Investigation of the Water Splitting Reaction on ZnO Surfaces in the Excited State

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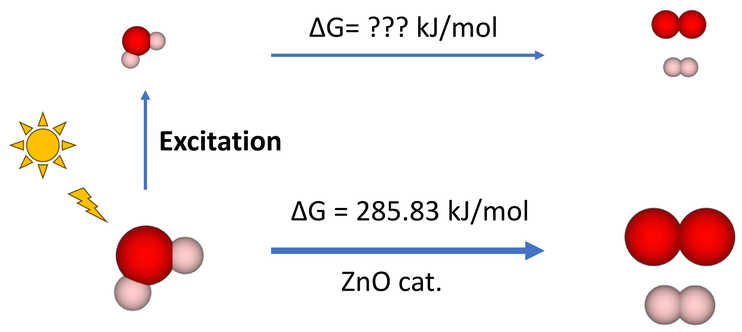
Introduction



Single-Point calculations have been performed on top of Ground-State optimized structures[1] in order to obtain the **water splitting reaction path** on the **triplet excited state (T_1)** over $(000\bar{1})$, (0001), $(10\bar{1}0)$ and $(11\bar{2}0)$ ZnO surfaces.

Objectives

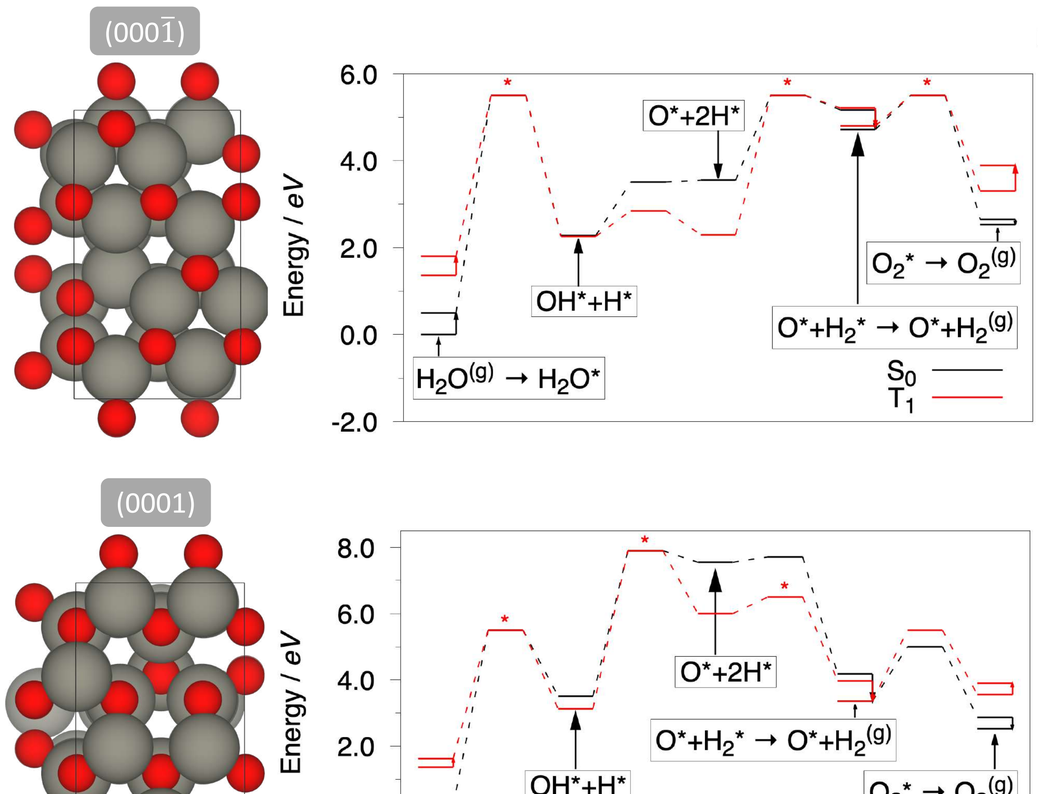
- Obtain the **band gap energy** for $(000\bar{1})$, (0001), $(10\bar{1}0)$ and $(11\bar{2}0)$ surfaces.
- Investigation of the **water splitting mechanism** in the ground and excited potential energy surface.
- Compare **adsorption energies** between ground and excited state.
- Locate the **limiting step** for each surface path.

Computational details

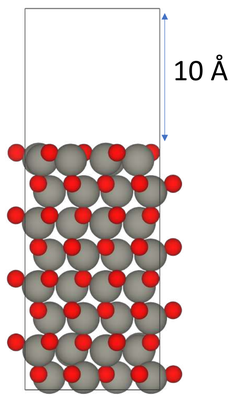
- **VASP** software
- **DFT** with **PBE** *xc* funcional
- **Grimme's D3** correction
- **CI-NEB** and **Improved Dimer** method for transition states

Ongoing work

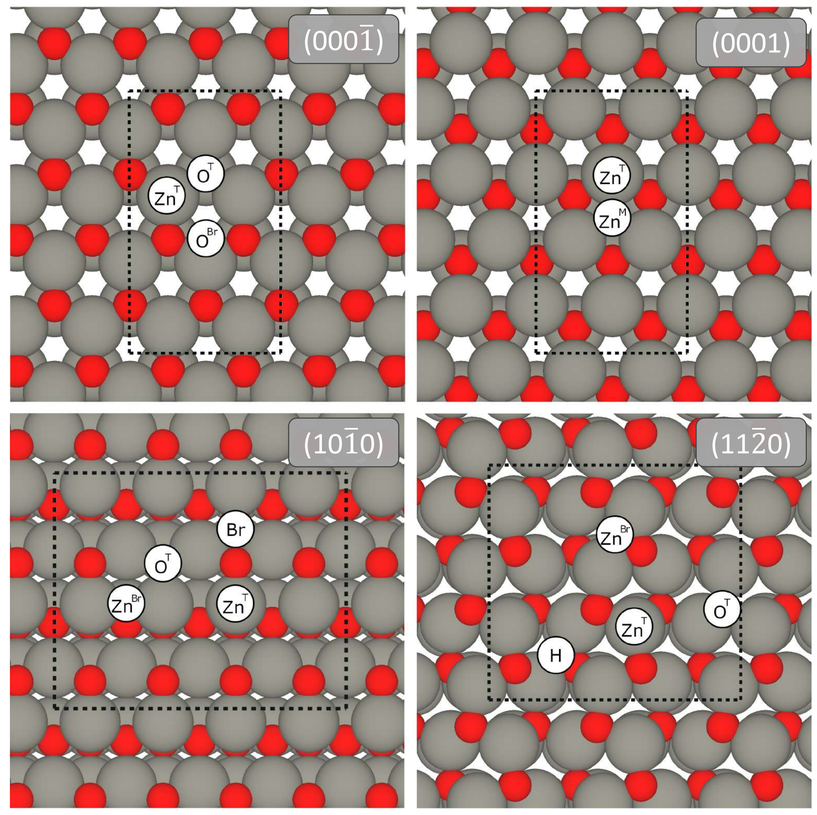
$(000\bar{1})$ and **(0001)** polar surfaces have been reoptimized neglecting **1/4 of the first** and **last layer atoms** to prevent charge transfer and obtain semiconducting behavior.[2]



