Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

X-ray diffraction studies.

The X-ray structural localization of the dipole moment of water molecules in cordierite is a complex methodological task. The problem lies both in the fact that extremely small scattering from a single electron of the hydrogen atom overlaps the signal from the large number of electrons present in the entire unit crystal cell, and in that the center of the electron of the hydrogen atom determined by X-ray diffraction data cannot, in principle, coincide with the center of the hydrogen nuclei due to chemical interactions within water molecule. The localization of carbon dioxide molecules in the pores of an imperfect crystal lattice of a natural mineral is also difficult due to their small amount.

To solve the complex problem of identification of a number of water molecules in the studied natural cordierite crystal, an accurate X-ray diffraction analysis was carried out using a number of effective original techniques. The main approaches for improving the accuracy and reliability of structural results involve careful preparation of the sample, measuring a large number of reflection intensities (by about an order of magnitude exceeding those in regular experiments), and calibrating the experimental setup. To eliminate errors and achieve reproducibility of results, the method was used that involves comparison of results obtained in multiple experiments [A.P.Dudka, Crystallogr. Rep. **47** 145 (2002)]: 10 experiments were carried out with different samples in the range of nominal temperatures of 85-295 K. To further increase the accuracy, the sample was treated with the el'bor abrasive papers with grains size 3-80 micrometers to get spherical samples of ~0.4 mm diameter and surface with roughness not exceeding 3 micrometers (Fig. SM1).

The sets of diffraction reflection intensities were collected on an Xcalibur diffractometer equipped with a EOS S2 CCD detector (Rigaku Oxford Diffraction). To reduce the influence of thermal atomic vibrations on the accuracy of structural analysis, the most thorough measurements were performed at a nominal temperature of 85 K. These results are discussed below. An open cryosystem Cobra Plus (Oxford Cryosystems) cooled by gaseous nitrogen flow was used for sample cooling. The calibration [A.P.Dudka, I.A.Verin, and E.S.Smirnova, Crystallogr. Rep. **61** 692 (2016)] showed that the real temperature of the sample was 91 K in the lowest-temperature measurements. The reciprocal space was covered by more than 99.5% with maximum angle of scattering of reflexes $\theta = 74.3$ degrees and data redundancy more than 10, which potentially makes it possible to distinguish details of electron density of 0.36 Å in size.

The integrated intensities were obtained according to [Rigaku Oxford Diffraction, 2018, CrysAlisPro Software system, version 1.171.39.46, Rigaku Corporation, Oxford, UK]. Data processing and structure model refinement were performed using the ASTRA program [Dudka A. J. Appl. Cryst. **40**, 602 (2007)], including the X-ray absorption measurements of ellipsoidal samples [A.P.Dudka, Crystallogr. Rep. **50**, 1068 (2005)], the calibration of the diffractometer [Dudka A. J. Appl. Cryst. **43** 1440 (2010)], the extinction effect corrections [Becker P.J., Coppens P. Acta Cryst. A. **30** 129 (1974)], the half-wavelength contribution corrections [Dudka A. J. Appl. Cryst. **43** 102 (2010)]. Fourier electron density maps were plotted using the Jana2006 program [Petricek V., Dusek M., Palatinus L. Z. Kristallogr. **B. 229**. 345 (2014)].

An important quantity in the discussions of the crystal model is the residual factor R

$$R = \Sigma_{\mathrm{hkl}}\,[||F_{\mathrm{obs}}(\mathbf{H})| - |F_{\mathrm{calc}}(\mathbf{H})||\,]\,/\,\Sigma_{\mathrm{hkl}}\,[|F_{\mathrm{obs}}(\mathbf{H})|],$$

where $|F_{\mathrm{obs}}(\mathbf{H})|$ and $|F_{\mathrm{calc}}(\mathbf{H})|$ are modules of observed and calculated (model) structure factors; summation is performed over hkl indexes of reflections (over the reciprocal lattice points $\mathbf{H} = \mathbf{H}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$). Weighted R-factor is given by

$$wR = \sqrt{\{\Sigma_{\mathrm{hkl}}\,[w(|F_{\mathrm{obs}}(\mathbf{H})| - |F_{\mathrm{calc}}(\mathbf{H})|)^2]\,/\,\Sigma_{\mathrm{hkl}}\,[w\,|F_{\mathrm{obs}}(\mathbf{H})|^2]\}},$$

where w are weights of reflections.

