Supplementary Information for "Low-Frequency Vibrations of Saccharides Using Terahertz Time-Domain Spectroscopy and Ab-Initio Simulations"

Andreea Aura Paraipan, [1] Nicole Luchetti, [2,3] Adriano Mosca Conte, [4] Olivia Pulci, [5] and Mauro Missori, [4,6*]

[1] *Énergie, Matériaux et Télécommunications, Institut National de la Recherche Scientifique (INRS), 1650 Boulevard Lionel Boulet, Varennes, QC J3X 1S2, Canada.*

[2] *Department of Engineering, Campus Bio-Medico University of Rome, Via Álvaro del Portillo 21, 00128 Rome, Italy.*

[3] *Center for Life Nano- & Neuro-Science, Italian Institute of Technology, Viale Regina Elena 291, 00161 Rome, Italy.*

[4] *Institute of Complex Systems, National Research Council (CNR-ISC), Piazzale Aldo Moro 5, 00185 Rome, Italy.*

[5] *ETSF, Department of Physics, Tor Vergata University of Rome, Via della Ricerca Scientifica 1, 00133, Rome, Italy.*

[6] *Department of Physics, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy.*

[*] *Correspondence: mauro.missori@cnr.it*

THz-TDS system

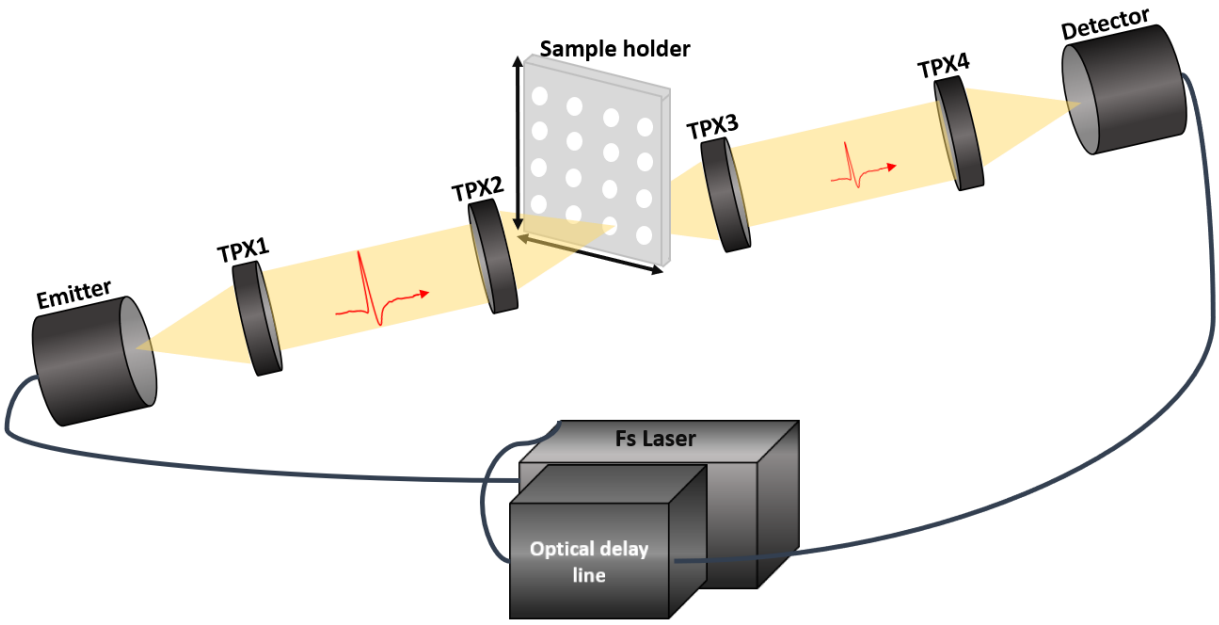

Figure S1: Sketch of the THz beamline used for the experiments with the multiple sample holder. TPX1 to TPX4 are polymethylpentene lenses with 50 mm focal length.

