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**STRUCTURAL AND DYNAMICAL STUDIES OF SUPERACIDS AND
SUPERACIDIC SOLUTIONS USING NEUTRON AND HIGH ENERGY
X-RAY SCATTERING**

A Thesis
Presented for the
Master of Science
Degree
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Jamie John Molaison
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DEDICATION

This work is dedicated to my parents, John and Chris Molaison, whose undying support proved invaluable to my success. I also dedicate this to my fiancée, Lauren, who never allowed me to quit in the face of adversity.

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ABSTRACT

The diffusive motions of the Brønsted superacid, hydrogen fluoride, have been studied using quasielastic neutron scattering. Neutron and high energy X-ray diffraction measurements on the Lewis superacid, antimony pentafluoride, are presented along with the results of three applied data models. Finally, structural information was obtained for a 9:1 $\text{FSO}_3\text{H}:\text{NH}_3$ solution using neutron diffraction with isotopic substitution and nuclear magnetic resonance.

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1 INTRODUCTION TO NEUTRON AND X-RAY SCATTERING AND AN OVERVIEW OF SUPERACIDS

This thesis presents aspects of the structural and dynamical characterization of superacids and solutes in superacidic media. The primary structural techniques employed to this end are neutron and X-ray diffraction; dynamics measurements using quasielastic neutron scattering were also used to supplement prior structural work. This chapter contains a brief introduction of the applicable concepts of neutron and X-ray scattering and introduces the chemistry and properties of superacids.

1.1 Properties of the neutron

The properties of the neutron are directly responsible for its applicability as a probe of matter. The definition of a thermal neutron is one that has an energy of 25.3 meV.¹ As a result of its mass, 1.675×10^{-27} kg, a thermal neutron has a de Broglie wavelength of 1.798 Å, which is on the order of the magnitude of the interatomic distances in solids and liquids. Thus, structural information can be obtained by measuring the effects of interference between neutrons scattered from sample nuclei. Another essential property of the neutron is its lack of electric charge. The neutron can interact with a nucleus without interacting electromagnetically with the electrons. For this reason, neutron scattering intensity is not dependent on the atomic number, Z . This is in contrast to X-ray scattering which is dominated by high- Z nuclei since X-rays interact with electrons. The relative intensities of neutron and X-ray scattering are shown in Figure 1.1 for several isotopes. The small Z -dependence of the neutron scattering cross-

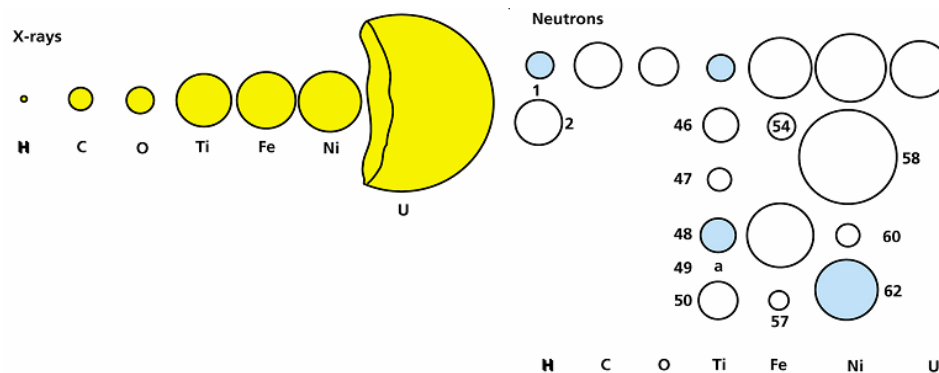


Figure 1.1: Relative X-ray and neutron scattering intensities. The blue shading represents a negative neutron scattering length. The numbers are the atomic masses of the elements.

section is obviously advantageous when studying hydrogen bonding and hydrogen containing species. Other properties of the neutron allow it to give insight into excitation energies and the magnetic properties of matter, but these were not explored in the work presented here.

1.2 Neutron production

Neutrons are produced in a number of ways, primarily through nuclear reactors and spallation sources. Reactor sources produce neutrons *via* a neutron capture reaction usually involving ^{235}U or ^{239}Pu . The resulting fission reaction produces two highly energetic fragments, an average of 2.5 neutrons, and ~ 190 MeV of energy per fission event. Nearly all reactors are operated in a steady state.

Spallation sources produce neutrons through the bombardment of a target made of heavy metal, such as uranium, tungsten, or mercury, with high energy protons. The

protons are produced from a beam of hydride ions. These ions are accelerated to very high velocities in a linear accelerator before passing through a layer of alumina or diamond, which strips the H^- ions of their electrons, leaving H^+ ions, or protons. The spallation process begins when a high energy proton collides with a nucleus in the target producing highly excited nuclei and releasing neutrons, protons, and pions. Some of the elementary particles released in this initial collision collide again to excite more target nuclei. All of the excited nuclei relax through a neutron evaporation process before undergoing beta and gamma decay. Most of the neutrons that exit the target area are from the evaporation process. However some of the neutrons released in the initial collisions do escape and have much higher energies; the highest of which approach the energy of the incident proton. The number of neutrons produced per incident proton is dependent on the energy of the proton, but more dependent on the mass number of the target nuclei. Experimental measurements give a range of 2 - 60 neutrons produced per incident proton, but the average is about 15.² For a spallation source only ~30 MeV of heat per useful neutron needs to be dissipated, opposed to ~200 MeV for a reactor source.³ The preference of spallation sources to reactor sources owes itself to a higher potential neutron peak flux and decreased heat production, among other reasons. Spallation sources produce neutrons in a pulsed manner with frequencies between 10 and 60 Hz. A pulsed neutron beam ensures that time-resolved measurements are possible.³⁻⁵

Neutrons produced *via* either mechanism are much too energetic to be used for structural techniques. Therefore, a moderator is placed between the target and the instrument, to thermalize the neutrons and sufficiently lower their energy to levels

suitable for characterization techniques. Common moderator materials, such as liquid deuterium, solid or liquid methane, and liquid water, serve to slow down the neutrons to the thermal range ($E = 5 - 100$ meV), thus making them useful as probes of material. A neutron loses a fraction of its energy every time it collides with a moderator atom, and eventually will reach thermodynamic equilibrium with the moderating material. The number of collisions necessary depends on the moderating material, specifically its scattering cross-section (σ), which is the probability of a nuclide interacting with an incident neutron and is given in terms of area.

The neutron flux produced from a reactor or a spallation source has a Maxwellian distribution if the neutrons are sufficiently moderated; i.e., if the moderator is thick enough. This distribution is given by

$$\Phi(v) \propto v^3 \exp\left(\frac{-m_N v^2}{2k_B T}\right), \quad (1.1)$$

where $\Phi(v)dv$ is the number of neutrons through unit area per second, k_B is

Boltzmann's constant, T is the temperature of the moderator, and v is the velocity.

Modern reactor sources have steady state fluxes on the order of 10^{15} neutrons per second per cm^2 , while the highest peak flux seen from a spallation source to date (ISIS at the Rutherford Appleton Laboratory near Oxford, England) is $\sim 10^{16} \text{ n s}^{-1} \text{ cm}^{-2}$. All structural studies using neutrons were performed on the Glass, Liquid and Amorphous materials Diffractometer (GLAD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory (ANL), Argonne, IL. IPNS, a spallation source, uses 450 MeV protons to produce a neutron flux of $\sim 10^{14} \text{ n s}^{-1} \text{ cm}^{-2}$. This source, like most

spallation sources, is under-moderated to allow for pulsed operation and time-of-flight measurements. Under-moderating is necessary to ensure that the process of slowing down the neutrons does not take longer than the pulse length of the proton beam, thus compromising the pulse spectrum.³ As a consequence, the resultant neutron wavelength distribution, shown for GLAD in Figure 1.2, shows a Maxwellian region (centered at 2.95 Å for GLAD) and a high energy, low wavelength region. The neutrons used by GLAD are moderated by solid methane at 28 K.

1.3 Scattering theory

As stated above in section 1.1, the neutron interacts directly with the nucleus *via* the strong nuclear force. Also, a neutron, having its own magnetic moment, can interact with the magnetic moment of a nucleus or unpaired spin density. Indeed, it is this

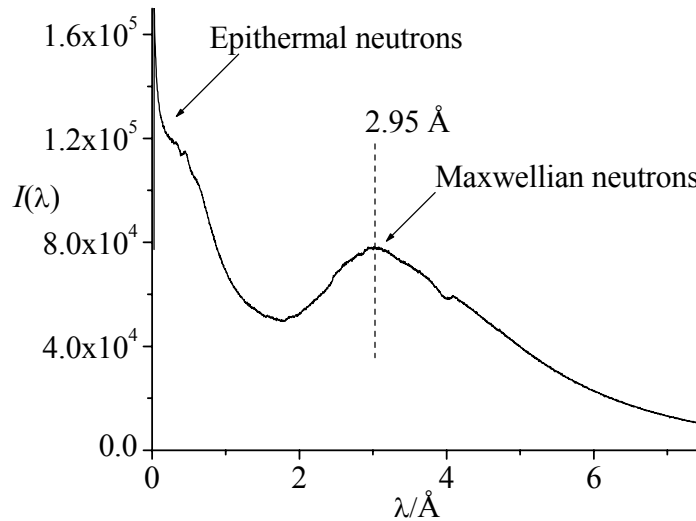


Figure 1.2: Incident neutron spectrum for GLAD.

phenomenon that facilitates the use of neutrons as a probe of the magnetic properties of materials. Contrast this to X-rays, which interact with the electron density in the sample.

Regardless of the probe, the wavefunction of the incident particle is approximated by a one-dimensional plane wave defined as

$$\Psi(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (1.2)$$

where $\mathbf{k}$ is the momentum vector of the incident particle and $\mathbf{r}$ is its position vector.

Similarly, once the incident particle is scattered from a single fixed nucleus its wavefunction is given by

$$\Psi'(\mathbf{r}) = c \exp(i\mathbf{k}' \cdot \mathbf{r}), \quad (1.3)$$

where $\mathbf{k}'$ is the momentum vector of the scattered particle and c is a constant scattering amplitude that is dependent on the type of incident particle and the sample composition.

If the incident particle does not lose or gain energy to or from the sample; i.e., the momentum vectors $\mathbf{k}$ and $\mathbf{k}'$ have the same magnitude, the scattering is termed elastic.

However, if energy is transferred to or from the sample; i.e., $\mathbf{k}$ and $\mathbf{k}'$ do not have the same magnitude, the scattering is known as inelastic. This type of neutron scattering is used to explore the excitations of normal modes of a system. A variation of inelastic neutron scattering, quasielastic neutron scattering (QENS), was used to observe the diffusive motions in anhydrous hydrogen fluoride. QENS will be briefly discussed later.

Elastic neutron and X-ray scattering are used extensively to study structural aspects of a sample. Although the momentum vectors are of equal magnitude in elastic techniques, the direction of these vectors is not identical. The resultant transferred wavevector, $\mathbf{Q}$, is then given by the difference between the scattered and the incident momentum vectors,

$$\mathbf{Q} = (\mathbf{k}' - \mathbf{k}). \quad (1.4)$$

The momentum transfer is now given by $\hbar\mathbf{Q}$. A diagram of this is given in Figure 1.3.

From this figure the relationship between Q , k , k' , and the scattering angle, θ , can be seen as

$$\sin \theta = \frac{Q/2}{k}. \quad (1.5)$$

Since de Broglie relates wavelength and momentum by $\lambda = h/k$, it follows that

$$|Q| = \frac{4\pi \sin \theta}{\lambda}, \quad (1.6)$$

where λ is the wavelength of the scattered neutron.

1.3.1 Diffraction

Diffraction techniques, regardless of the probe, measure the interference that results from elastic scattering of the probe off of the atoms in the sample. The intensity of this scatter is a function of momentum transfer and has the form

$$I(\mathbf{Q}) = \sum_{i,j} f_i f_j \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij}), \quad (1.7)$$

where $\mathbf{Q}$ is the momentum transfer vector, $\mathbf{r}_{ij}$ is the position vector between atoms i and j and f_i and f_j are the scattering factors for atoms i and j , respectively.

Since X-ray diffraction measures the interference of photons with the electron density of the atoms of the sample, the scattering intensity is dependent on the amount of electron density and thus the number of electrons in each atom. It follows that the

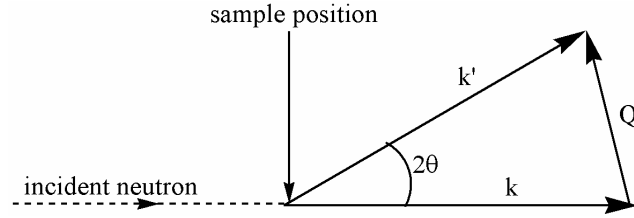


Figure 1.3: Geometry of incident and scattered wavevectors involving a fixed nucleus.

scattering intensity is also dependent on the concentration of each atom type in the sample. This dependence is represented by the atomic form factor, $f(\mathbf{Q})$. The atomic form factor shows an angular dependence because the wavelength of conventional X-rays, $\sim 1 \text{ \AA}$, is on the same order of the size of the scattering target, $\sim 1 \text{ \AA}$. There is less of a Q -dependence when high energy x-rays are employed, since their wavelength, $\sim 0.04 \text{ \AA}$, is not as close to the length scale of the microscopic structure of the target. Contrast this with neutron scattering, where the size of the target, a nucleus, is a few femtometers and the wavelength of the incident neutrons are $\sim 1 \text{ \AA}$. The substantial difference in the wavelength of the neutron and the size of the nucleus allows the target nucleus to be treated like a point source, thus the neutron form factor shows no angular dependence and is constant over all values of Q .

Neutron scattering form factors are the product of the concentration of the atom type in the sample and the scattering length, particularly the bound coherent scattering length, b , of the atom. The notion of bound coherent scattering length requires an explanation of coherent scattering and what the term ‘bound’ implies here. Coherent scattering is dependent on the correlation between the positions of the same nucleus at different times and on the correlation between the positions of different nuclei at different

times. Contrast this with incoherent scattering, which depends only on the correlation between the positions of the same nucleus at different times. As a consequence of their dependencies, coherent scattering results in interference effects and incoherent scattering does not.⁶ Therefore a diffraction experiment is only concerned with coherent scattering. The term ‘bound’ implies that the target nucleus is fixed.

Scattering length is independent of atomic number and varies between isotopes. This is exhibited by Figure 1.4.^{7,8} Isotopical variance of neutron scattering length allows experimenters to use a technique called **Neutron Diffraction with Isotopic Substitution (NDIS)** to obtain structural information that is very difficult to obtain with high energy X-rays. The work presented in the Chapter 4 took full advantage of NDIS. The value of b is the average over all spin states of the nucleus-neutron system. Since there is no adequate theory of nuclear forces, values of b must be determined experimentally.

Scattering lengths have a real and an imaginary component, the latter corresponding to absorption. Some nuclei, such as ^{121}Sb , ^{103}Rh , ^{113}Cd , ^{157}Gd , and ^{176}Lu , form compound nuclei (the target nucleus plus the incident neutron) possessing energies near that of an excited state. As a consequence these nuclei have large imaginary components of the scattering length, and are described as neutron absorbers. The phenomenon is known as neutron resonance and is often encountered in neutron diffraction experiments. This is evinced by the neutron diffraction data presented here for liquid antimony pentafluoride. The resonance due to ^{121}Sb causes a drop in intensity, which occurs across small ranges in Q , the values of which vary with detector bank.

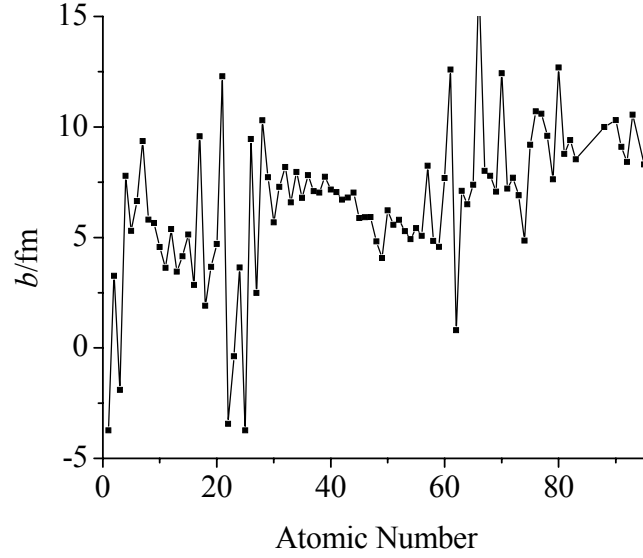


Figure 1.4: Bound coherent scattering lengths for the first 95 elements.

The technique of diffraction was first employed in the structural characterization of single crystals, which have atoms arranged in a fixed lattice resulting in their characteristic long-range order and periodicity. Hence the diffraction pattern of any crystalline system is non-zero only at discrete values of Q that correspond to a vector in reciprocal space, which defines a plane of atoms within the lattice. This is known as Bragg scattering⁹⁻¹¹ and is constrained by Bragg's law

$$n\lambda = 2d \left(\frac{Q/2}{k} \right) = 2d \sin \theta, \quad (1.8)$$

where n is an integer, λ is the wavelength of the incident particle, and d is the distance between lattice planes.

Bragg's law is inapplicable to liquids and other amorphous species since they do not have a periodic lattice and therefore have no long-range order. As a result, the

diffraction pattern of these systems contains no Bragg peaks, only what is termed diffuse scatter appearing as broad oscillations in the diffraction pattern. Diffuse scatter only gives insight to the local structure and intermediate-range order.

1.3.2 Neutron scattering measurements

Neutron diffraction experiments measure a quantity called the differential scattering cross-section, $d\sigma/d\Omega$, which has the following relationships:

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega_{\text{self}}} + \frac{d\sigma}{d\Omega_{\text{distinct}}} = \sum_{\alpha} c_{\alpha} b_{\alpha}^2 + P(\mathbf{Q}, \theta) + F_N(\mathbf{Q}), \quad (1.9)$$

where ‘distinct’ and ‘self’ refer to coherent and incoherent scattering, respectively, Ω is the angle of the scattered wavevector, and c_{α} and b_{α} are correspondingly the concentration and bound scattering length of atom type α . $P(\mathbf{Q}, \theta)$ represents the inelastic scattering and $F_N(\mathbf{Q})$ is interference function that describes the distinct scattering contribution. $F_N(\mathbf{Q})$ can be related to the better known total structure factor, $S^{\text{total}}(\mathbf{Q})$, by

$$S^{\text{total}}(\mathbf{Q}) = \frac{F(\mathbf{Q})}{\sum_{\alpha, \beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta}} + 1. \quad (1.10)$$

Functions, like $S(\mathbf{Q})$ in the above equation, are derived from the differential scattering cross-section to allow the calculation of numerous properties of the scattering system. From the intermediate function, $I(\mathbf{Q}, t)$, one can derive the scattering function, $S(\mathbf{Q}, \omega)$, the latter (a function of frequency, ω) being the time Fourier transform of the

former. The time-dependent pair correlation function, $G(\mathbf{r}, t)$ is the Fourier transform of $I(\mathbf{Q}, t)$ in space and represents the probability that a particle at the origin at time $t = 0$ is in the volume $d\mathbf{r}$ at time t .

The static approximation is used to simplify the two-dimensional correlation functions into one-dimensional functions. The static approximation assumes the time taken for the incident particle to interact with the sample is much less than the time needed for the scattering system to relax. In other words, the speed at which the probe moves is fast enough that the movement of atoms in a sample is negligible. This is definitely valid for X-rays, which travel at the speed of light, where the typical interaction time, that is the time taken for the incident photon to pass from one atom to another, is $\sim 10^{-18}$ seconds and common relaxation times for condensed matter systems are on the order of 10^{-13} seconds. However, thermal neutrons interact for about 10^{-13} seconds, leaving the validity of the static approximation in question for this application. Assuming the static approximation holds, the time-independent total scattering function and the time-independent total pair correlation function are given in terms of their partial functions by

$$S^{\text{total}}(\mathbf{Q}) = \frac{1}{\sum_{\alpha, \beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta}} \sum_{\alpha, \beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} (S_{\alpha\beta}(\mathbf{Q}) - 1) \quad (1.11)$$

and

$$G^{\text{total}}(\mathbf{r}) = \frac{1}{\sum_{\alpha, \beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta}} \sum_{\alpha, \beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} (g_{\alpha\beta}(\mathbf{r}) - 1). \quad (1.12)$$

The total structure factor and total pair correlation function are space Fourier transforms of each other. The same is true for the partial structure factors and partial pair correlation functions.

1.3.3 High energy X-ray measurements

High energy X-ray diffraction yields analogous measurements to neutron diffraction. One advantage to X-ray diffraction is the validity of the static approximation for the reasons stated above.¹² However, as previously discussed X-rays are not well-suited to determine the positions of low- Z atoms.

Again the measured quantity in a high energy X-ray diffraction experiment is the differential scattering cross section,

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega_{\text{Compton}}} + \frac{d\sigma}{d\Omega_{\text{self}}} + \frac{d\sigma}{d\Omega_{\text{distinct}}} = C_X(\mathbf{Q}) + \sum_{\alpha} c_{\alpha} f_{\alpha}^2(\mathbf{Q}) + I_X(\mathbf{Q}), \quad (1.13)$$

where $C_X(\mathbf{Q})$ is the $\mathbf{Q}$ -dependent Compton scattering function, which describes incoherent, inelastic X-ray scattering. $I_X(\mathbf{Q})$ is the intensity function for the distinct or coherent scattering. Analogous to the neutron total structure factor is the X-ray total pseudo-nuclear structure factor given by

$$S_X^{\text{total}}(\mathbf{Q}) = \frac{I_X(\mathbf{Q}) - C_X(\mathbf{Q}) - \sum_{\alpha} c_{\alpha} f_{\alpha}^2(\mathbf{Q})}{\sum_{\alpha, \beta} c_{\alpha} c_{\beta} f_{\alpha}(\mathbf{Q}) f_{\beta}(\mathbf{Q})}, \quad (1.14)$$

and given here in terms of the Faber-Ziman partial structure factors as

$$S_X^{\text{total}}(\mathbf{Q}) = \frac{1}{\sum_{\alpha,\beta} c_\alpha c_\beta f_\alpha(\mathbf{Q}) f_\beta(\mathbf{Q})} \sum_{\alpha,\beta} c_\alpha f_\alpha(\mathbf{Q}) c_\beta f_\beta(\mathbf{Q}) (S_{\alpha\beta}(\mathbf{Q}) - 1). \quad (1.15)$$

It follows that the space Fourier transform of the X-ray total pseudo-nuclear structure factor is the X-ray pair correlation function, $G_X^{\text{total}}(\mathbf{r})$.

1.3.4 Neutron diffraction from liquids

As stated above, liquids have no periodic lattice and thus no long-range order. However, intermolecular forces in liquids are comparable in magnitude to those in the solid state. This is evinced by similarities between the densities of liquids and solids. Intermolecular interactions in the liquid state give rise to diffuse scatter, which provides insight into the local structure and intermediate-range order. Also there is no proper theory of the liquid state, though it has been researched for some time.¹³⁻²⁵ These are some of the reasons that the interpretation of liquids structural data is considered to be much more difficult than that of solids.

Other major problems encountered in a liquids diffraction experiment include inelastic scattering, multiple scattering, and attenuation effects. Inelastic scattering is the most prominent problem in liquids diffraction. It is possible for translational and rotational modes of a molecule to be excited by the neutron scattering process. This results in the scattered neutron having energy other than its incident energy. The resultant structure factor must be corrected for the added inelastic intensity. Ignoring multiple scattering and attenuation effects, the measured total structure factor can then be considered as

$$S_M(\mathbf{Q}, \theta) = S(\mathbf{Q}) + P(\mathbf{Q}, \theta), \quad (1.16)$$

where $P(\mathbf{Q}, \theta)$ is known as the Placzek function and represents the difference due to inelasticity between the ideal $S(\mathbf{Q})$ and the measured $S_M(\mathbf{Q}, \theta)$. The Placzek function is a function of $\mathbf{Q}$ and scattering angle θ , and shows a direct relationship to temperature and an inverse relationship to neutron energy.²⁶

Another problem arises when the scattering system involves atoms of lower atomic number, especially hydrogen. Often the scattering intensity for a hydrogenous sample or a sample containing other low- Z atoms will fall off as $\mathbf{Q}$ increases. The shape of the fall-off is dependent on the position of the detector bank and must be accounted for when correcting the data. The effect can be attributed to deviation of bound-coherent scattering lengths from their ideal values according to the following equation:

$$b_{\text{effective}} = \left(\frac{M}{M+1} \right)^2 b, \quad (1.17)$$

where M is the mass of the nucleus. From this equation one can see that the effect should be far less profound with atoms of higher atomic number. The effect manifests itself in the form of a negative slope in the differential scattering cross-section data. Currently the best way to correct for this is to fit the measured differential scattering cross-section intensity with a Chebyshev polynomial.²⁷ These are a series of polynomials designed as solutions to the Chebyshev differential equation. The subtraction of the polynomial from the data yields the corresponding interference function, $F(\mathbf{Q})$.

