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

A Method of Calculating Surface Energies for Asymmetric Slab Models

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Table S1. TiO_2, SnO_2, MoO_3, MoP models with respective k-point grids

	TiO_2 rutile (001)	SnO_2 rutile (110)	SnO_2 rutile (101)	TiO_2 rutile (110)	MoO_3 (010)	MoP (001)	MoP (111)	MoP (100)
Optimized bulk	3x3x5	3x3x4	3x3x4	3x3x5	4x1x4	15x15x15	15x15x15	15x15x15
Slab models	3x3x1	2x2x1	3x3x1	5x3x1	4x4x1	5x5x1	5x8x1	4x5x1

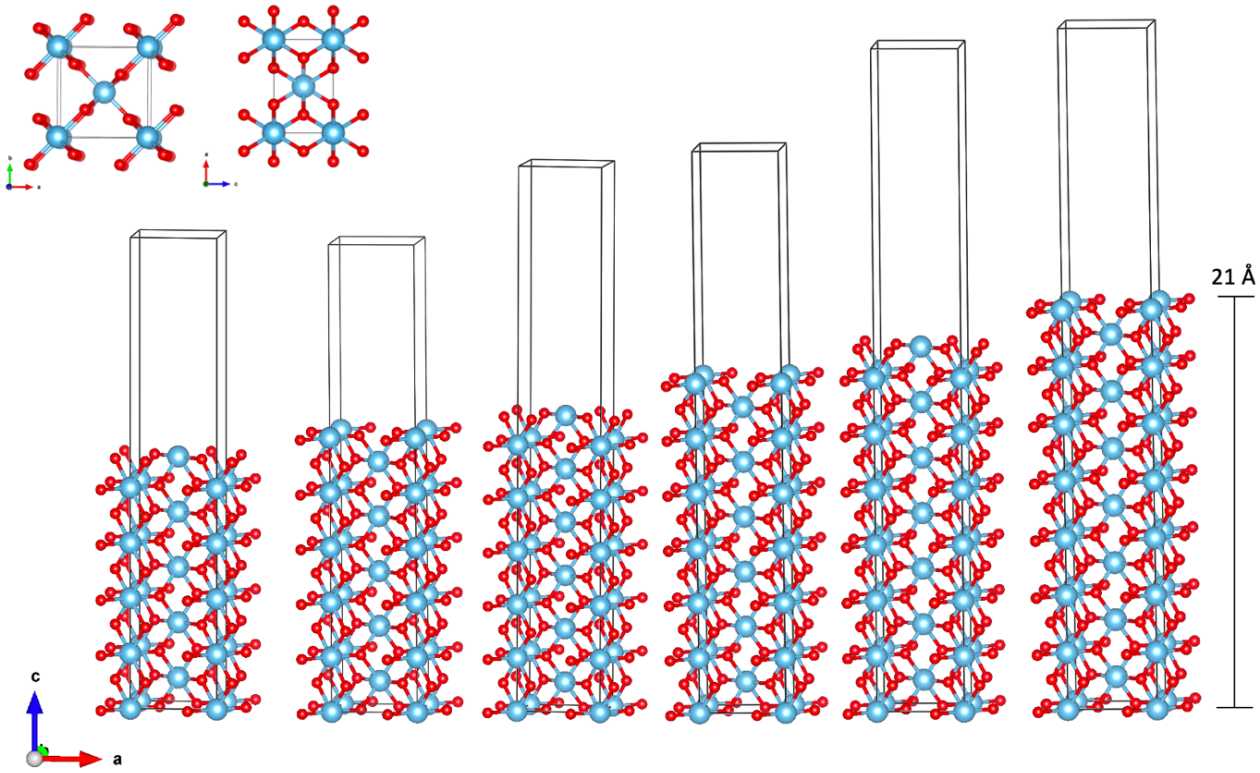

Figure S1. TiO_2 rutile optimized bulk & slab structures featuring both asymmetric and symmetric models. From left to right the models feature 10, 11, 12, 13, 14, and 15 layers. The slabs with even numbers of layers are asymmetric, while those with odd numbers of layers are symmetric.

