

The Impact of Chlorides on the Surface of Calcite: A Density Functional Theory Analysis of Calcium Carbonate

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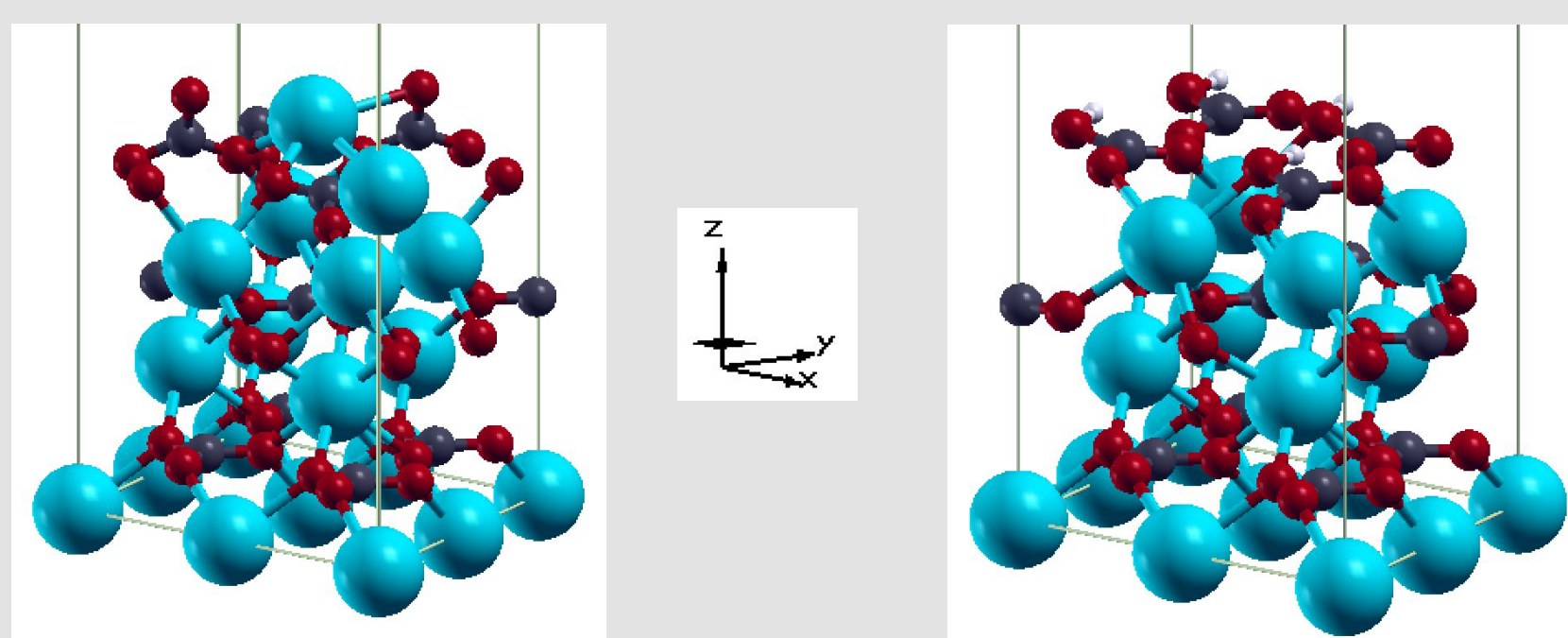


Introduction

- The mineral calcite has a variety of purposes including its historical use in pottery¹



- The crystal structure of calcite belongs to the trigonal crystal class and is hexagonal in shape
- One cleavage plane of calcite is calcium terminated, but the metal cations on the surface can interact with water products to generate a hydrogen terminated surface



