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

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

III-F-1 IR dip Spectra of Photochemical Reaction Products in a Phenol/Ammonia Cluster—Examination of Intracluster Hydrogen Transfer

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The vibrational transitions of the photochemical reaction products in phenol–$(NH_3)_3$ have been measured by IR dip spectroscopy. Two sharp bands at ~3200 cm^{-1} and a broad band in the region 2700~3100 cm^{-1} are observed. The spectrum is clearly different from that of the cluster in S_0, and also largely different from the IR spectrum of $NH_4^+(NH_3)_2$. This suggests that hydrogen transfer occurs in electronically excited phenol–$(NH_3)_3$. Evidence of hydrogen transfer has also been found in phenol–$(NH_3)_4$ based on the mass spectrum and the IR dip spectrum of the cluster.

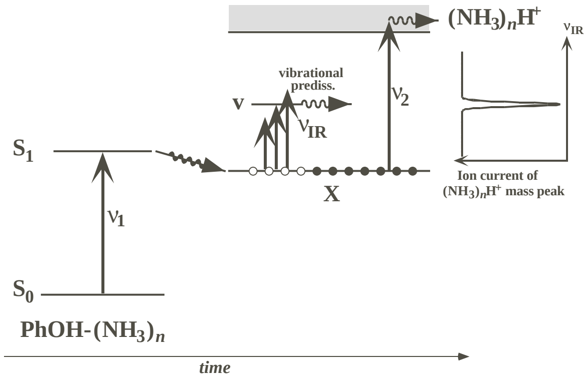

Figure 1. Schematic diagram showing the principle of IR dip spectroscopy which was employed in this work.

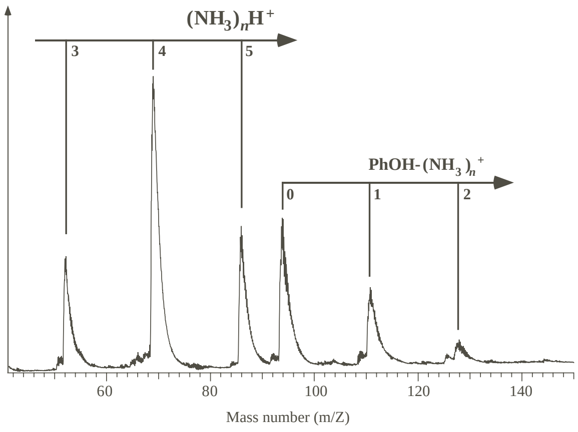

Figure 2. (a) IR dip spectrum of the reaction product which was observed by fixing ν_1 to the lower vibronic band in the S_1 state of PhOH–$(NH_3)_3$ (35498 cm^{-1}) and monitoring $(NH_3)_3H^+$. The third harmonics of the YAG laser was used as the ionization laser ν_2. Here, $(NH_3)_3H$ in the grand state can be ionized by one-photon of 355 nm light (IP = 3.31 eV). The IR laser ν_{IR} was irradiated after 180 ns from the excitation to S_1 due to ν_1. The solid curves and the dotted curves show the spectra obtained by adjusting the laser power of ν_{IR} to 0.2 mJ and 0.4 mJ, respectively. (b) IR dip spectrum of PhOH–$(NH_3)_3$ in S_0. The IR laser ν_{IR} was irradiated before 20 ns from the excitation to S_1 due to ν_1. All other conditions were the same as those for the IR dip spectrum of the reaction product (Figure 2a).

III-F-2 Structural Characterization of the Acridine–$(H_2O)_n$ (n = 1–3) Clusters by Fluorescence Dip Infrared Spectroscopy

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Vibrational spectra of supersonically cooled acridine–$(H_2O)_n$ (n = 1–3) clusters in the electronic ground state have been measured by fluorescence dip infrared spectroscopy. The observed O–H stretching fundamentals of the solvents have been analyzed with the aid of density functional calculations, to assign structures of the clusters. In the n = 1 cluster, the water molecule acts as a proton donor which is hydrogen-bonded to the N atom of acridine. The second (third) water in the higher clusters is further hydrogen-bonded to the first (second) one to form a linear “water chain,” which surrounds an edge of the acridine molecule approximately in the plane of the aromatic ring.

III-F-3 Internal Methyl Group Rotation in o-Cresol Studied by Pulsed Field Ionization-ZEKE Photoelectron Spectroscopy

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[*J. Electron. Spectrosc.* in press]

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-F-4 Pulsed Field Ionization-ZEKE Spectroscopy of Cresoles and Their Aqueous Complex: Internal Rotation of Methyl Group and Intermolecular Vibrations

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[*Faraday Discuss.* in press]

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-F-5 Butterfly Vibration of the Tetrafluorobenzene Cation Studied by Pulsed Field Ionization-ZEKE Photoelectron Spectroscopy

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[*J. Electron. Spectrosc.* in press]

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.