Dynamic range (DR) of the THz-TDS system

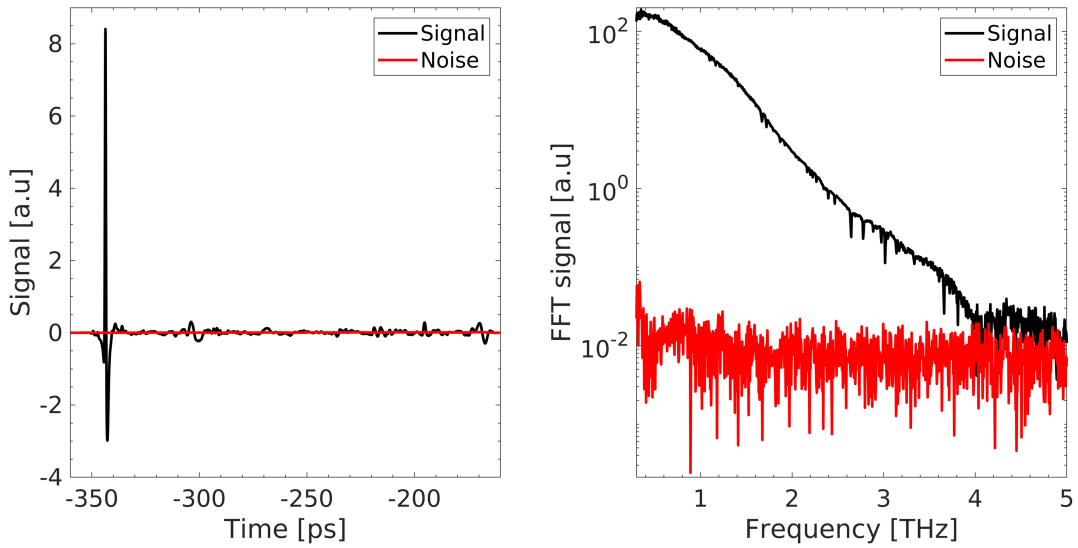

Figure S2: Time traces (left) and Fourier transform of the THz signal (right) propagating through the dry N_2 (black lines) and the noise floor of the system (red lines).

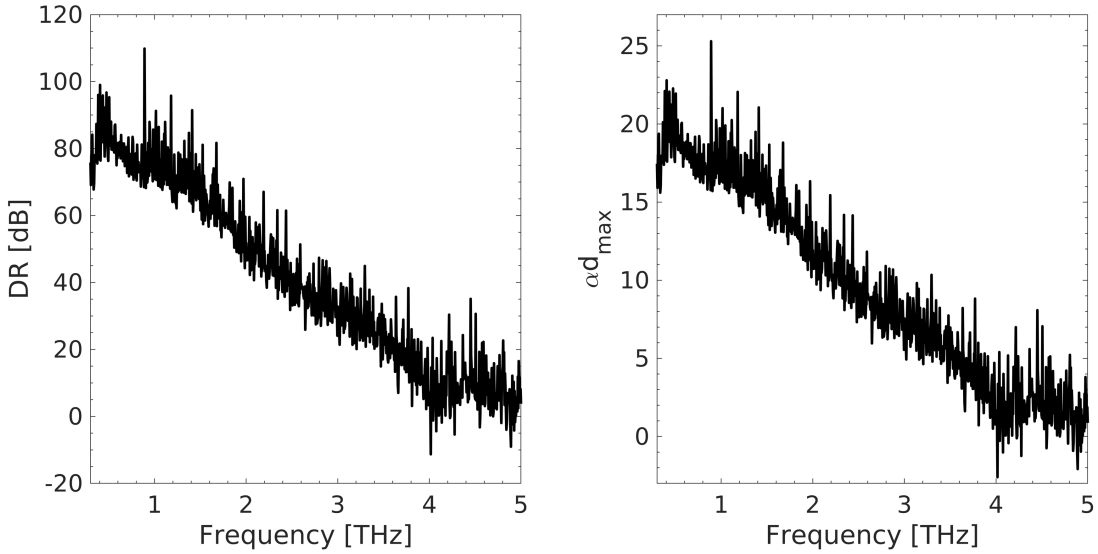

Figure S3: The DR (left) and highest measurable absorbance $(\alpha d)_{max}$ (right) of the THz-TDS system.

Mass density values

Sample label	Density [g/cm^3]	Refences
GLU	1.56	[61]
GAL	1.50	[*]
aLM	1.55	[61]
aLA	1.54	[39]
bLA	1.59	[61]
CBS	1.55	[57]
CEL	1.50	[60]
PET	0.96	[62]

Table S1: Typical nominal density of the investigated saccharides and PET, as reported in the literature [39, 57,60 – 62] and * from ChemSpider (http://www.chemspider.com/Chemical-Structure.2301265.html, accessed on 24 February 2020).

Experimental and simulated modes frequencies

Compound	Experimental frequency (THz)	Simulated frequency (THz)
CBS	1.24	0.89 (mode #1)
	1.54	1.53 (mode #2)
	2.07	2.01 (mode #4), 2.06 (mode #5), 2.15 (mode #6)
	2.31	2.42 (mode #7), 2.48 (mode #8)
	2.66	2.77 (mode #9)
βLA	1.85	1.79 (mode #2), 1.83 (mode #3)
	2.21	2.27 (mode #4)
CEL	2.15	2.23 (mode #2)
	2.73	2.73 (mode #3)
	3.00	3.00 (mode #4)
	3.19	3.27 (mode #5)
GLU	1.43	1.61 (mode #1)
	2.08	2.05 (mode #4)
	2.52	2.54 (mode #7)
	2.68	2.77 (mode #8)
	2.92	3.00 (mode #9)
GAL	2.13	2.17 (mode #3)
	2.32	2.33 (mode #5)
αLA	1.19	1.04 (mode #2)
	1.86	1.93 (mode #4)
	2.20	2.25 (mode #5)
	2.38	2.38 (mode #6)
	2.68	2.84 (mode #7)
αLM	0.53	1.12 (mode #1)
	1.37	1.40 (mode #2)
	2.55	2.51 (mode #6)
	2.87	2.82 (mode #7)

Table S2: Experimental THz frequencies modes associated with the simulated ones and the correspondent mode number.

