Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary materials

for

Exploring $PtSO_4$ and $PdSO_4$ phases: an evolutionary algorithm based investigation

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S1: Structural Information

Table S1: Structural parameters of the predicted structures of (a) $PdSO_4$ and (b) $PtSO_4$. For comparison available structural parameters are shown in parentheses.

(a) $PdSO_4$

Phase	Lattice parameter (in Å)			Lattice angle (in °)			Atomic coordinates			
	a	*b*	*c*	*α*	*β*	*γ*	Wyckoff position	*x*	*y*	*z*
Z = 2										
$P4_2/m$	4.442	4.442	8.908	90.00	90.00	90.00	8k (O) 2e (S) 2c (Pd)	0.1759 0.0000 0.0000	0.7809 0.0000 0.5000	0.1574 0.2500 0.0000
C2/c	7.495 (7.286)	6.323 (6.692)	7.778 (7.651)	90.00	100.48 (103.18)	90.00	8f (O) 8f (O) 4e (S) 4c (Pd)	0.1698 -0.0168 0.0000 0.2500	0.0554 0.2081 0.0737 0.2500	0.7911 0.4048 0.2500 0.0000
Ibam	4.097	9.477	8.943	90.00	90.00	90.00	16k (O) 4a (S) 4d (Pd)	0.7049 0.5000 0.5000	0.5962 0.0000 0.0000	0.3446 0.2500 0.0000
P_4/n	6.189	6.189	4.940	90.00	90.00	90.00	8g (O) 2b (S) 2c (Pd)	0.2500 0.2500 0.6838	0.2500 0.7500 0.4298	0.3457 0.5000 0.6847
I222	9.345	9.707	4.183	90.00	90.00	90.00	8k (O) 8k (O) 2c (S) 2d (S) 4h (Pd)	0.0876 0.5981 0.0000 0.0000 0.5000	0.0971 0.0860 0.0000 0.5000 0.2279	0.2990 0.2970 0.5000 0.0000 0.0000
I-4	5.995	5.995	4.366	90.00	90.00	90.00	8g (O) 2c (S) 2a (Pd)	0.0000 0.0000 0.8972	0.0000 0.5000 0.6755	0.0000 0.2500 0.0512
Z =4										
P1 (alpha)	6.1895	6.1895	10.097	89.26	89.15	90.01	1a (Pd) 1a (S) 1a (O)	0.5783 0.9179 0.0748 0.4213 0.0770 0.4196 0.9195 0.5770 0.7540 0.1018 0.7421 0.3947 0.4871 0.1415 0.0104 0.3564 0.8988 0.2379 0.5977 0.2582 0.8520 0.5145 0.6455 0.9828	0.9199 0.5768 0.4168 0.0798 0.9183 0.5788 0.0788 0.4182 0.3510 0.1470 0.0159 0.4817 0.4003 0.0966 0.7368 0.7597 0.9856 0.5125 0.6435 0.8549 0.2561 0.2406 0.6003 0.8967	0.9227 0.5736 0.0735 0.4228 0.9982 0.4983 0.4981 0.9980 0.0889 0.4080 0.4072 0.0880 0.4085 0.0881 0.0893 0.4071 0.9084 0.5894 0.5882 0.9070 0.5891 0.9070 0.9079 0.5881
P1 (beta)	7.8858	5.3736	8.7481	90.00	82.56	90.00	1a (Pd) 1a (S)	0.3270 0.3270 0.8270 0.8269 0.5635 0.5635	0.6932 0.1932 0.1931 0.6932 0.0346 0.8518	0.8940 0.3940 0.8940 0.3939 0.0877 0.5877

			1a (O)	0.0905	0.5347	0.2002
				0.0905	0.3517	0.7003
				0.0844	0.7472	0.3140
				0.1078	0.2657	0.5366
				0.1078	0.6207	0.0366
				0.0845	0.1391	0.8140
				0.5462	0.1206	0.2514
				0.5463	0.7658	0.7513
				0.2346	0.3607	0.2122
				0.2347	0.5257	0.7122
				0.4193	0.0258	0.5758
				0.4194	0.8605	0.0758
				0.9165	0.4172	0.2383
				0.5694	0.6393	0.4739
				0.5694	0.2470	0.9739
				0.9165	0.4693	0.7384
				0.7375	0.9171	0.0497
				0.7375	0.9693	0.5495