Complex structure factors $F_{\text{calc}} = |F_{\text{calc}}(\mathbf{H})|\exp[i\psi_{\text{calc}}(\mathbf{H})]$, which are calculated from the refined structure parameters, and observed structure factors $F_{\text{obs}} \cong |F_{\text{obs}}(\mathbf{H})| \exp[i\psi_{\text{calc}}(\mathbf{H})]$ are involved into the procedure of the difference Fourier synthesis of residual electron density to reveal the additional structure details that are not taken into account ($\psi_{\text{calc}}(\mathbf{H})$ is reflection phase). Residual electron density $\Delta\rho(\boldsymbol{r})$ at a point $\boldsymbol{r}$ of the unit cell is calculated as

$$\Delta\rho(\boldsymbol{r}) = (1/V)\,\Sigma_{\text{hkl}}\,[||F_{\text{obs}}(\mathbf{H})| - |F_{\text{calc}}(\mathbf{H})\,||\,\exp[i\,\psi_{\text{calc}}(\mathbf{H})]\,\exp(-2\pi i\,\mathbf{H}\boldsymbol{r})],$$

where V is a unit-cell volume and the summation is over the reciprocal lattice points.

Our refinement of the cordierite structure provided with the following results. Space group is *Cccm*, $Z = 4$, maximum angle of scattering of reflections is $\theta = 74.3$ degrees. Unit cell parameters are: $a = 17.05011$ (1) Å, $b = 9.71634$ (6) Å, $c = 9.34645$ (7) Å. Equivalent intensities difference is of 1.4%. The residuals that describe the differences between the experimental and modeling data are: R/wR=1.16/1.35%. Extremes of the difference Fourier synthesis of electron density are $\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}$=–0.17/+0.29 electrons/$\text{Å}^3$ for 5693 symmetry-independent reflections, for which the intensities $I \sim |F_{\text{obs}}(\mathbf{H})|^2$ exceed their doubled standard uncertainty, $I>2\sigma(I)$.

The results of performed X-ray structural experiments coincided with those of our chemical analysis. It was found that in the range of temperatures 91-295 K water molecules are found in several orientations. This follows from the difference Fourier synthesis of electron density, in which a blurred, unstructured maximum is contained in the region (0, 0, ¼). It was found that at these temperatures, switching between the orientations are very frequent; in other words, the time needed to change the orientation is comparable to the lifetime of the molecules in the “fixed” positions. In these “fixed” orientations, the vector connecting protons of the molecule is almost parallel to the crystallographic *c*-axis (1.985 degrees), and the vector of the molecular dipole moment is somewhat tilted relative to the *b*-axis (37.172 degrees). Note that the angles obtained in 91 K X-ray experiments are somewhat larger than these provided by DFT-MD simulations for helium temperatures (see main text).

According to our X-ray data, the orientation of carbon dioxide molecules was determined very reliably, despite the fact that they are located in the same region (0, 0, ¼) as water molecules. It was found that the CO_2 molecule does not change its orientation being elongated along the *a*-axis. The amplitudes of the molecular oxygens are not very large, and their propeller-shaped oscillations around the central carbon atom by about 10 degrees along the *b*-axis are observed (Fig.SM2).

As far as mutual orientations of the H_2O electric dipoles is concerned, the X-ray diffraction study shows that in the range of 91-295 K any such ferroelectric or antiferroelectric ordering is hampered by intense inter-orientation transitions and the relatively long time the water molecule stays in incoherent intermediate states.

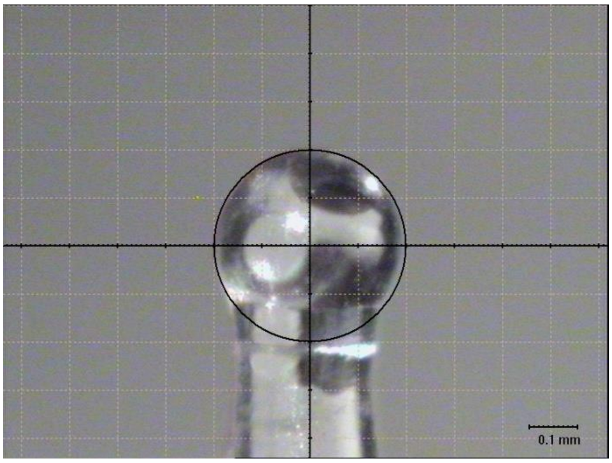


Fig. SM1. Photo image of cordierite sample made with Xcalibur diffractometer microscope.

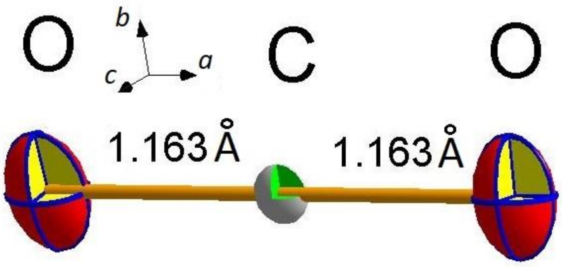


Fig. SM2. Orientation of the CO_2 molecule in cordierite at $z = 1/4$ level on X-ray diffraction data at 91 K.

Density-functional theory molecular dynamics simulations.