Simulated crystal structures

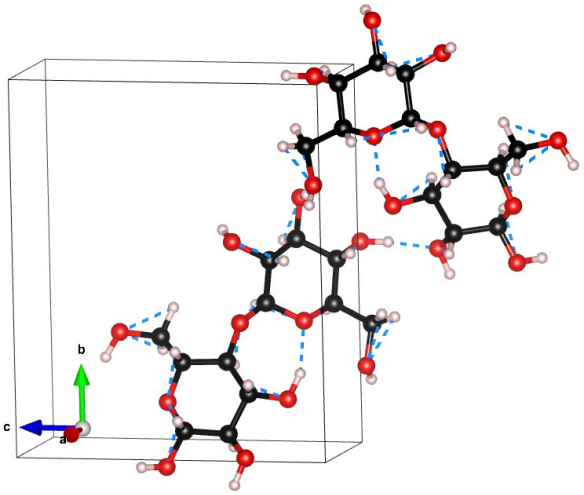

Figure S4: Ball and stick representation of CBS molecular crystal. The unit cell is indicated with a box. Black, red, and white spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the azure dotted lines the H-bonds.

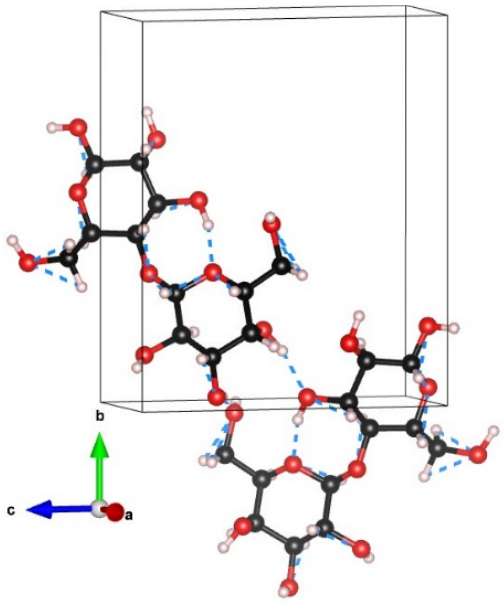

Figure S5: Ball and stick representation of βLA molecular crystal. The unit cell is indicated with a box. Black, red, and white spheres represent, respectively, carbon, oxygen, and hydrogen atoms, and the azure dotted lines the H-bonds.

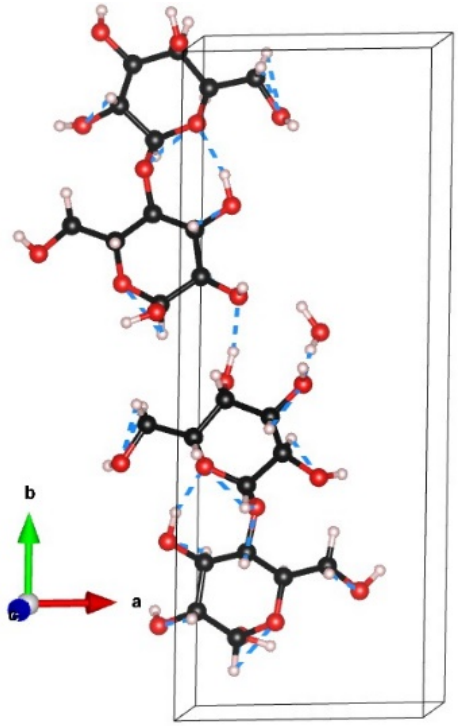

Figure S6: Ball and stick representation of αLM molecular crystal. The unit cell is indicated with a box. Black, red, and white spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the azure dotted lines the H-bonds.

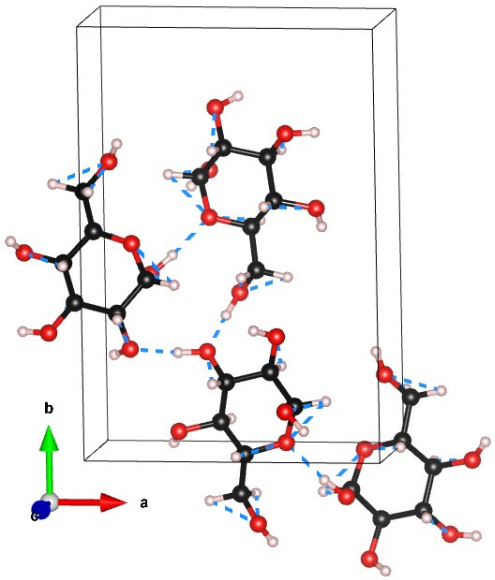

Figure S7: Ball and stick representation of GLU molecular crystal. The unit cell is indicated with a box. Black, red, and white spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the azure dotted lines the H-bonds.

