Supplementary Information

Modelling the bulk properties of ambient pressure polymorphs of zirconia

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1. Initial benchmarking

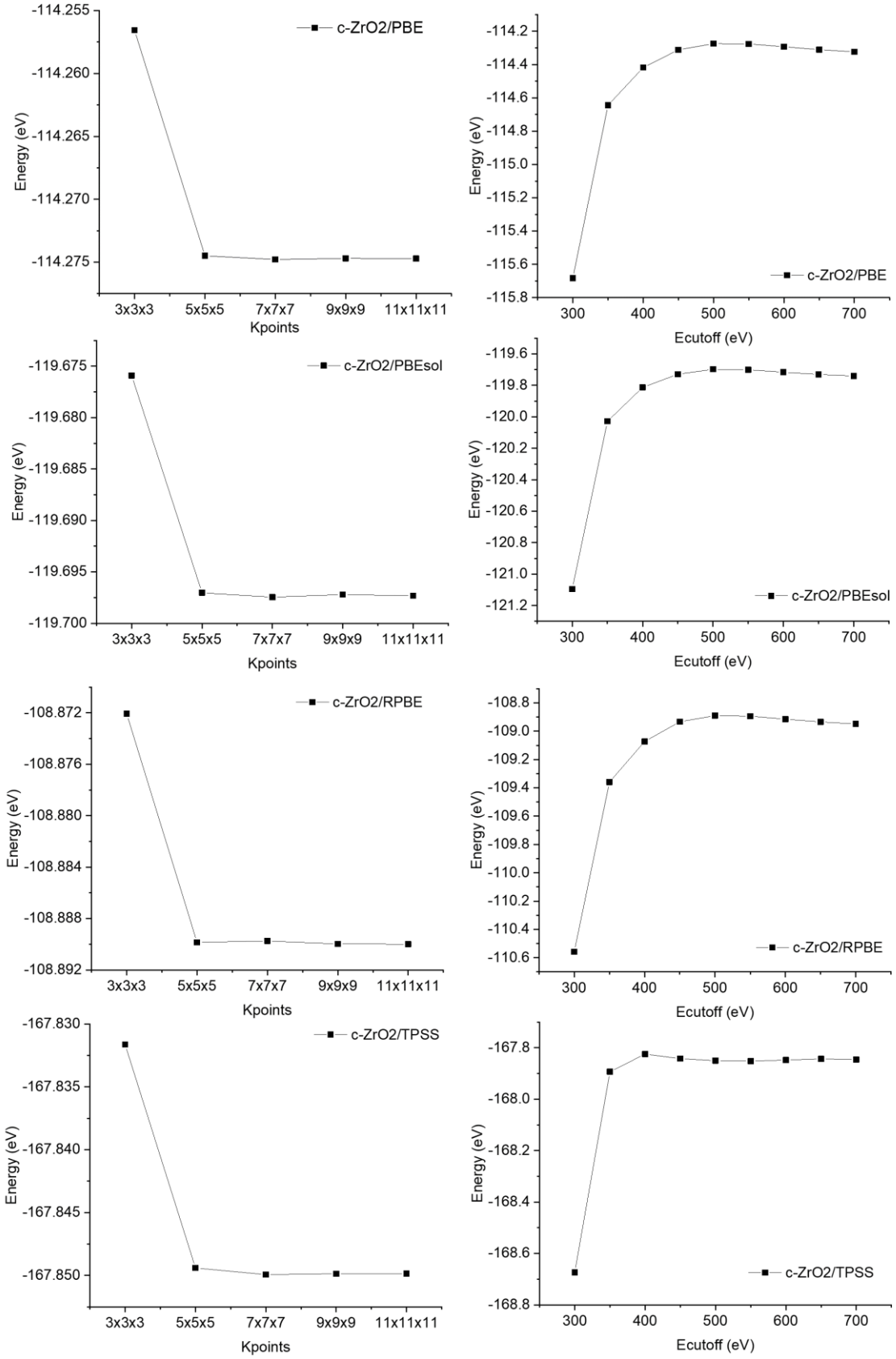

Figure S1. K-point mesh and cutoff energies tested for c-ZrO2 using PBE, PBEsol, RPBE, and TPSS functionals.

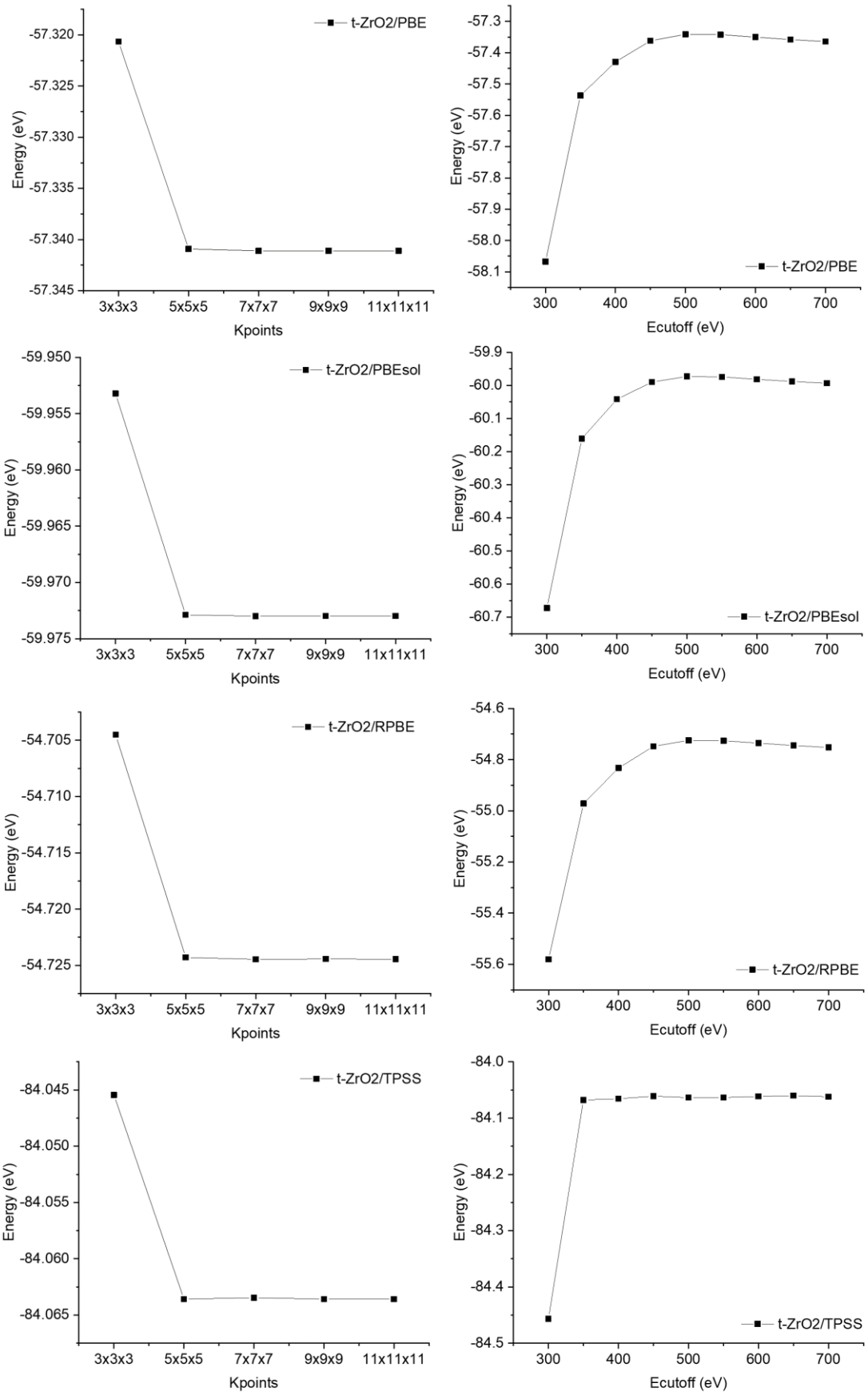

Figure S2. K-point mesh and cutoff energies tested for t-ZrO_2 using PBE, PBEsol, RPBE, and TPSS functionals.

