

Electronic Supporting Information

Effective sensing mechanisms of O₂ and CO on SnO₂ (110) surface: a DFT study

Felipe Lipsky,^{*a} Amanda F. Gouveia,^a Fabrício R. Sensato,^b Mônica Oliva,^a Elson Longo,^c Miguel A. San-Miguel^d and Juan Andrés^{*a}

^a Universitat Jaume I, Castelló de la Plana, Castelló 12071, Spain.

^b Universidade Federal de São Paulo, Diadema, São Paulo 09913-030, Brazil.

^c Center for the Development of Functional Materials - Universidade Federal de São Carlos, São Carlos, São Paulo 13565-905, Brazil.

^d Universidade Estadual de Campinas, Campinas, São Paulo 13083-970, Brazil.

*E-mail: lipsky@uji.es ; andres@qfa.uji.es

“This work is dedicated to Prof. Dr. Celso Aldao, who recently passed away. An excellent person and an innovative researcher in sensor materials. He opened the way for us to develop this investigation.”

1 Crystal data

The initial geometric data for bulk SnO₂ was retrieved from the Materials Project for SnO₂ (mp-856) from database version v2023.11.1. (Fig. SM1a).¹ The fitting for tetragonal SnO₂ was performed using the Natural Strain 3rd-order equation of state.² The calculated energy as a function of volume was obtained by varying the lattice scaling factor from 0.93 to 1.08. The quality of the fit was exceptional, with an R^2 value of 0.9998, indicating a near-perfect correlation. The minimum energy point from the fit was found at a volume of 12.0387 Å³/atom and an energy of -6.7996 eV/atom. (Fig. SM1b).

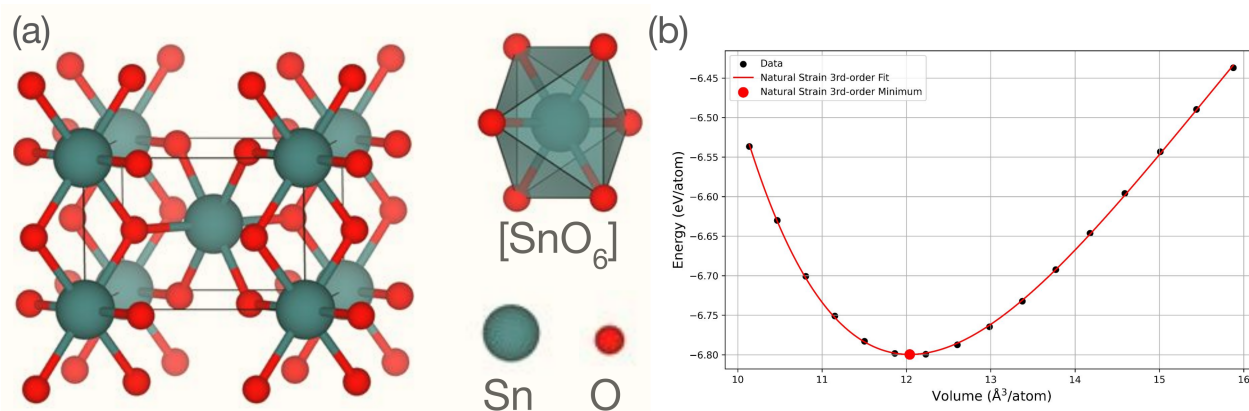


Fig. SM 1 (a) Conventional unit cell of tetragonal $P4_2/mmm$ SnO₂. Tin (Sn) atoms are represented in grey, and oxygen (O) atoms in red. The SnO₂ structure features Sn atoms coordinated by six oxygen atoms, forming [SnO₆] octahedral clusters. (b) Equation of state fitting of tetragonal SnO₂. The red circle indicates the minimum energy point.

Calculated electronic and geometric parameters with GGA (PBEsol) and hybrid functionals (HSE06) were compared. The results are shown in Table SM-1. The comparison highlights the underestimation of the band gap by GGA compared to experimental values, while the HSE06 functional provides a closer approximation. The bandstructure along a high symmetry path follows on Fig. SM-2 and it features a 2.78 eV direct $\Gamma \rightarrow \Gamma$ transition.

Table 1 Calculated structural parameters and band gap at Γ (E_g) of rutile SnO₂ using PBEsol and HSE06. The geometric and electronic experimental values (Expt.) are from Refs.¹ and ³.

Functional	a (Å)	c (Å)	E_g (eV)
PBEsol	4.748	3.208	1.02
HSE06	-	-	2.78
Expt.	4.740	3.188	3.60

2 Surface model

The surface energy (σ_{surf}) was the criterion chosen for assessing the convergence of the slab system with respect to its size, defined by the number of trilayers. It was calculated using Equation (S1):

$$\sigma_{\text{surf}} = \frac{1}{2A} (E_{\text{slab}}(n) - nE_{\text{bulk}}), \quad (\text{S1})$$

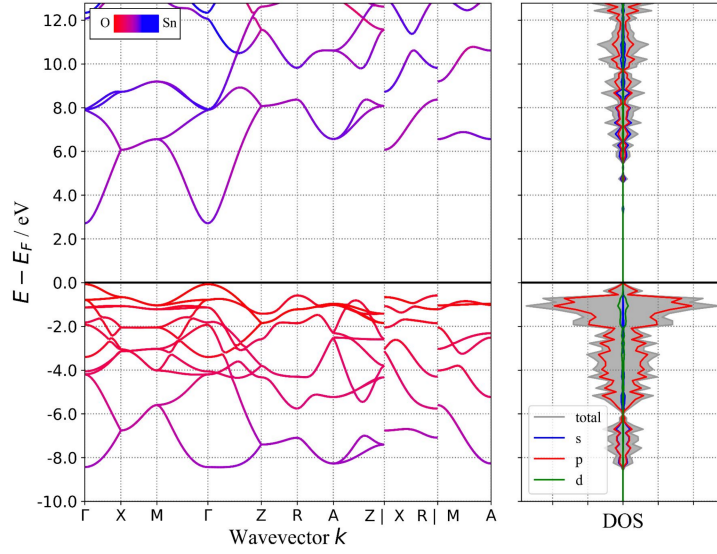


Fig. SM 2 The electronic band structure and density of states (DOS) for tetragonal $P4_2/mmm$ SnO_2 are presented. The band structure plot (left) shows the energy dispersion along high-symmetry points in the Brillouin zone, with contributions from O (red) and Sn (blue) atoms. The density of states plot (right) displays the total DOS (grey) and the projected DOS for s (blue), p (red), and d (green) orbitals. The Fermi level is set to 0 eV.

where $E_{\text{slab}}(n)$ is the energy of the surface model as a function of the number of O- Sn_2O_2 -O trilayers ((n)), A is the surface area, and E_{bulk} is the bulk energy. The bulk energy was determined using a linear-fit procedure.⁴

The linear fit of the slab energy ($E_{\text{slab}}(n)$) follows Equation (S2):

$$E_{\text{slab}}(n) = nE_{\text{bulk}} + 2A\sigma_{\text{surf}}, \quad (\text{S2})$$

where n represents the number of trilayers, and the fit started at $n = 3$ to ensure a flat σ_{surf} curve at model thicknesses of three and more trilayers. The fitted data follows in Fig. SM-3.

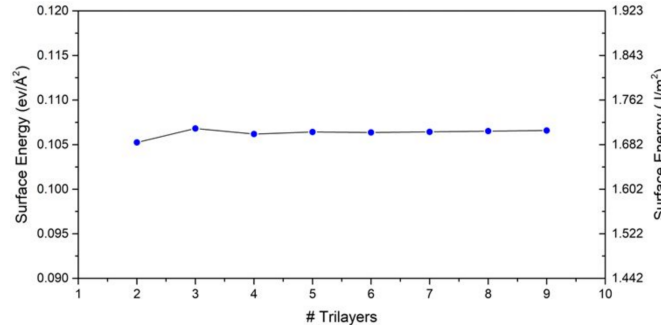


Fig. SM 3 Slab convergence study for the surface energy of the SnO_2 (110) surface. The plot shows the surface energy ($\text{eV}/\text{\AA}^2$ and J/m^2) as a function of the increasing number of constitutive trilayers, demonstrating the convergence behavior as the slab thickness increases.

