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THz–IR spectroscopy of single H₂O molecules confined in nanocage of beryl crystal lattice

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We have measured the terahertz–infrared (3–7000 cm⁻¹) spectra of the optical conductivity of iron-doped single crystals of beryl, (Mn,Fe):Be₃Al₂Si₆O₁₈, that contain lone water molecules isolated within nanometer-sized cages formed by the ions of beryl crystal lattice. By comparing the spectra with those of dehydrated crystals, we exclude phonon resonances and reconstruct the spectra determined exclusively by vibrations of the water molecules. At liquid-helium temperatures, well-known intramolecular H₂O modes are observed above 1000 cm⁻¹ and accompanied with satellite resonances that are combinations of intramolecular and external vibrations of H₂O molecules. At terahertz frequencies, a broad bump centred around 20 cm⁻¹ (at 5 K) is observed with three rather narrow resonances at its high-frequency shoulder (38, 42 and 46 cm⁻¹). The origin of these low-energy excitations is discussed.

Keywords: nano-confined water molecule; terahertz spectroscopy

1. Introduction

Properties of water confined to nano-sized spaces [1] become different compared to bulk water. The reasons for these differences are actively studied, both experimentally and theoretically. The present efforts are motivated by the widespread occurrence of water-confined phenomena in nature – in organic (cells, membranes, enzyme channels) and inorganic (carbon nanotubes, fullerenes, porous silica, molecular sieves, zeolites, rocks, clays) media. Though bulk water is one of the most widespread substances on the Earth, its physical properties are far from being fully understood. They become more diverse when clusters of H₂O molecules are confined in nanopores. A systematic approach is necessary to understand the complexity of these phenomena. One best begins with a very simple system, and crystals of the beryl family Be₃Al₂Si₆O₁₈ provide model objects in

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this respect. Beryl crystallizes in a hexagonal structure (space group $P6/mcc$) consisting of stacked six-membered rings of SiO_4 tetrahedra that leave open channels oriented parallel to the c -crystallographic axis.[2,3] The channels include ‘bottlenecks’ of about 2.8 Å diameter alternating with slightly larger (5.1 Å) cages. Crystals that are grown in aqueous environment contain H_2O molecules that enter the framework of the crystal lattice in such a way that single H_2O molecules reside within the cages in two orientations relative to the c -axis: type-I water molecules have the vector connecting two protons directed parallel to the c -axis (dipole moment perpendicular to c), while in type-II molecules (that are Coulomb-fixed to the alkali Na, K ions), the H–H vector is perpendicular to the c -axis (dipole moment parallel to c).[4] Thus, one most likely has the simplest possible case of nanoconfined water – just a single H_2O molecule located within a *well-defined crystallographic environment*. Since the molecule does weakly interact [4,5] with the cage walls, one may expect that this interaction leads to a new behaviour of the H_2O molecule as compared to that of water in its free state. Indeed, clear indications on specific vibrational states of H_2O molecule in beryl have been found by optical spectroscopy. It has been observed that the well-known high-frequency intramolecular modes (ν_1 , ν_2 , ν_3 [6]) are accompanied in the spectra by satellite peaks which were assigned to a mixture of ν_1 , ν_2 and ν_3 with the *external vibrations* of H_2O type-I molecule.[5,7] According to the experimental spectra of Kolesov et al. [5,7], these external excitations should have eigenfrequencies ranging from about 1000 cm^{-1} down to only several wavenumbers. A series of low-energy resonances has been detected in Raman spectra at frequencies as low as 100 cm^{-1} [5] and assigned to H_2O molecule external vibrations. An attempt was made to connect the observed excitations to combinations of the ν_3 vibration with Stokes and anti-Stokes components $\nu_3 \pm n\omega$ ($n = 1, 2, 3, \dots$) with $\omega = 6.3\text{ cm}^{-1}$ [7] or $\omega = 9\text{ cm}^{-1}$, [5] or to the ‘particle in the box’ like motions of the H_2O molecule within the beryl nanocavity.[8] However, severe discrepancies between these assignments and the experiment remained.

