Ab Initio Molecular Dynamics Study of a Mixture of HF(aq) and HCl(aq)[†]

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We have studied a mixture of HF and HCl molecules in water using Car−Parrinello ab initio molecular dynamics (CPMD). We have done simulations with 1 HF and 3 HCl molecules, 3 HF and 4 HCl, 6 HF and 8 HCl (6/8 simulation), and 14 HF molecules. All simulations consist of 32 molecules, and they were 10−96 ps long. The HF dissociation probability was around 30%, and HCl's was more than 90%. The solvation of the HF molecule was much better than the solvation of HCl. The solvation environment of F, both the F$^-$ ion and the F in HF, did not depend much on the acids concentration, whereas the Cl coordination numbers were rather sensitive to the concentration. In the 6/8 simulation, all XH−Y (X, Y = F, Cl) type molecules were observed and the FH−F was the most probable. In general, the molecular structures in mixed aqueous acid systems were similar to the pure HF(aq) and HCl(aq) systems.

1. Introduction

Hydrohalic acids are interesting acids. At low concentrations, the HCl, HBr, and HI molecules are all strong acids and they dissociate completely whereas hydrofluoric acid is a weak acid.[1] Low concentration HCl(aq) consists of well-solvated Cl$^-$ and H_3O^+ ions, but when the concentration of HCl increases, its dissociation becomes less easy. This is mainly due to the weakening of the solvation of the Cl$^-$ and hydronium ions, because there is less water to form solvation layers around the ions.[2,3] HF behaves differently, as mentioned earlier; at low concentrations, it is a weak acid, but when its concentration increases, it becomes a strong acid. The Hammett acidity increases rapidly around 50 mol % of HF.[4] This dramatic change of acidity of HF(aq) has been explained by the formation of $(HF)_n-F^-$ complexes where a proton has been easier to remove than from a HF molecule.[5−8] The equilibrium constant of HF + F$^-$ → HF$_2^-$ has been measured to be 5.1 (see ref 5) at concentrations below 6 mol kg^{-1}. The key difference between HF and HCl is that the HF molecule itself can take part in the solvation. Thus, the increase of HF does not reduce the solvation ability of the mixture, whereas in the case of HCl at some point all the water molecules are required for solvation of the Cl and hydronium ions.

The aqueous mixture of the HF and HCl is very interesting since it is not clear how the two acids will interact: how will the HF molecules solvate the Cl and hydronium ions, and what is the role of $(HF)_n-F^-$ complexes in such a mixture? Simultaneously, it will be interesting to see what happens to the HCl molecules. Will the HF molecules affect the dissociation of HCl molecules? Will there be mixed HF−Cl$^-$ or ClH−F$^-$ clusters? Can we say anything about the acidity of such a mixture? According to our knowledge, there is no experimental data for this system. Naturally, pure HF(aq) and HCl(aq) systems have been studied extensively.[4,5,9,10]

From the molecular modeling point of view, aqueous systems have been studied enormously. Recently also, ab initio molecular dynamics (AIMD) have been applied to aqueous systems. Pure water has been studied extensively both using Car−Parrinello MD (CPMD)[11−13] and path-integral AIMD.[14,15] Protons[15,16] and hydroxide ions have been studied.[17] Also, many other aqueous systems including various acids, especially HF,[18−22] HCl,[2,3,23] bases,[24] and ions[25] have been studied. Even the gas−water interface[26] can be simulated using CPMD. Also, many chemically important quantities, like pK_a[27] and redox potentials,[28] can be estimated using CPMD. Besides CPMD, there have been very many other theoretical studies of acids.[29,30]

2. Computational Details

All calculations reported here were done with the CPMD code (versions 3.7.2, 3.9.1, and 3.9.2).[31,32] The CPMD code describes the electrons using density functional theory (DFT) and the generalized gradient approximation (GGA). We used the PBE model of GGA.[33] This model was found to produce very similar results as the BLYP functional.[13] The core electrons have been replaced by pseudopotentials. We used the ultrasoft pseudopotentials by Vanderbilt.[34] In our simulations, all the hydrogens have been replaced with deuteriums. For simplicity in the discussion, we still use FH, HCl, etc. instead of FD and DCl, except in the part related to the frequencies. The Kohn−Sham wave functions have been expressed with plane waves, and the cutoff used was 30 Ry. In all simulations, the time step has been 5 au (= 0.124 fs) and the electronic effective mass was 500 au. The effective mass used is small enough that our deuterated simulations are not biased by the mass parameter.[13]

We have done several rather long CPMD simulations with different acid concentrations. In all simulations, there has been 32 molecules but the amount of HF and HCl has been varied. We have collected the different simulations in Table 1. Later, we refer to the simulations with the numbers of the acid molecules. The notation 1/3 means the simulation with 1 HF molecule, 3 HCl molecules, and 28 waters. All canonical simulations (NVT) used Nose−Hoover thermostats (the thermostat frequency was set to 100 cm^{-1}). In the microcanonical

TABLE 1: Simulations[a]

N(HF)/N(HCl)	length (ps)	type	temp (K)	code	density (g cm^{-3})
1/3	15	NVT	330	3.7.2	1.088
3/4	10.5	NVT	330	3.7.2	1.26
3/4	10	NVT	500	3.7.2	
6/8	55	NVT	350	3.9.1	1.28
6/8	20	NVE	320	3.9.1	
6/8	42	NVT	annealing[b]	3.9.2	
6/8	64	NVT	350	3.9.2	
14/0	22,34	NVT	350	3.9.1	1.09

[a] The systems have been identified by the number of acid molecules in them. The term 6/8 means that 6 HF and 8 HCl molecules have been used. In all systems, there are a total of 32 molecules. The length of the simulation was given in picoseconds. The simulations were either canonical (NVT) or microcanonical (NVE). In canonical simulations, the temperature was controlled using the Nose−Hoover thermostat. The code refers to the version of the CPMD code. The density is for a nondeuterated system. [b] Several heating and cooling cycles with a maximum temperature of 600 K.

simulation (NVE), the reported temperature was the average over the last 20 ps of the simulation. The longer 6/8 (98 ps) simulation was done with the CPMD code version 3.9.2. This simulation was a continuation of the earlier 6/8 (55 ps) simulation. This simulation had a 42 ps annealing part where a few heating cycles were done and the data was collected from the last 64 ps. Here, we focus on the last 6/8 simulation. The two shorter 6/8 simulations were only used for comparison.

We have also done two simulations of HF(aq). As in the other simulations, these systems had 32 molecules of which 14 were HFs. The simulation lengths were 22 and 34 ps. In this work, we do not go into the details of these simulations. They are used for comparison with the longer 6/8 simulation.