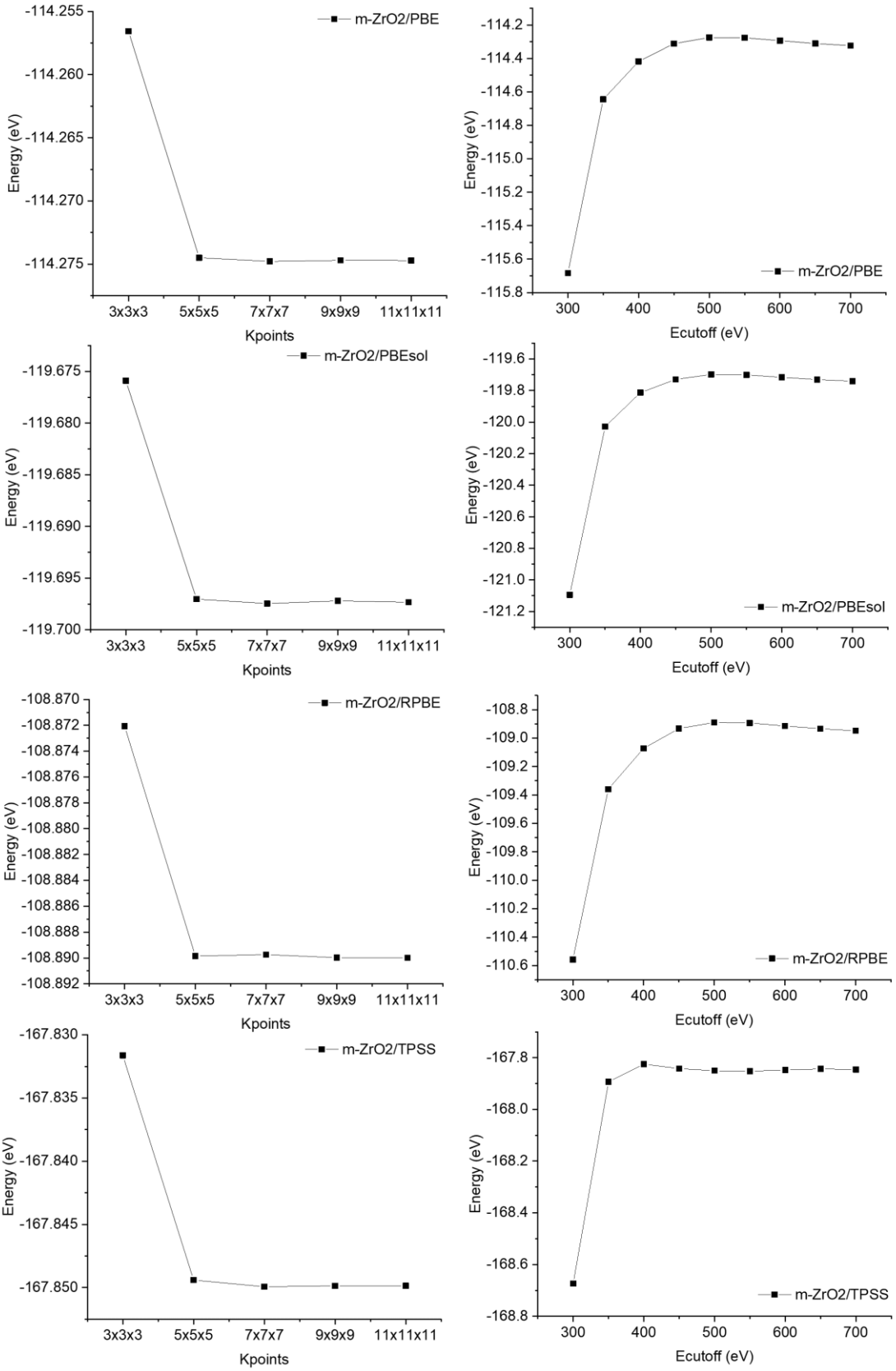

Figure S3. K-point mesh and cutoff energies tested for m-ZrO_2 using PBE, PBEsol, RPBE, and TPSS functionals.

2. Computed relative and total energies

Table S1. Total and relative energy of bulk m-, t-, and c-ZrO_2 obtained for each evaluated methodology. Relative energies of t- and c-ZrO_2 were calculated by taken the total energy of m-ZrO_2 as zero in each case.

m-ZrO2	PBE		PBEsol		RPBE		TPSS	
	Total Energy (eV)	Relative Energy (eV)	Total Energy (eV)	Relative Energy (eV)	Total Energy (eV)	Relative Energy (eV)	Total Energy (eV)	Relative Energy (eV)
None	-115.117	-	-120.266	-	-109.966	-	-168.444	-
D2	-118.298	-	-123.594	-	-113.057	-	-171.714	-
D3	-117.297	-	-122.050	-	-113.291	-	-170.645	-
U (2eV)	-110.550	-	-115.552	-	-105.475	-	-163.957	-
U (4eV)	-106.337	-	-111.193	-	-101.340	-	-159.821	-
U (6eV)	-102.463	-	-107.182	-	-97.544	-	-156.002	-
U (8eV)	-98.915	-	-103.504	-	-94.072	-	-152.510	-
D3-U (2eV)	-112.684	-	-117.302	-	-108.737	-	-166.114	-
D3-U (4eV)	-108.440	-	-112.907	-	-104.538	-	-161.928	-
t-ZrO2	PBE		PBEsol		RPBE		TPSS	
	Total Energy (eV)	Relative Energy (eV)	Total Energy (eV)	Relative Energy (eV)	Total Energy (eV)	Relative Energy (eV)	Total Energy (eV)	Relative Energy (eV)
None	-114.676	0.441	-119.950	0.316	-109.452	0.514	-168.124	0.320
D2	-118.035	0.263	-123.460	0.135	-112.685	0.373	-171.534	0.180
D3	-116.858	0.439	-121.760	0.291	-112.797	0.494	-170.342	0.303
U (2eV)	-110.167	0.384	-115.346	0.206	-104.950	0.526	-163.726	0.230
U (4eV)	-106.046	0.290	-111.151	0.042	-100.873	0.468	-159.732	0.089
U (6eV)	-102.329	0.134	-107.339	-0.158	-97.192	0.352	-156.110	-0.109
U (8eV)	-98.974	-0.059	-103.842	-0.338	-93.904	0.168	-152.787	-0.277
D3-U (2eV)	-112.319	0.365	-117.130	0.172	-108.278	0.459	-165.920	0.194
D3-U (4eV)	-108.196	0.244	-112.917	-0.010	-104.170	0.368	-161.902	0.026
c-ZrO2	PBE		PBEsol		RPBE		TPSS	
	Total Energy (eV)	Relative Energy (eV)	Total Energy (eV)	Relative Energy (eV)	Total Energy (eV)	Relative Energy (eV)	Total Energy (eV)	Relative Energy (eV)
None	-114.275	0.843	-119.707	0.559	-108.887	1.079	-167.852	0.592
D2	-117.706	0.593	-123.266	0.328	-112.233	0.824	-171.312	0.402
D3	-116.525	0.773	-121.554	0.496	-112.311	0.980	-170.120	0.525
U (2eV)	-109.980	0.571	-115.265	0.287	-104.673	0.802	-163.628	0.328
U (4eV)	-106.000	0.337	-111.144	0.050	-100.773	0.568	-159.715	0.107
U (6eV)	-102.329	0.134	-107.339	-0.157	-97.178	0.366	-156.104	-0.102
U (8eV)	-98.958	-0.042	-103.841	-0.337	-93.882	0.190	-152.787	-0.277
D3-U (2eV)	-112.184	0.500	-117.072	0.230	-108.039	0.697	-165.852	0.263
D3-U (4eV)	-108.162	0.278	-112.914	-0.008	-104.085	0.454	-161.896	0.033

3. Calculated elastic constants, Voigt's bulk moduli, shear elastic constant, Young's modulus, and Poisson ratio

Table S2. Computed elastic constants $\mathbf{C_{ij}}$ (GPa) bulk modulus $\mathbf{B_V}$ (GPa) for c-ZrO_2. Previously reported experimental and theoretical (LDA, GGA, FD and LD) values are also given for comparison. The derived shear modulus **G** (GPa), Young's modulus **E** (GPa), and Poisson ratio (**v**) are also presented for comparison.

PBE	$\mathbf{C_{11}}$	$\mathbf{C_{44}}$	$\mathbf{C_{12}}$	$\mathbf{B_V}$	**G**	**E**	**v**
None	534	65	95	242	127	324	0.28
D2	566	76	110	262	137	350	0.28
D3	544	66	98	247	129	329	0.28
U(2eV)	523	68	94	237	127	322	0.27
U(4eV)	513	70	93	233	126	320	0.27
U(6eV)	504	72	92	229	126	319	0.27
U(8eV)	495	74	91	226	125	317	0.27
D3-U(2eV)	532	68	96	241	128	326	0.27
D3-U(4eV)	521	71	95	237	128	325	0.27

PBEsol	$\mathbf{C_{11}}$	$\mathbf{C_{44}}$	$\mathbf{C_{12}}$	$\mathbf{B_V}$	**G**	**E**	**v**
None	564	71	109	261	134	342	0.28
D2	598	84	126	283	145	371	0.28
D3	573	72	112	265	135	347	0.28
U(2eV)	551	74	107	255	133	340	0.28
U(4eV)	539	76	105	250	132	338	0.27
U(6eV)	528	78	103	245	132	335	0.27
U(8eV)	517	80	102	241	131	333	0.27
D3-U(2eV)	559	75	109	259	135	345	0.28
D3-U(4eV)	546	77	107	253	134	342	0.28

RPBE	$\mathbf{C_{11}}$	$\mathbf{C_{44}}$	$\mathbf{C_{12}}$	$\mathbf{B_V}$	**G**	**E**	**v**
None	512	60	85	227	121	309	0.27
D2	543	71	99	247	131	335	0.27
D3	523	61	87	232	124	315	0.27
U(2eV)	503	63	84	223	122	309	0.27
U(4eV)	494	65	83	220	121	307	0.27
U(6eV)	486	67	82	217	121	306	0.26
U(8eV)	478	69	82	214	121	305	0.26
D3-U(2eV)	512	64	86	228	124	314	0.27
D3-U(4eV)	503	66	85	224	123	312	0.27

TPSS	$\mathbf{C_{11}}$	$\mathbf{C_{44}}$	$\mathbf{C_{12}}$	$\mathbf{B_V}$	**G**	**E**	**v**
None	553	71	105	254	132	338	0.28
D2	585	82	120	275	142	364	0.28
D3	563	71	107	259	134	342	0.28
U(2eV)	542	74	103	249	132	337	0.27
U(4eV)	531	76	102	245	131	334	0.27
U(6eV)	522	78	101	241	131	333	0.27
U(8eV)	512	80	100	237	130	331	0.27
D3-U(2eV)	551	74	105	254	134	341	0.28
D3-U(4eV)	539	76	104	249	133	338	0.27

	$\mathbf{C_{11}}$	$\mathbf{C_{44}}$	$\mathbf{C_{12}}$	$\mathbf{B_V}$	**G**	**E**	**v**
Experimental[1]	417	47	82	194	-	-	-
FD[2]	520	62	94	236	-	-	-
LD[3]	409	60	53	-	-	-	-
LDA[4]	499	63	111	240	-	-	-
GGA[5]	520	61	93	235	-	-	-

Table S3. Computed elastic constants $\mathbf{C_{ij}}$ (GPa) and bulk modulus $\mathbf{B_V}$ (GPa) for t-ZrO_2. Previously reported experimental and theoretical (LDA, GGA, FD and LD) values are also given for comparison. The derived shear modulus **G** (GPa), Young's modulus **E** (GPa), and Poisson ratio (**v**) are also presented for comparison.

