The Raman spectrum of CaCO3 polymorphs calcite and aragonite: A combined experimental and computational study.

SUPPLEMENTARY MATERIAL: The Raman spectrum of $CaCO_3$ polymorphs calcite and aragonite. A combined experimental and computational study

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I. SINGLE CRYSTAL DATA AT 300 K

		calc.	exp.	Δ	calc.	exp.	Δ	calc.	exp.	Δ	
	Symmetry	ν			a^2			b^2			$\gamma_{\rm exp}$
#	A_{1g}		1066.8			8			1		1.7
1		1089.1	1086.5	*2.6*	1000	1000		90	176	*-86*	1.8
#			1749.2			24			11		6.6
		ν			c^2			d^2			
2	E_g	155.1	155.4	*-0.3*	93	25	*68*	209	147	*62*	6.0
3		276.3	282.0	*-5.7*	99	71	*28*	708	428	*280*	9.3
4		711.0	712.5	*-1.5*	193	56	*137*	22	20	*2*	2.9
5		1433.3	1436.5	*-3.2*	17	11	*6*	51	6	*45*	3.8
$\overline{\lvert\Delta\rvert}$				*2.6*						*79*	
$\overline{\Delta}$				*-1.6*						*60*	
$\overline{\lvert\Delta\rvert}$%										*76*	
$\lvert\Delta\rvert_{max}$				*5.7*						*280*	

TABLE S1: Calculated and experimental Raman properties of single crystal calcite at T = 300 K. In the calculations the temperature effect was taken into account for integrated intensities only. Frequencies ν and peak widths γ_{exp} are in cm^{-1}; Raman integrated intensities were re-normalized so that the a^2 element of A_{1g} mode at 1089.1 cm^{-1} is equal to 1000. The symbols # indicate modes identified in the experiments with no correspondence in the calculations.

		calc.	exp.	Δ	calc.	exp.	Δ	calc.	exp.	Δ	calc.	exp.	Δ	
	Symmetry		ν			a^2			b^2			c^2		$\gamma_{\rm exp}$
1	A_g	148.7	143.0	*5.7*	6	1	*5*	2	4	*-2*	144	88	*56*	2.5
2		161.9	162.2	*-0.3*	85	16	*69*	11	0	*11*	79	55	*24*	4.8
3		195.8	194.3	*1.5*	6	4	*2*	87	6	*81*	31	4	*27*	5.8
4		205.0	214.9	*-9.9*	8	2	*6*	362	180	*182*	67	41	*26*	7.7
5		280.2	285.3	*-5.1*	1	0	*1*	117	51	*66*	48	26	*22*	10.4
6		704.2	705.7	*-1.5*	1	1	*0*	224	105	*119*	222	102	*120*	2.2
7		862.8	853.2	*9.6*	24	5	*19*	0	2	*-2*	0	3	*-3*	2.0
#			1059.7			1			4			4		2.0
8		1095.3	1085.3	*10.0*	169	218	*-49*	977	990	*-13*	1000	1000		1.7
9		1473.9	1464.0	*9.9*	2	0	*2*	6	0	*6*	5	13	*-8*	3.1
			ν			d^2			e^2			f^2		
10	B_{1g}	97.4	113.5	*-16.1*	192	74	*118*							9.4
11		152.1	153.4	*-1.3*	1672	1430	*242*							6.2
12		199.0	207.1	*-8.1*	3	3	*0*							5.0
13		213.4	225.5	*-12.1*	57	27	*30*							10.0
14		705.5	706.6	*-1.1*	16	15	*1*							2.1
15		1463.9	1462.3	*1.6*	51	28	*23*							3.1
16	B_{2g}	182.5	180.7	*1.8*				345	152	*193*				4.5
17		207.2	206.9	*0.3*				776	618	*158*				4.7
18		249.2	248.4	*0.8*				171	92	*79*				10.5
19		260.7	261.5	*-0.8*				8	71	*-63*				7.9
20		278.7						46						
21		714.6	716.9	*-2.3*				11	10	*1*				2.2
22		911.8	908.5	*3.3*				1	0	*1*				6.0
23		1091.6						0						
24		1591.8	1574.9	*16.9*				47	16	*31*				6.6
25	B_{3g}	101.3	125.0	*-23.7*							44	16	*28*	11.4
26		167.6	180.5	*-12.9*							238	23	*215*	7.0
27		177.8	190.9	*-13.1*							44	91	*-47*	6.2
28		271.4	272.9	*-1.5*							122	61	*61*	9.2
29		701.2	701.4	*-0.2*							211	98	*113*	2.0
30		1415.0									0			
$\overline{\lvert\Delta\rvert}$				*6.3*									*53*	
$\overline{\Delta}$				*-1.8*									*44*	
$\overline{\lvert\Delta\rvert}$%													*41*	
$\lvert\Delta\rvert_{max}$				*23.7*									*242*	

