The structure of liquid fluorosulfuric acid investigated by neutron diffraction

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The results of an investigation into the liquid structure of fluorosulfuric acid measured using neutron diffraction with isotopic substitution are reported. The first-order neutron difference function is extracted from data recorded at 300 and 193 K from isotopically labeled FSO₃H and FSO₃D. Analysis of the derived radial distribution functions shows that unique, multisite hydrogen bonding is present in the liquid. These results suggest hydrogen bonding between the hydrogen and fluorine as well as oxygen occurs in the liquid. The fraction of molecules that is hydrogen bound in each way varies with temperature, with the 193 K data showing a more tightly bound system. © 2002 American Institute of Physics. [DOI: 10.1063/1.1495395]

I. INTRODUCTION

Superacids are a class of fluids that possess extremely high acidities, which far exceed those observed for the strongest aqueous acid systems.¹–⁴ NMR spectroscopy has shown that the normal range of bases can be augmented in superacidic media by species such as methane, xenon, hydronium ion, and first-row diatomic molecules.⁵–¹⁰ It is the ability to protonate the C–H bond that gives these fluids their industrial and, in part, academic importance. They are used extensively for hydrocarbon management—the isomerization and cracking of petroleum products—as well as the investigation of reactive, carboxylic intermediates in organic chemistry.¹⁰ More recently, they have become popular as solvent systems for inorganic synthesis, where high valent and extremely-electron-poor metal centers can be synthesized and studied.¹¹–¹³

Superacids also differ from other hydrogen-bound systems, such as water, ammonia, and alcohols, in that they are highly-electron-poor hydrogen-bound systems. Previous systems on superacids and other acidic systems have usually relied on x-ray diffraction in the solid state to determine structure.¹⁴–²⁰ Studies of the structure of superacids in the liquid state have so far been confined to two total structure factor determinations of DF.²¹–²² In this paper, the determination of the [H/D] first-order difference function in neutron diffraction for a complex superacid are reported for the first time.
appearing in Eqs. (4) and (5). The distances that contribute to ΔG_{XX}(r) are therefore those between the heavy atoms S, O, and F.

In general, integration of \( g_{\alpha\beta}(r) \) gives the coordination number of atoms \( \alpha \) and \( \beta \) atoms between two distances, \( r_1 \) and \( r_2 \):

\[
n_{\alpha\beta}^2(r) = \frac{4\pi\rho}{r_2} \int_{r_1}^{r_2} g_{\alpha\beta}(r)r^2dr,
\]

where \( \rho \) corresponds to the atomic number density, which, in FSO₃H, is 0.0629 and 0.0683 atoms/A³ at 300 and 193 K, respectively.

### B. Experiment: Sample handling and preparation

Fluorosulfuric acid is an aggressive material and must be handled with caution only in rigorously dried glassware or Teflon apparatus. All manipulations of FSO₃H and FSO₃D were carried out under an argon atmosphere or under vacuum on a Schlenk link (\( p_{\text{min}} < 10^{-2} \) mbar). All glassware was flame-dried under vacuum at least four times and allowed to cool under an argon atmosphere. FSO₃D was prepared according to the literature with the exchange between D₂SO₄ and FSO₃H being performed three times. NMR measurements and neutron analysis (vide infra) revealed that the incorporation of D for H was greater than 99.6%. The purity of FSO₃H with respect to water was assayed using Raman spectroscopy and determined to be greater than 99.9% H₂O-free. The Raman spectra were acquired on a Dilor XY Raman spectrometer (Instruments S.A., Edison, NJ) using a 514-nm Rayleigh line. The density of FSO₃H was measured using a custom designed glass pycnometer, which was standardized against the density of methanol, which is well known. FSO₃H and FSO₃D were distilled into quartz tubes (0.4 cm ID, 0.5 cm OD) and were flame-sealed under vacuum to give a sample volume of 0.478 cm³.

