Water network-mediated, electron-induced proton transfer in $[\text{C}_5\text{H}_5\text{N}\cdot(\text{H}_2\text{O})_n]^-$ clusters

Andrew F. DeBlase,¹ Conrad T. Wolke,¹ Gary H. Weddle,^{1,2} Kaye A. Archer,³ Kenneth D. Jordan,^{3,a)} John T. Kelly,⁴ Gregory S. Tschumper,⁴ Nathan I. Hammer,^{4,a)} and Mark A. Johnson^{1,a)}

¹Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520, USA

²Department of Chemistry, Fairfield University, 1073 North Benson Road, Fairfield, Connecticut 06824, USA

³Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania 15260, USA

⁴Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, USA

(Received 3 August 2015; accepted 16 September 2015; published online 9 October 2015)

The role of proton-assisted charge accommodation in electron capture by a heterocyclic electron scavenger is investigated through theoretical analysis of the vibrational spectra of cold, gas phase $[\text{Py}\cdot(\text{H}_2\text{O})_{n=3-5}]^-$ clusters. These radical anions are formed when an excess electron is attached to water clusters containing a single pyridine (Py) molecule in a supersonic jet ion source. Under these conditions, the cluster ion distribution starts promptly at $n = 3$, and the photoelectron spectra, combined with vibrational predissociation spectra of the Ar-tagged anions, establish that for $n > 3$, these species are best described as hydrated hydroxide ions with the neutral pyridinium radical, $\text{PyH}^{(0)}$, occupying one of the primary solvation sites of the OH^- . The $n = 3$ cluster appears to be a special case where charge localization on Py and hydroxide is nearly isoenergetic, and the nature of this species is explored with *ab initio* molecular dynamics calculations of the trajectories that start from metastable arrangements of the anion based on a diffuse, essentially dipole-bound electron. These calculations indicate that the reaction proceeds via a relatively slow rearrangement of the water network to create a favorable hydration configuration around the water molecule that eventually donates a proton to the Py nitrogen atom to yield the product hydroxide ion. The correlation between the degree of excess charge localization and the evolving shape of the water network revealed by this approach thus provides a microscopic picture of the “solvent coordinate” at the heart of a prototypical proton-coupled electron transfer reaction. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4931928>]

I. INTRODUCTION

As an isolated species, the radical anion of pyridine, Py^- , exists as an unstable transient negative ion,¹⁻⁹ while in aqueous environment it is known¹⁰ to undergo rapid protonation to form the neutral pyridinium radical $\text{PyH}^{(0)}$ along with hydroxide. Consequently, the presence of water plays two essential roles underlying the chemical behavior of Py^- : one to provide a dielectric medium that can electrostatically prevent the valence anion from undergoing electron autodetachment, and the other to facilitate proton transfer by stabilizing the nascent hydroxide ion. Such a scenario provides an interesting opportunity to explore the detailed manner by which these two processes unfold as water molecules are sequentially added to the ionic ensemble $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$. This study is motivated by the earlier cluster work of Desfrancois and coworkers,¹ who made the important observation that the $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$ distribution begins promptly at $n = 3$ when formed using Rydberg electron transfer. Estimates^{1,2,4-9,11} of the Py electron affinity range from -0.48 to -0.79 eV, which means that the isolated anion is unstable with respect to electron detachment. Desfrancois

and coworkers¹ attributed the onset of the distribution at $n = 3$ in the hydrated clusters to the greater stabilization of the Py^- anion (relative to the neutral) with increasing hydration, as indicated schematically in Fig. 1. This raises the question, however, of whether such a radical ion can be prepared and isolated as a locally stable arrangement in the early hydration regime *prior* to the proton transfer event. Indeed, the values for the vertical detachment energies of the untagged $[\text{Py}\cdot(\text{H}_2\text{O})_{n \geq 3}]^-$ clusters measured in recent negative ion photoelectron spectra¹² have been interpreted to indicate that both $\text{PyH}^{(0)}$ created by electron-induced proton transfer and reactant hydrated Py^- anions were present at $n = 3$, while the spectra of the larger clusters were most consistent with the $\text{PyH}(\text{OH})^-\cdot(\text{H}_2\text{O})_{n-1}$ species.¹² This leaves open the questions of how these conclusions depend on the internal energies of the ions, as well as what internal rearrangements drive formation of the proton-transferred products. In particular, these results point to an interesting scenario where the proton is effectively titrated from water to Py^- according to the number and arrangement of water molecules in the spirit of our recent study of network-mediated, intracluster proton transfer in the conversion of nitrosonium NO^+ to nitrous acid HONO .¹³ Our approach involves an integrated analysis of the photoelectron angular distribution, vibrational predissociation, and

^{a)}Author to whom correspondence should be addressed. Electronic mail: jordan@pitt.edu; nhammer@olemiss.edu; and mark.johnson@yale.edu

FIG. 1. Schematic representation of the potential energy curves for converting $\text{Py} \cdot (\text{H}_2\text{O})_n$ to the lowest valence anion state of $[\text{Py} \cdot (\text{H}_2\text{O})_n]^-$ with $n = 2$ and 3 water molecules. While in the bottom case ($n = 3$) the charged species is energetically favored, removal of a single water molecule to give $n = 2$ (top trace) leads to autodetachment of the excess electron. This charge-stabilization by a critical number of solvent molecules has been used to rationalize the observed prompt onset of the $[\text{Py} \cdot (\text{H}_2\text{O})_n]^-$ distribution at $n = 3$ in Rydberg electron transfer.¹

photo-induced vibrational autodetachment spectroscopies of the Ar-tagged products from the reaction between neutral Py and the negatively charged water clusters,

and thus extends the recent photoelectron work of Wang *et al.*¹² We then explore the mechanism by which an excess electron, initially delocalized in a diffuse orbital of the system,^{14,15} becomes localized into a valence molecular orbital through the cooperative interplay between the water network and the key proton transfer reaction coordinate: $\text{N} \cdots \text{H} \cdots \text{OH}$.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Vibrational photodissociation, photo-induced vibrational autodetachment, and photoelectron spectroscopy

