

First principles investigation of water adsorption, dopant segregation and surface thermodynamics of Mg and Sr substituted CaO(001) for Ca(OH)₂/CaO thermochemical energy storage

Abdul Rauf

rauf72984@gmail.com

Orbit Design Hub

Abdul Shakoor Sabir

Orbit Design Hub

Muhammad Danish

Orbit Design Hub

Research Article

Keywords: Thermochemical energy storage, Calcium oxide hydration, Water adsorption, Surface segregation, Density functional theory, Ab initio thermodynamics

Posted Date: October 28th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11484746/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

First principles investigation of water adsorption, dopant segregation and surface thermodynamics of Mg and Sr substituted CaO(001) for Ca(OH)₂/CaO thermochemical energy storage

Abdul Rauf^{1,2*}, Abdul Shakoor Sabir² and Muhammad Danish²

¹Department of Physics and Astronomy, School of Natural Sciences, National University of Sciences and Technology (NUST), Islamabad, Pakistan.

²Department of Computational Engineering, Orbit Design Hub, Multan, Punjab, Pakistan.

*Corresponding author(s). E-mail(s): rauf72984@gmail.com;

Abstract

The Ca(OH)₂/CaO cycle releases stored heat when CaO takes up water, an uptake that begins at the oxide surface. Isovalent Mg and Sr barely move the bulk equilibrium of the cycle, but their surface effect is unknown. We study water at 1/4 monolayer on CaO(001) with Mg, Sr or both in the top layer, or Mg in the second layer, by density functional theory. On every surface the most stable state we found is split: a hydroxyl bridges two cations and the proton sits on a neighbouring surface oxygen. Water binds by 0.84 eV on CaO, 0.98 eV with Sr, 1.17 eV with Mg, 1.18 eV with both and 0.81 eV with Mg below the surface. Mg acts through the oxygen that takes the proton, Sr through the site of the hydroxyl, and their gains do not add. The stretching frequency of the new surface hydroxyl tracks the binding energy ($r = -0.96$). On the clean surface Sr prefers the top layer by 0.46 eV and Mg the second layer by 0.29 eV. Adsorbed water reverses the choice of Mg, but in equilibrium with the vapour only below 530 to 790 K at 1 bar. Relative to CaO, surface Sr raises the water desorption temperature by 65 to 105 K and surface Mg by 190 to 250 K, while the same ions move the bulk equilibrium temperature by only -5 to $+25$ K. Surface doping, most reliably with Sr, thus tunes water uptake almost independently of the storage temperature.

Keywords: Thermochemical energy storage, Calcium oxide hydration, Water adsorption, Surface segregation, Density functional theory, Ab initio thermodynamics

Abbreviations and notation

BFGS: Broyden, Fletcher, Goldfarb and Shanno optimiser

CaO:X: CaO(001) with dopant X in the top layer

CaO:Mg(sub): CaO(001) with Mg in the second layer

CS: Campbell and Sellers entropy correlation

D3: Grimme dispersion correction, third generation, with Becke and Johnson damping

DFT: density functional theory

ML: monolayer, one water molecule per surface cation

O_w, O_s: oxygen of the water molecule; surface oxygen that takes the proton

H_w, H_s: hydrogen kept by O_w; hydrogen transferred to O_s

PBE: Perdew, Burke and Ernzerhof exchange and correlation functional

PDOS: projected density of states

SCF: self consistent field

TCES: thermochemical energy storage

VBM: valence band maximum

ZPE: zero point energy

1 Introduction

Thermochemical energy storage (TCES) keeps heat in the form of a reversible reaction between a solid and a gas, and gives it back when the reaction runs the other way (Pardo et al, 2014). Few reactions have been studied as closely for this purpose as $\text{Ca(OH)}_2(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{g})$. The materials are cheap and abundant, the equilibrium sits near 780 K under 1 bar of steam (Schaube et al, 2012), and reactors have already run at the 10 kW scale (Schmidt et al, 2014). Charging dehydrates the hydroxide. Discharging hydrates the oxide and releases the heat, so the rate of hydration sets how quickly stored heat can be delivered. That rate falls as the temperature approaches equilibrium or as the steam pressure drops (Schaube et al, 2012; Criado et al, 2014; Lin et al, 2006), and it degrades further on cycling through sintering and agglomeration (Wang et al, 2015; Dai et al, 2018; Xu et al, 2017) and through carbonation by traces of CO_2 (Yan et al, 2017).

Additives are the usual remedy. Salts such as KNO_3 lower the dehydration temperature (Shkatulov and Aristov, 2017; Wang et al, 2020), composites keep a bed reactive over many cycles (Funayama et al, 2019), and lithium speeds up dehydration (Yan and Zhao, 2014, 2015). In a companion study (Rauf et al, 2026) we computed how the isovalent ions Mg^{2+} and Sr^{2+} , one smaller and one larger than Ca^{2+} (Shannon, 1976), change the bulk thermodynamics of the cycle. They order differently in the hydroxide and the oxide, but at 8 to 12.5 % of each ion they shift the equilibrium temperature by only -5 to $+25$ K. The bulk equilibrium hardly notices them. Hydration, however, does not begin in the bulk. It begins when a water molecule lands on the CaO surface, splits, and supplies the hydroxyl groups from which Ca(OH)_2 grows (Manzano et al, 2012). Whether Mg or Sr change this first step has not been examined.

Water on clean alkaline earth oxide surfaces is well understood. On $\text{MgO}(001)$ a lone molecule stays intact and binds by about 0.5 eV (Carrasco et al, 2008; Bajdich et al, 2015; Alessio et al, 2019); it splits only in dense layers (Odelius, 1999; Giordano et al, 1998) or at steps and point defects (Costa et al, 2006; Liu et al, 1998). $\text{CaO}(001)$ is more reactive. Calculations predict that a single molecule splits into a tightly bound hydroxyl and a surface proton (Carrasco et al, 2008; Hu et al, 2011), and experiments on CaO films show the split monomers and the chains that form at higher coverage (Fujimori et al, 2016; Zhao et al, 2015). Calorimetry gives an initial heat of adsorption of 85 to 90 kJ mol^{-1} on $\text{CaO}(001)$ (Seifert et al, 2021), and the binding strengthens from MgO to BaO (Hu et al, 2011), along with easier dissociation and stronger restructuring of the surface (Maleki et al, 2024). Work on doped CaO surfaces is scarce and comes from carbon capture: Fe substitution was studied for CO_2 adsorption in the presence of water (Kong et al, 2024), and Mg and Ni substitution for CO_2 adsorption and oxygen vacancies, where isovalent Mg changed the surface chemistry only weakly (Shi et al, 2025).

Two questions decide whether a dopant matters for the surface step of the storage cycle: how it changes the binding of water nearby, and whether it is at the surface in the first place. In rock salt oxides such as MgO, isovalent cations larger than the host segregate to the (001) surface in simulations and experiments (Tasker et al, 1985; Colbourn et al, 1983; McCune and Wynblatt, 1983; Cotter et al, 1989), and simulations predict that smaller ones are depleted there (Tasker et al, 1985). In CaO, then, Sr should sit at the surface and Mg below it. We address both questions from first principles for $\text{CaO}(001)$ with Mg, Sr or both in the top layer and with Mg in the second layer. We locate the most stable adsorption state on each surface, separate the contributions of the two dopants, compute their segregation with and without water, and turn the energies into free energies using the vibrations of the adsorbate. Finally we compare the temperature at which adsorbed water leaves each surface with the bulk equilibrium temperatures of the companion study, which used identical settings.

2 Computational methods

2.1 Electronic structure and slab models

We used Quantum ESPRESSO 6.7 (Giannozzi et al, 2009, 2017, 2020) with the PBE functional (Perdew et al, 1996), norm conserving scalar relativistic pseudopotentials from the PseudoDojo v0.4 standard table (van Setten et al, 2018; Hamann, 2013) (10 valence electrons for Ca, Mg and Sr, 6 for O and 1 for H), and cutoffs of 90 Ry for the wavefunctions and 360 Ry for the density. These are the settings of the companion study (Rauf et al, 2026), so surface and bulk energies can be compared directly. CaO(001) was modelled by a slab of four layers in a (2×2) surface cell ($6.83 \times 6.83 \text{ \AA}^2$, four Ca and four O per layer, 32 atoms) built with the PBE lattice constant of CaO ($4.827 \text{ \AA}$; Rauf et al, 2026) and separated from its images by $15 \text{ \AA}$ of vacuum. The two bottom layers were held at their bulk positions and the two top layers relaxed. Because water was adsorbed on one side only, a dipole correction was applied in the vacuum (Neugebauer and Scheffler, 1992; Bengtsson, 1999). The Brillouin zone was sampled with a $2 \times 2 \times 1$ mesh shifted off Γ in the surface plane (Monkhorst and Pack, 1976), a spacing of $0.46 \text{ \AA}^{-1}$ that stays within the $0.5 \text{ \AA}^{-1}$ limit of the bulk calculations.

Geometries were optimised with the BFGS algorithm at 70/280 Ry until the energy changed by less than 10^{-4} Ry and every force on a free atom fell below 10^{-3} Ry bohr $^{-1}$ (the pure clean slab, the three clean slabs with dopants in the top layer and the on top state on pure CaO) or 2×10^{-3} Ry bohr $^{-1}$ (all other structures). All energies reported here are single points at 90/360 Ry on the optimised geometries. The lower cutoff shifts the difference $E(\text{slab}+\text{H}_2\text{O}) - E(\text{slab})$ by 0.015 to 0.017 eV in all 13 states, so relative adsorption energies change by less than 2 meV (Online Resource 1, Fig. S1; all figures and tables numbered with S are in Online Resource 1). SCF cycles were converged to 10^{-10} Ry per atom.

