ESRF	**Experiment title: Quantum correlation dynamics of OH and OD vibrational modes in liquid water and H_2O-D_2O mixtures studied by inelastic x-ray scattering (IXS)**	**Experiment number**: HS1447
Beamline: ID16	**Date of experiment**: from: 22.3.2001 to: 1.4.2001	**Date of report**: 31.8.2001
Shifts: 30	**Local contact(s)**: Giulio Monaco	*Received at ESRF:*

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Report:

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 a first experiment at the beamline ID16 at the ESRF (HS1152), this technique (IXS) has been successfully applied to the energy transfer regime of intramolecular vibrations of covalently bonded H atoms in water mixtures. We verified that, by means of IXS also internal degrees of freedom like intramolecular vibrations, are accessible to x-rays and obtained, for the first time, convincing experimental evidence that IXS can be used for vibrational spectroscopy [7,8].
However, in this preliminary attempt the obtained signal to noise ratio didn’t allow us to determine the scattering cross sections of the vibrational bands that was originally the aim of the experiment. The OH and OD stretching vibrational bands centred at about 430 meV and 310 meV respectively, are superimposed to the „long tail“ of the 4 orders of magnitude more intense quasielastic peak.
Consequently, in HS1447 the intensity conditions were improved in order to determine cross sections. We used the Si(777)-reflection at an incident energy of 13.8 keV and performed energy scans at 29 nm^{-1} ranging from 200 meV to 550 meV covering the two typical well known molecular stretching modes of light and heavy water. One 350 meV wide scan took 9 hours with an improved count rate of 2cts/s at 10 meV energy resolution and 1 nm^{-1} momentum resolution. The gain of factor 4 in intensity enhanced the signal to noise ratio by 2. However, for the data analysis it is obligatory to have a common baseline as a reference for all molar compositions. An example for the two pure compounds of light and heavy water is illustrated in **Fig.1.** Here, although at first glance a common baseline seems to exist, in case we subtract the tail of the elastic line we observe several intensity fluctuations over the whole energy range shown in **Fig.2**. Several drops and even shape changes of the instrumental resolution function occured that are indicated by circles A,B,C in **Fig.1**. The statistical uncertainity described by Poisson statistics doesn’t explain these fluctuations that are bigger than the corresponding error bars. This induced important uncertainties in the determination of the baseline and the corresponding spectral intensities.
The fluctuations are related to mechanical instabilities of the beamline optics during the long temperature scans over 12 K leading to beam movements at the sample position by several hundreths of microns. This fact lead to daily reoptimization of the instrument such that recorded spectra taken in different series are not necessarily comparable to each other. It took several days of instrumental studies to find a way to stabilize the

beam position. The time loss limited our investigations to just the two pure compounds and the 1:1 mixture of light and heavy water.

Concerning anomalies in the scattering cross sections and/or the QE effect we can presently state:

1. About the OH-band of the 1:1 mixture we can say that it is weaker than classically expected. This decrease is possibly around 20% with an error conservatively estimated to ± 5%. The basic problem remains the baseline. The fluctuations are such, that doesn't allow us to make a clear quantitative statement. We need a stable baseline fit with a reliable convergence. The baseline fit strongly depends on the shape of the instrumental function.
2. About the OD vibration band we cannot make any statement. For this purpose we need a longer part of the elastic tail towards lower energies in order to describe it better.

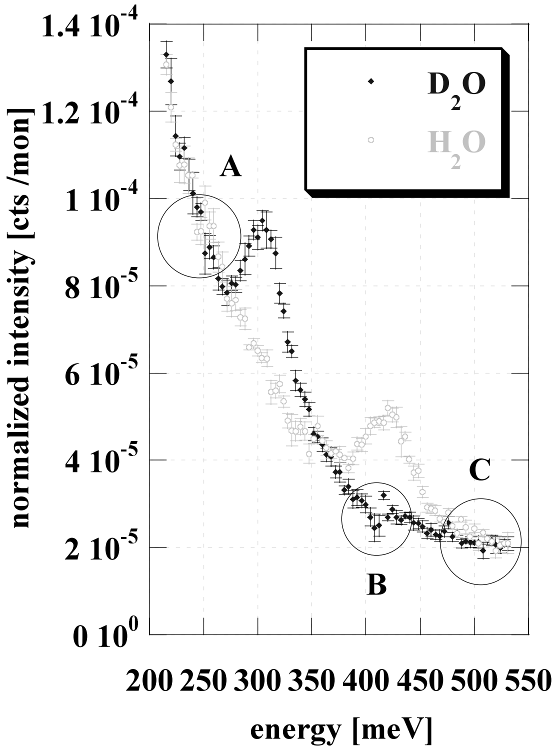

Fig. 1

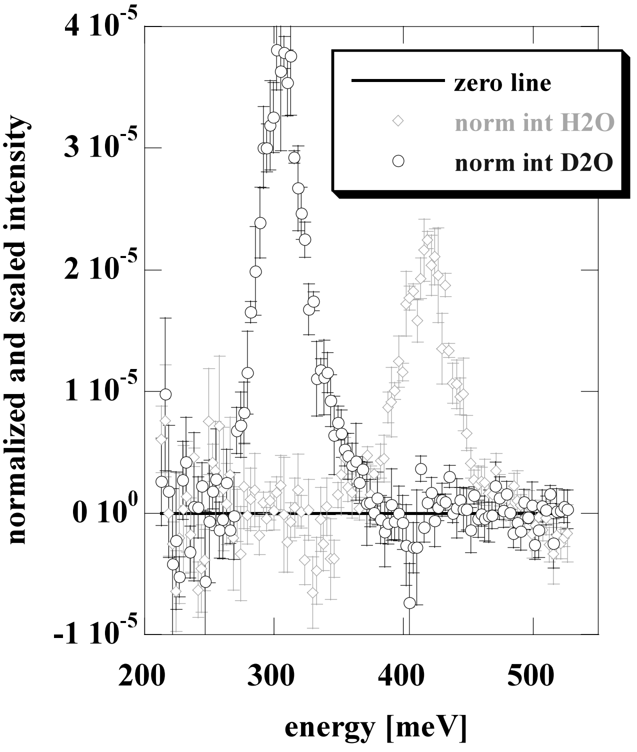

Fig.2

Our **aim** is to extend and complete previous quantum entanglement (QE) studies [4-5] performed by other probes and establish quantitatively the existence of an anomalous scattering component by applying x-rays. We already have strong indications for an anomaly in the OH-band. **Fig. 2** indicates that, the statistic error bars are smaller than baseline instabilities. The effect we are looking for, couldn’t be observed for the OD-band. In order to complete the present status of anomalies in scattering components, a significant improvement in a reliable baseline determination for both the OD-band and the OH-band as well is indispensable.

This can be achieved by extending the energy intervall towards lower energies keeping the instrumental conditions as stable as possible.

To complete our investigation we should also extend our strongly encouraging results to further molar compositions in order to vary the degree of quantum correlations.

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