The Role of Terahertz Polariton Absorption in the Characterization of Crystalline Iron Sulfate Hydrates

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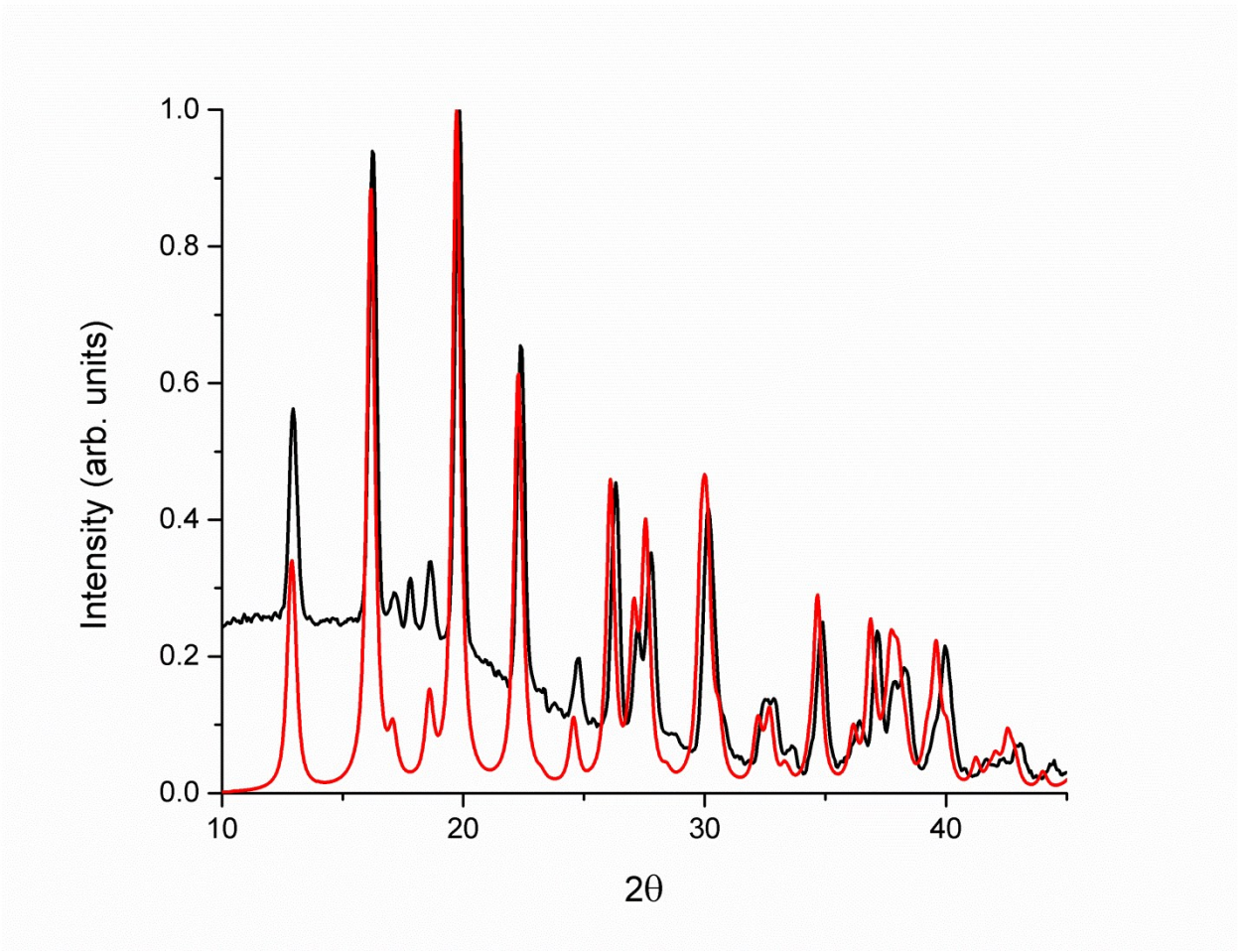

Figure S.1. Experimental (black) and calculated (red) PXRD of $FeSO_4 \cdot 4H_2O$.

