

Motivation

Self-assembled monolayers (SAMs) of organosulfur compounds on solid surfaces attract a lot of interest from both fundamental perspective and their potential applications.

SAMs on semiconductor surfaces and particularly on GaAs can be used for development of precursors for the growth of II-VI materials, creation of transition layers for ohmic contacts and Schottky diodes, passivation of GaAs surfaces, nanolithography, electrochemical applications and biosensing.

In contrast to alkanethiols on gold which are considered a prototype example of SAMs, there are no theoretical studies of thiols on GaAs.

In this work we present the theoretical study of alkanethiols adsorption on GaAs (001) under low coverage conditions as a first step towards understanding of the SAM formation process.

Model



TM2 pseudopotentials, PBE+NLCC DZP bases for Ga and As and TZP for As in top layer, S, C and H.

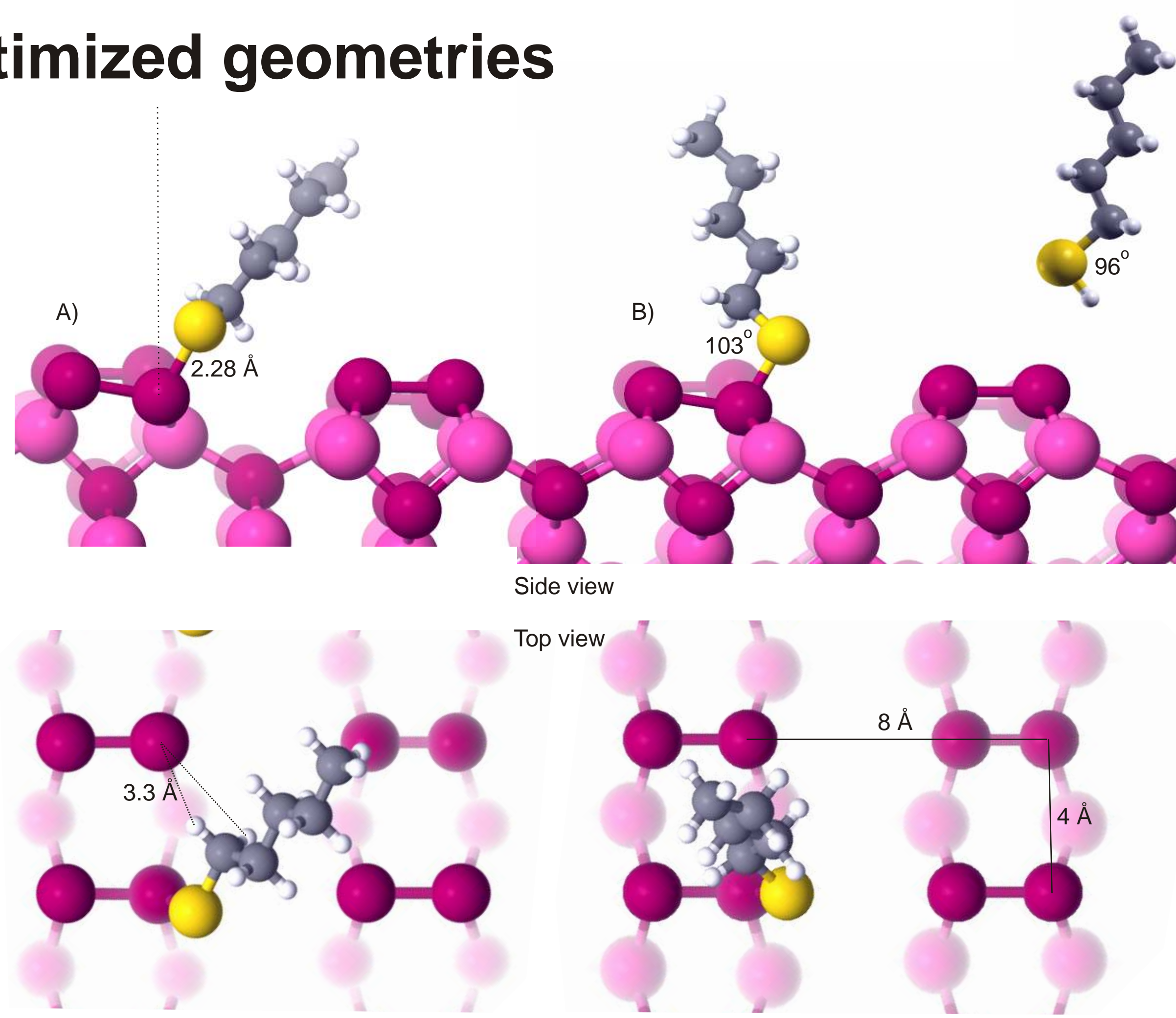
11 Å *k*-grid cutoff, 350 Ry equivalent plane wave energy cutoff (4x2) surface unit cell (16x8 Å²) with dimerized As

