Liquid Hydrogen Fluoride with an Excess Proton: Ab Initio Molecular Dynamics Study of a Superacid

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Proton transfer in the condensed phase is of great interest, not only because of its fundamental importance in chemical and biological systems, but also because it is a diverse and rich phenomenon. To date, most of the effort has been devoted to water and related systems.[1] However, here we present the ab initio molecular dynamcis study of a different hydrogen bonded system, namely, liquid hydrogen fluoride (HF) with an excess proton.

The significance of this system is obvious from the fact that liquid HF is a key solvent in the chemistry of superacids.[2,3] It is also an ideal candidate for studying the proton-transfer mechanism in a polar solvent. Superacidic HF solutions can be made by desolving the Group V pentafluorides (e.g., SbF_5, AsF_5, TaF_5) in anhydrous liquid HF: $XF_5 + 2HF \rightarrow XF_6^- + H_2F^+$, where X = Sb, As, Ta, etc., and the neutral and protonated liquid are denoted by 2HF and H_2F^+, respectively.

Indeed, Hyman et al.[4] and also Gillespie and Moss[5] found that the H_2F^+ ion, more precisely a proton solvated by HF, has an abnormally high mobility in the superacidic HF−SbF_5 solution. The estimated molar conductivity of the cationic species is 350 Ω^{-1} cm^2 mol^{-1}, which is comparable with ionic conductivity for H_3O^+. Moreover, they found that the electrical conductivity of HF−SbF_5 solutions showed a dramatic dependence on the SbF_5 concentration. At a low concentration, the conductivity of the solution quickly rose with the addition of SbF_5 and reached its maximum at about 10 mol % of SbF_5, and then sharply fell off.

These findings strongly suggest that the proton in superacidic HF solutions conducts by a proton jump mechanism. It is well-known that in liquid HF the majority of molecules exist as H-bonded chains.[6−10] When XF_5 is added to liquid HF, it becomes fluorinated and forms an XF_6^- anion, which is stabilized by the surrounding HF molecules through H-bonds. The proton resulting from the fluorination reaction is transferred to a preexisting HF chain to form a protonated HF oligomer. When the concentration of XF_5 is low, the addition of XF_5 results in increasing conductivity, simply because of the increasing number of ionic species in the solution. However, as the concentration of XF_6^- in solution further increases, more HF molecules are consumed to solvate XF_6^- ions and depolymerization of the protonated HF chains takes place. This depolymerization destroys the chain structures, which are effective media for the proton jump process.

To investigate the behavior of an excess proton in liquid HF, we have employed the Car−Parrinello molecular dynamics method,[11] where the interatomic forces are derived at each time step from ab initio electronic structure calculations based on the density functional theory.[12] The nuclear quantum effect is certainly of great interest and can be crucial for the system where the hydrogenic motion is important. However, because of enormous computational cost, we treated the nuclear motions classically. The valence electron wave functions are expanded in plane waves (energy cutoff = 60 Ry) and the interaction between the valence electrons and the ionic cores is described by the norm-conserving pseudopotentials. We employed the exchange energy expressions by Becke[13] and the correlation energy expression by Lee, Yang, and Parr,[14] the combination commonly known as BLYP. All calculations were done with the program CPMD.[15]

The simulation system comprising 54 HF molecules and one proton, which was contained in a $23a_o \times 23a_o \times 23a_o$ periodic cubic box, was prepared as follows. First, well-equilibrated neutral liquid HF at 290 K was generated following the procedure employed in an earlier study.[10] Next, one proton was added to the simulation system. To neutralize the excess charge, a uniform background negative charge was added to the system. The bare proton was quickly solvated by nearby HF molecules, and a protonated HF chain was formed. Then, the temperature, which had increased due to the solvation process, was readjusted to 290 K. After this, the system was reequilibrated for ∼1.5 ps. Finally, data were sampled for ∼2.5 ps.

At first, to analyze the simulation data, the excess proton should be unambiguously identified. From our previous ab initio MD study of gas-phase protonated HF clusters,[16] we have learned that, depending on the number of HF molecules in the chain, the excess proton is either bonded to an HF molecule to form H_2F^+ (bent, C_{2v} symmetry) or located symmetrically between two HF molecules to form $H_3F_2^+$ (planar, D_{2h} symmetry). In either case, the excess proton (H^+) is the hydrogen atom whose bond distances to the two nearby F atoms are most alike. The special fluorine atom (F^*) is also defined in a similar way. In the former case, H^+ is one of two hydrogen atoms bonded to the F^* atom. In the latter case, H^+ is shared by two F^* atoms.

Figure 1 shows a representative time evolution of the excess proton configurations. The protonated HF chain is drawn in color, along with normal HF chains as a black and white background. As evidently seen in Figure 1, H^+ (yellow sphere) and F^* (red sphere) are always adjacent to each other, forming an H_2F^+ or $H_3F_2^+$ structure. More importantly, these structures move along the chain at a fast rate. Note that, although actual atomic positions do not change much, the excess proton, and special F atom, travel across three bonds during a very short time (81.5 fs).