Calcium (left) and hydrogen (right) terminated surface

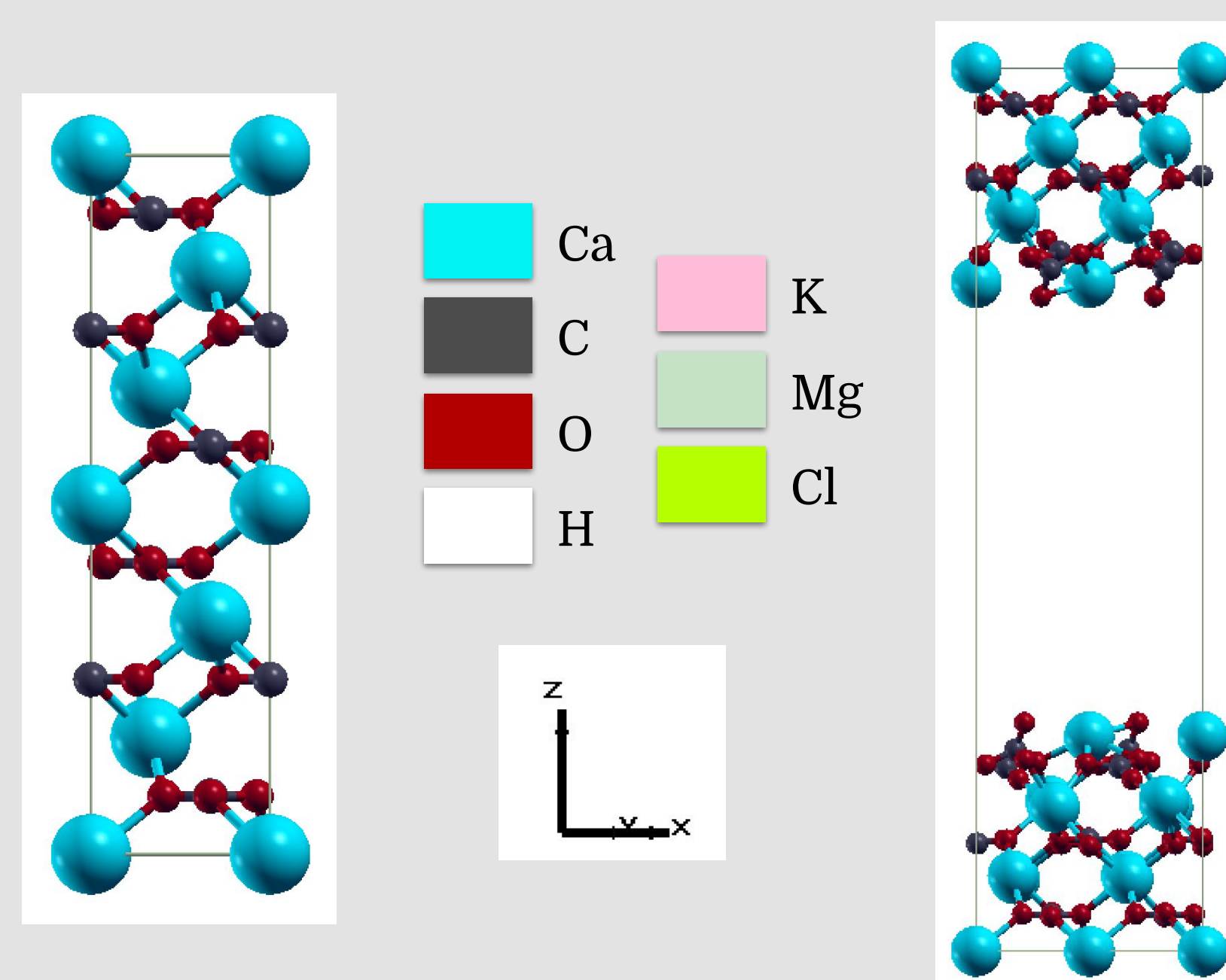
- Chloride anions occur naturally and have a -1 oxidation state
- They readily react and are known to be corrosive to calcium carbonate²

Acknowledgements

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Methodology

All calculations described here employ periodic DFT methods^{3,4} and are carried out using Quantum Espresso, an open source software package^{5,6}. All atoms are represented using GBRV-type ultrasoft pseudopotentials^{7,8}. A plane-wave cutoff of 40 Ry and charge density cutoff of 320 Ry are employed for all calculations, in line with similar surface studies^{9,10,11}. Bulk structural relaxations use a 6x6x6 k-point grid¹², and the convergence criteria for self-consistent relaxations is 5x10⁻⁶ eV. Geometry optimization of all surface-adsorbate interactions did not include fixing any layers, as detailed in Corum et al.¹³ where all atoms are free to relax. All calculations are performed at the GGA level using the Wu-Cohen (WC) modified PBE-GGA exchange correlation functional for solids^{14,15}.