	LDA	PBE	BLYP	RPBE	Expt
S-H length, 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
H-H length, 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

Unit cell used in calculations

Results

Optimized geometries



Optimized geometries of pentanethiol on As-rich GaAs (001) surface obtained from relaxation of (a) thiolate lying flat to the surface and (b) thiolate standing upright.

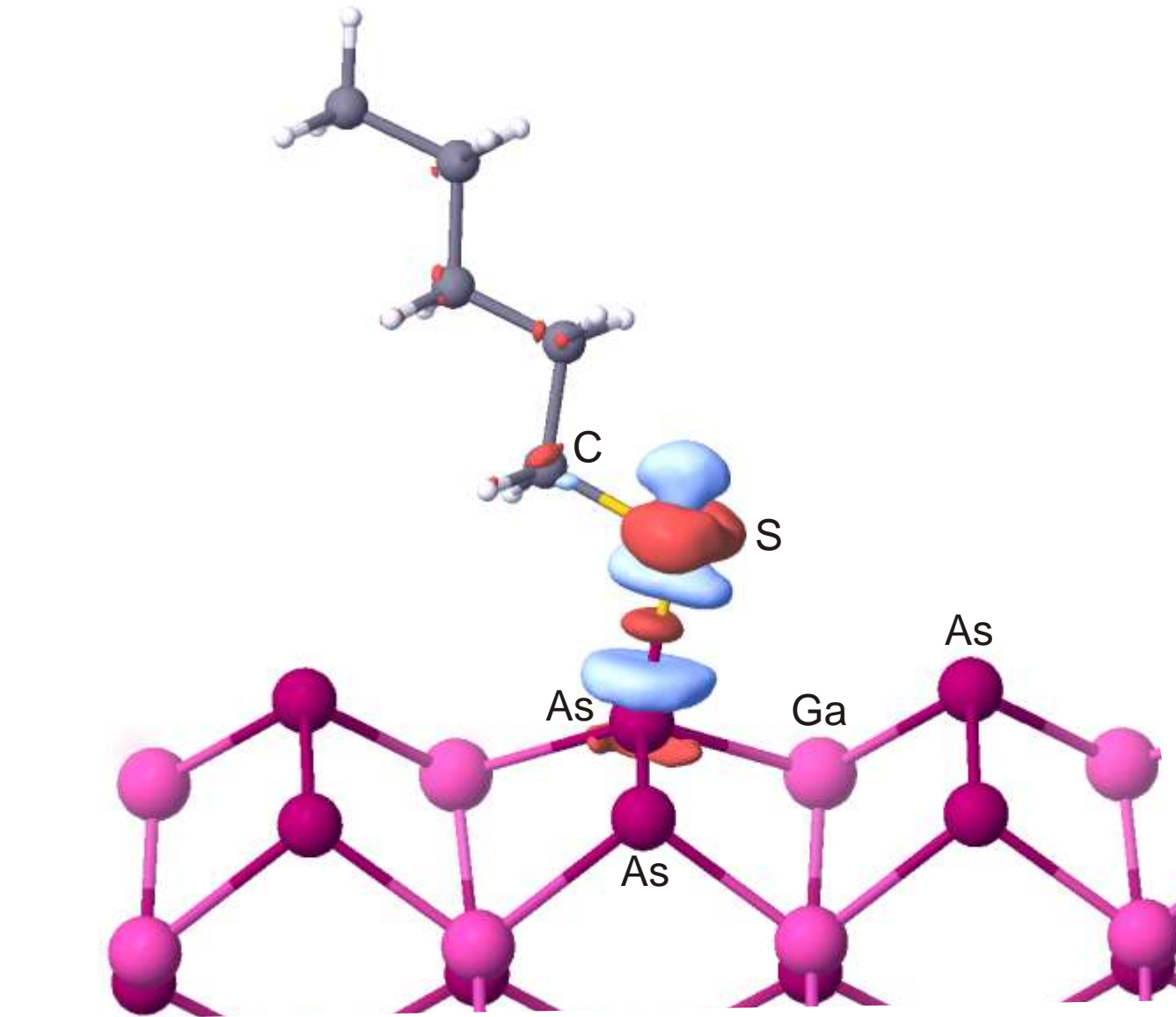
Strong dependence of total energy on tilt angle.

