A new technique for understanding quantum effects in water

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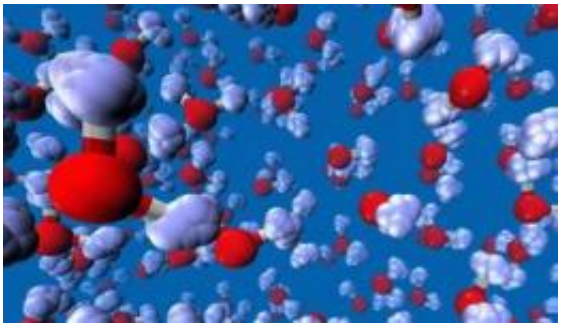

A snapshot taken from a path integral molecular dynamics simulation of liquid water. The oxygen atoms are shown by red spheres and the hydrogen atoms are shown by multiple white spheres (bubbles) which represent their positional uncertainty in the quantum simulation.

It covers over two thirds of our planet, is essential for life on Earth and its chemical formula is one of the few most people can name, but we still have much to learn about the structure of H2O. Now, scientists working in Grenoble have developed a new technique using oxygen isotopes to study in detail the structure of disordered oxide materials such as water in biological processes or glasses in lasers and telecommunication devices. This new technique allowed a team from the Institut Laue-Langevin (ILL), University of Bath, Oak Ridge National Laboratory and Stanford University to validate a new theoretical model for water's structure by measuring subtle differences between the molecular organisation of light and heavy water that result from quantum

mechanics.

At ILL the structural properties of materials are probed by using neutrons, which act like “super x-rays”, via a technique known as neutron scattering. As neutrons pass through materials they are often bounced (or scattered) by atomic nuclei which alters their trajectories, and these scattered neutrons can then be detected to create detailed maps of a sample’s molecular structure. To find out more about the positions of particular atoms within a sample, scientists use a trick called isotopic substitution where the scattering length (or ability to bounce neutrons) of a particular element is ‘tuned’ by substituting one of its isotopes for another. This allows them to zero in on the structure around the atoms of the chosen element.

In modern structural analysis, researchers commonly interchange hydrogen with its heavier isotope deuterium to probe the locations of atoms in water or other hydrogen containing materials. This technique of ‘H/D substitution’ is also commonly used in the analysis of hydrogen-storage materials or fuel cells. However, there are problems with using H/D substitution in neutron scattering. The lighter hydrogen isotope is comparable in mass to the neutron which generates imprecise scattering data and makes determination of structure more difficult. Also, you can’t use H/D substitution to study the difference between the positions of hydrogen atoms in H2O versus deuterium atoms in D2O as the technique assumes that H and D atoms have the same positions.

Oxygen has three isotopes: 16O, 17O and 18O and, like hydrogen, is a ubiquitous element on Earth and plays an important role across scientific disciplines. It is often found in structurally disordered materials like silicates in planetary science, glasses for lasers and optical communications, oxide layers in silicon-based electronic devices and water in biological processes. However, it was generally believed that the difference in scattering length between these isotopes is too small to

make isotopic substitution with neutron scattering feasible.

The team at ILL challenged this assumption via neutron interferometry – a technique where neutrons, acting as coherent quantum waves, allow for a very precise measurement of the scattering lengths of atoms in a sample. With the highly sensitive equipment at ILL, the team showed that the difference between the scattering lengths of two of the oxygen isotopes was actually six times larger than the literature suggested.

Professor Philip Salmon, from the University of Bath, said: "With this larger contrast, we showed the difference in the scattering lengths of the oxygen isotopes was just about large enough to make neutron scattering a plausible technique for studying the structure of oxide materials."

In order to demonstrate the powerful potential of their new technique, the team turned to the structure of the best-known oxide in nature - liquid water where the imprecise results from hydrogen isotope substitution had created some uncertainty. In particular, the team were interested in comparing structural differences between light water (H2O) and heavy water (D2O).

"The structure and dynamics of water have long been controversial subjects since they can have profound effects on biological processes, and there can be dramatic differences between heavy and light water. For example, most organisms eventually perish in a D2O environment, whereas they thrive in H2O", said Dr Henry Fischer, a physicist at ILL who worked alongside Prof Salmon on this paper.

Using oxygen isotope substitution, Prof Salmon and his team at ILL analysed the difference between the lengths of the O-H and O-D bonds within water molecules. They found that the O-H bonds were ½ % longer than the O-D bonds – the first time anyone had measured with such pin-point accuracy this important difference between the molecular

structures of light and heavy water.

Their findings were then compared with quantum mechanics predictions using path-integral methods to see if they could clarify some uncertainty around the structural model for liquid water. Earlier mathematical models often assumed simple rigid molecules, where the bond lengths do not vary, but it turns out that such models are not sufficient to account for the quantum effects leading to the observed structural differences between H2O and D2O. Quantum mechanics gives a fuzzy uncertainty to the positions of the H and D atoms in a water molecule, and since D is twice as heavy as H, the fuzzy effect is not as strong for D as compared to H. This leads to the observed structural differences which can be predicted using a more appropriate flexible model for the water molecule.

Salmon and his team thus identified the type of theoretical model that is needed for understanding the true structure of water, and confirmed that this model can explain the structural differences between H2O and D2O due to quantum mechanics.

More information: *Phys. Rev. Lett.*, 107, 145501 (30 September, 2011) prl.aps.org/abstract/PRL/v107/i14/e145501

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