Supporting Information

First ternary tungsten tellurate(IV) WTe_2O_7 with new crystal structure type

Raimund Ziegler, Felix R. S. Purtscher, Heidi A. Schwartz, Thomas S. Hofer, and Gunter Heymann*

Additional crystal structure data:

Table SI1. Atomic coordinates, site occupation, and isotropic equivalent displacement parameters U_{eq} /pm^2 for WTe_2O_7. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor (standard deviations in parentheses). All sites occupy Wyckoff site 2*i*.

Atom	*x*	*y*	*z*	*SOF*	U_{eq}
W1A	0.50630(4)	0.53362(4)	0.29649(2)	0.981(2)	42.0(4)
W1B	0.468(2)	0.503(2)	0.286(1)	0.019(2)	42.0(4)
Te1A	0.02845(3)	0.21413(2)	0.03050(2)	0.9677(7)	50.3(3)
Te1B	0.1585(9)	0.0956(7)	0.0994(6)	0.0323(7)	60(10)
Te2	0.19319(3)	0.08737(2)	0.57124(2)	1.00000	60.1(3)
O1	0.0710(3)	0.0666(3)	0.3544(2)	1.00000	60(3)
O2	0.1654(3)	0.5944(3)	0.1850(2)	1.00000	77(3)
O3	0.2599(3)	0.5657(3)	0.5062(2)	1.00000	73(3)
O4	0.5021(4)	0.2003(3)	0.7794(2)	1.00000	90(3)
O5	0.5066(3)	0.1843(3)	0.3890(2)	1.00000	62(3)
O6	0.7379(3)	0.4329(3)	0.1352(2)	1.00000	75(3)
O7	0.8231(3)	0.0326(3)	0.1070(2)	1.00000	71(3)

Table SI2. Anisotropic displacement parameters [Å^2] of WTe_2O_7 (space group $P\bar{1}$) with standard deviation in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1A	0.00474(5)	0.00355(5)	0.00410(4)	−0.00135(3)	0.00055(3)	−0.00120(4)
W1B	0.00474(5)	0.00355(5)	0.00410(4)	−0.00135(3)	0.00055(3)	−0.00120(4)
Te1A	0.00519(6)	0.00456(6)	0.00553(6)	−0.00108(4)	−0.00009(4)	−0.00226(4)
Te1B	0.007(2)	0.006(2)	0.004(2)	0.001(2)	−0.003(2)	−0.003(2)
Te2	0.00550(5)	0.00473(5)	0.00766(6)	−0.00290(4)	−0.00115(4)	−0.00062(4)
O1	0.0068(6)	0.0071(6)	0.0052(6)	−0.0018(5)	0.0002(5)	−0.0037(5)
O2	0.0075(7)	0.0081(6)	0.0064(7)	−0.0013(5)	−0.0011(5)	−0.0020(5)
O3	0.0066(6)	0.0076(6)	0.0069(7)	−0.0033(5)	0.0013(5)	−0.0010(5)
O4	0.0107(7)	0.0058(6)	0.0105(7)	−0.0027(6)	0.0012(6)	−0.0030(5)
O5	0.0055(6)	0.0038(6)	0.0078(7)	−0.0015(5)	0.0003(5)	−0.0002(5)
O6	0.0080(6)	0.0071(6)	0.0060(6)	−0.0026(5)	0.0014(5)	−0.0007(5)
O7	0.0087(7)	0.0066(6)	0.0087(7)	−0.0043(5)	0.0038(5)	−0.0048(5)

Atom		Distance	Atom		Distance	Atom		Distance
Te1A:	O7	190.28(17)	Te1B:	O7	200.1(5)			
	O2	191.96(17)		O1	203.1(5)			
	O6	205.56(16)		O7	207.9(5)			
	O7	217.22(16)		O4	217.3(5)			
	O1	248.18(17)						
Te2:	O5	191.56(16)	W1A:	O4	172.88(17)	W1B:	O2	168.3(12)
	O1	196.77(17)		O6	183.37(16)		O6	183.2(7)
	O1	202.79(17)		O3	188.74(18)		O4	201.2(14)
	O5	230.40(17)		O2	194.67(18)		O5	202.9(12)
	O7	246.75(18)		O3	207.59(17)		O3	209.3(7)
				O5	228.88(17)		O3	212.9(13)

Table SI3. Selected interatomic distances (pm) of WTe_2O_7 (standard deviations in parentheses).

Table SI4. Selected interatomic angles (°) of WTe_2O_7. (standard deviations in parentheses).

