Application of DFT Calculations to Self-Assembled Monolayers on Au(111)

NC State University

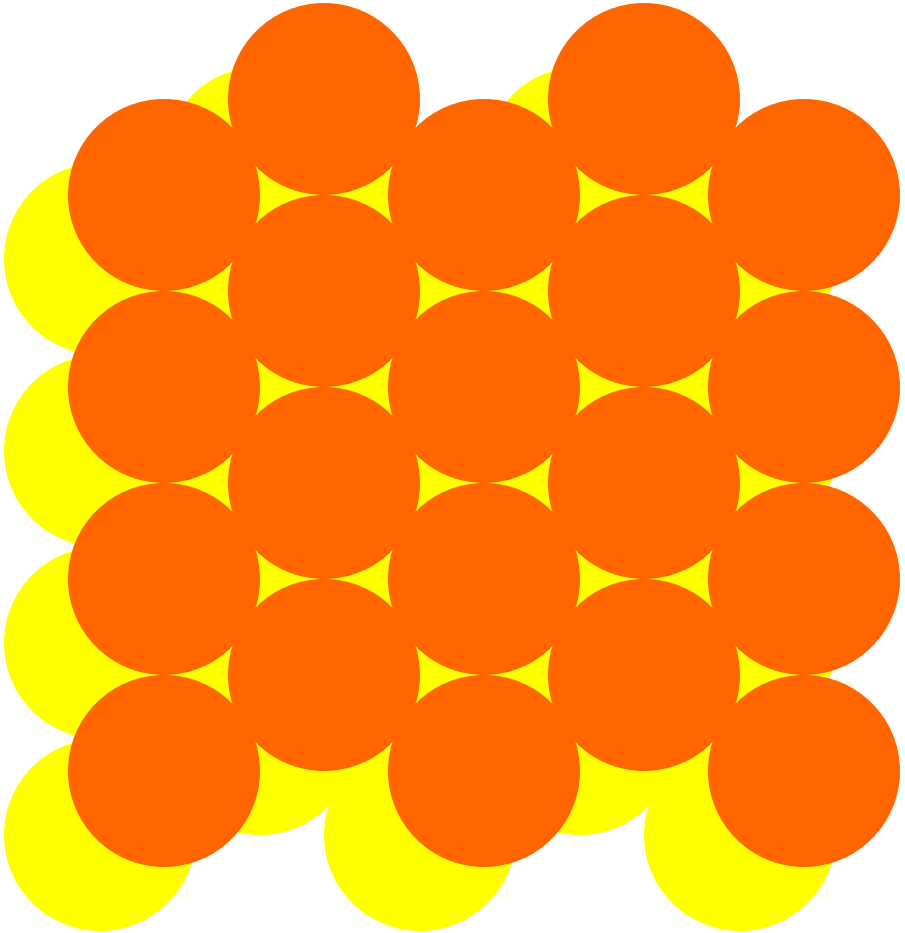
Computational modeling of the surface of Au(111)

- Structure of the ($\sqrt{3}$ x $\sqrt{3}$ R30^{o}) lattice
- Reconstruction of the Au(111) layer
- Studies of c(4x2) superlattice
- Mechanism of adlayer formation
- Modeling DNA adlayers
- Surface attachment of proteins
- Surface attachment of boronic acid biosensors