Anionic clusters of H_2O with Py were synthesized in an electron-impact ionized supersonic jet expansion of Ar carrier gas (60 psi) seeded with trace water and Py vapors, which were co-expanded through a single pulsed valve (Parker Hannifin General Valve Series 9, 0.030 in. aperture). A 1 keV electron beam counterpropagating along the axis of the supersonic expansion generated negatively charged cluster ions in the resulting neutral plasma. Conditions were optimized for attachment of weakly bound Ar atom “tags” to the cluster anions, thus enabling vibrational predissociation spectroscopy

by photoevaporation of the Ar atoms,

using the Yale double focusing, tandem time-of-flight photofragmentation mass spectrometer described previously.¹⁶

The parent $[\text{Py} \cdot (\text{H}_2\text{O})_n]^- \cdot \text{Ar}_p$ ion and the $[\text{Py} \cdot (\text{H}_2\text{O})_n]^- \cdot \text{Ar}_{p-q}$ photofragment were separated by a secondary (reflectron) mass spectrometer. The $[\text{Py} \cdot (\text{H}_2\text{O})_3]^- \cdot \text{Ar}_p$ cluster also exhibited vibrational autodetachment above 3000 cm^{-1} ,

The action spectrum for electron ejection through Eq. (3) was recorded as a function of photon energy by monitoring the electron signal on microchannel plates positioned below the laser interaction region.

All vibrational predissociation and photo-induced vibrational autodetachment spectra between 2250 and 3800 cm^{-1} were obtained using a *LaserVision* optical parametric oscillator/amplifier mid-infrared system pumped by a Nd:YAG laser (10 Hz, 8 ns pulse width). Radiation in the 600 – 2500 cm^{-1} region was produced by generating the difference frequency between the ~ 1.5 and $\sim 3 \mu\text{m}$ beams from the OPO/OPA in a AgGaSe₂ crystal. The spectra of the low and high frequency regions (600 – 2500 cm^{-1} vs. 2250 – 3800 cm^{-1}) were combined by normalizing the intensities of transitions that occur in the overlap region from 2250 to 2500 cm^{-1} that can be reached with both configurations. In addition, the photofragment signal was divided by the laser pulse energy to account for changes over the course of a scan. Experimental spectra represent the summation of 15–20 individual scans.

Photoelectron spectra were acquired by velocity map imaging at an excitation energy of 2.33 eV using an instrument described in detail elsewhere.^{17–21} Images were converted to photoelectron spectra using the BASEX transformation.¹⁹ The vibrational structure of the NO^- spectrum was used to calibrate the spectrometer.

B. Structure optimizations and harmonic frequency calculations

To aid in assigning the vibrational spectra, the geometries of various possible structures of the $[\text{Py} \cdot (\text{H}_2\text{O})_n]^-$, $n = 2$ – 5 clusters were optimized using M06-2X²² density functional method with the 6-31++G(d,p)^{23–25} basis set. This approach was chosen because it has recently been shown to accurately reproduce experimental photodetachment energies of hydrated azabenzene anions.¹² The X-H (X = N, O, C) stretching fundamentals were scaled by 0.980 for this level of theory, while the lower energy, non-stretching modes were not scaled. These calculations were performed using the Gaussian09 program.²⁶

C. Born-Oppenheimer molecular dynamics (BOMD) simulations

In order to gain insight into the rearrangement dynamics, we also carried out BOMD simulations of $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ starting from the structure corresponding to the dipole-bound anion. The simulations were carried out in the NVE ensemble with an excess energy corresponding to $T = 270 \text{ K}$,

randomized over all atoms. This temperature corresponds to $\sim 180\text{ cm}^{-1}$ per degree of freedom, whereas excitation of an OH stretch would deposit $\sim 120\text{ cm}^{-1}$ into each intermolecular degree of freedom (assuming validity of the equipartition theorem and that no energy is deposited into the high-frequency intramolecular modes after randomization). Thus, the simulations were carried out at an energy content in excess of that in play under the experimental conditions, which leads to accelerated dynamics. The BOMD simulations were carried out using the CP2K²⁷ code and were conducted using the BLYP density functional method,^{28,29} including the D2 long-range interaction correction of Grimme³⁰ and employing the Goedecker-Teter-Hutter pseudopotentials,³¹ aug-DZVP-GTH basis sets,^{31,32} and a plane wave cutoff of 280 Ry. The Martyna Tuckerman Poisson solver³³ was employed in the calculation of the electrostatic interactions. A cubic box of 18 Å sides was employed, and a time step of 1.0 fs was used.

III. RESULTS AND DISCUSSION

A. The $\text{Py}\cdot(\text{H}_2\text{O})_n^-$ cluster distribution: An abrupt onset at $n = 3$

The mass spectrum obtained from the ionized free jet, as described above, is displayed in Fig. 2, which shows the distribution of $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$ clusters (red) and their complexes with an argon atom (blue). Bare hydrated electron clusters with $n = 6$ and 7 (colored gray) and their Ar adducts (bronze) are also generated in abundance. The abrupt onset of $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$ anions at $n = 3$ is in accordance with the earlier observations by Desfrancois and co-workers,¹ as discussed in the Introduction. While not our focus in this work, we note in passing that we were able to generate the smaller $n = 2$ species using Ar-mediated condensation,

FIG. 2. Mass spectrum of electron-impact ionized species generated by coexpanding trace water and pyridine vapor in a supersonic jet with Ar carrier gas. The peaks due to the $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$ clusters are colored red, while the blue peaks designate the Ar-tagged species, $[\text{Py}\cdot(\text{H}_2\text{O})_n]^- \cdot \text{Ar}$. The hydrated electron clusters $(\text{H}_2\text{O})_n^-$ as well as their Ar-tagged derivatives, $(\text{H}_2\text{O})_n^- \cdot \text{Ar}$, are also present in the mass spectrum (gray and bronze, respectively). The dotted vertical red line points out that the $[\text{Py}\cdot(\text{H}_2\text{O})_2]^-$ species is not present under these source conditions.