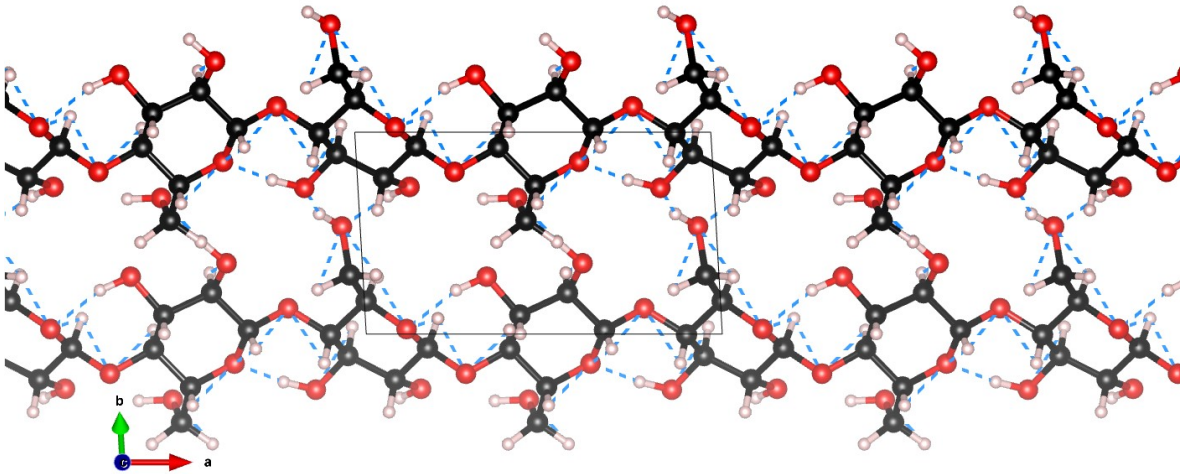

Figure S8: Ball and stick representation of CEL molecular crystal. The unit cell is indicated with a box. Black, red, and white spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the azure dotted lines the H-bonds.

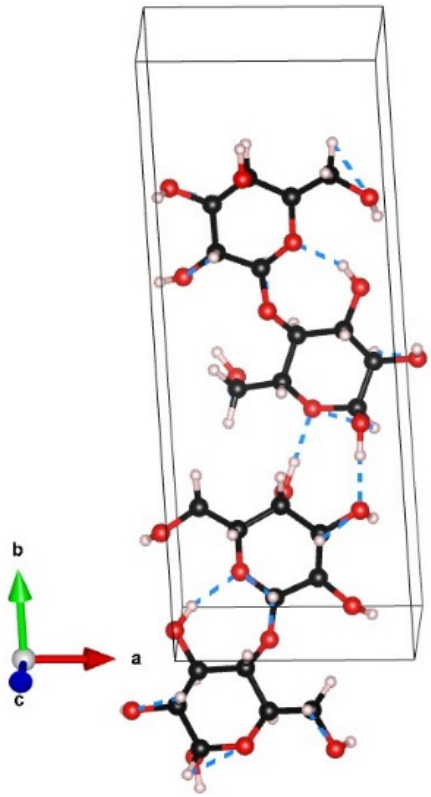

Figure S9: Ball and stick representation of αLA molecular crystal. The unit cell is indicated with a box. Black, red, and white spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the azure dotted lines the H-bonds.

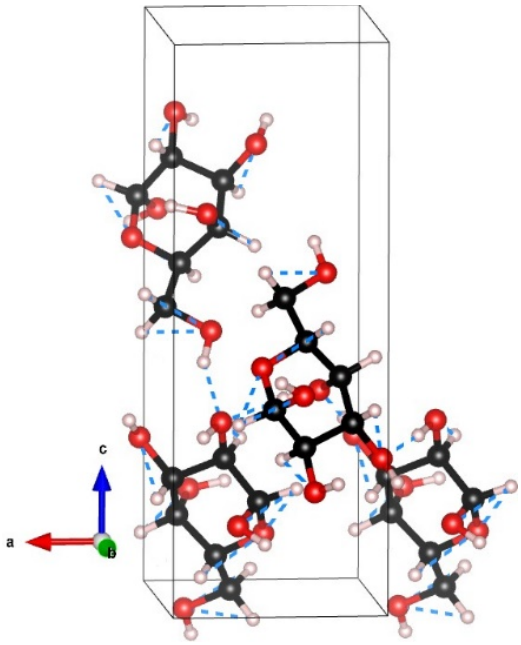

Figure S10: Ball and stick representation of GAL molecular crystal. The unit cell is indicated with a box. Black, red, and white spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the azure dotted lines the H-bonds.

Molecule	**a (Å)**	**b (Å)**	**c (Å)**	**α**	**β**	**γ**
CBS	4.72	12.60	10.55	90°	90°	90°
βLA	4.37	12.55	10.12	90°	92.8°	90°
αLM	8.04	21.12	4.62	90°	112.6°	90°
GLU	10.19	14.93	4.72	90°	90°	90°
CEL	10.23	8.04	6.06	46.2°	88°	91°
αLA	7.76	19.80	4.77	92.8°	107.1°	97.7°
GAL	5.69	7.65	15.29	90°	90°	90°

Table S3: Unit cell parameters for all simulated systems. a, b, and c are the primitive vectors lengths, and α, β, and γ are the axial angles.