Diffraction experiments were performed on the Glass Liquid and Amorphous Materials Diffractometer at the Intense Pulsed Neutron Source facility at Argonne National Laboratory. Data sets were collected at 300 and 193 K. The neutron diffraction data were corrected for container scattering, attenuation, multiple scattering, and inelastic scattering using standard analysis procedures. The data were not corrected for isotope quantum effects, which have recently been shown to be small for hydroxyl hydrogens in other hydrogen-bonded liquids such as methanol; moreover, they are expected to be smaller in this heavier molecule.

The small sample thickness minimizes multiple scattering effects due to the large amount of incoherent scattering from hydrogen. In addition, both tubes were blown from the same cane of tube to ensure that their wall geometries were as similar as possible, in order to minimize systematic errors in the difference experiments. The small error between the quartz tubes was additionally checked by comparison of the calculated intramolecular scattering contribution to the measured data. Both neutron differences agreed to within 5% to the expected intramolecular nearest-neighbor atoms [as discussed in the following sections (see Figs. 4 and 5)].

The following equations are used to calculate the structure factor of FSO₃D and FSO₃D-FO₃H in units of barn.

\[
S_{N}(Q) = \frac{F_{N}(Q)}{\sum_{a} c_{a}b_{a}}
\]

\[
= \frac{1}{\sum_{a} c_{a}b_{a}} \sum_{a,\beta} c_{a}b_{a}c_{\beta}b_{\beta}[S_{a\beta}(Q) - 1]. \quad (2)
\]

The first-order difference structure factor with the respect to the labeled site is calculated by subtraction of \( F_{N}(Q) \) for isostructural and isotopemic samples. In these experiments, the isotopomers used were FSO₃H and FSO₃D and so the corresponding structure factor is that related to the hydrogen/deuterium site, hereafter termed the derived from scattering for all nonhydrogen sites, \( \Delta F_{\text{HX}}(Q) \), where \( X \) includes hydrogen as well as the other heavy atoms. In a similar manner, the structure factor derived from scattering for all nonhydrogen sites, \( \Delta F_{\text{XX}}(Q) \), was extracted from the data by subtraction of \( \Delta F_{\text{HX}}(Q) \) from the measured total structure factor for FSO₃D.

The Fourier transform of any structure factor yields the associated radial distribution function \( G(r) \), which is the sum of the respective atom–atom correlation functions, \( g_{\alpha\beta}(r) \), each weighted by concentration and the bond coherent scattering length of the atomic species. The measured \( S(Q) \) is related to the total radial distribution function \( G(r) \) by the following equation:

\[
S(q) = 1 + \frac{4\pi\rho}{Q} \int_{0}^{\infty} r dr [G(r) - 1] \sin(Qr). \quad (3)
\]

Fourier transformation of \( \Delta F_{\text{HX}}(Q) \) yields the real-space counterpart \( \Delta G_{\text{HX}}(r) \). As intermo terms related only to the [H,D] site are present in \( \Delta F_{\text{HX}}(Q) \), \( \Delta G_{\text{HX}}(r) \) represents only the radial distribution functions associated with the [H,D] sites. Explicitly, \( \Delta G_{\text{HX}}(r) \) may be written as

\[
\Delta G_{\text{HX}}(r) = 2c_{H}c_{O}(b_{D}-b_{H})g_{\text{HO}}(r) + 2c_{H}c_{O}(b_{D}-b_{H})g_{\text{HO}}(r)
\]

\[
+ 2c_{H}c_{O}(b_{D}-b_{H})g_{\text{SS}}(r) + c_{H}^2(b_{D}^2 - b_{H}^2)g_{\text{HH}}(r).
\]

Fourier transformation of \( \Delta F_{\text{XX}}(Q) \) yields \( \Delta G_{\text{XX}}(r) \):

\[
\Delta G_{\text{XX}}(r) = 2c_{O}c_{S}(b_{O}g_{\text{SO}}(r) + 2c_{O}c_{S}b_{D}g_{\text{SS}}(r)
\]

\[
+ 2c_{O}c_{S}g_{\text{SO}}(r) + c_{O}^2b_{D}^2g_{\text{OO}}(r)
\]

\[
+ c_{S}^2b_{S}^2g_{\text{SS}}(r) + c_{F}^2b_{F}^2g_{\text{FF}}(r).
\]

