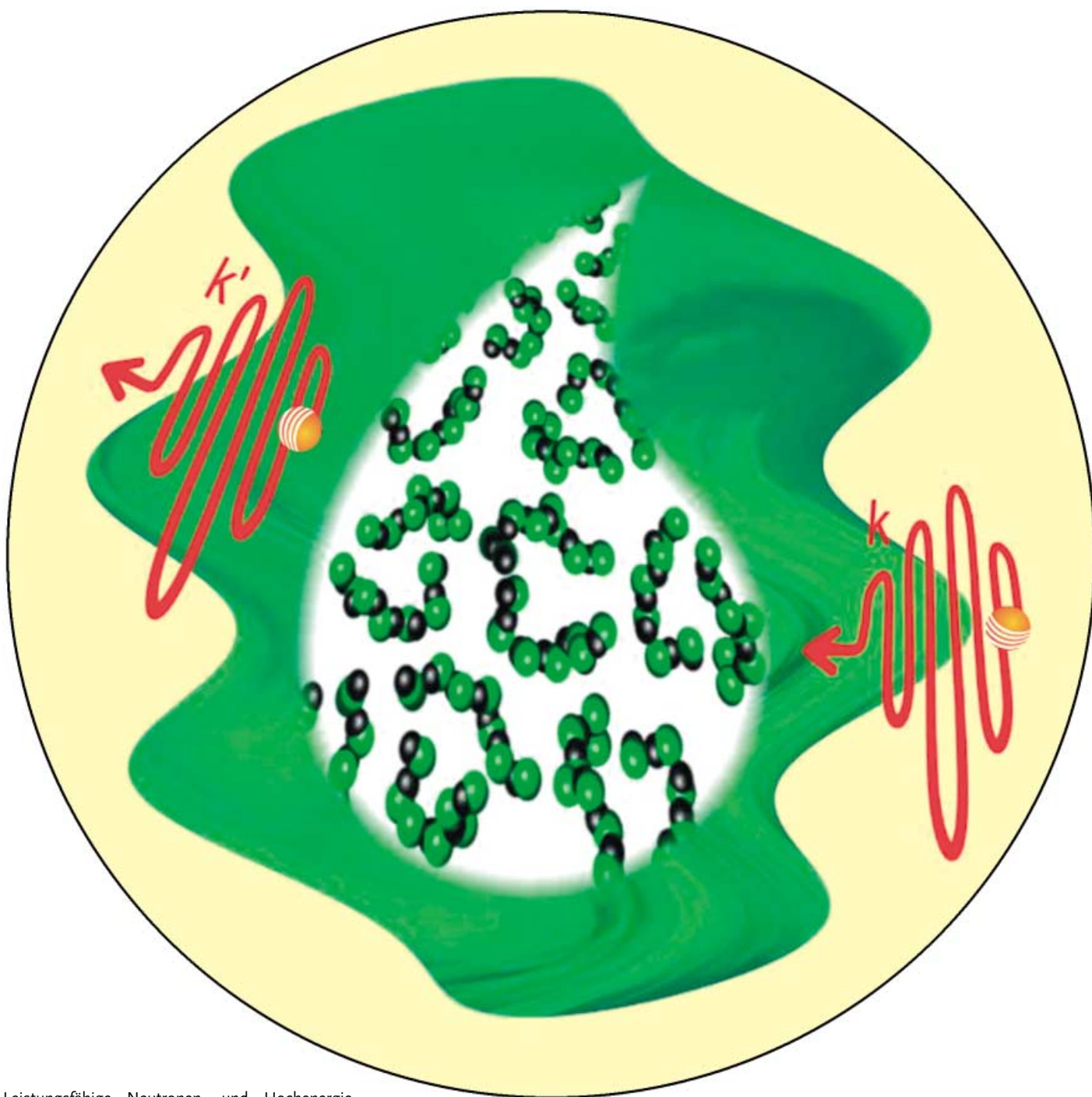# *Zuschriften*

Leistungsfähige Neutronen- und Hochenergie-röntgenbeugungsmethoden wurden zur Aufklärung der partiellen Strukturfaktoren von flüssigem Fluorwasserstoff verwendet. Die strukturellen Details der kurzen, durch starke Wasserstoffbrücken stabilisierten Ketten dienen als rigoroser Test für Modelle dieses fundamental wichtigen Lösungsmittels. Mehr dazu erfahren Sie in der Zuschrift von J. F. C. Turner et al. auf den folgenden Seiten.

