

# Interaction of H atoms with siliceous interstellar dust particles: **H-Forsterite**

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# INTRODUCTION

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- The formation of **molecular hydrogen in the ISM** is still an open question. Since the early 60's **interstellar dust particles** are invoked as possible **catalysts** to explain the **large abundance of H<sub>2</sub>** in diffuse clouds and PDR edges of dense molecular clouds
- Current knowledge of interstellar dust particles indicate that they have both a **carbonaceous and siliceous composition**. While several tens of theoretical studies exist for carbonaceous grains, there is only one (QM/MM: embedded cluster) study of H adsorption on silicates: Forsterite [1].
- We present a **periodic DFT study** of the interaction of an H atom with the **Forsterite [010] surface**, with the aim of characterizing the **properties of H atom adsorption** on that surface.

[1] *PM. Goumans, C. Richard, A. Catlow and W.A. Brown. MNRAS. 393,1403-1407 (2009)*

# SETUP: METHOD

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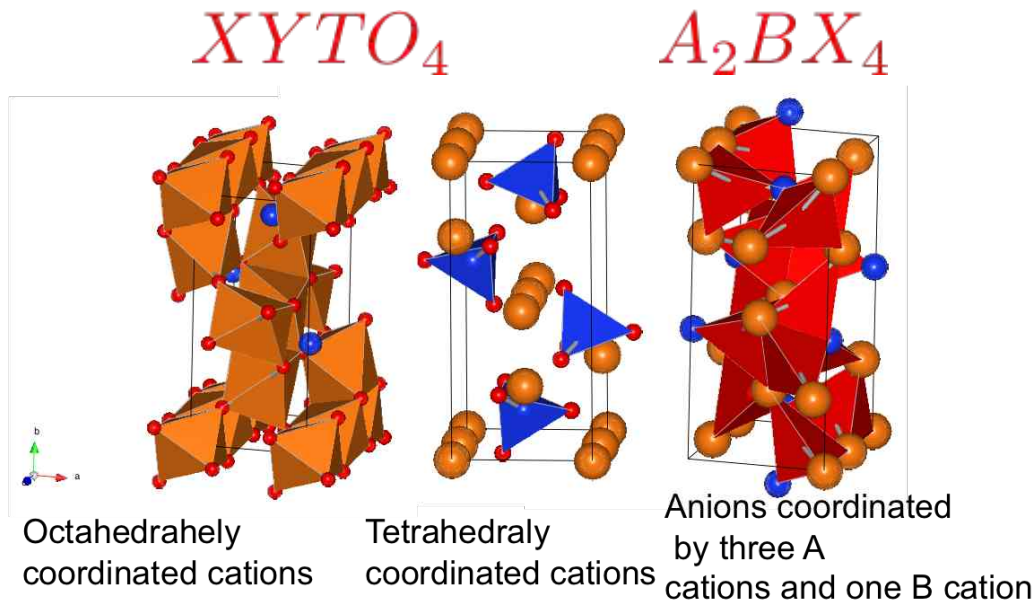
- **Spin-unrestricted periodic DFT with GGA-PBE and OptB88-VDW [1] functionals using the SIESTA code [2].**
- **Pseudopotentials.**
- **Basis: Localized orbitals (LCAO), DZP quality optimized for bulk Forsterite (0.02 GPa).**
- **Grid/K-points: 450 Ry and 4x4x4 sampling (convergence errors < 0.02 meV)**
- **NEB: Nudged elastic band (underway).**

[1] *J. limes, DR. Bowler and A. Michaelides. J. Phys.: Condens. Matter* **22**, 022201 (2010)

[2] *Soler. J. Phys.: Condens. Matter* **14**, 2745 (2002)

# SETUP: BULK

- Forsterite [ $Mg_2SiO_4$ ] is an end member of the olivines family.



Unit cell has 28 atoms  
(Wyckoff positions)

Mg <sub>1</sub>	x 4
Mg <sub>2</sub>	x 4
Si	x 4
O <sub>1</sub>	x 4
O <sub>2</sub>	x 4
O <sub>3</sub>	x 8

Orthorhombic  $P_{bnm}$  ( $b > c > a$ )

***Independent  $SiO_4$  tetrahedra linked by divalent cations in octahedral coordination.***

***The divalent cations occupy two distinct crystallographic sites with the oxygen sublattice deviating significantly from the ideal close packing arrangement***

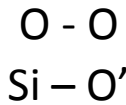
[4] N. de Leew. *J. Phys. Chem. C*, 105 (2001)

[5] M de la Pierre. *J. Comp. Chem.* 32,9 (2011)