O7–Te1A–O2	99.71(8)	O4–W1A–O6	95.65(8)
O7–Te1A–O6	85.67(7)	O4–W1A–O3	98.18(8)
O2–Te1A–O6	82.83(7)	O6–W1A–O3	101.46(8
O7–Te1A–O7	74.36(7)	O4–W1A–O2	95.96(8)
O2–Te1A–O7	85.56(7)	O6–W1A–O2	100.22(8
O6–Te1A–O7	154.83(7)	O3–W1A–O2	152.72(8
O7–Te1A–O1	70.88(7)	O4–W1A–O3	98.43(8)
O2–Te1A–O1	152.68(6)	O6–W1A–O3	165.76(7
O6–Te1A–O1	71.13(6)	O3–W1A–O3	74.53(8)
O7–Te1A–O1	114.84(6)	O2–W1A–O3	80.40(7)
		O4–W1A–O5	177.93(8
O7–Te1B–O1	79.78(18)	O6–W1A–O5	84.00(7)
O7–Te1B–O7	74.57(17)	O3–W1A–O5	83.89(7)
O1–Te1B–O7	145.5(2)	O2–W1A–O5	82.10(7)
O7–Te1B–O4	111.2(2)	O3–W1A–O5	82.00(6)
O1–Te1B–O4	81.05(17)		
O7–Te1B–O4	87.11(18)	O2–W1B–O6	111.2(5)
		O2–W1B–O4	95.1(3)
O5–Te2–O1	93.63(7)	O6–W1B–O4	86.7(5)

O5–Te2–O1	92.63(7)	O2–W1B–O5	97.2(8)
O1–Te2–O1	74.44(8)	O6–W1B–O5	91.9(4)
O5–Te2–O5	77.00(7)	O4–W1B–O5	167.3(7)
O1–Te2–O5	81.75(6)	O2–W1B–O3	86.2(3)
O1–Te2–O5	153.40(6)	O6–W1B–O3	162.4(8)
O5–Te2–O7	83.16(6)	O4–W1B–O3	89.5(5)
O1–Te2–O7	143.51(6)	O5–W1B–O3	88.1(3)
O1–Te2–O7	69.44(6)	O2–W1B–O3	155.5(4)
O5–Te2–O7	131.86(6)	O6–W1B–O3	93.0(5)
		O4–W1B–O3	82.6(6)
		O5–W1B–O3	84.9(3)
		O3–W1B–O3	69.4(3)

Table SI5: Comparison of the calculated MAPLE values of WTe_2O_7 and the binary compounds WO_3 ($P2_1/c$) and TeO_2 ($P2_12_12_1$).

Calculated MAPLE value for TeO_2 in kJ/mol	12288.9	2×
Calculated MAPLE value for WO_3 in kJ/mol	25828.2	
Calculated MAPLE value from the two educt compounds in kJ/mol	50406.0	
Calculated MAPLE value for WTe_2O_7 in kJ/mol	50129.4	
Deviation in %	0.55	