See Table I for a listing of the Faber–Ziman coefficients

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**Table I.** Faber–Ziman coefficients for FSO₃D and FSO₃D-FO₃H in units of barn.

| \( c_{a}b_{a}^2 \) | \( 2c_{H}c_{O}b_{D}b_{O} \) | \( 0.00888 \) |
| \( c_{a}^2b_{a}^2 \) | \( 2c_{O}c_{S}b_{D}b_{S} \) | \( 0.00225 \) |
| \( c_{a}c_{\beta}b_{a}b_{\beta} \) | \( 2c_{O}c_{S}b_{O}g_{\text{SO}} \) | \( 0.08419 \) |
| \( c_{a}^2b_{a}^2 \) | \( c_{D}b_{D} \) | \( 0.00388 \) |
| \( 2c_{H}c_{O}b_{S}b_{O} \) | \( 2c_{C}c_{D}b_{D}b_{H} \) | \( 0.00894 \) |
| \( 2c_{C}c_{D}b_{D}b_{H} \) | \( 0.05457 \) |
| \( 2c_{C}c_{D}b_{D}b_{H} \) | \( 0.01175 \) |

For any structure factor \( F_{N}(Q) \), the real-space counterpart \( G(r) \) may be written as

\[
G(r) = 2c_{H}c_{O}(b_{D}-b_{H})g_{\text{HO}}(r) + 2c_{H}c_{O}(b_{D}-b_{H})g_{\text{HO}}(r)
\]

\[
+ 2c_{H}c_{O}(b_{D}-b_{H})g_{\text{SS}}(r) + c_{H}^2(b_{D}^2 - b_{H}^2)g_{\text{HH}}(r).
\]

For the Faber–Ziman coefficients appearing in Eqs. (4) and (5). The distances that contribute to \( \Delta G_{\text{XX}}(r) \) are therefore those between the heavy atoms S, O, and F.

In general, integration of \( g_{\alpha\beta}(r) \) gives the coordination number of atoms \( \alpha \) and \( \beta \) atoms between two distances, \( r_1 \) and \( r_2 \):

\[
n_{\alpha\beta}^2(r) = 4\pi\rho\int_{r_1}^{r_2} g_{\alpha\beta}(r)r^2dr,
\]

where \( \rho \) corresponds to the atomic number density, which, in FSO₃H, is 0.0629 and 0.0683 atoms/A³ at 300 and 193 K, respectively.

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clearly indicates that the SiO₂ container corrections and the data normalization have been performed correctly.

C. Previous studies on the structure of fluorosulfuric acid

The structure of fluorosulfuric acid has been determined in the solid state by x-ray diffraction. The molecular structure consists of a pseudotetrahedral sulfur atom ligated by oxo-, fluoro-, and hydroxyl moieties. Salient bond lengths and angles from x-ray diffractometry are shown in Table II. The molecule is shown in Fig. 1, together with atom labels used in this paper. It may be noted from Table II that the hydroxyl O–H bond length, \( r(O_1-H) \), is very short, and this may be due to the inherent insensitivity of x-ray scattering to the presence of hydrogen.

III. RESULTS

In order to analyze the various radial distribution functions determined in these diffraction experiments, the structure of a single fluorosulfuric acid molecule was calculated using Møller-Plesset perturbation theory (MP2) with an augmented correlation consistent polarized valence double zeta (aug-cc-pVDZ) basis set with GAUSSIAN 98. The relevant calculated distances and angles are shown in Table II.