Structure of Liquid HF

On the Structure of Liquid Hydrogen Fluoride**

*Sylvia E. McLain, Chris J. Benmore, Joan E. Siewenie, Jacob Urquidi, and John F. C. Turner**

The liquid state is the most complex phase of matter. Densities of liquids are comparable to densities of the solids, implying that the forces between particles in the liquid are of the same magnitude as those forces present in the solid. However, there is no simplification due to the presence of a lattice and no satisfactory analytic theory of the liquid state exists. However, despite this complexity, the liquid state is an outstandingly important chemical milieu in which many reactions take place.

Strongly associated fluids are particularly complex and the structure and properties of these fluids provide an exacting and stringent test of theory. Here, we report the first investigation of the structure of hydrogen fluoride at the level of the distributions of pairwise interatomic distances, the partial pair correlation functions.

Liquid HF is an important chemical and it is widely used in the petrochemical industry, as a catalyst for hydrocarbon management, and in the glass and ceramics industries.[1,2] Academically, its superior properties as a solvent have found application in both organic and inorganic chemistry, and the superacidic properties have been exploited in both disciplines, in the study of reactive intermediates and reaction mechanisms[3,4] That these highly desirable properties are not more widely applied is mainly due to the exceedingly toxic and corrosive nature of the material,[5] which is severe when anhydrous and only somewhat lessened in solution. Indeed, given the properties of liquid HF, it has been stated that the calculation of its properties is to be preferred over measurement.[6]

The true importance of this fluid does not solely rest with its industrial and academic applications; it is the simplest archetype for the strong hydrogen bond, and the molecular simplicity of HF makes it an attractive model for strongly hydrogen-bonded systems. That hydrogen bonding should be so important to understand need not be reiterated, once the importance of this interaction in structural biology, materials science, chemistry and physics is appreciated.[7–9] This important, directional structural interaction is responsible, inter alia, for protein conformations, the stability of the structure of DNA and the properties of water and other associated fluids.

Both the bulk properties[6,10,11] and microscopic structure[12–15] of HF have been the focus of intense theoretical investigation; there have been many calculational approaches to the structure and properties of HF using a variety of methods.[6,10–24] The overarching feature of these calculations is the complete lack of experimental data with which to compare the results of calculation at the pair correlation function level. The only structural data reported to date are two total structure factor measurements for DF at a variety of thermodynamic state points.[25,26] Given that the total structure factor is the weighted sum of the partial structure factors, it is unsurprising that there is a variance in the results of the calculated structural models of HF at the pair correlation function level.

The hydrogen bond is the dominant feature of the structural chemistry of HF in all phases; the solid is composed of unbranched, zigzag chains[27] while the vapor is composed of cyclic oligomers and clusters.[28] 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.

To determine the atomic structure and therefore the hydrogen-bonded nature of HF, high-energy X-ray and neutron diffraction measurements were performed on samples of HF and DF at 296 ± 2 K and 1.2 ± 0.1 bar. Both types of radiation were used to provide complementary information on the structure.[29,30] X-rays scatter from electron density, weighting the contribution of each atom to the scattering pattern by Z the atomic number. In contrast, the interaction of neutrons with matter is dependent on the composition of the nucleus and therefore the isotopic nature of each sample defines magnitude of the scattering interaction. Assuming isostructurality between isotopomeric samples, it is possible, by taking linear combinations of diffraction patterns, to solve the structure factor equations and explicitly determine each of the individual structure factors. This technique has been widely applied to diffraction studies of liquids[31–36] as well as other disordered systems.[37] The pair correlation function is related to the scattered intensity by Fourier transformation as given in Equation (1), where ρ is the atomic number density.

$$S(Q) = 1 + \frac{4\pi\rho}{Q} \int r[G(r)-1]\sin(Qr)\mathrm{d}r \qquad (1)$$

Extraction of the partial structure factors therefore allows the determination of the distribution of pairwise atomic distances—the pair correlation functions.

