A comparison of sodium and hydrogen halides at the air-water interface

Collin D. Wick^{a)}

Louisiana Tech University, Ruston, Louisiana 71270, USA

(Received 23 March 2017; accepted 12 May 2017; published online 5 June 2017)

New molecular models, parameterized to *ab initio* calculations, were developed to describe HBr and HI at the air-water interface. These were used to compare how the air-water interface influenced dissociation of NaX and HX, with X being Cl, Br, or I, and also their propensity for the interface. The polarizable multistate empirical valence bond method, which explicitly describes proton sharing, was used to model HX. Results showed that the air-water interface suppressed HX dissociation from a contact ion pair to a solvent separated to a greater degree than NaX dissociation. Furthermore, HX had a greater propensity for the interface than NaX, which was a consequence of the hydronium ion having a greatest interfacial activity of all species studied. As a consequence of this, the average configuration of dissociated HX, while in both contact ion and solvent separated ion pairs near the air-water interface, is with the dissociated hydrogen oriented more towards the air than the X atom. *Published by AIP Publishing*, [<http://dx.doi.org/10.1063/1.4984114>]

I. INTRODUCTION

There is considerable interest in understanding how halides influence particle formation, and their role in fundamental atmospheric chemistry in the environment.^{1–5} In relation to atmospheric chemistry, any species that comes in contact with an atmospheric particle must first approach its interface. It serves as the first and potentially primary medium for chemical transformation for trace gases in contact with atmospheric particles. Because of this, elucidating the interfacial behavior of different species, including their propensities for the air-water interface, is an area of active research.^{6–9} In particular, comparing NaX with HX (X representing halide atoms), one can find some interesting differences. For instance, the addition of NaX to water increases its surface tension, while HX decreases it.¹⁰ This suggests that the exchange enhances the propensity for the air-water interface of HX with respect to NaX. Moreover, NaCl and HCl have opposite impacts on the electrophoretic mobility of water droplets with NaCl causing them to be more negatively charged and HCl more positively charged.¹¹ Overall, the experimental evidence points to hydronium ions being more surface active than halide anions, while alkali cations being less surface active. The dissociation mechanism, along with how the structure impacts the interfacial propensity, though, is difficult to probe experimentally.

Molecular simulation provides a valuable tool for the investigation of ion dissociation and a propensity for the air-water interface.^{8,9,12–14} There have been numerous investigations into sodium halide salts at the air-water interface, in which the general consensus is that as one goes from smaller to larger halide anions, their propensity for the air-water interface increases.^{8,9,15,16} This has been linked to both the size of the anions and their polarizability.¹⁷ Moreover, molecular

simulation has shown that the hydronium ion has a greater propensity for the interface than sodium.^{18,19} Many of these studies are of classical models, which do not account for the fact that hydronium ions can share protons with adjacent water molecules.²⁰ There are two ways to address this with molecular simulation. One of them is to run *ab initio* methods, such as *ab initio* molecular dynamics (AIMD) simulations or quantum mechanics/molecular mechanics (QM/MM) calculations.^{21–23} The other is to use semi-empirical potentials that include proton sharing in its formulation.^{24–27} The latter's greatest advantage is its lower computational requirements, allowing larger and more systems to be investigated with the same computational power. On the other hand, the former does not require any additional potential fitting, even though one has to choose the functional and correction factors that best describe the system of interest.^{28,29}

To describe proton sharing, the multistate empirical valence bond (MS-EVB) method has been widely used.^{25,26} This method has also been employed to examine the hydronium propensity at the air-water interface.^{30–33} To study halide anions, the type of model has been found to be important. Since anions (in contrast to cations) have a significant polarizability, its inclusion in molecular models may play an important role in their interfacial behavior. While not necessary for the observation that large halide anions have a propensity for the air-water interface,^{16,34} a definite link between the polarizability and interfacial activity has been formed.¹⁷ Because of these reasons, a molecular model that includes both proton sharing and polarizability would be expected to be important to describe the behavior of HX and NaX species at the air-water interface.

In previous work, it has been found that, using molecular simulation, molecular HCl and HCl in its contact ion pair state have a significant interfacial activity.^{21,22,35} Comparing HCl to NaCl, HCl has been found to have a greater propensity for the air-water interface,^{18,35} which is consistent with experimental surface tension measurements.³⁶ While HCl readily

^{a)} cwick@latech.edu

dissociates after it is solvated, including information from molecular HCl has been found to be important to describe its dissociation, and even to reproduce *ab initio* calculations for small HCl/water clusters (with dissociated HCl).³⁵ As such, modeling HBr and HI, which can provide some useful comparisons with HCl, will require new parameterizations to get a model that includes both proton sharing and polarizability. This paper describes the parameterization of new HBr and HI models with both proton sharing and polarizability. The interfacial behavior of the HX pairs is compared to that of NaX.

