Acid Dissociation in (HX)_n(H₂O)_n Clusters (X = F, Cl, Br, I; N = 2, 3)

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Acid dissociation in $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters

$(\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}; n = 2, 3)$

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Abstract

The interactions between two or three hydrogen halide molecules and the same number of water moieties are investigated through a systematic exploration of the corresponding potential energy surfaces using a stochastic methodology in conjunction with density functional theory computations. Our results indicate that HF, the weakest acid in the series, is partially dissociated. Similarly, HCl, HBr, and HI undergo dissociation in the presence of three, two, and two water molecules, respectively. The decrease in the number of water molecules required for dissociation, when compared with clusters with one single HX molecule, suggests cooperative effects. Interestingly, the hydrogen-bridged bihalide anions (XHX^-) are present in the global minimum of $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters with $\text{X} = \text{Br}, \text{I}$ and $n = 2, 3$. These anions are even persistent at room temperatures. Concomitantly, a broad spectrum of interactions is found, among them water $\cdots$ water, HX $\cdots$ water, and HX $\cdots$ HX hydrogen bonds, halogen bonds, ionic and long-range $\text{X}\cdots\text{H}$ interactions.

Introduction

Acid dissociation is a complex process affected by several factors, most prominently the environment and the strength of the proton-containing bond to be broken. In the aqueous phase, acidic strength is dictated by the pKa of the species in question. The hydrogen halide series covers a spectrum from the weak to the very strong acidity, as it is clear from Table 1. Interactions between hydrogen halides and water molecules are relevant because they participate in numerous biochemical and atmospheric reactions (Keesee, 1989; Müller et al., 1992; Rokita, 1992; Peter, 1997; De Haan et al., 1999; Domcke and Sobolewski, 2003). Moreover, the involved processes, such as proton transfer, acid dissociation, and the interactions that stabilize HX-water complexes, epitomize some central questions in chemistry. The nature of the interactions escapes descriptions in simple terms, rather it is necessary to invoke a complex mixture of electrostatic, covalent, induction, and dispersion contributions, varying in relative weights.

Table 1. Acidic power and properties of the H-X bond in the hydrogen halide series. pKas for dissociation in aqueous environments, bond lengths in Å, and dipole moments in Debyes (Cotton and Wilkinson, 1988; Weast et al., 1989; Sato and Hirata, 1999).

Property	HF	HCl	HBr	HI
pKa	3.2	-7.0	-9.5	-10.0
Bond lengths	0.92	1.27	1.41	1.60
Dipole moment	1.8	1.1	0.8	0.4

Microsolvation studies of a single acid molecule with one or more water molecules have expanded our understanding of acid dissociation and, in some cases, have pinpointed the number of solvent molecules needed to achieve the formation of the ion pair (Laasonen and Klein, 1994; Schindler et al., 1994; Lee et al., 1996; Ando and Hynes, 1999; Conley

and Tao, 1999; Gertner et al., 1999; Cabaleiro-Lago et al., 2002; Devlin et al., 2002; Hurley et al., 2003; Voegelé and Liedl, 2003; Kuo and Klein, 2004; Odde et al., 2004; Gutberlet et al., 2009; Vargas-Caamal et al., 2016a). These studies correspond to ideal situations that do not account for crucial factors such as increasing acid concentration via the explicit addition of new molecules. Indeed, there are fewer reports about microsolvation of clusters with more than one acid molecule compared with those for a single molecule, and many of them are focused on HCl. For instance, Morrison *et al.* reported an infrared spectroscopy study of mixed $(\text{HCl})_m(\text{H}_2\text{O})_n$ clusters ($m:n = 1:1, 2:1, 2:2, \text{ and } 3:1$) immersed in helium nanodroplets (Morrison et al., 2010). They discussed infrared spectra in the HCl stretch region ($2600\text{--}2900\text{ cm}^{-1}$) and determined that the 2:2 cluster has a nonalternating cyclic arrangement (Figure 1a). Chaban and coworkers analyzed the $(\text{HCl})_2(\text{H}_2\text{O})_2$ and $(\text{HCl})_4(\text{H}_2\text{O})_4$ aggregates during their discussion on the transition from hydrogen bonding to ionization (Chaban et al., 2001). The hydrogen-bonded isomer of $(\text{HCl})_2(\text{H}_2\text{O})_2$ (see Figure 1b) is 6.9 kcal mol^{-1} lower in energy than the ionic one (Figure 1c), both with an alternating cyclic structure. Conversely, the 4:4 complex adopts a cubic form, where the full dissociated isomer is almost 16 kcal mol^{-1} more stable than the hydrogen-bonded one. The authors consider that the incorporation of anharmonic effects is a crucial factor for the prediction of reliable vibrational spectra and that cooperative effects in the solvation of hydrogen halides are extremely important.

Recently, Zakai *et al.* performed classical molecular dynamics simulations to illustrate the transitions between the H-bonded and ionic isomers of $(\text{HCl})_2(\text{H}_2\text{O})_2$ (Figure 1b and 1c) and of $(\text{HF})_4(\text{H}_2\text{O})_4$ (Zakai et al., 2017). They reported that proton transfers were fully concerted in all trajectories for $[\text{Cl}\cdots\text{H}_3\text{O}^+]_2$, whereas for $[\text{F}\cdots\text{H}_3\text{O}^+]_4$, the fully concerted mechanism is dominant but partially concerted transfers of two or three protons

at the same time also occur. The authors remarked that the high symmetry of the ionic and the H-bonded structures plays a key role in the collective propagation of the protons and cooperative effects.

Structure for $(\text{HCl})_2(\text{H}_2\text{O})_2$ clusters found here and reported in other works: a) H-bonded nonalternating cyclic form (Morrison et al., 2010), b) H-bonded alternating structure, and c) ionic arrangement (Chaban et al., 2001).

In order to investigate some important questions such as how many water molecules are required to onset dissociation and underline the cooperativity in hydrogen-bonded systems, we systematically explore the potential energy surfaces (PES) of $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters, with $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ and $n = 2, 3$. This work contributes to the understanding of the process of microsolvation of acids supported by a large variety of structures and interactions, ranging from hydrogen bonds of different strengths to halogen interactions. Perhaps, one of the most remarkable results is the stabilization of hydrogen-bridged bihalide (XHX^-) moieties in the global minimum of $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters with $\text{X} = \text{Br}, \text{I}$. We hope that the formation of hydrogen-bridged bihalide anions and the increasing relevance of the $\text{X}\cdots\text{H}\cdots\text{X}$ interactions in the heavier halogens found here stimulate new perspectives on the general subject of acid microsolvation.