<table>
<thead>
<tr>
<th>Crystal (FSO₃H)</th>
<th>Interatomic distances/Å</th>
<th>Interbond angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r(S-O_1) )</td>
<td>1.51</td>
<td>106.8</td>
</tr>
<tr>
<td>( r(S-O_2) )</td>
<td>1.41</td>
<td>107.2</td>
</tr>
<tr>
<td>( r(S-O_3) )</td>
<td>1.42</td>
<td>120.9</td>
</tr>
<tr>
<td>( r(S-F) )</td>
<td>1.54</td>
<td>113.1</td>
</tr>
<tr>
<td>( r(O_1-H) )</td>
<td>0.63</td>
<td>97.6</td>
</tr>
<tr>
<td>( r(H\cdots O_3) )</td>
<td>2.02</td>
<td>105.7</td>
</tr>
</tbody>
</table>

a Reference 20.
b Reference 37.
c Reference 18.

Measurement of the density of fluorosulfuric acid in a high-vacuum pychnometer, previously calibrated with anhydrous methanol, yielded values of \( \rho_{300} = 1.743 \text{ g cm}^{-3} \) and \( \rho_{193} = 1.891 \text{ g cm}^{-3} \). Given that isostructurality between both isotopomers is assumed for the subtraction method to be applicable, these values of the number density were used for all the data analysis procedures.

The corrected total structure factors, \( F_N(Q) \), for FSO₃D for both temperatures are shown in Fig. 2. Figure 3 shows the hydrogen structure factors \( D_{FHX}(Q) \), extracted as described above, again for both temperatures. The radial distribution functions at 300 and at 193 K around the @H,D# site are shown in Fig. 4 and the extracted radial distribution functions for the heavy atoms, \( D_{GGX}(r) \), at 300 and 193 K, in Fig. 5.

Data analysis was performed by empirically fitting the derived \( D_{HHX}(r) \) function with Gaussian functions in order to determine the coordination number. Although approximate intramolecular distances between pairs of heavy atoms were available from x-ray crystallographic studies, there was no reliable estimate in the literature for intramolecular distances between hydrogen and the heavy atoms in FSO₃H. For instance, the x-ray structure indicates the covalent O–H
bond to be 0.63 Å, which is unreasonably short. Therefore, the equilibrium structure of an isolated FSO$_3$H molecule using Becke’s 3-parameter exchange DFT and the Lee-Yang-Parr correlation function $\text{~B2LYP~}$ with an aug-cc-pVDZ basis set and the intramolecular distances between hydrogen, and the F, S, and O atoms were taken from this structure. Intramolecular contributions to $\Delta G_{XX}(r)$ were fitted using distances taken from the x-ray crystal structure data for the fluorosulfate ion, FSO$_3^-$, and the [FSO$_3$HO$_2$SF]$^-$ anion (Table II), as well as those extracted from the density-functional calculations.  

The most important features in $\Delta G_{IX}(r)$ (Fig. 2) are the OH intramolecular peak at 0.98 Å and a broader peak at approximately 1.6 Å that corresponds to the intermolecular hydrogen bond. The solid-state x-ray data estimate this latter distance to be about 2.02 Å, presumably due to the exceedingly short OH intramolecular distance, and this distance is considerably longer than most common hydrogen bonds.  

At 300 K in the liquid, the hydrogen-bonding peak in $\Delta G_{IX}(r)$ is asymmetric and can be more accurately fitted as the sum of two peaks centered at 1.48 and 1.74 Å, showing a 1:4 area ratio with respective coordination numbers of 0.15 ($\sigma=\pm 0.1$) and 0.61 ($\sigma=\pm 0.1$), with respect to oxygen or fluorine as shown in Figs. 6 and 7. It should be noted that the coherent neutron scattering lengths of oxygen and fluorine are very similar and oxygen and fluorine cannot be distinguished in this experiment. At 193 K, where the hydrogen-bond peak is sharper, the two Gaussian peaks are centered at 1.48 and 1.73 Å and have coordination numbers with respect to oxygen or fluorine of 0.31 ($\sigma=\pm 0.1$) and 0.80 ($\sigma=\pm 0.1$), with the areas showing a 1:2.6 ratio. The 31% increase in hydrogen coordination, calculated from the Gaussian fits and clearly illustrated in the running coordination number plot, provides evidence of a significant increase in the hydrogen-bond chain length (and/or chain branching) upon cooling the liquid. The shift to lower $r$ upon cooling and the development of a more distinct inflection point in the running coordination number (Fig. 7) are consistent with the presence of stronger, better-defined hydrogen bonds at the lower temperature.

