Isotopic Quantum Effects in Water

Quantum mechanics plays an important role in describing the properties of water and intermolecular hydrogen bonding interactions in aqueous solutions. The most commonly recognized "quantum effect" is the freezing point of heavy water, D_2O, at 4°C [1] yet these effects also have implications for many biological processes, as high levels of D_2O are known to be toxic. From a chemical physics perspective, standard classical simulations on water using any simple potential will predict identical structural and thermodynamic properties for both H_2O and D_2O. The zero point motions of light and heavy water molecules therefore need to be included to provide an accurate description of the structure of liquid water. These motions are governed by quantum mechanical vibrations, rotations and translations.

Heavy water is closer to the classical approximation whereas light water exhibits larger degree of motion [2]. Quantum effects appear as small differences in the X-ray structure factor for different isotopic enrichments of water.

High energy diffraction technique experiments on H_2O and D_2O provide a direct insight into the quantum mechanical part of the hydrogen bond in water, information which is not accessible using neutron diffraction. At beamline **BL04B2** the effects of substituting the hydrogen for deuterium as well as the oxygen isotope ^{16}O for ^{18}O have been measured. The total mass change from $H_2{}^{16}O$ to $H_2{}^{18}O$ is the same as $H_2{}^{16}O$ to $D_2{}^{16}O$ but the mass distribution is different. Since the oxygen atom is nearly at the center of mass of the molecule, the effect of substitution at the proton sites (D for H) is dominated by rotational and vibrational molecular motions, while hindered translational motions may be expected to be the most prevalent effect in $^{16}O/^{18}O$ substitution. The structural isotope difference for the $^{16}O/^{18}O$ substitution is found to be approximately one quarter of the magnitude of the observed H *versus* D effect [3]. The experiment shows that the $^{16}O/^{18}O$ substitution effect is small and limited to the first coordination shell, while a simulation has predicted larger structural rearrangements in both the first and second coordination shells [4].

At 26°C it has been found that H_2O may be considered to have the same structure as D_2O at ~32°C [5]. This difference increases dramatically at lower temperatures due to quantum mechanical tunneling [1]. Quantum molecular dynamics simulations [2] have show that water is essentially tetrahedral with an additional loosely bound fifth molecule, and as the quantum effects increase the average distances of the tetrahedra increase. Our experiments have shown that the total structural isotope effect increases by a factor of 3.5 as the temperature is decreased from 45°C to -5°C [3].
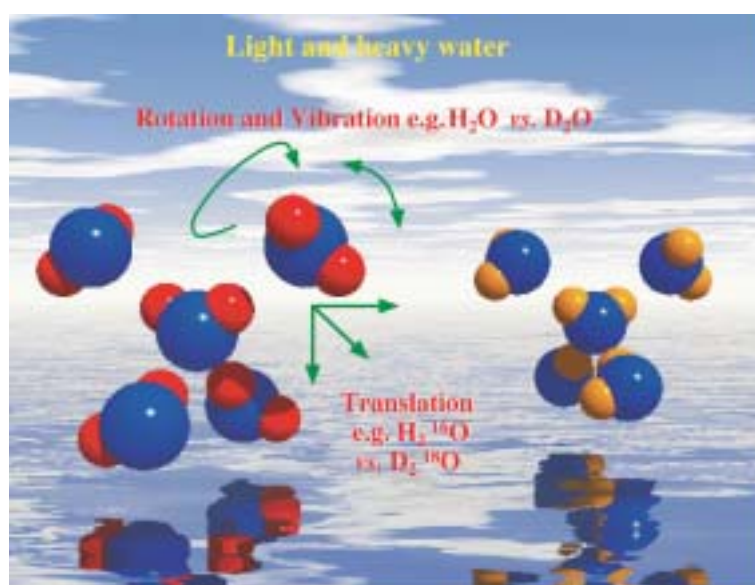