Computational details

In order to systematically explore the PES of the $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters (with $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ and $n = 2, 3$), a modified kick algorithm as is implemented in the GLOMOS code was used (Grande-Aztatzi et al., 2014; Ramirez-Manzanares et al., 2015; Cabellos et al., Cinvestav Mérida, Yuc. México. 2013). This heuristic has been employed by us to explore the PESs of several molecular clusters (Grande-Aztatzi et al., 2014; Vargas-Caamal et al., 2015; Vargas-Caamal et al., 2016a; Vargas-Caamal et al., 2016b; Murillo et al., 2017). A hierarchical screening is established, the initial structures were optimized at the PBE0/D95V level and then refined at the PBE0-D3/def2-TZVP level (Weigend and Ahlrichs, 2005; Grimme, 2006; Grimme, 2011). Each structure was characterized as a true minimum by harmonic vibrational frequency analysis. All computations were done using the *Gaussian* 09 (revision D.01) package (Frisch et al., Gaussian, Inc., Wallingford, CT. 2013). Temperature effects were analyzed using *Eyringpy* 1.0 (Dzib et al., 2019).

To examine the interactions, Wiberg bond indices (WBI) (Wiberg, 1968) were computed. Stern-Limbach (Limbach et al., 2009) plots were used to correlate the symmetry and length of hydrogen bonds. In these plots, q_1 measures the displacement of the proton from the center in idealized linear hydrogen bonds, while q_2 quantifies the distance between the two electronegative atoms (see Figure 2 for definition of variables). For hydrogen bonds involving equally electronegative atoms, $q_1 = 0$ indicates the point at which the proton is equally shared by both atoms, while positive or negative values denote that one of the electronegative atoms in the hydrogen bond is more strongly bound to the proton.-

Figure 2. Definition of hydrogen bond coordinates (Limbach et al., 2009), q_1 and q_2 . In our case, the A and B atoms are either oxygen or halogen. The large volume associated with the proton intends to suggest a high degree of delocalization.

Structures and Energetics

Table 2 contains the energy ranges and the number of structures obtained, which are 155 for the 2:2 systems and 815 for the 3:3 clusters, including enantiomers. As for other systems interacting with water molecules, the number and diversity of structures is huge in a relatively small energy range (Cabaleiro-Lago et al., 2002; Odde et al., 2004; Perez et al., 2008; Ramirez et al., 2011; Acelas et al., 2013; Vargas-Caamal et al., 2016a; Hadad et al., 2018).

Table 2. Number of structures and ZPE corrected electronic energies in kcal mol⁻¹ of the (HX)_n(H₂O)_n clusters.

	(HF) _n (H ₂ O) _n	(HCl) _n (H ₂ O) _n	(HBr) _n (H ₂ O) _n	(HI) _n (H ₂ O) _n	The
n = 2					
number of structures	18	24	45	68	
ΔE _{ZPE}	12.3	13.8	13.6	12.2	
n = 3					
number of structures	255	192	160	208	
ΔE _{ZPE}	12.8	12.3	26.4	25.4	

lowest ZPE-corrected energy structures for each molecularity are presented in Figure 3. The most stable forms for the F and Cl clusters and n = 2 adopt a nondissociated H-bonded alternating structure, in agreement with previous reports (Chaban et al., 2001). In the case of the bromine 2:2 complex, the global minimum can be described as a dissociated H-bonded nonalternating cyclic form in such a way that there is a transfer of a hydrogen atom to generate a H₃O⁺ cation. The most beautiful structure is the global minimum of (HI)₂(H₂O)₂ (see Figure 3), in which the IHI⁻ anion and the hydronium cation coexist! This C_s structure is a transition state for bromine, and it is not detected for clusters with fluorine and chlorine. Conversely, for 3:3 clusters, the lowest ZPE corrected energy clusters adopt cage-like arrays, but again the hydrogen bihalide anions are also present in the Br and I systems. It is important to comment that for the (HF)₃(H₂O)₃ cluster, there is a planar hexagonal structure at less than 0.1 kcal mol⁻¹ from the putative global minimum, so both arrangements are degenerate.

Figure 3. PBE0-D3/def2-TZVP lowest energy structures for the $(\text{HX})_2(\text{H}_2\text{O})_2$ and the $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters.

Note that hydrogen bihalide anions are stabilized only for the stronger acids (HBr and HI). These anions are linear with a hydrogen atom placed between two halide atoms and form strong intramolecular hydrogen bonds (Jiang and Anderson, 1974; Emsley, 1980; Kemp and Gordon, 2010; Grabowski, 2016; Grabowski et al., 2016). Grabowski *et al.* studied the XHX^- anions as a way to compare the similarity between hydrogen and gold (Grabowski et al., 2016). Although their analysis was based exclusively on the anions and our clusters include anions, hydronium, and water molecules, it seems plausible to compare their computed X-H bond lengths (1.70 and 1.90 Å for Br-H and I-H, respectively) against our results. Thus, while the IHI^- anion in the $(\text{HI})_2(\text{H}_2\text{O})_2$ global minimum has an I-H bond

length of 1.93 Å and it is symmetric, in 3:3 complexes there are differences between the $X\cdots H$ distances in transient symmetry, with ranges between 1.65-1.78 and 1.87-1.97 Å for $BrHBr^-$ and IHI^- , respectively. These asymmetries are due to the interactions with the solvent molecules (Pylaeva et al., 2017).

Kemp and Gordon conducted a study of $BrHBr^-(H_2O)_n$ and $IHI^-(H_2O)_n$ clusters with $n = 1$ to 6 in order to determine the preferred solvated structures (Kemp and Gordon, 2010). They found that for $n = 1, 2$, water molecules prefer to donate their hydrogen atoms for hydrogen bonding. Conversely, in this work, we started with neutral HX and H_2O and found the spontaneous formation of hydrogen bihalide anions!