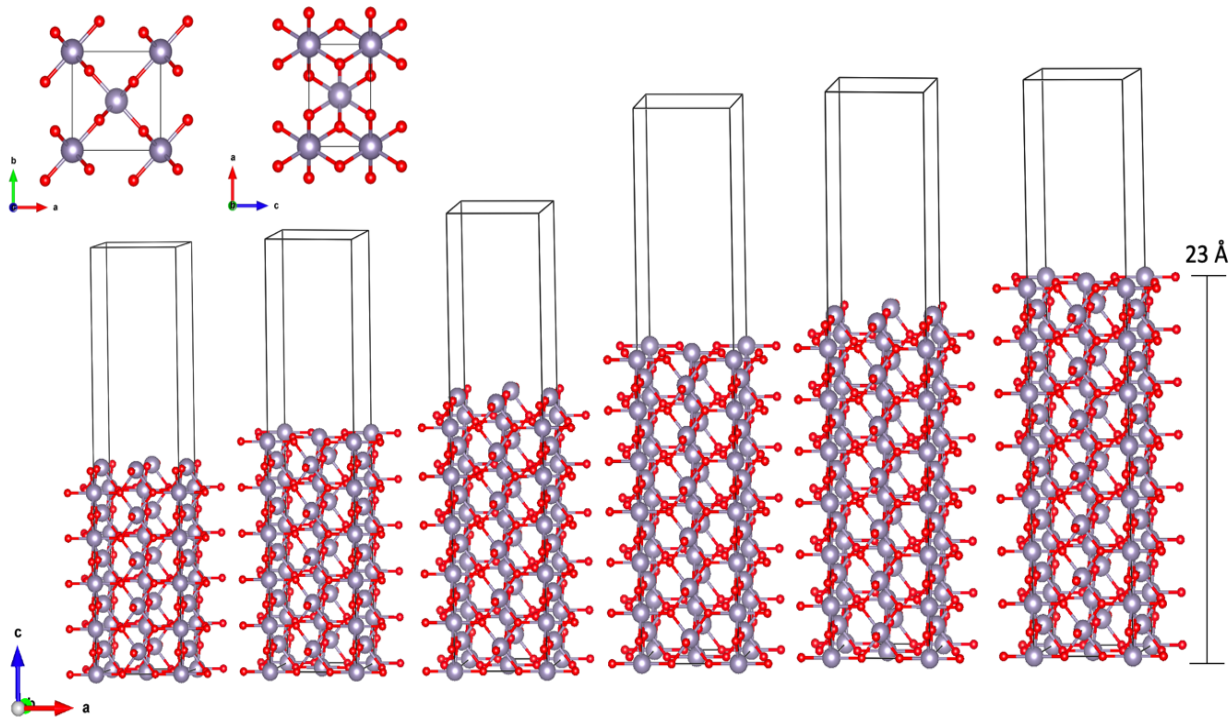

Figure S2. SnO_2 rutile optimized bulk & slab structures featuring both asymmetric and symmetric models. From left to right the models feature 10, 11, 12, 13, 14, and 15 layers. The slabs with even numbers of layers are asymmetric, while those with odd numbers of layers are symmetric.

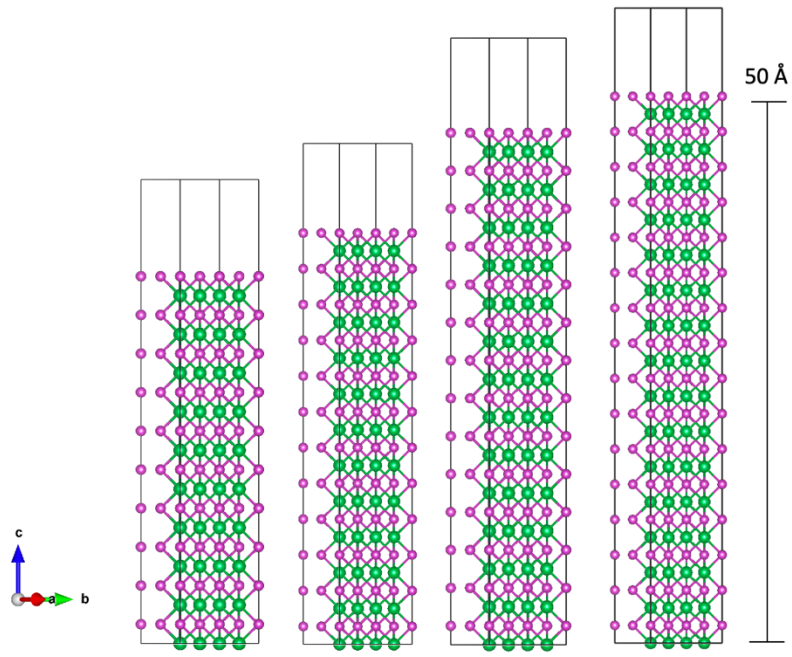

Figure S3. MoP (001) asymmetric slab models with 10, 12, 14, and 16 Mo-P layers.

