

	<b>Experiment title: Quantum correlation dynamics of OH and OD vibrational modes in liquid water and H<sub>2</sub>O-D<sub>2</sub>O mixtures studied by inelastic x-ray scattering (IXS)</b>	<b>Experiment number:</b> HS1152
<b>Beamline:</b> ID16	<b>Date of experiment:</b> from: 13.2.2000 to: 22.2.2000	<b>Date of report:</b> 25.8.2000
<b>Shifts:</b> 30	<b>Local contact(s):</b> Giulio Monaco	<i>Received at ESRF:</i>

**Names and affiliations of applicants (\* indicates experimentalists):**

Christina Halcoussis\* ESRF, Grenoble, France  
C. Aris Dreismann\* I.N.Stranski-Institute, Tech. University Berlin, Germany  
Tyno Abdul-Redah\* “  
Hendrik Naumann\* “

**Report:**

FIRST OBSERVATION OF MOLECULAR VIBRATIONAL EXCITATIONS OF WATER WITH INELASTIC X-RAY SCATTERING \*

C. Halcoussis<sup>1</sup>, T. Abdul-Redah<sup>2</sup>, H. Naumann<sup>2</sup>, G. Monaco<sup>1</sup> and C. A. Chatzidimitriou-Dreismann<sup>2</sup>

<sup>1</sup> ESRF, Experiments Division; <sup>2</sup> I. N.-Stranski Institute, Technical University of Berlin, Berlin, Germany

The inelastic X-ray scattering technique (IXS) has been applied to the energy transfer regime of molecular vibrations of covalently bonded H atoms, ca. 0-500 meV. We have obtained, for the first time, convincing experimental evidence that IXS can be used for vibrational spectroscopy.

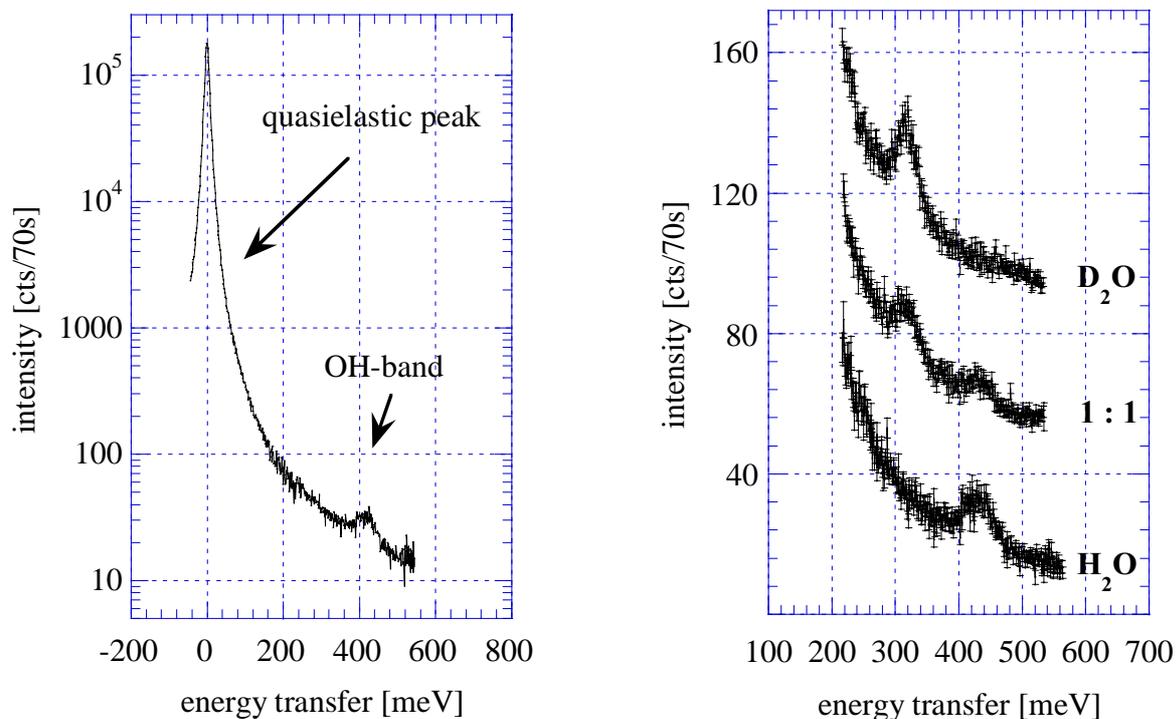
Nowadays it is widely known that most of the unique physicochemical properties of liquid water are intrinsically related to the huge amount of H-bonds, which determine its structure and dynamics, from the macroscopic to the microscopic spatial and temporal scales. Due to the small mass of the hydrogen atom, quantum mechanical effects appear to play a dominant role in the proper microdynamical description of water.

