

## Motivation

Semiconductors could offer potential benefits in using semiconductor-specific electronic properties for bio-sensing.

Self-assembled monolayers (SAMs) of thiols can passivate GaAs surface and at the same time provide a link for the attachment of specific biomolecules.

Very little information from relatively well studied thiols on noble metals can be applied to thiols on GaAs.

Theoretical modeling can help to understand the atomic level processes of thiols adsorption and self-assembly, verify robustness of the interface and improve the thiol deposition technique addressing specific applications.

## Calculation details

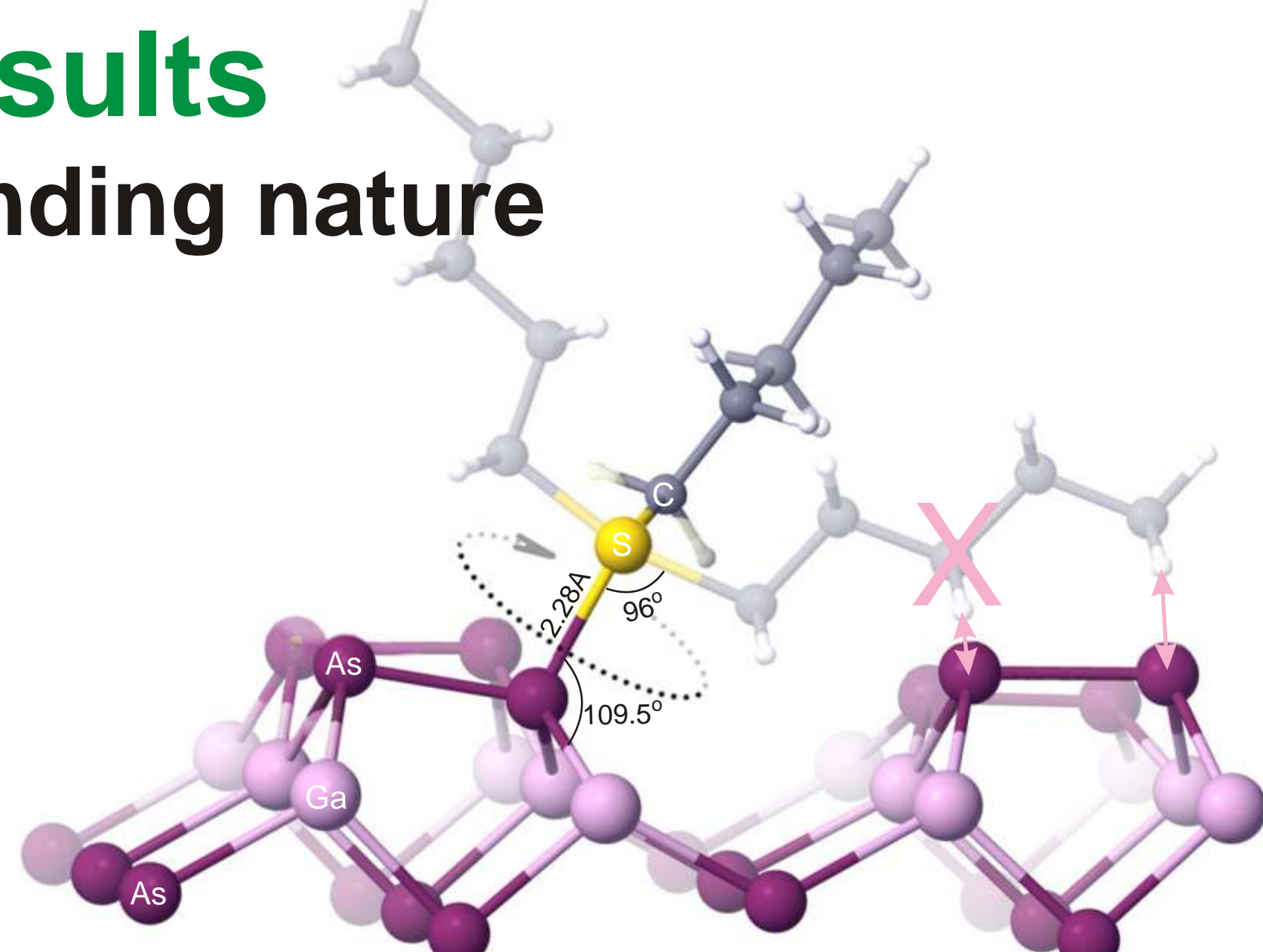


TM2 pseudopotentials, PBE+NLCC  
No 3d states included  
DZP bases for Ga and As and TZP for As in top layer, S, C and H.  
11 Å *k*-grid cutoff  
350 Ry real space grid energy cutoff  
Hydrogen terminated slabs of 7 to 10 atomic layers with surface unit cells from (2x1) to (4x4)

	LDA	PBE	BLYP	RPBE	Expt
$d_{S-H}$ , Å	1.361	1.359	1.360	1.359	1.35
$E_{S-H}$ , eV	4.27	3.781	3.749	3.696	3.73
$d_{H-H}$ , Å	0.768	0.752	0.748	0.749	0.742
$E_{H-H}$ , eV	4.935	4.567	4.769	4.609	4.75 (no ZPE)
$a_{GaAs}$ , Å	5.6	5.75	5.9	5.8	5.65
$d_{thiol-thiol}$ , Å	4.4	-	-	-	4.57
