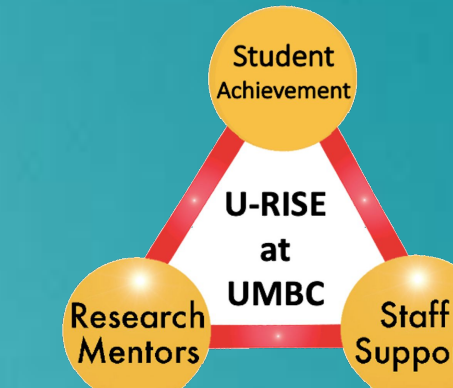


# A Non-Invasive Computational Investigation of the Photodegradation of Vermilion

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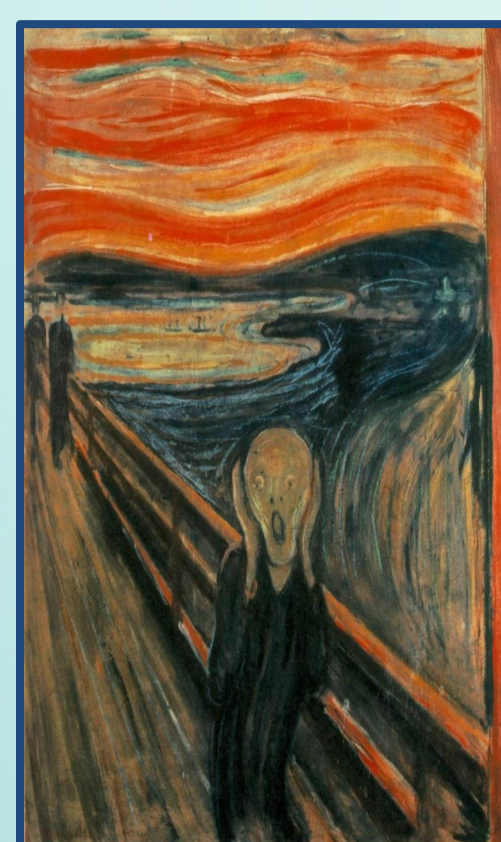
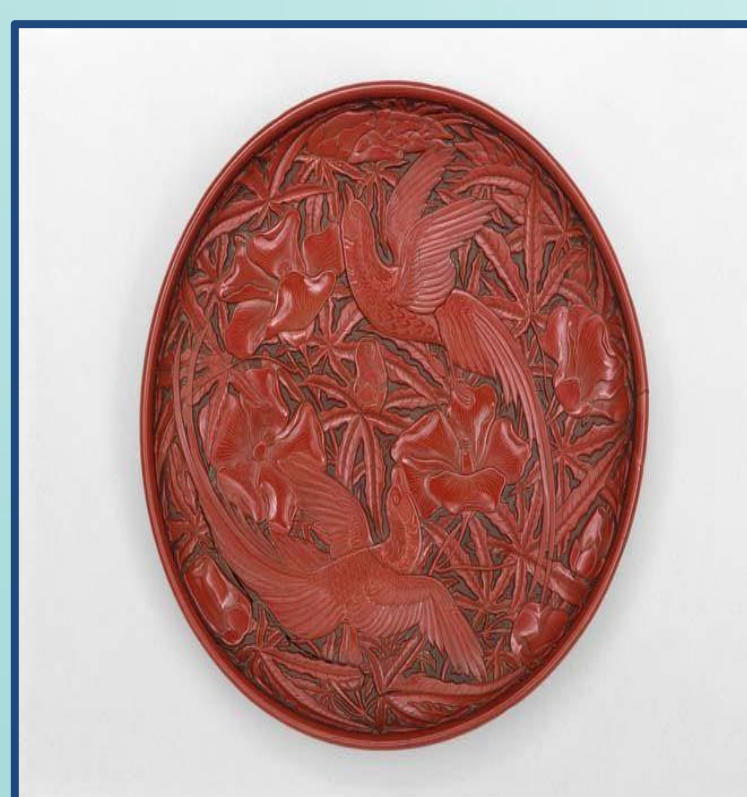
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## Introduction

Mercury sulfide (HgS), the primary component of cinnabar and vermilion, has been used in art as a pigment, a material in Chinese lacquer sculptures, and in other resin pigment inlays. The red color is known to photodegrade in the presence of chlorides, humidity, and light, causing irreparable damage. Such pieces are often recovered from caves, in proximity to chlorine containing minerals. While the method of degradation is known, the role of the chlorine in the degradation mechanism remains unknown.



