Supporting Information for

First Principles Calculation of Terahertz Spectroscopy of Molecular Crystals: the crucial role of periodic boundary conditions benchmarked with experimental L-ascorbic acid spectra†

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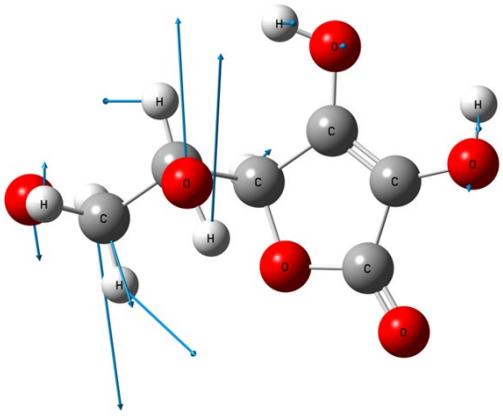
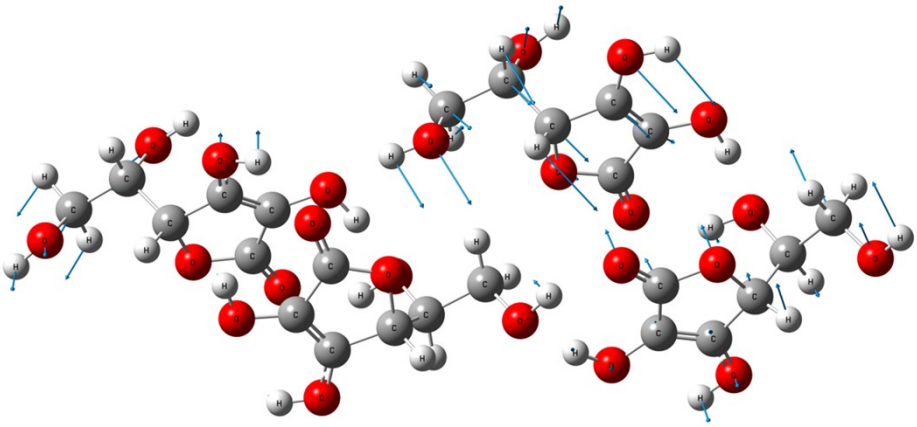
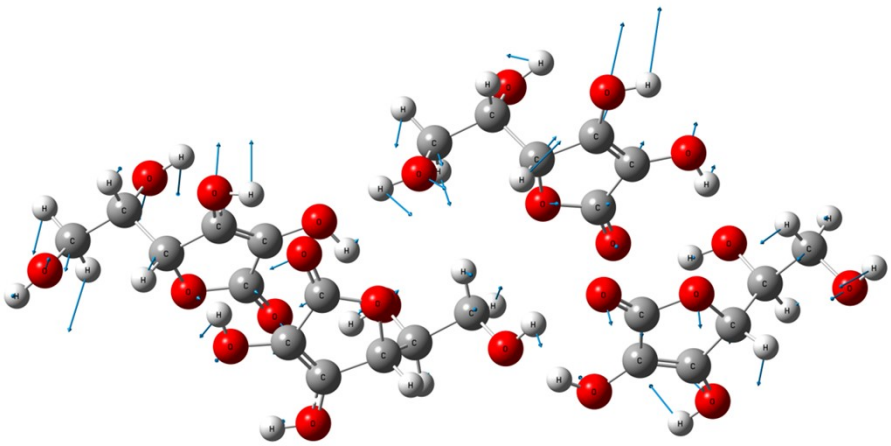


