



Experiment title: Role of Hydrogen Bonding in the High Frequency Dynamics of CH₄, CH₃OH, NH₃, H₂O and HF.

Experiment number:
HS - 1462

Beamline:	Date of experiment: from: 09-04-01 to: 16 04 01	Date of report: 23-04-01
Shifts:	Local contact(s): R. Angelini	<i>Received at ESRF:</i>

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Report:

In the experiment performed at the beamline ID16, we studied the Inelastic X-ray Scattering of two different mixtures of water and hydrofluoric acid (HF)_x(H₂O)_{1-x} with $x = 0, 0.2, 0.4$ at $T = 283$ K in the momentum transferred region $1 \div 15$ nm⁻¹. The sample cell is made in Teflon with thin (0.5 mm) windows to allow the passage of x-rays with a minimum scattering contribution from the Teflon.

This work is a part of the more extended project oriented to study the high frequency collective dynamics of hydrogen bonded liquids. We investigate (see previous report) the detailed shape of the dynamic structure factor $S(Q,E)$ of liquid HF at momentum transferred in the surrounding of the inverse of the intermolecular average distance to see whether this compound shows the same relaxational phenomenology as the one observed in water in the same Q range ⁽¹⁾.

When a relaxation is active in fluid the sound velocity is no longer a constant and can be generalized as a frequency (Q) dependent quantity being c_0 and c_∞ its zero and infinite frequency limiting values. While in liquid water the ratio c_0/c_∞ is 2.5, HF exhibits a large difference, in fact low frequency measurements give $c_0 \sim 500$ m/s, while numerical simulations ⁽²⁾ predict a $c_\infty \sim 3000$ m/s with a ratio of the order of 6. Furthermore on the basis of low frequency measurements, the isothermal sound velocity at room temperature goes from $c_0 \sim 500$ m/s for $x = 1$, $c_0 \sim 1350$ m/s for $x = 0.4$, $c_0 \sim 1450$ m/s for $x = 0.2$, to $c_0 \sim 1500$ m/s for $x = 0$. This steep dependence between the limit value of pure HF and pure water testifies that the hydrogen bond network is modified for different concentration of HF. For this reason the investigation of (HF)_x(H₂O)_{1-x} mixtures as a function of x is important to study the evolution of collective dynamics from the phenomenology of one liquid to that of the other. Up to now two mixtures with $x = 0.2$ and 0.4 at $T=283$ K have been studied. It is

evident, as shown in Fig.1, that even at a concentration as high as 40 % HF one observes almost no differences from the collective dynamics of pure H₂O. One explanation could be the fact that in water the tetrahedral co-ordination favours the formation of a three dimensional hydrogen bond network, while in HF the unidimensional nature of the hydrogen bond is responsible for a much weaker and spatially limited bonding pattern. To observe an HF-like dynamics, that means to disrupt the three dimensional network of H₂O, we need a sufficient number of HF molecules surrounding the H₂O ones. Further experimental work is then necessary to study a higher concentration of the HF to obtain a complete scenario of the phenomenon.

To allow a quantitative analysis, we subtracted the empty cell spectra from experimental spectra; we are fitting them using a model for the dynamic structure factor based on the memory function formalism in the infinite frequency limit i.e. using a simple fitting function composed by a delta for the central line and a damped harmonic oscillator for the inelastic signal. The model is convoluted with the resolution.

Fig.1 : HF, H₂O mixtures at T = 283 K

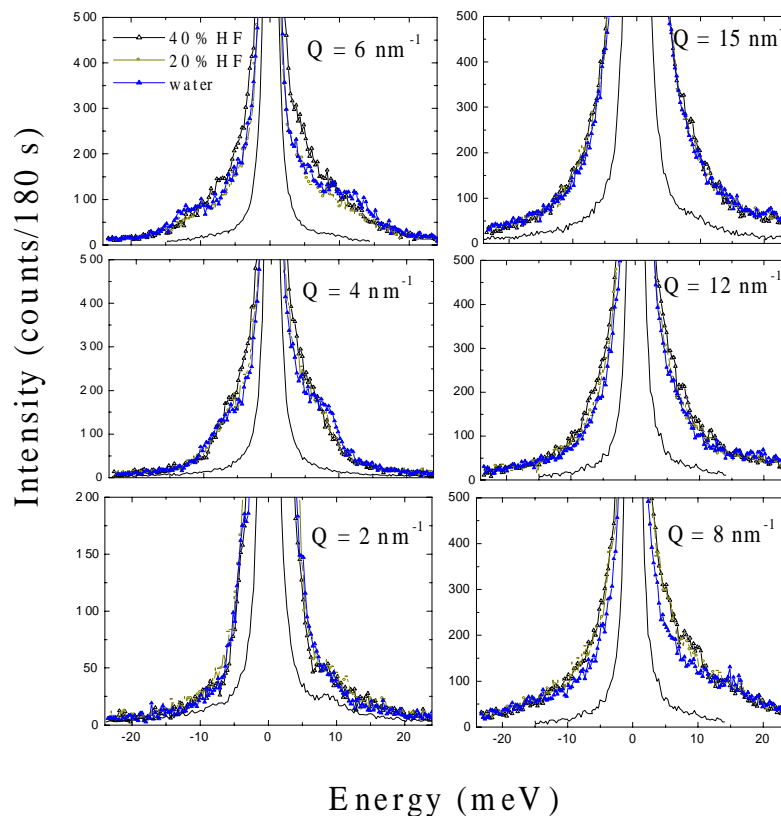


Fig.1 : example of IXS spectra at the indicated momenta Q for different concentrations of hydrofluoric acid. The solid line refers to the experimental resolution function. The spectra are normalized to their absolute scattering intensity and are subtracted of the contribution of empty cell.

References :

- 1) A.Cunsolo et al., *Phys. Rev. Lett.* **82**, 775 (1999)
- 2) D. Bertolini et al., *Phys. Rev. Lett.* **81**, 2080 (1998)