**Left:** Carved Red Lacquer, The Metropolitan Museum of Art, New York, USA

**Right:** "The Scream" by Edvard Munch, National Gallery and Munch Museum, Oslo, Norway

## Methodology

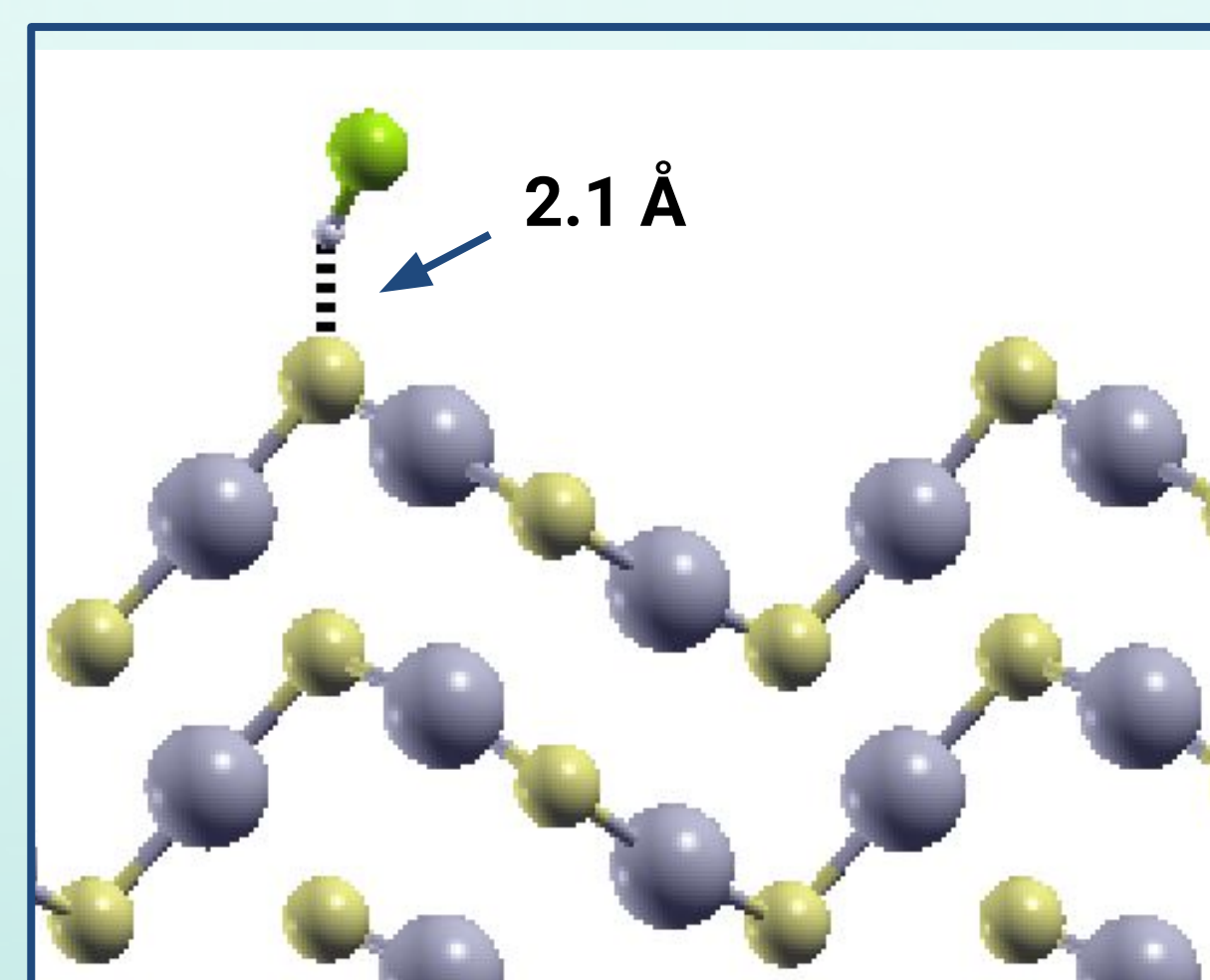
All computations in this project were performed using Quantum ESPRESSO, an open-source software package. Atoms were represented using GBRV ultra-soft pseudopotentials. A plane wave cutoff of 40 Ry and a charge density cutoff of 320 Ry were implemented for all calculations. Relevant surface interactions were identified by analyzing atomistic and electronic information such as the making and breaking of bonds, bond distances, surface transformations, changes in oxidation states, and small molecule adsorption energies.