One should not equate the time scale of this microscopic intrachain process, localized on a single protonated HF chain, to the macroscopic conductivity. Because the chain has a finite length, eventually, macroscopic long-range proton transfer will necessarily involve hydrogen bond making and breaking processes between the protonated chain and a neighboring neutral chain. The short MD run time precludes a reliable estimate of the time scale for this slower interchain process. However, examination of the trajectory revealed that the proton is transferred by the following processes, which takes roughly a picosecond: (i) the proton moves back and forth on the protonated chain as illustrated in Figure 1; (ii) the protonated chain is connected to a neutral

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Figure 1. Instant configurations of protonated liquid HF, which reveal apparent mobility of the excess proton.

chain by a hydrogen bond making process; (iii) the excess proton moves to a newly acquired location on the formerly neutral chain; and (iv) the H-bond breaking process disconnects the two chains and leaves the excess proton on a new chain. The overall mechanism is somewhat similar to that of the water system in the sense that macroscopic transport requires both the H-bond making and breaking processes. However, the transport mechanism in HF is unique because it involves interchain dynamics, rather than the second solvation shell dynamics as in water.[1]

The effects of an excess proton on the liquid structure are displayed in Figure 2, where the radial distribution functions (RDF), $g_{FF}(r)$, $g_{HF}(r)$, and $g_{HH}(r)$, are shown. The same RDF for the neutral liquid HF are also shown for comparison. Interestingly, the excess proton makes the liquid more structured. It is also noticeable that $g_{HF}(r)$ has a nonzero intensity around 1.2 Å, contrary to the neutral liquid HF. This nontrivial finding can be explained by the existence of the protonated HF chains and the stronger hydrogen bond between H_2F^+ and HF (35 kcal/mol[17]) than that of two HF molecules (4.81 kcal/mol[18]).

The signature of the protonated HF chain can be also found in Figure 3, where the Fourier transforms of the velocity autocorrelation functions for both the neutral and protonated liquid HF are displayed. Compared to the neutral liquid HF, the protonated liquid HF has small additional features between 1000 and 2500 cm^{-1}, which arise from the protonated HF chains.[16,19] Also, the downward shift of the peak at ∼3100 cm^{-1} agrees well with experiment.[19]

In summary, we have investigated the effect on the structure of the liquid HF of an excess proton by ab initio molecular dynamics simulation. We have observed very fast diffusion of the excess proton along the hydrogen bonded HF chains, which is likely relevant for the superacidity. Additionally, the dynamical

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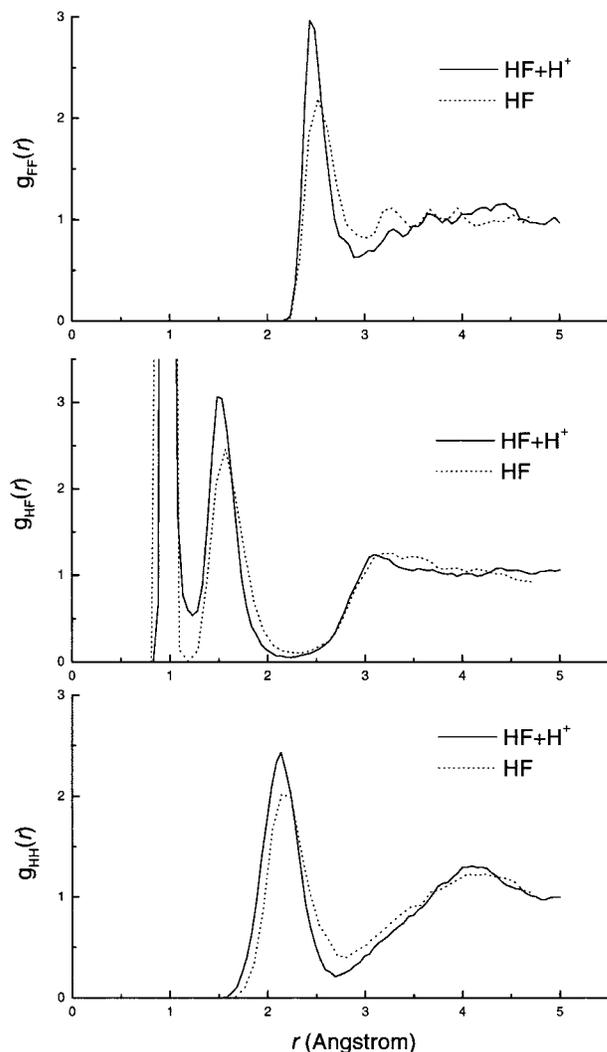
Figure 2. Radial distribution functions for (a) F−F, (b) H−F, and (c) H−H. The solid and dotted lines correspond to the liquid HF with an excess proton and the neutral liquid HF, respectively.
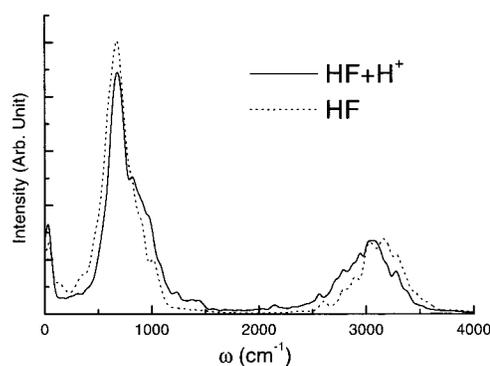
Figure 3. Power spectra for the liquid HF with an excess proton (solid line) and the neutral liquid HF (dotted line).

properties of the system show manifestations of the existence of the protonated HF chain. While further analysis and path integral calculations will be required to fully characterize the nature of the superacid, our findings are already consistent with a large body of experimental data.[3−5,19]