TABLE S2: Calculated and experimental Raman properties of single crystal aragonite at T = 300 K. In the calculations the temperature effect was taken into account for integrated intensities only. Frequencies ν and peak widths γ_{exp} are in cm^{-1}; Raman integrated intensities were re-normalized so that the c^2 element of A_g mode at 1095.3 cm^{-1} is equal to 1000. The symbols # indicate modes identified in the experiments with no correspondence in the calculations.

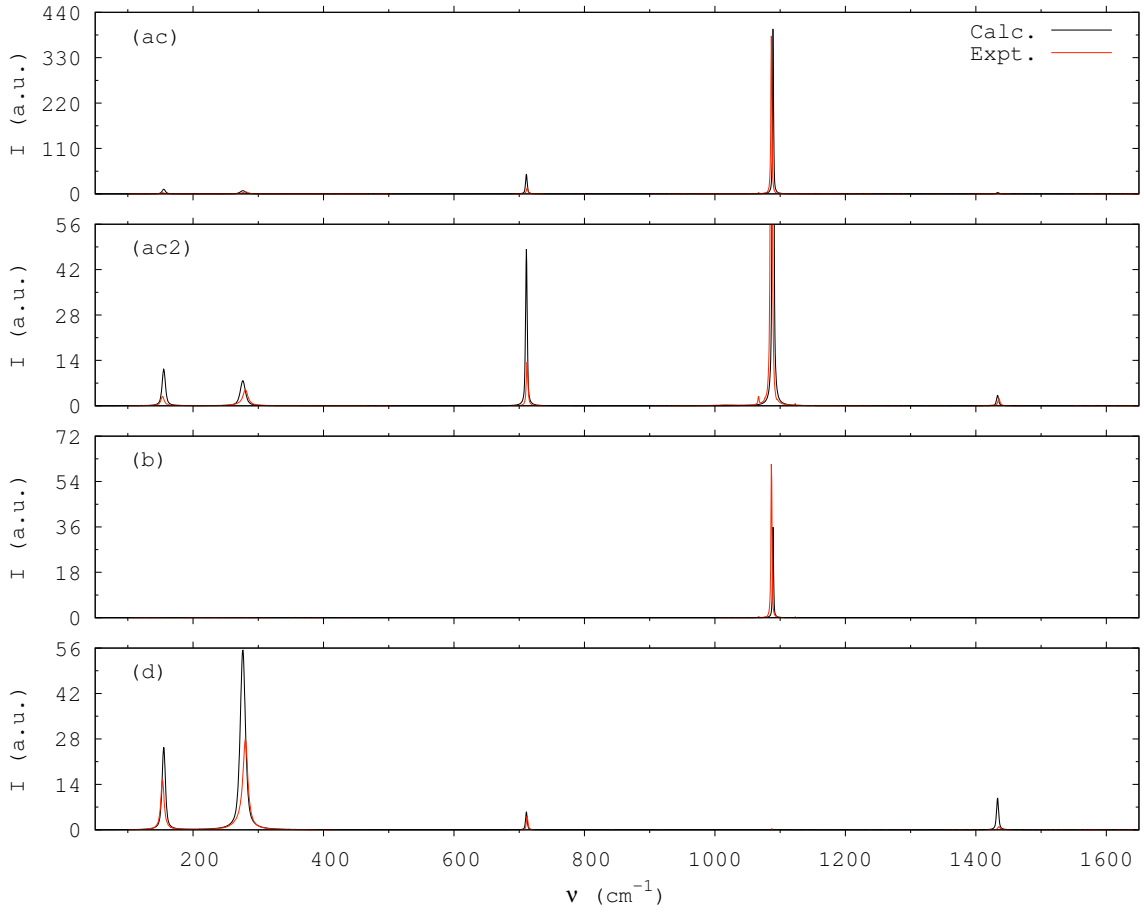

FIG. S1: Calculated and experimental Raman spectra of single crystal calcite at T = 300 K. In the calculations the temperature effect was taken into account for integrated intensities only. Raman integrated intensities were re-normalized so that the XX value for A_{1g} mode at 1089.1 cm^{-1} is equal to 1000. (ac) XX polarization, $a^2 + c^2$ contributions (A_{1g} plus E_g symmetries); (ac2) XX polarization, zoom on the c^2 contributions scale; (b) ZZ polarization, b^2 contributions (A_{1g}); (d) XZ polarization, d^2 contributions (E_g).