Bridge and hollow site positions are not favorable.

The thiolate adsorption site, tilt angle and its direction are dictated by high directionality of As dangling bond and sulfur 3p orbital and steric repulsion of the first CH₂ unit from the surface.

Bonding nature

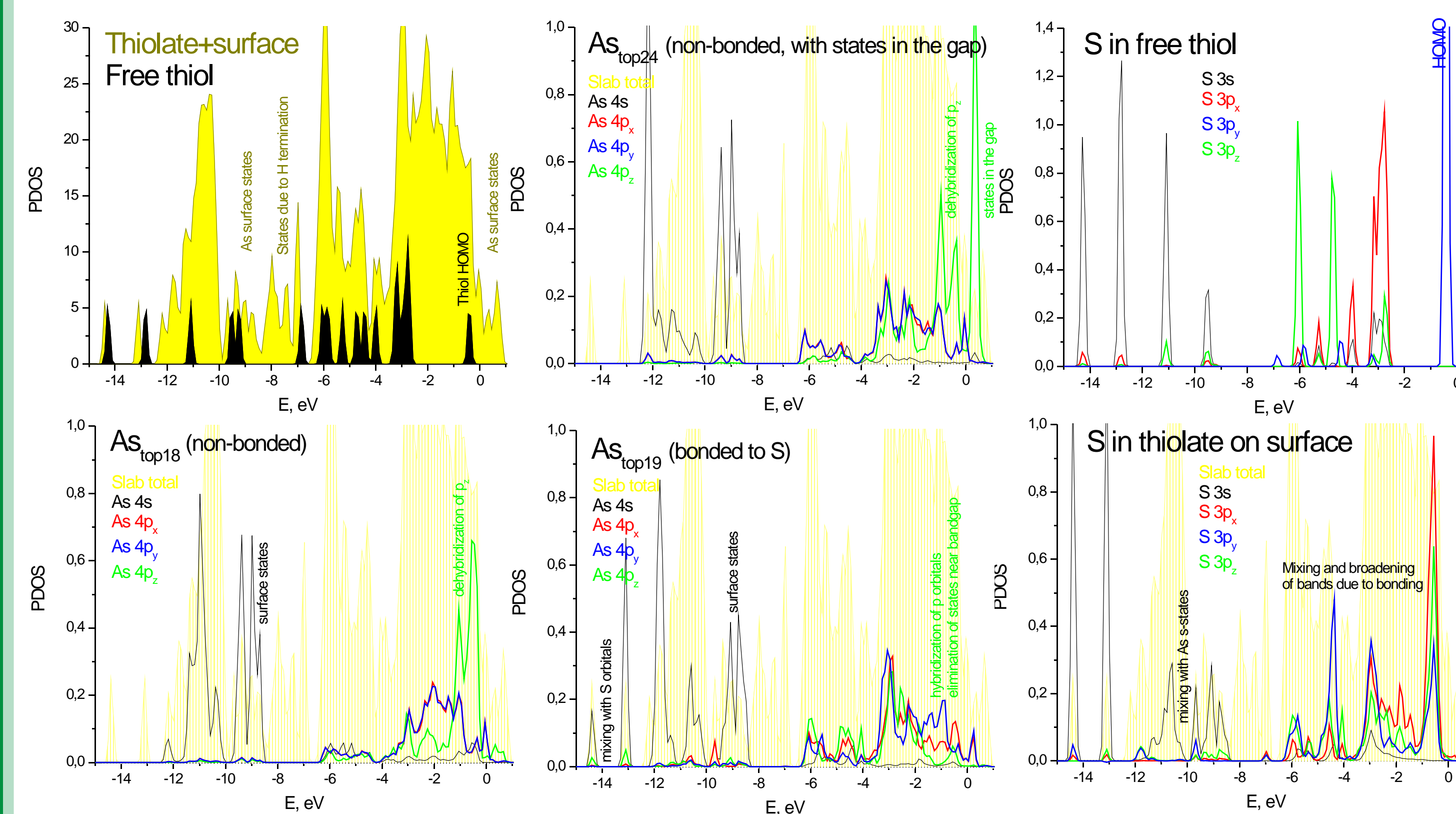
Absence of charge transfer between thiolate and surface, strong dependence of total energy on tilt angle and shorter S-As bond length (2.28 Å in comparison with 2.5 Å for S-Au and 2.31 Å for S-Cu) indicate a **highly covalent** nature of the bonding and stronger binding of thiolate to GaAs than to metal surfaces.