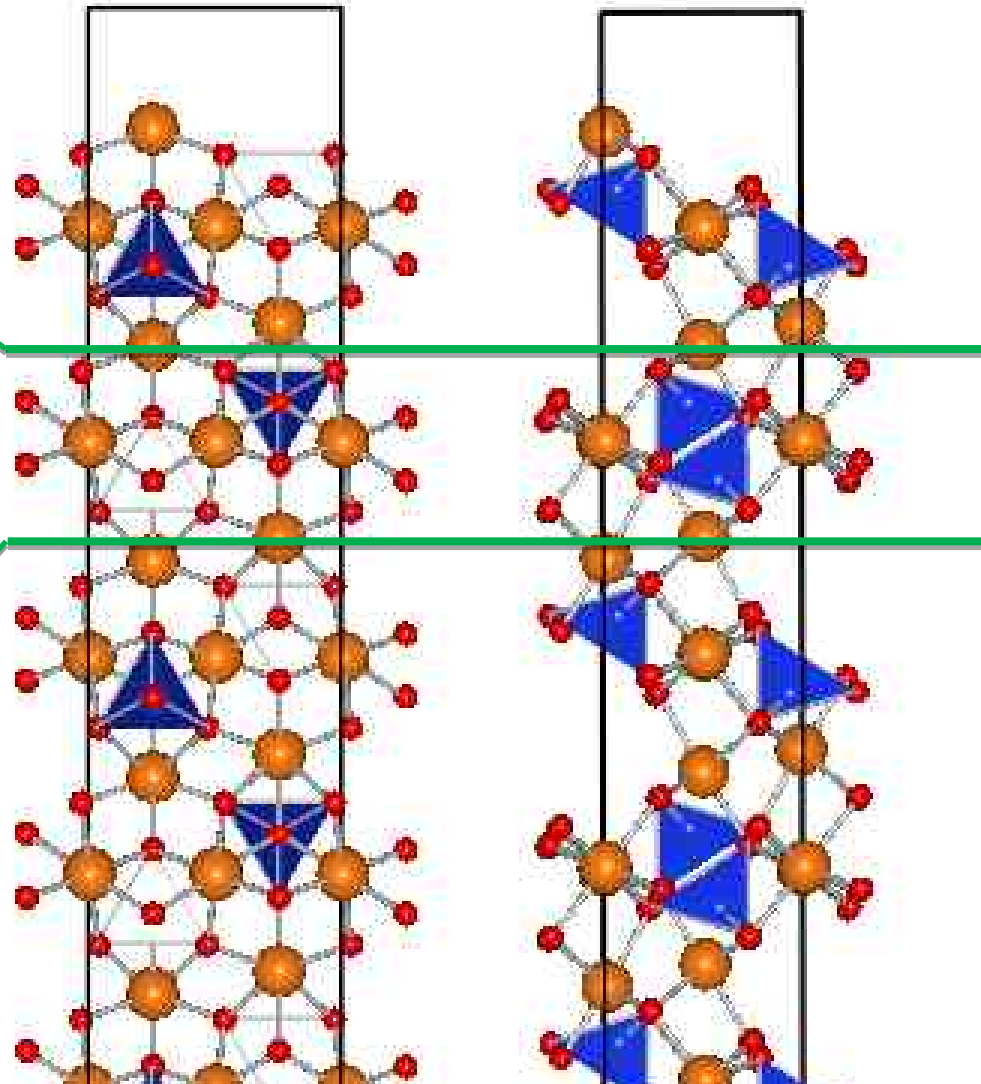
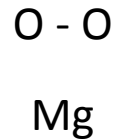
# SETUP: SURFACE

- Cut along the  $\{010\}$  plane [ $P_{bnm}$ ] and in between two Mg atoms leads to the most stable surface [1].

*The breaking of the Si-O bonds always results in less stable surfaces.*



*No dipole perpendicular to the surface in the repeat unit, because such a dipole leads to a divergent surface energy*



# SETUP: SURFACE

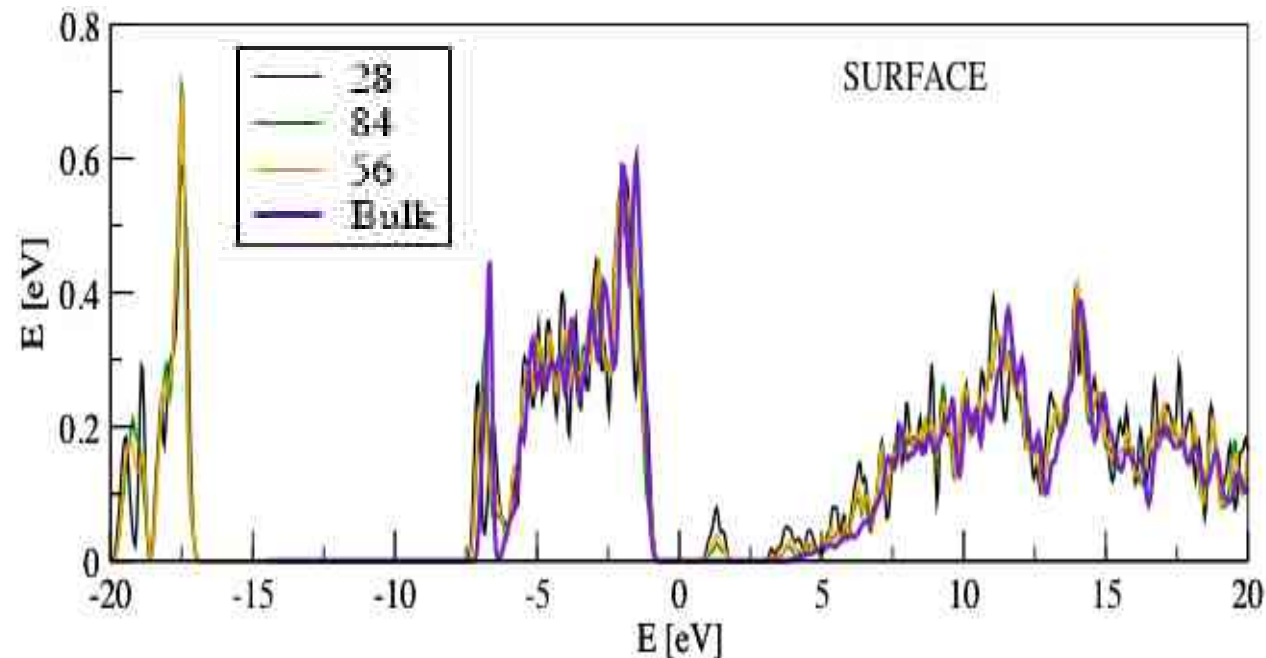
- Minimum number of unit cells chosen in order to correctly describe the surface: through and analysis of DOS, relaxation, Mulliken charges and surface energies.

