Searching for an explanation for remarkable behavior of ice on Earth

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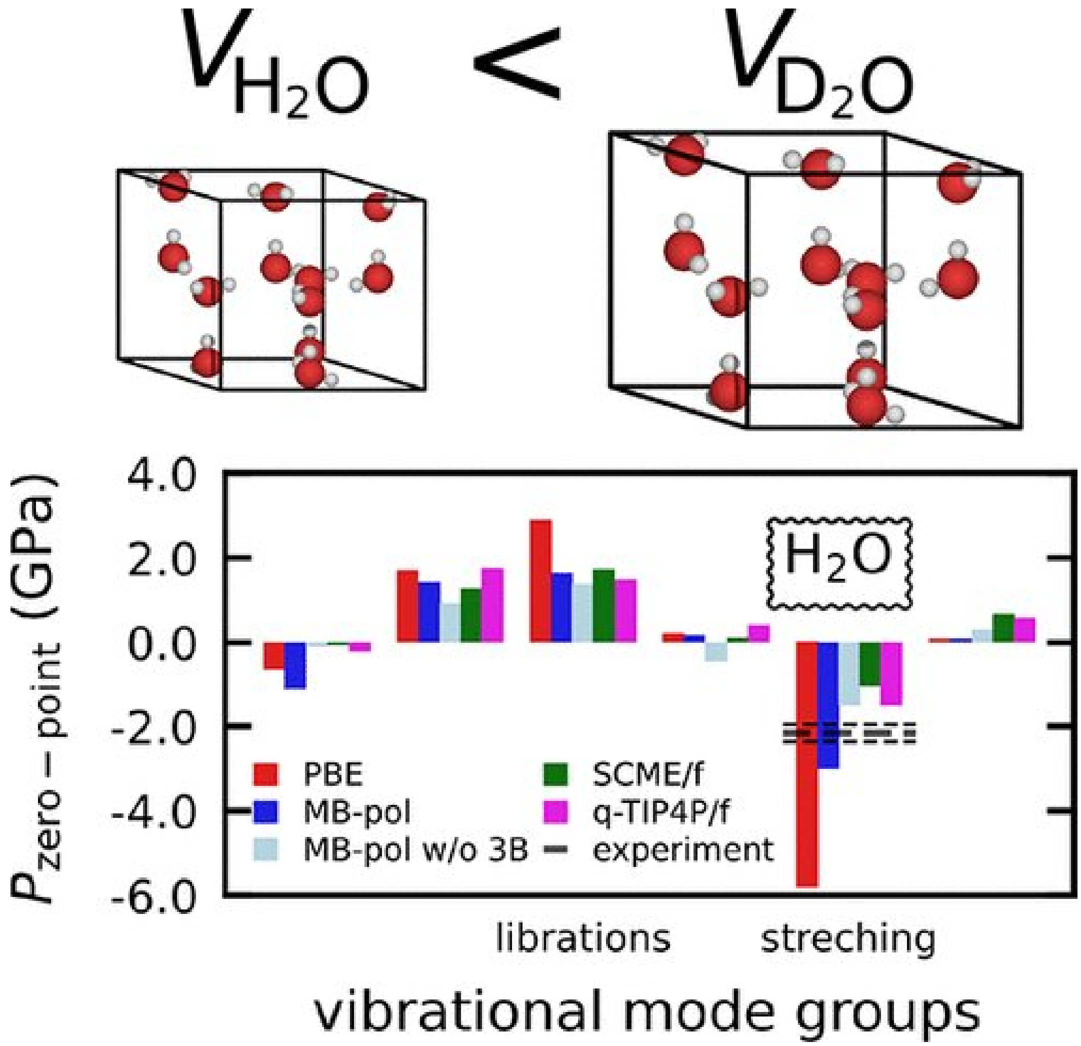

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If you replace the standard hydrogen atoms in ice with a heavier variant, something odd happens. The volume occupied by the molecules increases by 0.1%. Leiden chemist Jörg Meyer and his colleagues have created a theoretical model that describes this behavior. Their research appeared on the cover of the *Journal of Physical Chemistry Letters*.

The volume occupied by a certain type of molecule changes when you replace the atoms present for a heavier variant. This effect is called the volume isotope effect, abbreviated VIE. Variants of a chemical element with different weights, are called isotopes. For example, you have "regular" hydrogen and "deuterium," a hydrogen atom that is heavier due to the addition of a neutron in its nucleus.

Most materials have a normal VIE, where the volume of a given quantity of molecules decreases when you replace light isotopes with heavier ones. "In the most common form of ice on Earth, the volume actually increases," Meyer says. "That is counterintuitive. Simply put, heavier isotopes actually constrain the vibrations of molecules in a material. As a result, the molecules need less room to move and the volume decreases. But in ice, strangely enough, the volume seems to increase if you replace hydrogen with deuterium: the heavier isotope."

Hexagonal ice crystals

The researchers focused on ice Ih: the most common form of frozen water on Earth. The h indicates the crystal structure, which is hexagonal.

Ice is not the only material with an anomalous VIE. You also see it in semiconductors, for example. By finding a theoretical description of this counterintuitive behavior, the researchers hope to learn more about the properties of these materials and the chemical bonds that hold them together.

To theoretically describe the volume effect, the researchers use a so-called interaction potential formula. The formula approximates what happens at a molecule level, as it is impossible to precisely describe all quantum mechanical interactions that occur. "Almost all interaction potentials predicted that the volume of ice gets smaller when you replace hydrogen atoms with deuterium atoms," says Meyer. "Only the one from a U.S. research group gave a larger volume, as we see in reality."

Vibration modus influences the volume

The researchers analyzed the American interaction potential in detail. The analysis showed that the anomalous volume isotope effect of ice has to do with the different ways in which molecules can vibrate in a crystal structure. In a water molecule, for example, the hydrogen atoms can spring back and forth in the direction of the oxygen atom or the whole molecule bends back and forth.

In ice, this results in two vibration modes: In ice, there are therefore two possibilities: in the so-called stretch-vibration mode, water molecules exhibit a kind of internal vibration. For this, they do not need as much space and they can be close together. In the other, so-called vibrational mode, the molecules demand more space. "This is similar to someone forcing bystanders to make space by waving their elbows," says Meyer.

Heavier isotopes mean more vibration and more space

If you replace hydrogen atoms in ice with deuterium atoms, it turns out that the influence of the vibrational mode increases at the expense of the influence of the stretching mode. This causes the molecules to bump away from each other more, taking up more space and increasing the volume. Meyer says, "That is a simple analogy of the complex quantum mechanical effect that occurs in reality."

"One of the surprising things about the interaction potential is that three-body interactions, involving more than two molecules, turn out to play an important role for the volume effect, while in the case of inter-molecule bonding it hardly plays a role at all. Ice continues to amaze us."

More information: Soroush Rasti et al, New Insights into the Volume Isotope Effect of Ice Ih from Polarizable Many-Body Potentials, *The Journal of Physical Chemistry Letters* (2022). DOI: 10.1021/acs.jpclett.2c03212

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