in a different source scheme where the Py vapor is introduced with a second pulsed valve and entrained into the electron-beam ionized expansion. That approach was used earlier to form very low adiabatic electron affinity (AEA) anions [e.g., $(\text{H}_2\text{O})_4^-$] as well as metastable anions with diffuse excess electrons.^{34–37}

It is useful to consider the origin of the onset of the cluster distribution at $n = 3$ in the context of the behavior of related systems. For example, the $(\text{H}_2\text{O})_n^-$ distribution, at high water partial pressures,^{38,39} displays an abrupt onset at $n = 15$, which has been traced to a condition where the AEA becomes roughly equal to the water binding energy at this cluster size. In that case, the onset occurs because the smaller cluster anions are neutralized due to electron ejection when the condensation energy released upon attachment of a water monomer is larger than the AEA (i.e., a type of associative detachment reaction).⁴⁰ The onset of the $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$ cluster distribution at $n = 3$ therefore indicates that the AEA increases much more rapidly with increasing cluster size than for neat water clusters.

B. Velocity map imaging photoelectron spectroscopy of the $[\text{Py}\cdot(\text{H}_2\text{O})_3]^-$ cluster: Evidence for a valence anion

To assess the nature of the excess electron orbital in the $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$ clusters, the angular distributions of photoelectrons were obtained by velocity map imaging using an excitation wavelength of 532 nm (2.33 eV). These results for $n = 3$ are given in Fig. 3, where the raw image and photoelectron energy distributions (after BASEX transformation)¹⁹ are given in traces (a) and (b), respectively. The spectrum is very broad, consistent with that reported by Wang *et al.*,¹² displaying a full width at half maximum (FWHM) of 0.85 eV,

FIG. 3. Velocity map image (a) and resulting photoelectron spectrum (b) of $[\text{Py}\cdot(\text{H}_2\text{O})_3]^-$ after the BASEX transform procedure.¹⁹ This spectrum was obtained using an excitation energy of 2.33 eV and plotted as a function of the electron binding energy. The white arrow in the image indicates the direction of the electric field vector (E) of the laser. Arrows above the spectrum indicate the VDE values for $\text{Py}\cdot(\text{H}_2\text{O})_3^-$ and $\text{PyH}\cdot(\text{OH})\cdot(\text{H}_2\text{O})_2$ assigned by Wang *et al.*¹²

indicating that the vertical electron detachment energy (VDE) is much greater than the AEA. The peak photoelectron yield of the distribution occurs at 1.53 eV, corresponding to the VDE, which is in close agreement with the VDE of 1.56 eV reported by Wang *et al.*¹² Most importantly, the image in Fig. 3(a) exhibits a significantly negative anisotropy parameter⁴¹ of about -0.5 , indicating that photoelectrons are preferentially ejected *perpendicular* to the direction of the electric field vector (double-headed white arrow in Fig. 3(a)). This behavior is opposite to that displayed by the hydrated electron clusters, $(\text{H}_2\text{O})_n^-$, for which β values are observed close to $+2$,^{42,43} the limiting value expected for a $s \rightarrow p$ electron ejection scenario. Furthermore, anionic water clusters in the size range around $n = 5$ have much lower VDEs (<0.5 eV)^{34,44–46} with narrow photoelectron distributions closer resembling that displayed by diffuse, dipole-bound electrons.⁴⁷ These results indicate that the excess electron in the $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ cluster occupies a valence molecular orbital. Photoelectron spectra of the $n = 4$ and $n = 5$ clusters are also given in the supplementary material (Fig. S1).⁴⁸ As reported earlier,¹² the binding energy increases with hydration such that the band becomes distorted due to threshold effects^{49–51} when the VDE approaches the photon energy.

C. Calculated structures

The calculated [M06-2X/6-31++(d,p)] minimum energy structures for the $n = 3$ –5 clusters identified earlier by Wang *et al.*¹² are reproduced in Fig. 4. Interestingly, the $n = 3$ cluster has two nearly isoenergetic isomers: one that exhibits proton-transfer from a water molecule to the pyridine leaving a solvated hydroxide ion (Fig. 4(a)) and another that contains a hydrated Py^- ion (Fig. 4(b)). Thus, the $n = 3$ cluster appears to represent a tipping point in the electron-driven intracuster proton transfer reaction and indeed introduces the interesting possibility that vibrational excitation of the cold cluster can promote large amplitude rearrangements associated with this process.

FIG. 4. Calculated low energy M06-2X/6-31++G(d,p) structures. (a) and (b) are two low lying isomers of $n = 3$, where correction for the vibrational zero-point energy brings the intracuster proton transfer structure (a) lower in energy. The formation of the PyH radical is a robust feature of the larger clusters (c) $n = 4$ and (d) $n = 5$.

D. Vibrational predissociation and photo-induced vibrational autodetachment spectroscopies: Evidence for strong ionic H-bonding

1. Infrared photophysics of the Ar-tagged and bare clusters

The broad photoelectron spectra do not allow structural determination of the molecular nature of the species that bear the negative charge. To help clarify this situation, we obtained the vibrational predissociation spectra of the $[\text{Py} \cdot (\text{H}_2\text{O})_n]^-$ clusters tagged with Ar, with the results presented in Fig. 5. The average number of Ar atoms lost is found to be linearly dependent on the photon energy (see the supplementary material, Fig. S3),⁴⁸ establishing that each tag has a similar binding energy on the order of $750 \text{ cm}^{-1}/\text{Ar}$. In the case of the smallest persistent cluster at $n = 3$, it was only possible to observe fragment anions corresponding to Ar loss below 3300 cm^{-1} , while strong features were observed in the higher energy range for the $n = 4$ and 5 species. This type of behavior has been observed in $(\text{H}_2\text{O})_n^- \cdot \text{Ar}_m$ clusters,⁵² for which the

