Vacancy segregation on the FeS2(001) surface: DFT calculations

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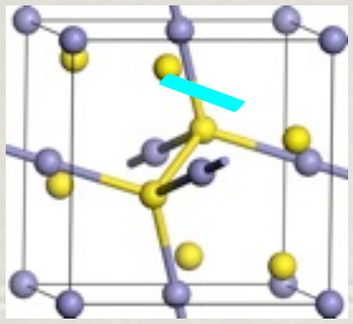
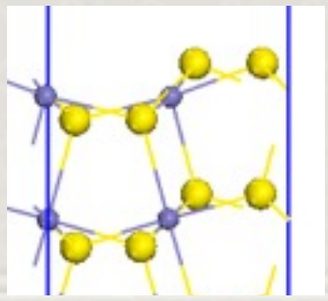
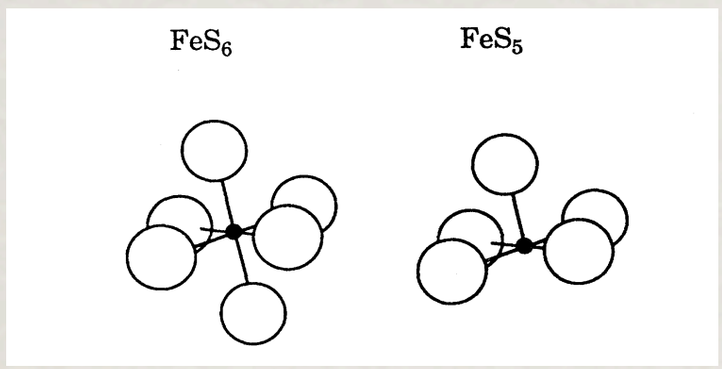
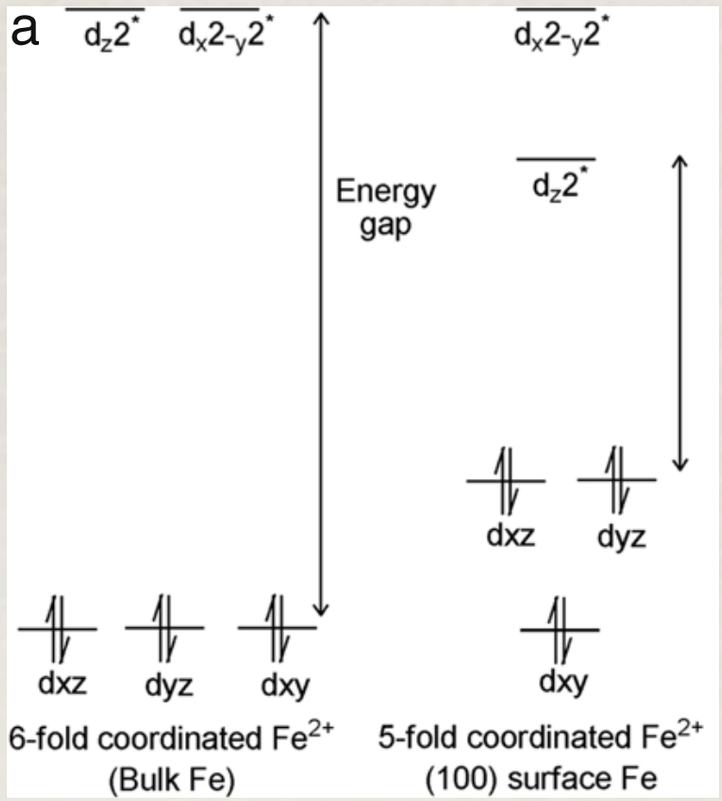
Sulfur vacancies in Pyrite