Theoretical Calculations and Analysis

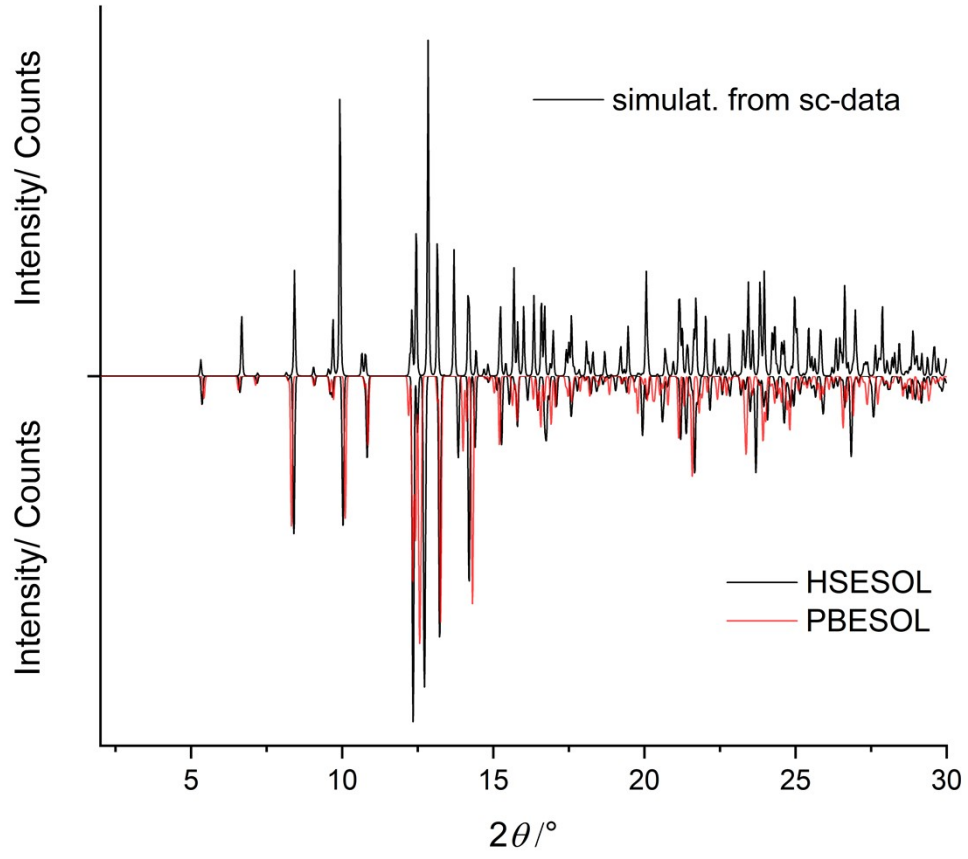

Figure SI1. Comparison of calculated powder XRD patterns derived from experimental singe crystal data (top) and from DFT optimized structures (bottom) using the solid-state functionals PBESOL (red curve) and HSESOL (black curve). Deviations may be caused by differences in the lattice parameters (room temperature vs 0K, accuracy of DFT methods, ...), thermal disorder in the lattice, uncertainties/approximations in the collision cross sections.

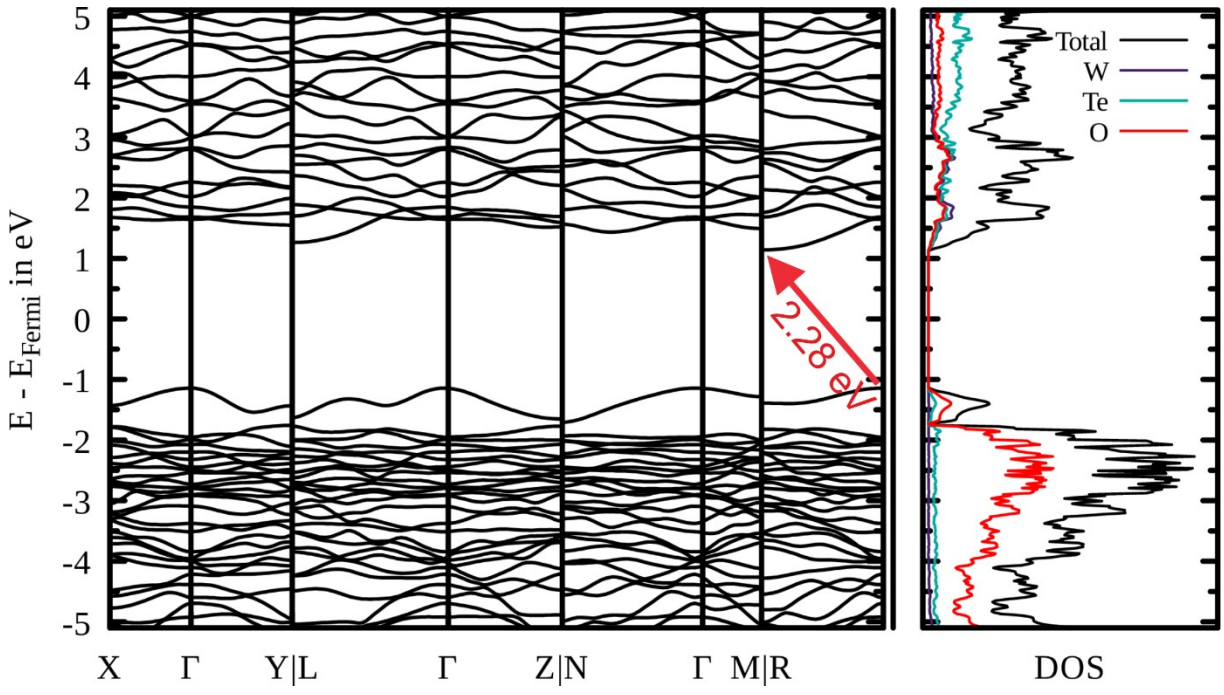

Figure SI2. Band structure and density of states (right part of the figure) of WTe_2O_7 determined by the PBESOL functional.

