Supporting Information

Relevance of dispersion and the electronic spin in the DFT+U approach for the description of pristine and defective TiO_2 anatase

Ana E. Torres,[a]* Janatan Rodríguez-Pineda,[a] and Rodolfo Zanella.[a]*

[a]Instituto de Ciencias Aplicadas y Tecnología, Universidad Nacional Autónoma de México, CU, Coyoacán, 04510, México City, Mexico.

Contents

I. Geometry Optimization procedure

1. The volume is varied +/-15% from its original volume and 7 deformed structure calculations are performed.
2. ISIF=2 followed by ISIF=4 calculations over the preoptimized structures were performed.
3. With the computed energies at each volume an EOS fitting was performed using a Birch-Murnaghan equation at fourth order as implemented in vaspkit. (See Figure S1 a and c)
4. The equilibrium volume is extracted and used as input for the next set of calculations.
5. For optimizing the a/c ratio with constant volume a maximum physical strain ϵ is defined as the percent variation of the a/c ratio (i.e.bn if there is a +/-5% variation in a/c then ϵ +/- 0.05), then the a/c of the distorted structure at the maximum physical strain is determined from $(a/c)=(a/c)_{initial}\cdot(1+\epsilon)$. Then 7 distorted structures were computed considering 7 ϵ_i values through variations of -5% to 5% of the a/c initial value with a step of 1.67%.
6. Then ISIF=2 calculations were computed for each distorted structure and the results of energy vs strain were plotted and fitted to a 4th order polynomial (See figure S1 b and d).

   $$E(x) = ax^4 + bx^3 + cx^2 + dx + c$$

   with $x=\epsilon$ and the minimum corresponds to the derivative $dE/dx=0$, i.e:

   $$0 = 4ax^3 + 3bx^2 + 2cx + d$$

   Then by solving the equation we use this new value of ϵ_{min} physical strain to compute the a/c ratio and build a new structure, that will be used to optimize the ratio a/c at ISIF=2 with fixed volume followed by ISIF=7 calculation, this final structure is used to reoptimize the volume at a fixed value of the ratio a/c through an EOS fitting as explained next.

7. The step one described previously is repeated by increasing the number of deformed structures for the volume calculations to 9. The procedure is repeated by following steps 2 to 4. Then for the a/c ratio optimization 9 distorted structures were used and steps 5 to 6 were followed.
8. Finally, after completing 4 calculation cycles (1st volume optimization – 1st a/c ratio optimization - 2nd volume optimization – 2nd a/c ratio optimization) the final structure is fully relaxed by ISIF=3 calculation.
9. The convergence between the volume, lattice parameters and energy were checked at each calculation cycle and the final structure is compared to the fully relaxed structure to verify a convergence < $1X10^{-6}$ Å in the lattice parameters and < $7X10^{-4}$ eV in the energy.

The convergence data for TiO_2 is presented in Table S1.

Ti_2O_3 geometry optimization was carried out by following a similar procedure as that previously described. However, instead of a/c ratio optimization at constant volume the α angle was optimized at constant volume (see figure S2 b and d). Four calculation cycles were performed (1st volume optimization (see Figure S2 a) – 1st α angle optimization - 2nd volume optimization (see Figure S2 c) – 2nd α angle optimization) the final structure was fully relaxed by ISIF=3 calculation. The convergence data for Ti_2O_3 is presented in table S2.

The relaxed structure at U_{n-1} is used as a starting structure for the next U_n (u=1,2,3,4) optimization procedure. The initial structures for the TiO_2 and Ti_2O_3 U=0 geometry optimization were taken from Howard et.al.[63] and Straumanis et.al [64], respectively.

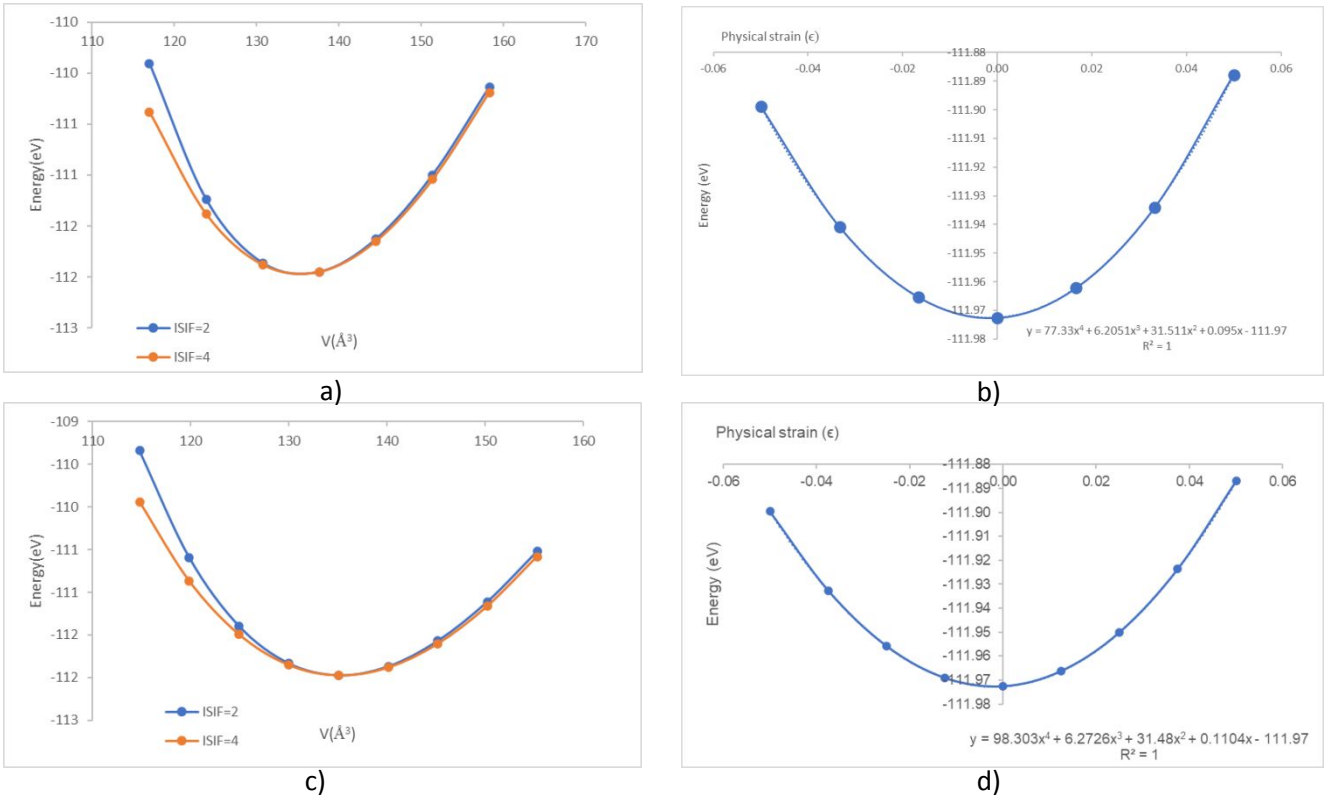

Figure S1. PBEsol U=1 Optimization steps until convergence is achieved for the geometry parameters of TiO_2. Volume optimization steps (a,c), and a/c optimization calculations (b,d).

