

Broad-Band Spectroscopy of Nanoconfined Water Molecules

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Abstract

We have performed broad-band spectroscopic investigations of vibrational and relaxational excitations of water molecules confined to nanocages within artificial beryl

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and mineral cordierite crystals. Signatures of quantum critical phenomena within the H₂O molecular network are registered in beryl. In cordierite, a density functional analysis is applied to reconstruct the potential energy landscape experienced by H₂O molecules, revealing a pronounced anisotropy with a potential well of about 10 meV for the molecular dipole moment aligned along the *b*-axis. This anisotropy leads to a strongly temperature dependent and anisotropic relaxational response of the dipoles at radiofrequencies with the activation energies corresponding to the barriers of the rotational potential. At $T \approx 3$ K, we identify signatures of a transition into a glassy state composed by clusters of H₂O dipoles. Rich set of anisotropic and temperature-dependent excitations are observed in the terahertz frequency range which we associate with rotational/translational vibrations.

Keywords

Nanoconfined water · Spectroscopy · Quantum criticality · Ferroelectricity

1 Introduction

A cutting edge of recent condensed-matter science is the study of phenomena occurring on the nanoscale, where qualitatively new properties can arise not known from the regular macroscopic bulk state of matter. Understanding the nature of the emerging new phases and their relations to the physical, chemical, geometrical, and morphological characteristics of the environment is of great fundamental and technological interest, but is presently still at its infancy. In the studies, special attention is paid to water due to its widespread prevalence and omnipresence on Earth and its critical importance for biological systems and organisms. Although the isolated H₂O molecule seems to be rather simple, bulk water remains one of the least understood liquids. Under the conditions of nanoconfinement, it acquires

an even greater variety of diverse and intriguing properties. Understanding such properties is important for geology, biology, mineralogy, ionic liquids, nanosciences and applications.

An ideal playground for the studies of confined water is provided by hydrated dielectric crystals whose ionic structure contains nanosized cavities with just a single water molecule. Among those systems, especially attractive are beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ and cordierite $(\text{Mg, Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$. Both include channels elongated along the *c*-axis that contain voids of 5.1 Å diameter, hosting single H_2O quasi-free molecule [1, 2]. The caged H_2O molecules are at a distance of approximately 5–10 Å and are thus free of H-bonds but coupled by electric dipole-dipole forces (the dipole moment of the water molecule is $p = 1.85$ Debye). In hexagonal beryl, water molecules experience a 6-well potential landscape with an amplitude of ≈ 1 meV. In orthorhombic cordierite the potential is fourfold and asymmetric with the deeper wells (≈ 10 meV) for the water dipole moment oriented along the *b*-axis. In this work we present the first experimental results demonstrating signatures of quantum critical phenomena within the H_2O molecular network within the crystalline matrix of beryl. First detailed measurements of broad-band dielectric spectra of cordierite reveal signatures of a transition into glassy state among clusters of H_2O dipoles. The results are obtained by applying radiofrequency and terahertz spectroscopic techniques supplemented by specific heat measurements and DFT analysis.

2 Experimental Details

All studied crystals were carefully analyzed by X-ray scattering and cut into slices needed for the polarization-dependent measurements. The results are obtained on artificial beryl [3] and mineral cordierite from India (the detailed location is unknown). The spectra of complex dielectric permittivity $\varepsilon^*(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu)$ were determined at radio and micro ($\nu = 1$ Hz–1.3 GHz) as well as terahertz ($\nu = 0.3$ –3 THz) frequencies in a broad temperature interval $T = 0.3$ –300 K and for three principle polarization directions $E||a$, $E||b$ and $E||c$. At radiofrequencies, we used a Novocontrol Alpha AN High Performance Frequency Analyzer, an Andeen-Hagerling 2500A capacitance bridge and a coaxial reflectometric technique employing an impedance analyzer (Keysight 4991B). For terahertz measurements, a commercial time-domain TeraView 3000 spectrometer was used. The dielectric experiments were complemented by measurements of the heat capacity in the relaxation method employing a PPMS system (Quantum Design). In all experiments, measurements on dehydrated samples allowed us to extract the characteristics determined exclusively by a network of water molecules.