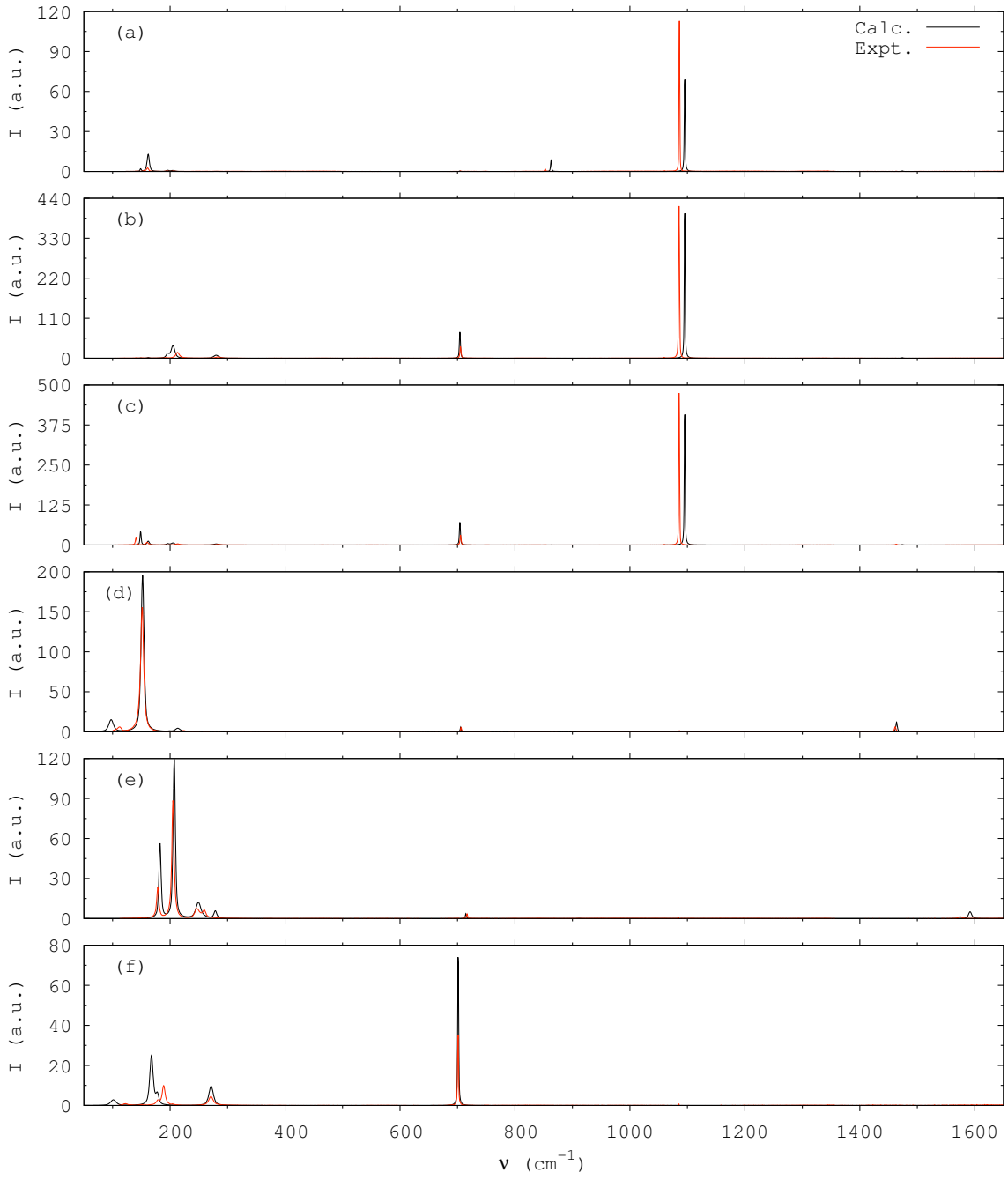

FIG. S2: Calculated and experimental Raman spectra of single crystal aragonite at T = 300 K. In the calculations the temperature effect was taken into account for integrated intensities only. Raman integrated intensities were re-normalized so that the ZZ value for A_g mode at 1095.3 cm^{-1} is equal to 1000. (a) XX polarization, a^2 contributions (A_g symmetry); (b) YY polarization, b^2 contributions (A_g); (c) ZZ polarization, c^2 contributions (A_g); (d) XY polarization, d^2 contributions (B_{1g}); (e) XZ polarization, e^2 contributions (B_{2g}); (f) YZ polarization, f^2 contributions (B_{3g}).