II. MOLECULAR MODEL

Classical many-body potentials were used to describe water, halide ions, and sodium as described in previous work.^{33,37} The MS-EVB model was utilized to describe hydrogen halides and hydronium ions.^{25–27} In this method, a Hamiltonian is constructed from N_S potential states for a system of interest,

$$H_{\text{EVB}} = \sum_{i=1}^{N_S} \sum_{j=1}^{N_S} \langle i | \hat{H} | j \rangle. \quad (1)$$

For hydronium in water, the number of states is determined as follows. A defect, or hydronium, oxygen is identified as described previously.³³ The water molecules it donates hydrogen bonds to, based on oxygen-oxygen and oxygen-hydrogen distance criteria,⁷ are identified. This will be a maximum of three water molecules (one for each hydronium hydrogen), and the oxygen for each of these first solvation shell water molecules will be considered for MS-EVB states. Next, the water molecules that accept hydrogen bonds from these first solvation shell waters will also be considered as MS-EVB hydronium states. In all, waters in the first two solvation shells of the hydronium ion will be considered as MS-EVB states.

When hydrogen halides are considered, the HX state (with X representing the halide) needs to be considered. Figure 1 represents a schematic of potential MS-EVB states when an HX molecule is in water. For an HX state to be considered, r_{HX} must be less than 3.0 Å. As for hydronium in water, two solvation shells around a hydronium cation are considered. For each state, a different system topology is considered.

For instance, in states 2 and 3, the HX molecule is explicitly considered, while in the remaining states, the X atom is treated as an anion, and a hydronium cation is present. For each of these states, the energy of the system is calculated via a classical potential. The total energy from these classical interactions is utilized to represent the diagonal states in an MS-EVB matrix to help form part of the Hamiltonian in Eq. (1). Non-diagonal terms, linking states that share hydrogen atoms between them, are parameterized to reproduce *ab initio* cluster calculations.

A. Diagonal terms

For classical electrostatic interactions, charges and point polarizabilities were utilized. These interactions were damped at short ranges with the procedure first introduced by Thole and outlined previously,^{38,39} in which the specific implementation utilized here is described by previous work.³⁷ Point polarizabilities allow induced dipoles to form in response to their local electric fields. The determination of these is a many-body problem that can be efficiently handled with the always stable predictor-corrector procedure.⁴⁰ Long ranged electrostatic interactions were calculated with the particle mesh Ewald summation technique.⁴¹ Van der Waals interactions were described with a Buckingham exponential-6 interaction potential, with interaction sites located at all heavy atomic positions,

$$U_{\text{vdw}} = \epsilon \left[\frac{6}{\lambda} \exp \left(\lambda \left[1 - \frac{r}{\sigma} \right] \right) - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2)$$

Further details, including parameters for the hydronium ion and water interaction parameters and potentials are described in previous work.³³ Alkali halide interaction parameters and potentials, including their parameterization procedure are also described in previous work.³⁷ A potential truncation of 9 Å was enforced for the exponential-6 potential with analytical tail corrections employed.

For the HX molecules, a Morse potential was used to describe their bond stretching,

$$U_{\text{Bond}}(r) = D \left[1 - e^{-\alpha(r-r_0)} \right]^2 + U_0, \quad (3)$$

where D is the classical dissociation constant, which can be extracted from experiment, U_0 is a zeroth energy term (described later), r_0 is the equilibrium bond length, and α affects the width of the Morse potential. The D term can be

FIG. 1. Schematic of potential MS-EVB states for HX in water.

extracted from a combination of the experimental dissociation energy (D_0) and the energy of the ground vibrational state, which can be found in the literature.⁴² The values of r_0 and α were parameterized to reproduce MP2 calculations of HX stretching with the aug-cc-pvtz basis set with an effective core potential (ECP) for HI only. For HBr, the D value was extracted from the *ab initio* calculations as well. The value of U_0 was parameterized to give the [HX + H₂O (separated)] energy difference with [H₃O⁺ + X⁻ (separated)] in agreement with counterpoise corrected MP2 calculations with the aug-cc-pvtz basis set with an ECP for HI. One should note that the energy of the [H₃O⁺ + X⁻ (separated)] is set to zero for the MS-EVB model. These are discussed later.

Point charges were on the hydrogen and X atomic positions of HX, which were extracted from MP2 calculations with the aug-cc-pvtz basis set with an ECP for HI, in which the electrostatic potential (ESP) charge method as utilized in the NWCHEM computational package was employed.⁴³ Point polarizabilities were placed on the X atomic positions, which were taken from the work of Applequist.⁴⁴ All HCl interactions were parameterized in previous work,³⁵ and the values arrived at for this work for HBr and HI are given in Table I.

B. Non-diagonal terms

The MS-EVB matrix to describe the system shown in Fig. 1 would have the following form:

$$H_{\text{EVB}} = \begin{bmatrix} h_1 & h_{12} & & h_{14} & & h_{16} \\ h_{12} & h_2 & & & & \\ & & h_3 & & & h_{36} \\ h_{14} & & & h_4 & h_{45} & \\ & & & h_{45} & h_5 & \\ h_{16} & & h_{36} & & & h_6 \end{bmatrix}, \quad (4)$$

where the diagonal terms are the classical potentials that represent the 6 states shown in Fig. 1, and the non-diagonal terms link states in which a hydrogen atom is shared with adjacent heavy atoms. For instance, in states 1 and 2, the same hydrogen atom is shared between two different heavy atoms, which is why there is a non-diagonal term to represent it. Non-diagonal terms linking two oxygen atoms [h_{14} , h_{16} , and h_{45} in Eq. (4)] were parameterized to reproduce *ab initio* calculations of clusters with a hydronium ion and one to four water molecules as described in previous work.³³ For states in which an X atom shares a hydrogen atom with an oxygen atom (terms h_{12} and h_{36}), the non-diagonal terms were parameterized to MP2 calculations of HX/water clusters with one and four water molecules present.