1.3.5 Neutron diffraction data analysis

Most neutron diffraction data, indeed all diffraction data presented here, are collected by a number of radially arranged detector banks. Often data will be collected in a series of runs. The data from each run must be summed and its intensity normalized to a beam monitor. Normalizing to the beam monitor ensures that any fluctuations in scattering intensity due to fluctuations in incident beam intensity are adjusted to their proper level.

In addition to the sample data, data are collected on an empty sample holder or can and on the instrument background; i.e., without anything in the beam. The data for the background and the empty container are subtracted from the sample data to leave only scattering intensity due to the sample material.

Data are also obtained on a vanadium rod of similar size to the sample can. The vanadium data are used in several ways, including establishing an absolute scale for and calibrating the intensity of the sample data. Vanadium is used for a number of reasons. It is mostly an incoherent scatterer, thereby generating a Q -independent calibration that is reliable at all detector angles. The fact that the density of vanadium is well known makes these calibrations more reliable. The vanadium data are also used to help correct for multiple scattering, attenuation, and absorption effects. Multiple scattering occurs any time a neutron interacts with more than one nucleus. No information about the position of a distinct nucleus can be extracted by analysis of a neutron that has interacted more than once. The notion of neutron absorption was discussed earlier and only appreciably occurs if the sample contains nuclei that have a scattering length with a significant

imaginary component (section 1.3.1). Attenuation effects are the lowering of scattering intensity due to sample size. This is easily corrected when the sample data are normalized to the vanadium data. Multiple scattering and attenuation correction is thoroughly discussed in the literature.²⁸⁻³⁰

At this point, the data are in the form of differential scattering cross-section. The Placzek correction is now applied and the self scattering intensity is subtracted. If a light atom effect is present, as discussed earlier, Chebyshev polynomials are fitted to and subtracted from the data. Once all corrections are applied, the differential scattering cross-section data for each detector bank are combined and averaged to give an interference function, $F(\mathbf{Q})$, which converts to the total static structure factor $S(\mathbf{Q})$ according to equation (1.10). Subsequent Fourier transform of $S(\mathbf{Q})$ yields the total pair correlation function, $G(\mathbf{r})$. Statistical background noise and the impossibility of measuring to an infinitely large $\mathbf{Q}$ value result in the Fourier transform of the structure factor, the pair correlation function, containing nonphysical peaks at low $\mathbf{r}$ values (typically less than ~ 1 Å). Similar error can arise if the low- Z atom effect is not completely corrected.

1.3.6 Quasielastic neutron scattering

Quasielastic neutron scattering, or QENS, is a technique used to study the dynamics and motions of atoms and molecules. The essence of the technique lies in the measurement of small energy transfers between neutrons and the atoms or molecules

being studied. Energy is transferred to or from the sample *via* neutron interaction with particles that are reorienting or diffusing on a timescale of $\sim 10^{-10} - 10^{-12}$ seconds. The amount of energy transferred is typically within ± 2 meV. Unlike diffraction data, QENS data points describe a single peak, the result of the broadening of the elastic line—that is the line representing neutrons scattered without the loss or gain of energy. It is the analysis of the shape of this single peak, which yields information about the motions of the sample. The small relevant energy range of a QENS experiment and the nature of the analysis make it necessary for any satisfactory QENS instrument to have superior resolution.

The notion of incoherent scattering was defined earlier as scattering that depends only on the correlation between the positions of the same nucleus at different times. Certainly the branch of neutron scattering concerned with the study of atomic and molecular motions must be concerned with incoherent scattering. Hence we begin by introducing a variation of the intermediate scattering function restricted to incoherent scattering,

$$I_{\text{inc}}(\mathbf{Q}, t) = \frac{1}{N} \sum_i \left\langle \exp\{i\mathbf{Q} \cdot \mathbf{R}_i(t)\} \exp\{-i\mathbf{Q} \cdot \mathbf{R}_i(0)\} \right\rangle, \quad (1.18)$$

where $\langle \dots \rangle$ denotes a thermal average. The general position vector, $\mathbf{r}(t)$, can be separated into two components and written as

$$\mathbf{r}(t) = \mathbf{r}_e(t) + \mathbf{u}(t), \quad (1.19)$$

where $\mathbf{r}_e(t)$ represents the instantaneous equilibrium position at time t , and $\mathbf{u}(t)$ is the displacement of a nucleus from its equilibrium position caused by internal vibrations that

result in the deformation of bond lengths and angles. $\mathbf{r}_e(t)$ is time-dependent with respect to the whole molecule, whereas $\mathbf{u}(t)$ depends on the time of the motions of molecular motions as well as internal vibrations.

The QENS work presented here was performed on a liquid sample; therefore, most of the following discussion will be restricted to liquids. For a general description of QENS, consult M. Bée's book *Quasielastic Neutron Scattering: Principles and Applications in Solid State Chemistry, Biology and Materials Science*.³¹ The external movements of a liquid essentially consist of molecular translations and rotations about its center of mass. Hence, the equilibrium position component vector can be further separated into rotational and translational components to give a more detailed description of the general position vector. The resultant equation is given as

$$\mathbf{r}(t) = \mathbf{r}_T(t) + \mathbf{r}_R(t) + \mathbf{u}(t), \quad (1.20)$$

where $\mathbf{r}_T(t)$ and $\mathbf{r}_R(t)$ are correspondingly the translational and rotational component of the position vector. The description of the position vector presented here assumes that a molecule in a bulk sample is free to translate anywhere in space and rotate freely about its center of mass. Of course, this isn't true since intermolecular interactions only allow translational and rotational reorientation to distinct equilibrium positions, though there would be several of these positions available for a molecule in a disordered phase, such as a liquid.

Taking into account the separation of the position vector, the intermediate scattering function can be written as

$$\begin{aligned}
I_{\text{inc}}(\mathbf{Q}, t) &= I_{\text{inc}}^{\text{T}}(\mathbf{Q}, t) + I_{\text{inc}}^{\text{R}}(\mathbf{Q}, t) + I_{\text{inc}}^{\text{V}}(\mathbf{Q}, t) \\
&= \langle \exp \{i\mathbf{Q} \cdot [\mathbf{r}_{\text{T}}(t) - \mathbf{r}_{\text{T}}(0)]\} \rangle \times \langle \exp \{i\mathbf{Q} \cdot \mathbf{r}_{\text{R}}(t)\} \exp \{-i\mathbf{Q} \cdot \mathbf{r}_{\text{R}}(0)\} \rangle \\
&\quad \times \langle \exp \{i\mathbf{Q} \cdot \mathbf{u}(t)\} \exp \{-i\mathbf{Q} \cdot \mathbf{u}(0)\} \rangle
\end{aligned} \tag{1.21}$$

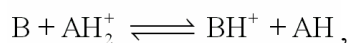
for a single scatterer. The time Fourier transform of the intermediate scattering function gives the scattering law, $S_{\text{inc}}(\mathbf{Q}, \omega)$.

QENS instrumentation and methods are briefly introduced in Chapter 2. A more detailed description of the specific diffusion model used for the QENS work in this thesis is given in section 2.2.5.

1.4 Introduction to the chemistry and properties of superacids

1.4.1 A brief history of superacids

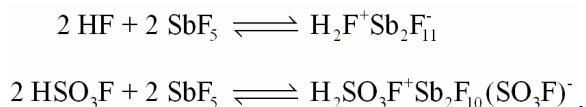
The term “superacid” was first used by J. B. Conant in 1927 in reference to any acid system that is more acidic than typical Brønsted acids such as sulfuric acid or Lewis acids such as aluminum trichloride.³² It was soon realized that the pH scale was not sufficient to describe the acidity of highly concentrated or nonaqueous systems. Five years later, Hammett and Deyrup proposed a method where degree of acidity can be derived from the degree of protonation of weakly basic indicators in acid solution.³³ The proton transfer equilibrium is given as



where AH_2^+ is the solvated proton. The resulting Hammett acidity function is given below in its usual form,

$$H_0 = \text{p}K_{\text{BH}^+} - \log \frac{[\text{BH}^+]}{[\text{B}]} . \quad (1.22)$$

Superacids were mostly unexplored until the 1960's when G. A. Olah used superacidic solvent systems to observe stable carbocations.³⁴ Later, Gillespie redefined the term superacid to mean any acid or acid system stronger than 100% sulfuric acid ($H_0 \leq -12$).^{35,36} Common Brønsted superacids include fluorosulfuric acid ($H_0 = -15.1$) and trifluoromethanesulfonic acid ($H_0 = -14.1$). The strongest acid system to date is the “magic acid” system, coined by Olah, of antimony pentafluoride dissolved in fluorosulfuric acid. A 90% solution of SbF_5 in FSO_3H has a Hammett acidity function value of -27.³⁷ It is thought that a concentrated solution of SbF_5 in HF may be more acidic ($H_0 \sim -30$), but this has yet to be proven. Gillespie has measured the H_0 value of 0.60 mol % SbF_5 in HF to be 21.13, which is much higher than its fluorosulfuric acid analogue.³⁸ The addition of SbF_5 to HF and FSO_3H yields complex fluoro anions that result in the delocalization of the negative charge. The equilibria for these two systems are given here.



Of course the unsolvated proton is unattainable in solution, but extrapolation of gas phase data place its H_0 value between -50 and -60.

1.4.2 Types of superacids

Fluorosulfuric acid and hydrofluoric acid are thought to represent the upper limit of acidity for a single species. This limit can be surpassed by adding a strong Lewis acid, which serves to shift the autoprotonation equilibrium forward.

As Gillespie's definition of superacids only pertains to Brønsted acids, Olah, Prakash and Sommer suggested that a superacid be any acid stronger than the Lewis acid aluminum chloride.^{39,40} This thesis presents studies of both Brønsted and Lewis superacids, however these two types do not constitute the whole of the superacid field.

Superacids can be divided into three major types: Brønsted and Brønsted-Lewis conjugate superacids, Lewis superacids, such as SbF_5 , TaF_5 , NbF_5 ,⁴¹⁻⁴⁷ and solid superacids. Brønsted and Brønsted-Lewis conjugate superacids can be further divided into four types. Firstly are perchloric (HClO_4),⁴⁸⁻⁵⁰ halosulfuric (e.g., FSO_3H),⁵¹⁻⁵⁶ and perfluoroalkane sulfonic (e.g., $\text{CF}_3\text{SO}_3\text{H}$) acids.⁵⁷⁻⁶⁴ Secondly are oxygenated Brønsted acids, such as H_2SO_4 , FSO_3H and $\text{CF}_3\text{SO}_3\text{H}$, mixed with Lewis acids, such as SO_3 , SbF_5 , AsF_5 .^{37,52,65-72} Thirdly are solutions of fluorinated Lewis acids, such as SbF_5 , TaF_5 , NbF_5 , BF_3 in anhydrous HF .^{65,73-87} Lastly are Friedel-Crafts acids including HBr-AlBr_3 and HCl-AlCl_3 .^{83,88-93}

Solid superacids can be subdivided into two groups: acidity-enhanced solid acids and supported or intercalated superacids. The former includes acid-treated metal oxides, mixed oxides and zeolites⁹⁴⁻¹⁰⁶ and perfluorinated resins and sulfonated cation exchange resins.¹⁰⁷ The latter consists of Lewis or Brønsted acids intercalated into graphite (or fluorographite)¹⁰⁸⁻¹²⁵ or into other inert supports such as alumina.¹¹⁹

The properties and chemistry of each superacid presented in this thesis are discussed in detail in their corresponding chapters.

2 DYNAMICAL STUDIES OF LIQUID ANHYDROUS HYDROGEN FLUORIDE

2.1 Introduction

Hydrogen fluoride is the simplest, strongly associated fluid in terms of the molecular structure of the material. In this respect, it is a highly attractive system for theoretical studies of hydrogen bonded fluids and it has received an intense level of investigation from the theoretical community recently.¹²⁶⁻¹⁴³ Moreover, the important industrial applications of this material have also stimulated simulations of its properties over a wide range of thermodynamic states. It has been stated that it is preferable to calculate the properties of HF, rather than to measure them, given the toxic and corrosive nature of the pure material.¹⁴⁴

The aggressive nature of the material has largely prevented the experimental investigation of its properties, a fact that has been highlighted previously in the literature.^{144,145} Given the shortage of experimental data and the archetypal nature of HF, to which we and others have referred elsewhere,^{138,144-146} a comprehensive investigation of its structure and properties has been undertaken, using appropriate experimental precautions,¹⁴⁷ in order to fill this apparent gap in the scientific body of data on strongly associated fluids.

The sensitivity of the calculated structure and dynamics of HF to the details of the model that is used for calculation is profound^{126,138} and therefore the need for the experimental community to provide such data is important for the further development of

specific models of HF and for the generalities of the theoretical treatment of associated hydrogen bonded fluids.

The structure of hydrogen fluoride is dominated by the hydrogen bond in all phases of matter;¹⁴⁸⁻¹⁵³ in this respect, the dynamics of the molecular constituents of the fluid within the structural framework that the fluid presents must be closely related to the dynamics within the hydrogen bond, as well as molecular translation and rotation in the context of the strong intermolecular forces that are undeniably present in HF.

Structural reports on liquid HF are scarce, with three total structure factor measurements^{146,149,153} and only one which reports the structure at the pair correlation function level.¹⁴⁶ Experimental measures of the dynamics of HF are more common, given the wider number of techniques that are available, which include vibrational spectroscopy,¹⁵⁴⁻¹⁶³ NMR measurements^{164,165} and inelastic and quasielastic neutron scattering.^{166,167}

NMR measurements performed by Karger, *et al* provide self-diffusion coefficient, D , values for HF and DF at several temperatures and pressures.^{164,165} These data show that D is only slightly dependent on pressure relative to its strong inverse dependence on temperature. They also observed an increase in the dynamic isotope effect with decreasing temperature. Two of the authors later reanalyzed these data after making density measurements on liquid HF. They observed a linear decrease in D with $1/T$ and the same with increasing density.

Neutron scattering is an extraordinarily potent probe of structure and dynamics in condensed matter for the reasons discussed in Chapter 1. Inelastic scattering has even

greater advantages over infra-red spectroscopy or Raman scattering as there are no selection rules that govern energy transfer to or from the normal vibrational modes, rotational modes or translational modes in the sample. There is also a very wide range of neutron energies available, allowing the recording of dynamical data over a very wide spectrum of energy transfers. Quasi- and inelastic neutron scattering are therefore both highly attractive tools for measurement of the total dynamical spectrum in the experimental energy range.¹⁶⁸⁻¹⁷²

Previous inelastic measurements by Egelstaff and Ring in the energy range 0.5 meV – 81.0 meV ($4.03 \text{ cm}^{-1} - 653 \text{ cm}^{-1}$) provided data that gave no diffusion coefficients ($D \leq 1 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) under the experimental conditions used.¹⁶⁷ Later, Ring analyzed the inelastic neutron scattering of liquid and solid HF by considering the vibrational modes of hydrogen-bonded chains.¹⁶⁶ He concluded that the features found in the inelastic spectra could not be accounted for by the chain modes alone. Therefore, there must be some other motion/structural feature that is responsible for the remaining inelastic and elastic scattering.

To gain insight to the translational mobility in pure liquid HF, quasielastic neutron scattering data are presented here as well as rotational and translational diffusion coefficients extracted from a parametric fit to the data.

2.2 Experimental

2.2.1 Sample preparation

In order to accurately measure their dynamics, high purity isotopic samples of hydrogen fluoride and deuterium fluoride were prepared on a high vacuum line constructed of Alloy 400 (Monel). Anhydrous HF or DF was produced from the reaction of H_2SO_4 or D_2SO_4 , respectively, with dry CaF_2 in a stainless steel pressure bomb under static vacuum. The gases were purified by cryogenic distillation, dried with fluorine, and degassed. HF or DF was barometrically measured and then cryogenically transferred into sample cells constructed of Alloy 400, which have been previously described.¹⁴⁷ Figure 2.1 shows a cross section of the sample cell. An annular volume was created by welding a tube of relatively small diameter concentrically inside a larger diameter tube. This assembly was then welded to a small flange, such that the HF or DF was contained between the two tubes. A PTFE gasket (not shown) was placed between the body of the cell (C) and the cell head (B). Threads on the cell head allowed for the final assembly to be made with a custom nut (D). The HF was delivered to and contained in the cell by manipulation of a stainless steel needle valve (A). The chemical and isotopic purity of all the samples was $> 99.9\%$ with $< 0.1\%$ H_2O . This was determined from neutron diffraction data¹⁷³ and the purity of starting materials. HF and DF were confined to annular volumes of 0.1319 mL and 1.138 mL, respectively.

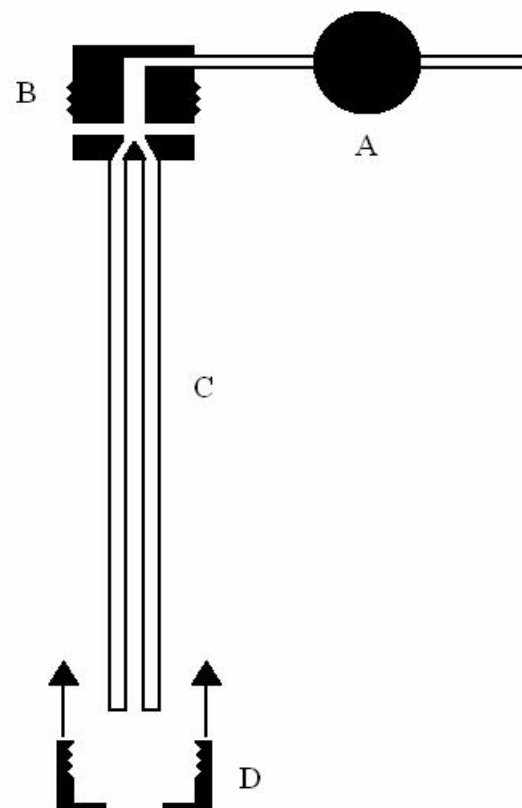


Figure 2.1: Cross-section of the Monel QENS cell used to measure the dynamics of HF. The valve, head, body, and nut are labeled as A, B, C, and D, respectively.

2.2.2 The QENS spectrometer

Quasielastic neutron scattering data for HF were obtained using the QENS spectrometer (Figure 2.2¹⁷⁴) at Argonne National Laboratory's Intense Pulsed Neutron Source.¹⁷⁵ Data were recorded for HF at 195 K, 246 K, and 296 K. Also, a resolution function was obtained from measurements on DF at 15 K. All temperatures are accurate to within ± 1 K. All data were collected at 22 momentum transfer values ranging from $0.37 \text{ \AA}^{-1} \leq Q \leq 2.55 \text{ \AA}^{-1}$. However, aberrant data from detector banks 9, 10, and 11 were not used in the analysis. QENS is an example of an inverse geometry, crystal analyzer instrument. Surrounding the sample are 22 detector arms each having a crystal analyzer that reflects the scattered neutrons onto ^3He detectors. The configuration of the detector arms give QENS a momentum transfer (Q) range of $0.3 - 2.6 \text{ \AA}^{-1}$. The total energy resolution is $90 \text{ \mu eV}$. QENS does not have a pre-sample monochromator, but rather uses a white beam of neutrons direct from the source. The benefits of this design are two fold. First the absence of a monochromator results in a higher incident flux, which permits the use of smaller samples. This is particularly beneficial to experimenters whose samples can not be produced in large quantities. Secondly, since the energies of the incident neutrons span the energy spectrum of the source, energy transfers resulting from myriad molecular and atomic motions can be measured with every pulse, specifically in the range of -2.5 to 200 meV .

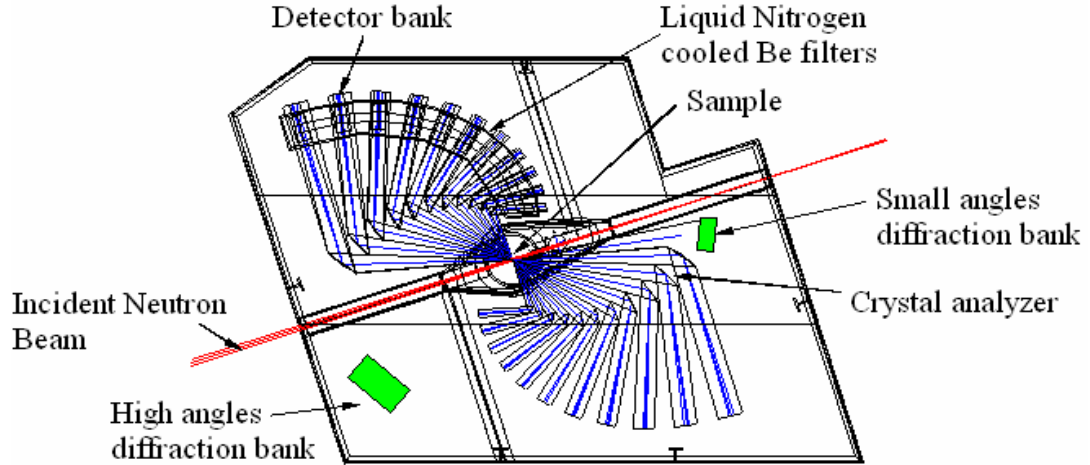


Figure 2.2: Schematic of the QENS spectrometer at IPNS showing its distinctive detector bank arrangement. The two diffraction banks allow for elastic measurements to be made while simultaneously measuring dynamics.

2.2.3 Time of flight measurements

As mentioned in Chapter 1, spallation neutron sources operate in a pulsed manner, at 60 Hz in the case of IPNS. This ensures that time-resolved measurements are possible. The measurements discussed in this and all subsequent chapters are known as time of flight, or TOF, measurements. This simply means that the energies of the scattered neutrons are determined *via* direct measurement of their velocities.

Making TOF measurements requires that the final energy of the scattered neutron, E_f , and the length from sample to detector, L_f , be precisely known. The former is elucidated by incorporating the scattering angle and the lattice spacing of the crystal along with Bragg's law into the de Broglie relationship as shown below.

The kinetic energy of a free neutron is simply

$$E = \frac{1}{2}mv^2, \quad (2.1)$$

where m and v are the mass and velocity of the neutron. Combined with the expression for the de Broglie wavelength, $\lambda = h/mv$, the energy is given by

$$E = \frac{h^2}{2m\lambda^2}, \quad (2.2)$$

where h is Planck's constant and λ is the wavelength of the neutron. Bragg's law was earlier written as

$$\lambda = 2d \sin \theta_C \quad (2.3)$$

for a crystal of lattice spacing, d , and scattering angle, θ_C . Substituting for λ in (2.2) yields

$$E_f = \frac{h^2}{8md^2 \sin^2 \theta_C}. \quad (2.4)$$

Specifically, this is the final energy of a neutron scattered from a crystal. The time of flight from sample to detector, t_f , can be calculated from equation (2.1) using the known path length, L_f . This time is subtracted from the total time of flight of the neutron to determine the time from source to sample and thus the incident energy of the neutron. For completeness, the incident energy of a neutron for a general spectrometer is derived below.

The total flight time, t , is the sum of the incident time of flight (source to sample), t_i , and the final time of flight (sample to detector), t_f . Thus, if

$$t = t_i + t_f, \quad (2.5)$$

and

$$E = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{L}{t}\right)^2, \quad (2.6)$$

then

$$\tau = L_i\left(\frac{2E_i}{m}\right)^{-\frac{1}{2}} + L_f\left(\frac{2E_f}{m}\right)^{-\frac{1}{2}}. \quad (2.7)$$

Dividing both sides by the final flight time gives

$$\frac{t}{L_f}\left(\frac{2E_f}{m}\right)^{\frac{1}{2}} = \frac{L_i\left(\frac{2E_i}{m}\right)^{-\frac{1}{2}}}{L_f\left(\frac{2E_f}{m}\right)^{-\frac{1}{2}}} + 1, \quad (2.8)$$

which, upon subtraction of the constant and the squaring of both sides, simplifies to

$$\left[\frac{t}{L_f}\left(\frac{2E_f}{m}\right)^{\frac{1}{2}} - 1\right]^2 = \frac{L_i^2/E_i}{L_f^2/E_f}. \quad (2.9)$$

Solving for the incident energy yields

$$E_i = E_f\left(\frac{L_i}{L_f}\right)^2\left(\frac{t}{L_f}\sqrt{\frac{2E_f}{m}} - 1\right)^{-2}. \quad (2.10)$$

2.2.4 Resolution and focusing

The technique described above is only valid if the measurements are made with a time focused instrument. Most crystal analyzer spectrometers use large (2 – 10 cm in diameter) single crystals as analyzers. Because of the large size, certain areas of a crystal will scatter to certain areas of a detector due to varying Bragg angles. However, remembering Bragg's law, only neutrons of certain wavelength, and thus energy and

velocity, will scatter from a particular spot on the crystal to a particular spot on the detector. By arranging the detectors so that the ratio of path length to velocity is constant, an instrument can achieve complete time resolution or time focusing.

QENS employs a somewhat different method involving analyzers that are each made up of several small crystals of (002) pyrolytic graphite. Each crystal only reflects neutrons to a specific area of the detector. For a particular detector, the variations in path length and velocity are minimized, such that L_f/V is essentially constant. By using this method, QENS obtains both time and final energy focusing, which is essential to any instrument capable of making both quasielastic and inelastic measurements.

