III-G Spectroscopy and Dynamics of Vibrationally Excited Molecules and Clusters

This research group is studying structure and dynamics of molecules and clusters by two-color double resonance spectroscopy. New spectroscopic methods will also be developed to observe the higher vibrational state under collision-free condition.

III-G-1 Picosecond Time-Resolved Infrared Spectra of Photo-Excited Phenol-$(NH_3)_3$ Cluster

ISHIUCHI, Shun-ichi; SAKAI, Makoto; DAIGOKU, Kota[1]; UEDA, Tadashi; YAMANAKA, Takaya; HASHIMOTO, Kenro[1]; FUJII, Masaaki
([1]Tokyo Metropolitan Univ. and ACT-JST)

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

Picosecond time-resolved IR spectra of phenol-$(NH_3)_3$ have been measured by UV-IR-UV ion dip spectroscopy for the first time (Figure 1). It was found that the time-evolution of two vibrational bands at 3180 cm^{-1} and 3250 cm^{-1} is different from each other. The results show that two transient species are generated from the photo-excited phenol-$(NH_3)_3$ cluster. From *ab initio* calculation, the transient species are assigned to two isomers of $(NH_3)_2NH_4$ (see Special Research Activity for more detail).

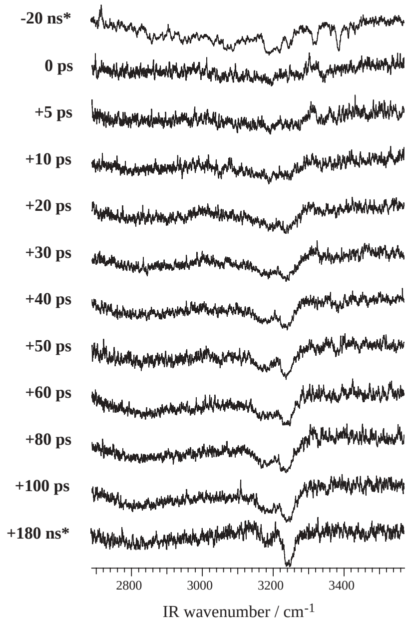

Figure 1. Picosecond time-resolved UV-IR-UV ion dip spectra of the transient species from the electronically excited PhOH-$(NH_3)_3$ which was observed by fixing the first laser ν_{UV} to the low vibronic band in the S_1 state of PhOH–$(NH_3)_3$ (281.49 nm) and monitoring $(NH_3)_2NH_4^+$ due to the ionization laser ν_{ION} (355 nm). Times indicated at the left side of each spectrum mean the delay times between ν_{UV} and the IR probe laser ν_{IR}. The spectra whose delay times are –20 ns and +180 ns (indicated by *) are obtained by nanosecond laser system, which have been reported in the previous paper (*Chem. Phys. Lett.* **322**, 27 (2000)).

III-G-2 Structure of Hydrogen-Bonded Clusters of 7-Azaindole Studied by IR Dip Spectroscopy and Ab Initio Molecular Orbital Calculation

YOKOYAMA, Hiroshi[1]; WATANABE, Hidekazu[2]; OMI, Takuichiro[1]; ISHIUCHI, Shun-ichi; FUJII, Masaaki
([1]Waseda Univ. and PRESTO; [2]AIST Shikoku, Natl. Inst. Adv. Ind. Sci. Tech.)

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

The IR spectrum of 7-azaindole monomer, 7-azaindole reactive and nonreactive dimers, and 7-azaindole $(H_2O)_n$ (n = 1–3) clusters in a supersonic jet from 2600 cm^{-1} to 3800 cm^{-1} have been measured using IR dip spectroscopy. The vibrational transitions in the ground state were clearly observed and were assigned to the CH and NH stretching vibrations of 7-azaindole and the OH stretching vibrations of water molecules in the clusters. The observed IR spectra of 7-azaindole monomer and 7-azaindole$(H_2O)_n$ (n = 1–3) clusters were compared to theoretical ones obtained by *ab initio* MO calculations. From a comparison, it is concluded that 7-azaindole$(H_2O)_n$ (n = 1–3) clusters have a ring structure due to a cyclic hydrogen-bond network. This conclusion is consistent with an analysis based on high-resolution spectroscopy. Similarly, the IR dip spectrum suggests that the 7-Azaindole reactive dimer has a cyclic hydrogen-bond network, forming a symmetric planer structure. It is strongly suggested from the IR spectrum and the ab initio calculations that the nonreactive dimer contains a water molecule between 7-azaindole molecules.

