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The Onset of Electron-Induced Proton-Transfer in Hydrated Azabenzene Cluster Anions

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Abstract

The prospect that protons from water may be transferred to N-heterocyclic molecules due to the presence of an excess electron is studied in hydrated azabenzene cluster anions using anion photoelectron spectroscopy and computational chemistry. In the case of *s*-triazine ($C_3H_3N_3$), which has a positive adiabatic electron affinity, proton transfer is not energetically favored nor observed experimentally. Heterocyclic rings with only 1 or 2 nitrogen atoms have negative electron affinities, but the addition of solvating water molecules can yield stable negative ions. In the case of the diazines ($C_4H_4N_2$: pyrazine, pyrimidine, and pyridazine) the addition of one water molecule is enough to stabilize the negative ion, with the majority of the excess electron density in a π^* orbital of the heterocycle but not significantly extended over the hydrogen bonded water network. Pyridine (C_5H_5N), with the most negative electron affinity, requires three water molecules to stabilize its negative ion. Although our computations suggest proton transfer to be energetically viable in all five N-heterocyclic systems studied here when three or more water molecules are present, proton transfer is not observed experimentally in the triazine nor in the diazine series. In pyridine, however, proton transfer competes energetically with hydrogen bonding (solvation), when three water molecules are present, i.e., both motifs are observed. Pyridine clusters containing four or more water molecules almost exclusively exhibit proton transfer along with solvated $[C_{6-x}H_{6-x+1}N_x{\cdot}OH]^-$ ions.

1. Introduction

Subtle non-covalent interactions between nitrogen-containing heterocyclic molecular building blocks, such as the azabenzenes shown in Figure 1, and hydrogen bonded aqueous environments play important roles in both biological structure and function. Such interactions are fundamental to the nature of macromolecular assemblies, ranging from DNA to proteins.[1-7] The interactions between water and ions are likewise important in many biochemical processes, in aqueous electrolyte chemistry, and in atmospheric chemistry.[8-10] Such hydrogen bonded networks have been studied at the nanoscopic level for decades in order to understand such interactions.[11,12] The addition of an excess electron to these systems further alters their energetic landscapes. Here, we explore how excess electrons are stabilized in hydrated azabenzene cluster anions as a function of stepwise hydration. Figure 1 shows the structures of the five N-heterocyclic molecules studied here.

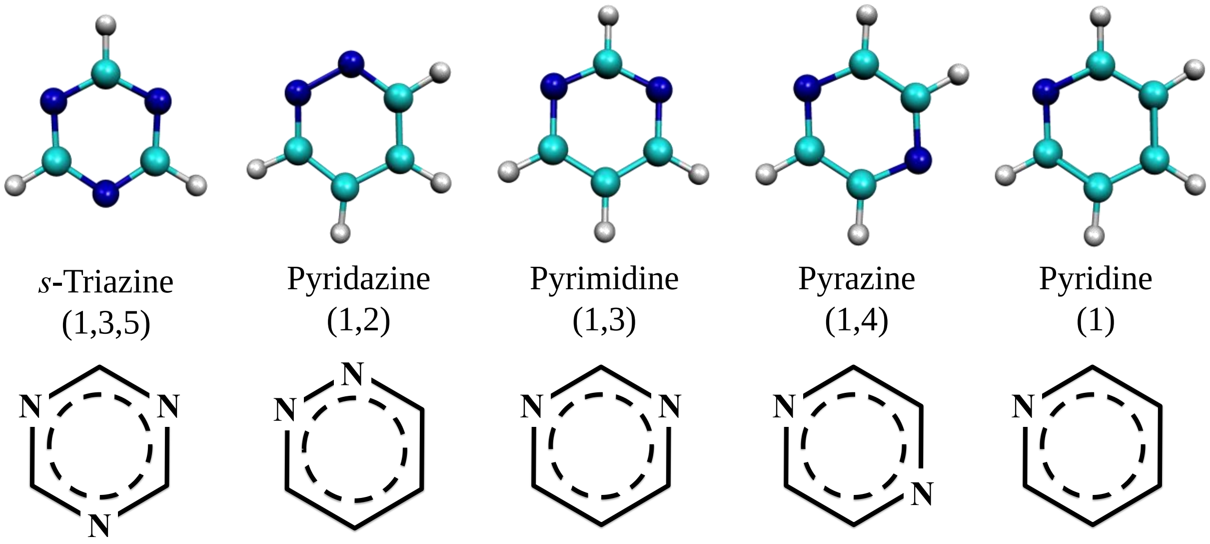

Figure 1: The five N-heterocyclic azabenzene anions studied in this work: *s*-triazine (Tz), pyridazine (Pd), pyrimidine (Pm), pyrazine (Pz), and pyridine (Py).

