Ab Initio Study of Aqueous Hydrochloric Acid

Kari E. Laasonen[†] and Michael L. Klein*

Center for Molecular Modeling and Department of Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania 19104-6323

Received: August 15, 1996; In Final Form: November 1, 1996[⊗]

Ab initio molecular dynamics simulations have been carried out for solutions of hydrochloric acid in water, under ambient conditions, over a wide range of concentrations. For acid-to-water mole ratios of 1:31 and 1:7 the hydrochloric acid molecules readily ionize to form hydrated chloride and hydronium ions. However, in a typical laboratory strength 1:3.6 solution, the textbook picture of separated solvated ions breaks down with the formation of a hydrogen-bonded species, $Cl-H\cdots Cl^-$. The presence of this species should be observable in experiment and its detection and characterization could provide a stringent test of the current *ab initio* simulation methodology.

1. Introduction

In the last few years, the development of powerful *ab initio* simulation algorithms[1] and their implementation on parallel computers[2] has lead to important insights into the behavior of condensed phase systems. These *ab initio* simulation techniques, based on density functional theory, have already had great success when applied to the study of covalently bonded atomic solids and liquids[3,4] and molecular systems such as hydrogen-bonded ice and water.[5−7] The technique has been used to study surface chemical reactions[8,9] and, more recently, ultradense high-temperature solid hydrogen.[10] The great advantage of an *ab initio* approach to condensed phase simulations is that it obviates the need for empirical interatomic potential functions. Herein, we report an application of the *ab initio* molecular dynamics methodology to a problem in “wet chemistry”; namely, we explore the nature of hydrochloric acid, one of the most common reagents found in any chemistry laboratory. Anticipating our results, we will see that, in addition to hydrated chloride and hydronium ions, which are present in dilute solutions, reagent strength hydrochloric acid is found to contain the bifluoride-like associated ionic species, $Cl-H\cdots Cl^-$. The predictions of our *ab initio* results on hydrochloric acid could be tested by a new generation of complementary spectroscopic and diffraction experiments.

Acid dissociation is one of the simplest and most important solvation reactions. One of the guiding chemical principles, found in standard texts, is that a strong acid such as HCl ($pK_a = -7$) readily dissociates in dilute aqueous solution to form hydrated chloride and hydronium ions, whereas, under the same conditions, a weak acid such as HF ($pK_a = 3$) barely ionizes.[11,12] These expectations have been borne out by numerous ingenious experimental studies spanning more than a century.[13,15] However, the behavior of the hydracids in *concentrated* aqueous solutions is somewhat less clear. For example, water has only a very limited solubility in concentrated HCl, but the solubility of HCl in water saturates at around 40 wt %.[13] Indeed, the HCl/water system is recognized as a classic nonideal liquid mixture.[13] Powerful physical techniques, such as the diffraction of X-rays and neutrons, and spectroscopic probes have confirmed the presence of hydronium in hydrochloric acid solutions and have also established that significant structural changes occur in the solution with increasing acid concentration.[14−16]

To further understand the nature of aqueous solutions, we extend earlier work on water[7] to include the *ab initio* molecular dynamics simulation of aqueous hydracids.[17] The present study is designed to gain some insight into the possible microscopic mechanisms that might limit acid solubility in water. Our investigation complements topical and ongoing research into the ionization of HCl on the surface of ice crystals.[18,19] In contrast to the latter works, the present study employs the Car−Parrinello (CP) density functional theory (DFT) based molecular dynamics (MD) method.[6,7] An *ab initio* approach is helpful because the dissociation of a water molecule is difficult to model with empirical potentials.[20] An advantage of the CP-MD technique is that it is able to describe both the bond-breaking ionization process and the dynamics of the system in a self-consistent fashion, subject to the limitation of DFT and the adiabatic propagation of nuclear degrees of freedom.[1] The present article reports the salient results of CP-MD simulations carried out for solutions of DCl in heavy water (D_2O) with acid-to-water mole ratios 1:31, 1:7, and 1:3.6. These particular values were chosen to be close to those employed in previous experimental studies.[14−16] The 1:3.6 system is near the saturation limit for aqueous solution.[13]

