Supplementary Information for:

Application of London-type dispersion corrections to the solid-state density functional theory simulation of the terahertz spectra of crystalline pharmaceuticals

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Table S1. Calculated bond lengths (Å) for naproxen and RMSDs as compared to the experimental X-ray data.

		fixed-geometry optimizations			full geometry optimizations		
bond	exp	PBE	PBE-D	PBE-D*	PBE	PBE-D	PBE-D*
C_1–C_2	1.5160	1.52386	1.52617	1.52587	1.52248	1.52064	1.52278
C_1–O_1	1.2120	1.23360	1.23307	1.23325	1.23503	1.23588	1.23502
C_1–O_2	1.3236	1.33130	1.33371	1.33301	1.32797	1.32804	1.32963
C_2–C_3	1.5298	1.53501	1.53745	1.53720	1.53626	1.53337	1.53493
C_2–C_4	1.5286	1.52663	1.52633	1.52810	1.52817	1.52359	1.52669
C_4–C_5	1.4200	1.42295	1.42444	1.42424	1.42389	1.42289	1.42354
C_4–C_6	1.3756	1.38667	1.38763	1.38754	1.38694	1.38526	1.38610
C_5–C_7	1.3726	1.38265	1.38335	1.38266	1.38277	1.38282	1.38240
C_6–C_8	1.4206	1.41987	1.42086	1.42049	1.42036	1.41817	1.41877
C_7–C_9	1.4197	1.42232	1.42320	1.42281	1.42318	1.42185	1.42206
C_8–C_9	1.4188	1.43516	1.43752	1.43683	1.43668	1.43524	1.43556
C_8–C_{10}	1.4190	1.42274	1.42456	1.42375	1.42462	1.42064	1.42171
C_9–C_{11}	1.4287	1.42662	1.42535	1.42623	1.42524	1.42636	1.42651
C_{10}–C_{12}	1.3659	1.37490	1.37745	1.37555	1.37650	1.37447	1.37412
C_{11}–C_{13}	1.3745	1.38907	1.39040	1.38986	1.38923	1.38994	1.38958
C_{12}–C_{13}	1.4187	1.42293	1.42603	1.42437	1.42500	1.42301	1.42295
C_{13}–O_3	1.3706	1.36864	1.36837	1.36916	1.36759	1.36793	1.36895
C_{14}–O_3	1.4278	1.43414	1.43747	1.43551	1.43466	1.43683	1.43552
	RMSD	**0.0091**	0.0104	0.0098	0.0097	0.0093	0.0092

Table S2. Calculated bond angles (°) for naproxen and RMSDs as compared to the experimental X-ray data.

		fixed-geometry optimizations			full geometry optimizations		
bond angle	exp	PBE	PBE-D	PBE-D*	PBE	PBE-D	PBE-D*
C_1–C_2–C_3	111.432	111.484	111.387	111.724	110.820	111.911	112.027
C_1–C_2–C_4	107.464	107.792	107.410	107.684	108.012	105.920	106.658
C_2–C_4–C_5	120.585	120.802	120.228	120.781	120.641	120.478	120.965
C_2–C_4–C_6	120.170	120.301	120.533	120.273	120.461	120.250	120.048
C_2–C_1–O_1	123.262	122.537	122.534	122.732	121.872	122.168	122.416
C_2–C_1–O_2	112.327	112.436	112.446	112.306	112.892	112.517	112.507
C_3–C_2–C_4	112.525	112.729	112.326	112.804	112.841	112.616	113.062
C_4–C_5–C_7	120.812	120.817	120.782	120.849	120.902	120.723	120.777
C_4–C_6–C_8	120.917	121.339	121.113	121.290	121.426	120.907	121.203
C_5–C_4–C_6	119.239	118.886	119.235	118.937	118.894	119.270	118.983
C_5–C_7–C_9	120.965	121.365	121.088	121.290	121.234	121.183	121.339
C_6–C_8–C_9	119.682	119.658	119.535	119.618	119.514	119.913	119.778
C_6–C_8–C_{10}	121.338	121.738	121.786	121.789	121.975	121.191	121.510
C_7–C_9–C_8	118.277	117.801	118.184	117.901	117.987	117.841	117.758
C_7–C_9–C_{11}	121.762	122.288	121.911	122.163	122.180	122.203	122.304
C_8–C_9–C_{11}	119.910	119.865	119.868	119.891	119.818	119.861	119.870
C_8–C_{10}–C_{12}	120.536	120.847	120.788	120.826	120.895	120.717	120.778
C_9–C_8–C_{10}	118.861	118.506	118.606	118.494	118.485	118.684	118.560
C_9–C_{11}–C_{13}	119.263	119.731	119.727	119.746	119.961	119.473	119.646
C_{10}–C_{12}–C_{13}	120.557	120.674	120.523	120.686	120.616	120.612	120.736
C_{11}–C_{13}–C_{12}	120.765	120.274	120.413	120.267	120.200	120.452	120.272
C_{11}–C_{13}–O_3	125.581	125.744	125.092	125.713	125.399	125.576	125.920
C_{12}–C_{13}–O_3	113.654	113.982	114.494	114.019	114.401	113.972	113.808
C_{13}–O_3–C_{14}	117.391	117.839	117.048	118.160	117.592	117.392	118.291
O_1–C_1–O_2	124.389	124.998	124.984	124.934	125.213	125.243	125.023
	RMSD	0.363	**0.349**	0.355	0.516	0.466	0.448