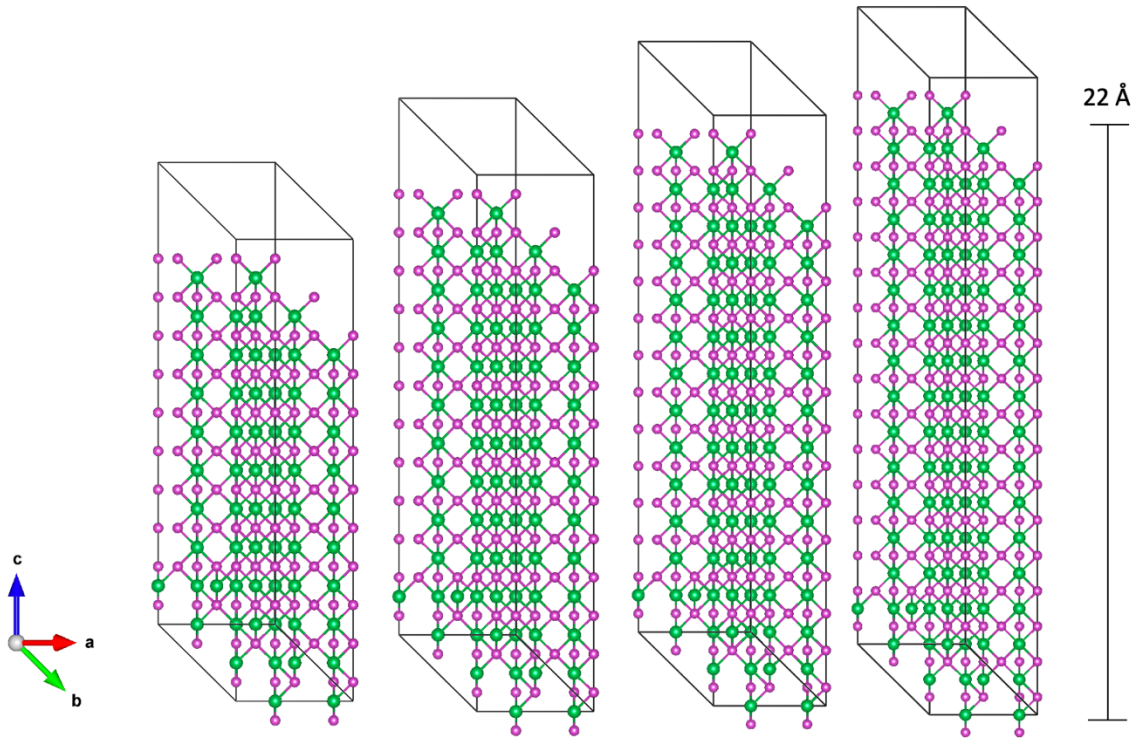

Figure S4. MoP (111) asymmetric slab models with 10, 12, 14, and 16 Mo-P layers.

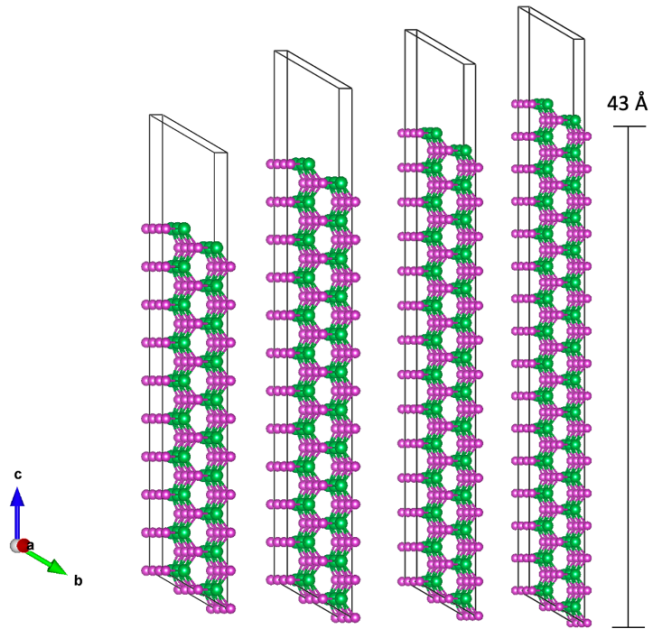

Figure S5. MoP slabs exposing the (100) surface. Asymmetric models are shown with 10, 12, 14, and 16 Mo-P layers.