The diffraction pattern of a sample of HF, collected with radiation source A and written as $S_T^A(Q)$, is related to the partial structure factors according to Equation (2), where $a_{YY'}^A$

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$$S_T^A(Q) = a_{HH}^A S_{HH}^A(Q) + a_{FF}^A S_{FF}^A(Q) + 2\,a_{HF}^A S_{HF}^A(Q) \qquad (2)$$

(Y,Y′ = H,F) is the weighting of the scattering from Y and Y′ due to number density and the inherent strength of the scattering interaction.

For neutrons, this factor is written as $a_{YY'}^N = c_Y c_{Y'} b_Y b_{Y'}$; for X-rays it is $a_{YY'}^X = c_Y c_{Y'} f_Y(Q) f_{Y'}(Q)$, where c_Y is the number density of nucleus Y, b_Y is the elastic coherent scattering length,[38] and $f_Y(Q)$ corresponds to the form factor. The weighting factors for these neutron and X-ray experiments are shown in Table 1.

Our measured neutron diffraction pattern of DF is presented in Figure 1. The diffraction pattern from our experiments is in good agreement with that of Deraman et al.[26] Given that the structure of the fluid at the partial structure factor level is determined solely by $S_{HH}(Q)$, $S_{HF}(Q)$, and $S_{FF}(Q)$, the collection of X-ray and neutron diffraction data on three isotopomeric samples allows the extraction of

Figure 2. a) Partial structure factors, $S_{HH}(Q)$, $S_{HF}(Q)$, and $S_{FF}(Q)$. b) partial pair correlation functions, $g_{HH}(Q)$, $g_{HF}(Q)$, and $g_{FF}(Q)$.

Table 1: Weighting factors for DF and HF neutron experiments and X-ray experiments.

	DF neutron	HF neutron	X-ray 0 Å^{-1}	X-ray 1 Å^{-1}	X-ray 2 Å^{-1}	X-ray 5 Å^{-1}	X-ray 10 Å^{-1}
a_{HH}^A	0.1113	0.0350	0.250	0.191	0.093	0.004	0.000
a_{FF}^A	0.0799	0.0799	20.250	18.253	13.715	3.569	0.435
$2a_{HF}^A$	0.1886	−0.1057	4.500	3.732	2.260	0.250	0.014

the partial structure factors and therefore, by way of Fourier transformation, the pair correlation functions. These are shown in Figure 2a in reciprocal space and in Figure 2b in real space.
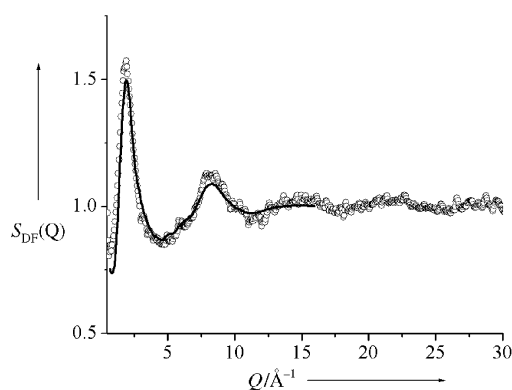

Figure 1. Total structure factor for DF measured by neutron diffraction (circles) compared with previous diffraction measurements (solid line).[26]

In the Fourier transform of the diffraction pattern of DF, the intramolecular H–F peak position in the $G_{DF}^N(r)$ is found at $r_{DF} = 0.93 \pm 0.02$ Å, in good agreement with the previously determined distances in liquid DF, namely 0.93 and 0.925 Å.[25,26]