Table S1. Convergence data and geometry parameters along each optimization step for TiO_2

Calculation	Step	a(Å)	c(Å)	Δa(Å)	Δc(Å)	E(eV)	ΔE(eV)	Vol(A³)	ΔVol(A³)
-	0	3.7800	9.510					136.2680	
Vopt1	1	3.7814	9.459	1.4078E-03	-5.0528E-02	-111.9726		135.2614	-1.0066E+00
1_a/c	2	3.7797	9.455	-3.0117E-04	-5.4811E-02	-111.9728	-2.0132E-04	135.0780	-1.1900E+00
Vopt2	3	3.7820	9.461	1.9674E-03	-4.9136E-02	-111.9726	2.0413E-04	135.3214	-9.4662E-01
2_a/c	4	3.7775	9.466	-2.4759E-03	-4.3629E-02	-111.9730	-3.6941E-04	135.0822	-1.1858E+00
ISIF=3	5	3.7775	9.466	-2.4760E-03	-4.3628E-02	-111.9723	6.4695E-04	135.0822	-1.1858E+00

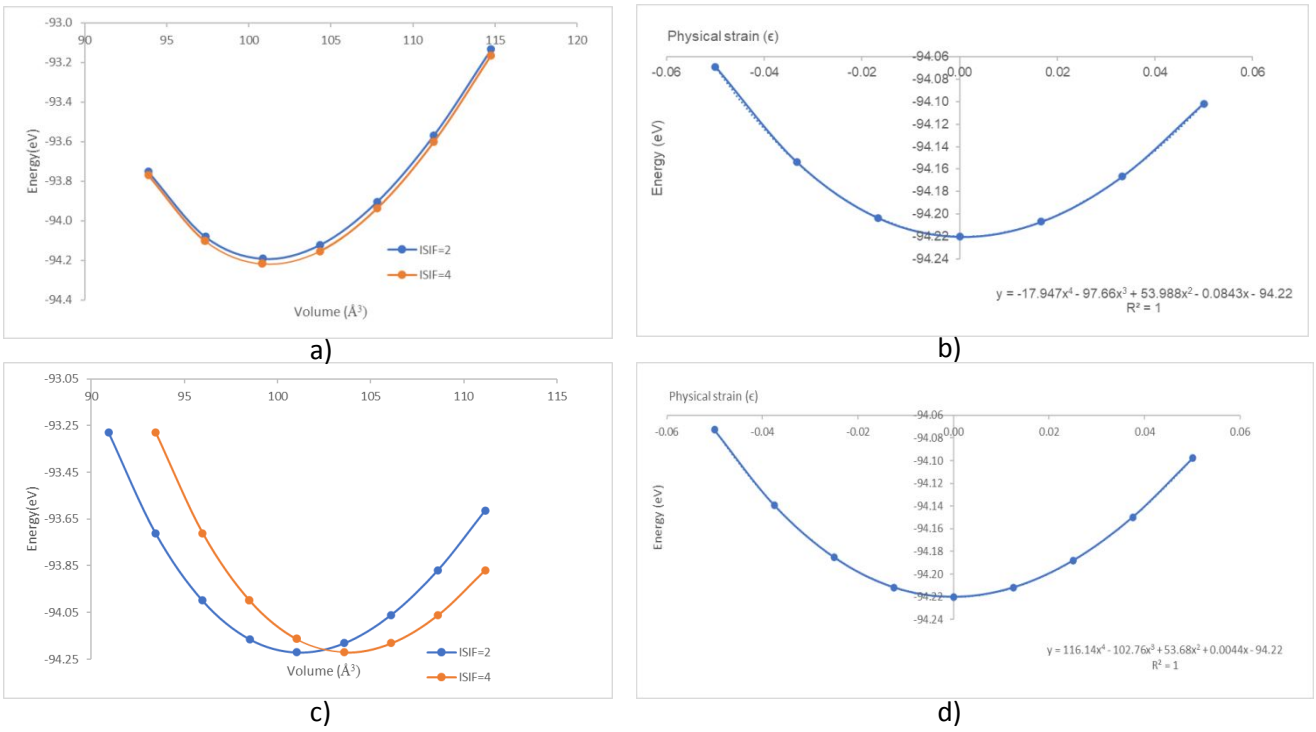

Figure S2. PBEsol U=1 Optimization steps until convergence is achieved for the geometry parameters of Ti_2O_3. Volume optimization steps (a,c), and α angle optimization calculations (b,d).

Table S2. Convergence data and geometry parameters along each optimization step for Ti_2O_3.

Calculation	Step	a(Å)	α(°)	Δa(Å)	Δα(°)	E(eV)	ΔE(eV)	Vol(Å³)	ΔVol(Å³)
-	0	5.4310	56.580					104.3219	
V1opt	1	5.4381	55.264	7.1100E-03	-1.3158E+00	-94.2202		101.2000	-3.1219E+00
Ang1	2	5.4331	55.307	-5.0000E-03	4.3200E-02	-94.2203	-1.3268E-04	101.0400	-1.6000E-01
V2opt	3	5.4363	55.307	3.1900E-03	0.0000E+00	-94.2202	1.7444E-04	101.2167	1.7666E-01
Ang2	4	5.4333	55.305	-3.0300E-03	-2.3000E-03	-94.2204	-2.2510E-04	101.0400	-1.7666E-01
ISIF=3	5	5.4333	55.305	0.0000E+00	0.0000E+00	-94.2199	4.6883E-04	101.0411	1.1130E-03

II. Converged geometries of TiO_2

1. TiO_2 PBEsol U=0

Ti O2
1.00000000000000
3.7729692360596809 0.0000000000000000 -0.0000000000000000
-0.0000000000000000 3.7729692360596809 -0.0000000000000000
0.0000000000000000 -0.0000000000000000 9.5561387893009861
Ti O
4 8
Direct
0.0000000000000000 -0.0000000000000000 -0.0000000000000000
0.5000000000000000 0.5000000000000000 0.5000000000000000
-0.0000000000000000 0.5000000000000000 0.2500000000000000
0.5000000000000000 0.0000000000000000 0.7500000000000000
-0.0000000000000000 0.0000000000000000 0.2076179618386709
0.5000000000000000 0.5000000000000000 0.7076179768386774
-0.0000000000000000 0.5000000000000000 0.4576179768386745
0.5000000000000000 0.0000000000000000 0.9576179768386774
0.5000000000000000 -0.0000000000000000 0.5423820231613226
0.0000000000000000 0.5000000000000000 0.0423820531613271
0.5000000000000000 0.5000000000000000 0.2923820231613255
0.0 -0.0000000000000000 0.7923820231613226

2. TiO_2 PBEsol U=1

Ti O2
1.00000000000000

3.7871192869247983 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.7871192869247983 0.0000000000000000

0.0000000000000000 0.0000000000000000 9.5668814005190317

Ti O

4 8

Direct

-0.0000000000000000 0.0000000000000000 -0.0000000000000000

0.5000000000000000 0.5000000000000000 0.5000000000000000

0.0000000000000000 0.5000000000000000 0.2500000000000000

0.5000000000000000 0.0000000000000000 0.7500000000000000

0.0000000000000000 0.0000000000000000 0.2076655252589770

0.5000000000000000 0.5000000000000000 0.7076655102589721

-0.0000000000000000 0.5000000000000000 0.4576655102589722

0.5000000000000000 -0.0000000000000000 0.9576655102589721

0.5000000000000000 -0.0000000000000000 0.5423344897410279

-0.0000000000000000 0.5000000000000000 0.0423345007410251

0.5000000000000000 0.5000000000000000 0.2923344897410278

-0.0000000000000000 0.0000000000000000 0.7923344897410279

3. TiO_2 PBEsol U=2

Ti O2

1.00000000000000

3.8008914404632632 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.8008914404632632 0.0000000000000000

0.0000000000000000 0.0000000000000000 9.5772813666030334

Ti O

4 8

Direct

-0.0000000000000000 0.0000000000000000 0.0000000000000000

0.5000000000000000 0.5000000000000000 0.5000000000000000

-0.0000000000000000 0.5000000000000000 0.2500000000000000
 0.5000000000000000 0.0000000000000000 0.7500000000000000
 0.0000000000000000 0.0000000000000000 0.2077279904936862
 0.5000000000000000 0.5000000000000000 0.7077279154936834
 0.0000000000000000 0.5000000000000000 0.4577279154936835
 0.5000000000000000 -0.0000000000000000 0.9577279154936834
 0.5000000000000000 -0.0000000000000000 0.5422720845063166
 0.0000000000000000 0.5000000000000000 0.0422720505063137
 0.5000000000000000 0.5000000000000000 0.2922720845063165
 0.0000000000000000 0.0000000000000000 0.7922720845063166