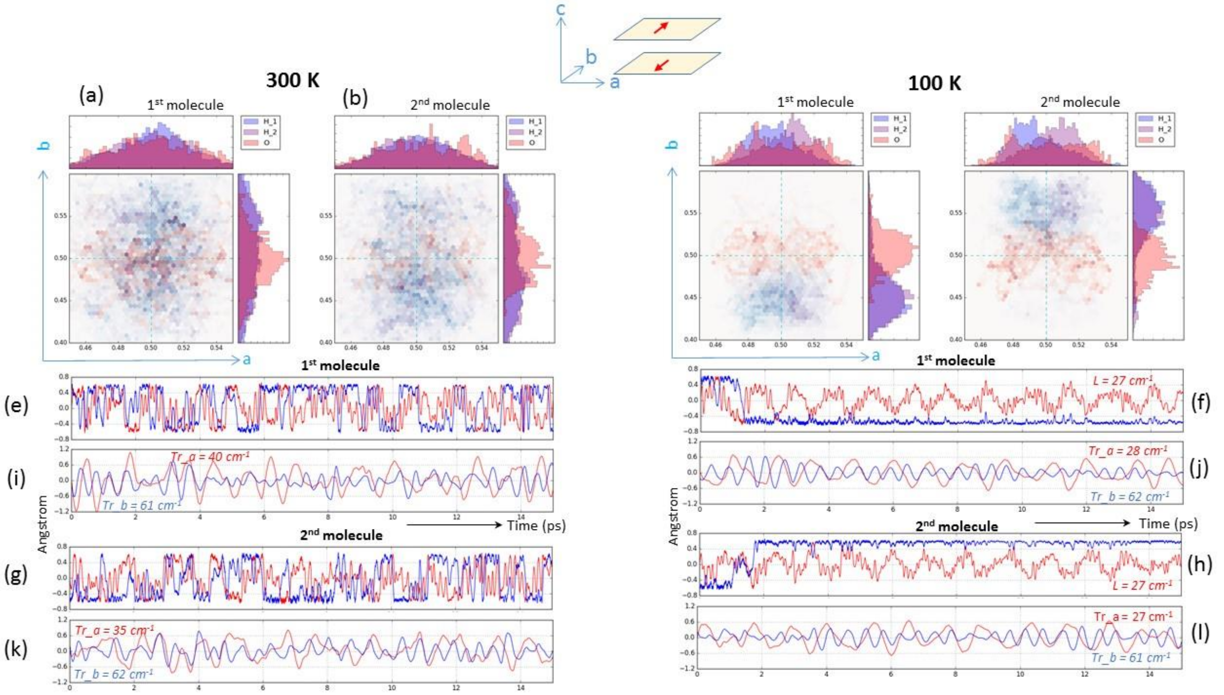


Fig.SM3. Molecular dynamics simulation during 15 ps at *T*=300 K and *T*=100 K of two water molecules within two nanopores of cordierite crystal lattice located next to each other along the channel *c*-axis with their dipole moments oriented antiparallel. Panels (a)-(d) display positions of oxygens and two protons in the (a,b) plane (shown in square frames) and projected on the a and b axes (shown in rectangular frames). Panels (e)-(h) display variations of the H_2O molecular dipole moment of the two molecules projected on the *a* (red color) and *b* (blue color) axes. These variations are related to librational motions of the molecules; corresponding frequencies in cm^{-1} are labeled with "*L*" and are calculated as inverse average distance between reproduced periodic oscillations. The dipole moment is represented by a distance (in Angstroms) between the center of oxygen ion and the middle between the two protons. Panels (i)-(l) display variations of position of oxygen ions of the two molecules projected on *a* (red color) and *b* (blue color) axes. These variations are related to translational motions of the molecules; corresponding frequencies in cm^{-1} are labeled with "*Tr*" and are calculated as inverse average distance between reproduced periodic oscillations. Numbers correspond the coordinates of atoms within the cages in fraction of translation vectors of cordierite unit cell.