Cooperativity

Leopold published a comprehensive review related to the dissociation of acids in aqueous environments, in which collects theoretical evidence about the number of water molecules needed to dissociate some simple acids, suggesting 4, 3, and 3 water molecules for HCl , HBr , and HI , respectively. For the case of HF , the acid is partially dissociated for $n > 7$. Remarkably, our computations indicate dissociation with just two (for HBr and HI) and three (for HCl) water molecules. This is, on one hand, consistent with the pK_a s listed in Table 1, and on the other hand, the decrease in the number of water molecules required for dissociation, when compared with clusters with one single HX molecule, suggests cooperative effects.

Cooperativity has been reported as an important effect in studies about acid ionization and hydration of ions (Tielrooij et al., 2010; Zakai et al., 2017). But even when cooperativity is one of those concepts that seems intuitively clear, it is not rigorously defined. Nonetheless, it seems generally accepted that it is related to non-additivity of the

energy of individual contacts, thus, it implies that the total interaction energy of a system is larger than the simple addition of the individual interactions. Several methods attempt to get a quantitative account of the cooperative effects by decomposing the interaction energy of a system of n bodies and by the inclusion of the many-body terms in the analysis (Dannenberg, 2002; Esrafil et al., 2011; Guevara-Vela et al., 2016; Mahadevi and Sastry, 2016). Here, just to illustrate cooperative effects, we take the total interaction energy of two structurally related geometries, that is, the same patterns of hydrogen bonds but with different sizes: the global minima for $(\text{HF})_2(\text{H}_2\text{O})_2$ and the planar hexagonal structure for $(\text{HF})_3(\text{H}_2\text{O})_3$ (see Figure 3), for those, total interaction energies are 32.2 and 54.0 kcal mol⁻¹, respectively, which afford 8.1 and 9.0 kcal mol⁻¹ per hydrogen bond, which clearly highlight the cooperative effects because if there were no cooperation, interaction energies per hydrogen bond would be the same.

Temperature Effects

Are these clusters stable at room temperature? The dissociation energies (ΔE_{diss}) of the $(\text{HX})_2(\text{H}_2\text{O})_2$ and $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters into water and HX are shown in Table 3. Clearly, all complexes are viable at 0 K with ΔE_{diss} in the range of 19.5-54.0 kcal mol⁻¹ and the 3:3 clusters require more energy to separate them than the 2:2 ones. The increase in temperature (or the increase of the entropic effects) causes havoc in the stability of the clusters, to such an extent that the dissociation into water and acid molecules tends to be exergonic for some of them at room temperature. This is consistent with the experimental evidence that the acid strength is inversely proportional to temperature for HF, HCl, and HBr aqueous solutions (Ayotte et al., 2005). {Ayotte, 2005 #3}{Ayotte, 2005 #3}From Table 1, it is also apparent that range (T_{max}) in which the complexes are viable depends on

the molecularity and on the acid strength. Note that the hydrogen bihalide anions are persistent for the 3:3 systems even at room temperature.

Table 3. Dissociation energies, ΔE_{diss} , and free dissociation energies, ΔG_{diss} , (298.15 K and 1 atm) of the $(\text{HX})_2(\text{H}_2\text{O})_2$ and $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters into water and HX in kcal mol⁻¹, and maximum temperature (K) for stability of the $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters.

	$(\text{HF})_n(\text{H}_2\text{O})_n$	$(\text{HCl})_n(\text{H}_2\text{O})_n$	$(\text{HBr})_n(\text{H}_2\text{O})_n$	$(\text{HI})_n(\text{H}_2\text{O})_n$
n = 2				
ΔE_{diss}	32.1	21.1	21.0	19.5
ΔG	8.4	-2.1	-3.4	-4.6
T_{max}	390	273	261	247
n = 3				
ΔE_{diss}	54.0	42.4	45.6	43.5
ΔG	12.9	-0.1	2.8	0.7
T_{max}	381	297	316	303

Bonding analysis

Wiberg bond index is a parameter related to the electron density shared between atoms, providing a reasonable quantification of bond order (Wiberg, 1968; Mayer, 2007). We provide in Figure 4 the distributions of the WBIs for $\text{H}\cdots\text{X}$ contacts for 2:2 and for 3:3 clusters. For both molecularities, most HF clusters fall in the 0.45-0.65 range, which denotes partial dissociation and just a few dissociated clusters are present for $n = 3$ (Figure 4b). For all the other acids, a clear separation between dissociated and undissociated complexes is noted. Dissociated/undissociated gaps are more defined for $n = 2$ than for $n = 3$. This is consistent with a greater variety of geometries and more advanced dissociation

stages as n grows. The halogen atom also plays an important role because the difference between the number of dissociated and undissociated groups is more evident in going from chlorine to iodine.

Figure 4. Wiberg bond indices (WBI) for the H–X interaction in a) $(\text{HX})_2(\text{H}_2\text{O})_2$, and b) $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters. Data taken from the PBE0-D3/def2-TVZP optimized geometries.

The Stern-Limbach plots for the $(\text{HX})_2(\text{H}_2\text{O})_2$ and $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters provide valuable complementary information about the interactions (see Figures 5 and 6). In general, the clusters exhibit two types of interactions between the hydrogen halide and water molecules, one by means of hydrogen bonds and the other through halogen bonds (see Figures 1-SI to 4-SI).

Figure 5. Correlation between q_1 and q_2 (See Figure 2 for definition of variables). Data taken from the PBE0-D3/def2-TVZP optimized geometries for the $(\text{HX})_2(\text{H}_2\text{O})_2$ clusters. Red squares indicate the lowest energy structure. Distances in Å.

The definition of q_1 and q_2 (Figure 2) corresponds to hydrogen bonding, however, large negative values of q_1 combined with large values of q_2 denote undissociated species with long $\text{A}\cdots\text{B}$ distances. These combinations of q_1 and q_2 are due to clusters with halogen interactions (see some examples on the left side of the Figures 5 and 6 for Cl, Br, and I) or to cases where the hydrogen atom of an undissociated HX molecule does not interact with another molecule, such as the examples on the left side of the Figures 5 and 6 for HF. In fact, no halogen bonds were formed for clusters with hydrogen fluoride, while the HCl,

HBr and HI clusters with halogen interactions had higher relative energies with respect to the global minima.

Figure 6. Correlation between q_1 and q_2 (see Figure 2 for definition of variables). Data taken from the PBE0-D3/def2-TVZP structures for the $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters. Red squares indicate the lowest energy structure. Distances in Å.

