Anion Photoelectron Spectroscopy of Solvated Transition State Precursors

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Anion photoelectron spectroscopy of solvated transition state precursors

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Photoelectron (PE) spectra have been collected for the clustered bihalide anions XHX−•(M) (X=Br, I) and BrHI−•(M), where M=H2O, HBr, and HI, in order to probe the effects of strongly solvating species on the PE spectra of transition state precursor anions. The PE spectra of the XHX−•(H2O) ions show similar vibrational progressions as the spectra of the bare BrHBr− and IHI− anions, indicating that photodetachment of the bare and hydrated ions accesses similar XHX transition state geometries on the X+HX reaction potential energy surfaces. These results are consistent with electronic structure calculations that predict a double hydrogen-bonded XHX−•(H2O) structure in which the symmetry of the strong XHX− hydrogen bond is largely preserved. In contrast, PE spectra of BrHBr−•(HBr)1,2 and IHI−•(HI)1,2 indicate that the addition of a single HBr or HI disrupts the symmetric XHX− bond, resulting in structures of the form X−•(HX)n, and altering the geometry of the Franck–Condon region accessed on the neutral potential energy surfaces. Similarly, PE spectra of BrH•−•(HI) and BrH•−•(HBr) suggest anion structures of the form I−•(HBr)HI and I−•(HBr)2, respectively. © 2003 American Institute of Physics. [DOI: 10.1063/1.1577331]

I. INTRODUCTION

The transition state region of a chemical reaction is of fundamental importance in chemical reaction dynamics. During the past 10–15 years, there have been numerous experimental and theoretical studies on transition state spectroscopy of isolated gas phase reactions, yielding new insights into the nature of the reaction potential energy surface near the transition state and the reaction dynamics that occur in this region of the surface.1–5 These experiments raise the fundamentally interesting question of how transition state spectroscopy and dynamics would differ in a condensed phase environment.6,7 This question can be addressed systematically by initiating transition state dynamics in size-selected clusters in which the reacting species are complexed to a known number of solvent atoms or molecules. Studies of this type are presented here, in which photoelectron (PE) spectroscopy of clustered transition state precursor anions is used to probe the effect of solvation on anion structure and on the neutral transition state.

We have previously shown that PE spectroscopy of stable negative ions can be used to study transition state species for gas phase bimolecular chemical reactions.5 The reactions studied include several heavy+light-heavy hydrogen transfer systems such as the I+HI, Br+HBr, and Br+HI reactions8–11 as well as the benchmark F+H2 and OH+H2 reactions.12–14 In these experiments, the PE spectrum is collected for anions such as IHI−, FH2−, etc., whose geometry is very similar to that of transition state species on the neutral potential energy surface. The region of the potential energy surface which is studied by photodetachment of this “precursor anion” is determined by the Franck–Condon overlap between the anion and the neutral reaction surface. Even though the neutral species dissociate to either reactants or products, the PE spectra yield resolved structure associated with vibrational motion in the neutral transition state region perpendicular to the reaction coordinate, for example, the antisymmetric H-atom stretching vibration in the IHI, BrHBr, and BrHI neutral complexes. The higher resolution zero electron kinetic energy (ZEKE) spectrum of IHI− revealed additional features assigned to the IHI symmetric stretch vibration, associated with reactive resonances in the transition state, and to IHI hindered rotor progressions.9

The effects of weakly interacting solvent species on the PE spectra of transition state precursor anions were investigated by Arnold et al.15,16 who measured the PE spectra of IHI− and IDI− clustered with multiple N2O and CO2 molecules, and by Liu et al.17,18 who obtained PE spectra for BrHI−•Ar and IHI−•(Ar)n 1–15. In all of these studies, the vibrational structure seen in the PE spectrum of the bare ion was preserved; the main effect of solvation was a shift of the photoelectron spectrum toward lower electron kinetic energy (eKE) because of stronger binding of the solvent species to the anion than the neutral. The PE spectra of IHI−•Ar and BrH•−•Ar were narrower than those of the bare ions, and the IHI−•Ar spectrum showed additional features that were not resolved in the IHI− PE spectrum (although most of them were seen in the ZEKE spectrum). These effects were attributed to the reduced contribution of vibrational hot bands in the PE spectra of the binary cluster ions; similar effects have been observed in the infrared (IR) spectra of clustered anions.19 In addition, PE spectra of the larger IHI−•(Ar)n clusters showed more pronounced hindered rotor progressions than were seen in the smaller clusters, an effect attributed to an increased lifetime of the IHI complex in the larger clusters from “caging” by the Ar atoms.5