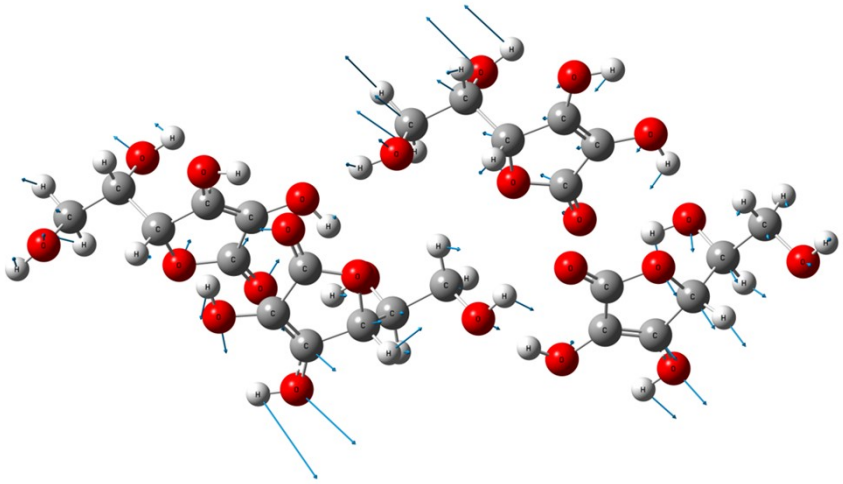
L-AA_1, 1.49 THz



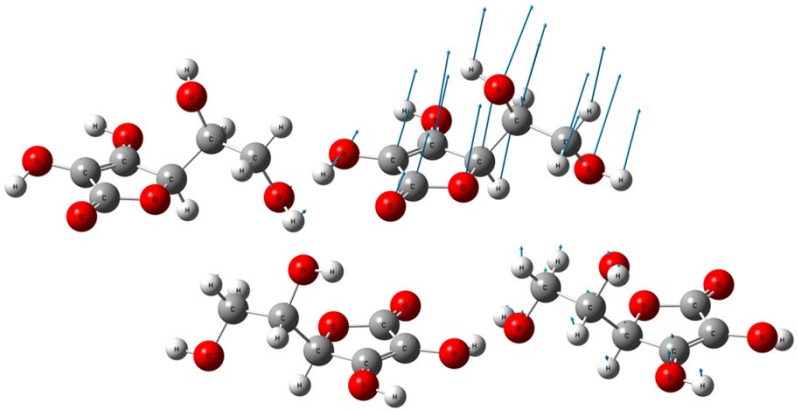
L-AA_4, 0.89 THz



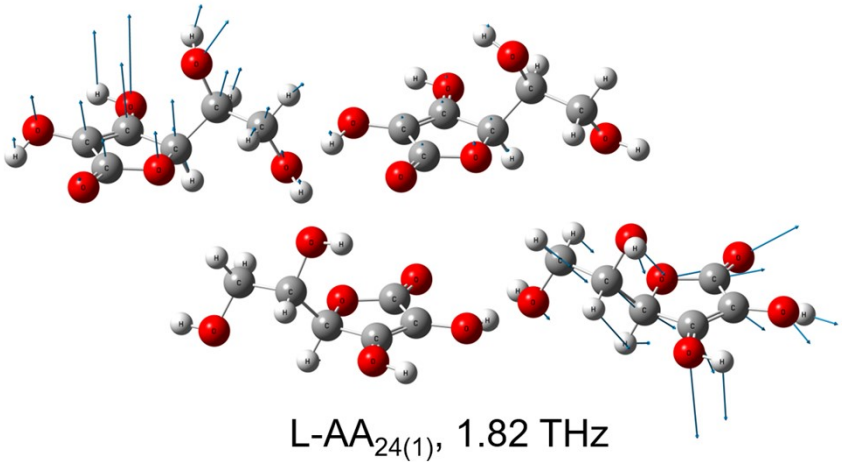
L-AA_4, 1.13 THz



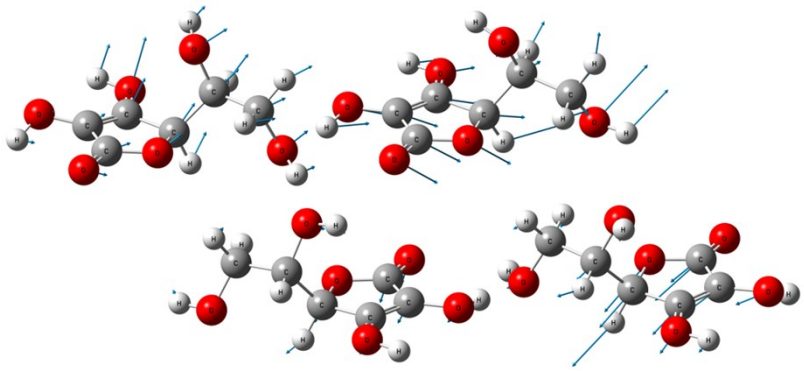
L-AA_4, 1.71 THz



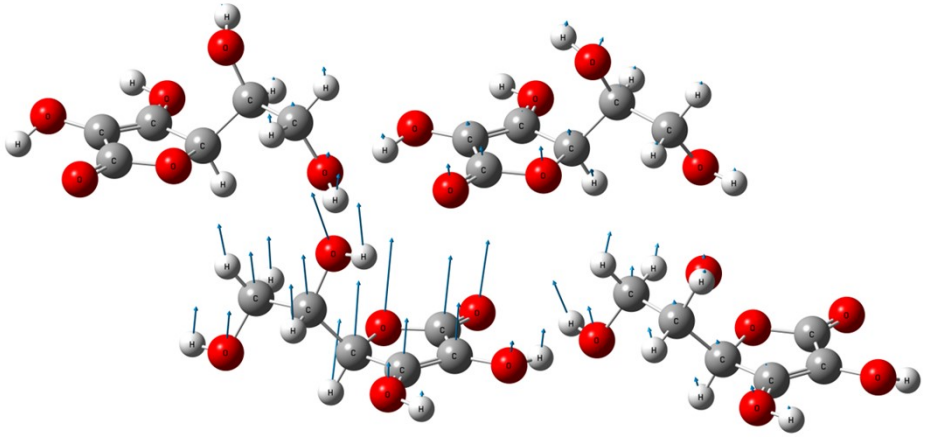
L-$AA_{24(1)}$, 1.61 THz



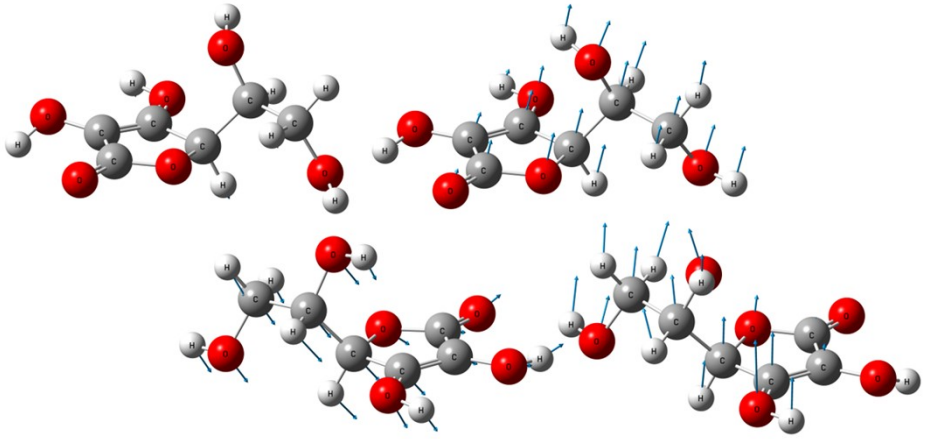
L-$AA_{24(1)}$, 1.82 THz



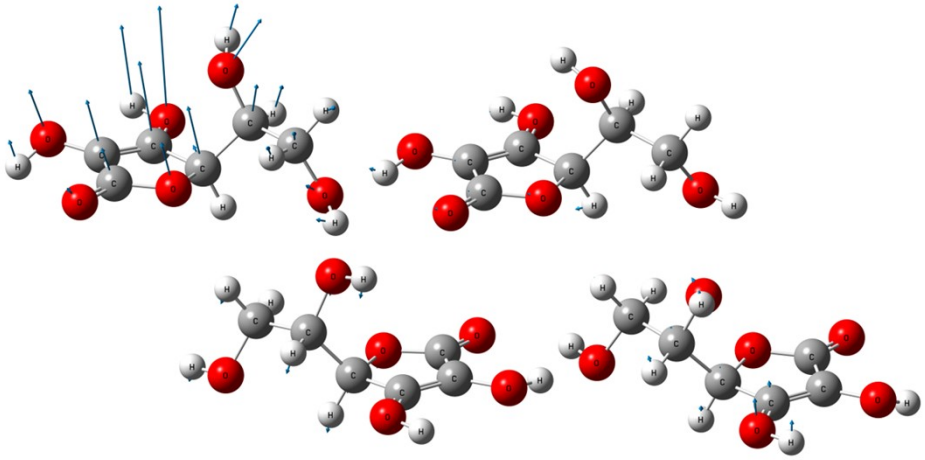
L-$AA_{24(1)}$, 1.97 THz



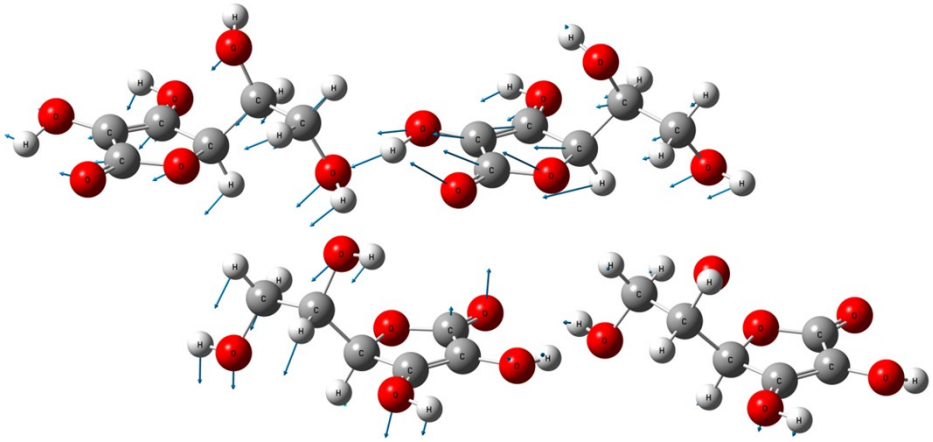
L-$AA_{24(2)}$, 1.56 THz



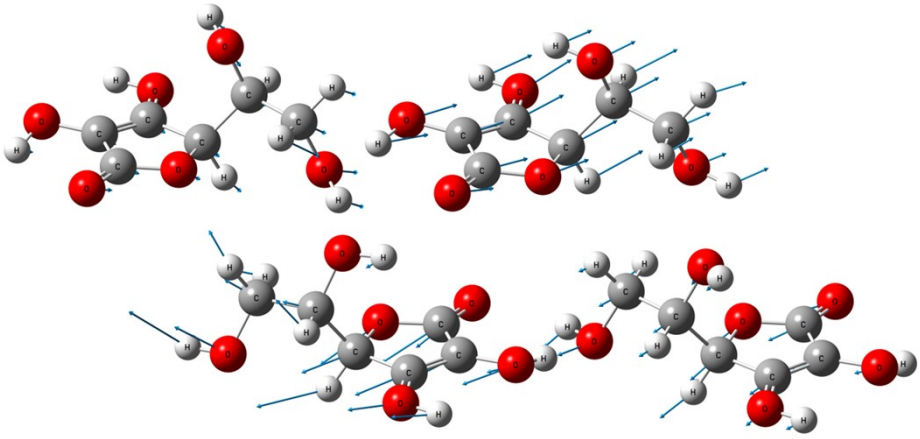
L-$AA_{24(2)}$, 1.72 THz



L-$AA_{24(2)}$, 1.82 THz