To get a deeper insight into the low-energy vibrational dynamics of water molecules confined within the cages of beryl crystal lattice, we have performed [9] infrared (IR) and terahertz (THz) optical measurements of water-containing beryl Mn: $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ single crystal in a broad frequency range from 7000 cm^{-1} down to only few wavenumbers (to quantum energies of fractions of meV). Below 1000 cm^{-1} , we have found a rich set of highly anisotropic features in the low-energy response of H_2O molecule in a crystalline nanocage. While for the light polarized with $\mathbf{E}\parallel c$, only two absorption water-related peaks were detected at ~ 90 and $\sim 160\text{ cm}^{-1}$; several absorption bands were discovered for $\mathbf{E}\perp c$, each consisting of several narrower resonances. These bands were assigned to librational ($400\text{--}500\text{ cm}^{-1}$) and translational ($150\text{--}200\text{ cm}^{-1}$) oscillations of type-I water molecule that is weakly (via weak hydrogen bonds) coupled to nanocage walls. In addition, a rather strong and broad bump was discovered at the lowest THz frequencies, around $10\text{--}20\text{ cm}^{-1}$. We suggested a simple model that explains the ‘fine structure’ of the bands by splitting of the energy levels due to quantum tunnelling between the minima in a six-well potential relief felt by the water molecule within the cage. The origin of the THz bump was assigned to transitions between the levels within the lowest energy band. Since the model we previously proposed [9] did not account for the details of the resonance absorption locations, their line shapes and temperature dependences, the aim of the present study is to get additional information on these characteristics by performing THz–IR measurements on other crystals of beryl with different chemical compositions.

2. Experiment

Light-blue-coloured crystals, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, containing Fe^{3+} , Fe^{2+} and Na^+ were grown in stainless steel autoclaves according to the standard hydrothermal growth method.[10] For our optical measurements, the crystals were oriented by X-rays and cut in thin slices with the crystallographic c -axis within their planes. This geometry allows us to measure the optical response in two principal polarizations with the electric field vector \mathbf{E} of the probing radiation oriented parallel and perpendicular to the c -axis. Optical measurements were performed using three spectrometers equipped with helium cryostats in order to reach low temperatures. In the IR range, a standard Fourier transform spectrometer Bruker IFS-113v was employed to record reflectivity $R(\nu)$ and transmissivity $\text{Tr}(\nu)$ coefficients. The THz and sub-THz spectra were recorded with the help of the frequency-domain spectrometer based on backward-wave oscillators (BWOs) as frequency sources. [11,12] Supplementary measurements in the THz range were performed using a custom-made time-domain spectrometer.[13] By applying the three spectroscopic techniques and merging correspondent data, we have finally obtained the broadband spectra of transmission and reflection coefficients and of the complex optical conductivity, $\sigma^* = \sigma_1 + i\sigma_2$, and dielectric permittivity, $\varepsilon^* = \varepsilon' + i\varepsilon''$, of the $\text{Fe}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ crystal, at frequencies from few wavenumbers up to $\nu = 7000 \text{ cm}^{-1}$, in the temperature interval from 5 to 300 K and for two principal polarizations, $\mathbf{E}\parallel c$ and $\mathbf{E}\perp c$. The spectra contained rich sets of features corresponding to absorption resonances that were fitted using Lorentzian expressions for the complex dielectric permittivity:

$$\varepsilon^*(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu) = \sum_j \frac{f_j}{i\nu_j\gamma_j + (\nu_j^2 - \nu^2)}, \quad (1)$$

where $f_j = \Delta\varepsilon_j^* \nu_j^2$ is the oscillator strength of the j th resonance, $\Delta\varepsilon_j$ is its dielectric contribution, ν_j represents the resonance frequency and γ_j the damping. Similar to what was done in [9] to distinguish water-related absorptions from phonon resonances, we have performed optical measurements of the samples before and after dehydration. In order to extract the crystal water from the samples, the specimens were heated to 1000 °C in vacuum for a few days leading to a weight loss of several percentage. The absorption features that disappear in the dehydrated samples (see example in Figure 1) are connected with the H_2O molecular response. Importantly, all phonon resonances stayed unchanged in the dehydrated crystals. With the water-related absorption lines identified, the phonon resonances have been ‘subtracted’ from $\sigma^*(\nu) = \sigma_1(\nu) + i\sigma_2(\nu)$ and $\varepsilon^*(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu)$ spectra by setting the corresponding oscillator strengths f_j in expression (1) to zero.

3. Results and discussion

Figure 2 presents the spectrum of optical conductivity (proportional to absorptivity) of $\text{Fe}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ together with the spectrum of $\text{Mn}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ [9] for the polarization $\mathbf{E}\perp c$ that shows a much richer spectral response compared to the other $\mathbf{E}\parallel c$ polarization. Both spectra correspond exclusively to vibrations of water molecules in the crystals with the phonon features ‘subtracted’. Due to phonons, the water-related absorptions were obscured at the respective spectral interval resulting in an uncertainty in extracting their characteristics; the corresponding band is denoted by the hatched area in Figure 2. It is seen that both spectra look similar. There are narrow resonances above 1000 cm^{-1} that