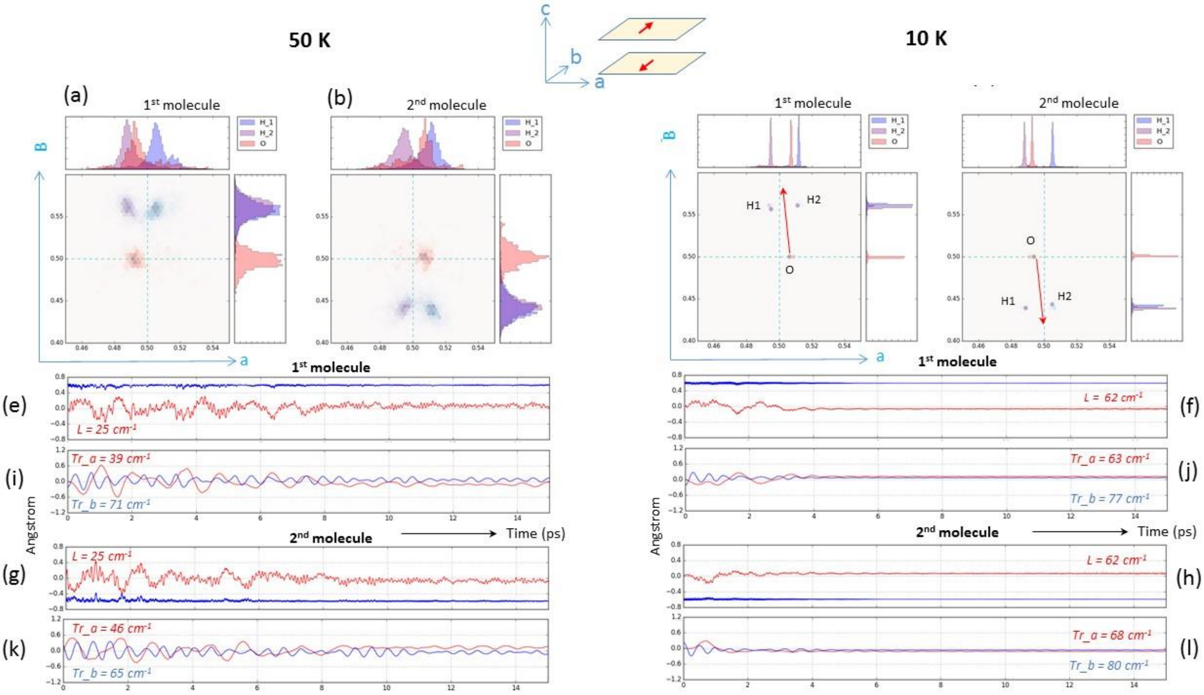


Fig.SM4. Same as in Fig.SM3 but for temperatures 50 K and 10 K.

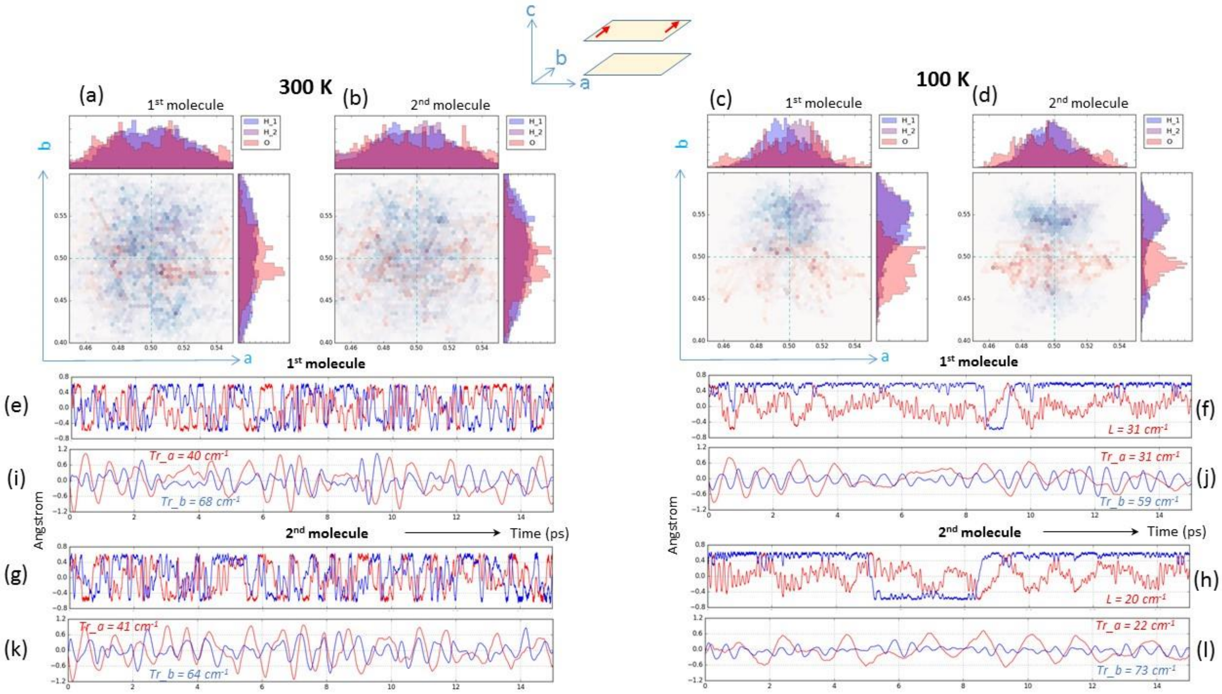


Fig.SM5. Molecular dynamics simulation during 15 ps at T=300 K and T=100 K of two water molecules within two nanopores of cordierite crystal lattice located next to each other in the (a,b) plane with their dipole moments oriented parallel. Panels (a)-(d) display positions of oxygens and two protons in the (a,b) plane (shown in square frames) and projected on the a and b axes (shown in rectangular frames). Panels (e)-(h) display variations of the H_2O molecular dipole moment of the two molecules projected on the a (red color) and b (blue color) axes. These variations are related to librational motions of the molecules; corresponding frequencies in cm^{-1} are labeled with "*L*" and are calculated as inverse average distance between reproduced periodic oscillations. The dipole moment is represented by a distance (in Angstroms) between the center of oxygen ion and the middle between the two protons. Panels (i)-(l) display variations of position of oxygen ions of the two molecules projected on a (red color) and b (blue color) axes. These variations are related to translational motions of the molecules; corresponding frequencies in cm^{-1} are labeled with "*Tr*" and are calculated as inverse average distance between reproduced periodic oscillations. Numbers correspond the coordinates of atoms within the cages in fraction of translation vectors of cordierite unit cell.

