THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 107, NUMBER 45, NOVEMBER 13, 2003

LETTERS

IR Photodissociation Spectroscopy of $Na^+[H_2O]_m[C_6F_6]_n$ Clusters: Evidence for Separation of Aqueous and Nonaqueous Phases

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Received: June 5, 2003; In Final Form: September 22, 2003

The structures of $Na^+[H_2O]_m[C_6F_6]_n$ cluster ions were investigated using IR photodissociation (IRPD) spectroscopy in the O−H stretching region. The IRPD spectra of $Na^+[H_2O]_1[C_6F_6]_n$ cluster ions indicate that even the addition of eight C_6F_6 moieties does not significantly alter the vibrational frequencies of the O−H stretches. In the case of $Na^+[H_2O]_4[C_6F_6]_n$ clusters, no changes were observed in the symmetric stretching vibration upon addition of 1−4 C_6F_6's. However, the width of the asymmetric stretching vibration increased with the number of C_6F_6, which can be attributed to vibrational relaxation. The absence of any evidence of a significant hydrogen-bonded interaction between H_2O and C_6F_6 for a wide range of cluster sizes and composition can best be explained as a separation between these two molecular species, that is, phase separation.

The physicochemical properties of hexafluorobenzene have been found to be significantly different from those of benzene or sometimes even from those of partially fluorinated benzenes. This difference has been called the "perfluoro" effect.[1] As an example, the evaluated gas-phase proton affinity of hexafluorobenzene (648 kJ/mol) is substantially lower than either that of benzene (750 kJ/mol) or that of other symmetrically substituted fluorobenzenes: 1,4-difluorobenzene (719 kJ/mol), 1,3,5-trifluorobenzene (742 kJ/mol), and 1,2,4,5-tetrafluorobenzene (746 kJ/mol).[2] Also notable is the difference in the quadrupole moment between benzene and hexafluorobenzene along the out-of-plane axis. Benzene has negative electrostatic potential above and below the plane of the ring and positive potential in the plane, giving rise to a net quadrupole moment of −8.5 B. Hexafluorobenzene has a potential comparable in magnitude but opposite in sign with a net quadrupole moment of +9.5 B. These differences between benzene and hexafluorobenzene significantly affect their interactions with other polar species. For instance, it is well-known that the hydrogen atoms in water interact with the benzene ring forming a π-hydrogen bond.[3] On the basis of electrostatic arguments, it was theoretically shown that water and hexafluorobenzene interact via O$\cdots\pi$ interaction, a reversal of the orientation of water relative to the water−benzene interaction.[4] Also, secondary minima exist on the water−hexafluorobenzene interaction potential (in 12 equivalent orientations), in which the water is above the plane of hexafluorobenzene with the O−H and C−F bond dipoles aligned.[4a] One curious result was the absence of the fully in-plane complex with F$\cdots$H−O hydrogen bonding. This contrasts with partially fluorinated benzenes, such as fluorobenzene and difluorobenzene, which are known to form fully planar complexes with water via F$\cdots$H−O hydrogen bonding.[5]

The water−hexafluorobenzene interaction is primarily between the oxygen atom and the electron-deficient region above and below the plane. At this stage, an interesting question arises. If the oxygen atom on water is unavailable to interact with hexafluorobenzene, can a F$\cdots$H−O hydrogen bond be induced? To probe this point, we investigated mixed clusters of Na^+ with water (H_2O) and hexafluorobenzene (C_6F_6). The calculated (MP2/6-31+G* level and ZPVE- and BSSE-corrected) binding

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10.1021/jp030715z CCC: $25.00

energies of Na^+ with H_2O and C_6F_6 are −25.7 and −12.4 kcal/mol, respectively. Although this level of calculation is of modest accuracy (within ±2 kcal/mol), it clearly indicates that Na^+ will preferentially bind to H_2O over C_6F_6. In the cluster formation process, water will preferentially locate in the first solvation shell around Na^+ because of the greater interaction energy, and the remaining positions will be occupied by C_6F_6. Once the first solvation shell is completely filled, the further addition of C_6F_6 moieties will trigger the formation of a second solvent shell. Should C_6F_6 in the second shell interact with H_2O in the first solvent shell leading to the formation of a F···H−O hydrogen bond, this could then be investigated and characterized through the vibrational spectroscopy of O−H stretching modes of H_2O. A similar approach was used in the investigation of $M^+(H_2O)_n(C_6H_6)_m$ clusters (M = Na and K), where π-hydrogen bonding was detected between water in the first shell and benzene in the second.[6]