In the present work, we use anion PE spectroscopy to investigate the effects of more strongly solvating species, namely, H2O, HBr, and HI, on the transition state precursor anions BrHBr−, IHI−, and BrH•−•(HBr). These solvating species
should bind much more strongly to the precursor anions, possibly inducing significant structural changes which must be understood if one hopes to interpret the effects of solvation on neutral TS dynamics. For example, structural changes in the transition state precursor will shift the Franck–Condon region of the neutral surface accessed by photodetachment, enabling one to probe regions of the reaction surface that are inaccessible from the bare ion. The PE spectra presented here are complementary to recent anion IR spectroscopy studies (using a free electron laser) of bare and complexed BrHBr\(^-\) by Pivonka et al.\(^{20,21}\) that suggested that the addition of HBr molecules to BrHBr\(^-\) breaks the D\(_{sh}\) symmetry of the bihalide anion. The IR spectra in conjunction with electronic structure calculations indicated that only one solvent molecule (HBr) is required to produce this effect, resulting in clusters of the form Br\(^-\)•(HBr)_n. In this work, we show how vibrational features in the PE spectra of the clustered bihalide ions reveal the extent of structural perturbations brought about by clustering.

II. EXPERIMENT

The negative ion time-of-flight (TOF) photoelectron spectrometer used in this study has been described in detail previously\(^{10,22}\) and only relevant details will be given here. BrHBr\(^-\)•(HBr)_n, IHI\(^-\)•(HI)_n, and BrH•(HX) (X=Br,I) clusters are prepared by coexpanding 4–40 psi of a HBr and/or HI argon mixture at room temperature through a pulsed molecular beam valve with a ~0.25 mm diam orifice. The concentrations of HBr and/or HI are modified depending on the size of the clusters of interest. Typical concentrations range from 0.01 to 1.0% HI/HBr in argon. Water-containing clusters are generated by adding couple of drops of distilled water to the gas lines. Negative ions are generated by a 1 keV, 300 mA electron beam that crosses the gas jet just downstream of the nozzle, in the continuum flow region of the expansion. The ions are extracted perpendicularly to the expansion by means of a pulsed electric field into a linear vacuum expansion tube. The ions are extracted perpendicularly to the laser and ion beam, and are energy-analyzed by TOF. The instrumental resolution is 8–10 meV for an electron kinetic energy (eKE) of 0.65 eV and degrades as (eKE)\(^{3/2}\). Approximately 25% of the ions are photodetached at 213 nm and about one electron is detected per laser shot. A typical spectrum requires 300 000–600 000 laser shots. Ultraviolet photons efficiently eject electrons from metal surfaces, resulting in a residual background photoelectron contribution of typically one electron per ten laser shots at 213 nm, primarily at low eKE. Background spectra were recorded on a daily basis, summed, and then subtracted from the acquired data.

All PE spectra presented here are plotted as a function of the electron kinetic energy. In the PE spectra the eKE is related to the internal energy of the anion and neutral complex by

\[ eKE = h\nu - EA - T_0 - E^0_v + E^-_v. \]  

In Eq. (1), \( h\nu \) is the photon energy of the detachment laser, EA is the electron affinity of the complex, and \( T_0 \) is the term value for various electronic states. \( E^0_v \) and \( E^-_v \) represent the vibrational energy of the neutral and anion complex, respectively. The angle between the laser polarization and the direction of electron collection can be varied by means of a half-wave plate. All spectra reported here were measured at a laser polarization angle of 90°.

III. RESULTS

A. Photoelectron spectra

The PE spectra of XHX\(^-\)•(H\(_2\)O), and XHX\(^-\)•(HX)\(_{1,2}\) (X = Br,I) collected at \( h\nu = 5.821 \) eV are shown in Figs. 1 and 2 along with the spectra of IHI\(^-\) and BrHBr\(^-\). Figure 3 shows the photoelectron spectra of BrHI\(^-\)•(HBr) and BrHI\(^-\)•(HI)
along with the spectrum of bare BrHI−. Peak positions for each spectrum are given in Table I. The bare BrHBr−, IHI−, and BrHI− spectra at \( h\nu = 5.821 \text{ eV} \) are similar to those reported previously.\(^8\,10,11,23\) The main vibrational progressions of IHI− (\( A_1, A_2, A_3 \)) and BrHBr− (\( A_1, A_2, A_3 \)) were attributed to the antisymmetric hydrogen vibrational stretch (\( v_3 \)) of the unstable neutral XHX complex with the vibrational assignment \( v_3 = 0, 2 \), and 4. The progression \( A_1, A_2, A_3 \) in BrHI− results from the same vibrational mode (\( v_3 \)) but with a slightly different vibrational assignment (\( v_3 = 0, 1, \) and 3), and corresponding to hydrogen vibrational motion more localized in the I−HBr valley of the neutral surface.\(^11\) For IHI− and BrHI−, the peaks located at low electron kinetic energy (\( B \)) are separated with respect to \( A_1 \) peaks by approximately the spin−orbit splitting of iodine (0.943 eV).\(^24\) In Figs. 1–3 peaks labeled as * at high electron kinetic energy correspond to photodetachment of bare halides (\( X^- \)). This signal is attributed to photodissociation followed by photodetachment of the atomic anion photofragment.