FIG. 5. Vibrational action spectra of the $[\text{Py} \cdot (\text{H}_2\text{O})_n]^-$ clusters. The full infrared spectrum for the $[\text{Py} \cdot (\text{H}_2\text{O})_3]^- \cdot \text{Ar}$ species was recorded by combining the photo-induced vibrational autodetachment channel above 3000 cm^{-1} (a) with the Ar-predissociation spectrum measuring formation of bare $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ photofragment ions (b). The spectra of $[\text{Py} \cdot (\text{H}_2\text{O})_4]^-$ (d) and $[\text{Py} \cdot (\text{H}_2\text{O})_5]^-$ (f) were obtained by Ar-predissociation between 800 and 3800 cm^{-1} . Calculated harmonic spectra [M06-2X/6-31++G(d,p) level] of the low energy proton transfer structures for $n = 3, 4$, and 5 are shown in the inverted grey traces of (d), (f), and (h), respectively, while the harmonic spectrum of the $\text{Py}^- \cdot (\text{H}_2\text{O})_3$ is shown in trace (c). Key features are indicated by the dotted guidelines, including free OH stretching ($\nu_{\text{OH}}^{\text{free}}$) and CH stretching (ν_{CH}) and other distinct bands (ν_{α} , ν_{β} , and ν_{γ}) that are addressed in the discussion.

nascent anionic fragment, $(\text{H}_2\text{O})_n^{*-}$, is unstable with respect to electron autodetachment,²⁰

unless it is sufficiently cooled by Ar evaporation. We, therefore, also monitored the electron photodetachment channel

with the results displayed in the inset in Fig. 5(a) for the Ar-tagged $n = 3$ cluster. The “missing” bands are indeed recovered in the electron loss channel, and these transitions can also be observed in the photofragmentation spectrum of $[\text{Py}\cdot(\text{H}_2\text{O})_3]^-$ tagged with 4 Ar atoms (see the supplementary material, Fig. S2).⁴⁸ This observation of vibrational autodetachment is significant in that it emphasizes the close proximity of the adiabatic electron continuum and the significant rearrangement that is required to access the intersection between the anionic and neutral potential surfaces.

2. Comparison with the vibrational spectrum of the $\text{OH}^-(\text{H}_2\text{O})_n$ anion

A striking qualitative aspect of the vibrational spectra is that they are extremely broad. For $n = 3$ and 4, for example, diffuse absorptions span most of the $900\text{--}3300\text{ cm}^{-1}$ range in contrast to the sharp features displayed by the water cluster anions in this size regime.^{53,54} This behavior is also unusual for the microhydration of small molecular anions (e.g., $\text{CO}_2^-(\text{H}_2\text{O})_n$)³⁵ of similar size. Even the intramolecular HOH bending mode is obscured in the $n = 3$ spectrum, and the only features that can be assigned by inspection are the relatively sharp bands near 3700 cm^{-1} due to the free OH stretching modes and those near 3000 cm^{-1} arising from the ring CH stretching fundamentals. Interestingly, the transitions in the lower energy range are much better defined in the larger ($n = 5$) cluster spectrum, with the onset of the diffuse band shifted toward higher energy, beginning at 2400 cm^{-1} .

The calculated harmonic spectra for the minimum energy structures displayed in Fig. 4 are included in Fig. 5 as inverted traces. Perhaps the most important conclusion from this comparison is that the spectra are so dominated by strong anharmonicities that even the most cursory assignments are not obvious. Rather than engage a very difficult exercise in simulating the anharmonic spectra of floppy systems clearly at play here, we find it more useful to empirically evaluate the chemical compositions of the $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$ clusters by comparing their vibrational spectra to that of the $\text{OH}^-(\text{H}_2\text{O})_4$ cluster reported earlier,⁵⁵ and included at the top of Fig. 6. Interestingly, a similarly diffuse band is also found in this species, where three water molecules are directly attached to the hydroxide ion and a fourth lies in the second solvation shell as illustrated in the inset structure. This diffuse band has been attributed to excitation of the OH groups engaged in H-bonds to the ion, while the sharp pattern highest in energy arises mostly from non-bonded OH groups or OH groups of the water molecule in the second solvation shell in a double H-bond donor (DD) configuration (ν_a). Note that the intensity of the hydroxide OH fundamental has been found to be dramatically

FIG. 6. Vibrational predissociation spectrum of the $\text{OH}^-(\text{H}_2\text{O})_4\cdot\text{Ar}$ cluster (a) with the minimum energy structure consistent with the spectrum depicted in the inset. Reprinted with permission from Robertson *et al.*, *Science* **299**, 1367 (2003). Copyright 2003 AAAS. Vibrational predissociation spectra of the Ar-tagged $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$ clusters with $n = 4$ (b) and 5 (c) are shown for comparison. Bands are assigned according to their number of H-bond acceptor (A) and donor (D) interactions of specific water molecules in the network.

suppressed upon completion of its hydration shell.⁵⁶ The fact that the spectral signatures of all three classes of OH environments (primary shell, secondary shell, and free) in hydrated hydroxide clusters are present in $[\text{Py}\cdot(\text{H}_2\text{O})_{4,5}]^-$ strongly suggests that these clusters adopt $\text{PyH}\cdot(\text{OH}^-(\text{H}_2\text{O})_{n-1})$ arrangements that would be consistent with an intracuster variation of the proton transfer process observed in solution (Eq. (1)).

3. Identification of the CH bending fundamentals of $\text{PyH}^{(0)}$

The reduction in complexity of the $n = 5$ spectrum in the fingerprint region warrants an effort to identify key well-defined peaks in the context of the hydroxide product, specifically the sharp features labeled ν_β and ν_γ in Fig. 5. This region of the spectrum is expanded in Fig. 7. The bands in question are quite close in frequency to those predicted for the ring CH bending modes of $\text{PyH}^{(0)}$, denoted ν_{23}^{Py} and ν_{21}^{Py} and colored green and orange, respectively, in Fig. 7. Here, the mode numbering is that for isolated $\text{PyH}^{(0)}$ with C_{2v} symmetry (numbered in order of highest to lowest symmetry and highest to lowest energy).

