, 3491 (2002)]

The local structure of acetic acid in protic and aprotic polar solvents have been studied by Raman spectroscopy and ab initio calculations with the self-consistent reaction field (SCRF) method. As acetic acid is diluted in water, the C=O stretching Raman band of acetic acid becomes broader and shows a higher wavenumber shift from 1666 to 1710 cm^{-1} , which arise from the generation of acetic acid microphases. In the region of $0.001 \leq \chi_A$ (acetic acid mole fraction) ≤ 0.2 , both the peak position and the bandwidth of the C=O band are hardly changed, indicating that the acetic acid microphases exist even in the diluted solution at $\chi_A = 0.001$.

In alcohols (methanol, 1-butanol, and 1-hexanol), the spectral changes in the C=O stretching band with the dilution are almost the same as those observed in water, suggesting that the same acetic acid microphases are formed in the alcohol solutions at $\chi_A \geq 0.001$. In acetonitrile, however, the spectral changes are apparently different from those in the protic solvents: two higher wavenumber C=O bands at 1725 and 1754 cm^{-1} appear in the region of $0.001 \leq \chi_A \leq 0.3$. From the ab initio SCRF calculations, we assign the 1725 and 1754 cm^{-1} bands to the cyclic dimer consisting of acetic acid and acetonitrile monomers and to the noncomplexed acetic acid monomer, respectively. Such two bands are also observed in other nitriles and ethers, suggesting that the monomeric molecules are preferentially formed in aprotic polar solvents. From these results, it is concluded that binary solution of acetic acid and the protic solvent do not get homogeneously mixed even in the low acid concentration region of $\chi_A \geq 0.001$, while homogeneously mixed states at molecular levels occur

in the binary solutions of acetic acid and the aprotic polar solvents when the acetic acid mole fraction is small.

III-C Ultrafast Dynamics and Scanning Tunneling Microscopy

We have constructed a low temperature scanning tunneling microscope system combined with an ultrafast light sources in addition to the femtosecond time-resolved ionization detected spectrometer.

III-C-1 Construction of an Apparatus for Direct Observation of Reactions Induced by Ultrafast Laser Pulses Using a Low Temperature STM

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(¹Univ. Tokyo)

Recent advances in laser technology have led to the development of ultrafast spectroscopic techniques that enable us to examine the dynamics of chemical reactions in the femto to picosecond time range. The next stage is to perform the real-space and high-resolution imaging of ultrafast chemical reactions. The ability to view molecular structural changes on an atomic scale in real time promises great progress in many fields of chemistry and physics. In the present study, we have constructed an apparatus for the visualization of photochemical reactions at surfaces by using a low-temperature UHV STM and a picosecond pulse laser system. Experimental arrangement is schematically depicted in Figure 1. The constructed system has two helium cooled STM cryostats, one of which operates to 8 K and has two optical windows for irradiation of laser beams. The angle of incidence is 45° with respect to the STM-tip axis. Optical illumination is provided by two independently tunable picosecond OPA systems. By using frequency mixings, we have obtained the tuning of light between 189 and 11200 nm with microjoule pulse energy and 4 ps pulse duration. Picosecond pump-probe experiments can be carried out with an optical delay stage. The other STM is constructed for low temperature STS studies. A sample in this cryostat can be controlled at any temperature between 4 K and 50 K and kept at 4 K for at least 24 hours without refilling He liquid. A sputtering and annealing system in a preparation chamber obtains a clean flat surface of a substrate. A molecular beam doser is equipped for the adsorption of target molecules onto a substrate. A pulse injection system with a high-speed solenoid valve is also installed for the deposition of nanoparticles and biomolecules. Both the STM cryostats have been confirmed to perform atomic resolution on topograph images of Si(111) surfaces at liquid helium temperatures. By using the former STM cryostat, we have observed Pd clusters with ≈ 6 nm diameters on Au(111) surfaces.