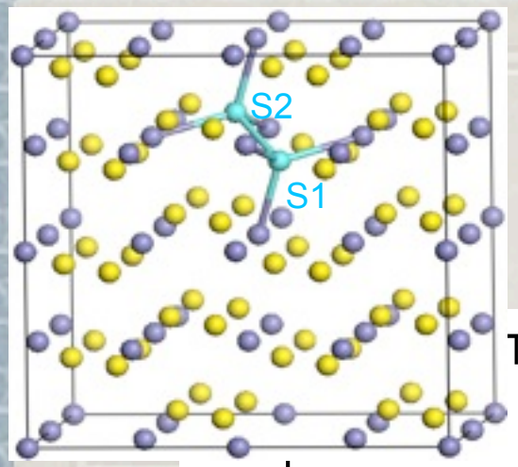


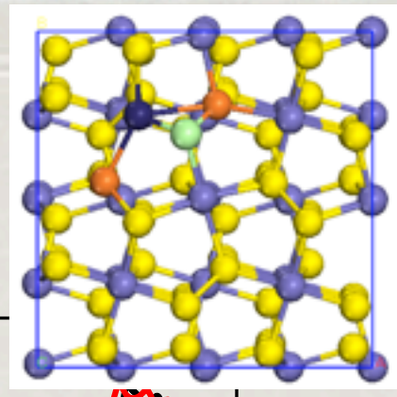


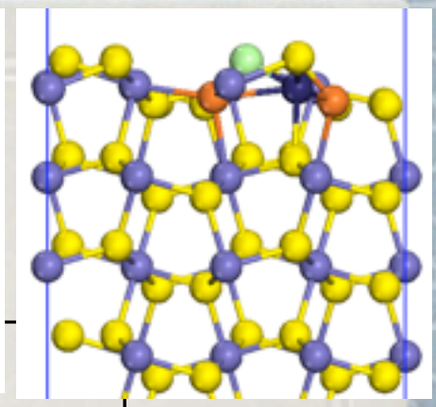


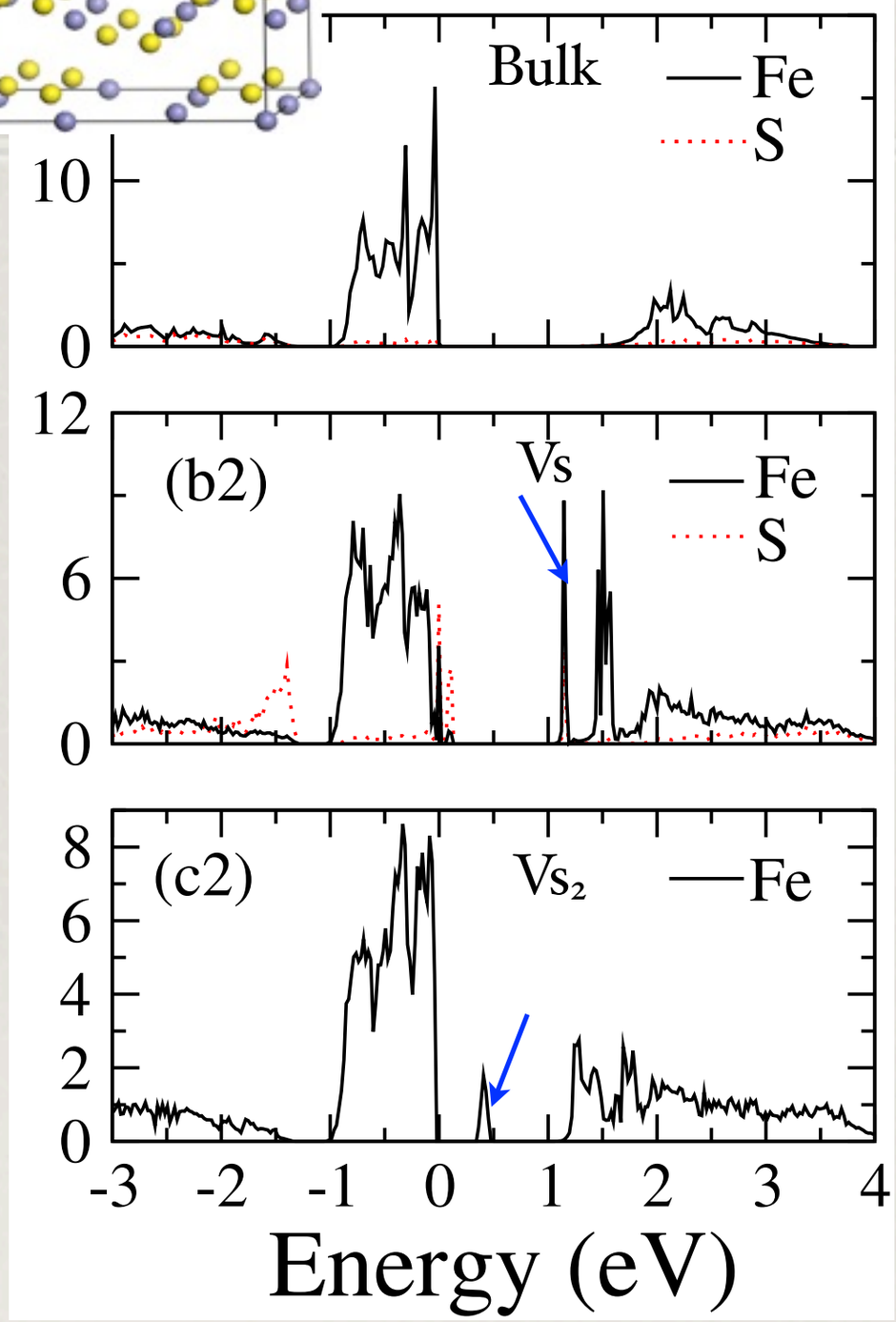
- The broken Fe-S and/or S-S bonds create vacancies and defects on Pyrite surfaces.
  - change electronic states
  - narrow the surface band gap
  - pin the Fermi level
  - reduce the photovoltage of pyrite samples

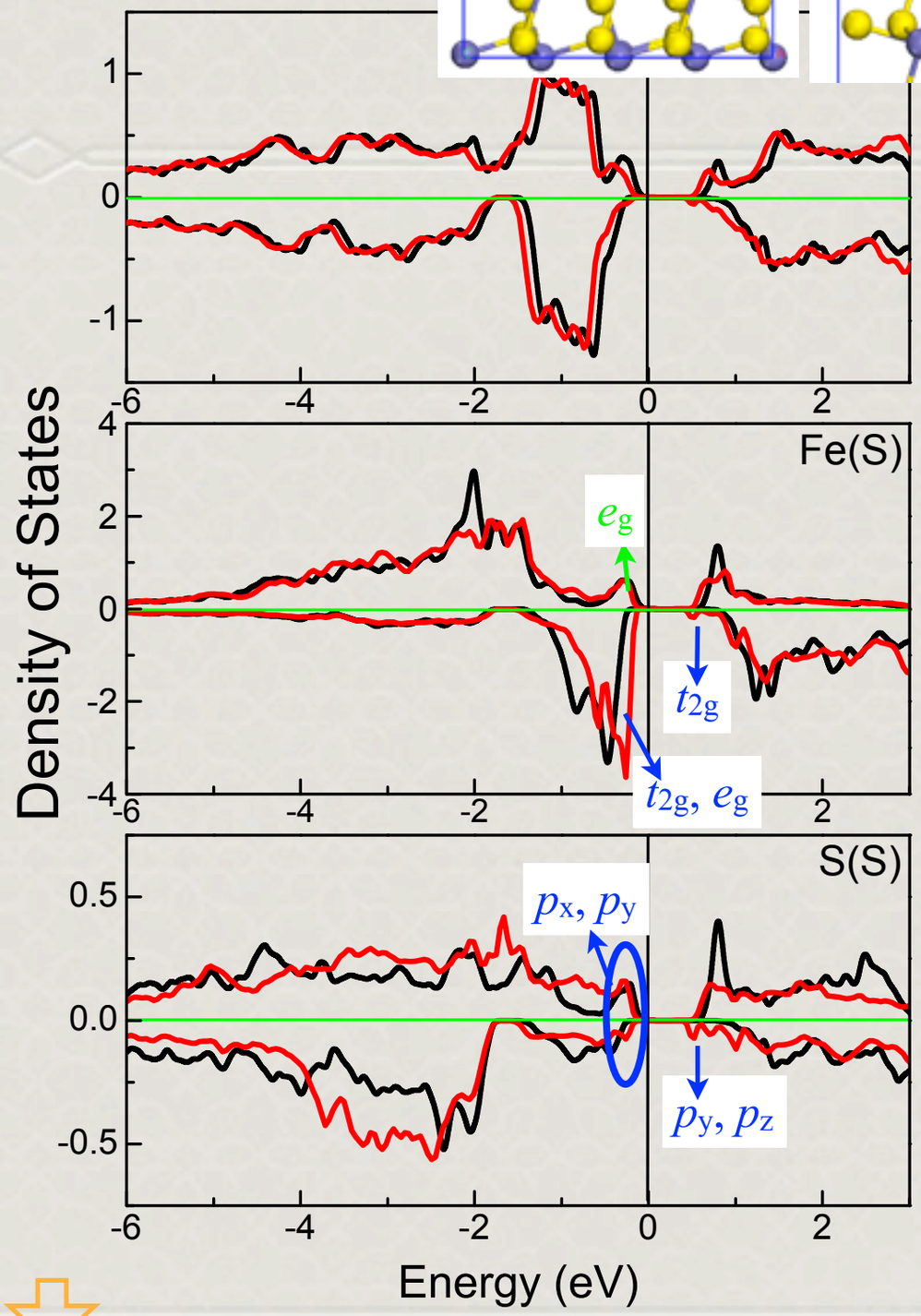
Effects of vacancy on electronic properties





