

Supplementary Information: Anhydrous cadmium oxalate polymorphism: a first principle study

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This file contains IR and Raman active modes and intensities for the three phases, and fractional coordinates of $\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$. Oscillator strengths are reported in separate files.

	ν_{IR}	Sym	I_{IR}	ν_{Raman}	Sym	I_p	I_{pl}	I_{pp}	I_{xx}	I_{xy}	I_{xz}	I_{yy}	I_{yz}	I_{zz}
1	78.8	A_u	2.94	86.1	A_g	285.27	168.79	116.48	27.08	0.00	69.65	260.26	0.00	17.95
2	90.6	B_u	27.58	184.7	B_g	161.98	92.56	69.42	0.00	123.81	0.00	0.00	4.23	0.00
3	97.0	A_u	5.28	189.3	A_g	449.34	324.36	124.98	388.63	0.00	39.84	112.18	0.00	55.09
4	113.5	B_u	3.13	199.8	B_g	135.78	77.59	58.19	0.00	56.79	0.00	0.00	50.54	0.00
5	123.9	A_u	15.12	232.0	B_g	258.40	147.66	110.74	0.00	52.02	0.00	0.00	152.23	0.00
6	163.6	B_u	6.75	234.3	A_g	324.65	222.55	102.10	31.21	0.00	9.32	4.31	0.00	418.09
7	172.3	A_u	0.09	504.8	A_g	652.59	612.46	40.13	209.92	0.00	32.47	430.09	0.00	61.63
8	197.5	A_u	11.16	539.2	B_g	73.15	41.80	31.35	0.00	24.40	0.00	0.00	33.43	0.00
9	205.5	B_u	16.84	592.1	A_g	84.44	62.26	22.18	7.95	0.00	3.34	14.52	0.00	88.85
10	267.8	B_u	82.36	599.4	B_g	51.68	29.53	22.15	0.00	4.49	0.00	0.00	36.37	0.00
11	279.2	A_u	2.78	833.4	A_g	112.41	64.61	47.79	24.67	0.00	22.50	97.46	0.00	10.16
12	433.5	A_u	1.71	836.6	B_g	11.37	6.50	4.87	0.00	0.76	0.00	0.00	8.23	0.00
13	437.1	B_u	11.71	904.3	B_g	76.75	43.86	32.89	0.00	55.88	0.00	0.00	4.79	0.00
14	517.0	B_u	49.51	906.9	A_g	133.09	128.09	5.01	57.45	0.00	2.60	75.80	0.00	14.37
15	524.7	A_u	26.48	1461.6	B_g	130.39	74.51	55.88	0.00	66.97	0.00	0.00	36.10	0.00
16	794.7	A_u	40.16	1472.3	A_g	1000.00	852.43	147.57	103.69	0.00	71.37	23.53	0.00	1000.00
17	796.6	B_u	26.95	1599.0	A_g	79.86	62.19	17.67	0.65	0.00	6.73	0.76	0.00	93.06
18	1328.1	A_u	100.04	1615.9	B_g	12.98	7.41	5.56	0.00	9.37	0.00	0.00	0.88	0.00
19	1333.3	B_u	83.50											
20	1588.1	B_u	1000.00											
21	1605.8	A_u	0.07											

Table 1: Computed IR and Raman active wavenumbers (ν , in cm^{-1}) for $\beta\text{-CdC}_2\text{O}_4$. Intensities (I , in arbitrary units) have been normalised, with the highest intensity assuming a value of 1000.00. For Raman spectra, the parallel (I_{pl}) and perpendicular (I_{pp}) components to the polycrystalline isotropic intensities (I_p) and the single crystal directional intensities (I_{xx} , I_{xy} , I_{xz} , I_{yy} , I_{yz} , I_{zz}) are reported. Raman spectra are calculated assuming an incident laser wavelength of 532 nm and a temperature of 300 K.

