

H₂O Molecules Hosted By A Crystalline Matrix – New State Of Water?

Elena S. Zhukova¹, M. A. Belyanchikov¹, M. Savinov², P. Bednyakov², V. G. Thomas³,
 L. S. Kadyrov¹, E. A. Simchuk¹, Z. V. Bedran¹, V. I. Torgashev⁴, A. Dudka⁵, M. Dressel^{1,6},
 B. P. Gorshunov¹.

¹ Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, 141700 Russia, zhukova.es@mipt.ru

² Institute of Physics AS CR, Na Slovance 2, 18221 Praha 8, Czech Republic

³ Institute of Geology and Mineralogy, RAS, 630090 Novosibirsk, Russia

⁴ Faculty of Physics, Southern Federal University, 344090 Rostov-on-Don, Russia

⁵ Shubnikov Institute of Crystallography, Federal Scientific Research Centre “Crystallography and Photonics”, Russian Academy of Sciences, 119333 Moscow, Russia

⁶ 1. Physikalisches Institut, Universität Stuttgart, 70569 Stuttgart, Germany

Along with the liquid and solid phases of water, there are many natural and artificial systems and objects - biological, geological, meteorological, physical, chemical, etc., in which water molecules are found in nano-confined state. As in the case of any other material, in such conditions water must acquire qualitatively new characteristics and properties that it did not possess in its macroscopic liquid state. Currently, there is a surge of active research on such properties, which is stimulated by the importance of obtaining new knowledge about the environment, the need to solve actual problems of medicine and public health, the creation of qualitatively new devices, mechanisms and technologies, materials with new characteristics that are promising for use in bio-sensors, diagnostics and in many other applications. It is known that the properties of liquid water remain less understood in comparison with other liquids, which is largely due to the ability of H₂O molecules to form hydrogen bonds with each other. Under the conditions of a nano-confinement these properties will become even more exotic, diverse and complex, especially in complex systems such as biological. Therefore, the most effective would be to study first as simple system as possible. We have studied an array of *single* H₂O molecules distributed over a periodical matrix of nano-sized cages inside the crystal lattice of dielectrics, see Fig. 1. The advantages of such objects are the absence of short-range intermolecular hydrogen bonds (the distance between the pores is 5-10 Angstroms), the complete certainty of the spatial arrangement of the cages, and hence the H₂O molecules, as well as the known type and magnitude of the interaction of molecules with the environment (weak van der Waals bonds) and between themselves (long-range electric dipole-dipole interaction). Importantly, these factors are essential from the point of view of simplifying and hanging the accuracy of the model analysis (molecular dynamics, density functional methods, ...) of the properties of the subsystem of water molecules.

Using broad-band spectroscopy (frequencies from ~1 Hz up to the visible, temperatures from 300 K down to 0.3 K) we have studied specific single-particle and collective excitations of water molecular ensemble hosted by dielectric crystalline matrices of hexagonal beryl Be₃Al₂Si₆O₁₈ and orthorhombic cordierite

(Mg,Fe)₂Al₄Si₅O₁₈. Experiments on dehydrated crystals allowed to identify spectral features connected exclusively with the response of water molecular subsystem. We observe well-known H₂O intramolecular modes together with librational and rattling-like translational excitations of separate water molecules confined within the nano-cages. Using density-functional and molecular dynamics approaches allowed us to identify the origin of the single-particle modes. In crystals of beryl containing both, regular and heavy water molecules we discovered an incipient ferroelectric state within water molecular subsystem that manifests itself in the form of a Curie-Weiss temperature dependence of quasi-static permittivity

$$\varepsilon'(T) = \varepsilon_{\infty} + C(T - T_C)^{-1},$$

where ε_{inf} is the high-frequency dielectric constant, C and T_C are the Curie constant and Curie temperature, respectively. Below ≈10 K the behavior $\varepsilon'(T)$ saturates that can be described by the Barrett expression [1]

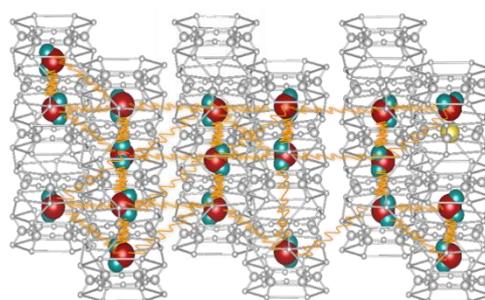
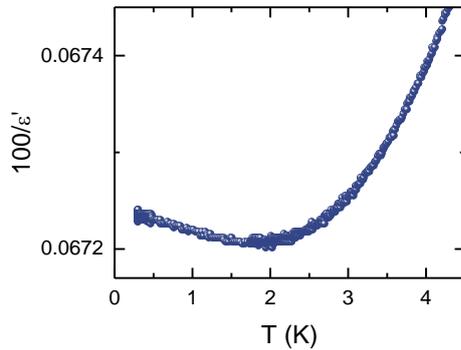


Fig. 1. Schematic view of a crystal lattice of beryl with nano-sized cages formed by ions of crystal lattice. The cages are arranged in channels that are elongated along crystallographic c-axis. Single water molecules are captured within the cages during crystal growth. The distance between H₂O molecules along the channels is about 5 Angstroms and between H₂O molecules in neighboring channels about 10 Angstroms. Orange lines denote intermolecular electric dipole-dipole interaction.

$$\varepsilon' = \varepsilon_{\infty} + \frac{C}{\frac{T_1}{2} \coth \frac{T_1}{2T} - T_C}$$

where C is constant and T_1 gives the energy scale of quantum fluctuations that are suppressing the macroscopic ferroelectric phase transition. We suggest that



quantum tunneling is responsible for the suppression of ferroelectric phase transition, as confirmed by neutron experiments [2].

Fig. 2. Temperature-dependent inverse dielectric permittivity of an array of nano-confined water molecules in beryl crystalline matrix measured at 1 kHz.

As seen from Fig.2, the inverse dielectric permittivity displays weak minimum at the lowest temperatures. This effect can be considered as either coming from onset of short-range spatial ferroelectric (antiferroelectric) correlations between the dipole moments or signs

of quantum critical behavior of water molecular electric dipoles. Further experiments are needed to clarify this point.

The specific potential profile experienced by the water molecules localized within the nano-cages of cordierite leads to emergence of an overdamped temperature dependent relaxation at radiofrequencies and a rich set of excitations in the terahertz range. The origin of both types of excitations needs detailed investigation.

In conclusion, spectroscopic studies of an array of dipole-dipole interacting water molecules localized within nano-sized cages of crystal lattice of dielectrics demonstrate a rich set of excitations that are not observed in liquid water. The corresponding H_2O molecular network can thus be considered as a model system whose studies will allow to proceed to investigations of more complicated water-containing objects.

The work was supported by Russian Foundation for Basic Research program Project No 18-32-00286.

References

1. *Barrett, J. H.* Dielectric constant in perovskite type crystals // *Phys. Rev.* 1952. V. 86, P. 118–120.
3. *Kolesnikov A. I.* et al. Quantum tunneling of water in beryl: a new state of the water molecule // *Phys. Rev. Lett.* 2016. V. 116, P. 167802.