TABLE I. Parameters used to describe the classical interactions of HBr and HI. Note that $q_{\text{H}} = -q_{\text{X}}$.

Atom	Nonbonded parameters				Morse parameters			
	σ_X (Å)	ε_X (kcal/mol)	q_X (e)	α_X (Å ³)	D (kcal/mol)	α (Å ⁻¹)	r_0 (Å)	U_0 (kcal/mol)
HBr	4.19	1.125	-0.1916	2.28 ^a	88.48	1.97	1.403	-158.3
HI	4.6	1.125	-0.1157	5.18 ^a	73.75	1.761	1.605	-149.59

^aTaken from Ref. 44.

The HCl parameterization was carried out in previous work.³⁵ The specific clusters used to parameterize HI are shown in Fig. 2, while the HBr clusters had very similar configurations. The aug-cc-pvtz basis set was used for the 1wat cluster, while the aug-cc-pvdz basis set was used for the 4wat clusters. For HI systems, an ECP was used. Binding energies with the counterpoise correction were calculated for the clusters, and a scan of the HX bond length, allowing all other coordinates to relax, for the 1wat and 4watA systems, was carried out for HBr and HI. The distance scanned was the HX bond in the 1wat system, and the distance between X and the hydrogen was directly above it in Fig. 2 for the 4watA system (both distances shown as a dotted line).

The simplest case is for the 1wat cluster, in which the MS-EVB matrix is given as

$$H_{\text{EVB}} = \begin{bmatrix} h_1 & h_{12} \\ h_{12} & h_2 \end{bmatrix}, \quad (5)$$

where the h_1 state represents the classical HX with H₂O and h_2 represents X⁻ and H₃O⁺. The h_{12} state (the non-diagonal term) was set to be a function of r_{HX} . No functional form was used for this, and a cubic spline interpolation was employed based on the values given in Table II for HBr and HI. The same spline fit used for h_{12} in Eq. (5) is used for all states in which a hydrogen atom is shared between an X and O atom, such as h_{12} and h_{36} in Eq. (4) (describing Fig. 1).

For clusters with more than one water molecule, an additional term is used as well. For hydronium in water, this additional term was present if the hydronium molecules linked with a specific non-diagonal term [e.g., for Fig. 1 and Eq. (4), h_{12} , h_{14} , and h_{16} are linked with state 1] donated two or three hydrogen bonds. In state 1, in Fig. 1, the hydronium molecule donates three hydrogen bonds. As a consequence, h_{14} and h_{16} are augmented by an additional term that is a function of r_{OO} distance. If there are only two hydrogen bonds (i.e., if the X was not present), then a different r_{OO} term is used. These are described in previous work.³³ For the non-diagonal term h_{12} in Eq. (4) and Fig. 1, it already is a function of r_{HX} as described previously. However, since the hydronium molecule donates two or more hydrogens, an additional constant is added to h_{12} of 5.0 kcal/mol. In summary, for non-diagonal terms linking a hydronium state that donates two or more hydrogen bonds, an additional term is present. When the non-diagonal term represents a hydrogen atom shared between two oxygens, it is augmented by a function of r_{OO} .³³ When this term represents a hydrogen atom shared between an oxygen and a Br or I atom, it is augmented 5.0 kcal/mol. This term stabilizes clusters of larger sizes and is necessary to simultaneously describe the 1wat, 4watA, and 4watB systems. To assure smoothness,

FIG. 2. Clusters used to parameterize non-diagonal terms for HI in water.

TABLE II. The values in which the cubic spline interpolation was parameterized to. Derived from *Ab Initio* (AI) calculations and those including Nuclear Quantum Effects (NQE). Units are in Å for r_{HX} and kcal/mol for h_{ij} .

r_{HX}	HBr		HI	
	h_{ij} (AI)	h_{ij} (NQE)	h_{ij} (AI)	h_{ij} (NQE)
1.1	0	31	0	0
1.2	0	22	0	0
1.3	0	12	20	29
1.4	12	11	19	27
1.5	12	10	18	20
1.6	5	6	16	16
1.7	5	6	13	12
1.8	4	5	8.4	10
1.9	4	4	8.2	11.9
2.0	4	4	9.0	11.5
2.1	4	1	10	11.0
2.2	4	1	10	12
2.3	1	1	12	12
2.4	1	1	13	13
2.5	1	1	14	14
2.6	1	1	12	12
2.7	1	1	12	12
2.8	1	1	8.0	8.0
2.9	1	1	0	0

a switching function between different states is utilized. For hydrogens shared between oxygens, the switching function is given elsewhere,³³ while for HX interactions, the switching function is as follows:

$$U_r^{\text{switch}} = \frac{1}{2} \{1 - \tanh[40(r_{\text{HX}} - r_0)]\}, \quad (6)$$

where r_0 is set to 2.7 Å for HBr and 2.85 for HI. This function will smoothly go to zero before $r_{\text{HX}} = 3.0$ Å, which is the criteria (as described above) for a MS-EVB state to be considered.