An instrument's overall energy resolution is largely dominated by either the uncertainty in time measurements or the uncertainty in energy measurements. By examination of the following equation, the factors affecting instrument resolution are evident:

$$(\Delta E)^2 = (\Delta E_f)^2 + E_f^2 \left(\frac{L_i}{L_f} \right)^4 \xi^6 \times \left[\left(\frac{\Delta E_f}{E_f} \right)^2 + 4 \left(\frac{\Delta L_f}{L_f} \right)^2 + \frac{4}{\xi^2} \left(\frac{\Delta L_i}{L_i} \right)^2 + 4 \left(\frac{\Delta t}{L_t} \sqrt{\frac{2E_f}{m}} \right)^2 \right]. \quad (2.11)$$

L_t is the total flight path and Δt is the uncertainty in the time measurement, which can arise from the time of flight measurement or from the source pulse width, the latter resulting in slightly different origination times of neutrons. ξ is the ratio between final flight time and incident flight time and is equal to the term contained in the second set of parentheses in equation (2.10).

Quasielastic scattering involves very small energy transfers between the neutron and the sample leading to similar final and incident neutron velocities. Therefore, the ratio of final flight time to incident flight time is very small, as the detectors are near the sample and the source is relatively far. Since this ratio is small, the total resolution of a quasielastic instrument is largely governed by the uncertainty in energy measurements. Conversely, inelastic resolution is dominated by uncertainty in the time domain. This is due to the relatively large energy transfer that occurs when a neutron is inelastically scattered. For the most part, a neutron loses energy to the sample and slows down as a result. Consequently, such a neutron requires more time to reach the detector than in an elastic or quasielastic experiment, and the ratio of final flight time to incident flight time is substantially larger.

2.2.5 Diffusion models

The simple analytical model used to describe the self-diffusion of HF was previously used to describe the diffusion of water.¹⁷⁶ The model assumes completely decoupled translational and rotational motions, which results in a viable computational model consisting of a convolution of translational and rotational contributions,

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \exp\left\{-\langle u^2 \rangle Q^2 / 3\right\} [T(\mathbf{Q}, \omega) \otimes R(\mathbf{Q}, \omega)]. \quad (2.12)$$

Here the first term (called the Debye-Waller factor), which includes the mean square displacement of the atom, $\langle u^2 \rangle$, gives the probability that the neutron is elastically or quasielastically scattered. $T(\mathbf{Q}, \omega)$ describes the translational motion of the molecule

and $R(\mathbf{Q}, \omega)$ represents the contribution for the low frequency rotational molecular motion. For rotation on the surface of a sphere, $R(\mathbf{Q}, \omega)$ is given by the Sears expansion,¹⁷⁷

$$R(\mathbf{Q}, \omega) = j_0^2(Qa)\delta(Qa) + \frac{1}{\pi} \sum_{l=1}^{\infty} (2l+1) j_l^2(Qa) \frac{l(l+1)D_r}{(l(l+1)D_r)^2 + \omega^2}, \quad (2.13)$$

where a is the radius of gyration, D_r is the rotational diffusion constant and j_l are the spherical Bessel functions. There is a relaxation time associated with rotational diffusion that is given by $\tau_r = 1/6D_r$. The translational component is a Lorentzian function

written as

$$T(\mathbf{Q}, \omega) = \frac{1}{\pi} \frac{\Gamma(\mathbf{Q})}{\Gamma^2(\mathbf{Q}) + \omega^2}, \quad (2.14)$$

with $\Gamma(\mathbf{Q})$ being equal to the half-width at half-height.

The simplest mode of translational diffusion is continuous and random. This notion was first described in one macroscopic dimension by Adolf Fick in 1855 and assumes constant particle concentration within the diffusion volume.^{178,179} This is known as Fick's first law. Fick's second law allows for changes in concentration about the diffusion volume and can be used to describe diffusion in all three dimensions. It takes the form,

$$D\nabla^2\phi = \frac{\partial\phi}{\partial t}, \quad (2.15)$$

where D is the translational diffusion coefficient, ∇^2 is the Laplace operator, ϕ is the concentration and is a function of the radius vector, $\mathbf{r}$, and time, t .

A truly microscopic description of random particle motion didn't exist until Brownian motion was completely and quantitatively described by Einstein in 1905.¹⁸⁰ The phenomenon had been discovered 78 years prior when Brown observed the random motion of pollen particles on the surface of water under a microscope.¹⁸¹ Under the conditions of Brownian motion, particle movement is caused exclusively by collisions with other particles. Between collisions, a particle moves in a straight line independent of its previous direction and with no memory of its path prior to the collision. For this reason, Brownian motion is sometimes called the “random walk model”, although the actual mathematical model of random walk is much simpler still.

The Brownian model is only useful in describing the motion of particles that have very little interparticle interaction and very small random displacements, such as liquid argon. Deviations from Fick's law arise in systems where one particle is not so independent of all others. Greater interaction yields greater deviation.

In response to the ever increasing examples of non-Fickian systems, Chudley and Elliott developed the jump diffusion model in 1961,¹⁸² a method later improved upon by Peter Egelstaff.¹⁸³ The jump model was initially developed to account for non-Fickian behavior in ordered liquids but soon saw application with a number of other types of systems, such as hydrogen diffusion in metals.

For translational diffusion *via* a jump mechanism, $\Gamma(Q)$ is given by

$$\Gamma(Q) = \frac{D_t Q^2}{1 + D_t Q^2 \tau_0}, \quad (2.16)$$

where $D_t = L^2 / 6\tau_0$ is the self-diffusion coefficient, τ_0 is the average residence time between jumps, and L is the average jump distance. For continuous diffusion, τ_0 approaches zero, and $\Gamma(\mathbf{Q}) \approx D_t Q^2$, which is what is given by Fick's law.

2.2.6 Corrections to the data

A large fraction of QENS measurements are performed on small samples confined to some container. The presence of this container greatly complicates matters, as data often display the effects of attenuation by multiple scattering, self-shielding, and absorption resulting from both sample and container. As described in section 1.3.5, diffraction experiments use data on an empty container to subtract from sample data in order to approximate the scattering intensity from the sample material alone. However, this alone is not a sufficient correction for QENS data, as the scattering intensity from the sample is often much too small relative to that of the container, such that reliable statistics are seldom obtained.

Also, it is frequently apparent that the measured total scattering intensity for a given sample in a container, I_{S+C}^{S+C} , is not merely the scattering intensity of the sample plus that of the container, but rather the sum of the scattering from the sample in the presence of the container, I_{S+C}^S , and the scattering from the can in the presence of the sample, I_{S+C}^C ,

$$I_{S+C}^{S+C} = I_{S+C}^S + I_{S+C}^C \quad (2.17)$$

This requires the introduction of attenuation factors into the scattering law of equation (1.21). The resulting scattering intensity for the sample in the presence of the can, the

can in the presence of the sample, and the can alone are given in terms of the theoretical intensity, I^C or I^S , with their respective attenuation factors, A :

$$\begin{aligned} I_{S+C}^S &= A_{S+C}^S I^S \\ I_{S+C}^C &= A_{S+C}^C I^C \\ I_C^C &= A_C^C I^C \end{aligned} \tag{2.18}$$

By combining (2.17) and (2.18), the theoretical scattering intensity is found to be

$$I^S = \frac{1}{A_{S+C}^S} \left(I_{S+C}^S - \frac{A_{S+C}^C}{A_C^C} I_C^C \right). \tag{2.19}$$

Proper correction of the data greatly hinges on the accurate determination of the attenuation factors, which are dependent on the nature of the sample and the container as well as the shape and orientation of the container.

Attenuation factors can be determined either analytically using the Sears' integral method¹⁷⁷, or by simulation using Monte Carlo techniques. The Sears' method works well in general, but the attenuation factors for many systems are more accurately determined with simulation. Indeed, this was the case for the HF and DF data presented here. Attenuation from the sample compounded with the absorption and multiple scattering from the container led to gross inaccuracies in the results of the initial data analysis. Special acknowledgement must be provided for Dr. Ken Herwig, who performed all the calculations and simulations described in this section.

Monel is composed of 66.5% nickel, 31.0% copper, and 2.5% other metals. Due to the considerable absorption cross-sections of Ni and Cu, a significant amount of

incident neutrons did not interact with the sample. Therefore, it was necessary to apply multiple corrections to the data.

The scattering intensity from a 6.4 mm diameter vanadium rod was measured and used to normalize the empty container and sample scattering intensity measured at the detectors. A Monte Carlo simulation using McStas software^{184,185} was used to calculate an absorption correction in the vanadium rod at a neutron wavelength of 4.35 Å. At this wavelength, the calculated absorption in the vanadium rod was 32% of the incident neutron beam. Sample self-shielding caused the calculated neutron intensity observed at the detectors to vary as a function of scattering angle by about 8% over the whole angular range. This correction was applied to the sample and background data. The calculated average scattered intensity observed at the detectors corresponded to the vanadium scattering about 9.5% of the incident neutron beam.

Below $Q \sim 2.5 \text{ \AA}^{-1}$, scattering from the Monel sample container is relatively featureless and approximately constant. After normalization to the measured vanadium standard, the measured intensity at the detectors for the empty Monel sample container was approximately 90% of that measured from the 6.4 mm diameter vanadium standard. The average scattered intensity measured at the detectors corresponds to the sample container scattering approximately 8.5% of the incident neutron beam. The sample container was modelled in McStas with an incoherent cross-section that reproduced the average measured intensity at the detectors and also included the considerable absorption cross-section due to the copper and nickel in the alloy. At a neutron wavelength of 4.35 Å, the calculated absorption in the sample cell was 26%.

The additional HF scattering measured in the detectors corresponds to a sample scattering intensity that is approximately 2.5% of the incident neutron beam. Due to attenuation of the neutron beam by HF, the data from the container had to be corrected before it was subtracted from the sample data. The attenuation factor was incorporated into another calculation of the empty Monel container. Yet another calculation was performed to model the angular dependence of absorption due to the container. The absorption was found to vary by 7% over the entire range of scattering angles. This correction was applied to the now background-subtracted HF sample data.

2.3 Results

2.3.1 Data and fits

Representative corrected and background-subtracted quasielastic neutron scattering data are displayed in Figure 2.3 for liquid HF at 195 K. The difference between the empty cell (light grey) and the cell filled with HF (dark grey) is given in the inset. These residuals, now representing only the scattering from HF, were fit using a jump diffusion model as described above. Although measurements were taken over the entire available Q range, poor statistics only allowed for the data in the range of 0.3 to $1.09 \text{ \AA}^{-1}$ to be properly analyzed. In fact, at the highest temperature, an even more truncated Q range was used. The low- Q data and their fits are shown in Figure 2.4, Figure 2.5, and Figure 2.6 for 195 K, 246 K and 296 K, respectively.

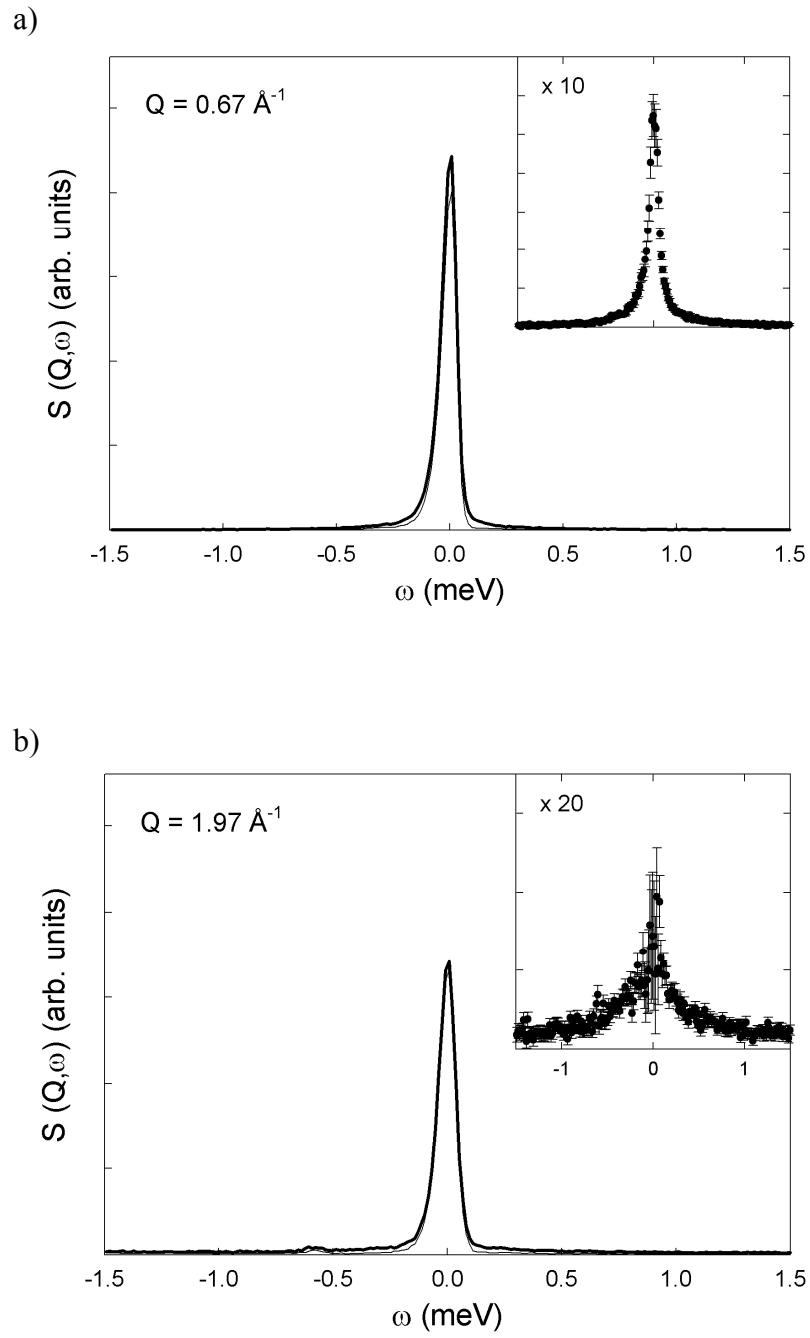


Figure 2.3: HF QENS spectra at 195 K from a) detector bank 3 and b) detector bank 14 showing the intensity due to the empty cell (light line), the cell with HF (dark line), and the difference in the inset scaled by the indicated amount.

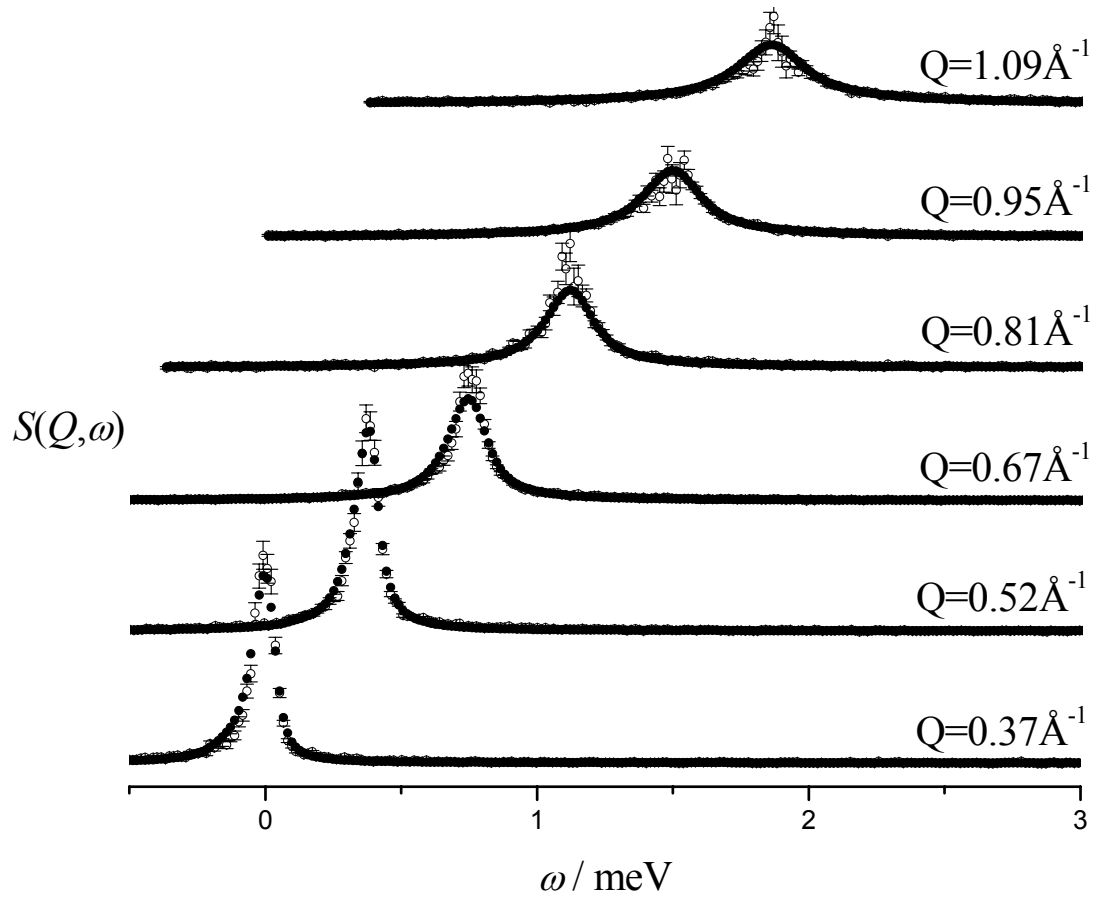


Figure 2.4: The low- Q spectra of $S(Q, \omega)$ vs. ω for HF at 195 K.

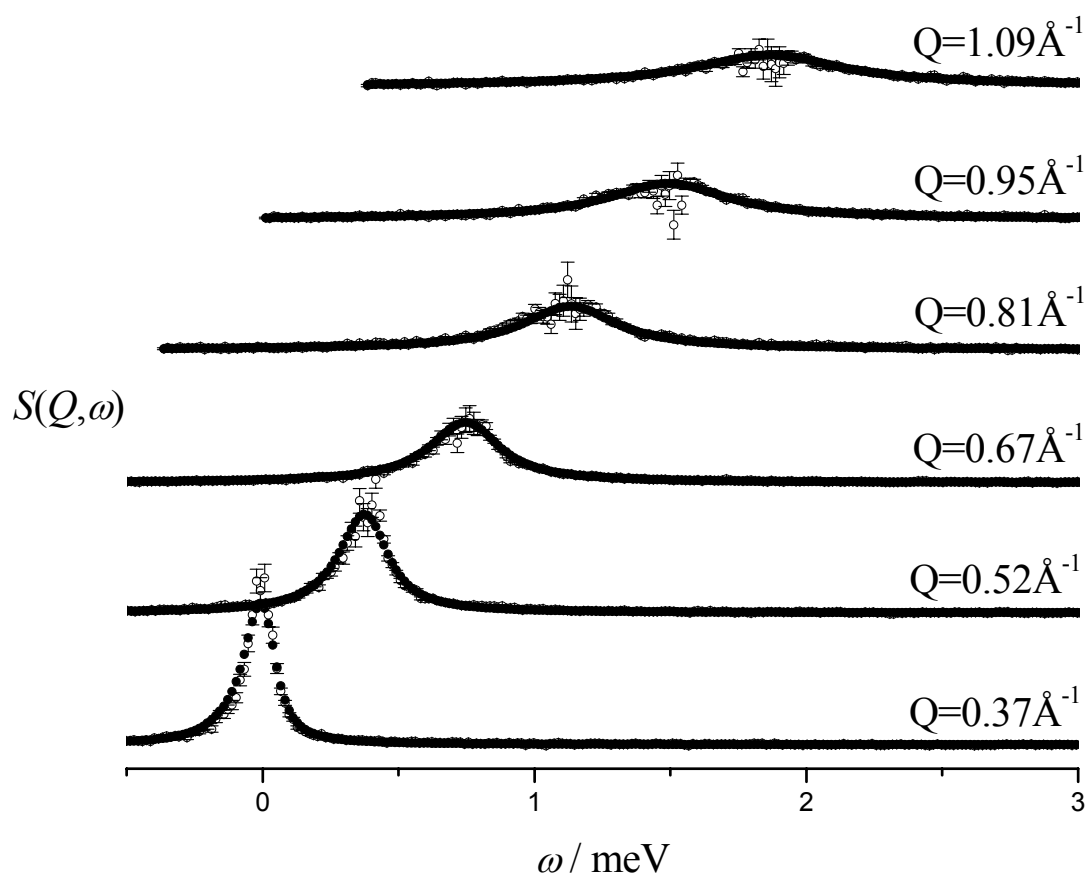


Figure 2.5: The low- Q spectra of $S(Q, \omega)$ vs. ω for HF at 246 K.

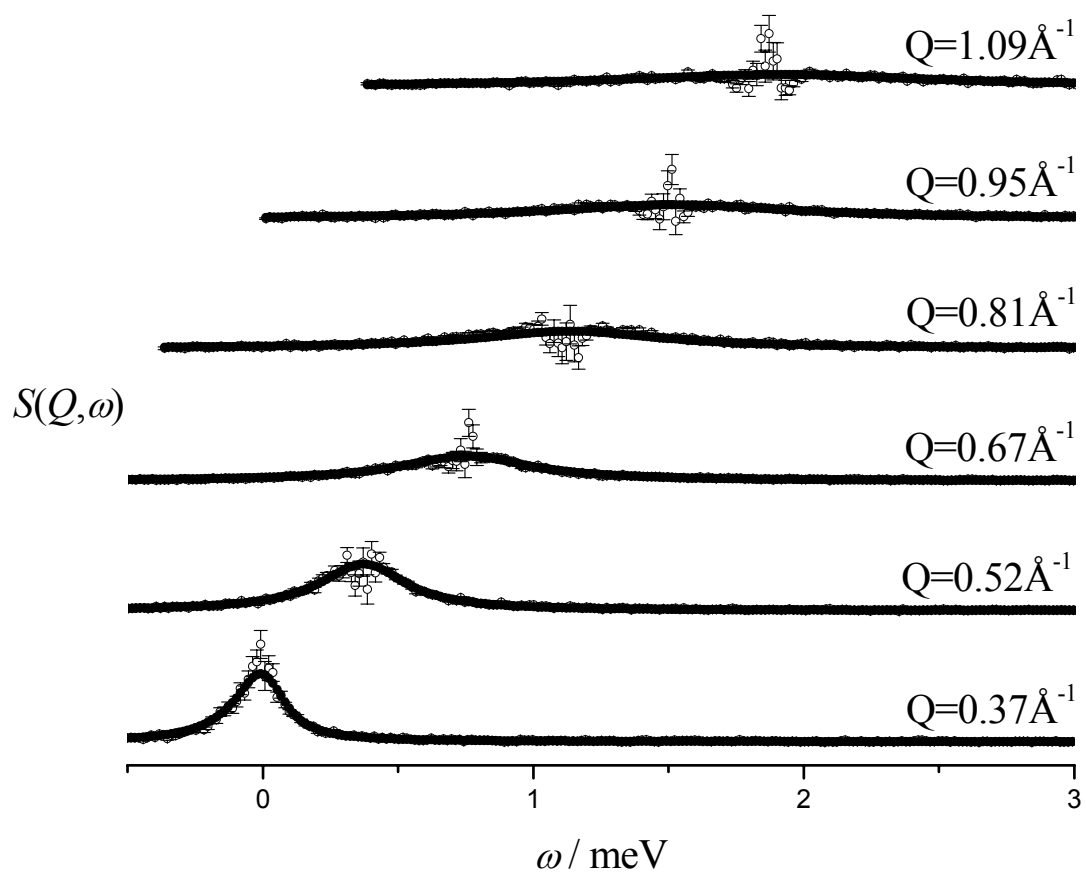


Figure 2.6: The low- Q spectra of $S(Q, \omega)$ vs. ω for HF at 296 K.

The main problem with the data analysis was the subtraction of the Monel sample container. Great lengths were taken to achieve an adequate subtraction (as was described in the previous section), but unfortunately the error in the data points near the elastic line ($\omega = 0$) is quite profuse, especially at higher temperature and higher Q values.

2.3.2 QENS and previous studies

The line width, $\Gamma(Q)$, of each fit was measured and the average diffusion parameters were extracted, the values of which are compiled in Table 2.1. Figure 2.7 shows the temperature dependence of D_t for the present work along with previous NMR measurements on HF,¹⁶⁵ and QENS measurements on water.¹⁷⁶ The NMR measurements were performed using the NMR spin echo technique, which uses a pulsed magnetic field gradient (PFG)^{186,187} to measure particle motions. Figure 2.8 and Figure 2.9 illustrate the temperature dependence of τ_t and L , respectively, for the present work compared with that of previous water measurements.

Table 2.1: Diffusion parameters extracted by fitting the QENS data to a jump diffusion model.