In general, the IHI−•(H₂O) and BrHBr−•(H₂O) spectra appear as broadened, shifted versions of the IHI− and BrHBr− spectra. The overall features of the spectra are similar to those of their corresponding bare ions. The peak spacing and relative intensities remain mostly unchanged for each complex compared with the bare ion. The IHI−•(H₂O) and BrHBr−•(H₂O) spectra are shifted to lower eKE compared to IHI− and BrHBr− by 355±20 meV and 455±20 meV, respectively (using peaks \( A_1 \) on each spectrum).

In contrast, photoelectron spectra of species solvated by HI or HBr show a noticeably different envelope than the corresponding bare ions, exhibiting fewer and broader peaks that are more widely spaced than in the bare ion PE spectra. The peaks are shifted by 430±20 meV, 745±20 meV, and 625±20 meV for IHI−•(HI), IHI−•(HI)₂, and BrHBr−•(HBr), respectively (from peaks \( A_1 \) and \( A \)). While the IHI− peak spacings are \( A_1–A_2 = \sim 1300 \text{ cm}^{-1}, A_2–A_3 = \sim 1400 \text{ cm}^{-1}, \) and \( A_3–A_4 = \sim 1550 \text{ cm}^{-1}, \) the peak spacings for IHI−•(HI)₁₂ are \( A–A’ = \sim 2200 \text{ cm}^{-1} \) and \( A’–A” = \sim 2200 \text{ cm}^{-1}, \) quite close to the vibrational frequency of 2230 cm\(^{-1} \) in diatomic HI. The \( A–B \) separation for IHI−•(HI) spectrum is 0.901±0.030 eV, similar to that in bare IHI−. The BrHBr−• peak spacings are \( A_1–A_2 = \sim 1550 \text{ cm}^{-1}, A_2–A_3 = 1700 \text{ cm}^{-1}, \) while the peak spacing for BrHBr−•(HBr) is \( A–A’ = \sim 2400 \text{ cm}^{-1}, \) close to but slightly smaller than the diatomic HBr vibrational frequency, 2558 cm\(^{-1} \). For BrHBr−•(HBr)₂, only one peak is accessible at 213 nm due to the large shift to lower eKE following the addition of an additional HBr.

The BrHI−•(HI) and BrHI−•(HBr) spectra shown in Fig. 3 are quite similar. Both spectra are shifted by approximately 540 meV with respect to BrHI−, also shown in Fig. 3 (from peaks \( A_1 \) and \( A \)). Both cluster PE spectra show a vibrational progression of around \( \sim 2500 \text{ cm}^{-1}, \) essentially the same as for the bare BrHI−, although the progressions are somewhat less extended in the clustered ions. The BrHI−•(HBr) progression is less congested than that for BrHI−•(HI). The \( A–B \) separation in all three spectra in Fig. 3 is 0.920±0.030 eV, again close to the spin−orbit splitting in atomic iodine.

### B. Electronic structure calculations

Electronic structure calculations were performed to assist in the interpretation of the data presented above. These calculations are aimed at determining the geometries of the solvated complexes. Geometries were optimized at the HF and UHF (unrestricted Hartree–Fock) levels of theory for the anion and neutral, respectively, then further explored.

#### Table I. Experimental peaks position and label.

<table>
<thead>
<tr>
<th>Species</th>
<th>Position (eV)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IHI</td>
<td>1.879(A₁), 1.719(A₂), 1.545(A₃), 1.353(A₄), 0.940(B)</td>
</tr>
<tr>
<td>IHI−•(H₂O)</td>
<td>1.502(A₁), 1.375(A₂), 1.187(A₃), 0.982(A₄), 0.530(B)</td>
</tr>
<tr>
<td>IHI−•(HI)</td>
<td>1.425(A₁), 1.160(A₂), 0.899(A₃), 0.522(B)</td>
</tr>
<tr>
<td>IHI−•(HI)₂</td>
<td>1.099(A₁), 0.835(A₂), 0.584(A₃), 0.522(B)</td>
</tr>
<tr>
<td>BrHBr</td>
<td>1.327(A₁), 1.125(A₂), 0.914(A₃), 0.723(B₂)</td>
</tr>
<tr>
<td>BrHBr−•(H₂O)</td>
<td>0.872(A₁), 0.680(A₂), 0.465(A₃)</td>
</tr>
<tr>
<td>BrHBr−•(HBr)</td>
<td>0.693(A₁), 0.397(A₂)</td>
</tr>
<tr>
<td>BrHBr−•(HBr)₂</td>
<td>0.306(A)</td>
</tr>
<tr>
<td>BrHI</td>
<td>1.935(A₁), 1.615(A₂), 1.365(A₃), 1.045(B₁), 0.739(B₂), 0.473(B₃)</td>
</tr>
<tr>
<td>BrHI−•(HBr)</td>
<td>1.391(A₁), 1.081(A₂), 0.817(A₃), 0.485(B)</td>
</tr>
<tr>
<td>BrHI−•(HI)</td>
<td>1.409(A₁), 1.103(A₂), 0.846(A₃), 0.502(B)</td>
</tr>
</tbody>
</table>

\(^a\)Error ±0.025 eV.
This is H₂O, HI, and HBr are included in Table II for comparison. These structures are shown in Fig. 4. Experimental and ab initio results for H₂O are summarized in Tables II–V. Calculated anion structures were explored at the HF and B3LYP level of theory. As starting geometries, we used singly and doubly hydrogen-bonded configurations, similar to the equilibrium structure TSI by Li et al., shown in Fig. 4(B), with the largest basis set. The bond angle for the water molecule is 108°. From Ref. 39. Harmonic frequency.