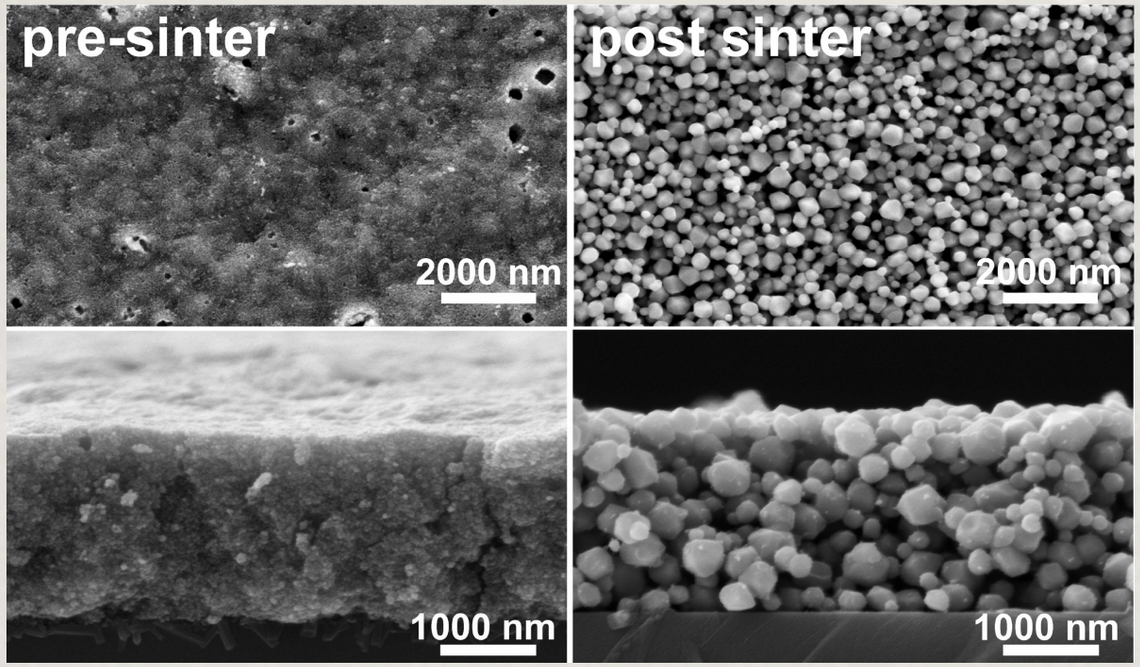




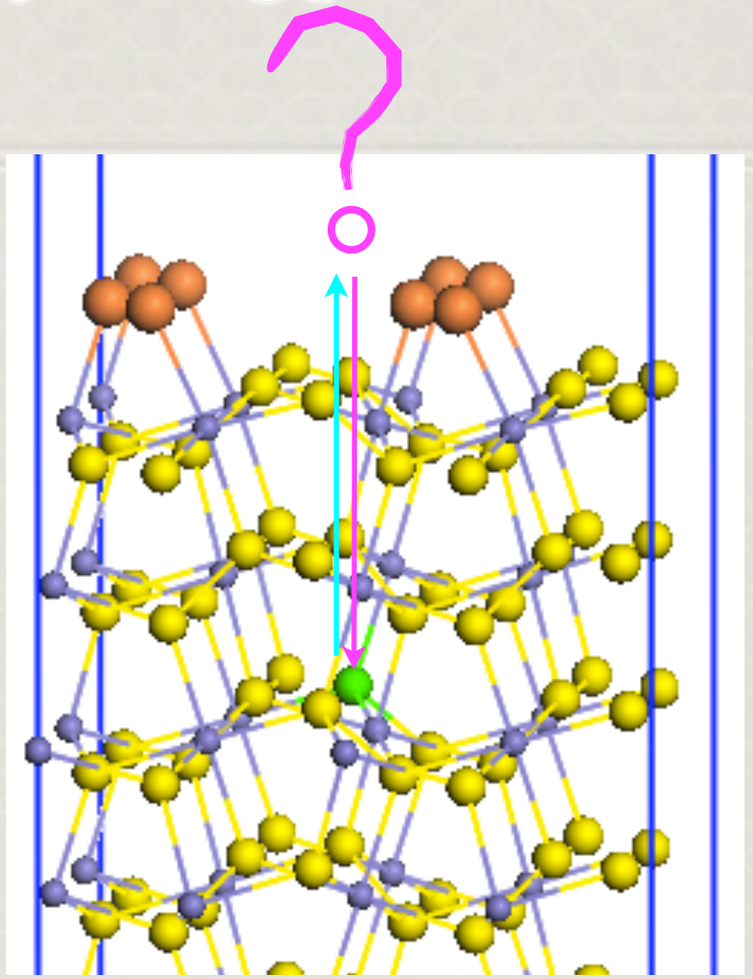


reduce the sulfur deficiency

Dynamic features of vacancy filling process



"The purpose of sintering the NC films (in the Sulfur vapor) was to increase the average grain size (and thus the carrier diffusion length), reduce possible sulfur deficiency, remove carbon, and densify the films. "

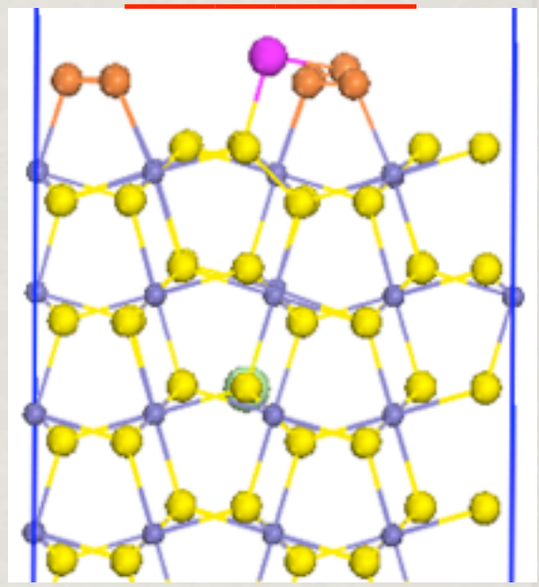


- How can the vacancy be filled?
- What's the energy barrier?
- How to control?
- other substitutions?
- .....

DFT calculation details

- DFT calculations with the plane-wave-based Vienna Ab initio Simulation Package (VASP)
- Potential: PAW-GGA(PBE)
- Energy cutoff: 300 eV
- Kpoints: 2×2×1 MK
- Atomic model: a seven-layer slab with a 2x2 unit cell in the lateral plane and a vacuum of ~15 Å thick.

