

Water adsorption on $\beta - PbO_2$: A surface orientation study

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Introduction

Lead dioxide $\beta - PbO_2$ is one of the main materials in the composition of the active material in lead acid batteries (LABs). The main failures of these batteries are the degradation of the active material, corrosion in the current collector, loss of water, etc. [1]. The loss of water in LABs could be related to the interaction between the water molecules and $\beta - PbO_2$. Therefore, studying the interaction between H_2O and $\beta - PbO_2$ is necessary to understand and reduce water loss in LABs.

The adsorption energy is a physical parameter that quantifies the ability of a system to attract smaller systems (atoms and molecules) [2]. In the field of electrochemistry, many researchers associate higher electrical conductivity with large values of adsorption energy.

In this work, the adsorption energy of the H_2O molecule is calculated on the surfaces (101) and (110) of lead dioxide in phase β . The same calculation is performed for the same surfaces, considering oxygen surface finishes (**cross-linked oxygen**) [3]. This study was carried out using the density functional theory (DFT), developed in the Quantum Espresso (QE) software.

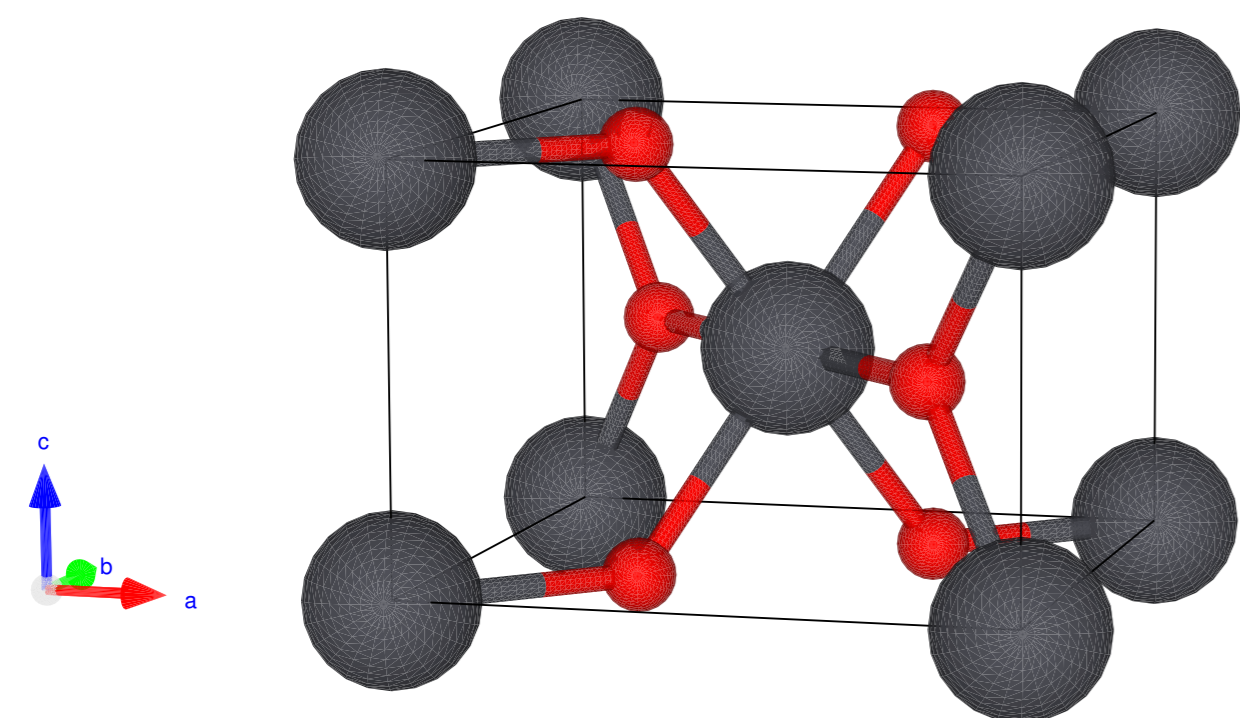


Fig.1 $\beta - PbO_2$ unit cell, red atom (oxygen), gray atom (lead). Lattice parameters: $a, b = 4.98581, c = 3.42809$ Angstroms.

Computational details

The adsorption energy is calculated using the following formula:

$$E_{ads} = E(total) - E(PbO_2) - E_{H_2O} \quad (1)$$

For negative values of the E_{Ads} , there is an attractive force (adsorption), while for positive values it indicates a repulsion (no adsorption). Geometric optimization was performed to calculate the network parameters ($a, b = 4.98581; c = 3.42809$). The electronic exchange and correlation energy was modeled using a Perdew – Burke – Ernzerhof (PBE) functional. The electron-atom interactions were modeled using an augmented plane wave potential (PAW), with a cut-off energy of 40 Ry, and a point density k (Monkhorst – Pack) $2 \times 2 \times 4$. With the lattice parameter values (a, b, c), slab systems were constructed, with a vacuum of 15 Angstroms, to avoid interactions between the films. The ground state for the different surfaces of the phases α and β of PbO_2 , were reached using a smearing of 0.02 eV. A four-layer slab model has been considered, where the atoms are allowed to relax, while the other atoms in the system remain fixed. Six adsorption points for H_2O were considered for the slab (110) – $\beta - PbO_2$, and 5 points for (101) – $\beta - PbO_2$. Initial positions for the H_2O molecules were considered in the XY and XZ planes, with a rotation of 90° degrees.