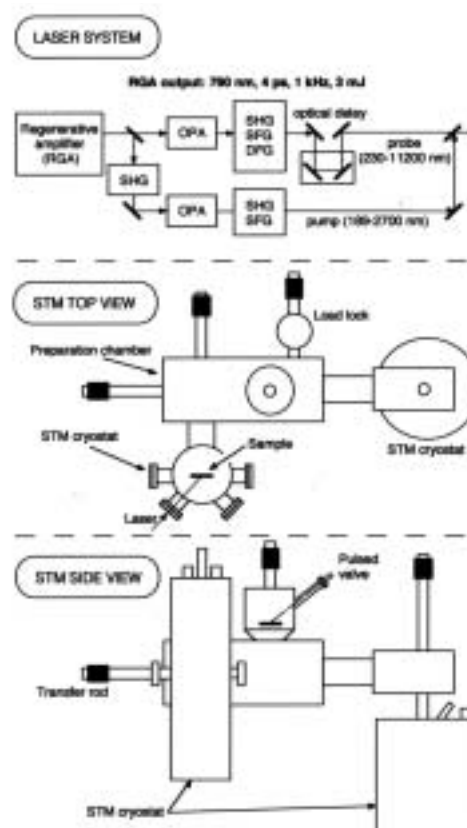


Figure 1. Schematic drawing of the experimental setup.

III-C-2 Construction of a Femtosecond Time-Resolved Ionization Detected Spectrometer

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A time-of-flight mass spectrometer combined with a supersonic molecular beam and a femtosecond laser system has been constructed to observe the ultrafast reaction dynamics of molecules and clusters in the gas phase. The femtosecond laser system consists of a mode-locked Ti:sapphire oscillator with a tunable wavelength from 720 to 850 nm, a regenerative amplifier pumped by a frequency-doubled Nd:YLF laser at 1 kHz, and an optical parametric amplifier (OPA) system. The output from the OPA is tuned between 300 and 10000 nm by mixing techniques and is used for pumping sample molecules to the photoexcited states. A portion

of the output from the regenerative amplifier is frequency doubled (or tripled) and used as a probe beam for ionizing transient molecules generated by the pump beam. After passing through fixed (for the pump beam) and variable (for the probe beam) optical delay lines, the pump and probe beams are superimposed by a dichroic mirror, and focused into a vacuum chamber with an $f = 350$ mm focal lens. Gas mixture of sample molecules and helium is expanded into the vacuum chamber through a pulsed nozzle with a 0.80 mm orifice diameter and a 300 microsec pulse duration. The laser beams merge with the molecular beam and ionize the sample molecules in the acceleration region. The product ions are mass analyzed in the time-of-flight mass spectrometer and are detected using a microsphere plate detector. The ion signals are collected at a 10 Hz repetition rate synchronized with the opening of the pulsed nozzle and are fed into a digital storage oscilloscope. The oscilloscope and the optical delay stage are controlled by a microcomputer through a GPIB interface. The instrumental response function is determined by the pump-probe ionization experiments on pyrazine and benzene that are known to exhibit an instrument-limited rise. It is estimated to be a Gaussian function with a full width at half maximum of 230 fs. Time-resolved multiphoton ionization intensities of N-salicylideneaniline and diarylethene derivatives have been observed by using this spectrometer.

III-C-3 Picosecond Time-Resolved Raman Studies on the Photochromic Reactions of Diarylethenes

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(¹Kyushu Univ.)

Diarylethenes are promising photochromic compounds for optoelectronic applications because of their fatigue-resistant and thermally irreversible properties. The open forms of diarylethenes are mostly colorless and turn to the closed forms by UV irradiation. The generated closed forms are thermally stable and exhibit absorption spectra in the visible region. Upon irradiation of visible light, the closed forms revert back to the original open forms. In the present study, we have first measured picosecond time-resolved Stokes and anti-Stokes Raman spectra of diarylethenes in solutions, in order to obtain the rates and mechanisms of these photochromic reactions. We have used 1,2-bis(2,5-dimethyl-

3-thienyl)perfluorocyclopentene for the ring-closure reaction, and 1,2-bis(3,4-dimethyl-5-phenyl-2-thienyl)-perfluorocyclopentene for the ring-opening reaction. Two common features of the ring-closure and ring-opening reactions are found: the photochromic reactions proceed in the time scale less than 4 ps and the vibrationally excited molecules in the ground electronic (S_0) state are generated as the intermediate state. Figure 1 shows the time-resolved anti-Stokes Raman spectra of 1,2-bis(3,4-dimethyl-5-phenyl-2-thienyl)perfluorocyclopentene. The observed two anti-Stokes Raman bands at 1545 and 1599 cm^{-1} are assignable to the C=C stretching modes of the thiophene and cyclopentene moiety of the generated S_0 open forms, respectively. The intensity of the cyclopentene moiety relative to that of the thiophene moiety becomes smaller with the delay time, indicating part of the excess energy generated via the ring-opening reaction is localized on the C=C stretching mode of the cyclopentene moiety. This means that the C=C stretching mode of the cyclopentene moiety is one of the promoting or the accepting modes in the ring-opening reaction.