(b) $PtSO_4$

Phase	Lattice parameter (in Å)			Lattice angle (in °)			Atomic coordinates			
	a	*b*	*c*	*α*	*β*	*γ*	*Wyckoff position*	*x*	*y*	*z*
Z = 2										
$P4_2/m$	4.451	4.451	8.859	90.00	90.00	90.00	2c (Pt)	0.0000	0.5000	0.0000
							2e (S)	0.0000	0.0000	0.2500
							8k (O)	0.1770	0.7804	0.1575
C2/c	7.045 (7.154)[1]	6.994 (6.553)[1]	7.683 (7.679)[1]	90.00	104.93 (102.19)[1]	90.00	4c (Pt)	0.2500	0.2500	0.0000
							4e (S)	0.0000	0.0676	0.2500
							8f (O)	-0.0118	0.1892	0.4073
							8f (O)	0.6847	0.4511	0.3017
Ibam	4.113	9.465	8.870	90.00	90.00	90.00	4c (Pt)	0.0000	0.0000	0.0000
							4b (S)	0.5000	0.0000	0.2500
							16k (O)	0.2055	0.5972	0.3447
P_4/n	6.201	6.201	4.900	90.00	90.00	90.00	2c (Pt)	0.2500	0.2500	0.3428
							2b (S)	0.2500	0.7500	0.5000
							8g (O)	0.6899	0.4301	0.6891
I222	9.442	9.776	4.108	90.00	90.00	90.00	4h (Pt)	0.5000	0.2286	0.0000
							2c (S)	0.0000	0.0000	0.5000
							2d (S)	0.0000	0.5000	0.0000
							8k (O)	0.0865	0.0976	0.2952
							8k (O)	0.5981	0.0847	0.2917
I-4	6.063	6.063	4.218	90.00	90.00	90.00	2a (Pt)	0.0000	0.0000	0.0000
							2c (S)	0.0000	0.5000	0.2500
							8g (O)	-0.0916	0.6771	0.0399
Z = 4										
P1 (alpha)	6.1992	6.1992	10.178	89.28	89.17	90.00	1a (Pt)	0.5782	0.9204	0.9228
								0.9182	0.5767	0.5734
								0.0748	0.4171	0.0733
								0.4217	0.0797	0.4229
							1a (S)			
								0.0767	0.9186	0.9980
								0.4199	0.5784	0.4982
								0.9198	0.0785	0.4983
								0.5767	0.4186	0.9981
							1a (O)			
								0.7544	0.3562	0.0893
								0.1023	0.1413	0.4076
								0.7422	0.0204	0.4069
								0.3943	0.4770	0.0889
								0.4824	0.4000	0.4075
								0.1356	0.0970	0.0887
								0.0147	0.7368	0.0894
								0.3615	0.7601	0.4068
								0.8985	0.9809	0.9074

								0.2379	0.5166	0.5895
								0.5981	0.6376	0.5888
								0.2586	0.8601	0.9068
								0.8573	0.2563	0.5895
								0.5189	0.2407	0.9067
								0.6398	0.6009	0.9075
								0.9780	0.8963	0.5890
								0.3271	0.6931	0.8940
							1a (Pt)	0.3270	0.1932	0.3940
								0.8269	0.1932	0.8940
								0.8270	0.6932	0.3940
							1a (S)	0.5588	0.0264	0.0825
								0.5588	0.8600	0.5825
								0.0951	0.5264	0.2054
								0.0951	0.3600	0.7055
							1a (O)	0.0903	0.7277	0.3194
								0.1113	0.2801	0.5416
P1 (beta)	7.8094	5.6949	8.7655	90.00	81.71	90.00		0.1113	0.6062	0.0416
								0.0902	0.1586	0.8194
								0.5427	0.1063	0.2464
								0.5427	0.7800	0.7464
								0.2406	0.3601	0.2145
								0.2407	0.5261	0.7145
								0.4133	0.0263	0.5735
								0.4134	0.8600	0.0735
								0.9175	0.4195	0.2483
								0.5636	0.6587	0.4685
								0.5636	0.2277	0.9685
								0.9175	0.4670	0.7483
								0.7365	0.9195	0.0396
								0.7365	0.9669	0.5396