**Surface Energy:**  $\gamma = \frac{E_{slab} - NE_{bulk}}{2A}$

**DOS**

	$\gamma$ [J/m <sup>2</sup> ]
Number of atoms (unit cells)	Surface Energy
→ 28	1.20
56	1.19
84	1.19

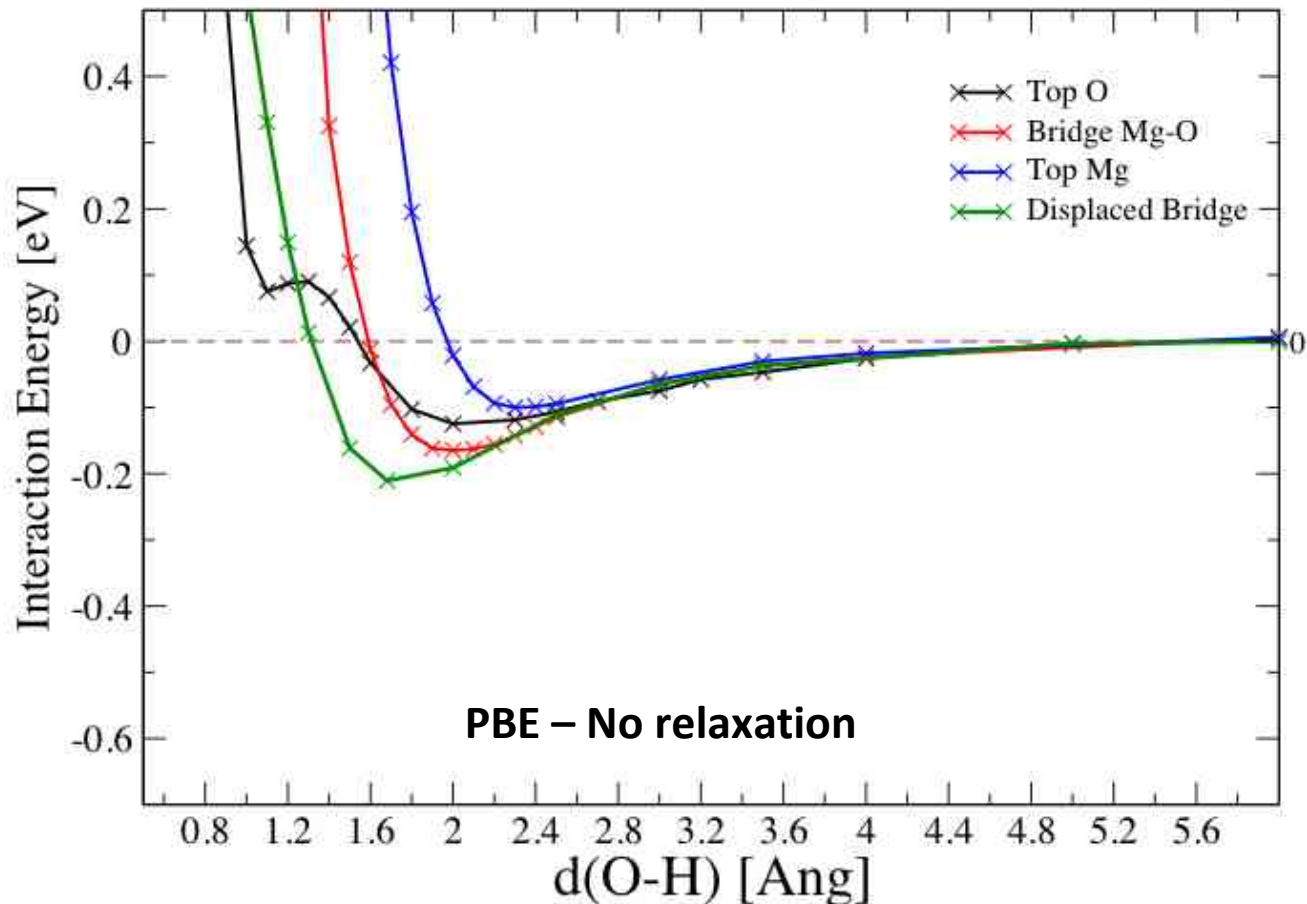
Very similar to the surface energy of MgO [1.20 J/m<sup>2</sup>] and in agreement with MM calculations (1.28)[1][2].