PBE	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	B_V	G	E	v
None	357	266	16	154	208	60	182	81	211	0.31
D2	395	309	37	165	215	71	201	97	251	0.29
D3	367	285	22	160	211	62	188	86	225	0.30
U(2eV)	359	292	36	167	207	58	184	94	240	0.28
U(4eV)	362	320	54	183	207	56	187	107	269	0.26
U(6eV)	367	380	71	200	211	63	199	120	300	0.25
U(8eV)	374	495	74	198	215	96	229	125	317	0.27
D3-U(2eV)	367	311	41	174	211	60	190	99	253	0.28
D3-U(4eV)	369	340	59	190	212	58	193	112	281	0.26

PBEsol	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	B_V	G	E	v
None	393	328	37	171	221	73	206	99	255	0.29
D2	430	374	58	183	231	87	227	115	295	0.28
D3	400	344	42	175	226	76	211	103	265	0.29
U(2eV)	391	354	55	186	222	71	207	111	282	0.27
U(4eV)	392	387	71	203	224	70	211	123	309	0.26
U(6eV)	401	528	78	208	232	109	248	131	335	0.27
U(8eV)	397	517	79	203	225	108	244	130	332	0.27
D3-U(2eV)	398	370	59	191	226	73	212	115	292	0.27
D3-U(4eV)	398	410	74	208	229	75	218	126	318	0.26

RPBE	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	B_V	G	E	v
None	327	218	-6	141	200	48	163	64	170	0.33
D2	366	259	17	153	205	57	181	82	214	0.30
D3	339	239	3	146	202	52	170	71	187	0.32
U(2eV)	331	243	16	154	197	46	165	78	203	0.29
U(4eV)	337	271	38	169	196	45	168	93	236	0.27
U(6eV)	342	303	57	185	197	44	173	107	265	0.24
U(8eV)	356	478	69	194	207	87	217	120	305	0.27
D3-U(2eV)	342	265	24	160	201	50	172	85	219	0.29
D3-U(4eV)	346	293	45	175	201	48	175	99	250	0.26

TPSS	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	B_V	G	E	v
None	384	316	37	167	216	72	201	96	249	0.29
D2	420	360	55	178	226	85	221	111	286	0.28
D3	393	336	42	173	221	75	207	101	262	0.29
U(2eV)	384	342	54	181	217	70	203	108	275	0.27
U(4eV)	386	371	69	197	219	69	206	119	300	0.26
U(6eV)	396	522	78	206	228	106	244	131	333	0.27
U(8eV)	392	512	79	202	221	105	240	130	330	0.27
D3-U(2eV)	392	361	58	188	222	73	209	113	286	0.27
D3-U(4eV)	393	395	72	205	225	72	213	124	311	0.26

	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	B_V	G	E	v
Experimental[6]	327	264	59	64	100	62	150	-	-	-
FD[2]	436	271	19	70	127	62	183	-	-	-
LD[3]	416	234	39	73	30	68	-	-	-	-
LDA[4]	382	346	42	167	221	72	204	-	-	-
GGA[5]	334	248	9	152	211	52	172	-	-	-

Table S4. Computed elastic constants C_{ij} (GPa) and bulk modulus B_V (GPa) for m-ZrO_2. Previously reported experimental and theoretical (LDA, GGA, FD and LD) values are also given for comparison. The derived shear modulus **G** (GPa), Young's modulus **E** (GPa), and Poisson ratio (**v**) are also presented for comparison.

PBE	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}	B_V
None	308	357	263	75	80	117	163	94	40	156	-4	3	-9	195
D2	286	411	190	94	83	134	166	60	62	114	13	43	-9	174
D3	301	374	240	80	83	122	168	82	44	156	-7	12	-10	192
U(2eV)	310	354	270	82	82	116	165	96	38	160	-8	2	-11	197
U(4eV)	313	344	279	87	82	115	165	100	36	163	-10	1	-11	199
U(6eV)	317	330	291	91	82	114	164	105	33	165	-11	**-2**	-12	201
U(8eV)	322	311	301	93	82	113	161	110	31	163	-11	-4	-12	200
D3-U(2eV)	303	371	244	87	85	121	169	85	41	161	-9	10	-11	194
D3-U(4eV)	308	354	264	91	86	120	173	92	38	172	-14	7	-11	200
PBEsol	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}	B_V
None	298	402	232	88	86	130	174	77	49	156	-6	19	-10	194
D2	307	434	234	110	85	142	179	94	66	110	24	58	-7	193
D3	290	414	219	92	85	135	172	70	55	142	-2	32	-10	188
U(2eV)	295	395	233	93	85	128	174	74	49	156	-8	23	-11	192
U(4eV)	318	370	269	97	88	127	184	104	39	182	-13	12	-12	196
U(6eV)	297	373	235	99	85	125	180	73	44	174	-14	21	-12	195
U(8eV)	315	330	263	100	86	122	189	92	36	198	-18	10	-12	207
D3-U(2eV)	288	407	222	97	87	133	170	69	53	144	-4	32	-11	187
D3-U(4eV)	295	397	240	101	89	131	179	79	46	159	-10	25	-12	196
RPBE	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}	B_V
None	299	322	259	63	76	106	140	91	38	131	1	-4	-7	178
D2	278	387	175	81	81	125	166	47	54	137	3	25	-10	171
D3	288	360	214	74	78	115	158	69	42	149	-7	8	-10	180
U(2eV)	305	326	273	74	77	107	147	98	35	142	-3	-5	-10	186
U(4eV)	298	385	237	97	86	127	179	76	46	166	-11	22	-12	298
U(6eV)	310	316	288	85	78	106	147	102	31	146	-7	-8	-11	190
U(8eV)	312	306	293	88	78	106	145	104	29	144	-8	-9	-11	188
D3-U(2eV)	280	360	217	82	79	115	160	63	42	150	-9	9	-12	178
D3-U(4eV)	292	351	229	87	79	114	163	75	37	161	-12	6	-12	186
TPSS	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}	B_V
None	291	395	216	87	84	127	167	75	50	145	-1	23	-10	186
D2	300	433	243	110	83	140	179	98	64	115	25	57	-6	196
D3	277	410	213	92	87	132	163	66	55	129	1	33	-9	180
U(2eV)	283	392	222	92	85	126	165	67	50	143	-4	25	-10	183
U(4eV)	284	384	224	96	85	125	169	67	48	149	-6	25	-11	185
U(6eV)	287	374	223	99	86	125	172	64	45	159	-10	23	-11	186
U(8eV)	296	353	244	98	85	118	172	78	39	165	-12	13	-11	192
D3-U(2eV)	277	401	215	97	87	131	162	65	54	129	1	34	-10	179
D3-U(4eV)	270	392	204	101	87	129	156	56	54	124	0	37	-11	171
	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}	B_V
Experimental[7]	361	408	258	100	81	126	142	55	-21	196	31	-18	-23	187
FD[2]	340	396	247	96	68	128	152	84	46	121	-6	21	-18	189
LD[3]	347	364	274	88	108	122	164	102	28	156	-17	11	-44	-
GGA[5]	337	351	268	79	70	114	155	84	26	153	-4	2	-15	193

Table S4. (Continued)

PBE	G	E	v
None	89	231	0.30
D2	99	249	0.26
D3	91	236	0.30
U(2eV)	90	235	0.30
U(4eV)	91	236	0.30
U(6eV)	91	237	0.30
U(8eV)	91	237	0.30
D3-U(2eV)	92	239	0.30
D3-U(4eV)	92	239	0.30

PBEsol	G	E	v
None	96	247	0.29
D2	107	271	0.27
D3	98	251	0.28
U(2eV)	96	246	0.29
U(4eV)	95	247	0.30
U(6eV)	94	242	0.29
U(8eV)	90	236	0.31
D3-U(2eV)	99	252	0.28
D3-U(4eV)	99	253	0.28

RPBE	G	E	v
None	84	217	0.30
D2	90	230	0.28
D3	86	222	0.29
U(2eV)	86	224	0.30
U(4eV)	95	246	0.29
U(6eV)	88	229	0.30
U(8eV)	89	231	0.30
D3-U(2eV)	87	225	0.29
D3-U(4eV)	88	227	0.30

TPSS	G	E	v
None	94	241	0.28
D2	106	268	0.27
D3	98	249	0.27
U(2eV)	95	244	0.28
U(4eV)	95	243	0.28
U(6eV)	95	243	0.28
U(8eV)	92	238	0.29
D3-U(2eV)	99	250	0.27
D3-U(4eV)	99	248	0.26

	G	E	v
Experimental[7]	-	-	-
FD[2]	-	-	-
LD[3]	-	-	-
GGA[5]	-	-	-

Shear modulus **G** (GPa), Young's modulus **E** (GPa), and Poisson ratio (**v**) were calculated by using the following equations:

$\mathbf{G} = \frac{1}{5}\,(C_{11} - C_{12} + 3C_{44})$, for c-$ZrO_2$;

$\mathbf{G} = \frac{1}{15}\,(2C_{11} + C_{33} - C_{12} - 2C_{13} + 6C_{44} + 3C_{66})$, for t-$ZrO_2$;

$\mathbf{G} = \frac{1}{15}\,[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})]$, for m-$ZrO_2$;

$\mathbf{E} = \frac{9B_V G}{3B_V + G}$;

and $\boldsymbol{\nu} = \frac{3B_V - 2G}{2(3B_V + G)}$.

4. Calculated elastic constants using higher cutoff energy in selected cases

Table S5. Computed elastic constants c_{ij} (GPa) of m-ZrO_2 using two values of E_{cutoff} (550 and 750 eV). The percentual difference Δ (%) is also given for comparison.