2. Technical Details

At the start of the CP-MD calculations, the simulation systems consist of solute DCl and solvent D_2O molecules. The computational details are very similar to those employed in earlier CP-MD calculations (see, for example, refs 7 and 17). The valence electronic wave functions are developed in plane waves, and their interactions with nuclei and the core electrons are described using ultrasoft pseudopotentials.[21] The psudopotentials were Vandebilt type, and the cutoffs were 1.4 au for oxygen, 0.7 au for hydrogen, and 1.5 au for Cl. The exchange-correlation was the LDA form parametrized by Perdew and Zunger,[22] and the gradient-corrected exchange term is taken from the work of Becke[22] with no gradient correction applied to the correlation terms. (The accuracy of this approximation is extensively discussed in ref 7.) Even though the size of our system is relatively small (in this case 32 molecules), the inclusion of periodic boundary conditions and Ewald summation makes the CP-MD approach more relevant for the discussion

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[*] To whom correspondence should be addressed: Laboratory for Research on the Structure of Matter, University of Pennsylvania, 3231 Walnut Street, Philadelphia, PA 19104-6202. Phone: (215) 898-8571. FAX: (215) 898-8296. Email: klein@lrsm.upenn.edu.

[†] K.E.Laasonen@helsinki.fi. Present address: Department of Chemistry, University of Oulu, Oulu, Finland.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

