Quantum behaviour of water molecule in gemstone: terahertz fingerprints

Elena S Zhukova[1,2,3], Boris P Gorshunov[1,2,3], Victor I Torgashev[4], Vladimir V Lebedev[2,5], Gil'man S Shakurov[6], Reinhard K Kremer[7], Efim V Pestrjakov[8], Victor G Thomas[8], Dimitry A. Fursenko[8] and Martin Dressel[2]

[1]A M Prokhorov General Physics Institute, Russian Academy of Sciences, Russia
[2]Physikalisches Institut, Universität Stuttgart, Germany
[3]Moscow Institute of Physics and Technology, Russia
[4]Faculty of Physics, Southern Federal University, Russia
[5]Landau Institute for Theoretical Physics, Russian Academy of Sciences, Russia
[6]Kazan Physical-Technical Institute, Russian Academy of Sciences, Russia
[7]Max-Planck-Institut für Festkörperforschung, Germany
[8]Institute of Laser Physics, Russian Academy of Sciences, Russia

E-mail: gorshunov@ran.gpi.ru

Abstract. We have shown that a weak interaction of a lone H2O molecule with the "walls" of nano-sized crystalline cage of gemstone (beryl) results in emergence of a rich set of molecular vibrational states. By analogy with translational and librational bands in liquid water and ice corresponding absorption bands are explained as due to translational (T) and librational (L) movements of the H2O molecule which is hydrogen bonded to the cage walls. In beryl crystal lattice, however, the six-fold symmetry of the cage brings about additional effect of splitting of the T and L bands into fine structure due to tunnelling within the six-well potential relief. The presented results will be of use for analysis of more complicated systems with confined water molecules like H2O chains in carbon nano-tubes, molecular clusters in e.g. zeolites, clays, silica gels and other natural or synthetic frameworks, as well as for interfacial water in biological systems.

1. Introduction and background

Water is a chemical compound most pervasive on the Earth, liquid is most studied by physics, chemistry and biology [1]. Nevertheless, despite a simple structure of the H_2O molecule, water probably is the least understood of all liquids because of the complex network of hydrogen bonds. Water in contact with solid surfaces [2],[3] or single macromolecules, for instance proteins [4], forms a hydration layer in which a gradual transition from bound towards bulk water takes place. Although the characteristic network becomes less dynamic, weak hydrogen bonds allow librations, i.e. restricted rotations of the water molecules, which survive even in solid ice. Here we investigate single water molecules confined to nano-scale cages present in the crystal lattice of gemstone beryl $Be_3Al_2Si_6O_{18}$. Such nano-cages provide a well-defined environment for the water molecules that can be modeled and understood in great detail.

2. Results

Using coherent source terahertz spectroscopy in combination with infrared Fourier-transform spectroscopy, we have measured the water-related absorption spectra in beryl crystal for two principle polarizations (electrical field vector of radiation **E** parallel and perpendicular to the c-axis) at frequencies 7 cm^{-1} to 7000 cm^{-1} and at temperatures from 300 K down to 5 K. We have observed quantum behavior of the confined H_2O molecules of type-I and type-II (figure 1). Via tunneling processes the wave functions of the type-I molecules hybridize and the discrete energy levels broaden to form bands. In highly anisotropic absorption spectra we identify transitions between and within these bands related to librational and translational motions similar to those present in ice and liquid water.

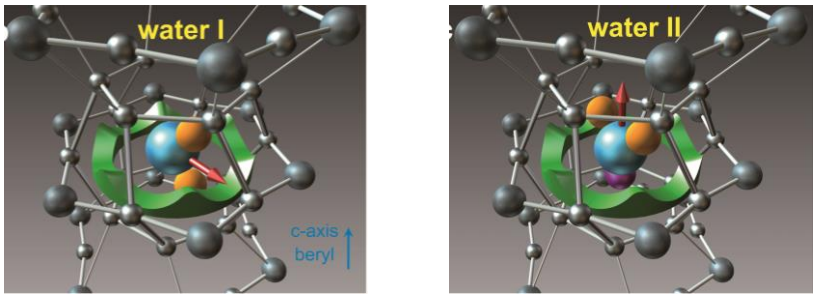

Figure 1. Honeycomb crystal structure (space group P6/mcc) of beryl contains open nano-channels that extend along the c-direction. They contain cavities of 5.1 Å diameter connected by bottlenecks of 2.8 Å size. Crystal water molecules enter the cavities and are oriented with the dipole moment (red arrows) either perpendicular (A) or parallel (B) to the c-direction. Hydrogen bonds weakly connect the water molecules to surrounding oxygen atoms as indicated by the green belt that resembles the periodic potential.

References

[1] Lynden-Bell R M, Morris S C, Barrow J D, Finney J L, Harper C L 2010 *Water and Life* (CRC Press, Boca Raton)
[2] Thiel P A and Madey T E 1987 The interaction of water with solid surfaces: fundamental aspects *Surf. Sci. Reports* **7** 211
[3] Henderson M A 2002 The interaction of water with solid surfaces: fundamental aspects revisited *Surf. Sci. Reports* **46** 1
[4] Ball P 2008 Water as an Active Constituent in Cell Biology *Chem. Rev.* **108** 74