

III-E 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.

A molecular cluster is a microscopic system of solution and/or crystal, and is thought to provide detailed information on relaxation and reaction dynamics in condensed phase. However the previous studies are concentrated to stable clusters which has no reaction pathway after photo-excitation. Consequently, spectroscopic information which concerns the reaction mechanism has not been obtained sufficiently. In this research project started from 2000, we will apply various laser spectroscopies to the reactive clusters to reveal detailed mechanism of intracuster reaction.

For the study of the ground state, the structure of the cluster can be determined by the combination of the IR dip spectroscopy and *ab initio* MO calculations.¹⁾ The IR dip spectroscopy is a kind of IR-UV double resonance spectroscopy which provides the spectrum which corresponds to the infrared absorption spectrum of the cluster (see Figure 1). A tunable IR laser is introduced to the clusters and is scanned its frequency over the fundamental vibrational region (typically 2400 ~ 4000 cm⁻¹). Then a tunable UV laser, of which the frequency is fixed to the S_1 origin of a specific cluster, is introduced and resonant enhanced multiphoton ionization signal *via* S_1 is monitored. When the IR laser is resonant to a vibrational level of the cluster, the ion signal decreases much because of loss of the population in the vibrational ground state. Thus, the IR absorption spectrum of the cluster can be measured by this depletion spectroscopy. The same spectrum can be obtained when the fluorescence intensity from S_1 is monitored instead of the ion current.

The IR spectrum in the excited state S_1 can also be measured by the depletion spectroscopy, when the UV laser is introduced before the IR laser (the UV-IR fluorescence dip spectroscopy; see Figure 2). The molecule is excited to S_1 by the UV laser, and the fluorescence intensity is monitored as well as the IR dip spectroscopy for S_0 . Then the S_1 molecules are further excited to the vibrationally excited level in S_1 by the IR laser. In general, the fluorescence quantum yield decreases in the higher vibronic level. Thus, the total fluorescence intensity decreases when the IR laser frequency is resonant to the vibrational level in S_1 .

Similarly, the IR spectrum of the ionic cluster can be measured by the depletion spectroscopy (mass-selected ion dip spectroscopy; see Figure 3). The ionic cluster can be prepared by the multiphoton ionization *via* S_1 , and the ion current due to the cation cluster of the specific size can be measured through a mass-filter. When the ionic cluster is vibrationally excited by the IR laser, the cluster is dissociated by the vibrational predissociation. Therefore, the IR transition can be measured by the decrease of the parent cluster. The same spectrum can be obtained by monitoring the enhancement of fragments (mass-selected multiphoton dissociation spectroscopy). In addition to these "dip" spectroscopies, the nonresonant ionization detected IR spectroscopy²⁾ and the PFI-ZEKE photoelectron spectroscopy³⁾ are also important tool to obtain the spectral information in the cation and the overtone states. Based on these spectroscopic techniques, we have measured the IR spectra of solvated clusters,⁴⁾ such as phenol/ammonia,⁵⁾ naphthol/alcohol,⁶⁾ carbazole/water⁷⁾ and 7-azaindole dimers,⁸⁾ and have discussed the relation among geometrical structure, electronic state and intracuster reactions.

From 2001, we have been developing the new ultrafast time-resolved IR spectroscopy for the reactive clusters. The pico second time-resolved vibrational spectroscopy is one of the ideal way to reveal the reaction mechanism directly. Here, we will demonstrate its usefulness by applying the hydrogen transfer reaction in photoexcited PhOH-

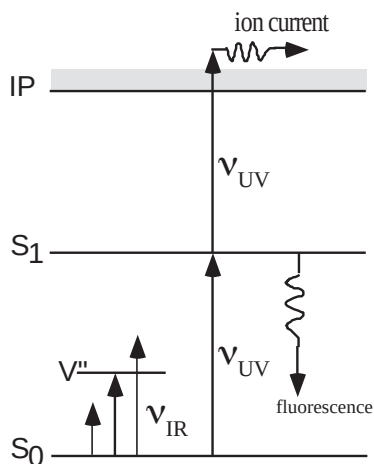


Figure 1. Principle of the IR Dip Spectroscopy. The IR transition in the ground state cluster can be measured.

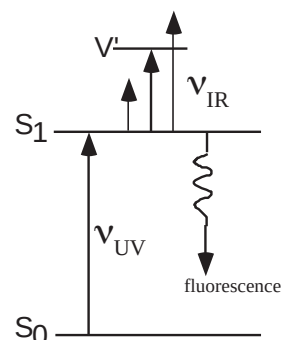


Figure 2. Principle of the UV-IR Fluorescence Dip Spectroscopy. The IR transition of the cluster in the S_1 state can be obtained.