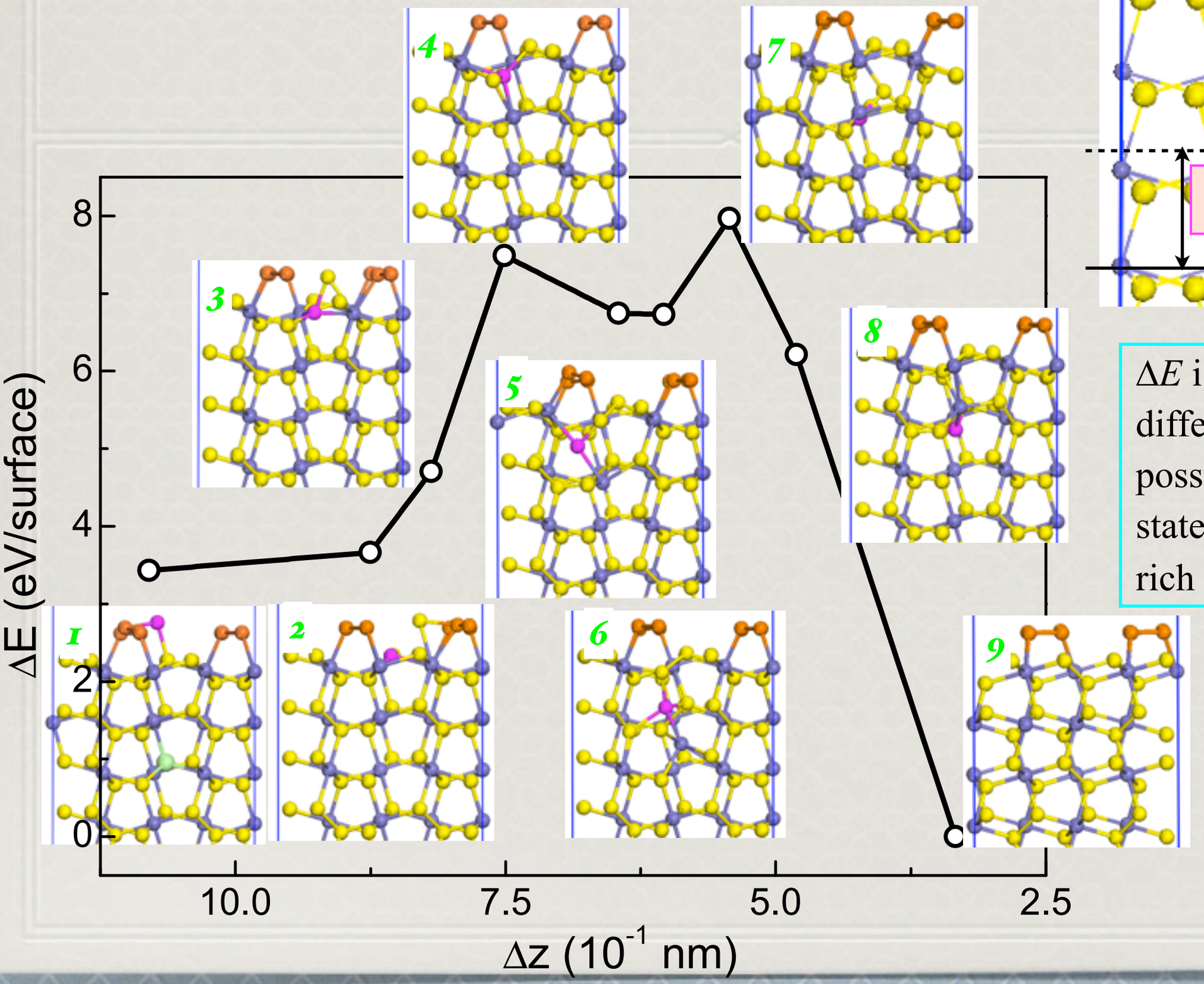
$Fe_{56}S_{128}$

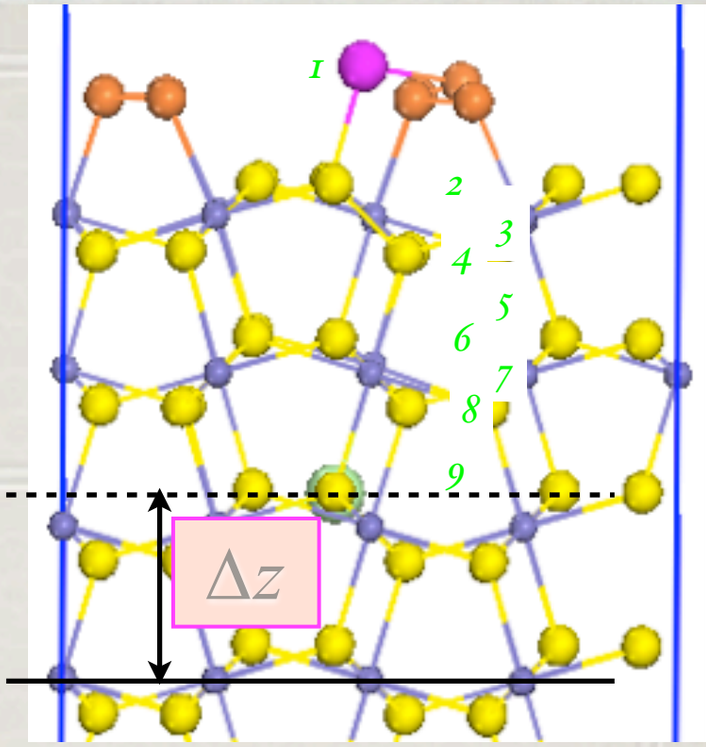


$\Delta E_{tot} = E_{tot}(def.) - E_{tot}(clean)$

$= +3.4$ eV/surface

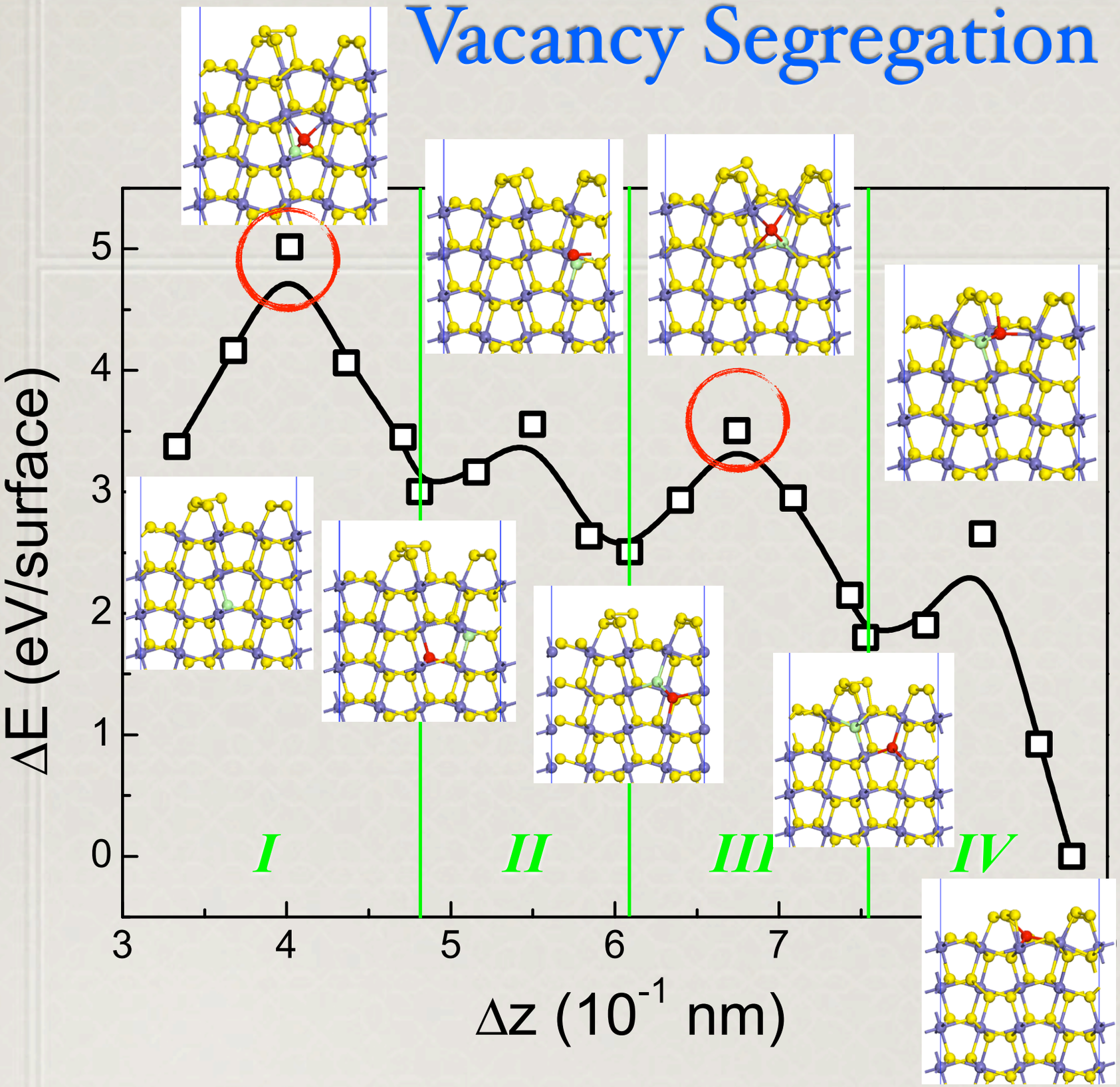
Sulfur Segregation