We now focus in the clusters with HX molecules exhibiting some degree of dissociation, say, those for which $q_1 > -0.8$. Unlike the plots of q_1 vs q_2 reported previously (Gonzalez et al., 2013; Vargas-Caamal et al., 2016a), there are now two curves according to the type of interaction, $\text{X}\cdots\text{H}\cdots\text{O}$ or $\text{X}\cdots\text{H}\cdots\text{X}$, the latter becoming increasingly important for the heavier elements (Br and I) and three water molecules. The global minima are

included in the plots to notice the type of interaction and are highlighted with red squares on the curves.

A detailed classification of the interactions and their percentages over the entire populations are given in Figures 5-SI to 7-SI. The assignment of interactions is based strictly on geometrical criteria. For $(\text{HF})_2(\text{H}_2\text{O})_2$, all the computed structures have hydrogen bonds as dominant interactions and dissociated structures are not present. The situation changes a little bit in $(\text{HCl})_2(\text{H}_2\text{O})_2$, where dissociated structures and halogen interactions rise to $\sim 8\%$ each one (see Figure 6-SI). For the $(\text{HBr})_2(\text{H}_2\text{O})_2$ clusters, the separation of curves corresponding to $\text{Br}\cdots\text{H}\cdots\text{O}$ and $\text{Br}\cdots\text{H}\cdots\text{Br}$ interactions is evident. Concomitantly, the number of structures with hydrogen bonds decrease ($\sim 73\%$ for water-water and HX-water interactions), while those with dissociated forms and halogen bonds increase ($\sim 13\%$ and 40% , respectively). The global minimum is located on the curve of $\text{Br}\cdots\text{H}\cdots\text{O}$ interactions and possesses a cyclic ion-pair geometry, which belongs to the Zundel-like form ($\text{X}\cdots\text{H}\cdots\text{O}$), which represent $\sim 13\%$ of population. For the iodine analogs, the percentages of water-water and HX-water interactions decrease to roughly 60% and the $\text{I}\cdots\text{H}\cdots\text{I}$ interactions become the most important since the global minimum belongs to this Zundel-type (notice that it is the only one structure of this category in Figure 6-SI), with the formation of a hydrogen bihalide anion (Zundel-like structure), supported by the fact that the global minimum is located at $q_1 = 0$, corresponding to the central-symmetric anion. Structures with halogen bond interactions increase considerably (almost 74%), while the Zundel-like $\text{I}\cdots\text{H}\cdots\text{O}$ structures decreases at $\sim 9\%$ compared with HBr-water clusters.

The zoo of forms found for the $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters is more diverse. The plot for HF (Figure 6) shows that the $\text{F}\cdots\text{H}\cdots\text{O}$ and $\text{F}\cdots\text{H}\cdots\text{F}$ curves are closer to each other.

Hydrogen bonds of the $F\cdots H\cdots O$ type are longer than $F\cdots H\cdots F$. The global minimum is undissociated (an alternating six-membered ring) and belongs to the type of HF-water hydrogen bonds, the dominant interaction ($\sim 95\%$, Figure 7-SI). The lowest energy dissociated form is a quasi-Eigen cation and has a relative free energy of $4.6 \text{ kcal mol}^{-1}$. There are no structures with halogen bonds, but some examples of dissociated (2.8%) and quasi-Eigen forms (2%) were found. F-H-O Zundel-like structures are 22.4% of the total. The gap between curves is more evident for the HCl species (Figure 6). Again, a reduction of hydrogen bond interactions (about 77% and 45% for HX-water and water-water interactions, respectively) and a significant increment of the dissociated complexes ($\sim 57\%$) are noted. The quasi-Eigen cations represent almost 10% of population (including the global minimum) and the structures containing Zundel-like cations is now present (about 5%), while Zundel-like Cl-H-O and halogen interactions contribute with ~ 5 and 1% , respectively. For the $(HBr)_3(H_2O)_3$ clusters, the highest percentages belong to HX-water interactions ($\sim 77\%$) and dissociated complexes (66%). Although the Zundel-like X-H-X interactions have a low percentage of occurrence (about 6%), leading to the same motif for the global minima, a cage-like geometry. Contributions increased in structures with halogen bond (about 12%), Zundel X-H-O type ($\sim 14\%$), Zundel (10%), and quasi-Eigen ($\sim 14\%$) cations. Finally, in $(HI)_3(H_2O)_3$ clusters, water $\cdots$ water and HX $\cdots$ water interactions decreased (about 29 and 62% , respectively). The percentage of dissociated structures is slightly lower ($\sim 61\%$) than those with bromine, but this is compensated by the increase of the special dissociated forms: quasi-Eigen ($\sim 18\%$), Zundel (11.5%), and Zundel I-H-I type ($\sim 9\%$). In this case, there are no Zundel-like I-H-O structures and the halogen interactions represent $\sim 59\%$ of the entire population. Another important remark is that the gap around q_1

= 0 in Figure 6 is decreasing from clusters with Cl to I, and for the latter, there are structures populating the whole range, including zero, which accounts for structures with bihalide ions being more symmetrical than those with bromine.

Summary and Outlook

The exploration of the PES for the microsolvation of hydrogen halides with more than one HX (X = F, Cl, Br, I) molecule reveals that it is viable to dissociate the hydrogen halides with few water molecules. Particularly, HCl is dissociated with three water molecules while HBr and HI only needed two. Since two water molecules may not be sufficient to dissociate a single hydrogen halide molecule, and the same number of water molecules do that in the presence of two HX molecules, strong cooperative effects are suggested. Intriguingly, for the stronger acids, bihalide anions (BrHBr^- and IHI^-) are formed. These fragments are persistent even at room temperature, indicating that at high acid concentrations, such species could be detected.

A diverse zoo of interactions and forms is found for $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters, such as water $\cdots$ water, HX $\cdots$ water, and HX $\cdots$ HX hydrogen bonds, halogen bonds, ionic and long-range X $\cdots$ H contacts, as well as quasi-Eigen, Zundel, and Zundel-like structures. The first three types are dominant in HF-water complexes and in going from F to I, these decrease to make way for the other types of interactions, so that the dissociated forms, although smaller in percentage, can become very important because they contain the global minimum, as is the case of Zundel-like structures.