### Table II. Results of DFT electronic structure calculations for XHX⁻ \( (X = H, Br, HI) \) complexes

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>( A_{H-X} )</th>
<th>( R_{H-X} )</th>
<th>( R_{O-H} )</th>
<th>( A_{H-O-H} )</th>
<th>( A_{H-X-H} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>C₂v</td>
<td>105.0</td>
<td>0.962</td>
<td>1602 3815 3920</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B3LYP/3-21G**</td>
<td>104.7</td>
<td>0.965</td>
<td>1614 3801 3906</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>104.5</td>
<td>0.965</td>
<td>1595 3755 3656</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R₂v</td>
<td></td>
<td></td>
<td>104.5</td>
<td>0.965</td>
<td>1614 3801 3906</td>
</tr>
<tr>
<td></td>
<td>B3LYP/6-311G**</td>
<td>180.0</td>
<td>2.356</td>
<td>1.729</td>
<td>197 703 829</td>
<td></td>
</tr>
<tr>
<td>BrHBr⁻</td>
<td>C₂v</td>
<td>180.0</td>
<td>2.356</td>
<td>1.729</td>
<td>197 703 829</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B3LYP/3-21G**</td>
<td>180.0</td>
<td>2.356</td>
<td>1.729</td>
<td>197 703 829</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>180.0</td>
<td>2.356</td>
<td>1.729</td>
<td>197 703 829</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R₂v</td>
<td></td>
<td></td>
<td>180.0</td>
<td>2.356</td>
<td>1.729</td>
</tr>
<tr>
<td>HI</td>
<td>C₂v</td>
<td>142.7</td>
<td>2.593</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>B3LYP/3-21G**</td>
<td>143.1</td>
<td>2.595</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>141.4</td>
<td>2.648</td>
<td></td>
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<tr>
<td></td>
<td>R₂v</td>
<td></td>
<td></td>
<td>142.7</td>
<td>2.593</td>
<td></td>
</tr>
</tbody>
</table>

Using density functional theory (DFT) with the B3LYP (Becke-3-parameter-Lee–Yang–Parr) exchange correlation functional. The STO-3G*, 3-21G**, 6-311G**, and aug-cc-pVDZ basis sets were used during the study. However, for iodine-containing clusters the biggest basis set used is 6-311G**. Calculations were performed using the GAUSSIAN 98 electronic structure package, and the results are summarized in Tables II–V. Calculated anion structures are shown in Fig. 4. Experimental and ab initio results for H₂O, HI, and HBr are included in Table II for comparison.

### Table III. Results of DFT electronic structure calculations for XHX⁻ (H₂O) clusters

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>( A_{H-X} )</th>
<th>( R_{H-X} )</th>
<th>( R_{O-H} )</th>
<th>( A_{H-O-H} )</th>
<th>( A_{H-X-H} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IHI⁻ (H₂O)</td>
<td>C₂v</td>
<td>175.8</td>
<td>2.873</td>
<td>1.947</td>
<td>0.970</td>
<td>101.2</td>
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<tr>
<td></td>
<td>B3LYP/3-21G**</td>
<td>177.1</td>
<td>2.973</td>
<td>1.950</td>
<td>0.971</td>
<td>102.0</td>
</tr>
<tr>
<td>BrHBr⁻ (H₂O)</td>
<td>C₂v</td>
<td>176.2</td>
<td>2.737</td>
<td>1.731</td>
<td>0.967</td>
<td>101.1</td>
</tr>
<tr>
<td></td>
<td>B3LYP/3-21G**</td>
<td>176.9</td>
<td>2.730</td>
<td>1.729</td>
<td>0.971</td>
<td>101.3</td>
</tr>
<tr>
<td>Cₛ</td>
<td>194.4</td>
<td>2.553</td>
<td>1.607</td>
<td>0.975</td>
<td>103.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B3LYP/aug-cc-pVDZ</td>
<td>179.1</td>
<td>2.487</td>
<td>1.611</td>
<td>0.979</td>
<td>102.0</td>
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<tr>
<td></td>
<td>B3LYP/aug-cc-pVDZ</td>
<td>179.1</td>
<td>2.487</td>
<td>1.611</td>
<td>0.979</td>
<td>102.0</td>
</tr>
</tbody>
</table>