T (K)	D_t ($\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)	τ_t (ps)	D_r (meV)	L (Å)
195±1	2.510±0.120	1.785±0.210	0.231±0.014	1.640±0.104
246±1	5.120±0.205	0.619±0.085	0.305±0.034	1.379±0.099
296±1	9.659±0.356	0.170±0.052	0.226±0.120	0.993±0.154

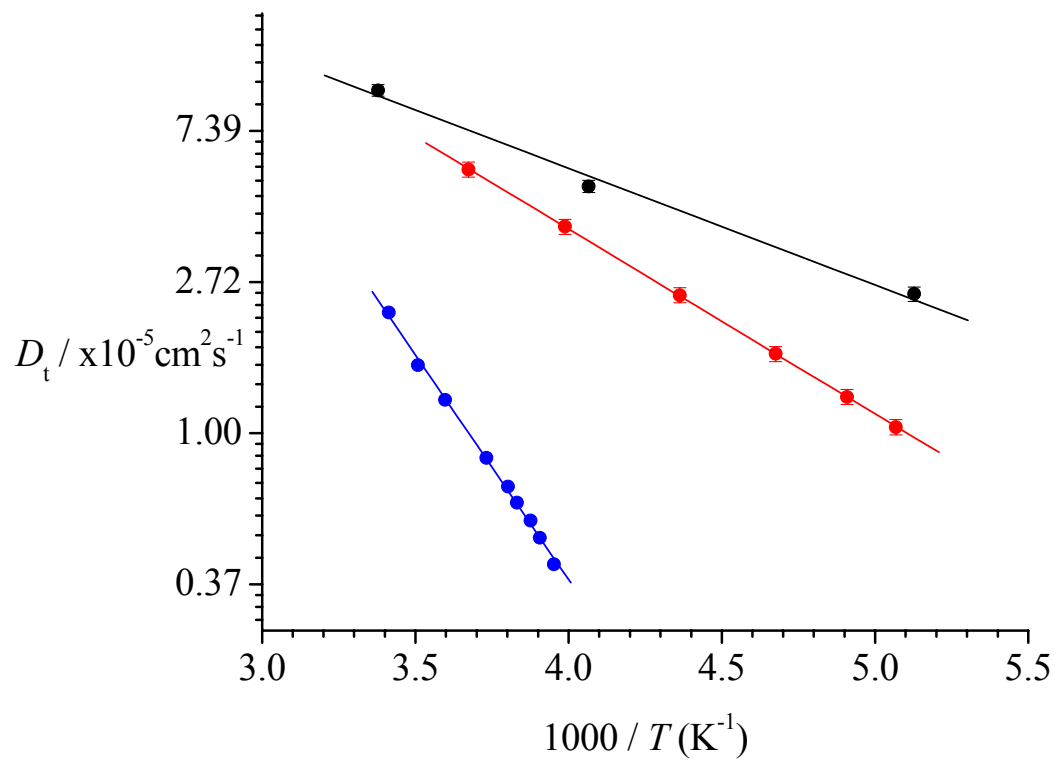


Figure 2.7: D_t vs. $1000/T$ for HF via QENS (black dots) and NMR (red dots), and water via QENS (blue dots). The y-axis is on a natural log scale to show Arrhenius behavior.

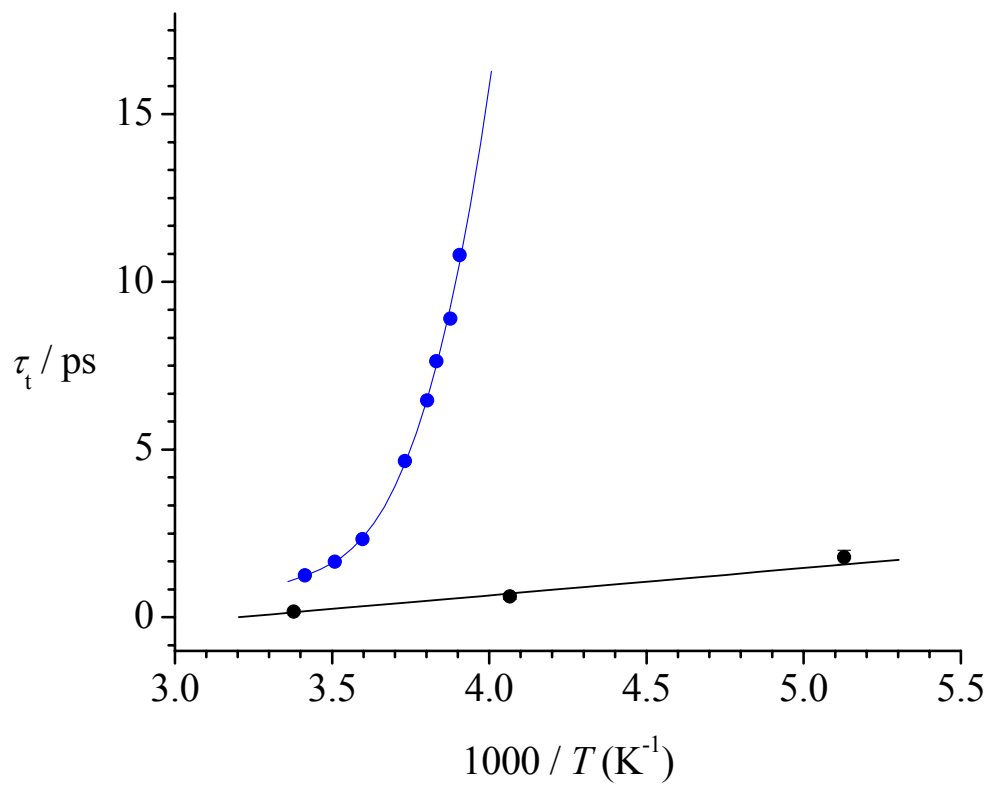


Figure 2.8: τ_t vs. $1000/T$ for HF (black dots) and H_2O (blue dots), both determined using QENS.

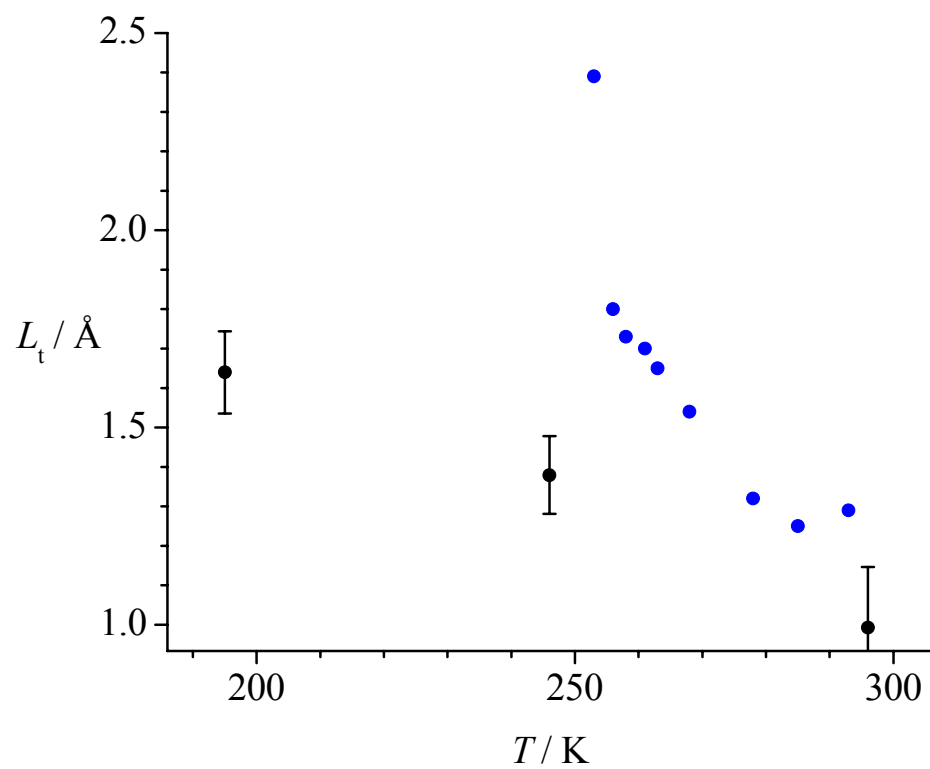


Figure 2.9: L_t vs. T for HF (black dots) and H_2O (blue dots) measured with QENS.

2.4 Discussion

2.4.1 Trends in the data

Upon examination of Figure 2.4, Figure 2.5, and Figure 2.6, two trends are noticed. $\Gamma(Q)$ is highly dependent on, unsurprisingly, Q and temperature. Both dependencies are direct ones; the line width increases with increasing temperature or momentum transfer. This is what is expected according to equation (2.16). Molecular motions slow down at lower temperatures. This implies that any system following a jump diffusion model contains particles that, upon cooling, “jump” less often. In other words, τ_t , the translational residence time or more simply the time between jumps, increases with temperature. $\Gamma(Q)$, being inversely proportional to τ_t , decreases. At high temperatures, τ_t becomes very small, thereby reducing the denominator of equation (2.16) to ~ 1 and $\Gamma(Q) \approx DQ^2$ (Fickian). Under such conditions, the mode of diffusion is indistinguishable from continuous diffusion. Similarly, $\Gamma(Q)$ is directly proportional to Q , so one goes as the other.

Also of note, the quasielastic intensity is highly Q -dependent and goes as

$$\exp\{-\langle u^2 \rangle Q^2 / 3\}, \quad (2.20)$$

which is the Debye-Waller factor from equation (2.12).

2.4.2 QENS vs. NMR

NMR spin echo with a pulsed magnetic gradient (PFG-NMR), mentioned in brief above, was the technique chosen by Karger *et al*¹⁶⁵ to determine the self-diffusion coefficients of anhydrous HF, the results of which are shown in Figure 2.7. A bit more detail is required to adequately compare such measurements with those of a QENS experiment.

The noninvasive nature of NMR makes it a method of choice for characterizing the motions of particles. The spin echo method employs a two-pulse, two-delay method. After the standard 90° pulse and delay time, a second 180° pulse is used to refocus the spins before a second delay equal to the first. The resultant signal is not unlike typical NMR FID, but the second pulse and delay provide a means for obtaining changes in the spatial orientations of molecules. The nuclear spins that are excited by the initial 90° pulse are then realigned to their orientation. The key is that spin echo NMR cannot refocus spins that are in a time varying external field, for example, the nuclear spins of a diffusing particle. Therefore, a measurable attenuation of the signal occurs if diffusion is ongoing.

The introduction of a pulsed magnetic field gradient *via* PFG during both delay periods provides the spin echo signal with spatial information. During the first delay, the first gradient is applied in one direction. This results in a partial dephasing of the nuclear spins. After the second rf pulse, a second gradient of equal magnitude is applied in the opposite direction. If the particle has not translationally diffused, the two fields cancel and the particle's spin is in phase again. If diffusion has occurred, the spin will remain

out of phase. The degree to which the phase has shifted is proportional to the displacement of the particle in the direction of the gradient.

In general, NMR is a bulk probe. Meaning it doesn't give direct evidence of phenomena occurring locally with respect to an atom or molecule. This distinction is important when comparing NMR measurements to quasielastic neutron scattering measurements. QENS is inherently a local probe. The neutron interacts directly with the nucleus. Figure 2.7 compares diffusion coefficients of HF made with QENS and with PFG-NMR. The former are noticeably higher than the latter, which initially caused concern. But some physicists make a logical argument for such discrepancies, citing a difference in time scales, and length scales. There are indeed large differences in both. NMR is useful for measuring on the order of $t > 10^{-4}$ s or greater and QENS on the order of $t < 10^{-8}$ s. NMR provides measurements on the micrometer length scale, whereas QENS instruments generally measure on the order of one to tens of angstroms. This shows the degree to which QENS is a local probe and NMR is a bulk probe. Therefore, NMR measures a sort of composite diffusion coefficient representative of all actions that affect particle diffusion.

Certain promoters of PFG-NMR admit that the time scale of the technique suggests that the measure is not directly comparable to that of other techniques. Oddly enough, there are a great many examples in the literature of QENS agreement with PFG-NMR. Therefore, a difference in results between the two techniques for a given system might imply that there are other modes of diffusion at play. And the converse may hold true as well, meaning that similar results might imply only one mechanism of diffusion is

present. In light of this notion, it is suggested that our elevated D_t measurements are indicative of at least two modes of translation present in HF.

There is one NMR method that measures on a time scale comparable to QENS.^{188,189} By measuring the relaxation on the picosecond time scale, the rotational correlation time, τ_c , can be determined. τ_c can be related to solution viscosity, η , via the Debye equation,

$$\tau_c = 4\pi\eta r_s^3(3kT), \quad (2.21)$$

where r_s is the Stokes hydrodynamic radius and k is Boltzmann's constant. Continuing, the viscosity relates to the coefficient of friction, f , by

$$f = 6\pi\eta r_s. \quad (2.22)$$

Finally, the translational diffusion coefficient can be calculated using the Stokes-Einstein equation,

$$D = \frac{kT}{f} \quad (2.23)$$

Though this method is indirect, it would provide an interesting comparison to this work.

2.4.3 HF vs. H₂O

Low temperature diffusion measurements for water were made by Teixeira *et al*¹⁷⁶. It is from this work that the decoupled rotation and translation model originated. This experiment provides a good comparison for our work, since it is a QENS experiment on a system possessing a substantial hydrogen bond network.

The diffusion coefficients determined in this experiment are plotted along with analogous HF results in Figure 2.7. At initial inspection, it is apparent that diffusion in water is much slower over all temperature ranges. This is to be expected, as the hydrogen bond network formed by water molecules is undoubtedly more extensive than that of HF. The diffusion of water also shows much greater temperature dependence than HF. This also is of no surprise, since it is known that water, upon supercooling, rapidly completes its hydrogen bond network, further decreasing mobility in the liquid.

Figure 2.8 gives the temperature dependence of τ_i for both HF and water. The respective values differ greatly. The residence time of water increases nearly exponentially with decreasing temperature. Analogous HF results, while exhibiting an inverse relationship to T , do so in a dramatically more linear trend.

The mean jump distance, L , for the two liquids are plotted versus T in Figure 2.9. There is very little correlation between the two sets of values, but it is clear that at higher temperatures, the disorder of the hydrogen bond network decreases the average jump length. Again water shows a much stronger dependence, as the mean jump distance rapidly deviates from the standard distance across the tetrahedral angle of the water network, which is 1.6 Å.

The mean jump distance for HF at 195 K was found to be 1.64 ± 0.102 Å. This is in good agreement with a D–F hydrogen bond length of 1.56 Å determined by McLain *et al.*¹⁹⁰ This suggests that translational diffusion is occurring predominantly *via* transport along a chain of hydrogen-bonded molecules. Again, a decrease in this value at higher temperatures indicates decreased order in the hydrogen bond network.

2.5 Conclusions

Although the data presented here have relatively poor statistics and required a great deal of correction, the results are interesting in their comparison with other techniques and species. From the extracted diffusion parameters, it is evident that the hydrogen bond network of HF is far weaker than that of water. Future work on this system should involve NMR measurements *via* picosecond relaxation measurement. This would perhaps provide a better comparison for diffusion measure with QENS.

It is likely that a jump diffusion model is best suited to describe the local translational and rotational diffusive modes. In fact, jump diffusion along a hydrogen bonded chain of HF molecules is likely the dominant mode, as the mean jump distance at 195 K agrees well with the D–F hydrogen bond length determined by neutron diffraction at 195 K.

3 THE STRUCTURE OF LIQUID ANTIMONY PENTAFLUORIDE

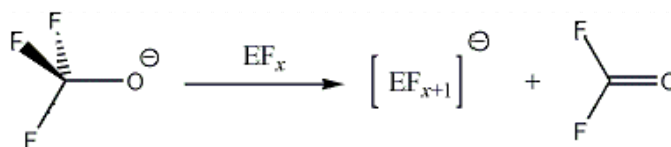
The work discussed in this chapter is published in an article by S. E. McLain, A. K. Soper, J. J. Molaison, C. J. Benmore, M. R. Dolgos, C. J. Benmore, J. L. Yarger, and J. F. C. Turner recently accepted to the *Journal of Molecular Liquids*.

3.1 Introduction

Since the first reported synthesis of antimony pentafluoride by Ruff in 1907¹⁹¹, there has been consistent interest in the chemical, physical, and structural properties of the substance. Interest in SbF₅ is in part due to its archetypal nature as an associated fluid bound by **3** center – **4** electron (3c-4e) interactions and as a strongly associated Lewis acid. SbF₅ is noteworthy for its high Lewis acidity and its ability to act as a fluoride ion acceptor or donor. Antimony pentafluoride is the strongest F[−] acceptor ($pF^- = 12.03$) according to the fluoride ion acceptor scale for Lewis acidity developed by Christie¹⁹². pF^- is defined by

$$pF^- = \frac{\varepsilon\{F^-\}}{10 \text{ kcal mol}^{-1}}, \quad (3.1)$$

where $\varepsilon\{F^-\}$ is the fluoride ion affinity for the Lewis acid referenced to the reaction



having $\varepsilon\{F^-\} = 49.9 \text{ kcal mol}^{-1}$.

The high Lewis acidity of SbF_5 implies that its conjugate Lewis base, SbF_6^- , is very weak. Often SbF_5 is used to abstract an F^- from a fluoride-containing species resulting in a highly electrophilic cation. It is the weak Lewis basicity of SbF_6^- that stabilizes the cation. It is for this reason that SbF_5 has found application in the production of reactive intermediates in organic¹⁹³⁻¹⁹⁷ and inorganic chemistry¹⁹⁸ as well as in other areas.

3.1.1 Previous studies

The structure of SbF_5 in all phase states is dominated by molecular association. In the gas phase at higher temperatures (400 °C), infra-red and Raman spectroscopic measurements indicate a trigonal bipyramidal structure with D_{3h} symmetry. However, electron diffraction data suggests that for the gas phase at lower temperatures, tri- and tetrameric units exist.¹⁹⁹

Antimony pentafluoride in the solid state consists of molecular, tetrameric units formed by corner-sharing octahedra. Its crystal structure, shown in Figure 3.1, is similar to that of NbF_5 and TaF_5 .²⁰⁰

Indirect structural evidence of the pure liquid was first obtained using ^{19}F NMR data at -10°C . The spectra showed three resonances which corresponds to three distinct types of F atoms residing in unique chemical environments.²⁰¹ The authors proposed the semi-infinite *cis*-linked chain structure seen in Figure 3.2, with F_A denoting the bridging fluorines, F_B are mutually *cis* and F_C are mutually *trans*. Note that the extended chain of

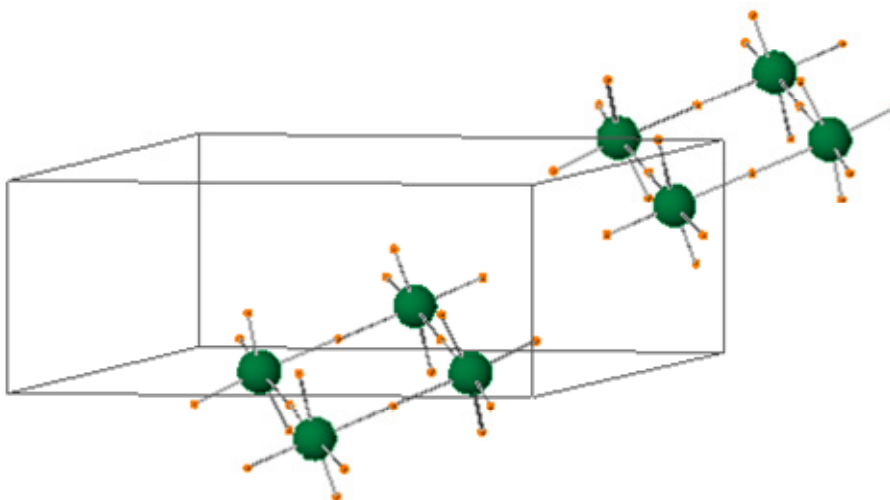


Figure 3.1: Schematic representation of the crystal structure of SbF_5 , with the green spheres being the central Sb atoms and the F atoms shown in orange.

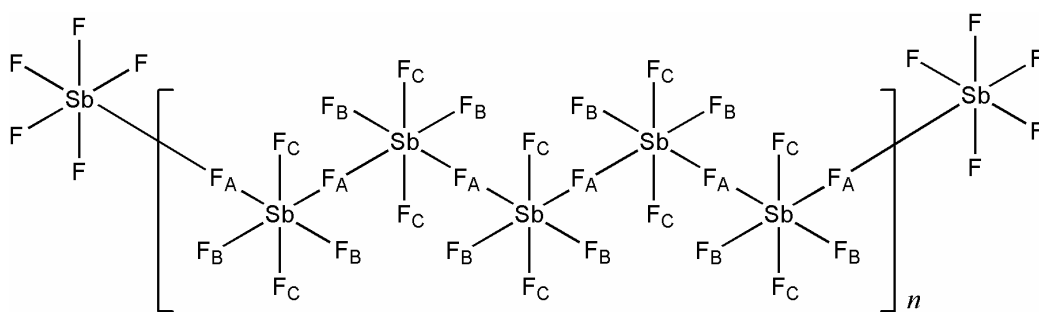


Figure 3.2: The structure of liquid SbF_5 as deduced from ^{19}F NMR data.

pseudooctahedra must be long since no resonances due to the terminal SbF_5 units are observed. Interestingly, one unpublished neutron diffraction experiment suggests the liquid contains cyclic tetramers.²⁰²

The reported density of SbF_5 in the crystalline state is 4.07 g cm^{-3} at 279 K, while the density of the liquid at 281.65 K, just above the melting point, is 3.16 g cm^{-3} .²⁰³ Such a large decrease in density, ~22 %, upon melting is indicative of a marked change in structure.

Surprisingly, theoretical studies of the liquid structure of SbF_5 are virtually nonexistent, with the only study to date being a recent *ab initio* molecular dynamics calculation.²⁰⁴ Here cis-linked chains of up to eight molecules were seen mixed with shorter chains and dimers. Thermochemical calculations have also been performed on SbF_5 .^{192,205-208}

3.1.2 Structure models

As stated in the first chapter, liquids and disordered materials do not have long-range order and structure but rather a local structure influenced by short range repulsive forces, long-range attractive forces and for molecular species, the orientation of the molecules. Diffraction experiments, be they X-ray or neutron, give insight into the local structure of disordered atomic and molecular substances. However, the insight gained is limited in its ability to provide a plausible visualization of the system. The end result of a diffraction measurement of an amorphous material is the pair correlation function. This real space function gives, as a function of distance and direction, weighted averages of

the density of different atom types around other atom types. Hence, a coordination number equal to six extracted from a single peak in $G(r)$ cannot be assumed to necessarily mean that all α atoms are surrounded by exactly six β atoms. The correct assumption is that the *average* number of β atoms around each α atom is six. It is apparent that this could mean some α 's have four or five β 's around them and some have seven or eight, and other combinations can be imagined. In order to know if the average coordination number can be assumed to be the actual number of atoms around another atom, prior information must be included in the analysis.

Empirical Potential Structure Refinement (EPSR) was developed by A. Soper to do what previous analytic techniques could not do for mildly complex systems.²⁰⁹ By incorporating previously determined information into a structural model of the system, EPSR can simulate, *via* standard Monte Carlo methods discussed elsewhere,²¹⁰ the sample material using the newly collected data and the additional information as constraints. EPSR simulations are constrained by including information such as reference potentials, partial atomic charges, and plausible molecular shapes. It is important to note that data modelling is currently not practical for many multi-component systems or systems consisting of large molecular units. However, ongoing efforts are aimed at extending the method to more complex systems.

The EPSR process begins by defining the molecules of the system. Intramolecular distances are defined using harmonic force constants, while intermolecular distances are defined by Lennard-Jones potentials. Ionic charges and partial charges are represented by a pseudo-Coulomb potential that does not give a

complete description of Coulombic interaction at large distances. These potentials combine to form the reference potential, from which an initial configuration of atoms or molecules is produced.

The initial configuration is then perturbed in one of four ways: whole molecule translations, whole molecule rotations, headgroup rotations, and the movement of an atom within a molecule. After a very small change of random magnitude in the position of a random atom or molecule, a decision is made. If the change in the potential energy of the system, $\Delta U = U_f - U_i$, is negative, the move is accepted. If the change is positive, the move is accepted with a certain probability, $\exp\left(-\Delta U/kT\right)$. The latter notion ensures the simulation does not stop after the first move that increases the potential energy; i.e., at a local minimum.

After a number of iterations, simulated diffraction data are extracted from the configuration and compared to the measured data at the $S(Q)$ level. The difference between the experimental data and the simulated data is represented by an empirical potential. When the empirical potential energy is minimized, the simulated data should mimic the measured data accurately. Ultimately a 3-D configuration of atoms or molecules is produced. Since EPSR, like all Monte Carlo methods, is a statistical method, the resulting configuration is the most disordered solution in an array of possible solutions that are compatible with the implemented constraints. This should also be the most probable solution. More information supplied when defining the reference potential results in greater confidence in the final solution.