The corresponding calculated phase diagram for SnO_2 is shown in Figure SM-4.

The modeling of an oxygen vacancy (V_O) hinged on the calculation of the formation energies G_f of neutral vacancies on both types of oxygen atoms found on the exposed surface layer of the pristine SnO_2 (110) system. The results follow on Table SM-2 .

Table 2 Calculated Gibbs formation energies (eV) for the formation of oxygen vacancies (V_O) in the bent (O_{2c}) and trigonal planar (O_{3c}) sites in oxygen poor (O-poor) and oxygen rich (O-rich) conditions at various temperatures (K).

Site	T = 298.15 K		T = 323.15 K		T = 523.15 K	
	O-rich	O-poor	O-rich	O-poor	O-rich	O-poor
O_{3c}	13.65	13.12	13.63	13.09	13.41	12.88
O_{2c}	2.77	2.24	2.74	2.21	2.56	2.03

The density of states (DOS) calculated with the HSE06 exchange and correlation functional for both the pristine and defect SnO_2 surface models are presented in Figure SM-5.

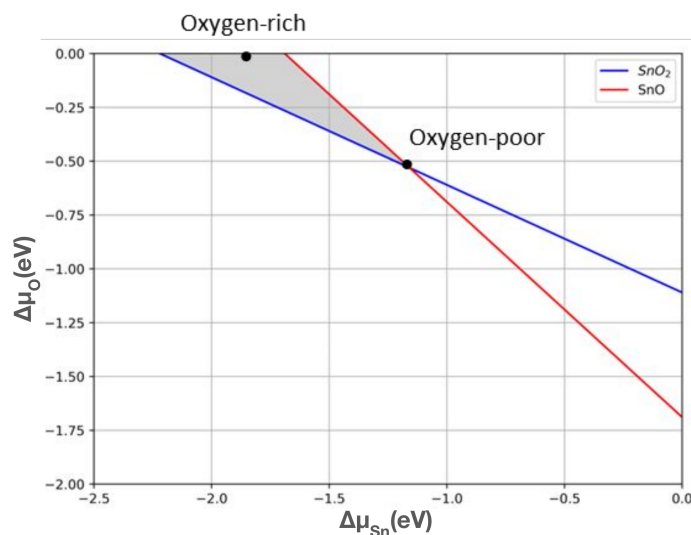


Fig. SM 4 Phase diagram for the formation of SnO_2 with varying chemical potentials of its constituent atoms. Values are shown for a temperature of 298.15 K and a pressure of 1 bar.

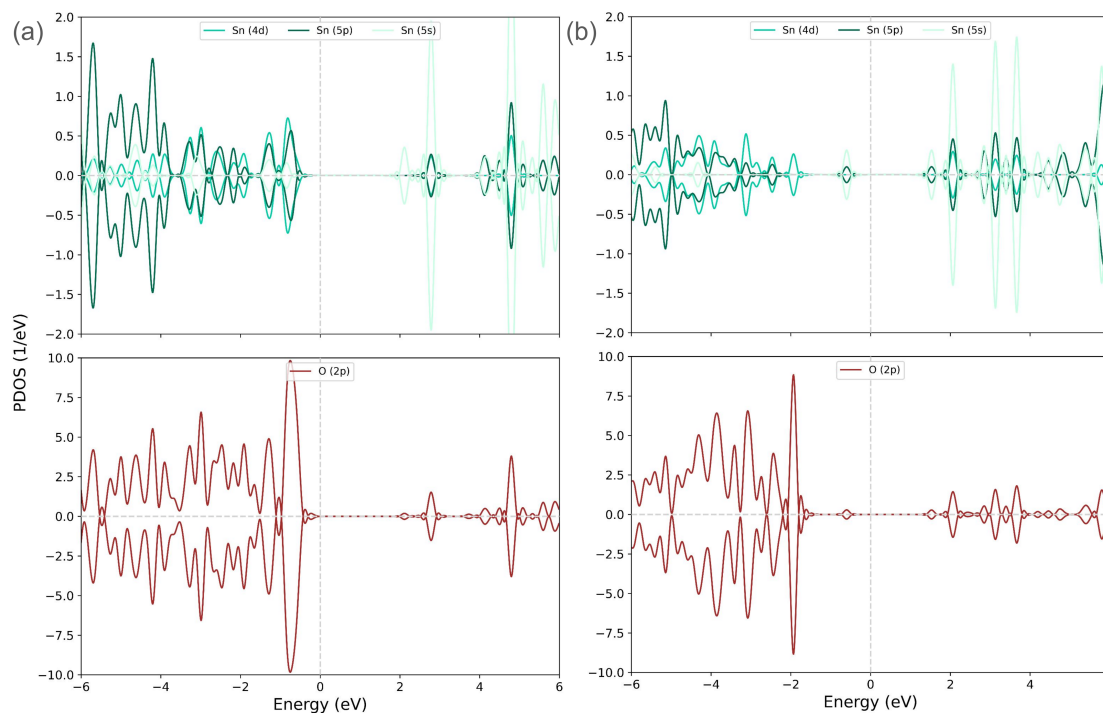


Fig. SM 5 Projected DOS of the first surface trilayer (Sn: green and O: red) of (a) SnO_2 (110) surface and (b) SnO_2 (110). V_O surface, neglecting the population densities below 0.1 1/eV. Band edges were aligned to the vacuum.

3 Adsorption site screening

In our study, adsorption site selection is conducted with XSORB,⁵ which integrates in its workflow two well-established Python libraries, ASE and Pymatgen. The relevant criteria for selecting sites are as follows:

1. **Symmetry analysis:** Pymatgen identifies high-symmetry points on the surface based on the crystallographic symmetry of the substrate. This selection avoids redundancy and ensures that symmetry-equivalent sites are chosen only once.
2. **Coordination environment:** Sites are chosen based on the coordination number of surface atoms. Lower-coordination sites, such as atop, bridge, and hollow sites, are preferred due to their tendency to bind more strongly, reflecting common adsorption preferences in catalysis.
3. **Stability and approximate binding preference:** While binding energies are not directly calculated at the initial site selection

stage, XSORB incorporates prior knowledge of stable sites for similar materials, ensuring that our selections reflect realistic adsorption behaviors.

The screening of potential adsorption positions was conducted solely for O₂ using XSORB, with the native initial input (settings.in), which generated the potential sites listed in Figure SM-6. This screening focused exclusively on O₂ because of our proposed mechanism for O₂ dissociation and CO oxidation, which occurs through a directly coupled, single-step pathway. In this mechanism, both molecules need to adsorb adjacently on the surface. Given that both molecules interact most favorably via their O atom with Sn cations on the surface—and considering the surface symmetry—there is only one symmetrically distinct co-adsorption site that meets these criteria for both molecules. In this configuration, CO adsorption consistently stabilizes in the same geometry, while O₂ adsorbs in two distinct configurations, leading to two activated forms: superoxide and peroxide, discussed in the main text. Other co-adsorption configurations would spatially separate the molecules, decoupling them and thereby precluding the study of the proposed mechanism.

@SETTINGS

&STRUCTURE

```

symm_reduce           = 0.1
near_reduce           = 0.2
surface_height        = 1.5

molecule_axis        = atoms 0 1
selected_atom_index    = 0

screening_atom_distance = 1.8
screening_min_distance = 1.5
relax_atom_distance    = 1.8
relax_min_distance     = 1.5
x_rot_angles          = 0
y_rot_angles          = 0 45 90
z_rot_angles          = 0 45 90
vertical_angles        = x
layers_height          = 0.5

```

The employed structural data for the surface and the adsorbate (O₂ molecule):

```

#=====
# CRYSTAL DATA
#-----
data_VESTA_phase_1

_chemical_name_common      'SnO2 (110) pristine'
_cell_length_a             6.416322
_cell_length_b             13.425858
_cell_length_c             27.317101
_cell_angle_alpha          90.000000
_cell_angle_beta           90.000000
_cell_angle_gamma          90.000000
_cell_volume               2353.221294
_space_group_name_H-M_alt  'P 1'
_space_group_IT_number     1

loop_
_space_group_symop_operation_xyz
  'x, y, z'

loop_
_atom_site_label
_atom_site_occupancy
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_adp_type
_atom_site_U_iso_or_equiv
_atom_site_type_symbol
Sn1          1.0      0.000000      0.000000      0.377130      Uiso  ? Sn

```


Sn2	1.0	0.000000	0.500000	0.377130	Uiso	? Sn
Sn3	1.0	0.500000	0.000000	0.377130	Uiso	? Sn
Sn4	1.0	0.500000	0.500000	0.377130	Uiso	? Sn
Sn5	1.0	0.000000	0.250000	0.501194	Uiso	? Sn
Sn6	1.0	-0.000000	0.750000	0.501194	Uiso	? Sn
Sn7	1.0	0.500000	0.250000	0.501194	Uiso	? Sn
Sn8	1.0	0.500000	0.750000	0.501194	Uiso	? Sn
Sn9	1.0	-0.000000	0.000000	0.619322	Uiso	? Sn
Sn10	1.0	0.000000	0.500000	0.619322	Uiso	? Sn
Sn11	1.0	0.500000	0.000000	0.619322	Uiso	? Sn
Sn12	1.0	0.500000	0.500000	0.619322	Uiso	? Sn
Sn13	1.0	0.250000	0.250000	0.377130	Uiso	? Sn
Sn14	1.0	0.250000	0.750000	0.377130	Uiso	? Sn
Sn15	1.0	0.750000	0.250000	0.377130	Uiso	? Sn
Sn16	1.0	0.750000	0.750000	0.377130	Uiso	? Sn
Sn17	1.0	0.250000	0.000000	0.498184	Uiso	? Sn
Sn18	1.0	0.250000	0.500000	0.498184	Uiso	? Sn
Sn19	1.0	0.750000	0.000000	0.498184	Uiso	? Sn
Sn20	1.0	0.750000	0.500000	0.498184	Uiso	? Sn
Sn21	1.0	0.250000	0.250000	0.629279	Uiso	? Sn
Sn22	1.0	0.250000	0.750000	0.629279	Uiso	? Sn
Sn23	1.0	0.750000	0.250000	0.629279	Uiso	? Sn
Sn24	1.0	0.750000	0.750000	0.629279	Uiso	? Sn
O1	1.0	0.000000	0.250000	0.329460	Uiso	? O
O2	1.0	0.000000	0.750000	0.329460	Uiso	? O
O3	1.0	0.500000	0.250000	0.329460	Uiso	? O
O4	1.0	0.500000	0.750000	0.329460	Uiso	? O
O5	1.0	0.000000	0.000000	0.451157	Uiso	? O
O6	1.0	0.000000	0.500000	0.451157	Uiso	? O
O7	1.0	0.500000	0.000000	0.451157	Uiso	? O
O8	1.0	0.500000	0.500000	0.451157	Uiso	? O
O9	1.0	0.000000	0.250000	0.576195	Uiso	? O
O10	1.0	-0.000000	0.750000	0.576195	Uiso	? O
O11	1.0	0.500000	0.250000	0.576195	Uiso	? O
O12	1.0	0.500000	0.750000	0.576195	Uiso	? O
O13	1.0	0.000000	0.250000	0.424800	Uiso	? O
O14	1.0	0.000000	0.750000	0.424800	Uiso	? O
O15	1.0	0.500000	0.250000	0.424800	Uiso	? O
O16	1.0	0.500000	0.750000	0.424800	Uiso	? O
O17	1.0	-0.000000	0.000000	0.546346	Uiso	? O
O18	1.0	-0.000000	0.500000	0.546346	Uiso	? O
O19	1.0	0.500000	0.000000	0.546346	Uiso	? O
O20	1.0	0.500000	0.500000	0.546346	Uiso	? O
O21	1.0	0.000000	0.250000	0.672555	Uiso	? O
O22	1.0	0.000000	0.750000	0.672555	Uiso	? O
O23	1.0	0.500000	0.250000	0.672555	Uiso	? O
O24	1.0	0.500000	0.750000	0.672555	Uiso	? O
O25	1.0	0.250000	0.096985	0.377130	Uiso	? O
O26	1.0	0.250000	0.596985	0.377130	Uiso	? O
O27	1.0	0.750000	0.096985	0.377130	Uiso	? O
O28	1.0	0.750000	0.596985	0.377130	Uiso	? O
O29	1.0	0.250000	0.250000	0.451157	Uiso	? O
O30	1.0	0.250000	0.750000	0.451157	Uiso	? O
O31	1.0	0.750000	0.250000	0.451157	Uiso	? O
O32	1.0	0.750000	0.750000	0.451157	Uiso	? O

#=====

```

2
02 molecule .xyz
0   7.764541   7.737161   6.869615
0   7.764541   7.737161   8.102387

```

The data generated by the XSORB package with the above input is presented in Table SM-3. The most favorable configurations

(Labels 26 and 40) were selected for further geometry optimization and resulted in the triplet and singlet O_2 detailed in the main text.

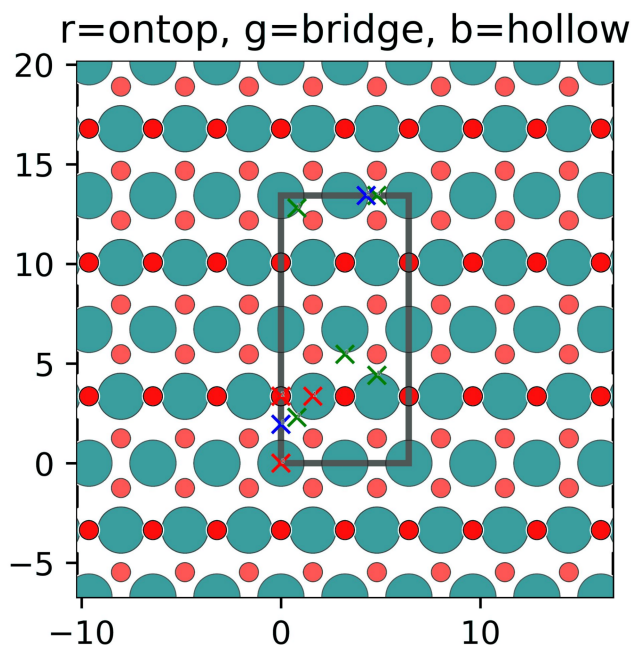


Fig. SM 6 Non-equivalent adsorption sites on the SnO_2 (110) surface. The three symmetry types (on-top, bridge, hollow) are colored in red, green, and blue, respectively.

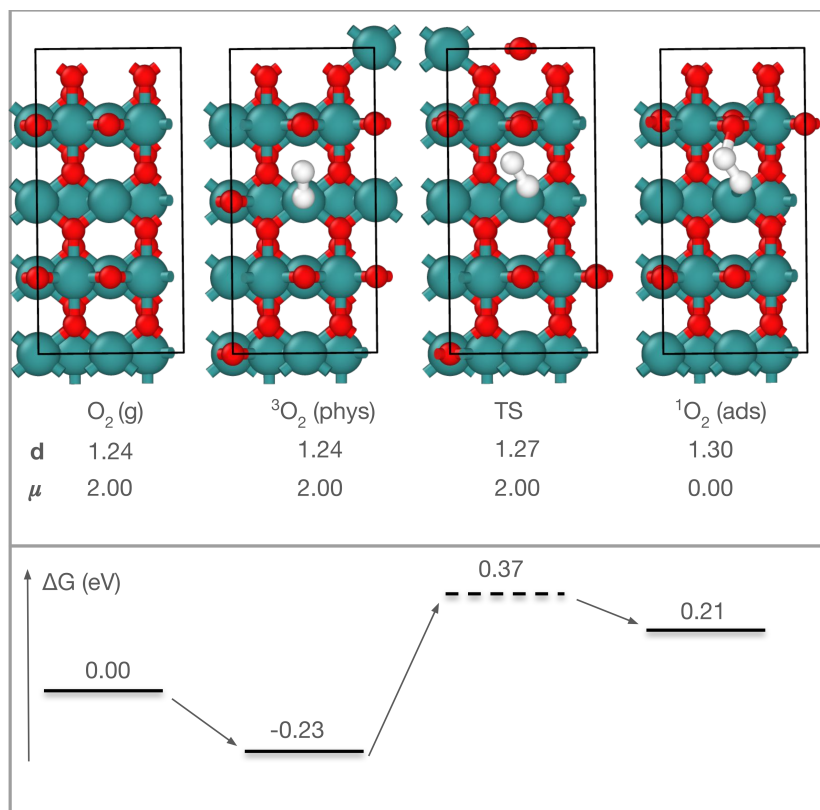


Fig. SM 7 The reaction sequence for the interaction of one molecule of oxygen gas with the pristine SnO_2 (110) surface (top view), from physisorption of triplet oxygen 3O_2 to the chemisorption of singlet oxygen 1O_2 . The relative Gibbs free energy (ΔG), molecular bond length d (Å) and molecular dipole moment μ (μ_B) in each step are signaled.

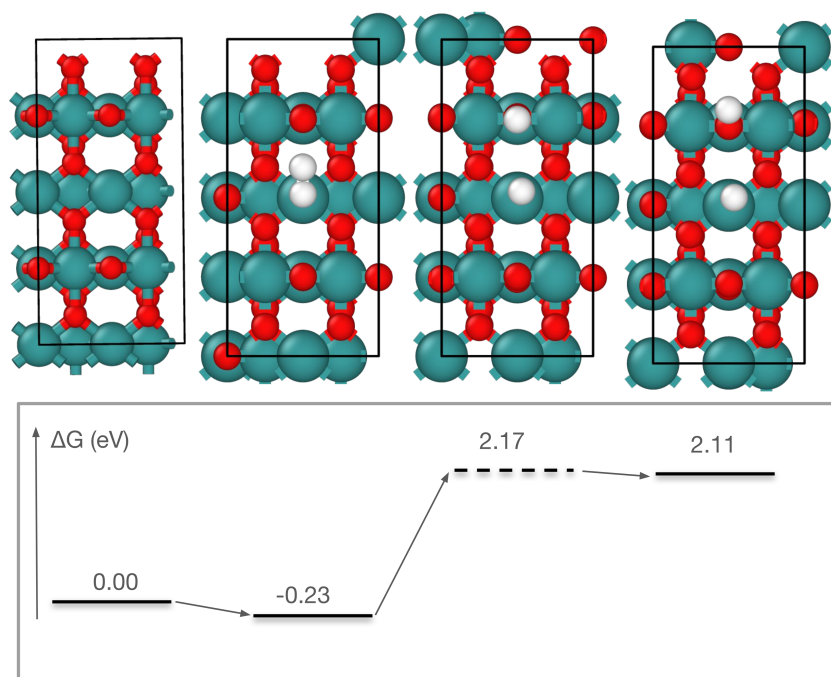


Fig. SM 8 The most favorable reaction path for the dissociation of one molecule of O_2 on the pristine SnO_2 (110) surface (top view), from physisorption of triplet oxygen 3O_2 to the chemisorption of two O^- anions. The relative Gibbs free energy (ΔG) in each step is signaled.

4 Transition state characterizations

The reaction pathways discussed in the main text for the formation of singlet oxygen from triplet oxygen upon O_2 adsorption on the pristine SnO_2 surface and for the dissociation of triplet oxygen into two O^- anions on the same surface follow in Figures SM-7 and SM-8, respectively.

We have characterized the transition states of all reactions discussed in the main text by analyzing the normal mode of vibration corresponding to the single imaginary frequency in the calculated spectrum (f/i). In each case, this mode is directly associated with the respective reaction coordinate.

Transition state in Figure SM-7:

78 f/i=	2.718684 THz		17.081994 2PiTHz	90.685528 cm-1	11.243567 meV	
	X	Y	Z	dx	dy	dz
	0.000000	0.000000	10.302098	0	0	0
	0.000000	6.712929	10.302098	0	0	0
	3.208161	0.000000	10.302098	0	0	0
	3.208161	6.712929	10.302098	0	0	0
	0.000221	3.372405	13.689649	0	0	0
	0.001975	10.086225	13.669051	0	0	0
	3.208392	3.364914	13.691915	0	0	0
	3.209714	10.085176	13.688952	0	0	0
	0.000035	13.420672	16.934296	-0.006418	-0.073309	0.018642
	0.000263	6.730556	16.877562	-0.005071	-0.002153	-0.016610
	3.207491	0.029662	16.922024	-0.007688	0.036932	-0.002124
	3.206168	6.733730	17.003832	-0.018396	0.037873	0.148160
	1.604080	3.356464	10.302098	0	0	0
	1.604080	10.069393	10.302098	0	0	0
	4.812241	3.356464	10.302098	0	0	0
	4.812241	10.069393	10.302098	0	0	0
	1.604153	0.010406	13.612363	0	0	0
	1.614762	6.717827	13.624820	0	0	0
	4.813034	0.010669	13.612245	0	0	0
	4.803056	6.717985	13.626273	0	0	0
	1.598438	3.382497	17.189660	-0.011815	0.013890	-0.004520
	1.580616	10.078352	17.138564	-0.099287	-0.060341	-0.069524
	4.816351	3.384280	17.188542	0.011061	0.026113	-0.005970
	4.846661	10.080849	17.128769	0.103896	-0.069697	-0.096398
	0.000000	3.356464	8.999892	0	0	0
	0.000000	10.069393	8.999892	0	0	0
	3.208161	3.356464	8.999892	0	0	0
	3.208161	10.069393	8.999892	0	0	0
	0.000456	0.005287	12.327873	0	0	0
	0.000333	6.747871	12.326989	0	0	0
	3.208641	0.013485	12.326326	0	0	0
	3.209275	6.744535	12.327605	0	0	0
	6.415980	3.390381	15.737223	-0.001599	-0.016169	-0.002677
	0.006037	10.208872	15.709507	0.003790	0.070960	-0.014390
	3.207394	3.372177	15.741101	0.000855	-0.022449	-0.000657
	3.211472	10.182270	15.766413	0.003319	0.039053	0.064730
	0.000000	3.356464	11.604305	0	0	0
	0.000000	10.069393	11.604305	0	0	0
	3.208161	3.356464	11.604305	0	0	0
	3.208161	10.069393	11.604305	0	0	0
	0.000274	13.402019	14.938335	0	0	0
	0.001748	6.662389	14.893691	0	0	0
	3.208679	13.410552	14.930447	0	0	0
	3.208106	6.676017	14.956407	0	0	0
	6.414863	3.312322	18.372612	-0.001231	-0.040618	-0.001323

0.001596	10.048964	18.353945	-0.006549	0.019258	0.011264
3.207827	3.353710	18.364559	0.000574	-0.033780	-0.011163
3.213307	10.011970	18.389603	-0.008610	-0.151957	0.108427
1.604080	1.302107	10.302098	0	0	0
1.604080	8.015036	10.302098	0	0	0
4.812241	1.302107	10.302098	0	0	0
4.812241	8.015036	10.302098	0	0	0
1.608442	4.679475	13.621143	0	0	0
1.611177	11.401555	13.627445	0	0	0
4.808505	4.679842	13.621769	0	0	0
4.808300	11.401409	13.629026	0	0	0
1.595816	1.255272	17.162417	-0.014842	-0.020753	-0.000362
1.577909	8.013506	16.964076	-0.031725	0.032594	-0.132972
4.819760	1.254309	17.161402	0.009587	-0.023534	0.003167
4.844020	8.019569	16.949441	0.037051	0.037120	-0.167282
1.604080	5.410822	10.302098	0	0	0
1.604080	12.123751	10.302098	0	0	0
4.812241	5.410822	10.302098	0	0	0
4.812241	12.123751	10.302098	0	0	0
1.601281	2.038899	13.665468	0	0	0
1.609630	8.765323	13.697369	0	0	0
4.815415	2.039045	13.665470	0	0	0
4.810388	8.765459	13.697247	0	0	0
1.575829	5.493474	17.219722	-0.022219	-0.002984	-0.012459
1.622360	12.183957	17.261319	0.022737	-0.031196	0.032867
4.836789	5.496217	17.213215	0.013716	0.006479	0.004184
4.792735	12.182957	17.264496	-0.034022	-0.037267	0.034036
3.458033	7.348567	19.149914	0.194432	0.492372	-0.295990
2.793293	8.386289	19.460349	-0.017824	0.482838	-0.462496

Transition state in Figure SM-8:

78 f/i=	2.714741 THz	17.057220 2PiTHz	90.554007 cm-1	11.227261 meV
	X	Y	Z	
			dx	dy
				dz
0.000000	0.000000	10.302098	0	0
0.000000	6.712929	10.302098	0	0
3.208161	0.000000	10.302098	0	0
3.208161	6.712929	10.302098	0	0
0.000486	3.355135	13.688179	0	0
6.415524	10.070692	13.659204	0	0
3.207253	3.350356	13.690292	0	0
3.208235	10.069451	13.689652	0	0
0.000153	13.420428	16.940098	0.001936	0.023022
6.412615	6.721799	16.884105	0.007226	0.013181
3.207243	0.041718	16.919260	0.002144	-0.000108
3.207509	6.697011	17.077333	-0.001765	0.031616
1.604080	3.356464	10.302098	0	0
1.604080	10.069393	10.302098	0	0
4.812241	3.356464	10.302098	0	0
4.812241	10.069393	10.302098	0	0
1.603788	13.425629	13.612242	0	0
1.614948	6.710205	13.632361	0	0
4.812239	0.000722	13.612561	0	0

4.799866	6.706757	13.637441	0	0	0
1.595933	3.375550	17.181476	0.005294	0.005883	0.005149
1.520699	10.063487	17.077928	0.006913	0.026821	-0.001660
4.821245	3.383330	17.167455	-0.001249	0.003553	0.006961
4.896644	10.075124	17.088321	-0.013238	0.018648	-0.003747
0.000000	3.356464	8.999892	0	0	0
0.000000	10.069393	8.999892	0	0	0
3.208161	3.356464	8.999892	0	0	0
3.208161	10.069393	8.999892	0	0	0
6.415982	13.399801	12.328737	0	0	0
6.414781	6.733060	12.331017	0	0	0
3.208231	13.412810	12.326413	0	0	0
3.208836	6.727427	12.331831	0	0	0
0.010502	3.270134	15.725780	-0.000759	0.013068	0.002649
6.412065	10.195740	15.678032	0.001045	-0.007101	0.000559
3.200760	3.272486	15.731066	0.001194	0.009208	0.001709
3.212551	10.133789	15.844242	-0.001074	0.008068	-0.009990
0.000000	3.356464	11.604305	0	0	0
0.000000	10.069393	11.604305	0	0	0
3.208161	3.356464	11.604305	0	0	0
3.208161	10.069393	11.604305	0	0	0
6.416311	13.408690	14.939112	0	0	0
0.001684	6.718995	14.899836	0	0	0
3.207817	13.419423	14.930134	0	0	0
3.204418	6.714103	14.969333	0	0	0
6.411383	3.332027	18.362057	0.001268	0.006985	0.001339
0.004584	10.134339	18.356472	-0.002255	0.006399	-0.003244
3.212871	3.389697	18.342755	0.000596	0.007112	0.002765
3.204943	10.088565	18.455569	0.001024	0.151982	-0.015803
1.604080	1.302107	10.302098	0	0	0
1.604080	8.015036	10.302098	0	0	0
4.812241	1.302107	10.302098	0	0	0
4.812241	8.015036	10.302098	0	0	0
1.606177	4.671401	13.649137	0	0	0
1.612212	11.388584	13.664119	0	0	0
4.809583	4.669380	13.648995	0	0	0
4.803445	11.389039	13.662367	0	0	0
1.594186	1.232468	17.241305	0.004499	0.006567	-0.000178
1.558231	8.026312	16.995370	0.001743	0.006168	0.029044
4.821594	1.237460	17.216741	-0.000968	0.005593	0.003670
4.858294	8.032888	17.037672	0.004894	0.007087	-0.005306
1.604080	5.410822	10.302098	0	0	0
1.604080	12.123751	10.302098	0	0	0
4.812241	5.410822	10.302098	0	0	0
4.812241	12.123751	10.302098	0	0	0
1.601633	2.025739	13.631563	0	0	0
1.609717	8.760821	13.681424	0	0	0
4.814380	2.026717	13.635554	0	0	0
4.805740	8.758558	13.684577	0	0	0
1.555265	5.469102	17.113886	0.006017	0.009634	0.018096
1.632036	12.157152	17.204202	-0.005824	0.009361	-0.013457
4.859426	5.451518	16.950232	-0.004103	0.011934	0.036036
4.783275	12.163009	17.221958	0.005640	0.007995	-0.016832

3.461410	7.020588	19.032716	0.073924	0.137784	-0.009931
3.199838	9.978799	19.763872	0.008410	-0.966948	-0.096005

TS1 in figure 5a in the main text:

84 f/i=	6.058837 THz	38.068793 2PiTHz	202.101035 cm-1	25.057324 meV
	X	Y	Z	
				dx
				dy
				dz
0.000000	0.000000	10.302098	0	0
0.000000	6.712929	10.302098	0	0
3.208161	0.000000	10.302098	0	0
3.208161	6.712929	10.302098	0	0
6.414268	3.345560	13.678809	0	0
6.413777	10.064348	13.686691	0	0
3.206208	3.354037	13.688817	0	0
3.205436	10.073886	13.687513	0	0
6.410930	0.039416	16.930466	0.003993	-0.046168
0.009882	6.750129	16.921531	-0.017225	0.008846
3.201676	13.400685	16.931913	0.004834	0.049070
3.218551	6.707474	16.960248	-0.019324	-0.031385
1.604080	3.356464	10.302098	0	0
1.604080	10.069393	10.302098	0	0
4.812241	3.356464	10.302098	0	0
4.812241	10.069393	10.302098	0	0
1.602428	13.423630	13.612253	0	0
1.604128	6.712281	13.624999	0	0
4.810516	13.423188	13.612693	0	0
4.805979	6.712998	13.622991	0	0
1.608240	3.376043	17.179116	-0.007041	-0.014586
1.591251	10.065233	17.133438	-0.092222	0.048866
4.816829	3.374247	17.180071	0.002332	-0.015023
4.779664	10.071379	17.120062	0.176690	0.010273
0.000000	3.356464	8.999892	0	0
0.000000	10.069393	8.999892	0	0
3.208161	3.356464	8.999892	0	0
3.208161	10.069393	8.999892	0	0
6.414756	0.001700	12.328156	0	0
6.414424	6.703637	12.325908	0	0
3.206857	13.418960	12.327312	0	0
3.205312	6.703575	12.326883	0	0
0.001485	3.311451	15.732858	-0.002013	0.019753
6.404939	10.169769	15.754648	0.007440	-0.034226
3.210897	3.337863	15.737751	-0.000009	0.012544
3.188810	10.185708	15.729594	0.011759	-0.021746
0.000000	3.356464	11.604305	0	0
0.000000	10.069393	11.604305	0	0
3.208161	3.356464	11.604305	0	0
3.208161	10.069393	11.604305	0	0
6.414600	0.012090	14.938670	0	0
6.411107	6.753098	14.908993	0	0
3.205800	13.422183	14.936415	0	0
3.205645	6.711299	14.932560	0	0
0.005072	3.305784	18.361684	-0.000970	0.031796
6.379427	9.884283	18.392154	0.088148	0.327585

3.212640	3.393198	18.362415	-0.001370	0.013298	0.003245
3.187489	10.092738	18.360116	0.028036	-0.131704	0.048759
1.604080	1.302107	10.302098	0	0	0
1.604080	8.015036	10.302098	0	0	0
4.812241	1.302107	10.302098	0	0	0
4.812241	8.015036	10.302098	0	0	0
1.599612	4.667328	13.671180	0	0	0
1.597727	11.393908	13.651322	0	0	0
4.812496	4.667706	13.670439	0	0	0
4.813805	11.393760	13.651629	0	0	0
1.621157	1.238481	17.203387	-0.012215	0.015075	-0.001106
1.621623	8.012363	16.974102	0.005497	-0.025515	0.064419
4.788682	1.237492	17.207887	0.012623	0.015006	-0.001576
4.802864	8.014686	16.940129	-0.010812	-0.031868	0.080506
1.604080	5.410822	10.302098	0	0	0
1.604080	12.123751	10.302098	0	0	0
4.812241	5.410822	10.302098	0	0	0
4.812241	12.123751	10.302098	0	0	0
1.608462	2.028979	13.638511	0	0	0
1.606308	8.754553	13.649261	0	0	0
4.804035	2.028664	13.639538	0	0	0
4.804400	8.755183	13.648900	0	0	0
1.590361	5.483580	17.150870	-0.005193	-0.000426	0.012376
1.567509	12.163405	17.256979	0.058012	0.025330	-0.026981
4.849119	5.483280	17.155223	-0.013463	0.004090	0.039025
4.828784	12.164394	17.242222	-0.040944	0.022520	-0.018260
3.217631	7.055372	19.261319	-0.216901	0.010518	0.039635
3.659400	8.162922	19.672605	-0.305146	0.025659	-0.034749
0.008175	7.392566	19.226612	-0.030044	-0.185176	0.113886
6.003632	8.419918	19.625576	0.258108	-0.293802	0.601874

TS1 in figure 5b in the main text:

81 f/i=	2.416328 THz	15.182236 2PiTHz	80.600025 cm-1	9.993125 meV		
	X	Y	Z	dx	dy	dz
	0.000000	3.356464	10.302098	0	0	0
	0.000000	10.069393	10.302098	0	0	0
	3.208161	3.356464	10.302098	0	0	0
	3.208161	10.069393	10.302098	0	0	0
	6.410848	6.707941	13.641298	0	0	0
	6.408701	13.423299	13.683226	0	0	0
	3.202265	6.705732	13.681998	0	0	0
	3.201086	13.418096	13.683120	0	0	0
	6.411170	3.369610	16.950095	-0.000705	0.020997	-0.003476
	6.410422	10.055064	16.941675	-0.002816	0.020513	-0.010260
	3.202810	3.335044	16.929399	-0.000610	0.009205	0.000012
	3.202133	10.101442	16.959984	-0.001353	0.014647	0.027947
	1.604080	6.712929	10.302098	0	0	0
	1.604080	0.000000	10.302098	0	0	0
	4.812241	6.712929	10.302098	0	0	0
	4.812241	0.000000	10.302098	0	0	0
	1.598538	3.347767	13.616028	0	0	0
	1.600305	10.065870	13.627655	0	0	0

4.806708	3.348038	13.618395	0	0	0
4.802100	10.065381	13.629596	0	0	0
1.526933	6.716835	17.108785	0.011706	0.020976	0.016703
1.593867	0.000939	17.187844	-0.001548	0.008311	-0.005860
4.879103	6.717205	17.107076	-0.018314	0.022458	0.021864
4.810762	0.000765	17.187666	0.001145	0.007908	-0.003872
0.000000	6.712929	8.999892	0	0	0
0.000000	0.000000	8.999892	0	0	0
3.208161	6.712929	8.999892	0	0	0
3.208161	0.000000	8.999892	0	0	0
6.411082	3.385483	12.342640	0	0	0
6.409619	10.021949	12.347080	0	0	0
3.203648	3.375897	12.339607	0	0	0
3.203242	10.040889	12.345011	0	0	0
6.412063	6.705698	15.700406	-0.001206	-0.007548	0.001790
6.410646	0.014078	15.740975	-0.000072	0.011727	-0.003182
3.202117	6.697358	15.856656	-0.000016	-0.007591	-0.007626
3.201572	0.010085	15.741724	0.000208	0.009769	-0.003646
0.000000	6.712929	11.604305	0	0	0
0.000000	0.000000	11.604305	0	0	0
3.208161	6.712929	11.604305	0	0	0
3.208161	0.000000	11.604305	0	0	0
6.410814	3.375753	14.954054	0	0	0
6.408472	10.031784	14.951348	0	0	0
3.200603	3.361572	14.942716	0	0	0
3.199383	10.057436	14.962357	0	0	0
6.410467	6.716240	18.372345	-0.000888	-0.005563	-0.000943
6.410377	13.422764	18.377069	0.000134	0.012292	-0.003946
3.202473	13.409820	18.367788	-0.000382	0.021827	-0.006750
1.604080	4.658571	10.302098	0	0	0
1.604080	11.371500	10.302098	0	0	0
4.812241	4.658571	10.302098	0	0	0
4.812241	11.371500	10.302098	0	0	0
1.609111	8.016217	13.722499	0	0	0
1.597519	1.319676	13.661889	0	0	0
4.795423	8.016299	13.735807	0	0	0
4.804661	1.319844	13.662937	0	0	0
1.622192	4.634125	17.236041	0.000682	0.002009	-0.000612
1.582092	11.308976	17.190214	-0.003799	0.010261	-0.025559
4.783843	4.634489	17.233541	-0.001629	0.002098	0.000301
4.822131	11.308765	17.190952	0.002286	0.010026	-0.023800
1.604080	8.767286	10.302098	0	0	0
1.604080	2.054357	10.302098	0	0	0
4.812241	8.767286	10.302098	0	0	0
4.812241	2.054357	10.302098	0	0	0
1.607095	5.394697	13.711149	0	0	0
1.593368	12.097324	13.664710	0	0	0
4.797907	5.394561	13.710144	0	0	0
4.808252	12.096637	13.675183	0	0	0
1.619549	8.794953	17.232714	-0.010308	0.007965	-0.016608
1.591899	2.123768	17.226723	-0.002455	0.007265	-0.002314
4.784859	8.794970	17.232153	0.007716	0.008255	-0.014477
4.813480	2.123886	17.226163	0.002151	0.007188	-0.002541

3.202880	6.694855	18.487556	-0.004164	0.038196	-0.007811
3.201611	7.111951	19.756356	-0.013159	0.097897	-0.000807
3.190793	10.140302	19.572958	-0.056341	-0.048288	-0.178556
3.168449	9.693974	20.630993	-0.234234	-0.815799	-0.472199

TS2 in figure 5a in the main text:

81 f/i=	9.393959 THz	59.023985 2PiTHz	313.348741 cm-1	38.850275 meV	
	X	Y	Z		
			dx	dy	dz
0.000000	0.000000	10.302098	0	0	0
0.000000	6.712929	10.302098	0	0	0
3.208161	0.000000	10.302098	0	0	0
3.208161	6.712929	10.302098	0	0	0
6.414560	3.334427	13.669334	0	0	0
6.414245	10.055395	13.689064	0	0	0
3.206586	3.349578	13.687293	0	0	0
3.205695	10.071584	13.688447	0	0	0
6.416129	0.065994	16.943931	-0.000199	0.001881	-0.001441
0.001355	6.738928	16.863925	-0.000710	-0.001368	-0.002145
3.207538	13.386798	16.934869	0.000275	0.010403	0.003122
3.209221	6.556595	17.047170	-0.003258	0.050147	-0.141410
1.604080	3.356464	10.302098	0	0	0
1.604080	10.069393	10.302098	0	0	0
4.812241	3.356464	10.302098	0	0	0
4.812241	10.069393	10.302098	0	0	0
1.603288	13.419690	13.614052	0	0	0
1.605627	6.711394	13.630229	0	0	0
4.811177	13.418872	13.614779	0	0	0
4.804324	6.712778	13.626627	0	0	0
1.550693	3.386157	17.093595	0.066415	-0.006214	0.054863
1.604428	10.029488	17.188555	-0.000052	0.013755	0.001834
4.863108	3.386353	17.093143	-0.065354	-0.004702	0.054068
4.814605	10.032393	17.185057	-0.001086	0.013585	0.004172
0.000000	3.356464	8.999892	0	0	0
0.000000	10.069393	8.999892	0	0	0
3.208161	3.356464	8.999892	0	0	0
3.208161	10.069393	8.999892	0	0	0
6.415269	0.000261	12.329817	0	0	0
6.414770	6.683465	12.325986	0	0	0
3.207528	13.410260	12.328428	0	0	0
3.204909	6.684276	12.327426	0	0	0
6.415351	3.091055	15.697199	0.001164	0.022597	0.006165
0.000904	10.018055	15.742263	-0.001186	-0.011701	0.001132
3.207035	3.210119	15.789739	0.000000	0.000198	-0.036555
3.207248	10.084837	15.744906	0.000164	-0.010250	0.000364
0.000000	3.356464	11.604305	0	0	0
0.000000	10.069393	11.604305	0	0	0
3.208161	3.356464	11.604305	0	0	0
3.208161	10.069393	11.604305	0	0	0
6.415767	0.034601	14.944268	0	0	0
6.409967	6.801724	14.900214	0	0	0
3.206562	0.006993	14.941304	0	0	0
3.206588	6.729924	14.936109	0	0	0

6.415068	3.433983	18.346096	0.000308	0.015480	-0.010280
0.000599	10.068956	18.371104	0.000027	-0.007963	0.000893
3.207547	3.759887	18.398626	0.004712	-0.170717	-0.032634
3.210494	10.125811	18.369243	-0.000862	-0.009999	0.002043
1.604080	1.302107	10.302098	0	0	0
1.604080	8.015036	10.302098	0	0	0
4.812241	1.302107	10.302098	0	0	0
4.812241	8.015036	10.302098	0	0	0
1.598227	4.660447	13.697823	0	0	0
1.594902	11.392918	13.662201	0	0	0
4.814539	4.661169	13.696704	0	0	0
4.817531	11.392645	13.662570	0	0	0
1.652411	1.282328	17.326107	-0.010393	-0.014184	-0.010369
1.620489	7.897446	17.249567	0.006255	0.002014	0.025110
4.762925	1.281888	17.327042	0.011183	-0.014055	-0.011367
4.801347	7.901759	17.237871	-0.011612	-0.002680	0.041969
1.604080	5.410822	10.302098	0	0	0
1.604080	12.123751	10.302098	0	0	0
4.812241	5.410822	10.302098	0	0	0
4.812241	12.123751	10.302098	0	0	0
1.613958	2.025737	13.624101	0	0	0
1.609788	8.754045	13.627831	0	0	0
4.799466	2.025117	13.625958	0	0	0
4.801411	8.755335	13.627340	0	0	0
1.507181	5.390601	16.719027	0.033427	0.021437	0.047417
1.573145	12.193907	17.171578	0.001240	-0.008496	-0.002029
4.911480	5.391767	16.719300	-0.027564	0.020836	0.029142
4.843437	12.194563	17.169872	-0.001474	-0.008669	-0.001512
3.217771	5.290710	18.767609	0.071298	0.628174	0.251225
3.680533	7.195861	20.768202	-0.044868	-0.121001	-0.170709
3.410302	6.957795	19.681655	-0.019140	-0.637308	-0.069313

TS2 in figure 5b in the main text:

78 f/i=	9.382939 THz	58.954742 2PiTHz	312.981141 cm-1	38.804698 meV	
X	Y	Z	dx	dy	dz
0.000000	3.356464	10.302098	0	0	0
0.000000	10.069393	10.302098	0	0	0
3.208161	3.356464	10.302098	0	0	0
3.208161	10.069393	10.302098	0	0	0
0.000316	6.703029	13.683088	0	0	0
0.000385	13.415939	13.690174	0	0	0
3.208651	6.704728	13.688245	0	0	0
3.208399	13.424909	13.691722	0	0	0
6.414171	3.361784	16.931402	-0.000101	0.006323	0.007508
6.414047	10.066019	16.880833	0.000258	0.006436	0.005015
3.205576	3.300189	16.921385	-0.000250	-0.026014	-0.005578
3.205747	9.993812	16.984589	0.000011	-0.015720	0.090592
1.604080	6.712929	10.302098	0	0	0
1.604080	0.000000	10.302098	0	0	0
4.812241	6.712929	10.302098	0	0	0
4.812241	0.000000	10.302098	0	0	0
1.604135	3.353133	13.610956	0	0	0

1.611571	10.067533	13.617208	0	0	0
4.813084	3.352968	13.610802	0	0	0
4.805914	10.068403	13.614525	0	0	0
1.571910	6.689408	17.132533	-0.089450	0.037642	-0.036642
1.600236	13.382926	17.192844	-0.003395	-0.015766	0.001251
4.837733	6.689424	17.136660	0.087382	0.038672	-0.034825
4.811389	13.382895	17.192458	0.003529	-0.015806	0.001237
0.000000	6.712929	8.999892	0	0	0
0.000000	0.000000	8.999892	0	0	0
3.208161	6.712929	8.999892	0	0	0
3.208161	0.000000	8.999892	0	0	0
0.000463	3.348947	12.326399	0	0	0
0.001169	10.053769	12.324960	0	0	0
3.208461	3.345298	12.326084	0	0	0
3.208013	10.052884	12.325001	0	0	0
6.412608	6.568062	15.715018	-0.000974	-0.026406	-0.001181
6.415032	13.365602	15.740673	-0.000183	0.015940	-0.002326
3.206508	6.603961	15.766353	-0.000841	-0.013213	0.131088
3.206711	13.405338	15.742964	-0.000038	0.014007	-0.000377
0.000000	6.712929	11.604305	0	0	0
0.000000	0.000000	11.604305	0	0	0
3.208161	6.712929	11.604305	0	0	0
3.208161	0.000000	11.604305	0	0	0
0.000538	3.382769	14.933439	0	0	0
6.415287	10.114383	14.900169	0	0	0
3.208714	3.370773	14.929966	0	0	0
3.210437	10.089681	14.943053	0	0	0
6.414302	6.713940	18.357775	0.000023	-0.025152	0.025317
6.413651	13.422302	18.372324	0.000001	0.024253	-0.001981
3.205873	0.022595	18.368643	-0.000002	0.021378	-0.004873
1.604080	4.658571	10.302098	0	0	0
1.604080	11.371500	10.302098	0	0	0
4.812241	4.658571	10.302098	0	0	0
4.812241	11.371500	10.302098	0	0	0
1.604584	8.027302	13.678263	0	0	0
1.600904	1.321632	13.664387	0	0	0
4.812594	8.027662	13.677418	0	0	0
4.816078	1.321694	13.664663	0	0	0
1.630250	4.589764	17.266644	0.034707	0.046875	0.033365
1.605639	11.263686	17.242815	-0.013115	0.001051	-0.018537
4.781120	4.589578	17.270589	-0.035785	0.047285	0.034110
4.805983	11.264199	17.242026	0.013004	0.001146	-0.018453
1.604080	8.767286	10.302098	0	0	0
1.604080	2.054357	10.302098	0	0	0
4.812241	8.767286	10.302098	0	0	0
4.812241	2.054357	10.302098	0	0	0
1.606685	5.385737	13.629733	0	0	0
1.609151	12.105048	13.634210	0	0	0
4.810468	5.385515	13.629221	0	0	0
4.807814	12.105852	13.632350	0	0	0
1.557518	8.756795	16.958049	-0.026049	-0.040548	-0.041461
1.584128	2.088864	17.155240	-0.003397	0.023975	0.003371
4.854107	8.757123	16.969006	0.026300	-0.040256	-0.040806