Table III gives a comparison between *ab initio* and the MS-EVB model for the binding energy of the 1wat, 4watA, and 4watB clusters for HBr and HI, along with the energy of the separated 1wat cluster. As stated previously, the U_0 value in Eq. (3) is set to reproduce the $\text{HX} + \text{H}_2\text{O}$ (separated) value. Figure 3 gives a comparison between *ab initio* and the model for the energy as a function of the HX distance for the 1wat and

TABLE III. Energy comparisons between *ab initio* and the MS-EVB model for different gas phase clusters.

	$E_{\text{ab initio}}$ (kcal/mol)	E_{model} (kcal/mol)
$\text{Br}^- + \text{H}_3\text{O}^+$ (separated)	0.0	0.0
$\text{HBr} + \text{H}_2\text{O}$ (separated)	-158.2	-158.3
$\text{HBr} + \text{H}_2\text{O}$ (1wat)	-162.8	-163.0
$\text{HBr} + 4\text{H}_2\text{O}$ (4watA)	-197.0	-197.0
$\text{HBr} + 4\text{H}_2\text{O}$ (4watB)	-198.3	-198.1
$\text{I}^- + \text{H}_3\text{O}^+$ (separated)	0.0	0.0
$\text{HI} + \text{H}_2\text{O}$ (separated)	-149.6	-149.6
$\text{HI} + \text{H}_2\text{O}$ (1wat)	-154.5	-154.5
$\text{HI} + 4\text{H}_2\text{O}$ (4watA)	-194.7	-194.9
$\text{HI} + 4\text{H}_2\text{O}$ (4watB)	-197.4	-197.4

FIG. 3. Energy as a function of distance for the 1wat system (bottom) and the 4watA system (top). The symbols represent *ab initio* results, while the solid lines represent model fits to HI, the dashed lines the fit to HBr, and the dotted lines the NQE fit.

4watA clusters. As with the minimum energies, the agreement between *ab initio* and the models are good for these.

As with the HCl model,³⁵ the inclusion of nuclear quantum effects (NQE) was deemed to potentially play an important role in HBr and HI dissociation. The method first utilized to describe hydronium-water interactions was used for this work.^{45,46} The exact parameterization and implementation are given in previous work,^{33,35} in which the 1wat cluster for HBr and HI were refit to the centroid from path integral Monte Carlo simulations. The new h_{ij} values from this refit are given in Table II, and the energy versus r_{HX} for the 1wat and 4watA clusters are given in Fig. 3. It can be observed that the inclusion of NQEs has a minimal impact on the energy versus r_{HX} for the clusters examined. This is in contrast to hydronium-water and hydroxide-water interactions, which are significantly impacted by NQEs.^{25,45–47}

III. SIMULATION DETAILS

All interfacial simulations were carried out in a box with dimensions of $28 \text{ Å} \times 28 \text{ Å} \times 120 \text{ Å}$ with periodic boundaries in all directions. A total of 1000 water molecules were placed in the box, along with a single halide atom and a single sodium or hydronium atom. All production simulations were carried out in the NVT ensemble in which the Berendsen thermostat was used to keep the temperature at 298 K.⁴⁸ The water molecules formed a liquid that occupied approximately a third of the simulation box along the z -dimension. As a consequence, approximately two thirds of the simulation box was vapor, and two air-water interfaces formed, perpendicular to the z -axis. The Gibbs dividing surface (GDS) for these interfacial simulations was defined by fitting a hyperbolic tangent function to the density profile along the z -axis.⁴⁹ For simulations in bulk water, the z component of the simulation box was approximately 38 Å and the simulations were first equilibrated in the NPT ensemble for 100 ps, only allowing the z component of the simulation box to vary, with the pressure controlled via the Berendsen barostat.⁴⁸ After the initial equilibration period, the NVT ensemble was used for production runs. The timestep for all simulations was set to 0.2 fs.

To understand the dissociation mechanisms of HX and NaX, and how they are influenced by their proximity to the

GDS of the air-water interface, umbrella sampling was used.⁵⁰ Umbrella sampling allows the preferential sampling of certain regions of phase space by utilizing a pseudo-potential of the form,

$$u(r, z) = k_r(r_{AX} - r_0)^2 + k_z(z_A - z_0)^2, \quad (7)$$

where r_{AX} is the distance between the halide atom X and atom A, which is either the closest hydronium H atom to X or a sodium cation. The value of z_A represents the distance of the mentioned hydrogen or sodium atom z position with the z position of the center of mass of all of the water molecules combined. The other values, k_r , r_0 , k_z , and z_0 , are parameters set for each simulation and were chosen as follows. For the bulk simulations, k_z was set to 0.0 kcal/mol, while for the interfacial simulations, it was set to 2.0 kcal/mol. For all simulations, k_r was set to 2.0 kcal/mol. The HX and NaX simulations are somewhat different due to the fact that the MS-EVB model was used for HX. It should be noted that all MS-EVB diagonal states use Eq. (7), but the overall energy is still calculated via Eq. (1).