In light of the difficulties with the harmonic predictions discussed above, it is again useful to compare the observed spectra with empirical data to further assess the viability of the $\text{PyH}\cdot(\text{OH}^-(\text{H}_2\text{O})_{n-1})$ motif. Figure 7 compares the vibrational predissociation spectrum of $[\text{Py}\cdot(\text{H}_2\text{O})_5]^-$ to the IR absorption spectrum of the $\text{PyH}^{(0)}$ radical isolated in a matrix of frozen *para*-hydrogen⁵⁷ and to the gas phase vibrational spectrum of neutral Py.⁵⁸ $\text{PyH}^{(0)}$ in the *para*-hydrogen matrix was synthesized by Lee *et al.* by electron bombardment and photolysis of $\text{Cl}_2/\text{Py}/p\text{-H}_2$. For a simplified comparison to our data, we have simulated their spectrum using the tabulated

FIG. 7. A comparison between the Ar-predissociation spectrum $[\text{Py} \cdot (\text{H}_2\text{O})_5]^-$ (a), the infrared spectrum of $\text{PyH}^{(0)}$ taken in solid *p*-hydrogen (b),⁵⁷ and the infrared spectrum of neutral pyridine vapor⁵⁸ in the OH and CH bending regions (c). The spectrum in trace (b) is a convolution of the tabulated frequencies and intensities in Ref. 57 with a Lorentzian (4 cm^{-1} FWHM). (c) is a convolution of tabulated peaks in Ref. 58, with 20 cm^{-1} half-width Lorentzians. The normal mode displacement vectors of the Py/ $\text{PyH}^{(0)}$ moiety in each of these species are illustrated next to the corresponding transitions. The green and orange dotted guidelines highlight the proximity of transitions in the two model compounds to those observed in the spectrum of $[\text{Py} \cdot (\text{H}_2\text{O})_5]^-$.

wavenumbers and intensities that were assigned to the $\text{PyH}^{(0)}$ species (convoluted using a Lorentzian with a FWHM of 4 cm^{-1}). Both ν_{23} and ν_{21} of the $\text{PyH}^{(0)}$ species are very close to the observed sharp bands in the $[\text{Py} \cdot (\text{H}_2\text{O})_5]^-$ vibrational predissociation spectrum (Fig. 7(a)) with similar relative intensities, albeit with a small red shift (14 and 30 cm^{-1} for ν_{23} and ν_{21} , respectively) in the solid *p*-hydrogen matrix. Most importantly, these bands are quite different from the pattern displayed by the neutral Py molecule, which has been obtained from vapor-phase measurements and is included in Fig. 7(c).

E. Theoretical exploration of the rearrangement pathways in $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$

1. Potential surface for intracluster proton transfer

The empirical evidence points to a situation where the system explores both $\text{Py}^-(\text{H}_2\text{O})_n$ and $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_{n-1}$ components with the latter dominating but with the relative weights of the two terms depending on the degree of solvation of the OH^- . Qualitatively, as the hydroxide-based clusters

FIG. 8. One-dimensional potential energy curves for proton transfer in $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ (solid blue line) and $\text{Py} \cdot (\text{H}_2\text{O})_3$ (dashed blue line). The minimum energy structure of the anion used in generating these potentials is shown in the inset on the left, while the minimum energy structure of the neutral is shown on the right. The potentials are calculated by varying the NH distance, keeping all other degrees of freedom frozen. On the left-hand side of the anion potential, the structure is dominated by $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$, while on the right-hand side, it is dominated by $\text{Py}^-(\text{H}_2\text{O})_3$. Estimates of the energies of the $v=0$ and $v=1$ levels of the anion are illustrated by red horizontal lines.

accommodate additional water molecules on the emergent network, the configuration with the excess charge on the OH is stabilized, while that with the charge on the Py becomes less important. Thus, in the $n=3$ case, the proton is more strongly shared in the $\text{N} \cdots \text{H} \cdots \text{O}$ motif, giving rise to very broad spectral features typical for shared protons.⁵⁹ At smaller n , excitation of the nominal NH stretch samples the $\text{Py}^-(\text{H}_2\text{O})_n$ configuration, in essence driving the proton transfer reaction with concomitant excess charge displacement. Such a scenario has been demonstrated to be at play in the binary complex $\text{F}^- \cdot \text{HOH}$,⁶⁰ where excitation of the bridging proton stretch samples a region in the potential surface corresponding to $\text{HF} \cdots \text{OH}^-$. When this occurs in a system where the associated water network responds to the change in the charge distribution, it is expected that vibrational excitation will induce substantial heavy particle rearrangements, thus rationalizing the nearly continuous nature of the spectrum for $n=3$.

To better quantify the nature of the potential surfaces governing the heavy particles and excess electron, we calculated one-dimensional potential energy curves for proton transfer in $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$ and $\text{Py} \cdot (\text{H}_2\text{O})_3$. The potentials were calculated starting from the M06-2X optimized structure shown in Fig. 4(a) with a $\text{PyH} \cdot (\text{OH}^-) \cdot (\text{H}_2\text{O})_2$ configuration, and then carrying out a series of single-point calculations for the anion and neutral for different values of the NH distance, assuming linear motion between the N atom and the O of the hydroxyl, and keeping all other degrees of freedom frozen. The resulting anion potential energy curve, shown in Fig. 8, is exceedingly anharmonic, such that even the zero-point level samples the $\text{Py}^-(\text{H}_2\text{O})_3$ structure. The vibrational zero-point level of the neutral potential along this slice lies above the $v=1$ level of the anion; however, relaxation of the geometry of the neutral causes its zero-point level to fall below the $v=1$ level of the anion (as evidenced by the experimentally observed opening

of the electron autodetachment channel). We note that the actual energy gap between the proton-transfer and non-proton transfer structures may be somewhat larger than predicted by the M06-2X method. In particular, preliminary results using the restricted open-shell MP2 method^{61,62} predict the non-proton transfer structure to be about 477 meV less stable than the proton-transfer structure, rather than being nearly isoenergetic as predicted by the M06-2X method. In either case, however, it is still anticipated that excitation of the $v = 1$ OH manifold will induce significant large amplitude motions that mediate interconversion between these two structures.

