Proton-coupled Electron Transfer in $[\text{Pyridine} \bullet (\text{H}_2\text{O})_n]^-$, $n = 3, 4$, Clusters

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Abstract

The equation-of-motion method is used to map out one-dimensional potentials for proton-coupled electron transfer in the $[\text{pyridine} \bullet (\text{H}_2\text{O})_n]^-$, $n = 3, 4$, clusters. In both cases there is an avoided crossing between valence-type pyridinyl $\bullet (\text{OH}^-) (\text{H}_2\text{O})_{n-1}$ and dipole-bound pyridine $\bullet (\text{H}_2\text{O})_n^-$ anion species. For the $n = 3$ cluster, the mixing is sufficiently strong that both limiting structures are predicted to be sampled in the vibrational zero-point level.

I. Introduction

The anions of pyridine $\bullet(\text{H}_2\text{O})_n$ clusters, $[\text{Py} \bullet (\text{H}_2\text{O})_n]^-$, have been the subject of experimental and theoretical investigation [1–3]. These are intriguing and challenging systems because of the possibility of three different types of anions that are expected to be close in energy. The limiting cases are $\text{Py} \bullet (\text{H}_2\text{O})_n^-$ in which the excess electron is dipole bound [4,5], $\text{Py}^- \bullet (\text{H}_2\text{O})_n$ in which the excess electron is localized in a valence π^* orbital of the pyridine, and the $\text{PyH} \bullet (\text{OH}^-) \bullet (\text{H}_2\text{O})_{n-1}$ species formed by proton-coupled electron transfer (PCET) from $(\text{H}_2\text{O})_n^-$ to pyridine. The isolated Py^- ion is unstable with respect to electron detachment, lying 0.62 eV in energy above the ground state of the neutral pyridine molecule [6], but upon sufficient solvation it will become stable, with respect to electron detachment. Fig. 1 schematically reports the relative energies of the various fragments and products for the $n = 3$ cluster. The $(\text{H}_2\text{O})_3^-$ dipole-bound anion has a vertical detachment of 0.13 eV and is nearly isoenergetic with the global minima structure of the neutral $(\text{H}_2\text{O})_3$ cluster [7]. In the case of the $\text{Py}^- \bullet (\text{H}_2\text{O})_3$ and $\text{Py} \bullet (\text{H}_2\text{O})_3^-$ complexes, the energies of the unmixed diabatic states were obtained from constrained geometry optimizations.

The photoelectron spectra of the $[\text{Py} \bullet (\text{H}_2\text{O})_n]^-$, $n \geq 3$, clusters are consistent with $\text{PyH} \bullet (\text{OH}^-) \bullet (\text{H}_2\text{O})_{n-1}$ structures. However, the vibrational spectrum of the $n = 3$ anion is fundamentally different from that of the $n = 4$ and 5 anions in the region of the NH stretch. Specifically the spectrum of the $n = 3$ cluster displays three broad features with $\sim 350 \text{ cm}^{-1}$

spacing ($\sim 2050, 2400, 2750 \text{ cm}^{-1}$) [1,2], while for the $n = 4$ and 5 clusters, the vibrational structure in the NH stretch region consists of a very broad feature peaked near 2600 cm^{-1} . These results suggest a change in the electronic structure of the cluster in going from $n = 3$ to $n = 4$.

Figure 1: Energies of the various non-interacting fragments as well as of the possible products of the $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ cluster. The energies of the neutral species were calculated using the MP2 method, and those of the anionic species were calculated using the EA-EOM-CCSD(2) method. All calculations employed the aug-cc-pVDZ+7s7p basis set, described in the text.

In this work we present electronic structure calculations on $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ and $[\text{Py} \cdot (\text{H}_2\text{O})_4]^-$ to better understand how these species evolve along the proton transfer coordinate. These systems pose a significant challenge to theory. Specifically, density functional methods, even with the inclusion of exact exchange, tend to strongly overbind dipole-bound anions with the basis sets typically used for such systems, and the spin-unrestricted Hartree-Fock method suffers from sizable spin contamination for the various $[\text{Py} \cdot (\text{H}_2\text{O})_n]^-$ structures calling into question the validity of spin-unrestricted second-order Møller-Plesset (MP2)[8–10] calculations. The spin-restricted (MP2) [11,12] method avoids the spin-contamination problem, but application of this approach to the $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ system gave a discontinuous potential energy curve as a result of the restricted Hartree-Fock (RHF) calculations converging to different

solutions at different geometries. To avoid this problem, we adopt the EA-EOM-CCSD(2) method [13,14]. In this approach one carries out MP2 calculations on the neutral closed-shell cluster, and the resulting doubles [15] amplitudes are used to carry out a similarity transformation of the Hamiltonian, which, in turn, is used to carry out one-particle ($1p$) plus two-particle-one-hole ($2p1h$) configuration interaction calculations on the anion states.