To construct a potential of mean force (PMF) with respect to r_{AX} , multiple simulations were carried out, each with a different r_0 value (0.5, 1.0, 1.5, 1.7, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0 Å). For each simulation, 40 ps of equilibration preceded 160 ps of production. A probability distribution with respect to r_{AX} was collected that is typically centered at r_0 from every production run. The distributions were matched in overlapping regions to construct a PMF as described in previous work.³⁵ For the interfacial simulations, z_0 was set to the average position of the GDS. The PMF with respect to z_A was calculated in a similar fashion, using multiple different simulations, each with a different value of z_0 (-8, -6, -4, -2, -1, 0, 1, and 2 Å), with these given with respect to the average GDS position. For all of them in a specific PMF curve, r_0 was set to a single value, which is given later. Each simulation had 40 ps of equilibration and 320 ps of production. The probability distribution with respect to z_A was matched in overlapping regions to construct the PMF. These details are applicable for the study of NaBr, NaI, HBr, and HI, while the results for NaCl and HCl were calculated previously,³⁵ but used nearly identical procedures. All calculations were carried out utilizing the Amber10 computational package, modified to include umbrella sampling and the MS-EVB method.⁵² There are other ways to sample z for the hydronium ion at the air-water interface, such as using an umbrella potential with respect to the center of charge.⁵¹ One may be concerned that the umbrella potential used in this work may bias the hydronium ion more towards the eigen cation. To test this, the average of the largest eigenvector squared (i.e., the charge on the hydronium ion) was compared between simulations in which $k_z = 0$ and $k_z = 2.0$ kcal/mol. If the usage of Eq. (7) for the z coordinate biased the hydronium ion in HBr more towards the eigen cation, then these should be significantly different. The value in the solvent separated ion pair in the bulk or with z_0 at least 6 Å from the GDS ranged from 0.91 to 0.92 for all cases. No major difference between cases where $k_z = 0$ and $k_z = 2.0$ kcal/mol was found. Nevertheless, studying different coordinates may lead to a more efficient sampling of z , which will be investigated in future work.

IV. RESULTS AND DISCUSSION

A. Comparing HX dissociation with NaX

The PMF with respect to the interatomic distance in bulk water is given in Fig. 4 for HX and NaX. The uncertainties were calculated by splitting the calculations into four separate 40 ps trajectories. The reason for not including instances of molecular HBr and HI in the PMF is that it was too difficult to sample transitions from the molecular to the contact ion pair (CIP) forms. Perhaps another dissociation coordinate would better describe this, which has been discussed by other authors for acid dissociation.^{22,53} For HX, the CIP is favored the most for HCl and least for HI. This is consistent with the *ab initio* results in Table III, which show that the difference between 4watB and 4watA is greater for HI than HBr (i.e., the solvent separated ion pair (SSIP) is more stabilized for HI than HBr for these small clusters). Also, NaX has the same trends in CIP stability as HX. The barrier for going from the CIP to the SSIP is very large for the HX systems, being approximately 4.0 kcal/mol for HCl, 3.5 kcal/mol for HBr, and 2.0 kcal/mol for HI. These barrier heights are much lower for NaX, which are less than 2.0 kcal/mol, but have the same trend, with NaCl having the highest and NaI having the smallest.

The PMF with respect to the HX and NaX distance at the average position of the GDS of water is given in Fig. 5. For HX, the free energy for the CIP is lower for all systems but is impacted by a greater degree for HCl and HBr than for HI. This is somewhat expected, as the polarizability of the anions would be anticipated to promote more ion pairing. On the other hand, the fact that iodide is the most polarizable anion studied, it may be expected that it would be impacted more than the others, which it is not. This will be further discussed in Sec. IV B.

Of interest is the fact that the NaX PMFs do not appear to be significantly impacted by the interface. This is in contrast to previous work studying NaCl dissociation with polarizable potentials.⁵⁴ One should understand the differences between these models, though. The inclusion of Thole damping³⁸ reduces how much induced dipoles form in response to the local environment, which also lowers the propensity for

FIG. 4. PMF with respect to the distance in bulk water for HX (top) and NaX (bottom).