	E_{cutoff}	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}
PBE	**550 eV**	308	357	263	75	80	117	163	94	40	156	-4	3	-9
	750 eV	304	364	255	76	81	118	161	88	42	150	-5	5	-9
	Δ ***(%)***	*1.38*	*-1.91*	*3.03*	*-1.39*	*-0.88*	*-0.59*	*0.96*	*5.57*	*-5.35*	*3.49*	*-8.79*	*-109.35*	*2.95*
PBEsol	**550 eV**	298	402	232	88	86	130	174	77	49	156	-6	19	-10
	750 eV	287	402	196	88	82	131	162	57	58	131	0	35	-10
	Δ ***(%)***	*3.46*	*-0.11*	*15.84*	*-0.18*	*4.97*	*-0.74*	*7.04*	*26.06*	*-18.30*	*16.03*	*91.97*	*-82.75*	*3.97*
PBEsol-D2	**550 eV**	307	434	234	110	85	142	179	94	66	110	24	58	-7
	750 eV	306	433	230	111	86	143	178	91	67	108	24	59	-7
	Δ ***(%)***	*0.35*	*0.34*	*1.84*	*-0.67*	*-0.85*	*-0.74*	*0.63*	*2.80*	*-1.30*	*2.14*	*-2.59*	*-1.94*	*-1.06*
PBEsol-D3	**550 eV**	290	414	219	92	85	135	172	70	55	142	-2	32	-10
	750 eV	291	415	221	93	87	136	173	71	55	143	-3	32	-10
	Δ ***(%)***	*-0.24*	*-0.21*	*-0.68*	*-1.31*	*-1.34*	*-0.58*	*-0.48*	*-1.62*	*0.22*	*-1.07*	*-14.15*	*0.88*	*-0.37*
PBEsol-U(4eV)	**550 eV**	298	385	237	97	86	127	179	76	46	166	-11	22	-12
	750 eV	299	387	237	98	87	128	180	77	46	167	-11	22	-12
	Δ ***(%)***	*-0.20*	*-0.41*	*-0.25*	*-1.20*	*-1.20*	*-0.89*	*-0.58*	*-1.08*	*-0.30*	*-0.47*	*0.68*	*-1.33*	*0.08*
PBEsol-U(6eV)	**550 eV**	297	373	235	99	85	125	180	73	44	174	-14	21	-12
	750 eV	304	369	245	100	87	126	186	81	42	181	-15	18	-12
	Δ ***(%)***	*-2.56*	*1.14*	*-4.31*	*-1.11*	*-1.98*	*-0.74*	*-2.88*	*-11.49*	*5.32*	*-4.30*	*-10.00*	*13.79*	*0.45*
PBEsol-U(8eV)	**550 eV**	315	330	263	100	86	122	189	92	36	198	-18	10	-12
	750 eV	315	333	263	102	87	123	192	93	37	200	-18	11	-12
	Δ ***(%)***	*-0.07*	*-1.02*	*-0.08*	*-1.41*	*-1.25*	*-1.12*	*-1.30*	*-0.51*	*-1.85*	*-1.09*	*0.78*	*-17.97*	*-2.12*

Table S5. (Continued)

	E_{cutoff}	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}
	550 eV	299	322	259	63	76	106	140	91	38	131	1	-4	-7
RPBE	**750 eV**	299	326	259	64	77	107	142	90	38	132	1	-4	-7
	Δ (%)	*0.09*	*-1.19*	*-0.18*	*-2.38*	*-1.82*	*-1.37*	*-1.42*	*0.88*	*-0.01*	*-0.39*	*-25.28*	*-2.96*	*-1.99*
	550 eV	291	395	216	87	84	127	167	75	50	145	-1	23	-10
TPSS	**750 eV**	281	395	214	87	84	128	164	65	53	139	-1	26	-10
	Δ (%)	*3.70*	*0.08*	*0.77*	*-0.63*	*0.39*	*-0.52*	*1.47*	*12.98*	*-4.52*	*4.18*	*52.81*	*-12.30*	*0.79*
	550 eV	300	433	243	110	83	140	179	98	64	115	25	57	-6
TPSS-D2	**750 eV**	295	422	228	110	84	140	172	91	65	102	27	59	-7
	Δ (%)	*1.57*	*2.51*	*6.34*	*-0.08*	*-1.48*	*-0.19*	*3.85*	*7.06*	*-2.06*	*11.02*	*-8.90*	*-3.42*	*-6.87*
	550 eV	277	410	213	92	87	132	163	66	55	129	1	33	-9
TPSS-D3	**750 eV**	276	407	211	93	86	133	162	66	56	127	3	34	-10
	Δ (%)	*0.25*	*0.76*	*1.13*	*-0.96*	*0.97*	*-0.44*	*0.07*	*0.19*	*-1.74*	*1.44*	*-197.70*	*-4.31*	*-2.73*
	550 eV	296	353	244	98	85	118	172	78	39	165	-12	13	-11
TPSS-U(8eV)	**750 eV**	297	355	244	99	86	120	174	79	39	168	-12	13	-11
	Δ (%)	*-0.45*	*-0.47*	*0.05*	*-1.34*	*-1.25*	*-1.10*	*-1.14*	*-0.82*	*-0.19*	*-1.46*	*-2.48*	*-2.11*	*-0.54*
	550 eV	270	392	204	101	87	129	156	56	54	124	0	37	-11
TPSS-D3-U(4eV)	**750 eV**	275	395	211	101	88	131	163	63	51	131	-2	34	-11
	Δ (%)	*-1.66*	*-0.58*	*-3.89*	*-0.14*	*-1.35*	*-1.06*	*-4.47*	*-13.05*	*3.99*	*-6.24*	*606.84*	*7.76*	*-0.07*

5. Calculated electronic and ionic contributions to total dielectric constant

Table S6. Electronic ($\varepsilon_{11}^{\infty}$, $\varepsilon_{22}^{\infty}$, and $\varepsilon_{33}^{\infty}$) and ionic ($\varepsilon_{11}^{\mathrm{Ion}}$, $\varepsilon_{22}^{\mathrm{Ion}}$, and $\varepsilon_{33}^{\mathrm{Ion}}$) contribution to the dielectric tensor, total electronic (ε^{∞}) and ionic contribution ($\varepsilon^{\mathrm{Ion}}$), and total dielectric constant (ε) of c-ZrO_2. Previously reported experimental and theoretical (LDA and PBE) values are also given for comparison. The derived refractive index values (*n*) is also presented for comparison.

PBE	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
None	5.82	5.82	5.82	40.78	40.78	40.78	5.82	40.78	46.61	2.41
D2	5.79	5.79	5.79	35.03	35.03	35.03	5.79	35.03	40.82	2.41
D3	5.80	5.80	5.80	36.58	36.58	36.58	5.80	36.58	42.39	2.41
U(2eV)	5.44	5.44	5.44	26.97	26.97	26.97	5.44	26.97	32.41	2.33
U(4eV)	5.11	5.11	5.11	19.87	19.87	19.87	5.11	19.87	24.98	2.26
U(6eV)	4.81	4.81	4.81	15.63	15.63	15.63	4.81	15.63	20.44	2.19
U(8eV)	4.55	4.55	4.55	12.84	12.84	12.84	4.55	12.84	17.40	2.13
D3-U(2eV)	5.43	5.43	5.43	24.94	24.94	24.94	5.43	24.94	30.37	2.33
D3-U(4eV)	5.09	5.09	5.09	18.68	18.68	18.68	5.09	18.68	23.77	2.26

PBEsol	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
None	5.86	5.86	5.86	33.35	33.34	33.34	5.86	33.34	39.20	2.42
D2	5.83	5.83	5.83	29.49	29.49	29.49	5.83	29.49	35.32	2.41
D3	5.84	5.84	5.84	30.88	30.88	30.88	5.84	30.88	36.73	2.42
U(2eV)	5.47	5.47	5.47	23.22	23.22	23.22	5.47	23.22	28.70	2.34
U(4eV)	5.14	5.14	5.14	17.59	17.59	17.59	5.14	17.59	22.73	2.27
U(6eV)	4.85	4.85	4.85	14.06	14.06	14.06	4.85	14.06	18.91	2.20
U(8eV)	4.59	4.59	4.59	11.68	11.68	11.68	4.59	11.68	16.27	2.14
D3-U(2eV)	5.46	5.46	5.46	21.93	21.93	21.93	5.46	21.93	27.39	2.34
D3-U(4eV)	5.13	5.13	5.13	16.79	16.79	16.79	5.13	16.79	21.92	2.26

RPBE	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
None	5.83	5.83	5.83	49.26	49.26	49.258	5.83	49.26	55.09	2.41
D2	5.80	5.80	5.80	40.97	40.97	40.97	5.80	40.97	46.76	2.41
D3	5.80	5.80	5.80	42.69	42.69	42.69	5.80	42.69	48.50	2.41
U(2eV)	5.45	5.45	5.45	30.85	30.85	30.85	5.45	30.85	36.29	2.33
U(4eV)	5.11	5.11	5.11	22.13	22.13	22.13	5.11	22.13	27.24	2.26
U(6eV)	4.81	4.81	4.81	17.14	17.14	17.14	4.81	17.14	21.95	2.19
U(8eV)	4.55	4.55	4.55	13.95	13.95	13.95	4.55	13.95	18.50	2.13
D3-U(2eV)	5.42	5.42	5.42	27.99	27.99	27.99	5.42	27.99	33.41	2.33
D3-U(4eV)	5.09	5.09	5.09	20.54	20.54	20.54	5.09	20.54	25.63	2.26

	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
Experimental[8-10]	-	-	-	-	-	-	4.8	-	27.2-29.3	-
DFPT/LDA[11]	5.8	5.8	5.8	-	-	-	5.8	-	-	-
DFPT/LDA[12]	6.1	6.1	6.1	40.6	40.6	40.6	-	-	46.6	-
DFPT/PBE[8]	5.8	5.8	5.8	31.2	31.2	31.2	5.8	31.2	37.0	-

Table S7. Electronic ($\varepsilon_{11}^{\infty}$, $\varepsilon_{22}^{\infty}$, and $\varepsilon_{33}^{\infty}$) and ionic ($\varepsilon_{11}^{\mathrm{Ion}}$, $\varepsilon_{22}^{\mathrm{Ion}}$, and $\varepsilon_{33}^{\mathrm{Ion}}$) contribution to the dielectric tensor, total electronic (ε^{∞}) and ionic contribution ($\varepsilon^{\mathrm{Ion}}$), and total dielectric constant (ε) of t-ZrO_2. Previously reported experimental and theoretical (LDA and PBE) values are also given for comparison. The derived refractive index values (*n*) is also presented for comparison.