3 Results and Discussion

In Ref. [3], incipient ferroelectricity was reported in a system of water molecules in beryl. It was shown that the ferroelectric phase transition was suppressed by quantum effects (tunneling of the dipole moments within the six-well crystalline potential [5, 6]) that emerge below 10–20 K. Here, we demonstrate that at these low temperatures the properties of the water subsystem reveal signatures of quantum critical behavior. The transition from the classical paraelectric regime to the state where quantum effects dominate is documented by the temperature behavior of the inverse dielectric permittivity, $(\varepsilon')^{-1}$, the parameter that is linked to the state of electrical polarization of the material. In particular, while cooling down below a certain classical-to-quantum regime crossover temperature, the Curie-Weiss behavior $(\varepsilon')^{-1} \sim T$ changes into a different form, $(\varepsilon')^{-1} \sim T^\gamma$, where the critical exponent γ approaches a value of $\gamma = 2$ or $\gamma = 3$ for multi-axial or uniaxial dipoles orientations, respectively [7–9]. Another dielectric indication of the closeness of the system to the quantum-critical point is provided by the existence of a shallow minimum in the temperature dependence of $(\varepsilon')^{-1}$ at the lowest temperatures. This minimum is considered to be caused by the coupling of the critical optical soft modes (lattice vibrations that drive the displacive ferroelectric transitions) to acoustical phonons. A similar minimum was observed, e.g., in the prototypical incipient ferroelectric SrTiO_3 , which is also close to quantum criticality at low temperatures [10]. According to Fig. 1, the observed temperature evolution of the low-frequency inverse permittivity $(\varepsilon')^{-1}$ in hydrous beryl exhibits these two typical signatures of quantum critical behavior in the form of its quadratic (not cubic—see lower inset in Fig. 1) variation with temperature over the 3–12 K interval and a shallow minimum in the $(\varepsilon')^{-1}(T)$ dependence below 3 K.

We thoroughly measured the dielectric response of nanoconfined water molecules in mineral cordierite in order to check for the possibility of a macroscopic ferroelectric phase transition that was not observed in beryl. According to our DFT analysis, the localizing potential is strongly asymmetric in this crystal and the H_2O molecules tend to align their dipole moment along the *b*-axis. From Fig. 2 it is seen that in the polarization $E||b$ the low-frequency permittivity is fully determined by single-particle excitations observed at terahertz frequencies, as discussed below. In the $E||a$ case, there is a pronounced peak in the $\varepsilon'(T)$ behavior that is caused by a strong temperature dependence of a broad relaxational excitation at radiofrequencies, as demonstrated in Fig. 3.

In Fig. 4 we present the peak frequency of this relaxation as a function of temperature. Though the data shown in Figs. 2, 3 and 4 resemble the dependences typical for relaxor

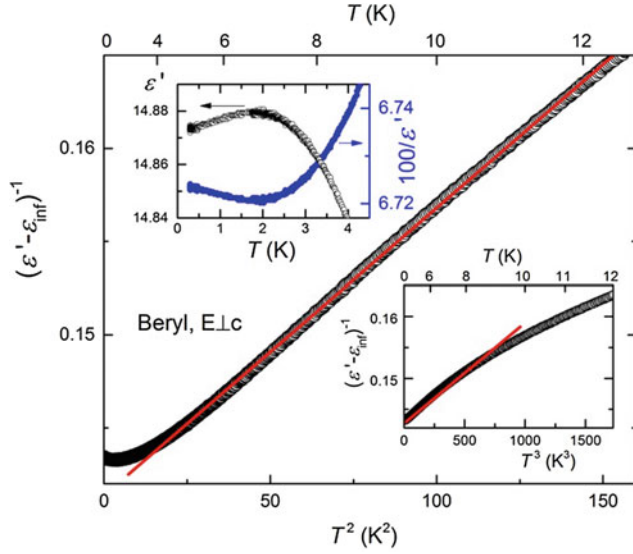


Fig. 1 Temperature dependence of the low-frequency (1 kHz) inverse dielectric permittivity $(\epsilon' - \epsilon_{\text{inf}})^{-1}$ plotted versus temperature squared, of a hydrous beryl crystal measured with $E \perp c$ polarization (dots). The red solid line demonstrates that the dependence is quadratic in temperature in the range 4–12 K and not cubic, as seen in the lower inset. $\epsilon_{\text{inf}} = 7.9$ is the high-frequency contribution to the permittivity from the lattice vibrations and interband transitions [4]. The upper inset shows the temperature dependence of dielectric permittivity and the inverse dielectric permittivity of nanoconfined water in beryl measured with polarization $E \perp c$. At around $T = 2$ K the dependences exhibit a shallow maximum and corresponding minimum, respectively