4. TiO_2 PBEsol U=3

Ti O2
  1.00000000000000
    3.8140727059167192   0.0000000000000000   0.0000000000000000
    0.0000000000000000   3.8140727059167192   0.0000000000000000
    0.0000000000000000   0.0000000000000000   9.5900726503956246
  Ti   O
    4   8
Direct
-0.0000000000000000 0.0000000000000000 0.0000000000000000
 0.5000000000000000 0.5000000000000000 0.5000000000000000
-0.0000000000000000 0.5000000000000000 0.2500000000000000
 0.5000000000000000 -0.0000000000000000 0.7500000000000000
 0.0000000000000000 -0.0000000000000000 0.2077591624932607
 0.5000000000000000 0.5000000000000000 0.7077590574932631
 0.0000000000000000 0.5000000000000000 0.4577590874932652
 0.5000000000000000 -0.0000000000000000 0.9577590574932631
 0.5000000000000000 0.0000000000000000 0.5422409425067369
 0.0000000000000000 0.5000000000000000 0.0422408865067398

0.5000000000000000 0.5000000000000000 0.2922409125067348

0.0000000000000000 0.0000000000000000 0.7922409425067369

5. TiO_2 PBEsol U=4

Ti O2

1.00000000000000

3.8265186425189275 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.8265186425189275 -0.0000000000000000

0.0000000000000000 -0.0000000000000000 9.6072785298340868

Ti O

4 8

Direct

0.0000000000000000 -0.0000000000000000 0.0000000000000000

0.5000000000000000 0.5000000000000000 0.5000000000000000

-0.0000000000000000 0.5000000000000000 0.2500000000000000

0.5000000000000000 0.0000000000000000 0.7500000000000000

0.0000000000000000 -0.0000000000000000 0.2077300525869028

0.5000000000000000 0.5000000000000000 0.7077299185869055

0.0000000000000000 0.5000000000000000 0.4577299485869085

0.5000000000000000 -0.0000000000000000 0.9577299185869055

0.5000000000000000 0.0000000000000000 0.5422700814130945

0.0000000000000000 0.5000000000000000 0.0422700104130919

0.5000000000000000 0.5000000000000000 0.2922700514130915

-0.0000000000000000 0.0000000000000000 0.7922700814130945

6. TiO_2 PBEsol U=6

Ti O2

1.00000000000000

3.8509222545303814 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.8509222545303814 -0.0000000000000000

0.0000000000000000 -0.0000000000000000 9.6449366076142251

Ti O

4 8

Direct

-0.0000000000000000 -0.0000000000000000 -0.0000000000000000

0.5000000000000000 0.5000000000000000 0.5000000000000000

-0.0000000000000000 0.5000000000000000 0.2500000000000000

0.5000000000000000 -0.0000000000000000 0.7500000000000000

-0.0000000000000000 0.0000000000000000 0.2076555746832124

0.5000000000000000 0.5000000000000000 0.7076553656832130

0.0000000000000000 0.5000000000000000 0.4576555146832074

0.5000000000000000 -0.0000000000000000 0.9576553656832130

0.5000000000000000 0.0000000000000000 0.5423446343167870

0.0000000000000000 0.5000000000000000 0.0423444813167923

0.5000000000000000 0.5000000000000000 0.2923444853167926

0.0 -0.0000000000000000 0.7923446343167870

7. TiO_2 PBEsol-D3 U=0

Ti O2

1.00000000000000

3.7638888359000000 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.7638888359000000 0.0000000000000000

0.0000000000000000 0.0000000000000000 9.4559316634999995

Ti O

4 8

Direct

0.0000000000000000 0.0000000000000000 0.0000000000000000

0.5000000000000000 0.5000000000000000 0.5000000000000000

0.0000000000000000 0.5000000000000000 0.2500000000000000

0.5000000000000000 0.0000000000000000 0.7500000000000000

0.0000000000000000 0.0000000000000000 0.2088565079999967

0.5000000000000000 0.5000000000000000 0.7088565230000015

0.0000000000000000 0.5000000000000000 0.4588565230000015

0.5000000000000000 0.0000000000000000 0.9588565230000015

0.5000000000000000 0.0000000000000000 0.5411434769999985

0.0000000000000000 0.5000000000000000 0.0411435070000010

0.5000000000000000 0.5000000000000000 0.2911434769999985

0.0000000000000000 0.0000000000000000 0.7911434769999985

8. TiO_2 PBEsol-D3 U=1

Ti O2

1.00000000000000

3.7775239944000001 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.7775239944000001 0.0000000000000000

0.0000000000000000 0.0000000000000000 9.4663715363000005

Ti O

4 8

Direct

0.0000000000000000 0.0000000000000000 0.0000000000000000

0.5000000000000000 0.5000000000000000 0.5000000000000000

0.0000000000000000 0.5000000000000000 0.2500000000000000

0.5000000000000000 0.0000000000000000 0.7500000000000000

0.0000000000000000 0.0000000000000000 0.2089503560000026

0.5000000000000000 0.5000000000000000 0.7089503409999978

0.0000000000000000 0.5000000000000000 0.4589503409999978

0.5000000000000000 0.0000000000000000 0.9589503409999978

0.5000000000000000 0.0000000000000000 0.5410496590000022

0.0000000000000000 0.5000000000000000 0.0410496699999996

0.5000000000000000 0.5000000000000000 0.2910496590000022

0.0000000000000000 0.0000000000000000 0.7910496590000022

9. TiO_2 PBEsol-D3 U=2

Ti O2

1.00000000000000

3.7906253338000000 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.7906253338000000 0.0000000000000000

0.0000000000000000 0.0000000000000000 9.4809303283999995

Ti O

4 8

Direct

0.0000000000000000 0.0000000000000000 0.0000000000000000

0.5000000000000000 0.5000000000000000 0.5000000000000000

0.0000000000000000 0.5000000000000000 0.2500000000000000

0.5000000000000000 0.0000000000000000 0.7500000000000000

0.0000000000000000 0.0000000000000000 0.2089729460000029

0.5000000000000000 0.5000000000000000 0.7089728710000003

0.0000000000000000 0.5000000000000000 0.4589728710000003

0.5000000000000000 0.0000000000000000 0.9589728710000003

0.5000000000000000 0.0000000000000000 0.5410271289999997

0.0000000000000000 0.5000000000000000 0.0410270949999969

0.5000000000000000 0.5000000000000000 0.2910271289999997

0.0000000000000000 0.0000000000000000 0.7910271289999997

10. TiO_2 PBEsol-D3 U=3

Ti O2

1.00000000000000

3.8034222126000001 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.8034222126000001 0.0000000000000000

0.0000000000000000 0.0000000000000000 9.4984664917000003

Ti O

4 8

Direct

0.0000000000000000 0.0000000000000000 0.0000000000000000

0.5000000000000000 0.5000000000000000 0.5000000000000000

0.0000000000000000 0.5000000000000000 0.2500000000000000

0.5000000000000000 0.0000000000000000 0.7500000000000000

0.0000000000000000 0.0000000000000000 0.2089217159999990

0.5000000000000000 0.5000000000000000 0.7089216110000010

0.0000000000000000 0.5000000000000000 0.4589216410000034

0.5000000000000000 0.0000000000000000 0.9589216110000010

0.5000000000000000 0.0000000000000000 0.5410783889999990

0.0000000000000000 0.5000000000000000 0.0410783330000015

0.5000000000000000 0.5000000000000000 0.2910783589999966

0.0000000000000000 0.0000000000000000 0.7910783889999990

11. TiO_2 PBEsol-D3 U=4

Ti O2

1.00000000000000

3.8157105445999999 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.8157105445999999 0.0000000000000000