FIG. 4. (a) $\Delta G_{IX}(r) + 3$ at 300 K and (b) $\Delta G_{IX}(r)$ at 193 K. The oxygen numbers correspond to the intramolecular structure shown in Fig. 1. The bond distances were calculated using density functional theory (Ref. 39).

FIG. 5. (a) $\Delta G_{XX}(R) + 1$ at 300 K and (b) $\Delta G_{XX}(r)$ at 193 K. The Gaussians were fitted empirically.

FIG. 6. $\Delta G_{IX}(r)$ hydrogen-bond peak fit with two Gaussians: (a) $\Delta G_{IX}(r) + 1.5$ at 300 K and (b) $\Delta G_{IX}(r)$ at 193 K.

FIG. 7. Running coordination number curve for the intermolecular O–H bond, showing the average number of oxygen of fluorine atoms around a central hydrogen atom at a given distance, $r$. The solid line represents the 300 K data and the dotted line represents the 193 K data.
These results imply that there are two distinct hydrogen bond distances, a phenomenon that does not occur in most other hydrogen-bound liquids such as water, methanol, or ethanol where only one hydrogen bonding atom type exists.26,27,34 This may be evidence that there are hydrogen bonds to both fluorine and oxygen in the liquid phase.

In the reported crystal structure of FSO₃H, linear chains of molecules are bound exclusively through S—OH···O=S linkages. The other heavy-atom distances in the crystal structure includes \( r_{S-OH} = 1.5118(1) \text{ Å} \), \( r_{S-O} = 1.412(1) \) and \( r_{S-F} = 1.540(1) \) Å. These distances are not atypical, as revealed by a search of the Cambridge Crystallographic Structural Database, where the mean distances for these values were found to be 1.54±0.04 Å (S=F) and 1.54±0.05 Å (S—OH), and 1.42±0.04 Å (S=O).40 It therefore appears, from this study in the solid state, that a different hydrogen-bonding structural motif is present that is not found in the solid state.

The Raman data, shown in Fig. 8, shows that the multisite hydrogen bonding cannot be due to H₂O contamination. The Raman data taken from FSO₃H used in this experiment is consistent with former measurements41 and with the addition of 0.1 mol % H₂O a new vibrational peak appears at 1080 cm⁻¹, and this peak continues to increase in intensity at higher water concentration. The variation of the area of this peak with concentration shows that the mol % H₂O present in FSO₃H to be virtually zero by extrapolation.

**IV. DISCUSSION**

Fluorosulfuric acid is a strongly hydrogen-bound fluid that is to be expected given the electronegative nature of the ligating atoms around S. Physically, it is a highly mobile liquid with a liquid range of 253.8 K (boiling point = 165.5 °C; melting point = −88.3 °C), this long liquid range being due to the hydrogen-bound nature of the fluid. For comparison, the melting and boiling points of sulfuryl difluoride, O₂SF₂, are −135.8 °C and −55.4 °C, respectively—a liquid range of 80.4 K.

Because the intermolecular O–H bonding peak is best described with two Gaussians and the distant change in the profile of the intermolecular O–H bonding peak with temperature, the presence of two possible hydrogen-bonding interactions, namely O−H···F and O−H···O is a reasonable conclusion. That F···H bonding may occur in the liquid structure is not surprising as fluorine is more electronegative than oxygen. The phase diagrams of the hydrates of the hydrohalic acids are rationalized on the exceptional strength of the hydrogen bond between H and F. The crystalline hydrates of HX (X = BrCl) have compositions written as HX·nH₂O (n = 1, 2, 3, 4, 6),42 whereas the crystalline hydrates of HF are in the form H₂O·mHF (m = 1, 2, 4).15,19,43 Indeed, the low \( pK_a \) of aqueous HF has been attributed to the strong hydrogen-bonding interaction between H and F, which leads to the formation of HF₂⁻ even in the presence of a large statistical excess of water. In addition, the strongest hydrogen bond known is between hydrogen and fluoride in the bifluoride ion \([\text{F}−\text{H}−\text{F}]^−\), and the strongest calculated hydrogen is between formic acid and the fluoride ion \([\text{HCO}_2−\text{H}−\text{F}]^−\).44,45