In these configurations, which have overall C₂v symmetry, the bond lengths and angles for the XHX⁻ (H₂O) cluster are in Å, angles in deg, and vibrational frequencies in cm⁻¹. Calculations were performed using the B3LYP level of theory. The lowest energy structures for BrHBr⁻ (H₂O) and IHI⁻ (H₂O) were found to be the double hydrogen-bonded complexes shown in Fig. 4(A). The lowest energy C₂v configurations, similar to the equilibrium structure TSI by Li et al., shown in Fig. 4(B), lie approximately 0.1 eV higher than structure A for BrHBr⁻ (H₂O) and IHI⁻ (H₂O). According to our computations, this structure has an imaginary frequency. Two other C₂v starting geometries, similar to the equilibrium structures EQU and TSII by Li et al., converged to the C₂v structure. Bond lengths and angles for the XHX⁻ (H₂O) complex computed at the B3LYP level of theory using different basis sets are summarized in Table III.

Vibrational analysis of the C₂v structures reveals no imaginary frequencies, showing that these are minima and not transition states. The water molecule binds to both the halogen atoms equally, and the charge of the complex is shared equally between the halogen atoms. The attraction in the complex is strong enough to cause small changes in the water and XHX⁻ molecules. The XHX⁻ bond angle changes from 180° in the bare ion to about 177° for both IHI⁻ and BrHBr⁻ with the largest basis set. The bond angle for the water molecule drops from 104.5° to about 102° for both anions. The HX and OH bond lengths in the clusters are very similar to the calculated values for bare XHX⁻ and H₂O in Table II.

Our results are slightly different than those reported by Li et al. on FHF⁻ (H₂O). They found a single hydrogen-bonded C₂v structure to be the minimum, and the double hydrogen-bonded C₂v structure to be either a transition state or local minimum, depending on the level of theory. However, the energy differences among these structures were very small (<1 meV at the highest level of theory used in their calculation) indicating a relatively flat potential energy landscape. The C₂v geometry found by us to be the global minimum for BrHBr⁻ (H₂O) and IHI⁻ (H₂O) is favored by the presence of two hydrogen bonds, and involves less of a perturbation of the H–O–H bond angle in free water compared to FHF⁻ (H₂O). A similar double hydrogen-bond has been proposed by Johnson and co-workers to explain the infrared spectrum of SO₂⁻ (H₂O).
TABLE IV. Results of DFT electronic structure calculations for IHI\textsuperscript{−}(HI)\textsubscript{n} clusters. All bond lengths are in \textAA{} and angles in deg.

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>(A_{4-H})</th>
<th>(R_{1-H})</th>
<th>(R_{1-\text{HI}})</th>
<th>(A_{1-\text{HI}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>IHI\textsuperscript{−}(HI)\textsubscript{2}</td>
<td>C\textsubscript{2v} B3LYP/3-21G**</td>
<td>107.7</td>
<td>1.780</td>
<td>2.196</td>
<td>177.6</td>
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<td></td>
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<td>107.6</td>
<td>1.753</td>
<td>2.254</td>
<td>177.7</td>
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<td>Experiment\textsuperscript{a}</td>
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<tr>
<td>IHI\textsuperscript{−}(HI)\textsubscript{2}</td>
<td>C\textsubscript{3v} B3LYP/3-21G**</td>
<td>107.9</td>
<td>1.728</td>
<td>2.332</td>
<td>179.0</td>
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<td></td>
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<td>108.1</td>
<td>1.698</td>
<td>2.414</td>
<td>179.5</td>
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<tr>
<td>Experiment\textsuperscript{a}</td>
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<td></td>
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</tr>
</tbody>
</table>

\textsuperscript{a}From Franck–Condon simulations in Fig. 6.

H\textsubscript{2}O to the bare ion using the relationship BE\textsuperscript{a} = \(|E(\text{XHX})| - |E(\text{XH}^\cdash)(\text{H}_2\text{O})| - |E(\text{H}_2\text{O})|\), where \(E(\text{XHX})\), \(|E(\text{XH}^\cdash)(\text{H}_2\text{O})|\), and \(|E(\text{H}_2\text{O})|\) are the computed total energy of XHX, XHX \textsuperscript{−}(\text{H}_2\text{O}), and \text{H}_2\text{O}. We obtained BE’s of 0.42 and 0.39 eV for BrHBr \textsuperscript{−}(\text{H}_2\text{O}) and IHI\textsuperscript{−}(\text{H}_2\text{O}), respectively. These values compare well with the experimental solvent shifts of 0.455 and 0.355 eV for BrHBr \textsuperscript{−}(\text{H}_2\text{O}) and IHI\textsuperscript{−}(\text{H}_2\text{O}).