Table 1. Crystal data and structure refinement for (S)-naproxen at 102 K.

Identification code	p2(1)	
Empirical formula	C14 H14 O3	
Formula weight	230.25	
Temperature	102(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.7354(11) Å	α= 90°.
	b = 5.7181(8) Å	β= 93.737(2)°.
	c = 13.3641(18) Å	γ = 90°.
Volume	589.86(14) $Å^3$	
Z	2	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	244	
Crystal size	0.35 x 0.25 x 0.21 mm^3	
Theta range for data collection	2.64 to 28.32°.	
Index ranges	-10<=h<=10, -7<=k<=7, -16<=l<=17	
Reflections collected	6007	
Independent reflections	1611 [R(int) = 0.0233]	
Completeness to theta = 28.32°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9812 and 0.9690	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1611 / 1 / 160	
Goodness-of-fit on F^2	1.108	
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0941	
R indices (all data)	R1 = 0.0367, wR2 = 0.0976	
Largest diff. peak and hole	0.287 and -0.204 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (S)-naproxen at 102 K. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3736(2)	3214(3)	4771(1)	38(1)
O(2)	3280(2)	-492(3)	4270(1)	29(1)
C(1)	2895(2)	1762(3)	4292(1)	23(1)
C(2)	1299(2)	2353(3)	3620(1)	22(1)
C(3)	1892(2)	2807(3)	2569(1)	20(1)
C(4)	1493(2)	1239(3)	1808(1)	20(1)
C(6)	1955(2)	1692(3)	815(1)	19(1)
C(7)	1459(2)	155(3)	13(1)	21(1)
C(8)	1749(2)	741(3)	-952(1)	24(1)
C(9)	2597(2)	2865(3)	-1168(1)	22(1)
C(10)	3173(2)	4351(3)	-409(1)	21(1)
C(11)	2836(2)	3792(3)	602(1)	18(1)
C(12)	3298(2)	5334(3)	1408(1)	22(1)
C(13)	2838(2)	4860(3)	2362(1)	22(1)
C(14)	317(3)	4429(4)	4030(1)	30(1)
O(3)	2761(2)	3227(3)	-2171(1)	28(1)
C(15)	3576(2)	5343(4)	-2456(1)	31(1)

Table 3. Bond lengths [Å] and angles [°] for (S)-naproxen at 102 K.

