# Structural and Spectral Properties of Aqueous Hydrogen Fluoride Studied Using ab Initio Molecular Dynamics

**Atte J. Sillanpää,**[†] **Christian Simon,**[‡] **Michael L. Klein,**[‡] **and Kari Laasonen\*,**[†]

*Department of Chemistry, University of Oulu, PO Box 3000, FIN-90014 Oulun Yliopisto, Finland, and Department of Chemistry and Center for Molecular Modeling, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323*

Aqueous solutions of deuterated hydrofluoric acid (DF) have been studied at three concentrations using ab initio molecular dynamics (AIMD). At low concentration, DF was found to form a strongly bound complex, dynamically fluctuating between $F-D \cdots D_2O$ and $F^- \cdots D_3O^+$ structures. The coordination number of molecular DF is as low as 2. The fluctuation behavior was observed also at higher concentrations, although in that case 40% of the DFs can be considered as dissociated into $F^-$ ions rather than being a part of $F^- \cdots D_3O^+$ complexes. No $FDF^-$ ions formed spontaenously at ambient temperature. One such complex was built, and it was stable for the whole simulation time (6 ps). The increasing acidity as a function of concentration is suggested to derive partly from the increasing stabilization of $F^-$ when its surroundings become more ionic. The $F^-$ ion can be also stabilized by HF molecule, which results in a bifluoride ion. The high DF concentration also lowers all coordination numbers and compresses the first solvation shell of heavy atoms (O and F), compared to low concentration or bulk water. Vibrational spectra obtained from the velocity autocorrelation functions agree with experimental results from spectroscopy. The increased intermolecular forces together with the weakening of the intramolecular ones can also be seen in the vibrational power spectra.

## Introduction

Acidity and proton activity are of fundamental importance in most chemical reactions. Therefore, it is not surprising that proton transfer has been studied extensively using computational tools.[1-3]

A natural model for the study of acidity in water is the series of hydrohalic acids (HF, HCl, HBr, and HI). They are the simplest of acids and form aqueous solutions in a wide range of concentrations. The three heaviest are strong acids, they dissociate completely upon solvation, and their strength increases toward heavier halides. The first in the series, HF, is an exception. In dilute solution, it behaves like a weak acid[4] but turns into a strong acid in concentrated solution.[5,6] The low acidity in dilute solution has been proposed to derive from strong association with a water molecule in the form of a proton-transfer complex.[7-11] Polyfluorides, $F^-(HF)_n$, have been invoked to explain the increase in acidity at higher concentrations.[6,12,13] However, this intepretation is based on indirect measurements, namely, IR and Raman spectra,[10,11,14-16] conductivity and transference number,[12,17,18] Hammet-acidity,[5,6] and potentiometric proton potential measurements.[13,19] Unfortunately, there exists no structural data from X-ray or neutron scattering experiments. The present article employs ab initio molecular dynamics (AIMD) to probe the structure and dynamics of aqueous HF. In AIMD, the forces between atoms are computed using quantum mechanics and, thus, make it possible for the molecules to dissociate and form any complexes or ions, not designed a priori, as in classical molecular mechanics. AIMD

has been successfully applied to a number of systems, where interpretation of experimental data has been inconclusive or where the physical conditions are extreme.[20-22]

To our knowledge, there have been few theoretical studies of HF solutions.[23-29] Most ab initio calculations have considered small clusters consisting of a hydrogen halide and water molecules[30] or different classical and continuum methods.[31] The main experimental results related to this work are the IR spectra of DF(aq).[10,16]

Aqueous HF provides a particularly interesting case study in the characterization of the fundamentals of hydrogen bonding and acidity. The approximations that are valid in dilute solutions for acid behavior very likely break down in concentrated solutions.[32] The conventional picture of a strong dilute acid is valid and useful for all chemists. We now seek a similar visualization and understanding of concentrated acid solutions, to be used as a tool in reasoning all phenomena related to them.

Regardless of the importance of concentrated acidic aqueous solutions, there is only one published AIMD simulation.[33] Such studies of condensed phase phenomena, where the inter- and intramolecular forces approach each other, illustrate the power of AIMD. The computational results bring new and independent structural information and also help and confirm the interpretation of experimental results. Hydrogen fluoride also forms the strongest hydrogen bonds known, which further makes it an interesting model in the study of hydrogen bonding in general.

We report simulations of aqueous DF from dilute (1:31, ∼1.7 mol dm$^{-3}$, 3.5 wt %) to concentrated (13:19, ∼22mol dm$^{-3}$, 43 wt %) solutions. Preliminary results of the low concentration simulation have been already reported,[25] but herein, the study has been extended to provide new results, e.g., vibrational spectra. The outline of the article is as follows. First, we will

\* To whom correspondence should be addressed. E-mail: kari.laasonen@oulu.fi. Phone: +358-8-5331640. Fax: +358-8-5331603.

† University of Oulu.

‡ University of Pennsylvania.

describe the computational method, then the different simulations, and before conclusions discuss the general features.

## Technical Details

The ab initio molecular dynamics have been carried out using the Car-Parrinello molecular dynamics approach (CPMD),[34−36] where only the valence electrons are treated explicitly. The core electrons are described using the Vanderbilt-type ultra soft pseudopotentials.[37] The electronic Kohn−Sham (KS) orbitals are expressed as a plane wave expansion with a 31 Ry energy cutoff, in a cubic box ($a$ = 9.87 Å) using periodic boundary conditions. The simulation of deuterium instead of hydrogen allows to use a time step of 0.145 fs and a fictitious electron mass $\mu$ = 800 au. We have used two different density functionals. The earlier part of the simulations were done using local density approximation corrected with the Becke-only (no correlation correction) as the exchange functional.[38−40] These simulations were then continued using the BLYP functional.[41] The simulations were done in the micro canonical ensemble (NVE), and the temperature was adjusted to approximately 300 K by slowly scaling the atomic velocities, typically during the first few hundred steps with a scaling factor of 1.0015. After this, no thermostats were used. For the parts that have been used for analysis, this resulted in average temperatures 320, 300, and 287 K for 1:31, 12:20, and 13:19 simulations, respectively. The (fictitious) kinetic energy of the electrons was always below 2 meV/electron ensuring accurate forces. All simulations have been done using the FINGER program.[42]

Simulations were performed at three concentrations. These are referred to using their mass percent concentrations and molecular ratios. All simulations had 32 molecules. The starting geometries for the 1:31 and 12:20 DF:$D_2O$ simulations, respectively, were created by replacing water molecules with DFs from an earlier Car-Parrinello equilibrated 32-molecule liquid water configuration. The systems were then run for 4 and 11 ps nominally at 300 K, respectively. The 13:19 simulation was started from the final 12:20 configuration, so that the replacement of one additional $D_2O$ with DF produced a DFDF pair. The technical details of all simulations are identical, apart from the functional, and we will refer to these briefly as the Becke-only simulations in this paper. The 1:31 and 13:19 simulations were continued from the last frame using the BLYP functional, for 12 and 6 ps, respectively. For analysis, we have used the last 5 ps of the 12:20 simulation. For the 1:31 and 13:19, we have used only the BLYP simulations and excluded 1 ps from the beginning of each from analysis, except where explicitly mentioned.