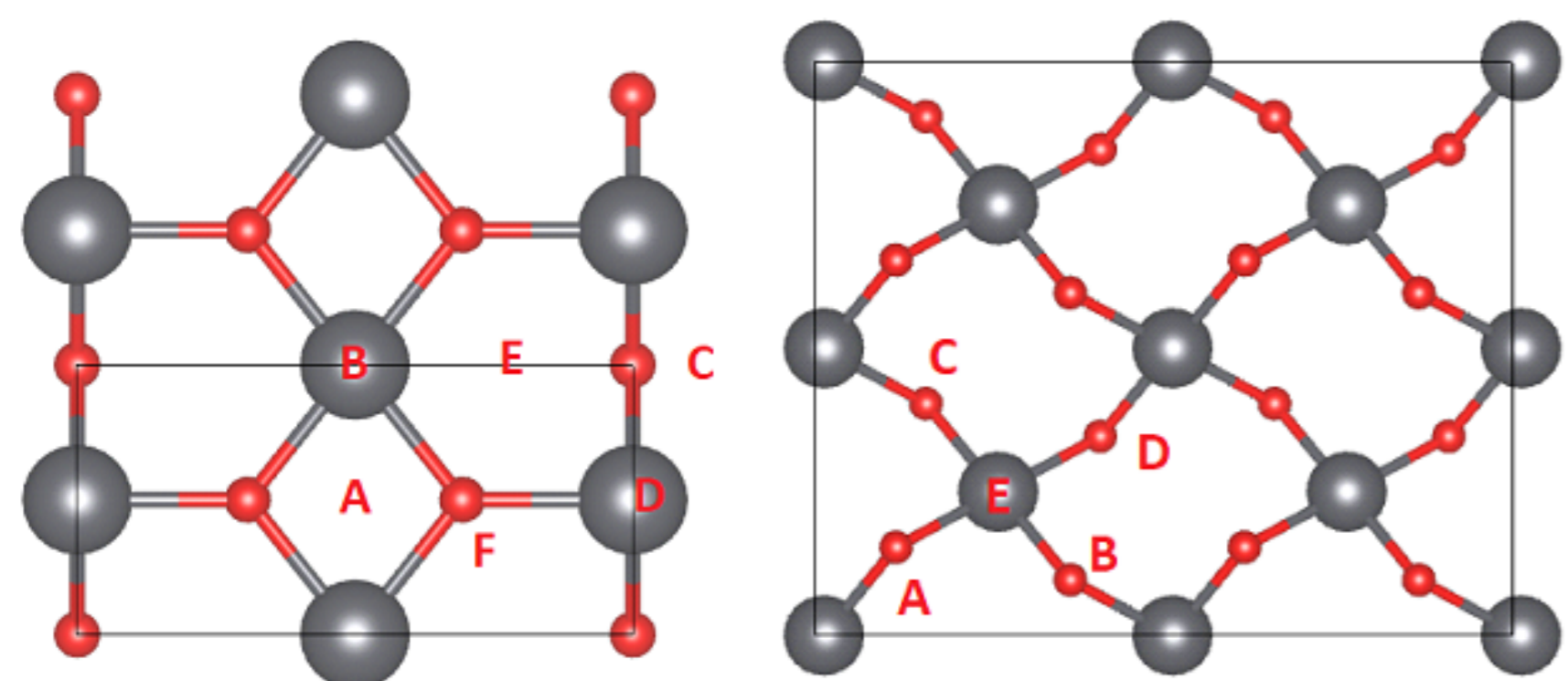


Fig.3 Main positions on the surface $\beta - PbO_2$. Figure left: surface (110), right: surface (101), for the adsorption of the H_2O molecule.

Results

Self-consistent calculations (scf) showed that surfaces (110) and (101), for the phase $\beta - PbO_2$, are the most stable, the latter being the surface with the lowest energy $-5,078$ keV.

The structural relaxation calculations for the surfaces $\beta - PbO_2$ (110) and $\beta - PbO_2$ -(101), showed values of very low adsorption energies, which change strongly depending on the initial state of the H_2O molecule (maximum peaks). The surface (110) shows a

maximum value of E_{ads} -0.16 eV. On the other hand, $\beta - PbO_2$ -OX surfaces, with reticular oxygen, have large E_{ads} values, showing the positive effect of reticular oxygen. For both surfaces peaks are shown, indicating the dependence of the E_{ads} with the initial state of H_2O . The surface (101) has a maximum adsorption value of -0.55 eV (strong physisorption). The surface (110) has a maximum E_{ads} value of -0.95 eV (chemisorption). The existence of these peaks in the E_{ads} could be caused by the interactions between the H_2O molecules. Therefore, the E_{ads} for the surface (110) was calculated, with a 5×5 supercell, to eliminate the interactions between the water molecules, obtaining an E_{ads} value of -1.05 eV. This value is slightly higher than for the initial case, indicating the negative effect of the interactions between the H_2O molecules.

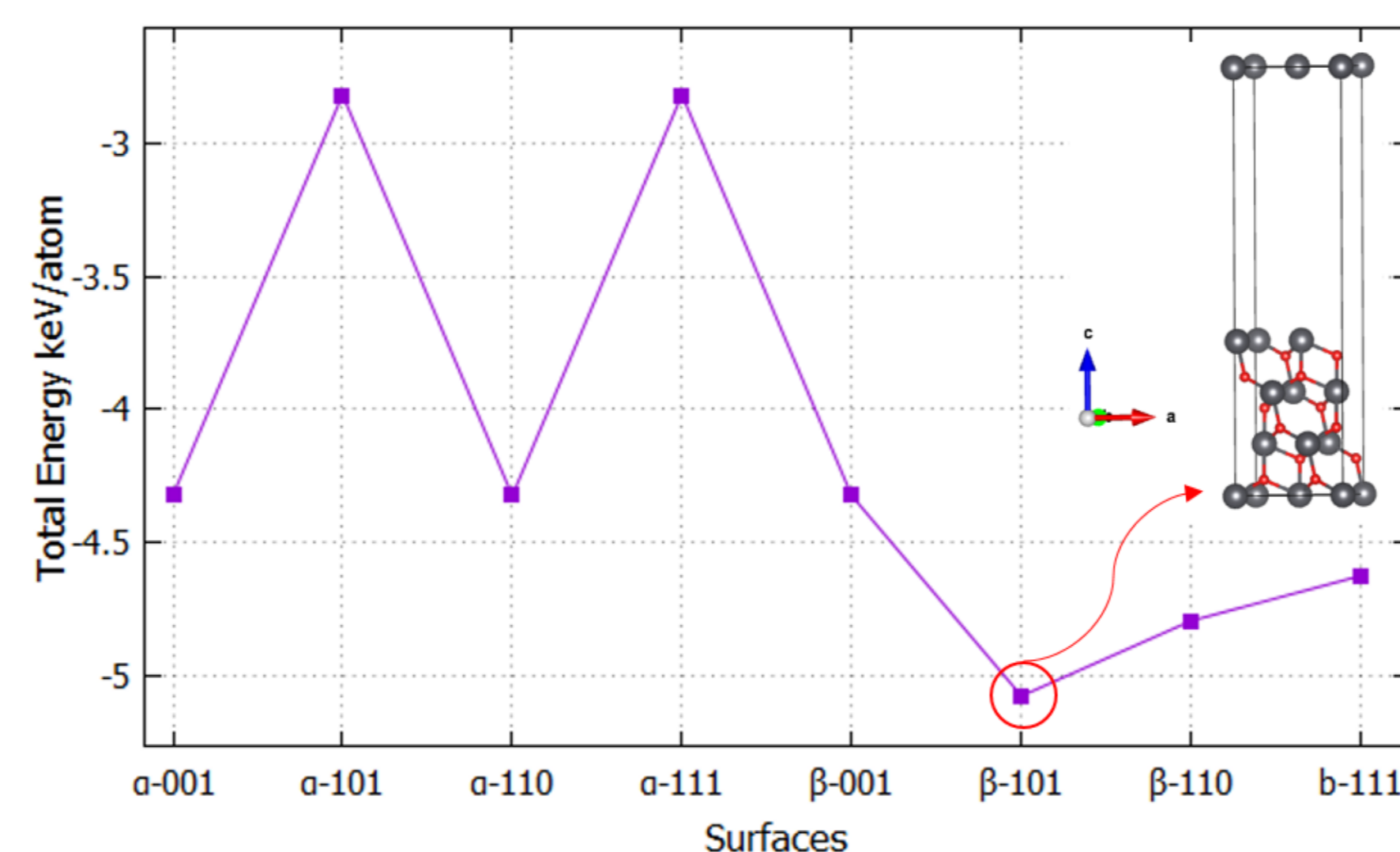


Fig.3 Total energy (keV) per atom, for different surfaces of the α and β phase of lead dioxide. The inner figure shows the crystal structure for supercell (101).

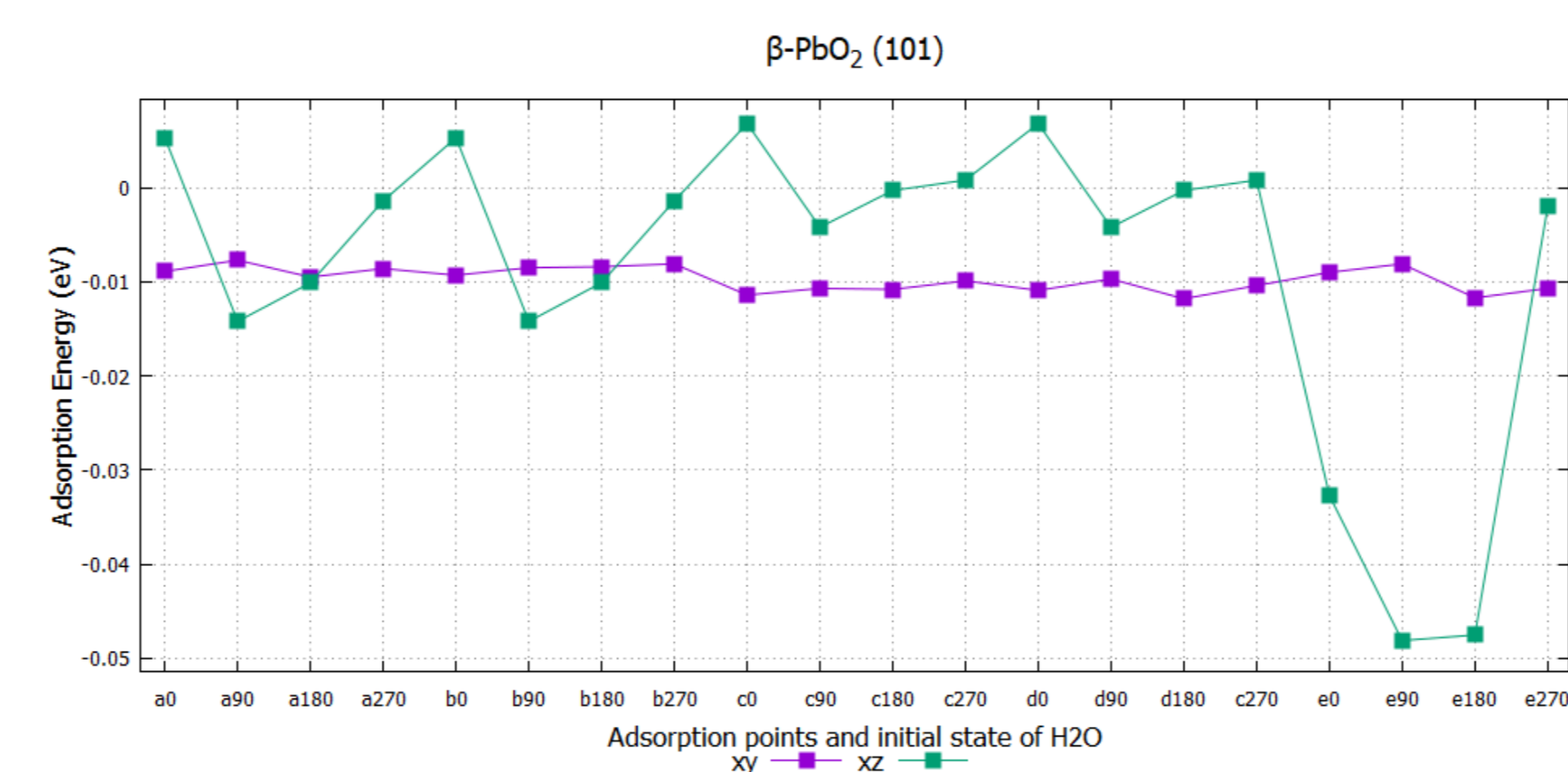


Fig.4 Adsorption energy calculations (eV), for different adsorption points in the structure $\beta - PbO_2$ (101).

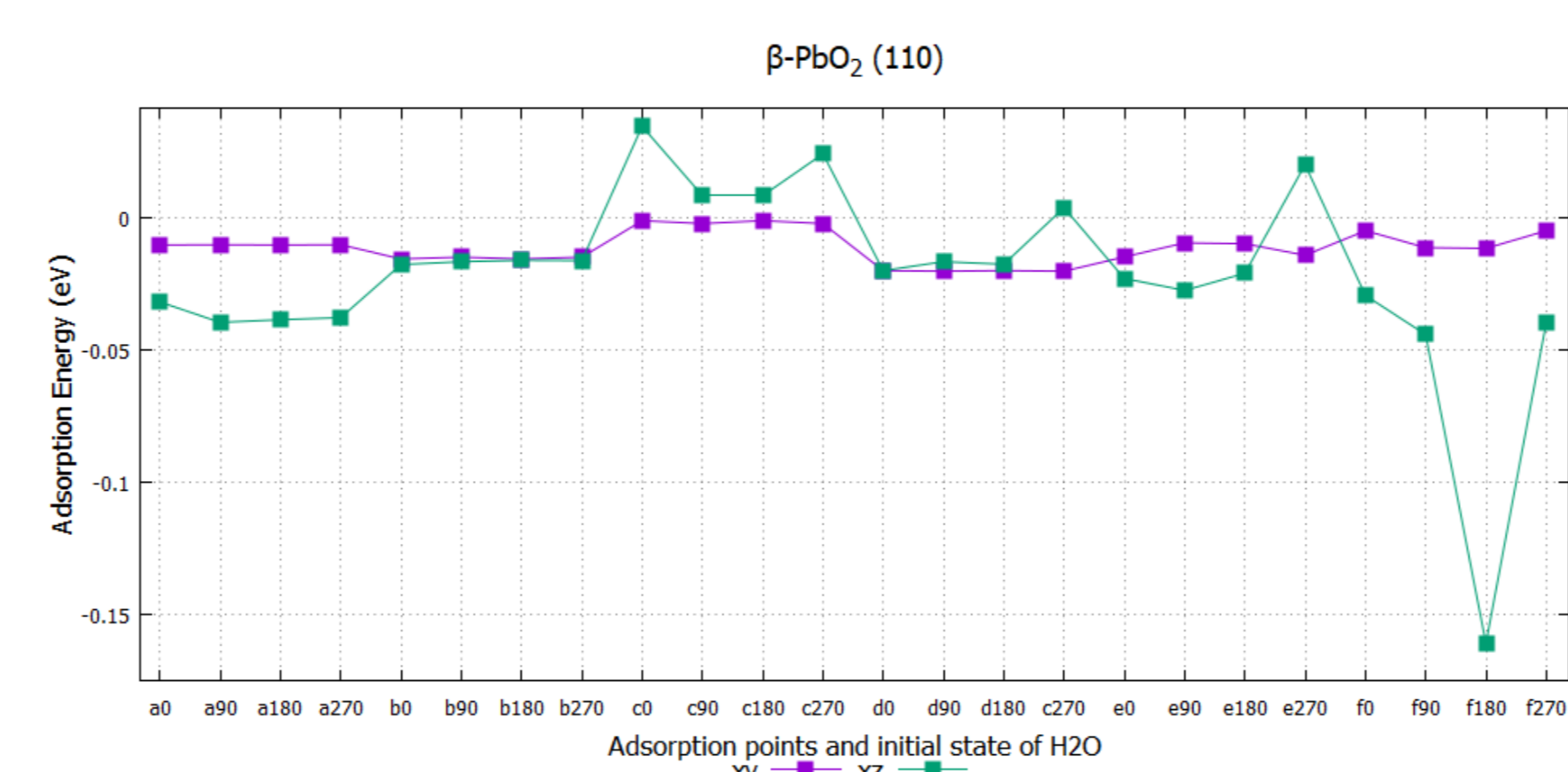


Fig.5 Adsorption energy calculations (eV), for different adsorption points in the structure $\beta - PbO_2$ (110).

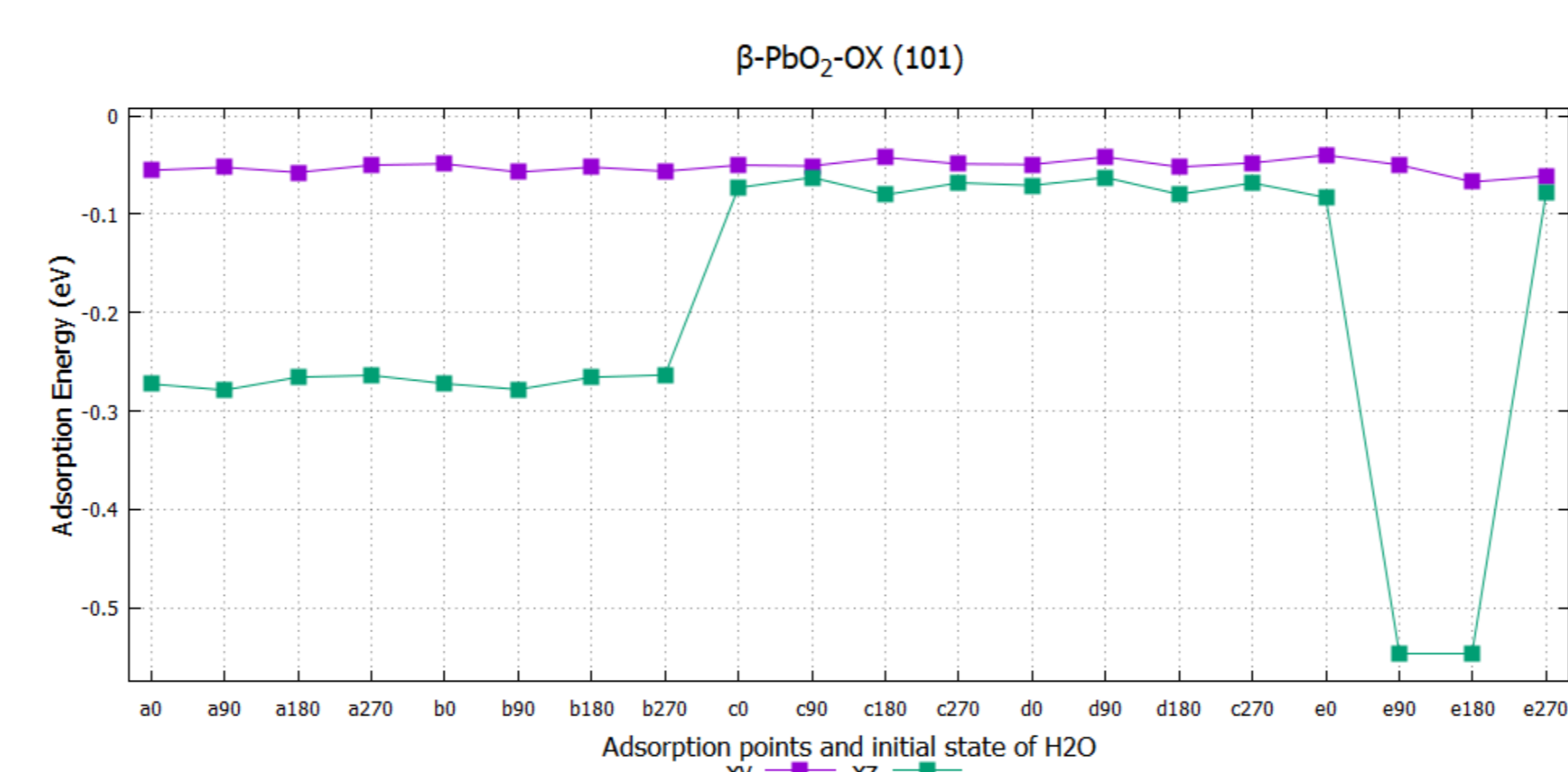


Fig.7 Adsorption energy (eV) calculations, for different adsorption points in the oxygen structure of $\beta - PbO_2$ -OX (101).

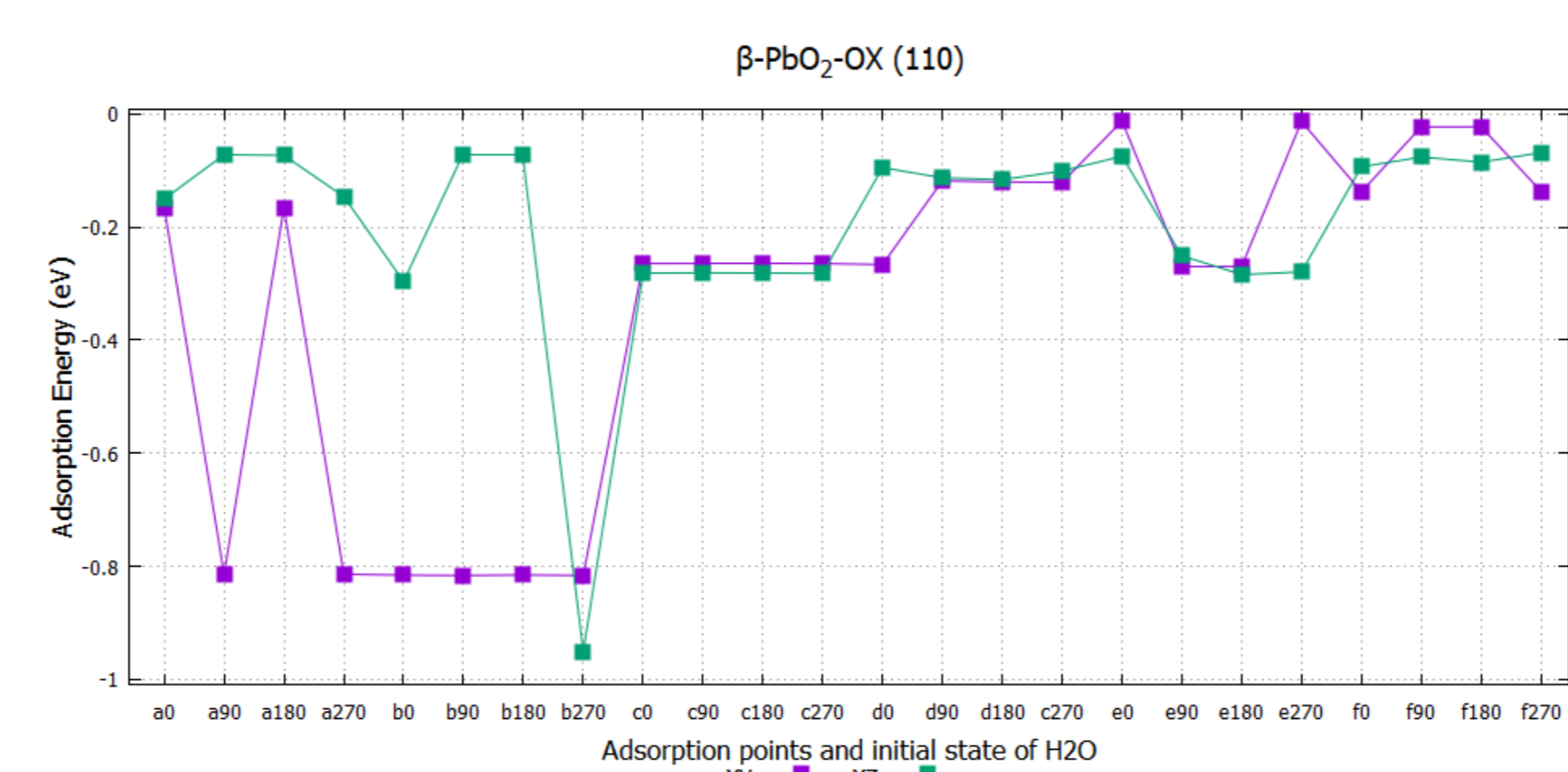


Fig.8 Adsorption energy (eV) calculations, for different adsorption points in the oxygen structure of $\beta - PbO_2$ -OX (110).

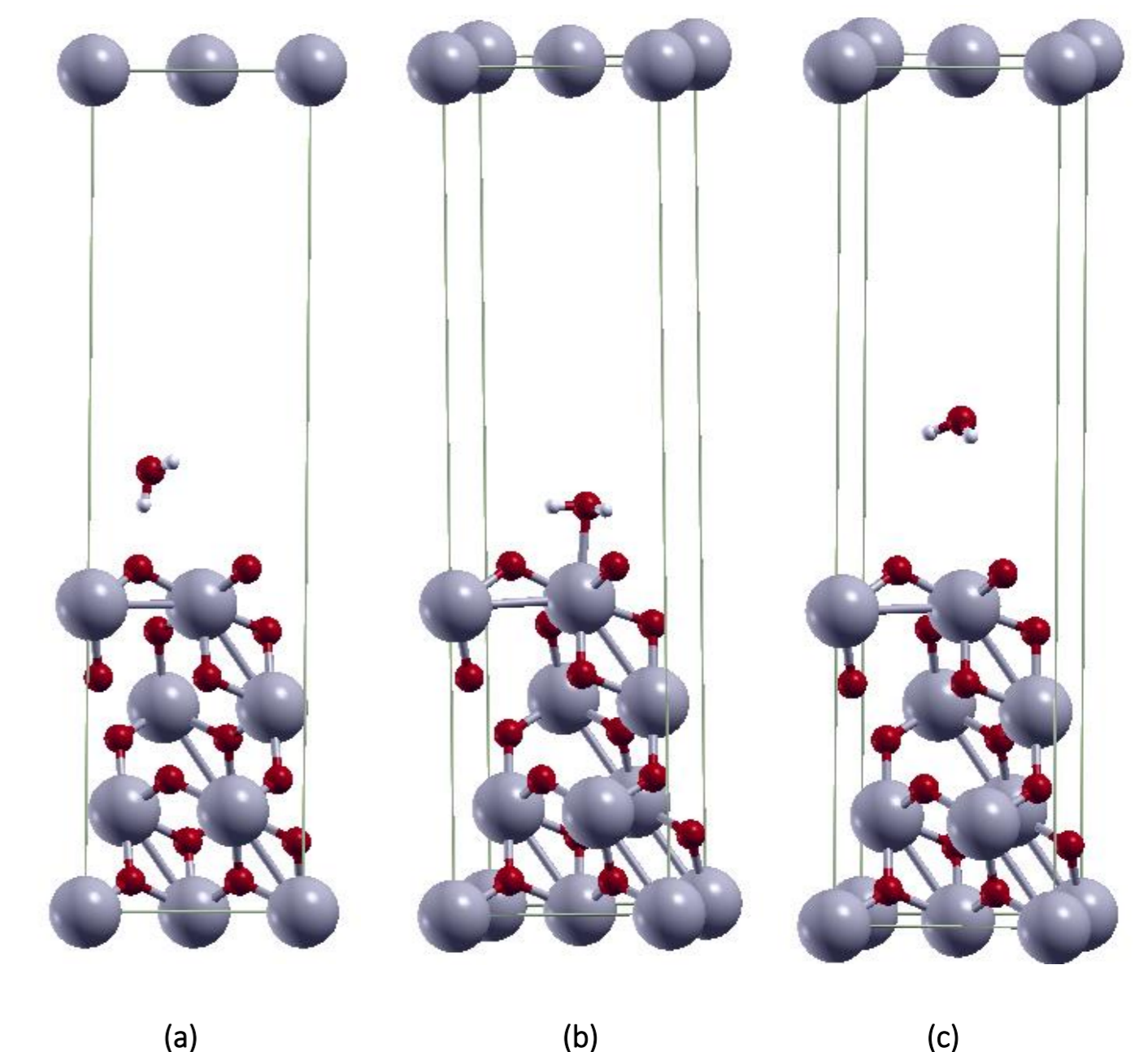


Fig.9 Results of the structural relaxation process for the oxygenated surface (OX-101). (a) Adsorption point b-90-xz. (b) Adsorption point e-90-xz. (c) Adsorption point a-90-xy.