PBE	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
None	5.73	5.73	4.99	83.15	83.15	13.65	5.48	59.98	65.47	2.34
D2	5.72	5.72	5.05	73.97	73.97	13.70	5.49	53.88	59.37	2.34
D3	5.72	5.72	5.05	66.08	66.08	13.80	5.50	48.65	54.15	2.35
U(2eV)	5.43	5.43	**4.97**	44.21	44.21	15.42	5.27	34.61	39.89	2.30
U(4eV)	5.12	5.12	4.91	25.27	25.27	16.21	5.05	22.25	27.30	2.25
U(6eV)	4.82	4.82	4.80	15.43	15.43	15.56	4.81	15.47	20.28	2.19
U(8eV)	4.55	4.55	4.55	12.42	12.42	12.91	4.55	12.58	17.13	2.13
D3-U(2eV)	5.42	5.42	5.02	36.66	36.66	15.49	5.28	29.60	34.89	2.30
D3-U(4eV)	5.11	5.11	4.95	21.72	21.72	16.11	5.05	19.85	24.90	2.25

PBEsol	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
None	5.79	5.79	5.19	49.25	49.25	14.533	5.59	37.68	43.27	2.36
D2	5.78	5.78	5.24	42.43	42.43	14.55	5.60	33.14	38.74	2.37
D3	5.79	5.79	5.23	42.82	42.82	14.63	5.60	33.42	39.02	2.37
U(2eV)	5.47	5.47	5.15	29.28	29.28	16.09	5.37	24.88	30.25	2.32
U(4eV)	5.15	5.15	5.07	18.36	18.36	16.41	5.12	17.71	22.83	2.26
U(6eV)	4.84	4.84	4.85	13.58	13.58	14.15	4.85	13.77	18.61	2.20
U(8eV)	4.59	4.59	4.59	11.31	11.31	11.74	4.59	11.45	16.04	2.14
D3-U(2eV)	5.47	5.47	5.19	26.22	26.22	16.10	5.37	22.85	28.22	2.32
D3-U(4eV)	5.14	5.14	5.09	16.80	16.80	16.27	5.12	16.63	21.75	2.26

RPBE	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
None	5.70	5.70	4.87	143.58	143.58	13.114	5.42	100.09	105.52	2.33
D2	5.69	5.69	4.92	163.15	163.15	13.22	5.44	113.17	118.61	2.33
D3	5.69	5.69	4.91	139.67	139.67	13.17	5.43	97.50	102.93	2.33
U(2eV)	5.41	5.41	4.85	70.27	70.27	15.05	5.23	51.86	57.09	2.29
U(4eV)	5.12	5.12	4.81	35.56	35.56	16.20	5.02	29.10	34.12	2.24
U(6eV)	4.83	4.83	4.73	19.88	19.88	15.97	4.79	18.57	23.37	2.19
U(8eV)	4.55	4.55	4.55	13.47	13.47	14.02	4.55	13.65	18.20	2.13
D3-U(2eV)	5.40	5.40	4.90	58.72	58.72	15.00	5.23	44.14	49.38	2.29
D3-U(4eV)	5.10	5.10	4.85	29.81	29.81	15.96	5.02	25.19	30.21	2.24

	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
Experimental[8-10]	-	-	-	-	-	-	4.9	-	34.5-39.8	-
DFPT/LDA[11]	5.7	5.7	5.3	-	-	-	5.6	**-**	**-**	**-**
DFPT/LDA[2,12]	-	-	-	41.6	41.6	14.9	-	-	-	-
DFPT/PBE[8]	5.8	5.8	5.3	42.1	42.1	15.8	5.6	33.4	39.0	-

Table S8. Electronic ($\varepsilon_{11}^{\infty}$, $\varepsilon_{22}^{\infty}$, and $\varepsilon_{33}^{\infty}$) and ionic ($\varepsilon_{11}^{\mathrm{Ion}}$, $\varepsilon_{22}^{\mathrm{Ion}}$, and $\varepsilon_{33}^{\mathrm{Ion}}$) contribution to the dielectric tensor, total electronic (ε^{∞}) and ionic contribution ($\varepsilon^{\mathrm{Ion}}$), and total dielectric constant (ε) of m-ZrO_2. Previously reported experimental and theoretical (LDA and PBE) values are also given for comparison. The derived refractive index values (*n*) is also presented for comparison.

PBE	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
None	5.33	5.36	5.01	18.86	17.19	13.11	5.23	16.39	21.62	2.29
D2	5.40	5.53	4.99	18.84	17.40	12.32	5.30	16.18	21.49	2.30
D3	5.33	5.38	5.01	17.93	16.36	12.38	5.24	15.56	20.80	2.29
U(2eV)	5.08	5.07	4.80	16.31	15.00	12.19	4.98	14.50	19.48	2.23
U(4eV)	4.83	4.79	4.59	14.04	12.99	11.14	4.74	12.72	17.46	2.18
U(6eV)	4.60	4.54	4.39	12.17	11.33	10.15	4.51	11.22	15.73	2.12
U(8eV)	4.38	4.31	4.20	10.71	9.99	9.28	4.30	9.99	14.29	2.07
D3-U(2eV)	5.07	5.08	4.80	15.51	14.26	11.53	4.99	13.77	18.75	2.23
D3-U(4eV)	4.83	4.80	4.59	13.39	12.37	10.58	4.74	12.11	16.85	2.18

PBEsol	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
None	5.40	5.46	5.06	17.29	15.56	11.57	5.31	14.81	20.11	2.30
D2	5.53	5.62	5.08	17.02	15.50	11.77	5.41	14.76	20.17	2.33
D3	5.41	5.49	5.07	16.68	15.08	11.14	5.32	14.30	19.62	2.31
U(2eV)	5.14	5.15	4.85	14.91	13.52	10.82	5.05	13.08	18.13	2.25
U(4eV)	4.89	4.86	4.64	12.93	11.78	9.99	4.79	11.57	16.36	2.19
U(6eV)	4.65	4.60	4.43	11.28	10.36	9.19	4.56	10.27	14.83	2.14
U(8eV)	4.43	4.36	4.24	9.98	9.22	8.49	4.34	9.23	13.58	2.08
D3-U(2eV)	5.15	5.18	4.85	14.44	13.09	10.42	5.06	12.65	17.71	2.25
D3-U(4eV)	4.89	4.89	4.64	12.52	11.42	9.65	4.81	11.20	16.00	2.19

RPBE	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
None	5.30	5.32	4.99	20.24	18.59	14.42	5.20	17.75	22.95	2.28
D2	5.33	5.46	4.95	20.34	18.77	13.21	5.25	17.44	22.69	2.29
D3	5.31	5.38	4.97	19.31	17.85	13.18	5.22	16.78	22.00	2.28
U(2eV)	5.06	5.04	4.79	17.63	16.43	13.49	4.96	15.85	20.81	2.23
U(4eV)	4.81	4.77	4.58	15.12	14.20	12.25	4.72	13.86	18.58	2.17
U(6eV)	4.58	4.52	4.38	13.03	12.30	11.07	4.49	12.13	16.62	2.12
U(8eV)	4.36	4.29	4.19	11.37	10.76	10.06	4.28	10.73	15.01	2.07
D3-U(2eV)	5.06	5.08	4.77	16.68	15.56	12.35	4.97	14.86	19.83	2.23
D3-U(4eV)	4.81	4.80	4.56	14.37	13.46	11.38	4.72	13.07	17.79	2.17

	$\varepsilon_{11}^{\infty}$	$\varepsilon_{22}^{\infty}$	$\varepsilon_{33}^{\infty}$	$\varepsilon_{11}^{\mathrm{Ion}}$	$\varepsilon_{22}^{\mathrm{Ion}}$	$\varepsilon_{33}^{\mathrm{Ion}}$	ε^{∞}	$\varepsilon^{\mathrm{Ion}}$	ε	*n*
Experimental[8-10]	-	-	-	-	-	-	4.8	-	16.0-25.0	-
DFPT/LDA[11,12]	5.6	5.6	5.2	22.8	20	16.5	-	-	25.3	-
DFPT/PBE[8]	5.5	5.5	5.1	18.3	16.4	11.8	5.4	15.5	20.8	-

Refractive index (*n*) was calculated by using the following relation:

$$n = (\varepsilon^{\infty})^{1/2}.$$

6. Calculated band gaps and band structures

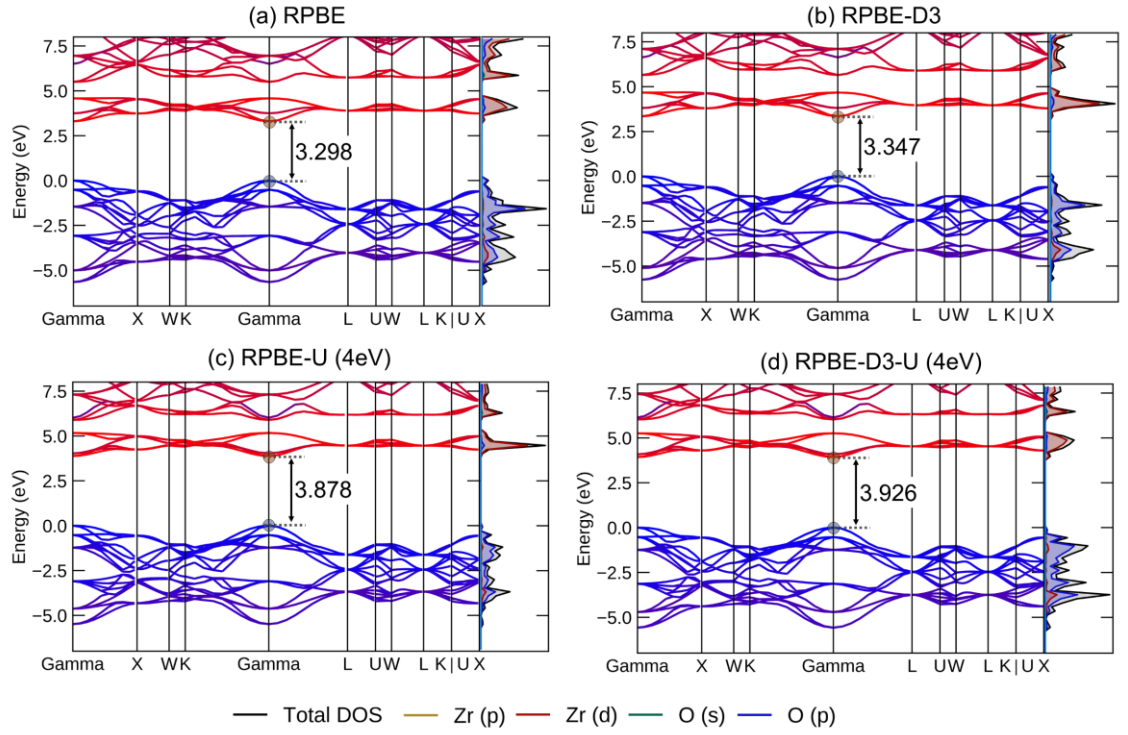

Figure S4. Band structures (left) and density of states (right) of c-ZrO_2 calculated using standard (a) RPBE, (b) RPBE-D3, (c) RPBE-U (4 eV), and (d) RPBE-D3-U (4 eV). The top of the valence band is taken a zero of energy.