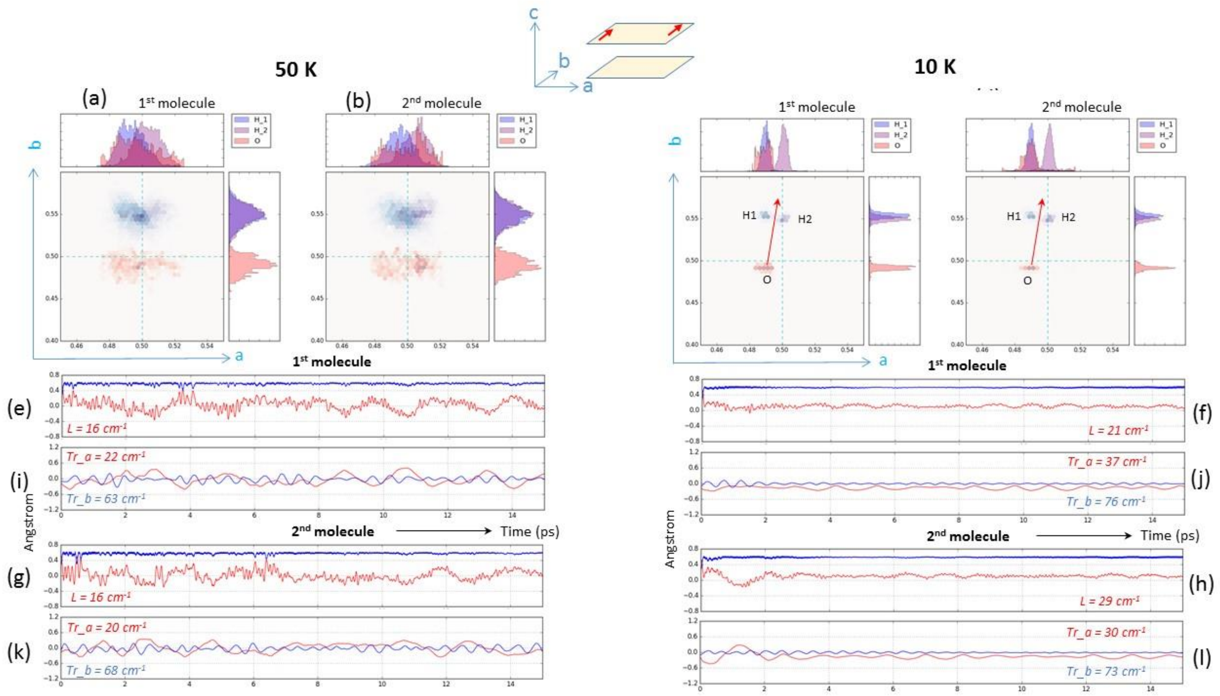


Fig.SM6. Same as in Fig.SM5 but for temperatures 50 K and 10 K.