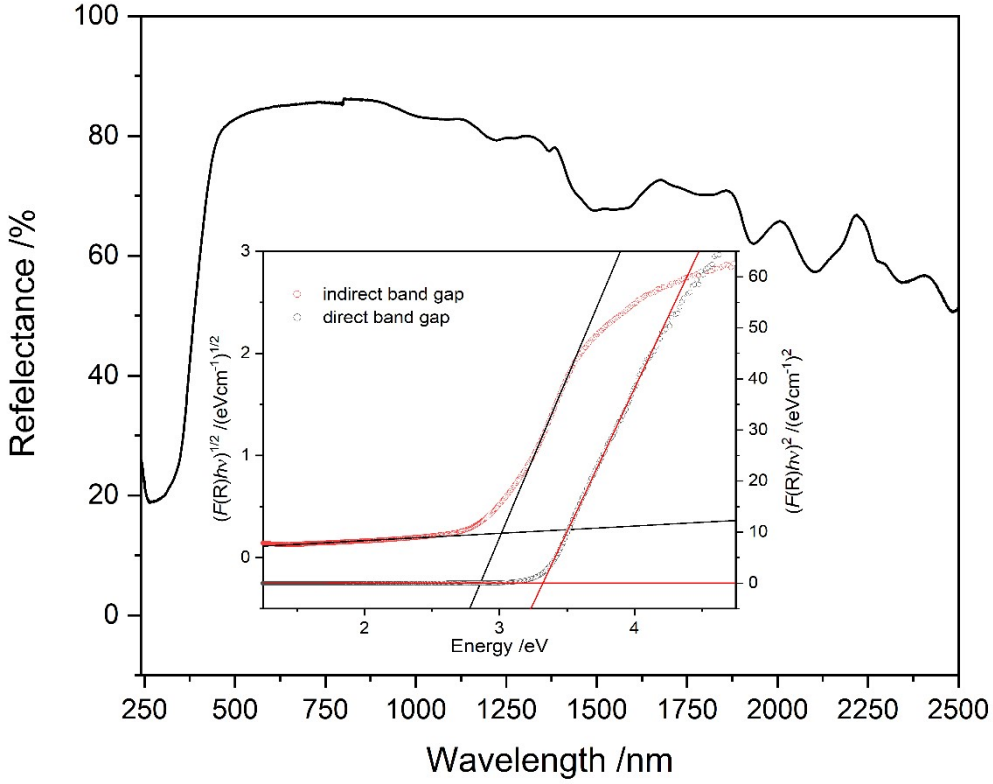

Figure SI3. UV/Vis spectrum measured in diffuse reflection geometry. As an inset, the plots $(F(\mathrm{R})h\nu)^{1/2}/(h\nu)$ for the indirect band gap (3.0 eV) and $(F(\mathrm{R})h\nu)^{2}/(h\nu)$ for the direct band gap (3.3 eV) are shown.

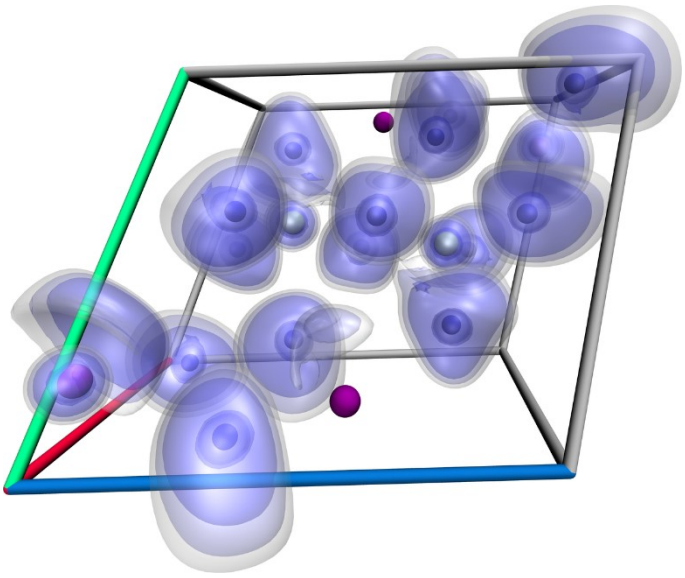

Figure SI4. 3D electron localization function (ELF) in perspective view. The orientation is indicated along a, b, c and red, green, blue respectively.