Dopants replaced one Ca ion in the top layer (CaO:Mg and CaO:Sr; 25 % of the surface cations and 6.25 % of all cations in the slab), two Ca ions in the top layer by one Mg and one Sr (CaO:(Mg,Sr)), or one Ca ion in the

second layer (CaO:Mg(sub) and its Sr analogue). In CaO:(Mg,Sr) the two dopants are second neighbours, $4.83 \text{ \AA}$ apart in the ideal lattice ($4.84 \text{ \AA}$ after relaxation) and joined through a surface oxygen on the line between them, the arrangement the companion study found most favourable in bulk CaO (Rauf et al, 2026). The adsorption energy of water is

$$E_{\text{ads}} = E(\text{slab}+\text{H}_2\text{O}) - E(\text{slab}) - E(\text{H}_2\text{O}) \quad (1)$$

where both slabs are relaxed and $E(\text{H}_2\text{O})$ is the energy of the isolated molecule in a cubic box of $10 \text{ \AA}$ with the Martyna and Tuckerman correction (Martyna and Tuckerman, 1999), taken from the companion study. One molecule per surface cell is a coverage of $1/4$ monolayer (ML). The segregation energy of a dopant is

$$E_{\text{seg}} = E(\text{dopant in 2nd layer}) - E(\text{dopant in top layer}) \quad (2)$$

so a positive value means the dopant prefers the top layer. With adsorbed water, each term refers to the most stable adsorption state found for that position of the dopant.

2.2 Search for the adsorption states

The search had two stages. First, the molecule was placed intact above a surface cation (Ca, Mg or Sr) with one OH bond tilted towards a neighbouring surface oxygen, or already split, with the hydroxyl on the cation and the proton on the neighbouring oxygen. Wherever the intact molecule was tried (CaO, CaO:Mg and CaO:Sr), it split during the optimisation, and on CaO:Mg the intact and split starts ended in the same state. Second, a split start next to Mg relaxed into a different and more stable state in which the hydroxyl bridges two surface cations. To treat all surfaces alike, this state was copied onto every symmetry distinct bridge of every surface using the eight point operations of the square surface net, keeping the heights of the adsorbed atoms relative to the mean height of the top layer Ca ions, and every copy was fully optimised. Altogether 13 states were optimised (Table S1 and Fig. S2). For Mg in the second layer we tried two placements, one with the proton on the oxygen directly above Mg and one with the adsorbate as far from Mg as the cell allows.

The settings were checked on the most stable state on pure CaO (Fig. S1, Table S2). A five layer slab gives $E_{\text{ads}} = -0.845$ eV, and $3 \times 3 \times 1$ and $4 \times 4 \times 1$ meshes also give -0.845 eV, against -0.843 eV in the production setup. The average surface energy of the clean slab is 0.645 and 0.644 J m⁻² for four and five layers, and the bulk energy of CaO recovered from the two slabs agrees with the bulk calculation (Rauf et al, 2026) to within 1.1 meV per formula unit. The SCF and BFGS histories of the five most stable states are shown in Fig. S4. To gauge dispersion, which PBE leaves out, we evaluated the D3 correction with Becke and Johnson damping (Grimme et al, 2010, 2011) on the PBE geometries of all states (PBE+D3, Fig. S8).

2.3 Electronic structure analysis

Löwdin charges (Löwdin, 1950) and projected densities of states (PDOS, Gaussian broadening 0.15 eV) were obtained with projwfc.x for the clean slab and the most stable adsorption state of each surface. Each PDOS is aligned at the highest occupied level of its system, the top of the O 2p valence band (VBM). The charge density difference

$$\Delta\rho = \rho(\text{slab}+\text{H}_2\text{O}) - \rho(\text{slab}) - \rho(\text{H}_2\text{O}) \quad (3)$$

was computed with all three densities at the geometry of the adsorbed state, the last two from separate calculations of the slab without the adsorbate and of the three adsorbate atoms without the slab. Its plane average $\Delta\bar{\rho}(z)$ and the cumulative charge $\Delta q(z) = \int_{-\infty}^z \Delta\bar{\rho}(z') dz'$ show how much charge crosses a plane at height z .

2.4 Vibrations and free energy of adsorption

Vibrations of the adsorbate were computed by central finite differences (± 0.015 Å) of the forces on its three atoms, with the slab frozen, at the cutoff of the geometry optimisation (70 Ry). This gives nine modes for each of the five most stable states, which we assigned from their eigenvectors. The adsorption free energy at temperature T and

water pressure p is (Reuter and Scheffler, 2001)

$$\Delta G_{\text{ads}}(T, p) = E_{\text{ads}} + F_{\text{vib}}^{\text{ads}}(T) - [G_{\text{H}_2\text{O}}(T, p) - E(\text{H}_2\text{O})] \quad (4)$$

where $F_{\text{vib}}^{\text{ads}}$ is the harmonic vibrational free energy of the adsorbate, zero point energy (ZPE) included,

$$F_{\text{vib}}^{\text{ads}}(T) = \sum_{i=1}^9 \left[\frac{\hbar\omega_i}{2} + k_{\text{B}}T \ln \left(1 - e^{-\hbar\omega_i/k_{\text{B}}T} \right) \right] \quad (5)$$

and the Gibbs energy of the gas molecule follows from the ideal gas, rigid rotor and harmonic oscillator model with the PBE frequencies of the companion study (ZPE 0.565 eV) (Rauf et al, 2026), as implemented in ASE (Larsen et al, 2017). Vibrations of the slab are taken as unchanged by adsorption. We define the desorption temperature $T_{\text{des}}(p)$ by $\Delta G_{\text{ads}}(T_{\text{des}}, p) = 0$. Above it, an isolated adsorbate at this coverage is less stable than the molecule in the gas, and the equilibrium occupation of the adsorption sites, $\theta = [1 + e^{\Delta G_{\text{ads}}/k_{\text{B}}T}]^{-1}$, drops below one half.

The harmonic model treats the soft frustrated translations and rotations of the adsorbate as small vibrations and may underestimate its entropy. As an independent estimate we also used the correlation of Campbell and Sellers (2012) (CS),

$$S_{\text{ads}}(T) = 0.70 S_{\text{gas}}^{\circ}(T) - 3.3R \quad (6)$$

for the adsorbate entropy, together with the harmonic enthalpy. The CS correlation was derived for adsorbates that keep much of their mobility, so for a split and strongly bound state it bounds the entropy from above. Together with PBE+D3 this gives three estimates of T_{des} , which we use to separate conclusions that depend on the model from those that do not.

2.5 Segregation in equilibrium with water vapour

Adsorbed water can change where a dopant prefers to sit, but only while the water stays on the surface. To include desorption, we treat each surface cell as a site that is either empty or holds one molecule in equilibrium with the vapour,

so that its free energy is $E(\text{slab}) - k_{\text{B}}T \ln[1 + e^{-\Delta G_{\text{ads}}/k_{\text{B}}T}]$. The effective segregation energy is then

$$E_{\text{seg}}^{\text{eff}}(T, p) = E_{\text{seg}} + k_{\text{B}}T \ln \frac{1 + e^{-\Delta G_{\text{ads}}^{\text{top}}/k_{\text{B}}T}}{1 + e^{-\Delta G_{\text{ads}}^{\text{2nd}}/k_{\text{B}}T}} \quad (7)$$

where E_{seg} refers to the clean surface and $\Delta G_{\text{ads}}^{\text{top}}$ and $\Delta G_{\text{ads}}^{\text{2nd}}$ are the adsorption free energies with the dopant in the top and in the second layer. It falls back to the clean surface value when water leaves both surfaces, and to the value with adsorbed water, vibrations included, when it stays on both.

3 Results and discussion

3.1 Water on pure CaO(001)

A water molecule placed intact above a surface Ca ion splits during the optimisation. The energy falls steadily over the 86 BFGS steps, and the proton crosses the midpoint between the two oxygens at step 62 (Fig. S3). A geometry optimisation is not a minimum energy path, so this does not rule out a small barrier along another route, but it shows that the intact molecule is not a stable state from this starting geometry. In the resulting state the proton sits on a neighbouring surface oxygen ($\text{O}_{\text{s}}\text{H}_{\text{s}} = 1.05 \text{ \AA}$) and the hydroxyl stays on top of the Ca ion ($\text{CaO}_{\text{w}} = 2.27 \text{ \AA}$), held by a short hydrogen bond to the new surface hydroxyl ($\text{O}_{\text{w}} \cdots \text{H}_{\text{s}} = 1.45 \text{ \AA}$). This state binds water by $E_{\text{ads}} = -0.778 \text{ eV}$. A second split state is more stable, $E_{\text{ads}} = -0.843 \text{ eV}$ (Fig. 1, Table 1): the hydroxyl leaves the top site and bridges two Ca ions (2.46 and 2.50 $\text{\AA}$), 1.83 $\text{\AA}$ above the surface plane, while the proton stays where it is.

These values agree with earlier work. Carrasco et al (2008) found the intact molecule at -0.80 eV and the split ion pair about 0.2 eV lower on CaO(001) at 1/16 ML, and the split monomer has been seen experimentally (Fujimori et al, 2016; Zhao et al, 2015). The small gap of 0.066 eV between our two split states fits the mobile hydroxyl of that ion pair, which Carrasco et al. found to visit neighbouring sites over barriers of about 0.05 eV . Our binding is about 0.15 eV weaker than theirs, a difference that may come from the four times higher coverage and the different computational setup. Microcalorimetry

gives an initial heat of adsorption of 0.88 to 0.93 eV (Seifert et al, 2021). PBE (-0.843 eV) binds slightly more weakly than this and PBE+D3 (-1.048 eV) more strongly, the same bracketing of experiment that we found for the bulk reaction energies (Rauf et al, 2026). We therefore keep PBE as the working functional and use PBE+D3 as a bracket.