II. CALCITE: SINGLE CRYSTAL DATA WITH EXTENDED RANGE

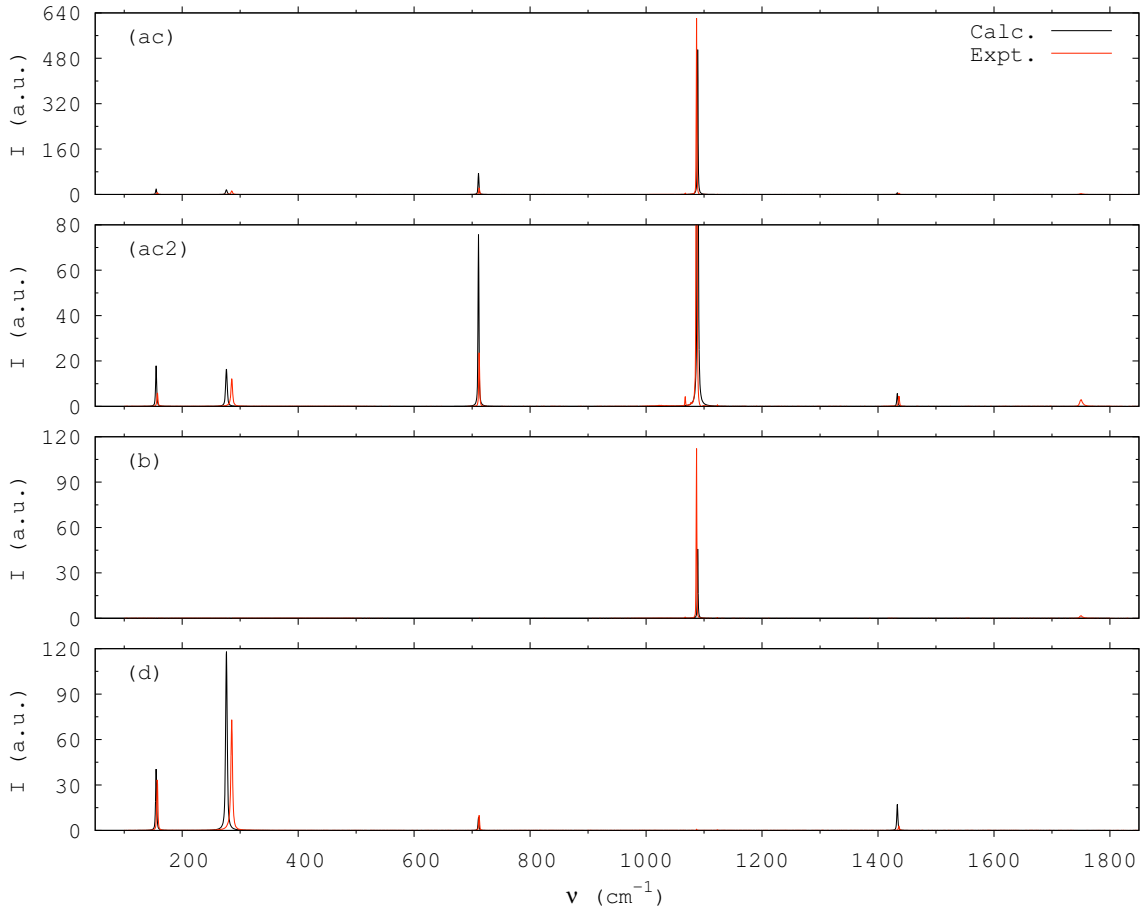

FIG. S3: Calculated and experimental Raman spectra of single crystal calcite at T = 80 K; the frequency range goes until 1850 cm^{-1}, to show the experimental peak around 1750 cm^{-1}. See caption to Figure S1 for more details.