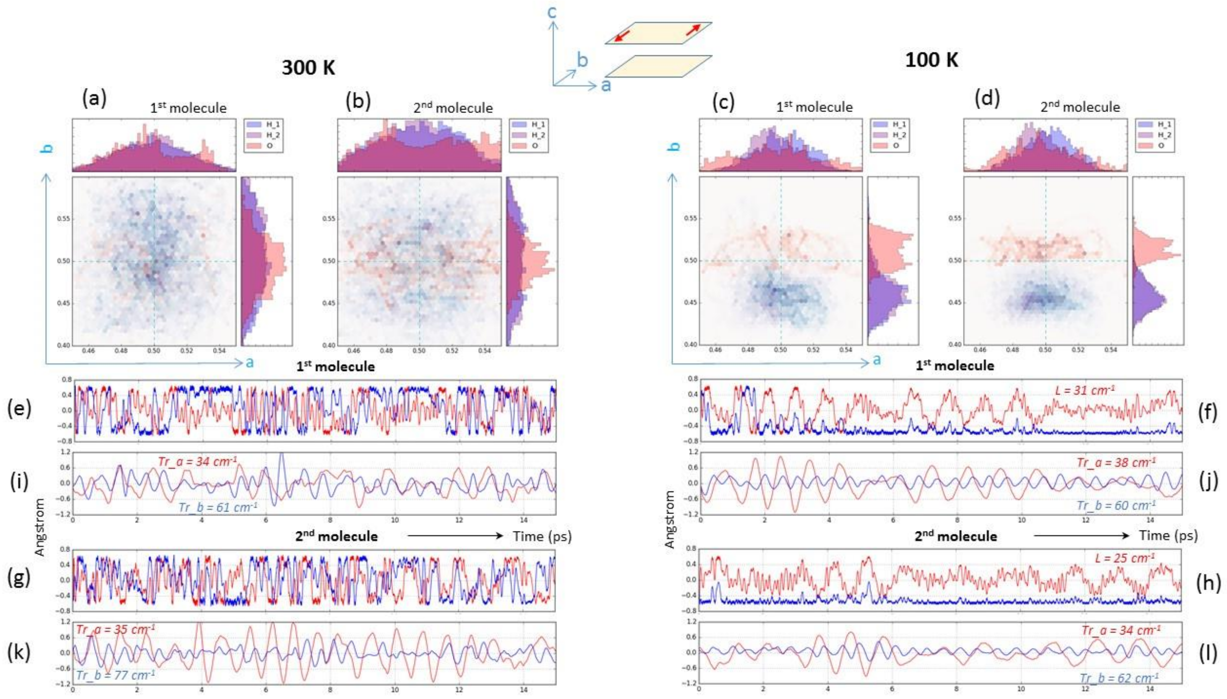


Fig.SM7. Molecular dynamics simulation during 15 ps at *T*=300 K and *T*=100 K of two water molecules within two nanopores of cordierite crystal lattice located next to each other in the (a,b) plane with their dipole moments oriented antiparallel. Panels (a)-(d) display positions of oxygens and two protons in the (a,b) plane (shown in square frames) and projected on the a and b axes (shown in rectangular frames). Panels (e)-(h) display variations of the H_2O molecular dipole moment of the two molecules projected on the a (red color) and b (blue color) axes. These variations are related to librational motions of the molecules; corresponding frequencies in cm^{-1} are labeled with "*L*" and are calculated as inverse average distance between reproduced periodic oscillations. The dipole moment is represented by a distance (in Angstroms) between the center of oxygen ion and the middle between the two protons. Panels (i)-(l) display variations of position of oxygen ions of the two molecules projected on a (red color) and b (blue color) axes. These variations are related to translational motions of the molecules; corresponding frequencies in cm^{-1} are labeled with "*Tr*" and are calculated as inverse average distance between reproduced periodic oscillations. Numbers correspond the coordinates of atoms within the cages in fraction of translation vectors of cordierite unit cell.

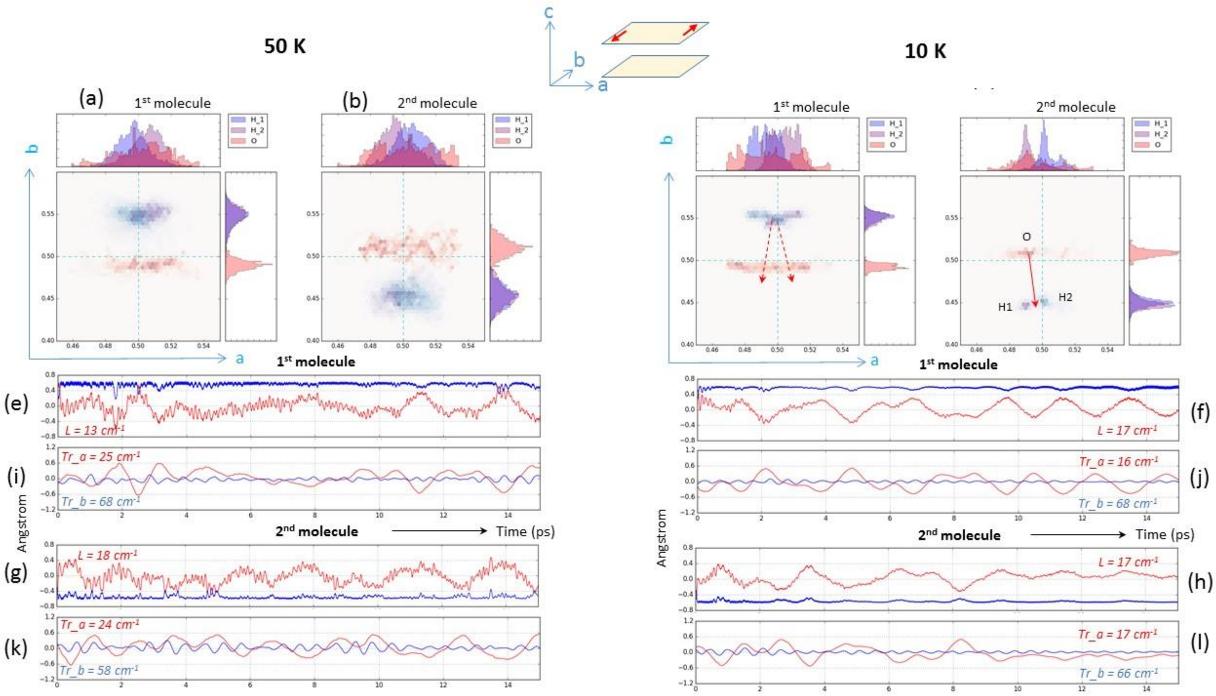


Fig.SM8. Same as in Fig.SM7 but for temperatures 50 K and 10 K.