L-$AA_{24(2)}$, 1.96 THz



L-AA_{108}, 1.50 THz

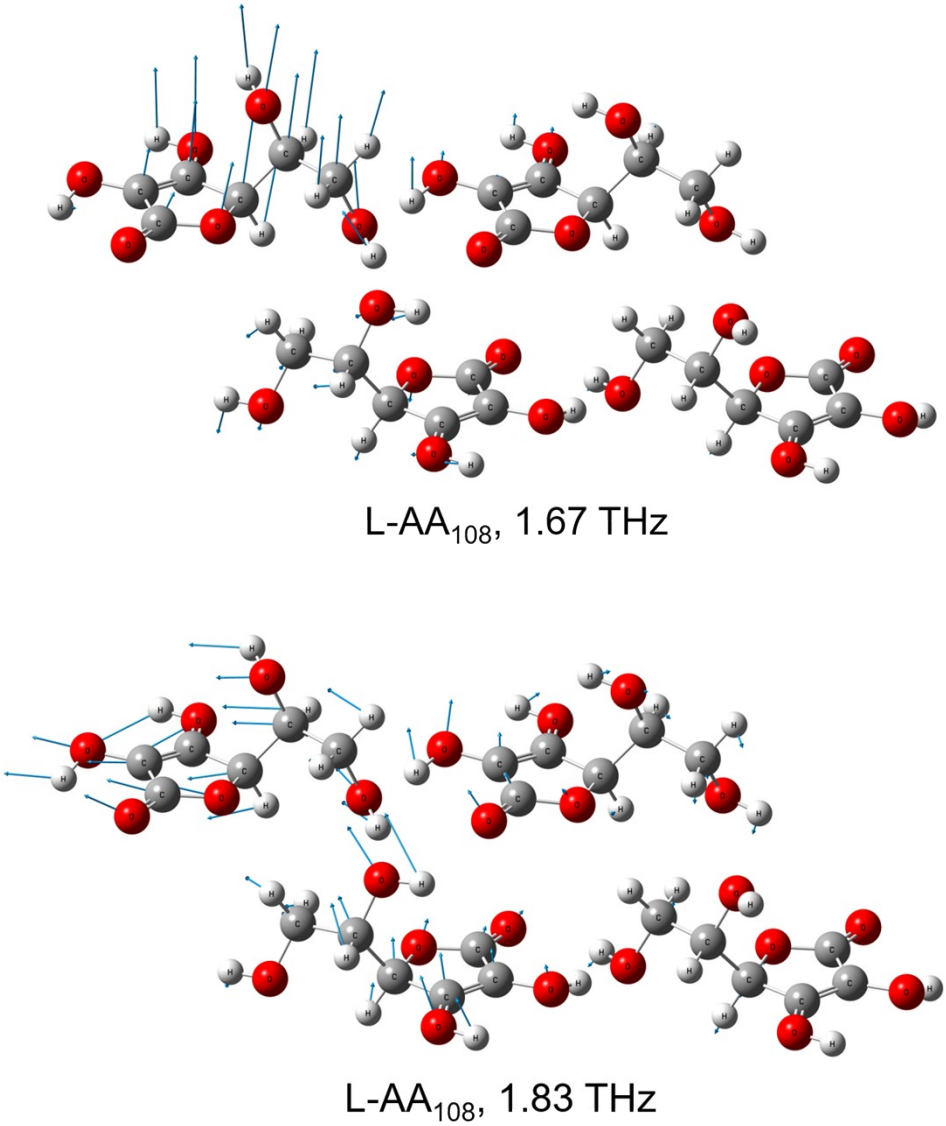


Fig. S1 The vibration modes corresponding to each absorption peak in the calculated spectrum of L-AA_1, L-AA_4, L-$AA_{24(1)}$, L-$AA_{24(2)}$, L-AA_{108}.

Table S1. The assignment of each vibrational mode in **Fig. S1** (the molecules 1, 2, 3, and 4 are the upper left, upper right, lower left, and lower right molecules in the model, respectively).

Model	Frequency/THz	Vibrational Mode
L-AA_1	1.49	The intra-rotation of the HCOH-CH_2OH group
L-AA_4	0.89	The collective vibration involving molecules 2, 4 and HCOH-CH_2OH group in molecule 1
