On the Structure of Liquid Hydrogen Fluoride

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Introduction

The hydrogen bond is the dominant feature of the structural chemistry of HF in all phases; the solid is composed of unbranched, zigzag chains while the vapor is composed of cyclic oligomers and clusters. In the liquid, the macroscopic properties are consistent with strong hydrogen bonds, though until this report, there has been no experimental data to confirm this at the pair correlation function level.

Methods and Materials

In order to determine the atomic structure and therefore the hydrogen bonded nature of HF, high energy X-ray diffraction measurements on 11-ID-C and neutron diffraction measurements on GLAD at IPNS were performed on samples of HF and DF at 296±2 K and 1.2±0.1 bar. It is possible, by taking linear combinations of the three diffraction patterns, to solve the structure factor equations and explicitly calculate each of the individual structure factors. The pair correlation function is related in general to the scattered intensity by Fourier transformation by

$$S(Q) = 1 + \frac{4\pi\rho}{Q}\int r\left[G(r)-1\right]\sin(Qr)\,dr$$

Extraction of the partial structure factors allows the determination of the distribution of atomic distances from the radial distribution functions. The X-ray diffraction signal is dominated by the Fluorine-Fluorine partial.

Results

The Fluorine-Fluorine radial distribution function is important in distinguishing between different calculational models. The first peak in this function occurs at 2.5±0.03 Å and is in close agreement with *ab initio* molecular dynamics and simulations, though most models predict this distance with reasonable accuracy. Moreover, figure 1 shows several peaks occurring beyond the first peak have been predicted to some extent by several simulations. The average HF-H angle gives an indication of the linearity of the hydrogen bonds and was found to be 104±8°, indicative of bent hydrogen bonds. The average FH-F angle is found to be 165±10° and defines the degree of orientation between different molecules in the chain.

Discussion

The degree of chain branching that occur in the liquid also varies widely between the different models, ranging from no branching to 20% branching. In order to visualize our data and to assess the degree of branching we have empolyed Reverse Monte Carlo (RMC) modeling. A snapshot of the RMC simulation (figure 2) indicates that short, winding, unbranched, hydrogen bonded chains of 6-8 molecules in length dominate the liquid state.

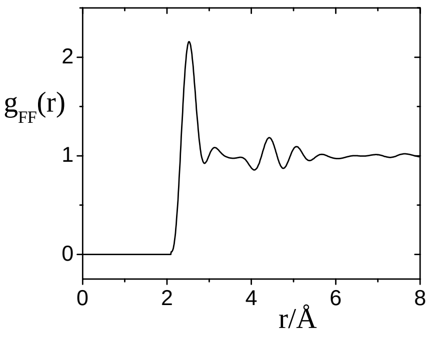

Fig 1. RMC Fluorine-Fluorine radial distribution function at 296K.

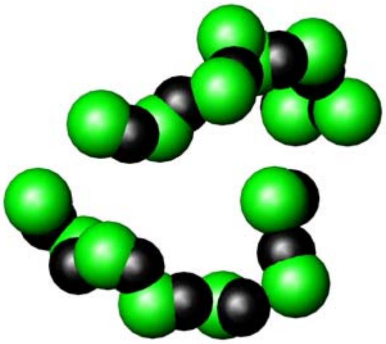

Fig.2.Typical hydrogen bonded chain in Liquid HF at room temperature obtained from a Reverse Monte Carlo fit to the diffraction data.

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