The vibrational spectra of $Na^+[H_2O]_m[C_6F_6]_n$ mixed clusters in the O−H stretching region were recorded in a tandem quadrupole mass spectrometer using the infrared-photodissociation (IRPD) technique, described in detail elsewhere.[7] Briefly, the neutral clusters of C_6F_6 and H_2O are formed in a supersonic jet by the coexpansion of the reagents in an argon buffer gas. Sodium ions, produced by thermionic emission from a tungsten filament coated with a salt-enriched suspension of zeolite paste, are injected into the neutral clusters about 30 mm downstream from a 180 μm diameter conical nozzle. The nascent cluster ions stabilize via evaporative cooling. From the ensemble of cluster ions formed in the molecular beam, the species of interest is mass-selected using a quadrupole mass filter. These mass-selected cluster ions are then passed on to a quadrupole ion guide, where they can interact with a tunable IR laser. The absorption of IR radiation by the cluster ion induces vibrational predissociation via loss of the most labile molecule to a specific cluster ion fragment, which is monitored using another quadrupole mass filter. The IR spectrum is measured by recording the percent fragmentation as a function of IR frequency. This action spectrum is reported as the predissociation cross section by correcting for the laser fluence. The IR source is the idler component of a $LiNbO_3$ optical parametric oscillator (3 cm^{-1} bandwidth) pumped by the fundamental of a custom 20 ns Nd:YAG laser (Continuum). Absolute frequency calibration (±2 cm^{-1}) for the spectrum is obtained by simultaneously measuring the photoacoustic spectrum of ambient water vapor. All of the IR spectra presented here were recorded by monitoring the loss of either one or two molecules, as noted in the figures. The choice of loss channel was based on signal-to-noise (S/N), because the IR spectral features remained unchanged.

The IRPD spectra of $Na^+[C_6F_6]_n[H_2O]_1$ clusters are presented in Figure 1. The spectra for n = 3−5 were recorded by monitoring the C_6F_6 loss channel, while those for n = 6−8 were recorded by monitoring the loss of two C_6F_6 moieties, which is the primary reason for the change in S/N. However, all six spectra show two bands around 3725 and 3640 cm^{-1}, which can be directly assigned to the asymmetric and symmetric stretching vibrations of H_2O, respectively. Both bands are slightly shifted to lower frequency relative to the gas-phase values of 3756 and 3657 cm^{-1} in water monomer because of the strong interaction between Na^+ and water. Similar shifts to lower frequencies were observed for $Cs^+(H_2O)Ar$.[8] These spectra point out that the environment around H_2O in all of the clusters is almost identical and, most significantly, they do not reveal any hydrogen-bonded interaction between H_2O and C_6F_6. This result is in complete contrast with the IRPD spectra of $Na^+[H_2O]_1[p\text{-}C_6H_4F_2]_n$, in which a hydrogen-bonded interaction was detected on the addition of the sixth p-$C_6H_4F_2$, marking the onset of formation of the second solvent shell.[9] Furthermore, from the present IRPD spectra of $Na^+[H_2O]_1[C_6F_6]_{3-8}$, the point of formation of the second shell cannot be determined. The slight

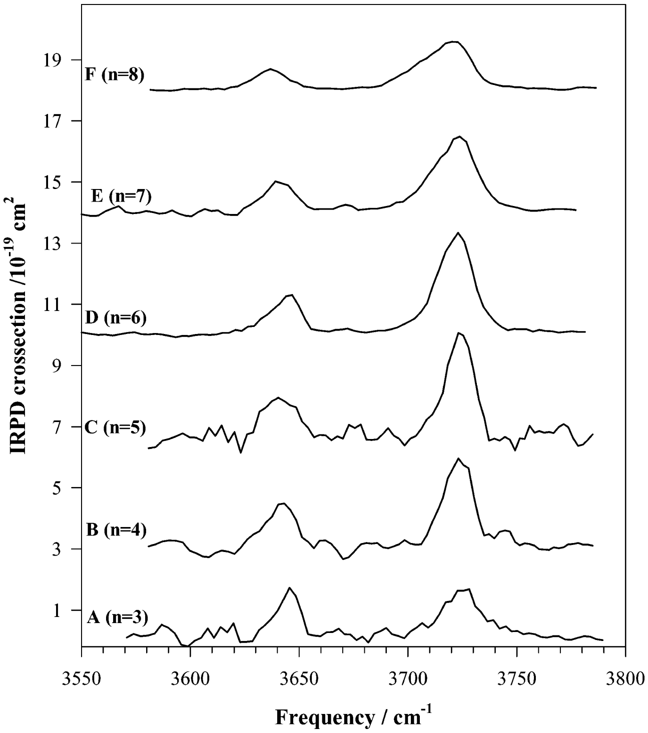

Figure 1. IRPD spectra of $Na^+[H_2O]_1[C_6F_6]_n$. Traces A−E correspond to n = 3−8, respectively. Traces A−C were recorded by monitoring the loss of one C_6F_6, and traces D−F were recorded by monitoring the two C_6F_6 loss channel.