III. ARAGONITE: SINGLE CRYSTAL DATA WITH ZOOM ON A SMALLER INTENSITY SCALE

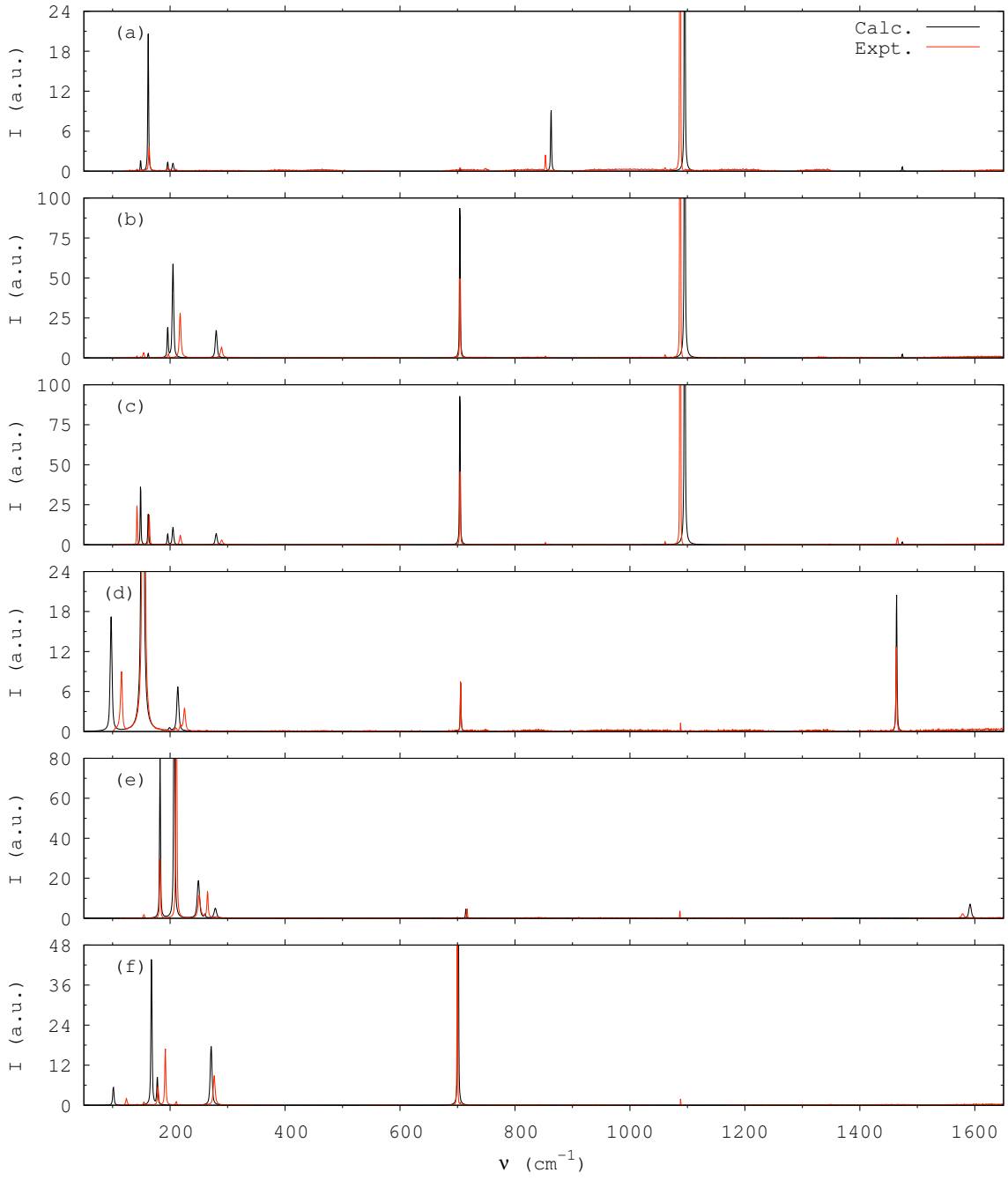

FIG. S4: Calculated and experimental Raman spectra of single crystal aragonite at T = 80 K; all spectra have been rescaled to the second most intense peak, to show less intense peaks. See caption to Figure S2 for more details.

IV. HARTREE-FOCK DATA FOR SINGLE CRYSTAL AT 80 K

		calc.	exp.	Δ	calc.	exp.	Δ	calc.	exp.	Δ	
	Symmetry		ν			a^2			b^2		$\gamma_{\rm exp}$
#	A_{1g}		1067.4			10			2		1.7
1		1193.1	1087.1	*106.0*	1000	1000		124	182	*-58*	1.4
#			1749.8			23			13		5.5
			ν			c^2			d^2		
2	E_g	163.3	159.6	*3.7*	49	17	*32*	98	99	*-1*	2.1
3		288.1	287.4	*0.7*	41	58	*-17*	493	354	*139*	3.2
4		783.2	712.6	*70.6*	202	56	*146*	11	23	*-12*	1.8
5		1583.6	1437.1	*146.5*	5	13	*-8*	22	7	*14*	2.1
$\overline{\lvert\Delta\rvert}$				*65.5*						*48*	
$\overline{\Delta}$				*65.5*						*26*	
$\overline{\lvert\Delta\rvert}$%										*53*	