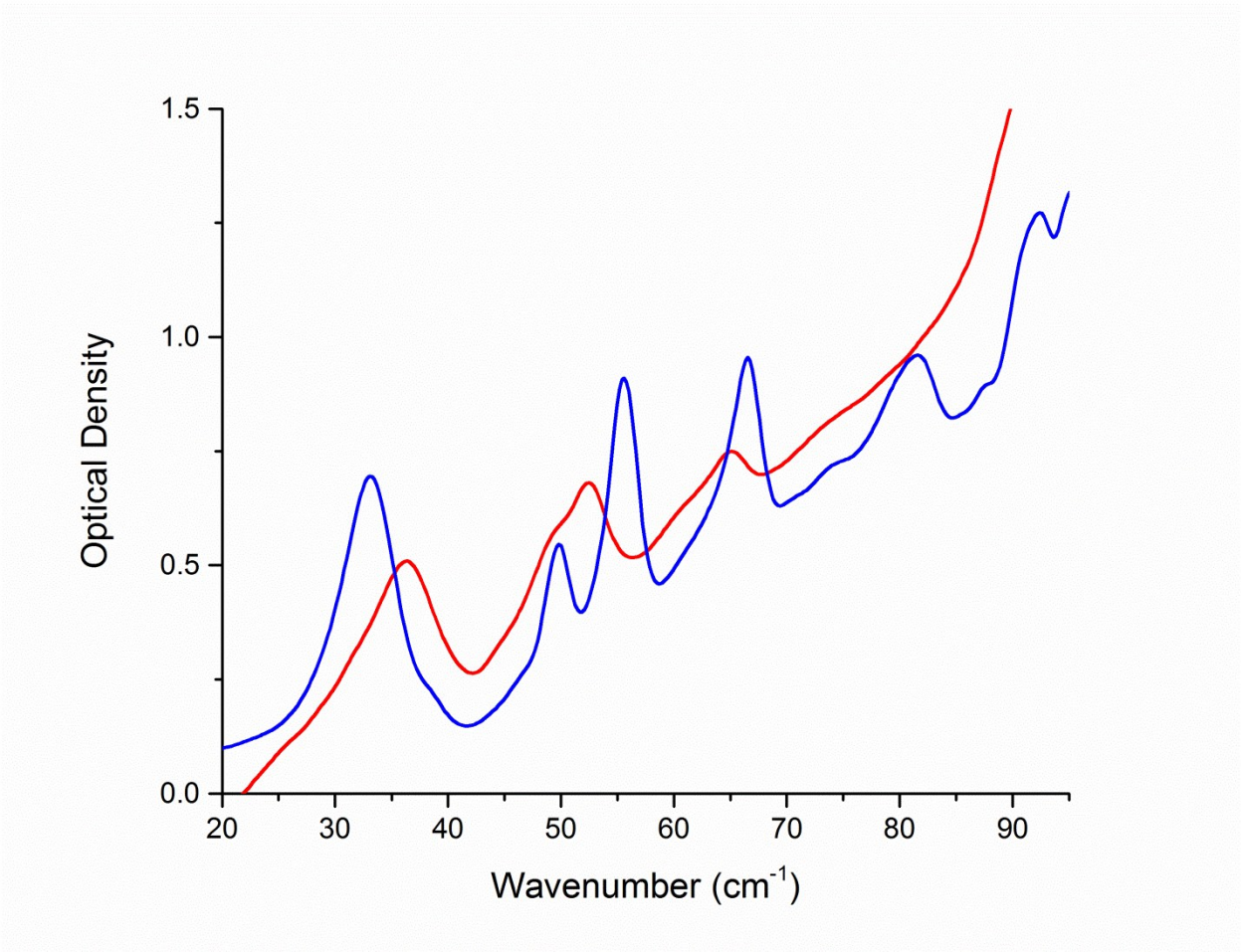

Figure S.2. Terahertz spectra of $FeSO_4 \cdot 7H_2O$ taken at 225 K (red) and 150 K (blue).

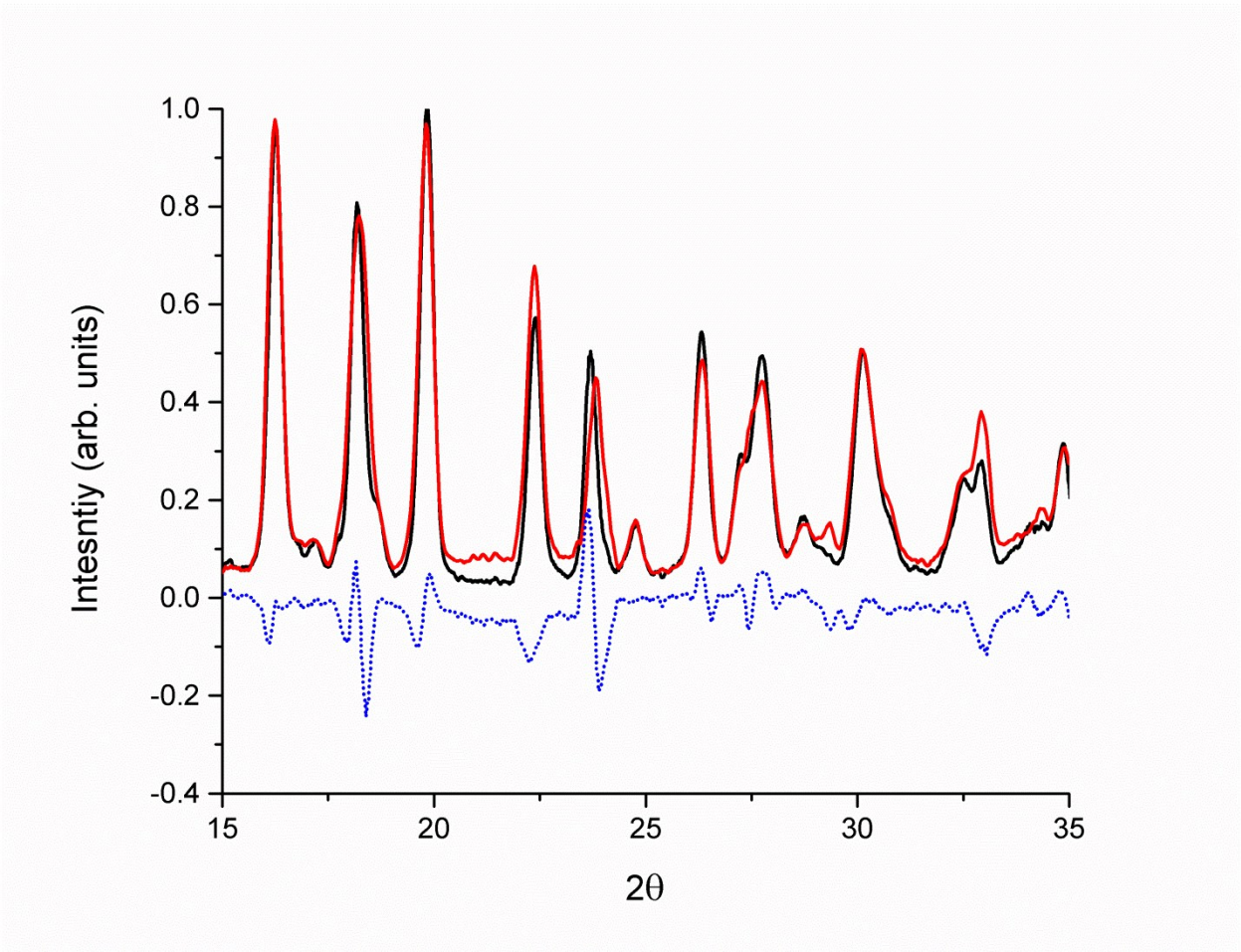

Figure S.3. Experimental PXRD of an $FeSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 4H_2O$ mixture (black), linear combination of the two individual patterns (red) and the difference (blue).