0.0000000000000000 0.0000000000000000 9.5184736252000004

Ti O

4 8

Direct

0.0000000000000000 0.0000000000000000 0.0000000000000000

0.5000000000000000 0.5000000000000000 0.5000000000000000

0.0000000000000000 0.5000000000000000 0.2500000000000000

0.5000000000000000 0.0000000000000000 0.7500000000000000

0.0000000000000000 0.0000000000000000 0.2088579679999967

0.5000000000000000 0.5000000000000000 0.7088578339999998

0.0000000000000000 0.5000000000000000 0.4588578640000023

0.5000000000000000 0.0000000000000000 0.9588578339999998

0.5000000000000000 0.0000000000000000 0.5411421660000002

0.0000000000000000 0.5000000000000000 0.0411420949999979

0.5000000000000000 0.5000000000000000 0.2911421359999977

0.0000000000000000 0.0000000000000000 0.7911421660000002

12. TiO_2 PBEsol-D3 U=6

Ti O2

1.00000000000000

3.8393427294256446 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.8393427294256446 0.0000000000000000

0.0000000000000000 -0.0000000000000000 9.5641177735926011

Ti O

4 8

Direct

-0.0000000000000000 0.0000000000000000 -0.0000000000000000

0.5000000000000000 0.5000000000000000 0.5000000000000000

-0.0000000000000000 0.5000000000000000 0.2500000000000000

0.5000000000000000 0.0000000000000000 0.7500000000000000

-0.0000000000000000 -0.0000000000000000 0.2087070713995634

0.5000000000000000 0.5000000000000000 0.7087068623995639

-0.0000000000000000 0.5000000000000000 0.4587070113995585

0.5000000000000000 -0.0000000000000000 0.9587068623995639

0.5000000000000000 -0.0000000000000000 0.5412931376004361

0.0000000000000000 0.5000000000000000 0.0412929846004412

0.5000000000000000 0.5000000000000000 0.2912929886004415

0.0 -0.0000000000000000 0.7912931376004361

Table S3. Optimized geometries for TiO_2 with different U values.

Method		*PBEsol*			*PBEsol- D3*	
Hubbard U value	*a(Å)*	*c(Å)*	*Vol(Å³)*	*a(Å)*	*c(Å)*	*Vol(Å³)*
0	3.76	9.46	133.96	3.76	9.46	133.96
1	3.79	9.57	137.21	3.78	9.47	135.08
2	3.80	9.58	138.36	3.79	9.48	136.23
3	3.81	9.59	139.51	3.80	9.50	137.41
4	3.83	9.61	140.67	3.82	9.52	138.59
6	3.85	9.64	143.03	3.84	9.56	140.98
Experimental value	3.78	9.51	136.27	3.78	9.51	136.27