Refractive indexes of the studied saccharides

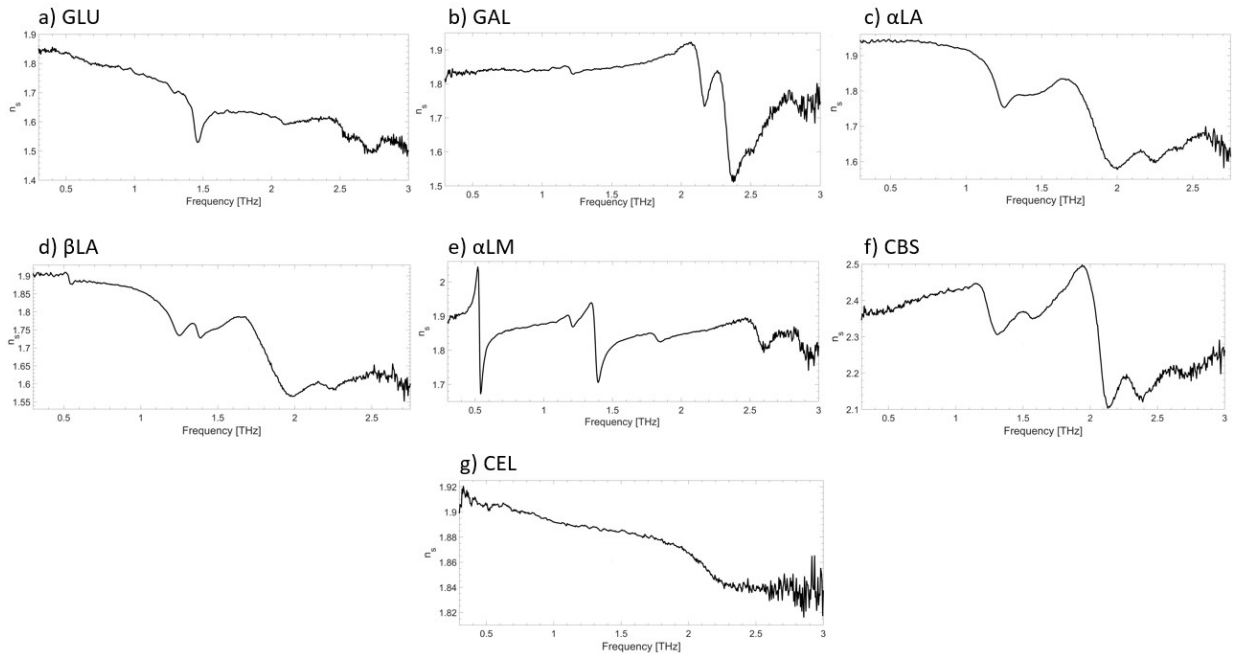

Figure S11: Refractive index, n_s, of (a) GLU, (b) GAL, (c) αLA, (d) βLA, (e) αLM, (f) CBS, (g) CEL.

Displacement vectors

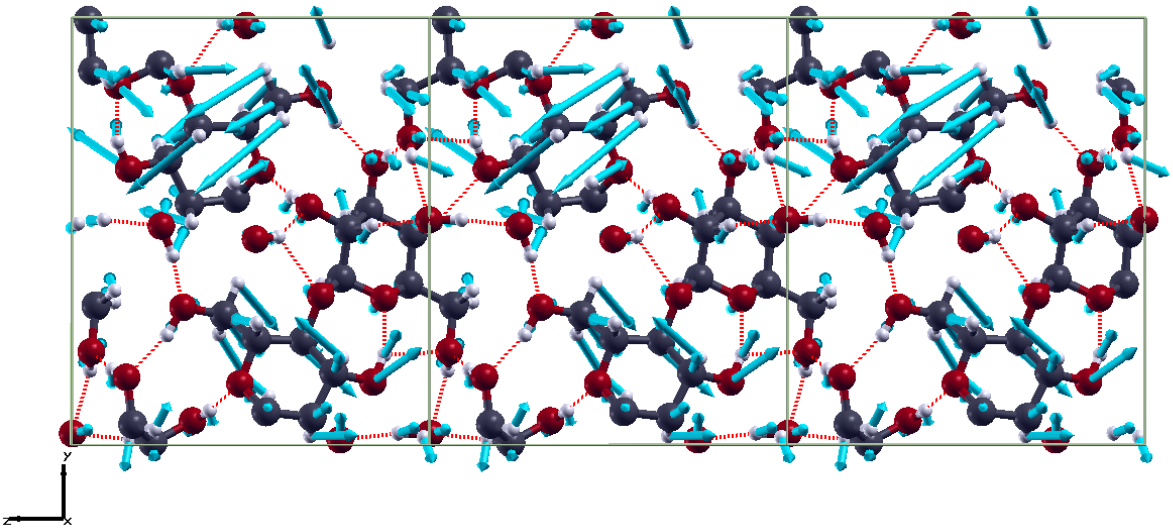

Figure S12: Atomic displacement vectors of CBS for mode 5 at 2.06 THz. Black, red, and white spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the red dotted lines the H-bonds.