The choice of the lattice parameter of an acid mixture is rather complicated. Experimentally, the HCl(aq) densities are known in different HCl concentrations at 20 °C.[36] We did not find similar data for HF(aq), but its density is known at around 50% solution.[37] From these data, we can estimate the volumes per molecule at 20 °C. We used these values: HF, 25; HCl, 30; and H$_2$O, 29.9 Å^3. We also need to know the thermal expansion of the solutions. For this, we have used the values of pure water.[36] The side of the simulation box of the 1/3 simulation was 9.89 Å, which corresponds to a density of 1.088 g cm^{-3} (nondeuterated molecules). For the 3/4 simulation, the box side was 9.84 Å and the system density was 1.26 g cm^{-3}. In all the 6/8 simulations, the box side was 9.85 Å and the density was 1.28 g cm^{-3}. In the 14/0 simulations, the box side was 9.72 Å and the density was 1.09 g cm^{-3}. It is also known that GGAs such as BLYP will produce a water density value that is too low.[26] We have not taken this into account since the determination of the equilibrium lattice constant using CPMD is very time-consuming; thus, all the lattice parameters were chosen to reproduce the experimental lattice parameters.

Most of our results are based on the two long simulations, 6/8 (55 ps) and the last 64 ps part of the 6/8 (98 ps) simulation. It turned out that the acid mixture had long relaxation times compared to simulations of single acid systems. To ensure that the system really was liquid, we calculated the diffusion constant. The diffusion constant of both of the NVT 6/8 simulations was $0.75 \pm 0.1 \times 10^{-9}$ m^2 s^{-1}. This is similar to the diffusion constants that have been calculated for pure water using CPMD,[12] $D = 0.4 \pm 0.2 \times 10^{-9}$ m^2 s^{-1}, and our previous calculations of HCl(aq).[3] One should note that these values are significantly smaller than the experimental value of pure water

TABLE 2: Coordination Numbers of Various Atoms in the Different Simulations[a]

atom pair	cutoff (Å)	1/3	3/4	6/8	14/0	0/7
Cl−H	1.5	0	0	0.11 (0.26)		0.3[b]
Cl−H	2.8	4.8	4.6	3.5 (3.3)		
Cl−O	3.7	5.7	5.1	4.7 (3.9)		
Cl−F	3.1	0	0.25	0.06 (0.28)		
F−F	2.8		0	0.68 (0.12)	0.75	
F−H	1.25	1	0.66	0.67 (0.72)	0.66	
F−H	2.3	2.6	2.9	2.7 (2.7)	2.8	
F−O	3.0	2.7	2.7	2.2 (2.4)	2.1	
O−H	1.25	2.13	2.23	2.60 (2.50)	2.41	
O−O	3.0[c]	2.69	2.21	1.07 (1.30)	1.43	

[a] The total coordination number with a given cutoff has been divided by the number of the first atom type. The systems have been identified by the number of acid molecules in them. The term 6/8 means that 6 HF and 8 HCl molecules have been used. In the 6/8 system, the old simulation results are in parentheses. [b] From ref 3. [c] In the case of OO, the minimum of the pair correlation varies quite a lot. The minimum and the corresponding coordination numbers were 3.2 Å, 3.2 (1/3); 3.15 Å, 2.6 (3/4); 3.0 Å, 1.3 (old 6/8); 2.85 Å, 0.9 (new 6/8); and 3.15 Å, 1.6 (14/0).

(3.5×10^{-9} m^2 s^{-1}, 318 K);[35] thus, the GGAs used seem to underestimate the diffusion.

We also calculated small FH−X$^-$ (X = F, Cl) type molecules in the gas phase and compared these results to Gaussian 03 (G03) to rule out any serious errors in the pseudopotentials, GGAs, or CPMD code used. In the Gaussian program, the PW91 GGA was used and the basis set was aug-cc-pVTZ. In CPMD, the molecules were put into a cubic box with a side length of 9 Å. All calculated results were very similar. In the gas phase, the FH−F$^-$ molecule was 85.90 (G03) or 82.67 kJ mol^{-1} (CPMD) more stable than the FH−Cl$^-$.

3. Results

We first focus on the lower concentration, 1/3 and 3/4, simulations.

3.1. Low Concentration Simulations, 1/3 System. The 1/3 simulation was started by randomly replacing some of the water molecules with HF or HCl. After this, an equilibration of 2 ps and a simulation of 10 ps with the wrong proton mass (12 amu) were performed. This simulation was followed by a simulation of 15 ps with the correct masses. Only the last data was used for analysis although the 10 ps simulations with the wrong proton mass produced essentially the same structural results. The total diffusion constant in the 15 ps simulation was $0.7 \pm 0.2 \times 10^{-9}$ m^2 s^{-1}.

In the 1/3 system, all HCl molecules dissociated and the Cl ions were well-solvated by water molecules. The Cl ions had an average of 4.8 hydrogens around them (cutoff 2.8 Å) and 5.7 oxygens (cutoff 3.7 Å[38]). These coordination numbers are in good agreement with the work of Heuft and Meijer.[39] The coordination numbers from all the simulations have been collected in Table 2. We did not observe any molecules or ions containing Cl or F atoms in the first solvation shell of Cl; thus, the Cl ions were mainly solvated by water or hydronium molecules. The HF molecule did not dissociate. It had 2.6 hydrogens near it (cutoff 2.3 Å, including its own hydrogen), and its first solvation shell contained only hydrogens and oxygens. The first solvation shell was asymmetric, and the FH−O bond was shorter (F−O distance ca. 2.4 Å) than the two OH−F bonds (F−O distances ca. 2.6 Å).

The total OH coordination number in the whole system was 59.7 (cutoff 1.25 Å). This means that there were in total 3.7 hydronium ions. Three of these extra protons come from the

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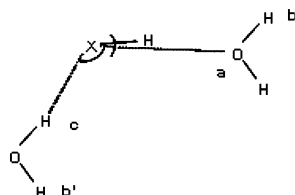
Figure 1. Schematic view of the different types of hydrogen bonds to the XH-molecule. The coordinate system for the projections in the following figures was defined as follows. The origin is at the heavy atom X, and the angles were defined by the (covalent) XH vector and, e.g., the XH (c) or XO (a) vectors. Thus, for example, small angles θ correspond to the space in front (H-side) of the molecule.