S1089-5639(96)02513-3 CCC: $14.00

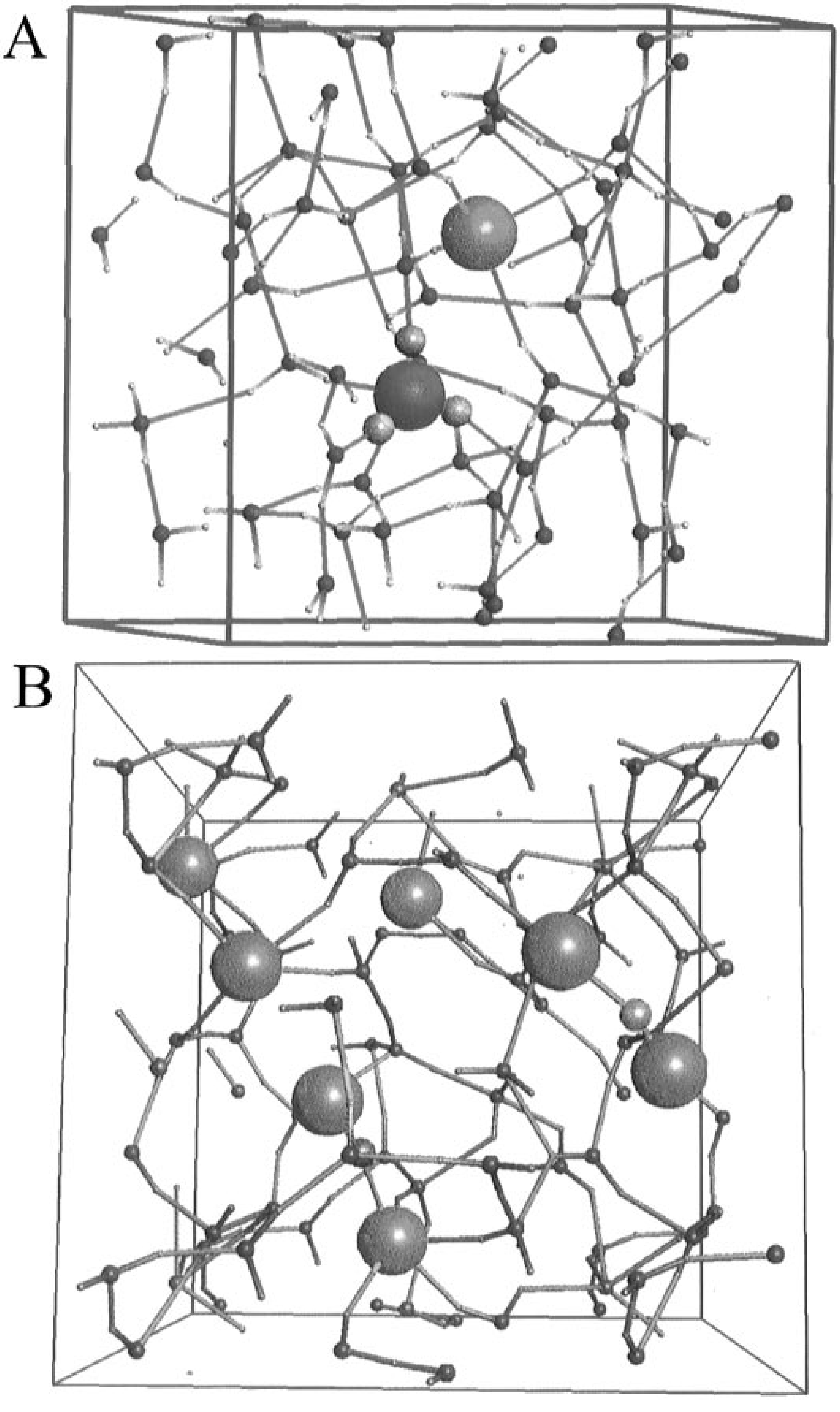

Figure 1. Snapshots of the *ab initio* CP-MD simulations. (A) A dilute (mole ratio 1:31) solution of DCl in D_2O showing hydrated chloride ion (blue) with four D_2O ligands and hydronium D_3O^+ (O red and D gray). Hydrogen bonds are shown as green lines. (B) A concentrated (mole ratio 1:3.6) solution. The large and small blue, red, and gray spheres are Cl, O, and D atoms, respectively. The bichloride $[Cl-D\cdots Cl^-]$ species are shown with enlarged Cl and D radii.

of the behavior of concentrated solutions than, for example, a cluster calculation. For the Ewald summation in *r*-space, the Gaussians employed $(\exp(-[r/r_c]^2)$ were very narrow with $r_c = 1.1$ au. In *k*-space, the cutoff is the same as used for the density, namely, $k_c^2 < 96$ Ry. We have replaced all of the hydrogen atoms in the periodic MD cell with deuterium so that