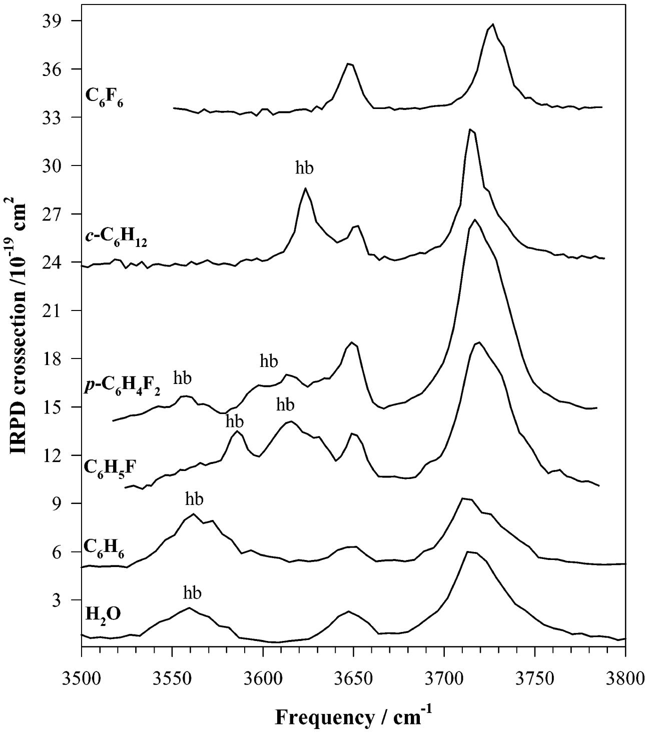

Figure 2. IRPD spectra of $Na^+[H_2O]_4[L]_1$, where "L" corresponds to various ligands. Peaks marked with "hb" correspond to hydrogen-bonded O−H stretches of water. All of the spectra were recorded by monitoring the loss of the fifth ligand.

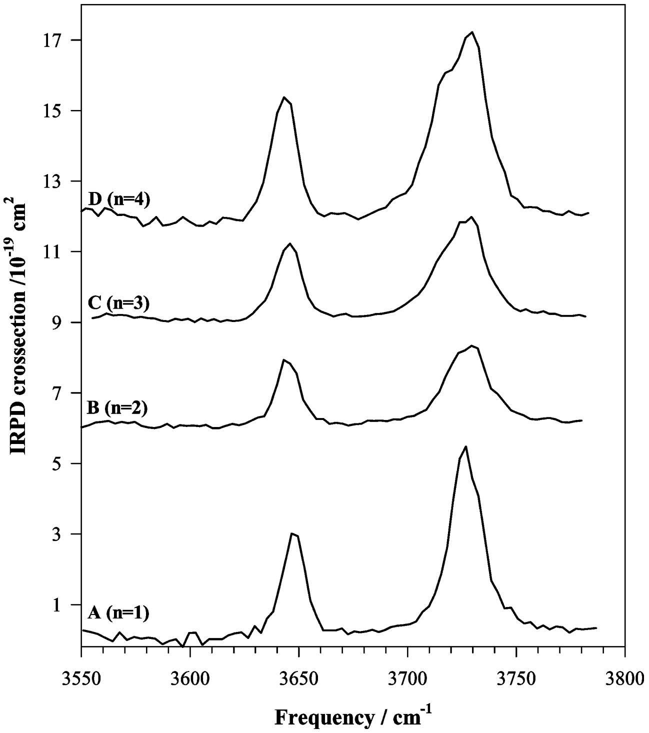

Figure 3. IRPD spectra of $Na^+[H_2O]_4[C_6F_6]_n$. Traces A−D correspond to $n = 1-4$, respectively. Trace A was recorded by monitoring the loss of one C_6F_6, and traces B−D were recorded by monitoring the two C_6F_6 loss channel.

broadening in the band of the asymmetric O−H stretch for $Na^+[H_2O]_1[C_6F_6]_{7,8}$ is the only notable change with size.