The motivation for the Becke-only functional is to be consistent with our previous studies on aqueous acids.[25,33,43] The use of BLYP, on the other hand, is motivated by its improved description of water[44,45] and hydrogen fluoride.[46] The use of two functionals also gives an estimate of the density functional dependence of the results. In the present case, the differences are insignificant and do not change the observed chemistry.

## Results

**Dilute DF Solution, (DF)·($D_2O$)$_{31}$.** Preliminary results based on the Becke-only functional at this concentration have already been published.[25] The main finding was that the DF formed a very strong hydrogen bond to a water molecule. This strong hydrogen bond split the first F−O RDF peak into two, indicating a significant difference between the FD···O*$D_2$ and DOD···FD hydrogen bonds (see Figures 1 and 2). The
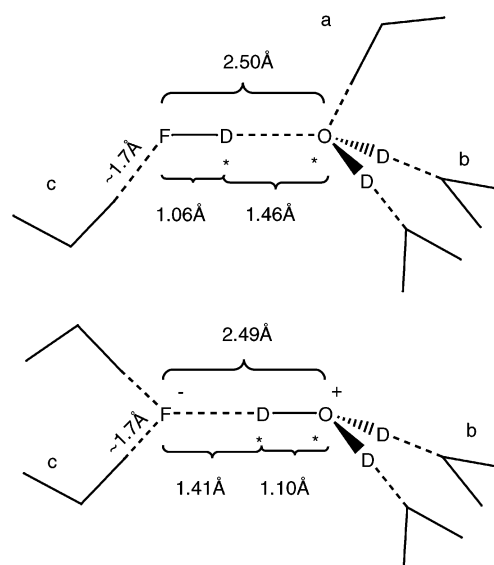


**Figure 1.** Ideal structures for FD···$OD_2$ in water. The two most probable configurations are presented with average bonding distances taken from the dilute solution simulation. Water molecules are presented as two lines in V shape. It should be noted that the hydronium is pyramidal and the O*−water plane is always bent with respect to the FO* bond. Hydrogen bond donor water (a) is not present in the lower configuration. Waters (b) were present all of the time and did not change. The number of H-bond donors (c) in the upper case is only 1−2, whereas in the lower, it is between 3 and 5.
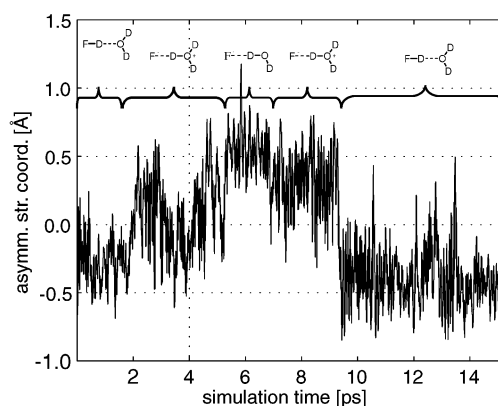


**Figure 2.** Asymmetric stretch coordinate, $x = r(FD^*) − r(OD^*)$ of the FD*$OD2$ moiety in the dilute solution simulations, as a function of time. $x$ below zero corresponds to undissociated DF. The left part, up to 5 ps, corresponds to the Becke-only simulation (see Technical Details) and the rest to the BLYP simulation. The part between 5.3 and 7.0 ps corresponds to the solvent separated ion pair.

FD···$OD_2$complex was found to oscillate between FD···$OD_2$ and F$^-$···$DOD_2^+$ type geometries.

These early results were mainly replicated by the new BLYP simulation except that now we observed both forms of the complex to persist on the pico second time scale. Moreover, the acidic deuterium was even observed to visit the F$^-$ second solvation shell momentarily. However, the resulting hydronium did not diffuse further but returned to the F$^-$ ion. This contrasts strongly what has been observed for HCl and HBr in similar simulations, where the hydronium is well-separated from the anion.[43,47]

The nature of the fluorine solvation shell is primarily determined by its protonation state. The simulation results can be divided roughly into two parts where the number of water molecules (or hydronium) in the first solvation shell is 2 (fluorine is protonated) or between 4 and 5 (fluorine is deprotonated). The coordination number includes the transferring
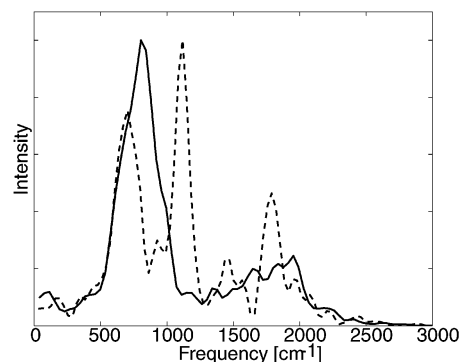
Ab Initio Aqueous Hydrofluoric Acid

*J. Phys. Chem. B, Vol. 106, No. 43, 2002* **11317**
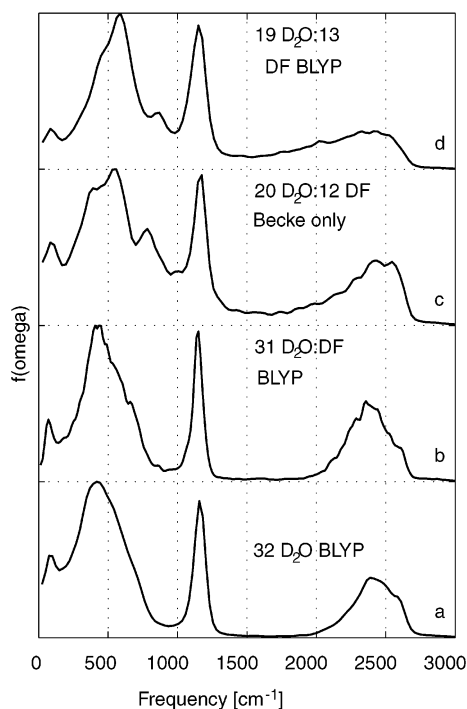


