

H₂O molecular network hosted by crystal lattice of a dielectric: new state of water?

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The physical properties of bulk water are extremely complex, be it liquid or solid, due to specific features of the H₂O molecule, such as highly-directional hydrogen bonds (H-bonds), relatively small moment of inertia or large dipole moments. Novel properties of water can arise when its molecules or molecular groups get confined within micro- or nano-sized spaces. Since these kinds of objects are widespread in various technological, geological, meteorological, biological, etc. systems, there is an urgent need to study their physical properties. However, along with large number of theoretical studies and computer simulations, the respective experimental observations are rather poor and often controversial.

We carried out a series of experiments using objects that are very convenient and thereby model systems for this type of research. These are dielectrics whose crystal lattice contains nano-sized cages in which distinct water molecules are placed during crystal growth. The H₂O molecules are weakly coupled through van der Waals forces to the lattice that serves as a matrix. This matrix holds the molecules at a distance (5-10 Å) large enough to suppress the H-bonding, but relatively close for an effective electrical dipole-dipole interaction. The resulting water molecular network can be considered to form a state that is intermediate between that of liquid water (H-bonded H₂O) and water vapor (quasi free molecules).

Using radio-frequency, terahertz, and infrared spectroscopy, we have studied the energetics of water subsystems in a number of dielectrics, such as beryl, cordierite, and bikitaite. We have discovered an incipient ferroelectric phase within the dipole-dipole interacting H₂O molecules in beryl and cordierite. Specific librational and translational excitations of separate water molecules confined within the nanocages in the crystals have also been observed. At infrared frequencies, combined excitations arising from the coupling between H₂O intramolecular and lower-frequency modes were seen. Isotope effects caused by replacement of H₂O with heavy water are also investigated, as well as the effects of symmetry of the hosting crystal lattice and the dimensionality on the water molecular subsystem. In order to analyze the observed effects, computer simulations within the density-functional-theory approach were performed.

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