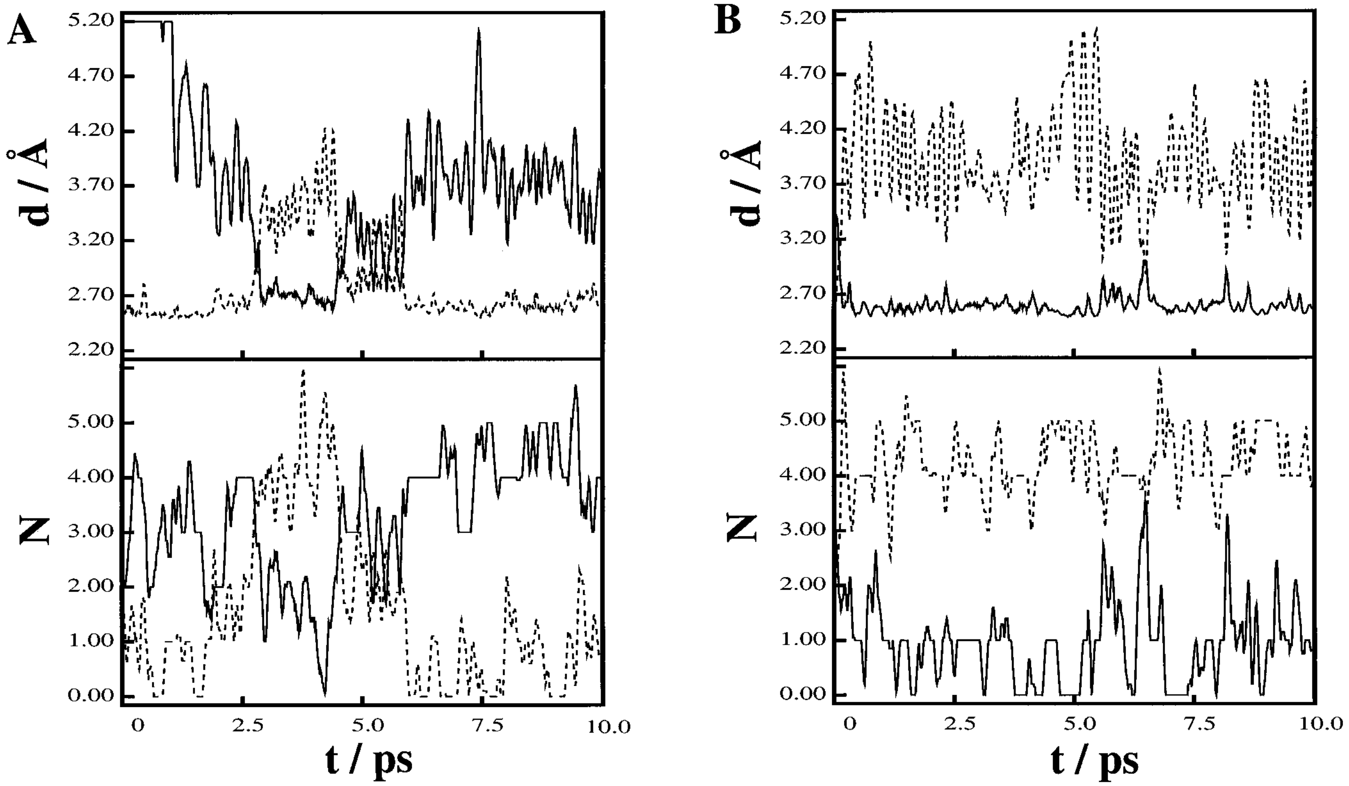

Figure 2. Evolution with time of the Cl−D distance, *d*, and Cl coordination number, *N*, for the [Cl−D···Cl$^-$] species. (A) The species exhibiting proton migration at $t = 2.6$, 4.6, and 5.8 ps. (B) The species that shows fluctuations but does not show an actual proton jump. The curves are running averages, with 60 fs averaging, of the actual CP-MD data.

the simulation actually refers to DCl in D_2O. This has the advantage that we can use a larger time step (0.145 fs) for integrating the equations of motion.

The CP-MD runs started from an equilibrated 32 molecule liquid water configuration[17] in which either one, four, or seven of the water molecules were replaced by DCl molecules and, simultaneously, the MD box was dilated to yield the desired density of the solution.[13] Although the DCl positions were chosen to maximize Cl−Cl distances, in the most concentrated solution there was actually one Cl−D···Cl−D near-neighbor pair (solute dimer) in the initial configuration. The starting Cl−D distances were set to the gas-phase value (1.27 Å). At the begining of the CP-MD calculation the system temperature intially increases. It was then gradually cooled over a time period of about 1 ps (i.e. 7000 time steps) to the desired value, which in the present case was 320 K. The CP-MD results discussed herein were obtained from subsequent trajectories of 10 ps for the most concentrated solution and 4 ps each for the other two runs.

3. Results and Discussion

In all of the simulations the DCl molecules typically dissociated to form Cl$^-$ and hydronium, D_3O^+, ions (Figure 1A). However, in the case of the most concentrated solution (Figure 1B), not all of the DCl molecules in the simulation system ionized during the CP-MD run. Indeed, two DCl molecules remained intact at the end of the 10 ps run and formed hydrogen-bonded Cl−D···Cl$^-$ species, analogous to a hydrated bifluoride ion.[11] One of these complexes began as a Cl−D···Cl−D dimer in the initial configuration of the simulation and persisted after ionization of one of the DCl molecules. The other complex formed spontaneously from initially well separated DCl molecules and stayed as such for the remainder of the run. The anion Cl−D···Cl$^-$ species is known; it has been studied in the gas phase[23] and in matrix isolation,[24] and its structure has been predicted by *ab initio* methods,[25] but as far as we are aware, it has not been reported heretofore in solution.

In the dilute solutions (Figure 1A), the chloride ion has a coordination number that fluctuates between 4 and 5, where the coordination number is determined here by counting the number of “bonds” with a D···Cl distance shorter than 2.90 Å. However, in the most concentrated solution, such a high coordination number is only possible if the hydrated Cl$^-$ ions share solvation sheath water molecules (Figure 1B). Another possibility[14] is the formation of Cl$^-$−Cl$^-$ contact-ion pairs, with a common water solvation sheath. Although this latter suggestion would seem to be electrostatically unfavorable, such ion-pairing structures have been reported in classical MD simulations based on empirical potential functions[26] and possibly seen in neutron diffraction studies of concentrated LiCl solutions.[27] However, in the present CP-MD simulations, no Cl$^-$−Cl$^-$ contact-ion pairs were observed.