As the charge becomes more stabilized on the OH^- , the spectra become simpler as excitation of one quanta of OH stretch no longer leads to sampling of the $\text{Py}^-(\text{H}_2\text{O})_n$ class of structures. A primitive manifestation of this type of blue-shifting by differential solvation of charge-localized, asymptotic partners (in this case $\text{Py}^-\cdot\text{H}_2\text{O}$ vs. $\text{PyH}\cdot\text{OH}^-$) has, in fact, been routinely invoked to understand the rare gas tag effects in binary complexes.^{63–65} The case of solvation by water can thus be viewed as an extreme example of a generic solvent response by an anionic, proton bound complex.

2. Calculation of the reaction path for water-mediated electron capture by Py

The preceding discussion emphasized the close energetic proximity of the $\text{PyH}\cdot(\text{OH}^-)\cdot(\text{H}_2\text{O})_{n-1}$ and $\text{Py}^-(\text{H}_2\text{O})_n$ valence-bond arrangements. There is actually a third low-lying valence-bond structure that corresponds to a dipole-bound $\text{Py}\cdot(\text{H}_2\text{O})_n^-$ anion with a diffuse excess electron, which is expected to be involved in early stages of $(\text{H}_2\text{O})_n^- + \text{Py}$ condensation. Our calculations indicate that excitation of one quanta into the NH or OH stretch vibrations of the most stable $\text{PyH}\cdot(\text{OH}^-)\cdot(\text{H}_2\text{O})_2$ species would deposit sufficient energy for the system to sample such dipole-bound structures as exit channel configurations leading to electron autodetachment. To further evaluate the dynamics of the interconversion between the $\text{Py}\cdot(\text{H}_2\text{O})_3^-$ and $\text{PyH}\cdot(\text{OH}^-)\cdot(\text{H}_2\text{O})_2$ structures, we performed BOMD simulations on the $[\text{Py}\cdot(\text{H}_2\text{O})_3]^-$ cluster (see Section II C for details). Ten trajectories, four between 1 and 5.5 ps and six for between 14.7 and 19.3 ps, were run. Of these only two gave rise to the solvated OH^- ion, one near 16 ps and the other near 1.6 ps. In these simulations, the $\text{Py}\cdot(\text{H}_2\text{O})_3^-$ isomer was heated to 270 K and changes to the geometry and electronic structure were recorded in 1 fs increments. An example video of one of these trajectories is given in the supplementary material.⁴⁸ Figure 9 plots the electron binding energy along one of the trajectories together with the differences in the charge densities of the anion and neutral, calculated at the MP2/aug-cc-pVDZ^{66,67} level, augmented with a $7s7p$ set of diffuse functions centered at the middle of the ring for the final, key intermediate, and product structures (MP2-level charge densities are employed rather than BLYP^{28,29} charge densities as the MP2 method is expected to give more reliable charge distributions). For the indicated trajectory, the electron remains dipole bound to the $(\text{H}_2\text{O})_3$ water network for about 1.65 ps, before evolving into an intermediate structure of the form $\text{Py}^- \cdots \text{H}^+ \cdots \text{OH}^-(\text{H}_2\text{O})_2$. This is followed by rapid formation of the pyridinium radical $\text{PyH}\cdot(\text{OH}^-)\cdot(\text{H}_2\text{O})_2$. In the product

FIG. 9. VDE of $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$ along a BOMD trajectory with an initial kinetic energy consistent with $T = 270$ K. The MP2 level charge differences (anion – neutral) for the reactant, intermediate, and product are displayed.

structure, both an electron and a proton have transferred to the Py, with the former occupying the π^* LUMO of the neutral Py molecule. Evolution to the product $\text{PyH}\cdot(\text{OH}^-)\cdot(\text{H}_2\text{O})_2$ structure requires the two H_2O monomers to adopt an arrangement that effectively solvates the OH^- . For the indicated trajectory, the system rapidly evolves from the intermediate to the product, although for other trajectories (not shown) there are fluctuations between the intermediate and reactant-like $\text{Py}\cdot(\text{H}_2\text{O})_3^-$ structures before the product is accessed. As seen in Fig. 9, the electron binding energy increases as the $\text{PyH}\cdot(\text{OH}^-)\cdot(\text{H}_2\text{O})_2$ product is formed, approaching a VDE similar to that observed from the photoelectron spectrum (1.53 eV).

IV. CONCLUSIONS

Gas phase cluster chemistry, together with analyses of the predissociation and photoelectron spectroscopies with electronic structure calculations, has been used to clarify the chemical rearrangements that occur when Py combines with hydrated electron clusters $(\text{H}_2\text{O})_n^-$ for $n = 3-5$. The photoelectron spectrum of the resulting $[\text{Py}\cdot(\text{H}_2\text{O})_n]^-$ species supports the presence of a valence anion, in which the VDE is much greater than its AEA. Analysis of the vibrational patterns then confirms the formation of neutral pyridinium radical $\text{PyH}^{(0)}$ and hydrated hydroxide, where the neutral radical occupies one of the sites in the primary solvation shell around the hydroxide anion: $\text{PyH}\cdot(\text{OH}^-)\cdot(\text{H}_2\text{O})_{n-1}$. Synthetic access to this arrangement now presents an attractive opportunity to follow the reaction chemistry of the $\text{PyH}^{(0)}$ radical in the microhydration regime. A particularly timely choice in this regard is the activation of CO_2 by proton coupled electron transfer, which has been proposed for the catalytic activity of Py by Musgrave⁶⁸ and Bocarsly.⁶⁹

ACKNOWLEDGMENTS

This work was supported by the Mississippi Center of Supercomputing Research and the National Science Foundation under Grant Nos. CHE-1338056 (G.S.T.) and CHE-0955550 (N.I.H.). Both G.S.T. and N.I.H. acknowledge NSF EPSCoR support under Grant No. EPS-0903787. M.A.J. and K.D.J.

want to thank the U.S. Department of Energy for support under Grant Nos. DE-FG02-06ER15800 and DE-FG02-06ER15066. M.A.J. also expresses gratitude to the staff and facilities of the Yale University Faculty of Arts and Sciences High Performance Computing Center, and NSF Grant No. CNS 08-21132, which partially funded acquisition of the facilities. K.D.J. also acknowledges use of computational facilities in the University of Pittsburgh's Center for Simulation and Modeling.

