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Hydrogen bonding of the naphthalene radical cation to water and methanol and attachment of the naphthalene ion to extended hydrogen bonding chains

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ABSTRACT

The binding energies of water and methanol to the naphthalene radical cation (7.8 and 8.3 kcal/mol, respectively) are reported. The naphthalene ion forms unconventional carbon-based ionic hydrogen bonds with H_2O and CH_3OH ($CH^{\delta+}\cdots OH_2$ and $CH^{\delta+}\cdots OHCH_3$, respectively) which can be extended to hydrogen bonding chains with additional solvent molecules. Both water and methanol molecules show a strong tendency for the external solvation of the naphthalene cation. These structures allow the PAH ion to reside on the surface of ice grains in interstellar medium where reactions with incoming organic molecules could take place to produce a variety of complex organics in space.

1. Introduction

Ionic hydrogen bonding (IHB) interactions involving ionized aromatics are important in radiation chemistry, electrochemistry, polymerization in aqueous solvents, and in astrochemical environments [1–3]. These interactions can form unconventional carbon-based IHBs where the hydrogen donors are the ionized aromatics containing CH groups and the hydrogen acceptors are electron lone pairs on hetero atoms such as O or N, olefin double bonds, or aromatic π systems [3]. Carbon-based $CH^{\delta+}\cdots O$ IHBs have been identified in the hydration of ionized aromatics such as benzene ($C_6H_6^{+\bullet}$), cyclic $C_3H_3^+$ and phenylacetylene ($C_8H_6^{+\bullet}$) [4–7]. For example, the benzene radical cation interacts with water molecules by $CH^{\delta+}\cdots O$ hydrogen bonds resulting in stepwise hydration energies, $\Delta H^\circ_{n-1,n}$ where n is the number of water molecules, that are nearly constant at 8.5 ± 1 kcal/mol for $n = 1$–6 [4,5]. However, the hydration energy of the cyclic $C_3H_3^+$ ion (11.7 kcal/mol) is significantly higher than those of the $C_6H_6^{+\bullet}$ and $C_8H_6^{+\bullet}$ ions reflecting the higher charge density on the $CH^{\delta+}$ sites of the $C_3H_3^+$ ion [6].

Ionic hydrogen bonding interactions involving small polar molecules such as water and methanol are also important for ionized polycyclic aromatic hydrocarbons (PAHs) which are considered to be the most abundant free interstellar organic molecules [8–10]. These compounds are also produced in solar nebulae which contain diverse environments suitable for rich organic chemistry [11–13]. Strong variations of physical conditions (temperature, density, ionization rate, UV/X-ray intensities) make a variety of chemical processes and transformations active in protoplanetary disks (PPDs), producing simple molecules in the gas phase and complex organic materials on the surfaces of dust grains [13–15]. Given the indications of PAHs in interstellar and nebula environments, the low ionization energies and high proton affinities of these compounds suggest that a large fraction of the PAHs are present in ionized states in space environments [16–22]. In turn, the ionized states make these compounds reactive in condensation and clusters' formation toward the build-up of increasingly more complex organics and aggregates. Interstellar molecules such as water, methanol and hydrogen cyanide can cluster with the PAH ions and condense to form large hydrogen-bonded networks around or on the surface of the PAH ions thus acting as nucleation centers for the formation of organic-doped icy grains. Such organic-doped icy grains can form complex organics including membrane-forming components under interstellar UV radiation [23–26].

The recent astrophysics discovery of new diffused interstellar bands (DIBs) assigned to the electronic transitions in the naphthalene radical cation based on complementary laboratory measurements, has initiated several experimental and theoretical studies of structures, spectroscopy and reactions of the