$E_{thiol-thiol}$ , eV	0.3	-0.13	-0.3	-0.43	0.25

## Results

### Bonding nature



Factors determining the optimal geometry of thiolate adsorption on GaAs(001) surface.

Thiolate adsorbs on GaAs(001) surface by saturating one of the dangling bonds.

Thiolate tilt angle and tilt direction are dictated by the direction of the dangling bond and sulfur unhybridized 3p orbital, and steric repulsion of the CH<sub>2</sub> units from the surface.

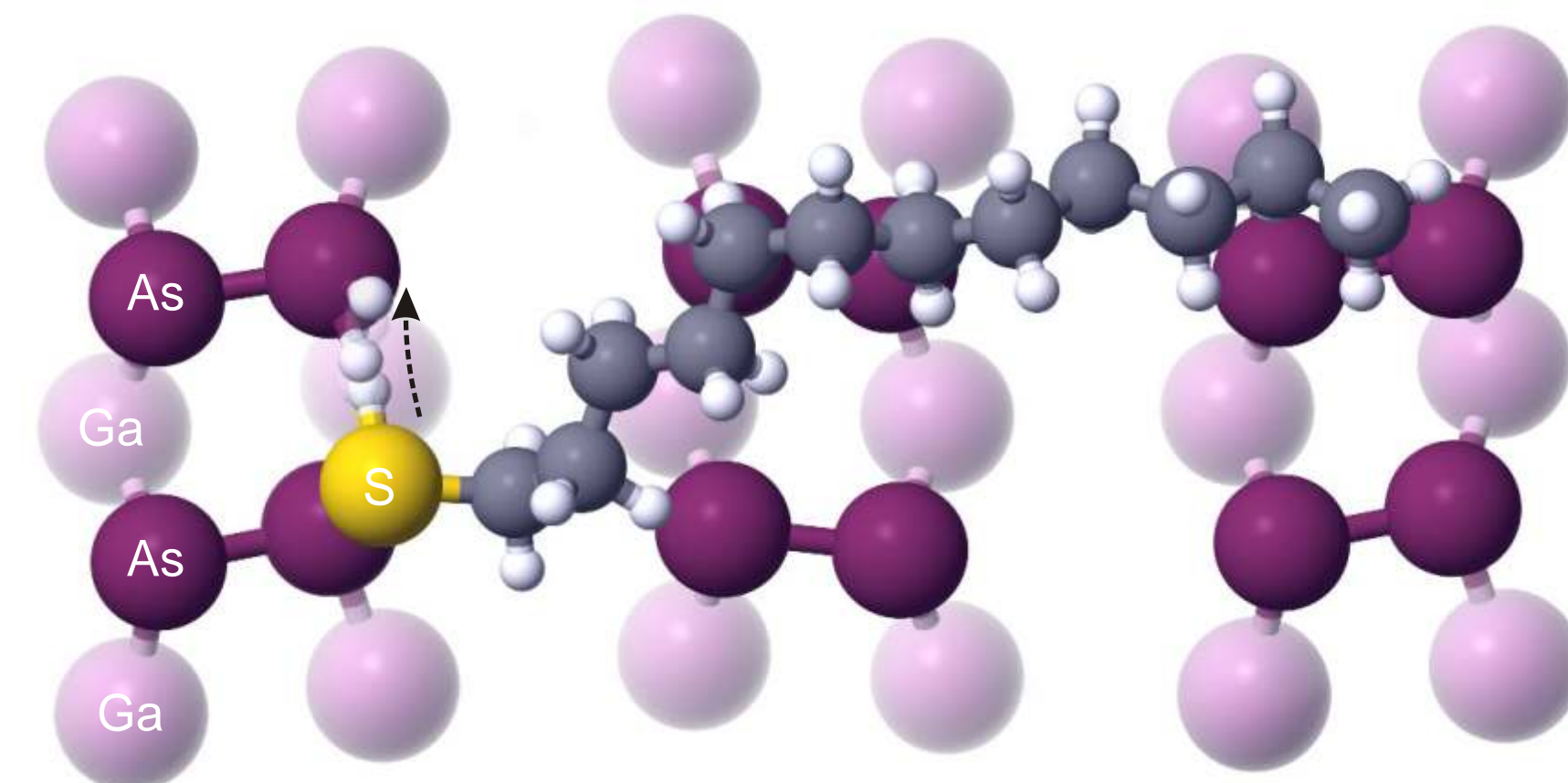
Relatively short bond and small charge transfer between thiolate and surface indicate a strong covalent bond with binding energy of 2.1 eV.