**Figure 3.** Power spectra obtained from Fourier transforms of the of the velocity autocorrelation functions of all of the hydrogen atoms. The spectra have been smoothed with the Blackman window.[49] All but the 20:12 simulation have used the BLYP functional (see Technical Details). Only the final 5−10 ps of the simulations have been used for the analysis.
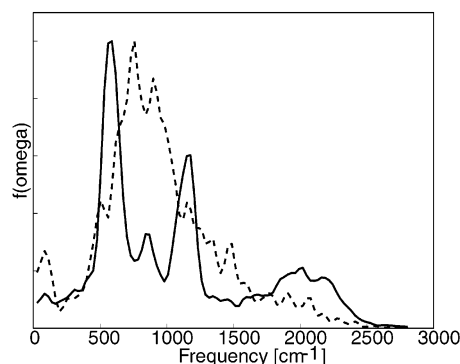


**Figure 4.** Total vibrational spectra of the D* in FD*···OD$_2$ (solid line, during interval 7.0−9.5 ps) and F$^-$···D*OD$_2$ (dashed line, during interval 10.0−15.0 ps) in the dilute simulation, see also Figure 3. Intensity is in arbitrary units. Note that the FD spectrum lacks the peak at 1200 cm$^{-1}$, which is very characteristic for water and hydronium and that the F$^-$···D$_3$O$^+$ part is very similar to those of other D$_3$O$^+$, in Figure 5.



**Figure 5.** Total vibrational spectra of the deuteriums belonging to "free" hydroniums during the last 2.3 ps of the 13:19 simulation (solid line) and those belonging to the ion pairs (dashed). The former is in good agreement with the theoretical spectrum by Schmitt et al., which has been computed using the multistate empirical valence bond method.[50] The peak at 850 cm$^{-1}$ does not appear in their spectrum but can be compared to the experimentally observed peak at 900 cm$^{-1}$, assigned to D$_3$O$^+$.[10] The "free hydroniums" were selected according to their coordination environment. Specifically, only those oxygens (their deuteriums), whose average coordination was above 2.95 with a 1.15 Å r(OD) cutoff and did not exchange deuteriums with fluorines, were selected.

deuterium[48] and has been determined using a 2.5 Å FD distance cutoff. The latter configuration can be further subdivided into two according to the coordination number. A coordination number of 4 is best described as an F$^-$ ion with four identical water molecules around it. In this case, the hydronium is located in the F$^-$ second solvation shell. The peaks of the FD- and FO-radial distribution functions (RDFs) are sharp, and their maxima are at 1.5 and 2.5 Å, respectively. A coordination number of 5 corresponds to the ion pair situation, where the hydronium is closer than other water molecules. The overall geometry switches between square pyramidal and trigonal bipyramidal, producing wide peaks in the RDFs.

The dynamics as inferred from the Fourier transform of the deuterium velocity autocorrelation functions are presented in Figure 3. In addition to these total vibrational spectra, we have examined certain atoms individually at time intervals, which correspond to a particular interesting configuration. In the Discussion section, these spectra will be compared to the experimental vibrational spectra reported in the literature.[10,11,14−16]

The hydrogen fluoride contribution to the spectrum is best evaluated by looking at the D*, F, and the special water explicitly at different parts of the simulation (see Figure 1 for D* definition). The spectrum of the molecular complex, i.e., FD···OD$_2$, can be decomposed into a FD stretching band 1200−2250 cm$^{-1}$ and FD librations at 500−1100 cm$^{-1}$. See Figure 4. The Fourier transform of the DF-bond time evolution reproduces the high frequency part but has practically no intensity at the libration range. The F and O* spectra have peaks at 450 cm$^{-1}$ corresponding to the FO* stretch. The ion-pair spectrum is different due to the much weaker F···D* bond, and the deuterium frequencies are very similar to the hydronium frequencies in Figure 5. This spectrum has, coincidentally, the deuterium libration (or hydronium bending) mode also within

the range of 600−800 cm$^{-1}$. A more detailed analysis is given in the Discussion section.

**40% DF Solution, (DF)$_{12}$(D$_2$O)$_{20}$.** For this concentration, the results are based on the Becke-only simulation. The FD and OD−RDFs are shown in Figures 6 and 7, and the rest are given in the Supporting Information as tabular data. Figure 6 shows the FD−RDFs of different fluorine species in solution. We will return to these in the Discussion section. The hydrogen related RDFs are strikingly different from those in pure water. In the latter, the intermolecular peaks are clearly distinguished from the intramolecular peaks, whereas here, they overlap because of the frequent hydrogen exchanges and very wide potential minima (see Figure 7). The second peak around 1.8 Å in pure water OD−RDF has shifted to 1.4 Å. In water, this peak corresponds to the acceptor H bonds to a given oxygen. Note, that this peak is also completely missing form the hydronium OH−RDF.[33] The average number of hydrogens around the oxygens was 2.2 (cutoff 1.22 Å) and 3.2 (cutoff 2.38 Å). These numbers correspond to 4 hydroniums in the system.

The difference between FO−RDF and OO−RDF at short distance is clear (see Supporting Information for the raw RDF-
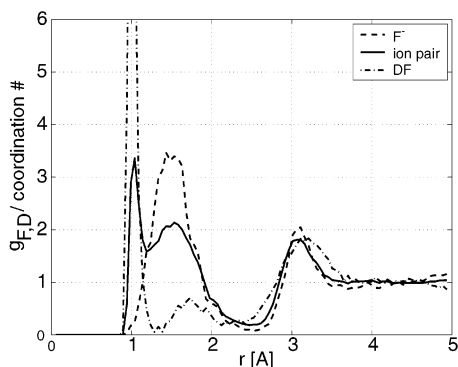
**Figure 6.** FD−RDFs from the last 2 ps of the 12:20 DF:D$_2$O simulation. See text for the division into the different fluorine types. Note the higher coordination of the ions and the low and diffuse coordination of the DF molecule. The DF molecule accepts only one hydrogen bond. The corresponding FO−RDFs have only one peak for all fluorine types.
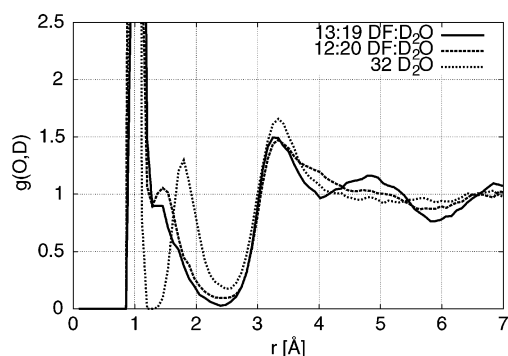


**Figure 7.** OD−RDFs from the most concentrated DF solutions and bulk water. The first peak in the former corresponds to 3.22 D atoms, and in water, the first two peaks correspond to 3.87 D atoms (cutoffs 2.5 Å). Note also the additional structure at distances above 4 Å in the 13:19 simulation and reduced intensity after the first two peaks in the DF solutions compared to bulk water.