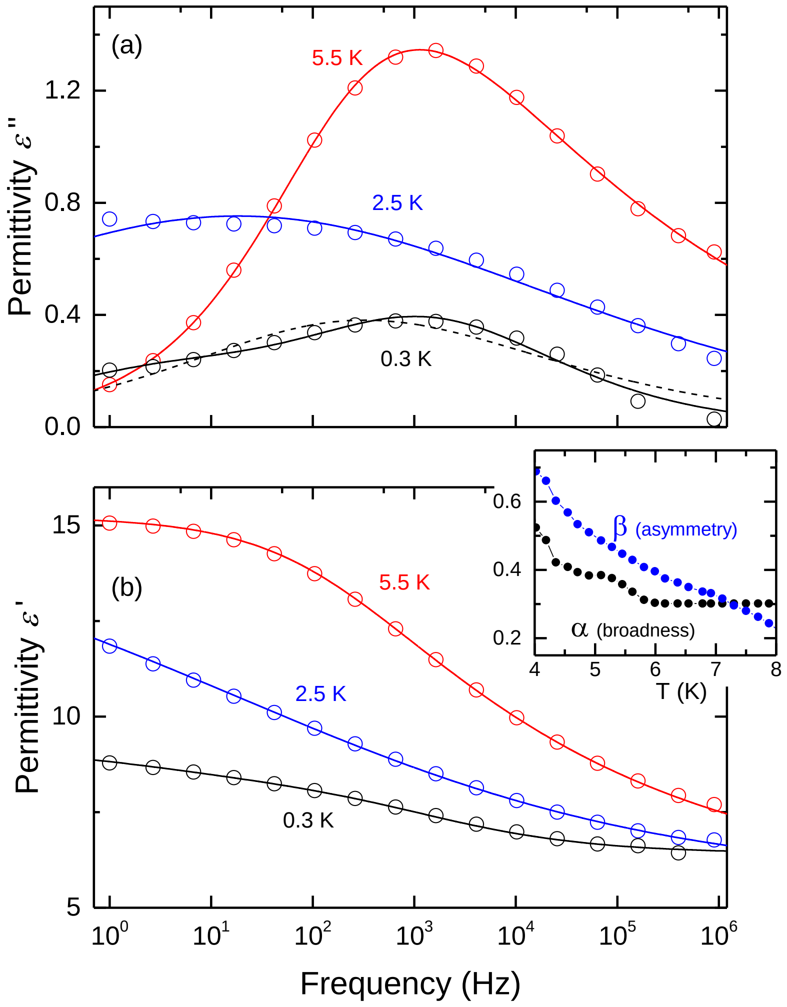


Fig. SM9. Radio-frequency spectra of imaginary (a) and real (b) parts of dielectric permittivity of water molecules confined in nanocages of cordierite crystal measured at different temperatures for polarization $E||a$. Lines represent the results of least-square fitting with the phenomenological Havriliak-Negami expression, Eq.1 in main text. Dielectric loss spectrum at T = 0.3 K can be fitted using two Havriliak-Negami terms. The best results using one term is shown by dashed line in panel (a). Inset presents temperature dependences of parameters α and β that characterize asymmetry and broadness of the observed relaxational peak, respectively.

Table SM1. Frequency positions (in cm^{-1}) of translational and librational excitations of water molecules confined within cages of cordierite crystal lattice. The values obtained from computer simulations (Figs.SM3-SM8) are presented together with experimentally observed values (Figs.5,6). Shown are the data that correspond to two H_2O molecules located along the channel *c*-axis and within the (*a*,*b*) plane; arrows correspond to mutual alignment of molecules dipole moments (ferroelectric or antiferroelectric). The values in brackets indicate frequencies of the second water molecule. Fonts sizes roughly correspond to relative modes' intensities.