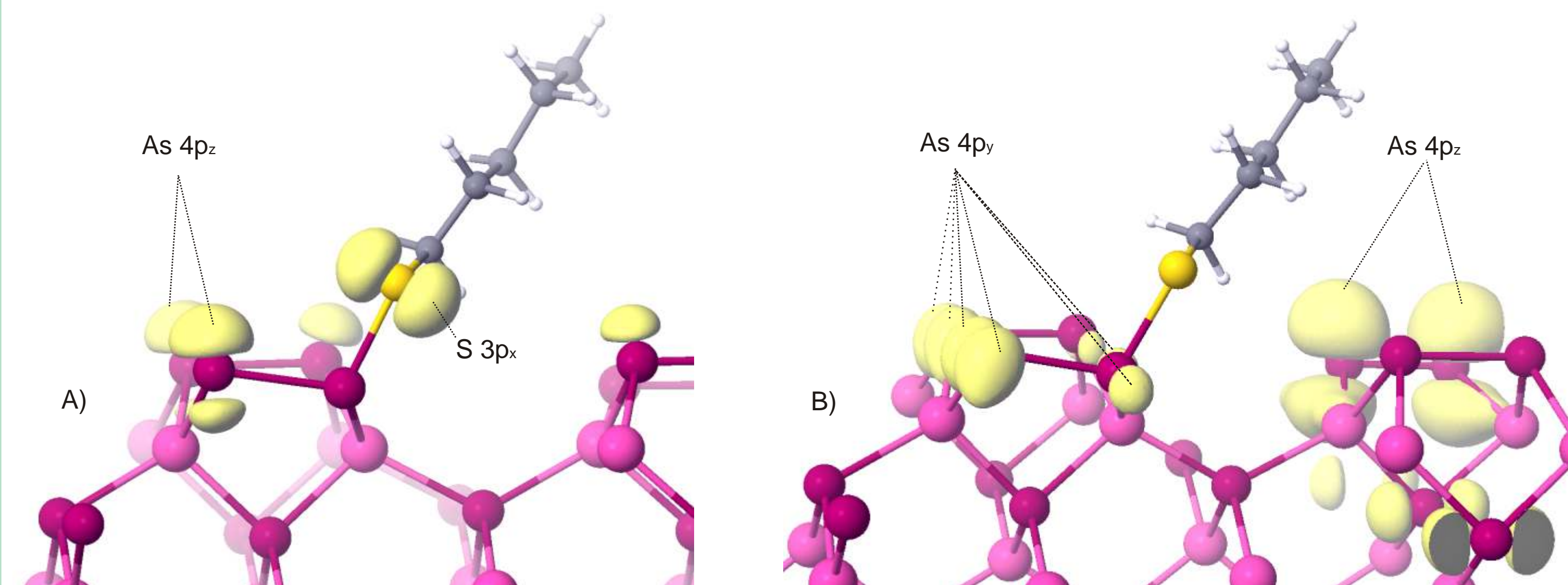
Regions of loss (light blue) and gain (red) of electron density induced by adsorption of thiolate on surface. Isodensity surfaces correspond to ±0.006 a.u.

Only electrons around sulfur and S-C bond are involved in bonding. Thus, binding energy doesn't depend on chain length.

Mulliken analysis shows very small charge transfer of 0.05e from thiolate to surface, comparing to transfer to thiol of 0.4e from gold surface and 0.7e from copper.



Analysis of density of states and molecular orbitals shows that thiol adsorption partially eliminates surface states, explaining the increase of PL intensity of thiol-passivated GaAs.