FIG. 5. PMF with respect to the distance near the GDS of water for HX (top) and NaX (bottom).

anions for the air-water interface.⁵⁵ Induced dipoles formed by polarizabilities are greater when the polarizabilities are greater (which they are for iodide), and when the distance between charges and the polarizability are smaller (which are smallest for chloride). Each anion has a balance between these, and this balance is impacted by the inclusion of electrostatic damping used in the existing model. This lowers, but does not eliminate, the impact of the environment. For instance, NaBr dissociation appears to be impacted the most by the interface, likely due to its relatively small diameter and larger polarizability.³⁷

B. PMF across the air-water interface

Figure 6 gives the PMF across the air-water interface for the HX pair while in the CIP state. The CIP state was enforced by setting r_0 in Eq. (7) to the minimum in the PMF with respect to r_{HX} at the air-water interface. These were set to 2.2 and 2.4 Å for HBr and HI, respectively, with the data for HCl taken from previous work.³⁵ There is not a large difference in the PMFs for different halide anions. Upon close inspection, the Br⁻ anion

FIG. 6. PMF across the air-water interface for CIP configurations for H⁺ (bottom) and X⁻ (top) for HX.

appears to have the greatest propensity for the air-water interface, while Cl⁻ and I⁻ have very similar PMFs. Moreover, H⁺ has a somewhat greater propensity for the interface for the HBr system than HCl and HI. While these are definitely subtle, they do not necessarily follow what would be expected: the HBr results would be in between the HCl and the HI results.

To provide further insight into this, the average dipole on the X⁻ atom as a function of its z_0 value used in Eq. (7) from the last 40 ps of the simulations used to calculate their PMFs with respect to z is shown in Fig. 7. The dipoles for all anions increase as they approach the GDS, but what is unexpected is that Br⁻ has the highest dipole of them all. For halides, alone in aqueous solution, I⁻ has the largest induced dipole due to its higher polarizability.⁵⁵ To further investigate this, the dipole of the 4watA cluster in Fig. 2 was calculated using the ESP method as implemented in the NWChem package⁴³ (from the same MP2 computations that are described in Sec. II). This represents a small cluster in the CIP configuration, so it will be used as a probe for what the dipole in solution may be. The average dipole for the HCl, HBr, and HI systems were 1.45, 1.97, and 1.93 D, respectively. This is consistent with the results in Fig. 7, as HBr has the highest dipole.

For the model used here, the polarizabilities allow induced dipoles to form in response to their local electric fields. The most potent factor for the local electric field in the CIP configuration is likely the hydronium ion donating a hydrogen bond to the anion. The electric field will be enhanced with a shorter HX distance, in which HCl is the shortest as can be observed in Fig. 5. However, the polarizability of the I⁻ anion is the largest.³⁷ The balance between these factors appears to favor HBr in its CIP, to have the highest dipole and HCl to have the smallest. One final aspect that should be noted is that for all cases, while the X⁻ atom has a more negative minimum in its PMF, it is located 1-2 Å from the GDS towards the liquid. On the other hand, the H⁺ PMFs do not increase with greater z until approximately 2.0 Å from the GDS towards the air. This shows that the average configuration for HX in its CIP configuration is with the hydronium ion oriented more towards the air.

The PMF across the air-water interface for HX in its SSIP state is given in Fig. 8. As with the CIP PMFs, they include the PMFs for both the H⁺ and X⁻ atoms. Also, the SSIP position was enforced by setting r_0 in Eq. (7) to 4.2 Å for both HBr and

FIG. 7. Average dipole on X⁻ atom with respect to z_0 value for CIP.

FIG. 8. PMF across the air-water interface for SSIP configurations for H^+ (bottom) and X^- (top) for HX.

HI. The HCl results are from previous work.³⁵ The X^- atoms appear to follow the expected trend in which the greater the polarizability and size, the greater propensity for the air-water interface.¹⁷ The PMFs for the H^+ atoms are fairly similar for all of the halides, with the H^+ in the HCl having a slightly lower propensity for the interface than the other two. As with the CIP, the H^+ PMF does not increase with greater z value until it has a position that is more towards the air than the GDS, while the X^- PMF increases on the liquid side of the GDS. This suggests, again, that for the SSIP, the H^+ atom is more likely to be oriented towards the air than the X^- atom. This is consistent with how the addition of HCl impacts capillary electrophoresis measurements,¹¹ which makes the surface of water droplets more positively charged. Moreover, the fact that HX has a propensity for the air-water interface is in agreement with predictions from surface tension measurements for aqueous HX solutions.³⁶ Overall, the computations show that the addition of HX to water will have a modest propensity for the

FIG. 9. PMF across the air-water interface for the X^- atom NaX in the CIP (top) and SSIP (bottom) configurations.

air-water interface with the H^+ atom more likely to be oriented towards the air than the X^- atom.

To compare with the HX systems, the PMF for the X^- atom in the CIP and SSIP configurations across the air-water interface are given in Fig. 9. The CIP configurations were enforced by setting r_0 in Eq. (7) to 2.9 and 3.2 Å for NaBr and NaI, respectively, and the SSIP configurations were enforced by setting r_0 equal to 4.5 Å for both NaBr and NaI. The NaCl data were taken from previous work.³⁵ The Na^+ ions are repelled from the air-water interface,³⁷ so they are not focused on in this work. For both the CIP and the SSIP, the trend of the larger, more polarizable halides having a propensity for the air-water interface is present. Consistent with HX, the SSIP Cl^- and Br^- have similar PMFs, while I^- has a greater propensity for the air-water interface.