Models

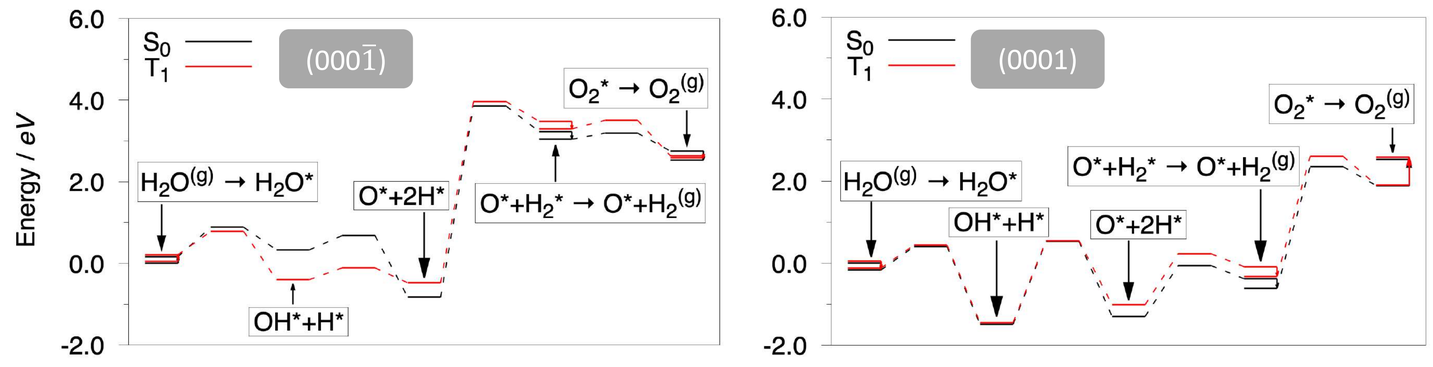


- (2×2) or (4×2) supercells
- 8 or 4 ZnO layers with 128 atoms

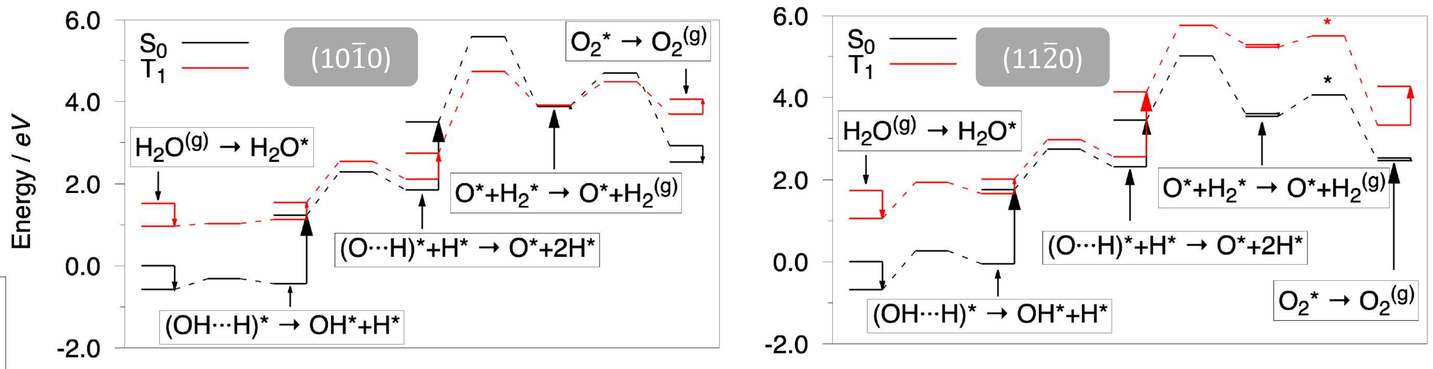


Results

- Polar **$(000\bar{1})$** and **(0001)** surfaces present **metallic character** obtaining a negligible band gap.
- **Hydrogen and oxygen** molecule formation are the **limiting steps** for $(000\bar{1})$ and (0001) surfaces.



- PBE *xc* funcional **underestimates band gap** on non-polar **$(10\bar{1}0)$** and **$(11\bar{2}0)$** surfaces.
- **Concatenation of endothermic steps** leads to high section energy points around 6 eV for GS and 4.5 eV for the T_1 state.



- Some cases have been optimized on the T_1 state to ensure that **SP calculations are a good approximation** for the excited state.

$E_{ads}(Opt) - E_{ads}(SP)$ (eV)	$(000\bar{1})$	(0001)	$(10\bar{1}0)$	$(11\bar{2}0)$
H_2O	0.00	-0.01	0.02	0.00
H_2	0.00	0.00	0.02	0.00
(OH···H)	0.11	-0.01	0.17	0.11
(H···H)	0.14	0.00	-1.00	-1.20

- The reaction path on the **T_1 state does not affect much on polar surfaces**, but there is a **reduction on the limiting step in $(10\bar{1}0)$** surface, and on the interaction of **(OH···H) on $(11\bar{2}0)$** surface.

References

(1) Morales-Salvador, R.; Bromley, S. T.; Viñes, F.; Catal. Today, 441, (**2024**)

(2) Noguera, C.; J. Phys.: Consens. Matter, 12, (**2000**)

Acknowledgements

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