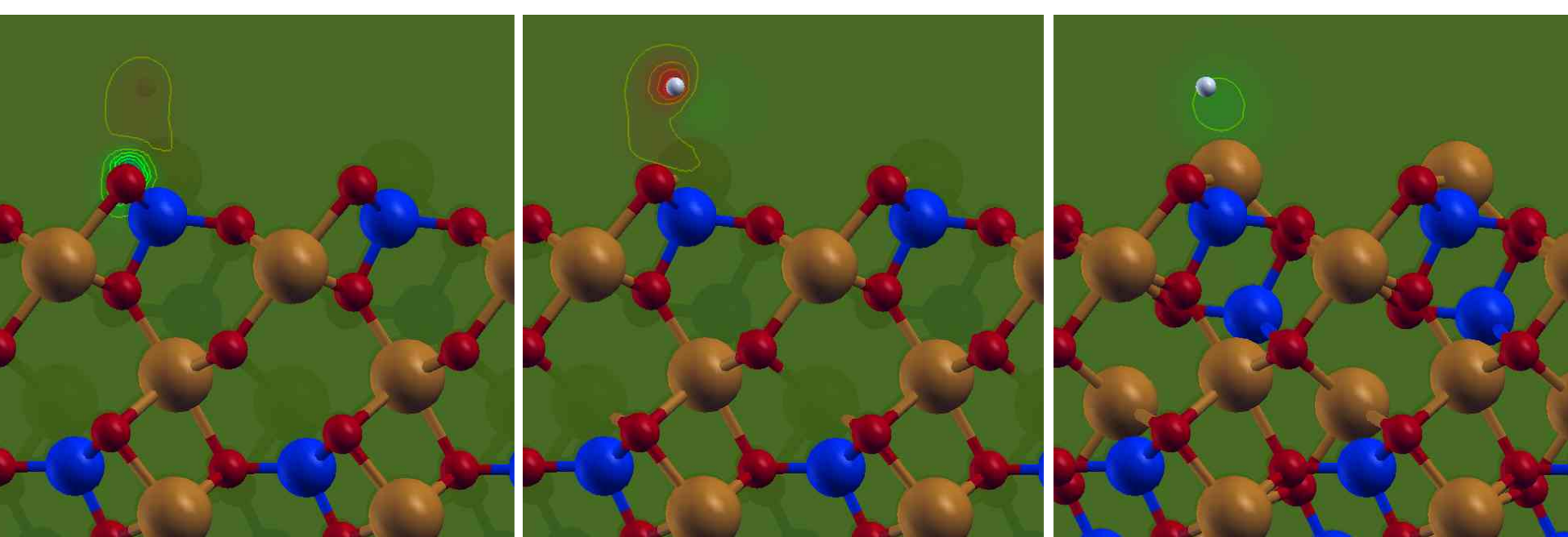
[1] G. W. Watson et al. *Phys. Chem. Minerals* (1997)25:70-78

[2] De Leew et al. *Phys. Chem. Miner.*27,332-341(2000)

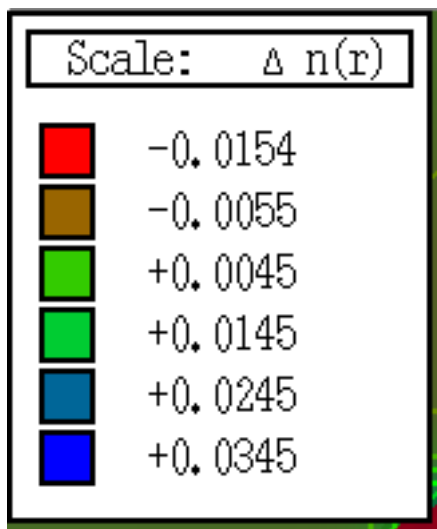
# H – PHYSISORPTION (VdW?)



- Our objective is to determine the potential energy as H approaches the surface, the easiest way is to make an initial study at **different sites without relaxation**
- The outer wells are not genuine VDW physisorption: **some charge transfer from the atom to the substrate exists** → **“Strong physisorption/weak chemisorption”**