S2: X-Ray Diffraction (XRD) Patterns

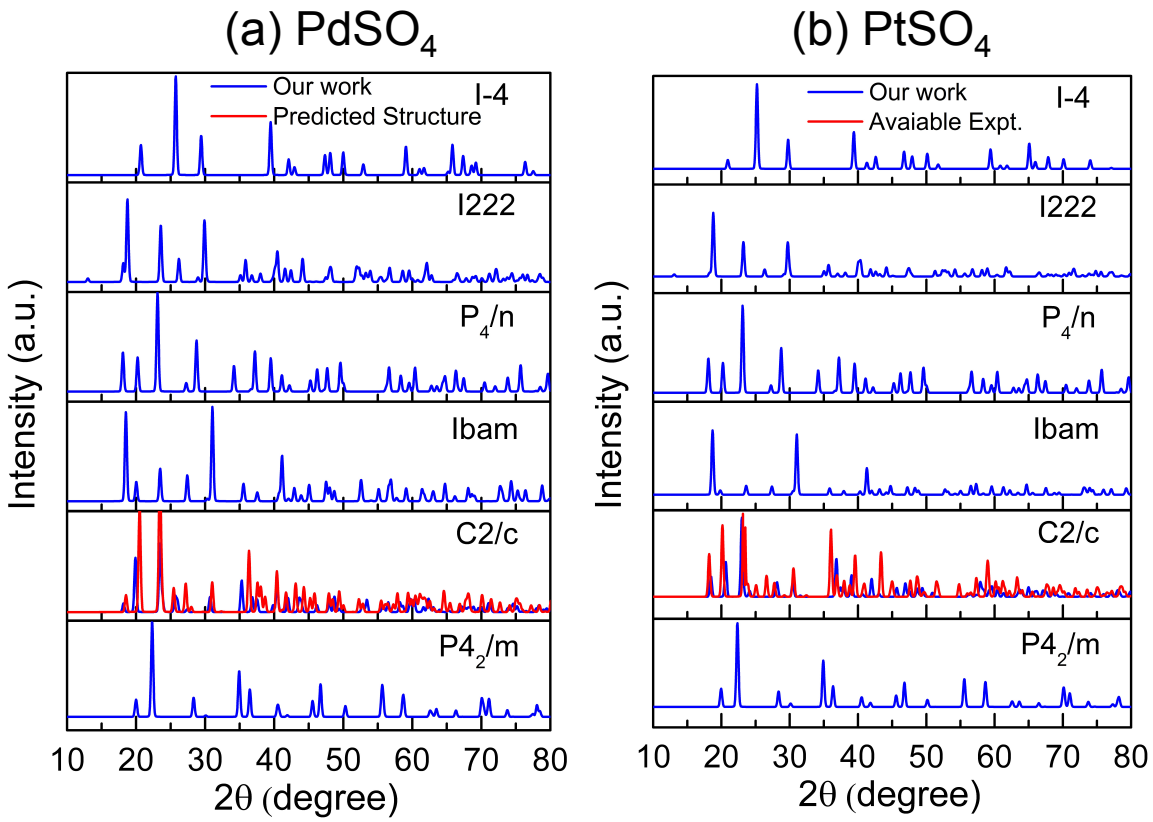
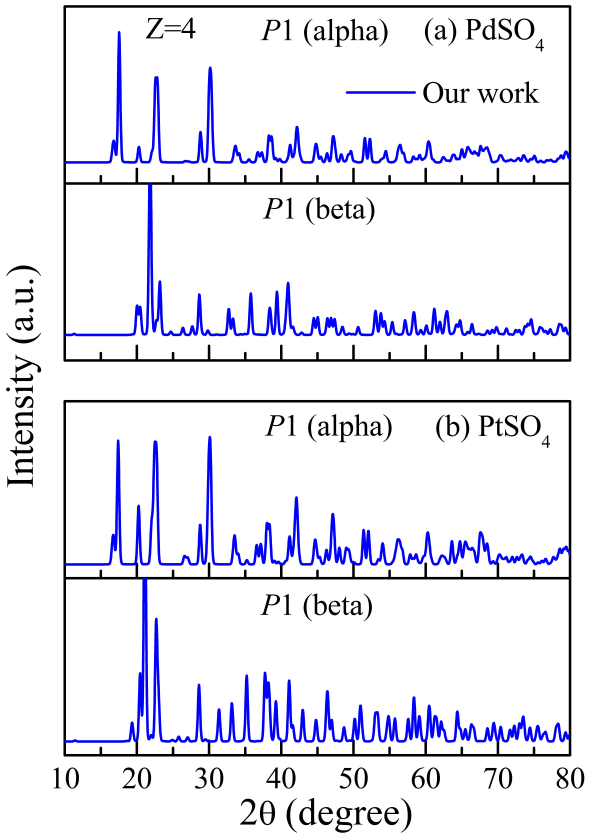