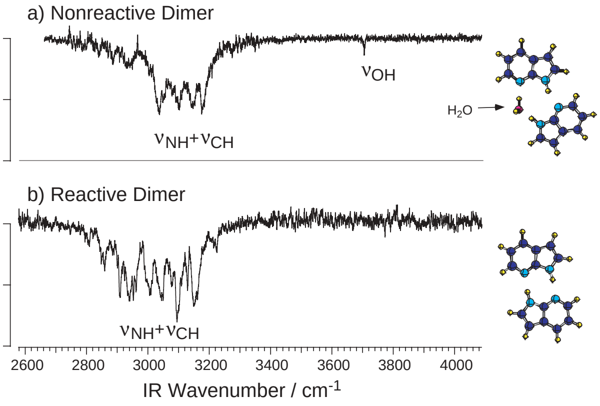

Figure 1. IR dip spectrum of (a) 7-azaindole reactive dimer and (b) nonreactive dimer. The structures concluded from the observed IR spectrum and *ab initio* calculations are also shown.

III-G-3 Structures of Carbazole-$(H_2O)_n$ (n = 1–3) Clusters Studied by IR Dip Spectroscopy and a Quantum Chemical Calculation

SAKAI, Makoto; DAIGOKU, Kota[1]; ISHIUCHI, Shun-ichi; SAEKI, Morihisa; HASHIMOTO, Kenro[1]; FUJII, Masaaki
([1]Tokyo Metropolitan Univ. and ACT-JST)

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

The IR spectra of carbazole and carbazole-$(H_2O)_n$ (n = 1–3) clusters in a supersonic jet have been measured by IR dip spectroscopy. The spectra show clear vibrational structures of both the monomer and the clusters in the 2900–3800 cm^{-1} frequency region. The observed vibrational bands are assigned to the NH stretch of carbazole and the OH stretches of H_2O molecules in the clusters. The geometries and IR spectra of carbazole-$(H_2O)_n$ clusters were calculated at the HF/6-31G and B3LYP/6-31++G(d,p) levels. From a comparison of the observed and calculated IR spectra, the structures of the cluster have been determined.

III-G-4 Structure of 1-Naphthol/Alcohol Clusters Studied by IR Dip Spectroscopy and Ab Initio Molecular Orbital Calculations

SAEKI, Morihisa; ISHIUCHI, Shun-ichi; SAKAI, Makoto; FUJII, Masaaki

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

The structures of 1-naphthol/alcohol clusters, 1-NpOH$(ROH)_n$ (n = 1–3; ROH = MeOH, EtOH, and t-BuOH), have been investigated by resonant two-photon ionization (R2PI) spectroscopy and ion-detected IR dip spectroscopy. Based on the calculated spectra obtained by *ab initio* MO calculations, the spectra of 1-NpOH-$(MeOH)_n$ was analyzed. The analysis elucidated that 1-NpOH$(MeOH)_{2,3}$ was a ring structure. From a similarity of the spectral pattern, the structures of 1-NpOH-$(EtOH)_n$ and 1-NpOH$(t\text{-}BuOH)_n$ were also determined to be a ring conformation. From a frequency shift of the hydrogen-bonded OH stretching vibration, the hydrogen bonding is weakened by a steric hindrance due to an alkyl group of ROH. The difference in the solvation mechanism between 1-NpOH$(MeOH)_n$ and 1-NpOH-$(H_2O)_n$ is discussed.

III-G-5 Structural and Dynamics of 9(10H)-Acridine and Its Hydrated Clusters. II Structual Characterization of Hydrogen-Bonding Networks

MITSUI, Masaaki[1]; OHSHIMA, Yasuhiro[1]; ISHIUCHI, Shun-ichi[2]; SAKAI, Makoto; FUJII, Masaaki
([1]Kyoto Univ.; [2]GUAS)

[*J. Phys. Chem. A* **104**, 8649 (2000)]