TABLE 3: Coordination Numbers of Various Bonds in Two Regions of Space[a]

system	bond	region	O	F	Cl	H	region	H
1/3	F−H	front	1.00		0.00	2.02	back	1.84
	O−H (H₂O)		0.70	0.03	0.26	1.47		1.75
	O−H (H₃O⁺)		0.83	0.07	0.10	1.90		0.14
3/4	F−H	front	0.50	0.00	0.51	1.36	back	1.90
	O−H (H₂O)		0.50	0.14	0.37	1.29		1.56
	O−H (H₃O⁺)		0.73	0.14	0.14	1.86		0.18
6/8 (old)	Cl−H	front	0.20	0.23	0.74	1.17	back	0.65
	F−H		0.55	0.06	0.39	1.39		1.55
	O−H (H₂O)		0.20	0.26	0.52	0.80		1.41
	O−H (H₃O⁺)		0.34	0.30	0.38	1.17		0.10
6/8 (new)	Cl−H	front	0.31	0.09	0.77	1.28	back	0.65
	F−H		0.37	0.59	0.05	1.63		1.57
	O−H (H₂O)		0.13	0.20	0.65	0.59		1.32
	O−H (H₃O⁺)		0.26	0.28	0.48	1.01		0.08

[a] Front corresponds to the region of $r < 3.5$ Å and $\theta < 40°$, for FH and OH and to $r < 4.0$ Å for HCl. The back region was $r < 2.4$ Å and $70° < \theta < 140°$, for all the bonds. In the 6/8 system, both the old and new simulation results have been reported.

HCls, and the 0.7 proton was shared with HF. This was possible because the F(H)−O distance was very small. Qualitatively, the bonding environment was similar to that in ref 3 or the higher concentration 6/8 simulation. The hydroniums were strongly bonded to oxygens or fluorine with O−O or O−F distances of 2.4−2.5 Å. Occasional bonding to chlorines was seen at bond lengths of ca. 3.0 Å. Similar Cl−hydronium bonding was seen by Heuft and Meijer.[39]

We also analyzed the bonding environment of the X−H (X = O, F) bonds. The coordinate system is shown in Figure 1. We defined the front region of the bond with $r < 3.5$ Å and $\theta < 40°$. The back region was $r < 2.4$ Å and $70° < \theta < 140°$. We have collected the amount of different atoms in these regions in Table 3. As one can see, even with this rather low Cl concentration, already 26% of the water OH groups were bonded to chlorines. Here, 90% of hydronium OH groups were bonded to oxygen or fluorine and only 10% were bonded to chlorines. The OH−Cl bonding difference between water and hydronium is interesting. It means that the Cl was better solvated with water than with hydronium.

This 1/3 system is a good example of an ideal acid system. There was enough water to solvate both the Cl and hydronium, and the HF role as solvent was not important. Most of our data here is in agreement with the previous HCl(aq) simulations.[3,39]

3.2. Low Concentration Simulations, 3/4 System. The 3/4 system was prepared in the same way as the 1/3 system. It was equilibrated at 500 K for 10 ps. Then, the system was cooled to 330 K and run for 10.5 ps. This data was used for the analysis. The total diffusion constant of this system was $1.3 \pm 0.2 \times 10^{-9}$ m² s⁻¹.

In the 3/4 system, all HCl molecules dissociated and the Cl ions were well-solvated by water and HF molecules. The Cl

ions had an average of 4.6 hydrogens around them (cutoff 2.8 Å) and 5.1 oxygens (cutoff 3.7 Å). The total heavy atom coordination number of Cl was 5.4 since a clear Cl−F pair was found with a Cl−F distance of 2.8 Å. The Cl−F pair was a FH−Cl⁻ complex. The hydrogen bonding to F and Cl in the FH−Cl⁻ complex was similar to the other F and Cl atoms. The Cl had an average of 4.65 hydrogens around it (cutoff 2.8 Å), and the F had 2.2 hydrogens within 2.3 Å. On average, only one of the HF molecules was dissociated. In the whole simulation, there were 2.0 hydrogens within 1.25 Å from the fluorines and 8.77 hydrogens within 2.3 Å. The HF molecules solvated with waters were not "stable", but they can borrow their proton from a neighboring water whereas the HF bonded to a Cl⁻ ion was stable for the whole simulation. The total OH coordination number was 55.7 (cutoff 1.25 Å). Thus, there were 5.7 hydronium ions (and 19.3 waters) in this system. Four of these protons come from the HCls, and the remaining 1.7, from the HFs.

As before, we analyzed the bonding environment of the X−H (X = O, F) bonds (Table 3). A significant fraction, 37%, of the waters' OH groups were bonded to chlorines. Also, 86% of the hydroniums' OH groups were bonded to oxygen or fluorine, and only 14% were bonded to chlorines. Also in this case, the Cl was better solvated with water than with hydronium.

3.3. 6 HF, 8 HCl Simulations. Several "different" 6/8 systems were prepared. One was started from the 3/4 simulation where seven waters were replaced by HF or HCl. This system was equilibrated for few picoseconds and the production run was done without thermostats. This simulation was 20 ps long, and the average temperature was 320 K. Another system was started from water coordinates and some of the water molecules were changed to HF or HCl. This system was equilibriated for 5 ps at 350 K, and then, a production run of 50 ps was done at 350 K. The third 6/8 system was prepared by heating and cooling the previous run a few times. The highest temperature used was 600 K. The total length of this annealing cycle was 42 ps. After this, a productions run of 64 ps was done. Most of our analysis and discussion are based on this last simulation. This last system is probably more reliable than the previous simulations since it was produced with a relatively long annealing cycle. The total energy was also slightly lower than in the first NVT simulation. The energy difference was 27.6 kJ mol⁻¹ for the whole system and 0.337 kJ mol⁻¹ per atom. In all of the 6/8 simulations, the simulation box side was 9.85 Å, which corresponds to a density of 1.289 g cm⁻³ (nondeuterated density).