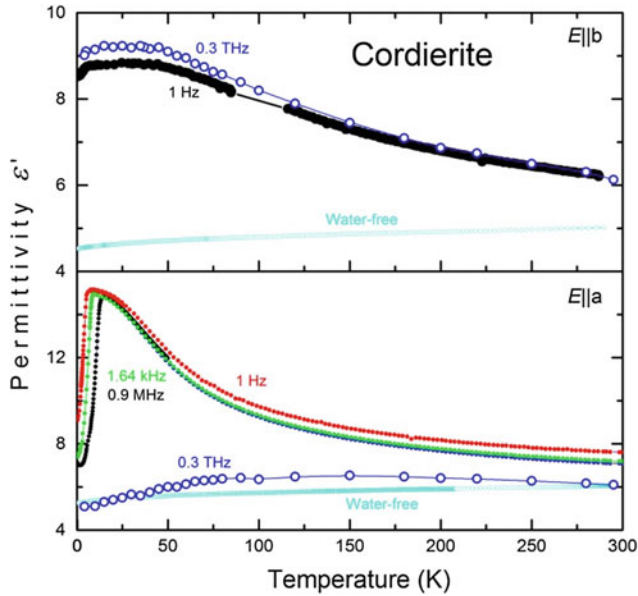


Fig. 2 Temperature dependences of real dielectric permittivity of nanoconfined water in mineral cordierite crystal measured at various frequencies for polarizations $E \parallel b$ (upper panel) and $E \parallel a$ (lower panel). WF denotes the data obtained on water-free (dehydrated) crystal

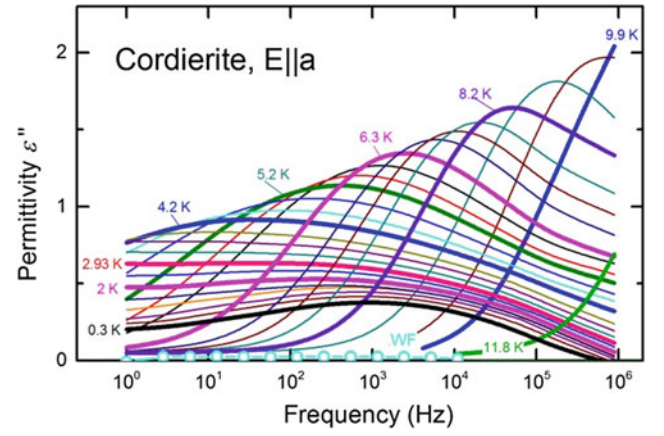


Fig. 3 Temperature-dependent relaxation in the radio-frequency spectra of nanoconfined water molecules in cordierite measured at various temperatures for polarization $E \parallel a$. WF (cyan symbols) denotes the spectrum measured on water-free (dehydrated) crystal

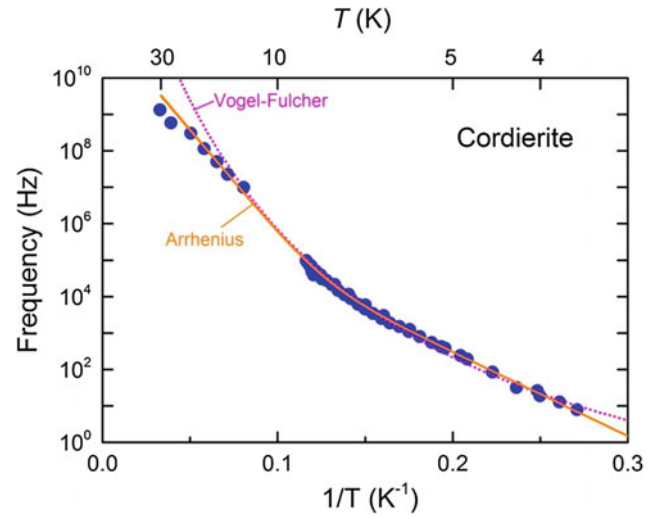


Fig. 4 Temperature dependence of the peak frequency of the relaxational excitation observed in the radio-frequency spectra of hydrous cordierite crystal, see Fig. 3. Solid line describes the data with the Arrhenius expression $A \exp(-E_1/k_B T) + B \exp(-E_2/k_B T)$ (A and B are constants) with two activation energies of 11.2 meV at $T \approx 10$ –30 K and 4.6 meV at $T \approx 4$ –7 K. Dotted line corresponds to the Vogel-Fulcher expression used to describe the dielectric response of relaxor ferroelectrics [11], $f_R = f_0 \exp[-U/kg(T - T_{VF})]$ where U is the activation energy, T_{VF} is the characteristic temperature and f_0 is the attempt frequency