D. IHI\textsuperscript{−}(HI)\textsubscript{n}

The IHI\textsuperscript{−}(HI)\textsubscript{2} structures share similar characteristics with experimental and theoretical results on clusters of the type XH\textsuperscript{−}*(HX)\textsubscript{n} (X = Br, I) ions.\textsuperscript{20,30,31} The lowest energy structures for \(n = 1\) and 2 are shown in Figs. 4(C)–4(D), and the geometries are given in Table IV. In contrast to the complex with \text{H}_2\text{O}, solvation by one or more HI molecules disrupts the symmetric hydrogen bond of IHI\textsuperscript{−}, resulting in a structure better described as I\textsuperscript{−}*(HI)\textsubscript{n+1}, in which I\textsuperscript{−} is solvated by multiple HI molecules. For example, the IHI\textsuperscript{−}(HI) complex has a C\textsubscript{2v} structure [Fig. 4(C)] and population analysis reveals that more than 58% of the complex charge is located in the central halogen atom, indicating that the anion complex behaves more like a single halogen solvated by two HI [i.e., I\textsuperscript{−}*(HI)\textsubscript{2}]. The IHI\textsuperscript{−}(HI)\textsubscript{2} complex exhibits an ammonialike structure with C\textsubscript{3v} symmetry [Fig. 4(D)]. This complex has an iodine center which carries most of the excess charge (51%) analogous to IHI\textsuperscript{−}(HI), although in this case it is surrounded by three HI molecules [i.e., I\textsuperscript{−}*(HI)\textsubscript{3}].

E. BrHI\textsuperscript{−}•(HX)

Results for BrHI\textsuperscript{−}•(HX) clusters are summarized in Table V. The BrHI\textsuperscript{−}•(HX) (X = Br, I) structures are similar to the IHI\textsuperscript{−}•(HI) clusters. The calculations show that the charge is mostly localized in a central iodine atom resulting in complexes of the type I\textsuperscript{−}•(HBr\textsubscript{2}) and I\textsuperscript{−}•(HBr\textsubscript{3})(HI). In I\textsuperscript{−}•(HBr\textsubscript{2}), the calculated HBr bond length at the B3LYP/6-311G** level of theory is 6% longer than diatomic HBr at the same level of theory, while the HI and HBr bond lengths in I\textsuperscript{−}•(HBr)(HI) are longer than free HI and HBr by 9% and 6%, respectively. In I\textsuperscript{−}•(HBr)(HI), the HI molecule is significantly closer to the central iodine than HBr, suggesting a stronger interaction between the central I\textsuperscript{−} and the HI, and consistent with the larger change in bond length in HI compared to HBr.

IV. DISCUSSION

The PE spectra in Figs. 1–3 show two effects attributed to solvation of the XHX\textsuperscript{−} and XHY\textsuperscript{−} anions. First, solvation by a water molecule or a HX species shifts the photoelectron spectrum to considerably lower eKE for all the systems reported here. On the other hand, the effect of solvation on vibrational structure is system-dependent. The BrHBr \textsuperscript{−}•H\textsubscript{2}O and IHI\textsuperscript{−}•H\textsubscript{2}O PE spectra show the same vibrational structure as the bare ions, and the same is true for the BrHI\textsuperscript{−}•HX PE spectra. The PE spectra of BrHBr \textsuperscript{−}•(HBr\textsubscript{2})\textsubscript{n} and IHI\textsuperscript{−}•(HI)\textsubscript{n} are quite different from those of the bare ions, with noticeably larger vibrational spacings that are very close to the diatomic HX frequencies.

The energetic shift upon clustering is the well-known “solvent shift” seen in negative ion photoelectron spectroscopy\textsuperscript{32} and reflects the stronger binding of the solvent to the charged anion than to the neutral species formed by photodetachment. The observed effects of clustering upon vibrational structure are more unusual. They reflect the degree of distortion in the XHX\textsuperscript{−} and XHY\textsuperscript{−} anions induced by solvation. If the bivalent chromophore is left relatively intact, then the PE spectrum will be similar to that of the bare ion (aside from the solvent shift), but if solvation produces a structural change, the PE spectrum will differ from that of the bare ion, because photodetachment will access a different region of the neutral potential energy surface. This interpretation is supported by the electronic structure calculations presented in Sec. III B. In the remainder of this section, individual PE spectra are analyzed and discussed with particular reference paid to the calculations.

TABLE V. Results of DFT electronic structure calculations for BrHI\textsuperscript{−}•(HBr) and BrHI\textsuperscript{−}•(HI) clusters. All bond lengths in \textAA{} and angles in deg.

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>(A_{4-H})</th>
<th>(R_{1-HBr})</th>
<th>(R_{1-\text{HI}})</th>
<th>(R_{H-\text{Br}})</th>
<th>(R_{H-\text{I}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrHI\textsuperscript{−}(HI)</td>
<td>C\textsubscript{3} B3LYP/3-21G**</td>
<td>110.2</td>
<td>2.344</td>
<td>2.135</td>
<td>1.505</td>
<td>1.810</td>
</tr>
<tr>
<td></td>
<td></td>
<td>110.6</td>
<td>2.387</td>
<td>2.198</td>
<td>1.498</td>
<td>1.773</td>
</tr>
<tr>
<td>Experiment\textsuperscript{c}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BrHI\textsuperscript{−}(HBr)</td>
<td>C\textsubscript{2v} B3LYP/3-21G**</td>
<td>114.9</td>
<td>2.277</td>
<td></td>
<td>1.524</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>100.5</td>
<td>2.340</td>
<td></td>
<td>1.512</td>
<td></td>
</tr>
<tr>
<td>Experiment\textsuperscript{c}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.549</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}R\textsubscript{1-HBr} is the distance between the central I and the H of HBr [see Fig. 5(C)].