## Project Goals

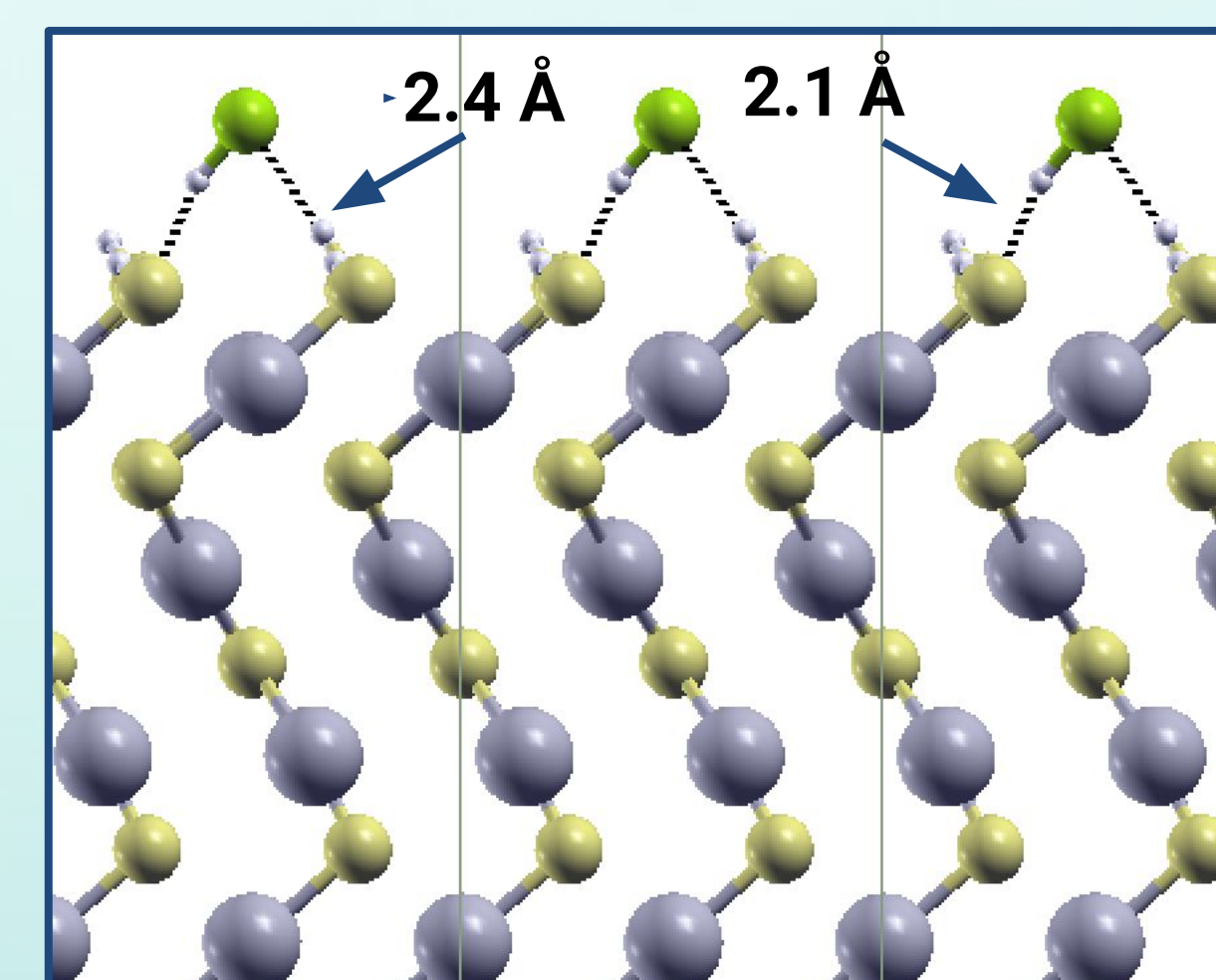
Density functional theory (DFT) provides an atomistic, non-invasive method of determining which chloride-containing compounds cause vermilion (HgS) to photodegrade. The objective of this research is to elucidate the environmental compounds implicated in the fading of HgS surfaces. DFT can be used as a probe to introduce a wide range of adsorbates, including chlorides and water products, to the surface in order to investigate the conditions that lead to surface instability.