O. Voznyy, J. J. Dubowski, *J. Phys. Chem. B* **110**, Iss.47 (2006).

## Physisorbed precursor

S-H bond (3.78 eV) is stronger than S-As bond (~2eV) making hydrogen abstraction not possible.

If thiol is not physisorbed, H rotates around S-C bond due to steric repulsion from surface, and never touches the surface at the same moment as S.

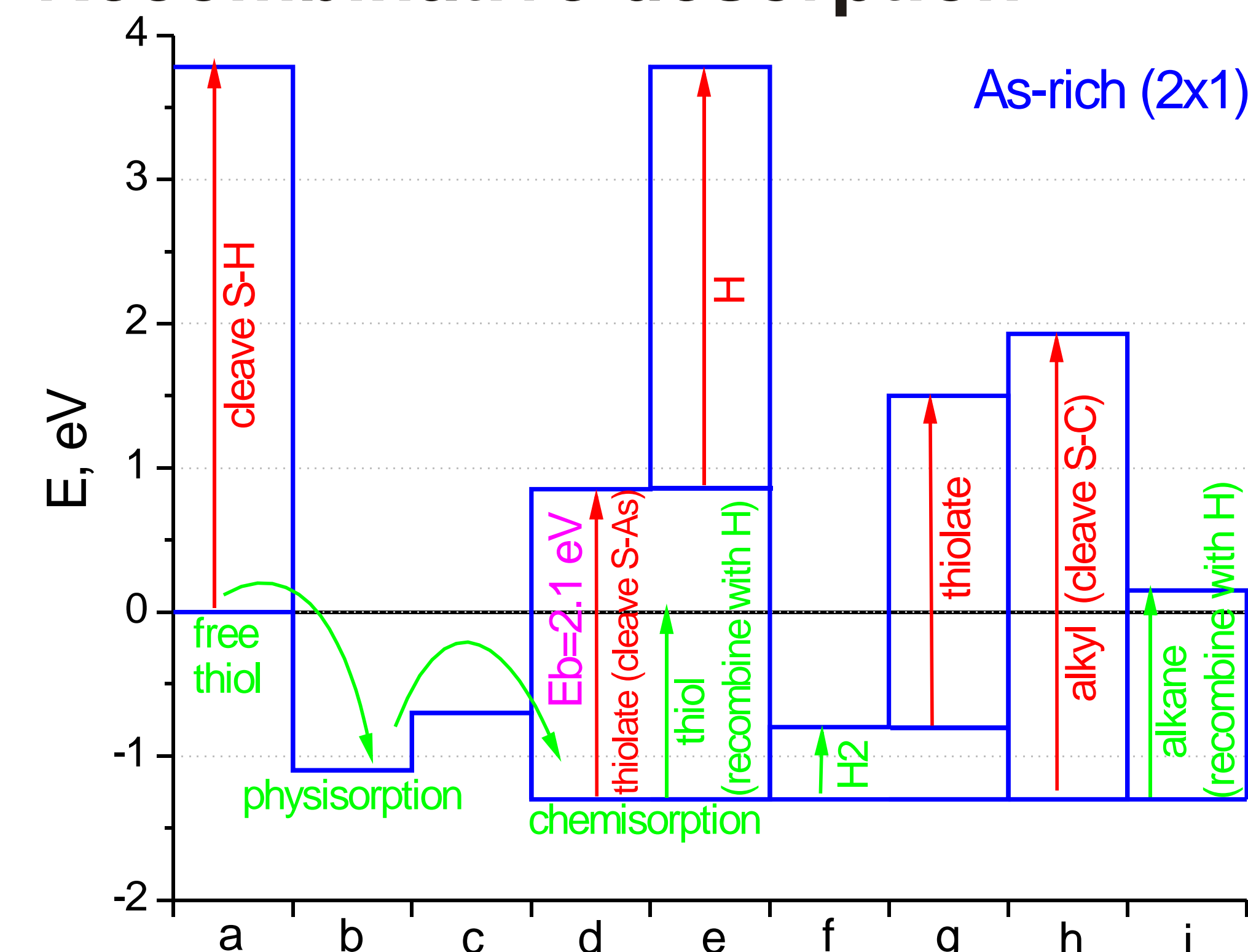


Transition from physisorption to chemisorption state. Lattice distortion and thiol bending due to thermal vibrations is visible.

In physisorbed state H stays near the surface. Physisorption energy is 1.1 eV for 11-chains thiol. Due to thermal vibrations, H can appear closer to nearby As than to S, leading to chemisorption of both thiolate and hydrogen.

This process requires ~0.5 eV, which is much less than the dissociation energy of the S-H bond.

## Recombinative desorption



Energy gain due to chemisorption of thiolate and H is 1.25 eV (d) comparable to that of physisorption (b).

Energy required to cleave S-As bond and to desorb thiolate (d) is 2.1 eV.

