

# Broadband Spectroscopy of H<sub>2</sub>O Molecule Confined in Nano-Cages of Crystal Lattice: Low-Energy Dynamics and Incipient Ferroelectric Behavior

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**Abstract**—Broadband (1 Hz to 100 THz) dielectric response of water-containing beryl crystals was measured at temperatures from 300 K down to 0.3 K. The low-energy dynamics of H<sub>2</sub>O molecules confined within nano-cages of the crystalline lattice was studied. We observe a THz-range soft mode indicating an incipient ferroelectric behavior due to interacting dipole moments of confined water molecules.

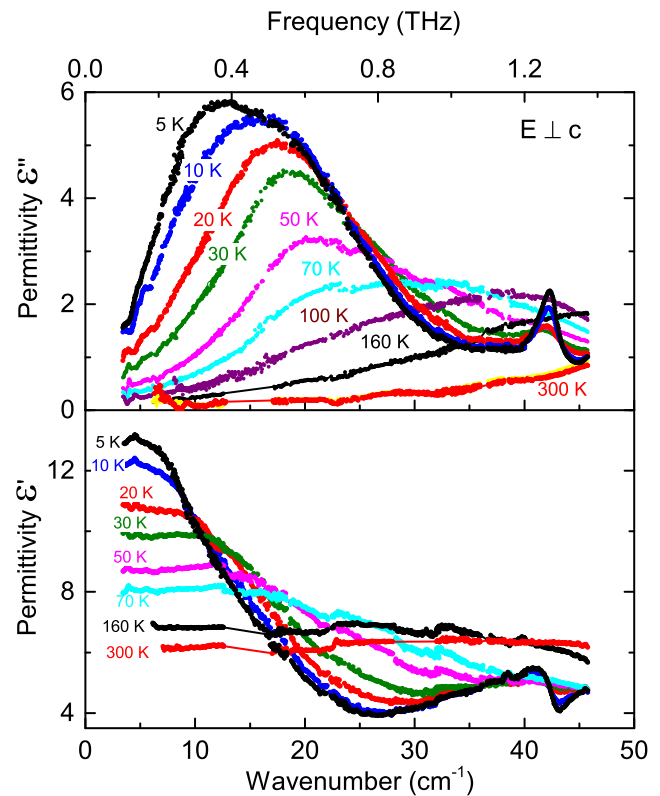
transform and impedance spectroscopies) we measured the spectra of complex dielectric permittivity  $\epsilon^* = \epsilon' + i\epsilon''$  of several water-containing beryl crystals in an extremely broad frequency interval (1 to 10<sup>14</sup> Hz) at temperatures 0.3 – 300 K. We studied several crystalline samples grown as described in [3] containing regular and heavy water molecules. Our

## I. INTRODUCTION

ALTHOUGH bulk water is one of the most widespread substances on the Earth, its physical properties are extremely complicated and far from being fully understood. They become more diverse when H<sub>2</sub>O molecules or molecular clusters are confined in nanosized cavities. Studying these properties is of great importance due to the widespread occurrence of confined water in nature: cells, membranes, enzyme channels, carbon nanotubes, fullerenes, porous silica, molecular sieves, zeolites, rocks, clays, etc. Due to an extreme complexity of the corresponding phenomena, it appears appropriate to begin with the “simplest” system possible. A model case is provided by beryl crystals Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>. Their hexagonal structure consists of stacked six-membered rings of SiO<sub>4</sub> tetrahedra that leave open channels along the *c* crystal axis [1]. The channels include 5.1 Å wide cages separated by “bottlenecks” 2.8 Å wide. During the crystal growth in an aqueous environment and under pressure, single H<sub>2</sub>O molecules reside within the cages [2]. Thus, beryl most likely represents the simplest possible case of nanoconfined water – single H<sub>2</sub>O molecules within a well-defined symmetric (crystallographic) environment. While interacting only weakly (via van der Waals interactions) with the cages’ “walls”, the H<sub>2</sub>O molecules are intercoupled via dipole-dipole interactions.

## II. RESULTS AND DISCUSSIONS

Using a set of spectroscopic techniques (frequency-domain backward-wave oscillator, pulsed time-domain, Fourier-



**Fig.1.** Temperature evolution of the *water-related* soft mode in the terahertz spectra of real (lower panel) and imaginary (upper panel) parts of the dielectric permittivity of H<sub>2</sub>O containing beryl crystal for the polarization with electric field vector perpendicular to the crystallographic *c*-axis.

measurements and analyses of both water-containing and water-free samples allowed us to extract the response determined *exclusively* by nanoconfined water molecules, with the phonon contributions subtracted.