The partial pair correlation functions, $g_{HH}(r)$, $g_{HF}(r)$, and $g_{FF}(r)$ (Figure 2b), define the radial structure of the fluid at
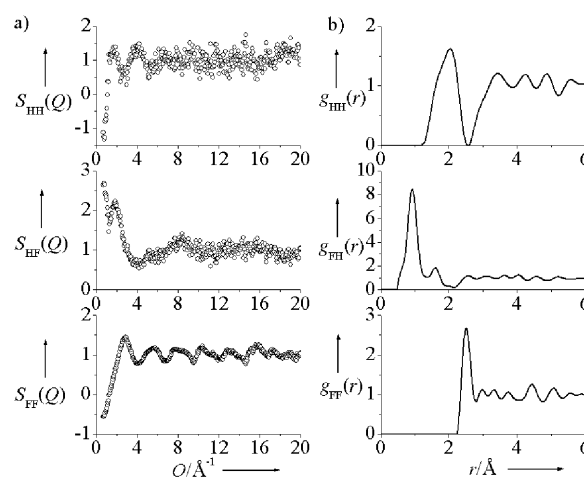
the pair correlation function level. $g_{HF}(r)$ illuminates the key structural feature of the liquid, the intermolecular hydrogen bond. The intermolecular peak position in $g_{HF}(r)$, r_{HF}, was found to be 1.60 ± 0.04 Å. This relatively short distance is indicative of a very strong hydrogen bond. Moreover, the average intermolecular hydrogen–fluorine coordination number, determined from integration of $g_{HF}(r)$, where

$$c_{HF} = 4\pi\rho \int_1^2 r^2 g_{HF}(r)\mathrm{d}r$$

is given by $c_{HF} = 0.86 \pm 0.10$ which consistent with the presence of hydrogen-bonded chains which are short and therefore not infinite. This result is in agreement with Raman and IR spectroscopy studies which have been interpreted by using a model with chains of six or seven HF molecules.[39]

$g_{HH}(r)$ shows a large peak at $r_{HH} = 2.1 \pm 0.1$ Å with a coordination number of $c_{HH} = 1.69 \pm 0.10$. This peak extends into the region at lower r and overlaps with the intermolecular hydrogen bond in $G_{DF}^N(r)$. This phenomenon has also been noted in the simulation literature, though at a different thermodynamic state point of the liquid.[13] The accurate separation of the overlapping peaks in $g_{HH}(r)$ and $g_{HF}(r)$ as well as the extraction of the $g_{FF}(r)$ function, is essential in understanding the complete structure of the liquid as well as in making accurate comparisons between calculational models.

The first peak in $g_{FF}(r)$ (Figure 2b) occurs at $r_{FF} = 2.51 \pm 0.03$ Å with a coordination number $c_{FF} = 2.1 \pm 0.1$ Å. In addition, $g_{FF}(r)$ shows several peaks occurring beyond the first peak, these peaks having been predicted to some extent by several simulations,[12,14,21,24] with the ab initio molecular dynamics and QM/MM simulations showing the closest agreement.

Angular information is available from a diffraction pattern from a liquid in a limited manner and represents a statistical average of the bulk configuration of the fluid.

Taking the peak maxima from the extracted pair correlation functions as the basis for intermolecular angular calculations is instructive. The average H-F-H angle gives an indication of the linearity of the hydrogen bonds and was found to be $\theta_{HFH} = 104 \pm 8°$, indicative of bent hydrogen bonds. The polarizable pair potential model predicts this value most accurately at $\theta_{HFH} = 107°$, although the bond lengths in this model vary from the present work.[15]

The average F-H-F angle is found to be $\theta_{FHF} = 165 \pm 10°$ and defines the degree of orientation between different molecules in the chain. The most accurate corresponding simulation value, from the ab initio MD calculations, is $\theta_{FHF} = 156°$.[14] Both non-polarizable and polarizable pair potential models predict this angle to be $\theta_{FHF} = 180°$.[15]

The degree of chain branching that occurs in the liquid also varies widely between the different models, ranging from 0%[21] to 20% branching.[23] To visualize our data and to assess the degree of branching we chose to model our data using reverse Monte Carlo (RMC) modeling.[40–42] Widely used in structural studies of disordered systems, the RMC model is thought to give the most disordered configurations that are consistent with the data[43,44] and has the advantage that no potential is prescribed in the calculations. The RMC simulation was performed simultaneously on the three measured partial structure factors using a cubic box containing 5000 HF molecules with the constraint that the average coordination number and peak positions in the simulation had to agree with the values obtained from direct the Fourier transform of the measured partial structure factor data. A comparison between the RMC partial structure factors (solid line) and the experimental partial structure factors (circles) is shown in Figure 3.