3.3.1. Structural Data, Cl Environment. The 6/8 system is quite complex, and we first analyze it from the point of view of the atom types. The system contained eight HCl molecules of which a majority are dissociated. On average, there were only 0.93 undissociated HCl molecules, yielding a dissociation ratio of 88%. The dissociation of HCl can be compared to our previous HCl(aq) simulations.[3] In both the 0/7 (340 K) and 0/10 (330 K) simulations, 70% of the HCls dissociated so the dissociation in the mixed system was more probable. The Cl ions had an average of 3.5 hydrogens around them (cutoff 2.8 Å) and 4.7 oxygens (cutoff 3.7 Å). Both of these numbers were slightly lower than in the lower concentration simulations. The lower hydrogen coordination number around the Cls was partly due to the undissociated HCl. The HCl molecule had only ca. 1.6 hydrogens around it (this includes the HCl's hydrogen), whereas the Cl⁻ ions had ca. 3.8 hydrogens around them. This phenomenon has been observed also in our previous simulations.[2,3] We also calculated a 2-dimensional projection of the
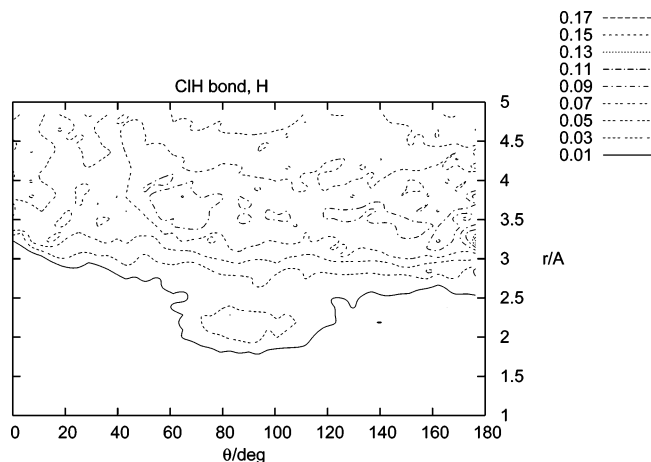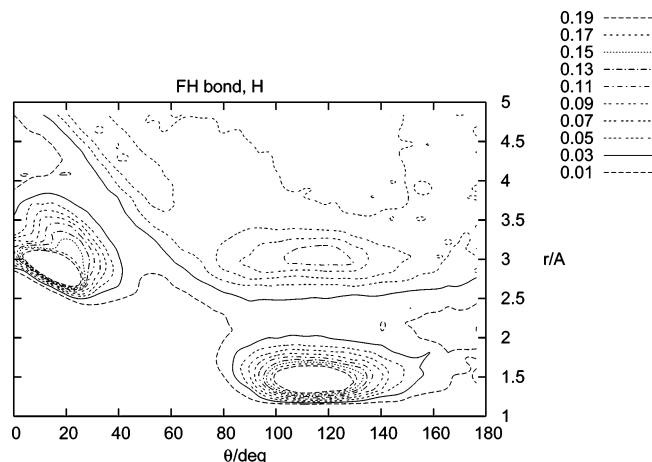
Figure 2. Projection of (θ, r) of hydrogens around the HCl molecule. See also Figure 1. The HCl molecule exists if a single proton is within 1.5 Å from the Cl. As one can see, there is not much structure in the hydrogen distribution around the HCl. There are some hydrogen bonds to the HCl around $r = 2$ Å, $\theta = 90°$, and some hydrogens can be detected in the front of HCl, around $r = 3.5$ Å, $\theta = 20°$.

Figure 3. Projection of (θ, r) of hydrogens around the HF molecule. The coordinate system was defined as in Figure 1. The HF molecule exists if a single proton is within 1.25 Å from the F. As one can see, there is much more structure around HF than around HCl. In this figure, the highest contour values were not shown for clarity.

bonding environment of all the X−H (X = O, Cl, F) bonds. The coordinate system is defined in Figure 1. This is a useful tool for visualizing the angular dependencies in bonding. The proton distribution around the HCl molecule is shown in Figure 2. There are some hydrogen bonds to the HCl molecule around $r = 2$ Å, $\theta = 90°$ (type c in Figure 1), but overall, the hydrogen distribution profile is rather flat. This peak contains only 0.65 hydrogens, whereas in the case of HF the same peak contained 1.57 hydrogens. We have collected the peak integrals of various atoms in Table 3.

The lower oxygen and hydrogen coordination number around Cl was due to the lack of water in the system. A significant proportion (55%) of all the OH groups (66% in the case of water and 47% in the case of hydronium) were bonded to Cls, and very likely, it was not possible to arrange the waters and hydroniums to make the coordination higher. In principle, the HF molecules could have participated in the Cl solvation, but the amount of fluorines in the first solvation shell was very small, 0.06. Thus, Cl was mainly solvated with water. The hydronium also had an important role. The same analysis for the Fs around Cl in the earlier 6/8 simulation yielded a coordination number of 0.28 which is much higher than in the later simulation. Although we consider the later simulation more reliable, we cannot exclude Cl solvation by HF, but its role in both simulations is small.

3.3.2. Structural Data, F Environment. Most of the HF molecules did not dissociate. The average amount of molecular HF was 4.0, and the dissociation ratio was 67%. This dissociation number varies quite a lot during the simulation, and we see this as an indication that the simulations are long enough to sample HF breaking.

As in the case of HCl, we have also computed the 2-dimensional projection of the hydrogens around the HF molecule (Figure 3). Compared to HCl, there is much more structure around the HF molecule. There is a very clear peak at $r = 3.0$ Å and $\theta = 10°$ which arises from protons of water molecules' acceptor hydrogen bonded to HF (type b in Figure 1). This peak contains 1.63 hydrogens (Table 3.). Since the number is less than 2, there is often a halide in this position instead of a water molecule. The second very clear peak at $r = 1.5$ Å and $\theta = 120°$ contains 1.57 hydrogens and comes from the donor hydrogen bonds to HF (type c in Figure 1). Note that the
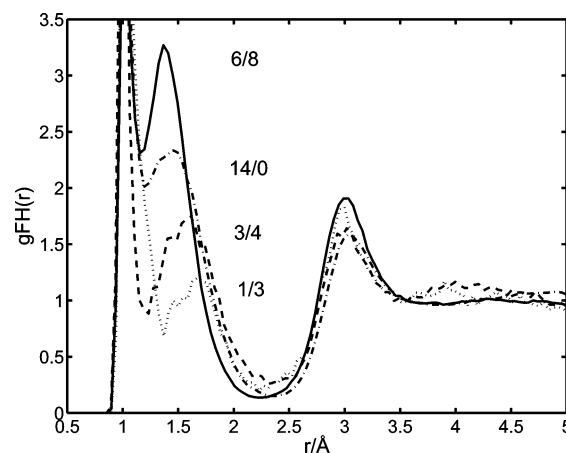
Figure 4. FH radial pair distribution functions. The $g_{FH}(r)$ of the 1/3 (15 ps), 3/4 (12 ps), 6/8 (50 ps), and 14/0 (25 ps) simulations are shown.

hydrogens come very close to the fluorine. This is due to the hydronium ions bonding to HF. The third peak at $r = 3.0$ Å and $\theta = 110°$ comes from the other hydrogens of the hydrogen bonded H_2O and H_3O^+ molecules (type b′).

