Molecular Dynamics

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Real-Time Observation of Ionization-Induced Hydrophobic→Hydrophilic Switching**

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Noncovalent interactions are responsible for fundamental properties of complex molecular systems that occur in our macroscopic world.[1] In particular, the structure, dynamics, and function of supramolecular systems such as DNA are entirely governed by noncovalent interactions.[2,3] Most of our understanding of noncovalent forces has come from quantum chemical calculations.[1,2] For example, a sophisticated ab initio treatment of intermolecular interactions in DNA base pairs has elucidated the competition between specific hydrogen-bonding and aromatic π-stacking interactions.[2] For the total stabilization energy of DNA, the stacking contribution was estimated to be about two-thirds of that of the hydrogen-bond contributions, substantially higher than it was previously thought.[2] This competition between hydrogen bonding and π stacking[4] can also be viewed as competition between hydrophilic and hydrophobic binding sites. Experimental work in the area of intermolecular forces is challenging and employs specific model systems to provide the detailed answers required to understand complex noncovalent interactions at the molecular level. Molecular clusters are one such model system,[5] and their spectroscopic characterization in molecular beams provides currently the most direct and most detailed experimental access to the intermolecular interaction potential[1,6] and excited-state dynamics.[7] In particular, clusters of acidic aromatic molecules with rare-gas atoms, such as phenol···Ar, constitute the simplest model systems to study the competition between hydrophobic and hydrophilic binding motifs, as they exhibit both dispersion interactions (binding to the π ring) and hydrogen bonding to the acidic functional group, which are essential forces for chemical and biological recognition.[2,3] As an example of such a chemical recognition process at the molecular level, we report here the first direct observation of a hydrophobic→hydrophilic site-switching process induced by ionization. This switching is initiated in the phenol···Ar_2 trimer by resonant photoionization. When the cation is prepared by photoionization, it is produced in the π-bound geometry of the neutral precursor, with argon binding to the hydrophobic ring site. On the timescale of a few picoseconds, one of the Ar atoms switches from the hydrophobic ring site to the hydrophilic OH site and creates a hydrogen bond. The dynamics of this isomerization process is monitored in real time by a change in the OH stretch vibrational wavenumber using time-resolved picosecond UV/IR pump-probe ionization depletion spectroscopy.

The competition between π bonding and hydrogen bonding in the phenol···Ar dimer cluster has been studied in the neutral ground electronic state (S_0), the electronically excited state (S_1), and the cation ground state (D_0).[4,8] In the neutral S_0 state, only the π-bound isomer is observed because dispersion forces between Ar and the aromatic π-electron system dominate the attraction. In contrast, in the ionic D_0 state the hydrogen-bound isomer is more stable, as the additional induction forces between Ar and the acidic OH group that arise from the excess charge override dispersion. Hence, Ar binds preferentially to the hydrophobic site in the neutral cluster and to the hydrophilic site in the cationic cluster. Figure 1 shows the two binding sites for the argon atom and the relevant potential energy diagrams along with the available energetic data.[4,8]

How does the system switch between the hydrophobic and hydrophilic sites? When the cation is prepared by photoionization, it is produced in the geometry of the neutral precursor (Franck–Condon principle), that is, argon binds to the hydrophobic site. Energetically, this π-bound cation is a metastable local minimum and could, in principle, switch by itself to the hydrogen-bound global minimum. However, the substantial energetic barrier between both minima[4] prevents this isomerization for the phenol···Ar dimer. In contrast, in the phenol···Ar_2 trimer the energetics change in a subtle way that enables us to present the first direct evidence for ionization-induced hydrophobic→hydrophilic site switching. The spectroscopic method employed is a sophisticated extension of the IR hole-burning technique[9] using three tuneable picosecond lasers. The excitation/ionization/depletion scheme is shown in Figure 2. Two UV lasers provide resonant ionization of phenol···Ar_2 via the S_1 state.[8] The first UV photon (UV1) excites the phenol···Ar_2 complex from the neutral S_0 state to its excited S_1 state. The second UV photon (UV2) ionizes phenol···Ar_2 from the excited S_1 state, thus producing the phenol···Ar_2 cation in its electronic ground

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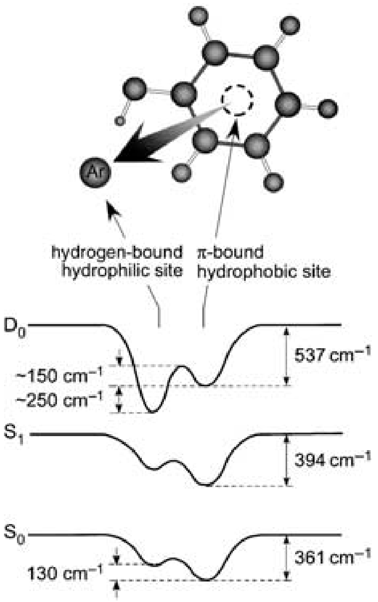

Figure 1. Hydrophobic ring site (π bonding) and hydrophilic OH site (hydrogen bonding) in the phenol···Ar cluster, along with potential diagrams[4,8] for the neutral S_0 ground state, the S_1 excited state, and the D_0 cation ground state.