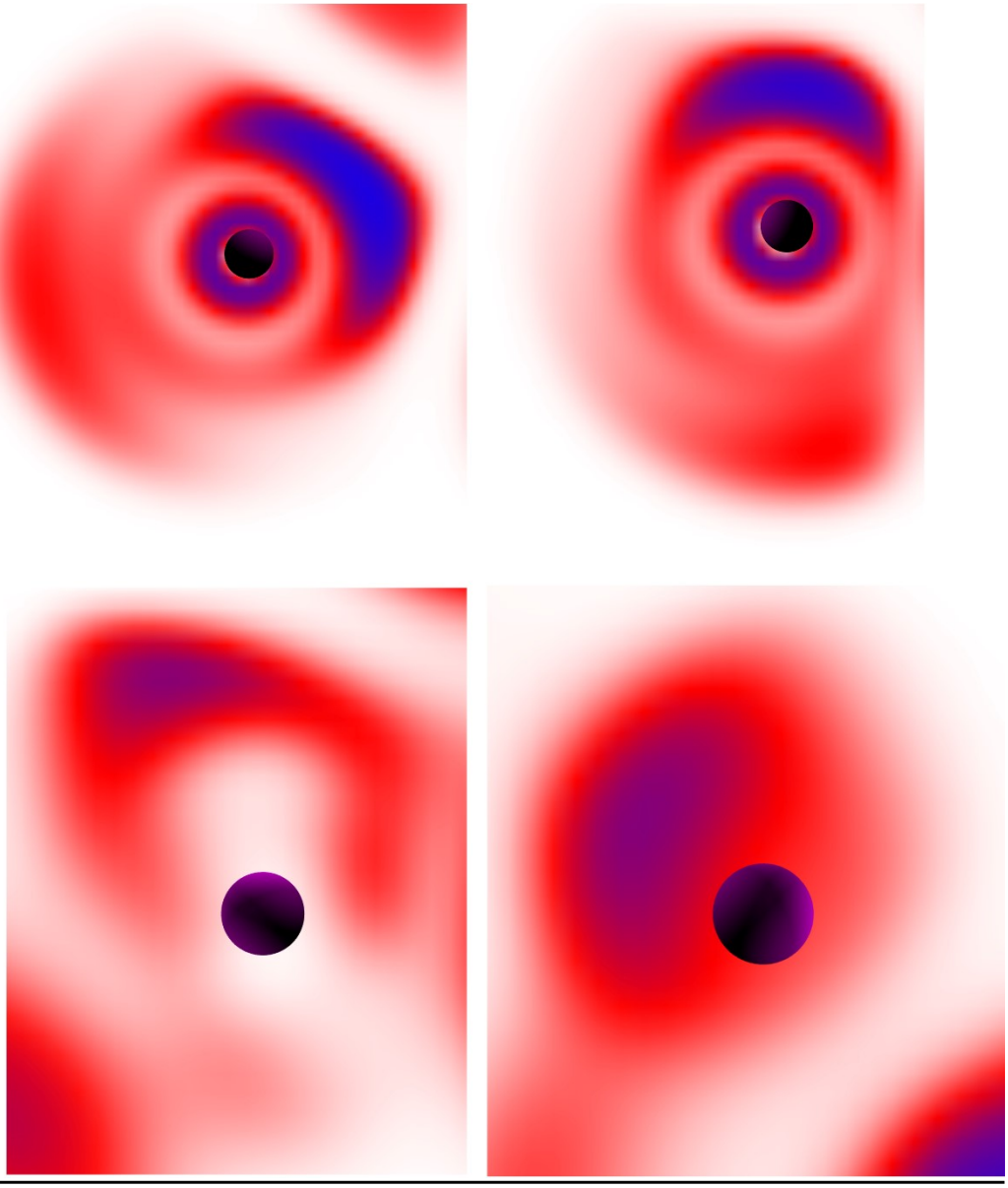

Figure SI5. Projection of the ELF density near the Te1 (top) and Te2 (bottom) atoms along the z- (left) and y-axes (right), respectively. The *p*-like character of the lone pair density is clearly visible.