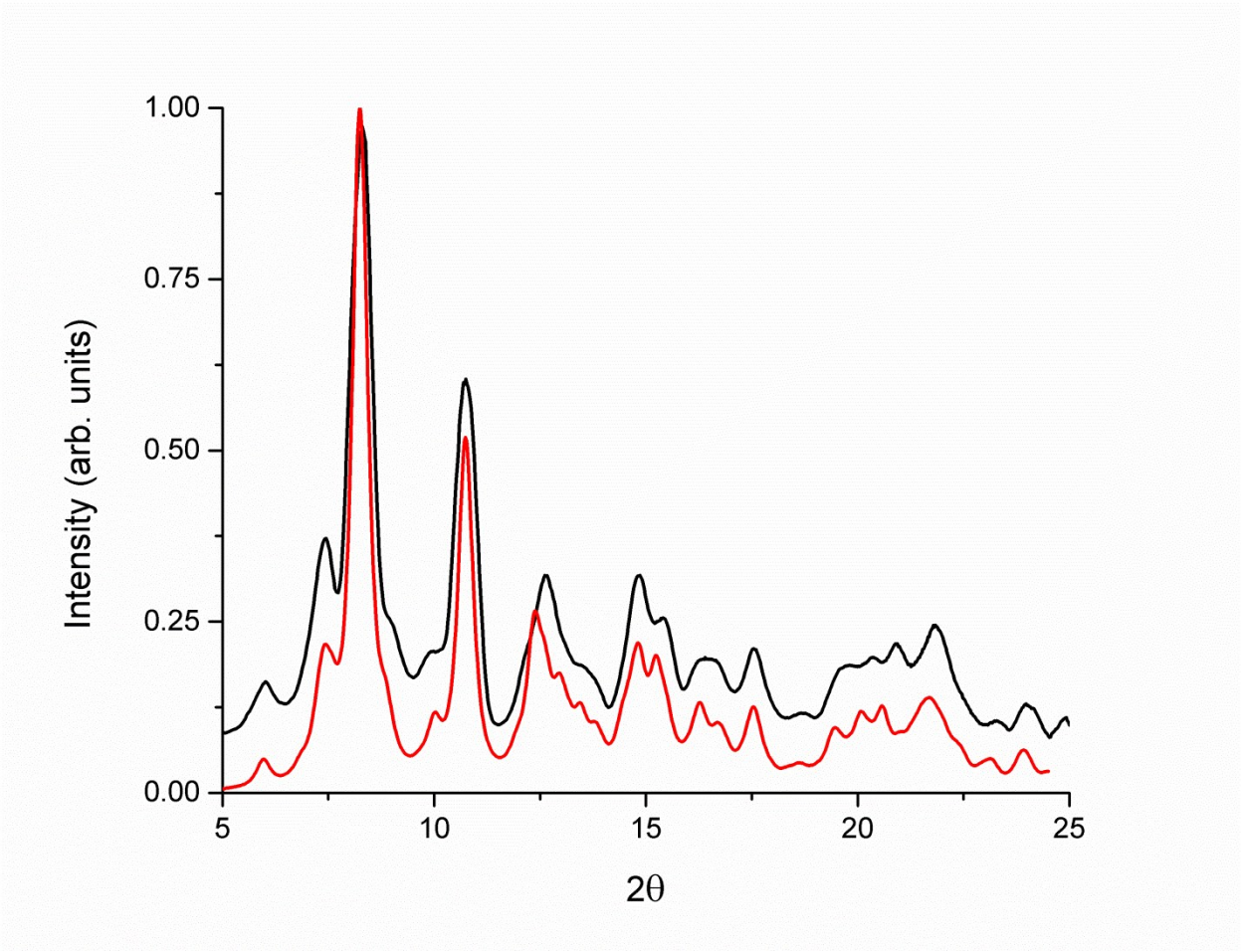

Figure S.4. Experimental (black) and calculated (red) PXRD of $FeSO_4 \cdot 7H_2O$.