III. Converged geometries of Ti_2O_3

1. Ti_2O_3 PBEsol U=0

Ti4 O6

1.00000000000000

5.4642519917672097 0.0013344319898459 0.0009107456149114

3.1343915680578145 4.4758955648586687 0.0009107456147785

3.1343915680578012 1.6320471772754752 4.1677408685983188

Ti O

4 6

Direct

0.3454939964066505 0.3454941024066522 0.3454941514066527

0.1545058835933538 0.1545058735933530 0.1545058465933472

0.6545054145933470 0.6545057235933477 0.6545060455933530

0.8454945104066504 0.8454939934066467 0.8454941644066502

0.9381278928058702 0.5618719931941275 0.2499999489999993

0.5618718761941285 0.2500000349999993 0.9381279568058684

0.2500001040000015 0.9381278468058735 0.5618720221941264

0.0618719721941293 0.4381277678058705 0.7500001339999969

0.4381283888058686 0.7499999389999985 0.0618719811941265

0.7500000200000017 0.0618719981941315 0.4381278298058685

2. Ti_2O_3 PBEsol U=1

Ti4 O6

1.00000000000000

5.4581862984483136 0.0004643471059587 0.0003188020878418

3.0610642566751234 4.5190356825129410 0.0003188020879977

3.0610642566751234 1.6239081019411896 4.2171798726059277

Ti O

4 6

Direct

0.3437001333189599 0.3437006083189602 0.3437003373189626

0.1562995956810355 0.1562996046810398 0.1562996026810396

0.6562999316810348 0.6562999756810385 0.6562994016810336

0.8437003593189644 0.8437006203189611 0.8437006903189669

0.9352501198109636 0.5647498731890394 0.2499999209999970

0.5647500341890349 0.2499998400000010 0.9352498258109606

0.2499998850000011 0.9352504138109666 0.5647499251890366

0.0647502771890374 0.4352498778109647 0.7500002170000002

0.4352499328109657 0.7500004070000017 0.0647501121890344

0.7500004540000020 0.0647501801890400 0.4352497858109642

3. Ti_2O_3 PBEsol U=2

Ti4 O6

1.00000000000000

5.4581862984483136 0.0004643471059587 0.0003188020878418

3.0610642566751234 4.5190356825129410 0.0003188020879977

3.0610642566751234 1.6239081019411896 4.2171798726059277

Ti O

4 6

Direct

0.3437001333189599 0.3437006083189602 0.3437003373189626

0.1562995956810355 0.1562996046810398 0.1562996026810396

0.6562999316810348 0.6562999756810385 0.6562994016810336

0.8437003593189644 0.8437006203189611 0.8437006903189669

0.9352501198109636 0.5647498731890394 0.2499999209999970

0.5647500341890349 0.2499998400000010 0.9352498258109606

0.2499998850000011 0.9352504138109666 0.5647499251890366

0.0647502771890374 0.4352498778109647 0.7500002170000002

0.4352499328109657 0.7500004070000017 0.0647501121890344

0.7500004540000020 0.0647501801890400 0.4352497858109642

4. Ti_2O_3 PBEsol U=3

Ti4 O6

1.00000000000000

5.4399007184043562 -0.0016528807938532 -0.0011411752877801

2.9848474874807880 4.5478795096712599 -0.0011411752875760

2.9848464284518750 1.6107055053492030 4.2530956146294567

Ti O

4 6

Direct

0.3427942868178331 0.3427945928178371 0.3427944398178351

0.1572055691821691 0.1572054591821671 0.1572055581821647

0.6572059871821683 0.6572057781821687 0.6572054711821682

0.8427944568178329 0.8427946828178303 0.8427951138178340

0.9343294244215328 0.5656707495784674 0.2499998999999988

0.5656712935784698 0.2499996940000031 0.9343287934215267

0.2499998669999997 0.9343289934215291 0.5656712285784680

0.0656715295784681 0.4343285984215283 0.7500005189999968

0.4343287954215268 0.7500003870000000 0.0656713435784740

0.7499999269999975 0.0656713415784739 0.4343287104215304

5. Ti_2O_3 PBEsol U=4

Ti4 O6

1.00000000000000

5.4334430732223202 -0.0007976099546275 -0.0005531206441553

2.9315567769540056 4.5747436135183728 -0.0005531206442028

2.9315583091404851 1.6029634969998634 4.2847145148939241

Ti O

4 6

Direct

0.3424327826993722 0.3424330126993699 0.3424330096993732

0.1575670913006316 0.1575670163006289 0.1575671253006273

0.6575674993006299 0.6575672913006269 0.6575670073006247

0.8424329696993699 0.8424333866993724 0.8424332846993711

0.9342825119310670 0.5657175640689321 0.2499998990000023

0.5657181320689294 0.2499997279999988 0.9342821169310663

0.2499996900000028 0.9342821809310716 0.5657183430689291

0.0657181680689323 0.4342819049310702 0.7500007060000016

0.4342823229310693 0.7500003299999989 0.0657181530689346

0.7500002210000005 0.0657180900689330 0.4342820659310658

6. Ti_2O_3 PBEsol U=6

Ti4 O6

1.00000000000000

5.4363960045795681 0.0022380481373034 0.0015626690242016

2.8593052092985305 4.6237193088848283 0.0015626690238983

2.8593067570147030 1.5944440122869035 4.3401062363304312

Ti O

4 6

Direct

0.3424307268039963 0.3424309358039958 0.3424309688039950

0.1575691641960054 0.1575690691960082 0.1575692151960061

0.6575696441960095 0.6575692911960052 0.6575690691960081

0.8424308468039921 0.8424313178039919 0.8424312648039911

0.9348931415645642 0.5651069104354330 0.2499998990000023

0.5651074574354321 0.2499996829999986 0.9348928205645625

0.2499997039999968 0.9348926075645626 0.5651077334354336

0.0651075054354363 0.4348924655645648 0.7500008020000024

0.4348928515645612 0.7500003239999984 0.0651075564354370

0.7500001619999992 0.0651074684354368 0.4348927465645632

7. Ti_2O_3 PBEsol-D3 U=0

Ti4 O6

1.00000000000000

5.4294943809999996 0.0000000000000000 0.0000000000000000

3.1133676909000001 4.4481851190999997 0.0000000000000000

3.1133676909000001 1.6211002490999999 4.1422680786999999

Ti O

4 6

Direct

0.3456154570000010 0.3456155630000026 0.3456156120000031

0.1543844230000033 0.1543844130000025 0.1543843859999967

0.6543839539999965 0.6543842629999972 0.6543845850000025

0.8456159710000009 0.8456154539999972 0.8456156250000006

0.9375987129999999 0.5624011729999978 0.2499999489999993

0.5624010559999988 0.2500000349999993 0.9375987769999981

0.2500001040000015 0.9375986670000032 0.5624012019999967

0.0624011519999996 0.4375985880000002 0.7500001339999969

0.4375992089999983 0.7499999389999985 0.0624011609999968

0.7500000200000017 0.0624011780000018 0.4375986499999982

8. Ti_2O_3 PBEsol-D3 U=1

Ti4 O6

1.00000000000000

5.4243292809000003 0.0000000000000000 0.0000000000000000

3.0416944504000001 4.4912629645999997 0.0000000000000000

3.0416944504000001 1.6136323342000001 4.1913761114000003

Ti O

4 6

Direct

0.3438728029999965 0.3438732779999967 0.3438730069999991

0.1561269259999989 0.1561269350000032 0.1561269330000030

0.6561272619999983 0.6561273060000019 0.6561267319999970

0.8438730499999991 0.8438733099999993 0.8438733030000023

0.9346486880000029 0.5653512820000017 0.2499999209999970

0.5653514660000027 0.2499998930000018 0.9346483639999974

0.2499999140000000 0.9346490579999980 0.5653513869999998

0.0653517590000021 0.4346484360000034 0.7500001599999990

0.4346484710000027 0.7500004070000017 0.0653515739999975

0.7500004640000029 0.0653516530000005 0.4346482959999989

9. Ti_2O_3 PBEsol-D3 U=2

Ti4 O6

1.00000000000000

5.4243292809000003 0.0000000000000000 0.0000000000000000

3.0416944504000001 4.4912629645999997 0.0000000000000000

3.0416944504000001 1.6136323342000001 4.1913761114000003

Ti O

4 6

Direct

0.3438728029999965 0.3438732779999967 0.3438730069999991

0.1561269259999989 0.1561269350000032 0.1561269330000030

0.6561272619999983 0.6561273060000019 0.6561267319999970

0.8438730499999991 0.8438733099999993 0.8438733030000023

0.9346486880000029 0.5653512820000017 0.2499999209999970

0.5653514660000027 0.2499998930000018 0.9346483639999974

0.2499999140000000 0.9346490579999980 0.5653513869999998

0.0653517590000021 0.4346484360000034 0.7500001599999990

0.4346484710000027 0.7500004070000017 0.0653515739999975

0.7500004640000029 0.0653516530000005 0.4346482959999989

10. Ti_2O_3 PBEsol-D3 U=3

Ti4 O6

1.00000000000000

5.4080031974775018 -0.0130688330168708 -0.0090055760720658

2.9796361468976977 4.5131405707170336 -0.0090055760721928

2.9796350979098336 1.5986109013787804 4.2205387941581103

Ti O

4 6

Direct

0.3430037870810937 0.3430040920810941 0.3430038890810951

0.1569960909189033 0.1569959789189012 0.1569960689189015

0.6569965129189028 0.6569963429189030 0.6569959429189054

0.8430039500810964 0.8430042160810971 0.8430045120811003

0.9335776354012127 0.5664225365987873 0.2499998870000013

0.5664231265987864 0.2499997629999982 0.9335769124012133

0.2499999560000035 0.9335772484012127 0.5664229775987847

0.0664233025987867 0.4335768724012171 0.7500004529999984

0.4335770154012183 0.7500004429999976 0.0664231175987820

0.7499999939999995 0.0664231265987863 0.4335769114012168

11. Ti_2O_3 PBEsol-D3 U=4

Ti4 O6

1.00000000000000

5.4005017281000001 0.0000000000000000 0.0000000000000000

2.9144510441000002 4.5465804761999999 0.0000000000000000

2.9144525576000002 1.5936101455000000 4.2581441859000000

Ti O

4 6

Direct

0.3426854120000016 0.3426856789999988 0.3426856230000013

0.1573144780000035 0.1573144030000009 0.1573145119999992

0.6573149049999998 0.6573146969999968 0.6573143379999991

0.8426855829999980 0.8426860000000005 0.8426858979999992

0.9335881089999987 0.5664119670000005 0.2499998990000023

0.5664125549999994 0.2499997480000005 0.9335876580000004

0.2499996900000028 0.9335877780000033 0.5664127459999975

0.0664125899999988 0.4335875220000034 0.7500006499999969

0.4335879200000008 0.7500003299999989 0.0664125560000031

0.7500003190000015 0.0664125030000022 0.4335876350000021

12. Ti_2O_3 PBEsol-D3 U=6

Ti4 O6

1.00000000000000

5.6212225725637550 -0.0003204180604673 -0.0002179030404288

3.2663941973264299 4.5748018822344862 -0.0002179030404364

3.2663936431801330 1.6812220375613252 4.2546795023393162

Ti O

4 6

Direct

0.3517274588797734 0.3517278208797749 0.3517279588797721

0.1482721911202261	0.1482721561202268	0.1482723321202271
0.6482725691202289	0.6482722661202287	0.6482722591202246
0.8517277898797759	0.8517282418797707	0.8517284598797745
0.9508552520878701	0.5491449609121297	0.2499998859999977
0.5491450459121332	0.2499996139999965	0.9508552690878680
0.2499993260000011	0.9508550480878675	0.5491453949121301
0.0491451809121338	0.4508548580878730	0.7500007800000006
0.4508549770878722	0.7500003019999966	0.0491452749121273
0.7500000750000027	0.0491451649121324	0.4508550470878709

Table S4. Optimized geometries for Ti_2O_3 with different U values.

Method		*PBEsol*			*PBEsol- D3*	
Hubbard U value	*a(Å)*	*α(°)*	*Vol(Å³)*	*a(Å)*	*α(°)*	*Vol(Å³)*
0	5.46	54.98	100.04	5.43	55.01	100.04
1	5.43	55.01	101.90	5.43	55.31	101.04
2	5.46	55.88	104.01	5.42	55.89	102.11
3	5.44	56.74	105.26	5.41	56.71	103.33
4	5.43	57.36	106.52	5.40	57.34	104.55
6	5.44	58.24	109.04	5.40	58.29	107.02
Experimental value	5.43	56.58	104.32	5.43	56.58	104.32

IV. **Calculation parameters**

INCAR TiO_2 U=3

Full optimization after preoptimization by following the procedure described in section I.