We have also done simulations of pure HF(aq) with the same acid concentration as in the 6/8 simulation. These simulations were 14/0 (35 ps) and 14/0 (22 ps). Here, we report data of the longer simulation. Also in this simulation, there were undissociated HF molecules. There were an average 9.3 HF molecules, or 66% of the HF molecules were undissociated. Thus, the dissociation ratio was very close to the total dissociation in the HF/HCl simulation.

From the pair correlation functions, we have examined the $g_{FH}(r)$. In Figure 4, we have plotted the $g_{FH}(r)$ of the three HF/HCl simulations and the 14/0 simulation. It is clear that the second peak height is sensitive to the acid concentration. Also, the peak position shifts to smaller distances. In the 1/3 simulation, this peak is rather low, ca. 1.2, and 1.7 Å away from F. In the 3/4 simulation, the peak height is 1.7 and the maximum is at 1.6 Å. In 14/0 simulation, the peak height is 2.2 and the maximum is at 1.5 Å. In the 6/8 simulation, the height is 3.3 and the maximum is at 1.4 Å. We found that the peak height correlated better with the hydronium ion concentration of the system than with the acid concentration. The ratio of the hydronium concentration and the peak height was close

to 0.3 at all acid concentrations. Although the peak height was sensitive to the hydronium ion concentration, the coordination number (the peak integral to the second minimum) was not. The hydrogen coordination numbers using a 2.3 Å cutoff were: 2.6 (1/3), 2.9 (3/4), 2.7 (6/8), and 2.8 (14/0).

The interpretation of the F−H coordination numbers is a bit complicated. In the lowest concentration, the HF molecule did not dissociate and, thus, the coordination reflects the solvation of a HF molecule. In the other simulations, part of the HF molecules dissociated and the coordination number is an average of HF molecules and F⁻ ions. In the 6/8 simulation, there were an average 2.0 F⁻ ions but none of the F atoms remained as an ion for the whole simulation. Somewhat surprisingly, the differences in FH and F⁻ coordination was not large. The F⁻ ion hydrogen coordination number was ca. 3.1, and the FH molecule coordination number was ca. 2.6. It is also interesting to note that the FH molecules belonging to the FH−Cl complexes had only a slightly lower hydrogen coordination, 2.45, than the other HF molecules. Compared to HCl, HF solvation is very different. The HCls had only 1.6 hydrogens around them, and the hydrogen solvation environment had very little structure.

To summarize, the hydrogen coordination number around the F⁻ and HF was quite similar and the coordination numbers were very similar in the different simulations; however, the solvation shell around the F was more compact in the higher concentration systems and, thus, the second peak in the pair correlation functions was higher.

3.3.3 Structural Data, O Environment. From the oxygen point of view, the most interesting quantity is the amount of hydrogens around it. The average hydrogen coordination number was 2.60 (cutoff 1.25 Å). This means that more than half of the waters were hydronium ions, H_3O^+. There were 10.8 "extra" protons around the oxygens. These protons came from the dissociated HCl and HF molecules. The HCl molecules relieved 7.1 protons, and the HFs, 2.0, for a total of 9.1 protons. The difference between this value and 10.8 was due to double counting protons in very tight FH−OH_2 and $O_2H_5^+$ groups. It is interesting to compare this number to the pure HF(aq) simulation, where the OH coordination number was 2.41 and there were 7.4 extra protons. In this system, the HF molecules relieved only 4.8 protons. The number of extra protons was smaller than in the mixture simulation; thus, the mixture is more acidic.

Another quantity that is sensitive to the hydronium concentration was the OO pair correlation function. Its first peak was around 2.68 Å in the 1/3 simulation, 2.50 Å in the 14/0 simulations, and 2.45 Å in the 6/8 simulation. The last very short O−O distance is in agreement with a high concentration of hydronium ions. Also, the O−O distance was shorter in the 6/8 simulation which had a higher hydronium concentration than in the 14/0 simulation. The O−O coordination numbers were very sensitive to the acid concentration (Table 2.). In the 6/8 simulation, there was only one oxygen in the oxygen's first solvation cell. This does not mean that the oxygens would make linear structures but that the first solvation cell is dominated by the other ions. In the 6/8 simulation, there were roughly 1 O, 2 Cl, and 1 F molecule(s) in the first solvation cell.

Another interesting pair correlation function is the OH one. In Figure 5, we have plotted the $g_{OH}(r)$ of the four simulations. As in the case of $g_{FH}(r)$, the second peak was very sensitive to the hydronium concentration. In the 1/3 and 3/4 simulations, this peak was clearly separated from the covalent OH peak. In the 6/8 simulation, the second peak joins the first peak and forms only a very shallow shoulder. Thus, there was very little
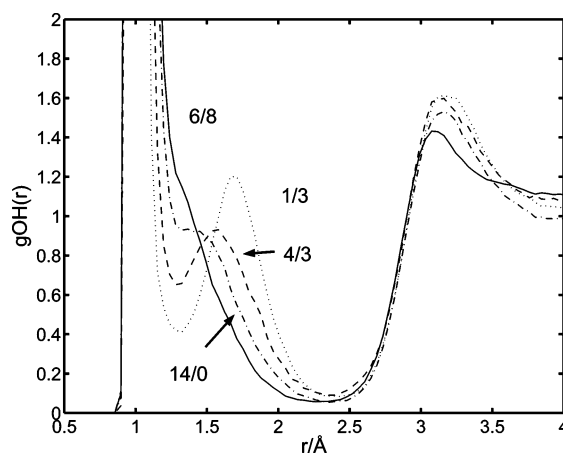
Figure 5. OH radial pair distribution functions. The $g_{OH}(r)$ of the 1/3 (15 ps), 3/4 (12 ps), 6/8 (50 ps), and 14/0 (25 ps) simulations are shown.
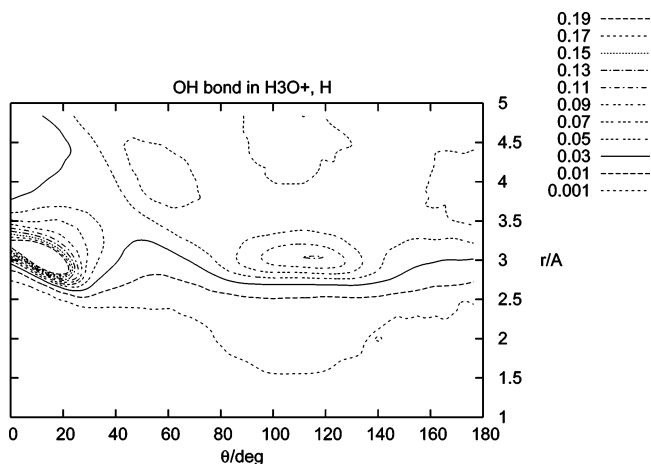
Figure 6. Projection of (θ, r) of hydrogens around the OH bond of a hydronium molecule. The coordinate system was defined as in Figure 1, and the hydronium molecule existed if three protons were within 1.25 Å from the O. The hydronium's own hydrogens were excluded from the plot. The main peak is at the front of the OH bond ($r = 3.0$ Å, $\theta = 20°$), and there are no hydrogens pointing toward the hydronium's oxygen. In this figure, the highest contour values were not shown for clarity.