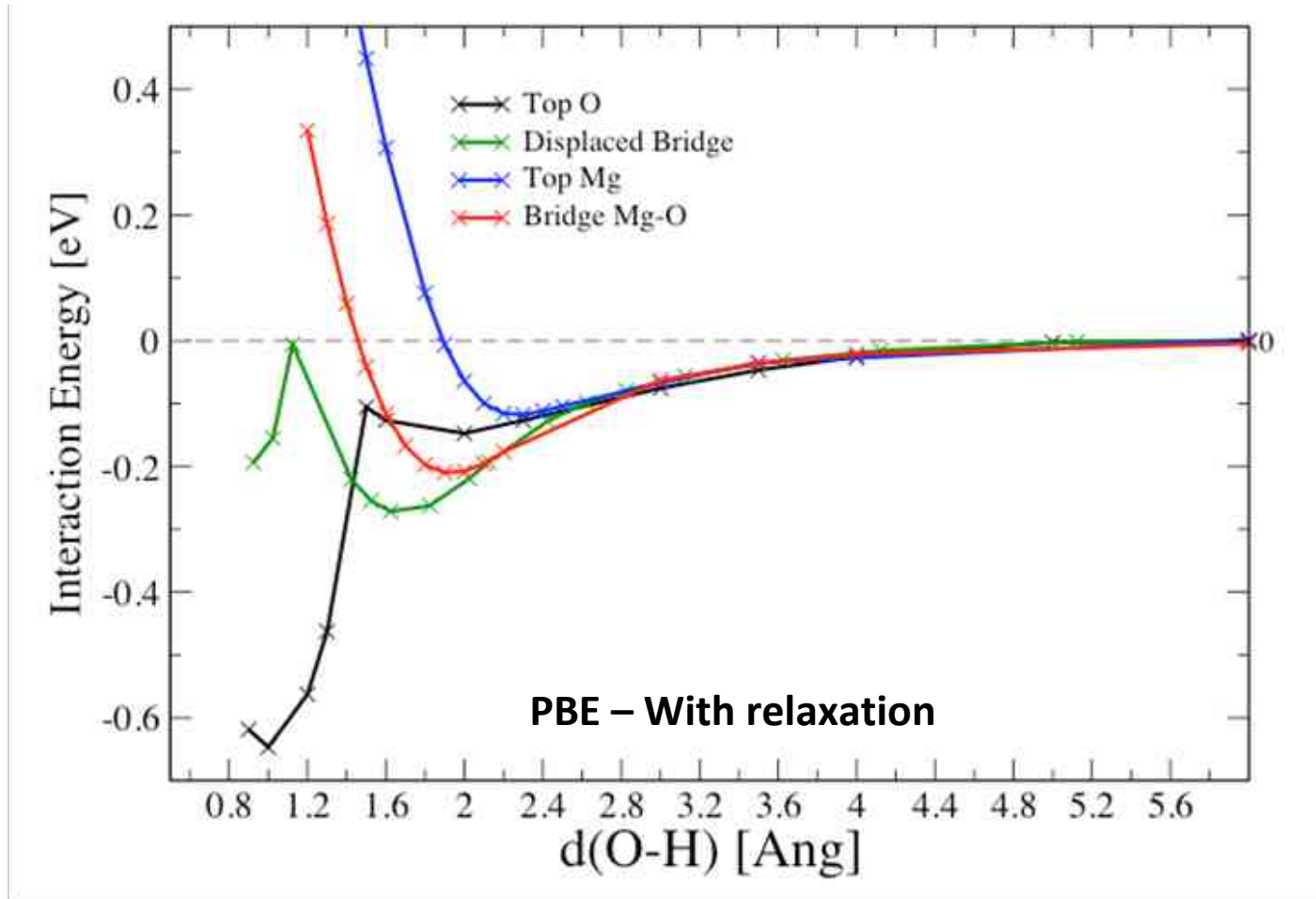


Charge transfer in the outer well: displaced bridge (2Å)



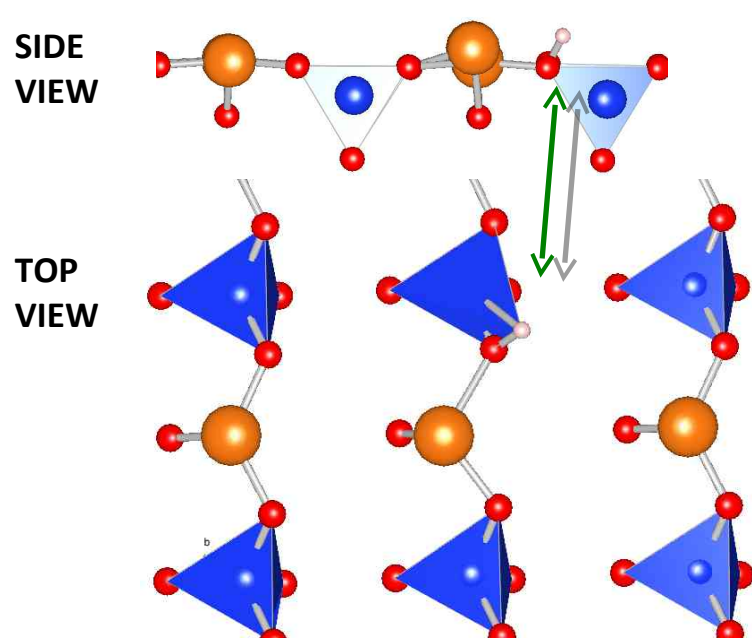


# “PHYSISORPTION” - CHEMISORPTION

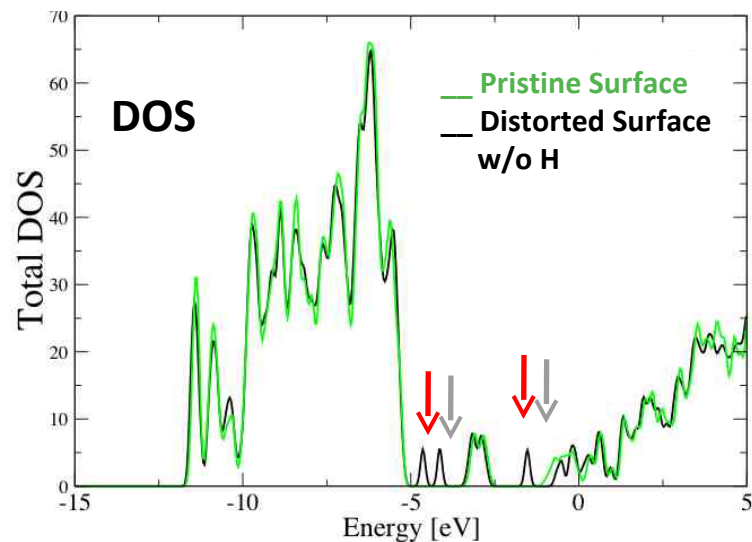


- Allowing the surface to relax, we find, in addition to the outer wells, new features at small H-substrate distance

# CHEMISORPTION



$$E_{\text{ads}} = -0.85 \text{ eV}$$



- H chemisorbs nearly atop O [bond distance = 0.99 Å]: the O-H bond is tilted by 19.98° with respect to the normal to the surface.