data). In particular, the OO−RDF first peak is rather small and corresponds to O−O coordination number of only 1.25 (cutoff 3.1 Å). The FO−RDF has a much higher first peak which also extends to shorter distances. The F−O coordination number is 1.8 (with a cutoff of 3.2 Å). The first F−O peak, at 2.45 Å, corresponds to the FD···OD$_2$ complexes. The first OO−RDF peak at 2.6 Å is significantly closer than in pure water ($r_{OO}$ = 2.8 Å). The peak position is close to O−O distance observed between water and hydronium ($r_{OO}$ = 2.5 Å) in a previous simulation.[22] This is expected because water molecules approach closer to hydroniums than to other water molecules. Even if these hydroniums primarily are bound to one fluorine, they also form two strong donor hydrogen bonds to water molecules as in Figure 1. In this simulation, the FF−RDF has only second solvation shell F−F interactions, where a water or hydronium ion acts as a bridge: F···DOD···F. The relatively clear peak at ca. 4 Å indicates significant correlation between these second neighbor F−F pairs.

The fluorines during the last 2 ps of this simulation can be divided into the three classes observed in the dilute simulation, namely, FD···OD$_2$, F$^-$···DOD$_2^+$, and F$^-$. Because of the large number of hydroniums in the system,[51] practically all fluorines have at least one hydronium in their first solvation shell, and therefore, no F$^-$ ions with *only* water around them were observed. The distinction between the F$^-$ ion and the F$^-$DOD$_2^+$ ion pair is made using the FD−RDFs over the 2 ps time period. The F$^-$ ions have an average coordination number of 3.5 and

have only one peak in the FD−RDF below 2.5 Å centered at 1.5 Å. During the last 2 ps of the simulation, there were four of these F$^-$ ions. Only one of the fluorines could be unequivocally assigned to an undissociated DF molecule. Its coordination number was only 2 (cutoff 2.75 Å), comprising the undissociated deuterium and one other within 1.5−2.75 Å range. We have assigned the rest of the fluorines to the ion pairs. The FD−RDFs of these seven atoms have a coordination number of 3. As seen in the dilute case, in the ion pair, the central deuterium is alternately close to either heavy atom. This can be seen in the FD−RDF as features from both extreme geometries. There are, indeed, two clear but connected peaks corresponding to the undissociated DF and the peak at 1.5−2.5 Å comprising the hydrogen bonded waters and hydroniums. The geometry has also been illustrated in Figure 8.

The Giguere model of aqueous HF was partly based on interpretation of vibrational spectra (infrared and Raman). To compare our results with these experiments directly, we have calculated the frequency spectra of all of the deuteriums in the simulation box. The spectrum, shown in Figure 3c, retains strong bands related to water. The O−D, F−D stretching band ranges from 2700 cm$^{-1}$ all the way down to the D−O−D bending bands centered around 1150 cm$^{-1}$. The O−D librations, heavy atom stretches, and translations constitute the broad peak below 600 cm$^{-1}$. The accustomed difference to pure water spectrum is the continuum of states between the high-frequency strecthes and the bendings at 1200 cm$^{-1}$. However, we find also a direct signature of aqueous DF. This is the additional peak around 750−800 cm$^{-1}$. This can be assigned to the FD libration in the undissociated complex *and* the corresponding librations in the ion pairs. The spectrum has also another new feature as the shoulder at 1000 cm$^{-1}$, which we associate to the same libration modes. See Figure 4.

We have a good agreement with the IR spectra of Giguere and Turrell, even if we do not observe a clear peak around 1500 cm$^{-1}$. However, this frequency is contained in the continuum below the DO stretches. Our frequency analysis is based on the motion of the atomic nuclei, which has been shown to correlate well with IR and Raman spectra.[52] However, even if the atomic velocities corresponded to the frequencies of the dipole moments, their weighting functions can be very different. We assume that this is the case in the D$_3$O$^+$ ion 1500 cm$^{-1}$ frequency. In the low concentration DF simulation, we observed a peak at 1500 cm$^{-1}$, which should be interpreted as a stretching frequency of the F···D···O deuterium, but the frequency data at this range is not conclusive. In general, our findings at this concentration are in agreement with the F$^-$···H$_3$O$^+$ model proposed by Giguere.[10,11]

Note, that this simulation did not reveal any (DF)$_n$···F$^-$ type complexes. There may be several reasons for this. The viscosity of the solution or memory effects from the starting configuration are among them. The importance of these factors is under investigation. However, as the polyfluorides have been invoked to explain experimental results,[10−12,17,53] we introduced one to study its behavior. We chose the simplest and a priori most stable of them: the bifluoride FDF$^-$.

**43% DF Solution, (DF)$_{13}$ (D$_2$O)$_{19}$, a System Containing FD···F$^-$.** Two simulations were performed: first, using Becke-only for 4.5 ps and then 6 ps using BLYP, as explained in the Technical Details section. The RDFs and the coordination numbers have been calculated using the last 5 ps from the BLYP simulation. These are mostly the same as in the 40% solution, except for the F−F, where a peak at 2.5 Å reveals the bifluoride (RDF given in the Supporting Information).

Ab Initio Aqueous Hydrofluoric Acid

*J. Phys. Chem. B, Vol. 106, No. 43, 2002* **11319**
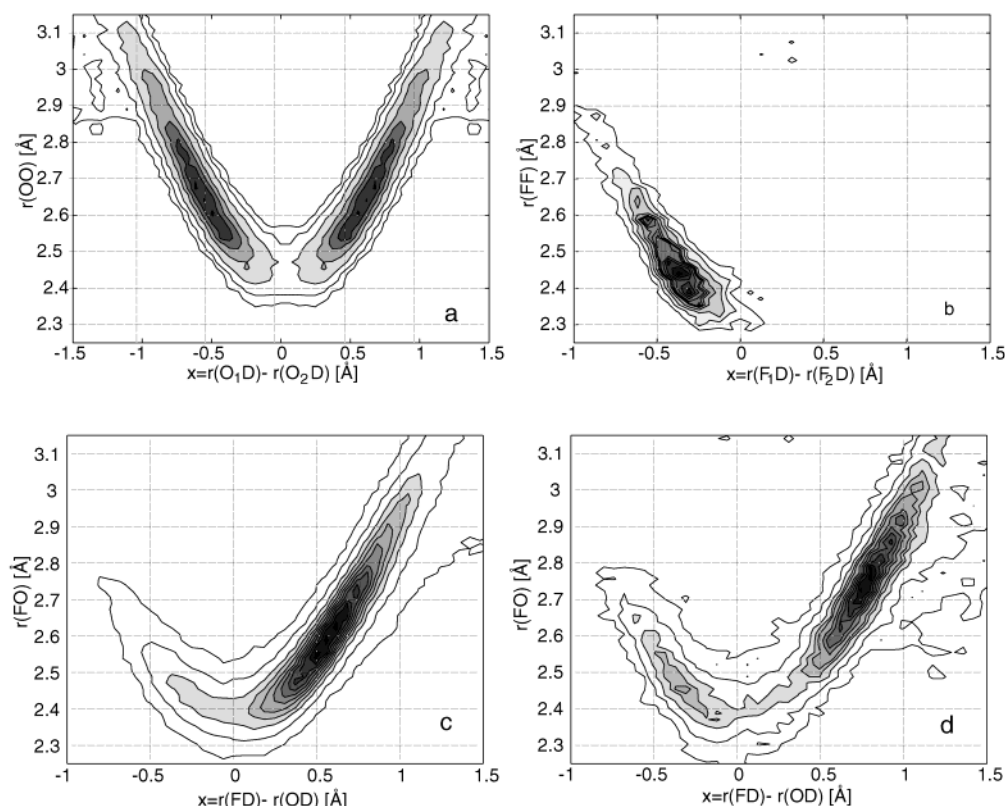