3.2 Effect of Mg and Sr on water adsorption

On every doped surface the most stable state we found is split as well, and it again consists of a hydroxyl bridging two cations and a proton on a neighbouring surface oxygen (Fig. 1). The dopants change its energy considerably (Fig. 2, Table 1). Relative to pure CaO, a Mg ion in the top layer strengthens the binding by 0.33 eV (-1.175 eV) and a Sr ion by 0.14 eV (-0.982 eV). With both ions in the top layer the binding is -1.178 eV , essentially the value for Mg alone, and a Mg ion in the second layer slightly weakens it (-0.807 eV).

The full set of states shows how each dopant works (Fig. 2 and Fig. 3b). On CaO:Mg, a hydroxyl bound on top of Mg itself (-0.954 eV , $\text{MgO}_{\text{w}} = 1.98 \text{ \AA}$) is less stable than one that bridges two Ca ions while its proton sits on an oxygen bonded to Mg (-1.175 eV). When the hydroxyl was started on a bridge between Ca and Mg, it moved away from Mg (to $2.88 \text{ \AA}$) and the binding dropped to -0.629 eV , weaker than on pure CaO. Mg therefore helps through the oxygen that takes the proton, not through the site of the hydroxyl. Sr works the other way round. On CaO:Sr the proton sits on an oxygen bonded to Sr in all three states, and the energy is set by where the hydroxyl goes: -0.777 eV on a bridge between two Ca, -0.822 eV on top of Sr and -0.982 eV on a bridge between Ca and Sr. The larger and more polarisable Sr ion offers a better site for the hydroxyl, in line with the stronger binding of water on SrO than on CaO (Hu et al, 2011).

3.3 Why the two dopants do not add

On the codoped surface both starting points we tried relaxed into the same state (-1.176 and -1.178 eV). It combines the two favourable features: the hydroxyl bridges Ca and Sr, and the proton sits on an oxygen bonded to Mg (and to

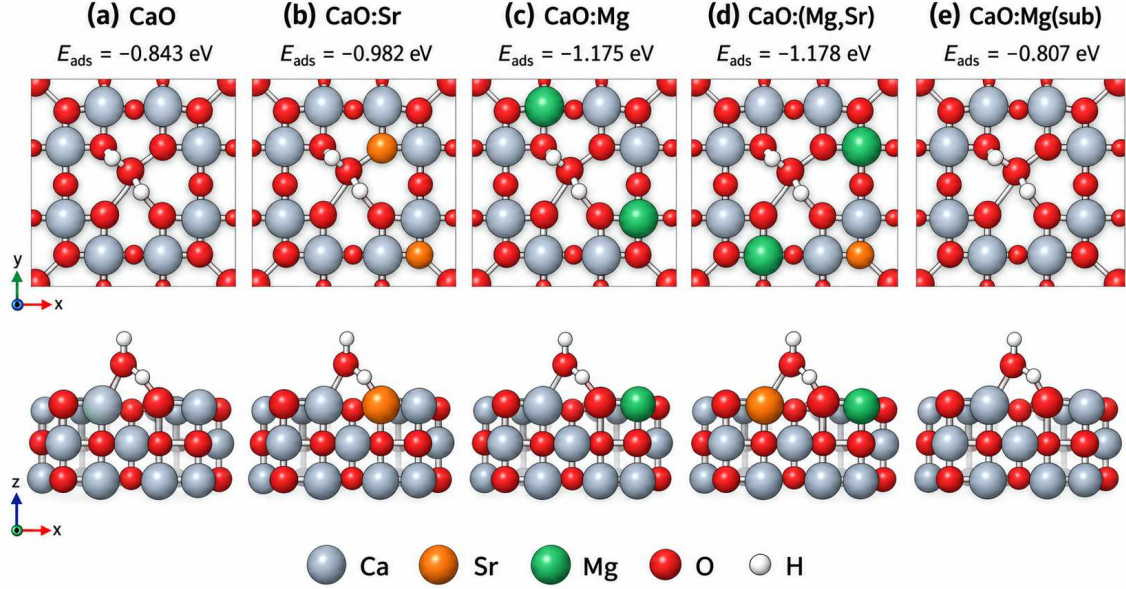


Fig. 1 Schematic of the most stable adsorption state of one water molecule on each surface (1/4 ML), with its adsorption energy. Top row: top view; bottom row: side view. The drawing illustrates the common bonding motif, a hydroxyl bridging two surface cations and a proton transferred to a neighbouring surface oxygen. It is not rendered from the optimised coordinates; the optimised geometries of all 13 states are shown in Fig. S2 and listed in Table S1

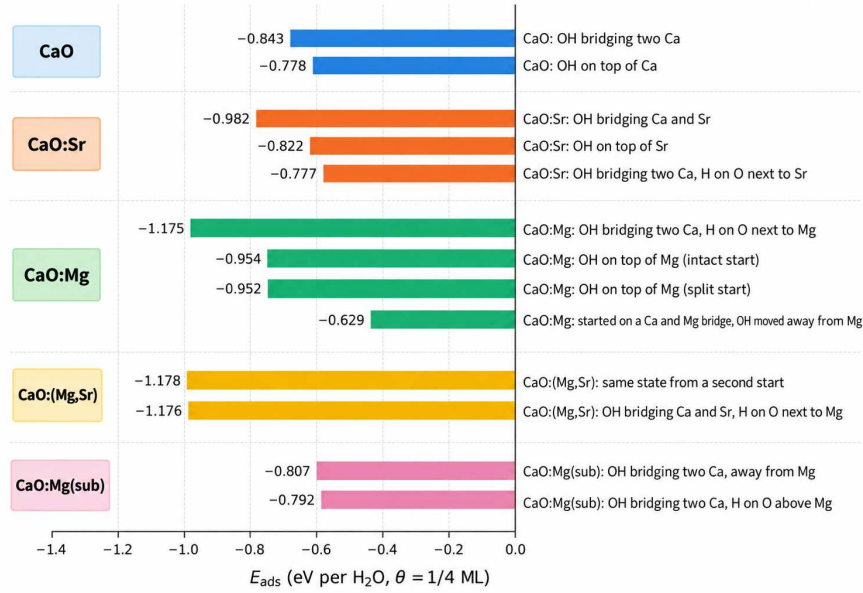


Fig. 2 Adsorption energies (Eq. 1) of all 13 optimised states, grouped by surface. Labels give the final position of the hydroxyl and, where it matters, of the transferred proton. All states are split

Table 1 Most stable adsorption state on each surface: adsorption energy (PBE, PBE with the ZPE difference, and PBE+D3), distances between the hydroxyl oxygen O_w and its two nearest cations, length of the hydrogen bond $O_w \cdots H_s$ and of the new surface hydroxyl $O_s H_s$, and stretching frequency of the new surface hydroxyl.

Surface	E_{ads} (eV)	+ ΔZPE (eV)	PBE+D3 (eV)	O_w to cations (Å)	$O_w \cdots H_s$ (Å)	$O_s H_s$ (Å)	$\nu(O_s H)$ (cm^{-1})	O_s bonded to
CaO	-0.843	-0.787	-1.048	2.46 (Ca), 2.50 (Ca)	1.478	1.033	2366	Ca
CaO:Sr	-0.982	-0.921	-1.154	2.45 (Ca), 2.61 (Sr)	1.525	1.028	2463	Ca, Sr
CaO:Mg	-1.175	-1.108	-1.361	2.37 (Ca), 2.53 (Ca)	1.537	1.018	2613	Ca, Mg
CaO:(Mg,Sr)	-1.178	-1.109	-1.353	2.43 (Ca), 2.52 (Sr)	1.574	1.014	2693	Ca, Mg, Sr
CaO:Mg(sub)	-0.807	-0.758	-1.003	2.51 (Ca), 2.54 (Ca)	1.457	1.045	2197	Ca

O_s bonded to: cations within 2.9 Å of O_s . In CaO:Mg(sub) the state with the proton on the oxygen directly above Mg is 0.015 eV less stable (Table S1). ΔZPE : zero point energy of the adsorbate minus that of the free molecule. $\nu(O_w H)$ of the bridging hydroxyl is 3773 to 3796 cm^{-1} on all surfaces.

Sr). The gains still do not add up (Fig. 3a). Sr alone strengthens the binding by 0.138 eV and Mg alone by 0.331 eV, so a simple sum predicts 0.470 eV, but the codoped surface gains only 0.335 eV. The missing 0.135 eV is almost unchanged when the ZPE is included (0.134 eV) and remains 0.114 eV with PBE+D3, so it is a robust feature of the energetics rather than an artefact of one treatment. The same holds for the desorption temperature at 1 bar (Fig. 3c): Sr raises it by 85 K and Mg by 203 K, but both together by 201 K instead of the 288 K a sum would give.

The site resolved energies explain why (Fig. 3b). Both gains act on the same proton shared between O_w and the surface. Mg stabilises the proton on the surface oxygen, and Sr stabilises the hydroxyl that the proton has left. Once Mg has pulled the proton firmly onto the surface, the hydrogen bond back to O_w is already weak (1.574 Å on CaO:(Mg,Sr) against 1.478 Å on CaO), and a better site for the hydroxyl has little left to add. In practice this means that, for the surface step, the larger dopant effect sets the result, and a second dopant does not compound it.

3.4 A vibrational signature of the binding strength

The geometry of the adsorbed state follows a common pattern (Table 1). The more strongly water binds, the more completely the proton has moved to the surface: the surface hydroxyl shortens from 1.045 Å (CaO:Mg(sub)) to 1.014 Å (CaO:(Mg,Sr)), and the hydrogen bond back to O_w lengthens from 1.457 to 1.574 Å. The stretching frequency of the new surface hydroxyl, which can be measured, follows the same order. It rises from 2197 to 2693 cm^{-1} , far below the 3773

to 3796 cm^{-1} of the bridging hydroxyl because of the strong hydrogen bond, and it correlates with the adsorption energy with $r = -0.96$ over the five surfaces (Fig. 4). With five points this is a trend rather than a calibrated relation, but it ties the energetics to a quantity that infrared spectroscopy of hydroxylated CaO can reach (Fujimori et al, 2016). The full assignment of the nine adsorbate modes is given in Fig. S5: three frustrated translations between 102 and 385 cm^{-1} , two librations of the bridging hydroxyl between 309 and 474 cm^{-1} , two bends of the surface hydroxyl between 1100 and 1242 cm^{-1} , and the two stretches. A dopant that binds water more strongly does so by holding the transferred proton more firmly, which also frees the bridging hydroxyl from part of its hydrogen bond.