differences between the covalent OH distance in H_2O/H_3O^+ and the hydrogen bonded XH···O distance. This was also seen in the O−H−O free energy plot which exhibited a very small (1.4 kJ mol⁻¹) barrier for the proton transfer (more details of the free energy plot are in the next section). The $g_{OH}(r)$ from the 14/0 simulation shows a small side peak around 1.5 Å.

As in the case of HCl and HF, we have also computed the 2-dimensional projection of the hydrogens around the OH-bond of hydronium molecules (Figure 6). The hydronium data can be compared to the HF (Figure 3). There is one very clear peak at $r = 3.0$ Å and $\theta = 10°$ which arises from the protons of water, HF, or hydronium molecules bonded to the hydronium (type b in Figure 1). The second peak at $r = 3.0$ Å and $\theta = 110°$ comes mostly from the same hydrogens but relative to another OH-bond in the hydronium ion. With very low contour values, we saw a weak hydrogen bonding at around $r = 2$ Å and $\theta = 110°$ to the hydronium oxygen. This corresponds to the "capping hydrogen" above the hydronium plane.[30,3] The integral of this peak amounts only to 0.08 hydrogens. The main peak ($r = 3.0$ Å, $\theta = 10°$) of hydronium contains 1.01 hydrogens, and the same peak calculated for water OHs contains only 0.59 hydrogens. These are interesting results since if the OH groups would have been bonded only to waters there would

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be 2 hydrogens in front of the them. The lower numbers mean that a significant amount of waters and a large part of the hydroniums are bonded to FH, F$^-$, and Cl$^-$. The same conclusion can be drawn from the integrals of OH bonding to heavy atoms (O, F, Cl) (Table 3).

3.3.4. Structural Data, XH$-$Y (X, Y = F, Cl) Pairs. A more detailed analysis of the X$-$Y (X, Y = F, Cl) pairs turned out to be very interesting. First, all XYs were hydrogen bonded, e.g., there was a hydrogen between them. So, they were in fact XH$-$Y type pairs.

We first concentrate on the FH$-$X, X = F, Cl, O, pairs. The HF molecules were associated to FH$-$O, FH$-$Cl, and FH$-$F complexes. The average numbers of these were ca. 2, 0.5, and 2.0, respectively. It was rather difficult to determine the number of FH$-$O complexes, due to the fast fluctuation between the FH$-$O and F$-$HO structures. The latter structure was difficult to distinguish from other F$-$HO bonds. Also, the F$-$HO structures were more common than the FH$-$O structures. The probability of H at the F$-$H$-$O bond gives the ratio of F$-$HO and FH$-$O structures to be roughly 7:1. Although the FH$-$O number is a bit uncertain, the interesting observation is the importance of the FH$-$F structures.

The FF distance in the FH$-$F$^-$ molecules was 2.35 Å, which is very close to the gas-phase value of FH$-$F$^-$, 2.32 Å. Unlike the gas phase, where the proton is exactly in the middle of the fluorines, in solution, the proton is mostly on one side of the molecule. The FH distances are typically 1.02$-$1.1 and 1.25$-$1.35 Å. The proton free energy profile showed a maximum of 1 kJ mol^{-1} at the middle of the FF bond. We found occasionally (FH)$_2$ type dimers. The ratio of (FH)$_2$ to FH$-$F type structures was a few percent. This small probability would suggest that the energy difference between (FH)$_2$ and FH$-$F is around 10 kJ mol^{-1}. It was interesting to note also that Braddy et al. mentioned the role of HF dimers in their potentiometric study of HF(aq), but they did not quantify the HF dimer concentrations.[5]

It is interesting to compare the FH$-$F molecules in the mixed acids and pure HF(aq) simulations. In the pure HF(aq) simulation, there were an average of 9.3 HF molecules or 66% of the HF molecules were undissociated. So, the dissociation ratio was very close to the mixed acid simulation. The number FH$-$F pairs were also similar. There were 5.2 such pairs in the pure HF(aq) simulation, or 74% of the fluorines were bonded to these pairs. In the HF/HCl simulation, there were 2.0 FHF pairs and 2.5 FHX (X = F, Cl) pairs. Also, 75% of all fluorines were bonded to the FHX pairs.

In the FH$-$Cl complex, the hydrogen prefers to be on the F side of this complex. This can be seen in Figures 7 and 8. Figure 7 shows the F$-$Cl, F$-$H, and Cl$-$H distances of one the Cl$-$H$-$F molecules. In the first half of the simulation, the proton is bonded to F. Around 15 ps, the proton will jump to the Cl side but return to F after ca. 2 ps. Around 24 ps, the proton again jumps to the Cl (and stayed there) and the Cl$-$F bond breaks. The ClH$-$F bond reforms around 30 and 49 ps but is not as stable as the FH$-$Cl form. Figure 7 shows only one example of the Cl$-$F pair, but analyzing them all allows for the computation of the proton probability distribution $P(x)$. The details of this analysis can be found in ref 3. A more informative quantity than the probability distribution is the effective Helmholz free energy associated with the proton position,