V. CONCLUSIONS

Molecular dynamics simulation utilizing the polarizable multistate empirical valence bond method was carried out to compare the behavior of HX with NaX, with X being Cl, Br, or I, at the air-water interface. A new model was parameterized to *ab initio* calculations for HBr and HI, and existing models were used for the remaining species. The barrier to go from a contact ion pair to a solvent separated ion pair was greater for HX at the air-water interface than in the bulk, while NaX showed similar barriers at both locations. Moreover, HX had a greater propensity for the interface than NaX. This was found to be a consequence of hydronium having more interfacial activity than any of the halide anions. Because of this, while NaX ion pairs had an average configuration of the X atom being oriented towards the air, HX had an average orientation with H located more towards the air than X. These results were found to be consistent with many experimental measurements, including surface tension and capillary electrophoresis measurements.

ACKNOWLEDGMENTS

This work is funded by the National Science Foundation under Award No. OIA-1541079 with additional support from the Louisiana Board of Regents. All major computations were carried out with resources from the Louisiana Optical Network Initiative.

- ¹E. M. Knipping, M. J. Lakin, K. L. Foster, P. Jungwirth, D. J. Tobias, R. B. Gerber, D. Dabdub, and B. J. Finlayson-Pitts, *Science* **288**, 301 (2000).
- ²Y. Q. Li, H. Z. Zhang, P. Davidovits, J. T. Jayne, C. E. Kolb, and D. R. Worsnop, *J. Phys. Chem. A* **106**, 1220 (2002).
- ³G. N. Robinson, D. R. Worsnop, J. T. Jayne, C. E. Kolb, E. Swartz, and P. Davidovits, *J. Geophys. Res.: Space Phys.* **103**, 25353, doi: 10.1029/98JD02085 (1998).
- ⁴P. Davidovits, C. E. Kolb, L. R. Williams, J. T. Jayne, and D. R. Worsnop, *Chem. Rev.* **106**, 1323 (2006).
- ⁵A. Laskin, D. J. Gaspar, W. H. Wang, S. W. Hunt, J. P. Cowin, S. D. Colson, and B. J. Finlayson-Pitts, *Science* **301**, 340 (2003).
- ⁶T. L. Tarbuck, S. T. Ota, and G. L. Richmond, *J. Am. Chem. Soc.* **128**, 14519 (2006).
- ⁷G. L. Richmond, *Chem. Rev.* **102**, 2693 (2002).
- ⁸T. M. Chang and L. X. Dang, *Chem. Rev.* **106**, 1305 (2006).
- ⁹P. Jungwirth and D. J. Tobias, *Chem. Rev.* **106**, 1259 (2006).
- ¹⁰P. K. Weissenborn and R. J. Pugh, *J. Colloid Interface Sci.* **184**, 550 (1996).
- ¹¹P. Creux, J. Lachaise, A. Gracia, J. K. Beattie, and A. M. Djerdjev, *J. Phys. Chem. B* **113**, 14146 (2009).