The present paper represents fluorescence-detected infrared measurements of 9(10H)-acridone (AD) and 10 of its fluorescent hydrated clusters, AD-$(H_2O)_n$ (n = 1–5 and more), which have been performed by monitoring the fluorescence from their $^1(\pi,\pi^*)$ electronic origin transitions. In the n = 1 and 2 clusters, free N–H stretching band has been identified in addition to O–H stretching bands characteristic to water molecules acting as single proton donors. As the next solvation step, the H-bonded O–H stretches are further developed in the red-shifted region and the N–H stretch becomes involved in the hydrogen-bonds for the n = 3–5 clusters. For $n \geq 6$, more than one pair of double-donor O–H stretches appear. These spectral features are well correlated to the stepwise evolution in the hydrogen-bonding networks in AD-$(H_2O)_n$, which have been predicted by the (π,π^*) spectral-shift analysis and DFT calculations presented in paper I: water units are bound to the C=O site for n = 1 and 2, a single water chain bridges between the C=O and N–H sites above the AD aromatic rings for n = 3–5, and water bridges become branched for ng 6 and probably form three-dimensional cages at higher aggregation levels. Differences in hydrogen-bonding topologies, stabilities, and dynamical behaviors among the conformers are discussed on the basis of the experimental observations, the DFT calculations, and comparison with other hydrated aromatic clusters.

III-G-6 Internal Methyl Group Rotation in o-Cresol Studied by Pulsed Field Ionization – ZEKE Photoelectron Spectroscopy

SUZUKI, Kazunari[1]; EMURA, Yuji[2]; ISHIUCHI, Shun-ichi[3]; FUJII, Masaaki
([1]YAMAHA; [2]Mitsui Chemical; [3]GUAS)

[*J. Electron Spectrosc.* **108**, 13 (2000)]

Pulsed field ionization – ZEKE photoelectron spectroscopy and (1+1) R2PI spectroscopy have been applied to cis- and trans-o-cresol. The internal rotational structure in S_1 has been re-assigned for the cis-isomer, and the potential curve for the internal rotation has been determined. In the PFI-ZEKE spectra recorded via different internal rotational levels in the S_1 state, well-resolved low-frequency bands have been observed. The low-frequency bands are assigned to internal rotational motion of the methyl group in the cation. Level energies and relative transition intensities are reproduced well by a one-dimensional rotor model with a three-fold axis potential. Potential curves for the internal rotation have been determined for both cis- and trans-o-cresol cations. The barrier height for the internal rotation is different for the two isomers in the cation, while it becomes similar in S_1. Contributions of steric and electronic factors to the rotational barrier are discussed.

III-G-7 Pulsed Field Ionization - ZEKE Spectroscopy of Cresoles and Their Aqueous Complex: Internal Rotation of Methyl Group and Intermolecular Vibrations

SUZUKI, Kazunari[1]; ISHIUCHI, Shun-ichi[2]; FUJII, Masaaki
([1]YAMAHA; [2]GUAS)

[*Faraday Discuss.* **115**, 229 (2000)]

Pulsed field ionization – ZEKE photoelectron spectroscopy and (1+1) R2PI spectroscopy have been applied to cis- and trans-m-cresol·H_2O clusters. The internal rotational structure in S_1 has been re-assigned, and the potential curve has been determined for the cluster. The PFI-ZEKE spectra of cis- and trans-isomer show low-frequency bands up to 1000 cm^{-1} above the adiabatic ionization potential IP_0. The low-frequency bands are assigned to the internal rotation of the methyl group, the intermolecular stretching and their combination bands in the m-cresol·H_2O cluster cation. Level energies and relative transition intensities are reproduced well by a one-dimensional rotor model with a three-fold axis potential. Potential curves for the internal rotation have been determined for both cis- and trans-isomers of m-cresol·H_2O cations. The effect of the cluster formation upon the internal methyl rotation, and interaction between the methyl rotation and the intermolecular vibration are discussed.

III-G-8 Butterfly Vibration of the Tetrafluorobenzene Cation Studied by Pulsed Field Ionization – ZEKE Photoelectron Spectroscopy

TAKAZAWA, Ken[1]; FUJII, Masaaki
([1]Natl. Res. Inst. Met.)

[*J. Electron Spectrosc.* **112**, 241 (2000)]

The pulsed field ionization - ZEKE photoelectron spectroscopy has been applied to 1,2,4,5-tetrafluorobenzene in a supersonic jet. The spectrum measured by selecting a specific vibronic level of butterfly vibrational mode in S_1 by the first laser shows well-resolved vibrational structure of the cation. A long progression has been assigned to the out-of-plane butterfly vibrational mode 11 with even quantum number in the cation. From the harmonisity and Franck-Condon factor, it has been concluded that the molecular structure of the tetrafluorobenzene cation is flat though that in S_1 is non-planer along the butterfly vibrational mode. The geometrical change upon ionization has been discussed in terms of the electronic structure.