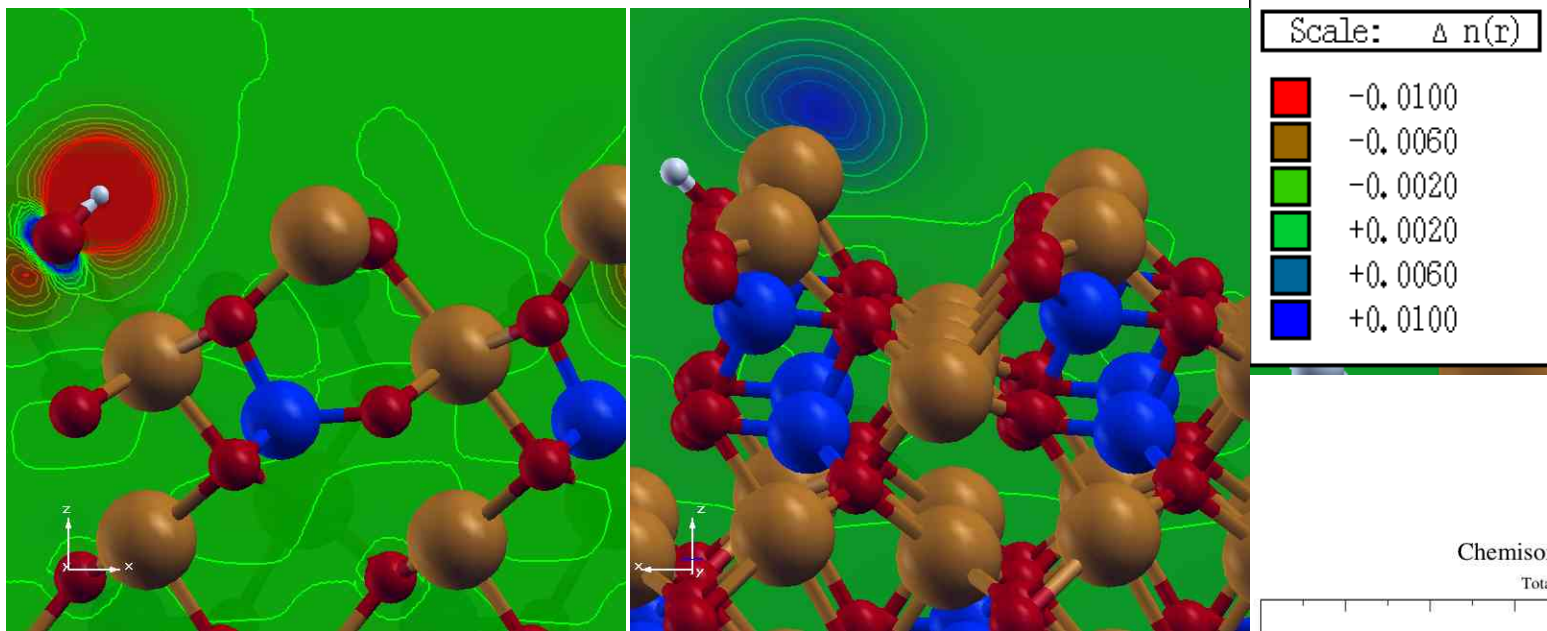
- The Mg and O atoms involved in the chemisorption get displaced towards the H atom:

$$\text{Mg } \{\Delta x = -0.29 \text{ \AA}, \Delta y = -0.12 \text{ \AA}, \Delta z = +0.32 \text{ \AA}\}$$

$$\text{O } \{\Delta x = -0.06 \text{ \AA}, \Delta y = +0.03 \text{ \AA}, \Delta z = +0.08 \text{ \AA}\}.$$