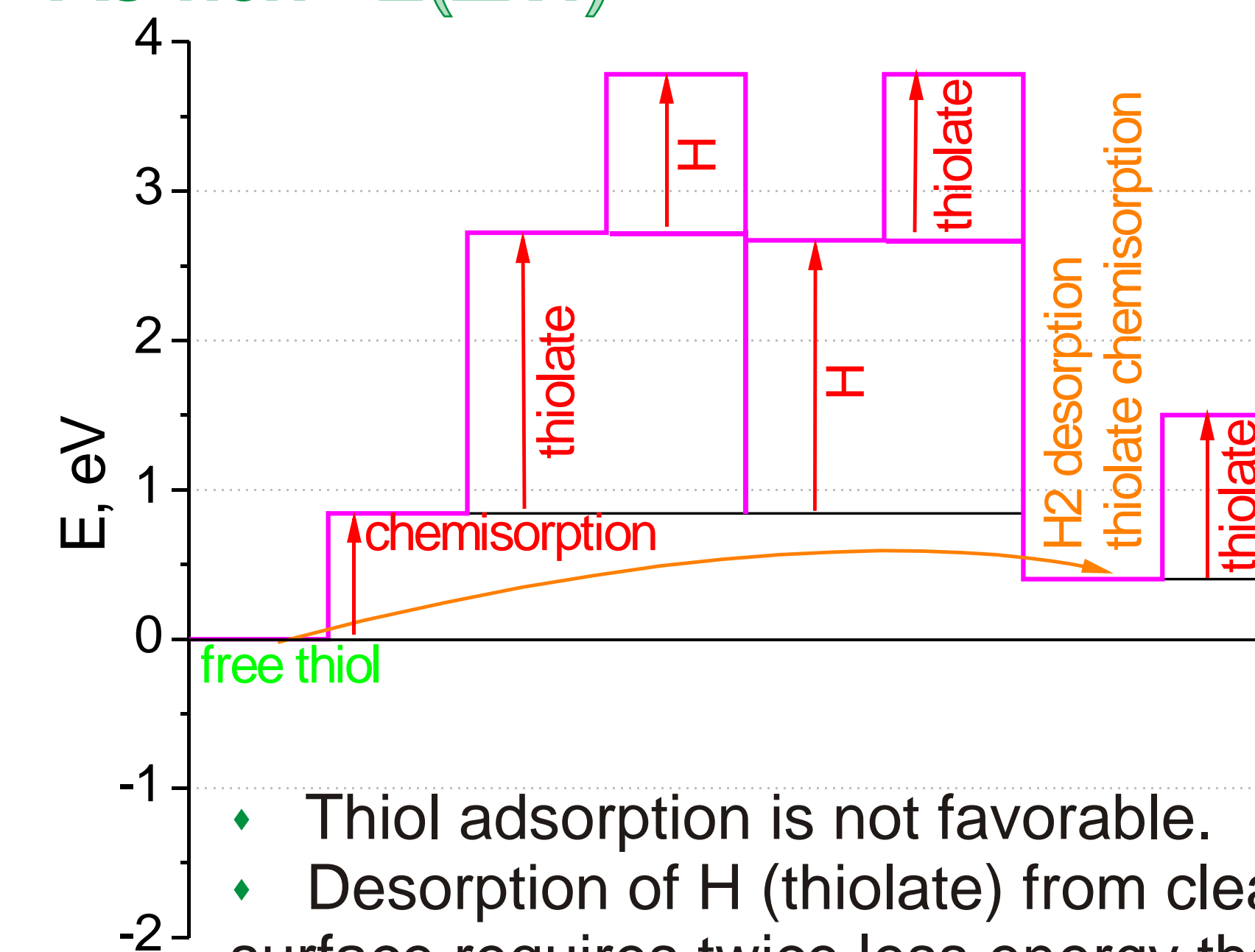
However, since hydrogen stays adsorbed on the surface near the thiolate, the recombinative desorption process (e) is possible, requiring aforementioned 1.25 eV, i.e., much less energy than needed for thiolate desorption.

Adsorbed hydrogen can also recombine with another hydrogen, desorbing as a H<sub>2</sub> (f), or with alkyl part of thiolate, desorbing as alkane (l), in agreement with experimental temperature desorption data\*.

