Supplementary Material (ESI) for PCCP

Supplementary Information for "A study into the effect of subtle structural details and disorder on the terahertz spectrum of crystalline benzoic acid"

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Contents of supplementary information:

A full listing of calculated vibrational frequencies in the terahertz region (Tables S1 and S2), lattice energy minimised unit cells of the disordered models (Table S3) and xyz trajectory files for visualisation of the calculated vibrational modes. These are supplied as xyz files in a format that can be visualised using JMol:
ba-dmarel_configA.xyz contains the vibrational modes calculated using the rigid molecule approximation (using DMAREL) and the fully ordered crystal structure model with dimers in configuration A

ba-dmarel_configB.xyz contains the vibrational modes calculated using the rigid molecule approximation (using DMAREL) and the fully ordered crystal structure model with dimers in configuration B

ba-castep_configA_fullyrelaxed.xyz contains the vibrational modes calculated using plane-wave DFT (using CASTEP) and the fully ordered crystal structure model with dimers in configuration A, with the crystal structure fully optimised (including unit cell dimensions)

ba-castep_configA_100K.xyz contains the vibrational modes calculated using plane-wave DFT (using CASTEP) and the fully ordered crystal structure model with dimers in configuration A, with the unit cell contrained at T = 100K dimensions during crystal structure optimisation

ba-castep_configB_100K.xyz contains the vibrational modes calculated using plane-wave DFT (using CASTEP) and the fully ordered crystal structure model with dimers in configuration B, with the unit cell contrained at T = 100K dimensions during crystal structure optimisation

ba-dmarel-disordered.xyz contains the vibrational modes calculated using the rigid molecule approximation (using DMAREL), using one of the models (model 1) of the disordered crystal structure (with a 2:1 ration of dimers in configurations A and B).

Table S1. Full listing of calculated **k**=0 vibrational mode frequencies from the rigid-molecule atom-atom model potential calculations on the ordered crystal structures.

ordered crystal structure with dimers in configuration A		ordered crystal structure with dimers in configuration B	
frequency / THz	symmetry	frequency / THz	symmetry
IR active modes		IR active modes	
0.84	Au	0.79	Au
1.16	Bu	1.16	Bu
1.31	Au	1.34	Au
2.37	Au	2.33	Bu
2.57	Bu	2.66	Au
3.12	Au	2.93	Au
3.32	Bu	3.08	Bu
3.80	Au	4.15	Bu
3.82	Bu	4.17	Au
IR inactive modes		IR inactive modes	
1.07	Bg	1.06	Bg
1.74	Ag	1.62	Ag

1.81	Ag	1.81	Ag
1.96	Bg	1.89	Bg
3.40	Ag	2.96	Bg
3.51	Bg	3.01	Ag
3.69	Bg	3.78	Bg
3.82	Ag	3.78	Ag
4.01	Ag	4.31	Ag
4.14	Bg	4.33	Bg
4.30	Bg	4.44	Bg
4.32	Ag	4.49	Ag

Table S2. Calculated **k**=0 vibrational mode frequencies from the rigid from plane-wave DFT calculations. All modes below 5 THz are listed.

ordered crystal structure with dimers in configuration A, using the unconstrained energy minimised structure		ordered crystal structure with dimers in configuration A, unit cell constrained at T = 100K dimensions		ordered crystal structure with dimers in configuration B, unit cell constrained at T = 100K dimensions	
frequency / THz	symmetry	frequency / THz	symmetry	frequency / THz	symmetry
IR active modes		IR active modes		IR active modes	
1.26	Au	1.52	Au	1.51	Au
1.30	Bu	2.00	Au	1.80	Bu
1.85	Au	2.11	Bu	2.12	Au
2.02	Bu	2.62	Bu	2.50	Au
2.13	Au	2.72	Au	2.71	Bu
2.34	Au	3.15	Au	2.99	Bu
2.37	Bu	3.26	Bu	3.18	Au
2.98	Au	3.54	Au	3.48	Au
2.99	Bu	3.55	Bu	3.55	Bu
4.18	Au	4.64	Bu	4.43	Bu
4.18	Bu	4.64	Au	4.43	Au
5.31	Au	5.71	Au	5.67	Au
5.37	Bu	5.75	Bu	5.69	Bu
IR inactive modes		IR inactive modes		IR inactive modes	
1.03	Bg	1.51	Bg	1.45	Bg
1.03	Ag	1.81	Ag	1.79	Ag
1.51	Ag	1.87	Ag	1.84	Ag
1.69	Bg	2.01	Bg	1.97	Bg
1.89	Ag	2.78	Ag	2.54	Ag
1.96	Bg	2.99	Bg	2.74	Bg
2.84	Ag	3.51	Bg	3.30	Bg
2.86	Bg	3.60	Ag	3.38	Ag
3.62	Ag	4.01	Ag	3.99	Bg
3.64	Bg	4.03	Bg	4.01	Ag
3.84	Bg	4.25	Bg	4.26	Ag
3.84	Ag	4.29	Ag	4.27	Bg
4.10	Bg	4.53	Bg	4.46	Bg
4.12	Ag	4.58	Ag	4.49	Ag

Table S3. Lattice energy minimised unit cell parameters of the two ordered and the four disordered models of benzoic acid, from the rigid-molecule atom-atom model potential calculations.

	Lattice Energy (kJ/mol)	a /Å	b /Å	c /Å	α /°	β /°	γ /°	Volume per molecule /Å^3
ordered (config. A)	-88.12	5.367	5.176	22.068	90	100.35	90	150.77
ordered (config. B)	-86.47	5.334	5.311	21.829	90	101.42	90	151.54
model 1	-87.55	5.360	5.213	22.000	90.01	100.66	89.99	151.04
model 2	-87.56	5.360	5.214	21.996	89.95	100.68	89.97	151.03
model 3	-87.56	5.361	5.214	21.997	90.05	100.68	90.03	151.03
model 4	-87.55	5.359	5.214	21.999	90.01	100.67	89.99	151.03