\textsuperscript{b}R\textsubscript{1-\text{HI}} is the distance between the central I and the H of HI [see Fig. 5(C)].

\textsuperscript{c}From Franck–Condon simulation in Fig. 6.
A. XHX⁻•H₂O

The PE spectra of the BrHBr⁻•H₂O and IHI⁻•H₂O clusters in Figs. 1 and 2 show vibrational progressions with similar peak spacings and intensities as were seen in the spectra of BrHBr⁻ and IHI⁻. This result indicates that photodetachment of the bare and hydrated anions accesses essentially the same region of the X+HX potential energy surface, namely the XHX transition state region, so that the PE spectra in both cases are dominated by a progression in the ν₃ antisymmetric stretch mode of the neutral XHX complex. Moreover, hydration by one water molecule induces minimal geometric distortion of the XHX⁻ anions.

These results are consistent with the double hydrogen-bonded Cᵥ, anion structures for BrHBr⁻•H₂O and IHI⁻•H₂O in Fig. 4(A) and Table III. These structures have a symmetric hydrogen bond in the XHX⁻ moiety, just as in bare XHX⁻. The comparison with Table II shows that the individual H–X bond lengths are virtually identical in the bare and hydrated anions. The bihalides are slightly bent in the clusters, and this may contribute to the increased width of the peaks in the hydrated vs bare ion PE spectra. Nonetheless, photodetachment from clusters with the Cᵥ structures will clearly access a very similar region of the neutral X+HX surface as does photodetachment of the bare ion. This is illustrated in Fig. 5, where a collinear model potential energy surface for the Br+HBr reaction is shown. The Franck–Condon (FC) region from the vibrational ground state of the bare ion is shaded. The calculated BrHBr⁻ geometry for the Cᵥ hydrated structure indicated by “●” lies in the center of the bare ion FC region.

The low-lying (~0.1 eV), single hydrogen-bonded Cᵥ structure in Fig. 4(B), on the other hand, is not consistent with the PE spectra. In the Cᵥ configuration of BrHBr⁻•H₂O, for which the calculated structure is given in Table III, the two H–Br bond lengths differ by 0.27 Å at the highest level of theory. Thus, as shown in Fig. 5, the BrHBr⁻ geometry, labeled “■,” is shifted significantly from the center of the bare ion FC region and lies more toward the entrance (or exit) valley of the Br+HBr potential energy surface. Such a shift would result in a noticeably higher frequency ν₁ progression, because as the two halogen atoms move away from one another, this vibrational mode evolves into the higher frequency vibration of diatomic HBr.¹⁰ Similar considerations apply to hydrated IHI⁻. Hence, while the rather small calculated energy differences between the doubly and singly hydrogen-bonded structures might not be convincing evidence that the Cᵥ structure for the hydrated anions is lower in energy than the Cᵥ structure, the experimental PE spectra strongly support this energy ordering.

The BrHBr⁻•H₂O and IHI⁻•H₂O PE spectra are shifted toward lower energy by 0.455 and 0.355 eV, respectively, compared to the PE spectra of the bare ions. These “solvent shifts” are similar to but smaller than those seen by Markovich et al.³³,³⁴ for Br⁻•H₂O (0.55 eV) and I⁻•H₂O (0.45 eV). While the solvent shifts reflect the difference in the solvent binding energies to the anion versus neutral cores, the considerably stronger solvent binding energies in the anions are largely responsible for trends in the solvent shifts. We therefore look to structural differences in the anions to explain the different solvent shifts in hydrated halide versus bihalide PE spectra. Infrared spectroscopy has shown that Br⁻•H₂O and I⁻•H₂O have a single hydrogen bond between the water and halide anion.¹⁹,³⁵,³⁶ In the hydrated bihalide anions, there are two hydrogen bonds, but each should be weaker than in X⁻•H₂O because the excess charge is shared equally between the two halogen atoms. While it is not clear whether the net effect from these differing hydrogen bond configurations would result in larger or smaller shifts for the hydrated bihalide anion, the calculated H–O–H bond angle in the hydrated bihalides is 2.5° smaller than in free water, and this additional “strain energy,” which is not present in the X⁻•H₂O clusters, may be the primary cause of the smallest solvent shift in the XHX⁻•H₂O clusters.