4.827788	2.088740	17.153297	0.003281	0.024108	0.003378
3.202329	6.908089	18.388190	-0.007135	0.422220	0.359180
3.190917	9.268983	19.187687	0.004982	-0.180898	-0.152804
3.176084	8.173848	19.670644	0.010588	-0.472885	-0.584448

References

- [1] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, *APL Materials*, 2013, **1**, 011002.
- [2] J. Poirier, *Introduction to the Physics of the Earth's Interior*, Cambridge University Press, 2000.
- [3] O. Mounkachi, E. Salmani, M. Lakhal, H. Ez-Zahraouy, M. Hamedoun, M. Benaissa, A. Kara, A. Ennaoui and A. Benyoussef, *Solar Energy Materials and Solar Cells*, 2016, **148**, 34–38.
- [4] Y. A. Mantz and Y.-L. Lee, *The Journal of Physical Chemistry C*, 2023, **127**, 9814–9822.
- [5] E. Pedretti, P. Restuccia and M. C. Righi, *Computer Physics Communications*, 2023, **291**, 108827.

Table 3 Adsorption energies for the screening ($E_{\text{ads_scr}}$) and full relaxation ($E_{\text{ads_rel}}$) of a single O_2 molecule on top of the pristine SnO_2 (110) surface. All symmetric distinct sites are labeled according to Figure SM-6. The degrees of rotation to obtain the initial configurations are indicated with respect to all axes. Values indicated as "nan" represent cases where the energy was not calculated.

Label	xrot (°)	yrot (°)	zrot (°)	site	$E_{\text{ads_scr}}$ (eV)	$E_{\text{ads_rel}}$ (eV)
0	0.0	0.0	0.0	1 ontop_Sn	-0.554	nan
1	0.0	0.0	0.0	1 ontop_Sn	0.226	-0.548
2	0.0	0.0	0.0	2 ontop_O	-0.467	nan
3	0.0	0.0	0.0	3 bridge	-0.338	nan
4	0.0	0.0	0.0	4 bridge	0.54	nan
5	0.0	0.0	0.0	5 bridge	-0.259	nan
6	0.0	0.0	0.0	6 bridge	-0.561	nan
7	0.0	0.0	0.0	7 bridge	0.501	nan
8	0.0	0.0	0.0	8 hollow	-0.337	nan
9	0.0	0.0	0.0	9 hollow	-0.795	nan
10	0.0	0.0	45.0	0 ontop_Sn	-0.606	nan
11	0.0	0.0	45.0	1 ontop_Sn	-0.323	nan
12	0.0	0.0	45.0	2 ontop_O	-0.371	nan
13	0.0	0.0	45.0	3 bridge	-0.273	nan
14	0.0	0.0	45.0	4 bridge	-0.583	nan
15	0.0	0.0	45.0	5 bridge	-0.052	-0.732
16	0.0	0.0	45.0	6 bridge	-0.568	nan
17	0.0	0.0	45.0	7 bridge	-0.512	nan
18	0.0	0.0	45.0	8 hollow	-0.371	nan
19	0.0	0.0	45.0	9 hollow	-0.492	nan
20	0.0	0.0	90.0	0 ontop_Sn	-0.633	nan
21	0.0	0.0	90.0	1 ontop_Sn	-0.404	nan
22	0.0	0.0	90.0	2 ontop_O	-0.427	nan
23	0.0	0.0	90.0	3 bridge	-0.491	nan
24	0.0	0.0	90.0	4 bridge	0.405	nan
25	0.0	0.0	90.0	5 bridge	0.288	nan
26	0.0	0.0	90.0	6 bridge	-0.742	-0.795
27	0.0	0.0	90.0	7 bridge	0.788	-0.754
28	0.0	0.0	90.0	8 hollow	0.036	-0.79
29	0.0	0.0	90.0	9 hollow	0.23	-0.792
30	0.0	45.0	0.0	0 ontop_Sn	-0.64	-0.747
31	0.0	45.0	0.0	1 ontop_Sn	-0.364	nan
32	0.0	45.0	0.0	2 ontop_O	-0.383	nan
33	0.0	45.0	0.0	3 bridge	-0.465	nan
34	0.0	45.0	0.0	4 bridge	-0.571	nan
35	0.0	45.0	0.0	5 bridge	-0.427	nan
36	0.0	45.0	0.0	6 bridge	-0.598	nan
37	0.0	45.0	0.0	7 bridge	0.593	-0.721
38	0.0	45.0	0.0	8 hollow	-0.435	nan
39	0.0	45.0	0.0	9 hollow	-0.581	nan
40	0.0	45.0	45.0	0 ontop_Sn	-0.671	-0.795
41	0.0	45.0	45.0	1 ontop_Sn	-0.485	nan
42	0.0	45.0	45.0	2 ontop_O	-0.391	nan
43	0.0	45.0	45.0	3 bridge	-0.378	nan
44	0.0	45.0	45.0	4 bridge	-0.444	nan
45	0.0	45.0	45.0	5 bridge	-0.395	nan
46	0.0	45.0	45.0	6 bridge	-0.579	nan
47	0.0	45.0	45.0	7 bridge	0.48	nan
48	0.0	45.0	45.0	8 hollow	-0.385	nan
49	0.0	45.0	45.0	9 hollow	-0.55	nan
50	0.0	45.0	90.0	0 ontop_Sn	-0.732	nan
51	0.0	45.0	90.0	1 ontop_Sn	-0.438	nan
52	0.0	45.0	90.0	2 ontop_O	-0.738	nan
53	0.0	45.0	90.0	3 bridge	-0.411	nan
54	0.0	45.0	90.0	4 bridge	-0.476	nan
55	0.0	45.0	90.0	5 bridge	-0.384	nan
56	0.0	45.0	90.0	6 bridge	-0.557	nan
57	0.0	45.0	90.0	7 bridge	0.489	nan
58	0.0	45.0	90.0	8 hollow	-0.422	nan
59	0.0	45.0	90.0	9 hollow	-0.544	nan
60	0.0	90.0	0.0	0 ontop_Sn	-0.548	nan
61	0.0	90.0	0.0	1 ontop_Sn	-0.321	nan
62	0.0	90.0	0.0	2 ontop_O	-0.397	nan
63	0.0	90.0	0.0	3 bridge	-0.388	nan
64	0.0	90.0	0.0	4 bridge	-0.421	nan
65	0.0	90.0	0.0	5 bridge	-0.384	nan
66	0.0	90.0	0.0	6 bridge	-0.576	nan
67	0.0	90.0	0.0	7 bridge	0.48	nan
68	0.0	90.0	0.0	8 hollow	-0.437	nan
69	0.0	90.0	0.0	9 hollow	-0.46	nan