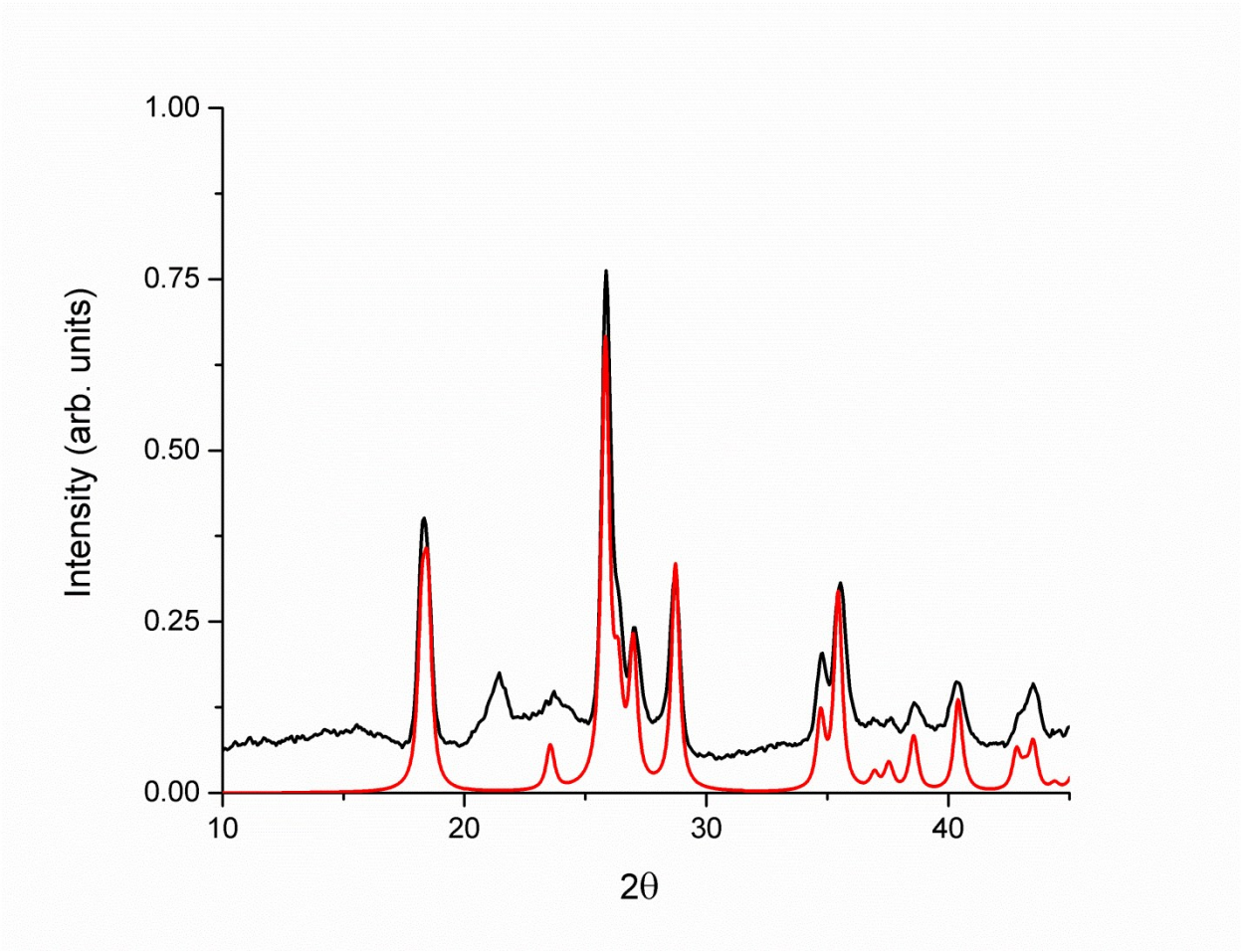

Figure S.5. Experimental (black) and calculated (red) PXRD of $FeSO_4 \cdot 4H_2O$.

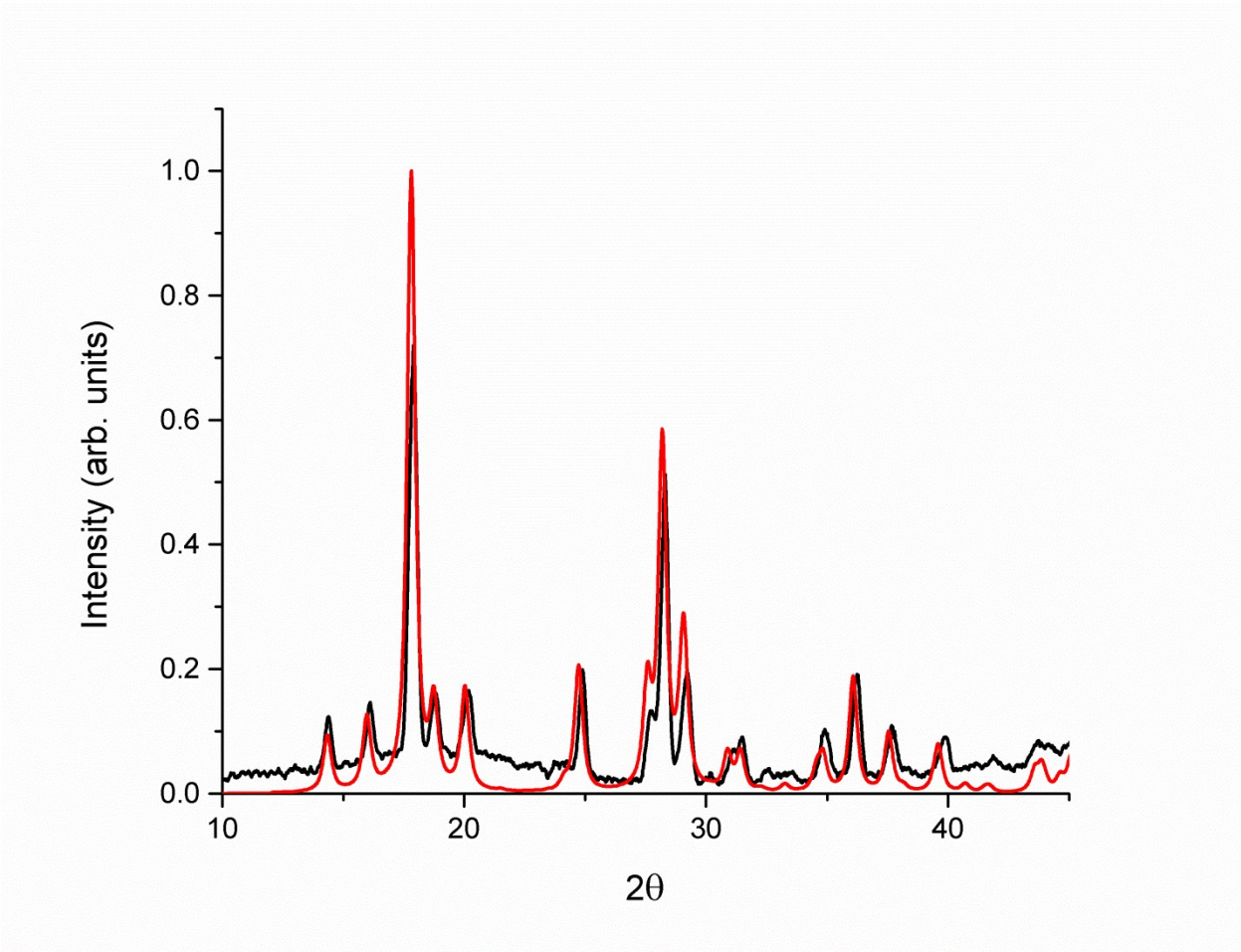

Figure S.6. Experimental (black) and calculated (red) PXRD of $Fe_2(SO_4)_3OH \cdot 2H_2O$.