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Acid dissociation in $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters

$(\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}; n = 2, 3)$

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Abstract

The interactions between two or three hydrogen halide molecules and the same number of water moieties are investigated through a systematic exploration of the corresponding potential energy surfaces using a stochastic methodology in conjunction with density functional theory computations. Our results indicate that HF, the weakest acid in the series, is partially dissociated. Similarly, HCl, HBr, and HI undergo dissociation in the presence of three, two, and two water molecules, respectively. The decrease in the number of water molecules required for dissociation, when compared with clusters with one single HX molecule, suggests cooperative effects. Interestingly, the hydrogen-bridged bihalide anions (XHX^-) are present in the global minimum of $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters with $\text{X} = \text{Br}, \text{I}$ and $n = 2, 3$. These anions are even persistent at room temperatures. Concomitantly, a broad spectrum of interactions is found, among them water $\cdots$ water, HX $\cdots$ water, and HX $\cdots$ HX hydrogen bonds, halogen bonds, ionic and long-range $\text{X}\cdots\text{H}$ interactions.

Introduction

Acid dissociation is a complex process affected by several factors, most prominently the environment and the strength of the proton-containing bond to be broken. In the aqueous phase, acidic strength is dictated by the pKa of the species in question. The hydrogen halide series covers a spectrum from the weak to the very strong acidity, as it is clear from Table 1. Interactions between hydrogen halides and water molecules are relevant because they participate in numerous biochemical and atmospheric reactions (Keese, 1989; Müller et al., 1992; Rokita, 1992; Peter, 1997; De Haan et al., 1999; Domcke and Sobolewski, 2003). Moreover, the involved processes, such as proton transfer, acid dissociation, and the interactions that stabilize HX-water complexes, epitomize some central questions in chemistry. The nature of the interactions escapes descriptions in simple terms, rather it is necessary to invoke a complex mixture of electrostatic, covalent, induction, and dispersion contributions, varying in relative weights.

Table 1. Acidic power and properties of the H-X bond in the hydrogen halide series. pKas for dissociation in aqueous environments, bond lengths in Å, and dipole moments in Debyes (Cotton and Wilkinson, 1988; Weast et al., 1989; Sato and Hirata, 1999).

Property	HF	HCl	HBr	HI
pKa	3.2	-7.0	-9.5	-10.0
Bond lengths	0.92	1.27	1.41	1.60
Dipole moment	1.8	1.1	0.8	0.4

Microsolvation studies of a single acid molecule with one or more water molecules have expanded our understanding of acid dissociation and, in some cases, have pinpointed

the number of solvent molecules needed to achieve the formation of the ion pair (Laasonen and Klein, 1994; Schindler et al., 1994; Lee et al., 1996; Ando and Hynes, 1999; Conley and Tao, 1999; Gertner et al., 1999; Cabaleiro-Lago et al., 2002; Devlin et al., 2002; Hurley et al., 2003; Voegelé and Liedl, 2003; Kuo and Klein, 2004; Odde et al., 2004; Gutberlet et al., 2009; Vargas-Caamal et al., 2016a). These studies correspond to ideal situations that do not account for crucial factors such as increasing acid concentration via the explicit addition of new molecules. Indeed, there are fewer reports about microsolvation of clusters with more than one acid molecule compared with those for a single molecule, and many of them are focused on HCl. For instance, Morrison *et al.* reported an infrared spectroscopy study of mixed $(\text{HCl})_m(\text{H}_2\text{O})_n$ clusters ($m:n = 1:1, 2:1, 2:2, \text{ and } 3:1$) immersed in helium nanodroplets (Morrison et al., 2010). They discussed infrared spectra in the HCl stretch region ($2600\text{--}2900\text{ cm}^{-1}$) and determined that the 2:2 cluster has a nonalternating cyclic arrangement (Figure 1a). Chaban and coworkers analyzed the $(\text{HCl})_2(\text{H}_2\text{O})_2$ and $(\text{HCl})_4(\text{H}_2\text{O})_4$ aggregates during their discussion on the transition from hydrogen bonding to ionization (Chaban et al., 2001). The hydrogen-bonded isomer of $(\text{HCl})_2(\text{H}_2\text{O})_2$ (see Figure 1b) is 6.9 kcal mol^{-1} lower in energy than the ionic one (Figure 1c), both with an alternating cyclic structure. Conversely, the 4:4 complex adopts a cubic form, where the full dissociated isomer is almost 16 kcal mol^{-1} more stable than the hydrogen-bonded one. The authors consider that the incorporation of anharmonic effects is a crucial factor for the prediction of reliable vibrational spectra and that cooperative effects in the solvation of hydrogen halides are extremely important.

Recently, Zakai *et al.* performed classical molecular dynamics simulations to illustrate the transitions between the H-bonded and ionic isomers of $(\text{HCl})_2(\text{H}_2\text{O})_2$ (Figure 1b and 1c) and of $(\text{HF})_4(\text{H}_2\text{O})_4$ (Zakai et al., 2017). They reported that proton transfers were fully concerted in all trajectories for $[\text{Cl}^-\cdots\text{H}_3\text{O}^+]_2$, whereas for $[\text{F}^-\text{H}_3\text{O}^+]_4$, the fully concerted

mechanism is dominant but partially concerted transfers of two or three protons at the same time also occur. The authors remarked that the high symmetry of the ionic and the H-bonded structures plays a key role in the collective propagation of the protons and cooperative effects.

Figure 1. Structure for $(\text{HCl})_2(\text{H}_2\text{O})_2$ clusters found here and reported in other works: a) H-bonded nonalternating cyclic form (Morrison et al., 2010), b) H-bonded alternating structure, and c) ionic arrangement (Chaban et al., 2001).

In order to investigate some important questions such as how many water molecules are required to onset dissociation and underline the cooperativity in hydrogen-bonded systems, we systematically explore the potential energy surfaces (PES) of $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters, with $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ and $n = 2, 3$. This work contributes to the understanding of the process of microsolvation of acids supported by a large variety of structures and interactions, ranging from hydrogen bonds of different strengths to halogen interactions. Perhaps, one of the most remarkable results is the stabilization of hydrogen-bridged bihalide (XHX^-) moieties in the global minimum of $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters with $\text{X} = \text{Br}, \text{I}$. We hope that the formation of hydrogen-bridged bihalide anions and the increasing relevance of the $\text{X}\cdots\text{H}\cdots\text{X}$ interactions in the heavier halogens found here stimulate new perspectives on the general subject of acid microsolvation.