For further reading on EPSR the literature should be consulted.^{209,211-213}

3.2 Experimental

3.2.1 Sample handling and preparation

Antimony pentafluoride (Aldrich Chemical Co.), a clear, viscous liquid, is quite aggressive and will slowly attack Pyrex glassware unless the liquid is extremely pure and the glassware is excessively dry. All manipulations of SbF_5 were handled under vacuum on a high vacuum line ($p_{\text{min}} < 10^{-4}$ mbar) or under inert atmosphere on a Schlenk line ($p_{\text{min}} < 10^{-2}$ mbar) in standard borosilicate glassware, which was flame dried under vacuum. The purchased liquid was transferred to a Schlenk flask and distilled under vacuum four times. The resulting liquid is much more viscous than the original. The decreased viscosity of the liquid as purchased results from the presence of dissolved HF in the liquid, and although the process described above significantly decreases the HF concentration, to obtain ultra-pure antimony pentafluoride further methods were employed. The quadruply distilled SbF_5 was then fractionally distilled on a glass high vacuum line. This involved the trapping of SbF_5 at 250 K with a CCl_4/N_2 bath and the subsequent trapping of HF and other volatiles at 77 K. Since HF condenses at ~ 293 K, some remains with the SbF_5 . Therefore it was necessary to repeat this process at least four times. The resultant liquid is noticeably more viscous than that obtained from vacuum distillation alone. The purity of the liquid was checked by ^1H NMR, which revealed a resonance due to HF impurity only after ~ 12 hours of data collection. Neutron

diffraction samples were prepared by cryogenic distillation of ~0.75 mL of SbF_5 into quartz tubes (5.0 mm ID x 7.0 mm OD) and flame sealed under vacuum. Samples consisting of ~0.35 mL of SbF_5 in 4.0 mm ID x 5.0 mm OD quartz tubes were prepared in an identical manner for high energy X-ray diffraction experiments.

3.2.2 Neutron diffraction

Neutron diffraction experiments were performed on 0.0110 moles SbF_5 on the Glass Liquid and Amorphous Materials Diffractometer at the Intense Pulsed Neutron Source facility of Argonne National Laboratory (ANL) at 296 K error of ± 2 K. The neutron data have been corrected for detector efficiency, empty cell scattering, attenuation, inelastic scattering, and multiple scattering using standard analysis methods.²¹⁴ In addition separate diffraction experiments were performed on the SiO_2 container at 296 K to ensure correct container normalization and successful container subtraction from the sample data.

3.2.3 High energy X-ray diffraction

High energy X-ray diffraction measurements on 0.005125 moles of SbF_5 were performed on the 11-IDC line at BESSRC-CAT at the Advanced Photon Source facility of ANL at 296 ± 2 K. In addition, a separate experiment was performed on the blank SiO_2 container, again to ensure accurate subtraction. The high energy X-ray data were corrected for detector efficiency, instrumental geometrical effects and polarization using standard analysis procedures.²¹⁵

3.2.4 EPSR

Both the X-ray and neutron diffraction data were modelled using the EPSRshell program.²¹⁶ Three distinct models based on a *cis*-linked polymeric structure were employed before satisfactory fits were achieved. The three models are hereafter called the *cis* monomer model, the tetramer model, and the *cis*-linked chain model. The ensemble for each model consisted of 500 Sb atoms and 2500 F atoms. The density ($\rho = 0.05271$ atoms $\text{\AA}^{-3}$) and temperature (298 K) were likewise identical for each simulation. As discussed in section 3.1.2, a reference potential must be formulated prior to establishing an initial configuration. Calculated Lennard-Jones parameters from methyl fluoride were used for fluorine.²¹⁷ Since similar parameters for antimony could not be found in the literature, the parameters were taken from values calculated for an iodine atom²¹⁸. Charges placed on specific F atoms and interaction sites (labeled as Q) give rise to a Coulombic potential component of the reference potential. Charges are contained within a sphere of radius r_e . Values for the Lennard-Jones parameters are given in Table 3.1 along with the charges and charge radii.

The first model used was the *cis* monomer model with an ensemble of 500 SbF_5 monomers identical to the one pictured in Figure 3.3. The monomer's central atom is shown in black, the uncharged F atoms in white, the charged F atom, F_{ch} , in light grey, and the positively charged interaction site, Q, in dark grey. The Sb–Q bond (grey) is not a bond at all, rather the distance between the central Sb atom and the positive interaction site, where an F_{ch} of another monomer would bind. F_{ch} and Q were assigned charges of -0.5 and $+0.5$, respectively, to allow for intermolecular bonding. Both charges were

Table 3.1 Lennard-Jones parameters, charges and charge radii used for EPSR reference potential.

Atom type	$\sigma / \text{\AA}$	$\varepsilon / \text{kJ mol}^{-1}$	q / e	$r_e / \text{\AA}$
Sb	4.989	0.41840	0.0	0.0
F	2.94	0.25522	0.0	0.0
F _{ch}	2.94	0.25522	-0.5	0.1
Q	0.0	0.0	+0.5	0.1

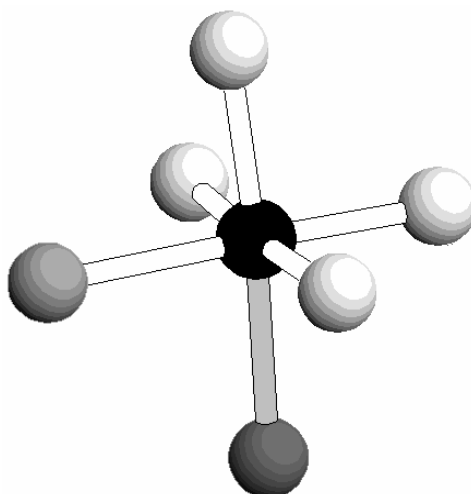


Figure 3.3: Representative ensemble unit used in the cis monomer model.

contained in a sphere of radius 0.1 Å. The Sb–Q and Sb–F_{ch} distances were set at 2.03 Å and the Sb–F distances were given a value of 1.86 Å.

The next simulations were performed using a tetramer model similar to the molecular units present in crystalline SbF₅. Again 500 SbF₅ molecules or 125 tetramer units were used for the ensemble. A representation of the tetramer is shown in Figure 3.4. Again the white spheres represent non-bridging F atoms, the central Sb atoms are in black, and the bridging fluorines are in light grey. The intramolecular distances used in the *cis* monomer model were used here. Additional constraints taken from the crystal structure were also introduced. The four Sb–F–Sb angles were assigned values of 170° and 141°, with two identical angles being opposite one another. Also, intermolecular Sb–Sb distances of 3.96 Å, 3.75 Å, and 5.55 Å were included. The first of these values is the distance between two Sb atoms of the 170° Sb–F–Sb bridge. The second value corresponds to the distance between two Sb atoms of the 141° Sb–F–Sb bridge. The last distance is that which spans between two corners of the tetramer. A scheme of the additional constraints used for the tetramer model is exhibited in Figure 3.5.

The last fits were achieved *via* the *cis*-linked chain model. The model employed an ensemble consisting of units formed from four *cis*-linked SbF₅ molecules (Figure 3.6). Each unit has an additional F_{ch} (light grey sphere with a white bond) attached to one terminal Sb and a Q site (dark grey sphere with a grey bond) attached to the other terminal Sb. The charged sites allow the acyclic tetramers to attach and form longer chains. The intramolecular bond lengths are identical to those of the *cis* monomer model.

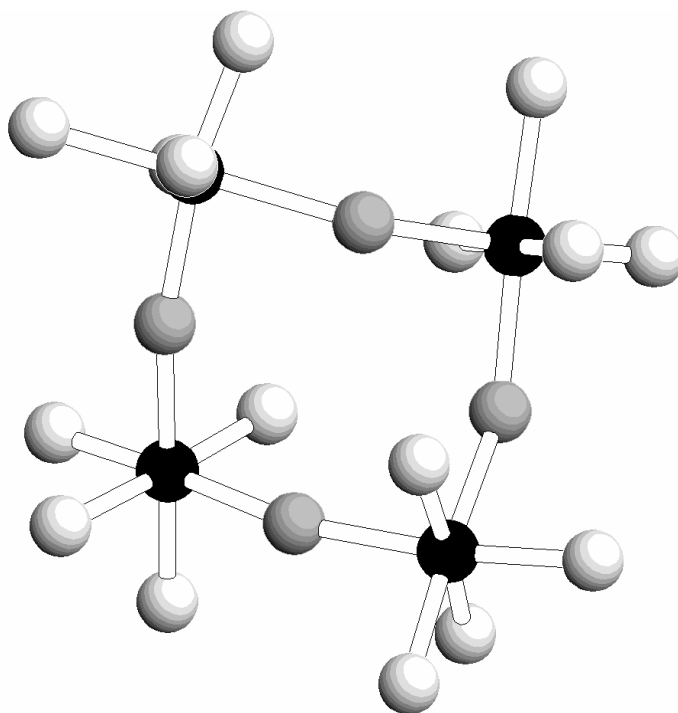


Figure 3.4: Representation of the units constructed for the tetramer model.

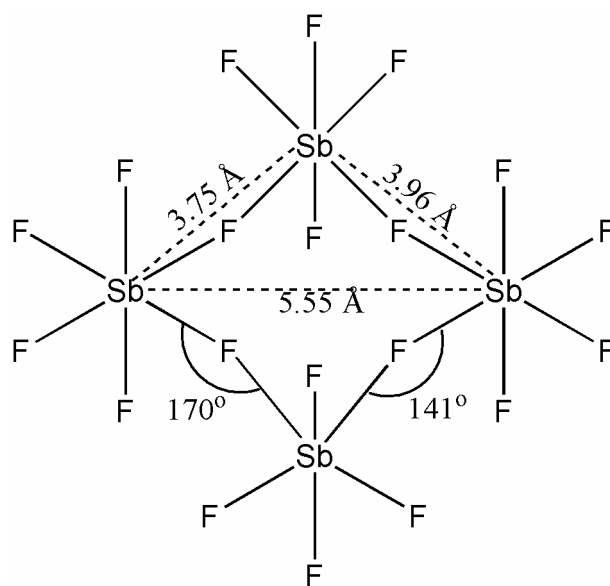


Figure 3.5: Schematic representation of additional constraints used for the tetramer model.

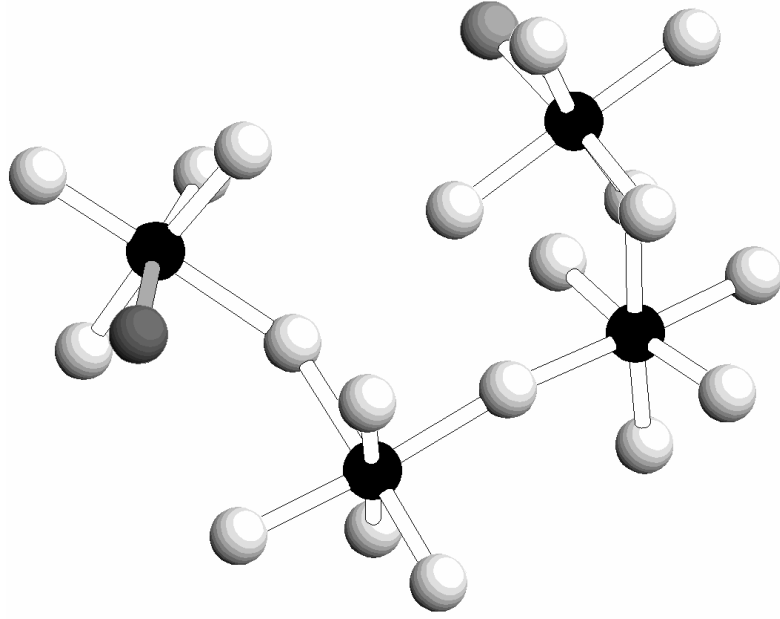


Figure 3.6: Representation of the acyclic tetrameric unit used in the cis-linked chain model.

3.3 Results

3.3.1 Neutron Diffraction

The measured neutron diffraction data, $S_{\text{SbF}_5}^{\text{N}}(Q)$, are given in Figure 3.7 at 296 K and are expressed in terms of the sum of the weighted partial structure factors by

$$\begin{aligned} S_{\text{SbF}_5}^{\text{N}}(Q) &= c_{\text{F}}^2 b_{\text{F}}^2 S_{\text{FF}}(Q) + 2c_{\text{F}} c_{\text{Sb}} b_{\text{F}} b_{\text{Sb}} S_{\text{SbF}}(Q) + c_{\text{Sb}}^2 b_{\text{Sb}}^2 S_{\text{SbSb}}(Q) \\ &= 0.698 S_{\text{FF}}(Q) + 0.276 S_{\text{SbF}}(Q) + 0.027 S_{\text{SbSb}}(Q). \end{aligned} \quad (3.2)$$

Since the total neutron structure factor is largely influenced by the light atom component, mostly the F–F partial structure factor but also the Sb–F component, neutron diffraction

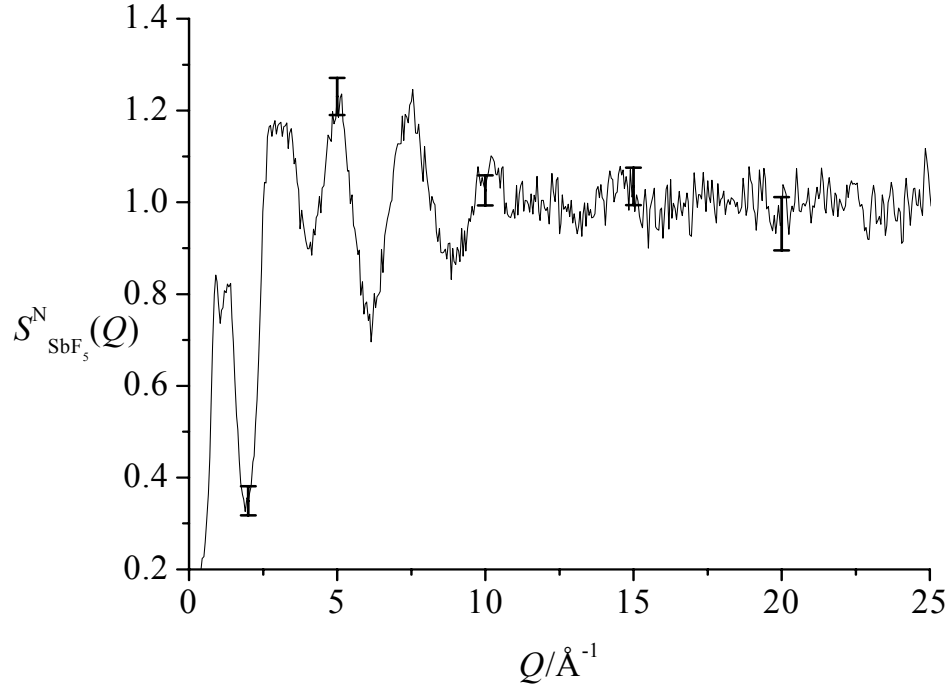


Figure 3.7: Total neutron structure factor for SbF_5 at 296 K with representative error bars at 2, 5, 10, 15, and 20 $\text{\AA}^{-1}$.

is the method of choice for determining these correlations. The corresponding pair correlation function, $G^N_{\text{SbF}_5}(r)$, is presented in Figure 3.8 at 296 K.

3.3.2 High energy X-Ray diffraction

The measured X-ray total structure factor for SbF_5 at 296 K, $S^X_{\text{SbF}_5}(Q)$, is displayed in Figure 3.9. The X-ray total structure factor can be expressed as the sum of the weighted partial structure factors by

$$\begin{aligned} S^X_{\text{SbF}_5}(Q) &= c_F^2 f_F^2 S_{\text{FF}}(Q) + 2 c_F c_{\text{Sb}} f_F f_{\text{Sb}} S_{\text{SbF}}(Q) + c_{\text{Sb}}^2 f_{\text{Sb}}^2 S_{\text{SbSb}}(Q) \\ &= 0.282 S_{\text{FF}}(Q) + 0.498 S_{\text{SbF}}(Q) + 0.220 S_{\text{SbSb}}(Q). \end{aligned} \quad (3.3)$$

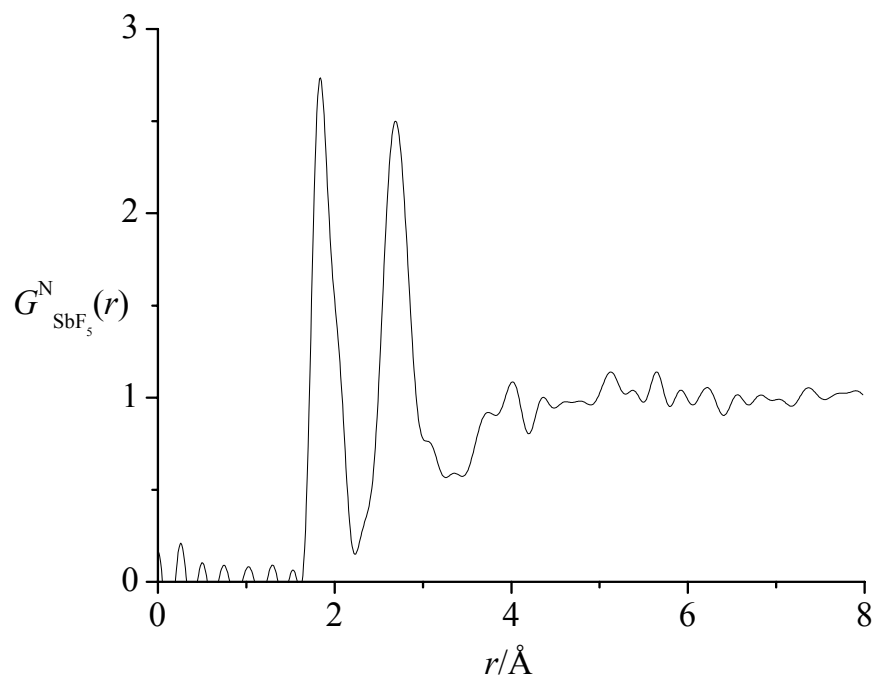


Figure 3.8: Total neutron pair correlation function for SbF_5 at 296 K.

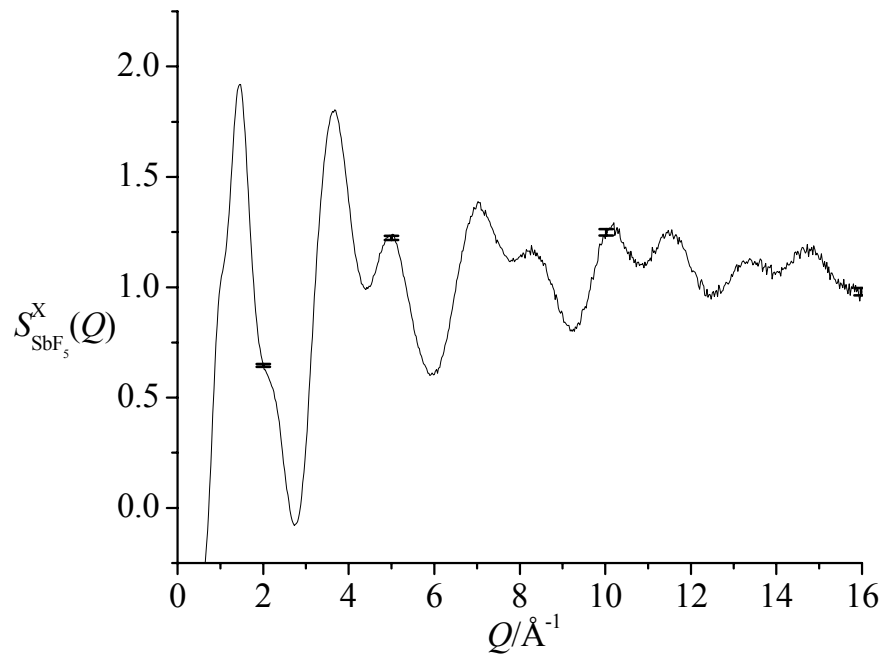


Figure 3.9: Total X-ray scattering function of SbF_5 at 296 K with representative error bars at 2, 5, 10, and 15 $\text{\AA}^{-1}$.

Its real-space counterpart, $G_{\text{SbF}_3}^{\text{X}}(r)$, is shown in Figure 3.10. The electronic form factors, f , at $Q = 0 \text{ \AA}^{-1}$, which are equal to the number of electrons in the atom, are used to determine the weighting factors. The rather large difference in the weighting of the Sb–Sb and Sb–F contributions is evident *via* comparison of equations (3.2) and (3.3). For this reason, X-ray diffraction is unsuitable for the determination of light atom positions in the present case.

3.4 Discussion

3.4.1 Pair correlation functions

In $G_{\text{SbF}_3}^{\text{N}}(r)$, Figure 3.8, the first peak at $r_{\text{SbF}} = 1.86 \pm 0.03 \text{ \AA}$ corresponds to the Sb–F intramolecular distance. In the X-ray analogue, $G_{\text{SbF}_3}^{\text{X}}(r)$, shown in Figure 3.10, the position of the first peak is at $r_{\text{SbF}} = 1.83 \pm 0.03 \text{ \AA}$. In either function, this peak is asymmetric, having a shoulder on its right side. This is evidence for the presence of a slightly longer Sb–F bond, which is expected since in any structural model other than one consisting of just monomers, the bridging fluorines would be farther away from either adjoining antimony atom. The shoulder is less pronounced in the X-ray version, no doubt due to the relative light atom insensitivity of X-ray diffraction. In $G_{\text{SbF}_3}^{\text{N}}(r)$, the shoulder lies at approximately $r_{\text{SbF}} = 2.03 \pm 0.03 \text{ \AA}$. Both of the Sb–F distances are comparable to the corresponding average bond lengths of $1.82 \text{ \AA}$ and $2.02 \text{ \AA}$ in the crystalline state.²⁰⁰

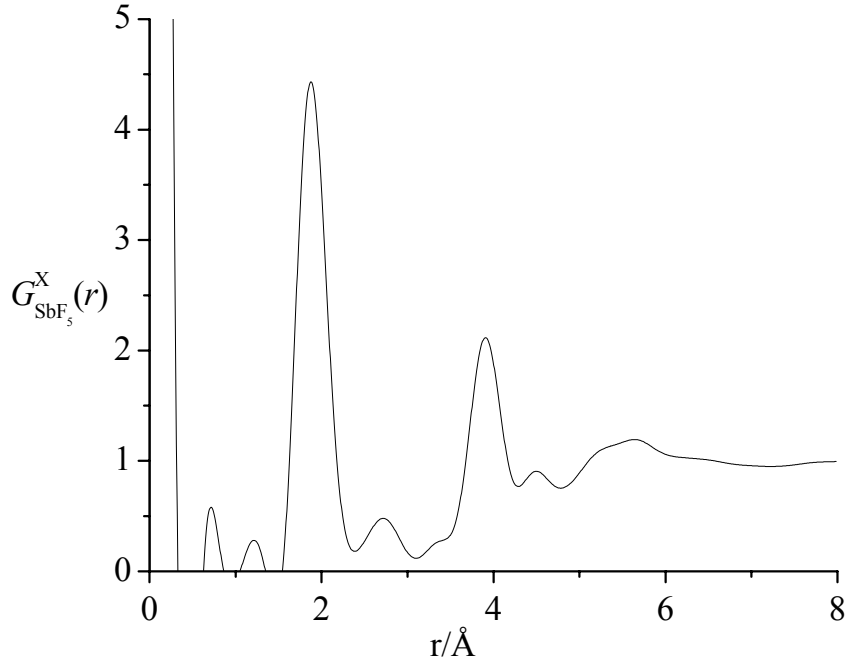


Figure 3.10: X-ray total pair correlation function for SbF_5 at 296 K.

In $G_{\text{SbF}_5}^{\text{N}}(r)$ and $G_{\text{SbF}_5}^{\text{X}}(r)$, the second peak lies at $r_{\text{FF}} = 2.70 \pm 0.05 \text{ \AA}$ and $r_{\text{FF}} = 2.72 \pm 0.05 \text{ \AA}$, respectively. The peak is much smaller in the Fourier transform of the X-ray data, since the F–F contribution to the X-ray scattering function is 60 % less than that of the neutron analogue. This distance is about what would be expected if every Sb is octahedrally coordinated by six F atoms. Indeed, the average F–Sb–F angle, $\theta_{\text{FSbF}} = 93.7 \pm 0.8^\circ$, calculated from the above distances is indicative of octahedral coordination. An average F–Sb–F angle of 100° would be expected if the liquid primarily consisted of trigonal bipyramidal monomers.

Upon further comparison of $G_{\text{SbF}_5}^{\text{N}}(r)$ and $G_{\text{SbF}_5}^{\text{X}}(r)$, a peak at $3.93 \pm 0.3 \text{ \AA}$ is noticed in the latter that is absent in the former. This peak corresponds to an Sb–Sb

distance, and should be attributed as such since it is only present in the X-ray pair correlation function whose Sb–Sb contribution is nearly 10 times greater than that of its neutron counterpart.

3.4.2 Coordination number analysis

Running coordination numbers were taken for the first and second peaks in $G_{\text{SbF}_5}^{\text{N}}(r)$. A coordination number for the first peak ($r_{\text{SbF}} = 1.86 \pm 0.03 \text{ \AA}$) of $C_{\text{Sb}}^{\text{F}} = 6.34 \pm 0.14$ (i.e., on average there are ~ 6.34 nearest neighbor F atoms around every Sb atom) further evinces the likely octahedral coordination around each Sb atom. Likewise, the coordination can be expressed in terms of the number of Sb atoms around each F atom, in which case the coordination number is $C_{\text{F}}^{\text{Sb}} = 1.27 \pm 0.03$. This is consistent with the expected F coordination in most polymeric structural models that require only one bridging fluorine per molecular unit. For example, in the tetrameric units found in crystalline SbF_5 (Figure 3.1), or the semi-infinite *cis*-bridged chain structure (Figure 3.2) based on NMR data, $\frac{1}{5}$ of the F atoms in an SbF_5 unit is bonded to two Sb atoms, while $\frac{4}{5}$ of the F atoms are bonded to only one Sb atom. Thus, the average number of nearest neighbor Sb atoms around each F atom is 1.20.

