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Ab Initio Molecular Dynamics Study of Hydrochloric Acid in Water

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Some of the simplest and most important reactions in water involve acids. In the case of strong acids, like HCl, almost all of the molecules dissociate in aqueous solution to form hydrated Cl^- and H^+ ions. Although there are very few experiments on the structure of aqueous HCl, X-ray data shows significant structural changes with increased concentration of HCl.[1]

On the theoretical side, empirical potentials combined with classical molecular dynamics (MD) have been used widely for studying ions in water;[2] but to describe ionization of an acid HCl in water[3] and the pH of water[4] is very difficult using empirical potentials. *Ab initio* quantum chemistry has concentrated on ions[5] or protons[6] in small water clusters, but mixed clusters of hydrohalic acids and water have also been studied.[7] These cluster calculations provide information on the binding energy and energy barriers for protonation, but neglect the actual atomistic dynamics. To date, the size of the clusters studied has necessarily been rather small. A more realistic approach was been taken by Ando and Hynes[8] who embedded a relatively large quantum mechanically treated cluster ($HCl(H_2O)_{10}$) in classical water. The fluctuations of the solvent were modeled using Monte Carlo sampling. In this way Ando and Hynes were able to estimate the activation barriers of the first two proton transfers.

We have used the Car−Parrinello (CP) density functional theory (DFT) based *ab initio* molecular dynamics method[9] to study HCl molecules in water. This approach is able to describe both the bond breaking and the dynamics of the system in a self−consistent fashion subject to the limitations of the DFT and the adiabatic propagation of nuclear degrees of freedom. Even though the size of our system is relatively small (32 molecules), the inclusion of a periodic boundary condition makes our approach much more relevant for the discussion of bulk behavior than the cluster calculations. The scheme we use has already proven to be successful for several different phases of water[10,11] and an excess proton in water.[12] In this communication we give few computational details because they are essentially the same as in earlier calculations.[10,13] The valence electronic wave functions are developed in plane waves, and their interactions with nuclei and the core electrons are described using Vanderbilt ultrasoft pseudopotentials.[14] The time step employed is 0.145 fs. We have also replaced all of the hydrogen atoms with deuterium.

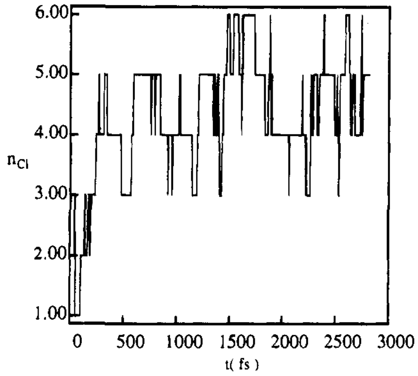

Figure 1. Coordination number, n_{Cl}, of the Cl^- ion from the longer CP run. The coordination number has been calculated as the number of hydrogens closer than 2.65 Å to the Cl.

We report here the results of two different CPMD simulations. In one, the run started from a liquid water configuration in which one water molecule was replaced by an HCl molecule. The starting Cl−H distance (1 Å) was chosen to be much shorter than the equilibrium value to aid bond breaking. In this case, the whole system was also heated to ≈450 K and then cooled to 320 K over a time period of about 0.8 ps to encourage the rearrangement of solvent molecules. The aim of this simulation was to investigate the equilibrium configuration of dissociated H^+ and Cl^-, including quantities such as the Cl coordination and diffusion of the proton. The MD trajectory was followed for an additional 2 ps after cooling to 320 K.

To further study the dissociation process we started a second CPMD run from a new 32 molecule configuration in which one molecule was replaced by HCl with the gas-phase Cl−H distance. This system is not in equilibrium, because solvated HCl does not necessarily have the same bonding pattern as pure water.

In both cases, dissociation occurs in a similar way and on a roughly similar time scale. The H originally bonded to Cl moves first along the H-bond to a neighboring water molecule, forming H_3O. Very soon thereafter (~100 fs) one of the other hydrogens of H_3O moves to another water molecule. Immediately after breaking of the HCl bond the proton hopping time is short (~100 fs), but on approaching the equilibrium state it increases to ~500 fs. The formation of the equilibrium coordination cell around the Cl^- is also time dependent and has a relaxation time of ~1 ps (see Figure 1). The fast dissociation of HCl in our simulations is in agreement with the estimation by Ando and Hynes of almost activationless breaking of HCl.[8]

We have calculated the atomic pair correlation functions from the longer CPMD run. The Cl−O pair correlation function is shown in Figure 2. The nearest neighbor Cl−O peak is at 3.2 Å, and the coordination number is about 5.0. These values can be compared to experimental data on Cl^- in water.[1,15] Experimentally, the first Cl−O peak occurs at 3.1−3.2 Å and the coordination number is 5.5−6.0 for most of the chloride salts[15] and around 4 for HCl.[1] Our structural data agree well with the available experimental data.

After dissociation, the proton was found in two different configurations: either bonded to a single H_2O molecule, forming H_3O^+ or located between two water molecules, forming the

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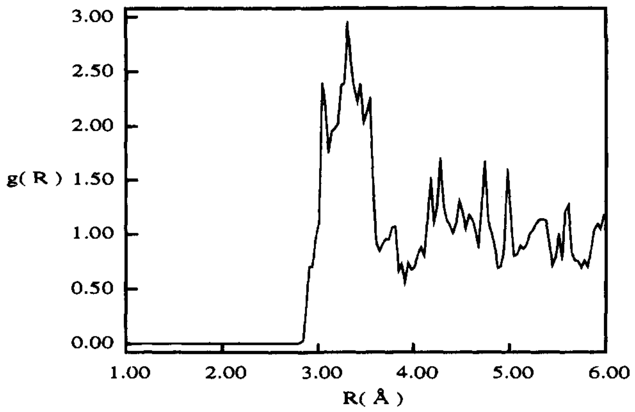

Figure 2. The Cl–O pair correlation function, $g(R)$. The correlation function was calculated from the last 2 ps of the longer CP run.

$(H_5O_2)^+$ complex. The additional proton does not break the hydrogen-bonded network, and both the H_3O^+ and the molecules in $(H_5O_2)^+$ are tetrahedrally coordinated. This finding is in agreement with quantum chemistry calculations[6] and is similar to the earlier simulation for an excess proton in water.[12] We followed the separation between Cl^- and H_3O^+ and found that the proton never comes back to the nearest neighbor of the Cl^- but was located, most of the time, at the next nearest neighbor distance (i.e., the maximum separation allowed by the simulation cell[17]). This observation suggests an effective repulsion between the Cl^- and H_3O^+ ions at the nearest neighbor distance which at larger separation turns attractive. Similar solvent-separated ions were found in the potential of mean force calculations for Na^+Cl^- in water by Smith and Dang.[16] Their mean force curve is clearly repulsive at 3.5 Å and has an attractive minimum at ~5 Å. Since in our case the positive charge is well localized on H_3O^+ (or $H_5O_2{}^+$), the analogy with Na^+Cl^- is not inappropriate.

To conclude, simple chemical reactions in solution (here water) are now accessible to *ab initio* computer simulation. We have shown that small but rather realistic systems can be studied on the picosecond time scale. The same CPMD scheme has been applied recently to proton transfer reactions.[18] We are currently studying aqueous HF and a more concentrated solution of HCl.

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