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	ν_{IR}	Sym	I_{IR}	ν_{Raman}	Sym	I_p	I_{pl}	I_{pp}	I_{xx}	I_{xy}	I_{xz}	I_{yy}	I_{yz}	I_{zz}
1	51.7	B_{1u}	0.12	40.6	B_{1g}	197.72	112.99	84.74	0.00	132.60	0.00	0.00	0.00	0.00
2	68.6	B_{3u}	0.29	57.1	B_{1g}	77.93	44.53	33.40	0.00	52.27	0.00	0.00	0.00	0.00
3	88.3	B_{1u}	0.30	78.1	B_{3g}	0.12	0.07	0.05	0.00	0.00	0.08	0.00	0.00	0.00
4	93.4	B_{2u}	23.60	88.0	B_{3g}	47.70	27.26	20.44	0.00	0.00	31.99	0.00	0.00	0.00
5	123.2	B_{3u}	22.05	106.1	B_{1g}	2.66	1.52	1.14	0.00	1.78	0.00	0.00	0.00	0.00
6	132.9	B_{2u}	27.78	109.6	A_g	25.59	22.28	3.31	0.04	0.00	0.00	4.64	0.00	22.45
7	139.6	B_{2u}	15.17	110.7	B_{2g}	270.25	154.43	115.82	0.00	0.00	0.00	0.00	181.24	0.00
8	162.0	B_{1u}	5.11	131.1	B_{3g}	472.07	269.75	202.31	0.00	0.00	316.59	0.00	0.00	0.00
9	173.8	B_{3u}	0.02	152.5	B_{2g}	268.48	153.42	115.06	0.00	0.00	0.00	0.00	180.05	0.00
10	200.0	B_{2u}	11.54	154.2	A_g	149.23	87.66	61.57	93.34	0.00	0.00	19.16	0.00	85.42
11	210.1	B_{1u}	123.71	179.7	A_g	233.35	141.11	92.24	28.88	0.00	0.00	159.18	0.00	117.63
12	251.5	B_{1u}	2.57	184.4	B_{2g}	158.52	90.59	67.94	0.00	0.00	0.00	0.00	106.31	0.00
13	251.8	B_{3u}	98.70	194.7	B_{1g}	509.16	290.95	218.21	0.00	341.47	0.00	0.00	0.00	0.00
14	273.0	B_{3u}	0.85	206.5	B_{3g}	88.78	50.73	38.05	0.00	0.00	59.54	0.00	0.00	0.00
15	418.7	B_{1u}	11.53	222.3	A_g	306.73	182.40	124.33	1.48	0.00	0.00	91.90	0.00	311.35
16	423.3	B_{3u}	0.00	222.8	B_{2g}	17.28	9.88	7.41	0.00	0.00	0.00	0.00	11.59	0.00
17	442.8	B_{3u}	0.48	237.7	B_{1g}	0.40	0.23	0.17	0.00	0.27	0.00	0.00	0.00	0.00
18	456.6	B_{1u}	0.30	248.3	B_{3g}	395.32	225.89	169.42	0.00	0.00	265.12	0.00	0.00	0.00
19	502.5	B_{2u}	32.82	508.6	A_g	425.19	419.28	5.91	92.87	0.00	0.00	91.11	0.00	220.78
20	517.1	B_{1u}	4.21	510.2	B_{2g}	29.80	17.03	12.77	0.00	0.00	0.00	0.00	19.99	0.00
21	517.3	B_{3u}	34.87	522.4	A_g	330.45	226.42	104.03	397.25	0.00	0.00	1.33	0.00	9.37
22	786.2	B_{1u}	37.44	533.5	B_{2g}	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
23	789.3	B_{2u}	52.69	594.0	B_{1g}	6.49	3.71	2.78	0.00	4.36	0.00	0.00	0.00	0.00
24	791.6	B_{3u}	9.61	616.4	B_{3g}	98.33	56.19	42.14	0.00	0.00	65.94	0.00	0.00	0.00
25	1333.4	B_{2u}	174.21	618.2	B_{2g}	29.54	16.88	12.66	0.00	0.00	0.00	0.00	19.81	0.00
26	1338.9	B_{1u}	61.46	618.6	A_g	71.44	54.75	16.69	4.16	0.00	0.00	1.56	0.00	77.03
27	1340.5	B_{3u}	125.75	846.1	B_{1g}	3.20	1.83	1.37	0.00	2.15	0.00	0.00	0.00	0.00
28	1599.9	B_{1u}	1000.00	846.8	B_{3g}	8.16	4.66	3.50	0.00	0.00	5.47	0.00	0.00	0.00
29	1627.2	B_{3u}	806.20	851.7	B_{1g}	22.25	12.71	9.53	0.00	14.92	0.00	0.00	0.00	0.00
30	1628.2	B_{1u}	148.17	852.4	B_{3g}	0.16	0.09	0.07	0.00	0.00	0.11	0.00	0.00	0.00
31	1693.9	B_{3u}	57.70	901.5	B_{2g}	7.18	4.11	3.08	0.00	0.00	0.00	0.00	4.82	0.00
32				905.6	B_{2g}	23.32	13.33	9.99	0.00	0.00	0.00	0.00	15.64	0.00
33				906.3	A_g	86.95	63.60	23.36	9.94	0.00	0.00	78.98	0.00	14.65
34				910.5	A_g	210.97	187.59	23.37	175.61	0.00	0.00	1.39	0.00	43.02
35				1463.5	B_{2g}	444.91	254.24	190.68	0.00	0.00	0.00	0.00	298.38	0.00
36				1463.8	A_g	286.67	200.58	86.09	27.85	0.00	0.00	280.26	0.00	41.89
37				1466.0	B_{2g}	7.15	4.09	3.07	0.00	0.00	0.00	0.00	4.80	0.00
38				1468.4	A_g	1000.00	805.94	194.06	8.77	0.00	0.00	112.33	0.00	1000.00
39				1605.4	B_{1g}	8.95	5.11	3.84	0.00	6.00	0.00	0.00	0.00	0.00
40				1644.5	B_{3g}	29.11	16.64	12.48	0.00	0.00	19.52	0.00	0.00	0.00
41				1650.9	B_{2g}	149.83	85.62	64.21	0.00	0.00	0.00	0.00	100.49	0.00
42				1655.7	A_g	9.49	8.74	0.76	4.80	0.00	0.00	4.73	0.00	0.09