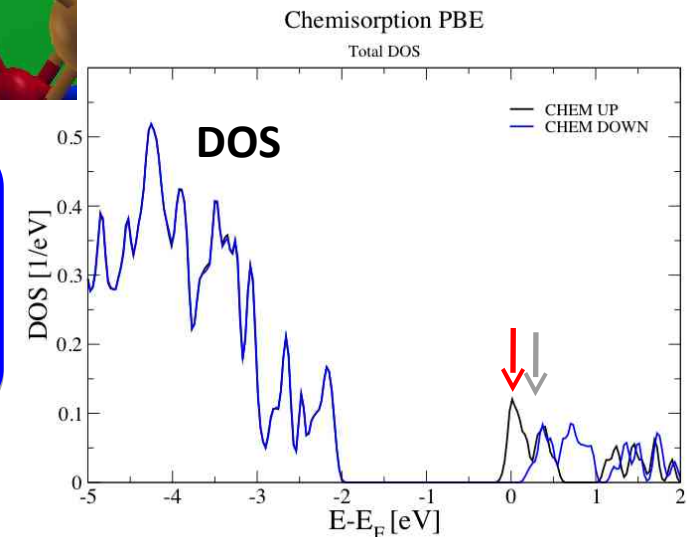
# CHEMISORPTION

## Induced Charge density.

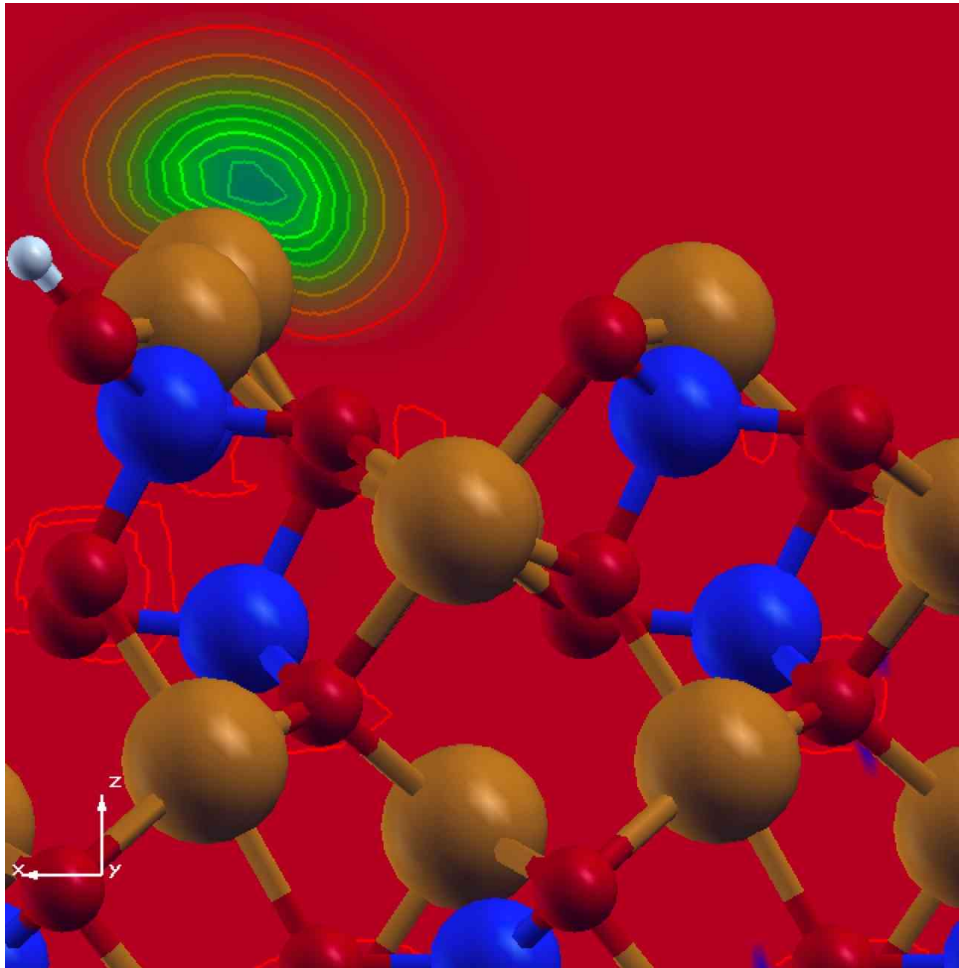


**Electron density is transferred from the H atom to the surface [1 electron]. It gets localized on the nearest Mg atom of the surface plane [O protonation with localization of the surface electron on Mg][1].**

[1] PM. Goumans, C. Richard, A. Catlow and Wendy A. Brown.  
Mon. Not. R. Astron. Soc. 393,1403-1407 (2009)