The vertical electron affinities (EA_v) of several azabenzenes were determined by electron transmission spectroscopy (ETS) and compared to benzene. The EA_v of benzene (–1.15 eV) was found to be more negative than that of pyridine (–0.62 eV), while the EA_v values of the diazines were determined to be near zero.[13] When ETS was applied to the related molecule, naphthalene, both its EA_v and its adiabatic electron affinity (EA_a) values were both found to be –0.19 eV.[14] Anion photoelectron spectroscopy determined the EA_a value of *s*-triazine to be positive at +0.03 eV,[17] while by extrapolation, it estimated the EA_a values of Py to be between –0.67 eV and –0.15 eV and of Pz to be –0.01 eV.[16,18] Mass spectra of hydrated pyridine cluster anions showed that water was stabilizing otherwise unstable pyridine anions.[15] Other mass spectral measurements showed the minimum number of water molecules needed to stabilize pyridine (3), and the diazines (1), and also estimated the negative electron affinity values for each of them.[16] Theory also computed both EA_v and EA_a (negative) values for pyridine, pyrimidine, and related molecules.[17] Both Rydberg electron transfer and anion photoelectron spectroscopy were applied to the study of the hydrated nucleobase anions.[18-21] Anion photoelectron spectroscopy was also used to study hydrated 7-azaindole cluster anions from their threshold size at three water molecules through six of them.[22] Negative ion photoelectron spectroscopic studies were also conducted on hydrated amino acid anions,[23] on hydrated naphthalene anions,[24] and on other hydrated aromatic molecular anions.[25] Recently, in a combined anion photoelectron and computational study, we studied hydrated pyrimidine (Pm) cluster anions, where we found that a single water molecule stabilized the Pm negative ion.[26] The azabenzene series has also shown interesting “associative” bond formation with CO_2 upon electron attachment.[27,28]

Here, in a combined anion photoelectron spectroscopic and computational study, we explore and compare the structures and energetics of sequentially hydrated azabenzene cluster anions, where the N-heterocyclic molecules under investigation were *s*-triazine, pyridazine, pyrimidine, pyrazine, and pyridine. While *s*-triazine forms stable parent anions without hydration, the above listed diazines require solvation by at least one water molecule in order to stabilize their anions, and pyridine needs at least three. The focus of this study is on determining the number of water solvent molecules needed to induce proton transfer from H_2O to a given N-heterocyclic molecular anion. This work continues our practice of studying electron-induced proton-transfer (EIPT), where in this case water is the proton donor. [29-46]

2. Experimental Details

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photoelectrons. It is governed by the energy-conserving relationship, hν = EBE + EKE, where hν is the photon energy, EBE is the electron binding (transition) energy, and EKE is the electron kinetic energy.

The hydrated N-heterocycle cluster anions were produced by two different kinds of anion photoelectron spectrometers in our lab. Hydrated *s*-triazine cluster anions were produced and characterized on our pulsed photoelectron instrument.[47] In general, the anions were generated in a photoemission ion source by focusing a pulsed (10 Hz), second harmonic (532 nm) beam of a Nd:YAG laser onto a continuously rotating, translating copper rod. The ultrahigh purity He carrier gas was pulsed through a pulsed valve with a backing pressure of ~150 psi. The mixture of water and *s*-triazine were directly put into the pulsed valve. The resultant anions were then extracted into a linear time-of-flight mass spectrometer, mass-selected by a mass gate, decelerated by a momentum decelerator, and photodetached by a Nd:YAG laser operated at third harmonic (355 nm, 3.49 eV). The resultant photoelectrons were analyzed by a magnetic bottle electron energy analyzer with a resolution of 35 meV at EKE=1 eV. The photoelectron spectra were calibrated against the well-known photoelectron spectrum of Cu^-. [48]

All of the other cluster anions were produced and characterized on our continuous anion photoelectron spectrometer. As previously described,[49] a nozzle expansion source was used. Briefly, the N-heterocyclic samples along with water were heated to 70-80 °C in a stagnation chamber (biased at- 500V) and co-expanded together with 30-50 psig argon gas through the 23 μm nozzle orifice into $\sim 10^{-4}$ Torr vacuum. Low-energy electrons from a biased thoriated-iridium filament were injected into the expanding jet to form negative ions in the presence of a weak magnetic field. The anions were then extracted and transported via a series of ion lenses through the flight tube of a 90◦ magnetic sector mass spectrometer (mass resolution, ~400). Mass-selected anions were then crossed with an intra-cavity argon ion laser beam, where photodetachment occurred. The resultant photoelectrons were then analyzed by a hemispherical electron energy analyzer with a resolution of 25 meV. The photoelectron spectrum reported here was recorded with 488 nm (2.540 eV) photons and calibrated against the well-known photoelectron spectrum of the O^- anion.[50]

3. Computational Details

A similar computational approach from our previous study has been employed using the Gaussian09 software package to perform full geometry optimizations as well as harmonic frequency calculations.[51] A hybrid meta-GGA functional, M06-2X,[52-54] was employed for the hydrated azabenzene anions to compare relative energetics as well as to compute vertical detachment energies (VDE). Pure angular momentum (5*d*,7*f*) atomic orbital basis functions along with a pruned numerical integration grid composed of 99 radial shells and 590 angular points per shell were employed. All electronic structure methods utilized a Pople-style double-ζ basis set, 6-31++G(*d*,*p*). Our previously optimized neutral[55] and anionic[26] structures were taken as starting geometries for all of the hydrated azabenzene series. Additional starting geometries were generated by attaching an azabenzene molecule to a free hydrogen atom from known water cluster geometries[56-62] and hydrated electron clusters.[37-49,63,64] Though not an exhaustive conformational search, this study identifies low energy structures that should be close to the global minimum. VDE values were calculated as the difference between the optimized electronic energy of the anion and that of the corresponding neutral species with identical geometry. A previously developed solvent polarized continuum model (PCM) linear extrapolation[65] revealed that the ordering of the vertical electron affinities are as follows: pyridine (1) < pyrimidine (1,3) < pyridazine (1,2) < pyrazine (1,4) < *s*-triazine (1,3,5).