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naphthalene radical cation [27–33]. Previous studies indicated unusual stability of the PAH radical cations in amorphous water ices up to 120 K [26,25], but no laboratory studies have focused on the gas phase interactions of the naphthalene radical cation with simple molecules such as water and methanol. Here, we present the first study on the interactions of the naphthalene radical cation with the astrophysically relevant molecules water and methanol in the gas phase. We report measured binding energies for the $(C_{10}H_8^{+\bullet})(H_2O)$ and $(C_{10}H_8^{+\bullet})(CH_3OH)$ complexes and calculated structures and binding energies of 1–6 water and methanol molecules associated with the naphthalene radical cation in the $(C_{10}H_8^{+\bullet})(H_2O)_n$ and $(C_{10}H_8^{+\bullet})(CH_3OH)_n$ clusters, respectively. The results indicate that the naphthalene radical cation is attached to a hydrogen bonding chain of water or methanol molecules with no evidence for internal solvation. We also investigate the proton transfer products $(C_{10}H_7^{\bullet})H^+(CH_3OH)_n$ that could lead to the formation of a reactive naphthalene radical ($C_{10}H_7^{\bullet}$) on the surface of methanol ice grains in interstellar medium. This work aims to establish a molecular level understanding of the role of hydrogen bonding interactions in determining the structures of the solvated naphthalene radical cations within clusters of polar molecules relevant to astrophysical environments.

2. Experimental

The experiments were performed using the VCU mass-selected ion mobility spectrometer. The details of the instrument can be found in several publications and only a brief description of the experimental procedure is given here [5,7,34].

Mass-selected $C_{10}H_8^{+\bullet}$ ions (generated by electron impact ionization of naphthalene vapor) are injected (in 25–45 μsec pulses) into the drift cell containing 1.0 Torr helium and 0.5–0.6 Torr of H_2O, D_2O or CH_3OH vapor. The temperature of the drift cell can be controlled to better than ±1 K using six temperature controllers. The reaction products can be identified by scanning a second quadrupole mass filter located coaxially after the drift cell. The injection energies used in the experiments (10–14 eV, laboratory frame) are slightly above the minimum energies required to introduce the ions into the cell against the H_2O/He or CH_3OH/He flow. Most of the ion thermalization occurs outside the cell entrance by collisions with the water vapor escaping from the cell entrance orifice. The ion intensity ratio $C_{10}H_8^{+\bullet}(H_2O)/C_{10}H_8^{+\bullet}$ or $C_{10}H_8^{+\bullet}(CH_3OH)/C_{10}H_8^{+\bullet}$ is measured from the ion intensity peaks as a function of decreasing cell drift field corresponding to increasing reaction time, and equilibrium is achieved when a constant ratio is obtained. Equilibrium constants are then calculated from $K = [I(C_{10}H_8^{+\bullet}(A))/I(C_{10}H_8^{+\bullet})\,P(A)]$ where I is the ion intensity taken from the mass spectrum and $P(A)$ is the partial pressure of the neutral A (water or methanol) in the drift cell. All the equilibrium experiments at different temperatures are conducted at correspondingly low drift fields and long residence times. The measured equilibrium constant is independent of the applied field across the drift cell in the low field region. The equilibrium constant measured as a function of temperature yields ΔH° and ΔS° from the van't Hoff equation $[\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R]$.

3. Computational section

Density functional theory (DFT) computations of the lowest energy geometries for the $(C_{10}H_8^{+\bullet})(H_2O)_n$ and $(C_{10}H_8^{+\bullet})(CH_3OH)_n$ clusters with $n = 1$–6 were performed at the B3LYP/6-311++G** level of theory using the Gaussian 03 program suite [35]. Calculations of the $(C_{10}H_8^{+\bullet})(H_2O)$ and $(C_{10}H_8^{+\bullet})(CH_3OH)$ complexes were also carried out at the M06-2X/6-311++G(d,p) level using the Gaussian 09 program suite [36], for comparison with the B3LYP method. Vibrational frequency calculations were also performed for all the optimized geometries at the same level of theory in order to obtain zero point vibrational energy (ZPVE) and also to verify the absence of any imaginary frequencies. The binding energy (ΔE) is calculated at 0 K, for example, for the $(C_{10}H_8^{+\bullet})(H_2O)_n$ clusters according to:

$$\Delta E[(C_{10}H_8^{+\bullet})(H_2O)_n] = E[(C_{10}H_8^{+\bullet})(H_2O)_{n-1}] + E[H_2O] - E[(C_{10}H_8^{+\bullet})(H_2O)_n] \quad (1)$$