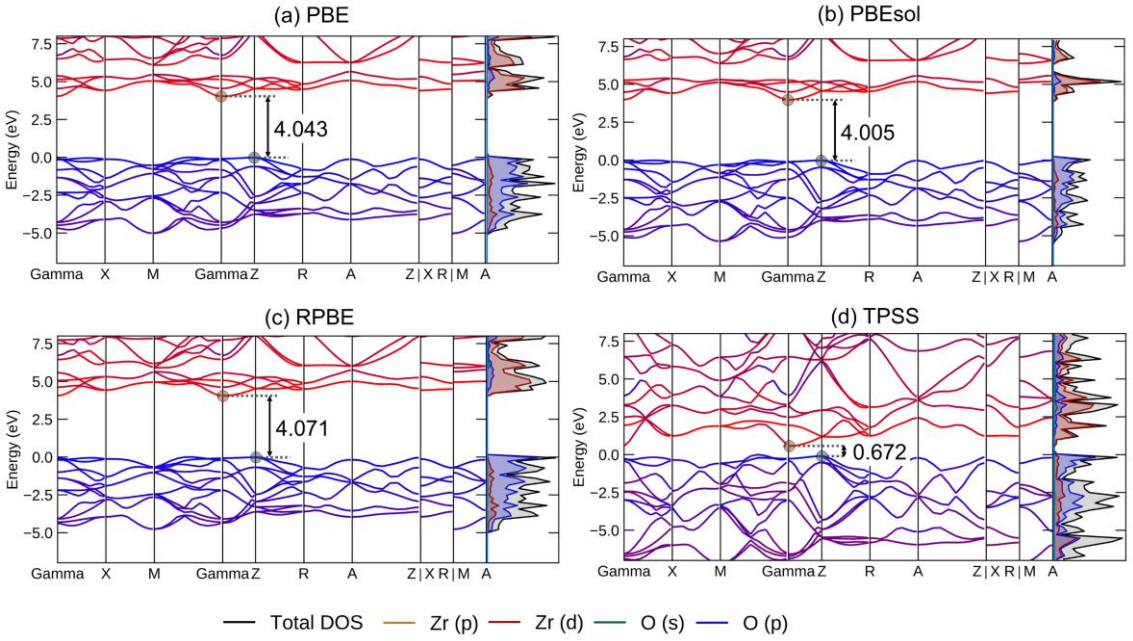

Figure S5. Band structures (left) and density of states (right) of t-ZrO_2 calculated using standard (a) PBE, (b) PBEsol, (c) RPBE, and (d) TPSS. The top of the valence band is taken a zero of energy.

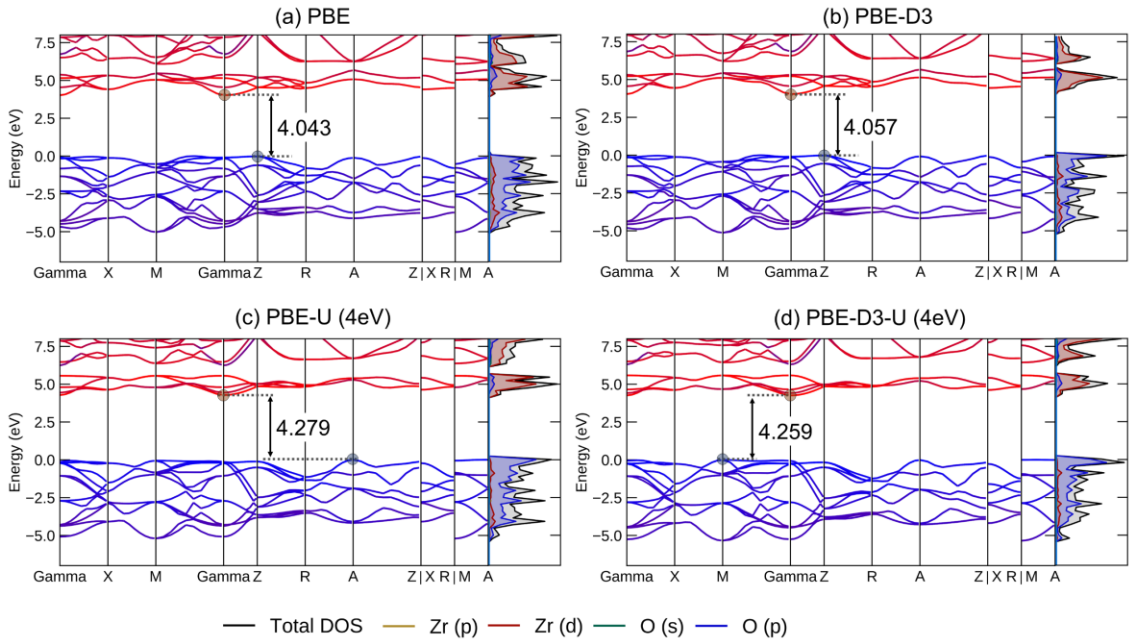

Figure S6. Band structures (left) and density of states (right) of t-ZrO_2 calculated using standard (a) PBE, (b) PBE-D3, (c) PBE-U (4eV), and (d) PBE-D3-U (4eV). The top of the valence band is taken a zero of energy.

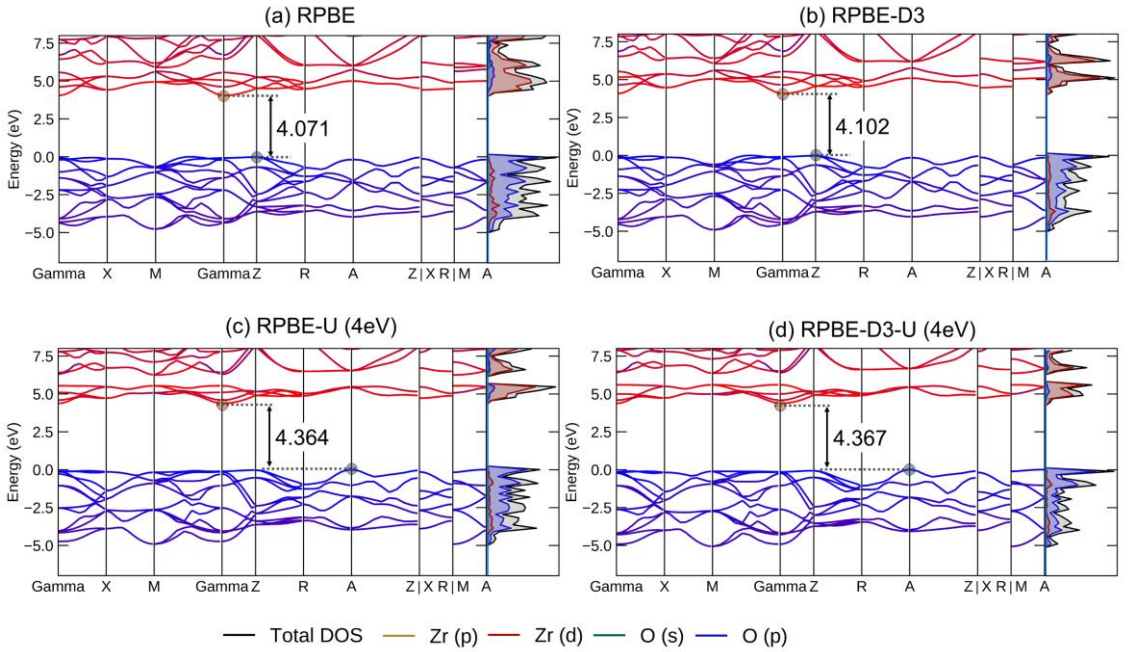

Figure S7. Band structures (left) and density of states (right) of t-ZrO_2 calculated using standard (a) RPBE, (b) RPBE-D3, (c) RPBE-U (4eV), and (d) RPBE-D3-U (4eV). The top of the valence band is taken a zero of energy.