Left: Calcite bulk structure

Right: Ca-terminated 2x2x1 inversion symmetric supercell with ~17 Å vacuum in between the layers

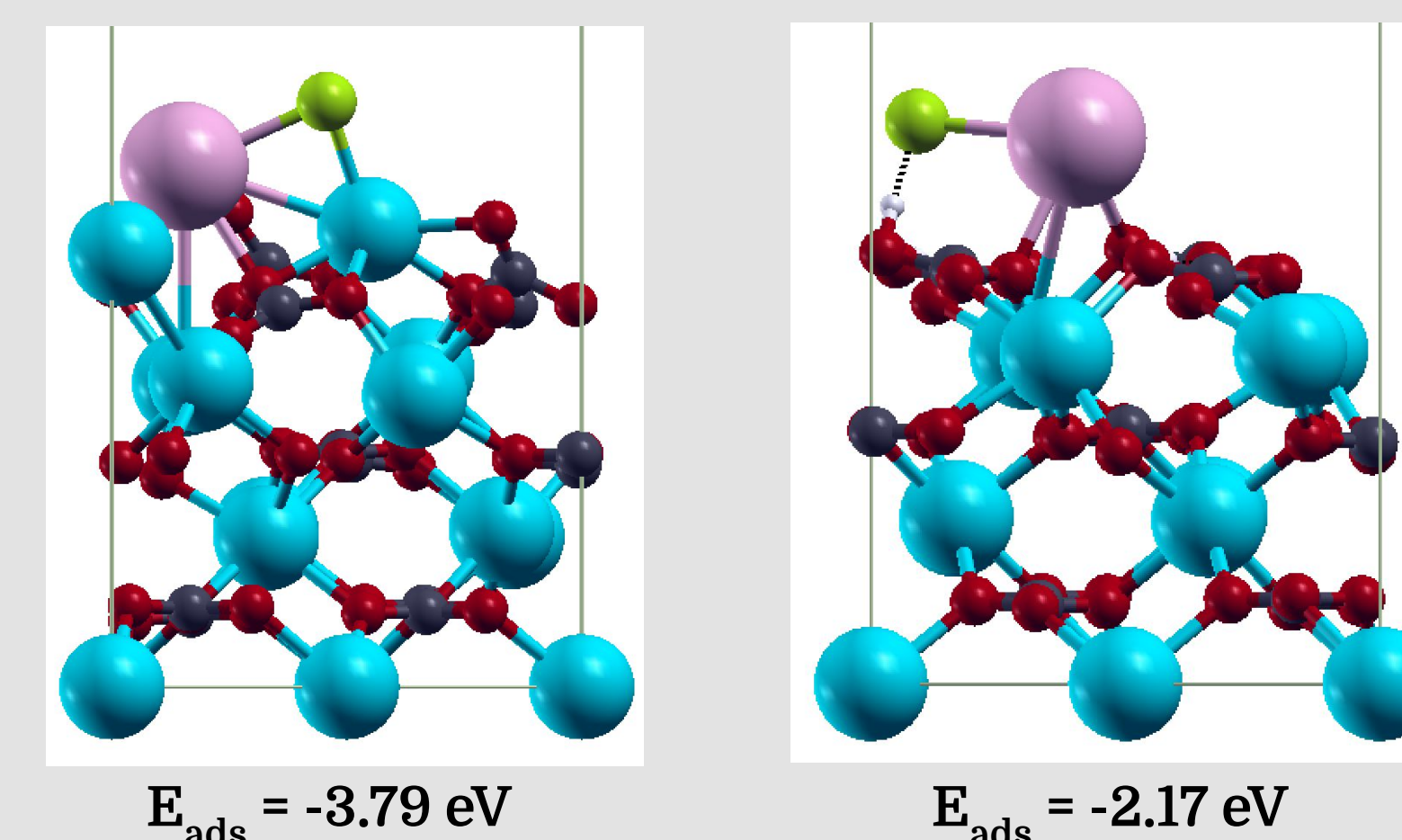
Project Goals

To identify the interactions that occur between calcite and chloride salts in an effort to aid the preservation and conservation of works of art. These calculations produce adsorption energy values that provide insight into the strength of interactions between the surface and adsorbate.