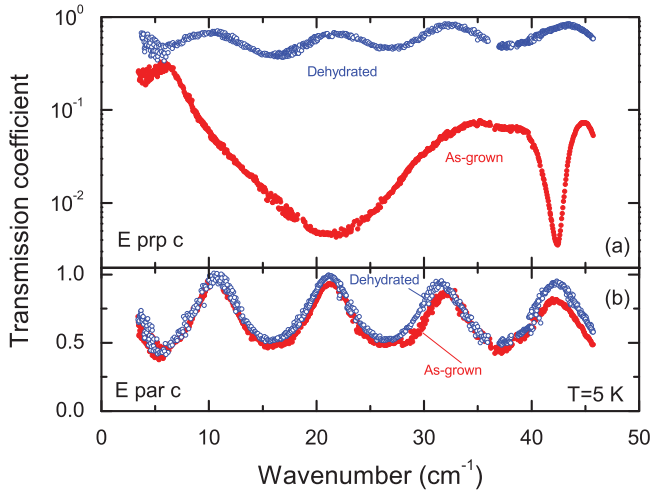


Figure 1. Terahertz spectra of the transmission coefficient of plane-parallel plates of crystalline beryl $\text{Fe}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ (Fe_2O_3 mass content about 0.05%) of thickness $200\ \mu\text{m}$ measured on as-grown and dehydrated samples for the polarizations $\mathbf{E}\perp c$ (a) and $\mathbf{E}\parallel c$ (b). The oscillations in the spectra are due to interference of monochromatic radiation due to multiple reflections at the plane-parallel surfaces of the samples. The deep minima (note logarithmic scale on the Y-axis) in the spectrum of as-grown sample for $\mathbf{E}\perp c$ are caused by absorption due to vibrations of water molecule encapsulated within the nano-sized cage formed by ions of beryl crystal lattice. The spectra of as-grown and dehydrated samples for polarization $\mathbf{E}\parallel c$ practically coincide since no intensive water-related absorptions were detected for this polarization at terahertz frequencies.

correspond to intramolecular ν_1 , ν_2 , ν_3 modes accompanied with satellites – combinations of ν_1 , ν_2 , ν_3 with lower frequency excitations. Resonance at $5300\ \text{cm}^{-1}$ relates to the combination $\nu_1 + \nu_2$. These high-frequency vibrations together with sharp resonances at 2400 and $3100\ \text{cm}^{-1}$ will be discussed in a subsequent publication; we concentrate on lower frequency absorption spectra later.

Below $\approx 400\ \text{cm}^{-1}$, an intensive absorption band is observed in $\text{Fe}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, which looks similar to that seen in $\text{Mn}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$. In both crystals, the band has basically the same strength (amplitude) indicating a similar amount of crystal water. However, it is noticeable that the band in $\text{Fe}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ is composed of more narrow components. The considered low-energy absorption lines are caused by external (no intramolecular degrees of freedom involved) vibrations of the H_2O molecules; these vibrations gain optical activity due to local fields, which lead to a finite dipole moment of the complex ‘ $\text{H}_2\text{O} + \text{crystalline surrounding}$ ’.[14,15] These molecules should be of type I; they are more loosely coupled to the crystalline surrounding than the molecules of type II that are fixed to the alkali ions via Coulomb forces. By analogy with the IR spectra of liquid water and ice, the band at $100\text{--}300\ \text{cm}^{-1}$ was assigned in $\text{Mn}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ [9] to the translational motions of the water molecule. The ‘fine structure’ of the band was connected with the splitting of the molecular energy levels due to quantum tunnelling between the minima of a six-well potential relief felt by a molecule within the crystalline cage of hexagonal symmetry. Already in our previous publication,[9] we noted that the simplified model used could only roughly account for the observations made for $\text{Mn}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, like for the number of observed resonances in the translational and