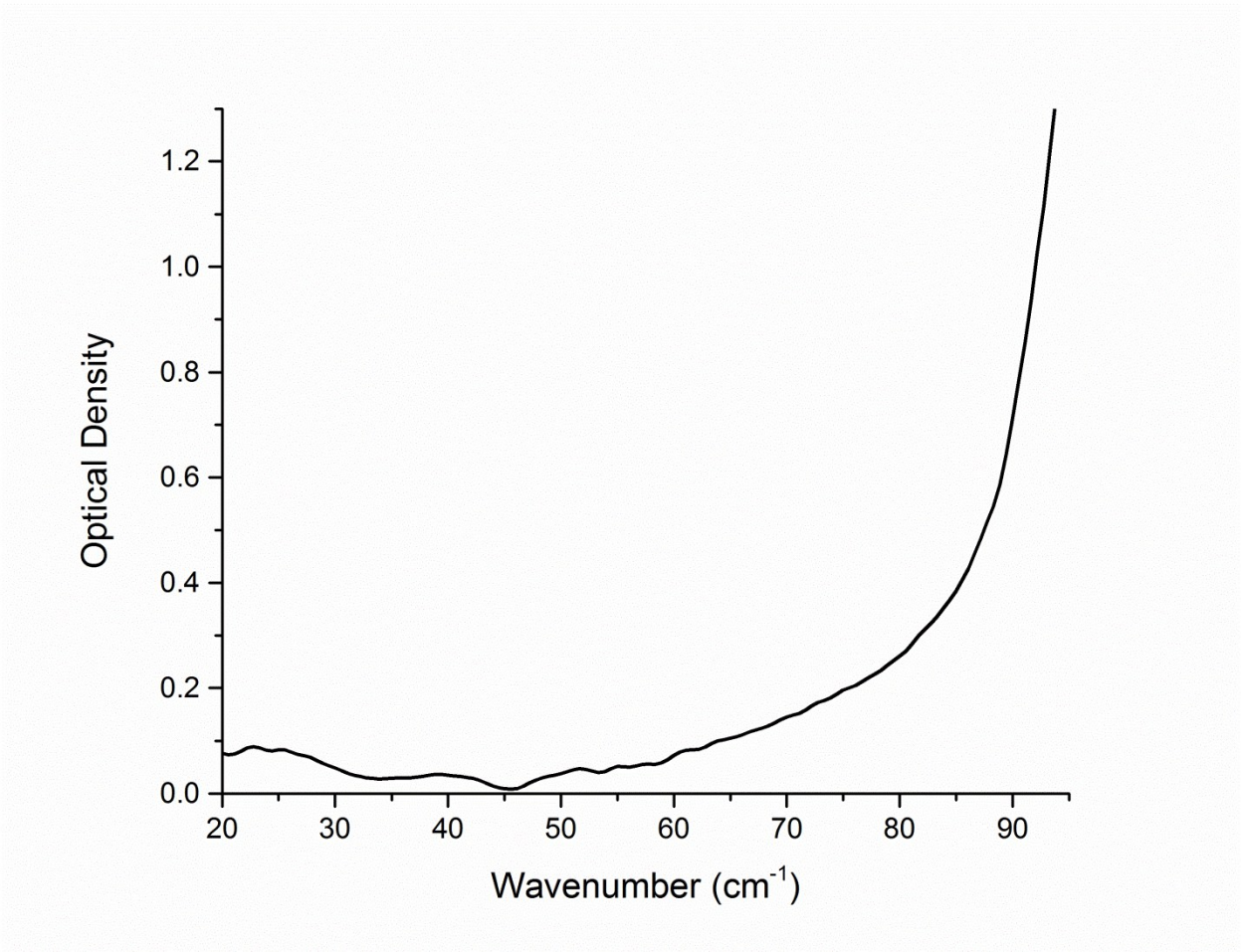

Figure S.7. Terahertz spectrum of $FeSO_4 \cdot H_2O$ taken at 77 K.