O(1)-C(1)	1.212(2)
O(2)-C(1)	1.324(2)
O(2)-H(1)	0.88(3)
C(1)-C(2)	1.516(2)
C(2)-C(3)	1.529(2)
C(2)-C(14)	1.530(2)
C(2)-H(2)	1.0000
C(3)-C(4)	1.375(2)
C(3)-C(13)	1.420(2)
C(4)-C(6)	1.420(2)
C(4)-H(4)	0.9500
C(6)-C(11)	1.419(2)
C(6)-C(7)	1.419(2)
C(7)-C(8)	1.366(2)
C(7)-H(7)	0.9500
C(8)-C(9)	1.419(3)
C(8)-H(8)	0.9500
C(9)-O(3)	1.371(2)
C(9)-C(10)	1.375(2)
C(10)-C(11)	1.429(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.420(2)
C(12)-C(13)	1.373(2)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
O(3)-C(15)	1.428(2)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(1)-O(2)-H(1)	113(2)

O(1)-C(1)-O(2)	124.38(18)
O(1)-C(1)-C(2)	123.26(18)
O(2)-C(1)-C(2)	112.33(15)
C(1)-C(2)-C(3)	107.45(13)
C(1)-C(2)-C(14)	111.44(15)
C(3)-C(2)-C(14)	112.53(14)
C(1)-C(2)-H(2)	108.4
C(3)-C(2)-H(2)	108.4
C(14)-C(2)-H(2)	108.4
C(4)-C(3)-C(13)	119.23(15)
C(4)-C(3)-C(2)	120.19(15)
C(13)-C(3)-C(2)	120.58(14)
C(3)-C(4)-C(6)	120.94(15)
C(3)-C(4)-H(4)	119.5
C(6)-C(4)-H(4)	119.5
C(11)-C(6)-C(7)	118.87(14)
C(11)-C(6)-C(4)	119.68(14)
C(7)-C(6)-C(4)	121.34(15)
C(8)-C(7)-C(6)	120.52(15)
C(8)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(7)-C(8)-C(9)	120.56(15)
C(7)-C(8)-H(8)	119.7
C(9)-C(8)-H(8)	119.7
O(3)-C(9)-C(10)	125.58(16)
O(3)-C(9)-C(8)	113.66(15)
C(10)-C(9)-C(8)	120.77(15)
C(9)-C(10)-C(11)	119.25(15)
C(9)-C(10)-H(10)	120.4
C(11)-C(10)-H(10)	120.4
C(6)-C(11)-C(12)	118.29(14)
C(6)-C(11)-C(10)	119.92(14)
C(12)-C(11)-C(10)	121.74(15)
C(13)-C(12)-C(11)	120.94(15)
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5

C(12)-C(13)-C(3)	120.82(15)
C(12)-C(13)-H(13)	119.6
C(3)-C(13)-H(13)	119.6
C(2)-C(14)-H(14A)	109.5
C(2)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(2)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(9)-O(3)-C(15)	117.39(14)
O(3)-C(15)-H(15A)	109.5
O(3)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
O(3)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (S)-naproxen at 102 K. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	40(1)	33(1)	40(1)	-5(1)	-13(1)	-5(1)
O(2)	30(1)	26(1)	30(1)	1(1)	-5(1)	3(1)
C(1)	26(1)	25(1)	20(1)	1(1)	3(1)	-2(1)
C(2)	23(1)	21(1)	21(1)	0(1)	2(1)	-1(1)
C(3)	19(1)	19(1)	22(1)	1(1)	-1(1)	2(1)
C(4)	19(1)	15(1)	25(1)	2(1)	-1(1)	1(1)
C(6)	18(1)	16(1)	22(1)	0(1)	-1(1)	2(1)
C(7)	21(1)	16(1)	27(1)	-1(1)	1(1)	0(1)
C(8)	24(1)	22(1)	25(1)	-5(1)	0(1)	2(1)
C(9)	21(1)	23(1)	21(1)	-1(1)	3(1)	3(1)
C(10)	20(1)	19(1)	24(1)	-1(1)	3(1)	0(1)
C(11)	16(1)	16(1)	23(1)	-1(1)	1(1)	1(1)
C(12)	23(1)	17(1)	26(1)	-2(1)	1(1)	-3(1)
C(13)	23(1)	19(1)	22(1)	-4(1)	-1(1)	-2(1)
C(14)	32(1)	30(1)	28(1)	-1(1)	8(1)	5(1)
O(3)	32(1)	30(1)	22(1)	-2(1)	5(1)	-2(1)
C(15)	36(1)	32(1)	26(1)	4(1)	9(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (S)-naproxen at 102 K.