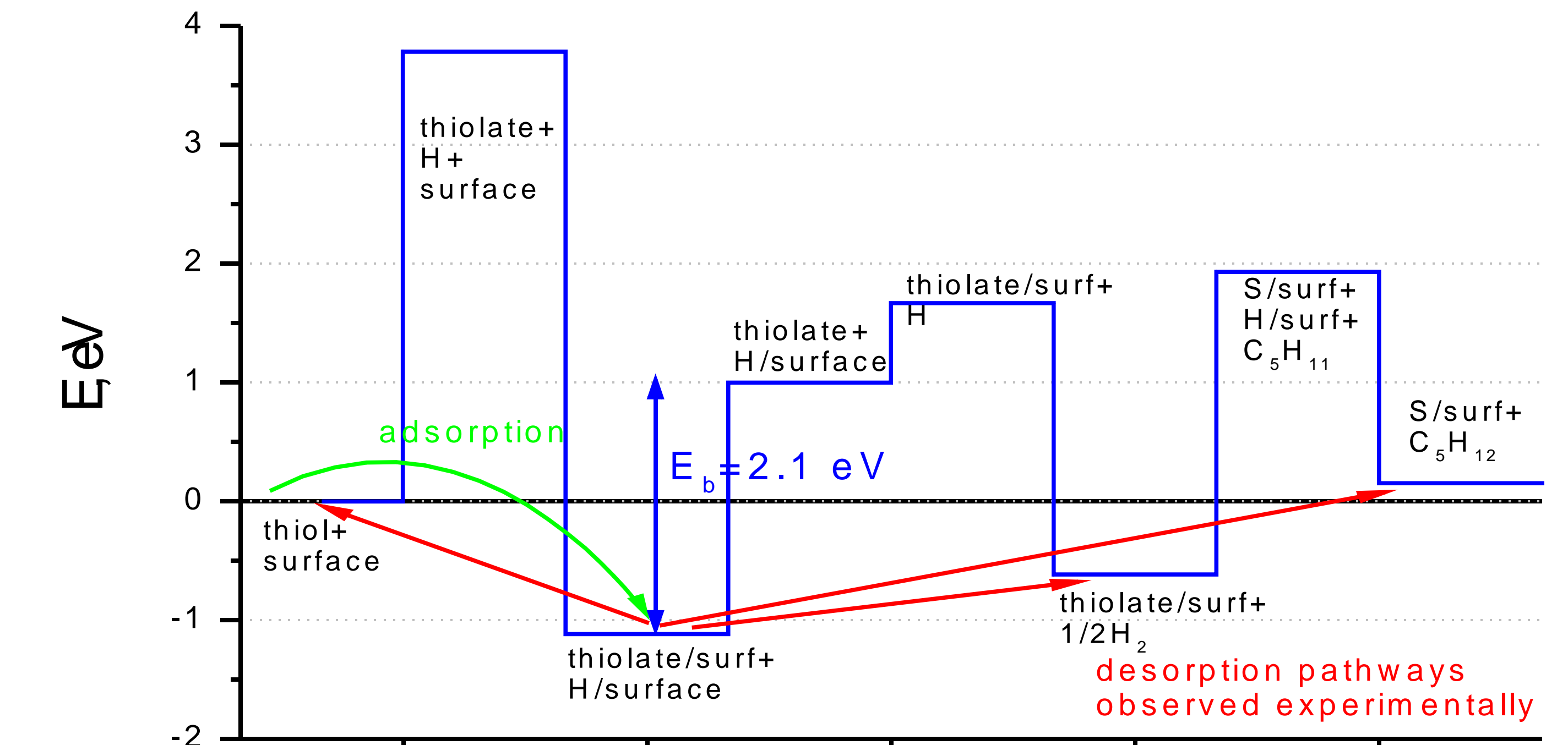


Molecular orbitals in 1 eV energy window (a) below Fermi level and (b) above Fermi level.

Sulfur 3s and 3p orbitals do not hybridize forcing C-S-As angle to be close to 90°.

Top layer arsenic 4p orbitals dehybridize and create states close to valence band maximum.