**Figure 8.** Distributions of the heavy atom distance and asymmetric stretch coordinates of deuteriums in between. Note that the proton in the FDF⁻ ion resides practically on one side of the ion, which means a long lifetime for the complex. The asymmetric stretch coordinate has been defined, e.g., $x(\text{FDO}) = r(\text{FD}) - r(\text{OD})$. Thus, the negative asymmetric stretch coordinate value means that the deuterium is closer to the fluorine. Contours a−c correspond to the 13DF:19D$_2$O simulation, and d corresponds to the 1:31 simulation.

The FDF⁻ ion set up at the beginning of the simulation remained the only observed. The asymmetric structure, FD···F⁻, was dominant with both density functionals. Only in the beginning of the Becke-only simulation, between 2 and 3 ps, the structure was symmetric, that is, the central deuterium fluctuated around the midpoint of the FF axis. During the rest of the simulation, the deuterium was clearly closer to the other fluorine. The presence of the single well structure can be correlated with the hydration of the DF part and the FF distance. When the DF was poorly solvated (coordination number 1−2, excluding the central D and the other fluorine atom), the asymmetric structure was dominant, whereas for the symmetric structure, both fluorines had higher and roughly equal coordination numbers. The FF distance has been plotted against the asymmetric stretch coordinate in Figure 8b. The gas-phase FHF⁻ has been exhaustively characterized by Thorson et al.[54] They have shown that the potential energy surface has a single minimum at FF separation of 2.27 Å, consistently with experimental data.[55] Thorson et al. also find two minima for the asymmetric proton coordinate if the FF distance is increased. Our data agrees with this. The shape of the distribution of the FDF⁻ geometry in Figure 8 is very similar to the distribution produced by the potential energy surface of Thorson et al. The solvation of the fluorines pulls them apart to the extent that the deuterium in the middle experiences two minima and resides in one of them, depending on the solvation of the fluorines: the one with smaller number of hydrogen bonds gets the common deuterium.

[F$_{(n+1)}$D$_n$]⁻ molecules are known experimentally from potassium HF salts, KF·$n$HF,[56,57] and theoretical simulations.[23,24,53,54] For comparison, the F−F distances of the FD···F are 2.30−2.44 and 2.28 Å for the F−H−F complex in these crystals.[57] The frequency for the deuterium transfer from one fluorine to the other seems slow, at least in the order of our simulation time. The inclusion of quantum effects on the transferring proton would facilitate the transition.

Ionic character is dominant in the heavy atom interactions. At the end of the simulation, there were five clear F⁻ ions and hydroniums. The ion−hydronium structure is described in previous sections. The F⁻ ions (hydroniums) had one to three hydroniums (fluorides) in their first solvation shell, so that the most likely arrangement was two hydroniums in the fluorine solvation shell.

The total deuterium frequency spectrum is very similar to the previous ones (Figure 3d). The spectrum shows a continuum of states between the D−O−D bending peak and the high-frequency OD and FD stretchings. This is in good agreement with the data by Giguere and Turrell.[10] The deuteriums associated with fluorines are in a very strong interaction with the coordinated water molecule. This manifests itself by the water bending frequency (or better D$_3$O⁺) showing up in the spectrum. A clear peak at 750 cm⁻¹ is associated with the libration frequencies of FD···OD$_2$ and F⁻···DOD$_2$⁺, as before. The spectrum of the deuterium in the [FD···F]⁻ complex exhibited also a strong libration peak at 650 cm⁻¹, and stretching at 1600−2500 cm⁻¹, see Figure 9. The first coincides well with the experimental peak at 730 cm⁻¹,[10] but again, no clear peaks at 1500 cm⁻¹ were found.

In contrast to the interpretation of Giguere,[11] and in agreement with experimental spectra and interpretation of Taylor and Vidale[58] as well as the theoretical spectra of von Rosenvinge et al.,[53] the FDF⁻ libration at 500−800 cm⁻¹ is a valid assignment. This result illustrates the power of AIMD, where we can identify the species responsible for the observed frequency unequivocally.
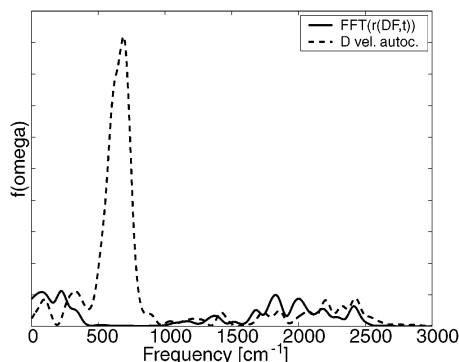
**Figure 9.** 13:19 DF:D$_2$O simulation. Deuterium total vibrational spectrum of the FDF$^-$ ion computed from the last 5 ps of the simulation. The solid line has been obtained by Fourier transform of the FD bond length as function of time, and the dashed line is from the velocity autocorrelation function. The intensity is arbitrary. The librational and translational motion appear only in the latter.

## Discussion

At low concentration, the F$\cdots$D$\cdots$O structure has two minima for the deuterium position along the FO axis. The hydrogen bonds formed by the fluorine can be sorted in three categories, according to the distance to its closest deuteriums. (a) The asymmetric stretch coordinate $\sim -0.3$ Å corresponds to undissociated DF. (b) The same positive value corresponds to the ion pair. These structures have an average FO distance of 2.4 Å. These two major configurations have average coordination numbers of 3.2 and 4.6, respectively (using the FO distance cutoff of 3.2 Å). (c) The third option is the solvent separated ion pair. In this case, fluorine accepts four hydrogen bonds in a tight tetrahedral arrangement, constituting a sharp peak at 1.6 Å in the FD$-$RDF.