$$\Delta F(q) = -RT \ln\left(\frac{P(q)}{\max(P(q))}\right) \tag{1}$$

where q is the asymmetric stretching coordinate $q = r_{FH} - r_{ClH}$
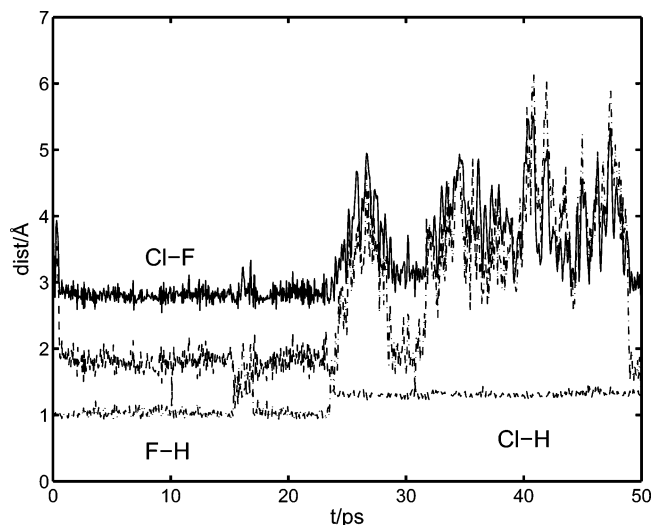
Figure 7. F$-$Cl, F$-$H, and Cl$-$H distances (in Å) of one of the Cl$-$F pairs. In the first half of the simulation, the proton was bonded to the F. Around 15 ps, the proton jumped to the Cl side but returned after 2 ps. At 23 ps, the proton moved to the Cl. The HCl molecule was bonded to F only around 30 ps and after 48 ps.
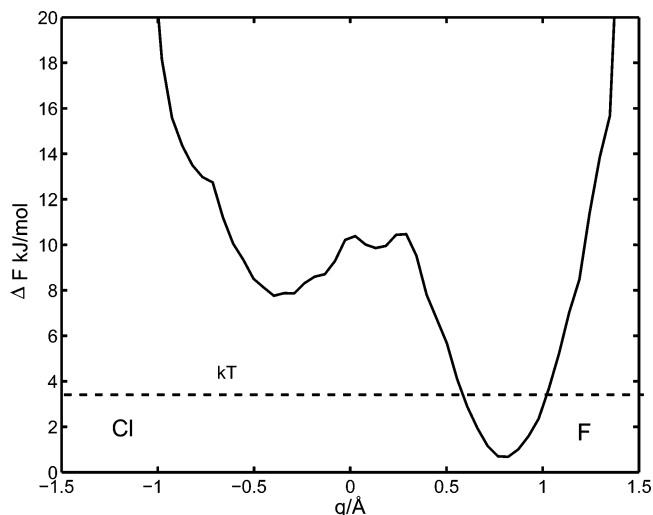

Figure 8. Helmholtz free energy profile of a proton in the Cl$-$H$-$F molecule. Cl is on the left side of the graph.

(for a F$-$Cl pair), R is Boltzmann's constant, and T is the temperature. As can be seen from Figure 8, the protons are more likely to be around the Fs. The barrier is around 10 kJ mol^{-1}, and the minimum in the Cl side is 7 kJ mol^{-1} higher than in the F-side. The lifetime of a FH$-$Cl complex was quite long, up to 20 ps. None of the FH$-$Cl complexes were stable over the whole simulation. Note that this analysis was done from the older 6/8 run; the new run revealed similar results but the statistic was poorer.

As observed in the 3/4 simulations, the hydrogen bonding to the F and Cl in the FH$-$Cl$^-$ complex was similar to the other F and Cl atoms. In this simulation, the Cl$^-$ (in FH$-$Cl$^-$) had an average of 3.6 hydrogens around it, which is close to the overall Cl$-$H coordination in this simulation, 3.5, and it is between the HCl coordination, 1.6, and the Cl$^-$ coordination, 3.7. The F (in FH$-$Cl$^-$) had 2.45 hydrogens within 2.3 Å, which is a bit below the average.

In this simulation, the previously seen ClH$-$Cl$^-$ molecules were rather difficult to find since the Cl$-$Cl pair correlation function did not have any clear first peak. Using a cutoff of 3.5 Å, we found on average 0.9 ClH$-$Cl$^-$ complexes. The undis-
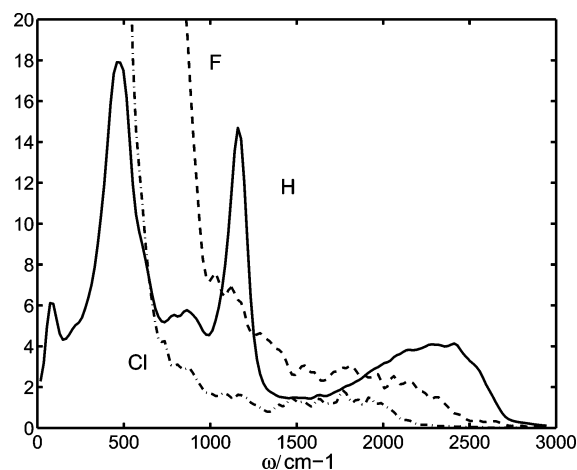
Figure 9. Computed total frequency spectra calculated as the Fourier transformation of the velocity−velocity autocorrelation function. The spectrum has been computed from the hydrogen, fluorine, and chlorine atoms of the 6/8 (350 K) simulation. The heavy solid line is the hydrogen spectrum, the dashed line is the F spectrum, and the dash−dotted line is the Cl one. The F and Cl spectra have been scaled by factors 10 and 20, respectively.

sociated HCl molecules were mostly (77%; see Table 3) associated with the ClH−Cl⁻ complexes. The lifetime of a ClH−Cl⁻ complex was quite long, 5−10 ps.

There were, in total, 3.4 XH−Y (X, Y = F, Cl) pairs. This can be compared to the pure HF(aq) simulations which had 5.2 FH−F pairs. So in the mixed simulation, there were less XH−Y pairs. This is mostly due to the low number of the ClH−Cl complexes, since the fluorines were bound to the FH−X structures in a similar manner in both the last 6/8 and 14/0 simulations.

3.3.5. Other Analysis. To estimate the variations of results in our last simulation, we divided the trajectory into four pieces and did part of the analysis to these separated pieces. All data related to the structural properties were well-converged. But as expected, the diffusion coefficients had rather large variations, the total diffusion constant varying with factor of 2. We performed similar analysis presented here also to the older 6/8 (NVT) and 6/8 (NVE) simulations. The results of these two simulation were very similar, and the main difference in the latest 6/8 simulation was the formation of the FHF complexes and the disappearance of the FHCl complexes.