3.5 Electronic structure of the adsorbed state

The charge density difference shows where electrons move on adsorption (Fig. 5a). In the plane through O_w and the proton accepting oxygen, charge builds up in the $O_s H_s$ bond and on the side of O_w facing the surface, and it is depleted between O_w and H_s . This is the signature of a proton that has moved from O_w to O_s while keeping a strong hydrogen bond. The plane average confirms that electron density leaves the top layer and the region just above it for the adsorbate (Fig. 5b). The cumulative charge reaches its minimum of -0.20 to -0.22 e at 1.2 to 1.4 Å above the top layer on all five surfaces. The Löwdin charges agree (Table S3, Fig. S7): the adsorbate gains 0.26 to 0.28 e relative to its neutral atoms, the slab loses 0.28

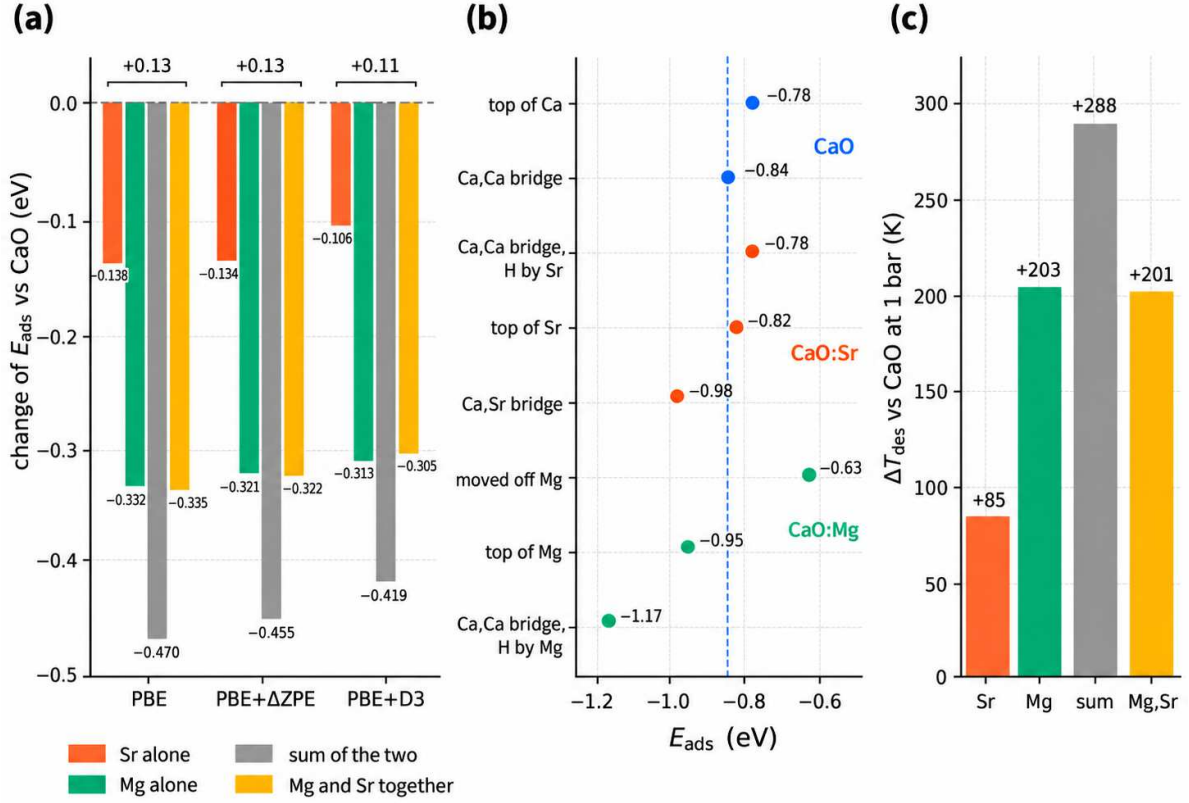


Fig. 3 Codoping analysis. (a) Change of the adsorption energy relative to CaO for Sr alone, Mg alone, their sum and the codoped surface, in three energy treatments; the number above each group is the nonadditive part (eV). (b) Site resolved adsorption energies on CaO, CaO:Sr and CaO:Mg; the dashed line marks the most stable state on CaO. “H by Sr” and “H by Mg” mean that the proton sits on an oxygen bonded to that dopant. (c) Shift of the desorption temperature at 1 bar relative to CaO (harmonic PBE model)

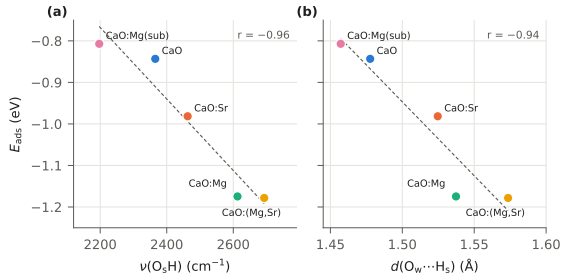


Fig. 4 Adsorption energy of the most stable state on each surface against (a) the stretching frequency of the new surface hydroxyl O_sH and (b) the length of the hydrogen bond between O_w and the transferred proton H_s . Dashed lines: linear fits; r : correlation coefficient

to 0.30 e , and the bridging hydroxyl carries -0.57 to -0.60 e on every surface.

None of these integrated quantities follows the adsorption energy. The charge transferred is the same on CaO and on CaO:Mg to within 0.01 e , although the binding differs by 0.33 eV, so the dopants do not act by donating or withdrawing charge. The PDOS shows three groups of adsorbate states below the O 2p band (Fig. 6). The deepest, at -6.27 to -6.45 eV, carries weight on both oxygens and on the transferred proton and belongs to the $\text{O}_s\text{H}_s \cdots \text{O}_w$ unit that shares the proton. The level at -4.25 to -4.41 eV holds about half of the weight of the hydroxyl hydrogen and little of the transferred proton; it is mainly the σ level of the bridging hydroxyl, mixed with O_s . The 2p states of the

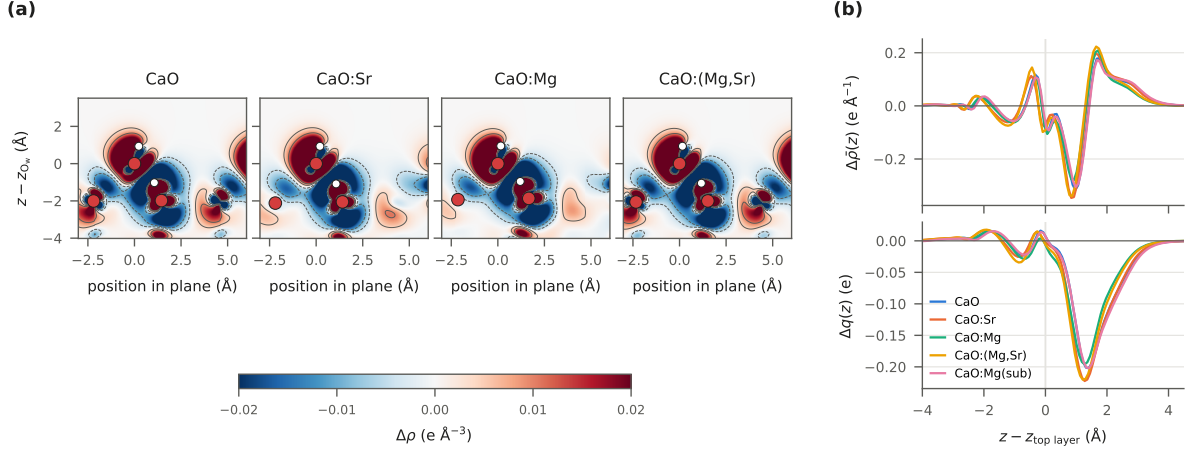


Fig. 5 Charge density difference on adsorption (Eq. 3). (a) $\Delta\rho$ on CaO and on the three surfaces with dopants in the top layer, in the vertical plane through the hydroxyl oxygen and the proton accepting surface oxygen (red: gain, blue: loss of electrons; contours at ± 0.004 and ± 0.01 $e \text{ \AA}^{-3}$); atoms within $0.8 \text{ \AA}$ of the plane are shown. (b) Plane average $\Delta\bar{\rho}(z)$ and cumulative charge $\Delta q(z)$ along the surface normal, with z measured from the top layer

protonated surface oxygen form a third peak, at -2.44 eV on pure CaO, split off from the O 2p band of the clean surface, while the 2p states of O_w lie near the VBM (-1.17 to -1.25 eV).

The dopants move these levels by a few tenths of an eV at most. On the two Mg surfaces the shared proton level lies 0.09 to 0.13 eV higher than on CaO, as expected from the longer hydrogen bond to O_w , and the 2p peak of the protonated oxygen splits into components at -2.41 and -2.71 eV (CaO:Mg) or -2.43 and -2.83 eV (CaO:(Mg,Sr)), with the lower edge of this band 0.21 to 0.33 eV deeper. On CaO:Sr and CaO:Mg(sub) the peak stays single, at -2.51 and -2.43 eV. The splitting reflects the bond of the protonated oxygen to Mg. Together with the shorter and stiffer surface hydroxyl, it points to a local stabilisation of that hydroxyl next to Mg, although no single level in the PDOS accounts for the difference in binding energy. On the clean surfaces (Fig. S6) the 2p states of the top layer oxygens lie 0.3 to 0.4 eV closer to the VBM than those of the second layer, and Mg extends the bottom of the valence band to lower energy (by 0.30 to 0.38 eV in the top layer and 0.60 eV in the second layer), the same Mg and O mixing that splits the peak of the protonated oxygen.

3.6 Free energy of adsorption and the link to the storage reaction

All nine vibrational modes of the adsorbate are real on every surface (Table S4, Fig. S5). The adsorbate has a ZPE 0.049 to 0.070 eV larger than the free molecule, which weakens the binding by 0.05 to 0.07 eV on all surfaces (Table 1). The breakdown of the free energy (Fig. 7) shows where the temperature dependence comes from. The thermal enthalpy terms nearly cancel (-0.04 eV at 300 K and below 0.01 eV at 700 K), and the loss of translational and rotational entropy on adsorption dominates: $-T\Delta S$ is $+0.47$ to $+0.48$ eV at 300 K and $+1.05$ to $+1.07$ eV at 700 K, nearly the same on every surface. At 300 K and 1 bar, ΔG_{ads} is therefore -0.35 eV on CaO, -0.48 eV on CaO:Sr, -0.67 eV on the two Mg surfaces in the top layer and -0.32 eV on CaO:Mg(sub). At 700 K adsorption on CaO, CaO:Sr and CaO:Mg(sub) has already become unfavourable ($+0.27$, $+0.14$ and $+0.29$ eV), while CaO:Mg and CaO:(Mg,Sr) stay just below zero (-0.04 eV). Since the entropy term is common to all surfaces, the order of the free energies is set by the adsorption energy alone, and ΔG_{ads} rises almost linearly with T (Fig. 8a).

The desorption temperatures follow the order of the adsorption energies (Table 2, Fig. 8b, Table S5). In the harmonic model at 1 bar, water leaves pure CaO at 524 K, CaO:Sr at 609 K, CaO:Mg and CaO:(Mg,Sr) at 725 to 727 K,

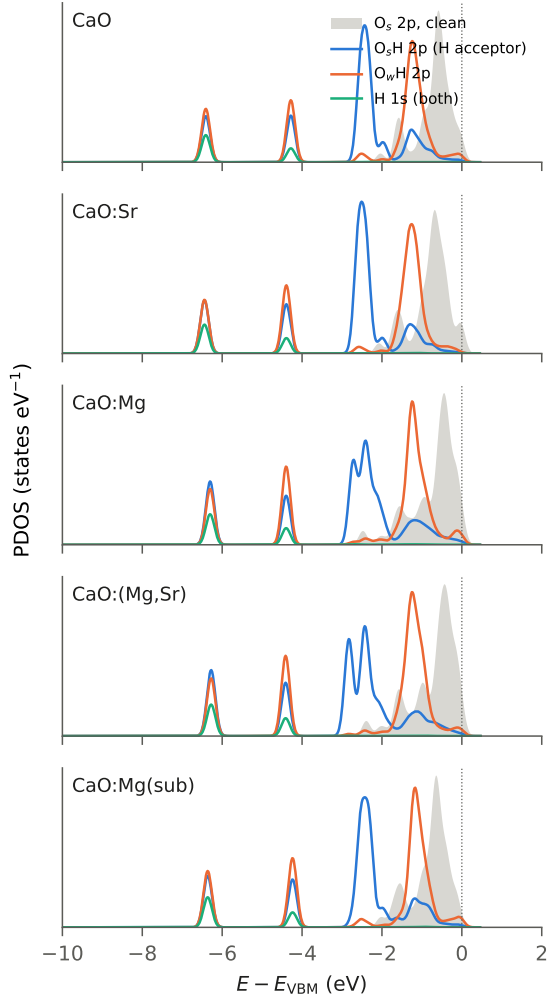


Fig. 6 Projected densities of states of the most stable adsorption state on each surface, aligned at the highest occupied level (VBM): 2p states of the proton accepting surface oxygen O_s (blue) and of the hydroxyl oxygen O_w (orange), 1s states of both hydrogen atoms (green), and 2p states of the same surface oxygen in the clean slab (grey). The clean surfaces are shown in Fig. S6

and CaO:Mg(sub) at 507 K. At 0.023 bar, the vapour pressure of water at room temperature, all values fall by 88 to 127 K. The absolute values depend on the model. At 1 bar, dispersion raises them by 114 to 134 K and the CS entropy by 258 to 313 K, so T_{des} of pure CaO at 1 bar ranges from 524 to 788 K. The bulk equilibrium temperature of $\text{Ca}(\text{OH})_2/\text{CaO}$ computed with the same functional is 695 K at 1 bar (Rauf et al, 2026). Whether a lone water molecule on the flat terrace of pure CaO survives up to this

temperature therefore depends on the model. In the harmonic PBE model it does not, whereas CaO:Mg and CaO:(Mg,Sr) keep their water above it.

The equilibrium site occupation makes the same point more concretely (Fig. 9). At 1 bar and the bulk equilibrium temperature of 695 K, the adsorption sites are 1 % occupied on CaO and CaO:Mg(sub), 10 % on CaO:Sr and 68 to 69 % on CaO:Mg and CaO:(Mg,Sr). At 0.023 bar and its bulk equilibrium temperature of 563 K, the occupations are 0.4 to 0.7 %, 9 % and 80 to 81 %. These numbers come from the harmonic PBE model and a single coverage, so they illustrate the contrast between the surfaces rather than predict measured coverages.

The effect of the dopants, unlike the absolute temperatures, is robust: its sign and order are the same in all three models (Fig. 8c). Relative to pure CaO, Mg in the top layer raises T_{des} by 193 to 248 K, Mg and Sr together by 182 to 249 K and Sr by 65 to 105 K, while Mg in the second layer lowers it by 16 to 23 K. In the companion study the same ions at 12.5 % each shifted the bulk equilibrium temperature by only -5 K (Mg), $+25$ K (Sr) and $+8$ K (both) (Rauf et al, 2026). The dopants thus act several times (Sr) to more than an order of magnitude (Mg) more strongly on the binding of water at the surface than on the bulk equilibrium of the storage reaction.

3.7 Dopant segregation with and without water

A dopant can only change adsorption if it is at the surface. On the clean surface the two ions behave as their size suggests (Fig. 10a, Table S5). The large Sr ion prefers the top layer by $E_{\text{seg}} = +0.457$ eV, and the small Mg ion prefers the second layer by -0.287 eV. This agrees with simulations and experiments on MgO, where larger isovalent cations segregate to the (001) surface (Tasker et al, 1985; Colbourn et al, 1983; McCune and Wynblatt, 1983; Cotter et al, 1989), and with simulations that predict the depletion of smaller ones (Tasker et al, 1985). The segregation of Sr is convenient, since its gain in water binding comes from a site the ion occupies anyway. For Mg the clean surface result suggests that its larger gain is out of reach.

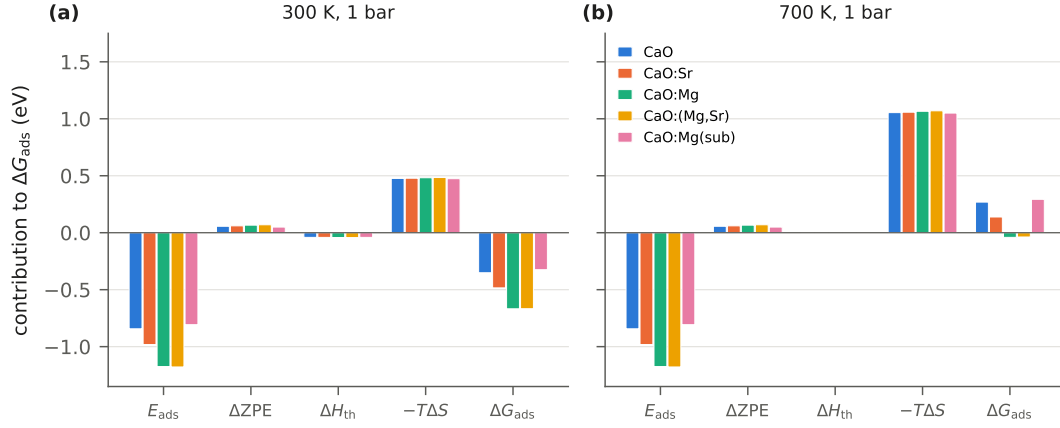


Fig. 7 Contributions to the adsorption free energy at 1 bar and (a) 300 K and (b) 700 K (harmonic PBE model): adsorption energy, ZPE difference, thermal enthalpy difference, entropy term and total

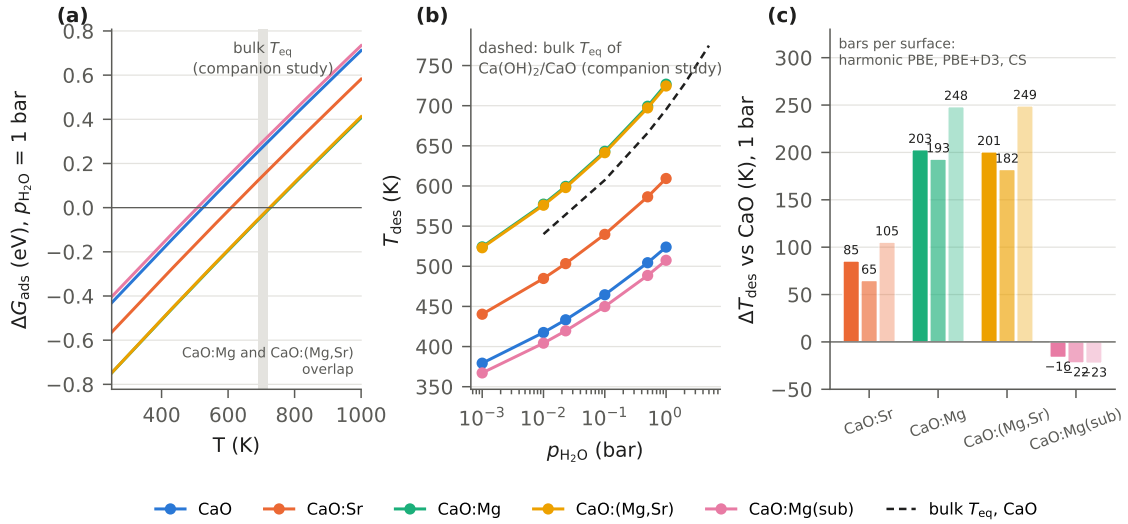


Fig. 8 Free energy of adsorption. (a) ΔG_{ads} (Eq. 4) at a water pressure of 1 bar (harmonic PBE model); the grey band marks the bulk equilibrium temperatures of the $\text{Ca(OH)}_2/\text{CaO}$ reaction for pure CaO and for 12.5 % Mg, Sr or both, from the companion study (Rauf et al, 2026). (b) Desorption temperature against water pressure, with the bulk equilibrium temperature of pure $\text{Ca(OH)}_2/\text{CaO}$ (dashed). (c) Shift of the desorption temperature relative to CaO at 1 bar in three models: harmonic PBE, harmonic PBE+D3, and the Campbell and Sellers (CS) entropy with PBE energies

Table 2 Desorption temperature T_{des} (K) of water at 1/4 ML for three water pressures in the harmonic PBE model, and at 1 bar with PBE+D3 energies and with the Campbell and Sellers (CS) entropy. The last column gives the bulk equilibrium temperature T_{eq} of the $\text{Ca(OH)}_2/\text{CaO}$ reaction at 1 bar for the nearest bulk composition of the companion study (Rauf et al, 2026).

Surface	0.023 bar	0.1 bar	1 bar	1 bar, PBE+D3	1 bar, CS	Shift vs CaO, 1 bar	Bulk T_{eq} , 1 bar
CaO	433	465	524	658	788	reference	695 (CaO)
CaO:Sr	503	540	609	723	894	+65 to +105	720 (12.5 % Sr)
CaO:Mg	599	643	727	851	1037	+193 to +248	690 (12.5 % Mg)
CaO:(Mg,Sr)	598	641	725	840	1038	+182 to +249	703 (12.5 % Mg and Sr)
CaO:Mg(sub)	420	450	507	636	766	-23 to -16	690 (12.5 % Mg)

Shifts give the range over the three models. The bulk values are PBE with harmonic phonons and lie 83 K below the measured T_{eq} of pure Ca(OH)_2 (778 K; Schaube et al, 2012); the PBE+D3 bulk value is 807 K (Rauf et al, 2026).

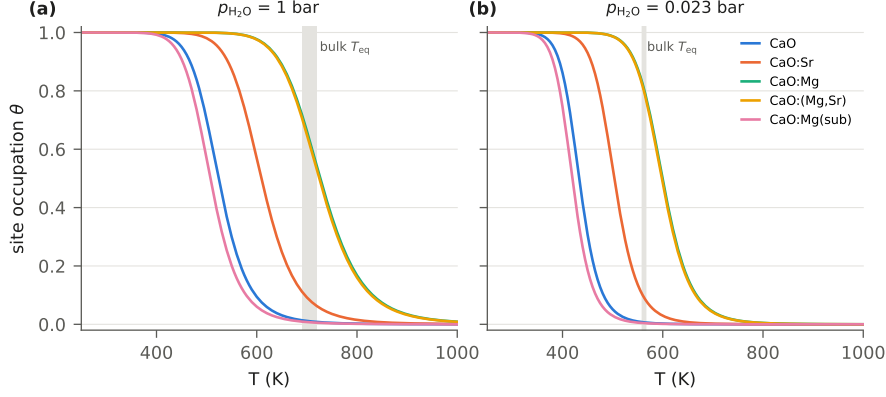


Fig. 9 Equilibrium occupation of the adsorption sites, $\theta = [1 + e^{\Delta G_{\text{ads}}/k_B T}]^{-1}$, at (a) 1 bar and (b) 0.023 bar (harmonic PBE model, independent sites at 1/4 ML). Grey marks: bulk equilibrium temperature of $\text{Ca(OH)}_2/\text{CaO}$ (Rauf et al, 2026); at 0.023 bar it is taken from the van 't Hoff line through the companion study values at 0.01 and 0.1 bar (563 K)

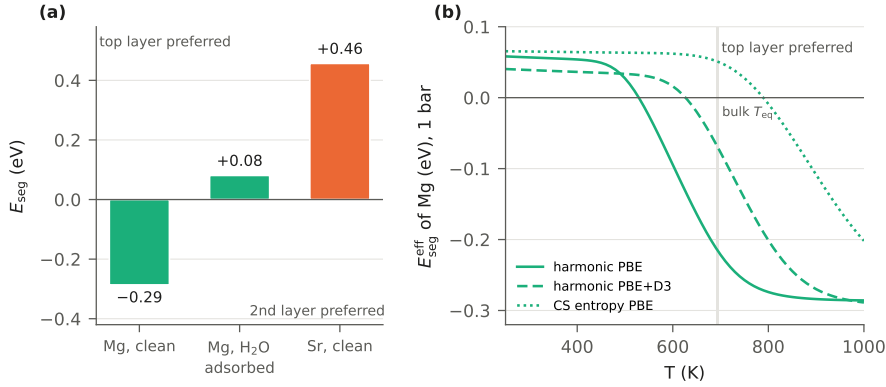


Fig. 10 (a) Segregation energies (Eq. 2) of Mg and Sr on the clean $\text{CaO}(001)$ surface and of Mg with one adsorbed water molecule per surface cell (static energies). (b) Effective segregation energy of Mg in equilibrium with water vapour at 1 bar (Eq. 7) in the three thermochemical models; the grey band marks the bulk equilibrium temperature of pure and 12.5 % Mg substituted Ca(OH)_2 (Rauf et al, 2026). Positive values mean that Mg prefers the top layer

Adsorbed water changes this, but only at moderate temperature. With Mg in the second layer, the most stable adsorption state binds water by -0.807 eV, close to pure CaO, whereas Mg in the top layer gives -1.175 eV. The difference of 0.368 eV more than offsets the segregation penalty of the clean surface, and with one adsorbed molecule per cell Mg prefers the top layer by $E_{\text{seg}} = +0.081$ eV (Fig. 10a). Dispersion changes this value by less than 0.02 eV ($+0.063$ eV with PBE+D3), and the ZPE difference between the two adsorbed states lowers it by 0.017 eV to $+0.064$ eV. The preference holds only while water stays on the surface, and CaO:Mg(sub) loses its water at a lower temperature than CaO:Mg

(Section 3.6). In equilibrium with the vapour (Eq. 7), Mg prefers the top layer below 529 K at 1 bar and below 442 K at 0.023 bar in the harmonic PBE model, below 627 and 526 K with PBE+D3, and below 789 and 633 K with the CS entropy (Fig. 10b, Table S5). Below the crossover the preference for the top layer is small, at most 0.04 to 0.07 eV, so adsorbed water at most balances the segregation of Mg rather than driving it strongly.

The full temperature and pressure map places these results next to the operating conditions of the cycle (Fig. 11). In every model the boundary between the two regions runs nearly parallel to the bulk equilibrium line, because both are set by the free energy of gas phase water. What differs

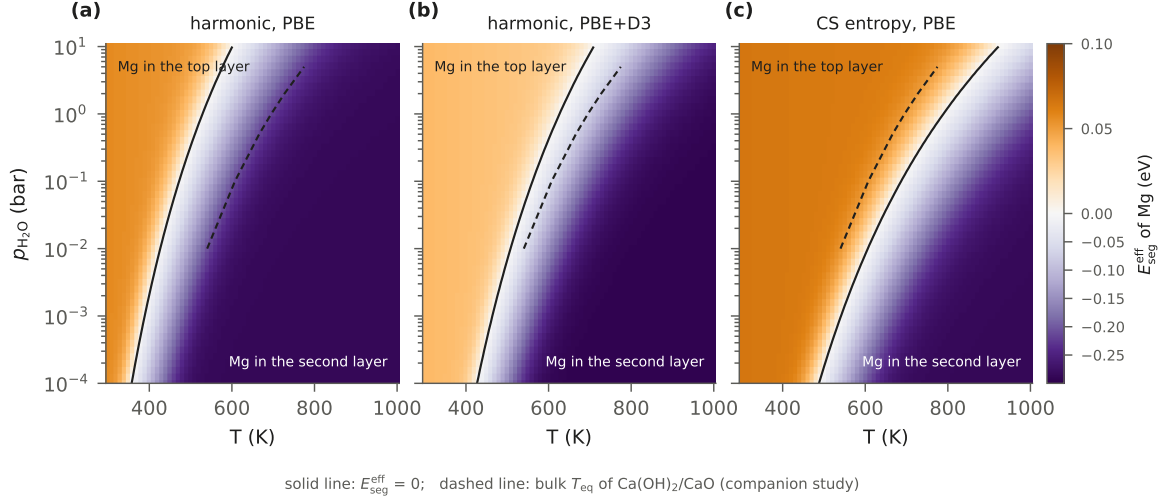


Fig. 11 Effective segregation energy of Mg (Eq. 7) as a function of temperature and water pressure in (a) the harmonic PBE model, (b) the harmonic PBE+D3 model and (c) the model with the Campbell and Sellers entropy. Orange: Mg prefers the top layer; purple: Mg prefers the second layer. Solid line: $E_{\text{seg}}^{\text{eff}} = 0$. Dashed line: bulk equilibrium temperature of $\text{Ca}(\text{OH})_2/\text{CaO}$ (Rauf et al, 2026)

is where the boundary lies relative to that line. Along the bulk equilibrium line between 0.01 and 5 bar, the effective segregation energy is -0.21 to -0.22 eV in the harmonic PBE model and -0.05 to -0.08 eV with PBE+D3, so Mg stays below the surface there, whereas with the CS entropy it is $+0.05$ eV and Mg sits in the top layer. Close to equilibrium, where the storage cycle releases its heat at the highest temperature, Mg is therefore expected to stay mostly in the second layer in the two harmonic models. Further below equilibrium, as in a hydration step run for faster kinetics or during cooling under steam, adsorbed water favours Mg at the surface in all three models. Whether Mg actually reaches the surface of a real material then depends on how fast cations move at these temperatures and on the history of the oxide.