where E [H_2O], E [$(C_{10}H_8^{+\bullet})(H_2O)_{n-1}$] and E [$(C_{10}H_8^{+\bullet})(H_2O)_n$] are the total electronic energies for H_2O, the lowest energy isomer of $C_{10}H_8^{+\bullet}(H_2O)_{n-1}$, and the lowest energy isomer of $C_{10}H_8^{+\bullet}(H_2O)_n$, respectively obtained at the B3LYP/6-311++G** level. Corrections to BSSE were made only for the $C_{10}H_8^{+\bullet}(H_2O)$ and $C_{10}H_8^{+\bullet}(CH_3OH)$ clusters since these corrections were found to be small (0.5–0.7 kcal/mol).

4. Results and discussion

4.1. Mass spectra and thermochemical results

Figure 1a and b displays the mass spectra obtained following the injection of the mass-selected naphthalene ions ($C_{10}H_8^{+\bullet}$) into the drift cell containing water/He and methanol/He vapors, respectively. In the presence of 0.60 Torr H_2O vapor in the drift cell at 298 K, the first association product $C_{10}H_8^{+\bullet}(H_2O)$ along with small intensities corresponding to the clusters $C_{10}H_8^{+\bullet}(H_2O)_n$ with $n = 2$–4 and protonated water clusters $H^+(H_2O)_n$ with $n = 6$–11 are also observed as shown in Figure 1a(ii). As the temperature decreases the ion intensity of the $C_{10}H_8^{+\bullet}(H_2O)$ cluster increases and at 249 K, small peaks corresponding to the $C_{10}H_8^{+\bullet}(H_2O)_n$ clusters with $n = 2$–6 can be detected as shown in Figure 1a(iv). Similar results are obtained following the injection of the $C_{10}H_8^{+\bullet}$ ions into the drift cell containing methanol/He vapor mixtures as shown in Figure 1b. Here, the $C_{10}H_8^{+\bullet}(CH_3OH)_n$ clusters with $n = 1$ and 2 and the protonated methanol clusters $H^+(CH_3OH)_n$ with $n = 5$–7 are observed at 249 K as shown in Figure 1b(iv). At lower temperatures (below 240 K), the intensities of the naphthalene-containing ions ($C_{10}H_8^{+\bullet}$ and $C_{10}H_8^{+\bullet}(CH_3OH)_n$ with $n = 1$–2) decrease and they eventually disappear at 238 K and only the protonated methanol clusters $H^+(CH_3OH)_n$ with $n = 5$–9 are observed along with small intensities of the $C_{10}H_8^{+\bullet}(CH_3OH)_n$ clusters with $n = 3$–5 as shown in Figure 1b(v).

The appearance of very small ion intensities of the protonated water clusters is most likely due to the injection energies of the injected naphthalene cations which could induce the ionization of water inside the drift cell followed by proton transfer to form the observed protonated water clusters. However, this mechanism cannot explain the simultaneous disappearance of the naphthalene-containing ions and the appearance of protonated methanol clusters $H^+(CH_3OH)_n$ starting with $n \geq 5$ at 238 K as shown in Figure 1b(v). This suggests that the large $C_{10}H_8^{+\bullet}(CH_3OH)_n$ clusters with $n \geq 5$ undergo intracluster dissociative proton transfer (DPT) reactions to produce the observed large $H^+(CH_3OH)_n$ clusters with $n = 5$–9 along with naphthalene radicals ($C_{10}H_7^{\bullet}$). Similar reactions have been observed within the $C_6H_6^{+\bullet}(H_2O)_n$ clusters but with $n \geq 4$ [5]. The higher proton affinity (PA) of the naphthalene radical ($C_{10}H_7^{\bullet}$, 234 kcal/mol) [37] as compared to that of the phenyl radical ($C_6H_5^{\bullet}$, 212 kcal/mol)[5] and the higher PA of methanol (182 kcal/mol) [38,39] as compared to water (167 kcal/mol) [38,39] make the PT reaction within the $C_{10}H_8^{+\bullet}(CH_3OH)_n$ clusters exothermic at $n = 5$ as will be discussed in Section 4 below.