A snapshot of the RMC simulation (Figure 4) indicates that short, winding, unbranched, hydrogen-bonded chains
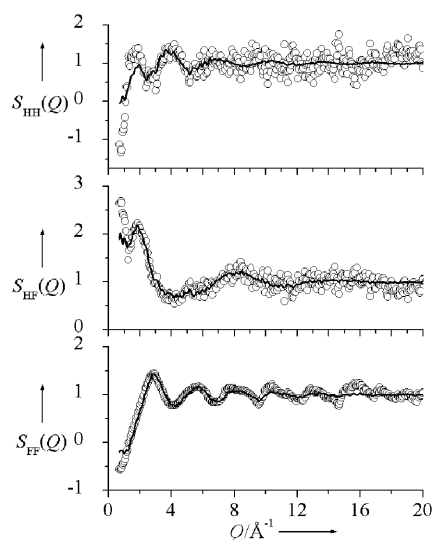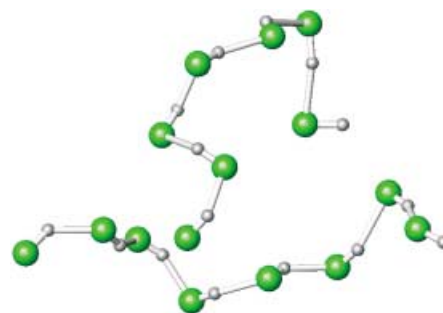

Figure 4. Two representative molecular groups taken from the RMC simulation show winding hydrogen-bonded chains dominate the liquid structure.

dominate the liquid state. Integration of $g_{HF}^{RMC}(r)$ to $r_{min} = 2.15$ Å, reveals only 8% of the molecules form branched chains, this compares to values of 3.5% predicted by the ab initio simulation and 7% predicted by the polarizable potential model.[14,15]

In summary, diffraction data from liquid hydrogen fluoride at the temperature and pressure of this measurement is consistent with the presence of short, bent, strongly hydrogen-bonded chains, with strong interchain interactions and very little branching. Despite the strength of the hydrogen bond in the liquid, the chains appear to be curtailed in length at around an average of seven molecules per chain.

As well as defining the structure of liquid HF at the partial pair correlation function level for the first time, these data provide the theoretical community with detailed experimental information required to improve simulations of HF and the methods for the calculational investigation of strongly associated fluids.

Experimental Section

Isotopic samples of HF, DF, and an $HF_{0.5}DF_{0.5}$ mixture were prepared as described elsewhere.[45] The chemical and isotopic purity of all the samples was $> 99.9\%$ with $< 0.1\%$ H_2O.

A series of neutron and high-energy X-ray diffraction measurements were conducted on the liquid at 296 ± 2 K and 1.2 ± 0.1 bar. Neutron diffraction data from DF and HF were recorded on the Glass, Liquid and Amorphous Diffractometer at the Intense Pulsed Neutron Source, Argonne National Laboratory (ANL), USA. High-energy X-ray diffraction data from analogous samples were measured on the 11-IDC line at BESSERC-CAT, Advanced Photon Source at ANL. The neutron data were corrected for detector efficiency, attenuation, multiple scattering, and inelastic scattering using standard methods.[46] The primary difficulties in the data correction arose from Bragg scattering from the cell and achieving correct normalization. Accordingly, each empty cell was measured separately and filled with D_2O, to correct each data set and to account for variations in the cells used. Careful empirical subtraction of the individual Bragg peaks was then performed.

High-energy X-ray data were corrected for detector efficiency, instrumental geometrical effects, polarization, and empty container scattering, and were then normalized to the sum of the form factors plus Compton scattering. X-ray experiments were performed on all of the isotopic mixtures at the same state conditions as the neutron experiments and showed no significant isotopic quantum effect, within the limits of the experimental error ($\sim 5\%$), supporting the use

Figure 3. RMC fit (solid line) to the experimental partial structure factors (circles).

of the isotopic substitution technique in neutron diffraction in this case.

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