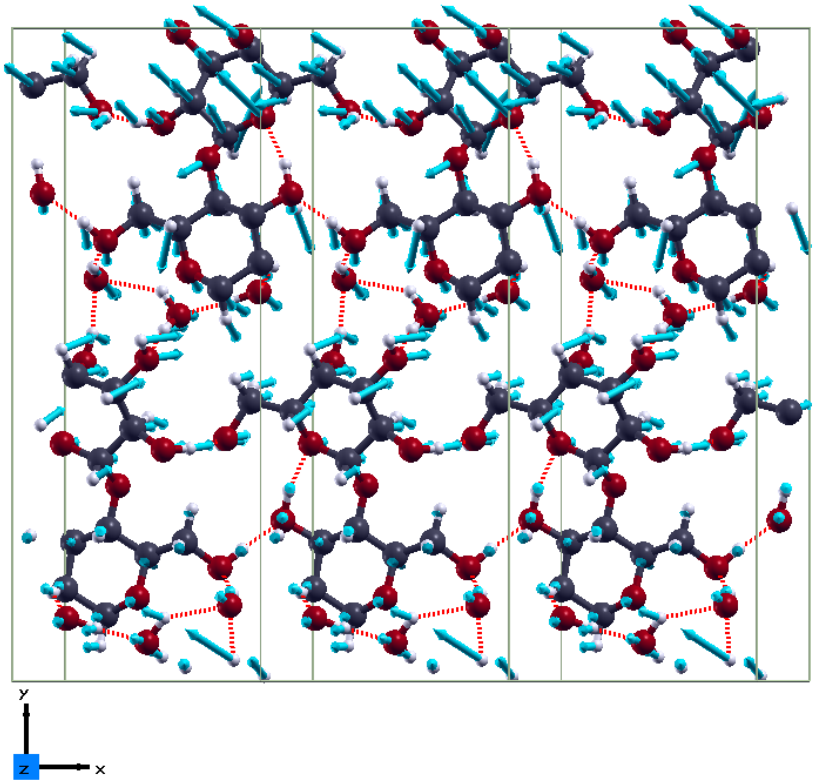

Figure S13: Atomic displacement vectors of αLM for mode 2 at 1.40 THz. Yellow, red, and cyan spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the red dotted lines the H-bonds.

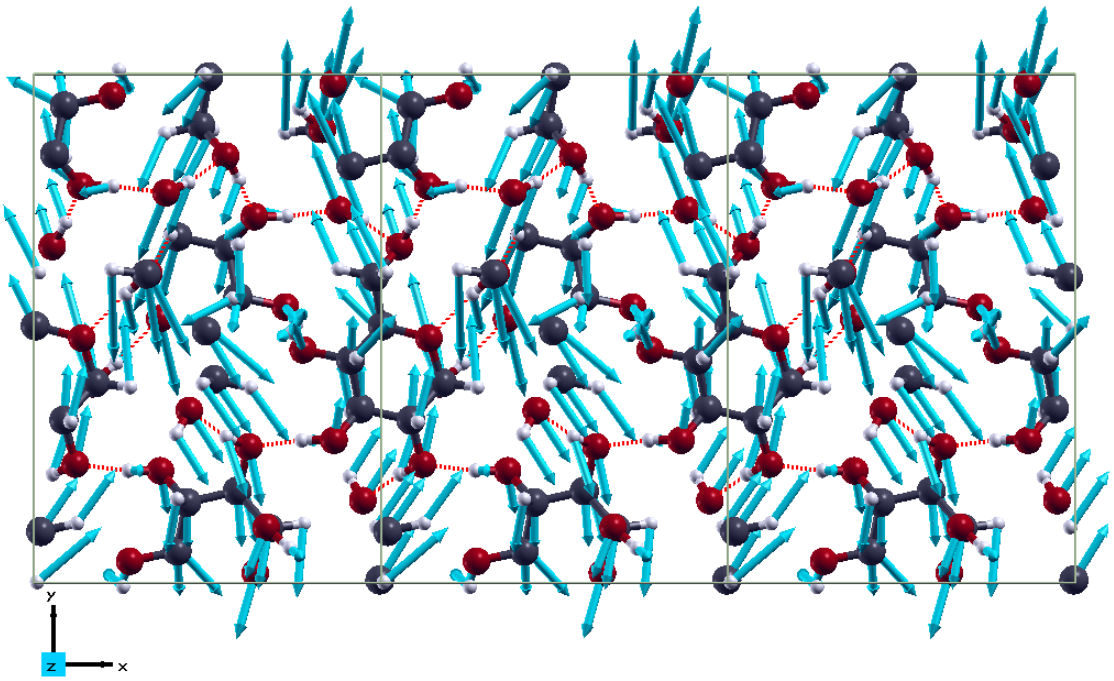

Figure S14: Atomic displacement vectors of GLU for mode 7 at 2.54 THz. Yellow, red, and cyan spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the red dotted lines the H-bonds.