(NH_3) $_n$ cluster.⁹⁾ Figure 4 shows the principle of the picosecond time-resolved UV-IR-UV ion dip spectroscopy. The reactive cluster ($\text{PhOH}(\text{NH}_3)_n$ in present case) is excited to S_1 by a picosecond UV laser ν_{UV} and the photochemical reaction (hydrogen transfer) is triggered. The final reaction product, *i. e.* (NH_3) $_{n-1}\text{NH}_4^+$, is ionized by a nanosecond UV laser ν_{ION} which is irradiated after 100 ns from ν_{UV} and the population of the reaction product is monitored as a mass peak of (NH_3) $_{n-1}\text{NH}_4^+$. A picosecond tunable IR laser ν_{IR} is irradiated after t ps from ν_{UV} and is scanned over vibrational region. If ν_{IR} is resonant to vibrational levels of the transient species, the population of the final reaction product decreases due to the vibrational predissociation of the transient species. Therefore, the vibrational transitions of the transient species at t ps can be observed as decrease of ion current of the final reaction product.

Time resolved UV-IR-UV ion dip spectra of phenol-(NH_3) $_3$ are shown in Figure 5. The numbers in the left hand sides of each spectrum indicate the delay time from ν_{UV} to ν_{IR} . Here the spectrum at -20 ns corresponds to the IR spectrum of $\text{PhOH}(\text{NH}_3)_3$ in S_0 , in which the sharp bands around 3400 cm^{-1} , the broad bands at $\sim 3200\text{ cm}^{-1}$ and the very broad background are assigned to the degenerated antisymmetric stretch vibration ν_3 in NH_3 , the totally symmetric stretch vibration ν_1 in NH_3 and the OH stretch vibration ν_{OH} in phenol, respectively. The spectrum at $+180$ ns shows the vibrational transitions of the final reaction product *via* S_1 , *i. e.* (NH_3) $_2\text{NH}_4^+$, and 1) two intense bands at 3180 cm^{-1} and 3250 cm^{-1} and 2) a broad band at $2700 \sim 3100\text{ cm}^{-1}$ which have been assigned to

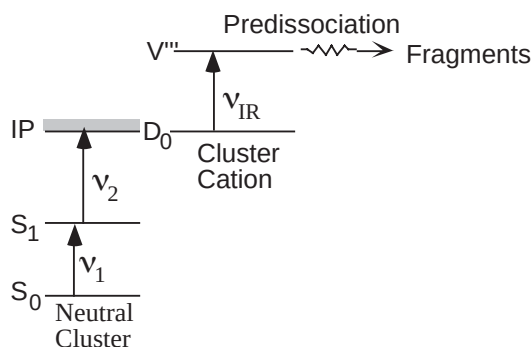


Figure 3. Principle of the mass-selected IR Ion Dip Spectroscopy. The IR transition of the cluster cation can be measured by the depletion of the parent cluster cation. The same spectrum can be measure by monitoring the enhancement of the fragments produced by the IR predissociation.

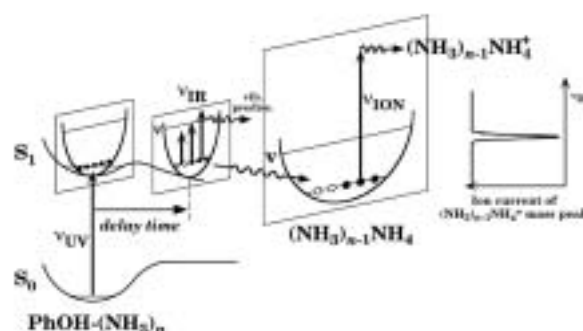


Figure 4. Principle of picosecond time-resolved UV-IR-UV ion dip spectroscopy. Potential curves of S_0 and S_1 are schematically drawn along O-H stretch coordinate. Potential curves in different sections on the S_1 O-H stretch coordinate are drawn along arbitrary N-H stretch coordinates.

