



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

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The inelastic X-ray scattering (IXS) technique 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.

The ubiquitous condensed matter system called "liquid water" has always been in the focus of fundamental research. In particular, the manner in which it renders the earth fit as a habitat for life, and its involvement in life processes at all levels has inspired generations of researchers. 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. Additionally, the role of water in the formation and stabilisation of biologically significant structures is well known.

In the last few decades it has been recognised that quantum mechanical

effects appear to play a dominant role in the proper microdynamical description of water due to the small mass of the hydrogen atom. Nowadays, modern spectroscopic techniques like neutron and X-ray scattering are indispensable for the study of matter in the mesoscopic and microscopic spatio-temporal domains. Extending the basic results obtained with inelastic neutron scattering, the recent development of the novel inelastic X-ray scattering (IXS) technique at a third generation synchrotron radiation source, the ESRF, has also led to a new interpretation of an important phenomenon in liquid water, i.e. a propagating "fast sound" collective mode at the mesoscopic scale [1].

The primary goal of our recent experiment (February 2000) at beamline

ID16 was to take the first measurement of the spectra of intramolecular vibrations (or, in other terms, localised vibrational excitations) using the IXS method. The OH stretching vibrational modes of water are about 400 meV. Before our experiment was performed, the possibility of observing such spectra had been questioned by many due to the very low intensity available at the spectral regime under consideration. Figure 1 shows the vibrational spectra of pure H₂O, pure D₂O and a H₂O-D₂O mixture with an equimolar H:D composition, i.e. H:D = 1:1. The accumulation time required for each of the spectra shown was about 40 hours. The spectra are presented as measured, i.e. no smoothing has been applied. The peaks due to the OH and OD stretching vibrational modes are clearly

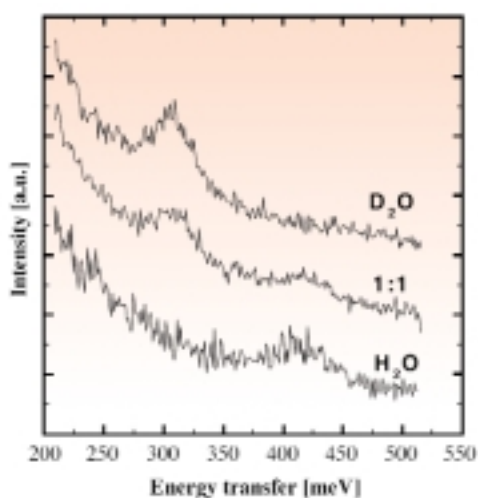


Fig. 1: The IXS spectra of the intramolecular OH and OD stretching modes of H₂O, D₂O, and a H₂O-D₂O mixture with an equimolar H:D composition (H:D = 1:1). The spectra are parallelly shifted, for illustration. Intensities are given in arbitrary units. (For the H₂O spectrum, a typical count rate at 400 meV was about 0.4 - 0.5 counts/s).

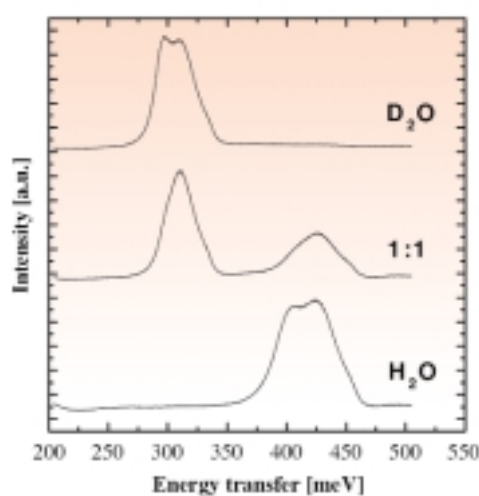


Fig. 2: The corresponding spectra of H₂O, D₂O, and the equimolar H₂O-D₂O mixture (H:D = 1:1) obtained with the conventional Raman light scattering technique (after standard data analysis). The spectra are parallelly shifted, for illustration. Intensities are given in arbitrary units. (Typical count rates at the maximum of the OH peaks were ca. 100 to 200 counts/s).



visible, and they are centred about 400 meV and 300 meV, respectively. These peaks are superimposed on the "long tail" of the much more intensive quasielastic peak. For the sake of visibility, the spectra are parallelly shifted. For the H₂O spectrum, a typical count rate at 400 meV was about 0.4 - 0.5 counts/second. The momentum transfer chosen in these experiments was 2.9 Å⁻¹. The incident energy was 13.8 keV. The spectral resolution used was about 12 meV. For comparison, the corresponding Raman light scattering spectra are shown in Figure 2. (An Argon-ion laser with excitation wavelength of 5140 Å was used. Typical count rates at the maximum of the OH peak were ca. 100 to 200 counts/second.) One can easily see that with both methods the same spectral positions of the OH and OD peaks were obtained. Obviously, the determination of the spectral peak shapes and widths of the IXS spectra require better counting statistics.