Figure S1: (i) Simulated X-ray diffraction patterns of all the low-energy structures predicted for Z=2 of (a) $PdSO_4$ and (b) $PtSO_4$ at ambient pressure. For $PdSO_4$, XRD pattern for the monoclinic (space group C2/c) is simulated using available experimental parameters. [1] While for $PtSO_4$, XRD pattern is compared with the structure suggested by Derzsi *et al.*[2]



(ii) Simulated X-ray diffraction patterns of all the low-energy structures predicted for Z= 4 of (a) $PdSO_4$ and (b) $PtSO_4$ at ambient pressure.

S3: Phonon density of states

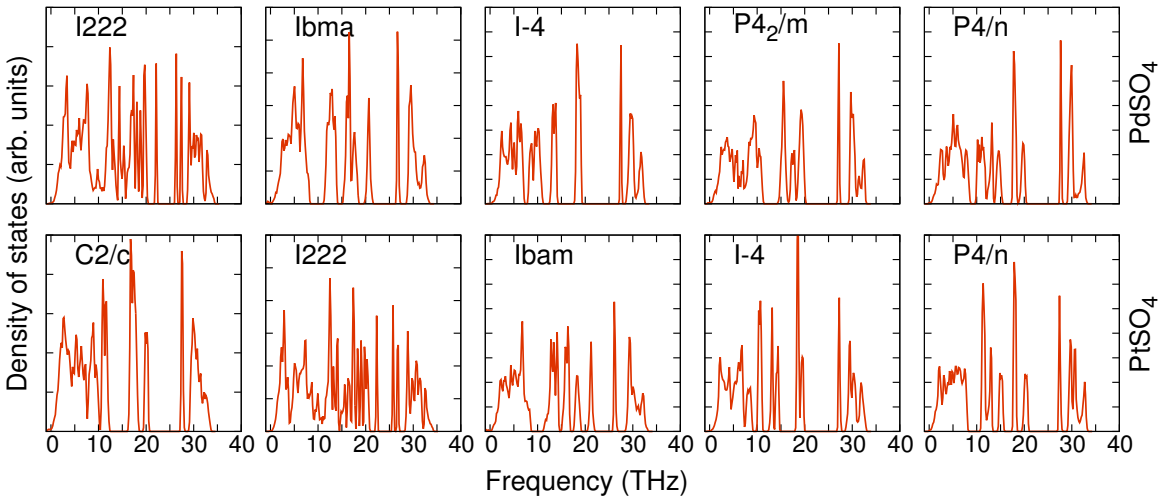


Fig S2: (i) phonon density of the state for the selected stable phases of $PtSO_4$ (lower panels) and $PdSO_4$ (upper panels) predicted by USPEX. Phonon densities of the state of the most stable phases of both sulfates are shown in the main text.