4. Experimental Results

Figure 2 shows the photoelectron spectra (PES) of four of the five hydrated azabenzene cluster anions studied here. Additional photoelectron spectra are included in the Supporting Information. Also, we recently reported PES of the hydrated pyrimidine series for n = 1-8, and we have included those results here for comparison.[26] Broad, vibrationally-unresolved spectral features are typical of such hydrated valence anions. Moreover, their spectral onsets (E_0) increase with each additional water solvent that is added ,i.e., $A^{-}\cdot(H_2O)_n + H_2O \rightarrow [A\cdot(H_2O)_{n+1}]^{-}$.[66,67] In cases where there is Franck-Condon overlap between the lowest vibrational levels of the cluster anion and its neutral counterpart and where there are no vibrational hot bands present, the EBE of the onset is equal to the adiabatic electron affinity (EA_a). In that case $E_0 = EA_a$. However, in the absence of a clear spectral assignment or explicit computational results, it is best not to assume that they are the same. In anion photoelectron spectra, the vertical detachment energy (VDE) is the EBE value at the photoelectron intensity maximum, i.e., where the Franck-Condon overlap in a given transition is maximized. The EA_a value, which is the thermodynamic energy difference between the lowest vibrational levels of the anion and its corresponding neutral, can only be determined with confidence under the conditions described above.[68] Between VDE and EA_a values, the former is usually the better defined, when no vibrational structure is present. The vertical electron affinity (EA_v) is the energy measured from the lowest vibrational level of a neutral molecule or cluster vertically to its corresponding anion at the structure of the relaxed neutral. While VDE is a *detachment* quantity, EA_v is an electron *attachment* quantity. Anion photodetachment spectra do not reveal direct information about EA_v values. Only in the case where the anion and its neutral counterpart have identical (relaxed) structures is the EA_v equal to the EA_a, and there VDE = EA_a = EA_v.

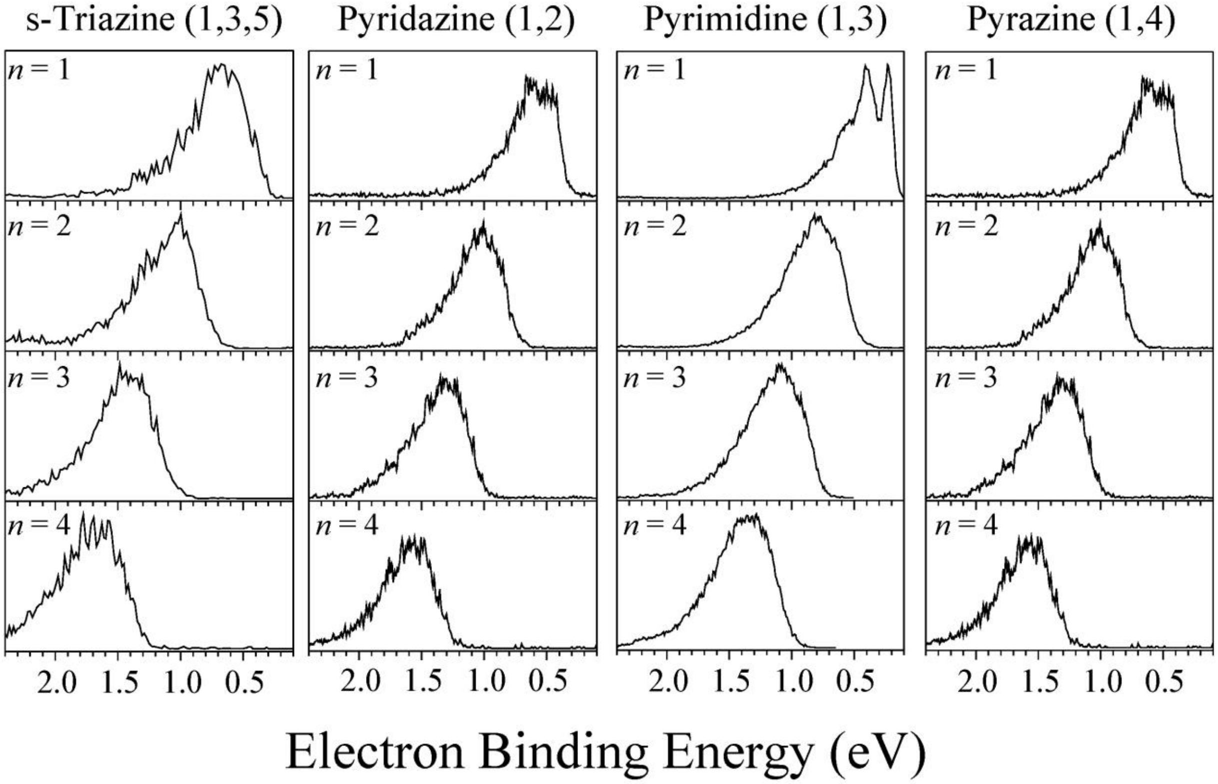

Figure 2: Photoelectron spectra of four of the five hydrated azabenzene cluster anions studied here: $Tz^{-}\cdot(H_2O)_n$, $Pd^{-}\cdot(H_2O)_n$, $Pm^{-}\cdot(H_2O)_n$, and $Pz^{-}\cdot(H_2O)_n$,where $n = 1 – 4$.