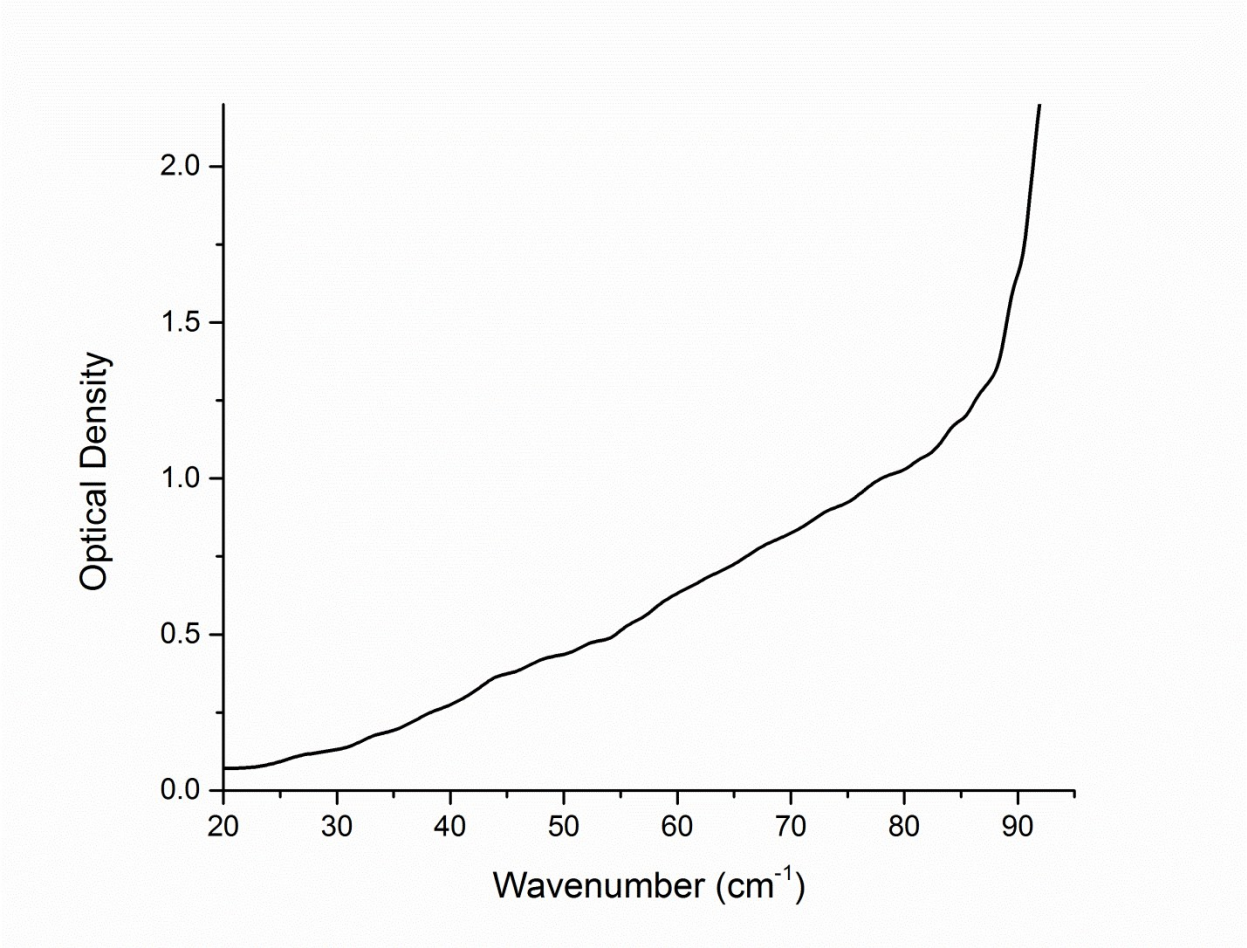

Figure S.8. Terahertz spectrum of $Fe_2(SO_4)_3OH \cdot 2H_2O$ at 77 K.

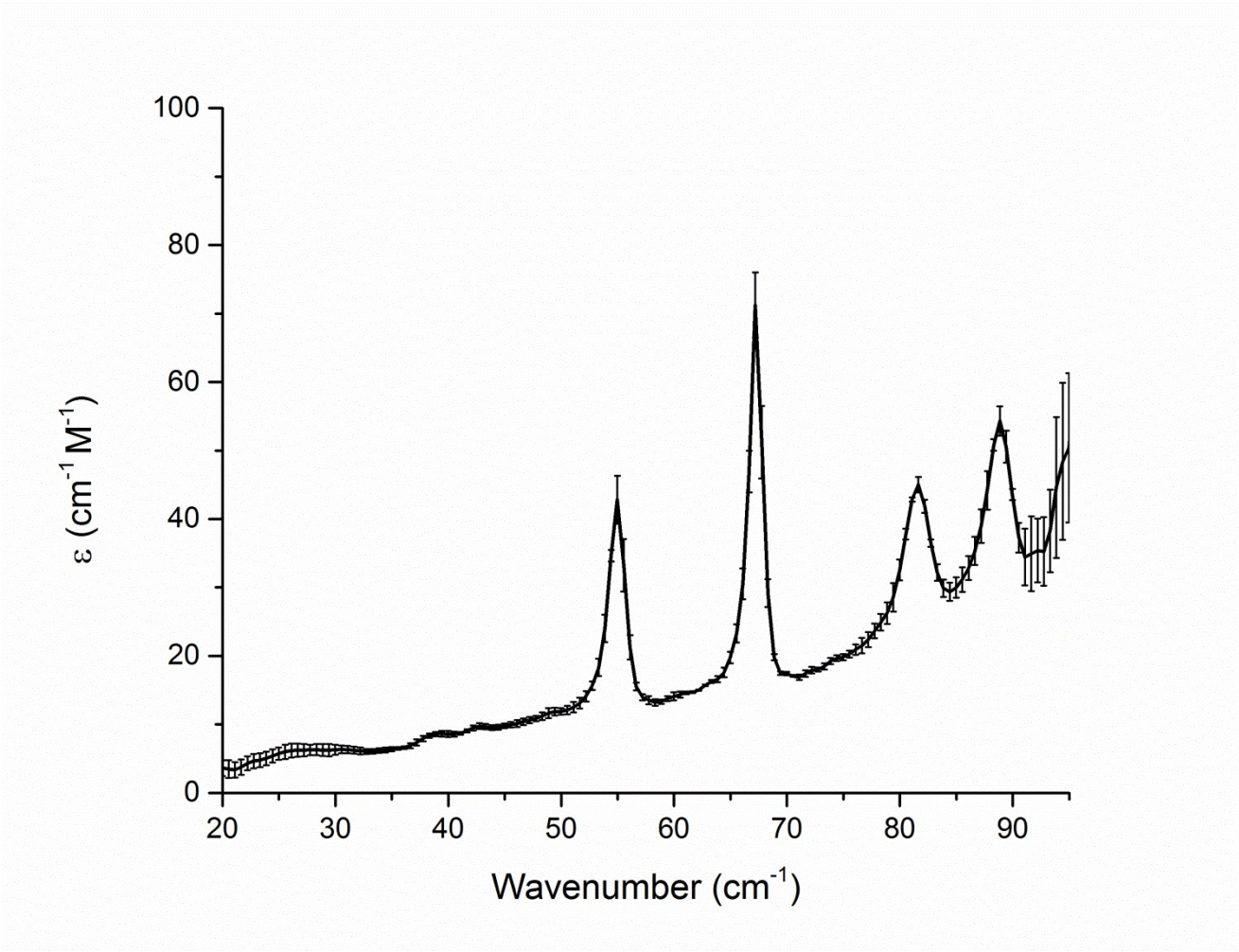

Figure S.9. 78 K terahertz spectrum of $FeSO_4 \cdot 4H_2O$ with standard deviation in the absorption shown.