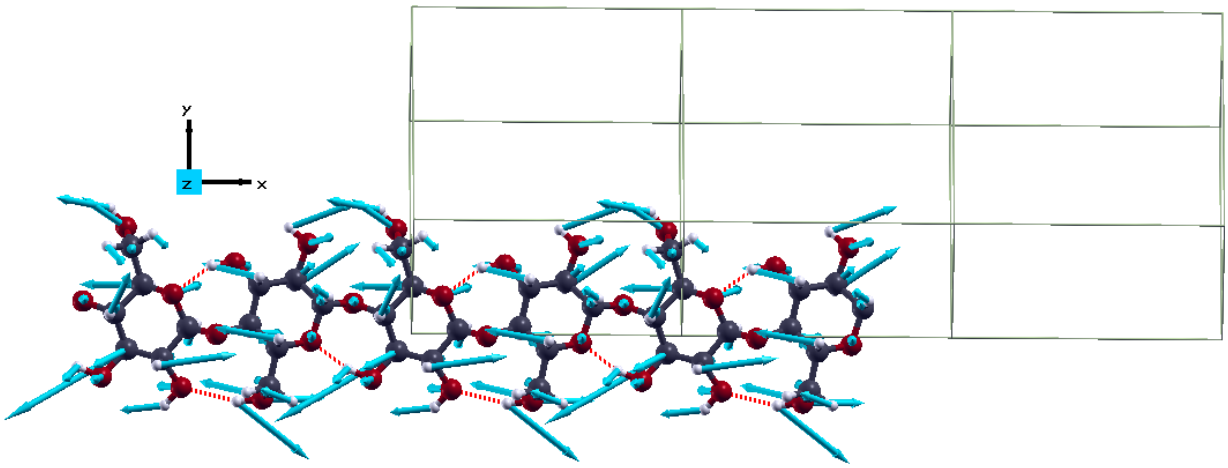

Figure S15: Atomic displacement vectors of CEL for mode 2 at 2.23 THz. Yellow, red, and cyan spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the red dotted lines the H-bonds.

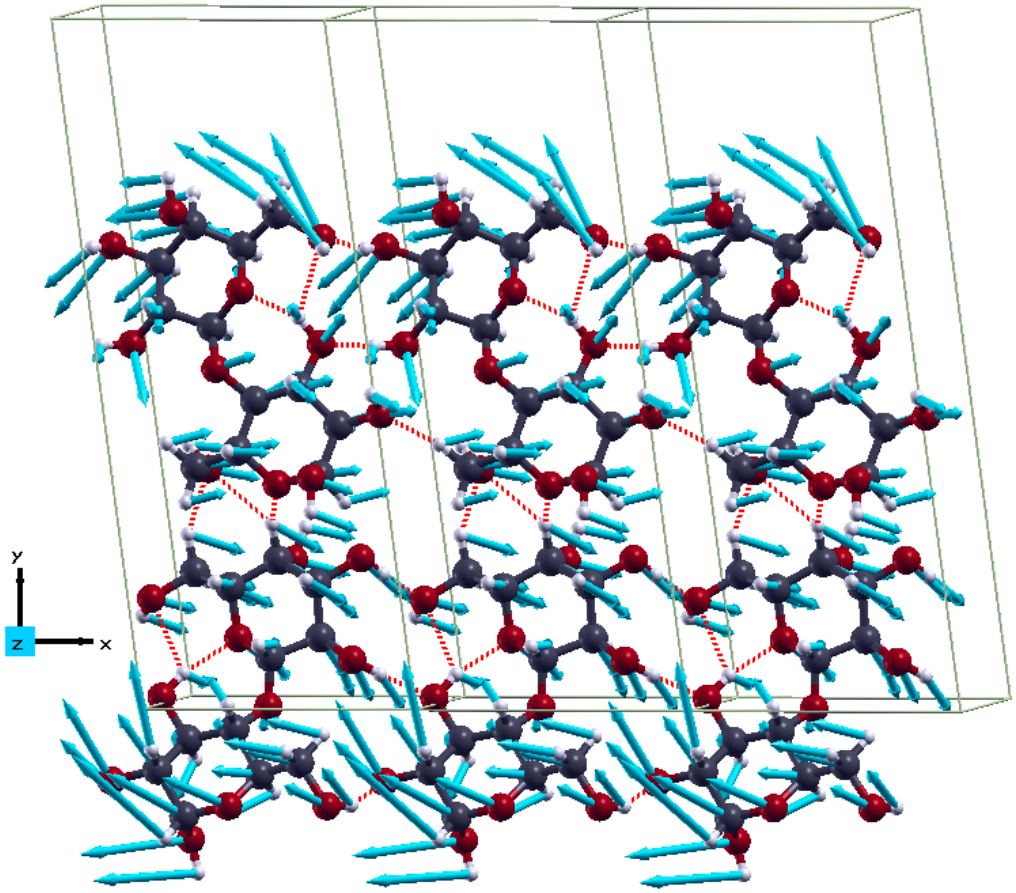

Figure S16: Atomic displacement vectors of αLA for mode 4 at 1.93 THz. Yellow, red, and cyan spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the red dotted lines the H-bonds.