The dynamics of the ion pair follows general principles established earlier.[22,59,60] The coordination number of the fluorine atom increases prior to the deprotonation and decreases before accepting the deuterium again. The special water has a coordination number of three only when it is part of the ion pair. Four and Five hydrogen bonds at other times prevent it from accepting the extra deuterium from the fluorine to form hydronium. The hydrogen bond donor water molecule, labeled *a* in Figure 1, is present at other times.

To fully dissociate DF, one of the deuteriums associated with the D$_3$O$^+$ should jump to one of the neighboring water molecules and thus create a charge separation between the F$^-$ and D$_3$O$^+$. At low concentration, the extra deuterium remained close to the fluorine. The behavior of HCl and HBr is different, as the ions formed upon dissociation do not form ion pairs but rather avoid each other.[47,61,62] At higher concentrations, some of the fluorines were better described as isolated F$^-$ ions. Although, now because of the very high concentration of hydroniums, these always stayed close to the F$^-$ ions. We propose that this interion attraction is the factor that diminishes the acidity, i.e., proton activity in dilute solutions.

Even in short simulations such as the dilute case (4 + 12 ps), we can expect the system to display the experimental acidity as a time average. The weights of the configurations FD$\cdots$OD$_2$, F$^-\cdots$DOD$_2{}^+$, and F$^-\cdots$(DOD)$_n$ are 60%, 30%, and 10%, respectively. See Figure 2. Thus, if we, following Giguere, interpret the ion pair as a nonfree proton,[11,14] the two first conformations sum up to give $\alpha$, the extent of dissociation, as 0.1. Estimating the proportion of "free", i.e., active, D$_3$O$^+$ (or F$^-$) in solution using simple dissociation equilibrium and experimental acidity constant for DF,[4] $K_a = 3.34 \times 10^{-4}$ M

gives the percentage of F$^-$ ($c_{DF} = 1.7$ M, $[F^-] \approx \sqrt{(K_a[DF])}$) $\approx 2.4\%$, which is a factor of 4 less than our simulation, but still in qualitative agreement. Note, that if the ion pair was considered as dissociated DF then the disagreement would be more pronounced. Note also, that hydronium momentarily in the second solvation shell would still not be completely free.

The CPMD data suggest the presence of both FD$\cdots$OD$_2$ and F$^-\cdots$D$_3$O$^+$ structures in dilute solution. Both of these would also contribute to the experimental absorption ranging from 600 to 1000 cm$^{-1}$. The D$_3$O$^+$ has been interpreted to produce a signal at 900 cm$^{-1}$, which is consistent with our simulations.[10] We could not unequivocally determine individual configurations that produce the two features appearing in the total frequency spectra. At present, we will conclude, that the absorption at that range derives from both species but, the acidic proton is bound in either case, and thus represents undissociated hydrogen fluoride in the sense that the activity of the proton is expected to be small.

The F$\cdots$D*$\cdots$OD$_2$ potential well is not symmetric. The shape of the potential is determined by the coordination of the fluorine and accepting water. In dilute solution, high solvation prefers the ion complex form, where the fluorine end is solvated by four waters. The special water, i.e., the occasional hydronium ion, is closer than the other solvating waters. In the concentrated case, the surroundings become more ionic. The interaction of these hydroniums and corresponding fluorides is stronger than with water. This competition leads to the accumulation of hydroniums in the first solvation shell of F$^-$. Simultaneously, the first peak in the FO$-$RDF (and FD$-$RDF) shifts to shorter distance and the coordination number diminishes. This is reasonable, because the coordination sphere gets crowded as the bonds are shortened. The presence of hydroniums in the system induces the dissociation of the remaining hydrogen fluorides.

The overall RDFs can be decomposed to those of dissociated and undissociated DFs, see Figure 6. It is clear, that the free F$^-$ ions are solvated more strongly; they form linear hydrogen bonds, have a coordination number between 3 and 4, and have a FO$-$RDF maximum at 2.5 Å. The undissociated DFs represent the other type of unsymmetrical proton potential. Now the fluorine is poorly solvated and, hence, keeps the proton, which in turn forms one strong hydrogen bond to a neighboring water molecule. The solvation shell of this type of fluorines is more diffuse; (excluding the deuterium and the water oxygen bonded to it) the coordination number is 1$-$2, and the first RDF peak is wide, and has a maximum at 2.8 Å.

In the low concentration simulation, the FO and OO$-$RDFs coincide beyond the first peak. The first peak has shifted to begin 0.2 Å before the OO$-$RDF. We interpret this to mean that the fluorine sits in a water coordination site and has not perturbed significantly the long-range water structure. In the higher concentrations, there is difference in the number of either atom type in the first and second shell or in the FO and OO$-$RDFs, but the peaks appear qualitatively at the same places. It is therefore instructive to look at the total heavy atom structure, XX$-$RDFs, where X means both O and F atoms. Apart from the first peak, the RDFs have all of the same features as the pure water OO$-$RDF. See Figure 10. This means, that the fluorines fit in the general water structure and have not completely disrupted the hydrogen bond network, even after the substantial changes in the short-range structure.

We will now describe the short range differences in more detail. The main feature is the absence of the second peak at ca. 1.8 Å in the OD$-$RDF suggesting that the hydrogen bonding

Ab Initio Aqueous Hydrofluoric Acid

*J. Phys. Chem. B, Vol. 106, No. 43, 2002* **11321**
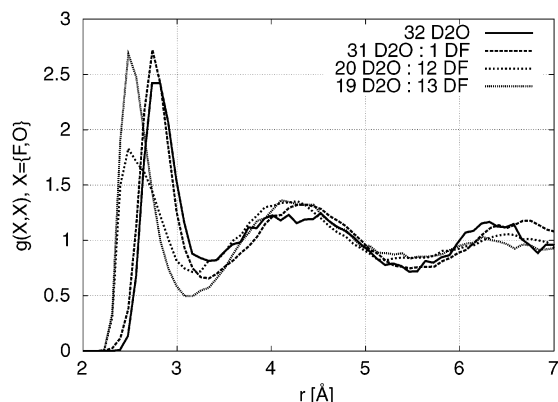


**Figure 10.** Heavy atom RDFs, i.e., $g_{XX}$, X = {F,O}, from bulk water through all simulated DF concentrations. Note the shifting of the first peak to shorter distance at high concentration. The peak in the highest concentration comes from the FDF complex. The second peak at 4.3 Å and third at 6.5 Å are quite similar in all cases.

network is mostly dominated by the $(D_3O)^+$ or $(D_5O_2)^+$ complexes. The short average O$-$O distance is also consistent with the existence of hydroniums. The ions tend to cluster, that is, the fluorides preferably bind hydroniums. This clustering prevents the usual tetrahedral network from breaking down completely. The average oxygen coordination number is 3.2, which is less than in pure water. See Figure 7. Yet the second and third peaks of the combined O$-$O and F$-$O are quite similar to pure water. See Figure 10. This demonstrates again that the general hydrogen bond network has not disintegrated. This lower coordination is achieved by not occupying all (tetrahedral) water sites at the same time. Three-coordinate hydroniums are not planar, but pyramidal, and the same applies to central F$^-$ ions, and generally most heavy atoms. Fluctuations in the 3D-network structure elongate one of the bonds so that the average coordination is achieved.