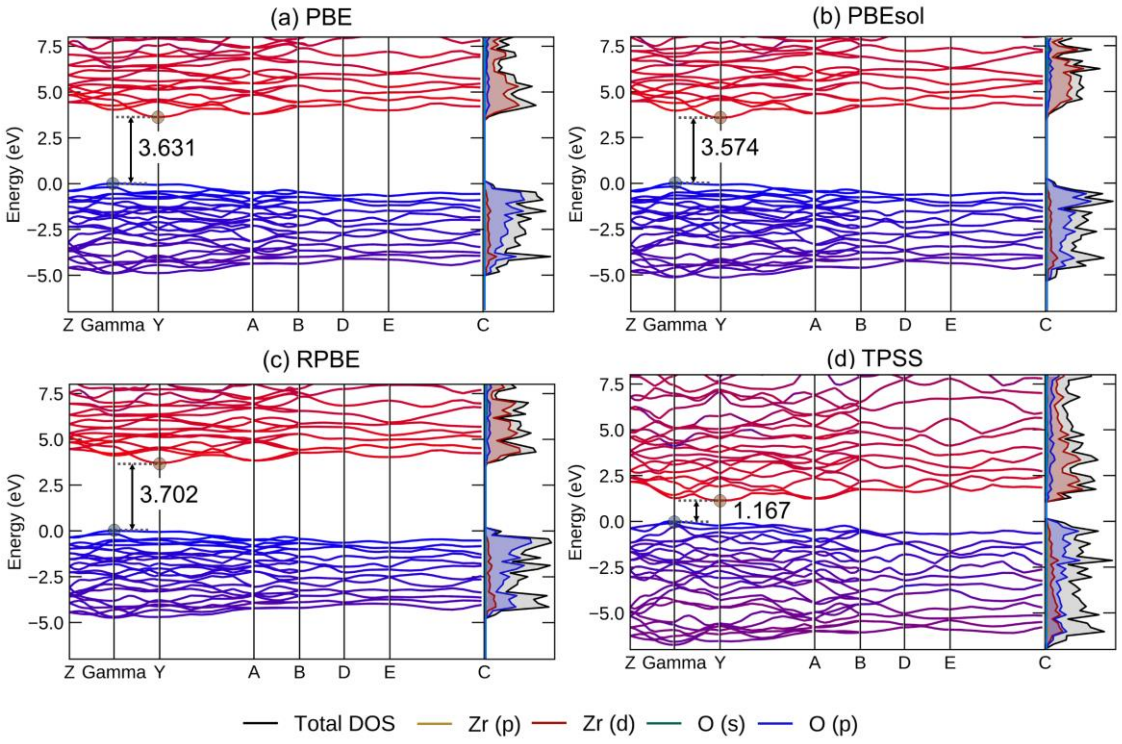

Figure S8. Band structures (left) and density of states (right) of m-ZrO_2 calculated using standard (a) PBE, (b) PBEsol, (c) RPBE, and (d) TPSS. The top of the valence band is taken a zero of energy.

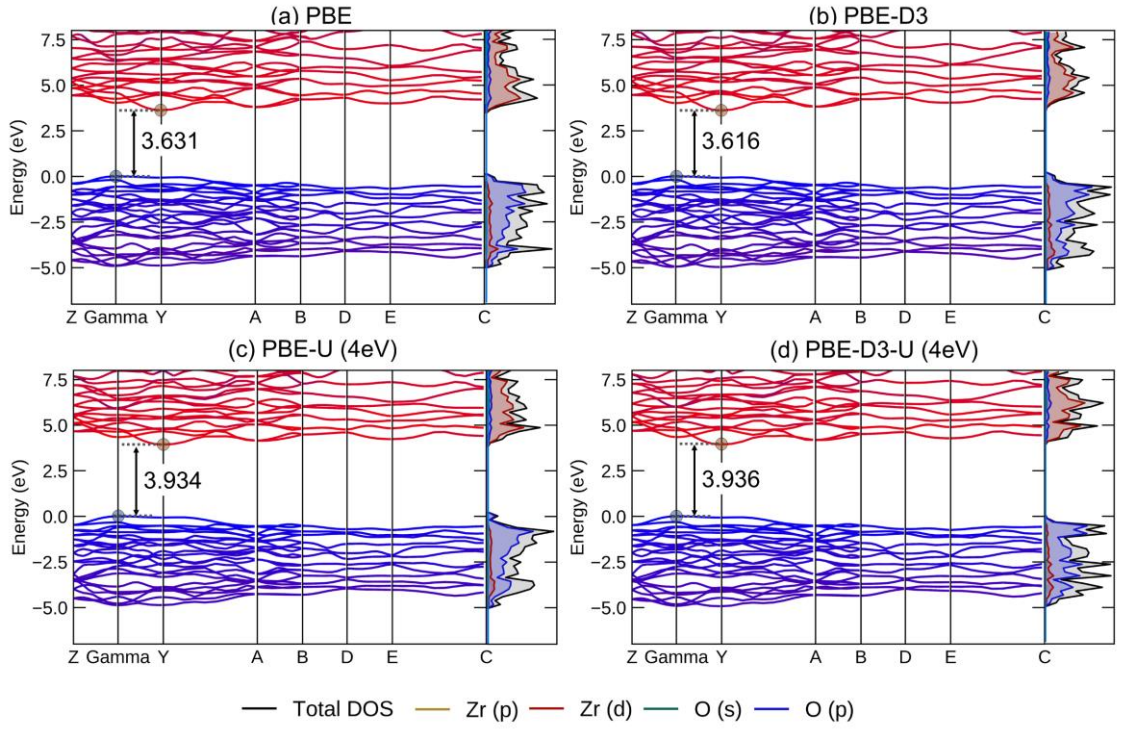

Figure S9. Band structures (left) and density of states (right) of m-ZrO_2 calculated using standard (a) PBE, (b) PBE-D3, (c) PBE-U (4eV), and (d) PBE-D3-U (4eV). The top of the valence band is taken a zero of energy.

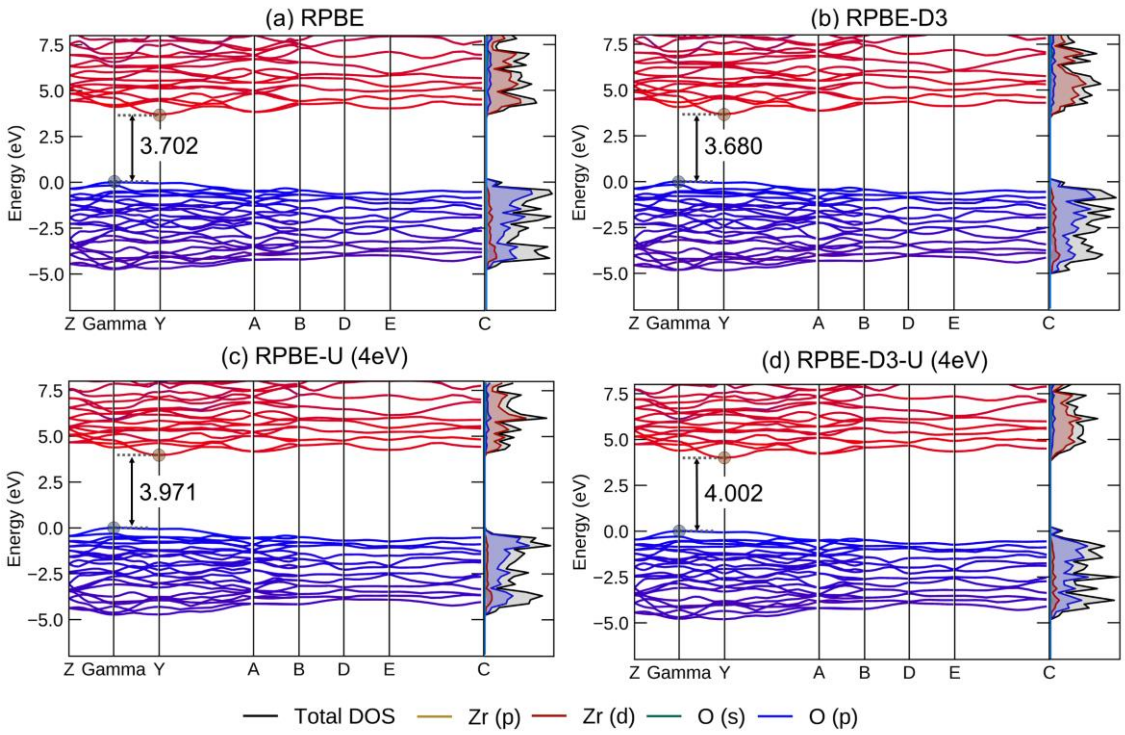

Figure S10. Band structures (left) and density of states (right) of m-ZrO_2 calculated using standard (a) RPBE, (b) RPBE-D3, (c) RPBE-U (4eV), and (d) RPBE-D3-U (4eV). The top of the valence band is taken a zero of energy.