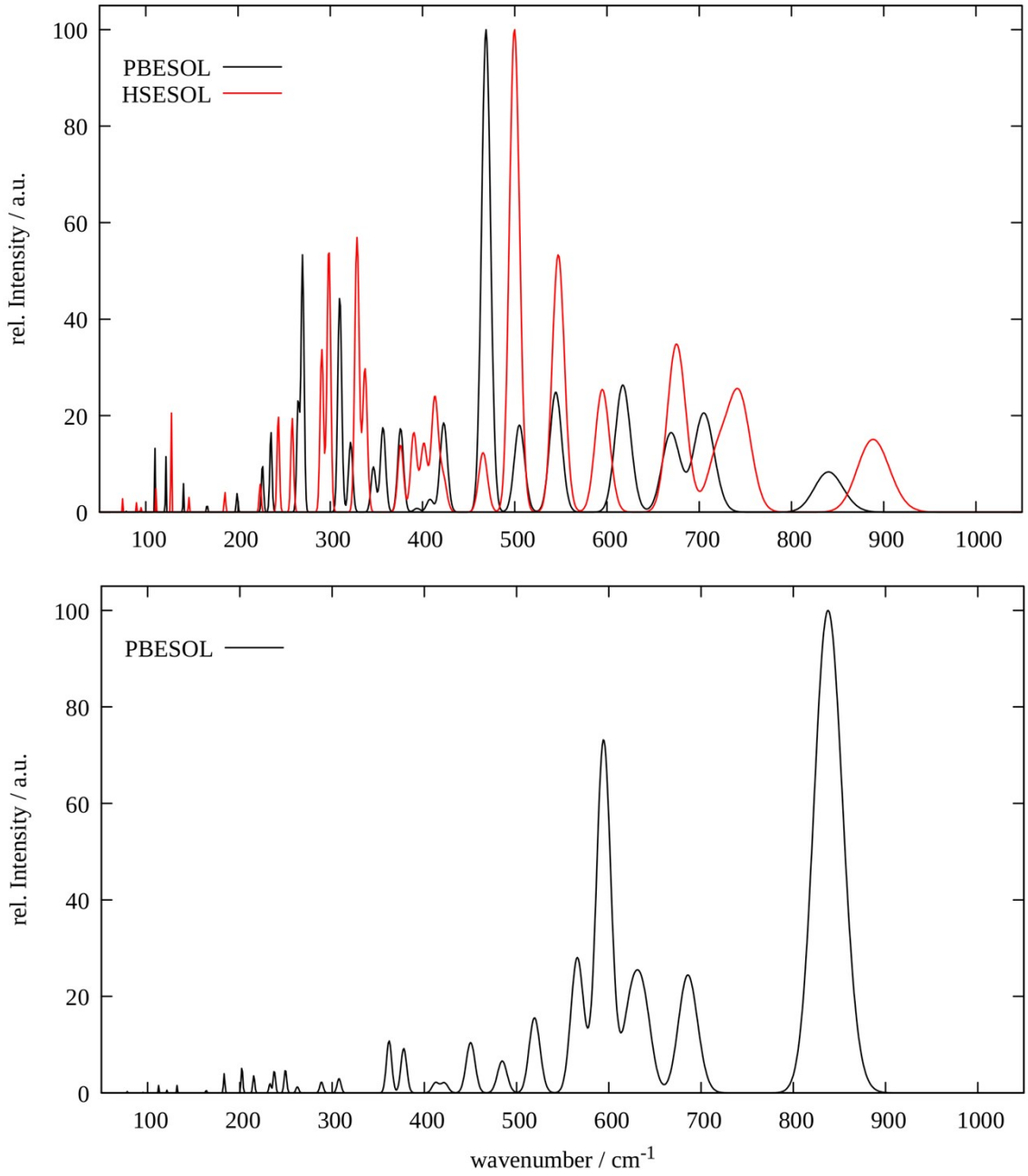

Figure SI6. Calculated IR spectrum on PBESOL and HSESOL level (top) and calculated Raman spectrum with the GGA functional PBESOL (bottom).

Table SI6. Analysis of the individual atoms contributing to the vibrational modes calculated at HSESOL level. For each pair of bonded atoms A and B (based on their respective van-der-Waals distance) the relative motion is evaluated and decomposed into i) a stretch (S) component along the A-B bond, ii) a bending (B) component when considering a third atom C and iii) an out-of-plane (O) component relative to the plane when considering a third atom C. For both stretch and bending components the default threshold of 0.85 has been employed (i.e. 85% of the relative motion has to be attributed to the respective mode). Otherwise the motion is assumed to be out-of-plane. In addition, collective vibrational motion of entire structural units are designated as R. Attention: Atom labeling of the crystal structure and the theoretical calculation is different. Therefore, at the end of the

table the fractional coordinates and the corresponding atomic index are given (atomic labels in brackets correspond to the atom labeling of the single-crystal structure).

Mode	Freq / cm^{-1}	Irrep	Type	Atom A	Atom B	Atom C
1	74,7902	Au	R	O 13	TE 3	O9
			R	O 14	TE 4	O10
2	85,3929	Ag	R	O 11	W 5	O16
			R	O 12	W 6	O15
3	88,0539	Ag	R	O 17	TE 1	O18
			R	O 18	TE 1	O19
			R	TE 1	O 19	TE2
			R	O 20	TE 1	O19
			R	O 17	TE 2	O20
			R	O 18	TE 2	O17
			R	TE 2	O 19	TE1
			R	O 20	TE 2	O19
4	90,0008	Au	R	O 8	TE 3	O9
			R	O 7	TE 4	O10
5	95,3997	Au	S	O 17	TE1	
			R	O 18	TE 1	O17
			R	TE 2	O 17	TE1
			S	O 18	TE2	
6	100,1662	Ag	O	O 11	W 5	O13
			O	O 12	W 6	O14
7	111,3139	Au	B	O 8	TE 3	O10
			S	O 13	TE 3	O10
			B	O 7	TE 4	O9
			S	O 14	TE 4	O9
8	123,427	Ag	O	O 10	TE 3	O8
			O	O 9	TE 4	O7
			B	O 11	W 5	O12
			B	O 12	W 6	O11
9	127,6667	Au	S	O 13	TE 3	O8
			S	O 14	TE 4	O7
10	133,8238	Ag	B	TE 3	O 13	W5
			B	TE 4	O 14	W6
			B	O 7	W 5	O11
			S	O 11	W 5	O7
			B	O 8	W 6	O12
			S	O 12	W 6	O8
11	144,2185	Ag	O	O 10	TE 3	O8
			S	O 13	TE 3	O9
			O	O 9	TE 4	O7
			S	O 14	TE 4	O10
12	146,8072	Au	B	O 7	W 5	O16
			B	O 8	W 6	O15
13	183,6314	Ag	B	O 16	W 5	O7
			B	O 15	W 6	O8
14	185,889	Au	O	TE 3	O 13	W5
			O	TE 4	O 14	W6
			B	O 16	W 5	O13
			B	O 15	W 6	O14
15	200,5396	Ag	B	O 13	W 5	O11
			B	O 16	W 5	O13