The water bending peak can be used as an estimate of the accuracy of our frequencies and to calibrate them against experimental data. We find the peak at 1150$-$1200 cm$^{-1}$, in all simulations, compared to the 1200 cm$^{-1}$ peak observed experimentally. We have not included the description of nuclear quantum effects in our simulations. However, because comparisons are made to the experimental results for deuterated samples, we expect quantum effects to play a reduced role.

The libration and stretching frequencies of FD$\cdots$OD$_2$ are very sensitive to the FO distance. The simulations can be windowed so that the Fourier transform of the D* velocity autocorrelation function results in narrow bands within the libration and stretching bands of the whole simulations. The continuous fluctuations in the solvation environment and therefore the FO separation result in the wide bands seen in the overall spectra. These frequencies do not extend to the experimentally observed sharp peak at 2640 cm$^{-1}$, which has been assigned to undissociated DF.[10] The highest frequencies found in the undissociated DF molecules are around 2500 cm$^{-1}$ and clearly less than OD stretching in water molecules. This suggests that the experimental spectra should be reinterpreted.

The whole libration peak range 200$-$700 cm$^{-1}$ has blue shifted starting from pure water with increasing DF concentration. This can be understood with the strengthening of the intermolecular forces as the ionicity of the system increases: The first neighbor heavy atoms are closer to each other, which creates a stronger field and restoring force for the oscillating molecule (e.g., DF libration). The opposite applies for the high-frequency XD stretchings: Now, because of the stronger

hydrogen bonding to the neighboring molecule, the intramolecular frequencies decrease.

In addition to the vibrational spectrum, structural aspects of the HF solvation could be studied experimentally using neutron and X-ray scattering techniques. Combined neutron and X-ray experiments are able to resolve the average radial distribution functions, and neutron scattering with isotope substitution can now even resolve individual radial distribution functions. Also, dynamical aspects of the DF$\cdots$D$_2$O complex could perhaps be probed by ultrafast spectroscopy. These experiments thus would complement the IR studies and our simulation results.

One has to be careful in interpreting the results. Water and especially concentrated acids are viscous liquids and have long relaxation times. This means that we might be looking at some statistically less important conformations. We did not observe large structures such as the polyfluorides in KD:2FD simulation by von Rosenvinge et al., but only the bifluoride ion, FDF$^-$.[53] Nevertheless, we are confident that despite the small size of our system our results bring important new insight to the strongly ionized liquid solvation. Further studies on the relaxation of the concentrated systems and higher polyfluoride ion formation are in progress.

## Conclusions

We have studied the structure and dynamics of aqueous hydrogen fluoride solutions. Low concentration (7 wt %) DF-(aq) has FD$\cdots$OD$_2$ $\leftrightarrow$ F$^-\cdots$D$_3$O$^+$ as its basic unit, which accounts for over 90% of the configurations. The fluorine end of the unit is poorly solvated when in the neutral form. Counting the hydrogens within 2.5 Å of the fluorine, the coordination numbers in the neutral and ionic form are 2 and 4$-$5, respectively.

At the end of the high concentration (40 wt %) simulation, the 12 fluorines were sorted as follows: four were F$^-$ ions, one was a DF molecule, and the remaining seven were best described as ion pairs. The RDFs of F$^-$, DF, and F$^-\cdots$D$_3$O$^+$ are distinct: the first has one clear peak at 1.0$-$2.0 Å including 3.5 hydrogens. Undissociated DF has two peaks; the first corresponds to the covalently bonded deuterium below 1.2 Å, and the second corresponds to one water or hydronium the within 1.5$-$2.5 Å. The ion pair is a combination of these two, i.e., has two peaks and a total coodination number of three (see Figure 6). The ionized fluorine is thus most coordinated. As no spontaneous formation of the bifluoride ion, FDF$^-$, was observed, we built one, and in the 43 wt % simulation, it appeared to be stable. The F$^-$ ions and DF's in the latter simulation were similar to the previous one.

The most appropriate way to describe solvated DF is to view it as a complex dynamically fluctuating between F$-$D$\cdots$OD$_2$ and F$^-\cdots$D$_3$O$^+$ structures. At all concentrations, we find also long-lived, in the order of picoseconds, F$^-\cdots$D$_3$O$^+$ complexes as proposed by Giguere.[10,11] The equilibrium between the dissociated and undissociated species can be seen as a result of competetition between the covalent bond energy in DF and high solvation energy of F$^-$.

The frequency spectra obtained from the velocity autocorrelation function has been compared to experimental data. We have confirmed the peak at 750 cm$^{-1}$ as a D* libration in FD*$\cdots$OD$_2$ and F$^-\cdots$D*OD$_2$, in agreement with Giguere et al.[10] No clear intensity at 1400 cm$^{-1}$, corresponding to D$_3$O$^+$ bending was found, but the continuum of stretching frequencies between the OD stretch and DOD bending of pure water were faithfully reproduced.

Overall, in addition to the new peaks, the total spectra have two general features: the libration band has blue shifted and the stretching band red shifted because of the strengthening of the intermolecular and weakening of the intramolecular forces as the ionicity increases.

We have shown that both dissociated and undissociated hydrogen fluoride molecules are present in the concentrations below 43 wt %. The equilibria between these species is clearly dynamical. X-ray or neutron diffraction studies would be useful to confirm our structural results.

**Supporting Information Available:** Tabular data for the FD and OD-RDFs. This material is available free of charge via the Internet at http://pubs.acs.org.

### References and Notes

(1) Bountis, T. *Proton Transfer in Hydrogen-Bonded Systems*; Kluwer Academic Publishers: Norwell, MA, 1992; Vol. 291.

(2) Ando, K.; Hynes, J. T. *Adv. Chem. Phys.* **1999**, *110*, 381−430.

(3) Hammes-Schiffer, S. B.; Salomon, R. *Int. Rev. Phys. Chem.* **2001**, *20*, 591−616.

(4) Kresge, A. J.; Chiang, Y. *J. Phys. Chem.* **1973**, *77*, 822.