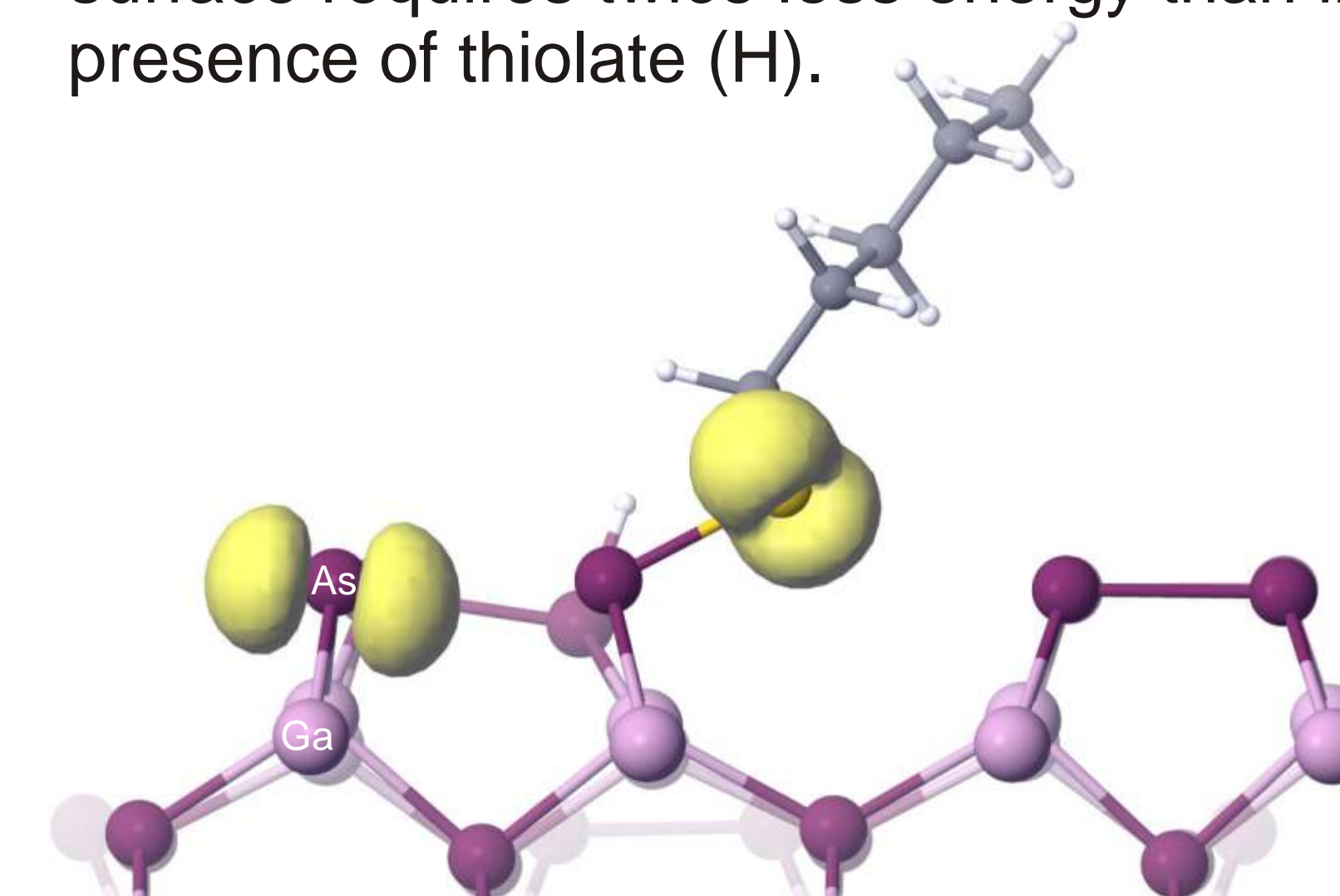
\* N. K. Singh, D. C. Doran, *Surf. Sci.* **422**, 50 (1999).

## Effect of surface reconstruction

### As-rich 2(2x4)



- Thiol adsorption is not favorable.
- Desorption of H (thiolate) from clean surface requires twice less energy than in the presence of thiolate (H).



Highest occupied molecular orbitals for thiol adsorption on As-rich 2(2x4) surface.

Adsorption of thiolate and hydrogen on As dangling bonds leads to the excess of 2 electrons.