4.1 Hydrated s-Triazine Anions

The s-triazine anion, Tz^-, is the only azabenzene considered here that exhibits a stable bound state with respect to autodetachment, i.e., it has a positive EA_a value. Kim et al. previously reported the gas phase photoelectron spectrum of the Tz^- molecular anion and determined its adiabatic electron affinity to be +0.03 eV.[69] The photoelectron spectra of the hydrated *s*-triazine cluster anion series is shown in Figure 2. Its experimental VDE for $n = 1$ is 0.68 eV. The VDE values are observed to increase continuously with hydration and are 1.01 eV, 1.41 eV, 1.69 eV, 1.89 eV, and 2.09 eV, for $n = 2 – 6$, respectively.

4.2 Hydrated Pyridazine, Pyrimidine, and Pyrazine Anions

Pyridazine is the diazine derivative of pyridine with the second nitrogen atom in the *ortho*-position (i.e. 1,2 diazine). The electron affinity of the pyridazine molecular anion is thought to be slightly negative. [13] With the addition of a single water molecule, the monohydrated cluster anion is stabilized and exhibits a VDE of 0.53 eV. Addition of subsequent water molecules leads to VDE values of 0.93 eV, 1.27 eV, and 1.53 eV for n=2–4, respectively.

Previously, we reported PES of the hydrated pyrimidine (1,3 diazine) cluster anion series up to $n = 8$ and we have included those results here. The VDEs of the hydrated pyrimidine cluster anion series are 0.42 eV, 0.78 eV, 1.11 eV, 1.34 eV, 1.58 eV, and 1.62 eV, respectively, while the extrapolated electron affinity (E_0) of the pyrimidine monomer was –0.2 eV.

Pyrazine is another derivative of pyridine, but with its second nitrogen atom in the *para*- or 1,4 position of the heterocycle (see Figure 1). Kim measured the PES of $Pz^-(H_2O)$. Using a sequential argon extrapolation method, the estimated the adiabatic electron affinity of pyrazine to be –0.01 ± 0.01 eV.[70] The photoelectron spectra of hydrated Pz cluster anion series is shown in

Figure 2. The measured VDE values for n = 1 - 4 are 0.66 eV, 1.05 eV, 1.32 eV, and 1.60 eV, respectively.

4.3 Hydrated Pyridine Anions

The photoelectron spectra of hydrated pyridine cluster anions are shown in Figure 3. The $[A\cdot(H_2O)_n]^-$, n = 1,2, clusters are unstable in the gas phase with respect to autodetachment. The PES for n=3 exhibits two broad overlapping features with the smaller feature (shoulder) located between 0.5 and 1.0 eV. and with the stronger feature (peak) centered at 1.56 eV, it VDE value. The photoelectron spectra for n = 4 - 6 species each exhibit single broad peaks with VDE values of 1.79 eV, 1.98 eV, and 2.18 eV, respectively.

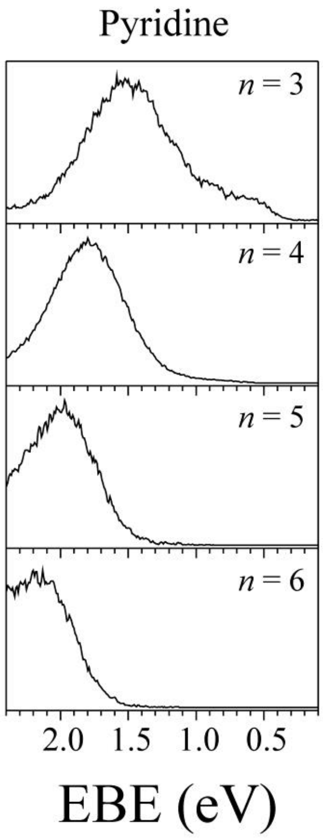

Figure 3: Photoelectron spectra of $[Py\cdot(H_2O)_n]^-$, cluster anions, n = 3 – 6.

5. Theoretical Results

Over 80 hydrated cluster anion structures, these corresponding to minima (no imaginary frequencies), were characterized and are included in the Supporting Information. The lowest energy structures identified through this calibrated DFT procedure[71] exhibited two motifs. One group of structures can simply be classified as hydrated azabenzene anions, $A^{-}\cdot(H_2O)_n$, in which a water molecule (or hydrogen bonded network of water molecules) tends to form a hydrogen bond with one N atom of the heterocycle. DFT computations indicate that the majority of the excess electron density resides in a π* orbital of the azabenzene rather than significantly interacting with the extended hydrogen bonded network of water molecules. The lowest-energy $A^{-}\cdot(H_2O)_n$ structures exhibiting this motif are shown in Figure 4 for n = 1 – 4 and A = Tz, Pd, Pm, and Pz.