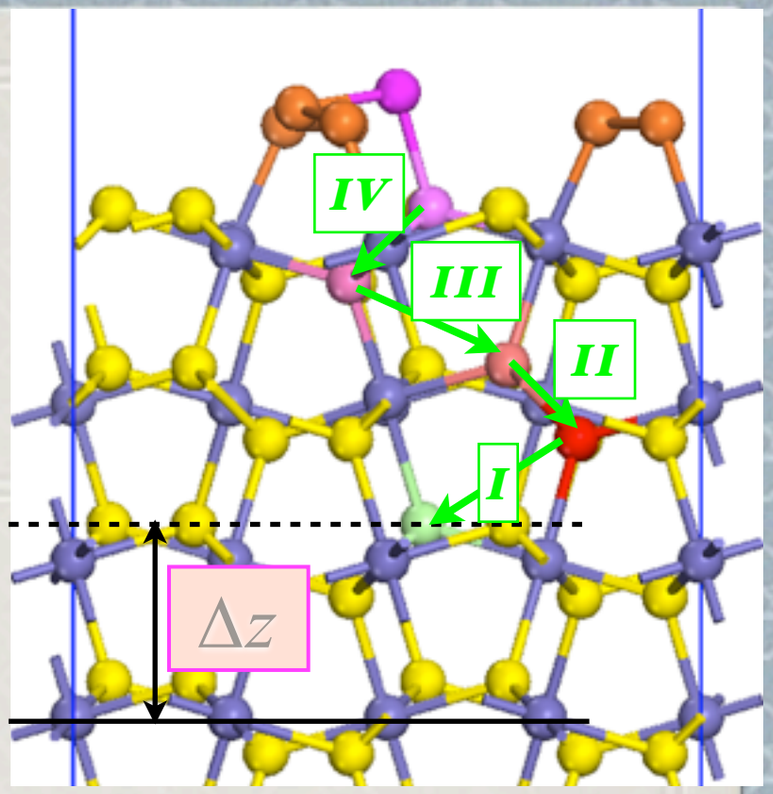


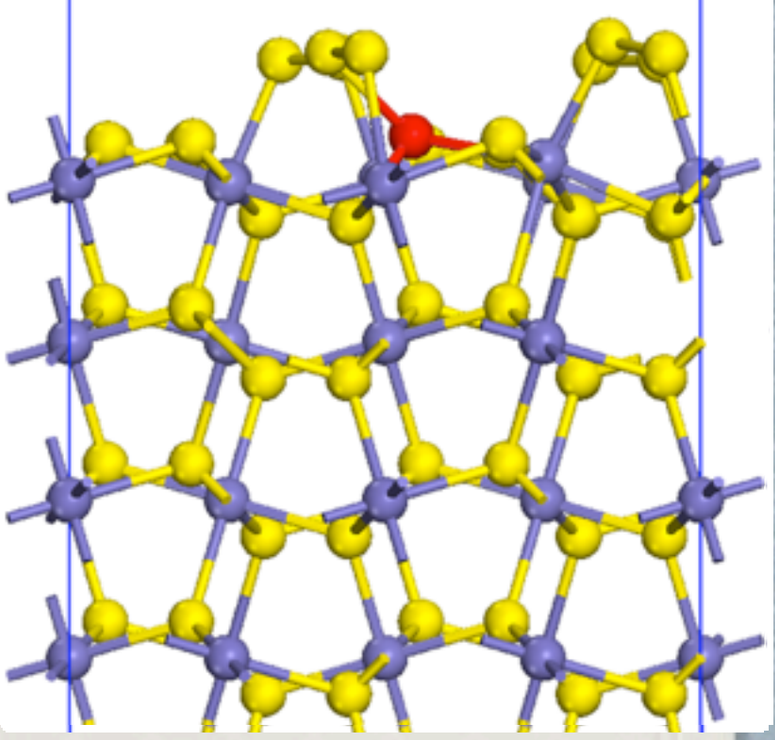


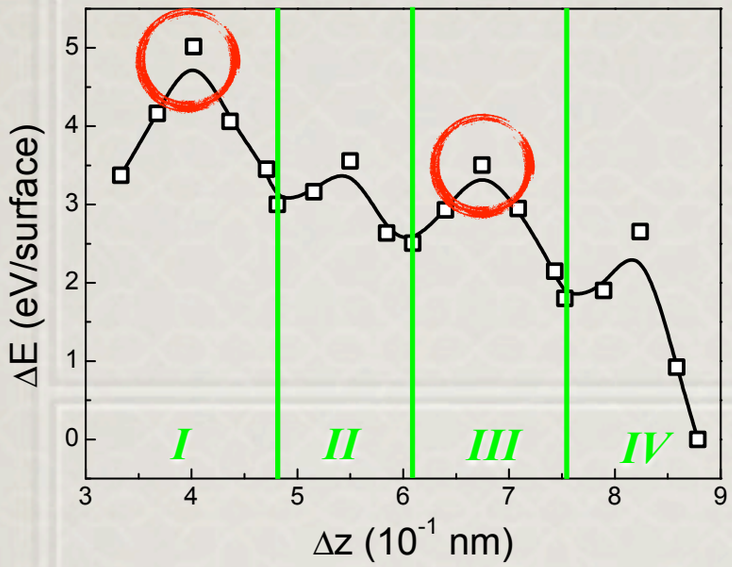
ΔE is the total energy difference between the possible intermediate states and the clean S-rich $FeS_2(001)$ surface.