			B	O 14	W 6	O12
			B	O 15	W 6	O14
16	219,3378	Ag	O	O 20	TE 1	O17
			O	O 19	TE 2	O18
17	224,1441	Au	B	O 17	TE 1	O19
			O	O 18	TE 1	O19
			O	O 17	TE 2	O20
			B	O 18	TE 2	O20
			B	O 13	TE 3	O9
			B	O 14	TE 4	O10
			O	O 13	W 5	O11
			O	O 16	W 5	O7
			O	O 14	W 6	O12
			O	O 15	W 6	O8
18	235,0493	Ag	B	O 17	TE 1	O20
			B	O 18	TE 2	O19
19	243,6719	Au	O	O 7	W 5	O13
			B	O 13	W 5	O7
			O	O 8	W 6	O14
			B	O 14	W 6	O8
20	247,6554	Ag	S	O 17	TE 1	O19
			S	O 18	TE 2	O20
21	251,7256	Ag	B	O 17	TE 1	O19
			B	O 18	TE 2	O20
22	258,8362	Au	B	O 17	TE 1	O19
			B	O 18	TE 1	O19
			B	O 19	TE 1	O18
			B	O 20	TE 1	O18
			B	O 17	TE 2	O20
			B	O 18	TE 2	O20
			B	O 19	TE 2	O17
			B	O 20	TE 2	O17
23	270,6559	Ag	B	O 9	TE 3	O8
			B	O 10	TE 3	O8
			B	O 9	TE 4	O7
			B	O 10	TE 4	O7
24	284,995	Ag	B	O 8	TE 3	O10
			B	O 7	TE 4	O9
			O	O 7	W 5	O13
			O	O 8	W 6	O14
25	290,9127	Au	B	O 8	TE 3	O13
			B	O 7	TE 4	O14
			B	O 7	W 5	O13
			B	O 8	W 6	O14
26	298,5195	Au	B	O 9	TE 3	O8
			B	O 10	TE 3	O8
			B	O 9	TE 4	O7
			B	O 10	TE 4	O7

			S	O 11	W 5	O16
			O	O 12	W 5	O13
			O	O 11	W 6	O14
			S	O 12	W 6	O15
27	306,2203	Ag	B	O 18	TE 1	O19
			B	O 17	TE 2	O20
28	322,0576	Ag	B	O 13	TE 3	O10
			B	O 14	TE 4	O9
			B	O 7	W 5	O16
			B	O 13	W 5	O7
			B	O 8	W 6	O15
			B	O 14	W 6	O8
29	329,0506	Au	O	O 9	TE 3	O10
			S	O 10	TE 3	O8
			S	O 9	TE 4	O7
			O	TE 4	O 10	TE3
30	337,7205	Au	S	O 17	TE 1	O19
			O	TE 1	O 18	TE2
			O	TE 2	O 17	TE1
			S	O 18	TE 2	O20
31	371,0673	Ag	B	O 16	W 5	O12
			B	O 15	W 6	O11
32	376,3711	Au	B	O 9	TE 3	O13
			S	O 10	TE 3	O8
			S	O 9	TE 4	O7
			B	O 10	TE 4	O14
33	390,6297	Au	O	O 19	TE 1	O18
			B	O 20	TE 1	O18
			B	O 19	TE 2	O17
			O	O 20	TE 2	O17
34	401,5544	Au	O	TE 3	O 13	W5
			O	TE 4	O 14	W6
			B	O 13	W 5	O16
			B	O 14	W 6	O15
35	401,8035	Ag	B	TE 3	O 13	W5
			B	TE 4	O 14	W6
			B	W 5	O 13	TE3
			B	W 6	O 14	TE4
36	413,3845	Au	B	O 7	W 5	O12
			B	O 8	W 6	O11
37	422,4202	Au	B	O 8	TE 3	O9
			B	O 7	TE 4	O10
			B	O 7	W 5	O16
			B	O 16	W 5	O12
			B	O 8	W 6	O15
			B	O 15	W 6	O11
38	425,9121	Ag	B	TE 3	O 8	W6