- ¹V. Periquet, A. Moreau, S. Carles, J. P. Schermann, and C. Desfrancois, *J. Electron Spectrosc. Relat. Phenom.* **106**, 141–151 (2000).
- ²S. Y. Han, J. K. Song, J. H. Kim, H. B. Oh, and S. K. Kim, *J. Chem. Phys.* **111**, 4041–4050 (1999).
- ³K. Aflatooni, G. A. Gallup, and P. D. Burrow, *Chem. Phys. Lett.* **282**, 398–402 (1998).
- ⁴C. Desfrancois, H. Abdoul-Carime, and J. P. Schermann, *Int. J. Mod. Phys. B* **10**, 1339–1395 (1996).
- ⁵J. P. Ziesel, I. Nenner, and G. J. Schulz, *J. Chem. Phys.* **63**, 1943 (1975).
- ⁶P. D. Burrow, A. J. Ashe, D. J. Bellville, and K. D. Jordan, *J. Am. Chem. Soc.* **104**, 425–429 (1982).
- ⁷D. Mathur and J. B. Hasted, *Chem. Phys.* **16**, 347–352 (1976).
- ⁸K. D. Jordan and P. D. Burrow, *Chem. Rev.* **87**, 557–588 (1987).
- ⁹G. J. Schulz, *Rev. Mod. Phys.* **45**, 423 (1973).
- ¹⁰J. Grimshaw, *Electrochemical Reactions and Mechanisms in Organic Chemistry* (Elsevier, Amsterdam, 2000).
- ¹¹K. Aflatooni, G. A. Gallup, and P. D. Burrow, *J. Phys. Chem. A* **102**, 6205–6207 (1998).
- ¹²Y. Wang, X. Zhang, S. Lyapustina, M. M. Nilles, S. Xu, J. D. Graham, K. H. Bowen, J. T. Kelly, G. S. Tschumper, and N. I. Hammer, “The onset of electron-induced proton-transfer in hydrated azabenzene anions,” *Phys. Chem. Chem. Phys.* (submitted).
- ¹³R. A. Relph, T. L. Guasco, B. M. Elliott, M. Z. Kamrath, A. B. McCoy, R. P. Steele, D. P. Schofield, K. D. Jordan, A. A. Viggiano, E. E. Ferguson, and M. A. Johnson, *Science* **327**, 308–312 (2010).
- ¹⁴T. Sommerfeld and K. D. Jordan, *J. Am. Chem. Soc.* **128**, 5828–5833 (2006).
- ¹⁵T. Sommerfeld, A. DeFusco, and K. D. Jordan, *J. Phys. Chem. A* **112**, 11021–11035 (2008).
- ¹⁶M. A. Johnson and W. C. Lineberger, in *Techniques for the Study of Ion-Molecule Reactions*, edited by J. M. Farrar and W. H. Saunders, Jr. (Wiley, New York, 1988), Vol. XX, p. 591.
- ¹⁷A. Sanov and R. Mabbs, *Int. Rev. Phys. Chem.* **27**, 53–85 (2008).
- ¹⁸A. T. J. B. Eppink and D. H. Parker, *Rev. Sci. Instrum.* **68**, 3477–3484 (1997).
- ¹⁹V. Dribinski, A. Ossaditchi, V. A. Mandelshtam, and H. Reisler, *Rev. Sci. Instrum.* **73**, 2634–2642 (2002).
- ²⁰B. M. Elliott, L. R. McCunn, and M. A. Johnson, *Chem. Phys. Lett.* **467**, 32–36 (2008).
- ²¹H. K. Gerardi, K. J. Breen, T. L. Guasco, G. H. Weddle, G. H. Gardenier, J. E. Laaser, and M. A. Johnson, *J. Phys. Chem. A* **114**, 1592–1601 (2010).
- ²²Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* **120**, 215–241 (2008).
- ²³T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. V. R. Schleyer, *J. Comput. Chem.* **4**, 294–301 (1983).
- ²⁴P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **28**, 213–222 (1973).
- ²⁵W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257–2261 (1972).
- ²⁶M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *GAUSSIAN 09*, Gaussian, Inc., Wallingford, CT, 2009.
- ²⁷See <http://www.cp2k.org> for CP2K.
- ²⁸A. D. Becke, *Phys. Rev. A* **38**, 3098–3100 (1988).
- ²⁹C. T. Lee, W. T. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785–789 (1988).
- ³⁰S. Grimme, *J. Comput. Chem.* **27**, 1787–1799 (2006).
- ³¹S. Goedecker, M. Teter, and J. Hutter, *Phys. Rev. B* **54**, 1703–1710 (1996).
- ³²C. Hartwigsen, S. Goedecker, and J. Hutter, *Phys. Rev. B* **58**, 3641–3662 (1998).
- ³³G. J. Martyna and M. E. Tuckerman, *J. Chem. Phys.* **110**, 2810–2821 (1999).
- ³⁴J.-W. Shin, N. I. Hammer, J. M. Headrick, and M. A. Johnson, *Chem. Phys. Lett.* **399**, 349–353 (2004).
- ³⁵K. J. Breen, A. F. DeBlase, T. L. Guasco, V. K. Voora, K. D. Jordan, T. Nagata, and M. A. Johnson, *J. Phys. Chem. A* **116**, 903–912 (2012).
- ³⁶R. Nakanishi and T. Nagata, *J. Chem. Phys.* **130**, 224309 (2009).
- ³⁷H. Motegi, T. Takayanagi, T. Tsuneda, K. Yagi, R. Nakanishi, and T. Nagata, *J. Phys. Chem. A* **114**, 8939–8947 (2010).