ferroelectrics [10] (see also caption for Fig. 4), we exclude such scenario here for the following reasons: (i) the Vogel-Fulcher fit to the data (Fig. 4) leads to a *negative* divergence temperature $T_{VF} = -10 \pm 1$ K, that is of no physical meaning and (ii) the obtained Vogel-Fulcher attempt frequency $f_0 \approx 10^{16}$ Hz is unreasonably high—one

expects it to be of the order of phonon frequencies, i.e., 10^{12} – 10^{13} Hz. Fitting the temperature dependence of the peak frequency of the relaxational band at $3.5 \text{ K} < T < 30 \text{ K}$ with the Arrhenius expression $A \exp(-E_1/k_B T) + B \exp(-E_2/k_B T)$ (A and B are constants, k_B is the Boltzmann constant) results in the activation energies $E_1 = 11.2 \text{ meV}$ for $3.5 \text{ K} < T < 30 \text{ K}$ and $E_2 = 4.6 \text{ meV}$ for $4 \text{ K} < T < 7 \text{ K}$. We associate these energies with the potential barriers experienced by nanoconfined water molecules.

At lower temperatures, $T < 3 \text{ K}$, we observe a broad relaxation that *hardens* upon cooling (Fig. 3). We connect this behavior to smeared-out polar phase transition into a disordered low-temperature state among the 3D dipolar complexes of H_2O molecules that are coupled along the three crystallographic axes. This transition is also confirmed by an anomaly in the temperature dependence of the specific heat of the water subsystem detected at close temperature of $T \approx 6 \text{ K}$.

Figure 5 displays the terahertz spectra of the optical conductivity of water subsystem in cordierite. The response is strongly anisotropic. For the $E||a$ polarization it is in qualitative agreement with the predictions of the mean-field model described in Nakajima and Naya [12]: during cooling, the spectral weight of hindered rotational modes is transferred to librational oscillations of the dipole moments. The fine structure seen in the terahertz spectra at the lowest temperatures can be connected to transitions between the

tunnel-split energy levels caused by rotational tunneling of the H_2O molecule within the potential.

For the polarization $E||b$ we observe two terahertz excitations that significantly soften while cooling down. We associate them with translational vibrations of H_2O molecules located in the wells of the localizing potential. The softening of these modes should be connected with strong anharmonicity of the localizing potential.

4 Conclusions

Broad-band (radio-frequency up to terahertz) dielectric studies are performed of a network of interacting water molecules each confined to nanocage within the crystal lattice of hydrous beryl and cordierite. In hexagonal beryl, we identify signatures of quantum critical phenomena within the H_2O molecular network. In orthorhombic cordierite, radio-frequency relaxation is observed for the $E||a$ polarization that hardens at low temperatures. This behavior indicates a transition to a glass state within water molecular clusters. Anisotropic sets of excitations are detected at terahertz frequencies, which we assign to complex translational and librational vibrations of confined water molecules.

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Conflict of Interest The authors declare that they have no conflict of interest.

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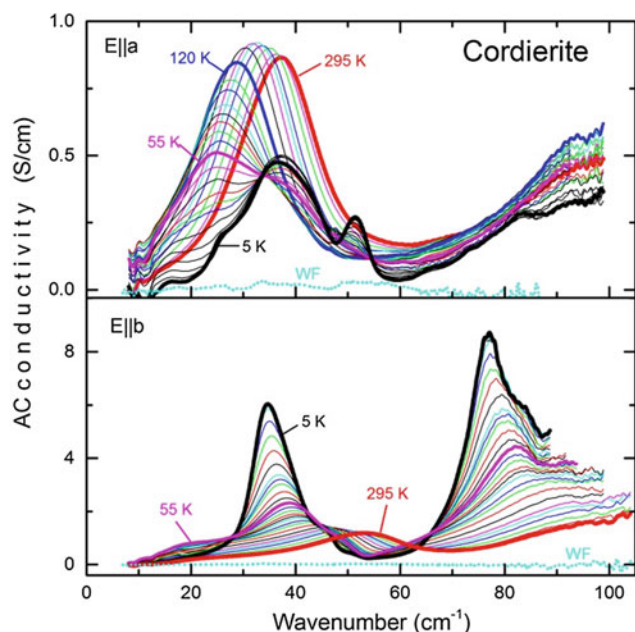


Fig. 5 Terahertz spectra of optical conductivity of nanoconfined water molecules in cordierite crystal measured at different temperatures for polarizations $E||a$ (upper panel) and $E||b$ (lower panel). WF denotes spectra obtained for water-free (dehydrated) crystals

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