3.8 Implications for thermochemical storage

The separation of surface and bulk effects is the main practical result. In the discharge step, CaO is hydrated below the equilibrium temperature, and the closer it operates to equilibrium, the higher the temperature of the released heat but the slower the reaction (Schaube et al, 2012; Criado et al, 2014). Hydration begins with water that is adsorbed and split at the surface (Manzano

et al, 2012). A surface that holds water up to higher temperatures, or at lower steam pressure for a given temperature, should therefore keep this first step supplied in exactly the conditions where pure CaO is weakest, while the equilibrium temperature, and with it the temperature level of the stored heat, stays where it is.

Of the two dopants, Sr is the more dependable. It segregates to the surface on its own and raises T_{des} by 65 to 105 K. Mg has the larger effect, 190 to 250 K, but only from the top layer, which it prefers under adsorbed water only below the crossover temperatures of Section 3.7. Near the equilibrium temperature of the cycle it is expected to stay mostly in the second layer, where it slightly weakens the binding. On the codoped surface the effect of Mg dominates and the gains do not add, so for the surface step codoping offers no advantage over Mg alone in our model. Its benefit lies in the bulk, where linear bridges of Mg, O and Sr stabilise the dissolved state of both ions in CaO (Rauf et al, 2026). Sr substitution is thus the most direct way to strengthen the surface step without moving the equilibrium, and Mg is an option for hydration at lower temperatures or wherever Mg can be kept at the surface.

These conclusions carry the limits of the model. We considered one coverage ($1/4$ ML), one dopant arrangement per surface cell and the flat

terrace only. Steps, corners and vacancies bind water more strongly and split it more readily on CaO and MgO (de Leeuw and Purton, 2001; Costa et al, 2006; Seifert et al, 2021), and on real particles they may dominate the first steps of hydration. At higher coverage water forms chains on CaO(001) (Zhao et al, 2015; Fujimori et al, 2016), and the transition to a hydroxide layer (Manzano et al, 2012) was not addressed. In our (2×2) cell every surface oxygen is a neighbour of the dopant, so whether the proton ends up on an oxygen bonded to Mg is decided by the relaxation; larger cells would allow dopant contents closer to those of the companion study and a cleaner separation of the two effects. We report thermodynamics only. The barriers of proton transfer and of hydroxide growth, which control the rate, and the diffusion of the dopants, which controls how fast segregation equilibrium is reached, remain to be calculated. The strong correlation between the adsorption energy and the stretching frequency of the surface hydroxyl offers a way to test the predicted trends by infrared spectroscopy of doped CaO.

4 Conclusions

We have studied the first step of CaO hydration, the adsorption and splitting of water at the CaO(001) surface, on pure, Mg, Sr and Mg and Sr substituted surfaces by density functional theory. The main findings are as follows.

First, the most stable state found on every surface is split: a hydroxyl bridges two surface cations and the proton sits on a neighbouring surface oxygen. On pure CaO this state binds water by 0.84 eV (PBE), slightly less than the measured heat of adsorption (0.88 to 0.93 eV), which lies between the PBE and PBE+D3 values. The result is converged with respect to slab thickness and k point sampling to within about 2 meV.

Second, Mg and Sr strengthen the binding in different ways. Mg in the top layer stabilises the proton on its neighbouring oxygen and strengthens the binding by 0.33 eV, while Sr provides a better site for the hydroxyl and strengthens it by 0.14 eV. The two effects do not add: 0.11 to 0.135 eV of the expected combined gain is missing in all three energy treatments, because both dopants act on the same shared

proton. The stretching frequency of the new surface hydroxyl rises from 2197 to 2693 cm^{-1} with the binding strength ($r = -0.96$), whereas the total charge transferred to the adsorbate (0.26 to 0.28 e) hardly changes.

Third, on the clean surface Sr prefers the top layer by 0.46 eV and Mg the second layer by 0.29 eV. Adsorbed water reverses the preference of Mg (+0.08 eV at one molecule per cell), but in equilibrium with the vapour only below 530 to 790 K at 1 bar, depending on the thermochemical model. Near the bulk equilibrium temperature Mg is expected to stay mostly below the surface in the two harmonic models.

Fourth, the dopants raise the temperature at which adsorbed water leaves the surface by 193 to 248 K (Mg), 182 to 249 K (Mg and Sr) and 65 to 105 K (Sr) across three thermochemical models, whereas they shift the bulk equilibrium temperature of the storage reaction by only -5 to $+25$ K. The entropy lost on adsorption is nearly the same on every surface, so the adsorption energy alone sets this order.

For the $\text{Ca}(\text{OH})_2/\text{CaO}$ storage cycle this points to Sr substitution as a dependable way to strengthen the surface step of hydration without moving the equilibrium, and to Mg as a stronger but temperature dependent option. Steps and defects, higher coverage, the diffusion of the dopants and the barriers of proton transfer and hydroxide growth are the next steps towards a kinetic model of doped CaO hydration.

Supplementary information. Online Resource 1 (ESM.1.pdf) contains Figs. S1 to S8 and Tables S1 to S5: convergence checks, all 13 optimised adsorption states, the relaxation from an intact molecule, the calculation histories, the vibrational fingerprint, the clean surface densities of states, the Löwdin charges and the dispersion correction.

Declarations

Funding. This research did not receive any specific grant from funding agencies in the public, commercial, or not for profit sectors.

Competing interests. The authors have no relevant financial or non financial interests to disclose.

Author contributions. Abdul Rauf: Conceptualization, Methodology, Software, Formal analysis, Investigation, Data curation, Validation, Visualization, Writing (original draft), Writing (review and editing). Abdul Shakoor Sabir: Conceptualization, Methodology, Supervision, Validation, Writing (review and editing), Project administration. Muhammad Danish: Conceptualization, Methodology, Supervision, Validation, Writing (review and editing), Project administration. All authors read and approved the final manuscript.

Ethics approval and consent. This study is entirely computational. It involved no human participants, no animals and no laboratory experiments, so ethics approval and consent to participate were not required. Consent for publication: not applicable.

Data availability. The datasets generated and analysed during the current study are available from the corresponding author on reasonable request.

Code availability. All calculations used the open source codes Quantum ESPRESSO and ASE. Input files and analysis scripts are available from the corresponding author on reasonable request.

Use of AI assisted technologies. During the preparation of this work the authors used Grammarly in order to correct grammatical errors. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

References

- Alessio M, Usvyat D, Sauer J (2019) Chemically accurate adsorption energies: CO and H₂O on the MgO(001) surface. *Journal of Chemical Theory and Computation* 15(2):1329–1344. <https://doi.org/10.1021/acs.jctc.8b01122>
- Bajdich M, Nørskov J, Vojvodic A (2015) Surface energetics of alkaline-earth metal oxides: trends in stability and adsorption of small molecules. *Physical Review B* 91(15):155401. <https://doi.org/10.1103/PhysRevB.91.155401>
- Bengtsson L (1999) Dipole correction for surface supercell calculations. *Physical Review B* 59(19):12301–12304. <https://doi.org/10.1103/PhysRevB.59.12301>
- Campbell C, Sellers J (2012) The entropies of adsorbed molecules. *Journal of the American Chemical Society* 134(43):18109–18115. <https://doi.org/10.1021/ja3080117>
- Carrasco J, Illas F, Lopez N (2008) Dynamic ion pairs in the adsorption of isolated water molecules on alkaline-earth oxide (001) surfaces. *Physical Review Letters* 100(1):016101. <https://doi.org/10.1103/PhysRevLett.100.016101>
- Colbourn E, Mackrodt W, Tasker P (1983) The segregation of calcium ions at the surface of magnesium oxide: theory and calculation. *Journal of Materials Science* 18(7):1917–1924. <https://doi.org/10.1007/BF00554983>
- Costa D, Chizallet C, Ealet B, et al (2006) Water on extended and point defects at MgO surfaces. *The Journal of Chemical Physics* 125(5):054702. <https://doi.org/10.1063/1.2212407>
- Cotter M, Campbell S, Cao L, et al (1989) Surface segregation of Ba in MgO. *Surface Science* 208(3):267–284. [https://doi.org/10.1016/0039-6028\(89\)90003-4](https://doi.org/10.1016/0039-6028(89)90003-4)
- Criado Y, Alonso M, Abanades J (2014) Kinetics of the CaO/Ca(OH)₂ hydration/dehydration reaction for thermochemical energy storage applications. *Industrial & Engineering Chemistry Research* 53(32):12594–12601. <https://doi.org/10.1021/ie404246p>
- Dai L, Long XF, Lou B, et al (2018) Thermal cycling stability of thermochemical energy storage system Ca(OH)₂/CaO. *Applied Thermal Engineering* 133:261–268. <https://doi.org/10.1016/j.applthermaleng.2018.01.059>
- Fujimori Y, Zhao X, Shao X, et al (2016) Interaction of water with the CaO(001) surface. *The Journal of Physical Chemistry C* 120(10):5565–5576. <https://doi.org/10.1021/acs.jpcc.6b00433>