Computational details

In order to systematically explore the PES of the $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters (with $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ and $n = 2, 3$), a modified kick algorithm as is implemented in the GLOMOS code was used (Grande-Aztatzi et al., 2014; Ramirez-Manzanares et al., 2015; Cabellos et al., Cinvestav Mérida, Yuc. México. 2013). This heuristic has been employed by us to explore the PESs of several molecular clusters (Grande-Aztatzi et al., 2014; Vargas-Caamal et al., 2015; Vargas-Caamal et al., 2016a; Vargas-Caamal et al., 2016b; Murillo et al., 2017). A hierarchical screening is established, the initial structures were optimized at the PBE0/D95V level and then refined at the PBE0-D3/def2-TZVP level (Weigend and Ahlrichs, 2005; Grimme, 2006; Grimme, 2011). Each structure was characterized as a true minimum by harmonic vibrational frequency analysis. All computations were done using the *Gaussian 09* (revision D.01) package (Frisch et al., Gaussian, Inc., Wallingford, CT. 2013). Temperature effects were analyzed using *Eyringpy* 1.0 (Dzib et al., 2019).

To examine the interactions, Wiberg bond indices (WBI) (Wiberg, 1968) were computed. Stern-Limbach (Limbach et al., 2009) plots were used to correlate the symmetry and length of hydrogen bonds. In these plots, q_1 measures the displacement of the proton from the center in idealized linear hydrogen bonds, while q_2 quantifies the distance between the two electronegative atoms (see Figure 2 for definition of variables). For hydrogen bonds involving equally electronegative atoms, $q_1 = 0$ indicates the point at which the proton is equally shared by both atoms, while positive or negative values denote that one of the electronegative atoms in the hydrogen bond is more strongly bound to the proton.

Figure 2. Definition of hydrogen bond coordinates (Limbach et al., 2009), q_1 and q_2 . In our case, the A and B atoms are either oxygen or halogen. The large volume associated with the proton intends to suggest a high degree of delocalization.

Structures and Energetics

Table 2 contains the energy ranges and the number of structures obtained, which are 155 for the 2:2 systems and 815 for the 3:3 clusters, including enantiomers. As for other systems interacting with water molecules, the number and diversity of structures is huge in a relatively small energy range (Cabaleiro-Lago et al., 2002; Odde et al., 2004; Perez et al., 2008; Ramirez et al., 2011; Acelas et al., 2013; Vargas-Caamal et al., 2016a; Hadad et al., 2018).

Table 2. Number of structures and ZPE corrected electronic energies in kcal mol⁻¹ of the (HX)_n(H₂O)_n clusters.

	(HF) _n (H ₂ O) _n	(HCl) _n (H ₂ O) _n	(HBr) _n (H ₂ O) _n	(HI) _n (H ₂ O) _n
n = 2				
number of structures	18	24	45	68
ΔE _{ZPE}	12.3	13.8	13.6	12.2
n = 3				
number of structures	255	192	160	208
ΔE _{ZPE}	12.8	12.3	26.4	25.4

The lowest ZPE-corrected energy structures for each molecularity are presented in Figure 3. The most stable forms for the F and Cl clusters and $n = 2$ adopt a nondissociated H-bonded alternating structure, in agreement with previous reports (Chaban et al., 2001). In the case of the bromine 2:2 complex, the global minimum can be described as a dissociated H-bonded nonalternating cyclic form in such a way that there is a transfer of a hydrogen atom to generate a H₃O⁺ cation. The most beautiful structure is the global minimum of (HI)₂(H₂O)₂ (see Figure 3), in which the IHI⁻ anion and the hydronium cation coexist! This C_s structure is a transition state for bromine, and it is not detected for clusters with fluorine and chlorine. Conversely, for 3:3 clusters, the lowest ZPE corrected energy clusters adopt cage-like arrays, but again the hydrogen bihalide anions are also present in the Br and I systems. It is important to comment that for the (HF)₃(H₂O)₃ cluster, there is a planar hexagonal structure at less than 0.1 kcal mol⁻¹ from the putative global minimum, so both arrangements are degenerate.

Figure 3. PBE0-D3/def2-TZVP lowest energy structures for the $(\text{HX})_2(\text{H}_2\text{O})_2$ and the $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters.

Note that hydrogen bihalide anions are stabilized only for the stronger acids (HBr and HI). These anions are linear with a hydrogen atom placed between two halide atoms and form strong intramolecular hydrogen bonds (Jiang and Anderson, 1974; Emsley, 1980; Kemp and Gordon, 2010; Grabowski, 2016; Grabowski et al., 2016). Grabowski *et al.* studied the XHX^- anions as a way to compare the similarity between hydrogen and gold (Grabowski et al., 2016). Although their analysis was based exclusively on the anions and our clusters include anions, hydronium, and water molecules, it seems plausible to compare their computed X-H bond lengths (1.70 and 1.90 Å for Br-H and I-H, respectively) against our results. Thus, while the IHI^- anion in the $(\text{HI})_2(\text{H}_2\text{O})_2$ global minimum has an I-H bond length of 1.93 Å and it is symmetric, in 3:3 complexes there are differences between the $\text{X}\cdots\text{H}$ distances in transient

symmetry, with ranges between 1.65-1.78 and 1.87-1.97 Å for BrHBr^- and IHI^- , respectively. These asymmetries are due to the interactions with the solvent molecules (Pylaeva et al., 2017).

Kemp and Gordon conducted a study of $\text{BrHBr}^-(\text{H}_2\text{O})_n$ and $\text{IHI}^-(\text{H}_2\text{O})_n$ clusters with $n = 1$ to 6 in order to determine the preferred solvated structures (Kemp and Gordon, 2010). They found that for $n = 1, 2$, water molecules prefer to donate their hydrogen atoms for hydrogen bonding. Conversely, in this work, we started with neutral HX and H_2O and found the spontaneous formation of hydrogen bihalide anions!