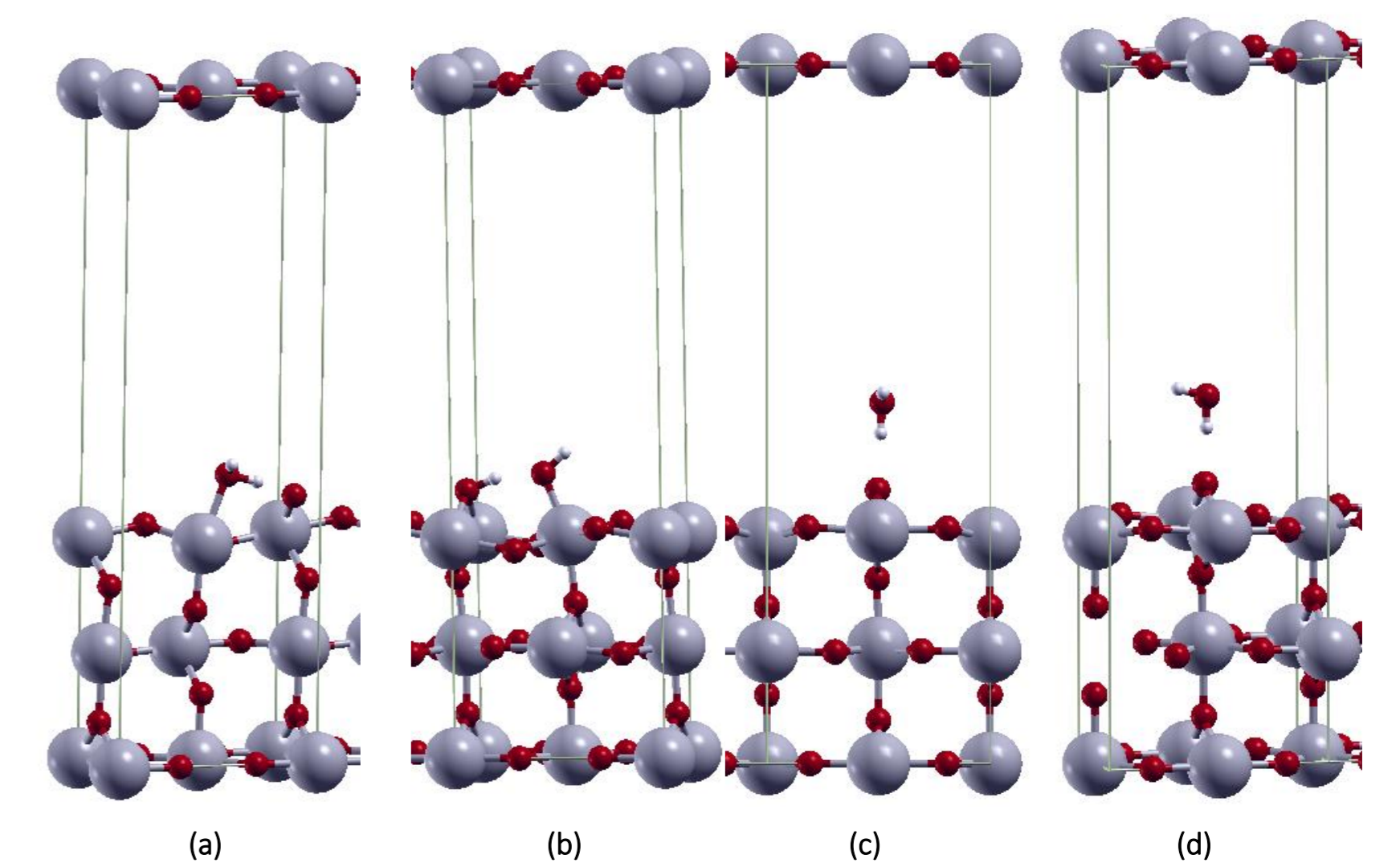
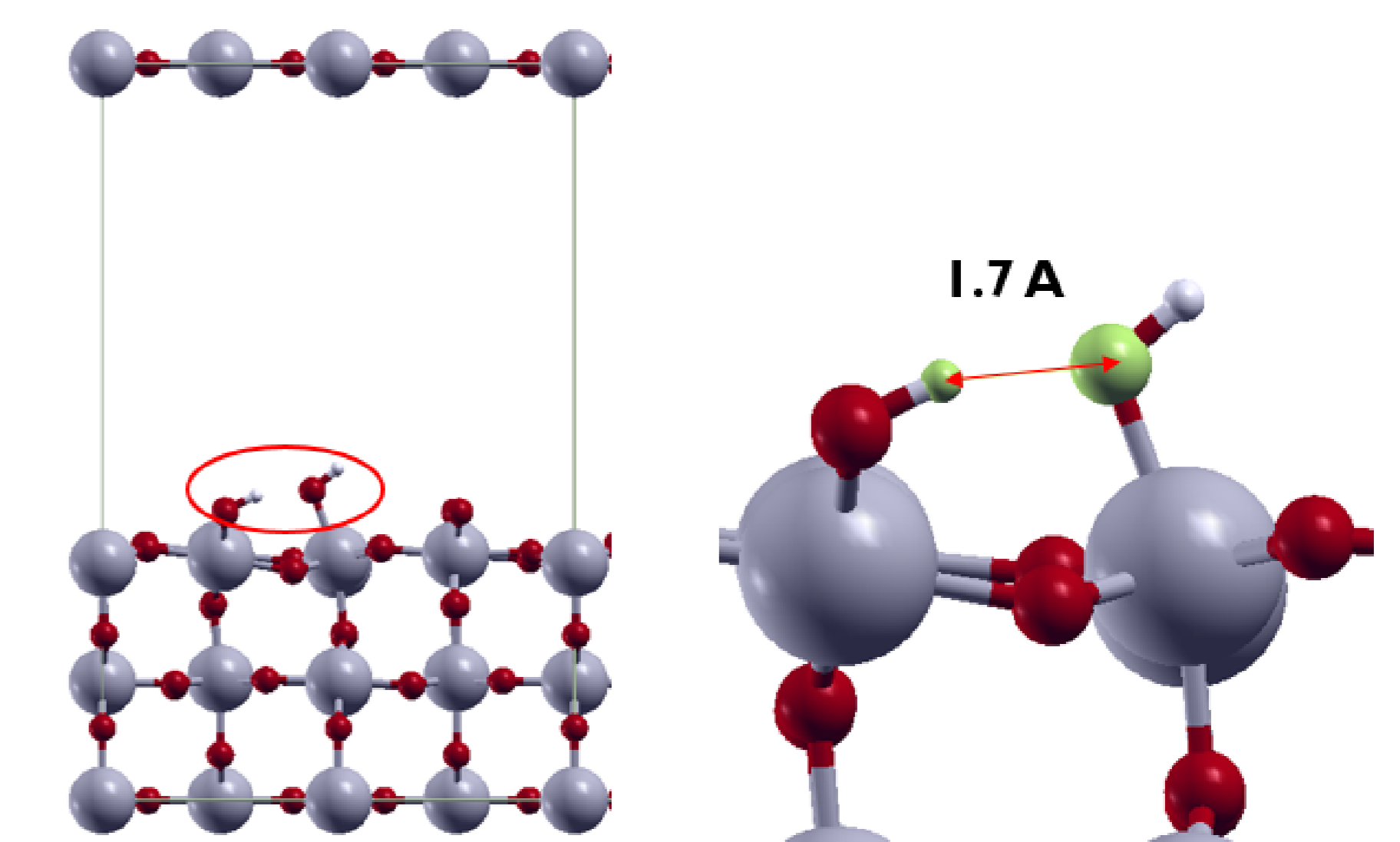


Fig.10 Results of the structural relaxation process for the oxygenated surface (OX-110). (a) Adsorption point b-270-xy. (b) Adsorption point b-270-xz. (c) Adsorption point c-270-xy. (d) Adsorption point c-270-xz.



Supercell 5x5 $E_{ads} = -1.052$ eV

Fig.10 Relaxed structure for the $\beta - PbO_2$ -OX-110 surface, with a 5×5 supercell. The value of the adsorption energy and the distance between the bonded H atom in a reticular oxygen atom and an oxygen atom of the OH group formed on the metal surface is shown.

Conclusions

• Surfaces (110) and (101), without oxygenated terminations, have low adsorption energy. The effect of cross-linked oxygen terminations increases the adsorption energy for surfaces (101) and (110), achieving mechanisms of physisorption and chemisorption. The interactions between H_2O molecules negatively affect the adsorption energy (competitive effect), which is shown by calculating the adsorption energy for a 5×5 supercell, obtaining an adsorption energy of -1.05 eV.

References

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