$\lvert\Delta\rvert_{max}$				*146.5*						*146*	

TABLE S3: Calculated and experimental Raman properties of single crystal calcite at T = 80 K; the Hartree-Fock Hamiltonian was adopted in the calculations. Data can be compared to those in Table IV of the main Paper. See caption to Table S1 for more details.

V. EFFECT OF BASIS SET ON SINGLE CRYSTAL DATA AT 80 K

		calc.	exp.	Δ	calc.	exp.	Δ	calc.	exp.	Δ	
	Symmetry	ν			a^2			b^2			γ_{exp}
#	A_{1g}		1067.4			10			2		1.7
1		1099.9	1087.1	*12.8*	1000	1000		97	182	*-85*	1.4
#			1749.8			23			13		5.5
		ν			c^2			d^2			
2	E_g	156.6	159.6	*-3.0*	52	17	*35*	108	99	*8*	2.1
3		275.4	287.4	*-12.0*	74	58	*16*	530	354	*176*	3.2
4		714.1	712.6	*1.5*	177	56	*121*	21	23	*-3*	1.8
5		1449.5	1437.1	*12.4*	15	13	*3*	43	7	*36*	2.1
$\overline{\lvert\Delta\rvert}$				*8.3*						*54*	
$\overline{\Delta}$				*2.3*						*34*	
$\overline{\lvert\Delta\rvert}$%										*60*	
$\lvert\Delta\rvert_{max}$				*12.8*						*176*	