Symmetric TiO2 and SnO2 slabs:

The (001) surface of TiO_2 exhibits very similar atomic structure for the A and B terminations, which feature a combination of titanium and oxygen atoms. Thus, it is to be expected that these surfaces have very similar energy values. The simultaneous equations method yields surface energies of 1.28 J/m^2 for both A and B. The cleavage energy method yields surface energies of 1.27 and 1.28 J/m^2 for A and B, respectively. The values of (E_a', E_b') generated by the simultaneous equations method and (γ_A, γ_B) generated by the cleavage energy method are, on average, only 0.28 percent different from each other. Using the single surface approximation (Equation 1), the surface energies of A and B are both 1.28 J/m^2. All of the computed surface energies differ by <3% from the literature value of 1.25 J/m^2 reported by Perron et al.[1]

The (110) surfaces of tin dioxide rutile are also comprised of stacked metal-oxide layers. The two terminations are more nearly equivalent than the analogous (*hkl*) surfaces of the isostructural titanium dioxide. Thus, again it is expected that there should not be a difference in surface energy between A and B. Application of the simultaneous equations method generated energies of 1.86 and 1.86 J/m^2 for relaxed A and B surfaces, respectively, whereas application of the cleavage energy method yielded surface energies of 1.88 and 1.85 J/m^2. The values of (E_a', E_b') generated by the simultaneous equations method and (γ_A, γ_B) generated by the cleavage energy method differ by only 0.25 percent on average. The single-surface approximation via Equation 1 yields a surface energy of 1.86 J/m^2. All of the computed surface energies differ by <4.1% from the literature value of 1.80 J/m^2 reported by Wexler et al. for both A and B surfaces of (110) SnO_2.[2]

Table S3. Calculated Surface Energies for Low-Index Surfaces of MoP Generated using the Simultaneous Equations Method

		Energy values (J/m^2)						
Material	**Surface**	**Energies**	**10 layers**	**12 layers**	**14 layers**	**16 layers**	Literature (Tian et al 2018)	**Single surface approximation**
MoP	111	A	2.34	2.34	2.34	2.34	2.48	2.30 J/m^2
		B	2.27	2.27	2.27	2.27	2.19	
	100	A	1.95	1.93	1.91	1.89	1.93	1.97 J/m^2
		B	2.09	2.06	2.05	2.03	2.28	
	001	A	2.80	2.79	2.77	2.76	2.98	2.69 J/m^2
		B	2.61	2.60	2.58	2.57	2.56	

Table S4. Calculated Surface Energies for Low-Index Surfaces of MoP using Cleavage Energy Method

		Energy values (J/m^2)						
Material	**Surface**	**Energies**	**10 layers**	**12 layers**	**14 layers**	**16 layers**	Literature (Tian et al 2018)	**Single surface approximation**
MoP	111	A	2.38	2.38	2.38	2.37	2.48	2.30 J/m^2
		B	2.22	2.23	2.22	2.22	2.19	
	100	A	1.87	1.84	1.83	1.83	1.93	1.97 J/m^2
		B	2.17	2.15	2.14	2.14	2.28	
	001	A	2.92	2.91	2.89	2.88	2.98	2.69 J/m^2
		B	2.49	2.49	2.46	2.45	2.56	

Table S5. Calculated Surface Energies for Low-Index Surfaces of TiO_2 and SnO_2 with respect to Slab Height. All surface energies are in J/m^2.