Basic setup:

ISPIN = 2

ISTART = 1

ICHARG = 1

Accuracy controls:

PREC = Accurate

```
# Electronic loop controls:
 ALGO = Fast
 EDIFF = 0.000001
 ENCUT = 600
 NELM = 200
 NELMIN = 5
 NELMDL = -10
 MAXMIX = -100
 ISMEAR = 0
 SIGMA = 0.05

# Relaxation control:
 IBRION = 1    # Conjugate gradients
 NSW = 50
 ISIF = 3     # Ions
 EDIFFG = -0.01

# Properties:
 LCHARG = .TRUE.
 LWAVE = .TRUE.
 LELF = .FALSE.
 LVTOT = .FALSE.
 LVHAR = .FALSE.
 GGA = PS
 LDAU = .TRUE.

# HUBBARD
 LDAUU = 3.00 0.00
 LDAUJ = 0.00 0.00
 LDAUL = 2    -1
 LDAUPRINT = 1
```

LMAXMIX = 4

LASPH = .TRUE.

V. TiO2 (001) anatase surface

Ti O

1.00000000000000

15.2136999999999993 0.0000000000000000 0.0000000000000000

0.0000000000000000 15.2136999999999993 0.0000000000000000

0.0000000000000000 0.0000000000000000 29.0000000000000000

Ti O

64 128

Selective dynamics

Direct

0.0000000000000000 0.0000000000000000 0.2750532313799594 T T T

0.0000000000000000 0.2499998170000026 0.2750532313799594 T T T

0.0000000000000000 0.4999996339999981 0.2750532313799594 T T T

-0.0000000000000000 0.7499994499999971 0.2750532313799594 T T T

0.2499998170000026 -0.0000000000000000 0.2750532313799594 T T T

0.2499998170000026 0.2499998170000026 0.2750532313799594 T T T

0.2499998170000026 0.4999996339999981 0.2750532313799594 T T T

0.2499998170000026 0.7499994499999971 0.2750532313799594 T T T

0.4999996339999981 0.0000000000000000 0.2750532313799594 T T T

0.4999996339999981 0.2499998170000026 0.2750532313799594 T T T

0.4999996339999981 0.4999996339999981 0.2750532313799594 T T T

0.4999996339999981 0.7499994499999971 0.2750532313799594 T T T

0.7499994499999971 -0.0000000000000000 0.2750532313799594 T T T

0.7499994499999971 0.2499998170000026 0.2750532313799594 T T T

0.7499994499999971 0.4999996339999981 0.2750532313799594 T T T

0.7499994499999971 0.7499994499999971 0.2750532313799594 T T T

0.1249999079999995 0.1249999079999995 0.1119448770623885 T T T

0.1249999079999995 0.3749997250000021 0.1119448770623885 T T T

0.1249999079999995	0.6249995419999976	0.1119448770623885	T	T	T
0.1249999079999995	0.8749993590000003	0.1119448770623885	T	T	T
0.3749997250000021	0.1249999079999995	0.1119448770623885	T	T	T
0.3749997250000021	0.3749997250000021	0.1119448770623885	T	T	T
0.3749997250000021	0.6249995419999976	0.1119448770623885	T	T	T
0.3749997250000021	0.8749993590000003	0.1119448770623885	T	T	T
0.6249995419999976	0.1249999079999995	0.1119448770623885	T	T	T
0.6249995419999976	0.3749997250000021	0.1119448770623885	T	T	T
0.6249995419999976	0.6249995419999976	0.1119448770623885	T	T	T
0.6249995419999976	0.8749993590000003	0.1119448770623885	T	T	T
0.8749993590000003	0.1249999079999995	0.1119448770623885	T	T	T
0.8749993590000003	0.3749997250000021	0.1119448770623885	T	T	T
0.8749993590000003	0.6249995419999976	0.1119448770623885	T	T	T
0.8749993590000003	0.8749993590000003	0.1119448770623885	T	T	T
0.0000000000000000	0.1249999079999995	0.0301591937929970	F	F	F
0.0000000000000000	0.3749997250000021	0.0301591937929970	F	F	F
0.0000000000000000	0.6249995419999976	0.0301591937929970	F	F	F
0.0000000000000000	0.8749993590000003	0.0301591937929970	F	F	F
0.2499998170000026	0.1249999079999995	0.0301591937929970	F	F	F
0.2499998170000026	0.3749997250000021	0.0301591937929970	F	F	F
0.2499998170000026	0.6249995419999976	0.0301591937929970	F	F	F
0.2499998170000026	0.8749993590000003	0.0301591937929970	F	F	F
0.4999996339999981	0.1249999079999995	0.0301591937929970	F	F	F
0.4999996339999981	0.3749997250000021	0.0301591937929970	F	F	F
0.4999996339999981	0.6249995419999976	0.0301591937929970	F	F	F
0.4999996339999981	0.8749993590000003	0.0301591937929970	F	F	F
0.7499994499999971	0.1249999079999995	0.0301591937929970	F	F	F
0.7499994499999971	0.3749997250000021	0.0301591937929970	F	F	F
0.7499994499999971	0.6249995419999976	0.0301591937929970	F	F	F
0.7499994499999971	0.8749993590000003	0.0301591937929970	F	F	F
0.1249999079999995	0.0000000000000000	0.1944816089138053	T	T	T
0.1249999079999995	0.2499998170000026	0.1944816089138053	T	T	T

0.1249999079999995	0.4999996339999981	0.1944816089138053	T	T	T
0.1249999079999995	0.7499994499999971	0.1944816089138053	T	T	T
0.3749997250000021	-0.0000000000000000	0.1944816089138053	T	T	T
0.3749997250000021	0.2499998170000026	0.1944816089138053	T	T	T
0.3749997250000021	0.4999996339999981	0.1944816089138053	T	T	T
0.3749997250000021	0.7499994499999971	0.1944816089138053	T	T	T
0.6249995419999976	0.0000000000000000	0.1944816089138053	T	T	T
0.6249995419999976	0.2499998170000026	0.1944816089138053	T	T	T
0.6249995419999976	0.4999996339999981	0.1944816089138053	T	T	T
0.6249995419999976	0.7499994499999971	0.1944816089138053	T	T	T
0.8749993590000003	-0.0000000000000000	0.1944816089138053	T	T	T
0.8749993590000003	0.2499998170000026	0.1944816089138053	T	T	T
0.8749993590000003	0.4999996339999981	0.1944816089138053	T	T	T
0.8749993590000003	0.7499994499999971	0.1944816089138053	T	T	T
0.0000000000000000	0.0000000000000000	0.0167046872410026	F	F	F
0.0000000000000000	0.2499998170000026	0.0167046872410026	F	F	F
0.0000000000000000	0.4999996339999981	0.0167046872410026	F	F	F
0.0000000000000000	0.7499994499999971	0.0167046872410026	F	F	F
0.2499998170000026	0.0000000000000000	0.0167046872410026	F	F	F
0.2499998170000026	0.2499998170000026	0.0167046872410026	F	F	F
0.2499998170000026	0.4999996339999981	0.0167046872410026	F	F	F
0.2499998170000026	0.7499994499999971	0.0167046872410026	F	F	F
0.4999996339999981	0.0000000000000000	0.0167046872410026	F	F	F
0.4999996339999981	0.2499998170000026	0.0167046872410026	F	F	F
0.4999996339999981	0.4999996339999981	0.0167046872410026	F	F	F
0.4999996339999981	0.7499994499999971	0.0167046872410026	F	F	F
0.7499994499999971	0.0000000000000000	0.0167046872410026	F	F	F
0.7499994499999971	0.2499998170000026	0.0167046872410026	F	F	F
0.7499994499999971	0.4999996339999981	0.0167046872410026	F	F	F
0.7499994499999971	0.7499994499999971	0.0167046872410026	F	F	F
0.1249999079999995	0.1249999079999995	0.1803623868732818	T	T	T
0.1249999079999995	0.3749997250000021	0.1803623868732818	T	T	T