Energetics at low coverage

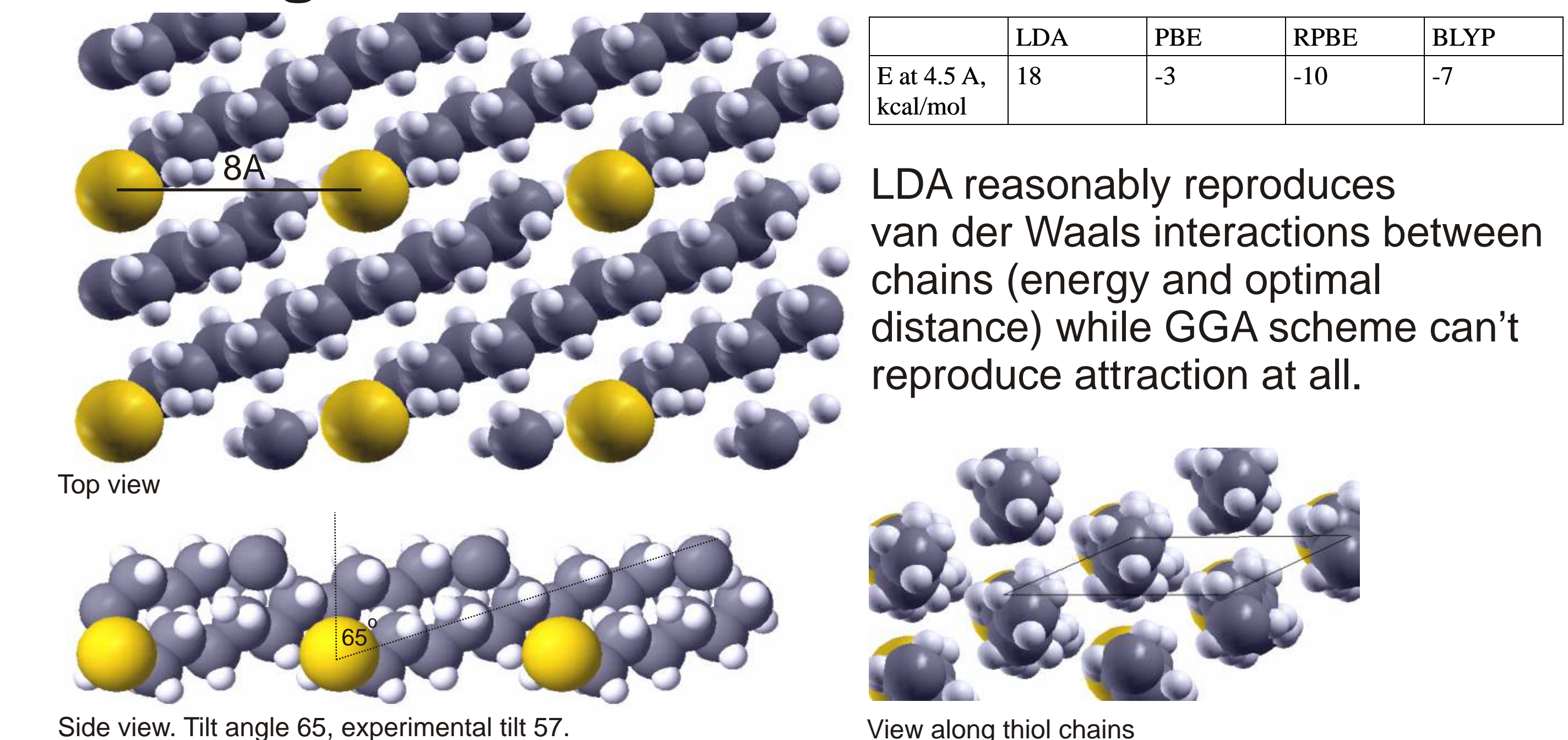


Calculated binding energy of 2.1 eV is bigger than 1.7 eV for thiols on gold and 2.03 eV for thiols on copper.

Atomic hydrogen desorption is highly unfavorable. Hydrogen stays adsorbed on the adjacent As near adsorbed thiolate.

At high temperatures hydrogen participates in recombinative desorption with creation of molecular hydrogen, thiol and pentane, in agreement with experimental results [N.Singh, D.Doran. *Surf.Sci.* 422 pp.50-64. (1999)].

Packing of free alkanethiols



Thickness of the optimally packed monolayer is about half of that observed on GaAs surface.

Geometry of free alkanethiol packing is not possible on GaAs surface due to high directionality of the As-S bond and steric repulsion of the first CH₂ unit from surface.

Outlook

- Calculation of binding energy with different XC functionals
- Study of different surface reconstructions
- Ga-rich surface
- Potential energy surface for thiol diffusion
- Investigation of physisorption state which serves as a precursor for chemisorption
- High coverage conditions and formation of SAMs

Acknowledgements

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