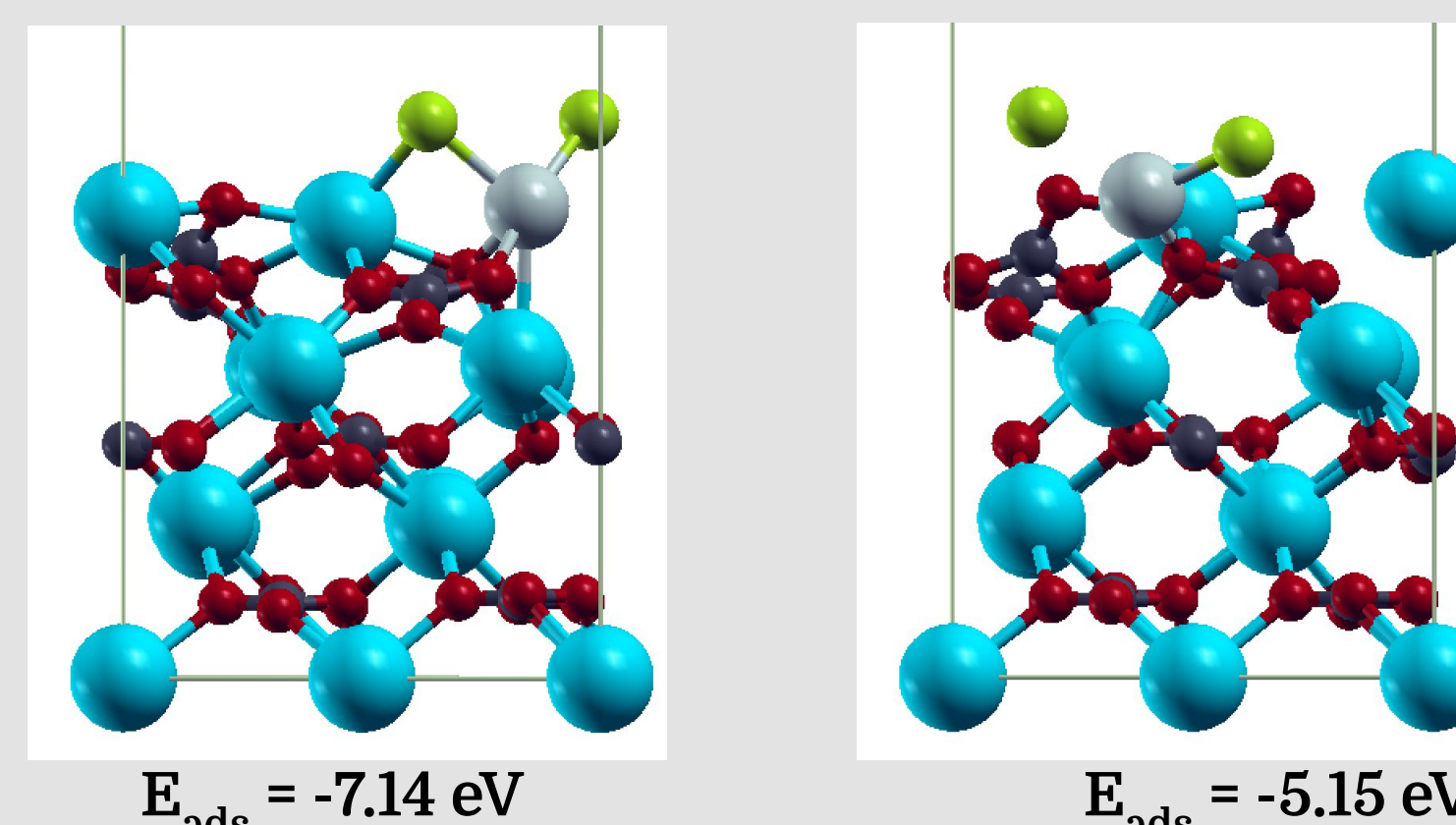
Results

| Adsorbate | Ca-Terminated Surface | | H-Terminated Surface | |
|--------------------|-----------------------|-----------|----------------------|-----------|
| | Config. 1 | Config. 2 | Config. 1 | Config. 2 |
| HCl | -2.77 | -2.67 | -0.29 | -0.18 |
| LiCl | -4.98 | -3.99 | -3.51 | -2.66 |
| NH ₄ Cl | -3.35* | -2.98 | -1.23 | -0.98 |
| NaCl | -5.05 | -3.53 | -2.55 | -0.20 |
| MgCl ₂ | -7.14 | -5.15 | -2.06 | -2.57 |
| KCl | -3.79 | -3.31 | -2.17 | -2.17 |
| CaCl ₂ | -7.67 | -7.67 | -3.48 | -3.48 |