(5) Hyman, H. H.; Kilpatrick, M.; Katz, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 3668−3671.

(6) Bell, R. P.; Bascombe, K. N.; McCourbey, J. C. *J. Chem. Soc.* **1956**, 1286−1291.

(7) Pauling, L. *J. Chem. Educ.* **1976**, *53*, 762.

(8) Pauling, L. *J. Chem. Educ.* **1956**, *33*, 16−17.

(9) Myers, R. T. *J. Chem. Educ.* **1976**, *53*, 17−19.

(10) Giguere, P. A.; Turrell, S. *J. Am. Chem. Soc.* **1980**, *102*, 5473−5477.

(11) Giguere, P. A. *Chem. Phys. Lett.* **1976**, *41*, 598−600.

(12) Davies, C. W.; Hudleston, L. J. *J. Chem. Soc.* **1924**, *125*, 260−268.

(13) Braddy, R.; McTigue, P. T.; Verity, B. *Fluorine Chem.* **1994**, *66*, 63−7.

(14) Giguere, P. A.; Martel, C.; Turrell, S. *Chem. Phys. Lett.* **1978**, *56*, 231−234.

(15) Giguere, P. A.; Turrell, S. *Can. J. Chem.* **1976**, *54*, 3477−3482.

(16) Khorami, J.; Beaudoin, R.; Menard, H. *Can. J. Chem.* **1987**, *65*, 817−820.

(17) McTigue, P.; O'Donnell, T. A.; Verity, B. *Aust. J. Chem.* **1985**, *38*, 1797−1807.

(18) Simons, J. H. *Fluorine Chemistry*; Academic Press, Inc.: New York, 1950; Vol. I.

(19) Broene, H. H.; Vries De, T. *J. Am. Chem. Soc.* **1947**, *69*, 1644−1646.

(20) Tuckerman, M. E.; Marx, D.; Klein, M. L.; Parrinello, M. *Science* **1997**, *275*, 817−820.

(21) Laasonen, K.; Sprik, M.; Parrinello, M. *J. Chem. Phys.* **1993**, *99*, 9080−9089.

(22) Tuckerman, M.; Laasonen, K.; Sprik, M.; Parrinello, M. J. *J. Chem. Phys.* **1995**, *103*, 150−161.

(23) Simon, C.; Cartailler, T.; Turq, P. *J. Chem. Phys.* **2002**, submitted.

(24) Simon, C.; Cartailler, T.; Turq, P. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3119−3124.

(25) Laasonen, K.; Klein, M. L. *Mol. Phys.* **1996**, *88*, 135−142.

(26) Röthlisberger, U.; Parrinello, M. *J. Chem. Phys.* **1997**, *106*, 4658−4664.

(27) Raugei, S.; Klein, M. L. *J. Phys. Chem. B* **2001**, *105*, 8212−8219.

(28) Kim, D.; Klein, M. L. *J. Phys. Chem. B* **2000**, *104*, 10074−10079.

(29) Kim, D.; Klein, M. L. *J. Am. Chem. Soc.* **1999**, *121*, 11251−11252.

(30) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *11*, 199.

(31) Sato, H.; Hirata, F. *J. Am. Chem. Soc.* **1999**, *121*, 3460−3467.

(32) Laurs, N.; Bopp, P. *Ber. Bunsen−Ges. Phys. Chem.* **1993**, *97*, 982−96.

(33) Laasonen, K. E.; Klein, M. L. *J. Phys. Chem. A* **1997**, *101*, 98−102.

(34) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.

(35) Laasonen, K.; Pasquarello, A.; Car, R.; Lee, C.; Vanderbilt, D. *Phys. Rev. B* **1993**, *47*, 10142−10153.

(36) Galli, G., Pasquarello, A., Allen, M. P., Tildesley, D. J., Eds.; *NATO ASI series C*; Kluwer: Dordecht, The Netherlands, 1993; Vol. 397, p 261.

(37) Vanderbilt, D. *Phys. Rev. B.* **1990**, *41*, 5048.

(38) Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155.

(39) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(40) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048.

(41) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(42) The FINGER program has mainly been developed in the Helsinki University of Technology, Espoo, Finland.

(43) Laasonen, K.; Klein, M. L. *J. Am. Chem. Soc.* **1994**, *116*, 11620−11621.

(44) Silvestrelli, P. L.; Parrinello, M. *J. Chem. Phys.* **1999**, *111*, 3572−3580.

(45) Sprik, M.; Hutter, J.; Parrinello, M. *J. Chem. Phys.* **1996**, *105*, 1142−1152.

(46) Maerker, C.; Von R. Schleyer, P.; Liedl, K. R.; Ha, T.-K.; Quack, M.; Suhm, M. A. *J. Comput. Chem.* **1997**, *18*, 1695−1719.

(47) Raugei, S.; Klein, M. L. *J. Chem. Phys.* **2002**, *116*, 196−202.

(48) Note: In the protonated case, the solvation should be considered as bonds both to the fluorine and deuterium. During our simulations, the latter was always hydrogen-bound to the special water molecule, see Figure 1, and thus counted as one in the coordination number.

(49) Allen, M. P.; Tildesley, D. J. *Computer simulations of liquids*; Clarendon press: Oxford, U.K., 1989.

(50) Schmitt, U. W.; Voth, G. A. *Chem. Phys. Lett.* **2000**, *329*, 36−41.

(51) Note: Recall that, in addition to the long-lived "free" hydroniums, the ion pairs can be considered as hydroniums next to fluorines.

(52) Lyubartsev, A. P.; Laasonen, K.; Laaksonen, A. *J. Chem. Phys.* **2001**, *114*, 3120−3126.

(53) Rosenvinge, v. T.; Parrinello, M.; Klein, M. *J. Chem. Phys.* **1997**, *107*, 8012−8019.

(54) Epa, V. C.; Choi, M.; Klobulowski, M.; Thorson, W. R. *J. Chem. Phys.* **1990**, *1*, 466−472.

(55) Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1987**, *87*, 6838−6841.

(56) Mootz, v. D.; Poll, W. *Z. Anorg. Allg. Chem.* **1982**, *484*, 158−164.

(57) Mootz, D.; Boenigk, D. *J. Am. Chem. Soc.* **1986**, *108*, 6634.

(58) Vidale, G. L.; Taylor, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 294.

(59) Day, T. J. F.; Schmitt, U. W.; Voth, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 12027−12028.

(60) Tuckerman, M. E.; Ungar, P. J.; von Rosenvinge, T.; Klein, M. L. *J. Chem. Phys.* **1996**, *100*, 12878−12887.

(61) Laasonen, K.; Klein, M. L. *J. Am. Chem. Soc.* **1994**, *116*, 11620−11621.

(62) Raugei, S.; Klein, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 9484−9485.