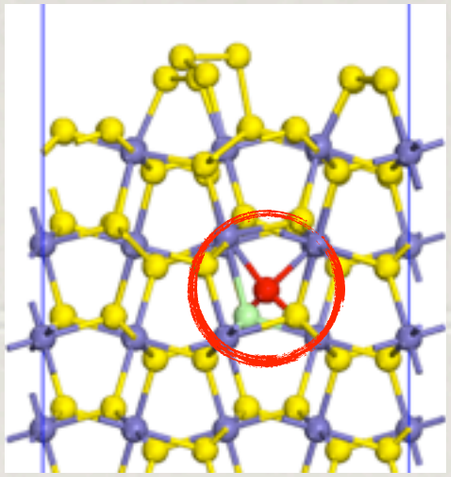
Vacancy Segregation

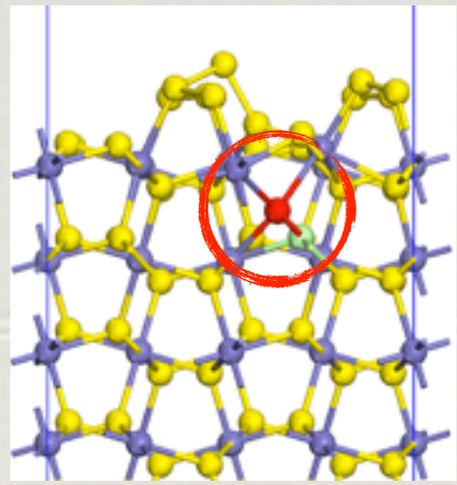












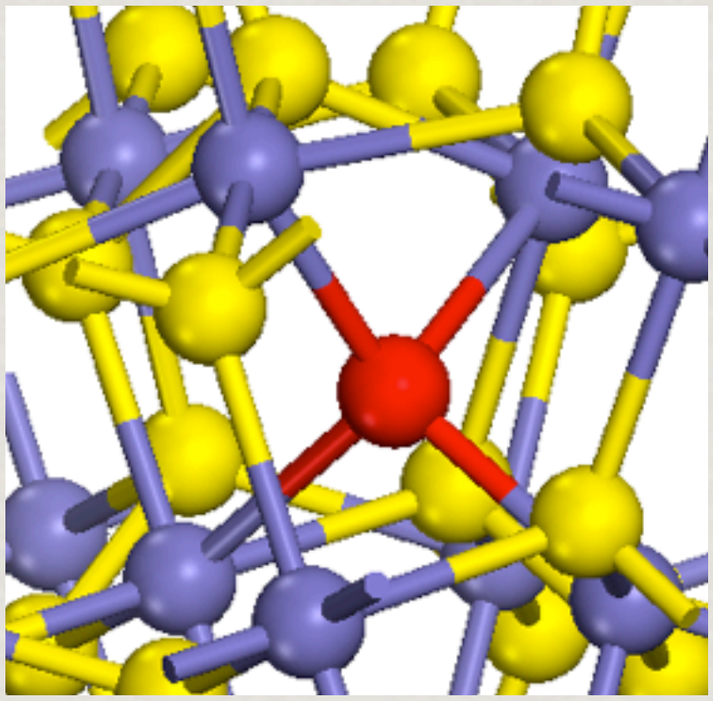
$d_{S\text{-}Fe}$= 2.25~2.62 Å

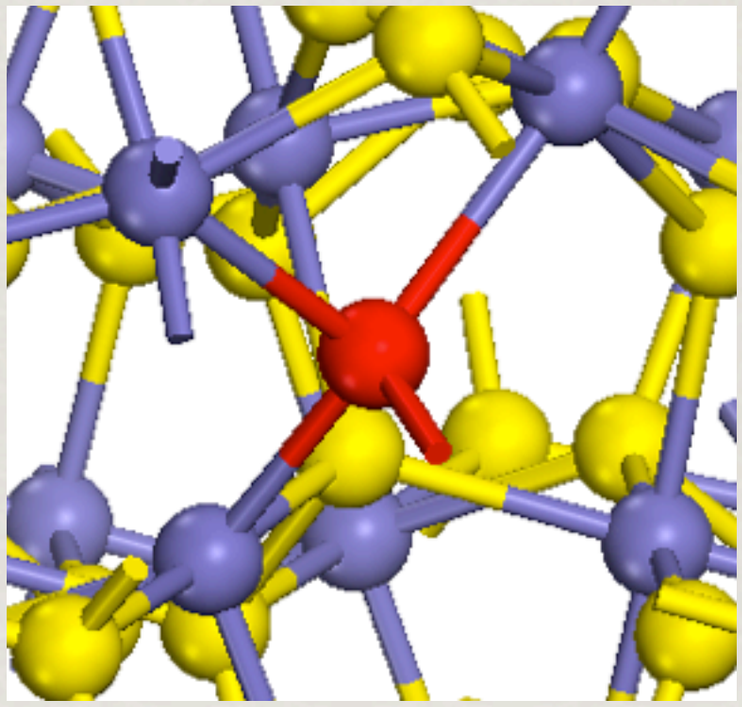
$d_{S\text{-}S}$ = 2.60~3.17 Å

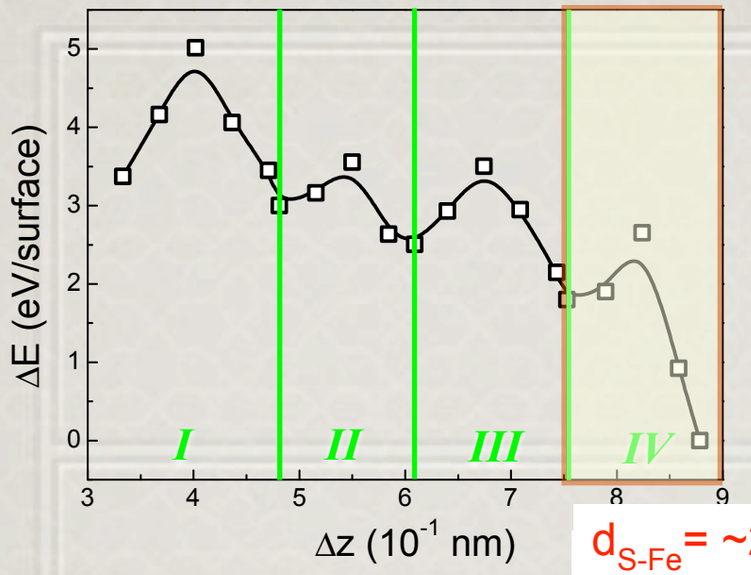
in bulk

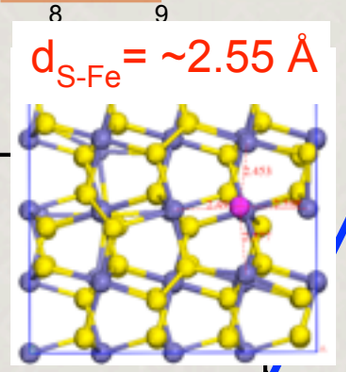
$d_{S\text{-}Fe}$= 2.27 Å

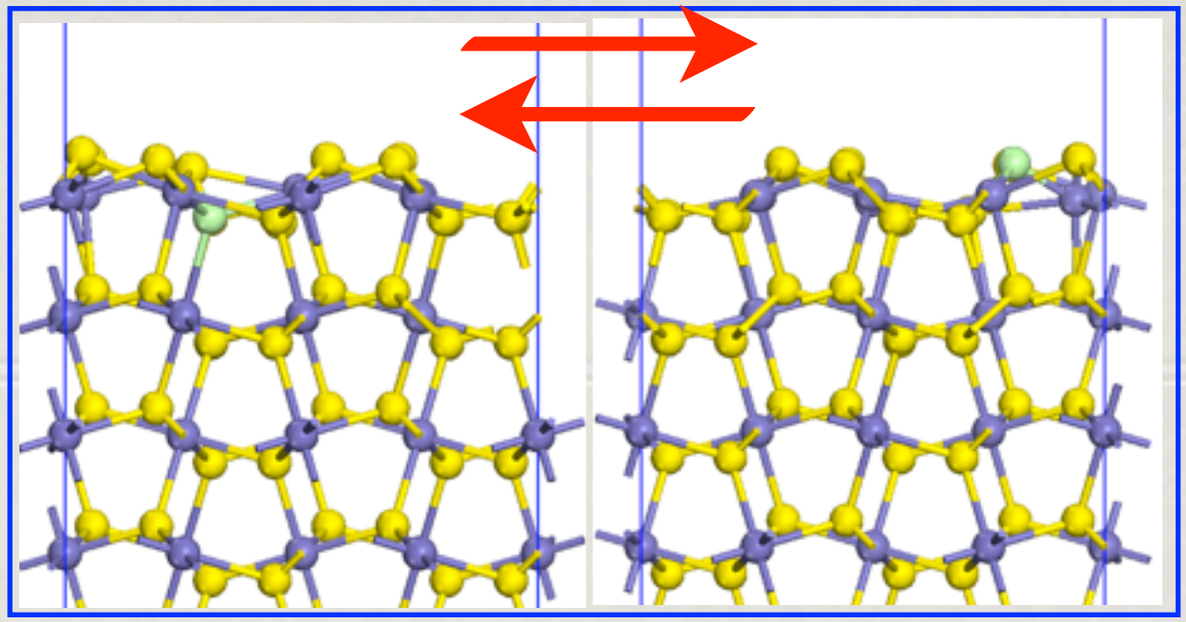
$d_{S\text{-}S}$ = 2.16 Å



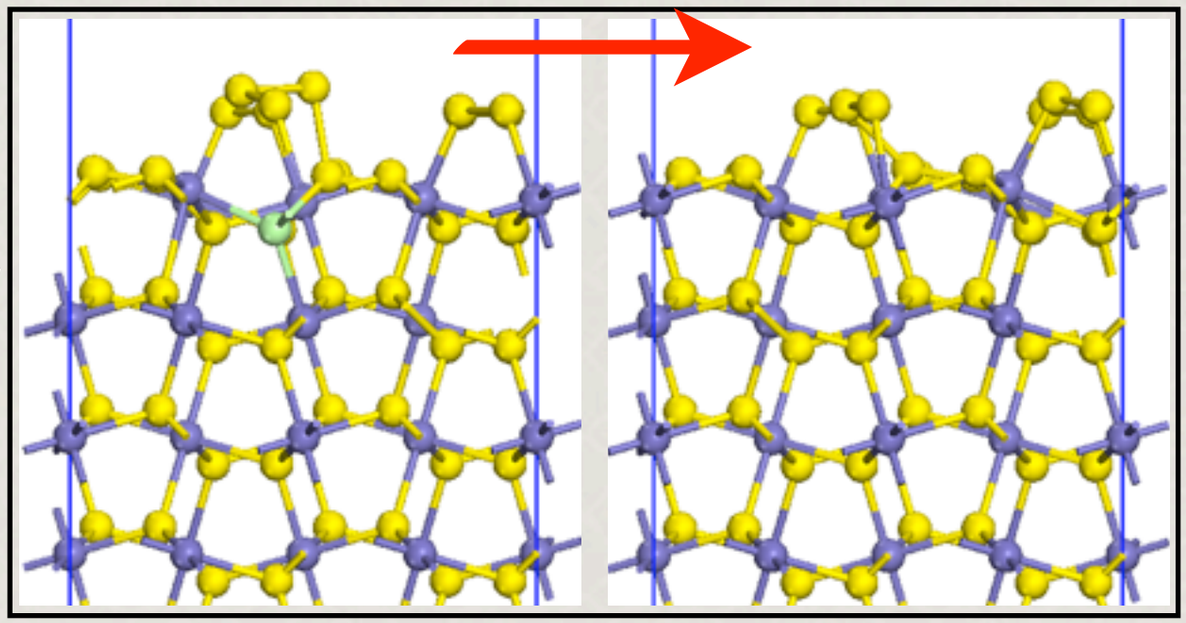



ΔE (eV/surface)
Δz (10^{-1} nm)
I
II
III
IV