	300 K						**100 K**					
	E||a			**E||b**			**E||a**			**E||b**		
	Channel	**Plane**		**Channel**	**Plane**		**Channel**	**Plane**		**Channel**	**Plane**	
	↑↓	↑↑	↑↓	↑↓	↑↑	↑↓	↑↓	↑↑	↑↓	↑↓	↑↑	↑↓
Librations							27(27)	31(20)	31(25)			
Translations	40(35)	40(41)	34(35)	61(62)	68(64)	61(77)	28(27)	31(22)	38(34)	62(61)	59(73)	60(62)
Experiment	**36**			**23, 52**			**26**			**20, 40, 86**		

	50 K						**10 K**					
	E||a			**E||b**			**E||a**			**E||b**		
	Channel	**Plane**		**Channel**	**Plane**		**Channel**	**Plane**		**Channel**	**Plane**	
	↑↓	↑↑	↑↓	↑↓	↑↑	↑↓	↑↓	↑↑	↑↓	↑↓	↑↑	↑↓
Librations	25(25)	16(16)	13(18)				62(62)	21(29)	17(17)			
Translations	39(46)	22(20)	25(24)	71(65)	63(68)	68(58)	63(68)	37(30)	16(17)	77(80)	76(73)	68(66)
Experiment	**16, 22, 36**			**19, 38, 82**			**19, 36**			**35, 77**		

Table SM2. Results of increased-accuracy calculations (VASP keyword PREC=Accurate) for the configuration of water molecules with the smallest primitive cell (two cages per cell).

Lowest energy configuration:

1) space group C2/c (antiferroelectric ordering), atomic positions:

O x=0, y=-.00484605, z=1/4, WP=4e

H x=.00744953, y=.05639072, z=.33159283, WP=8f

2) lowest vibrational frequencies in the harmonic approximation at Γ-point (in cm^{-1}) and their interpretation in terms of the motion of the two water molecules in the primitive cell:

32.2	librations around c-axis (antiphase displacement of the two oxygen atoms along a-axis)
41.8	translations along a-axis (mixed with librations around c-axis)
60.9	translations along b-axis
65.7	antiphase displacement along b-axis + other motions
67.2	antiphase displacement along c-axis mixed with librations around a-axis
78.6	translations along c-axis
79.0	antiphase displacement along b-axis
88.2	lowest-frequency lattice mode

Saddle point corresponding to 180°-flip of the water dipoles:

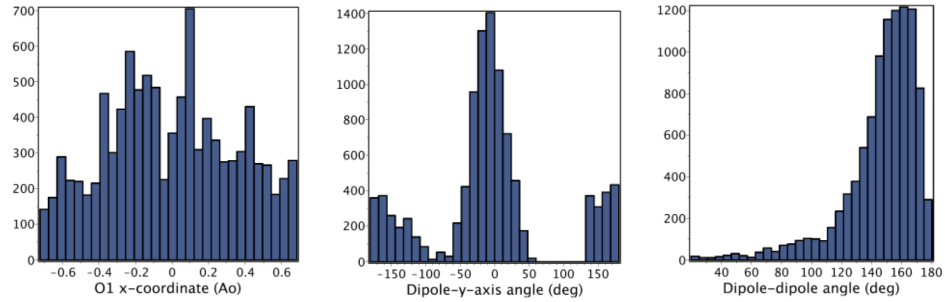
1) space group C2/c11 (antiferroelectric ordering), atomic positions:

O x=-.03208112, y=0, z=1/4, WP=4e

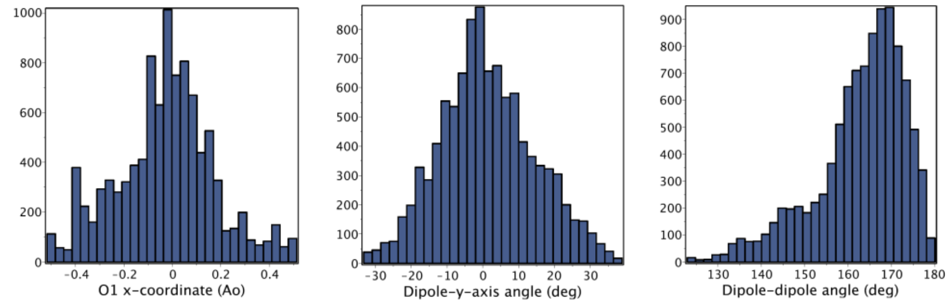
H x=.00245316, y=.03614103, z=.32416370, WP=8f

2) relative energy is 26.5 meV per water molecule

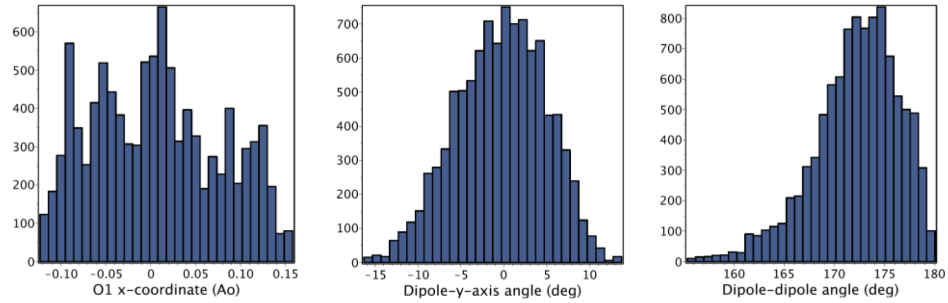
Histograms from 10-ps molecular dynamics:



at 100 K:



at 50 K:



at 10 K: