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

Theoretical Investigation of CH-Bond Activation by photocatalytic excited SO_2 and Effects of (C-, N-, S-, Se-) doped TiO_2

Supporting Information

Luca Gerhards, Thorsten Klüner*

Institute of Chemistry, Carl-von-Ossietzky University of Oldenburg, Carl-von-Ossietzky
Strasse 9-11, D-26129 Oldenburg, Germany

S1 Lattice Parameter for Periodic Boundary Condition

Table s1-1 Calculated lattice parameters of the TiO_2-rutile and -anatase unit cell. (PBE0/POB_TZVP)

Modification	Lattice parameter	PBE0	Experiment
Rutile	a, b [Å]	4.594	4.594[1] | 4.587[2]
	c [Å]	2.959	2.953[1] | 2.954[2]
	α, β, γ [°]	90.000	90.000 | 90.000
	E_{gap} [eV]	3.92	3.03[3]
Anatase	a, b [Å]	3.748	3.785[4] | 3.765[5]
	c [Å]	9.674	9.514[4] | 9.545[5]
	α, β, γ [°]	90.000	90.000
	E_{gap}	4.26	3.2[6]

S2 Construction of Cluster Model

The modeling of embedded clusters has made significant progress in the last 30 years. Usually a stoichiometric free cluster is used, which is placed over a boundary region in an embedding potential. The embedding potential can be described by various approaches such as a point charge field (PCF) or a molecular mechanics region (MM). [7-10] The boundary region is usually defined by effective core potentials (ECP) to prevent overpolarization of the electron density.[10] These approaches work well for the description of adsorption energies of closed-shell molecules. However, problems arise when open-shell molecules or excited states are considered. Between the boundary region and the stoichiometric cluster, dangling bonds form at the under-coordinated atoms on the cluster. These lead to energetically artificial and unfavorable states that cause problems such as non-convergence or local spin-density at the edge of the cluster. [8] In figure s2-1, an example of two embedded stoichiometric cluster models is shown for rutile[110] ($Ti_{37}O_{74}$) and anatase[101] ($Ti_{42}O_{84}$).

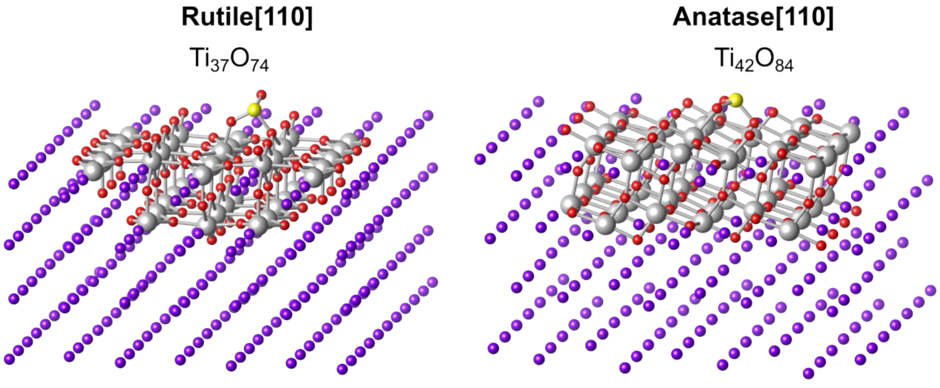


Figure s2-1 Stoichiometric embedded cluster model for rutile[110] and anatase[101]. The cluster models were embedded in a point charge field of ~21700 point charges. (Colour scheme: red – oxygen, grey – titanium, yellow – sulfur, dark violet – effective core potential)

Here, the adsorption energy and geometry agrees well with the periodic boundary conditions (PBC) (table s2-1). However, if higher spin multiplicities or an unrestricted Hartree-Fock singlet state are calculated, it becomes apparent that radicals are formed at the edge of the cluster that are energetically more stable than the closed-shell solution. (table s2-2).

Table s2-1 Comparison of stoichiometric cluster models with periodic boundary condition (PBC) calculations regarding bond length and adsorption energy E_{ads} on PBE0 level (No BSSE correction).

Model	S─(Br-O) [Å]	O_{SO2}─Ti [Å]	O_{SO2}─S [Å]	E_{ads} [eV]
Rutile[110] – PBC(2x2)	1.754	1.878	1.496 / 1.629	-1.08
Rutile[110] – Cluster	1.666	1.866	1.406 / 1.548	-0.94
Anatase[101] – PBC(2x2)	1.668	2.030	1.579 / 1.579	-1.45
Anatase[101 - Cluster	1.655	2.076	1.491 / 1.489	-1.50

When calculating excited states using CASSCF, the same artificial problems arise leading to unphysical excitation energies. In table s2-3, two examples of a state-averaged CAS active space for both cluster models are shown. For the rutile[110] cluster the excitation energy from the HOMO to the LUMO of the cluster is unreasonable small while for the anatase[101] cluster the "excited state" with an occupation of [1100] (each number represents one orbital and its occupation) is energetically more stable than the ground state [0200].

Table s2-2 Energies and spin contamination of different multiplicities of a stoichiometric $Ti_{37}O_{74}$ rutile[110] cluster model on Hartree-Fock level (WF 11 = wavefunction of undecet state as initial guess for singlet state).

Multiplicity	Energy [a.u.]	ΔE [eV]	Spin contamination
1 (RHF)	-41699.01545	0	-
3	-41699.32387	-8.39	0.011
11	-41699.74843	-19.95	10.006
1 (WF 11)	-41699.70992	-18.90	10.006

Table s2-3 CASSCF calculations for a stoichiometric cluster model of two state averaged states (0 – ground state, 1 – first excited state).

System	State	Occupation	ΔE [eV]
Rutile[110] SA-CAS(8,8)	0	[22220000]	-
	1	[22120010]	0.78
Anatase[101] SA-CAS(2,4)	0	[1100]	-
	1	[0200]	0.84

When considering the involved orbitals it becomes clear that the dangling bonds at the titanium centers near the boundary region play a significant role in artificial states (figure s2-2). In earlier works the same behavior could be observed, and the dangling bonds had to be included in the active space to avoid convergence problems.[8]

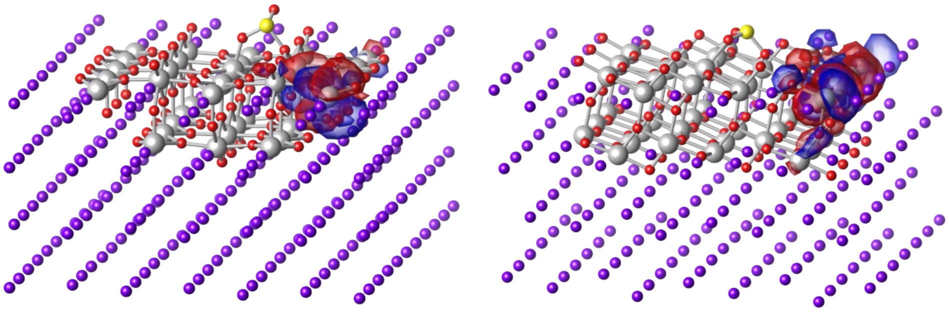


Figure s2-2 Dangling bond orbitals located at the boundary region of stoichiometric cluster models leading to artificial states in CASSCF calculation.

Therefore, in order to describe open-shell systems and electronic excitations in a more accurate way, a new cluster model has to be constructed. The saturation of dangling bonds via hydrogen-atoms or pseudo atoms has been successfully used in many works. [11-13] One disadvantage of this approach is the exclusion of long-range-Coulomb interaction of an external field like in embedding schemes. Our strategy is now to combine the saturation of dangling bonds with the inclusion of an external point charge field. For that we apply the rules given by *Casarin* et al. regarding the chemical bond situation in TiO_2 from a local point of view. [12] They stated that in the bulk of TiO_2 titanium atoms are octahedrally coordinated by six oxygen atoms and have four valence electrons to share for each bond. In conclusion Ti distributes 4/6 (2/3) electrons into each Ti-O bond. On the other hand, oxygen is trigonal planar coordinated by three titanium atoms. Because of its trigonal geometry, two of the six valence electrons of oxygen are not involved in chemical bonding and are forming a lone pair.[12] The other four electrons distribute over the three Ti-O bonds leading to an electron distribution of 4/3 electrons per bonding.[12] When summing the electron distribution of one titanium atom and one oxygen atom to a Ti-O bond two electrons per bonding arise. Respecting those rules, the construction of our cluster models can be done as follows.

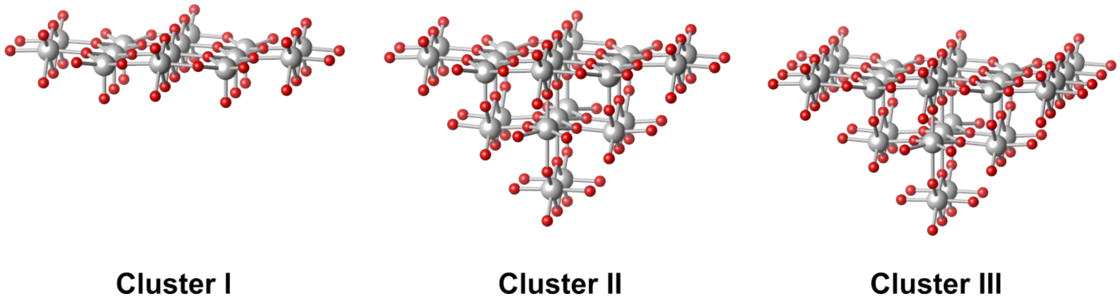


Figure s2-3 Three different cluster model sizes for charged cluster model approach. Every Ti atom (grey) except the 5f-Ti on the surface is fully coordinated by O atoms (red). (Cluster I – $Ti_{14}O_{28}[O_{20}]^{40-}$, cluster II – $Ti_{23}O_{48}[O_{30}]^{60-}$ & cluster II – $Ti_{27}O_{54}[O_{34}]^{68-}$)

The cluster model is constructed in such a way that no dangling bonds can form on Ti atoms and therefore, all titanium atoms receive their complete coordination (figure s2-3). Thus, the edges of the cluster are only surrounded by under-coordinated oxygen atoms. In order to completely electronically saturate them, the missing bond partners must be counted for all oxygen atoms. For each missing bonding partner, the cluster model receives 2/3 electrons to fill the empty cluster level. Three clusters with this approach are shown in Figure s2-3. For cluster I, this rule gives a stoichiometry of $Ti_{14}O_{28}[O_{20}]^{40-}$, where the oxygen atoms in the square brackets represent the under-coordinated edge atoms. It can be seen that this calculation introduces exactly the number of valence electrons of titanium that occur in a stoichiometric cluster of the form $Ti_{14}O_{28}[Ti_{10}O_{20}]$. It is therefore iso-valence-electronic to the stoichiometric cluster and the electronically relevant cluster levels are completely filled.

The inclusion of an external field via point charges requires a special treatment of the boundary region. In order to counter the negative charge of the cluster and the point charge field, the effective core potentials in the boundary region must have a different charge compared to their counterparts in a stoichiometric embedded cluster. For this purpose, the ECPs located directly at the cluster are charged according to the following formula:

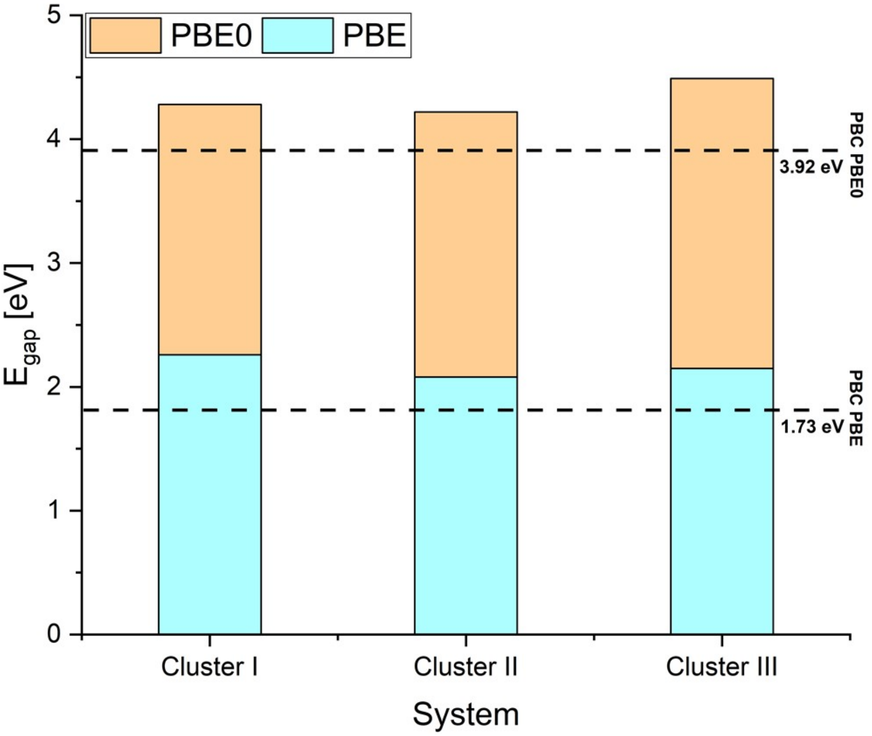
$$Z_{ECP} = \frac{|Z_{cluster} + Z_{PCF}|}{N_{ECP}} \qquad \textbf{(eq. s2-1)}$$

Here, Z_{ECP} is the charge of each ECP, $Z_{cluster}$ is the charge of the cluster, Z_{pcf} is the charge of the point charge field and N_{ECP} is the number of ECP's directly at the cluster. Thus, the system is fully neutrally charged and has both the long-range coulomb effect and the saturation of dangling bonds, respectively. A validation of these cluster models is performed in S3 and the cartesian coordinates of an example cluster can be found in section S10, table s10-1. A detailed and more general investigation of these cluster models will be provided in later works.

S3 Validation of Cluster Models

For the validation of our cluster models several properties were investigated as suggested by *Kick* and *Oberhofer*.[14] The first parameter is the correct description of the band gap. In figure s3-1 the three cluster models and their band gap using PBE0 and PBE in comparison to the periodic boundary conditions calculations are shown.

Figure s3-1 Comparison of band gap for different cluster sizes and bulk periodic boundary conditions (PBC) calculations with PBE0 and PBE. (POB_TZVP)



In all three cases, the band gap is slightly overestimated but still in reasonable agreement with periodic slab calculations. When investigating the orbitals near the band gap one can observe that the cluster models represent the electronic structure accurately (figure s3-2). Here, the HOMO of cluster I and II are highly dominated by 2p orbitals of oxygen while the LUMO is mostly populated by 3d orbitals of titanium. The same behavior can be observed in periodic calculations and literature.[14] Besides that, no artificial localization of the orbitals at on edge atoms can be found, and the contributions are distributed over the whole cluster simulating a band-like structure.

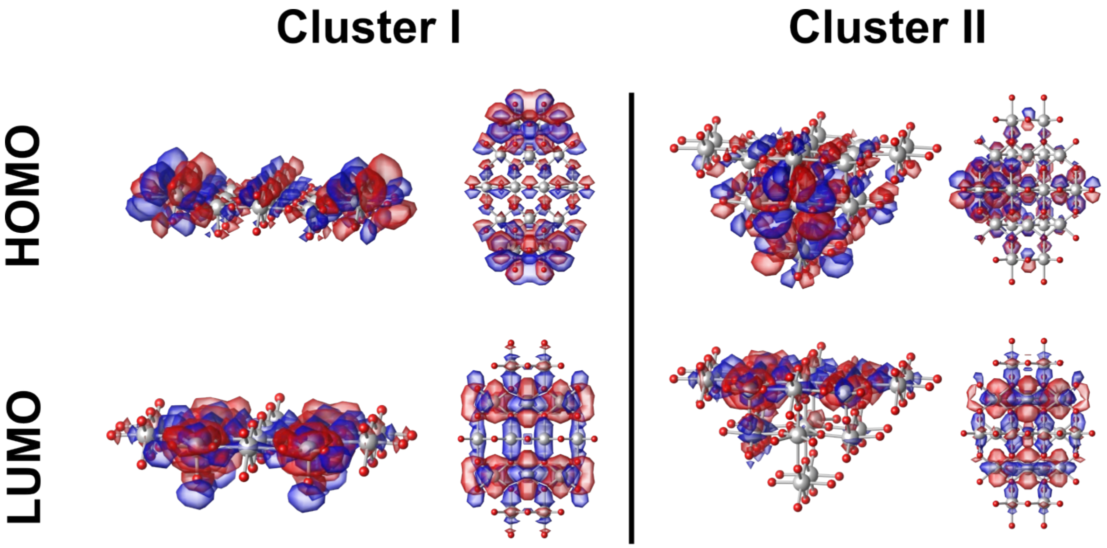


Figure s3-2 Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of cluster I and II. The HOMO is dominantly populated by 2p oxygen orbitals and the LUMO by 3d titanium orbitals. (PBE0/POB_TZVP)

The last three properties to validate are the charge distribution of the clusters, the geometrical relaxation and the control for possible dangling bonds. In Table s3-1 a comparison between the Mulliken population analysis of the PBC with the cluster models is shown. Both values are similar, and the cluster models can represent the same charge distribution as the PBC calculations. When performing geometry optimizations the cluster model atoms were relaxed excluding the edge atoms at the boundary region. The root mean square Error (*RMSE*) of the deviation after geometry optimization from the PBC geometry was calculated using the following equation:

$$RMSE = \frac{\sum_{i=1}^{N} \sqrt{\left(x_{i}^{cluster} - x_{i}^{PBC}\right)^2 + \left(y_{i}^{cluster} - y_{i}^{PBC}\right)^2 + \left(z_{i}^{cluster} - z_{i}^{PBC}\right)^2}}{N} \qquad \text{(s3-1)}$$

Here, $x_{i}^{cluster}$, $y_{i}^{cluster}$ and $z_{i}^{cluster}$ are the cartesian coordinates of the cluster after geometry optimization, x_{i}^{PBC}, y_{i}^{PBC} and z_{i}^{PBC} are the cartesian coordinates of the cluster in PBC geometry and N is the number of atoms in the cluster model, respectively. All three clusters differ only marginally from the PBC geometry and the external potential (PCF) can represent the periodic potential in an accurate way.

Table s3-1 Averaged *Mulliken* population, geometrical deviation and energetically difference between triplet and singlet ground state of cluster models in comparison to PBC calculations. Atoms at the edge are not included. For the periodic slab calculation the KS E_{gap} of the bulk is shown. (PBE0/POB-TZVP)

System	Relaxed atoms	*Mulliken* charges (Ti / O)	Geometry RMSE	$\Delta E_{Triplet\text{-}Singlet}$ [eV]
PBC (2x1)	20	+2.02 / -0.97	-	3.92
Cluster I	19	+2.08 / -0.96	0.015	3.78
Cluster II	27	+2.04 / -0.99	0.030	3.65
Cluster III	53	+2.06 / -1.10	0.021	3.77

When calculating the energy difference between the triplet and singlet state of the cluster it can be observed that in contrast to the stoichiometric cluster models no energetically more favorable triplet state can be found. Moreover the energy difference is significantly close to the Kohn-Sham band gap of bulk rutile[110] with PBE0 and periodic boundary conditions. Therefore, we can justify using this new approach for a charged surface cluster of rutile[110].

Additionally, when adsorbing SO_2 on the clusters similar electronic structures compared to the periodic slab model can be observed. Figure s3-3 illustrates the HOMO of cluster I in comparison to the crystalline orbital HOCO-1 of a periodic slab 2x2 supercell and the HOMO of SO_3^{2-} in gas phase. Significant similarities can be found leading to the conclusion that the electronic structure is described sufficient enough for further qualitative investigations.

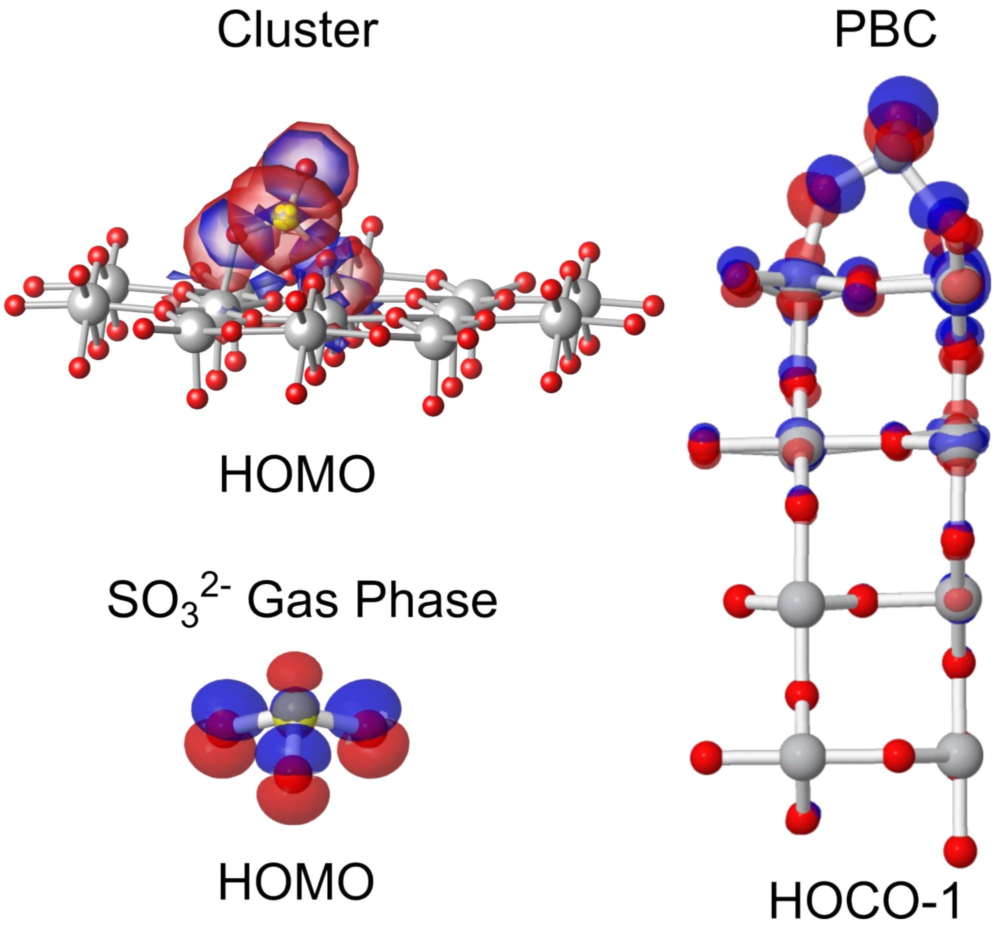


Figure s3-3 Comparison of molecular orbitals between cluster model, periodic slab model and SO$_3^{2-}$ in gas phase (HOMO = Highest occupied molecular orbital / HOCO = Highest occupied crystalline orbital).

S4 Comparison TD-DFT and triplet state geometry and CASSCF-excitations of Pristine Surface

Table s4-1 Geometrical parameter of ground state, triplet state and optimized TD-PBE0 excited state. (Cluster I/PBE0/POB_TZVP)

State	S─(Br-O) [Å]	O_{SO2}─Ti [Å]	O_{SO2}─S [Å]
Ground State	1.776	1.949	1.501 / 1.601
Triplet State	1.612	2.259	1.507 / 1.535
Excited TD-DFT State	1.622	2.169	1.513 / 1.550

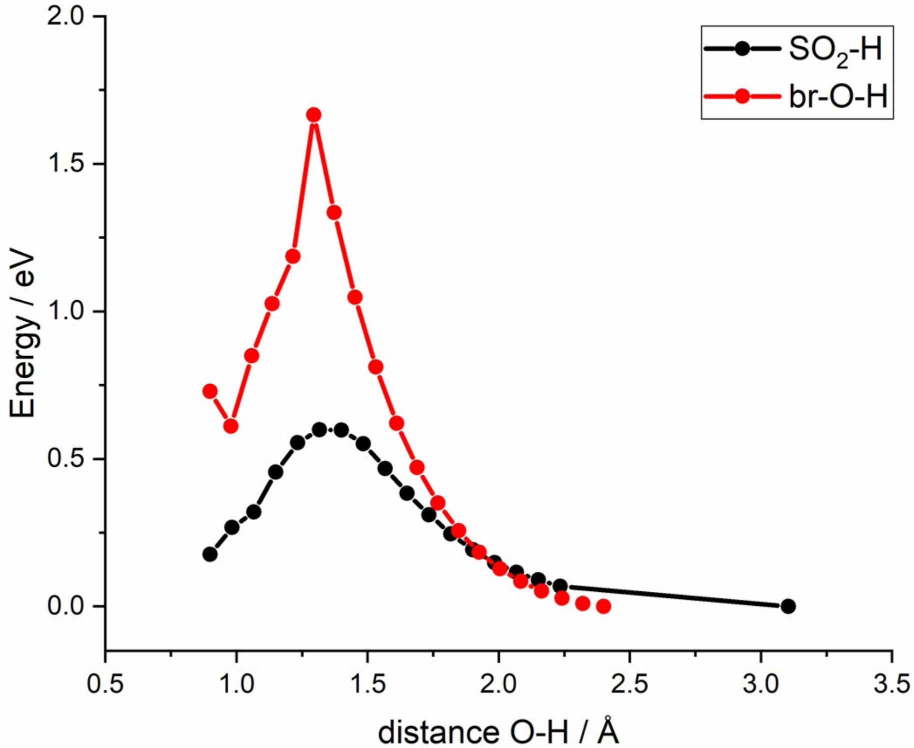


Figure s4-1 Reaction coordinate scans of triplet state system. The black curve describes the CH-bond activation via oxygen atom from adsorbed SO_2 (SO_3-like) and the red curve represents the bond activation via br-O. (Cluster I/PBE0/POB_TZVP)

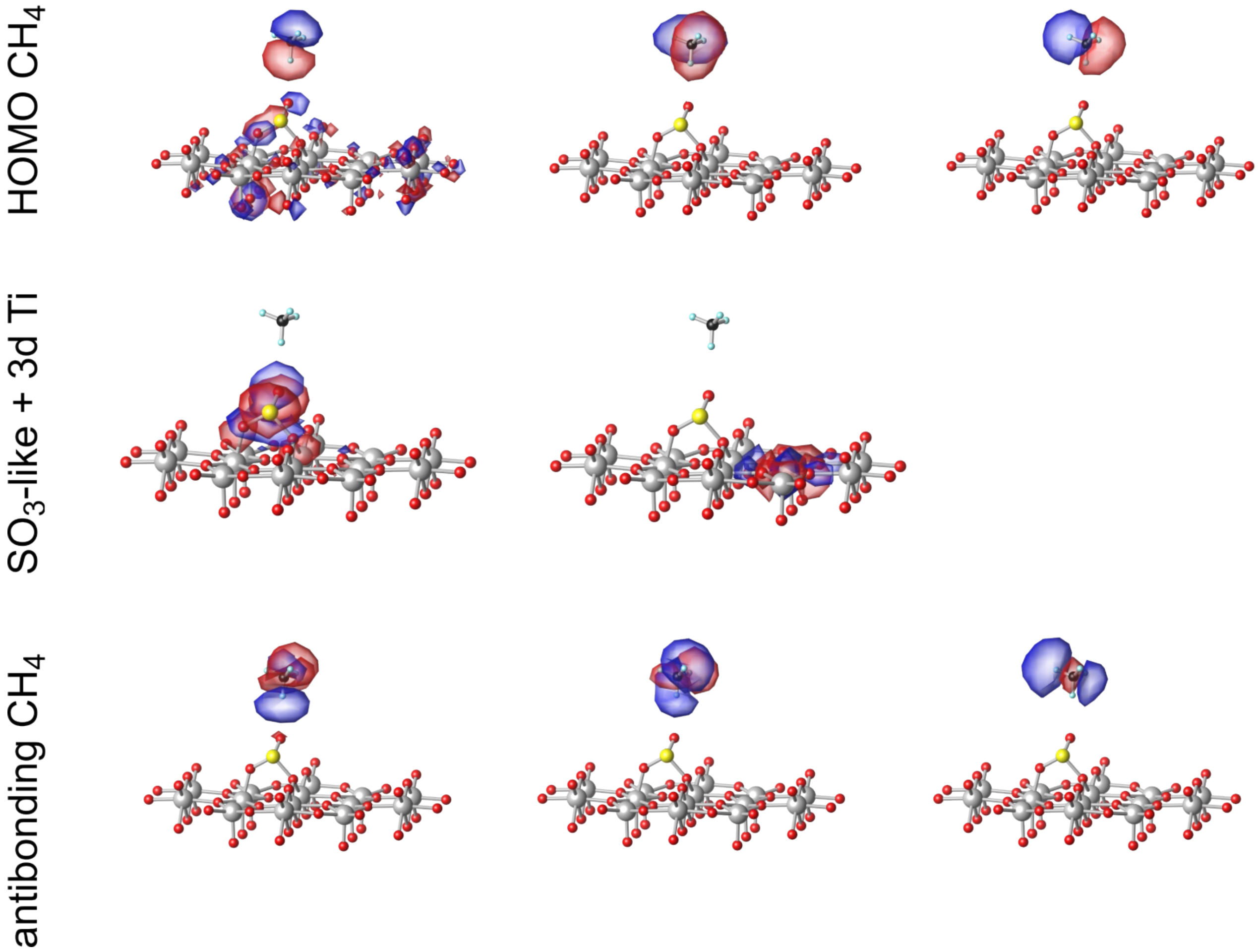


Figure s4-2 Included molecular orbitals in CAS(8,8) space.

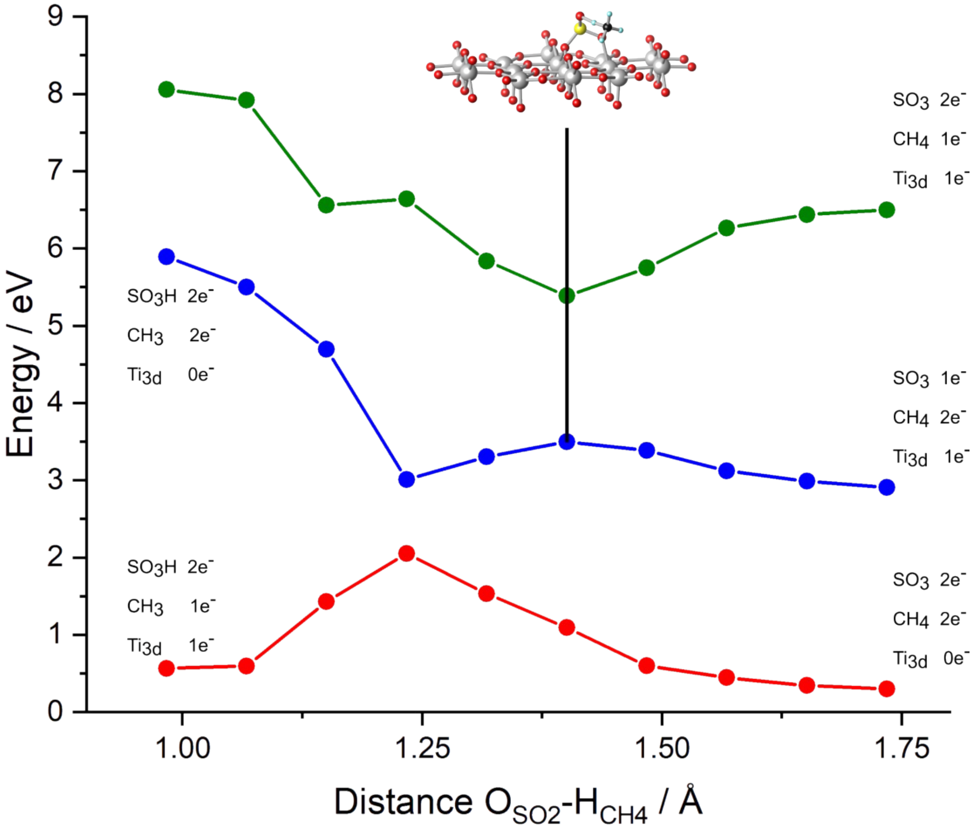


Figure s4-3 SA-CAS(8,8) reaction scan over three states with weighting 0.5,0.25,0.25. At the transition state of the blue curve a possible conical intersection between state 2 and 3 occur. The simplified occupation numbers of the corresponding species are shown for each state.

S5 Relative Energies of doped TiO_2

Table s5-1 Calculated energies of doped anatase[101] with different dopants at different positions. (PBC/PBE0/POB_TZVP/2x2)

Dopant	Position	Energy [a.u.]	ΔE [eV]
C-O	us2-O	-32263.82496	0.00
	pl-O	-32263.78917	0.97
	br-O	-32263.80059	0.66
	us1-O	-32263.80575	0.52
C-Ti	6f-Ti	-31489.6844	0.00
	5f-Ti	-31489.70772	-0.63
N	us2-O	-32280.59328	0.00
	pl-O	-32280.58175	0.31
	br-O	-32280.57479	0.50
	us1-O	-32280.57233	0.57
S-O	us2-O	-32623.8849	0.00
	pl-O	-32623.90615	-0.58
	br-O	-32623.92147	-1.00
	us1-O	-32623.85596	0.79
S-Ti	6f-Ti	-31849.51252	0.00
	5f-Ti	-31849.53178	-0.52
Se-O	us2-O	-34627.12879	0.00
	pl-O	-34627.15561	-0.73
	br-O	-34627.17879	-1.36
	us1-O	-34627.0975	0.85
Se-Ti	6f-Ti	-33852.78679	0.00
	5f-Ti	-33852.8058	-0.52

Table s5-2 Calculated energies of doped rutile[110] with different dopants at different positions. (PBC/PBE0/POB_TZVP/2x2)

Dopant	Position	Energy [a.u.]	ΔE [eV]
C	us2-O	-32263.65634	0.00
	pl-O	-32263.63526	0.57
	br-O	-32263.63015	0.71
	us1-O	-32263.64834	0.22
C-Ti	6f-Ti	-31489.52734	0.00
	5f-Ti	-31489.53356	-0.17
N	us2-O	-32280.42515	0.00
	pl-O	-32280.41916	0.16
	br-O	-32280.41011	0.41
	us1-O	-32280.42200	0.09
S	us2-O	-32623.67970	0.00
	pl-O	-32623.72440	-1.22
	br-O	-32623.73457	-1.49
	us1-O	-32623.71704	-1.02
S-Ti	6f-Ti	-31849.35973	0.00
	5f-Ti	-31849.36795	-0.22
Se	us2-O	-34626.91204	0.00
	pl-O	-34626.97411	-1.69
	br-O	-34626.98431	-1.97
	us1-O	-34626.95589	-1.19
Se-Ti	6f-Ti	-33852.6272	0.00
	5f-Ti	-33852.64723	-0.54

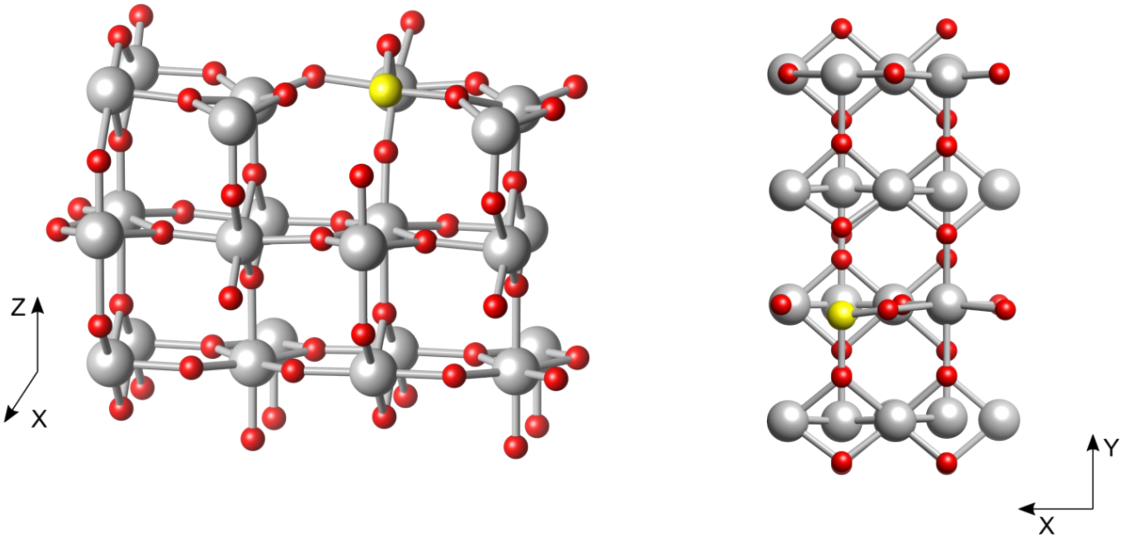


Figure s5-1 Deformation of rutile[110] surface by substitution 6f-Ti with sulfur atom. (PBC/PBE0/POB_TZVP/2x2)

