III-J Electronic Spectroscopy and Excited-State Dynamics of Aromatics Clusters

Clusters are model systems for elucidating intermolecular interactions that control macroscopic properties of the molecules in condensed phases, such as liquids and crystals. We are investigating geometry and bonding topology of clusters containing aromatic molecules as well as their dynamical behavior after photoexcitation. This year we focus on detailed reexamination of electronic spectra of (benzene)$_n$ clusters. Because benzene is a fundamental aromatic molecule with high symmetry, their aggregates have been subjected to vast numbers of experimental and theoretical studies for more than a quarter of a century. Still, there remain not a few issues under debate especially concerning to their electronic spectra. We succeeded in solving some of them by the present reexamination.

III-J-1 S_1–S_0 Vibronic Spectrum of the Benzene Tetramer

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We reinvestigated the S_1–S_0 electronic transitions of (benzene)$_n$ clusters by two-color mass-selective resonantly enhanced two-photon ionization (R2PI) and UV–UV hole burning spectroscopies. In this study, we explored the band system that has been assigned to the trimer for two decades. Hole burning measurements by monitoring the trimer ion isotopomer channels in the expansion of a mixture of C_6H_6 and C_6D_6 have shown the contribution of six spectral carriers in the R2PI spectra, two of which are isotopically pure clusters. The other hetero isotopic species containing at least one C_6H_6 moiety appear in two adjacent isotopomer channels. It is argued that the band system should be reassigned to the neutral tetramer having four equivalent sites, which are detected in daughter ion mass channels due to efficient fragmentation after ionization even with two-color excitation. The experimental results are consistent with a distorted tetrahedral structure with S_4 symmetry predicted as the global minimum by several model calculations. This conclusion is further supported by an analysis of exciton splittings in the C_6H_6-localized origin band, and this analysis provides coupling constants for the excitation exchange in the S_1 state. Other experimental results reported so far pertaining to this species are reconsidered on the basis of the new assignment.

III-J-2 S_1–S_0 Vibronic Spectrum of the Benzene Trimer

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We further reexamined the S_1–S_0 transition of the (benzene)$_n$ cluster that appears only in the dimer ion channel and thus has been assigned to an isomer of the neutral dimer other than the extensively studied T-shaped form. Mass-selective resonantly enhanced two-photon ionization (R2PI) excitation and UV–UV hole burning spectra are measured in the 0_0^0 and 6_0^1 vibronic regions. It is established from the observed spectra monitoring three isotopomer channels, $(C_6H_6)_2{}^+$, $[(C_6H_6)(C_6D_6)]^+$, and $(C_6D_6)_2{}^+$, that efficient fragmentation following ionization prohibits one to observe the two-color R2PI spectra in the parent ion channels, similar to the case for the benzene tetramer as presented in III-J-1. Three neutral isotopomers containing at least one C_6H_6 moiety are identified, and this result argues the reassignment of the band system to the neutral benzene trimer with a cyclic form, where the three benzene sites are equivalent. The spectra of the homo isotopomers $[(C_6H_6)_3$ and $(C_6D_6)_3]$ in the two vibronic regions exhibit small splittings due to the excitation exchange interactions, and this observation is discussed on the symmetry of the cluster geometry. Energetics pertaining to neutral and ionic benzene clusters are also discussed with previous experimental studies to assess a reason of the efficient fragmentation in the ionic states after R2PI for the trimer and larger clusters but not for the dimer.

III-K Electronic Spectroscopy of Molecules in Pendular States

When a molecule is subjected to a strong external electric field, pendular states are realized, where the electrostatic interaction by the field exceeds the molecular rotational energy and free rotation of the molecule changes to libration confined in the interaction potential. Thus, spectroscopic studies of pendular states will provide fundamental information toward establishing artificial manipulation of molecular orientation. We recently started investigation of electronic spectra of aromatic molecules in a strong DC electric field.