L-AA_4	1.13	Mainly the intramolecular O-H vibration
L-AA_4	1.71	Mainly the O-H vibration of molecules 2, 3
L-$AA_{24(1)}$	1.61	The vibration of CH_2OH-CH_2O and five-membered ring in molecule 2
L-$AA_{24(1)}$	1.82	The vibration of five-membered ring, CH_2O, two OH groups in molecule 1 and vibration of molecule 4
L-$AA_{24(1)}$	1.97	Mainly the horizontal vibration involving molecules 1, 2, 4, respectively
L-$AA_{24(2)}$	1.56	The vibration involving molecule 3 and CH_2OH group in molecule 4
L-$AA_{24(2)}$	1.72	Collective vibration of molecules 2, 3 and 4
L-$AA_{24(2)}$	1.82	The vibration of five-

		membered ring, CH_2O, two OH groups in molecule 1
L-$AA_{24(2)}$	1.96	Mainly the horizontal vibration involving molecules 1, 2 and vertical vibration involving 3
L-AA_{108}	1.50	The vibration of molecule 2 relative to molecule 3
L-AA_{108}	1.67	The vibration of five-membered ring, CH_2OH-CH_2O, one OH group in molecule 1 and vibration of CH_2OH in molecule 4
L-AA_{108}	1.83	Mainly the vibration involving molecules 1 and 3

Table S2 The numerical value of the internal product of the vibration of the absorption peak in the calculation results of the periodic model.