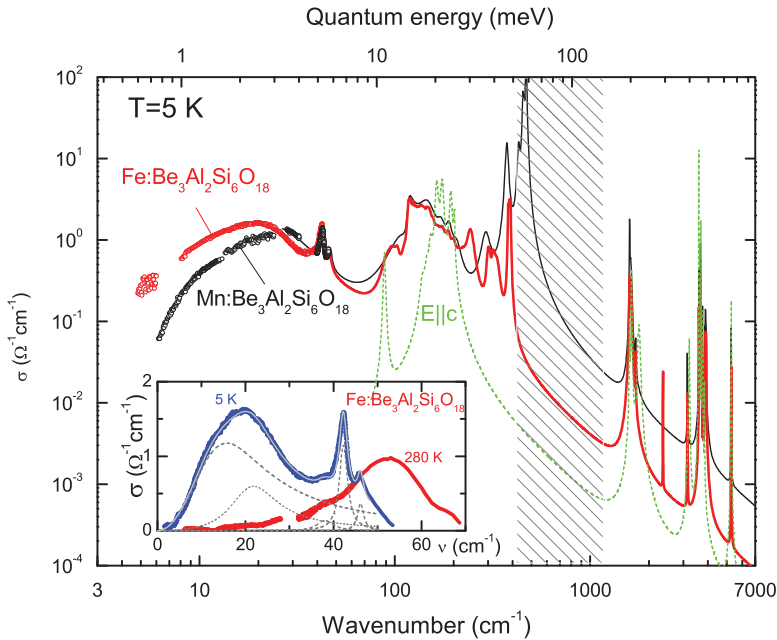


Figure 2. (Colour online) Terahertz–infrared spectrum of dynamical conductivity caused by the response of water molecules in nanopores of beryl crystal $\text{Fe}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ (red line) together with the spectrum for $\text{Mn}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ (black line, MnO mass content about 0.09%) from [9]. The spectra are taken at liquid helium temperature for the polarizations $\mathbf{E}\perp\mathbf{c}$ and $\mathbf{E}\parallel\mathbf{c}$. The hatched area denotes the frequency range where the response of phonon resonances was ‘subtracted’ as described in the text. The inset shows terahertz absorption bands at two temperatures, 5 and 280 K. For $T=5\text{ K}$, the spectrum was fitted (grey colour) with the sum of five Lorentzians (1) shown separately by dashed lines.

librational bands, but not, for example, for their spectral positions. The present data confirm the more complicated nature of the vibrational states of the water molecule captured within the nanopore in beryl lattice. The fact that the frequency position (around 140 cm^{-1}) of the considered band is so close to the location of translational band in liquid water (around 190 cm^{-1}) may indicate that mainly the translational character of the H_2O vibrations contributes to the absorption. At this point, however, one cannot exclude contributions from restricted rotations (librations) that could lead to the features around 300 cm^{-1} (Figure 2).

The THz-frequency spectra of both crystals ($\text{Fe}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ and $\text{Mn}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) contain broad bumps around $10\text{--}20\text{ cm}^{-1}$ with relatively narrow peaks at their high-frequency shoulders. The structures are perfectly reproduced in both series of measurements. For the $\text{Fe}:\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ crystal, using the BWO and the time-domain spectroscopy (TDS) techniques, we were able to precisely record the spectral shape of the THz resonances. The inset of Figure 2 clearly shows that five absorption components contribute to the low-temperature absorption below 60 cm^{-1} . The bump centred at 20 cm^{-1} can be fitted by a sum of two Lorentzians, and the structure at higher frequencies contains three narrower Lorentzian-like peaks. Unlike IR resonances, the structures at THz frequencies are strongly temperature-dependent. At room temperature, there is a single broad peak that softens while cooling down from $\approx 53\text{ cm}^{-1}$ (280 K) to 20 cm^{-1} (5 K) with three narrow resonances appearing below $50\text{--}70\text{ K}$. Presently, we can assume that the relatively

broad THz component could be connected with H₂O vibrations that involve bending the H-bonds.[16–19] However, no explanation can be given for its pronounced low-temperature softening and complicated spectral shape. The narrow components at 38, 42 and 46 cm⁻¹ (at 5 K, Figure 2) might be associated with transitions between rotational states of *ortho*-H₂O (hydrogen spins parallel) and *para*-H₂O (hydrogen spins antiparallel). Corresponding transition energies fall into the THz range,[20] and have been recently observed by IR absorption spectroscopy for water molecules encapsulated in a cage of fullerene C₆₀; they appear at 20, 37 and 56 cm⁻¹. [21] In beryl, the energies of the transitions can be modified by interaction of the H₂O molecule with surrounding ions of the beryl crystal lattice.

In conclusion, the spectra of the dynamical conductivity of single crystalline beryl Fe:Be₃Al₂Si₆O₁₈ are measured in the frequency range from a few wavenumbers up to $\nu = 7000$ cm⁻¹, i.e. covering the complete THz and IR range, at temperatures from 5–300 K and for two principal polarizations relative to the crystallographic axis *c*: **E**||*c* and **E**⊥*c*. We could construct spectra exclusively connected with dynamics of lone water molecules encapsulated within the nanocages of beryl crystal lattice. These spectra are compared with those earlier obtained for Mn:Be₃Al₂Si₆O₁₈ and their overall similarity is found. At the same time, it is found that for **E**⊥*c*, the IR band around 100–300 cm⁻¹ contains richer fine components in Fe:Be₃Al₂Si₆O₁₈ compared with Mn:Be₃Al₂Si₆O₁₈ indicating a more complicated nature of the vibrational states of the H₂O molecule within the crystalline nanocage.

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