			B	TE 4	O 7	W5
			B	W 5	O 7	TE4
			B	W 6	O 8	TE3
39	455,3932	Ag	S	O 17	TE1	
			B	O 18	TE 1	O20
			B	O 17	TE 2	O19
			S	O 18	TE2	
40	465,7085	Au	B	O 19	TE 1	O17
			S	O 20	TE 1	O17
			S	O 19	TE 2	O18
			B	O 20	TE 2	O18
41	472,9355	Ag	S	O 11	W5	
			B	O 12	W 5	O11
			B	W 6	O 11	W5
			S	O 12	W6	
42	498,0106	Ag	B	TE 1	O 19	TE2
			S	O 20	TE1	
			S	O 19	TE2	
			B	O 20	TE 2	O19
43	499,7479	Au	B	O 11	W 5	O12
			S	O 12	W5	
			S	O 11	W6	
			B	O 12	W 6	O11
44	527,0718	Ag	B	O 9	TE 3	O10
			S	O 10	TE3	
			S	O 9	TE4	
			B	TE 4	O 10	TE3
45	547,2665	Au	S	O 19	TE1	
			B	O 20	TE 1	O19
			B	TE 2	O 19	TE1
			S	O 20	TE2	
46	563,3358	Ag	S	O 8	TE3	
			S	O 7	TE4	
47	595,0192	Au	S	O 9	TE3	
			B	TE 3	O 10	TE4
			B	O 9	TE 4	O10
			S	O 10	TE4	
48	620,2016	Ag	S	O 18	TE1	
			S	O 17	TE2	
			S	O 12	W 5	O11
			S	W 6	O 11	W5
49	637,2332	Ag	S	TE 1	O 19	TE2
			B	O 20	TE 1	O19
			B	TE 2	O 19	TE1
			S	O 20	TE 2	O19
50	670,2464	Ag	S	O 18	TE1	
			S	O 19	TE 1	O20

			S	O 17	TE2	
			S	TE 2	O 20	TE1
51	675,4702	Au	B	TE 1	O 17	TE2
			S	O 18	TE1	
			S	O 17	TE2	
			B	O 18	TE 2	O17
52	677,7719	Ag	S	O 9	TE3	
			S	O 10	TE4	
53	720,3913	Au	S	O 8	TE3	
			S	O 7	TE4	
54	734,2399	Ag	S	O 8	TE3	
			S	O 7	TE4	
			S	O 7	W 5	O12
			S	O 13	W5	
			S	O 8	W 6	O11
			S	O 14	W6	
55	743,5881	Au	S	O 9	TE3	
			B	O 10	TE 3	O9
			S	O 13	TE3	
			B	TE 4	O 9	TE3
			S	O 10	TE4	
			S	O 14	TE4	
			S	O 13	W5	
			S	O 14	W6	
56	888,5776	Au	S	O 16	W5	
			S	O 15	W6	
57	899,1912	Ag	S	O 16	W5	
	^		S	O 15	W6	

Unit Cell:

a (Ang)	*b* (Ang)	*c* (Ang)	*α* (°)	*β* (°)	*γ* (°)
5,35385	6,94821	7,95395	72,57597	85,89739	67,80648

Fractional Coordinates:

Atom Index	Element	x	y	z
1(2)	TE	-0,19712	-0,09513	0,43855
2(2)	TE	0,19712	0,09513	-0,43855
3(1A)	TE	-0,02839	-0,20998	-0,02638
4(1A)	TE	0,02839	0,20998	0,02638
5(1A)	W	0,47748	0,46037	-0,29052
6(1A)	W	-0,47748	-0,46037	0,29052
7(2)	O	-0,16049	0,39821	-0,19382
8(2)	O	0,16049	-0,39821	0,19382
9(7)	O	0,19183	-0,03980	-0,09698
10(7)	O	-0,19183	0,03980	0,09698
11(3)	O	-0,26270	0,42908	0,48666
12(3)	O	0,26270	-0,42908	-0,48666
13(6)	O	0,27278	-0,43605	-0,13146
14(6)	O	-0,27278	0,43605	0,13146
15(4)	O	-0,48631	-0,21141	0,22586
16(4)	O	0,48631	0,21141	-0,22586

17(5)	O	-0,49951	-0,17904	-0,39169
18(5)	O	0,49951	0,17904	0,39169
19(1)	O	-0,06467	-0,06691	-0,34983
20(1)	O	0,06467	0,06691	0,34983