Functional / Frequencies	opt-B88 opt-B86	opt-B86 opt-PBE	opt-B88 opt-PBE
1.06/1.07/1.01 THz	0.975	0.999	0.975
1.51/1.54/1.64 THz	0.993	0.985	0.963
1.62/1.65/1.77 THz	0.998	0.996	0.997

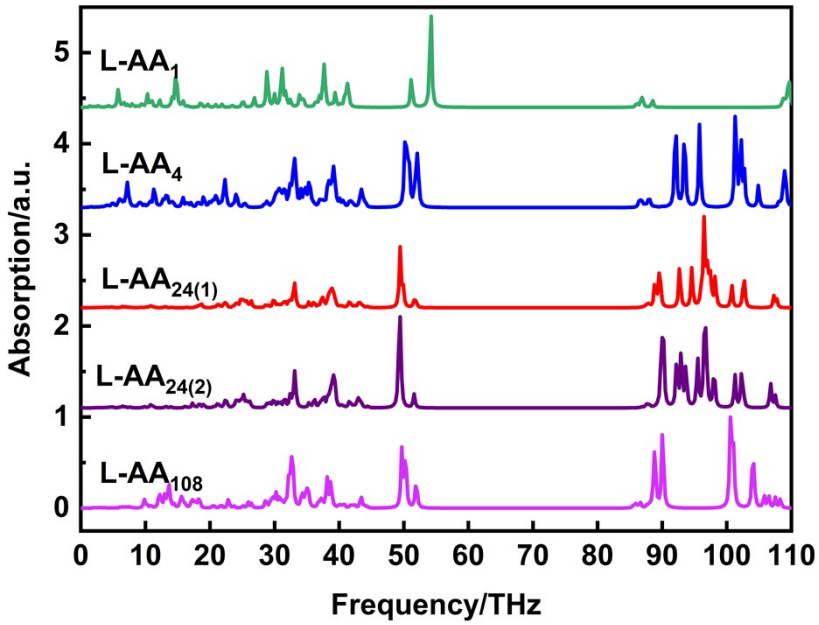


Fig. S2 Full spectra calculated by the cluster models.

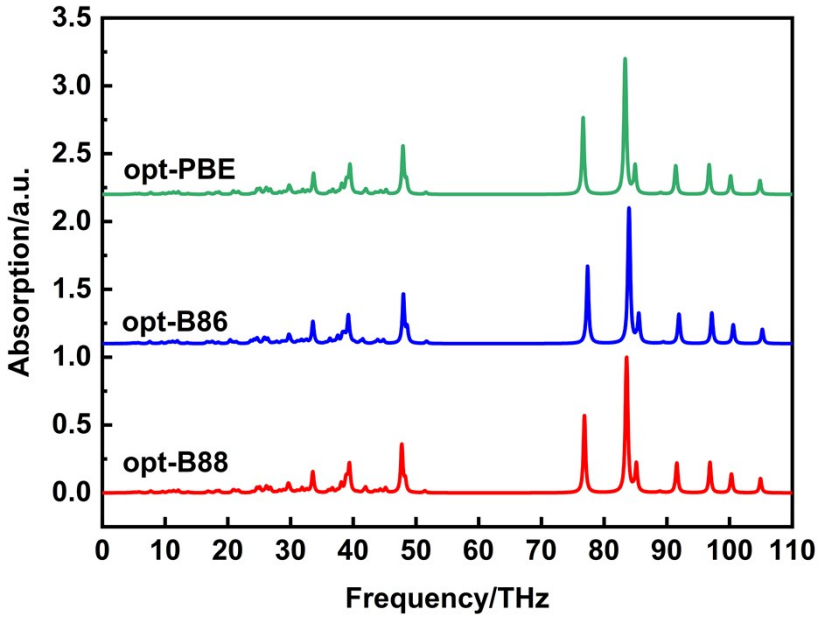


Fig. S3 Full spectra calculated by the periodic structure model.