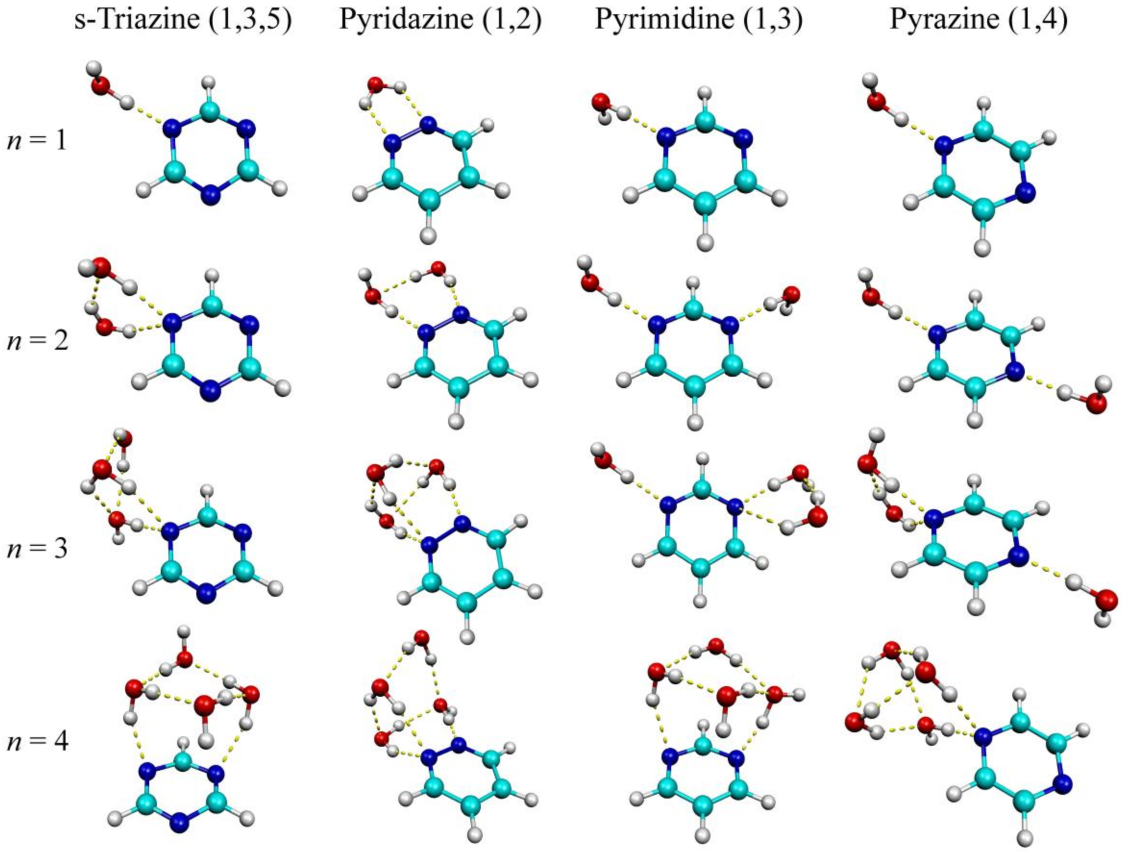

Figure 4: Lowest energy structures of $Tz^{-}\cdot(H_2O)_n$, $Pd^{-}\cdot(H_2O)_n$, $Pm^{-}\cdot(H_2O)_n$, and $Pz^{-}\cdot(H_2O)_n$ cluster anions for $n = 1 – 4$ using M06-2X/6-31++G(*d*,*p*) level of theory.

Starting at $n = 3$ for Py and for Pd and at $n = 4$ in Pm, Pz, and Tz, the other interaction motif begins to emerge. This second class of structures exhibits proton transfer from a water molecule to the azabenzene effectively creating a solvated anion complex, $[AH{\cdot}OH]^{-}{\cdot}(H_2O)_{n\text{-}1}$. The M06-2X/6-31G(*d*,*p*) computations suggest neither the charge nor the spin of the excess electron is appreciably localized on either fragment of the $[AH{\cdot}OH]^{-}$ complex (although this characteristic could change with the method and/or basis set). In the cases of Tz, Pd, Pm, and Pz, the structures exhibiting proton transfer are not the lowest energy structures (with the exception of Pz for $n = 5$, 6), as shown in Table I. However, in the case of Py, the lowest energy structures identified in this study for each cluster size ($n \geq 3$) all exhibit proton transfer, although $Py^{-}{\cdot}(H_2O)_3$ also has a low-lying, hydrogen bonded solvation network, i.e., non-proton transfer, structure. These are shown in Figure 5, and both motifs described in greater detail in the following sections for the various azabenzene systems.

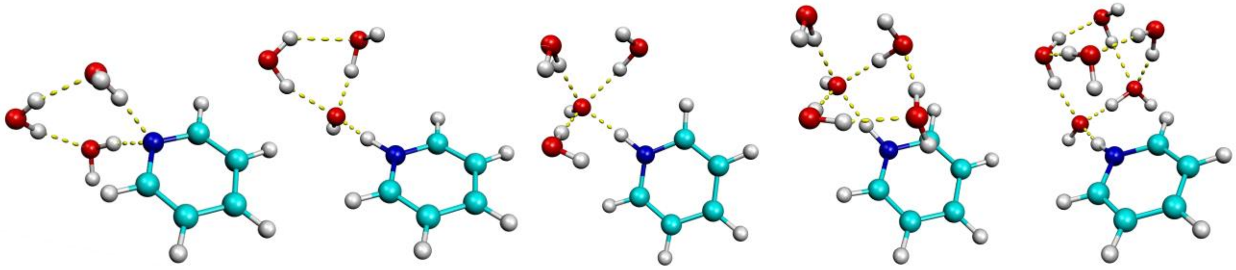

Figure 5: From left to right: Low-energy structures for $Py^{-}{\cdot}(H_2O)_3$, $[PyH{\cdot}OH]^{-}{\cdot}(H_2O)_2$, $[PyH{\cdot}OH]^{-}{\cdot}(H_2O)_3$, $[PyH{\cdot}OH]^{-}{\cdot}(H_2O)_4$, and $[PyH{\cdot}OH]^{-}{\cdot}(H_2O)_5$.