7. Calculated phonon dispersion curves

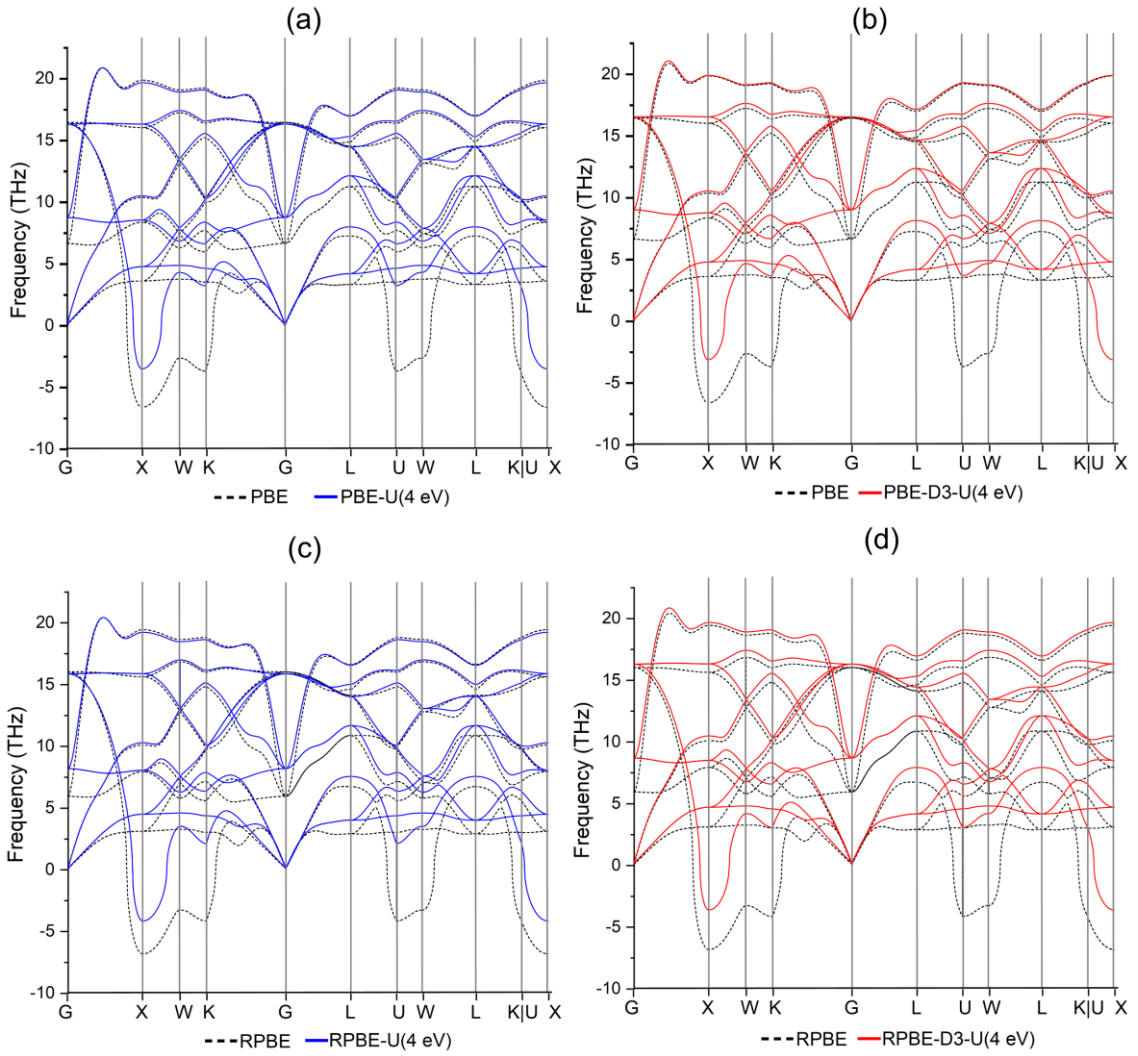

Figure S11. Comparison of the phonon dispersion curves of c-ZrO_2 obtained using (a) PBE and PBE-U(4 eV), (b) PBE and PBE-D3-U(4 eV), (c) RPBE and RPBE-U(4 eV), and (d) RPBE and RPBE-D3-U(4 eV).

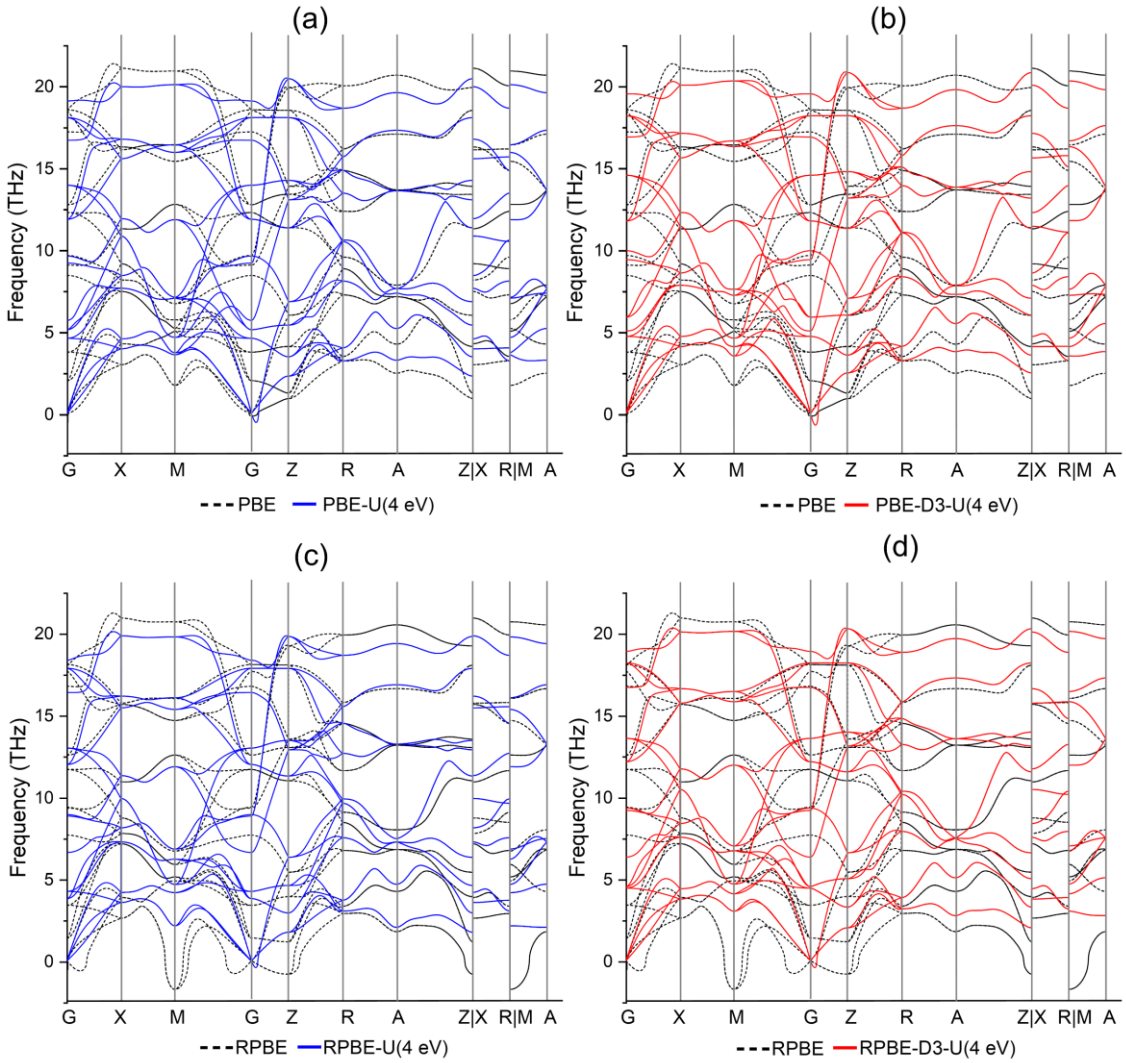

Figure S12. Comparison of the phonon dispersion curves of t-ZrO_2 obtained using (a) PBE and PBE-U(4 eV), (b) PBE and PBE-D3-U(4 eV), (c) RPBE and RPBE-U(4 eV), and (d) RPBE and RPBE-D3-U(4 eV).

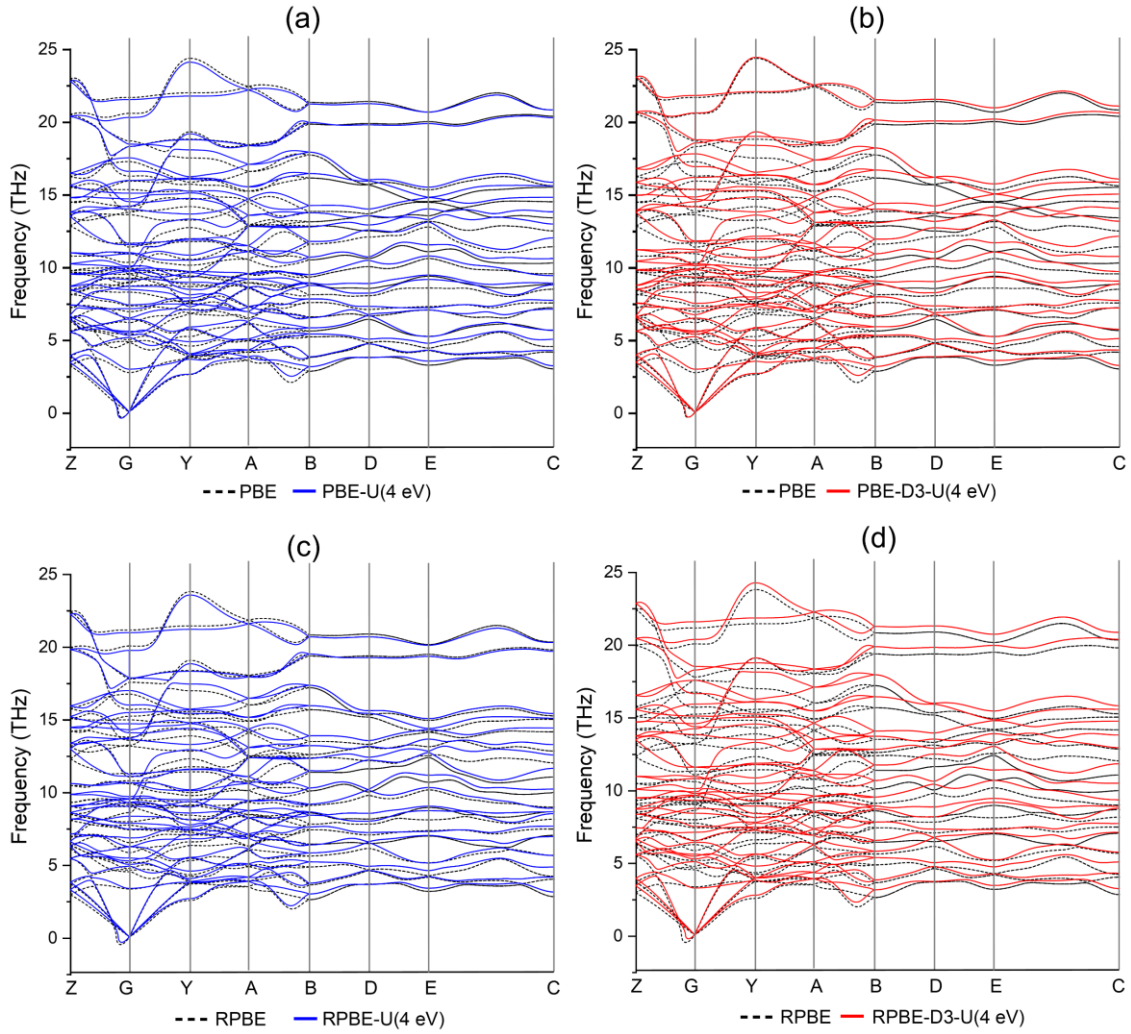

Figure S13. Comparison of the phonon dispersion curves of m-ZrO_2 obtained using (a) PBE and PBE-U(4 eV), (b) PBE and PBE-D3-U(4 eV), (c) RPBE and RPBE-U(4 eV), and (d) RPBE and RPBE-D3-U(4 eV).

8. References

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