Table 2: Computed IR and Raman active wavenumbers and intensities for γ -CdC₂O₄. Symbols and units as in Table 1.

	x	y	z
Cd	-0.44654	-0.18456	0.21023
O11	0.41763	0.11092	0.31170
O12	0.37387	0.24957	-0.47889
C1	0.44044	0.10293	0.45237
O21	0.27717	-0.05227	0.03728
O22	-0.03859	-0.20511	0.17623
C2	0.06800	-0.07443	0.06168
O3	-0.33837	-0.49700	0.13565
H31	-0.21532	0.41544	0.18944
H32	-0.45508	0.41124	0.15738
O4	0.23067	-0.35001	0.38768
H41	0.11582	-0.32239	0.32021
H42	0.27251	0.49763	0.42761
O5	-0.05935	0.24823	0.31465
H51	0.10609	0.21233	0.29424
H51	-0.10874	0.27280	0.42374

Table 3: Calculated (B3LYP) fractional coordinates for $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$.

	$\nu_{IR} (Au)$	I_{IR}	$\nu_{Raman} (Ag)$	I_p	I_{pl}	I_{pp}	I_{xx}	I_{xy}	I_{xz}	I_{yy}	I_{yz}	I_{zz}
1	81.5	2.17	72.0	301.08	172.10	128.97	12.19	6.20	138.25	134.30	48.45	202.77
2	88.9	4.11	81.3	307.34	186.78	120.55	181.59	22.66	152.42	10.39	81.41	26.43
3	101.4	5.18	92.3	346.40	210.52	135.88	121.90	12.68	45.06	206.71	103.66	172.95
4	115.8	3.97	100.5	330.34	273.64	56.70	127.73	0.31	41.93	68.74	114.97	150.64
5	128.3	8.91	103.8	21.53	14.92	6.61	0.41	11.67	0.02	10.63	5.40	2.88
6	135.2	10.05	116.3	103.47	75.58	27.89	0.14	17.30	32.70	95.13	7.03	15.20
7	140.8	5.68	123.2	116.33	67.05	49.29	24.93	92.91	17.71	19.06	3.68	10.49
8	158.8	17.43	140.5	135.15	96.51	38.63	7.23	21.54	0.07	116.58	39.90	50.18
9	168.2	2.45	148.7	361.28	212.25	149.03	219.92	191.83	21.11	90.57	63.37	9.13
10	171.4	12.22	161.3	75.04	59.29	15.75	0.08	0.42	15.92	9.98	0.32	111.81
11	186.8	7.01	198.9	280.91	164.01	116.90	72.48	9.08	32.11	8.58	98.01	320.51
12	218.7	27.71	204.7	305.93	176.76	129.17	47.89	66.46	142.31	16.29	6.47	249.04
13	240.3	23.10	220.2	202.62	130.48	72.14	345.96	1.13	2.37	86.93	6.94	15.88
14	252.5	27.56	229.9	90.55	64.43	26.12	8.56	14.91	0.18	8.65	0.31	151.42
15	277.2	3.16	248.2	80.98	46.87	34.11	8.15	0.25	2.87	79.47	13.29	76.28
16	291.8	28.64	282.3	58.32	47.97	10.35	79.23	2.71	1.66	26.96	0.87	0.74
17	340.1	13.59	287.3	178.44	163.61	14.82	40.52	1.76	12.42	78.24	20.21	142.78
18	406.4	3.15	349.3	48.79	42.40	6.39	0.03	0.95	3.39	36.55	0.26	48.52
19	426.4	48.91	506.8	245.16	222.33	22.83	136.02	13.21	2.31	164.71	39.54	47.22
20	438.5	3.74	529.7	239.82	191.38	48.43	138.01	15.24	100.70	12.14	2.63	105.41
21	504.5	18.22	540.9	124.49	71.64	52.86	13.76	10.84	62.52	35.00	43.05	21.56
22	512.7	23.46	588.5	49.20	28.55	20.65	1.47	11.94	7.00	46.71	0.02	33.31