We note that the vibrational spectrum of solitary water molecules in liquid C_6F_6 has been measured.[10] In this environment, the observed frequencies of 3725 and 3634 cm^{-1} for the asymmetric and symmetric modes of H_2O are very close to the values reported for the above clusters. We further note that the widths of the asymmetric and symmetric modes are different,[10] the former over twice the width (24 cm^{-1}) of the latter (11 cm^{-1}). This was attributed to more rapid vibrational relaxation of the asymmetric mode.

It is well-known, both experimentally[6,9,11] and theoretically,[12] that the first hydration shell of Na^+ in the gas phase consists of four H_2O molecules. Addition of a fifth H_2O molecule to $Na^+[H_2O]_4$ triggers the formation of a second solvent shell, which is reflected by the appearance of a hydrogen-bonded O−H stretching vibration. Apart from H_2O, the addition of various other molecules as a fifth ligand (L) to $Na^+[H_2O]_4$ also triggers the formation of a second solvation shell, again detected via IR spectroscopy of the hydrogen-bonded O−H stretch. This suggests that perhaps addition of C_6F_6 to $Na^+[H_2O]_4$, would force the formation of a hydrogen bond between C_6F_6 and H_2O. Figure 2 shows the IRPD spectra of $Na^+[H_2O]_4[L]_1$ clusters, where L, the fifth ligand, is one of the following: H_2O (water), C_6H_6 (benzene), C_6H_5F (fluorobenzene), *p*-$C_6H_4F_2$ (1,4-difluorobenzene), *c*-C_6H_{12} (cyclohexane), and C_6F_6 (hexafluorobenzene). The appearance of a hydrogen-bonded O−H stretching transition below 3640 cm^{-1} can be seen in all of the spectra, with the exception of $Na^+[H_2O]_4[C_6F_6]_1$. In this last case, the IRPD spectrum of $Na^+[H_2O]_4[C_6F_6]_1$ shows only the two bands at 3727 and 3647 cm^{-1} and is almost identical to those depicted in Figure 1. Even the IRPD spectrum of $Na^+[H_2O]_4[c\text{-}C_6H_{12}]_1$ with a band at 3623 cm^{-1} suggests some type of hydrogen-bonded interaction, albeit a weak one, although cyclohexane is normally considered to be hydrophobic.[13] Figure 2 clearly demonstrates that these shifts decrease in the ligand order given above and disappear completely in the case of C_6F_6. It appears that hexafluorobenzene exhibits no ability to act as a proton acceptor in a hydrogen bond with water.

In an attempt to initiate a $O-H\cdots C_6F_6$ interaction, C_6F_6 molecules were successively added to $Na^+[H_2O]_4$. Figure 3 shows the IRPD spectra of $Na^+[H_2O]_4[C_6F_6]_{1-4}$ clusters. All four spectra show only the two bands around 3727 and 3647 cm^{-1}, the respective asymmetric and symmetric stretching vibrations of H_2O. As noted in Figure 2 for the $Na^+[H_2O]_4[L]_1$ clusters, the presence of any $O-H\cdots L$ interaction gives rise to a hydrogen-bonded O−H stretching transition, appearing at a lower frequency to the symmetric stretch. Even the limiting case of a very weak hydrogen-bond interaction would lead to a broadening of the symmetric stretching vibration to lower frequency. However, in the IRPD spectra of $Na^+[H_2O]_4[C_6F_6]_{1-4}$, the width and the position of the symmetric stretching vibration remain unchanged, signifying the absence of any $O-H\cdots C_6F_6$ interaction. While the symmetric stretching is unaltered, the width of the asymmetric stretch increases as the number of C_6F_6 moieties increases from 2 to 4. For $Na^+[H_2O]_4[C_6F_6]_4$, the width (~28 cm^{-1}) of the asymmetric stretch is about twice that of the symmetric stretch. The similarity in these observed widths to that for solitary water in liquid C_6F_6 cited earlier[10] suggests a common source of broadening in the asymmetric stretch, that is, vibrational relaxation[10] resulting from the presence of C_6F_6 near some of the H_2O molecules.