The present investigation, thus, has two goals: (1) to provide insights into the difference in the electronic structure of the $n=3$ and 4 clusters and the implications of this difference on the vibrational spectra, and (2) to provide benchmark electronic structure results for assessing the performance of more approximate electronic structure methods for describing proton-coupled electron transfer in anionic complexes.

II. Computational Details

The EA-EOM-CCSD(2) calculations were carried out using the CFOUR code [16] and employed the aug-cc-pVDZ basis set [17,18] supplemented with a set of $7s7p$ diffuse functions [19]. The exponents of the supplemental functions were chosen to be in a geometric ratio of 3.33, with the tightest of these functions having exponents 3.33 times smaller than those of the corresponding “aug” functions. The supplemental diffuse functions were centered on the C atom situated opposite the N atom of the pyridine ring and were included primarily for the purpose of describing dipole-bound anions. For the $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ form of the $n=3$ cluster, EA-EOM-CCSD(2) calculations were also carried out with the aug-cc-pVTZ basis set [17,18] supplemented with the $7s7p$ set of diffuse functions, in order to check the convergence of the electron binding energy with basis set expansion. Starting with the $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_{n-1}$ species, optimized [20,21] using the ROHF-MP2 method in the frozen core approximation, a series of single-point calculations, in which the shared proton was moved along the line connecting the N atom of the pyridine ring and the O atom of the OH^- ion, were carried out. The resulting potential energy curves for the $n = 2$ and $n = 3$ clusters are shown in Figs. 2 and 3, respectively. The figures also display the dominant natural orbitals for the unpaired electron as obtained for the EOM calculations.

Figure 2: One-dimensional potential energy curves for the $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2 \rightarrow \text{Py} \cdot (\text{H}_2\text{O})_3^-$ rearrangement. The energies of the anion states were calculated using the EOM-EA-CCSD(2) method, using the aug-cc-pVDZ+7s7p basis set, with the starting structure being that of $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ optimized using the ROMP2 method. At each step along the reaction coordinate, the MP2 energy of the neutral cluster is also reported. There is an avoided crossing between the valence-like and dipole-bound anions near $\Delta\text{NH} = 0.45 \text{ \AA}$.

III. Results

From Fig. 2 it is seen that at the minimum energy structure of the $n = 3$ anion, the calculated vertical detachment energy (VDE) at the EOM-EA-CCSD(2)/aug-cc-pVDZ+7s7p level is 1.16 eV, as compared to the experimental result of 1.56 eV [1]. Upon enlarging the basis set to aug-cc-pVTZ+7s7p, the calculated vertical detachment energy increases to 1.35 eV, in reasonable agreement with experiment. At this geometry there is also a dipole-bound anion lying about 0.3 eV below the neutral cluster. The natural orbitals associated with the unpaired electron are also shown in Fig 2. As the proton is displaced along the reaction coordinate (from the $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ toward the $\text{Py} \cdot (\text{H}_2\text{O})_3^-$), the energy of the valence-type ground state anion rises, while that of the dipole-bound anion descends, with there being an avoided crossing between the two anion states near $\Delta\text{NH} = 0.44 \text{ \AA}$. In the measured vibrational spectrum, the peak of the feature due to the NH stretch vibration of $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ is observed near

0.30 eV [1], which implies that the $v=1$ level of this vibration lies about 0.4 eV above the potential energy minimum. Thus, as seen from Fig. 2, the vibrationally excited state of the anion samples the $\text{Py} \cdot (\text{H}_2\text{O})_3^-$ structure.

Table 1: Vertical detachment energies of $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ and $[\text{Py} \cdot (\text{H}_2\text{O})_4]^-$.