The second peak at $r_{\text{FF}} = 2.70 \pm 0.05 \text{ \AA}$ represents the shortest intramolecular F–F distance, namely the distance between two F atoms *cis* to each other. Based on simple geometrical analysis of the tetramer and extended chain structures, $\frac{1}{5}$ of the F atoms in an SbF_5 molecule is this distance from eight other F atoms and $\frac{4}{5}$ are this distance from

four other F atoms. This gives an average of 4.8 F atoms around every F atom.

However, the coordination number for this peak is actually $C_F^F = 5.58 \pm 0.38$; quite the discrepancy, for which there is currently no explanation.

3.4.3 EPSR fits

The EPSR fits to the neutron and X-ray diffraction data and the fits to the corresponding pair distribution functions are shown in Figure 3.11 for the *cis* monomer model. The fit to the neutron data is reasonable, but the model doesn't fit the X-ray data very well. Upon observation of the X-ray real-space fit, it is obvious that the model can't reproduce the pronounced peak at 3.93 Å. Therefore, the *cis* monomer model is unable to account for the corresponding Sb–Sb correlation. In the final configuration, chains of up to five molecules in length were observed, but the sufficient constraints were not implemented to allow for the formation of longer chains. Given sufficient computational time, this model probably would reproduce the diffraction data rather well. However, this would take an unreasonable amount of time for a system as complex as this.

The tetramer model proved to be more successful in fitting the data than the *cis* monomer model. This fact is clearly illustrated in Figure 3.12 for the data sets and their Fourier transforms. With the exception of some discrepancy in the amplitude of the $S(Q)$ oscillations, the model replicates the measured data nicely. The Fourier transforms of the fits account for most of the correlations seen in the experimental $G(r)$ functions, though not with exact peak heights. Notice for the X-ray pair distribution function the

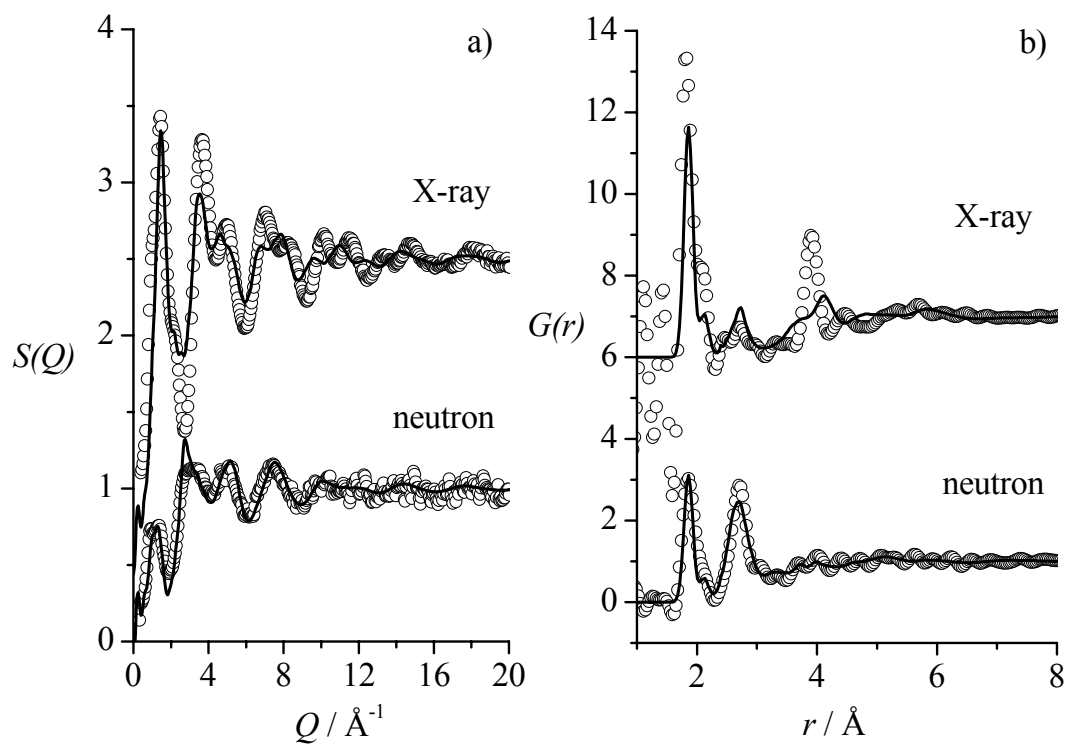


Figure 3.11: EPSR fits (solid line) produced by the cis monomer model and experimental functions (circles) for a) $S_{\text{SbF}_5}^N(Q)$ and $S_{\text{SbF}_5}^X(Q) + 1.5$ and b) $G_{\text{SbF}_5}^N(r)$ and $G_{\text{SbF}_5}^X(r) + 6.0$.

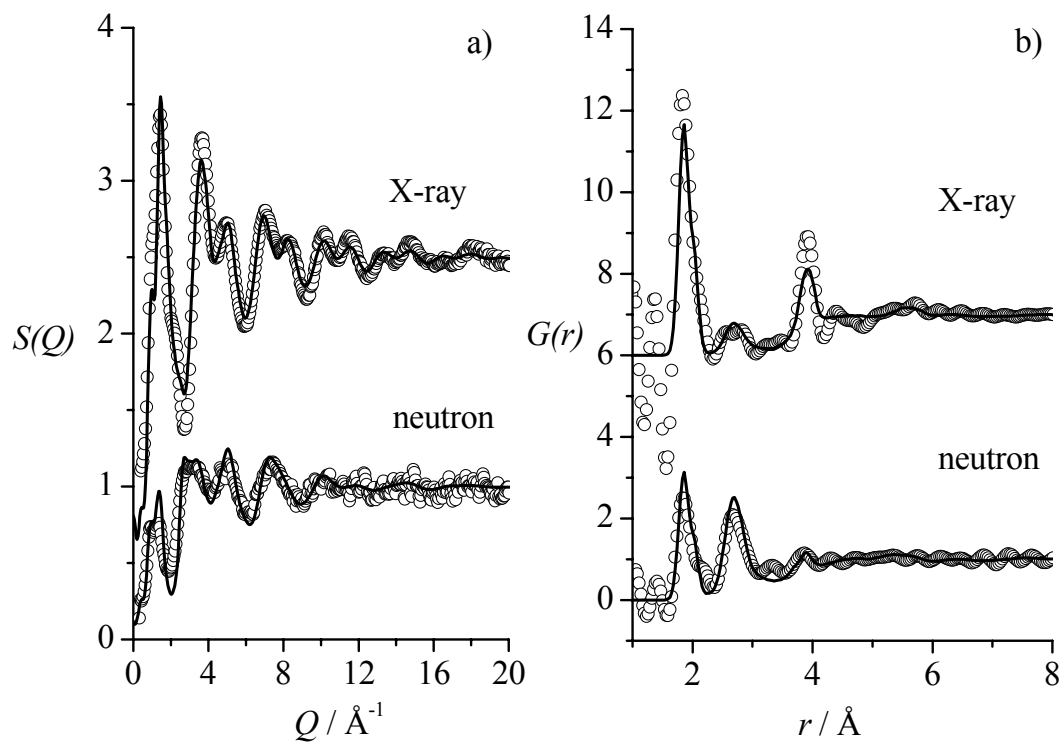


Figure 3.12: EPSR fits (solid line) produced by the tetramer model and experimental functions (circles) for a) $S_{\text{SbF}_5}^N(Q)$ and $S_{\text{SbF}_5}^X(Q) + 1.5$ and b) $G_{\text{SbF}_5}^N(r)$ and $G_{\text{SbF}_5}^X(r) + 6.0$.

Sb–Sb correlation peak at 3.93 Å that was absent from the *cis* monomer fit is now accounted for, but again with less than ideal peak height, a measure of the influence of the additional constraints used in this model. Overall, the tetramer simulations provide good fits to the data and represent the important correlations seen in the radial distribution functions. However, a liquid consisting of cyclic tetrameric units is not consistent with previous NMR data. In the ^{19}F NMR data collected by Hoffman *et al.*,²⁰¹ three resonances are observed at $\sim -10^\circ$, which indicates the presence of three chemically different types of F atoms. However, measurements at room temperature show a significant loss of detail; specifically the three resonances become much broader and begin to converge to a single resonance. It is believed that if the structure was the constrained cyclic tetramer, the fluorine atoms would retain their chemical uniqueness even at room temperature. Thus, three well resolved peaks would be observed in the ^{19}F NMR spectrum. This is not the case for an acyclic chain structure at higher temperatures, where free rotation about the Sb–F–Sb bridge promotes the exchange of the F atoms. Also, the sizeable change in the density of SbF_5 seen upon melting, would suggest a significant structural rearrangement occurs. Therefore, it is unlikely that cyclic tetramers comprise the majority of the liquid and crystalline phases.

The *cis*-linked chain model was employed to obtain accurate fits to the data with a model unlike what is seen in the crystal structure, while preserving agreement between the model and the NMR data. The fits to the X-ray and neutron data and pair correlation functions (Figure 3.13) very much resemble those produced by the tetramer model (Figure 3.12). In fact, much scrutiny is required to find differences at all. The fit

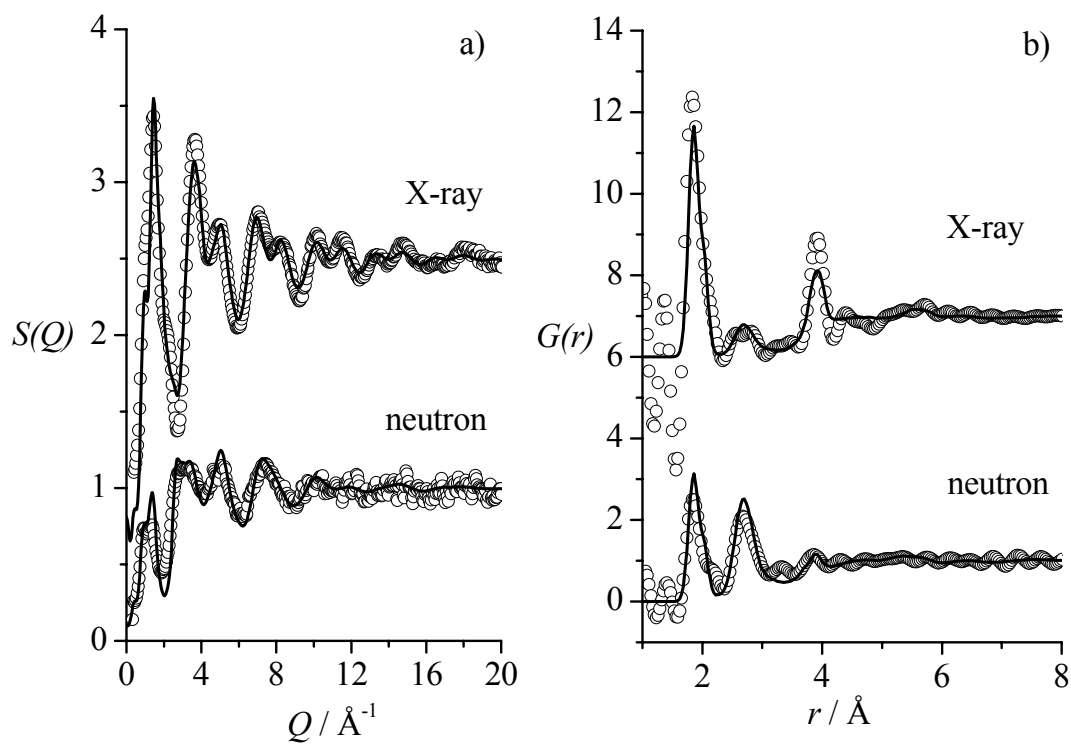


Figure 3.13: EPSR fits (solid line) produced by the cis-linked chain model and experimental functions (circles) for a) $S_{\text{SbF}_5}^N(Q)$ and $S_{\text{SbF}_5}^X(Q) + 1.5$ and b) $G_{\text{SbF}_5}^N(r)$ and $G_{\text{SbF}_5}^X(r) + 6.0$.

accuracy of the *cis*-linked chain model is then equal to that of the tetramer model. Since the additional Sb–Sb distances used in the tetramer model were also used to constrain this model, similarities in the resulting fits of both models were expected.

In the final configuration, no chains of more than eight molecules were present, which is consistent with the lone structure calculation performed on the liquid.²⁰⁴ A typical molecule seen in the final configuration is shown in Figure 3.14. An average Sb–F–Sb angle of 150.9° was extracted from the final configuration, while the same angle in the crystal structure has an average of 155.5°.

3.5 Conclusions

The viscous nature of SbF₅ implies that the liquid structure is polymeric and thus possesses a high degree of order. This is corroborated by neutron diffraction measurements, which show that on average each antimony atom is surrounded by more than five fluorine atoms (~ 6.34 F atoms to be specific). This study also shows that neutron data alone are insufficient for a complete description of the local structure. In fact, a significant Sb–Sb correlation ($r_{\text{SbSb}} = 3.93 \text{ \AA}$) is only seen in the X-ray pair distribution function. Also, inclusion of additional Sb–Sb distances in the initial configuration of EPSR models is needed to reproduce that peak. Both the tetramer and the *cis*-linked chain models are consistent with the diffraction data, though the former does not agree with NMR data and is not consistent with an assumed structural change from the crystalline state to the liquid phase. The *cis*-linked chain model produces open

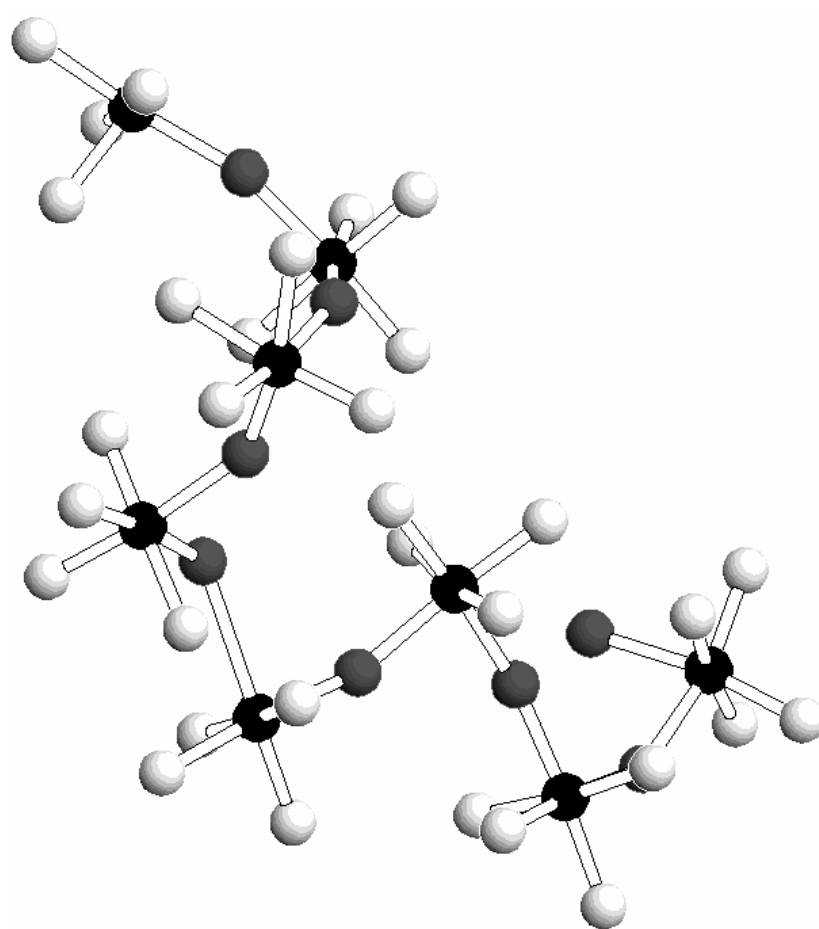


Figure 3.14: Representative SbF_5 chain from the final configuration of the cis-linked chain model.

chains of up to 8 SbF_5 molecules, which is consistent with the only existing structure calculation.

4 STRUCTURAL STUDIES OF AMMONIA IN FLUOROSULFURIC ACID

4.1 Introduction

4.1.1 Structural studies of solutes

The determination of liquid structures is important to many branches of chemistry, biology and physics. Much effort has been made to determine the molecular and hydrogen bonding structures of biological molecules, such as proteins and amino acids, in aqueous solution. Small molecule structure determination in aqueous and nonaqueous solution is also the subject of frequent study. However, only recently have researchers become interested in structures of solutes in superacids.

Superacids have been used for decades in the fields of hydrocarbon management and as reagents in organic synthesis.^{123,124,219-233} The application of superacid chemistry has recently been extended to inorganic synthesis, specifically in the production of compounds with high-valent, electron-poor metal centers.²³⁴⁻²³⁷ Despite their widespread application, there is very little structural evidence of superacids and superacidic solutions. The few direct structural studies of superacidic systems have mostly been *via* solid state X-ray diffraction.²³⁸⁻²⁴⁴ To date, only four liquid structure determinations of superacids have been published. They include three structure factor determinations of anhydrous deuterium fluoride and one of fluorosulfuric acid. Total structure factors were achieved in two of DF studies^{149,153}, with the third taking advantage of Neutron Diffraction with Isotopic Substitution (NDIS) to give the partial structure factors as well.¹⁴⁶ The study of FSO₃H also used NDIS to elucidate the structure factor due to only the hydrogen

correlations, $S_{\text{HX}}(Q)$, and another, which involved only the non-hydrogen or heavy atom correlations, $S_{\text{XX}}(Q)$.²⁴⁵

There has been only one neutron diffraction measurement of a solute dissolved in a superacid. NDIS performed on a solution of 10% H₂O in FSO₃H was used to determine the structure of the hydronium ion in fluorosulfuric acid.²⁴⁶ It was previously thought that the formation of H₄O²⁺ was energetically favorable.²⁴⁷ However, the results indicated no appreciable concentration of the doubly protonated species. These measurements suggest a possible hydrogen bond between H₃O⁺ and FSO₃H solvent molecules, the existence of which may indicate a deprotonation/protonation mechanism for the formation of the hydronium ion. The proposed mechanism, which may involve a transition state, is shown in Figure 4.1.

4.1.2 The solid state structure of ammonium fluorosulfate

Crystalline ammonium fluorosulfate can be prepared by the reaction of ammonium chloride and fluorosulfuric acid, that is



O'Sullivan *et al* determined its structure by X-ray crystallography in 1970.²⁴⁸ A view of the structure along the *b* axis is shown in Figure 4.2. It crystallizes in the P_{nma} space group, and the fluorosulfate sublattice is observed to be only partially ordered. This is unlike potassium fluorosulfate, which is completely disordered. Evidence suggests that and an oxygen atom on the anion. As a consequence of the disorder, the structure was

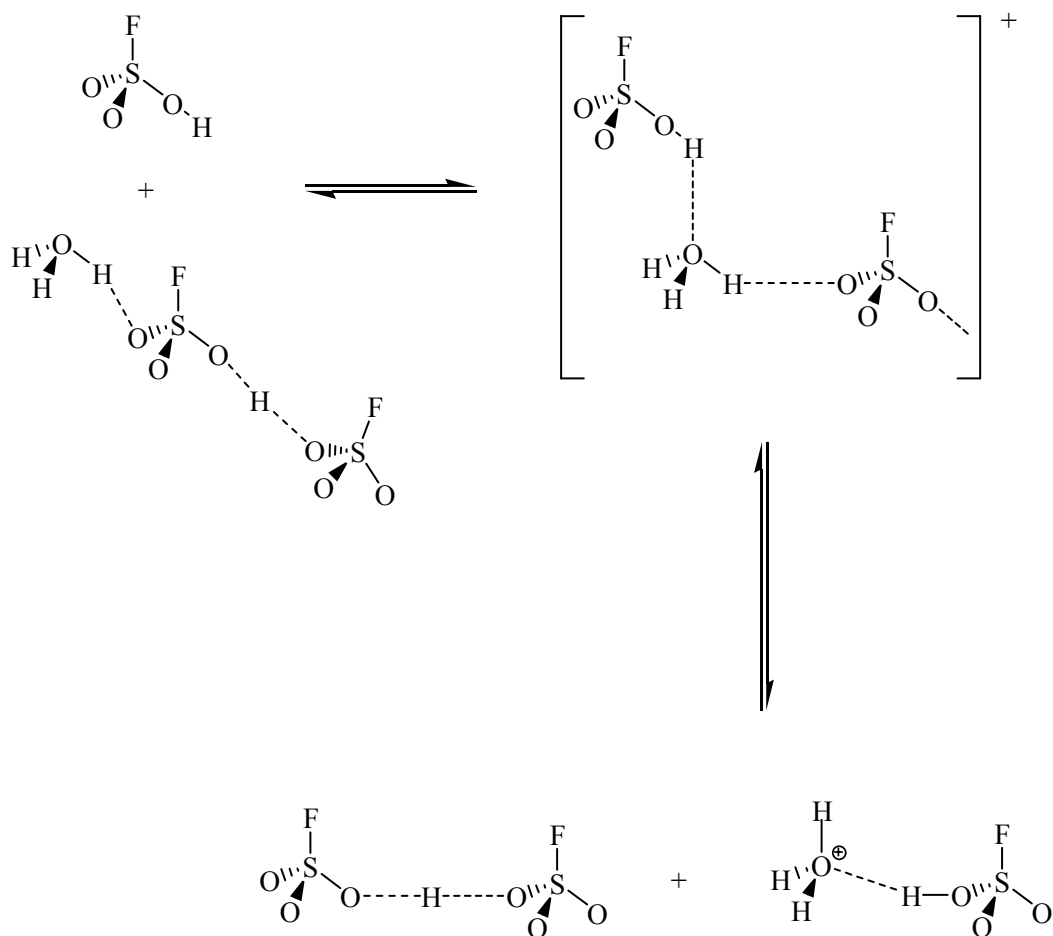


Figure 4.1: Proposed mechanism for the protonation of water by fluorosulfuric acid.

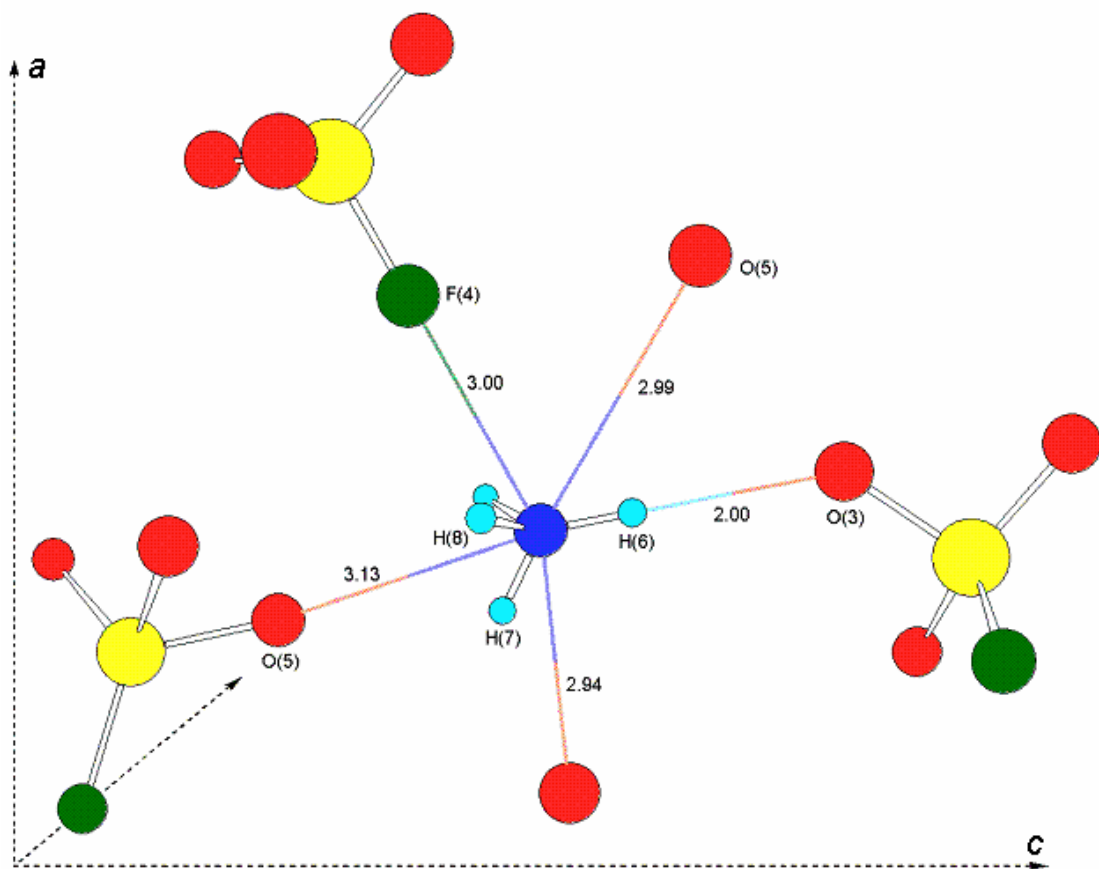
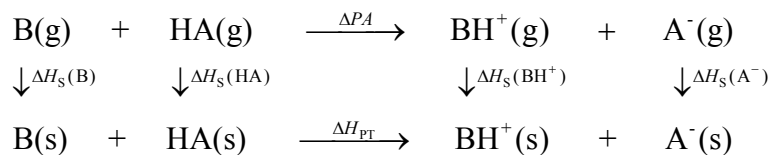


Figure 4.2: The crystal structure of ammonium fluorosulfate as determined by X-ray crystallography. The view is along the *b* axis.

refined twice—once with atom 4 being O and once as F. The observed distances and angles are given in Table 4.1.