In the concentrated solution, Cl$^-$ ions participating in the bichloride-like Cl−D···Cl$^-$ complex can be regarded as being surrounded by a hydration sphere that includes an undissociated DCl molecule. This view is supported by a more detailed analysis of the solvent structure. The coordination number of the Cl$^-$ ion in the complex is ∼4, which is similar to the other Cl$^-$ ions in the system, whereas the Cl in the undissociated DCl molecule has a significantly lower coordination number, typically between 1 and 2; see Figure 1B and Figure 2. In principle, the proton in the hydrated bichloride species Cl−D···Cl$^-$ can migrate from one Cl to the other without causing dissociation of the bound complex, i.e. Cl−D···Cl$^-$ $\Leftrightarrow$ Cl$^-$···DCl. We have observed such jumps and verified that they are indeed correlated with variations in the coordination numbers of the Cl atoms (see Figure 2). Analysis of the electronic density also confirms the ionicity change.

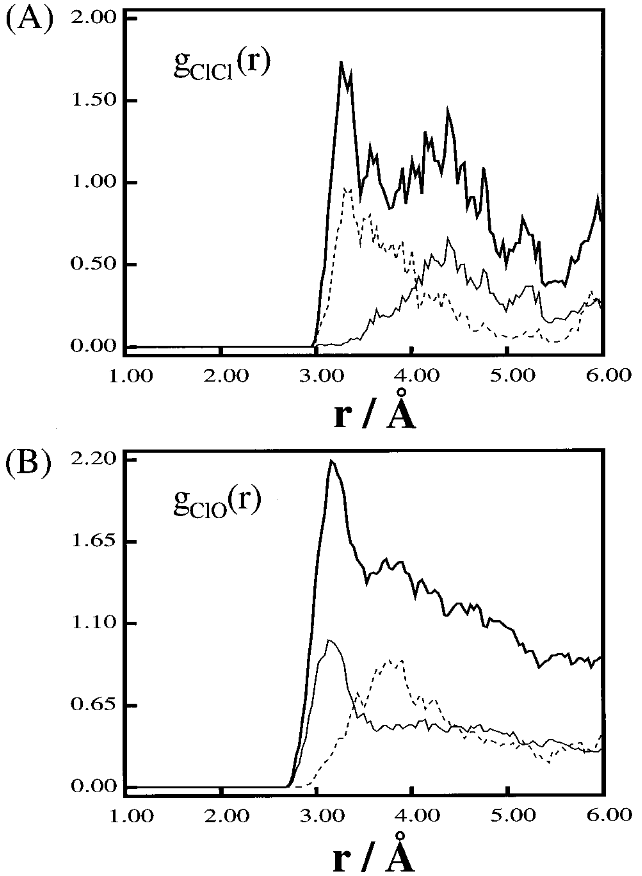

Figure 3. Radial distribution functions (RDFs) for the concentrated solution calculated from the last 8 ps of the simulation. (A) Cl−Cl, Cl^-−Cl, Cl(DCl)−Cl, and (B) Cl−O, Cl^-−O, Cl(DCl)−O. The total Cl−Cl RDF is drawn with a bold solid line, Cl^-−Cl, as a thin solid line, and Cl(DCl)−Cl, as a thin dashed line. The latter two have been scaled by a factor of 1/3. Similarly, the total Cl−O RDF is drawn with a bold solid line, Cl^-−O, as a thin solid line, and Cl(DCl)−O, as a thin dashed line. The latter two RDFs have also been scaled by a factor of 1/3.