23	603.3	44.69	600.3	20.48	11.73	8.75	5.28	0.10	0.70	10.21	16.38	0.11
24	617.4	16.48	608.4	79.29	54.49	24.80	18.77	3.51	5.10	51.13	16.05	58.70
25	689.8	54.92	626.5	48.25	27.89	20.35	15.60	1.38	8.13	34.26	24.19	0.00
26	713.4	51.70	691.7	29.75	17.83	11.92	39.56	5.69	7.15	0.96	0.17	4.68
27	765.9	109.39	730.1	17.24	10.97	6.27	1.48	5.82	1.84	0.00	0.01	23.38
28	785.5	6.55	811.8	13.76	11.36	2.40	7.42	0.00	0.01	4.90	6.47	2.35
29	793.2	77.11	852.7	12.96	8.65	4.31	0.12	5.29	2.40	0.03	0.13	13.69
30	929.7	119.21	856.7	28.80	18.32	10.48	48.60	0.80	0.27	9.84	2.87	0.79
31	978.3	5.53	893.2	70.72	61.14	9.57	112.33	1.46	0.12	0.67	1.15	18.76
32	1042.0	60.56	900.7	50.30	46.99	3.31	9.99	4.86	1.88	29.21	0.19	38.57
33	1333.4	171.15	980.5	108.19	87.35	20.83	88.25	1.45	19.71	45.25	21.44	1.84
34	1335.4	17.52	986.9	39.54	27.75	11.79	19.46	0.02	26.90	0.08	0.22	13.93
35	1571.0	375.28	1047.7	16.13	10.63	5.50	18.53	2.32	0.00	4.09	2.39	4.93
36	1622.1	312.18	1465.4	359.76	281.07	78.69	15.80	0.03	12.09	109.17	177.94	244.35
37	1628.2	104.12	1474.0	542.51	434.75	107.76	170.90	75.62	213.91	83.34	4.10	269.98
38	1652.5	46.26	1604.3	29.82	18.37	11.46	4.16	7.69	7.01	7.85	9.38	10.37
39	1692.4	63.28	1611.7	12.22	8.73	3.49	0.03	1.03	5.81	0.82	0.00	12.32
40	3191.8	622.68	1655.2	35.77	24.10	11.67	1.78	0.04	16.13	37.68	2.99	3.28
41	3296.1	239.48	1661.4	38.84	22.57	16.27	35.37	0.39	9.13	14.71	3.61	17.86
42	3331.1	1000.00	1698.7	20.29	11.64	8.65	7.71	0.11	5.42	0.31	10.79	8.82
43	3495.0	196.29	3197.6	885.41	758.73	126.68	657.19	152.76	157.27	186.96	9.84	246.05
44	3636.3	256.00	3296.9	1000.00	910.19	89.81	228.22	76.06	70.40	785.43	67.30	421.58
45	3719.3	81.77	3337.1	329.03	190.86	138.17	22.14	34.44	61.20	389.68	55.39	84.69
46			3489.9	264.89	188.58	76.32	11.66	0.01	26.77	0.29	111.91	293.88
47			3638.1	494.91	361.80	133.12	1000.00	18.74	10.14	0.73	5.98	3.02
48			3716.5	427.34	378.31	49.03	140.33	50.01	5.42	402.11	47.18	66.58

Table 4: Computed IR and Raman active wavenumbers and intensities for $\text{CdC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$. Symbols and units as in Table 1. As mentioned in the paper, the values $>3000 \text{ cm}^{-1}$ are expected to be red-shifted by about 200 cm^{-1} due to the highly anharmonic behaviour of the OH oscillator. To realte these data with the figures in the main text, a correction of -200 cm^{-1} should be applied to values $>3000 \text{ cm}^{-1}$.