Cluster	Experimental (eV)		Isomer	Theory (eV)	
	Wang <i>et al</i> ^a	Deblase <i>et al</i> ^b		Wang <i>et al</i> ^a M06-2X/ 6-31++G(<i>d,p</i>)	Current work EOM-EA CCSD(2)/ aug-cc-pVDZ+7s7p
$[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$	0.75 1.56	1.53	$\text{Py}^-(\text{H}_2\text{O})_3$	0.84	0.39 ^c
			$\text{Py} \cdot (\text{H}_2\text{O})_3^-$	0.74 ^d	0.12
			$\text{PyH} \cdot \text{OH}^- \cdot (\text{H}_2\text{O})_2$	1.44	1.16 (1.35 ^e)
$[\text{Py} \cdot (\text{H}_2\text{O})_4]^-$	1.79	1.63	$\text{Py}^-(\text{H}_2\text{O})_4$	1.13	–
			$\text{Py} \cdot (\text{H}_2\text{O})_4^-$	–	0.71
			$\text{PyH} \cdot \text{OH}^- \cdot (\text{H}_2\text{O})_3$	1.7	1.45

a. Ref. [2].

b. Ref. [1].

c. Calculated at the M06-2x/6-31++G(*d,p*) optimized geometry.

d. Calculated at the ROMP2/aug-cc-pVDZ optimized geometry.

e. The value in the parentheses was obtained using the aug-cc-pVTZ+7s7p basis set.

The potential energy curves depicted in Fig. 2 were generated by simply stretching the NH bond, keeping all other degrees of freedom frozen. Separate calculations indicate that the energy of the neutral cluster drops by 0.40 eV upon geometry relaxation. At the potential energy minimum of the neutral, $\Delta\text{NH} = 0.77 \text{ \AA}$, and at the geometry the dipole-bound anion is calculated to lie only by 0.03 eV below the neutral. Thus on the relaxed potential the dipole-bound anion near $\Delta\text{NH} = 0.77 \text{ \AA}$ would be expected to lie only a few hundredths of an eV above the $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ species at its optimized structure. We have optimized the geometry of the anion at the ROMP2 level for ΔNH values between -0.2 and 0.35 $\text{\AA}$. The relaxed potential has a barrier of ~ 0.12 eV near $\Delta\text{NH} = 0.25 \text{ \AA}$. This result establishes that, both limiting $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ and $\text{Py} \cdot (\text{H}_2\text{O})_3^-$ configurations are sampled in the vibrational zero-point level of the $n=3$ anion. This is consistent with the fact that the peak in the photodetachment spectrum for the $n=3$ cluster extends from 0 to 2 eV. Our calculations also predict that autoionization should become an open channel for $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ following excitation of one quanta of the NH stretch mode. The experimental vibrational spectrum of $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ was obtained by

use of Ar-tagged $[\text{Py} \cdot (\text{H}_2\text{O})_3]^- \cdot \text{Ar}$ cluster. For this species electron detachment is observed at energies above 0.4 eV [1], while at lower energies the vibrational excited anion decays by Ar-atom loss. The Ar atom is expected to stabilize the valence anion state relative to the neutral cluster, acting so as to suppress the electron detachment channel. It is also likely that the Ar tag causes a reduction of the amount of $\text{Py} \cdot (\text{H}_2\text{O})_3^-$ character in the wavefunction for the ground state anion.