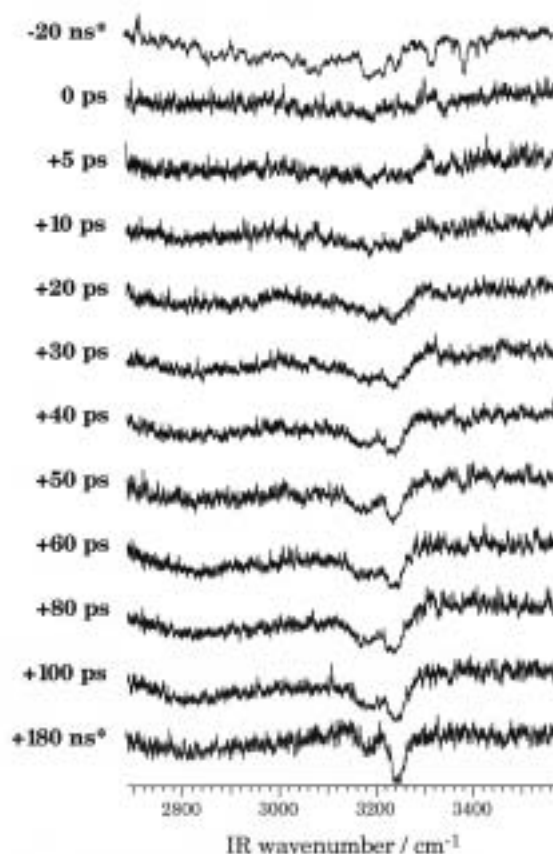


Figure 5. Picosecond time-resolved UV-IR-UV ion dip spectra of the transient species from the electronically excited $\text{PhOH}(\text{NH}_3)_3$ which was observed by fixing ν_{UV} to the low vibronic band in the S_1 state of $\text{PhOH}(\text{NH}_3)_3$ (281.49 nm) and monitoring (NH_3) $_2\text{NH}_4^+$ due to ν_{ION} (355 nm). Times indicated at the left side of each spectrum mean the delay times between ν_{UV} and ν_{IR} . The spectra whose delay times are -20 ns and $+180\text{ ns}$ (indicated by *) are obtained by nanosecond laser system, which have been reported in the previous paper.⁵⁾

vibrational transitions concerned with NH_4 .

One can see that the vibrational bands rise with increasing delay time. The spectral feature at +100 ps is already similar to that of the final reaction product (+180 ns). Here, the intense band at 3250 cm^{-1} rises slower than the band at 3180 cm^{-1} . The relative intensities of the two bands become comparable at 40 ps, thereafter, the higher band at 3250 cm^{-1} clearly grows further. Thus, the rising time constant of the band at 3250 cm^{-1} is apparently different from that of the 3180 cm^{-1} -band. This remarkable difference between the two intense bands suggests that each vibrational transition is derived from different species. The existence of two transient species are naturally interpreted by considering the isomers of $(\text{NH}_3)_2\text{NH}_4$; the most stable $\text{NH}_3\text{--NH}_4\text{--NH}_3$ and the meta-stable $\text{NH}_4\text{--NH}_3\text{--NH}_3$. The co-existence of isomers is strongly supported by *ab initio* calculations.

As described above, we have successfully measured the picosecond time resolved IR spectra of the transient species for the ESHT of $\text{PhOH}\text{--}(\text{NH}_3)_3$ for the first time. It proves that the picosecond UV-IR-UV ion dip spectroscopy is a powerful tool to explore the dynamics of the intracluster reaction.

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III-E-1 Hydrogen Transfer in Photo-Excited Phenol/Ammonia Clusters by UV-IR-UV Ion Dip Spectroscopy and Ab Initio MO Calculations I: Electronic Transitions

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[J. Chem. Phys. in press]

The electronic spectra of reaction products via photo-excited phenol / ammonia clusters (1:2~5) have been measured by UV-near-IR-UV ion dip spectroscopy. Compared with the electronic spectra of hydrogenated ammonia cluster radicals the reaction products have been proven to be $(\text{NH}_3)_{n-1}\text{NH}_4$ ($n = 2 \sim 5$), which are generated by excited-state hydrogen transfer in $\text{PhOH}\text{--}(\text{NH}_3)_n$. By comparing the experimental results with *ab initio* molecular orbital calculations at multi-reference single and double excitation CI level, it has been found that the reaction products, $(\text{NH}_3)_{n-1}\text{NH}_4$ (for $n = 3$ and 4), contain some isomers.

III-E-2 Hydrogen Transfer in Photo-Excited Phenol/Ammonia Clusters by UV-IR-UV Ion Dip Spectroscopy and Ab Initio MO Calculations II: Vibrational Transitions

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[J. Chem. Phys. in press]

The vibrational spectra of phenol/ammonia clusters (1:2 ~ 5) in S_0 and those of their photo chemical reaction products, $(\text{NH}_3)_{n-1}\text{NH}_4$ ($n = 2 \sim 5$), which are generated by excited-state hydrogen transfer, have been measured by UV-IR-UV ion dip spectroscopy. The geometries, IR spectra and normal modes of phenol- $(\text{NH}_3)_n$ ($n = 1 \sim 5$) have been examined by *ab initio* molecular orbital calculations, at the second-order Møller-Plesset perturbation theory level with large basis sets. For the $n = 2$ and 3 reaction products, similar vibrational analyses have been carried out. From the geometrical information of reactants and products, it has been suggested that the reaction products have memories of the reactant's structure, which we call "memory effect."