## Results

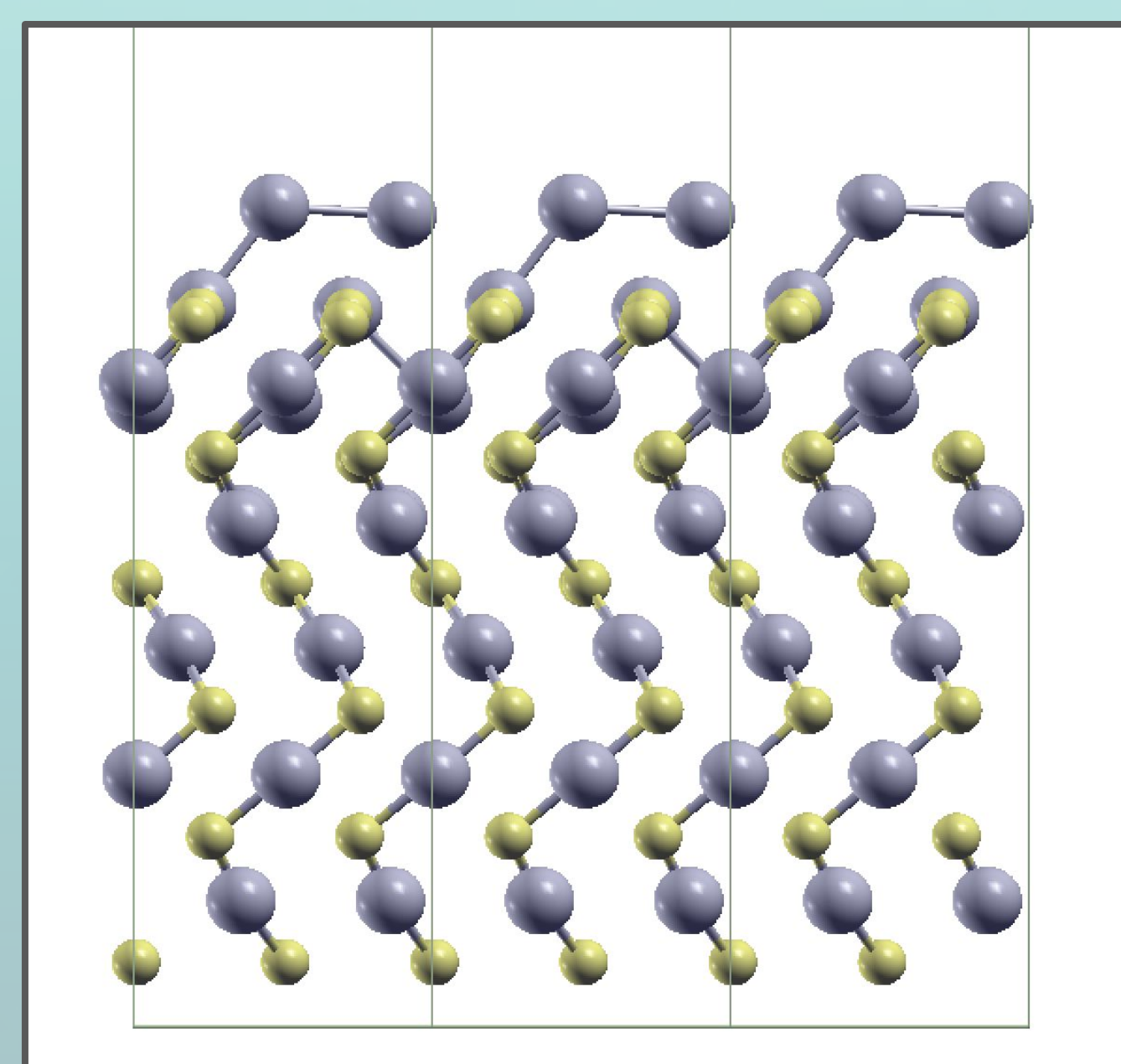
Computational results suggest that chlorine-containing compounds with a lower oxidation number (such as in HCl) are more likely to interact with the different surfaces of HgS (i.e. have lower adsorption energies)