Material	Method	GGA PW91	Number of atomic layers												Literature value (J/m^2)
		Energies (J/m^2)	10	10 FIL	11	11 FIL	12	12 FIL	13	13 FIL	14	14 FIL	15	15 FIL	
(001) TiO_2 rutile	Cleavage Energy	γ_A	1.31	1.31	1.26	1.26	1.26	1.26	1.27	1.27	1.27	1.27	1.25	1.25	1.25 (GGA PW91) Perron et al. 2007[2]
		γ_B	1.31	1.31	1.32	1.32	1.26	1.26	1.26	1.26	1.27	1.27	1.28	1.28	
	Simultaneous Equations	E_a^f	2.43	2.39	2.40	2.39	2.42	2.40	2.39	2.40	2.44	2.43	2.44	2.43	
		E_b^f	2.43	2.39	2.35	2.39	2.43	2.40	2.40	2.40	2.44	2.43	2.42	2.43	
		E_a^r	1.19	1.33	1.32	1.32	1.21	1.33	1.29	1.29	1.22	1.28	1.28	1.28	
		E_b^r	1.19	1.33	1.32	1.32	1.21	1.33	1.29	1.29	1.22	1.28	1.28	1.28	
Slab Thickness (Å)			13.2	13.2	14.7	14.7	16.1	16.1	17.6	17.6	19.1	19.1	20.5	20.5	
(110) SnO_2 rutile	Cleavage Energy	γ_A	1.85	1.87	1.84	1.86	1.84	1.86	1.85	1.85	1.84	1.86	2.12	1.85	1.80 (GGA PBE) Wexler et al. 2014[3]
		γ_B	1.85	1.87	1.85	1.86	1.84	1.86	1.85	1.85	1.84	1.86	1.85	1.85	
	Simultaneous Equations	E_a^f	2.37	2.38	2.37	2.38	2.38	2.38	2.39	2.39	2.40	2.40	2.34	2.41	
		E_b^f	2.37	2.35	2.37	2.38	2.38	2.38	2.39	2.39	2.40	2.40	2.56	2.41	
		E_a^r	1.85	1.88	1.86	1.86	1.85	1.85	1.85	1.86	1.85	1.86	1.90	1.86	
		E_b^r	1.85	1.85	1.86	1.86	1.85	1.85	1.85	1.86	1.85	1.86	1.86	1.85	
Slab Thickness (Å)			14.4	14.4	16.0	16.0	17.5	17.5	19.2	19.2	20.7	20.7	22.3	22.3	

Table S6. Percent differences in relaxed surface energy values for TiO_2 and SnO_2 surfaces, as calculated via Simultaneous Equations and Cleavage Energy methods.

Material	Compared Values	Number of atomic layers											
		10	**10 FIL**	**11**	**11 FIL**	**12**	**12 FIL**	**13**	**13 FIL**	**14**	**14 FIL**	**15**	**15 FIL**
(001) TiO_2 rutile	γ_A vs E_a^r	8.95	1.87	4.18	4.64	4.53	5.28	1.96	2.02	3.56	0.919	2.05	2.09
	γ_B vs E_b^r	8.95	1.87	0.436	0.507	3.90	5.22	2.72	2.96	3.60	0.885	0.178	0.385
(110) SnO_2 rutile	γ_A vs E_a^r	0.293	0.829	0.655	0.124	0.515	0.725	0.452	0.166	0.524	0.0276	10.8	0.210
	γ_B vs E_b^r	0.328	0.689	0.328	0.178	0.550	0.647	0.488	0.166	0.524	0.0348	0.490	0.0862

Table S7. Percent Differences Between Summed Surface Energies of Relaxed A, B Terminations and Total Relaxed Surface Energy for Both Methods.

Material	Compared Values	Number of atomic layers											
		10	**10 FIL**	**11**	**11 FIL**	**12**	**12 FIL**	**13**	**13 FIL**	**14**	**14 FIL**	**15**	**15 FIL**
(001) TiO_2 rutile	Cleavage Energy ($\gamma_A + \gamma_B$) vs δ	10	1.8	2.6	2.6	4.7	5.3	2.7	2.7	4.0	0.87	1.3	1.3
	Simultaneous Equations ($E_a^r + E_b^r$) vs δ	1.1	0.07	0.32	0.06	0.50	0.02	0.31	0.23	0.43	0.04	0.14	0.03
(110) SnO_2 rutile	Cleavage Energy ($\gamma_A + \gamma_B$) vs δ	0.38	0.09	0.61	0.19	0.66	0.09	0.58	0.21	0.65	0.04	6.7	0.18
	Simultaneous Equations ($E_a^r + E_b^r$) vs δ	0.07	0.02	0.12	0.04	0.13	0.77	0.11	0.04	0.12	0.01	1.2	0.03