d_{S-Fe}= ~2.55 Å



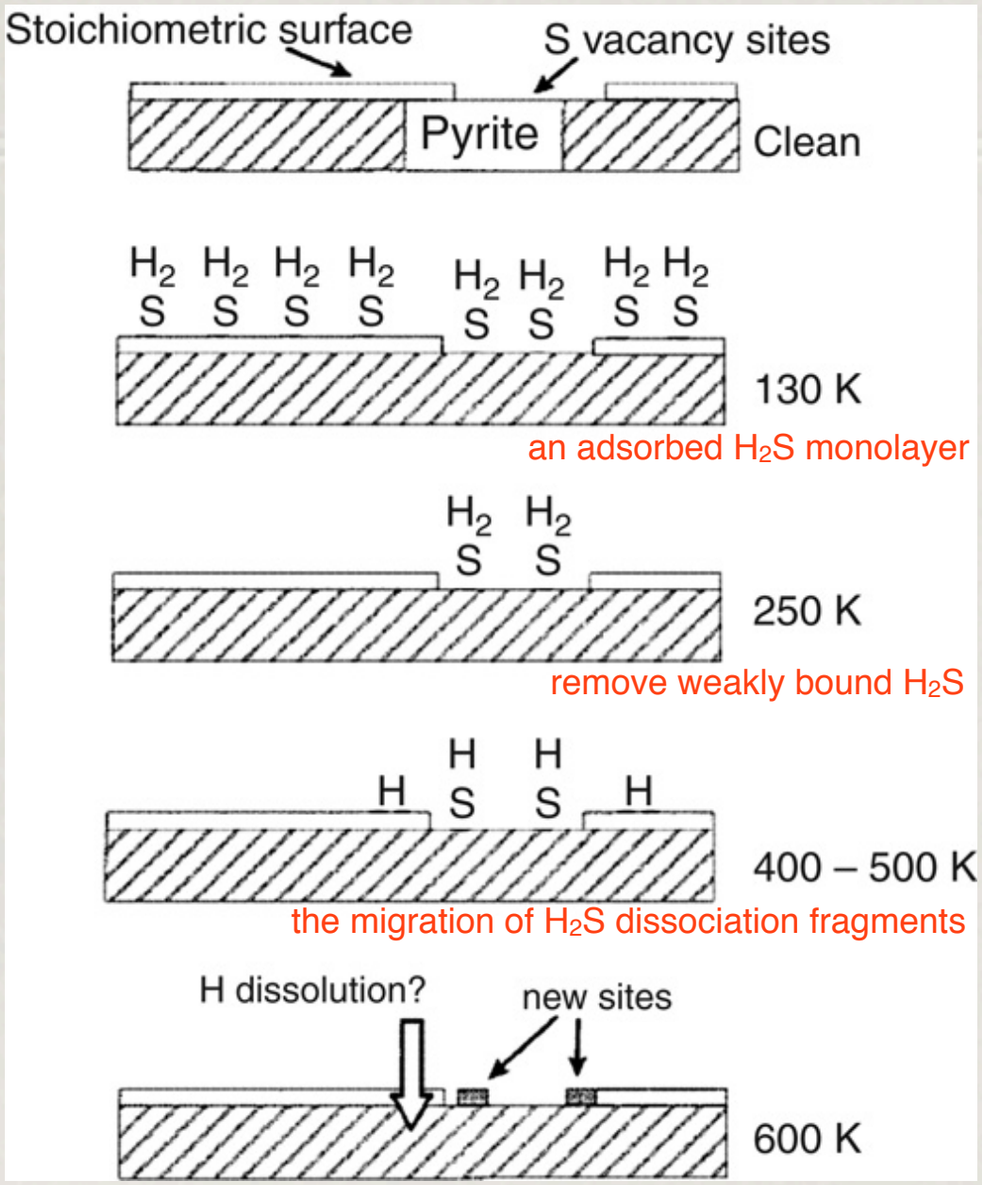
ΔE (eV/surface)
Δz (10^{-1} nm)



A proposed model for the thermal chemistry of H_2S on $FeS_2(100)$.

Guevremont et al. American Mineralogist 83 (1998) 1246

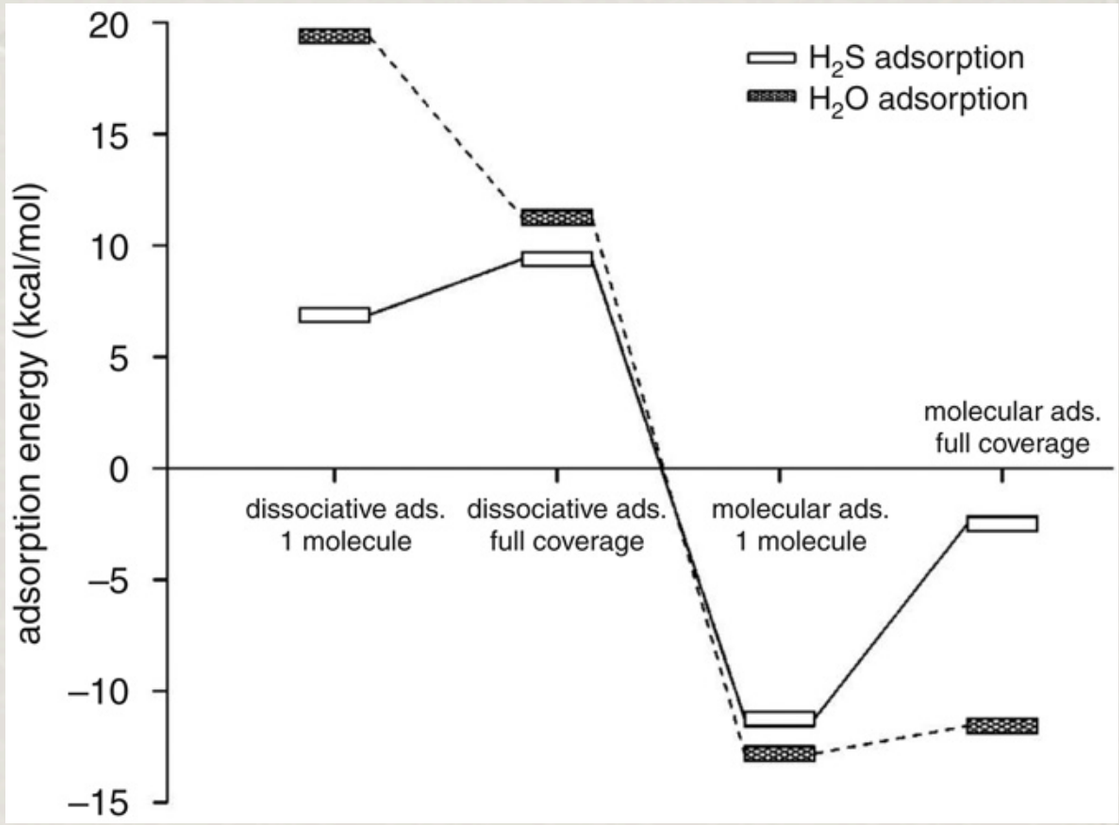
Temperature programmed desorption (TPD)



"Whereas the diffusion of H is well supported by our data, it cannot be determined unambiguously whether S-containing species also migrate."

denser, more uniform pyrite films with H2S annealing at low temperatures.

H_2S



Comparison of the adsorption energies in different adsorption states for H_2S and H_2O.

A. Stirling, M. Bernasconi, M. Parrinello, *J. Chem. Phys.* 119 (2003) 4934.

Whether H_2S shows a tendency to dissociate on a defective pyrite surface was not investigated.

Conclusions

- *DFT calculations were performed to study the filling process of the single vacancy at different Pyrite(001) surfaces.*
- *Efforts are being made to understand the effect of surface condition on the vacancy filling, so as to find out the factors that control the sulfur deficiency segregation.*