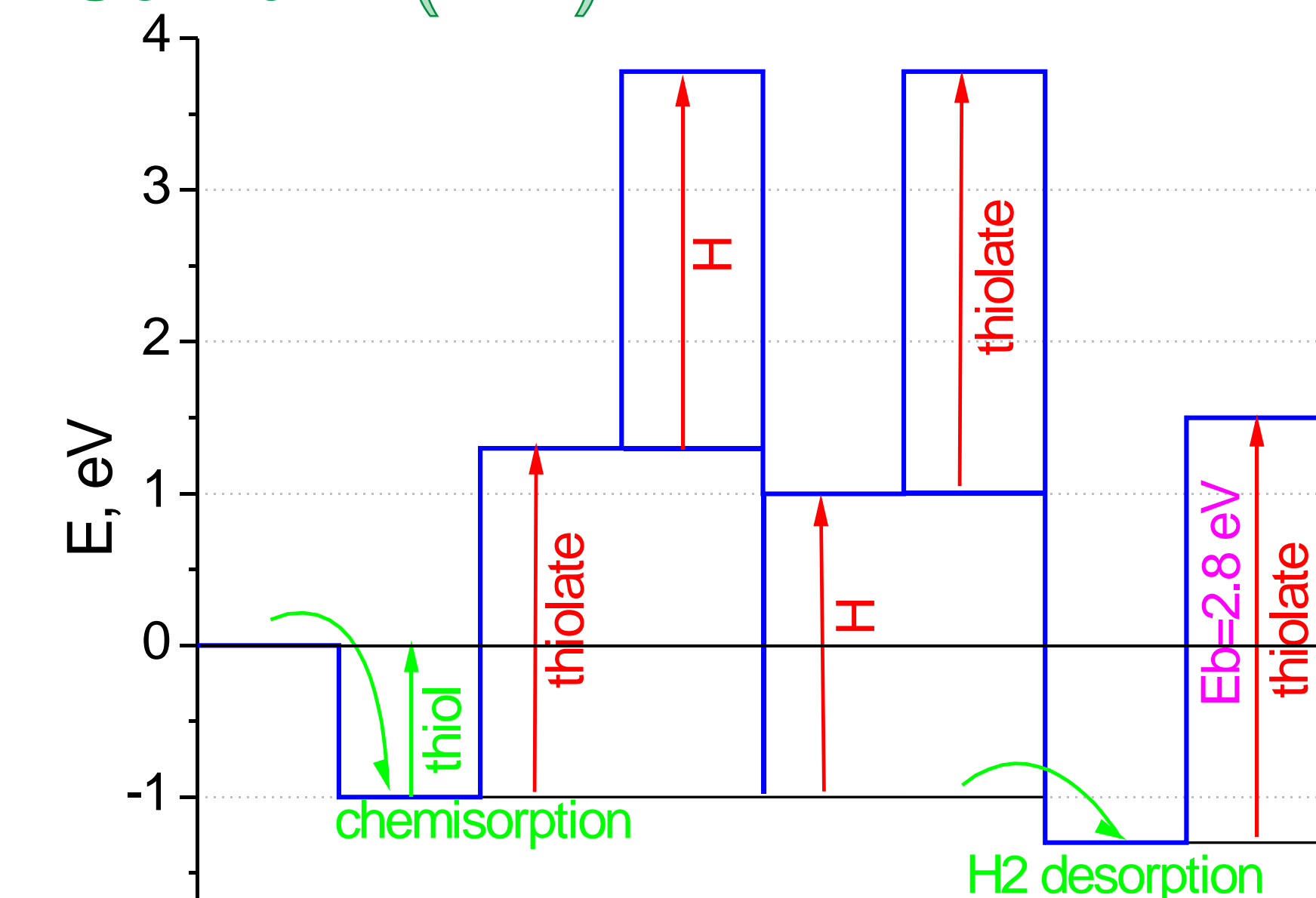
To satisfy the electron counting rule, surface relaxes by breaking the As dimer, creating 2 new dangling bonds instead of 1 dimer bond.

This raises the energy of surface significantly, making thiol adsorption not favorable.

