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

Supplementary Information For

Vibrational states of nano-confined water molecules in beryl investigated by first principles calculations and optical experiments

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Table S1. Chemical composition (in wt. %) of the hydrous beryl crystals used for the measurements of terahertz-infrared excitation spectra of nanocaged water molecules.

Sample name (water molecule type)	SiO_2	Al_2O_3	BeO	Fe_2O_3	MnO	Cr_2O_3	CuO	Li_2O	Na_2O	LOI*	Total
FeNa (H_2O)	66.12	18.27	13.86	0.60	0.00	0.00	0.01	0.02	0.05	0.85	99.78
Mn (H_2O)	66.79	17.32	13.75	1.30	0.09	0.00	0.00	0.15	0.00	1.93	101.18
3902 (D_2O, DHO)	66.18	18.66	13.80	0.05	0.00	0.00	0.00	0.04	0.00	1.14	99.87

*LOI: loss on ignition.

Table S2. Calculated geometries of water molecules in nanopores of beryl crystal lattice. The data for 50% and 100% fillings of crystalline pores are presented. Results corresponding to water molecules that are spatially arranged in vacuum in an arrangement as in the beryl lattice, but with the lattice ions absent (see text) are also given.

Water geometry	HOH angle (deg.)	OH distance (Å)	HH distance (Å)
Water type I in vacuum, 50% filling	104.39	0.972	1.536
Water type I in vacuum, 100% filling	104.33	0.972	1.536
Water vapor (exp.[S1])	104.47	0.957	1.513
Water type I in beryl, 50% filling	105.07	0.973	1.545
Water type I in beryl, 100% filling	104.59	0.973	1.540
Water type II + Li in beryl	105.08	0.983	1.560
Water type II + Na in beryl	103.69	0.979	1.541

Table S3. Comparison of the vibrational frequencies (in cm^{-1}) of the modes calculated by different methods. Here DFPT refers to density functional perturbation theory, and FD means finite differences, PBE - Perdew-Burke-Ernzerhof exchange-correlation functional,[S2] MBD - many-body dispersion energy correction.[S3] Negative values indicate imaginary frequencies.

Mode type	PBE/DFPT	PBE/FD	PBE-MBD/FD
L_{z1}	32	-73	-50
T_x	71	54	49
T_z	90	78	86
L_{z2}	109	107	92
L_y	222	219	220
L_x	228	230	222
bending	1587	1586	1580
sym. stretch	3701	3708	3702
asym. stretch	3805	3807	3805

Table S4. Normal modes and their frequencies (in cm^{-1}) of complexes involving water-II molecules and alkali ions. ν_1, ν_2 and ν_3 denote internal H_2O molecular modes. L and T stand for librational and translational motions, respectively. The numbers in the brackets indicate relative intensities for two principle polarizations, parallel (||) and perpendicular ($\perp$) to the crystallographic *c*-axis. The cases of modes labeled Lw2 (Lw2TLi, LwTNa) correspond to H_2O libration around c (a, b) axes. TLi, TNa correspond to translational modes of alkali ions with corresponding H_2O translations negligibly small.