Despite our efforts to form an $O-H\cdots C_6F_6$ hydrogen bond, no evidence for its formation was observed in the IRPD spectra. Indeed, for Na^+ clusters with one or four H_2O molecules, the addition of C_6F_6 to a total of nine or eight ligands, respectively, does not appreciably alter the appearance of the vibrational

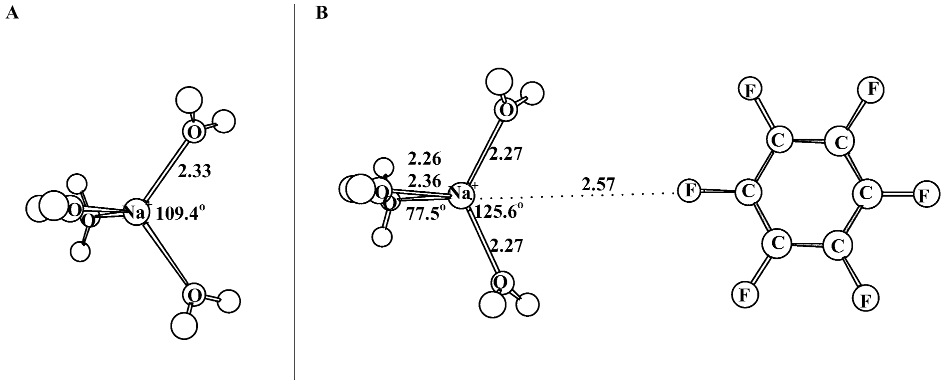

Figure 4. Calculated structures of (A) $Na^+[H_2O]_4$ and (B) $Na^+[H_2O]_4[C_6F_6]_1$. All of the atoms except hydrogens are labeled, and distances are shown in angstroms. For better presentation, C_6F_6 is shown at slightly larger distance, not to scale.

spectrum of H_2O, save for an increase in width of the asymmetric stretch for the largest clusters. However, C_6F_6 molecules are present in the cluster. Is there an explanation of the remarkably subtle impact of C_6F_6 on the water molecules?

To gain insight as to the mode of interaction of C_6F_6 with the $Na^+[H_2O]_4$ cluster ion, we calculated the structures of $Na^+[H_2O]_4$ and $Na^+[H_2O]_4[C_6F_6]_1$ cluster ions at MP2/6-31G* level using Gaussian 98.[14] Figure 4 shows the fully optimized structures. In the case of $Na^+[H_2O]_4$, the four water molecules are arranged in a tetrahedral geometry around the Na^+ ion. In $Na^+[H_2O]_4[C_6F_6]_1$, C_6F_6 distorts the tetrahedral arrangement of water molecules and interacts directly with Na^+ through ligation of the lone pair on the F atom, effectively forming a pentacoordinated complex. Structurally, the angle between the two in-plane water molecules widens to 125.6°, and the angle between the two out-of-plane water molecules contracts to 77.5°. The hexafluorobenzene is slightly above the plane containing the first two water molecules with a Na^+-F distance of 2.57 Å. This structure explains the absence of a hydrogen-bonded feature or any distortion of the O−H stretching modes in the IRPD spectrum of $Na^+[H_2O]_4[C_6F_6]_1$ (Figure 3A). The continued absence of any hydrogen-bonded interaction upon successive addition of C_6F_6 to the $Na^+[H_2O]_4[C_6F_6]_1$ cluster indicates that C_6F_6 avoids water in favor of $C_6F_6-C_6F_6$ interactions. This picture is supported by two observations. The most favorable $C_6F_6-C_6F_6$ interaction results from an offset face-to-face configuration,[15] which can be readily accommodated given the structure in Figure 4B. Successive C_6F_6 molecules will likely add to the cluster in a similar manner based on neutron diffraction and MD studies of liquid C_6F_6,[16] where nearest neighbors have both parallel and perpendicular configurations with the former favored at the shortest distances. Thus C_6F_6 will gravitate away from locations in the cluster where water is present.

As the number of C_6F_6 molecules increase, a boundary or interface will be established between the H_2O and C_6F_6 molecules. For solitary water in liquid C_6F_6, this led to a characteristic broadening of the asymmetric (24 cm^{-1}) and symmetric (11 cm^{-1}) O−H stretching modes but only a slight shift in the vibrational frequencies.[10] In our cluster ions, when the number of C_6F_6 molecules is sufficient, a similar effect occurs where additional broadening in the asymmetric mode is observed for both $Na^+[H_2O]_1[C_6F_6]_{n\geq 6}$ and $Na^+[H_2O]_4[C_6F_6]_{m\geq 2}$. The simplest interpretation of this collective behavior is for a phase separation between the aqueous and nonaqueous components in this cluster ion. To our knowledge, this effect has not been previously observed in ion clusters.

Acknowledgment. This material is based upon work supported by the National Science Foundation, Experimental Physical Chemistry, under Grant No. CHE-0071278. Authors thank Prof. K. S. Kim, Dr. P. Tarakeshwar, and Mr. T. Vaden for useful discussions.

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