Table S.1. Simulated IR-active vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) of anhydrous $FeSO_4$.

Frequency	Intensity
136.89	0.06
150.15	108.13
157.41	41.93
191.81	146.45
209.69	413.13
227.76	0.08
245.50	177.13
305.82	239.99
343.84	205.31
471.56	85.16
472.56	0.00
584.42	83.47
587.20	149.13
663.45	252.24
942.36	268.15
978.20	2179.02
1095.32	1744.22
1142.05	1562.27

Table S.2. Simulated IR-active vibrational frequencies (cm^{-1}) and intensities ($km\ mol^{-1}$) of $FeSO_4 \cdot H_2O$.

Frequency	Intensity
121.63	7.14
127.52	40.94
165.68	130.80
178.83	40.36
191.74	24.47
229.45	226.35
235.39	176.87
277.29	615.90
303.30	52.85
306.78	125.88
325.34	27.15
329.17	90.45
426.25	0.09
527.57	47.17
586.41	300.91
608.21	112.09
613.05	691.31
708.16	231.31
886.72	1954.31
943.45	35.10
961.57	268.56
1042.18	598.61
1086.05	1564.54
1140.22	1759.60
1617.19	167.13
3428.36	1385.50
3449.11	3867.82

Table S.3. Simulated IR-active vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) of $FeSO_4 \cdot 4H_2O$.

Frequncy	Intensity
58.27	8.75
63.54	2.36
68.62	0.00
72.25	11.94
81.75	0.00
85.87	2.96
96.44	4.16
98.26	0.00
101.95	0.00
103.36	24.39
108.00	0.00
115.00	27.16
119.47	4.55
120.56	0.00
123.95	0.00
129.67	0.10
131.77	162.59
132.07	0.20
135.90	48.91
139.19	0.00
147.83	0.01
148.56	94.71
148.72	40.45
153.24	18.68
153.73	0.33
156.94	22.73
158.05	0.01
158.64	0.01
160.54	154.88
164.09	0.00
164.85	0.02
172.12	200.30
173.02	0.01
174.70	3.62
177.39	0.01
184.95	2.17

185.55	39.80
189.46	244.79
189.50	0.01
190.78	0.23
193.94	100.20
195.22	43.78
196.41	0.02
201.05	250.94
206.06	0.00
208.54	0.02
216.17	0.01
218.10	68.23
219.91	0.81
225.32	0.00
228.24	0.01
228.74	5.57
230.60	67.03
236.90	0.00
238.23	0.01
247.24	376.19
247.36	111.03
249.00	0.00
250.15	0.07
250.46	3.54
255.04	27.13
260.36	47.34
261.31	0.01
267.79	137.70
270.35	0.01
310.22	0.23
311.47	85.87
313.29	3.61
314.57	23.30
358.53	192.21
364.82	0.01
369.39	0.04
370.34	0.02
374.04	69.38
377.05	2.41
377.89	141.38
378.69	0.05

407.80	39.68
412.78	46.22
413.06	1.59
417.90	0.02
442.82	80.24
443.42	19.32
443.56	192.75
445.71	0.04
459.59	0.00
462.81	35.24
463.08	542.67
472.00	15.61
476.51	0.00
478.12	244.04
478.59	0.15
497.09	0.01
516.63	0.03
522.85	7.37
524.98	767.98
528.23	19.76
556.30	0.16
567.73	666.68
569.73	1.77
571.63	971.77
585.43	84.33
586.41	0.22
588.80	0.01
590.39	213.03
590.99	45.16
591.48	362.87
592.91	0.01
594.80	0.23
596.33	1075.58
598.56	0.04
598.95	0.03
601.47	132.97
605.93	430.52
610.95	0.03
613.53	0.02
629.26	100.41
639.28	1947.07

648.56	0.01
649.95	175.51
659.46	0.10
677.16	0.00
688.79	0.39
697.07	159.71
712.53	0.01
714.89	140.08
716.47	474.71
718.04	49.79
728.06	0.20
742.49	116.20
748.12	0.01
757.09	191.48
765.37	81.73
769.95	0.29
783.31	44.52
789.89	449.15
792.07	0.92
794.98	0.39
802.97	86.60
805.27	2.95
812.47	47.66
821.32	0.07
822.92	0.08
831.79	4.45
842.55	270.18
871.90	0.00
880.77	97.08
890.40	0.03
893.57	48.76
949.03	11.97
950.05	0.14
950.53	85.36
951.22	0.00
1033.66	3578.84
1034.61	81.23
1046.34	0.00
1048.40	0.02
1073.95	0.00
1082.00	0.03

1085.56	865.60
1087.54	3199.14
1123.55	1827.06
1129.91	0.00
1138.02	25.98
1163.39	0.00
1618.29	0.01
1622.71	370.79
1623.85	3.03
1629.62	92.16
1645.85	415.58
1653.31	0.01
1656.64	50.83
1666.72	0.33
1667.42	181.88
1671.43	12.64
1676.89	278.12
1678.56	0.02
1681.08	0.00
1684.82	538.74
1749.67	0.00
1749.89	0.00
3451.20	4285.27
3452.21	11.22
3459.34	2445.12
3467.56	0.05
3533.42	472.93
3535.08	60.81
3535.19	452.70
3536.23	280.11
3549.86	719.34
3554.76	3537.25
3556.28	10.23
3559.88	61.73
3614.00	0.30
3614.18	0.00
3619.50	386.88
3623.02	2915.85
3623.71	0.00
3623.98	6.44
3639.95	1595.83

3641.58	0.06
3642.35	876.95
3646.76	12.04
3655.39	541.48
3659.75	6647.16
3706.42	0.50
3709.33	1024.14
3714.87	2606.74
3729.42	0.96
3787.12	1576.44
3791.10	516.00
3796.34	0.26
3807.43	0.03

Table S.4. Simulated IR-active vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) of $FeSO_4 \cdot 7H_2O$.