Cooperativity

Leopold published a comprehensive review related to the dissociation of acids in aqueous environments, in which collects theoretical evidence about the number of water molecules needed to dissociate some simple acids, suggesting 4, 3, and 3 water molecules for HCl, HBr, and HI, respectively. For the case of HF, the acid is partially dissociated for $n > 7$. Remarkably, our computations indicate dissociation with just two (for HBr and HI) and three (for HCl) water molecules. This is, on one hand, consistent with the pKas listed in Table 1, and on the other hand, the decrease in the number of water molecules required for dissociation, when compared with clusters with one single HX molecule, suggests cooperative effects.

Cooperativity has been reported as an important effect in studies about acid ionization and hydration of ions (Tielrooij et al., 2010; Zakai et al., 2017). But even when cooperativity is one of those concepts that seems intuitively clear, it is not rigorously defined. Nonetheless, it seems generally accepted that it is related to non-additivity of the energy of individual contacts, thus, it implies that the total interaction energy of a system is larger than the simple

addition of the individual interactions. Several methods attempt to get a quantitative account of the cooperative effects by decomposing the interaction energy of a system of n bodies and by the inclusion of the many-body terms in the analysis (Dannenberg, 2002; Esrafil et al., 2011; Guevara-Vela et al., 2016; Mahadevi and Sastry, 2016). Here, just to illustrate cooperative effects, we take the total interaction energy of two structurally related geometries, that is, the same patterns of hydrogen bonds but with different sizes: the global minima for $(\text{HF})_2(\text{H}_2\text{O})_2$ and the planar hexagonal structure for $(\text{HF})_3(\text{H}_2\text{O})_3$ (see Figure 3), for those, total interaction energies are 32.2 and 54.0 kcal mol⁻¹, respectively, which afford 8.1 and 9.0 kcal mol⁻¹ per hydrogen bond, which clearly highlight the cooperative effects because if there were no cooperation, interaction energies per hydrogen bond would be the same.

Temperature Effects

Are these clusters stable at room temperature? The dissociation energies (ΔE_{diss}) of the $(\text{HX})_2(\text{H}_2\text{O})_2$ and $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters into water and HX are shown in Table 3. Clearly, all complexes are viable at 0 K with ΔE_{diss} in the range of 19.5-54.0 kcal mol⁻¹ and the 3:3 clusters require more energy to separate them than the 2:2 ones. The increase in temperature (or the increase of the entropic effects) causes havoc in the stability of the clusters, to such an extent that the dissociation into water and acid molecules tends to be exergonic for some of them at room temperature. This is consistent with the experimental evidence that the acid strength is inversely proportional to temperature for HF, HCl, and HBr aqueous solutions (Ayotte et al., 2005). From Table 1, it is also apparent that range (T_{max}) in which the complexes are viable depends on the molecularity and on the acid strength. Note that the hydrogen bihalide anions are persistent for the 3:3 systems even at room temperature.

Table 3. Dissociation energies, ΔE_{diss} , and free dissociation energies, ΔG_{diss} , (298.15 K and 1 atm) of the $(\text{HX})_2(\text{H}_2\text{O})_2$ and $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters into water and HX in kcal mol⁻¹, and maximum temperature (K) for stability of the $(\text{HX})_n(\text{H}_2\text{O})_n$ clusters.

	$(\text{HF})_n(\text{H}_2\text{O})_n$	$(\text{HCl})_n(\text{H}_2\text{O})_n$	$(\text{HBr})_n(\text{H}_2\text{O})_n$	$(\text{HI})_n(\text{H}_2\text{O})_n$
n = 2				
ΔE_{diss}	32.1	21.1	21.0	19.5
ΔG	8.4	-2.1	-3.4	-4.6
T_{max}	390	273	261	247
n = 3				
ΔE_{diss}	54.0	42.4	45.6	43.5
ΔG	12.9	-0.1	2.8	0.7
T_{max}	381	297	316	303

Bonding analysis

Wiberg bond index is a parameter related to the electron density shared between atoms, providing a reasonable quantification of bond order (Wiberg, 1968; Mayer, 2007). We provide in Figure 4 the distributions of the WBIs for $\text{H}\cdots\text{X}$ contacts for 2:2 and for 3:3 clusters. For both molecularities, most HF clusters fall in the 0.45-0.65 range, which denotes partial dissociation and just a few dissociated clusters are present for $n = 3$ (Figure 4b). For all the other acids, a clear separation between dissociated and undissociated complexes is noted. Dissociated/undissociated gaps are more defined for $n = 2$ than for $n = 3$. This is consistent with a greater variety of geometries and more advanced dissociation stages as n grows. The halogen atom also plays an important role because the difference between the

number of dissociated and undissociated groups is more evident in going from chlorine to iodine.

Figure 4. Wiberg bond indices (WBI) for the H–X interaction in a) $(\text{HX})_2(\text{H}_2\text{O})_2$, and b) $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters. Data taken from the PBE0-D3/def2-TVZP optimized geometries.

The Stern-Limbach plots for the $(\text{HX})_2(\text{H}_2\text{O})_2$ and $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters provide valuable complementary information about the interactions (see Figures 5 and 6). In general, the clusters exhibit two types of interactions between the hydrogen halide and water molecules, one by means of hydrogen bonds and the other through halogen bonds (see Figures 1-SI to 4-SI).

Figure 5. Correlation between q_1 and q_2 (See Figure 2 for definition of variables). Data taken from the PBE0-D3/def2-TVZP optimized geometries for the $(\text{HX})_2(\text{H}_2\text{O})_2$ clusters. Red squares indicate the lowest energy structure. Distances in Å.

The definition of q_1 and q_2 (Figure 2) corresponds to hydrogen bonding, however, large negative values of q_1 combined with large values of q_2 denote undissociated species with long $\text{A}\cdots\text{B}$ distances. These combinations of q_1 and q_2 are due to clusters with halogen interactions (see some examples on the left side of the Figures 5 and 6 for Cl, Br, and I) or to cases where the hydrogen atom of an undissociated HX molecule does not interact with another molecule, such as the examples on the left side of the Figures 5 and 6 for HF. In fact, no halogen bonds were formed for clusters with hydrogen fluoride, while the HCl, HBr and

HI clusters with halogen interactions had higher relative energies with respect to the global minima.

Figure 6. Correlation between q_1 and q_2 (see Figure 2 for definition of variables). Data taken from the PBE0-D3/def2-TVZP structures for the $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters. Red squares indicate the lowest energy structure. Distances in Å.