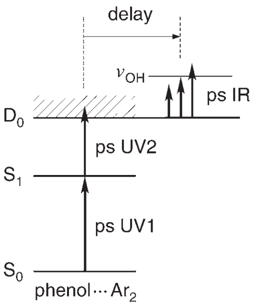

Figure 2. Excitation scheme for time-resolved picosecond UV-UV-(pump)-IR(probe) ionization depletion spectroscopy of phenol···Ar$_2$.

state, D_0. Two different colors for the UV photons are required to prevent the dissociation of the cluster cation upon ionization. The energy of the second photon results in an excess energy of less than 300 cm^{-1}, which is sufficiently small to prevent direct dissociation of the doubly π-bonded phenol···Ar$_2$ trimer cation. After an adjustable delay, the IR laser is fired to probe if one of the Ar atoms of the cation produced by the two UV lasers has moved from the ring to the OH group. To this end, the IR laser is tuned from 3400 to 3600 cm^{-1} through the range of the OH stretch wavenumber, $\tilde{\nu}_{OH}$, to distinguish between the free OH ($\tilde{\nu}_{OH} = 3537$ cm^{-1}) and the hydrogen-bonded OH···Ar vibration ($\tilde{\nu}_{OH} = 3467$ cm^{-1}).[4] The ν_{OH} wavenumber is substantially reduced by hydrogen bonding of argon to the OH group, whereas π-bound ligands have virtually no effect.[4] When the IR laser is resonant to the OH stretch vibration, the trimer is vibrationally excited and subsequently dissociated. Thus, the wavenumber of the OH stretch vibration, that is, the spectroscopic signature of the binding site of the Ar atom, is detected in the experiment by the depletion of the signal of the parent ion.

Figure 3 shows the results of the UV-UV(pump)-IR-(probe) experiment for pump-probe delay times between 1 and 50 ps. Because ionization occurs in the geometry of the neutral cluster, in which the OH bond is free (both Ar atoms are π-bound), the cation is initially produced in the same geometry (Franck–Condon principle). This "free OH" structure is indeed detected immediately after ionization for IR probe delay times of up to 3 ps, for which only the free OH band is observed at $\tilde{\nu} = 3537$ cm^{-1}. With increasing probe delay, from around 7 ps onwards, an additional peak is observed at $\tilde{\nu} = 3467$ cm^{-1}. This peak corresponds to hydrogen-bonded OH···Ar and it grows with delay time, whereas the free OH band disappears. For delay times of 10, 20, and 50 ps, only the "bound OH" structure is seen. This result can only be explained by switching of one Ar atom from the π-bonding hydrophobic to the hydrogen-bonding hydrophilic site, which has been initiated by the ionization and is completed after around 10 ps. Such a timescale for the π-to-hydrogen-bonding isomerization is consistent with a (nearly) barrierless intermolecular isomerization process.

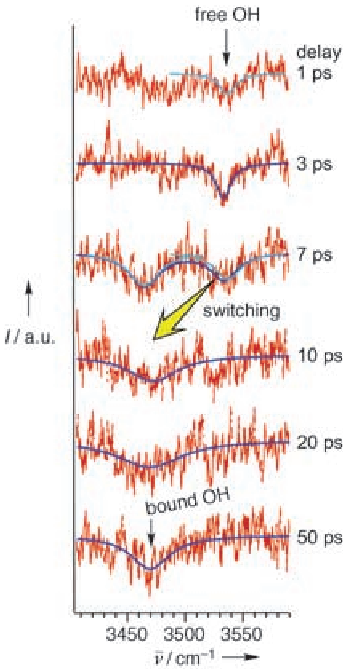

Figure 3. Time-resolved IR spectra of phenol···Ar$_2$ at various pump-probe delay times as indicated beside each spectrum. The vertical axis shows the signal for the phenol···Ar$_2$ ion, while the horizontal axis presents the wavenumber of the IR laser. When the IR laser is resonant to the OH stretch vibration, the ion signal is depleted because of vibrational predissociation of the parent cluster. Least-squares fits to the experimental data are included to guide the eyes.

This first observation in real time of the dynamics of a molecular hydrophobic→hydrophilic switch represents a fundamental example of molecular recognition dynamics. The direct observation of this intermolecular reorganization process has been possible because the change in the charge state of the aromatic molecule phenol from 0 to +1 induces the switch in the preferred aromatic solvent recognition motif from π bonding to hydrogen bonding.[10] Thus, these experiments represent a milestone in the characterization of dynamical processes of noncovalent interactions and solute–solvent binding-site specificity. The experimental approach will be used to investigate the dynamics of other molecular recognition mechanisms, such as the ionization-triggered π-to-hydrogen-bonding switch in the fundamental benzene–water interaction.[10,11]

Experimental Section

Phenol···Ar_2 complexes were produced in a supersonic molecular beam expansion of phenol seeded in Ar carrier gas. The UV1 and UV2 lasers were tuned to 36280 and 32260 cm^{-1} to prepare phenol···Ar_2 cations through resonant ionization via the S_1 origin with an excess energy of ca. 300 cm^{-1} above the ionization threshold. After an adjustable delay time, the phenol···Ar_2 cations interacted with a tuneable IR laser. Resonant vibrational excitation induces cleavage of one of the intermolecular bonds, leading to a depletion of the phenol···Ar_2 ion current. Ions were extracted in a time-of-flight (TOF) mass spectrometer and monitored as a function of the IR laser wavenumber to obtain the IR depletion spectrum. Further details of the experimental setup and the three-color picosecond laser system are provided in the Supporting Information.

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