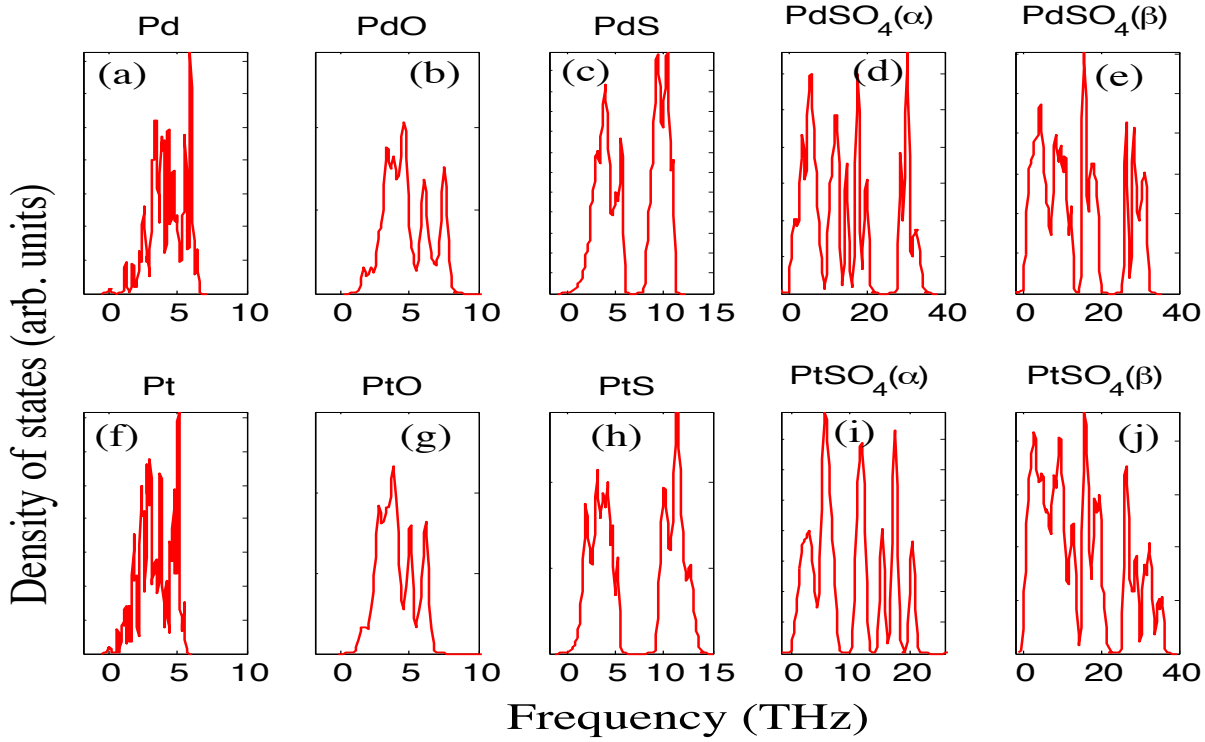


Fig S2: (ii) phonon density of the state for the most stable phases of (a) Pt, (b) PdO, (c) PdS, (d) Z4 $PdSO_4$ (α), (e) Z4 $PdSO_4$ (β), (f) Pt, (g) PtO, (h) PtS, (i) Z4 $PtSO_4$ (α), and (j) Z4 $PtSO_4$ (β), phases.

S4: Free energy diagram (Ellingham Diagram).