Frequency	Intensity
51.63	2.60
54.01	1.91
58.09	0.00
62.97	12.01
70.42	9.05
77.69	0.29
87.05	5.38
90.99	3.67
94.23	6.70
103.00	0.06
109.62	35.94
117.65	1.80
118.49	3.23
125.94	77.26
128.72	20.09
131.48	43.09
135.02	143.00
140.27	94.72
142.37	140.68
149.56	12.14
149.57	57.79
155.37	73.05
157.17	1.15
163.32	1.73
163.72	51.46
163.93	85.14
173.06	9.38
174.45	39.05
177.59	0.86
185.89	52.44
187.18	96.88
190.82	3.16
192.47	5.05
202.64	11.64

204.30	137.31
205.90	2.30
206.95	56.83
221.09	31.12
222.45	315.06
235.00	221.42
238.31	45.98
239.85	78.91
246.75	65.47
250.43	79.54
262.45	33.93
279.89	120.71
284.71	21.69
286.29	74.52
290.52	147.35
298.66	83.47
301.37	0.09
307.41	21.81
317.90	59.65
351.89	23.85
356.65	361.90
384.57	39.05
389.65	122.21
403.25	11.66
405.51	120.80
417.25	146.14
423.99	168.07
434.84	7.23
437.43	74.16
453.63	38.49
456.67	21.44
461.98	116.88
463.30	6.78
477.16	783.35
483.65	74.48
488.61	257.46
504.28	167.44
557.75	499.76
565.85	26.57
570.34	1098.79
573.70	42.10

577.70	117.63
585.06	104.38
594.71	218.94
599.18	393.71
599.24	595.47
602.77	703.03
607.10	64.62
614.63	766.13
629.19	145.38
642.01	501.69
654.19	594.41
675.60	85.43
676.96	279.35
692.66	196.83
700.06	34.49
717.91	545.30
723.31	91.51
728.64	155.93
737.81	375.96
751.26	587.76
761.66	224.89
762.50	1173.24
768.99	578.21
776.59	239.45
783.91	88.77
790.56	103.20
808.21	807.26
819.11	208.71
842.04	36.72
844.01	37.67
853.56	346.83
864.26	49.37
885.62	226.40
891.01	235.66
896.29	5.32
910.77	187.14
935.94	28.88
938.30	223.05
954.82	877.21
966.33	722.25
1029.70	2865.38

1032.94	20.97
1053.21	192.58
1069.10	1343.64
1071.91	1346.03
1079.19	1.31
1116.24	1482.03
1123.68	940.77
1602.89	53.07
1604.50	311.04
1657.53	72.43
1660.32	482.53
1678.17	265.68
1680.85	16.67
1694.46	67.09
1694.47	55.63
1701.06	23.90
1705.03	223.49
1705.05	100.49
1707.90	167.71
1735.99	289.78
1737.16	97.56
3304.97	5063.57
3319.87	2273.69
3400.38	114.00
3414.15	6948.60
3461.74	931.49
3463.44	10.13
3477.20	5618.75
3480.08	355.64
3514.32	4109.33
3518.63	4162.44
3537.70	6155.89
3543.87	528.38
3548.73	2073.99
3561.39	23.70
3591.22	2400.28
3591.75	1103.93
3594.35	292.36
3594.52	47.16
3609.49	7691.99
3612.09	106.18

3615.76	3215.99
3622.41	323.70
3666.19	503.79
3667.18	1119.07
3680.34	1279.37
3681.46	2585.53
3712.15	2875.65
3714.40	649.02

Table S.5. Simulated IR-active vibrational frequencies (cm^{-1}) and intensities ($km\ mol^{-1}$) of $Fe_2(SO_4)_3OH \cdot 2H_2O$.

Frequency	Intensity
109.33	16.97
127.94	0.31
138.42	60.39
159.18	110.57
164.11	104.01
174.80	128.52
180.97	82.28
209.85	224.33
244.69	169.78
250.86	12.10
271.10	91.62
294.69	190.06
302.67	269.31
327.93	293.12
433.73	73.11
436.00	16.00
445.62	218.70
471.61	906.30
476.27	209.25
484.40	0.26
524.67	877.07
537.29	527.26
580.01	270.89

590.22	228.46
651.00	0.58
705.51	32.25
723.42	168.13
794.30	833.24
835.60	47.66
909.68	106.28
925.47	2398.45
963.04	268.88
1033.67	334.01
1058.23	2600.35
1128.62	1453.04
1672.50	22.54
1713.74	383.75
3400.72	1816.96
3447.43	3091.65
3453.35	5598.98
3538.55	4434.23
3802.21	342.48

Table S.6. Solid-state DFT optimized atomic positions of anhydrous $FeSO_4$, which crystallizes *Cmcm*, with lattice parameters a = 5.251 Å, *b* = 8.020 Å, *c* = 6.642 Å.

	a	b	c
Fe	0.000	0.000	0.000
Fe	0.000	0.000	-0.500
S	0.000	0.350	0.250
O	0.000	0.250	0.064
O	0.000	-0.250	-0.436
O	-0.265	-0.040	0.250

Table S.7. Solid-state DFT optimized atomic positions of $Fe_2(SO_4)_3OH \cdot 2H_2O$, which crystallizes $P2_1/m$, with lattice parameters a = 6.826 Å, b = 7.404 Å, c = 5.809 Å, β =90.254°.

	a	b	c
Fe	0.000	0.000	0.000
O	0.180	0.085	0.251
O	0.230	-0.026	-0.222
H	-0.345	0.403	0.174
H	-0.278	-0.421	0.309
S	0.305	0.250	0.285
O	0.378	0.250	-0.475
O	0.468	0.250	0.117
O	0.049	-0.250	0.115
H	0.136	-0.250	0.247