We now focus in the clusters with HX molecules exhibiting some degree of dissociation, say, those for which $q_1 > -0.8$. Unlike the plots of q_1 vs q_2 reported previously (Gonzalez et al., 2013; Vargas-Caamal et al., 2016a), there are now two curves according to the type of interaction, $\text{X} \cdots \text{H} \cdots \text{O}$ or $\text{X} \cdots \text{H} \cdots \text{X}$, the latter becoming increasingly important for

the heavier elements (Br and I) and three water molecules. The global minima are included in the plots to notice the type of interaction and are highlighted with red squares on the curves.

A detailed classification of the interactions and their percentages over the entire populations are given in Figures 5-SI to 7-SI. The assignment of interactions is based strictly on geometrical criteria. For $(\text{HF})_2(\text{H}_2\text{O})_2$, all the computed structures have hydrogen bonds as dominant interactions and dissociated structures are not present. The situation changes a little bit in $(\text{HCl})_2(\text{H}_2\text{O})_2$, where dissociated structures and halogen interactions rise to ~8% each one (see Figure 6-SI). For the $(\text{HBr})_2(\text{H}_2\text{O})_2$ clusters, the separation of curves corresponding to $\text{Br}\cdots\text{H}\cdots\text{O}$ and $\text{Br}\cdots\text{H}\cdots\text{Br}$ interactions is evident. Concomitantly, the number of structures with hydrogen bonds decrease (~73% for water-water and HX-water interactions), while those with dissociated forms and halogen bonds increase (~13% and 40%, respectively). The global minimum is located on the curve of $\text{Br}\cdots\text{H}\cdots\text{O}$ interactions and possesses a cyclic ion-pair geometry, which belongs to the Zundel-like form ($\text{X}\cdots\text{H}\cdots\text{O}$), which represent ~13% of population. For the iodine analogs, the percentages of water-water and HX-water interactions decrease to roughly 60% and the $\text{I}\cdots\text{H}\cdots\text{I}$ interactions become the most important since the global minimum belongs to this Zundel-type (notice that it is the only one structure of this category in Figure 6-SI), with the formation of a hydrogen bihalide anion (Zundel-like structure), supported by the fact that the global minimum is located at $q_1 = 0$, corresponding to the central-symmetric anion. Structures with halogen bond interactions increase considerably (almost 74%), while the Zundel-like $\text{I}\cdots\text{H}\cdots\text{O}$ structures decreases at ~9% compared with HBr-water clusters.

The zoo of forms found for the $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters is more diverse. The plot for HF (Figure 6) shows that the $\text{F}\cdots\text{H}\cdots\text{O}$ and $\text{F}\cdots\text{H}\cdots\text{F}$ curves are closer to each other. Hydrogen

bonds of the $F\cdots H\cdots O$ type are longer than $F\cdots H\cdots F$. The global minimum is undissociated (an alternating six-membered ring) and belongs to the type of HF-water hydrogen bonds, the dominant interaction ($\sim 95\%$, Figure 7-SI). The lowest energy dissociated form is a quasi-Eigen cation and has a relative free energy of $4.6 \text{ kcal mol}^{-1}$. There are no structures with halogen bonds, but some examples of dissociated (2.8%) and quasi-Eigen forms (2%) were found. F-H-O Zundel-like structures are 22.4% of the total. The gap between curves is more evident for the HCl species (Figure 6). Again, a reduction of hydrogen bond interactions (about 77% and 45% for HX-water and water-water interactions, respectively) and a significant increment of the dissociated complexes ($\sim 57\%$) are noted. The quasi-Eigen cations represent almost 10% of population (including the global minimum) and the structures containing Zundel-like cations is now present (about 5%), while Zundel-like Cl-H-O and halogen interactions contribute with ~ 5 and 1% , respectively. For the $(HBr)_3(H_2O)_3$ clusters, the highest percentages belong to HX-water interactions ($\sim 77\%$) and dissociated complexes (66%). Although the Zundel-like X-H-X interactions have a low percentage of occurrence (about 6%), leading to the same motif for the global minima, a cage-like geometry. Contributions increased in structures with halogen bond (about 12%), Zundel X-H-O type ($\sim 14\%$), Zundel (10%), and quasi-Eigen ($\sim 14\%$) cations. Finally, in $(HI)_3(H_2O)_3$ clusters, water $\cdots$ water and HX $\cdots$ water interactions decreased (about 29 and 62% , respectively). The percentage of dissociated structures is slightly lower ($\sim 61\%$) than those with bromine, but this is compensated by the increase of the special dissociated forms: quasi-Eigen ($\sim 18\%$), Zundel (11.5%), and Zundel I-H-I type ($\sim 9\%$). In this case, there are no Zundel-like I-H-O structures and the halogen interactions represent $\sim 59\%$ of the entire population. Another important remark is that the gap around $q_1 = 0$ in Figure 6 is decreasing

from clusters with Cl to I, and for the latter, there are structures populating the whole range, including zero, which accounts for structures with bihalide ions being more symmetrical than those with bromine.

Summary and Outlook

The exploration of the PES for the microsolvation of hydrogen halides with more than one HX ($X = \text{F, Cl, Br, I}$) molecule reveals that it is viable to dissociate the hydrogen halides with few water molecules. Particularly, HCl is dissociated with three water molecules while HBr and HI only needed two. Since two water molecules may not be sufficient to dissociate a single hydrogen halide molecule, and the same number of water molecules do that in the presence of two HX molecules, strong cooperative effects are suggested. Intriguingly, for the stronger acids, bihalide anions (BrHBr^- and IHI^-) are formed. These fragments are persistent even at room temperature, indicating that at high acid concentrations, such species could be detected.

A diverse zoo of interactions and forms is found for $(\text{HX})_3(\text{H}_2\text{O})_3$ clusters, such as water $\cdots$ water, HX $\cdots$ water, and HX $\cdots$ HX hydrogen bonds, halogen bonds, ionic and long-range $\text{X}\cdots\text{H}$ contacts, as well as quasi-Eigen, Zundel, and Zundel-like structures. The first three types are dominant in HF-water complexes and in going from F to I, these decrease to make way for the other types of interactions, so that the dissociated forms, although smaller in percentage, can become very important because they contain the global minimum, as is the case of Zundel-like structures.

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HX_n-H₂O_n-clusters_final.pdf (1.05 MiB)

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