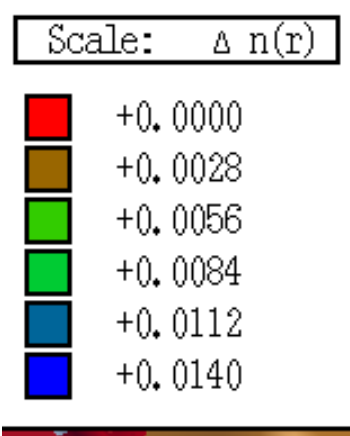


# CHEMISORPTION

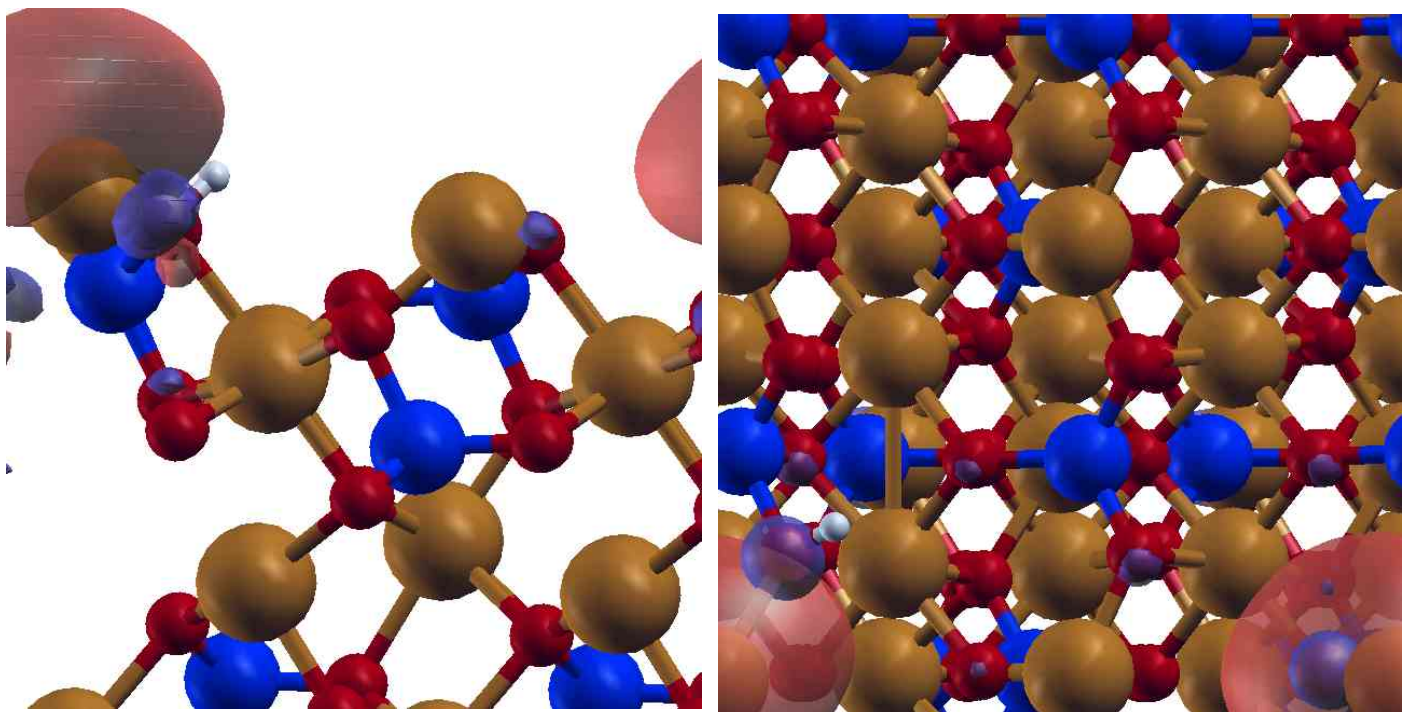


SPIN DENSITY MAP ( $n_{\uparrow} - n_{\downarrow}$ ).

Local magnetization on the Mg site.  
The spin is balanced everywhere  
except on the magnesium.



# CHEMISORPTION



**View of the wavefunction involved in the process of chemisorption. The hydrogen is injecting an electron in this state located in the top surface layer. This state is a hybrid of  $s$ ,  $p_x$  and  $p_z$  orbitals.**

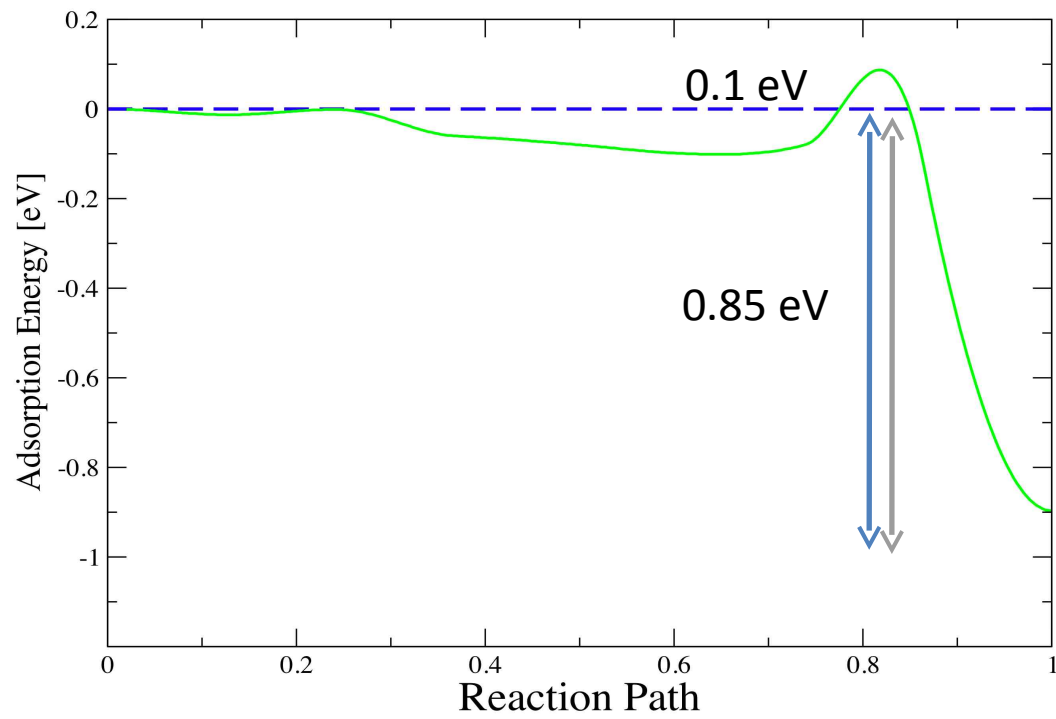


# CONCLUSIONS

- The present results indicate that an **H atom can adsorb without barrier on the [010] surface of Forsterite** whatever in the **outer wells [strong physisorption/weak chemisorption]** or in the **inner [chemisorption] well**.
- **Pure VDW physisorption is not found**: the binding in the **outer wells** involves some **electron transfer from the H atom to the surface** [strong physisorption/weak chemisorption binding]. The **outer wells depths are deeper than that of H-graphene** ( $\approx 44$  meV) by a factor of 2-7. Comparatively, **this should considerably increase the residence time of H atoms adsorbed in these wells at typical temperatures of the diffuse ISM**.
- The **present periodic PBE results** for chemisorption [well depth, bonding characteristics] **agree with the QM/MM-MPWB1K [embedded cluster] ones** obtained by Goumans et al. [1].
- NEB calculations are underway to determine the potential energy curve along the minimum energy path. The next stage will consist of studying **the interaction of a second H atom with the already chemisorbed one and with the surface in presence of the H chemisorbate**.

[1] PM. Goumans, C. Richard, A. Catlow and Wendy A. Brown.  
Mon. Not. R. Astron. Soc. 393,1403-1407 (2009)

# NEB



### KBM-No Relax