- Funayama S, Takasu H, Zamengo M, et al (2019) Composite material for high-temperature thermochemical energy storage using calcium hydroxide and ceramic foam. *Energy Storage* 1(2):e53. <https://doi.org/10.1002/est2.53>
- Giannozzi P, Baroni S, Bonini N, et al (2009) QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter* 21(39):395502. <https://doi.org/10.1088/0953-8984/21/39/395502>
- Giannozzi P, Andreussi O, Brumme T, et al (2017) Advanced capabilities for materials modelling with Quantum ESPRESSO. *Journal of Physics: Condensed Matter* 29(46):465901. <https://doi.org/10.1088/1361-648X/aa8f79>
- Giannozzi P, Basergio O, Bonfà P, et al (2020) Quantum ESPRESSO toward the exascale. *The Journal of Chemical Physics* 152(15):154105. <https://doi.org/10.1063/5.0005082>
- Giordano L, Goniakowski J, Suzanne J (1998) Partial dissociation of water molecules in the (3×2) water monolayer deposited on the MgO(100) surface. *Physical Review Letters* 81(6):1271–1273. <https://doi.org/10.1103/PhysRevLett.81.1271>
- Grimme S, Antony J, Ehrlich S, et al (2010) A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics* 132(15):154104. <https://doi.org/10.1063/1.3382344>
- Grimme S, Ehrlich S, Goerigk L (2011) Effect of the damping function in dispersion corrected density functional theory. *Journal of Computational Chemistry* 32(7):1456–1465. <https://doi.org/10.1002/jcc.21759>
- Hamann D (2013) Optimized norm-conserving Vanderbilt pseudopotentials. *Physical Review B* 88(8):085117. <https://doi.org/10.1103/PhysRevB.88.085117>
- Hu X, Carrasco J, Klimeš J, et al (2011) Trends in water monomer adsorption and dissociation on flat insulating surfaces. *Physical Chemistry Chemical Physics* 13(27):12447–12453. <https://doi.org/10.1039/c1cp20846b>
- Kong D, Zhang Y, Nie B, et al (2024) CO₂ adsorption and desorption across the Fe-doped Ca-based composites in the presence of H₂O: a DFT approach. *Physica B: Condensed Matter* 673:415483. <https://doi.org/10.1016/j.physb.2023.415483>
- Larsen AH, Mortensen JJ, Blomqvist J, et al (2017) The atomic simulation environment—a Python library for working with atoms. *Journal of Physics: Condensed Matter* 29(27):273002. <https://doi.org/10.1088/1361-648X/aa680e>
- de Leeuw N, Purton J (2001) Density-functional theory calculations of the interaction of protons and water with low-coordinated surface sites of calcium oxide. *Physical Review B* 63(19):195417. <https://doi.org/10.1103/PhysRevB.63.195417>
- Lin S, Harada M, Suzuki Y, et al (2006) CaO hydration rate at high temperature (~ 1023 K). *Energy & Fuels* 20(3):903–908. <https://doi.org/10.1021/ef050257o>
- Liu P, Kendelewicz T, Jr. GB, et al (1998) Reaction of water with MgO(100) surfaces. Part I: Synchrotron X-ray photoemission studies of low-defect surfaces. *Surface Science* 412-413:287–314. [https://doi.org/10.1016/S0039-6028\(98\)00444-0](https://doi.org/10.1016/S0039-6028(98)00444-0)
- Löwdin PO (1950) On the non-orthogonality problem connected with the use of atomic wave functions in the theory of molecules and crystals. *The Journal of Chemical Physics* 18(3):365–375. <https://doi.org/10.1063/1.1747632>
- Maleki F, Inico E, Liberto GD (2024) Hydration of MgO, CaO, SrO, and BaO (001) surfaces from first principles. *ChemistrySelect* 9(18):e202401864. <https://doi.org/10.1002/slct.202401864>
- Manzano H, Pellenq RM, Ulm FJ, et al (2012) Hydration of calcium oxide surface predicted by reactive force field molecular dynamics.

- Langmuir 28(9):4187–4197. <https://doi.org/10.1021/la204338m>
- Martyna GJ, Tuckerman ME (1999) A reciprocal space based method for treating long range interactions in ab initio and force-field-based calculations in clusters. The Journal of Chemical Physics 110(6):2810–2821. <https://doi.org/10.1063/1.477923>
- McCune R, Wynblatt P (1983) Calcium segregation to a magnesium oxide (100) surface. Journal of the American Ceramic Society 66(2):111–117. <https://doi.org/10.1111/j.1151-2916.1983.tb09985.x>
- Monkhorst H, Pack J (1976) Special points for Brillouin-zone integrations. Physical Review B 13(12):5188–5192. <https://doi.org/10.1103/PhysRevB.13.5188>
- Neugebauer J, Scheffler M (1992) Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al(111). Physical Review B 46(24):16067–16080. <https://doi.org/10.1103/PhysRevB.46.16067>
- Odelius M (1999) Mixed molecular and dissociative water adsorption on MgO[100]. Physical Review Letters 82(19):3919–3922. <https://doi.org/10.1103/PhysRevLett.82.3919>
- Pardo P, Deydier A, Anxionnaz-Minvielle Z, et al (2014) A review on high temperature thermochemical heat energy storage. Renewable and Sustainable Energy Reviews 32:591–610. <https://doi.org/10.1016/j.rser.2013.12.014>
- Perdew J, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. Physical Review Letters 77(18):3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>
- Rauf A, Sabir AS, Danish M (2026) First principles investigation of coupled structural, electronic, optical and thermochemical properties of $\text{Ca}_{1-x-y}\text{Mg}_x\text{Sr}_y(\text{OH})_2/\text{Ca}_{1-x-y}\text{Mg}_x\text{Sr}_y\text{O}$ for thermochemical energy storage, computational Condensed Matter, submitted
- Reuter K, Scheffler M (2001) Composition, structure, and stability of $\text{RuO}_2(110)$ as a function of oxygen pressure. Physical Review B 65(3):035406. <https://doi.org/10.1103/PhysRevB.65.035406>
- Schaube F, Koch L, Wörner A, et al (2012) A thermodynamic and kinetic study of the de- and rehydration of $\text{Ca}(\text{OH})_2$ at high H_2O partial pressures for thermo-chemical heat storage. Thermochimica Acta 538:9–20. <https://doi.org/10.1016/j.tca.2012.03.003>
- Schmidt M, Szczukowski C, Roßkopf C, et al (2014) Experimental results of a 10 kW high temperature thermochemical storage reactor based on calcium hydroxide. Applied Thermal Engineering 62(2):553–559. <https://doi.org/10.1016/j.applthermaleng.2013.09.020>
- Seifert J, Carey S, Schauer mann S, et al (2021) Water and carbon dioxide adsorption on $\text{CaO}(001)$ studied via single crystal adsorption calorimetry. Topics in Catalysis 64(17-20):1030–1040. <https://doi.org/10.1007/s11244-021-01431-2>
- van Setten M, Giantomassi M, Bousquet E, et al (2018) The PseudoDojo: training and grading a 85 element optimized norm-conserving pseudopotential table. Computer Physics Communications 226:39–54. <https://doi.org/10.1016/j.cpc.2018.01.012>
- Shannon RD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica Section A 32(5):751–767. <https://doi.org/10.1107/S0567739476001551>
- Shi W, Li R, Bao X, et al (2025) DFT investigation into adsorption-desorption properties of Mg/Ni-doped calcium-based materials. Crystals 15(8):711. <https://doi.org/10.3390/cryst15080711>
- Shkatulov A, Aristov Y (2017) Calcium hydroxide doped by KNO_3 as a promising candidate for thermochemical storage of solar heat. RSC Advances 7(68):42929–42939. <https://doi.org/10.1039/c7ra06639b>

- Tasker P, Colbourn E, Mackrodt W (1985) Segregation of isovalent impurity cations at the surfaces of MgO and CaO. *Journal of the American Ceramic Society* 68(2):74–80. <https://doi.org/10.1111/j.1151-2916.1985.tb15268.x>
- Wang A, Deshpande N, Fan LS (2015) Steam hydration of calcium oxide for solid sorbent based CO₂ capture: effects of sintering and fluidized bed reactor behavior. *Energy & Fuels* 29(1):321–330. <https://doi.org/10.1021/ef502021d>
- Wang T, Zhao C, Yan J (2020) Investigation on the Ca(OH)₂/CaO thermochemical energy storage system with potassium nitrate addition. *Solar Energy Materials and Solar Cells* 215:110646. <https://doi.org/10.1016/j.solmat.2020.110646>
- Xu M, Huai X, Cai J (2017) Agglomeration behavior of calcium hydroxide/calcium oxide as thermochemical heat storage material: a reactive molecular dynamics study. *The Journal of Physical Chemistry C* 121(5):3025–3033. <https://doi.org/10.1021/acs.jpcc.6b08615>
- Yan J, Zhao C (2014) First-principle study of CaO/Ca(OH)₂ thermochemical energy storage system by Li or Mg cation doping. *Chemical Engineering Science* 117:293–300. <https://doi.org/10.1016/j.ces.2014.07.007>
- Yan J, Zhao C (2015) Thermodynamic and kinetic study of the dehydration process of CaO/Ca(OH)₂ thermochemical heat storage system with Li doping. *Chemical Engineering Science* 138:86–92. <https://doi.org/10.1016/j.ces.2015.07.053>
- Yan J, Zhao C, Pan Z (2017) The effect of CO₂ on Ca(OH)₂ and Mg(OH)₂ thermochemical heat storage systems. *Energy* 124:114–123. <https://doi.org/10.1016/j.energy.2017.02.034>
- Zhao X, Shao X, Fujimori Y, et al (2015) Formation of water chains on CaO(001): what drives the 1D growth? *The Journal of Physical Chemistry Letters* 6(7):1204–1208. <https://doi.org/10.1021/acs.jpcclett.5b00223>

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [ESM1.pdf](#)