III-K Structure and Exited-State Dynamics of Aromatic Clusters

Clusters containing aromatic molecules are model systems for elucidating intermolecular interactions that control macroscopic properties of the molecules in condensed phases, such as liquids and crystals. We focus on detailed correlation of dynamical behavior of photo-excited aromatic chromophore to geometry and bonding topology of the clusters. Especially, it is critically important to definitely characterize the cluster structure, and we implement various laser-based methods, such as IR–UV double resonance and rotational coherence spectroscopy (RCS), in conjunction with molecular-orbital calculations. The following subjects have been studied; 1) hydrogen-bonding networks and nonradiative dynamics of a bi-functional aromatic solvated by water molecules, 2) experimental determination of solvation structure of aromatic clusters by RCS, and 3) reexamination of electronic spectra of (benzene)$_n$ clusters.

III-K-1 Electronic Spectroscopy of 9(10H)-Acridone and Its Hydrated Clusters

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The lowest $^1(\pi,\pi^*)$ electronic transition of 9(10H)-acridone (AD) and its hydrated clusters has been studied by fluorescence-based laser spectroscopy and mass-selective two-color resonance-enhanced two-photon ionization (2C-R2PI). Thirteen fluorescent hydrates as well as the monomer have been identified in fluorescence-excitation and UV–UV hole-burning measurements, and size assignments for relatively smaller clusters, AD–$(H_2O)_n$ (n = 1–6), have been conducted by 2C-R2PI. The origin bands for larger-size clusters show larger red shifts converging at *ca.* 2200 cm^{-1}, but the changes are non-monotonic with a substantial increase from n = 2 to 3. DFT calculations at the B3LYP/6–31G(d,p) level have predicted that the energy difference between the C=O and N–H bonded isomers is quite small (only ≈ 1 kcal/mol) for n = 1 and 2. The observed spectral shifts of fluorescent hydrates with n = 1 and 2 are well reproduced by the HOMO–LUMO gap in the calculated orbital energies of either of the N–H or C=O bonded isomers, leaving the definitive structural assignments to fluorescence-detected infrared spectroscopy described in the next section. For the larger clusters (n = 3–5), several minimum-energy structures have been identified within 2 kcal/mol in binding energy, among which the conformers with water molecules bridging between the C=O and N–H sites over the AD's aromatic rings are identified as the observed species, based on good agreement between the calculated and observed spectral shifts.

III-K-2 Characterization of Hydrogen-Bonding Networks in 9(10H)-Acridone and Its Hydrated Clusters

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Fluorescence-detected infrared measurements have been performed for 9(10H)-acridone (AD) and ten of its fluorescent hydrated clusters, AD–$(H_2O)_n$ (n = 1–5 and more). 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 come to 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 the above section: waters 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's aromatic rings for n = 3–5, and water bridges become branched for $n \geq 6$ and probably form three dimensional cages at higher aggregation level.

III-K-3 Microscopic Solvation Effects on Nonradiative Dynamics in 9(10H)-Acridone and Its Hydrated Clusters

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Nonradiative dynamics and energy-level structure of relevant electronic excited states in 9(10H)-acridone (AD) and its hydrated clusters have been studied. The fluorescence decay is very fast (≈ 10 ps) for bare AD but drastically lengthened (> ns) in the clusters. Bare AD has been observed by delayed ionization and sensitized phosphorescence, which indicates the efficient formation of molecules in triplet manifold after the $^1(\pi,\pi^*)$ excitation. Several weak peaks attributable to $^3(n,\pi^*)$ transitions are identified in bare AD, but such satellites completely disappear in the fluorescent cluster spectra with $n \geq 1$. The dominant nonradiative pathway in bare AD is the $S_1(\pi,\pi^*) \rightarrow T_2(n,\pi^*)$ intersystem crossing (ISC) followed by the $T_2(n,\pi^*) \rightarrow T_1(\pi,\pi^*)$ internal conversion. This direct ISC process becomes prohibited by the energy-level inversion between S_1 and

T_2 induced by the H-bonding to the C=O site. The relaxation pathway is switched to the second-order ISC [$S_1(\pi,\pi^*) \rightarrow T_1(\pi,\pi^*)$] in the fluorescent hydrated clusters, where the carbonyl site is H-bonded. Owing to the increasing S_1–T_2 separation, the fluorescence quantum yield becomes larger for the higher clusters, which is approaching to the bulk solution value. A small fall-off in the decay constants from n = 2 to 3 is correlated to the crossover in H-bonding topologies (the C=O bonded → the bridged form), which has been established in the above sections. The delayed ionization has identified new spectral features that are absent in the fluorescence excitation spectrum. They are assigned to the N–H bonded isomer(s) with $n \leq 3$, in which the ISC should be as fast as in bare AD because of the lack of the S_1–T_2 level inversion. These experimental findings demonstrate the site-specific solvation effects on the nonradiative dynamics in the hydrated clusters of AD.