Interestingly, our calculations do not provide evidence for a bound $\text{Py}^- \cdot (\text{H}_2\text{O})_3$ ion. This suggests that this form of the anion, at least for the geometries considered, lies energetically above the neutral, and is thus subject to electron detachment. However, this temporary anion state could be involved in the initial electron capture with rapid decay to the dipole-bound and/or valence anion, and thus lead to the observed $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ product. Calculations using the M06-2X density functional method [22], in contrast to those with the EA-EOM-CCSD (2) methods, predict the $\text{Py}^- \cdot (\text{H}_2\text{O})_3$ ion to be stable with respect to electron detachment. This appears to be an artifact of the DFT calculations. Table 1 summarizes experimental and calculated detachment energies of $[\text{pyridine} \cdot (\text{H}_2\text{O})_3]^-$ and $[\text{pyridine} \cdot (\text{H}_2\text{O})_4]^-$. Unless noted otherwise the M06-2X detachment energies were calculated using M06-2X optimized geometries and using the 6-31++G(*d,p*) basis set [23,24], and the EOM detachment energies were calculated using ROMP2 optimized geometries and the aug-cc-pVDZ+7s7p. The exceptions are the M06-2X calculations on the $\text{Py} \cdot (\text{H}_2\text{O})_3^-$ form of the anion, which were carried out at the ROMP2 optimized geometry and the EOM calculations on the $\text{Py}^- \cdot (\text{H}_2\text{O})_3$ form of the anion, which were carried out at the M06-2X optimized structure. The M06-2X calculations predict the $\text{Py}^- \cdot (\text{H}_2\text{O})_3$ and $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ species to be isoenergetic, with the $\text{Py} \cdot (\text{H}_2\text{O})_3^-$ form of the anion lying 0.13 eV higher in energy. In contrast the EOM calculations predict the $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ form of the anion to be most stable, with the $\text{Py} \cdot (\text{H}_2\text{O})_3^-$ and $\text{Py}^- \cdot (\text{H}_2\text{O})_3$ forms lying, respectively, 0.06 eV and 0.12 eV higher in energy.

Figure 3: One-dimensional potential energy curves for the $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_3 \rightarrow \text{Py} \cdot (\text{H}_2\text{O})_4^-$ rearrangement. The energies of the anion states were calculated using the EOM-EA-CCSD(2) method, using the aug-cc-pVDZ+7s7p basis set. The initial structure of $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_3$ was optimized using the ROMP2 method. At each step along the reaction coordinate, the MP2 energy of the neutral cluster is reported. There is an avoided crossing between the lowest valence-type and dipole-bound anion near $\Delta\text{NH} = 0.60 \text{ \AA}$.

For the $n = 4$ cluster, the calculated vertical electron detachment energy at the minimum energy structure of the anion is 1.45 eV, which is in reasonable agreement with the experimental VDE value of 1.63 eV [2]. As for the $n = 3$ cluster, the adiabatic ground state of the anion of the $n = 4$ cluster evolves from valence-bound at $\Delta\text{NH} \sim 0 \text{ \AA}$ to dipole-bound at large ΔNH values ($\sim 0.6 \text{ \AA}$). The energy of the $n = 4$ cluster drops by 0.50 eV when the geometry is fully relaxed. At the relaxed geometry $\Delta\text{NH} = 0.85 \text{ \AA}$. Thus the relaxed potential for proton transfer in the ground state anion is much steeper for the $n = 4$ than for the $n = 3$ anion. As a result, the cluster in its zero-point level is essentially $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_3$ in nature, but in its $\nu = 1$ NH stretch level, it could acquire a small amount of dipole-bound anion character. From Fig. 3 it is seen that in addition to the ground state valence-type anion and the dipole-bound anion, the $n = 4$ cluster also has a bound excited state valence-type anion, in which the excess electron occupies the second lowest lying π^* orbital of the pyridine ring.

IV. Conclusion

Our calculations of the potential energy curve for proton transfer in $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ provide evidence that even in its vibrational zero-point level the anion samples both the dipole-bound $\text{Py} \cdot (\text{H}_2\text{O})_3^-$ and valence-type $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ configurations. This conclusion is consistent with the complex vibrational spectrum observed for the anion in the $[\text{Py} \cdot (\text{H}_2\text{O})_4]^-$ cluster. The presence of the additional water molecule in $[\text{Py} \cdot (\text{H}_2\text{O})_4]^-$ causes the PCET limiting structure to be preferentially stabilized with respect to the dipole-bound anion [compared to $\text{Py}(\text{H}_2\text{O})_3^-$]. At the ROMP2 level of theory the preferential stabilization is about 0.21 eV. This suppresses the large amplitude motion along the proton transfer coordinate and the sampling of dipole-bound structures in the zero-point and first vibrationally excited (NH stretch) levels. While M06-2X calculations indicate strong mixing between $\text{Py}^- \cdot (\text{H}_2\text{O})_3$ and $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ the present EA-EOM-CCSD(2) calculations indicate that the strong mixing is between the $\text{Py} \cdot (\text{H}_2\text{O})_3^-$ and $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$.

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Graphical Abstract