5.1 Hydrated s-Triazine Anions

The heterocycle, *s*-triazine is the only azabenzene in this study that has a positive electron affinity. The addition of an excess electron lowers the symmetry of *s*-triazine from D_{3h} to C_{2v} due to Jahn-Teller distortions.[69] The $Tz^{-}{\cdot}(H_2O)_{n=1\text{-}6}$ cluster anions have calculated VDE values of 0.74 eV, 1.16 eV, 1.45 eV, 1.50 eV, 1.87 eV, and 2.09 eV respectively. Our relative energy calculations suggest that 2 or 3 water molecules tend to prefer interacting with *s*-triazine at a single nitrogen atom, instead of individually forming hydrogen bonds with the heterocycle at multiple sites (see first column of Figure 4).

5.2 Hydrated Pyridazine, Pyrimidine, and Pyrazine Anions

For the hydrated diazine series, the position of the two nitrogen atoms plays an important role in the solvation of the anion at each hydration step (see second, third and fourth column of Figure 4). Unlike the stable Tz^{-} anion, all three of the diazine (Pd, Pm and Pz) monomeric anions are unstable with respect to autodetachment of the excess electron. However, with the addition of a single water molecule, the energy of the hydrated cluster anion becomes lower than that of its corresponding neutral molecular cluster in each case. Only one structure for each of the monohydrated diazines, $A^{-}\cdot(H_2O)$ was found at the M06-2X/6-31++G(*d*,*p*) level of theory, with computed VDE values of 0.61 eV, 0.59 eV, and 0.69 eV for Pd, Pm and Pz, respectively. Stepwise hydration of each negatively charged diazine cluster anion, $A^{-}\cdot(H_2O)_n$, resulted in increasing VDE values. Interestingly, the hydrated Pm cluster anions, $Pm^{-}\cdot(H_2O)_n$, have lower computed VDE values than those of the hydrated Pz and Pd cluster anions at the same values of n. Structures exhibiting proton transfer for a given value of n have computed VDE values that are up to 0.7 eV higher than those that do not. Moreover, hydrated diazine cluster anion structures that display proton transfer are not their lowest energy minima (with the exception of Pz for $n = 5, 6$).

5.3 Hydrated Pyridine Anions

Dozens of low-lying minimum energy structures were identified for the negatively charged hydrated pyridine series, and many of them exhibit proton transfer from associated water molecules. For $n = 3$, even though the lowest energy structure exhibits proton transfer (shown in

Figure 5), another structure only 0.02 kcal mol^{-1} lower in energy (also shown in Figure 5) does not. For n = 3, the computed VDE value of the non-proton transfer structure is 0.84 eV, whereas the middle of the shoulder region in the actual photoelectron spectrum is ~0.75 eV. Also for n = 3, the computed VDE value for the proton transferred structure is 1.44 eV, whereas the VDE value for the main peak is 1.56 eV. The computed and experimental VDE values for both interaction motifs are in good agreement. For n = 4 - 6, the lowest energy structures possess a transferred proton from a water molecule and have calculated VDE values of 1.70 eV, 1.87 eV, and 2.07 eV, respectively. These are shown in Figure 5. For n = 4 - 6, these compare well with experimentally-determined VDE values of 1.79 eV, 1.98 eV, and 2.18 eV, respectively. The corresponding lowest energy structures with intact water molecules lie at least 1 kcal mol^{-1} higher in energy and have computed VDE values of 1.13 eV, 1.33 eV, and 1.51 eV, respectively. For structures exhibiting proton transfer, only a single deprotonated water molecule interacts directly with the heterocycle. While the other n - 1 water molecules form a hydrogen-bonded network around the deprotonated water molecule.

6. Discussion

6.1 Assignment of Photoelectron Spectral Features

The combination of negative ion photoelectron spectroscopy with density functional theory provides insight into important molecular interactions at play in negatively charged cluster anions. In the case of the N-heterocyclic molecular anion clusters studied here, two types of structural motifs are theoretically predicted to occur as a result of the attachment of an excess electron. In one case, the excess electron density primarily resides in a π* orbital with n intact water molecules solvating the azabenzene anion at nitrogen atom sites. The other case involves the transfer of a proton from a water solvent to the azabenzene sub-anion solute: $A\cdot(H_2O)_n + e^-$

→ $[AH{\cdot}OH]^{-}{\cdot}(H_2O)_{n\text{-}1}$. Table I summarizes the experimental and theoretical results of this study. For Tz, Pd, Pm, and Pz the quantitative agreement between the computed VDE values for non-proton transfer isomers and the experimental VDE values is relatively good, whereas the agreement between the computed VDE values for proton transferred isomers and experiment is poor. This suggests that proton transfer is not occurring in these systems. In the case of n=3 for Py, however, the same comparison indicates both structural motifs are likely to be present. For the Py systems with $n > 3$, the VDE data suggests that only structures exhibiting proton transfer, $[PyH{\cdot}OH]^{-}{\cdot}(H_2O)_{n\text{-}1}$, are present. These results are strongly supported by unpublished infrared spectroscopic studies on the same clusters anions by Johnson and co-workers.

Table I: Computed VDE values for the lowest energy structural isomers for $A^{-}{\cdot}(H_2O)_n$ and $[AH{\cdot}OH]^{-}{\cdot}(H_2O)_{n\text{-}1}$ (A = Tz, Pd, Pm, Pz, and Py); ΔE_{rel}, the energy difference between the isomers (in kcal mol^{-1}, where a negative value indicates a structure exhibiting proton transfer is lower in energy); and the experimentally-determined spectral onsets, E_0, as well as vertical detachment energies, VDE.