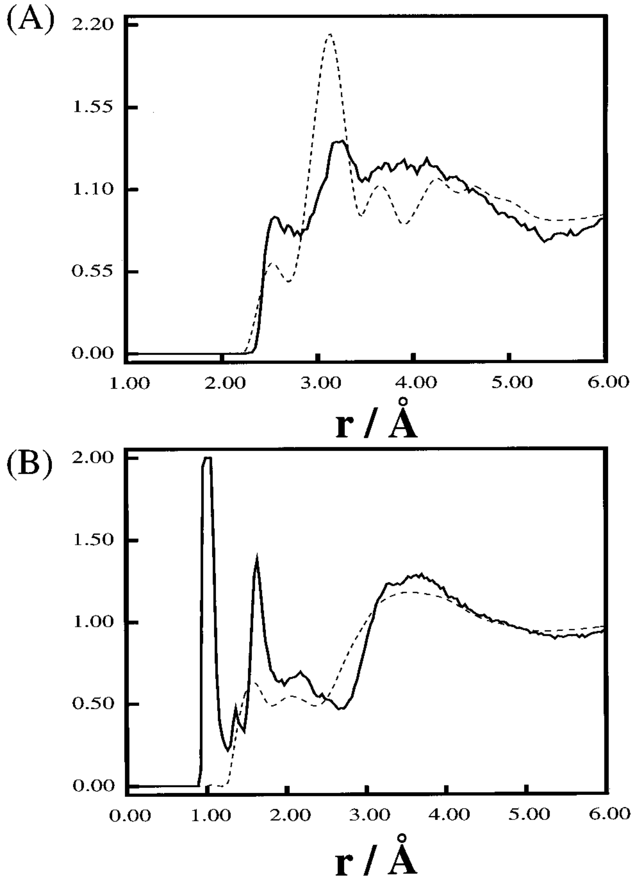

Figure 4. Comparison between the CP-MD X-ray (A) and neutron (B) RDFs, $G_{n,x}(R)$, and the measurements of ref 14. Here, $G_{n,x}(R) = \sum c_i c_j b_i b_j\, g_{ij}(R)/\sum c_i c_j b_i b_j$, where, $g_{ij}(R)$ is the atom−atom RDF, c_i the concentration of species $_i$, and b_i the relative value of the X-ray or neutron scattering length: $b_{x,O} = 10.0$, $b_{x,Cl} = 18.0$, $b_{x,D} = 0.0$ and $b_{n,O} = 0.58$, $b_{n,Cl} = 0.96$, $b_{n,D} = 0.667$, respectively.

The sensitivity of the Cl−D···Cl^- structure to the local environment likely also explains its apparent stability. If we link the dissociation of the DCl with the formation of a higher coordination state of Cl, the stability of the hydrated bichloride-like complex is enhanced by the fact that even though the DCl molecule ionizes, the structure of the complex is still preserved. Dissociation will likely happen only when *both* of the chlorine atoms in the complex become fully (four) coordinated. Unfortunately, due to the short duration of the MD run, we cannot rule out the possibility that the bichloride species will *eventually* dissociate. However, as evidence for the likely stability of this complex, we note that we did actually observe the spontaneous formation of one of the Cl−D···Cl^- complexes during the MD run. Thus, taken at face value, the simulation suggests that hydrated bichloride-like species should exist in a concentrated solution.[29]

We have used atomic radial distribution functions (RDFs) to explore, more quantitatively, the structure of the solutions.[27] The RDFs (see Figure 3 and Figure 4) confirm that the saturated solution is really a multicomponent mixture of water (D_2O), chloride (Cl^-), hydrated hydronium (as in ref 7, we observe both D_3O^+ and $D_5O_2{}^+$ structures), and bichloride (Cl−D···Cl^-), with distinct coordination numbers for atoms associated with the different species. The calculated hydronium O(D_3O^+)−O(D_2O) RDF has a sharp first peak at 2.5 Å, which is in excellent accord with the diffraction data (see the dashed line in Figure 4A). The solvent O(D_2O)−O(D_2O) first peak occurs at ~2.7 Å, as expected for the model.[7]