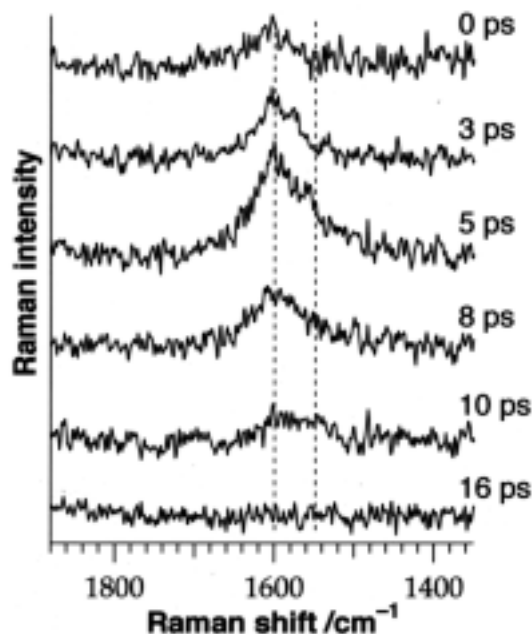


Figure 1. Picosecond time-resolved anti-Stokes Raman spectra of 1,2-bis(3,4-dimethyl-5-phenyl-2-thienyl)-perfluorocyclopentene in acetonitrile. Pump, 480 nm; probe, 395 nm. The delay time is given on the right side of each spectrum.

III-D Spectroscopic and Dynamical Studies of Molecular Cluster Ions

Electron deficiency of molecular cluster cations can attract electron rich groups or atoms exhibiting charge transfer or charge resonance interaction in the clusters. This causes dynamical structural change such as proton transfer or ion-core switching in hot cluster ions or clusters in solution.

III-D-1 Intermolecular Interactions in Aniline/Benzene Hetero-Trimer and Aniline Homo-Trimer Ions

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[*Chem. Phys. Lett.* **357**, 223 (2002)]

The charge distribution and binding features of aniline/benzene hetero-trimer and aniline homo-trimer ions are investigated by vibrational spectroscopy and by near-infrared photodissociation and spontaneous unimolecular dissociation of mass-selected cluster ions. The absence of the charge resonance absorption indicates the charge localization in the trimer ions. Substantial red-shifts and enhanced intensities of the NH-stretching transitions suggest large intermolecular perturbations. The trimer ions are stabilized by the hydrogen-bonding interaction through the NH₂ group of the charged aniline with the neutral molecules rather than the charge-delocalization interaction among the component molecules.

III-D-2 Infrared Photodissociation Spectroscopy of Protonated Formic Acid-Water Binary Clusters, H⁺·(HCOOH)_n·H₂O (*n* = 1–5). Spectroscopic Study of Ion Core Switch Model and Magic Number

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[*J. Phys. Chem. A* **106**, 4529 (2002)]

Infrared spectra of protonated formic acid-water binary clusters, H⁺·(HCOOH)_n·H₂O (*n* = 1–5), are investigated by infrared photodissociation spectroscopy and ab initio molecular orbital calculations. The asymmetric OH stretching vibration of water is observed in the infrared photodissociation spectra of the clusters with *n* = 1–3; it disappears in the spectra of the *n* = 4 and 5 clusters. On detailed comparison of the observed infrared spectra with calculated ones, the most stable geometric structures are obtained for the *n* = 1–5 clusters. These results suggest that the clusters switch the ion cores from HCOOH₂⁺ for *n* = 1–3 to H₃O⁺ for *n* = 4 and 5. The *n* = 5 cluster has a cyclic-type structure; the H₃O⁺ ion core is fully surrounded and stabilized by five formic acid molecules. This characteristic nature produces a magic number of the *n* = 5 cluster.