The second goal of our IXS experiment was to investigate the possibility of observing quantum entanglement (QE, cf. side panel) between the vibrational modes of liquid water. QE and/or Schrödinger's cat states of quantum particles play a dominant role in numerous present day investigations of fundamental (theoretical and experimental) physics. Moreover, articles about "quantum

computer", "quantum cryptography" and "quantum teleportation" can be found even in rather popular journals; see for instance [2]. However, one conventionally expects that the observation of QE effects is impossible in condensed matter at room temperature, due to the extremely fast decoherence process [2,3] which destroys these quantum effects.

In our neutron Compton scattering (NCS) experiment on water and H₂O-D₂O mixtures [3] we have provided the first direct experimental evidence for QE between protons in water at room temperature. The NCS technique is characterised by a short scattering time (or interaction time of neutrons with protons) of about 1 femtosecond. The most surprising result was that, due to protonic QE, the cross-section density of H becomes reduced anomalously by up to 30%. In simple terms, QE seems to effectuate destructive quantum interference between protons, in the sub-femtosecond time scale [3]. Since OH oscillators contain protons, this striking NCS result indicates that the quantum dynamics of OH vibrations (and H-bonds), and the associated IXS spectra, could also be affected by protonic QE.

In future work, after further IXS data accumulation, we intend to determine the integral scattering intensities of the OH and OD peaks of the samples mentioned

above (see Figure 1). If QE between vibrational degrees of freedom is present in water, then an anomalous change of the X-ray scattering cross-section density of the OH mode will be measurable. Concretely, the integral cross-section density of the OH mode of the H₂O-D₂O mixture would then be smaller (say, by ca. 10%) than that of the pure H₂O. In this case, one would observe the surprising effect that ca. 10% of the OH oscillators of the H₂O-D₂O mixture would become "invisible" to the X-rays. It may be noted that neutron scattering is due to the strong interaction, whereas IXS is due to the electromagnetic interaction. Thus it will be interesting to compare the anomalies found with NCS [3] with the associated IXS results. If successful, our IXS experiment on water will reveal novel characteristics of short-time quantum dynamics of protons (and H-bonds) in condensed matter. ■

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QUANTUM ENTANGLEMENT (QE) OF TWO SYSTEMS

Consider two dice (say, A and B) which are rolled. As conventionally assumed, each dice on its own should be fair and yield random results. The two outcomes of a throw with the two dice are then completely uncorrelated.

Of course, dice are classical objects. Nevertheless let us now make the (fictitious) assumption that the two dice are quantum objects. After rolling of the dice pair, its wavefunction, say Ψ_{AB} , can be constructed with the aid of the "single-dice" wavefunctions $\Psi_A(i)$ and $\Psi_B(j)$, where i and j are possible outcomes, that is, natural numbers from 1 to 6. There are many different forms of Ψ_{AB} that are permissible according to quantum theory. Some of them – in fact, the majority of them – appear to have completely counter-intuitive properties. Here let us give a particular example of

such a state (which is adapted from Ref. [2]). E.g., for the specific case of "equal outcomes", the following dice-pair wavefunction (before an actual measurement of the outcomes; see below) is permissible according to the fundamental Superposition Principle of quantum mechanics (see any textbook):

$$\Psi_{AB} = \text{const.} * [\Psi_A(1) * \Psi_B(1) + \Psi_A(2) * \Psi_B(2) + \dots + \Psi_A(6) * \Psi_B(6)] \quad (1)$$

The physical meaning of this Ψ_{AB} may be described as follows: The outcomes of both dice A and B are equal to 1 and, at the same time, they are equal to 2,, and, at the same time, they are equal to 6. This specific quantum state has no classical analogue and thus it is completely counter-intuitive.

An actual measurement of the two outcomes "reduces" Ψ_{AB} to another wavefunction, say Φ_{AB} . E.g., if one

actually measures a "double 5", then the wavefunction of the dice pair after the measurement is

$$\Phi_{AB} = \Psi_A(5) * \Psi_B(5) \quad (2)$$

[This is according to the standard theory of measurement; in technical terms, applying the von Neumann projection postulate.] Clearly, in contrast to (1), the wavefunction (2) has a classical analogue.

A pair of quantum systems being in a quantum state like (1) – but not like (2) – is called entangled. Quantum states like (1) are also called Schrödinger's cat states, Einstein-Podolsky-Rosen states, etc. Nowadays, entangled pairs of quantum objects (e.g., photons or ions, which must be very well isolated from their environment) can be produced in the laboratory; cf. [2].