Until now, in the field of dynamics of liquid matter, IXS with meV energy resolution has been extensively applied in order to study their collective excitations [1-3]. In our recent experiment (HS1152), at the beamline ID16 at the ESRF, the primary goal was to detect by IXS intramolecular vibrations or, in other terms, localised vibrational excitations. We verified for the first time, that, by means of IXS, also internal degrees of freedom like single intra-molecular vibrations in liquid water, are accessible. We measured at room temperature the spectral distribution of the intensities of the OH and OD molecular stretching vibration modes of different H<sub>2</sub>O-D<sub>2</sub>O mixtures centred at about 430 meV and 310 meV respectively [6]. **Fig. 2** shows the vibrational IXS spectra of pure H<sub>2</sub>O, pure D<sub>2</sub>O and a H<sub>2</sub>O-D<sub>2</sub>O mixture with an equimolar H:D composition, i.e. H:D=1:1. They reveal clearly the OH and OD stretching vibrational bands, which are superimposed to the „long tail“ of the much more intense quasielastic peak. For the sake of visibility, the spectra are parallelly shifted.

Before our experiment was performed, the possibility to observe such spectra has been questioned by many, due to the very low intensity available at the spectral regime under consideration. **Fig.1** illustrates, why these

excitations are difficult to observe. These high frequency intra-molecular vibrations of single molecules have a cross section that is about 4 orders of magnitude smaller than the central quasi-elastic scattering line and still 3 orders of magnitude weaker than the acoustic-like collective excitations in water [3] situated in an energy span of 10-30 meV.

We used the Si(777)-reflection at an incident energy of 13.8 keV and performed energy scans at  $29 \text{ nm}^{-1}$  momentum transfer that corresponds to the x-ray structure factor maximum of the oxygen-oxygen pair correlation function to which x-rays are more sensitive. The energy transfers ranged from 250 meV to 500 meV covering the two typical well known molecular stretching modes of light and heavy water. This corresponds at 13.8 keV to a temperature difference of  $\Delta T=12 \text{ K}$  between the two energy analysing crystals. One 250 meV energy scan takes 4-5 hours. For the  $\text{H}_2\text{O}$  spectrum, a typical count rate at 400 meV was about 0.4-0.5 counts/second. We used an energy resolution of  $\sim 10 \text{ meV}$  and a momentum resolution of  $\sim 1 \text{ nm}^{-1}$ .



Our scientific **aim** is now to extend our previous quantum entanglement (QE) studies [4-5] and establish quantitatively the existence of an anomalous scattering component by applying x-rays. The dependence on the different radiation-matter coupling mechanisms will provide us with new information about the QE effect and quantum dynamics in liquid water. The DOS of the OH and OD vibration modes are well separated in frequency, so that the integrated intensities over the DOS of the OH and OD stretching modes are strictly proportional to their cross-sections  $\sigma_{\text{OH}}$  and  $\sigma_{\text{OD}}$ .

The IXS technique is particular suited for the determination of spectral intensities of collective excitations in liquids [1-3]. For this purpose we should extend our strongly encouraging results [6] to further molar compositions in order to vary the degree of quantum correlation. One can easily see in **Fig. 2** that, the size of the error bars is still bigger ( $< 20\%$ ) than the effect we are looking for. Consequently, a significant improvement of statistics quality is indispensable. According to our preliminary results we need an accumulation of 8–16 spectra depending on mixture to obtain sufficient statistics.

[1] F. Sette et al., *Science*, **280**, 1550-1555, 1998; [2] H. Sinn et al., *PRL* **78**, 1715 (1997)

[3] G. Ruocco and F. Sette, *J. Phys.: Condens. Matter* **11** (1999) R259-R293

[4] C. A. C.-Dreismann et al., *PRL* **79**, 2839 (1997);

[5] C. A. C.-Dreismann et al., *J. Chem. Phys.*, **113** (7), p. 2784-2792 (15.8.2000)

(\*): First results are published in

[6] C. Halcoussis, T. Abdul-Redah, H. Naumann, G. Monaco and C. A. C.-Dreismann, "First observation of molecular vibrational excitations of water with inelastic x-ray scattering", *ESRF Newsletter* (sept. 2000);