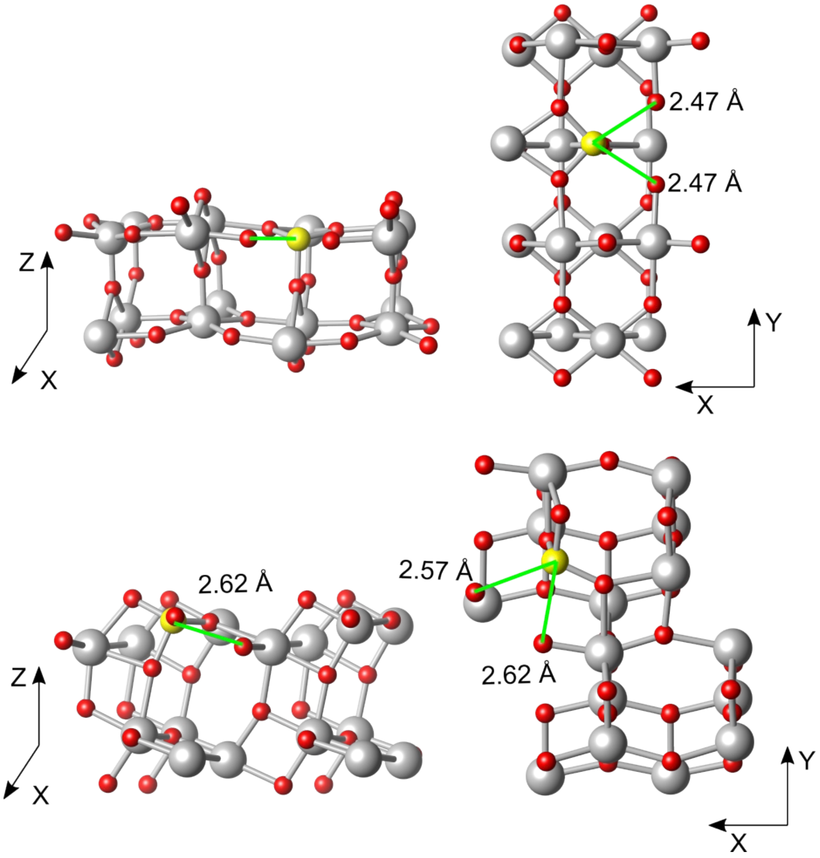


Figure s5-2 S-O bond lengths of S-5f-Ti doped rutile[110] and anatase[101] surfaces. (PBC/PBE0/POB_TZVP/2x2)

S6 Calculated Adsorption Geometries for doped TiO_2

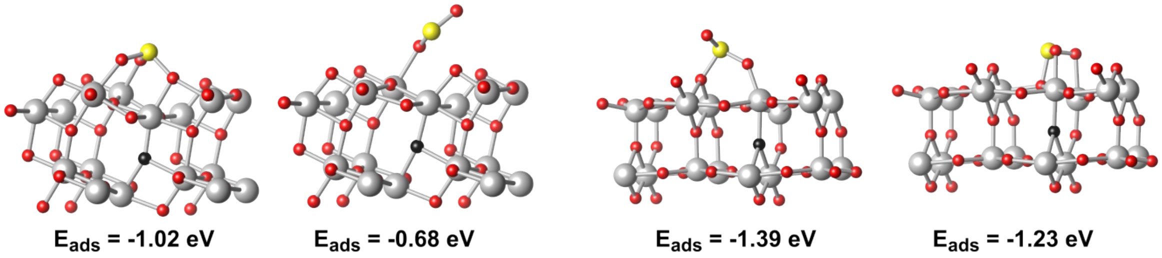


Figure s6-1 Adsorption geometries for C-O-substituted anatase[101] and rutile[110]. Adsorption energies are not BSSE-corrected.

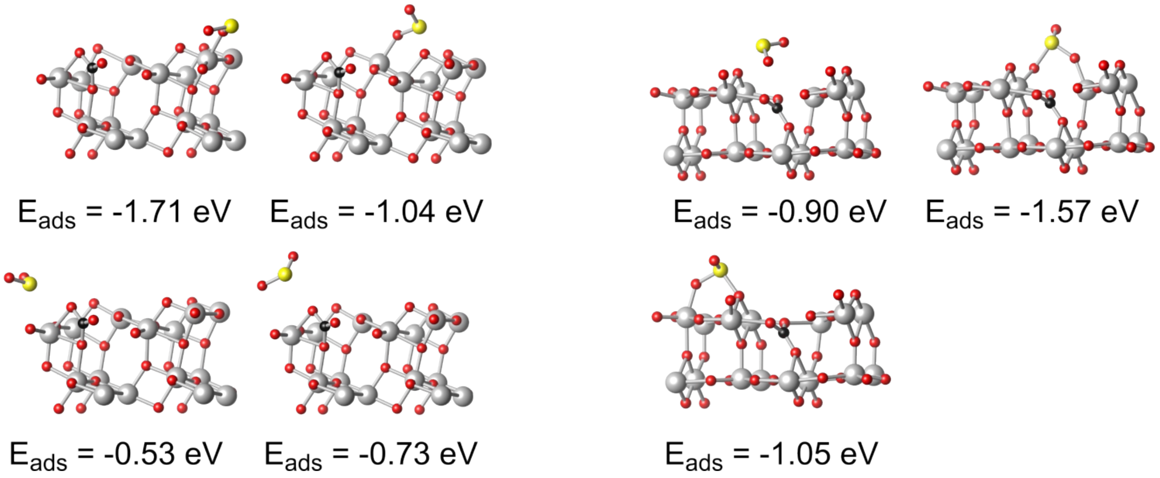


Figure s6-2 Adsorption geometries for C-Ti-substituted anatase[101] and rutile[110]. Adsorption energies are not BSSE-corrected.

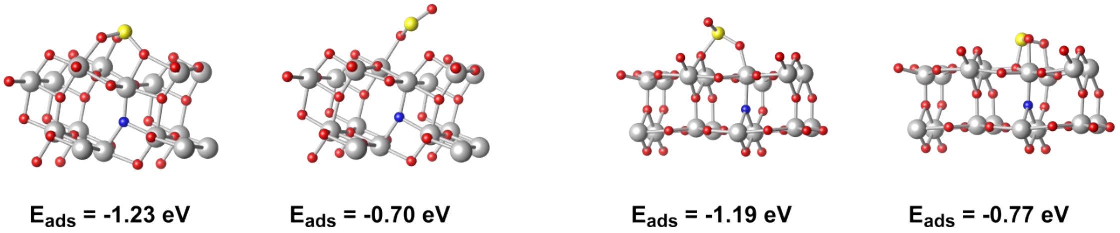


Figure s6-3 Adsorption geometries for N-O-substituted anatase[101] and rutile[110]. Adsorption energies are not BSSE-corrected.

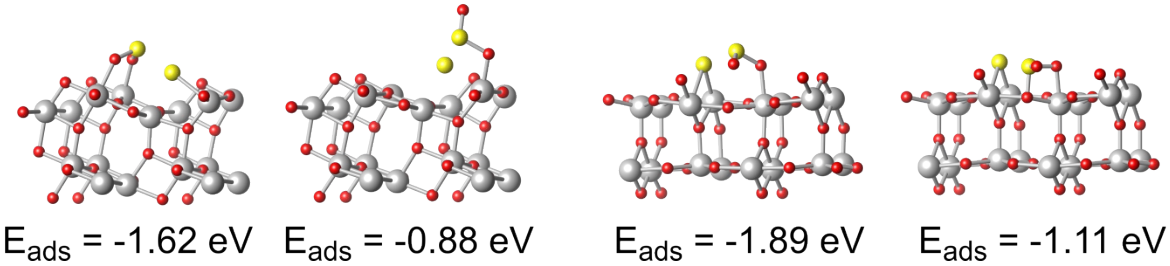


Figure s6-4 Adsorption geometries for S-O-substituted anatase[101] and rutile[110]. Adsorption energies are not BSSE-corrected.

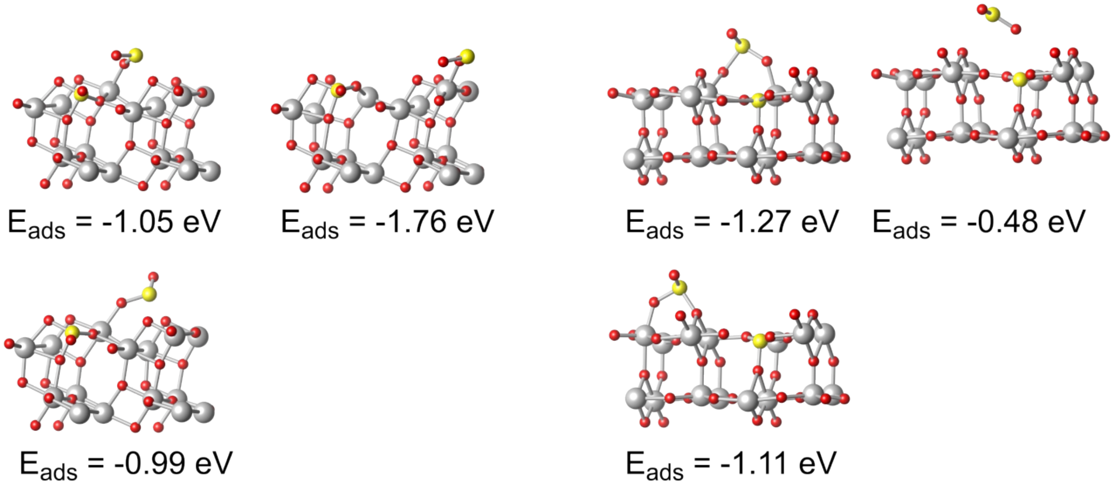
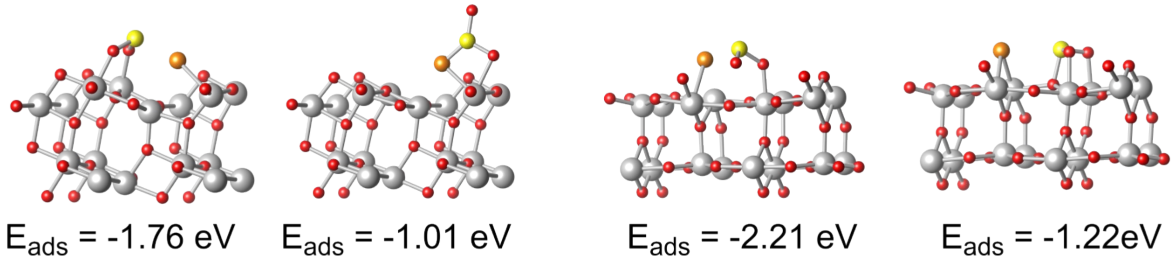
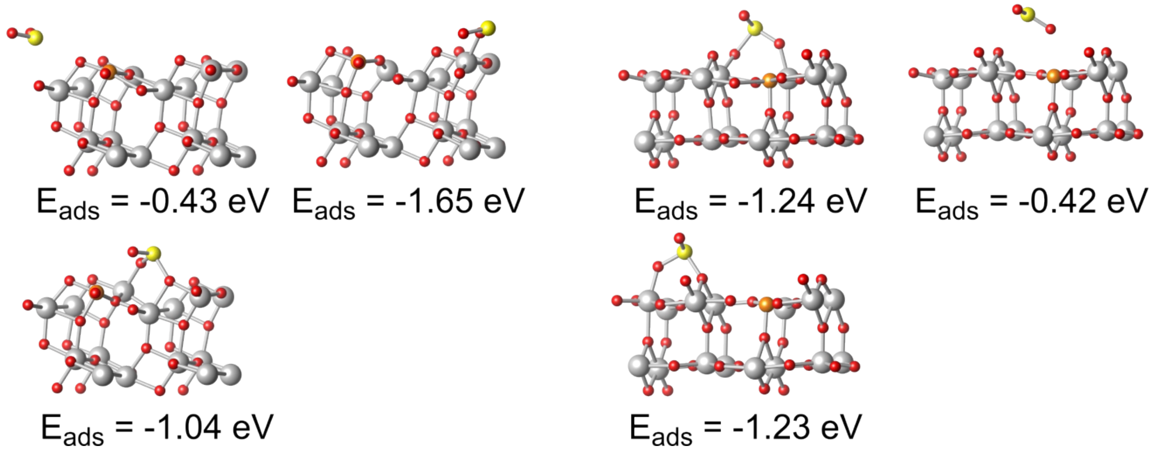


Figure s6-5 Adsorption geometries for S-Ti-substituted anatase[101] and rutile[110]. Adsorption energies are not BSSE-corrected.



E_{ads} = -1.76 eV E_{ads} = -1.01 eV E_{ads} = -2.21 eV E_{ads} = -1.22eV

Figure s6-6 Adsorption geometries for Se-O-substituted anatase[101] and rutile[110]. Adsorption energies are not BSSE-corrected.



E_{ads} = -0.43 eV E_{ads} = -1.65 eV E_{ads} = -1.24 eV E_{ads} = -0.42 eV

E_{ads} = -1.04 eV E_{ads} = -1.23 eV

Figure s6-6 Adsorption geometries for Se-Ti-substituted anatase[101] and rutile[110]. Adsorption energies are not BSSE-corrected.

S7 Comparison between Periodic and Cluster Geometries

In the following tables the comparison between PBC and cluster model calculations for the pristine rutile[110] and the doped systems in respect to adsorption energy E_{ads} and geometries are represented. Significant deviations in adsorption energy between periodic slab and cluster models regarding the doped scenarios may occur due to the lower doping concentration on the cluster model in contrast to the PBC calculations, the greater influence of the BSSE or the geometrical relaxation of the atoms in the cluster model. However, the geometrical parameters are in reasonable agreement. Additionally, the electronic structure of the clean doped surfaces was found to be in good agreement in with the PBC calculations in the manuscript.

Table s7-1 Comparison between periodic and cluster model adsorption geometry on pristine rutile[110] TiO_2. Values in brackets show BSSE-corrected values.

Model	S─(Br-X) [Å]	O_{SO2}─Ti [Å]	O_{SO2}─S [Å]	E_{ads} [eV]
PBC (2x2)	1.754	1.878	1.496 / 1.629	(-0.54) -1.08
PBC (4x2)	1.709	1.839	1.496 / 1.658	(-0.66) -1.24
Cluster I	1.776	1.949	1.501 / 1.601	(-0.83) -1.39
Cluster II	1.777	2.051	1.513 / 1.585	(-0.89) -1.44
Cluster III	1.714	1.895	1.504 / 1.6321	(-0.77) -1.36

Table s7-2 Comparison between periodic and cluster model adsorption geometry on C-O-substituted TiO_2. Values in brackets show BSSE-corrected values.

Model	S─(Br-X) [Å]	O_{SO2}─Ti [Å]	O_{SO2}─S [Å]	E_{ads} [eV]
PBC (2x2)	1.777	1.905	1.496 / 1.616	(-0.81) -1.39
Cluster II	1.727	1.972	1.513 / 1.604	-1.88

Table s7-3 Comparison between periodic and cluster model adsorption geometry on C-Ti-substituted TiO_2. Values in brackets show BSSE-corrected values.

Model	S─(Br-X) [Å]	O_{SO2}─Ti [Å]	O_{SO2}─S [Å]	E_{ads} [eV]
PBC (2x2)	1.812	1.914	1.494 / 1.585	(-1.07) -1.57
Cluster II	1.862	2.122	1.515 / 1.545	-1.25

Table s7-4 Comparison between periodic and cluster model adsorption geometry on N-O-substituted TiO_2. Values in brackets show BSSE-corrected values.

Model	S─(Br-X) [Å]	O_{SO2}─Ti [Å]	O_{SO2}─S [Å]	E_{ads} [eV]
PBC (2x2)	1.778	1.883	1.496 / 1.626	(-0.64) -1.19
Cluster II	1.741	1.995	1.513 / 1.597	-1.70

Table s7-5 Comparison between periodic and cluster model adsorption geometry on S-O-substituted TiO_2. Values in brackets show BSSE-corrected values.

Model	S─(Br-X) [Å]	O_{SO2}─Ti [Å]	O_{SO2}─S [Å]	E_{ads} [eV]
PBC (2x2)	2.296	2.014	1.566 / 1.5678	(-1.30) -1.89
Cluster II	2.316	2.071	1.522 / 1.576	(-1.36) -1.88

Table s7-6 Comparison between periodic and cluster model adsorption geometry on S-Ti-substituted TiO_2. Values in brackets show BSSE-corrected values.

Model	S─(Br-X) [Å]	O_{SO2}─Ti [Å]	O_{SO2}─S [Å]	E_{ads} [eV]
PBC (2x2)	1.789	1.909	1.496 / 1.610	(-0.75) -1.27
Cluster II	1.825	2.122	1.519 / 1.569	-1.43

Table s7-7 Comparison between periodic and cluster model adsorption geometry on Se-O-substituted TiO_2. Values in brackets show BSSE-corrected values.

Model	S─(Br-X) [Å]	O_{SO2}─Ti [Å]	O_{SO2}─S [Å]	E_{ads} [eV]
PBC (2x2)	2.357	1.994	1.579 / 1.573	(-1.58) -2.21
Cluster II	2.422	2.075	1.548 / 1.565	-1.87

Table s7-8 Comparison between periodic and cluster model adsorption geometry on Se-Ti-substituted TiO_2. Values in brackets show BSSE-corrected values.

Model	S─(Br-X) [Å]	O_{SO2}─Ti [Å]	O_{SO2}─S [Å]	E_{ads} [eV]
PBC (2x2)	1.789	1.917	1.497 / 1.609	(-0.71) -1.24
Cluster II	1.821	2.129	1.518 / 1.564	-1.41

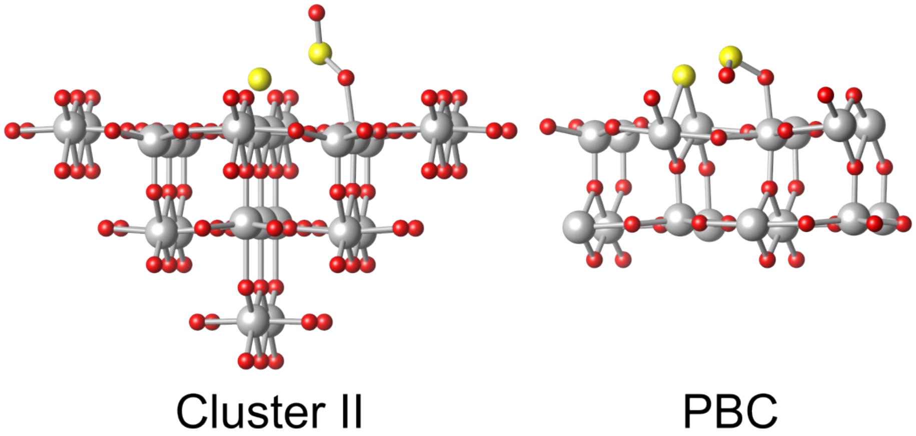


Figure s7-1 Geometrical comparison between PBC and cluster model of adsorbed SO_2 on S-O-substituted rutile[110].

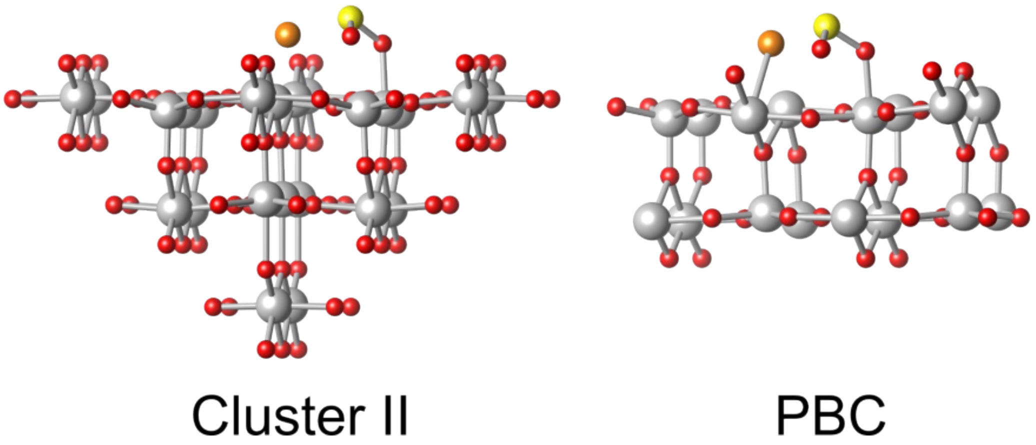


Figure s7-2 Geometrical comparison between cluster model II and PBC of adsorbed SO_2 on Se-O-substituted rutile[110].

S8 Contributing Orbitals of specific Electronic Transitions

Table s8-1 Significant TD-PBE0 transition of adsorbed SO_2 on pristine rutile[110]. (Cluster II/PBE0/POB_TZVP)

STATE 3: E= 0.134637 au 3.664 eV 29549.4 cm^{-1} Oscillator strength: 0.010137889

602a -> 603a : 0.171555 (c= 0.41419251)

602a -> 604a : 0.252043 (c= -0.50203860)

602a -> 605a : 0.060674 (c= -0.24632169)

602a -> 607a : 0.265000 (c= -0.51478196)

602a -> 609a : 0.021673 (c= 0.14721653)

602a -> 610a : 0.062010 (c= 0.24901765)

602a -> 612a : 0.011294 (c= 0.10627142)

602a -> 613a : 0.018001 (c= 0.13416672)

602a -> 614a : 0.011473 (c= 0.10711323)

602a -> 615a : 0.014874 (c= -0.12195976)

602a -> 618a : 0.016925 (c= 0.13009542)

Table s8-2 Significant TD-PBE0 transition of adsorbed SO$_2$ on C-O-substituted rutile[110]. (Cluster II/PBE0/POB_TZVP)

STATE 10: E= 0.103202 au 2.808 eV 22650.2 cm^{-1} Oscillator strength: 0.015151615

```
601a -> 603a  :    0.028000 (c= -0.16733153)
601a -> 604a  :    0.069583 (c= -0.26378671)
601a -> 609a  :    0.262041 (c=  0.51189969)
601a -> 610a  :    0.249205 (c=  0.49920401)
601a -> 611a  :    0.020667 (c=  0.14375982)
601a -> 613a  :    0.046548 (c= -0.21574875)
601a -> 617a  :    0.099908 (c=  0.31608291)
601a -> 619a  :    0.013458 (c= -0.11601062)
601a -> 620a  :    0.048854 (c= -0.22102841)
601a -> 624a  :    0.033313 (c= -0.18251906)
```

STATE 19: E= 0.114534 au 3.117 eV 25137.4 cm^{-1} Oscillator strength: 0.005088605

```
599a -> 602a  :    0.083109 (c=  0.28828643)
600a -> 603a  :    0.078044 (c= -0.27936286)
600a -> 605a  :    0.042684 (c= -0.20660034)
600a -> 607a  :    0.093128 (c= -0.30516932)
600a -> 608a  :    0.024040 (c=  0.15504880)
600a -> 609a  :    0.069381 (c=  0.26340329)
600a -> 610a  :    0.013497 (c= -0.11617815)
600a -> 611a  :    0.265693 (c= -0.51545461)
600a -> 612a  :    0.011754 (c= -0.10841552)
600a -> 616a  :    0.035118 (c=  0.18739834)
600a -> 619a  :    0.012225 (c=  0.11056813)
600a -> 623a  :    0.010759 (c= -0.10372716)
600a -> 626a  :    0.017078 (c=  0.13068106)
600a -> 629a  :    0.014894 (c=  0.12204206)
600a -> 633a  :    0.010714 (c=  0.10350704)
```

600a -> 635a : 0.013404 (c= -0.11577427)

601a -> 620a : 0.021592 (c= -0.14694145)

601a -> 621a : 0.012584 (c= 0.11217845)

STATE 22: E= 0.116116 au 3.160 eV 25484.5 cm^{-1} Oscillator strength: 0.001186291

596a -> 602a : 0.231644 (c= -0.48129456)

597a -> 602a : 0.138378 (c= 0.37199185)

598a -> 602a : 0.214639 (c= 0.46329131)

599a -> 602a : 0.160905 (c= -0.40112968)

600a -> 602a : 0.068352 (c= 0.26144285)

601a -> 614a : 0.014175 (c= -0.11905675)

601a -> 621a : 0.021717 (c= 0.14736556)

601a -> 622a : 0.025808 (c= 0.16064869)

601a -> 626a : 0.014629 (c= -0.12095237)

601a -> 633a : 0.010321 (c= -0.10159206)

STATE 26: E= 0.120851 au 3.289 eV 26523.8 cm^{-1} Oscillator strength: 0.010093899

600a -> 604a : 0.073843 (c= 0.27174158)

600a -> 609a : 0.167332 (c= 0.40906268)

600a -> 610a : 0.160282 (c= 0.40035236)

600a -> 612a : 0.030420 (c= 0.17441387)

600a -> 614a : 0.021009 (c= 0.14494390)

600a -> 617a : 0.092240 (c= 0.30371025)

600a -> 620a : 0.054335 (c= -0.23309822)

600a -> 628a : 0.015989 (c= -0.12644737)

600a -> 632a : 0.035698 (c= 0.18893818)

600a -> 633a : 0.019347 (c= -0.13909320)

600a -> 634a : 0.054081 (c= -0.23255228)

600a -> 640a : 0.012299 (c= -0.11090070)

601a -> 616a : 0.035148 (c= -0.18747780)

601a -> 630a : 0.012700 (c= 0.11269574)

601a -> 636a : 0.012996 (c= 0.11400112)
601a -> 638a : 0.012159 (c= 0.11026584)

Table s8-3 Significant TD-PBE0 transition of adsorbed SO_2 on N-O-substituted rutile[110]. (Cluster II/PBE0/POB_TZVP)

STATE 2: E= 0.076706 au 2.087 eV 16835.0 cm^{-1} Oscillator strength: 0.000428593
551b -> 602b : 0.011581 (c= 0.10761466)
554b -> 602b : 0.010245 (c= -0.10121686)
557b -> 602b : 0.021805 (c= -0.14766594)
564b -> 602b : 0.010231 (c= 0.10115075)
567b -> 602b : 0.015295 (c= 0.12367189)
571b -> 602b : 0.013387 (c= -0.11570277)
574b -> 602b : 0.014270 (c= 0.11945666)
589b -> 602b : 0.018000 (c= 0.13416337)
592b -> 602b : 0.119679 (c= -0.34594708)
593b -> 602b : 0.254859 (c= -0.50483582)
597b -> 602b : 0.073736 (c= 0.27154282)
599b -> 602b : 0.060778 (c= -0.24653194)
600b -> 602b : 0.219573 (c= 0.46858648)

STATE 3: E= 0.107352 au 2.921 eV 23561.1 cm^{-1} Oscillator strength: 0.001426502
597b -> 602b : 0.143915 (c= -0.37936173)
599b -> 602b : 0.290287 (c= 0.53878308)
600b -> 602b : 0.491005 (c= 0.70071785)

STATE 4: E= 0.109729 au 2.986 eV 24082.7 cm^{-1} Oscillator strength: 0.001022343
588b -> 602b : 0.012910 (c= 0.11362229)
592b -> 602b : 0.090412 (c= -0.30068599)
593b -> 602b : 0.210424 (c= -0.45871974)

594b -> 602b : 0.010518 (c= 0.10255569)

597b -> 602b : 0.127169 (c= -0.35660806)

599b -> 602b : 0.236848 (c= 0.48666981)

600b -> 602b : 0.221847 (c= -0.47100688)

STATE 6: E= 0.120028 au 3.266 eV 26343.0 cm^{-1} Oscillator strength: 0.000317162

601b -> 603b : 0.111183 (c= -0.33344055)

601b -> 605b : 0.159650 (c= -0.39956190)

601b -> 607b : 0.306524 (c= -0.55364654)

601b -> 608b : 0.044805 (c= 0.21167278)

601b -> 610b : 0.092002 (c= -0.30331785)

601b -> 611b : 0.169699 (c= 0.41194569)

601b -> 618b : 0.010314 (c= 0.10155725)

601b -> 624b : 0.017461 (c= -0.13214022)

STATE 7: E= 0.120126 au 3.269 eV 26364.6 cm^{-1} Oscillator strength: 0.003141870

586b -> 602b : 0.012575 (c= 0.11213619)

588b -> 602b : 0.041300 (c= -0.20322438)

589b -> 602b : 0.027755 (c= 0.16659773)

591b -> 602b : 0.034599 (c= 0.18600799)

595b -> 602b : 0.013403 (c= -0.11577242)

596b -> 602b : 0.015199 (c= -0.12328453)

597b -> 602b : 0.520750 (c= -0.72163037)

599b -> 602b : 0.286420 (c= -0.53518240)

Table s8-4 Significant TD-PBE0 transition of adsorbed SO_2 on S-O-substituted rutile[110]. (Cluster II/PBE0/POB_TZVP)

STATE 1: E= 0.112339 au 3.057 eV 24655.7 cm^{-1} Oscillator strength: 0.017662363

606a -> 607a : 0.071269 (c= 0.26696306)

606a -> 608a : 0.486233 (c= 0.69730386)

606a -> 609a : 0.231051 (c= -0.48067796)

606a -> 611a : 0.075139 (c= -0.27411411)

606a -> 613a : 0.049370 (c= -0.22219323)

STATE 2: E= 0.114984 au 3.129 eV 25236.2 cm^{-1} Oscillator strength: 0.009632908

606a -> 607a : 0.666377 (c= -0.81631920)

606a -> 608a : 0.016700 (c= 0.12922933)

606a -> 609a : 0.012425 (c= -0.11146578)

606a -> 611a : 0.189674 (c= -0.43551535)

606a -> 613a : 0.021190 (c= 0.14556806)

606a -> 614a : 0.023765 (c= -0.15415780)

606a -> 618a : 0.020282 (c= 0.14241571)

STATE 3: E= 0.118237 au 3.217 eV 25950.1 cm^{-1} Oscillator strength: 0.010162205

605a -> 607a : 0.072872 (c= -0.26994770)

605a -> 608a : 0.028730 (c= -0.16949978)

605a -> 609a : 0.112435 (c= 0.33531317)

606a -> 608a : 0.183873 (c= -0.42880399)

606a -> 609a : 0.391777 (c= -0.62592089)

606a -> 610a : 0.023367 (c= -0.15286207)

606a -> 613a : 0.028938 (c= 0.17011040)

606a -> 614a : 0.036308 (c= -0.19054651)

Table s8-5 Significant TD-PBE0 transition of adsorbed SO_2 on Se-O-substituted rutile[110].

STATE 2: E= 0.108107 au 2.942 eV 23726.8 cm^{-1} Oscillator strength: 0.006119101

615a -> 617a : 0.251222 (c= -0.50122039)

615a -> 618a : 0.350995 (c= -0.59244823)

615a -> 619a : 0.037394 (c= -0.19337435)

615a -> 620a : 0.010099 (c= 0.10049195)

```
   615a -> 621a  :     0.025559 (c= -0.15987168)
   615a -> 623a  :     0.193959 (c=  0.44040733)
   615a -> 624a  :     0.018637 (c=  0.13651795)
   615a -> 629a  :     0.010652 (c=  0.10320892)

STATE  3:  E=   0.110279 au      3.001 eV    24203.4 cm-1 Oscillator strength: 0.008155221
   615a -> 616a  :     0.131110 (c= -0.36209158)
   615a -> 617a  :     0.128434 (c=  0.35837732)
   615a -> 618a  :     0.252756 (c= -0.50274864)
   615a -> 619a  :     0.028274 (c=  0.16814869)
   615a -> 620a  :     0.041595 (c= -0.20394813)
   615a -> 621a  :     0.043574 (c=  0.20874394)
   615a -> 622a  :     0.113404 (c=  0.33675531)
   615a -> 623a  :     0.028266 (c= -0.16812431)
   615a -> 625a  :     0.119179 (c=  0.34522359)
   615a -> 626a  :     0.019983 (c=  0.14136104)
   615a -> 639a  :     0.015295 (c=  0.12367117)

STATE  4:  E=   0.111548 au      3.035 eV    24482.0 cm-1 Oscillator strength: 0.004767871
   615a -> 616a  :     0.150475 (c=  0.38791146)
   615a -> 617a  :     0.340680 (c= -0.58367837)
   615a -> 619a  :     0.036858 (c=  0.19198347)
   615a -> 620a  :     0.145514 (c= -0.38146270)
   615a -> 622a  :     0.056280 (c=  0.23723366)
   615a -> 623a  :     0.071810 (c= -0.26797458)
   615a -> 625a  :     0.070635 (c=  0.26577261)
   615a -> 626a  :     0.026983 (c=  0.16426518)
   615a -> 627a  :     0.025707 (c= -0.16033460)
   615a -> 630a  :     0.011718 (c=  0.10824898)
   615a -> 639a  :     0.010187 (c=  0.10093031)
```

S9 TD-PBE0 Spectra for Ti-substitution

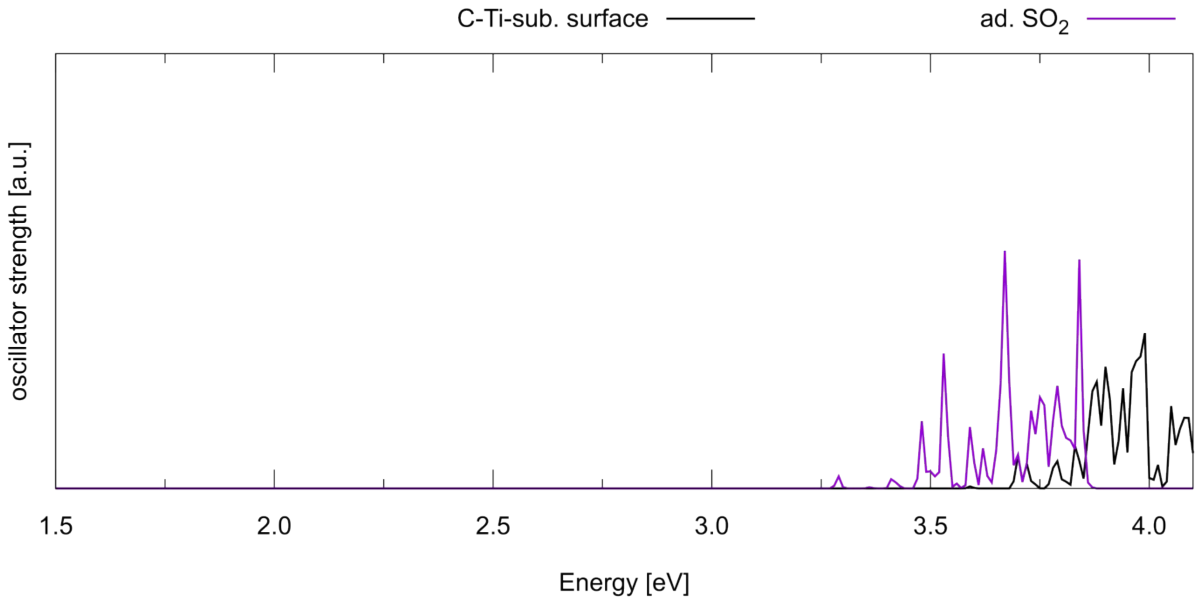


Figure s9-1 TD-PBE0 spectra of C-Ti-substituted rutile[110] (first 40 roots). (Cluster II/PBE0/POB_TZVP)

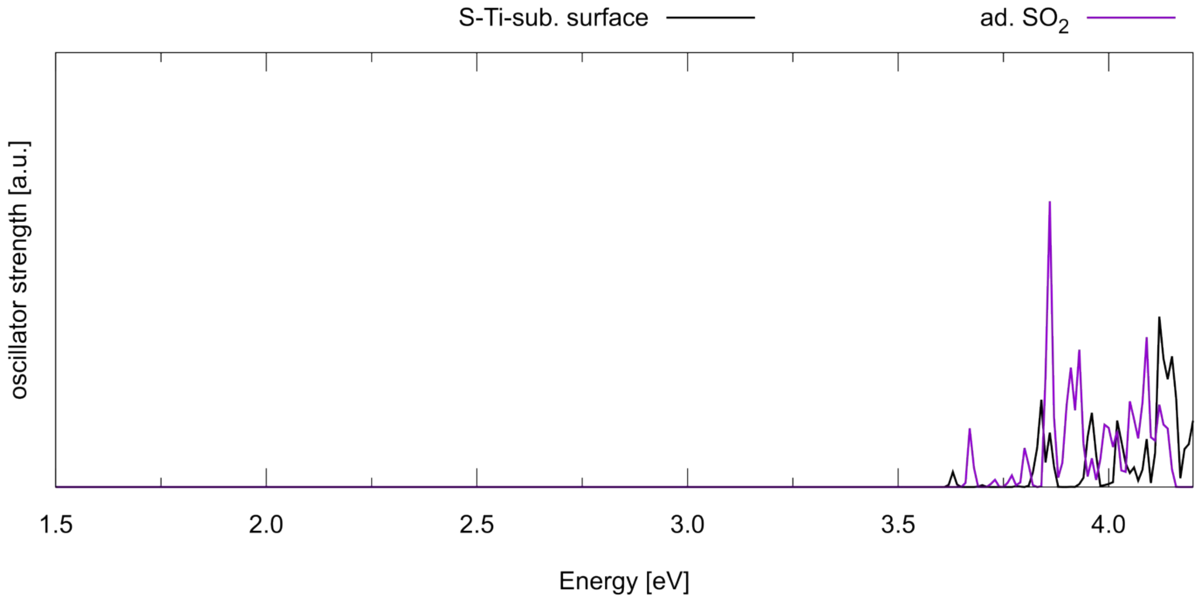


Figure s9-2 TD-PBE0 spectra of S-Ti-substituted rutile[110] (first 40 roots). (Cluster II/PBE0/POB_TZVP)

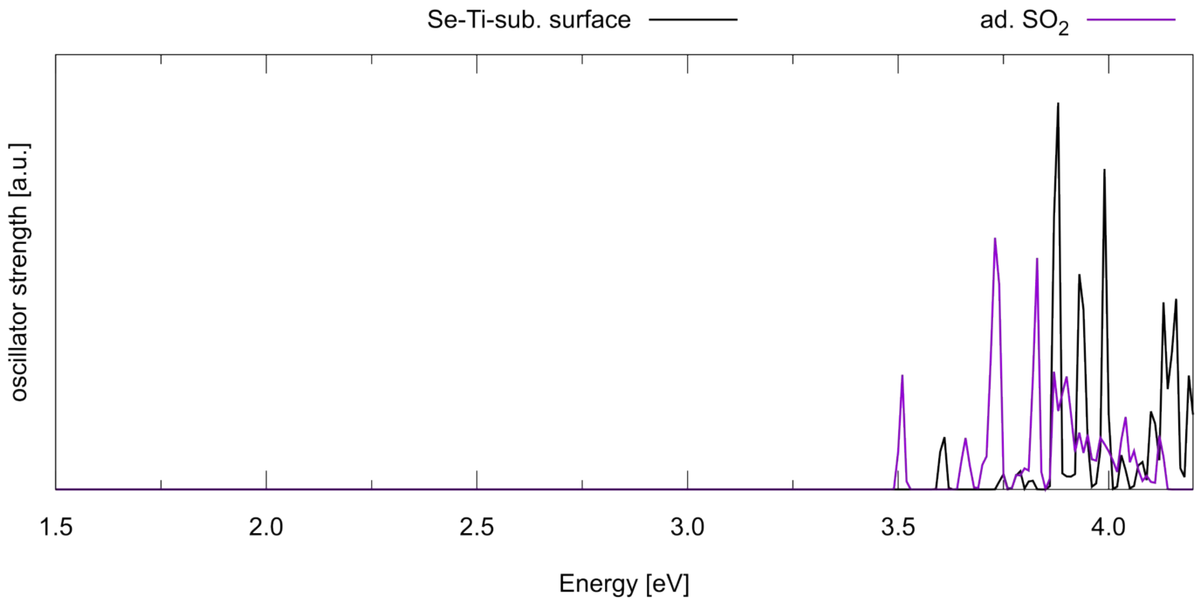


Figure s9-3 TD-PBE0 spectra of Se-Ti-substituted rutile[110] (first 40 roots). (Cluster II/PBE0/POB_TZVP)

S10 Geometries of Cluster Models

Table s10-1 Cluster I coordinates an as an example. TI> are effective core potentials in the boundary region.

Atom	Charge	X [Å]	Y [Å]	Z [Å]
O		0.000000000	0.000000000	0.000000000
O		0.000000000	6.466462000	0.000000000
O		0.000000000	-6.466462000	0.000000000
O		2.951373000	0.000000000	0.000000000
O		2.951373000	6.466462000	0.000000000
O		2.951373000	-6.466462000	0.000000000
O		5.902745000	0.000000000	0.000000000
O		-5.902745000	0.000000000	0.000000000
O		-2.951373000	0.000000000	0.000000000
O		-2.951373000	6.466462000	0.000000000
O		-2.951373000	-6.466462000	0.000000000
Ti		0.000000000	3.233231000	-1.490336000
Ti		0.000000000	-3.233231000	-1.490336000
Ti		2.951373000	3.233231000	-1.490336000
Ti		2.951373000	-3.233231000	-1.490336000
Ti		-2.951373000	3.233231000	-1.490336000
Ti		-2.951373000	-3.233231000	-1.490336000
Ti		1.475686000	0.000000000	-1.048681000
Ti		1.475686000	6.466462000	-1.048681000
Ti		1.475686000	-6.466462000	-1.048681000
Ti		4.427059000	0.000000000	-1.048681000
Ti		-4.427059000	0.000000000	-1.048681000
Ti		-1.475686000	0.000000000	-1.048681000
Ti		-1.475686000	6.466462000	-1.048681000
Ti		-1.475686000	-6.466462000	-1.048681000

O	1.475686000	4.445757000	-1.143849000
O	1.475686000	-8.487167000	-1.143849000
O	1.475686000	-2.020705000	-1.143849000
O	4.427059000	4.445757000	-1.143849000
O	4.427059000	-2.020705000	-1.143849000
O	-4.427059000	4.445757000	-1.143849000
O	-4.427059000	-2.020705000	-1.143849000
O	-1.475686000	4.445757000	-1.143849000
O	-1.475686000	-8.487167000	-1.143849000
O	-1.475686000	-2.020705000	-1.143849000
O	1.475686000	2.020705000	-1.143849000
O	1.475686000	8.487167000	-1.143849000
O	1.475686000	-4.445757000	-1.143849000
O	4.427059000	2.020705000	-1.143849000
O	4.427059000	-4.445757000	-1.143849000
O	-4.427059000	2.020705000	-1.143849000
O	-4.427059000	-4.445757000	-1.143849000
O	-1.475686000	2.020705000	-1.143849000
O	-1.475686000	8.487167000	-1.143849000
O	-1.475686000	-4.445757000	-1.143849000
O	0.000000000	0.000000000	-2.535988000
O	0.000000000	6.466462000	-2.535988000
O	0.000000000	-6.466462000	-2.535988000
O	2.951373000	0.000000000	-2.535988000
O	2.951373000	6.466462000	-2.535988000
O	2.951373000	-6.466462000	-2.535988000
O	5.902745000	0.000000000	-2.535988000
O	-5.902745000	0.000000000	-2.535988000
O	-2.951373000	0.000000000	-2.535988000
O	-2.951373000	6.466462000	-2.535988000
O	-2.951373000	-6.466462000	-2.535988000

O		0.000000000	3.233231000	-3.274489000
O		0.000000000	-3.233231000	-3.274489000
O		2.951373000	3.233231000	-3.274489000
O		2.951373000	-3.233231000	-3.274489000
O		-2.951373000	3.233231000	-3.274489000
O		-2.951373000	-3.233231000	-3.274489000
TI>	2.57142857100	1.47568600000	3.23323100000	-4.67344500000
TI>	2.57142857100	1.47568600000	-3.23323100000	-4.67344500000
TI>	2.57142857100	-1.47568600000	3.23323100000	-4.67344500000
TI>	2.57142857100	-1.47568600000	-3.23323100000	-4.67344500000
TI>	2.57142857100	0.00000000000	0.00000000000	-4.35009300000
TI>	2.57142857100	2.95137300000	0.00000000000	-4.35009300000
TI>	2.57142857100	-2.95137300000	0.00000000000	-4.35009300000
TI>	2.57142857100	4.42705900000	6.46646200000	-1.04868100000
TI>	2.57142857100	4.42705900000	-6.46646200000	-1.04868100000
TI>	2.57142857100	-4.42705900000	6.46646200000	-1.04868100000
TI>	2.57142857100	-4.42705900000	-6.46646200000	-1.04868100000
TI>	2.57142857100	0.00000000000	9.69969300000	-1.49033600000
TI>	2.57142857100	0.00000000000	-9.69969300000	-1.49033600000
TI>	2.57142857100	2.95137300000	9.69969300000	-1.49033600000
TI>	2.57142857100	2.95137300000	-9.69969300000	-1.49033600000
TI>	2.57142857100	5.90274500000	3.23323100000	-1.49033600000
TI>	2.57142857100	5.90274500000	-3.23323100000	-1.49033600000
TI>	2.57142857100	-5.90274500000	3.23323100000	-1.49033600000
TI>	2.57142857100	-5.90274500000	-3.23323100000	-1.49033600000
TI>	2.57142857100	-2.95137300000	9.69969300000	-1.49033600000
TI>	2.57142857100	-2.95137300000	-9.69969300000	-1.49033600000
TI>	2.57142857100	7.37843200000	0.00000000000	-1.04868100000
TI>	2.57142857100	-7.37843200000	0.00000000000	-1.04868100000
TI>	2.57142857100	0.00000000000	6.46646200000	-4.35009300000
TI>	2.57142857100	0.00000000000	-6.46646200000	-4.35009300000

```
TI>   2.57142857100   2.95137300000    6.46646200000   -4.35009300000
TI>   2.57142857100   2.95137300000   -6.46646200000   -4.35009300000
TI>   2.57142857100   5.90274500000    0.00000000000   -4.35009300000
TI>   2.57142857100  -5.90274500000    0.00000000000   -4.35009300000
TI>   2.57142857100  -2.95137300000    6.46646200000   -4.35009300000
TI>   2.57142857100  -2.95137300000   -6.46646200000   -4.35009300000
TI>   2.57142857100   4.42705900000    3.23323100000   -4.67344500000
TI>   2.57142857100   4.42705900000   -3.23323100000   -4.67344500000
TI>   2.57142857100  -4.42705900000    3.23323100000   -4.67344500000
TI>   2.57142857100  -4.42705900000   -3.23323100000   -4.67344500000
TI>   2.00000000000   0.00000000000    3.23323100000   -7.92502000000
TI>   2.00000000000   0.00000000000   -3.23323100000   -7.92502000000
TI>   2.00000000000   2.95137300000    3.23323100000   -7.92502000000
TI>   2.00000000000   2.95137300000   -3.23323100000   -7.92502000000
TI>   2.00000000000  -2.95137300000    3.23323100000   -7.92502000000
TI>   2.00000000000  -2.95137300000   -3.23323100000   -7.92502000000
TI>   2.00000000000   1.47568600000    0.00000000000   -7.75408200000
TI>   2.00000000000  -1.47568600000    0.00000000000   -7.75408200000
TI>   2.00000000000   4.42705900000    0.00000000000   -7.75408200000
TI>   2.00000000000  -4.42705900000    0.00000000000   -7.75408200000
TI>   2.00000000000   5.90274500000    9.69969300000   -1.49033600000
TI>   2.00000000000   5.90274500000   -9.69969300000   -1.49033600000
TI>   2.00000000000  -5.90274500000    9.69969300000   -1.49033600000
TI>   2.00000000000  -5.90274500000   -9.69969300000   -1.49033600000
TI>   2.00000000000   7.37843200000    6.46646200000   -1.04868100000
TI>   2.00000000000   7.37843200000   -6.46646200000   -1.04868100000
TI>   2.00000000000  -7.37843200000    6.46646200000   -1.04868100000
TI>   2.00000000000  -7.37843200000   -6.46646200000   -1.04868100000
TI>   2.00000000000   5.90274500000    6.46646200000   -4.35009300000
TI>   2.00000000000   5.90274500000   -6.46646200000   -4.35009300000
TI>   2.00000000000  -5.90274500000    6.46646200000   -4.35009300000
```

```
TI>   2.00000000000   -5.90274500000    -6.46646200000    -4.35009300000
TI>   2.00000000000    0.00000000000     0.00000000000   -11.01674500000
TI>   2.00000000000    2.95137300000     0.00000000000   -11.01674500000
TI>   2.00000000000   -2.95137300000     0.00000000000   -11.01674500000
TI>   2.00000000000    8.85411800000     3.23323100000    -1.49033600000
TI>   2.00000000000    8.85411800000     9.69969300000    -1.49033600000
TI>   2.00000000000    8.85411800000    -9.69969300000    -1.49033600000
TI>   2.00000000000    8.85411800000    -3.23323100000    -1.49033600000
TI>   2.00000000000   -8.85411800000     3.23323100000    -1.49033600000
TI>   2.00000000000   -8.85411800000     9.69969300000    -1.49033600000
TI>   2.00000000000   -8.85411800000    -9.69969300000    -1.49033600000
TI>   2.00000000000   -8.85411800000    -3.23323100000    -1.49033600000
TI>   2.00000000000   -1.47568600000    12.93292400000    -1.04868100000
TI>   2.00000000000   -1.47568600000   -12.93292400000    -1.04868100000
TI>   2.00000000000    1.47568600000    12.93292400000    -1.04868100000
TI>   2.00000000000    1.47568600000   -12.93292400000    -1.04868100000
TI>   2.00000000000    4.42705900000    12.93292400000    -1.04868100000
TI>   2.00000000000    4.42705900000   -12.93292400000    -1.04868100000
TI>   2.00000000000    7.37843200000    12.93292400000    -1.04868100000
TI>   2.00000000000    7.37843200000   -12.93292400000    -1.04868100000
TI>   2.00000000000   -7.37843200000    12.93292400000    -1.04868100000
TI>   2.00000000000   -7.37843200000   -12.93292400000    -1.04868100000
TI>   2.00000000000   -4.42705900000    12.93292400000    -1.04868100000
TI>   2.00000000000   -4.42705900000   -12.93292400000    -1.04868100000
TI>   2.00000000000    8.85411800000     0.00000000000    -4.35009300000
TI>   2.00000000000    8.85411800000     6.46646200000    -4.35009300000
TI>   2.00000000000    8.85411800000    -6.46646200000    -4.35009300000
TI>   2.00000000000   -8.85411800000     0.00000000000    -4.35009300000
TI>   2.00000000000   -8.85411800000     6.46646200000    -4.35009300000
TI>   2.00000000000   -8.85411800000    -6.46646200000    -4.35009300000
TI>   2.00000000000   -1.47568600000     9.69969300000    -4.67344500000
```

TI>	2.00000000000	-1.47568600000	-9.69969300000	-4.67344500000
TI>	2.00000000000	1.47568600000	9.69969300000	-4.67344500000
TI>	2.00000000000	1.47568600000	-9.69969300000	-4.67344500000
TI>	2.00000000000	4.42705900000	9.69969300000	-4.67344500000
TI>	2.00000000000	4.42705900000	-9.69969300000	-4.67344500000
TI>	2.00000000000	7.37843200000	3.23323100000	-4.67344500000
TI>	2.00000000000	7.37843200000	9.69969300000	-4.67344500000
TI>	2.00000000000	7.37843200000	-9.69969300000	-4.67344500000
TI>	2.00000000000	7.37843200000	-3.23323100000	-4.67344500000
TI>	2.00000000000	-7.37843200000	3.23323100000	-4.67344500000
TI>	2.00000000000	-7.37843200000	9.69969300000	-4.67344500000
TI>	2.00000000000	-7.37843200000	-9.69969300000	-4.67344500000
TI>	2.00000000000	-7.37843200000	-3.23323100000	-4.67344500000
TI>	2.00000000000	-4.42705900000	9.69969300000	-4.67344500000
TI>	2.00000000000	-4.42705900000	-9.69969300000	-4.67344500000
TI>	2.00000000000	5.90274500000	3.23323100000	-7.92502000000
TI>	2.00000000000	5.90274500000	-3.23323100000	-7.92502000000
TI>	2.00000000000	-5.90274500000	3.23323100000	-7.92502000000
TI>	2.00000000000	-5.90274500000	-3.23323100000	-7.92502000000
TI>	2.00000000000	-1.47568600000	6.46646200000	-7.75408200000
TI>	2.00000000000	-1.47568600000	-6.46646200000	-7.75408200000
TI>	2.00000000000	1.47568600000	6.46646200000	-7.75408200000
TI>	2.00000000000	1.47568600000	-6.46646200000	-7.75408200000
TI>	2.00000000000	4.42705900000	6.46646200000	-7.75408200000
TI>	2.00000000000	4.42705900000	-6.46646200000	-7.75408200000
TI>	2.00000000000	7.37843200000	0.00000000000	-7.75408200000
TI>	2.00000000000	-7.37843200000	0.00000000000	-7.75408200000
TI>	2.00000000000	-4.42705900000	6.46646200000	-7.75408200000
TI>	2.00000000000	-4.42705900000	-6.46646200000	-7.75408200000
TI>	2.00000000000	5.90274500000	0.00000000000	-11.01674500000
TI>	2.00000000000	-5.90274500000	0.00000000000	-11.01674500000

TI>	2.00000000000	-1.47568600000	3.23323100000	-11.01674500000
TI>	2.00000000000	-1.47568600000	-3.23323100000	-11.01674500000
TI>	2.00000000000	1.47568600000	3.23323100000	-11.01674500000
TI>	2.00000000000	1.47568600000	-3.23323100000	-11.01674500000
TI>	2.00000000000	4.42705900000	3.23323100000	-11.01674500000
TI>	2.00000000000	4.42705900000	-3.23323100000	-11.01674500000
TI>	2.00000000000	-4.42705900000	3.23323100000	-11.01674500000
TI>	2.00000000000	-4.42705900000	-3.23323100000	-11.01674500000

Table s10-2 Adsorption geometry of SO_2 on cluster I using PBE0.

Atom	X [Å]	Y [Å]	Z [Å]
O	-0.01515555520592	0.25571455705926	0.02994773855872
O	-0.00000038478665	6.46647223692738	0.00000043833760
O	0.00000017873979	-6.46645864909114	-0.00000046646539
O	2.91395202215041	-0.00700235538693	-0.03387674969996
O	2.95137305771800	6.46646490168210	0.00000017354422
O	2.95137291242138	-6.46646064793958	0.00000006433766
O	5.90274505849588	-0.00001857142977	0.00000005300928
O	-5.90274534061610	-0.00001410531932	-0.00000042009008
O	-2.90582475579669	0.00621797136085	-0.03353540312208
O	-2.95137341237283	6.46646443130626	0.00000007753100
O	-2.95137280333276	-6.46646081753988	-0.00000014334593
Ti	-0.00164325273890	3.23482618459540	-1.31833237515512
Ti	0.00769878188680	-3.15336600847040	-1.46064946998788
Ti	2.98764059304630	3.29809651287481	-1.44395505754077
Ti	2.98130872671800	-3.28359952237293	-1.42334046869176
Ti	-2.98451396010139	3.29668446383198	-1.44920236608776
Ti	-2.97702857290333	-3.29247604392580	-1.42409679716083
Ti	1.56012265537787	0.09155436686758	-1.19003972192600
Ti	1.47568548446104	6.46644329238610	-1.04868118862722

Ti	1.47568731030065	-6.46646939549147	-1.04868027007862
Ti	4.42706111937553	0.00007564437800	-1.04868198844749
Ti	-4.42705923590460	0.00003299200250	-1.04868013920956
Ti	-1.55479917778354	0.06316282071808	-1.21976462863105
Ti	-1.47568387086087	6.46644748223328	-1.04868104889768
Ti	-1.47568822044104	-6.46646816862578	-1.04868015451758
O	1.49336919643492	4.41063591876584	-1.18880657722702
O	1.47568591739002	-8.48716673417276	-1.14384928764249
O	1.46686329456116	-1.98980465727588	-1.16864980114428
O	4.42705784002482	4.44575725597008	-1.14384955217977
O	4.42705983265952	-2.02070706034026	-1.14384717682988
O	-4.42705650937412	4.44576036323560	-1.14385200977912
O	-4.42705952948313	-2.02070528501520	-1.14384859346324
O	-1.49655512101976	4.41215345755075	-1.18751432815749
O	-1.47568570297500	-8.48716675973980	-1.14384925038533
O	-1.47075870468558	-1.98861737820325	-1.17314795630627
O	1.57584046959393	1.97460669731857	-1.35632726861478
O	1.47568603062596	8.48716750121619	-1.14384908256756
O	1.47961980899606	-4.39501736739479	-1.15168454108462
O	4.42705890085505	2.02070190651618	-1.14384732461798
O	4.42705448110901	-4.44576493999478	-1.14385479554963
O	-4.42705949230270	2.02070384088997	-1.14384811851235
O	-4.42705676902602	-4.44576113839382	-1.14385229078056
O	-1.58049121815386	1.97421105567563	-1.34952088325257
O	-1.47568643906525	8.48716739331856	-1.14384905059630
O	-1.48100526063499	-4.39322904356865	-1.14544734995757
O	0.00000139686702	0.00002008790901	-2.53598951348858
O	-0.00000030404437	6.46646549737989	-2.53598771446966
O	0.00000016176453	-6.46645973712779	-2.53598826986436
O	2.95137080751969	-0.00002569951884	-2.53598819020806
O	2.95137290086123	6.46646813288452	-2.53598784529988

O	2.95137296545852	-6.46645976744224	-2.53598803195492
O	5.90274418856323	-0.00004576423560	-2.53598832101827
O	-5.90274515442939	-0.00000711628772	-2.53598828446014
O	-2.95137262058552	-0.00002618818548	-2.53598792467709
O	-2.95137333204984	6.46646617772413	-2.53598810717131
O	-2.95137276674181	-6.46646060651901	-2.53598807373207
O	-0.00000001137526	3.23322568563605	-3.27448813278438
O	0.00000000514043	-3.23323378328421	-3.27448836470138
O	2.95137290377573	3.23322592703262	-3.27448826363871
O	2.95137332744965	-3.23323272147350	-3.27448815090680
O	-2.95137318678416	3.23322780983993	-3.27448824340319
O	-2.95137316904938	-3.23323173229476	-3.27448852448688
S	-0.18175763385915	1.40418660535515	1.37458437571964
O	1.04337587742572	1.18035157970644	2.21266678254656
O	0.01386697636259	2.77837693327258	0.57661976826180

References

1. Diebold, U., The surface science of titanium dioxide. *Surf. Sci. Rep.* **2003,** *48* (5), 53-229.
2. Burdett, J. K.; Hughbanks, T.; Miller, G. J.; Richardson, J. W.; Smith, J. V., Structural-electronic relationships in inorganic solids: powder neutron diffraction studies of the rutile and anatase polymorphs of titanium dioxide at 15 and 295 K. *J. Am. Chem. Soc.* **1987,** *109* (12), 3639-3646.
3. Amtout, A.; Leonelli, R., Optical properties of rutile near its fundamental band gap. *Phys. Rev. B. Condens. Matter* **1995,** *51* (11), 6842-6851.
4. Esch, T. R.; Gadaczek, I.; Bredow, T., Surface structures and thermodynamics of low-index of rutile, brookite and anatase – A comparative DFT study. *Appl. Surf. Sci.* **2014,** *288*, 275-287.
5. Howard, C.; Sabine, T.; Dickson, F., Structural and thermal parameters for rutile and anatase. *Acta Crystallogr., Sect. B: Struct. Sci.* **1991,** *47* (4), 462-468.
6. Tang, H.; Lévy, F.; Berger, H.; Schmid, P. E., Urbach tail of anatase TiO_2. *Phys. Rev. B.* **1995,** *52* (11), 7771-7774.
7. Petersen, T.; Klüner, T., Photodesorption of H_2O from Anatase-TiO_2 (101): A Combined Quantum Chemical and Quantum Dynamical Study. *J. Phys. Chem. C* **2020,** *124* (21), 11444-11455.
8. Teusch, T.; Klüner, T., Photodesorption mechanism of water on WO_3(001) – a combined embedded cluster, computational intelligence and wave packet approach. *Phys. Chem. Chem. Phys.* **2020,** *22* (34), 19267-19274.
9. Kubas, A.; Berger, D.; Oberhofer, H.; Maganas, D.; Reuter, K.; Neese, F., Surface Adsorption Energetics Studied with "Gold Standard" Wave-Function-Based Ab Initio Methods: Small-Molecule Binding to TiO_2(110). *J. Phys. Chem. Lett.* **2016,** *7* (20), 4207-4212.
10. Berger, D.; Logsdail, A. J.; Oberhofer, H.; Farrow, M. R.; Catlow, C. R.; Sherwood, P.; Sokol, A. A.; Blum, V.; Reuter, K., Embedded-cluster calculations in a numeric atomic orbital density-functional theory framework. *J. Chem. Phys.* **2014,** *141* (2), 024105.
11. Casarin, M.; Ferrigato, F.; Maccato, C.; Vittadini, A., SO_2 on TiO_2 (110) and Ti_2O_3 (1012) nonpolar surfaces: A DFT study. *J. Phys. Chem. B* **2005,** *109* (25), 12596-12602.
12. Casarin, M.; Maccato, C.; Vittadini, A., Molecular chemisorption on TiO_2 (110): A local point of view. *J. Phys. Chem. B* **1998,** *102* (52), 10745-10752.
13. He, H.; Zapol, P.; Curtiss, L. A., A Theoretical Study of CO_2 Anions on Anatase (101) Surface. *J. Phys. Chem. C* **2010,** *114* (49), 21474-21481.
14. Kick, M.; Oberhofer, H., Towards a transferable design of solid-state embedding models on the example of a rutile TiO_2 (110) surface. *J. Chem. Phys.* **2019,** *151* (18), 184114.