0.1249999079999995	0.6249995419999976	0.1803623868732818	T	T	T
0.1249999079999995	0.8749993590000003	0.1803623868732818	T	T	T
0.3749997250000021	0.1249999079999995	0.1803623868732818	T	T	T
0.3749997250000021	0.3749997250000021	0.1803623868732818	T	T	T
0.3749997250000021	0.6249995419999976	0.1803623868732818	T	T	T
0.3749997250000021	0.8749993590000003	0.1803623868732818	T	T	T
0.6249995419999976	0.1249999079999995	0.1803623868732818	T	T	T
0.6249995419999976	0.3749997250000021	0.1803623868732818	T	T	T
0.6249995419999976	0.6249995419999976	0.1803623868732818	T	T	T
0.6249995419999976	0.8749993590000003	0.1803623868732818	T	T	T
0.8749993590000003	0.1249999079999995	0.1803623868732818	T	T	T
0.8749993590000003	0.3749997250000021	0.1803623868732818	T	T	T
0.8749993590000003	0.6249995419999976	0.1803623868732818	T	T	T
0.8749993590000003	0.8749993590000003	0.1803623868732818	T	T	T
0.0000000000000000	0.1249999079999995	0.0985879896550017	F	F	F
0.0000000000000000	0.3749997250000021	0.0985879896550017	F	F	F
0.0000000000000000	0.6249995419999976	0.0985879896550017	F	F	F
0.0000000000000000	0.8749993590000003	0.0985879896550017	F	F	F
0.2499998170000026	0.1249999079999995	0.0985879896550017	F	F	F
0.2499998170000026	0.3749997250000021	0.0985879896550017	F	F	F
0.2499998170000026	0.6249995419999976	0.0985879896550017	F	F	F
0.2499998170000026	0.8749993590000003	0.0985879896550017	F	F	F
0.4999996339999981	0.1249999079999995	0.0985879896550017	F	F	F
0.4999996339999981	0.3749997250000021	0.0985879896550017	F	F	F
0.4999996339999981	0.6249995419999976	0.0985879896550017	F	F	F
0.4999996339999981	0.8749993590000003	0.0985879896550017	F	F	F
0.7499994499999971	0.1249999079999995	0.0985879896550017	F	F	F
0.7499994499999971	0.3749997250000021	0.0985879896550017	F	F	F
0.7499994499999971	0.6249995419999976	0.0985879896550017	F	F	F
0.7499994499999971	0.8749993590000003	0.0985879896550017	F	F	F
0.1249999079999995	0.0000000000000000	0.2624964526750593	T	T	T
0.1249999079999995	0.2499998170000026	0.2624964526750593	T	T	T

0.1249999079999995	0.4999996339999981	0.2624964526750593	T	T	T
0.1249999079999995	0.7499994499999971	0.2624964526750593	T	T	T
0.3749997250000021	-0.0000000000000000	0.2624964526750593	T	T	T
0.3749997250000021	0.2499998170000026	0.2624964526750593	T	T	T
0.3749997250000021	0.4999996339999981	0.2624964526750593	T	T	T
0.3749997250000021	0.7499994499999971	0.2624964526750593	T	T	T
0.6249995419999976	-0.0000000000000000	0.2624964526750593	T	T	T
0.6249995419999976	0.2499998170000026	0.2624964526750593	T	T	T
0.6249995419999976	0.4999996339999981	0.2624964526750593	T	T	T
0.6249995419999976	0.7499994499999971	0.2624964526750593	T	T	T
0.8749993590000003	0.0000000000000000	0.2624964526750593	T	T	T
0.8749993590000003	0.2499998170000026	0.2624964526750593	T	T	T
0.8749993590000003	0.4999996339999981	0.2624964526750593	T	T	T
0.8749993590000003	0.7499994499999971	0.2624964526750593	T	T	T
0.1249999079999995	-0.0000000000000000	0.1260453038172506	T	T	T
0.1249999079999995	0.2499998170000026	0.1260453038172506	T	T	T
0.1249999079999995	0.4999996339999981	0.1260453038172506	T	T	T
0.1249999079999995	0.7499994499999971	0.1260453038172506	T	T	T
0.3749997250000021	-0.0000000000000000	0.1260453038172506	T	T	T
0.3749997250000021	0.2499998170000026	0.1260453038172506	T	T	T
0.3749997250000021	0.4999996339999981	0.1260453038172506	T	T	T
0.3749997250000021	0.7499994499999971	0.1260453038172506	T	T	T
0.6249995419999976	-0.0000000000000000	0.1260453038172506	T	T	T
0.6249995419999976	0.2499998170000026	0.1260453038172506	T	T	T
0.6249995419999976	0.4999996339999981	0.1260453038172506	T	T	T
0.6249995419999976	0.7499994499999971	0.1260453038172506	T	T	T
0.8749993590000003	0.0000000000000000	0.1260453038172506	T	T	T
0.8749993590000003	0.2499998170000026	0.1260453038172506	T	T	T
0.8749993590000003	0.4999996339999981	0.1260453038172506	T	T	T
0.8749993590000003	0.7499994499999971	0.1260453038172506	T	T	T
-0.0000000000000000	0.1249999079999995	0.2916580201061817	T	T	T
0.0000000000000000	0.3749997250000021	0.2916580201061817	T	T	T

0.0000000000000000	0.6249995419999976	0.2916580201061817	T	T	T
-0.0000000000000000	0.8749993590000003	0.2916580201061817	T	T	T
0.2499998170000026	0.1249999079999995	0.2916580201061817	T	T	T
0.2499998170000026	0.3749997250000021	0.2916580201061817	T	T	T
0.2499998170000026	0.6249995419999976	0.2916580201061817	T	T	T
0.2499998170000026	0.8749993590000003	0.2916580201061817	T	T	T
0.4999996339999981	0.1249999079999995	0.2916580201061817	T	T	T
0.4999996339999981	0.3749997250000021	0.2916580201061817	T	T	T
0.4999996339999981	0.6249995419999976	0.2916580201061817	T	T	T
0.4999996339999981	0.8749993590000003	0.2916580201061817	T	T	T
0.7499994499999971	0.1249999079999995	0.2916580201061817	T	T	T
0.7499994499999971	0.3749997250000021	0.2916580201061817	T	T	T
0.7499994499999971	0.6249995419999976	0.2916580201061817	T	T	T
0.7499994499999971	0.8749993590000003	0.2916580201061817	T	T	T
0.1249999079999995	0.1249999079999995	0.0436137220689972	F	F	F
0.1249999079999995	0.3749997250000021	0.0436137220689972	F	F	F
0.1249999079999995	0.6249995419999976	0.0436137220689972	F	F	F
0.1249999079999995	0.8749993590000003	0.0436137220689972	F	F	F
0.3749997250000021	0.1249999079999995	0.0436137220689972	F	F	F
0.3749997250000021	0.3749997250000021	0.0436137220689972	F	F	F
0.3749997250000021	0.6249995419999976	0.0436137220689972	F	F	F
0.3749997250000021	0.8749993590000003	0.0436137220689972	F	F	F
0.6249995419999976	0.1249999079999995	0.0436137220689972	F	F	F
0.6249995419999976	0.3749997250000021	0.0436137220689972	F	F	F
0.6249995419999976	0.6249995419999976	0.0436137220689972	F	F	F
0.6249995419999976	0.8749993590000003	0.0436137220689972	F	F	F
0.8749993590000003	0.1249999079999995	0.0436137220689972	F	F	F
0.8749993590000003	0.3749997250000021	0.0436137220689972	F	F	F
0.8749993590000003	0.6249995419999976	0.0436137220689972	F	F	F
0.8749993590000003	0.8749993590000003	0.0436137220689972	F	F	F
-0.0000000000000000	0.0000000000000000	0.2082683807298407	T	T	T
-0.0000000000000000	0.2499998170000026	0.2082683807298407	T	T	T