III-K-1 Construction of an Apparatus for Measurements of Fluorescence Excitation Spectra in a Strong DC Electric Field

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We have recently constructed an experimental apparatus that enables measurements of fluorescence excitation spectra of molecules in a strong DC electric field. The apparatus is consisted of two differentially pumped vacuum chambers, as shown in Figure 1. A sample vapor diluted in He carrier gas is expanded through a heated pulsed nozzle, collimated by a conical skimmer, and passed through the center of two parallel electrodes in the second chamber. A linearly polarized light from a pulsed dye laser goes across the molecular beam in right angles, and the resultant fluorescence propagating to the downstream of the molecular beam is filtered and imaged onto a photomultiplier tube (PMT). The output of PMT is pre-amplified and fed into a boxcar. A combination of a Glan-laser polarizer and a variable wave plate is used to obtain highly polarized laser light with arbitrary orientation of linear polarization. The electrodes are so-called of Rogowski-type, which are designed to minimize the field inhomogenity at their edges. By applying positive and negative high voltages to each of the electrodes, a uniform DC electric field up to 200 kV/cm can be achieved.

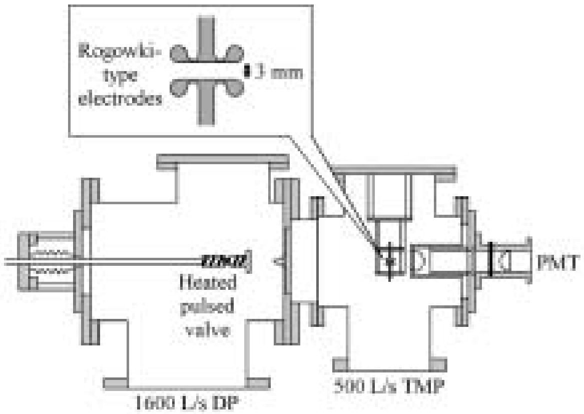

Figure 1. Schematic diagram of the experimental apparatus for measurements of fluorescence excitation spectra in a strong DC electric field. Close up of the Rogowski-type electrodes is shown as an inset.

III-K-2 Laser-Induced Fluorescence Spectra of Pendular-State Aromatics in a Strong DC Electric Field

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With the experimental setup described in III-K-1, electronic transitions of several aromatic molecules like 9-cyanoanthracene (CNA) and *p*-aminobenzonitrile were observed under various DC electric field strengths. Figure 1 shows the S_1–S_0 origin of CNA in the external electric filed. The band contour changes drastically as the increase of the external field. In addition, altering polarization of the laser against the field provides an entirely different shape in the spectra.

Because it is highly demanding computation to derive oscillator strength in a strong electric field for large asymmetric-top molecules like aromatics, some approximate method is indispensable. Considering that the interaction between the field and the molecular permanent dipole is dominant, we adopt a molecule-fixed axis system that is appropriate for the interaction. Then, the Hamiltonian is separated into zero-order terms that manifest pendular states for a symmetric top and remaining off-diagonal terms. Perturbation-theory treatments of the latter terms afford acceptably accurate calculations with greatly reduced computational time. Besides, we derived analytically, for the first time, energy levels and wavefunctions of a symmetric top in the pendular limit with corresponding quantum numbers.

Gross features of asymmetric-top pendular spectra are described in terms of the zero-order energy levels and selection rules. Indeed, the observed dependences for CNA on the electric field and the laser polarization are explained consistently, and its electric dipole moment is found to be increased by ~ 1.3 D after the $S_1 \leftarrow S_0$ excitation.

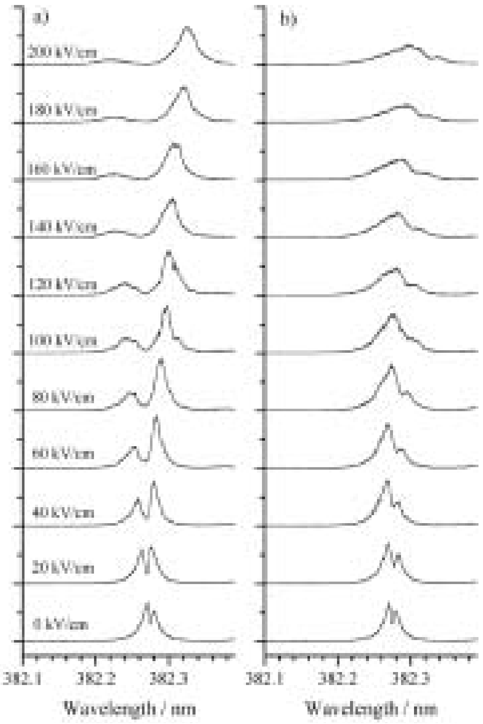

Figure 1. Electric field effects in LIF spectra of the S_1–S_0 origin band of CNA. An angle between the laser polarization and the field is a) parallel, and b) perpendicular.