		Theoretical			Experimental	
	n	$A^{-}{\cdot}(H_2O)_n$ VDE	$[AH{\cdot}OH]^{-}{\cdot}(H_2O)_{n\text{-}1}$ VDE	ΔE_{rel}	E_0	VDE
Tz	1	0.74	---	---	0.38	0.68
	2	1.16	---	---	0.72	1.01
	3	1.45	---	---	1.03	1.41
	4	1.50	2.04	4.20	1.28	1.69
	5	1.87	2.63	1.91	1.43	1.89
	6	2.09	2.84	1.40	1.51	2.09
Pd	1	0.61	---	---	0.40	0.53
	2	1.12	---	---	0.67	0.93
	3	1.46	2.02	6.48	1.09	1.27
	4	1.79	2.37	4.05	1.30	1.53
	5	1.96	2.55	4.14	---	---
	6	1.95	2.79	2.22	---	---
Pm	1	0.59	---	---	0.23	0.42
	2	0.87	---	---	0.62	0.78
	3	1.26	---	---	0.93	1.11
	4	1.36	2.07	3.00	1.16	1.34
	5	1.37	2.34	1.24	1.36	1.58
	6	1.64	2.42	0.00	1.45	1.62
	1	0.69	---	---	0.34	0.66

	2	1.24	---	---	0.73	1.05
Pz	3	1.64	---	---	1.05	1.32
	4	1.67	2.40	2.25	1.31	1.60
	5	1.66	2.55	–3.37	---	---
	6	2.21	2.75	–0.13	---	---
	1	–0.04	---	---	---	---
	2	0.41	---	---	---	---
Py	3	0.84	1.44	–0.02	0.93	0.75, 1.56
	4	1.13	1.70	–1.21	1.23	1.79
	5	1.33	1.87	–4.32	1.48	1.98
	6	1.51	2.07	1.96	1.61	2.18

6.2 Role of Symmetry

The *s*-triazine is the only negatively-charged azabenzene molecule in this study that is stable with respect to autodetachment. Previous work on *s*-triazine and its anion compared the high symmetry neutral *s*-triazine (D_{3h}) to the reduced symmetry anion (C_{2v}).[17] A nascent Jahn-Teller distortion has also been recently reported in buckminsterfullerene, C_{60}, upon the addition of an excess electron perturbing the electronic structure.[72-77] This structural change transforms a number of chemical properties, including but not limited to electron affinities, vertical detachment energies, electronic states, charge distributions, and relative energetics between isomers. There are instances, however, where the addition of an excess electron to a closed-shell neutral system can increase the symmetry of the molecular framework.[78]

The diazines (Pd, Pm, Pz) maintain their symmetric geometries upon excess electron attachment. Delocalization of the excess charge over the ring minimizes changes in the structure of the anion relative to its neutral. The 1,4 diazine monomer has D_{2h} symmetry in its neutral state, whereas both the 1,3 and 1,2 diazine monomers have C_{2v} symmetry.

6.3 Extrapolation of Experimentally-Determined E_0 Values

Previously, we utilized the experimental E_0 values of the $Pm^{-}\cdot(H_2O)_n$ cluster anion series to extrapolate to $n = 0$, giving an E_0 value of –0.2 eV for the Pm molecule.[26] As described earlier, in the absence of a vibrational assignment of the origin transition, there is no *a priori* assurance that EA_0 values are equal to EA_a values. Often, in fact, they are not due to a lack of Franck Condon overlap between the lowest vibrational levels of the anion and its neutral counterpart. Nevertheless, the –0.2 eV value agreed well with the earlier electron transmission spectroscopy (ETS) measurement of $EA_v = –0.25$ eV. (Technically, ETS provides EA_v values.) The value of EA_a only equals the value of EA_v when the structures of the anion and its neutral counterpart are similar. As noted in previous studies, however, this is the case for pyrimidine and the other diazines studied here. Thus, the implication is that the measured E_0 values of $Pm^{-}\cdot(H_2O)_n$ spectra were close to EA_a values. The structural similarity between these anions and their neutral counterparts is the reason that both $E_0 \sim EA_a$ and $EA_a \sim EA_v$. Nevertheless, the anion and corresponding neutral structures are not identical, since if they were the observed photoelectron spectral bands would be quite narrow, not broadened, as in fact they are. Similar extrapolations of experimental E_0 values for the $Pd^{-}\cdot(H_2O)_n$, $Pz^{-}\cdot(H_2O)_n$, and $Py^{-}\cdot(H_2O)_n$ cluster anion series gave E_0 values at $n = 0$ of ~0.0 eV, –0.1 eV, and –0.5 eV respectively. The E_0 value of –0.5 eV for the pyridine molecule is comparable to the previously measured ETS value of $EA_v = –0.67$ eV for pyridine.[13]