III-K-4 Structural Characterization of 9-Cyanoanthracene–(Ar)$_n$ (n = 0–3)

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Rotational coherence spectroscopy implemented with time-resolved fluorescence depletion has been applied in a structural study of 9-cyanoanthracene (CNA) and its clusters with Ar up to three atoms. For bare CNA, C-type transients for the S_1 and S_0 states have been observed separately, yielding independent sets of rotational constants for the two states. For the Ar clusters, rotational constants as averages for S_1 and S_0 have been derived to fix the cluster geometry. The Ar atom in CNA–Ar is located 3.46 ± 0.03 Å above the central aromatic ring of CNA and displaced slightly from the ring center toward the cyano group. The plane–Ar distance is quite close to those in clusters with other polycyclic aromatic molecules. Two values (≈ 0.2 or 0.6 Å) for the displacement to the cyano group are consistent with the experimental data, and results on related aromatics–Ar show that the former is preferable. The dominant conformer of CNA–(Ar)$_2$ has been determined as a two-sided (1 + 1) type: structures for each sides of the CNA plane are the same as that of CNA–Ar within the experimental uncertainties. CNA–(Ar)$_3$ has a (2 + 1)-type structure: one side of the substrate is the same as CNA–Ar and an Ar dimer lies 3.48 ± 0.04 Å above the other side. The determined conformations of CNA–(Ar)$_{1,3}$ are the same as the corresponding anthracene clusters, but that of CNA–(Ar)$_2$ is in contrast to anthracene–(Ar)$_2$, which has been identified as a (2 + 0) type. Model potential calculations have been employed to explain the difference in structural motifs of the two closely related clusters.

III-K-5 Structural Characterization of 9-Cyanoanthracene–Water

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Rotational coherence spectroscopy has been applied to determine rotational constants of the two isotopic species of the 9-cyanoanthracene–water complex, CNA–H_2O and CNA–D_2O. To support the experimental observation DFT calculations [B3LYP/6-31G(d,p)] have been also performed to identify several stable conformations. The structure of the complex is found to be such that water is hydrogen-bonded to the π-electrons of the cyano group of CNA. Geometrical parameters consistent with the experimental results are evaluated.

III-K-6 Structural Characterization of 1:1 van der Waals Complexes of 9-Cyanoanthracene with Aprotic Solvents

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Structures of 9-cyanoanthracene (CNA) clusters microsolvated with single molecule of aprotic solvents (carbon dioxide, two isotopomers of acetonitrile, and fluoroform) have been studied by rotational coherence spectroscopy. All the observed traces exhibit pronounced C-type transients, which suggests that these species are quite close to planar asymmetric tops with their electronic transition moments pointing to in-plane directions. Weak J-type transients have been also identified for CNA–CO_2 and –CF_3H, latter of which shows A-type transients in addition. By comparing the experimental observations with B3LYP/6-31G(d,p) calculations, it is concluded that the solvent molecule is located by the side of the CN group of CNA with its molecular axis lying in the CNA molecular plane. All the cluster geometries are of C_s symmetry, in which a positively charged atom of the solvents (C, H, or H for CO_2, CH_3CN, and CF_3H, respectively) is close to the cyano nitrogen of CNA, while an electonegative part (O, N, or F) contacts with the 1-position hydrogen of CNA. Some geometrical parameters including the centers of mass separation are obtained from the derived rotational constants.

III-K-7 Size Reassignments of the S_1–S_0 Vibronic Spectra of Benzene Clusters

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The vibronic band systems of (benzene)$_n$ clusters in the S_1–S_0 vibronic region are revisited by mass-selective resonant two-photon ionization and ultraviolet–ultraviolet hole-burning spectroscopies. A detailed examination of the spectra of isotopomers with isotopic mixture of C_6H_6 and C_6D_6 reveals that there is substantial fragmentation for $n \geq 3$ following photoionization. This observation concludes that it is necessary to correct the size assignments. Transitions which have been formerly identified to the trimer are most probably due to the tetramer. Instead, reassigned to the trimer is the band system which has been believed to be of an isomeric form of the dimer.