In the most concentrated solution studied herein, the Cl−Cl RDF (Figure 3) has a first peak at 3.2 Å (Figure 3A), which is related to the bichloride species, plus a broad peak between 3.8 and 4.8 Å arising from the Cl^-−Cl^- interactions. Typically, Cl^- ions form Cl^-−H_3O^+−Cl^- clusters, with Cl−O distances of ~3 Å (Figure 3B) and a Cl−O−Cl angle of ~90°. This finding is in good qualitative agreement with the structural features present in the trihydrate crystal.[30] One conclusion to emerge from the RDF structural analysis of the CP-MD simulations is that no Cl^-−Cl^- contact-ion pairs formed during the simulation. For aqueous LiCl and $NiCl_2$ the ion−ion RDFs have been measured.[27] The reported Cl−Cl RDFs suggest anion pairing in the former case but not the latter. Also, in a recent study of the more dilute system LiCl:$6H_2O$, the Cl^- ions were reported to be completely solvated and no evidence was presented concerning Cl^-−Cl^- ion pairs.[28] The experimental values reported in refs 27 and 28 for the coordination number of the chlorine in LiCl were ~5.3 and ~5.8, respectively, which compare to the average value of ~4.6 calculated here from consideration of the Cl−D coordination and ~5.1 from the Cl−O in the concentrated solution.

At high concentration the experimental X-ray RDF (the dashed line in Figure 4A) shows a small peak at 2.52 Å, identified as due to hydronium (O−O), and a peak at 3.13 Å, which has been attributed to Cl−O (see Figure 3B).[14] According to our simulations, the latter peak might well be interpreted as a combination of the first Cl^-−O hydration peak (recall

Figure 3B) plus the Cl(DCl)−Cl bichloride peak. The neutron RDF data[14] show two new peaks at high concentration, one at 1.6 Å and the other at 2.1 Å (the dashed line in Figure 4B). The latter is likely related to Cl···D interactions from chloride hydration, but if this is the only contribution, then its measured peak height should *increase* with acid concentration, which it does not.[14] The reported relative constancy of this peak height, as the acid concentration increases, could perhaps be explained by increasing amounts of undissociated HCl and a reduction in the Cl-ion coordination number (from, say, ∼5 to ∼4). The neutron peak observed at 1.6 Å (Figure 4B) is mostly likely related to hydronium, i.e. $O(D_3O^+)\cdots D$, interactions.[14] To make explicit comparison with X-ray and neutron data, we have constructed the appropriately weighted RDFs, which are shown in Figure 4. It should be noted that the intramolecular H−H and O−H contributions have been subtracted from the experimental neutron data.

The CP-MD technique can also probe the short time dynamical behavior of the acid solutions. Indeed, we have identified frequencies related to the different species in the solution.[7] For example, the DCl stretching frequency (recall that all of the H atoms have been replaced with D) is calculated to be ∼1400 cm^{-1}, which is near a broad feature in the infrared spectrum attributed to hydronium D_3O^+ vibrations.[15] The low-frequency bichloride Cl−Cl breathing vibration falls in the water "lattice-mode" region, around 150 cm^{-1}, where peaks are seen in the Raman spectrum.[16]

4. Conclusion

The present *ab initio* MD simulations confirm that for aqueous hydrochloric acid the conventional picture of solvated chloride and hydronium is obtained at mole ratios of acid-to-water of 1:31 and 1:7. However, according to our calculation, there is likely to be undissociated, but complexed, HCl present in more concentrated solutions of aqueous HCl. Thus, in a bottle of reagent grade HCl some of the acid molecules will likely be undissociated; they are stabilized by participating in the first coordination shell of hydrated Cl^- ions, thereby forming a hydrated bichloride-like species $Cl-H\cdots Cl^-$. To date the available experimental data[14−16] have been interpreted without invoking the presence of the $Cl-D\cdots Cl^-$ species. The experimental situation is sufficiently unclear that a new generation of diffraction experiments, focused on aqueous hydracids, would seem to be worthwhile. Individual RDFs can now be measured using neutron diffraction with isotopic substitution.[27] If our prediction is valid, the signal arising from $Cl-D\cdots Cl^-$ should be quite clear in the diffraction data. New spectroscopic[15,16] and NMR studies should also give valuable additional information on this species, which has already been studied in matrix isolation and in the gas phas.[23,24]

Acknowledgment. We thank Michele Parrinello and Michiel Sprik for sharing with us details of their related studies on aqueous systems before publication and Kechuan Tu and Preston Moore for useful discussions. This research was supported by the National Science Foundation under Grant CHE 96-23017 and benefited, in part, from facilities provided under DMR 91-20668. Some of the calculations were conducted with allocation MCA 93 S020 on the IBM SP2 parallel machine at the Cornell Theory Center.

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