0.0000000000000000 0.4999996339999981 0.2082683807298407 T T T

0.0000000000000000 0.7499994499999971 0.2082683807298407 T T T

0.2499998170000026 0.0000000000000000 0.2082683807298407 T T T

0.2499998170000026 0.2499998170000026 0.2082683807298407 T T T

0.2499998170000026 0.4999996339999981 0.2082683807298407 T T T

0.2499998170000026 0.7499994499999971 0.2082683807298407 T T T

0.4999996339999981 0.0000000000000000 0.2082683807298407 T T T

0.4999996339999981 0.2499998170000026 0.2082683807298407 T T T

0.4999996339999981 0.4999996339999981 0.2082683807298407 T T T

0.4999996339999981 0.7499994499999971 0.2082683807298407 T T T

0.7499994499999971 -0.0000000000000000 0.2082683807298407 T T T

0.7499994499999971 0.2499998170000026 0.2082683807298407 T T T

0.7499994499999971 0.4999996339999981 0.2082683807298407 T T T

0.7499994499999971 0.7499994499999971 0.2082683807298407 T T T

VI. Geometries comparison

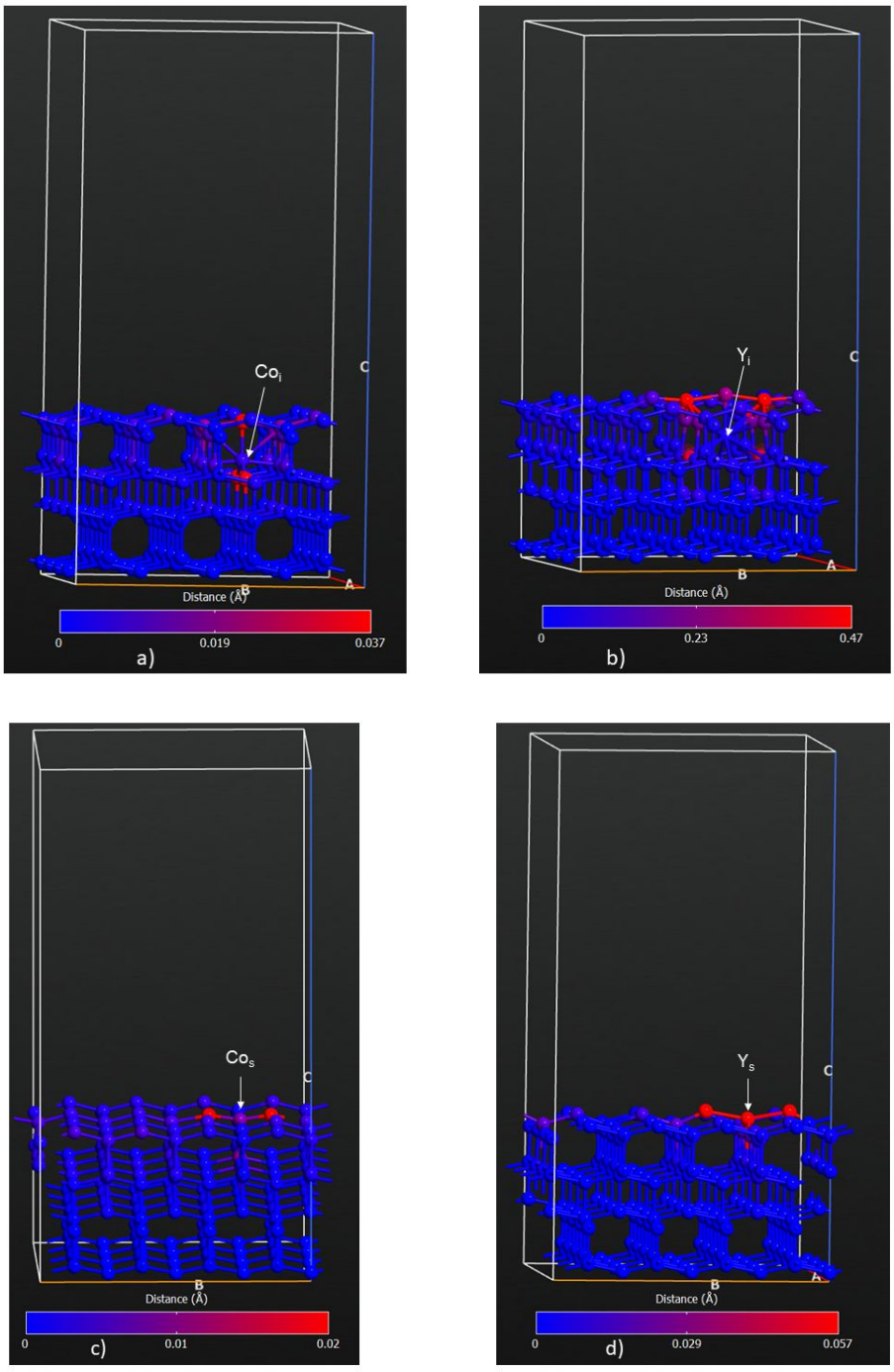

Figure S3. Geometries comparison between U=0 and U=3 optimized geometries for cobalt and yttrium interstitially doped (a and b, respectively) TiO_2 (001) anatase surface. The substitutional Co and Y doped structures are shown in c and d. Red in the color gradient and in the TiO_2 surface shows the highest change in the bond distances.

VII. CO_2 adsorption energy over the TiO_2(001) anatase surface

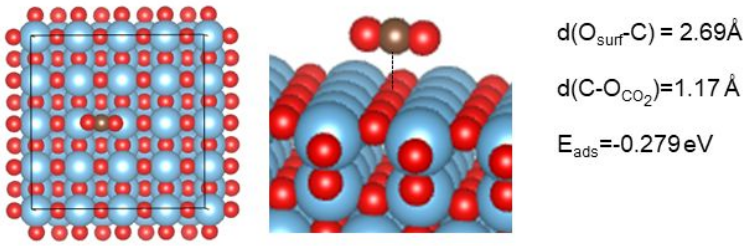

Figure S4. Adsorption of a CO_2 molecule over a TiO_2 (001) surface, some geometry parameters are presented.

The adsorption energy (E_{ads}) of a CO_2 molecule over a TiO_2 (001) surface was computed at PBEsol-D3(BJ) with U=3 in a similar configuration as that reported by Araujo et al.[1] The adsorption energy is in agreement with that previously reported by Araujo et al.[1] and Huygh et al.[2]

VIII. DOS plot of the pristine TiO_2(001) anatase

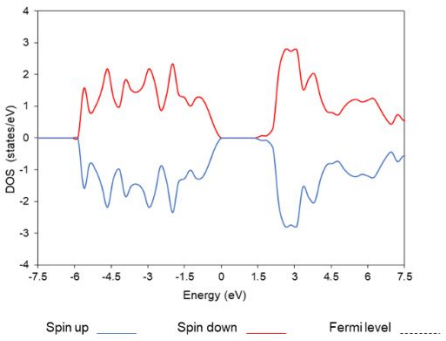

Figure S5. Density of states plot of the TiO_2 (001) anatase pristine surface.

References

(1) Araujo-Lopez, E.; Varilla, L. A.; Seriani, N.; Montoya, J. A. TiO2 Anatase's Bulk and (001) Surface, Structural and Electronic Properties: A DFT Study on the Importance of Hubbard and van Der Waals Contributions. *Surf. Sci.* **2016**, *653*, 187–196. https://doi.org/10.1016/j.susc.2016.07.003.

(2) Huygh, S.; Bogaerts, A.; Neyts, E. C. How Oxygen Vacancies Activate CO2 Dissociation on TiO2 Anatase (001). *J. Phys. Chem. C* **2016**, *120* (38), 21659–21669. https://doi.org/10.1021/acs.jpcc.6b07459.