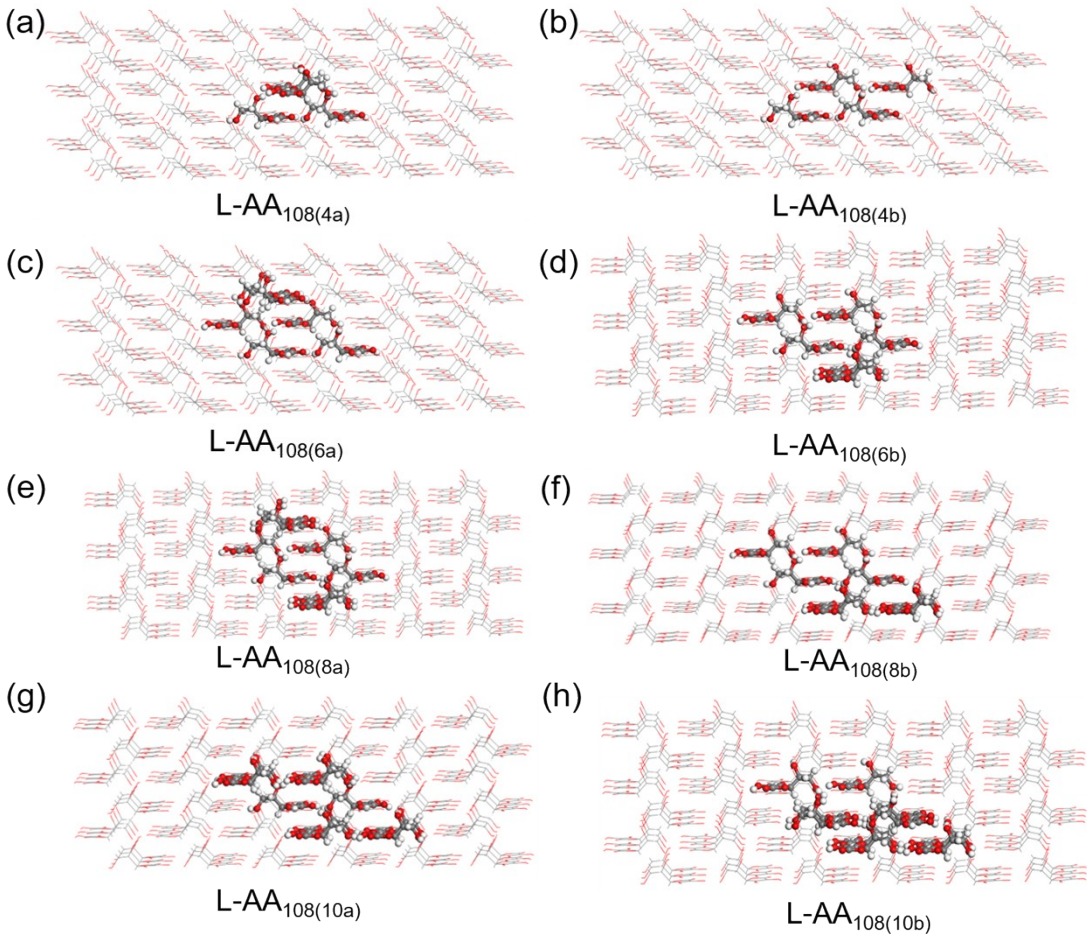


Fig. S4 Cluster models the of L-AA crystal with 4 (a, b), 6 (c, d), 8 (e, f), and 10 (g, h) monomers allowed to be relaxed in a 108-molecule matrix. The inner (ball-sticks) and outer (lines) layers represent the cluster models and their surroundings, respectively, treated with quantum chemical and semiempirical methods. For each size of the cluster, we built two different models by selecting different monomers. Gray, red, and white balls and lines denote carbon, oxygen, and hydrogen atoms, respectively.