*Cl initially at C1:(0.5, 0.5, z) and C2:(0.75, 0.5, z)

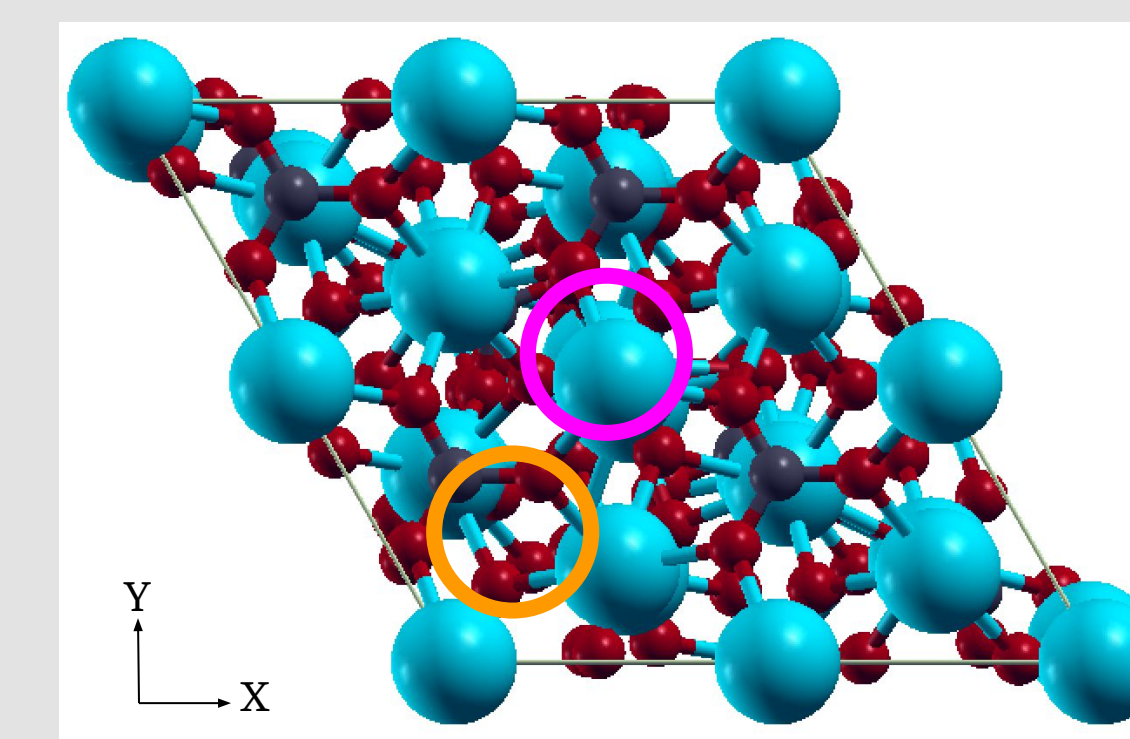


Above: KCl on a Ca (left) and H (right) terminated surface. Interaction with the Ca-terminated surface is more energetically favorable than with the H-terminated surface.



Above: MgCl₂ on a Ca terminated surface, C1 and C2. A larger positive charge on the cation leads to a stronger interaction with the surface. Moreover, introducing a greater number of ions (related to charge) onto the surface strengthens the interactions.

Right: Standardized starting configurations
Config. 1: 0.5, 0.5
Config. 2: 0.25, 0.25
The coordinates given are expressed as (x,y) in fractional form



Conclusion

- On the H-terminated surface, E_{ads} is a more positive value, suggesting that removal might be easier from this surface compared to the Ca-terminated surface (H-bonds vs. M-O bonds)
- Cations with higher positive charges exhibit stronger integration into the surface. This also suggests that the presence of more ions on the surface results in a more negative E_{ads} (e.g. MgCl₂ vs NaCl)
- Among the chloride salts tested here, stronger interactions were generally observed in configuration 1

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