4.1.3 Proton transfer between ammonia and fluorosulfuric acid

The nature of a basic solute in acidic solution is greatly determined by the type and degree of solvation present. Solvation effects are responsible for discrepancies between analogous gas and solution phase reactions. The likelihood of proton transfer in acid-base reactions can be quantitatively described by standard thermodynamic properties. A relationship between the reaction in the gas phase and that in solution is established by taking advantage of Hess' law. The spontaneity of gas phase proton transfer between a neutral base and a neutral acid is evaluated by the difference in the proton affinity (PA) values of the base, B , and the product anion, A^- . Spontaneity of the same reaction in solution is determined by examining the change in free energy for the proton transfer reaction. The free energy is dominated, in this case, by ΔH_{PT} , which is related to ΔPA by the scheme shown below.



ΔH_S is the heat of solvation for each species.

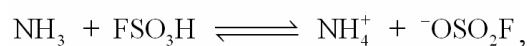
A positive ΔH_{PT} value implies that the proton is not exchanged and the covalent X-H bond of the acid remains intact. In such a case, the solute most likely forms a

Table 4.1: Atomic distances ($\text{\AA}$) and angles ($^\circ$) obtained from the partially disordered ammonium fluorosulfate structure. Values are given both from the refinement with F at position four, and with O at the position.

Parameter	Atom 4 refined as O	Atom 4 refined as F
S–F(4)	1.513	1.502
S–O(3)	1.467	1.476
S–O(5)	1.443	1.443
N–H(6)	1.00	1.00
H(6)⋯O(3)	2.00	2.00
N⋯O(3)	2.96	2.96
O(3)–S–F(4)	106.1	106.1
O(5)–S–F(4)	107.8	108.1
O(5)–S–O(3)	110.8	110.5
O(5)–S–O(5')	113.3	113.2
N–H(6)⋯O(3)	3.0	3.0

hydrogen bond with the acidic proton on the neutral acid, resulting in a lengthening of the X–H covalent bond. Reactions which have negative ΔH_{PT} values are exothermic and full proton transfer occurs. The species in solution are now BH^+ and A^- , for which there are likely a number of possible solvated environments.

The gas phase proton transfer enthalpy for the reaction between ammonia and fluorosulfuric acid,



was calculated from

$$\Delta H_{\text{PT}}(g) = \Delta PA = PA_{\text{FSO}_3^-} - PA_{\text{NH}_3} \quad (4.1)$$

to be endothermic by $+103 \text{ kcal mol}^{-1}$.^{249,250} This means that in the gas phase, disregarding entropic terms, this strong neutral base and strong neutral acid don't react spontaneously. However, in fluorosulfuric acid solution, the reaction is exothermic by 43 kcal mol^{-1} .²⁵¹ This illustrates the role a polar solvent plays in separation of charge.

Recent calculational work²⁵² at the B3LYP-MP2 level involving one free FSO_3H and one NH_3 molecule suggests the gas phase interaction of the two does not result in a proton transfer reaction according to the calculated structural parameters. Only after a water molecule was introduced, did the transfer favorably occur. Addition of a second water molecule further decreased the free energy, however, the energy increased when a third was introduced. The intent of the authors was to determine the effect of trace amounts of water on an endothermic gas phase reaction.

It is not likely that the same effects would be observed for the reaction in acid solution, since the proton transfer is calculated to be exothermic under solution conditions. However, the confirmation of such a phenomenon that would be contrary to classical thermodynamics is quite provocative.

On the opposite end of the spectrum, the double protonation of ammonia by fluorosulfuric acid would also be an important discovery, the mechanism for which is given in Figure 4.3. There is no theoretical or experimental evidence for the existence of the NH_5^{2+} ion, however, the notion of an H_4O^{2+} ion is still supported by some.

To explore the nature of ammonia as a solute in fluorosulfuric acid, neutron diffraction measurements were obtained for a 10% NH_3 solution in FSO_3H . Isotopic substitution (NDIS) on the H and N sites was incorporated to gain further insight into the structural characteristics. This work was undertaken in hopes of adding to the scientific knowledgebase of superacid chemistry and, in particular, the characterization of solutes in superacid solutions.

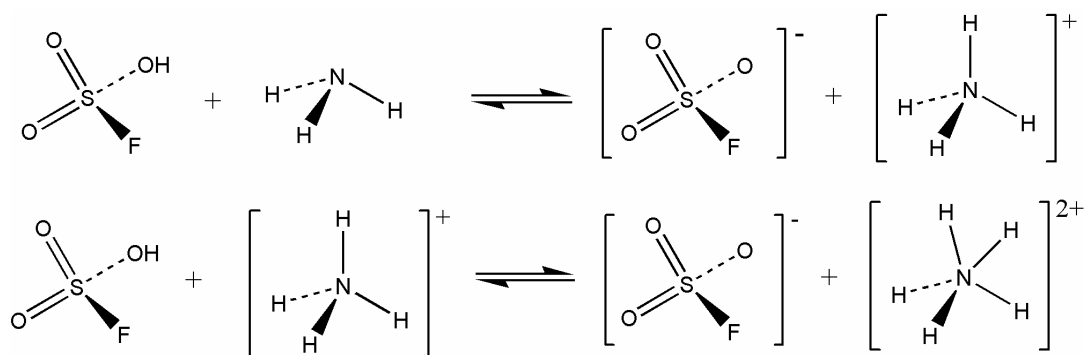


Figure 4.3: Scheme for the double protonation of ammonia by fluorosulfuric acid.

4.2 Experimental

4.2.1 Sample preparation

Fluorosulfuric acid is an aggressive material and must be handled with caution in rigorously dried glassware. All manipulations of FSO₃H and FSO₃D were carried out under an argon atmosphere or under vacuum on a Schlenk line ($p_{\min} < 10^{-3}$ mbar) or on an all glass high vacuum line ($p_{\min} < 10^{-5}$ mbar). All glassware was flame-dried under vacuum at least four times and allowed to cool under vacuum. FSO₃H (Allied Chemical Co.) was triply distilled prior to use. FSO₃D was prepared according to the literature with the exchange between D₂SO₄ and FSO₃H being performed three times.²⁵³ NMR measurements and neutron analysis (vide infra) revealed that the incorporation of D for H was greater than 99.8%. The purity of FSO₃H with respect to water was assayed using Raman spectroscopy and determined to be greater than 99.9% H₂O free as previously reported. All Raman spectra were acquired on a Dilor XY Raman spectrometer (Instruments S.A., Inc, Edison, NJ) using a 514 nm Rayleigh line.

The scope of the experiment required the use of three different high purity ammonia supplies: ¹⁵ND₃, ND₃ and NH₃. ND₃ and NH₃ were necessary to extract the first order difference with respect to the hydrogen sites, and ¹⁵ND₃ and ND₃ made possible the extraction of the first order difference with respect to the nitrogen. The notion of NDIS was mentioned in section 1.3.1. Briefly, once diffraction data are obtained for two samples differing only by their isotopes of one atom type, a simple subtraction of the normalized differential scattering cross-section gives a difference

function that, upon Fourier transformation, gives a partial pair correlation function that only contains the correlations involving the isotopically labeled element.

NH_3 (Matheson), ND_3 (Isotec, 98% D), or $^{15}\text{ND}_3$ (Cambridge Isotopes, 99.9%D) was condensed into an ampoule containing sodium metal with liquid nitrogen. The ammonia was allowed to melt at -78°C and react with the sodium. This served to remove any trace water. The ammonia was frozen and a high vacuum was pulled on the ampoule remove any non condensable gases that may have come from the stock ammonia cylinders. The amount of ammonia needed to make a 10 mole % solution was expanded into a known volume of the high vacuum line. The number of moles was determined by assuming ideal behavior and measuring the pressure in the vacuum line. All of the ammonia in the line was then condensed into a quartz sample tube on top of the appropriate amount of either FSO_3D or FSO_3H that was previously cryogenically distilled into the tube. After all the gas was condensed, the quartz tube was flame-sealed under dynamic vacuum, while the sample material was held at -196°C .

Neutron diffraction measurements were performed at 195 K on 0.585 mL of $\text{NH}_3/\text{FSO}_3\text{H}$ (1:9) or 2.262 mL of either $\text{ND}_3/\text{FSO}_3\text{D}$ or $^{15}\text{ND}_3/\text{FSO}_3\text{D}$. The measurements were made on GLAD at IPNS and data were recorded and corrected in a manner identical to what is described in section 3.3.2.

4.3 Results

Measured neutron diffraction data are given in Figure 4.4 for $\text{NH}_3/\text{FSO}_3\text{H}$, $\text{ND}_3/\text{FSO}_3\text{D}$, and the difference of D-H. The corresponding pair correlation functions are

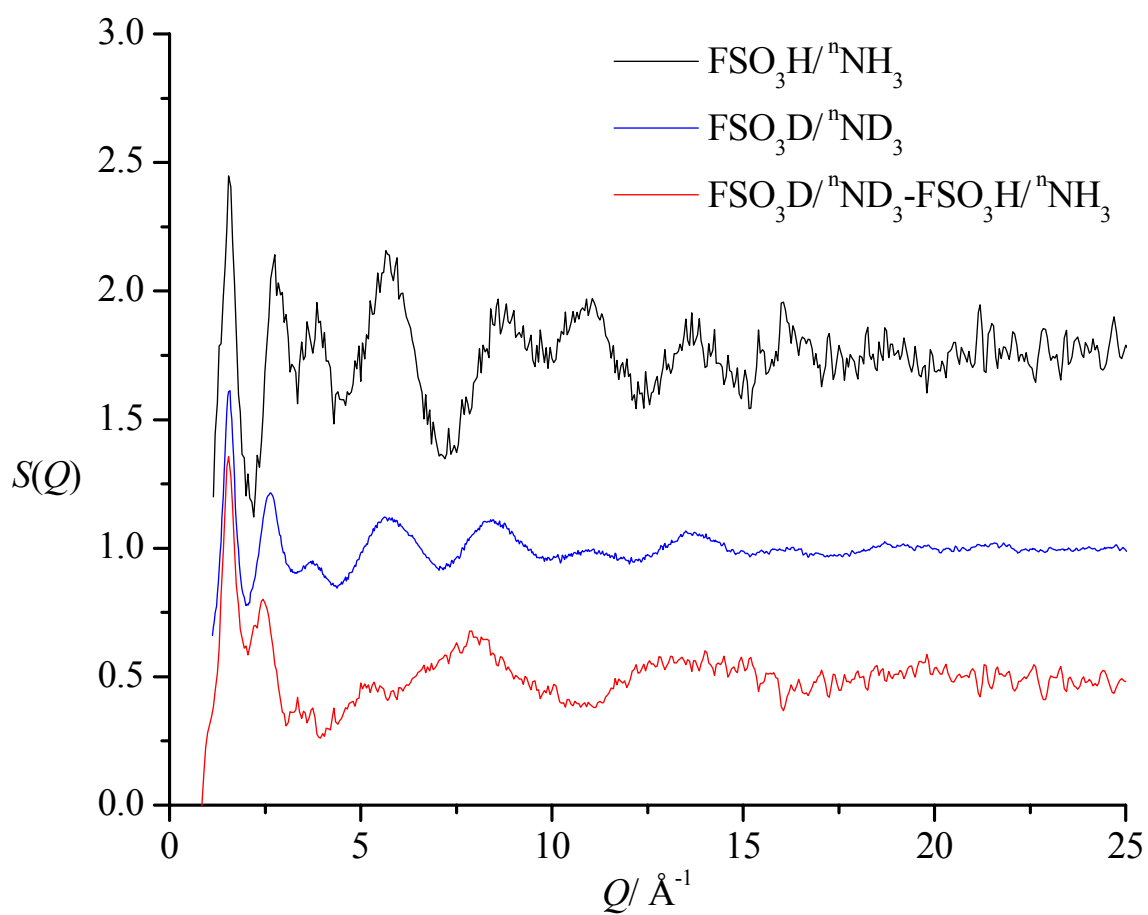


Figure 4.4: $S_{\text{H/H}}^{\text{N}}(Q)$ (black line), $S_{\text{D/D}}^{\text{N}}(Q)$ (blue line) and the difference function, $S_{\text{D/D-H/H}}^{\text{N}}(Q)$ (red line), at 195 K.

shown in Figure 4.5. The measured data for $\text{ND}_3/\text{FSO}_3\text{D}$ can be compared to the nitrogen labeled sample, $^{15}\text{ND}_3/\text{FSO}_3\text{D}$ in Figure 4.6. There is very little difference between the two, but there are unique features present in the difference Fourier transform, as seen in Figure 4.7.

It is obvious to compare these data to that of neat FSO_3H ²⁴⁵ and to the only other known neutron diffraction measurement of a solute dissolved in a superacid, namely H_2O in FSO_3H .²⁴⁶ The latter was part of the author's research and therefore will be freely discussed in the subsequent sections. The comparison between all three can be seen in Figure 4.8 and Figure 4.9 for $S(Q)$ and $G(r)$, respectively.

To complement the neutron diffraction data, preliminary NMR measurements have been performed. The ^1H NMR spectrum of $\text{NH}_3/\text{FSO}_3\text{D}$ (1:9) at 400 MHz is presented in Figure 4.10. The peak at 11.7 ppm is the residual FSO_3H . The large triplet centered at 5.0 ppm has an peak intensity ratio of 1:1:1 and a coupling constant, $J = 54 \text{ Hz}$.

4.4 Discussion

4.4.1 Scattering functions and pair correlation functions

Upon addition of a solute to fluorosulfuric acid, the first sharp diffraction peak in the measured data decreases in intensity. This is true for both NH_3 and H_2O as seen in Figure 4.8. It is believed that the intensity of this peak is often related to the degree of short-range and intermediate-range ordering in a liquid. That notion is supported by the

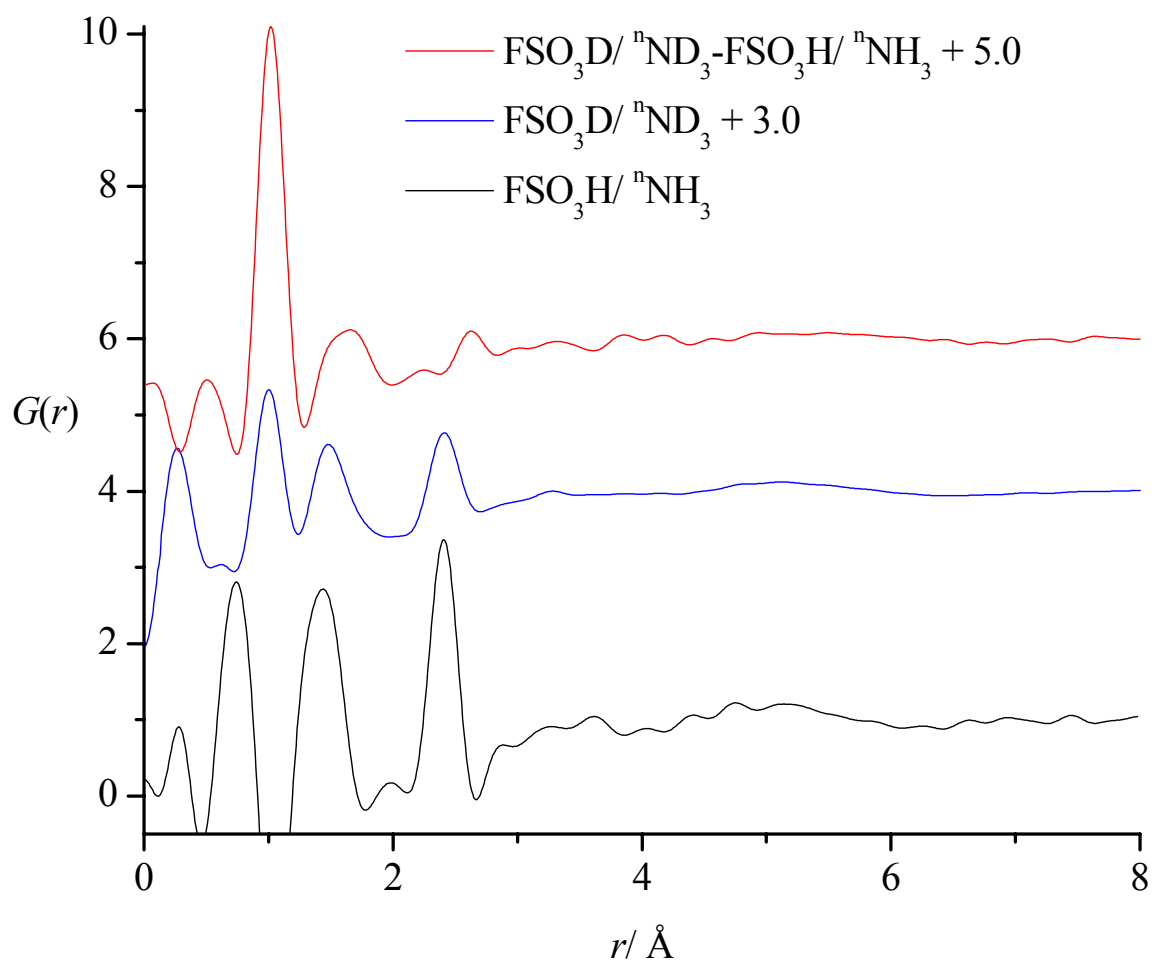


Figure 4.5: $G_{\text{H/H}}^{\text{N}}(r)$ (black line), $G_{\text{D/D}}^{\text{N}}(r)$ (blue line) and the difference function, $G_{\text{D/D-H/H}}^{\text{N}}(r)$ (red line), at 195 K.

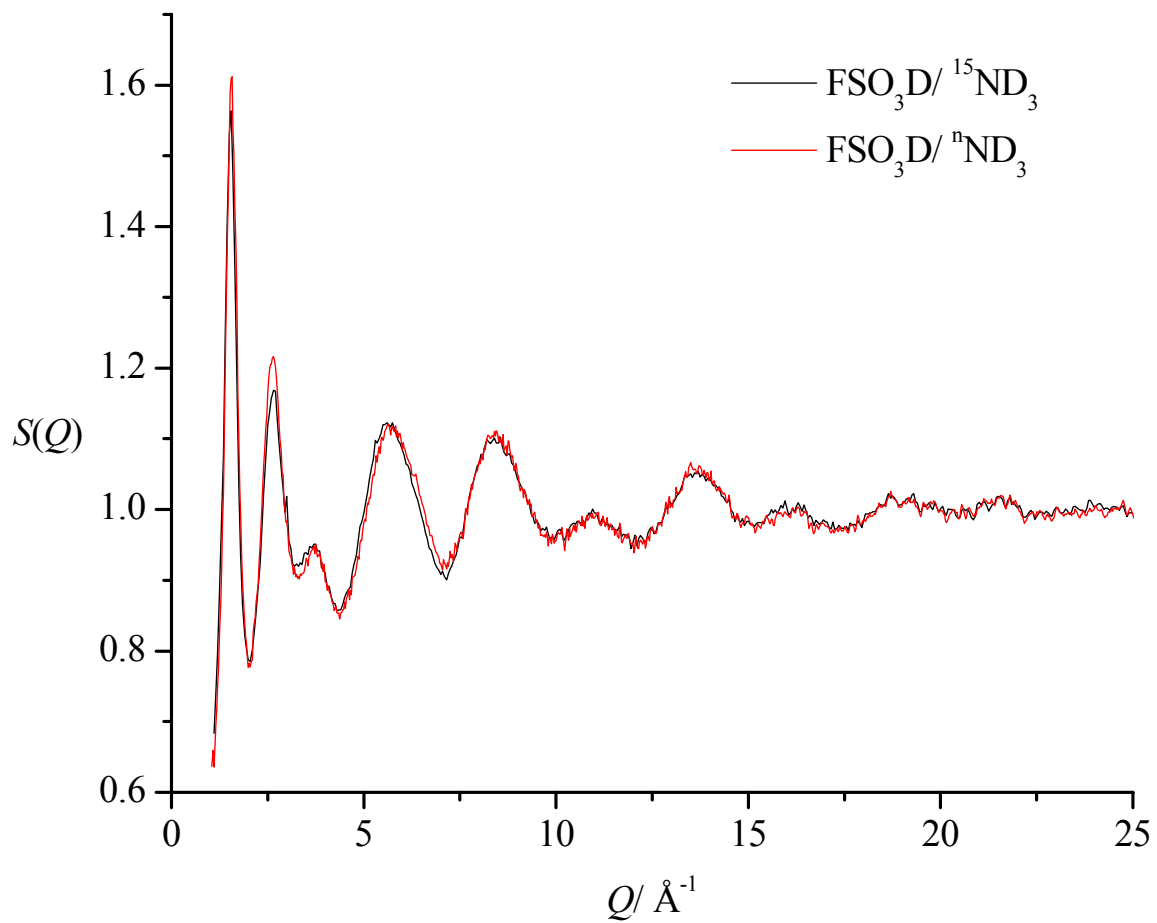


Figure 4.6: $S_{\text{D/D}}^{\text{N}}(Q)$ (red line), $S_{^{15}\text{ND}_3/\text{D}}^{\text{N}}(Q)$ (black line) at 195 K.

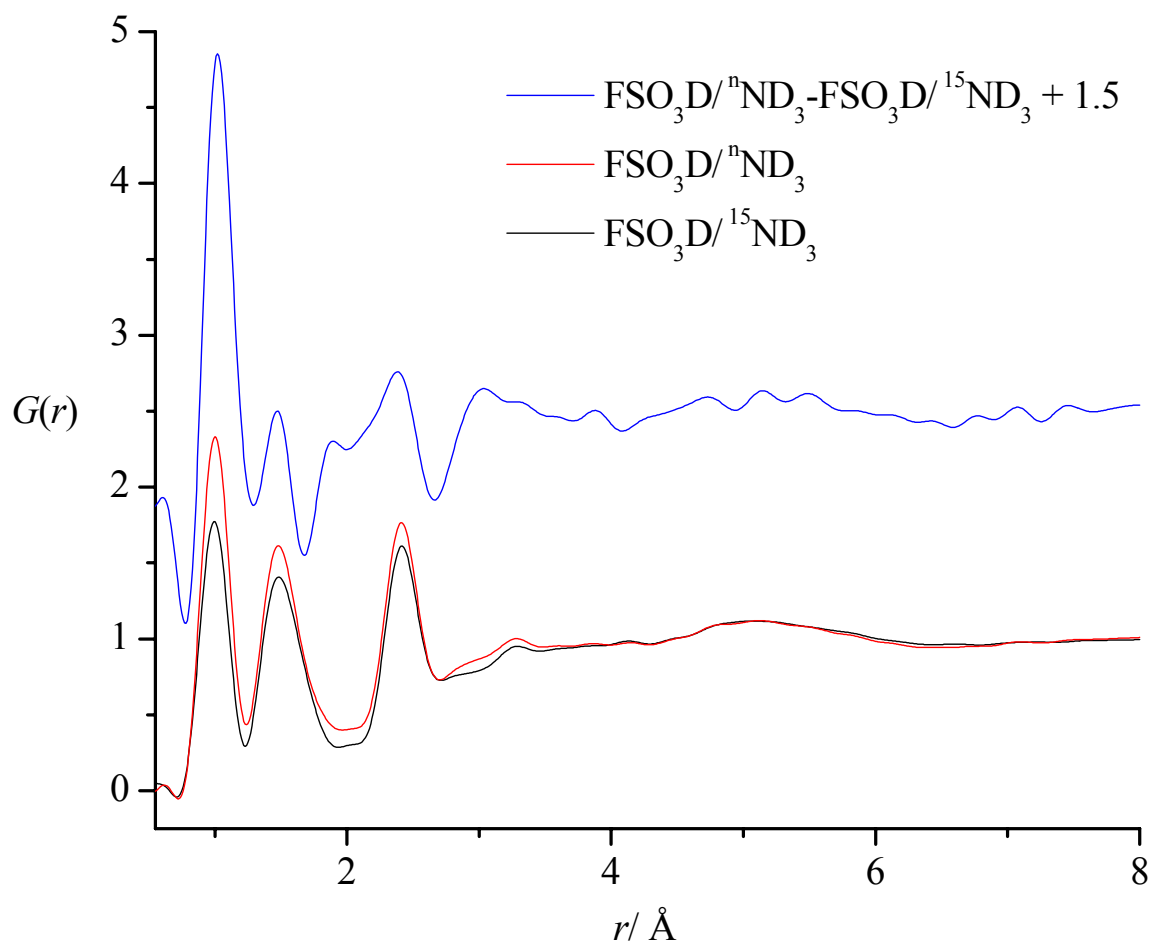


Figure 4.7: $G_{15\text{ND3/D}}^{\text{N}}(r)$ (black line), $G_{\text{D/D}}^{\text{N}}(r)$ (red line) and the nitrogen difference function, $G_{15\text{ND3/D-D/D}}^{\text{N}}(r)$ (blue line), at 195 K.