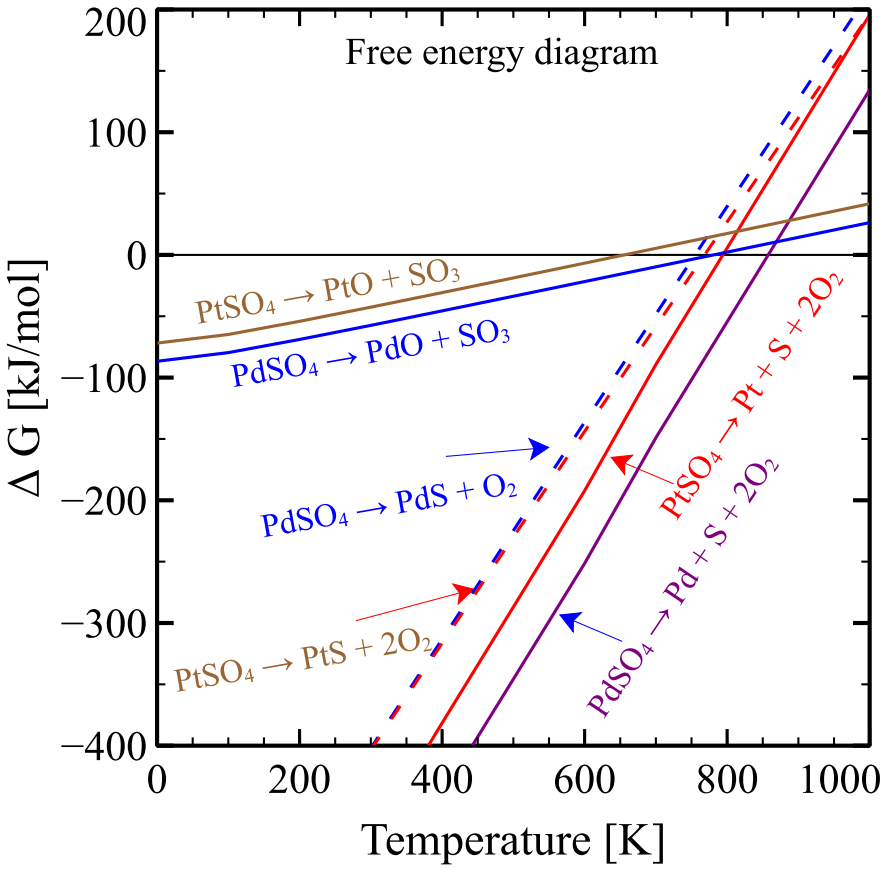


Figure S3: Free energy plot for the decomposition of $PdSO_4$ and $PtSO_4$ to their metal oxides, sulfur tri-oxide, metal sulfides, and elemental compositions. Negative value of ΔG suggests that the compound is stable towards decomposition. For the reaction Pd/PtSO4 → Pt/Pd + S + O_2, the latent heat of fusion (1.73 kJ mol^{-1}) and latent heat of vaporization (9.8 kJ mol^{-1}) of sulfur are also considered while computing ΔG given the melting of 388.36 K and boiling point of 717.87 K. [3, 4] Small shift in ΔG value can be seen at ~700 K due to the phase change in sulfur. In the positive ΔG range, the sulfates are no longer thermodynamically stable.