	x	y	z	U(eq)
H(2)	512	963	3590	26
H(4)	901	-166	1949	24
H(7)	920	-1294	150	26
H(8)	1380	-282	-1484	28
H(10)	3787	5735	-555	25
H(12)	3935	6714	1286	26
H(13)	3156	5919	2890	26
H(14A)	-79	4030	4691	45
H(14B)	-686	4796	3571	45
H(14C)	1086	5791	4091	45
H(15A)	2935	6685	-2213	47
H(15B)	3581	5415	-3189	47
H(15C)	4770	5382	-2163	47
H(1)	4280(30)	-820(50)	4596(18)	41(7)

Table 6. Hydrogen bonds for (S)-naproxen at 102 K [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(1)...O(1)#1	0.88(3)	1.79(3)	2.6703(19)	174(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y-1/2,-z+1

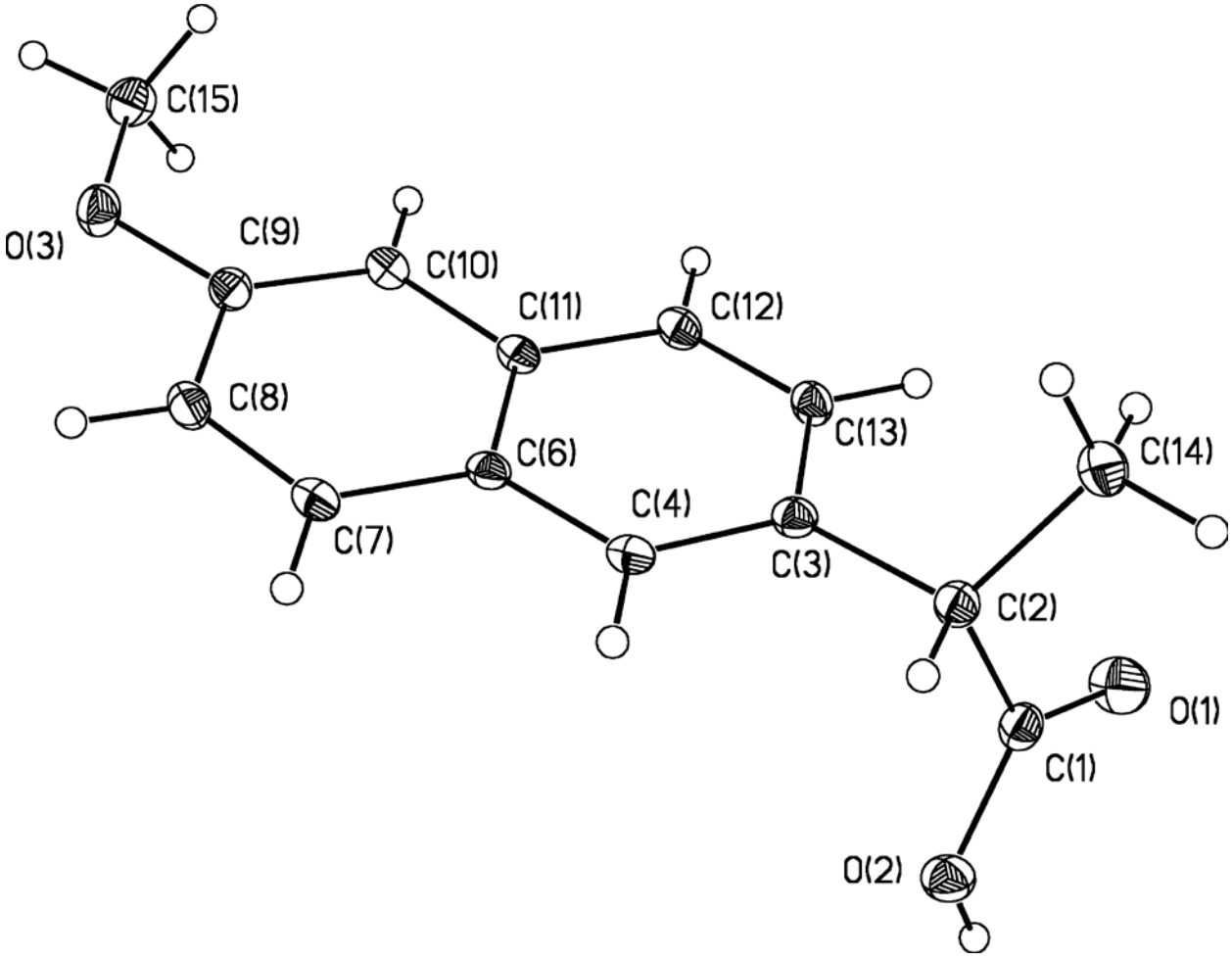

Figure 1. Molecular structure and atomic labeling scheme for (S)-naproxen.