III-E-3 Picosecond Time-Resolved Infrared Spectra of Photo-Excited Phenol- $(\text{NH}_3)_3$ Cluster

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[Chem. Phys. Lett. **347**, 87 (2001)]

Picosecond time-resolved IR spectra of phenol- $(\text{NH}_3)_3$ have been measured by UV-IR-UV ion dip spectroscopy for the first time. 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)₂NH₄.

III-E-4 Picosecond Time-Resolved Nonresonant Ionization Detected IR Spectroscopy on 7-Azaindole Dimer

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[*Eur. Phys. J. D* in press]

The picosecond time-resolved IR spectrum of the 7-azaindole dimer has been measured by picosecond time-resolved nonresonant ionization detected IR spectroscopy. This new time-resolved technique was developed by combining nonresonant ionization detected IR (NID-IR) spectroscopy with tunable picosecond IR and UV lasers. The time-resolved NID-IR spectrum from 2600 cm^{-1} to 3800 cm^{-1} shows a drastic change from 1.5 ps to 11 ps time evolution. A mode-specific vibrational redistribution has been suggested.

III-E-5 Structure of Hydrogen-Bonded Clusters of 7-Azaindole Studied by IR Dip Spectroscopy and Ab Initio Molecular Orbital Calculation

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[*J. Phys. Chem. A* **105**, 9366 (2001)]

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.

III-E-6 Structures of Carbazole-(H_2O)_{*n*} (*n* = 1–3) Clusters Studied by IR Dip Spectroscopy and a Quantum Chemical Calculation

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[*J. Phys. Chem. A* **105**, 8651 (2001)]

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-E-7 Structure of 1-Naphthol/Alcohol Clusters Studied by IR Dip Spectroscopy and Ab Initio Molecular Orbital Calculations

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[*J. Phys. Chem. A* **105**, 10045 (2001)]

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*-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-E-8 Pulsed Field Ionization Zero Kinetic Energy Photoelectron Study on Methylanisole Molecules in a Supersonic Jet

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[*Phys. Chem. Chem. Phys.* **3**, 4889 (2001)]

Pulsed-field ionization zero kinetic energy (PFI-ZEKE) photoelectron spectra were measured for jet-cooled *o*-, *m*-, and *p*-methylanisoles for the first time. The low-frequency bands observed at around the origin band in the spectra were assigned to the methyl internal rotational bands of the cations. The potential curves and the Franck-Condon factors for the methyl internal rota-

tional motion were calculated by the one-dimensional free-rotor approximation. The potential barrier height was found to change drastically on ionization, suggesting that the electronic structure should mainly affect the potential barrier of the methyl internal rotation.

bution. The spectroscopic and theoretical results are in agreement with a relatively weak intramolecular hydrogen bond.

III-E-9 The PFI-ZEKE Photoelectron Spectrum of *m*-Fluorophenol and its Aqueous Complexes: Comparing Intermolecular Vibrations in Rotational Isomers

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[*Phys. Chem. Chem. Phys.* **4**, 2534 (2002)]

Pulsed Field Ionization–Zero Kinetic Energy (PFI-ZEKE) Photoelectron spectroscopy has been applied to study the cationic ground states of the rotational isomers of *m*-fluorophenol and its hydrogen-bonded clusters with H₂O and D₂O. The *cis*- and *trans*- monomer isomers are assigned by comparing the observed ionization potentials with values obtained from *ab initio* calculations (HF/6-31G*). Both monomers display very similar vibrational frequencies, indicating that the geometric structures of the two cations are similar. In contrast, the *cis*- and *trans*-aqueous clusters display distinctive intermolecular vibrational frequencies (*e.g.* the intermolecular stretching vibrations appear at 239 and 228 cm⁻¹ in the *cis*- and *trans*-isomers respectively). The origin of the different intermolecular interactions in the isomeric clusters is discussed with reference to the *ab initio* calculations.

III-E-10 OH- and CH-Stretching Overtone Spectra of Catechol

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[*J. Phys. Chem. A* **106**, 258 (2002)]

We have recorded the CH-, OH-, and OD-stretching fundamental and overtone spectra of catechol (1,2-dihydroxybenzene, pyrocatechol) and selectively deuterated catechol. Conventional and intracavity photoacoustic spectroscopy were used to record room temperature spectra of catechol in solution and in the vapor phase, whereas nonresonant ionization detected spectroscopy was used to study catechol in a supersonic jet. The spectra can be explained in terms of a local mode model with one oscillator for each of the non-equivalent CH, OH, or OD bonds. Intensities of the CH-, OH-, and OD-stretching transitions were calculated with an anharmonic oscillator local mode model and *ab initio* determined dipole moment functions. Our simple calculations are in good agreement with the observed intensities. Line widths in the jet-cooled spectra are discussed in terms of intramolecular vibrational redistri-