- ¹²B. C. Garrett, G. K. Schenter, and A. Morita, *Chem. Rev.* **106**, 1355 (2006).
- ¹³K. Ando and J. T. Hynes, *J. Phys. Chem. B* **101**, 10464 (1997).
- ¹⁴D. Clifford, T. Bartels-Rausch, and D. J. Donaldson, *Phys. Chem. Chem. Phys.* **9**, 1362 (2007).
- ¹⁵T. Ishiyama and A. Morita, *J. Phys. Chem. C* **111**, 738 (2007).
- ¹⁶M. Fyta, I. Kalcher, J. Dzubiella, L. Vrbka, and R. R. Netz, *J. Chem. Phys.* **132**, 024911 (2010).
- ¹⁷L. Vrbka, M. Mucha, B. Minofar, P. Jungwirth, E. C. Brown, and D. J. Tobias, *Curr. Opin. Colloid Interface Sci.* **9**, 67 (2004).
- ¹⁸T. Ishiyama and A. Morita, *J. Phys. Chem. A* **111**, 9277 (2007).
- ¹⁹L. X. Dang, *J. Chem. Phys.* **119**, 6351 (2003).
- ²⁰N. Agmon, *Chem. Phys. Lett.* **244**, 456 (1995).
- ²¹D. Ardura and D. J. Donaldson, *Phys. Chem. Chem. Phys.* **11**, 857 (2009).
- ²²M. D. Baer, D. J. Tobias, and C. J. Mundy, *J. Phys. Chem. C* **118**, 29412 (2014).
- ²³M. D. Baer, I.-F. W. Kuo, D. J. Tobias, and C. J. Mundy, *J. Phys. Chem. B* **118**, 8364 (2014).
- ²⁴A. A. Kornyshev, A. M. Kuznetsov, E. Spohr, and J. Ulstrup, *J. Phys. Chem. B* **107**, 3351 (2003).
- ²⁵G. A. Voth, *Acc. Chem. Res.* **39**, 143 (2006).
- ²⁶J. M. J. Swanson, C. M. Maupin, H. Chen, M. K. Petersen, J. Xu, Y. Wu, and G. A. Voth, *J. Phys. Chem. B* **111**, 4300 (2007).
- ²⁷U. W. Schmitt and G. A. Voth, *J. Chem. Phys.* **111**, 9361 (1999).
- ²⁸C. J. Mundy, I. F. W. Kuo, M. E. Tuckerman, H. S. Lee, and D. J. Tobias, *Chem. Phys. Lett.* **481**, 2 (2009).
- ²⁹T. Todorova, A. P. Seitsonen, J. Hutter, I. F. W. Kuo, and C. J. Mundy, *J. Phys. Chem. B* **110**, 3685 (2006).
- ³⁰Y. Wu, H. Chen, F. Wang, F. Paesani, and G. A. Voth, *J. Phys. Chem. B* **112**, 467 (2008).
- ³¹M. K. Petersen, S. S. Iyengar, T. J. F. Day, and G. A. Voth, *J. Phys. Chem. B* **108**, 14804 (2004).
- ³²Y.-L. S. Tse, C. Chen, G. E. Lindberg, R. Kumar, and G. A. Voth, *J. Am. Chem. Soc.* **137**, 12610 (2015).
- ³³C. D. Wick, *J. Phys. Chem. C* **116**, 4026 (2012).
- ³⁴B. L. Eggimann and J. I. Siepmann, *J. Phys. Chem. C* **112**, 210 (2008).
- ³⁵C. D. Wick, *J. Phys. Chem. C* **117**, 12359 (2013).
- ³⁶L. M. Pegram and M. T. Record, Jr., *Proc. Natl. Acad. Sci. U. S. A.* **103**, 14278 (2006).
- ³⁷O. T. Cummings and C. D. Wick, *J. Chem. Phys.* **139**, 64708 (2013).
- ³⁸B. T. Thole, *Chem. Phys.* **59**, 341 (1981).
- ³⁹J. Sala, E. Gurdia, and M. Masia, *J. Chem. Phys.* **133**, 234101 (2010).
- ⁴⁰J. Kolafa, *J. Comput. Chem.* **25**, 335 (2004).
- ⁴¹U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen, *J. Chem. Phys.* **103**, 8577 (1995).
- ⁴²D. A. McQuarrie, *Statistical Mechanics* (Harper Collins, New York, NY, 1976).
- ⁴³R. J. Harrison, J. A. Nichols, T. P. Straatsma, M. Dupuis, E. J. Bylaska, G. I. Fann, T. L. Windus, E. Apra, F. De Jong, S. Hirata, M. T. Hackler, J. Anchell, D. E. Bernholdt, P. Borowski, T. Clark, D. Clerc, H. Dachsel, M. J. O. Deegan, K. Dyall, D. Elwood, H. Fruchtl, E. Glendening, M. Gutowski, K. Hirao, A. Hess, J. Jaffe, B. Johnson, J. L. Ju, R. A. Kendall, R. Kobayashi, R. Hutteh, Z. Lin, R. Littlefield, X. Long, B. Meng, T. Nakajima, J. Nieplocha, S. Niu, M. Rosing, G. Sandrone, M. Stave, H. Taylor, G. Thomas, J. van Lenthe, K. Wolinski, A. T. Wong, and Z. Zhang, NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.1, 2002.
- ⁴⁴J. Applequist, J. R. Carl, and K. K. Fung, *J. Am. Chem. Soc.* **94**, 2952 (1972).
- ⁴⁵G. Brancato and M. E. Tuckerman, *J. Chem. Phys.* **122**, 224507 (2005).
- ⁴⁶D. E. Sagnella and M. E. Tuckerman, *J. Chem. Phys.* **108**, 2073 (1998).
- ⁴⁷C. D. Wick and L. X. Dang, *J. Phys. Chem. A* **113**, 6356 (2009).
- ⁴⁸H. J. C. Berendsen, J. P. M. Postma, W. F. Vangunsteren, A. Dinola, and J. R. Haak, *J. Chem. Phys.* **81**, 3684 (1984).
- ⁴⁹L. X. Dang and T. M. Chang, *J. Chem. Phys.* **106**, 8149 (1997).
- ⁵⁰G. M. Torrie and J. P. Valleau, *J. Comput. Phys.* **23**, 187 (1977).
- ⁵¹S. Iuchi, H. Chen, F. Paesani, and G. A. Voth, *J. Phys. Chem. B* **113**, 4017 (2009).
- ⁵²D. A. Case, T. A. Darden, T. E. Cheatham III, C. L. Simmerling, J. Wang, R. E. Duke, R. Luo, M. Crowley, R. C. Walker, W. Zhang, K. M. Merz, B. Wang, S. Hayik, A. Roitberg, G. Seabra, I. Kolossváry, K. F. Wong, F. Paesani, J. Vanicek, X. Wu, S. R. Brozell, T. Steinbrecher, H. Gohlke, L. Yang, C. Tan, J. Mongan, V. Hornak, G. Cui, D. H. Mathews, M. G. Seetin, C. Sagui, V. Babin, and P. A. Kollman (2008), *Amber 10*, University of California, San Francisco, CA.
- ⁵³J. M. Park, A. Laio, M. Iannuzzi, and M. Parrinello, *J. Am. Chem. Soc.* **128**(35), 11318–11319 (2006).
- ⁵⁴C. D. Wick, *J. Phys. Chem. C* **113**, 2497 (2009).
- ⁵⁵C. D. Wick, *J. Chem. Phys.* **131**, 84715 (2009).