III-D-3 Infrared Photodissociation Spectroscopy of Aniline⁺-(Water)_{1,2} and Aniline⁺-(Methanol)_{1,2}

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[*Chem. Phys. Lett.* **358**, 419 (2002)]

Infrared photodissociation spectra of the aniline ion

solvated by water and methanol molecules are measured in the 2600–3800 cm⁻¹ region. Substantially red-shifted and broadened transition is distinctly observed at 3105 and 2915 cm⁻¹ for aniline⁺-(H₂O)₁ and aniline⁺-(CH₃OH)₁, respectively, and assigned to the stretching vibration of the hydrogen-bonded NH oscillator of the aniline⁺ moiety. The spectra of aniline⁺-(H₂O)₂ and aniline⁺-(CH₃OH)₂ demonstrate a large perturbation to both of the NH oscillators, indicating that each NH bond is bound to a solvent molecule in the most stable structure.

III-D-4 Intracuster Proton Transfer in Aniline–Amine Complex Ions

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[*Chem. Phys. Lett.* **359**, 283 (2002)]

The intracuster proton transfer in aniline–amine complex ions is investigated by infrared photodissociation spectroscopy and density functional theory calculations. The proton acceptors include ammonia, methylamine, dimethylamine and trimethylamine in ascending order of proton affinity. The spectra of (aniline–ammonia)⁺ and (aniline–methylamine)⁺ demonstrate the persistence of the aniline ion unit in the complexes. For (aniline–dimethylamine)⁺ and (aniline–trimethylamine)⁺, the spectra imply the transformation to the anilino radical (C₆H₅NH) unit, suggesting the occurrence of the proton transfer.

III-D-5 LIF and IR Dip Spectra of Jet-Cooled *p*-Aminophenol–*M* (*M* = CO, N₂): Hydrogen-Bonded or van der Waals-Bonded Structure?

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(¹Kyushu Univ.)

[*J. Phys. Chem. A* **106**, 4886 (2002)]

Intermolecular interaction and stable structures of the *p*-aminophenol–*M* (*M* = CO, N₂) 1:1 complexes have been studied by measuring the S₁–S₀ fluorescence excitation spectra and the IR dip spectra in the OH and NH stretch region. We also have performed ab initio calculations to obtain stable structures and calculated infrared spectra of the complexes. The S₁–S₀ electronic origin of the CO complex is 141 cm⁻¹ red shifted from that of the monomer. This shift is smaller than that of the N₂ complex (153 cm⁻¹), although the molecular polarizability of CO is larger than that of N₂. The IR dip spectrum of the CO complex shows that the OH stretching frequency is 26 cm⁻¹ lower than that of the monomer. On the other hand, the N₂ complex displays no shift. We conclude that the CO molecule is bonded to the OH group via a hydrogen bond in *p*-aminophenol–CO, whereas the N₂ molecule is van der Waals-

bonded to the π cloud of the aromatic ring in *p*-aminophenol- N_2 .

III-D-6 Structure and Intermolecular Hydrogen Bond of Jet-Cooled *p*-Aminophenol-(H_2O)₁ Studied by Electronic and IR-Dip Spectroscopy and Density Functional Theory Calculations

MORI, Hirotoshi¹; KUGISAKI, Hitomi¹; INOKUCHI, Yoshiya; NISHI, Nobuyuki; MIYOSHI, Eisaku¹; SAKOTA, Kenji¹; OHASHI, Kazuhiko¹; SEKIYA, Hiroshi¹
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[*Chem. Phys.* **277**, 105 (2002)]

The structure and hydrogen bonding interaction in jet-cooled *p*-aminophenol- H_2O 1:1 complex have been studied by measuring the fluorescence excitation, dispersed fluorescence, and IR-dip spectra. In the electronic spectrum we identified only one isomer, where the oxygen atom of water is bonded to the hydroxy proton of *p*-aminophenol. Four stable isomers are obtained by ab initio calculations at the MP2/6-31G(d) level, while density functional theory calculations provide four or three isomers depending on the basis sets. It has been shown that theoretical IR spectra with small basis sets are not in agreement with the experimental IR spectrum. The experimental IR spectrum has been well reproduced by the B3LYP/6-311+G(d,p) calculations, showing that diffuse functions are necessary to describe the intermolecular hydrogen bond in *p*-aminophenol- H_2O . The vibronic levels in the S_1 state of *p*-aminophenol- H_2O have been assigned with the aid of the dispersed fluorescence spectra. The formation of the intermolecular hydrogen bond substantially reduces the frequency of the amino inversion mode in the S_1 state due to nonlocal character of this mode.