- ³⁸L. A. Posey and M. A. Johnson, *J. Chem. Phys.* **89**, 4807–4814 (1988).
- ³⁹P. J. Campagnola, D. M. Cyr, and M. A. Johnson, *Chem. Phys. Lett.* **181**, 206–212 (1991).
- ⁴⁰M. T. Bowers, *Gas Phase Ion Chemistry* (Academic Press, New York, 1979).
- ⁴¹J. Cooper and R. N. Zare, *J. Chem. Phys.* **48**, 942–943 (1968).
- ⁴²P. J. Campagnola, L. A. Posey, and M. A. Johnson, *J. Chem. Phys.* **92**, 3243–3245 (1990).
- ⁴³A. E. Bragg, J. R. R. Verlet, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, *J. Am. Chem. Soc.* **127**, 15283–15295 (2005).
- ⁴⁴J. V. Coe, G. H. Lee, J. G. Eaton, S. T. Arnold, H. W. Sarkas, K. H. Bowen, C. Ludewigt, H. Haberland, and D. R. Worsnop, *J. Chem. Phys.* **92**, 3980–3982 (1990).
- ⁴⁵J. Kim, I. Becker, O. Cheshnovsky, and M. A. Johnson, *Chem. Phys. Lett.* **297**, 90–96 (1998).
- ⁴⁶J. R. R. Verlet, A. E. Bragg, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, *Science* **307**, 93–96 (2005).
- ⁴⁷J. V. Coe, S. T. Arnold, J. G. Eaton, G. H. Lee, and K. H. Bowen, *J. Chem. Phys.* **125**, 014315 (2006).
- ⁴⁸See supplementary material at <http://dx.doi.org/10.1063/1.4931928> for photoelectron spectra of $[\text{Py} \cdot (\text{H}_2\text{O})_n]^-$ clusters, tag dependence study of the vibrational predissociation spectra of the $[\text{Py} \cdot (\text{H}_2\text{O})_3]^-$, calculated isomeric forms of $\text{PyH} \cdot (\text{H}_2\text{O})_n \cdot \text{OH}^-$, with $n = 3-5$, double resonance spectroscopy of $[\text{Py} \cdot (\text{H}_2\text{O})_4]^-$ and video of a trajectory of the interconversion between the $\text{Py} \cdot (\text{H}_2\text{O})_3^-$ and $\text{PyH} \cdot (\text{OH})^- \cdot (\text{H}_2\text{O})_2$ structures.
- ⁴⁹C. L. Adams, B. J. Knurr, and J. M. Weber, *J. Chem. Phys.* **136**, 064307 (2012).
- ⁵⁰E. P. Wigner, *Phys. Rev.* **73**, 1003–1009 (1948).
- ⁵¹C. L. Adams, H. Schneider, and J. M. Weber, *J. Phys. Chem. A* **115**, 8588 (2011).
- ⁵²P. Ayotte, C. G. Bailey, J. Kim, and M. A. Johnson, *J. Chem. Phys.* **108**, 444–448 (1998).
- ⁵³N. I. Hammer, J.-W. Shin, J. M. Headrick, E. G. Diken, J. R. Roscioli, G. H. Weddle, and M. A. Johnson, *Science* **306**, 675–679 (2004).
- ⁵⁴N. I. Hammer, J. R. Roscioli, M. A. Johnson, E. M. Myshakin, and K. D. Jordan, *J. Phys. Chem. A* **109**, 11526 (2005).
- ⁵⁵W. H. Robertson, E. G. Diken, E. A. Price, J.-W. Shin, and M. A. Johnson, *Science* **299**, 1367–1372 (2003).
- ⁵⁶M. Morita, H. Takahashi, S. Yabushita, and K. Takahashi, *Phys. Chem. Chem. Phys.* **16**, 23143–23149 (2014).
- ⁵⁷B. Golec, P. Das, M. Bahou, and Y. P. Lee, *J. Phys. Chem. A* **117**, 13680–13690 (2013).
- ⁵⁸K. N. Wong and S. D. Colson, *J. Mol. Spectrosc.* **114**, 129–151 (1984).
- ⁵⁹C. J. Johnson, L. C. Dzugas, A. B. Wolk, C. M. Leavitt, J. A. Fournier, A. B. McCoy, and M. A. Johnson, *J. Phys. Chem. A* **118**, 7590–7597 (2014).
- ⁶⁰J. R. Roscioli, E. G. Diken, M. A. Johnson, S. Horvath, and A. B. McCoy, *J. Phys. Chem. A* **110**, 4943–4952 (2006).
- ⁶¹C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618–622 (1934).
- ⁶²M. Head-Gordon, J. A. Pople, and M. J. Frisch, *Chem. Phys. Lett.* **6**, 503–506 (1988).
- ⁶³G. H. Gardenier, M. A. Johnson, and A. B. McCoy, *J. Phys. Chem. A* **113**, 4772–4779 (2009).
- ⁶⁴S. A. Corcelli, J. A. Kelley, J. C. Tully, and M. A. Johnson, *J. Phys. Chem. A* **106**, 4872–4879 (2002).
- ⁶⁵S. G. Olesen, T. L. Guasco, J. R. Roscioli, and M. A. Johnson, *Chem. Phys. Lett.* **509**, 89–95 (2011).
- ⁶⁶T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007–1023 (1989).
- ⁶⁷R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *J. Chem. Phys.* **96**, 6796–6806 (1992).
- ⁶⁸C. H. Lim, A. M. Holder, and C. B. Musgrave, *J. Am. Chem. Soc.* **135**, 142–154 (2013).
- ⁶⁹A. J. Morris, R. T. McGibbon, and A. B. Bocarsly, *ChemSusChem* **4**, 191–196 (2011).