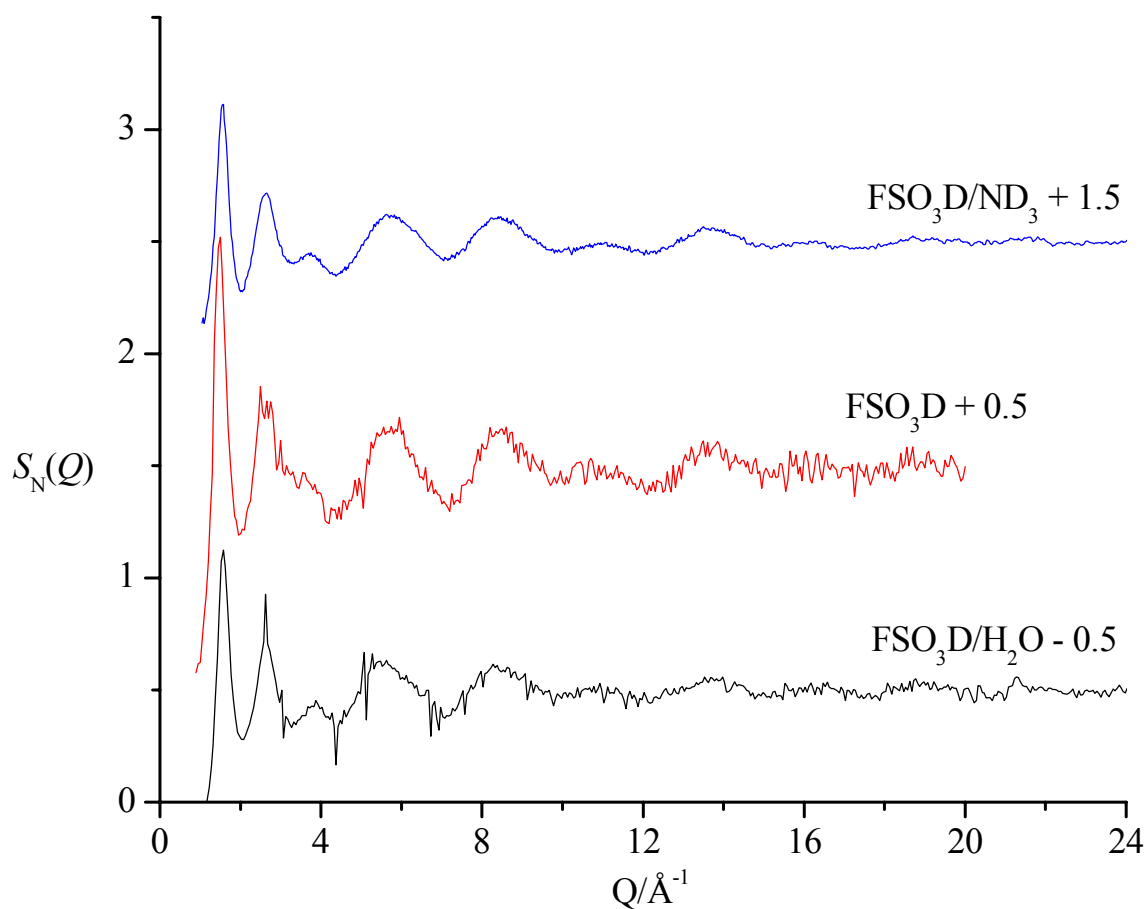


Figure 4.8: The $S(Q)$ functions for pure FSO_3D , 10% ND_3 in FSO_3D and 10% H_2O in FSO_3D . The decrease in the intensity of the first sharp diffraction peak is often indicative of a loss in short- and intermediate-range order, such as the weakening of a hydrogen bond network.

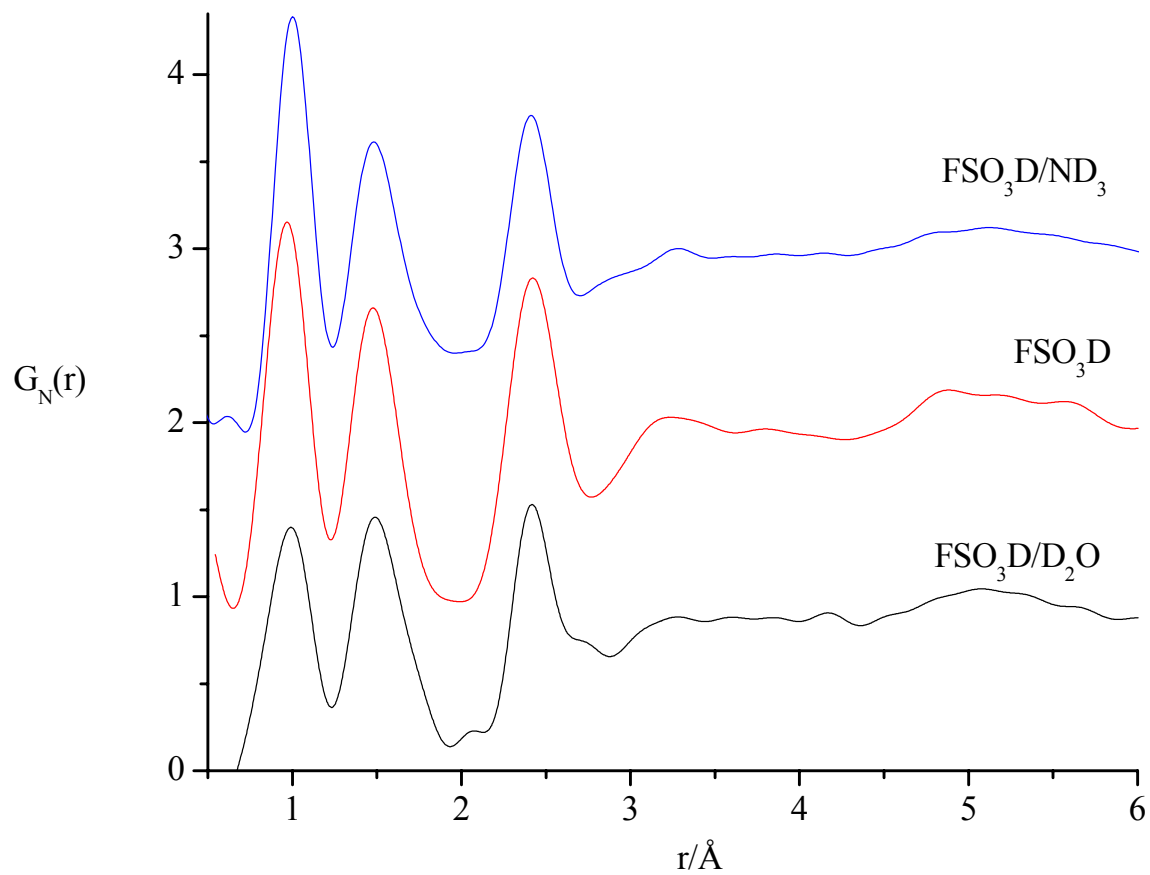


Figure 4.9: The $G(r)$ functions for pure FSO_3D , 10% ND_3 in FSO_3D and 10% H_2O in FSO_3D .

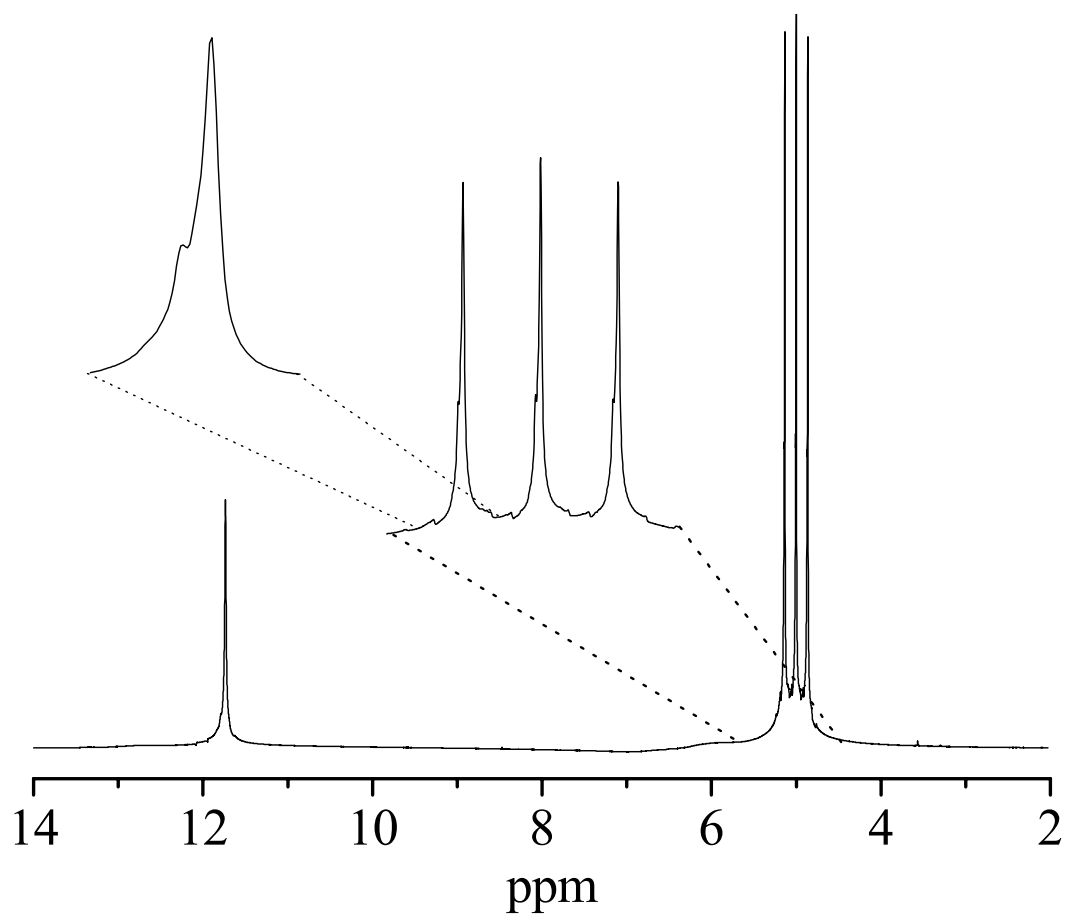


Figure 4.10: The 400 MHz ^1H NMR spectrum of $\text{NH}_3/\text{FSO}_3\text{D}$ (1:9). The triplet (expanded in the inset) centered at 5.0 ppm ($J = 54\text{ Hz}$) is representative of N-H scalar coupling to the ammonium ion. The peak at 11.7 ppm is attributed to fluorosulfuric acid.

observed disappearance of a possible second hydrogen bonding peak in the neat acid upon addition of water. This is best observed in the difference Fourier transforms for the respective data sets, which are given in Figure 4.11. If intensity of the first sharp diffraction peak is indeed an indication of local order in liquids, then it must be said that ammonia is equal to water in its ability to decrease the local order of FSO₃H.

A few other definite differences are visible in Figure 4.11. There is a small peak around 2.24 Å in $\Delta G(r)_{\text{NH}_3/\text{H}}$ that is not present for the neat acid or the water solution. However, $\Delta G(r)_{\text{H}_2\text{O}/\text{H}}$ does show a small peak at 1.96 Å that is absent for the ammonia solution or the neat acid. In fact the entire region of $\Delta G(r)_{\text{FSO}_3\text{H}}$ from about 1.8 – 2.4 Å is featureless, which implies the peaks at 2.24 Å and 1.96 Å in the ammonia sample and the water sample, respectively, correspond to either a solute intramolecular distance or a solute – solvent hydrogen bond. And since the largest intramolecular solute distance, regardless of exactly what species they may be, can be no larger than ~1.7 Å based on simple geometry, the peak likely corresponds to a solute – solvent hydrogen bond. Here, the term solute definitely includes the fluorosulfate anion, since it would likely be present if proton transfer occurs.

Also somewhat noticeable in the same figure is the dependence of the position of the first peak on solute. The average distance in the first correlation peak shifts to a higher value ($r = 1.02$ Å) upon the addition of ammonia and a lower value ($r = 0.97$ Å) when water is added. In pure FSO₃H(D) that distance is 0.98 Å, which is taken as the intramolecular O–H bond length. This is completely reasonable since the O–H bond length in the hydronium ion, most likely the adopted conformation of a water molecule in

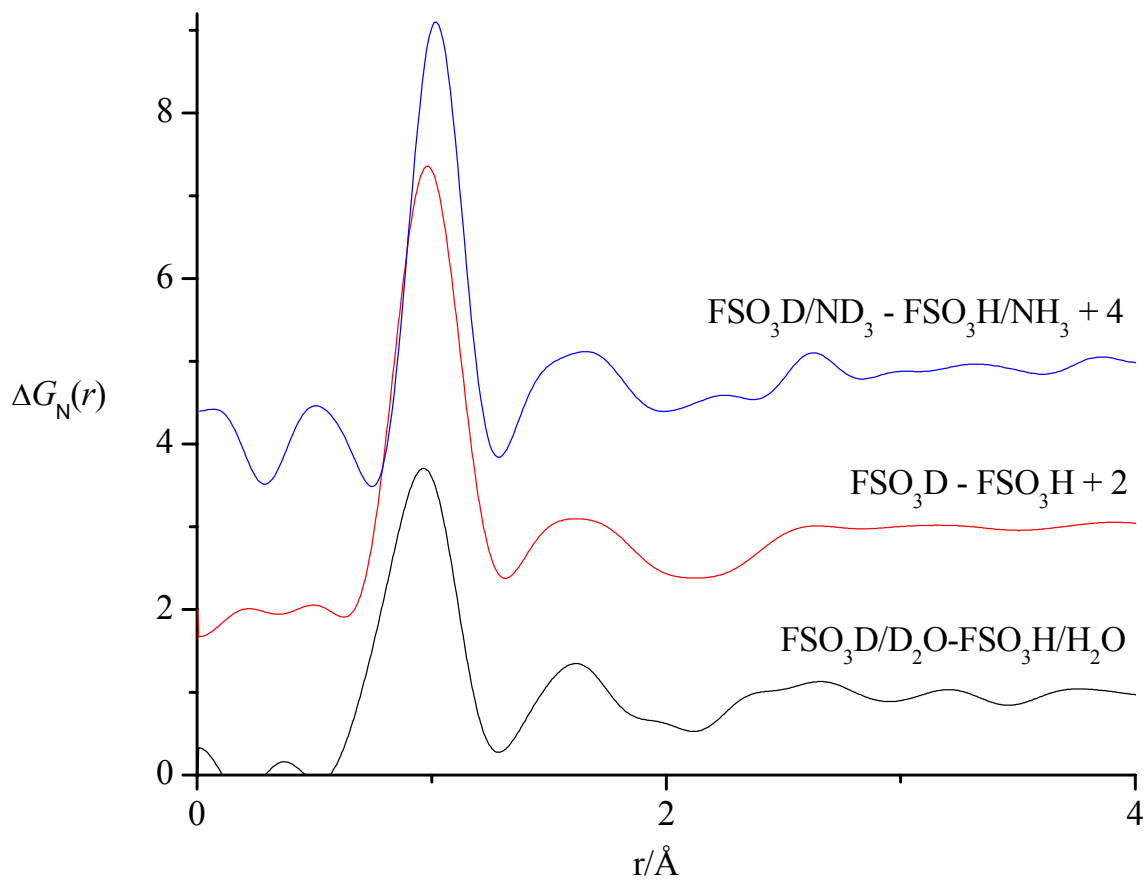


Figure 4.11: The hydrogen first order difference correlation functions for the neat acid, a 10% ammonia solution and a 10% water solution. Note the sharpening of the second peak at 1.6 Å with the addition of water.

a superacid, is 0.90 Å, as determined by neutron diffraction of hydronium triflate.

Likewise, the average N–H bond length taken from a calculational study²⁵² is 1.026 Å.

4.4.2 Coordination number analysis

Typical coordination number analysis of peaks in the pair distribution function, as described in section 3.4.2, proved difficult with these data. For these measurements, the first peak of $G(r)$ (except the first order difference with respect to nitrogen) contains N-H(D) and O-H(D) coordination. Usually the first peak in $G(r)$ only contains one type of correlation. As such, the portion of the peak representative of a singular correlation is not explicitly known. In this case, the peak must be deconvolved before average coordination can be determined. For this particular case, the peak was fit to two Gaussian functions. By allowing the fitting program to vary the Gaussian parameters, the common issue of overconstraint is avoided. An example of this technique is exhibited in Figure 4.12 for the first correlation peak of ND₃/FSO₃D.

There are a number of possible configurations of species in solution. This further complicates the coordination number analysis, since it is not certain what types of correlations are under a given peak. Apart from the possible, nitrogen-containing products mentioned in section 4.1.3, one can imagine many different ionic or hydrogen-bonded species formed in solution. For example, if proton transfer occurs, then the resulting fluorosulfate ion will not exist without coordination to its counter ion or solvation by FSO₃H molecules. If, for instance, an FSO₃[−] ion is coordinated to the

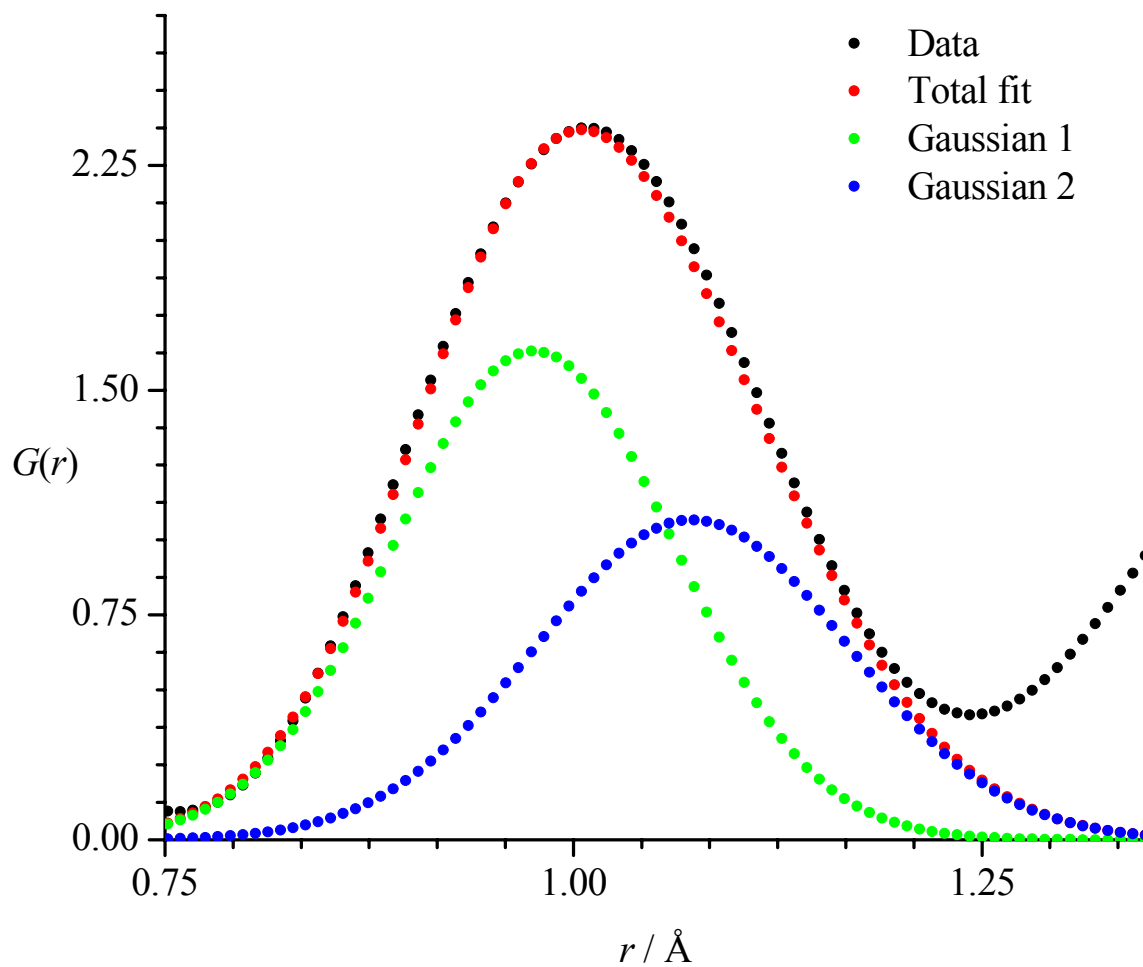


Figure 4.12: Two-Gaussian fit to the first correlation peak in $G(r)$ for $\text{ND}_3/\text{FSO}_3\text{D}$ (1:9). If the area of each peak is determined, the average coordination about the X atom, $X=\text{O}$ or N in this case, can be calculated. Such information is not available without proper deconvolution of the peak.

ammonium ion, then one of the four covalent N–H bonds will be stretched, in this case, resulting in additional distances under the first correlation peak. If the same anion were to be solvated by acid molecules, there would likely be an additional hydrogen bonding peak other than the ones seen in the neat acid.²⁴⁵

By taking the first order difference with respect to nitrogen, an attempt is made to eliminate all correlations except ones concerning nitrogen. This would greatly simplify the coordination number analysis, particularly regarding that of the first peak. The intramolecular O–H correlation would be removed, leaving only one peak corresponding to the intramolecular N–H distance. NDIS is effective when the difference in scattering length between two isotopes is very large. Thus, the ubiquitous choice for NDIS is the hydrogen / deuterium couple ($b_{\text{H}} = -3.739, b_{\text{D}} = 6.67$). The difference in the scattering lengths for naturally abundant N and ^{15}N ($b_{\text{N}} = 9.36, b_{^{15}\text{N}} = 6.44$) is rather small and this experiment approaches the limit of instrument capability. This point is illustrated by Figure 4.6, which shows very little difference between $S_{\text{D/D}}^{\text{N}}(Q)$ and $S_{^{15}\text{ND3/D}}^{\text{N}}(Q)$. The residual scattering intensity is essentially signal noise and the resulting $G(r)$, though seemingly featured, cannot be used to obtain accurate structural information.

Coordination numbers for nearest neighbor deuterium atoms around O and N, were extracted from the total pair distribution function by fitting the first peak with two Gaussian functions (Figure 4.12). The optimal configuration of the two peaks gave areas that correspond to $C_{\text{O}}^{\text{D}} = 0.23$ and $C_{\text{N}}^{\text{D}} = 2.42$. These numbers are significantly low (at least ~20 % low), as $C_{\text{N}}^{\text{D}} = 3$ would correspond to free ammonia in solution and the lowest possible value. The actual number of D around O is probably closer to 4, since

the most likely solute is NH_4^+ . This suggests the presence of a severe error in the data collection or analysis. The chance of the latter has been minimized through repetition of the analysis. It is likely that mistakes were made during collection, or that any the method used to extract coordination numbers is invalid.

The inability to obtain proper coordination numbers through standard methods suggests that data modelling, such as that described in chapter 3, is perhaps the best and only way to extract any significant structural information from these data.

4.4.3 NMR

In the ^1H NMR data, the triplet is representative of through-bond coupling of hydrogen to the dominant isotope of nitrogen, ^{14}N , which has spin, $I = 1$. This is an uncommon phenomenon. Any nucleus having a nuclear spin greater than one-half is known as a quadrupole. In other words, the charge density of the nucleus is asymmetrical, which causes rapid relaxation of the nucleus to a preferred orientation after it is subjected to an rf pulse. Fast relaxation times result in very broad, often immeasurable resonances. However, in a highly symmetrical environment such as a molecule possessing T_d or C_{3v} symmetry, there is no preferred orientation for a quadrupolar nucleus. Therefore, its relaxation time is much slower and can be measured on the usual NMR timescale.

Upon magnification (Figure 4.10), each line of the triplet shows further splitting, which is a result of two-bond coupling to deuterium. Since the only source of deuterium is FSO_3D , we must assume that full proton transfer did occur and a new N–H covalent

bond was formed. This is hardly surprising, based on thermodynamical calculations and evidence for the similar protonation of water.

Further NMR experiments are needed to better characterize the solute, but based on this evidence, NH_4^+ is the most likely species.

4.5 Conclusions

The neutron diffraction data at 195 K reveals some information on the solute structure of ammonia in fluorosulfuric acid. The data suggest that the short-range order, and thus the extent of the hydrogen bond network, of FSO_3H is lessened upon addition of the solute. This is indicated by a decrease in the intensity of the first diffraction peak. Although both water and ammonia likely undergo a one proton transfer in fluorosulfuric acid solution, there are structural differences in the two data sets.

^1H NMR data suggest the presence of ammonium ions, which supports thermodynamical calculations. Future 1-D and 2-D NMR studies are suggested to further characterize the ammonia – fluorosulfuric acid system.

Valid coordination numbers could not be extracted from the data; as such the amount of structural information obtained from this experiment is limited. Data modelling techniques such as Reverse Monte Carlo and Empirical Potential Structure Refinement should be employed to fully elucidate the solute structure of ammonia in fluorosulfuric acid.

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