Li				Na			
Mode type	H_2O	D_2O	DHO	Mode type	H_2O	D_2O	DHO
ν_3	$3540.4^{(\perp 0.62)}_{(\parallel 0.00)}$	$2591.4^{(\perp 0.28)}_{(\parallel 0.00)}$	$3508.9^{(\perp 0.37)}_{(\parallel 0.10)}$	ν_3	$3634.0^{(\perp 0.75)}_{(\parallel 0.00)}$	$2659.5^{(\perp 0.70)}_{(\parallel 0.00)}$	$3599.1^{(\perp 0.52)}_{(\parallel 0.15)}$
ν_1	$3475.4^{(\perp 0.00)}_{(\parallel 0.13)}$	$2505.0^{(\perp 0.00)}_{(\parallel 0.18)}$	$2547.0^{(\perp 0.17)}_{(\parallel 0.06)}$	ν_1	$3562.7^{(\perp 0.00)}_{(\parallel 0.26)}$	$2567.8^{(\perp 0.00)}_{(\parallel 0.29)}$	$2613.1^{(\perp 0.23)}_{(\parallel 0.10)}$
ν_2	$1544.3^{(\perp 0.00)}_{(\parallel 1.00)}$	$1132.3^{(\perp 0.00)}_{(\parallel 1.00)}$	$1357.7^{(\perp 0.02)}_{(\parallel 1.00)}$	ν_2	$1575.0^{(\perp 0.00)}_{(\parallel 1.00)}$	$1152.8^{(\perp 0.00)}_{(\parallel 1.00)}$	$1382.8^{(\perp 0.02)}_{(\parallel 1.00)}$
$Tw2TLi$	$459.8^{(\perp 0.04)}_{(\parallel 0.15)}$	$451.9^{(\perp 0.05)}_{(\parallel 0.28)}$	$457.3^{(\perp 0.05)}_{(\parallel 0.20)}$	$Lw2$	$353.0^{(\perp 1.00)}_{(\parallel 0.00)}$	$254.5^{(\perp 1.00)}_{(\parallel 0.00)}$	$315.8^{(\perp 1.00)}_{(\parallel 0.00)}$
$Lw2TLi$	$390.3^{(\perp 0.49)}_{(\parallel 0.00)}$	$304.8^{(\perp 0.41)}_{(\parallel 0.00)}$	$337.1^{(\perp 0.55)}_{(\parallel 0.00)}$	$Lw2$	$300.7^{(\perp 0.23)}_{(\parallel 0.00)}$	$248.3^{(\perp 0.00)}_{(\parallel 0.01)}$	$264.6^{(\perp 0.13)}_{(\parallel 0.00)}$
$Lw2$	$290.4^{(\perp 1.00)}_{(\parallel 0.00)}$	$209.7^{(\perp 1.00)}_{(\parallel 0.00)}$	$256.8^{(\perp 0.91)}_{(\parallel 0.00)}$	$Tw2TNa$	$252.7^{(\perp 0.00)}_{(\parallel 0.01)}$	$228.1^{(\perp 0.33)}_{(\parallel 0.00)}$	$243.5^{(\perp 0.12)}_{(\parallel 0.00)}$
TLi	$203.4^{(\perp 0.87)}_{(\parallel 0.00)}$	$202.3^{(\perp 0.26)}_{(\parallel 0.00)}$	$203.8^{(\perp 1.00)}_{(\parallel 0.00)}$	$Lw2$	$215.9^{(\perp 0.00)}_{(\parallel 0.00)}$	$177.3^{(\perp 0.32)}_{(\parallel 0.00)}$	$177.5^{(\perp 0.26)}_{(\parallel 0.00)}$
$Lw2$	$168.9^{(\perp 0.04)}_{(\parallel 0.00)}$	$125.7^{(\perp 0.38)}_{(\parallel 0.00)}$	$136.0^{(\perp 0.19)}_{(\parallel 0.00)}$	TNa	$176.9^{(\perp 0.18)}_{(\parallel 0.00)}$	$170.1^{(\perp 0.15)}_{(\parallel 0.00)}$	$173.0^{(\perp 0.14)}_{(\parallel 0.00)}$
$Lw2TLi$	$132.1^{(\perp 0.48)}_{(\parallel 0.00)}$	$117.1^{(\perp 0.09)}_{(\parallel 0.00)}$	$127.0^{(\perp 0.43)}_{(\parallel 0.00)}$	$Lw2TNa$	$174.6^{(\perp 0.14)}_{(\parallel 0.00)}$	$152.6^{(\perp 0.00)}_{(\parallel 0.00)}$	$172.2^{(\perp 0.01)}_{(\parallel 0.00)}$
$Tw2TLi$	$111.9^{(\perp 0.00)}_{(\parallel 0.10)}$	$107.1^{(\perp 0.00)}_{(\parallel 0.17)}$	$108.3^{(\perp 0.02)}_{(\parallel 0.12)}$	$Tw2TNa$	$99.9^{(\perp 0.03)}_{(\parallel 0.00)}$	$89.3^{(\perp 0.05)}_{(\parallel 0.00)}$	$92.9^{(\perp 0.04)}_{(\parallel 0.00)}$
$Tw2TLi$	$95.8^{(\perp 0.26)}_{(\parallel 0.00)}$	$89.2^{(\perp 0.14)}_{(\parallel 0.00)}$	$90.9^{(\perp 0.23)}_{(\parallel 0.00)}$	$Lw2$	$90.9^{(\perp 0.01)}_{(\parallel 0.00)}$	$84.8^{(\perp 0.02)}_{(\parallel 0.00)}$	$86.3^{(\perp 0.01)}_{(\parallel 0.00)}$
$Lw2$	$88.2^{(\perp 0.01)}_{(\parallel 0.00)}$	$83.3^{(\perp 0.01)}_{(\parallel 0.01)}$	$83.3^{(\perp 0.01)}_{(\parallel 0.00)}$	$Tw2TNa$	$87.6^{(\perp 0.00)}_{(\parallel 0.03)}$	$66.4^{(\perp 0.00)}_{(\parallel 0.06)}$	$67.2^{(\perp 0.00)}_{(\parallel 0.04)}$

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