B. XHX⁻•(HX)ₙ

The PE spectra of IHI⁻•(HI) and BrHBr⁻•(HBr) show similar characteristics. Compared to the bare ions and the hydrated bihalides, the peaks are broader and their spacing is significantly larger (see Table I), much closer to free HI and HBr for IHI⁻•(HI) and BrHBr⁻•(HBr), respectively. The infrared spectra of BrHBr⁻•(HBr)ₙ (n = 0–2) and accompanying electronic structure calculations²⁰,²¹ indicate that the addition of HBr to the BrHBr⁻ complex distorts the symmetry of these clusters, which are better described as a central ha-
The PE spectra of BrHI\textsuperscript{−}, BrH\textsuperscript{−}•(HBr), and BrH\textsuperscript{−}•(HI) in Fig. 3 are quite similar. All show a visible progression with a peak spacing close to 2500 cm\textsuperscript{−1}, but the BrH\textsuperscript{−}•(HI) spectrum is more congested than the other two. Since the proton affinity of Br\textsuperscript{−} is about 0.5 eV higher than that of I\textsuperscript{−}, the BrHI\textsuperscript{−} anion can be thought of as I\textsuperscript{−}•HBr, a result confirmed by recent high level electronic structure calculations by Kaledin et al.\textsuperscript{37} As a result, the Franck–Condon region of anion photodetachment lies in the I+HBr product valley, and the photoelectron spectrum is dominated by a vibrational progression in the nascent HBr product.\textsuperscript{11} Since the anion is already asymmetric, with most of the charge located on the iodine atom, the addition of an additional HBr or HI molecule should not significantly change the spectral envelope, consistent with the experimental spectra. Hence, the BrHI\textsuperscript{−}•(HBr) and BrHI\textsuperscript{−}•(HI) anions are more accurately pictured as I\textsuperscript{−}•(HBr)\textsubscript{2} and I\textsuperscript{−}•(HBr)(HI), respectively. These qualitative considerations are consistent with the electronic structure calculations in Table V.

The length of the vibrational progression in the PE spectrum of bare BrHI\textsuperscript{−} primarily reflects the difference between the (longer) H–Br bond length in the anion and in diatomic HBr. The shorter vibrational progression in the BrH\textsuperscript{−}•(HBr) spectrum indicate that the analogous bond length changes upon photodetachment are smaller, consistent with interaction between the I\textsuperscript{−} and HBr becoming smaller with the addition of more solvent molecules. In the BrHI\textsuperscript{−}•(HI) spectrum, one expects activity in the HBr and HI stretches because of solvent interactions with the central I\textsuperscript{−} ion. The
HBr and HI vibrational frequencies are similar but not identical, and this is why the BrHI•−(HI) spectrum is more congested than the BrHI•−(HBr) spectrum.

Figure 6 shows reduced dimensionality simulations of the BrHI•−(HBr) (X = Br, I) photoelectron spectra, which were performed just like the simulations for the XHX•−(HX)n simulations in the same figure. For BrHI•−(HBr), only the totally symmetric solvent HBr stretch mode was assumed to be active, while for BrHI•−(HI) the HBr and HI stretches were allowed to be active. The HX bond lengths in the anion clusters that gave the best fit to the spectra are listed in Table 2, where they can be compared to calculated anion geometries. We note that in BrHI•−(HI), theory and experiment indicate that the HBr and HI bond lengths are both longer than in the diatomic species, indicating that both solvent molecules interact strongly with the central I− ion. In addition, both PE spectra undergo a similar solvent shift (~540 meV) compared to BrHI•−, indicating that it makes relatively little difference whether HBr or HI is added to BrHI•−.

V. CONCLUSIONS

The results presented here show how anion PE spectroscopy probes the effects of the polar solvent molecules H2O, HI, and HBr, on strongly hydrogen-bonded transition state precursor bhalide ions. The structural changes induced by clustering depend on the solvent molecule and on whether the bhalide ion is symmetric or asymmetric. We find that for XHX•−(H2O) (X = Br, I) clusters, the PE spectra retain the vibrational structure of the bare XHX− PE spectra, indicating that photodetachment of the singly hydrated clusters probes the X+HX transition state region. This result is consistent with a double hydrogen bonded structure in the anion complex, in which the water molecule bonds equally to the two halogens X in a planar C2v structure, maintaining the symmetric hydrogen bond characteristic of XHX− anions. We plan to confirm the doubly hydrogen-bonded structure by measurement of the IR spectrum of these ions using the same method used to investigate BrHBr•−(HBr)n clusters.20

For the other clusters XHX•(M)12 (M=HBr, HI), charge localization on one halogen is responsible for breaking the symmetry of the XHX− complex. This is reflected by a large difference in the PE spectra compared to the bare ion. As a result, the anion PE spectrum probes a region of the neutral potential energy surface quite distant from the transition state in the asymptotic region of the X+HX surface. The XHX•(M)12 (M=HBr, HI) clusters are better described as X−•(MX)2,3. Finally, we observed that the addition of an additional HBr or HI molecule to the asymmetric bhalide anion BrHI•− induces only small changes in the PE spectrum, because of the already asymmetric structure of BrHI•− with its charge localized mostly on the iodine atom.

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