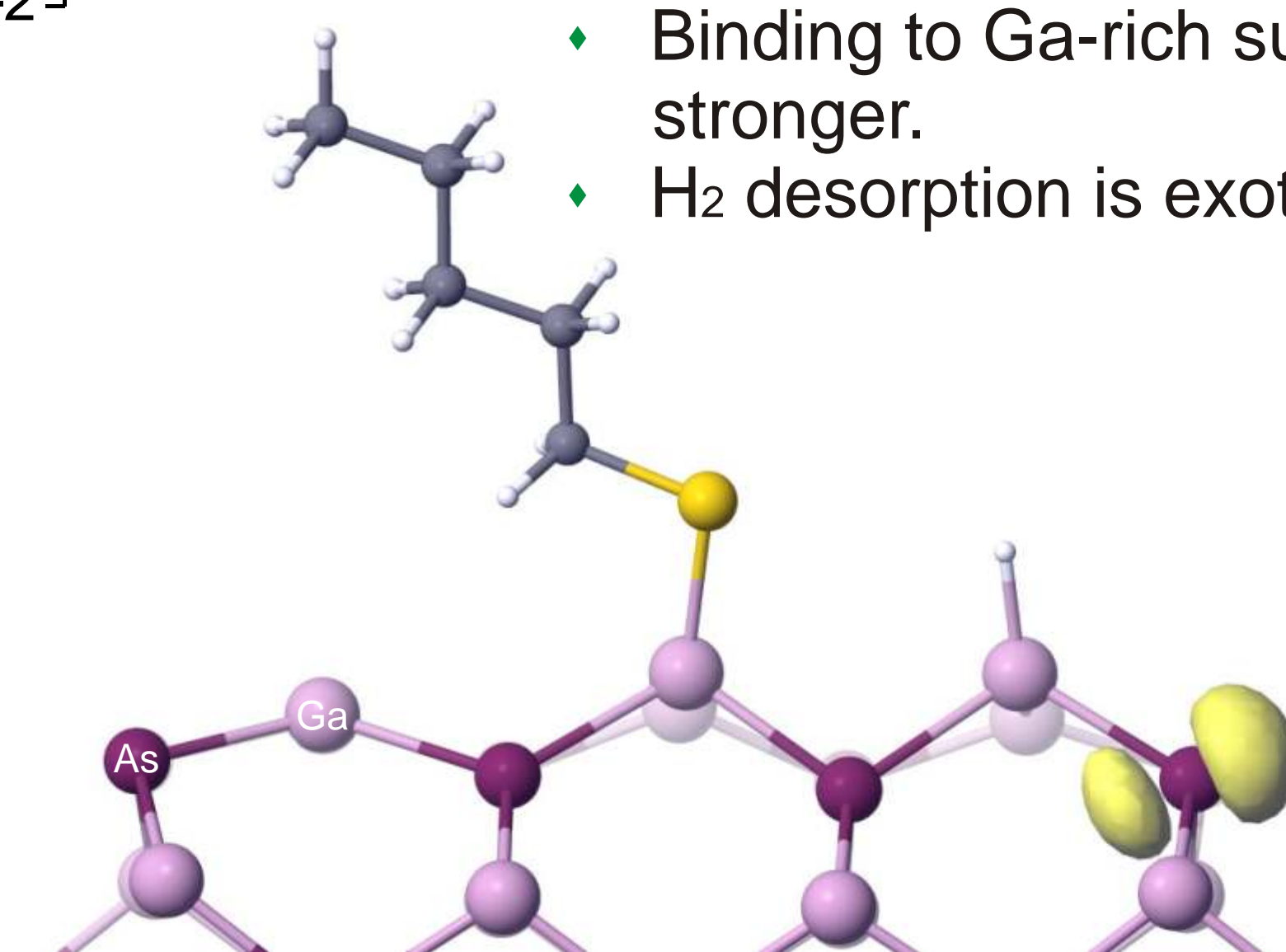
The energy of the surface after hydrogen (thiolate) desorption becomes even higher, since now there is an excess of only one electron and the electron counting rule can't be satisfied even after relaxation.

This results in a much smaller energy needed to desorb the thiolate (hydrogen) and return the surface to its ideal state.

### Ga-rich (4x2)



- Binding to Ga-rich surface is stronger.
- H<sub>2</sub> desorption is exothermic.



Partially empty molecular orbital on As due to thiol adsorption on Ga-rich (4x2) surface.

Adsorption of thiolate and hydrogen on empty Ga dangling bonds leads to a deficit of 2 electrons, since now each previously empty bonds should contain 2 electrons.

These electrons are taken partially from As dangling bonds (not changing their hybridization) and partially from the thiolate itself.

Ga atoms change hybridization from sp<sup>2</sup> to sp<sup>3</sup>, which lowers their energy and also helps to reduce strain.

Energy gain due to formation of Ga-H and Ga-S bonds, rehybridization and strain relaxation becomes greater than the loss due to partial emptying of As dangling bonds, resulting in favorable thiol adsorption

## Conclusions

Our theoretical study of alkanethiols adsorption on GaAs (001) have shown that upon transition from physisorbed to chemisorbed state hydrogen atom stays on surface affecting significantly desorption products and energies, in agreement with available experimental data.

Strong dependence of adsorption energetics on surface reconstruction emphasizes the importance of the right choice of surface treatment before thiolation.

Simple electron counting can be used to predict the possibility of thiol adsorption on other semiconductor surface reconstructions.

## Acknowledgements

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