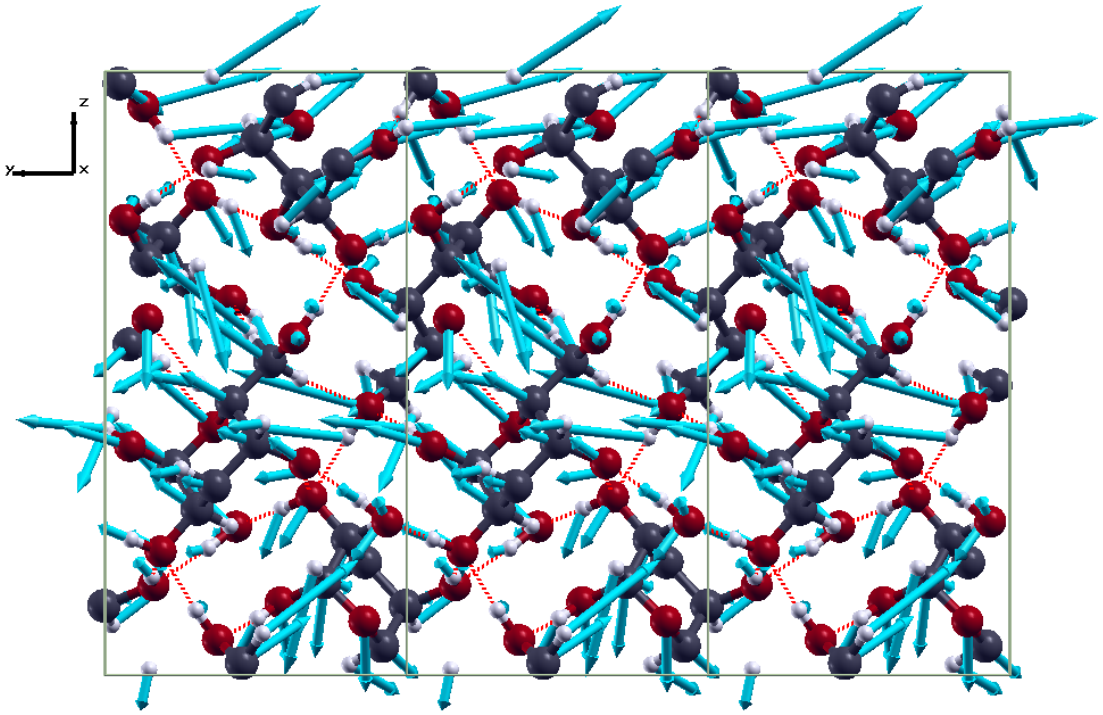

Figure S17: Atomic displacement vectors of GAL for mode 5 at 2.33 THz. Yellow, red, and cyan spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the red dotted lines the H-bonds.

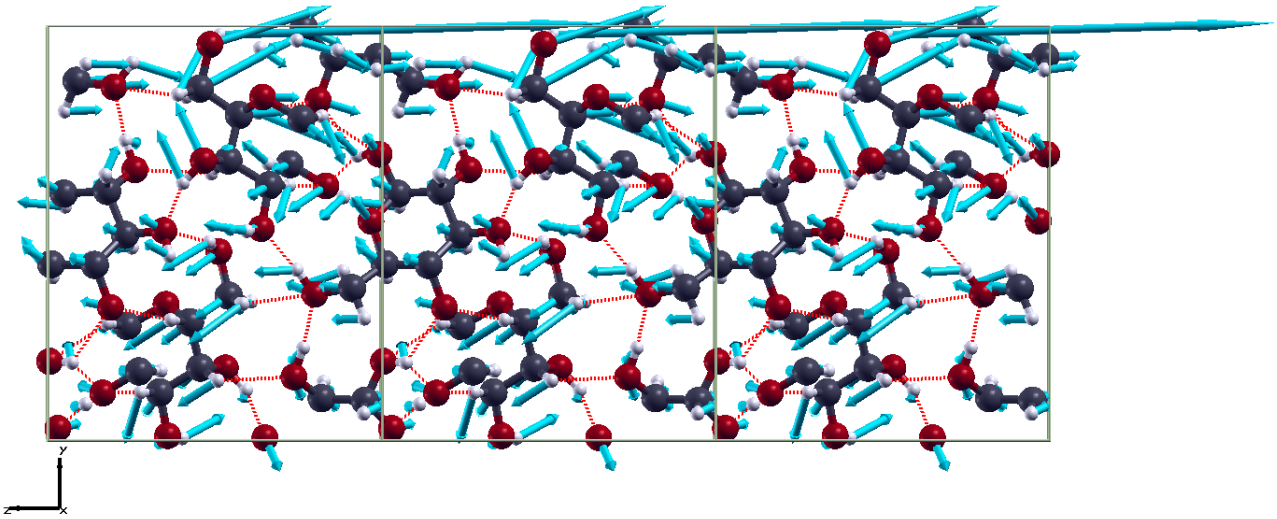

Figure S18: Atomic displacement vectors of βLA for mode 2 at 1.79 THz. Yellow, red, and cyan spheres represent, respectively, carbon, oxygen and hydrogen atoms, and the red dotted lines the H-bonds.