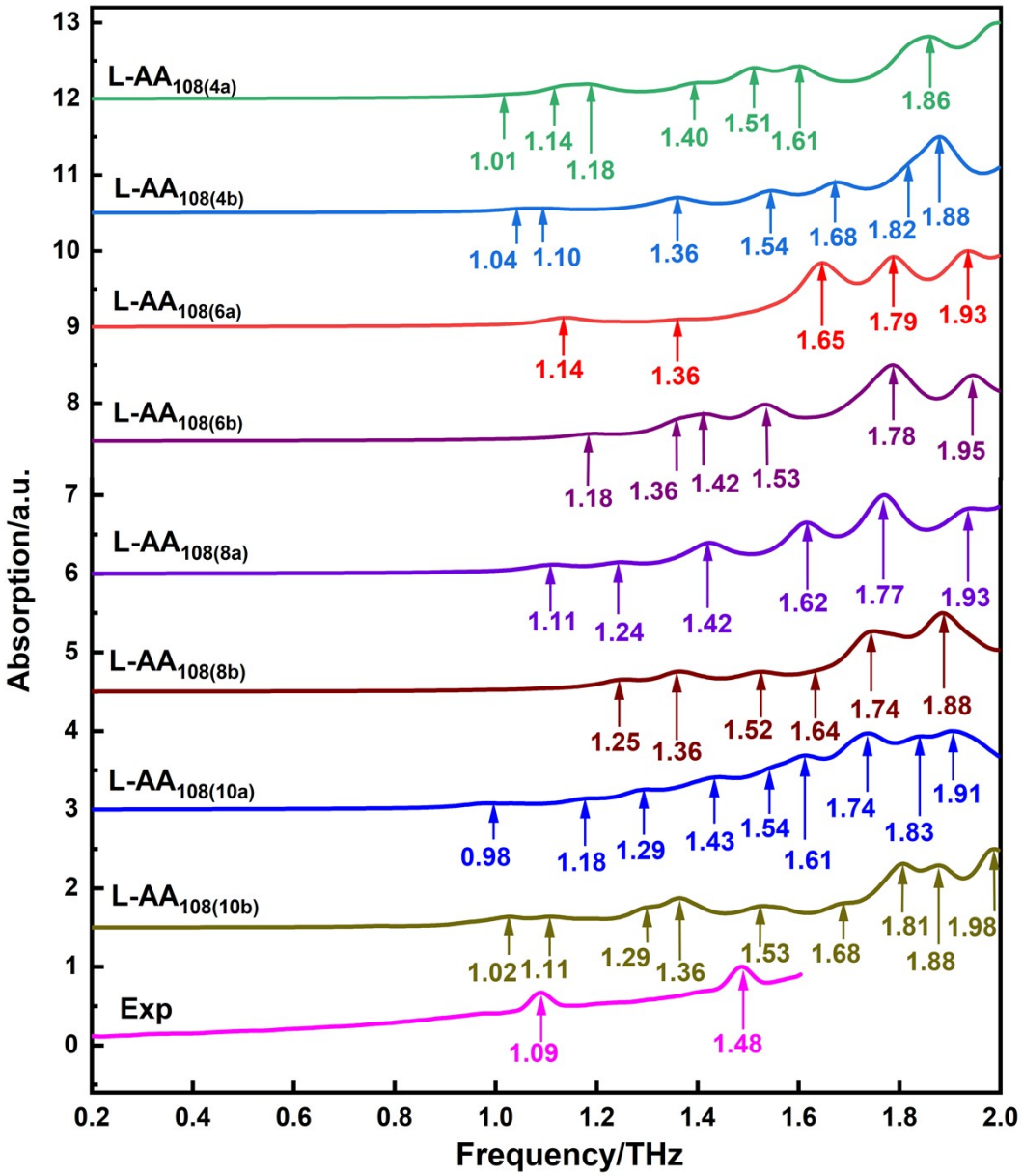


Fig. S5 Comparison of the calculated THz absorption spectra of L-AA crystal. Calculations are based on different cluster models (**Fig. S4**).

Table S3 Calculation results of single molecule using B3LYP functional in VASP compared with Gaussian.

Gaussian/B3LYP/6-311g(d,p)	VASP/B3LYP/500 eV
1.49	1.29
2.10	2.17
2.73	3.08
3.96	3.80
4.33	4.24
5.84	4.95
6.67	5.56
7.29	6.05
8.01	6.65
8.79	8.01
9.49	9.22
10.35	9.78
10.99	11.81
12.24	12.49
14.19	12.82
14.80	13.85
15.85	15.68
16.62	16.92
18.67	18.08
19.70	19.87
20.94	20.16
21.94	22.15
23.53	23.85
25.19	24.99
26.95	28.54
28.98	28.97
30.11	30.04
31.24	30.69
31.26	30.95
31.86	32.15
32.58	32.39
34.05	33.64
34.58	34.22
36.52	35.95
37.10	37.06
37.74	37.35
37.91	37.68
38.95	38.36
39.56	39.29
40.35	40.24

41.10	40.37
41.48	41.54
41.60	42.11
43.69	44.14
51.41	51.04
54.39	52.77
86.40	87.00
87.02	87.46
87.31	88.53
88.86	88.70
109.13	109.06
109.53	110.43
109.96	111.73
110.17	112.71