III-D-7 Positive Charge Distribution in (Benzene)₁(toluene)₂⁺ and (Benzene)₂(toluene)₁⁺ Studied by Photodissociation Spectroscopy

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

The positive charge distribution in benzene-toluene hetero-trimer ions is investigated by photodissociation spectroscopy in the near-infrared (6000–14000 cm^{-1}) and infrared (2800–3150 cm^{-1}) regions. The electronic spectra of (benzene)₁(toluene)₂⁺ and (benzene)₂(toluene)₁⁺ in the near-infrared region display a strong band at 9430 and 8330 cm^{-1} , respectively. These bands are ascribed to the charge resonance band; the positive charge is not localized on a single molecule. The vibrational spectrum of (benzene)₁(toluene-*d*₈)₂⁺ shows three distinct bands at 3054, 3084, and 3108 cm^{-1} ; these bands are assigned to the CH stretching vibrations of the benzene moiety. The similarity of the spectral features to those of the neutral benzene monomer suggests that

the benzene molecule in the (benzene)₁(toluene)₂⁺ ion has a neutral character. The positive charge is localized on the toluene dimer unit with a structure written as (toluene)₂⁺⋯(benzene). The vibrational spectrum of (benzene)₂(toluene)₁⁺ bears a resemblance to that of (benzene)₂⁺. The vibrational spectrum of (benzene-*d*₆)₂(toluene)₁⁺ shows dissimilar features to the spectrum of the neutral toluene monomer, suggesting that a certain amount of the positive charge is carried by the toluene moiety. These results are explained by the charge resonance interaction between (benzene)₂ and (toluene)₁. A simple perturbation theory is applied for determining the positive charge distribution in (benzene)₂(toluene)₁⁺. The probability of finding the charge on the (benzene)₂ and (toluene)₁ moieties is analyzed to be 58 and 42 %, respectively.

III-D-8 Infrared Photodissociation Spectroscopy of [Aniline-(Water)_{*n*}]⁺ (*n* = 1–8)

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Infrared photodissociation spectra of [aniline-(H_2O)_{*n*}]⁺ (*n* = 1–8) are measured in the 2700–3800 cm^{-1} region. The spectra are interpreted with the aid of density functional theory calculations. A substantially red-shifted and broadened transition is distinctly observed at 3105 cm^{-1} for the *n* = 1 ion, and assigned to the stretching vibration of the hydrogen-bonded NH oscillator of the aniline⁺ moiety. The spectrum of the *n* = 2 ion demonstrates a large perturbation to both of the NH oscillators, indicating that each NH bond is bound to a water molecule in the most stable structure. For the *n* = 3 ion, three broad bands exist at 3070, 3230, and 3420 cm^{-1} , and there are two maxima and a weak hump at 3637, 3723, and 3696 cm^{-1} . The calculated spectrum of the 2-1 branch structure resembles the observed one very well. For the *n* = 4 ion, there exist three strong bands at 2960, 3100, and 3430 cm^{-1} , and a very weak one at 3550 cm^{-1} . The observed spectrum in the 3600–3800 cm^{-1} region is decomposed into four bands at 3640, 3698, 3710, and 3734 cm^{-1} . These bands are originated from the 2-2 branch isomer except for the 3550 and 3710 cm^{-1} bands. These two bands are due to the other isomer that has the five-membered ring. A characteristic transition in the observed spectrum of the *n* = 5 ion is the 3684 cm^{-1} band, which hardly emerges in the spectra of *n* = 1–4. This band is assigned to the free OH stretching vibration of the three-coordinated (double-acceptor–single-donor) H_2O , indicating the ring structure. The *n* = 5 ion has the five-membered ring structure with the fifth water molecule bound to the terminal (double-acceptor) H_2O . The observed spectra of the *n* = 6–8 ions show features quite different from those of *n* = 1–5; a very strong and broad band emerges around 3400 cm^{-1} . It is suggested that the *n* = 6–8 ions have the proton transfer form with some ring structure.