We identified infrared range resonances caused by translational and librational movements of individual H<sub>2</sub>O molecules, as well as the intramolecular H<sub>2</sub>O vibrational modes [4]. We present a model that explains the “fine structure” of the infrared translational and librational bands (around 200 cm<sup>-1</sup> and 600 cm<sup>-1</sup>, respectively) by a splitting of the energy levels due to quantum tunneling between the minima in a six-well potential governing the motion of molecules within the nanocavities. At terahertz frequencies, below 60 cm<sup>-1</sup>, we have discovered an absorption resonance whose temperature evolution closely resembles the behavior of ferroelectric soft modes (Fig.1). The temperature dependence of its contribution to the dielectric permittivity is well described by the Curie-Weiss law which is typical for the paraelectric state in ferroelectrics. At the lowest temperatures we observe saturation of the dielectric contribution of the soft mode, of its eigenfrequency and of the lower-frequency dielectric constant, that are well described with the Barrett expression for incipient ferroelectrics [5], see Fig.2. The above-mentioned behavior is observed only for the polarization of the probing radiation where its electric vector is perpendicular to the crystallographic *c*-axis.

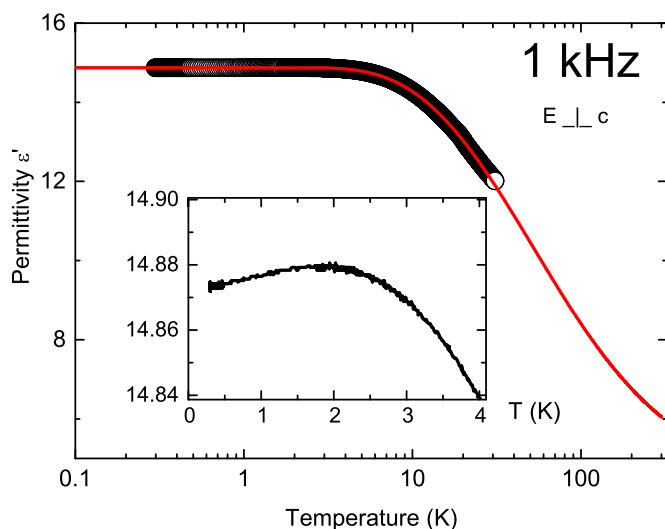


Fig.2. Temperature dependence of low-frequency dielectric permittivity of a water-containing beryl crystal for the polarization with electric-field vector perpendicular to the crystallographic *c*-axis. The line represents a fit to the data using the model by Barrett [5]. The inset shows the low-temperature part in an expanded scale: lowest temperature decrease of the permittivity can be an indicator of fluctuating ferroelectric order in the network of nanoconfined H<sub>2</sub>O molecules.

Our observations allow us to consider the broadband electrodynamic response of nanoconfined water molecules as a fingerprint of an incipient ferroelectric behavior in the network of H<sub>2</sub>O molecules that are periodically located within

the matrix of beryl crystal lattice at distances large enough to weaken hydrogen bonding but sufficiently close to keep the H<sub>2</sub>O-H<sub>2</sub>O dipole-dipole coupling strong, of order of 20 meV. Since the molecules have their dipole moments aligned perpendicular to the *c*-axis and these moments can loosely rotate, we assume that their reorientational-like motions are at the origin of incipient ferroelectric features seen in the water molecular subsystem, in accordance with computer simulations [6, 7]. At temperatures below about 100 K and frequencies of 30 – 60 cm<sup>-1</sup>, a series of narrow resonances were detected. We assign them to transitions between energy levels imposed to the water molecules by the minima of a six-fold potential relief that appears due to the interactions of the molecules with the cavity walls. Tunneling between potential minima can act as disorder mechanism that suppresses the ferroelectric phase transition.

### III. SUMMARY

Using a set of spectroscopic techniques, broadband (1 to 10<sup>14</sup> Hz) dielectric response of water-containing beryl crystals was measured at temperatures from 300 down to 0.3 K. Absorption resonances are recorded and studied that are connected with vibrations of single water molecules confined within nano-cages composed by ions of beryl crystal lattice. At terahertz and subterahertz frequencies (few wavenumbers to 60 cm<sup>-1</sup>) an absorption resonance is discovered whose frequency location strongly decreases while cooling: from ≈60 cm<sup>-1</sup> at 300 K to ≈15 cm<sup>-1</sup> at 5 K. Our analysis shows that the excitation can be associated with the ferroelectric soft mode that originates within the network of nanoconfined water molecules that interact via dipole-dipole interaction. Below ≈10 K this soft mode’s frequency saturates indicating an incipient ferroelectric behavior.

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