6.4. Electron-Induced Proton Transfer

The work presented here continues a line of work that focuses on electron-induced proton-transfer (EIPT) in the electronic ground state.[29-46] Among these are the thymine-glycine dimeric anion complex, $(TG)^{-}$, where the excess electron first goes to the thymine base. This then enables the extraction of a proton from the glycine, resulting in a complex composed of a "thymine hydride" and a deprotonated glycine.[31] Another example of EIPT involves the ammonia-hydrogen chloride dimeric anion complex, $[NH_3(HCl)]^-$. In this case, the excess electron first goes to the ammonia side of the linear, high dipole moment ammonia-hydrogen chloride dimeric (neutral) complex, leading to the formation of a temporary dipole bound anion. The additional negative charge, associated with the ammonia molecule, then helps to pull the proton from the HCl and onto ammonia, which in turn becomes NH_4^+, albeit with the diffuse excess electron still nearby. These latter two entities then form the neutral Rydberg molecule, NH_4. Thus, the formal nature of the ammonium chloride molecular anion is a neutral NH_4 Rydberg molecule interacting with a Cl^- anion, which in turn polarizes the NH_4, *viz.*, $NH_4 \cdots Cl^-$.[32] Yet another example of EIPT may be the hydrated electron itself, although unlike those mentioned above, this one may be hypothetical. While the cavity model is the generally accepted picture of the hydrated electron, an alternative model was espoused by Robinson et al. [79] and then studied theoretically by Domcke et al. [80,81] In that model, an excess electron induces a water molecule, which resides in a sea of other water molecules, to donate a proton to a neighboring water molecule, thereby forming H_3O^+, with the excess electron nearby. Together, the latter two entities are envisioned as forming the H_3O Rydberg molecule. Since an OH^- anion was also formed in the deprotonation step, the net outcome is the hydrated radical-anion complex, $(H_3O \cdots OH^-)_{aq}$. Unlike the other examples mentioned above, however, this species has not been demonstrated experimentally. Perhaps, this is a higher energy isomer of the hydrated electron. In all of these examples, the lowest EBE photodetached electron would be expected to originate from the net neutral "base hydride", i.e., "thymine hydride", NH_4, or H_3O, rather than from the deprotonated "acid", i.e., deprotonated glycine, Cl^-, or OH^-.

The present study differs from our previous work with EIPT in that here, water is the proton donor. Proton transfer by water is facilitated by the fact that, while neutral N-heterocyclic molecules are themselves bases, negatively-charged N-heterocyclic molecules are even better bases (proton acceptors). Of the hydrated azabenzene anions studied here, pyridine is the most prone to accept a proton from water, because pyridine has the most negative value of EA_v, the pyridine anion is the best Lewis base among them. As in other EIPT examples discussed above, the excess electron goes first to the base, after which proton transfer from the “acid” occurs. Thus, we believe that proton transfer from water occurred only after the solvated pyridine anion had formed at $n = 3$. For the four non-pyridine, hydrated azabenzene cluster anions studied here, notice that the VDE values for their threshold cluster anion sizes are all significantly smaller than the VDE value of $Py^-(H_2O)_{3.}$ Once enough water is present to initiate proton transfer, the resulting cluster anion is greatly stabilized compared to the stabilization afforded by simple solvation. A relatively high VDE value at a given cluster anion’s threshold size is a signature of proton transfer having occurred. In fact, in photoelectron work on 7-azaindole-water cluster anions by Nakajima et al.,[22] where the VDE value was found to be ~1.3 eV at the $n = 3$ threshold size, this was likely an unrecognized indication that electron induced proton transfer had occurred.

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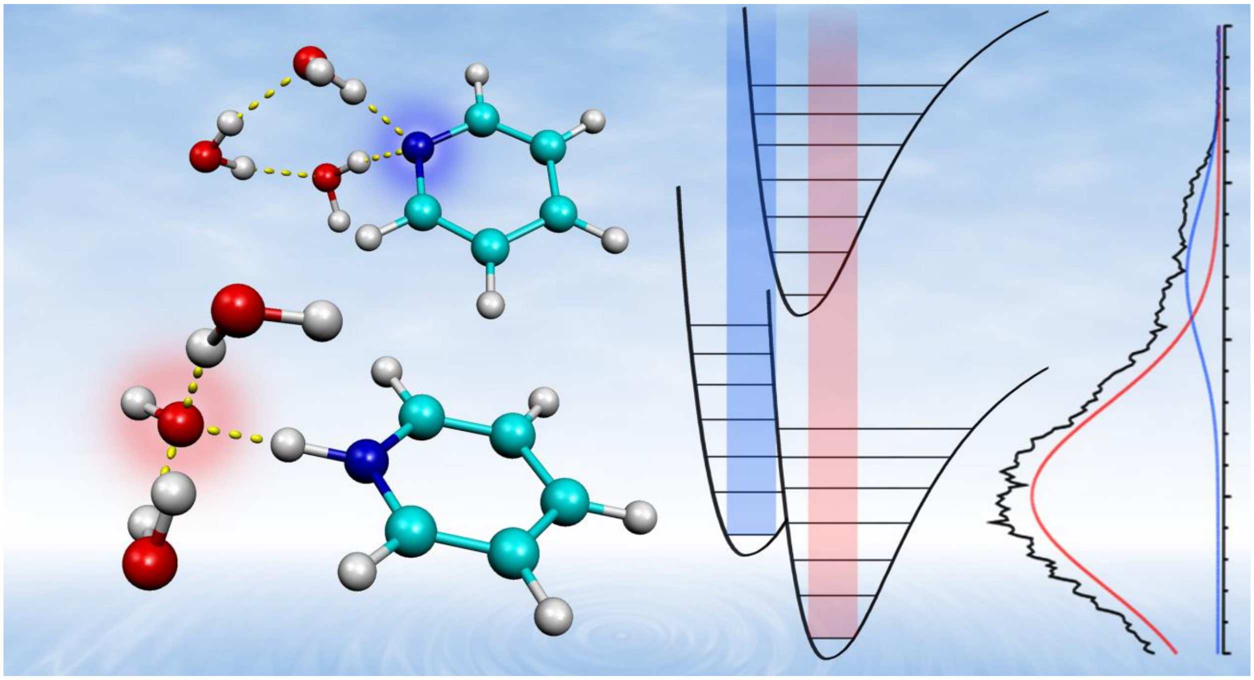

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