However, the partial charge assigned to fluorine in isolated FSO₃H (determined from a molecular electrostatic potential analysis, CHELP, at the B3LYP/aug-cc-pVDZ level of theory)39 is only −0.20 electrons, while the partial charges assigned to the oxygen atoms are substantially larger in magnitude, at −0.36 electrons (S−O=H) and −0.42 and −0.44 electrons (S=O). It may be noted that the distribution of the electron density may differ in a hydrogen-bound or otherwise condensed system, where the formal sharing of electron density between molecules, in a 3c−4e manner, and the presence of a dielectric may be contributing and perturbing factors.

Whereas the experimental resolution does not allow for the assignment of individual heavy-atom distances, \( G_{XX}(r) \) reveals two features, an asymmetric peak with a maximum at −1.47 Å with a coordination number of 4.16 \( (σ = ±0.1) \) fluorine or oxygens bound to sulfur and a second peak with a maximum at −2.41 Å with a coordination number of 6.22 \( (σ = ±0.1) \) with respect to oxygen and fluorine distances. These distances are in accord with the literature values,16 as well as those extracted from the Cambridge Crystallographic Structural Database and the other literature sources and calculations specifically cited above for the directly bonded and nonbonded distances, respectively. Given that the heavy-atom structure of fluorosulfuric acid is essentially unchanged at the two experimental temperatures within the resolution of the experiment, the largest change in the structure of the liquid is due mainly to the change in hydrogen-bond structure. Moreover, this change in hydrogen-bond structure may be due to a change in the mole fraction of molecules bound as O−H···F and O−H···O, as is shown by the change in coordination number for the double Gaussian fits to the intermolecular hydrogen-bond peak.

Preliminary density-functional theory (DFT) calculations on an isolated dimer of fluorosulfuric acid show that the dimer is stable in configurations where both O−H···F and O−H···O are present between the molecules.39 However, given the multiple number of possible hydrogen-bonding sites in the FSO₃H molecule, the liquid structure is likely to be comprised of a three-dimensional network. Consequently, while the DFT calculations show the inherent stability of these types of linkages, calculating the relative strengths of these bonds and their temperature dependence is difficult due...
to the effects of many-body intermolecular interactions in the liquid state.

Further experimental and theoretical work is needed to clarify the relative importance of $\text{O} \cdots \text{H} \cdots \text{O}$ and $\text{O} \cdots \text{H} \cdots \text{F}$ hydrogen bonding in liquid FSO$_3$H. Modeling efforts towards this end are currently in progress, utilizing molecular dynamics and $(N,V,T)$ ensemble Monte Carlo simulations that employ periodic boundary conditions and a customized variant of the optimized potential for liquid simulations (OPLS) intermolecular potential tailored to the charge distribution in FSO$_3$H.

V. CONCLUSIONS

The hydrogen bond peak profile in the measured radial distribution neutron difference function for liquid fluorosulfuric acid is asymmetric and the asymmetry varies in temperature. The temperature variation of the neutron difference function, combined with the changes in the running coordination number, imply that a multi-site hydrogen-bonding motif may be present in the liquid. Although from these measurements the nature of the atoms involved in this $\text{O} \cdots \text{H} \cdots \text{X}$ bond cannot be determined, due to the similarity of the scattering cross section for O and F, $\text{O} \cdots \text{H} \cdots \text{F}$ and $\text{O} \cdots \text{H} \cdots \text{O}$ bonding being simultaneously present cannot be excluded. Indeed, a multisite hydrogen-bonded structure involving only O would imply a frustrated hydrogen-bonded picture.

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37 A. Frisch and M. Frisch, GAUSSIAN 98 (Gaussian, Pittsburgh, 1998).