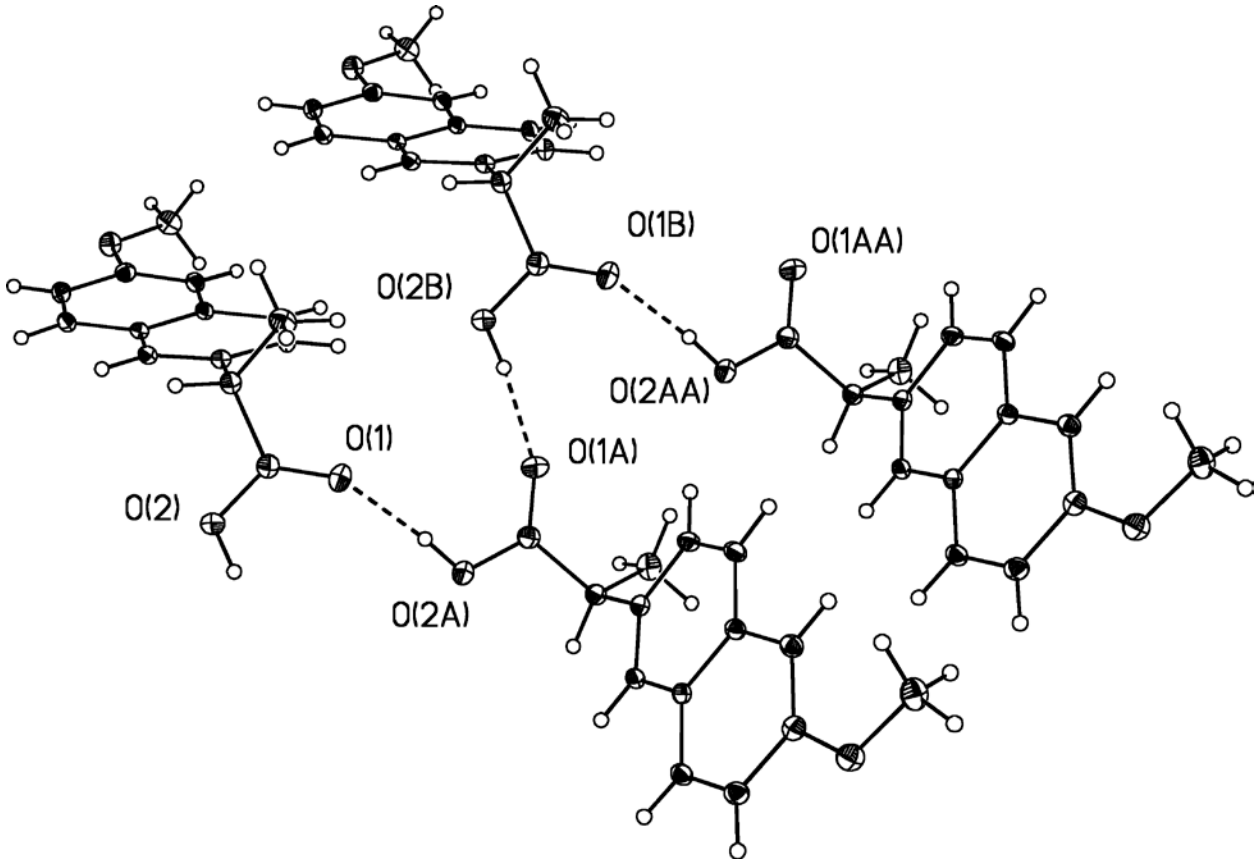

Figure 2. Hydrogen bonding pattern for (S)-naproxen.