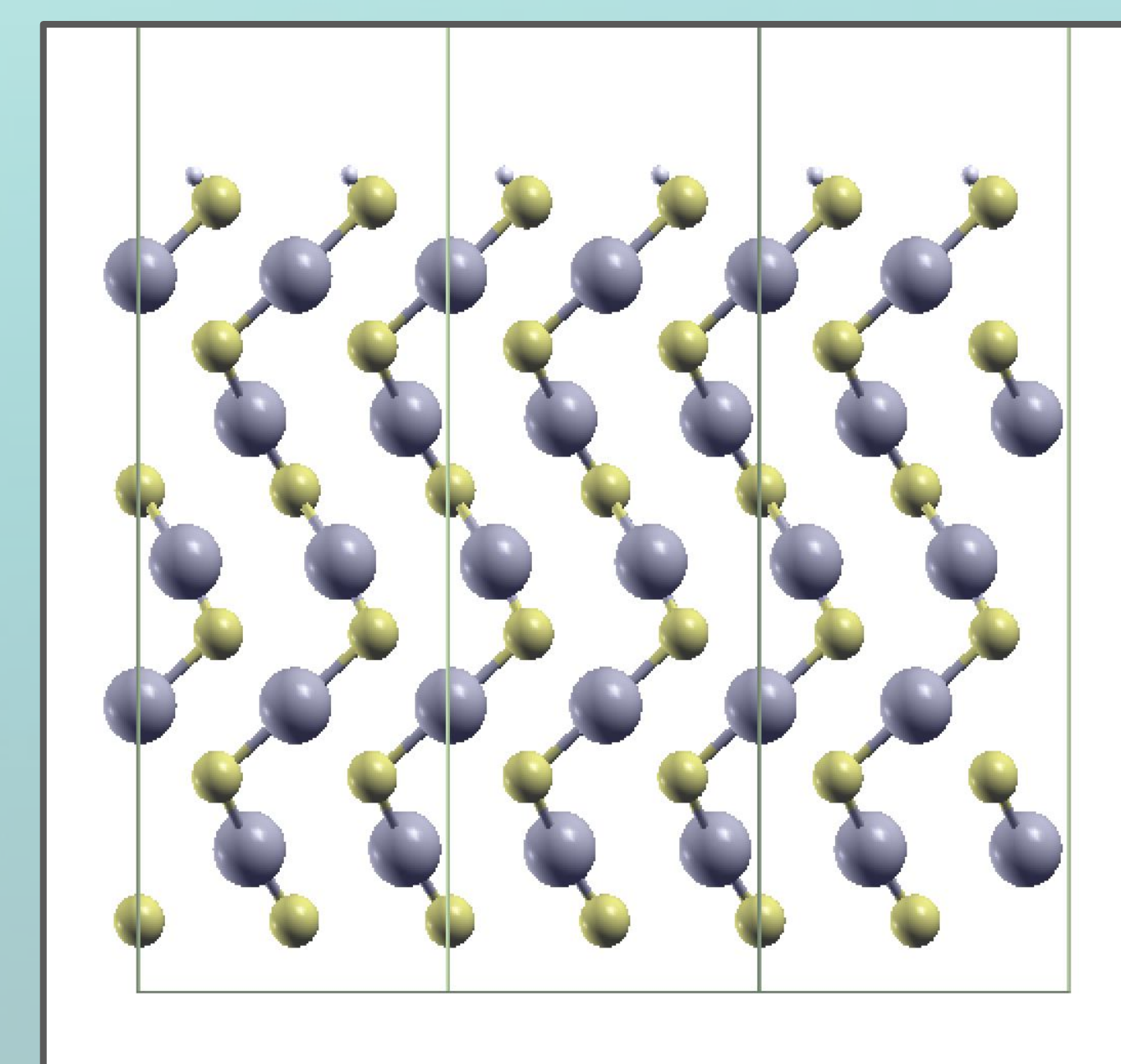
**Left:** Relaxed Corrugated (100) HgS surface interacting with a HCl adsorbate. One hydrogen bond per HCl molecule is observed.



**Right:** Relaxed Proton-terminated (001) surface interacting with a HCl adsorbate. Two hydrogen bonds per HCl molecule are observed.



**Left:** Hg-terminated surface



**Right:** Proton-terminated surface

The Hg-terminated metal surface (001) is likely unstable. As a result, a charge neutral proton-terminated surface was used to probe the surface adsorption reactivity of the (001) cleavage plane.

## Conclusions

- DFT was effectively employed to screen a large variety of atmospheric pollutants, spatially relevant chloride-containing minerals, and water products.
- Certain surface terminations and cleavage planes of HgS provide a range of stability and surface reactivity.
- Mercury-terminated (001) HgS is likely too unstable. As protonation of the surface increases, stability is achieved. However, the corrugated surface of HgS is the most stable.
- Adsorbates containing chlorine with lower oxidation states were more reactive with multiple surface terminations, forming H bonds with the surface.

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