S5: Electronic density of states

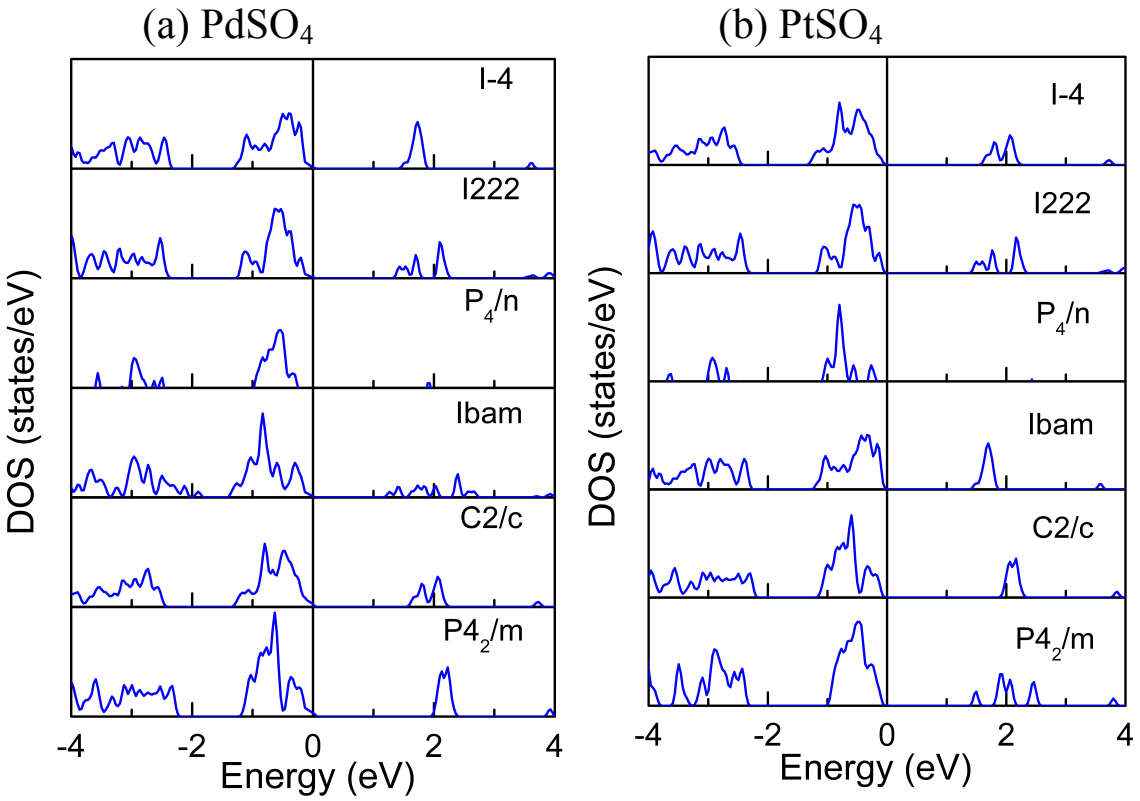
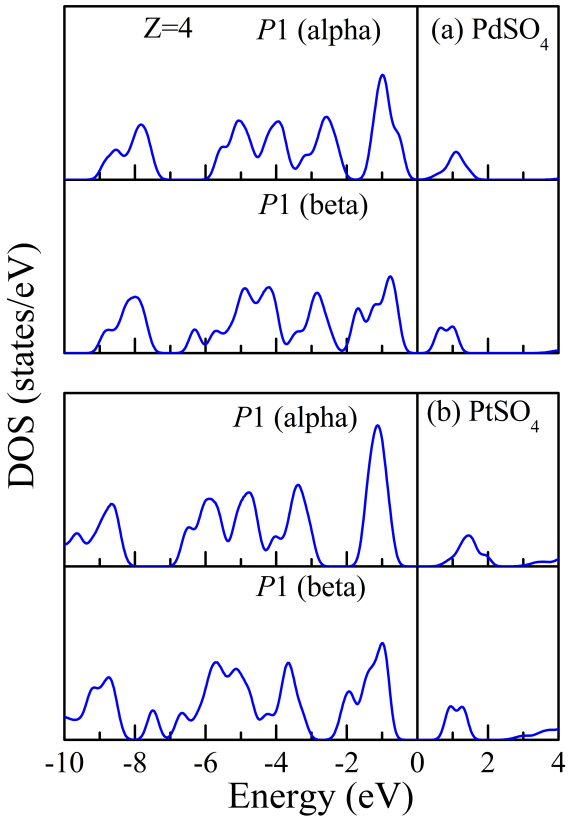


Figure S4: (i) Electronic density of states of the $Z = 2$ low-energy phases of (a) $PdSO_4$ and (b) $PtSO_4$. The bottom of valence bands (below -4 eV) and the top of conduction band (above 4 eV), not shown, consist of bands mainly due to P (2*p*) and S (2*s*) states.



(ii) Electronic density of states of $Z = 4$ low-energy structures of (a) $PdSO_4$ and (b) $PtSO_4$.

References

[1] D. L. Mowery and R. L. McCormick, Appl. Catal. B: Env. **34**, 287 (2001).
[2] M. Derzsi, A. Hermann, R. Ho_mann, and W. Grochala, Eur. J. Inorg. Chem. 2013, 5094 (2013).
[3] R.H. Schumm, D.D. Wagman, S. Bailey, W.H. Evans, and V.B. Parker in National Bureau of Standards (USA) Technical Notes 270-1 to 270-8, 1973.
[4] J.D. Cox, DD., Wagman, and V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere Publishing Corp., New York, USA, 1989.