TABLE S4: Calculated and experimental Raman properties of single crystal calcite at T = 80 K; a basis set with additional f polarization functions was adopted in the calculations. Data can be compared to those in Table IV of the main Paper. See caption to Table S1 for more details.

		calc.	exp.	Δ	calc.	exp.	Δ	calc.	exp.	Δ	calc.	exp.	Δ	
	Symmetry		ν			a^2			b^2			c^2		γ_{exp}
1	A_g	147.6	144.7	*2.9*	4	1	*3*	0	2	*-2*	102	51	*51*	1.5
2		162.3	166.1	*-3.8*	41	11	*30*	9	0	*9*	38	44	*-6*	1.7
3		194.7	199.2	*-4.5*	1	3	*-2*	113	5	*108*	25	2	*23*	2.1
4		203.9	219.9	*-16.0*	6	1	*5*	183	120	*63*	29	27	*2*	2.9
5		277.6	291.5	*-13.9*	1	0	*1*	94	39	*55*	38	18	*20*	3.7
6		705.6	705.0	*0.6*	1	1	*0*	208	104	*104*	204	99	*105*	1.6
7		864.8	854.0	*10.8*	24	5	*19*	0	2	*-2*	1	4	*-3*	1.8
#			1061.2			1			3			3		1.6
8		1105.7	1087.2	*18.5*	174	210	*-36*	973	980	*-7*	1000	1000		1.4
9		1489.3	1466.2	*23.1*	2	0	*2*	5	0	*5*	6	12	*-6*	1.8
			ν			d^2			e^2			f^2		
10	B_{1g}	90.0	117.6	*-27.6*	103	47	*56*							3.7
11		152.6	156.2	*-3.6*	930	918	*12*							2.8
12		198.0	211.7	*-13.7*	3	5	*-2*							3.5
#			220.0			3								3.0
13		212.6	227.0	*-14.4*	34	23	*11*							4.1
14		708.1	705.9	*2.2*	16	14	*2*							1.6
15		1478.1	1464.1	*14.0*	49	29	*20*							1.8
16	B_{2g}	180.2	184.6	*-4.4*				236	87	*149*				1.9
17		207.7	212.8	*-5.1*				473	415	*58*				2.2
18		247.5	252.5	*-5.0*				124	75	*49*				4.7
19		261.7	267.0	*-5.3*				2	53	*-51*				2.4
20		277.0	284.1	*-7.1*				38	6	*32*				5.0
21		716.1	716.9	*-0.8*				11	10	*1*				1.7
22		914.8	911.1	*3.7*				1	0	*1*				2.0
23		1102.0						0						
24		1605.4	1579.0	*26.4*				44	17	*27*				4.8
25	B_{3g}	97.6	126.2	*-28.6*							17	8	*9*	2.7
26		164.3	181.0	*-16.7*							149	17	*132*	2.3
27		178.1	193.7	*-15.6*							18	50	*-32*	2.3
28		271.5	278.5	*-7.0*							92	47	*45*	3.7
29		703.9	700.1	*3.8*							191	96	*95*	1.5
30		1428.8									0			
$\overline{\lvert\Delta\rvert}$				*10.7*									*32*	
$\overline{\Delta}$				*-3.1*									*26*	
$\overline{\lvert\Delta\rvert}$%													*32*	
$\lvert\Delta\rvert_{max}$				*28.6*									*149*	

TABLE S5: Calculated and experimental Raman properties of single crystal aragonite at T = 80 K; a basis set with additional *f* polarization functions was adopted in the calculations. Data can be compared to those in Table V of the main Paper. See caption to Table S2 for more details.