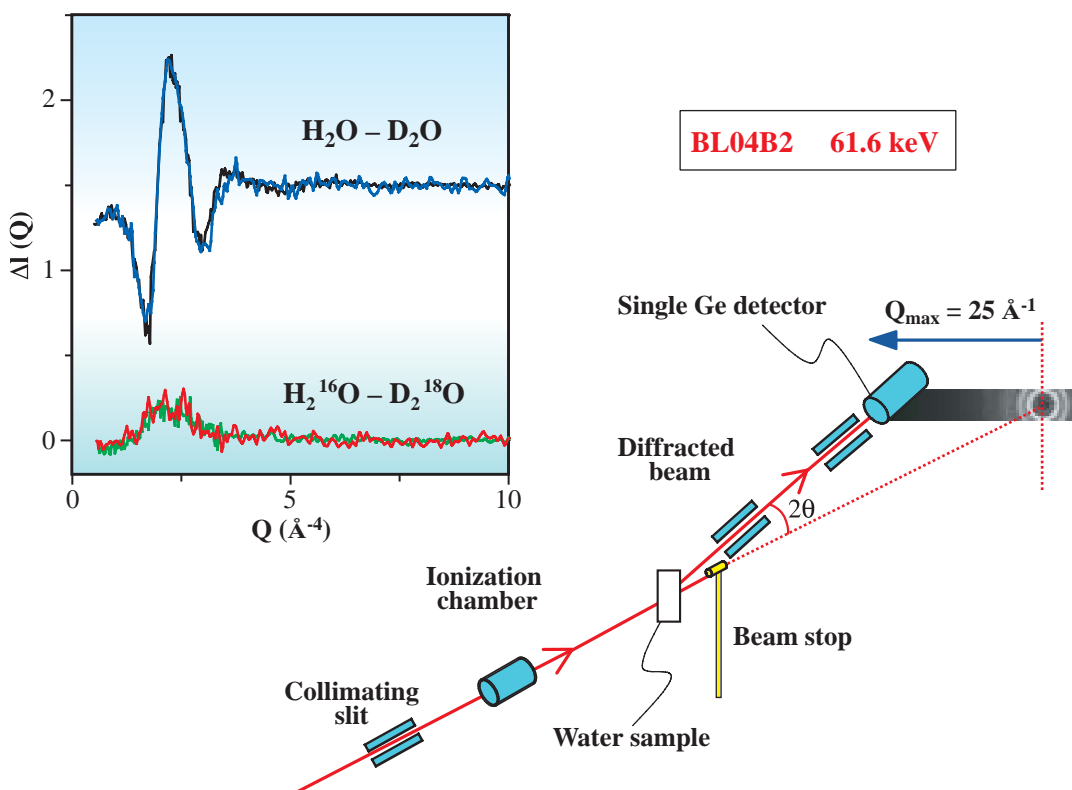Fig. 1. Representation of the local structure and motion of water molecules.

BL04B2   61.6 keV

Fig. 2. Schematic diagram of high energy diffraction set-up and isotopic differences for H/D and $^{18}O/^{16}O$ substitutions.
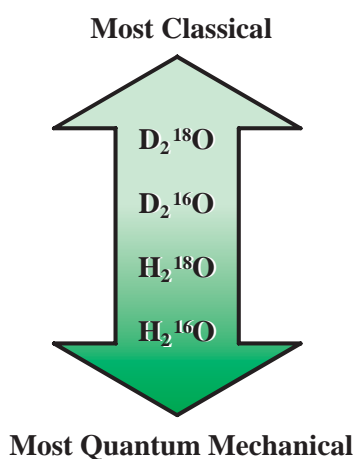

Fig. 3. Variations in quantum mechanical behavior of different isotopes of water.

C. J. Benmore[a,*], J. Neuefeind[b] and S. Kohara[c]

[a] Intense Pulsed Neutron Source and Advanced
   Photon Source, Argonne National Laboratory, USA
[b] Spallation Neutron Source, Oak Ridge National
   Laboratory, USA
[c] SPring-8 / JASRI

*E-mail: Benmore@anl.gov

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