We also calculated the total frequency spectrum as the Fourier transformation of the velocity−velocity autocorrelation function. The deuterium spectrum was very similar to the previously calculated HF(aq) spectrum, but the fluorine and chlorine spectra are interesting since they showed small maxima or shoulders at around 2000 and around 1800 cm⁻¹, respectively (see Figure 9). These can be assigned to the FD and ClD stretching frequencies. The stretching frequencies of DF are similar, as seen in our earlier DF(aq) simulations.[20] The small peak in the deuterium spectrum around 850 cm⁻¹ is seen in the previous DF(aq) simulations but not in the DCl(aq) simulations. Here, we studied the deuteriums bonded to fluorines and we usually saw a mild peak between 800 and 1000 cm⁻¹, whereas the deuteriums bonded to oxygens (water and hydroniums ions) are much more waterlike and have a low intensity near 900 cm⁻¹. Qualitatively, our spectra can be compared to the IR adsorption experiments of HF(aq) of Khorami et al.[8] and Giguere and Turell.[7] The DF spectra of Giguere and Turell showed a peak similar to the one we had around 850 cm⁻¹ at 730 cm⁻¹.[7] One should remember that we obtained the spectra from the velocity−velocity autocorrelation function and not from the

dipole moments. More details of the calculations of IR spectra using CPMD can be found in an article by Iftimie and Tuckerman.[40]

4. Discussion

When starting these simulations, we were interested to see what kind of structures this mixture would reveal. In our previous simulations, we have seen FH−F and ClH−Cl complexes,[20,3] and it would also be logical that in the mixture FH−Cl molecules would be present. But, at which proportions would these species appear? As described above, the FH−F was the most common bihalide ion in our mixed acid simulations. In the 14/0 systems, there were also several FH−F pairs as inferred in the experiments.[5] In the gas phase, the FH−F⁻ molecule has a 70.7 kJ mol⁻¹ lower enthalpy than FH−Cl⁻ but HF has a 31.0 kJ mol⁻¹ higher binding energy to Cl⁻ than water.[41] So, there is a competition of the HF molecules by the F⁻ and Cl⁻ ions. According to the gas-phase data, the fluorine should win. Also, the solvation energy of FH−F⁻ is ca. 33.5 kJ mol⁻¹ larger than that of FH−Cl⁻.[42] So, it is reasonable that the FH−F ions were the most stable, but it was not easy to get these FHF complexes. We have done several simulations of the acid mixture, and only in the last 6/8 simulation were these complexes seen. We assume that the last simulation is the most reliable one due to the long annealing cycle before it. On the other hand, the lifetime of the FHF complexes were very long. So once they were formed, they stayed for the rest of the simulation and we did not see their breaking; therefor, even the latest simulation was too short.

In our simulations, all fluorines had some protons very close to them and so the FH−F⁻ complexes were something between FH−F⁻ and FH−FH. In both the 6/8 and 14/0 simulations, several FH−F⁻ complexes were seen but also HF dimers were observed. On the other hand, the chlorines in FH−Cl⁻ were clearly ions. This would favor the FH−Cl⁻ complex since the binding energy of the HF dimer in the gas phase is 58.5 kJ mol⁻¹ higher in energy than the FH−Cl⁻ complex. Overall, this system contains several types of ions and, even if some trends are correct in the gas-phase calculations, it is necessary to perform dynamical atomistic simulations at real temperatures to capture the explicit solvation effects.

We were also interested to see if the 6/8 system is more acidic than the corresponding 14/0 or hypothetical 0/8 system. Unfortunately, this question is very difficult to answer using molecular dynamics simulations since one should compute the activity of the proton or use some indicator molecules.[21] If we use the number of extra protons around the waters or the average O−O distance as an indication of acidity, the mixed 6/8 system is more acidic than the 14/0 system. The 0/8 system is probably less acidic than the 6/8 system, since the HCl dissociation was lower in the pure HCl(aq) simulations. So, the mixed HF/strong acid systems are good candidates for superacids. We did not have experimental data of this mixed system, but the acidity of HCl(aq) and HF(aq) has been discussed in depth in refs 4 and 9.

Another observed general trend was that the HF molecule was much better solvated than HCl. This can be seen from the HCl coordination numbers which are much lower than the corresponding HF numbers. Also, the bonding environment of HCl is much less structured than that of HF. Also at the atomic level, F and Cl had different solvation trends. This was seen in the coordination numbers of F and Cl atoms (Table 2). The fluorine coordination numbers were not very sensitive to the acid concentrations, whereas the chlorine coordination numbers were. This can be explained partly by the increase of the undissociated HCl, which were not well-solvated. But, the

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concentration of HCl molecules was rather small so other factors had effects on the Cl coordination numbers. The second and more important factor was the higher coordination number of Cl. Cl needs more solvent molecules than F around it, and when the Cl concentration increased, there were not enough solvent molecules for good solvation. This is clearly seen in the OO coordination numbers. The OO coordination number is very sensitive to the acid concentration, and in the 6/8 systems, there was only one oxygen molecule at the first solvation cell of oxygen. An important observation from our simulations was that the Cl$^-$ ions were mostly solvated by waters not by hydroniums or HFs. Thus in the case of Cl, the other molecules cannot easily replace water as a solvent and Cl solvation gets worse when its concentration increases. Fluorine solvation was easier since its solvation numbers were smaller. Also, the HF and hydronium molecules could participate well in the solvation of F. These observations are consistent with the fact that HF can mix with water at any concentration but HCl can mix only up to ca. 30 mol %.

5. Conclusions

CPMD simulations are possible for very small acid systems (32−64 molecules); however, the simulations need to be "long", at least 50 ps, or preferably, one should conduct careful annealing cycles and productions simulations of hundreds of picoseconds. The main reason for such long simulation times is the stability of XHY (X, Y = F, Cl) dimers. One needs to simulate some dimer breaking and forming. Of these dimers, ClHCl and FHCl have lifetimes of the order of 20 ps but the FHF dimers are more stable. Their lifetime is more than 100 ps, and even the simulations done here were not long enough to sample the FHF breaking. Also, larger systems than those shown here should be studied[39] but the computational scaling of the present AIMD codes makes the increase of the system size very expensive.

Our key finding is that the FH−F$^-$ complexes are more probable than the FH−Cl$^-$ ones. This is based on the assumption that our latest 6/8 simulation is the most reliable due to the annealing cycle. This is in agreement with the pure HF(aq) systems where FH−F$^-$ complexes were observed. Also in the gas phase, the FH−F$^-$ molecule is more stable than the FH−Cl$^-$ molecule.

Another interesting observation was that the Cl$^-$ ions were preferentially solvated by water molecules instead of hydroniums or HFs but the fluorine atoms are equally well-solvated by water and hydroniums. This means that good solvation of Cl$^-$ ions requires water molecules, and this could explain, on a molecular level, the lower soluability of HCl compared to HF. Also, the fact that as a molecule HF is well-solvated whereas HCl is not will effect the soluability of HCl and HF. HCl has a strong tendency to break, and the resulting ions need to be solvated. The later is getting harder as the number of water molecules decreases.

Last, the molecular structure in a mixed HF−HCl aqueous system is surprisingly similar to that in the pure HF(aq) and HCl(aq) systems.

Supporting Information Available: Data of the pair correlation functions of the 1/3, 3/4, 6/8, and 14/0 simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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