Top view of the Au(111) Surface

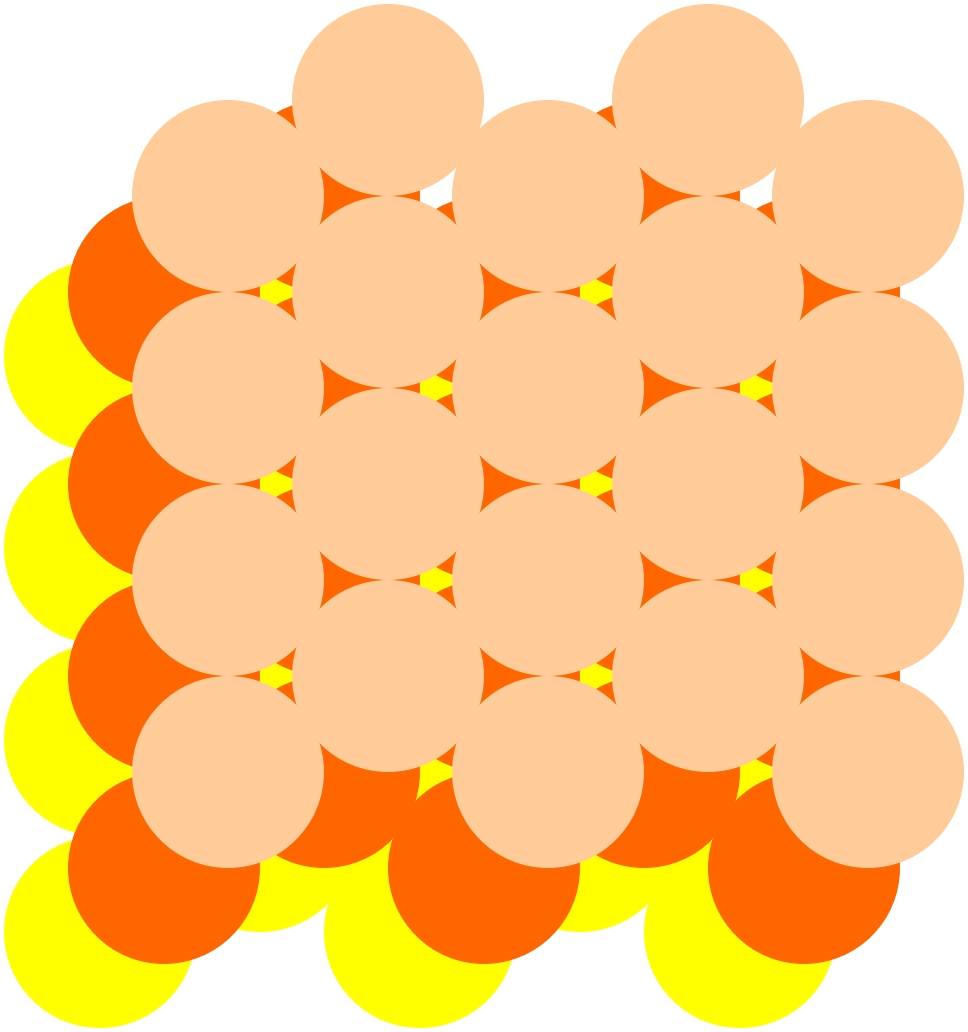
A

Face-centered cubic lattice is ABC



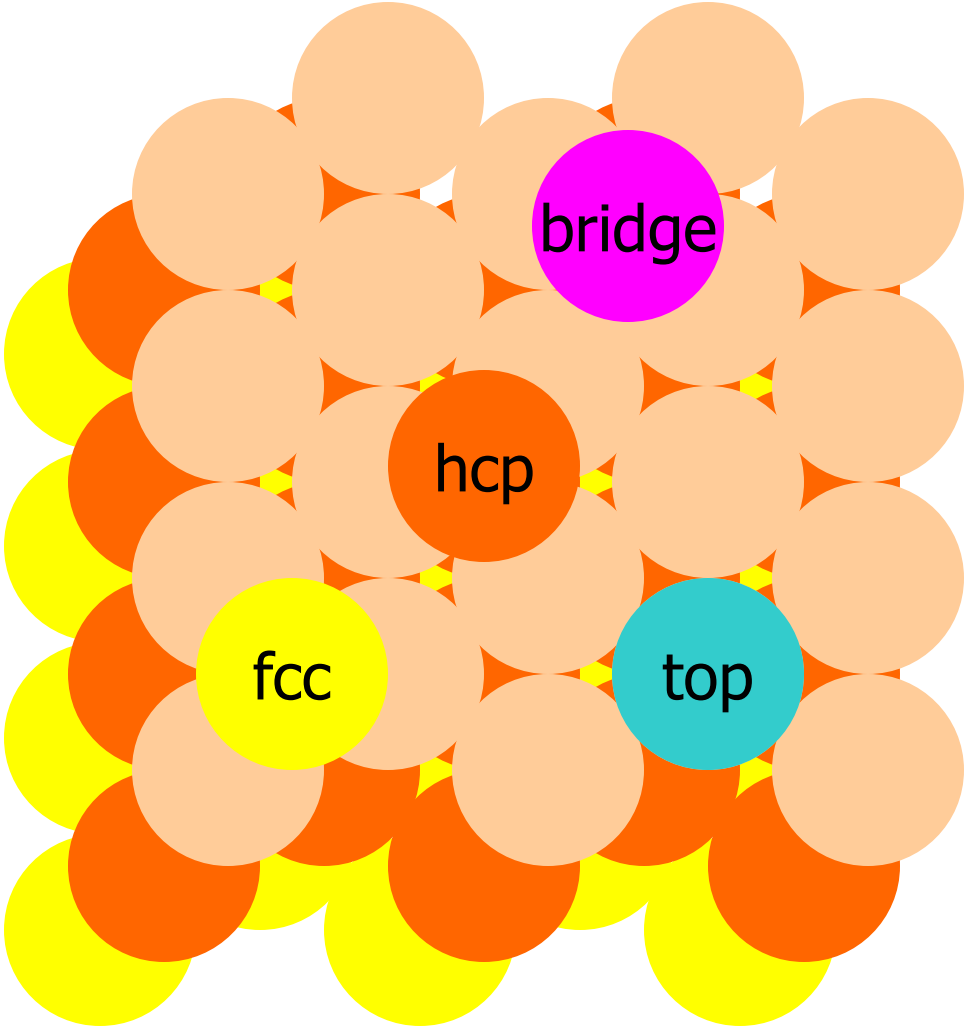
A B

Face-centered cubic lattice is ABC

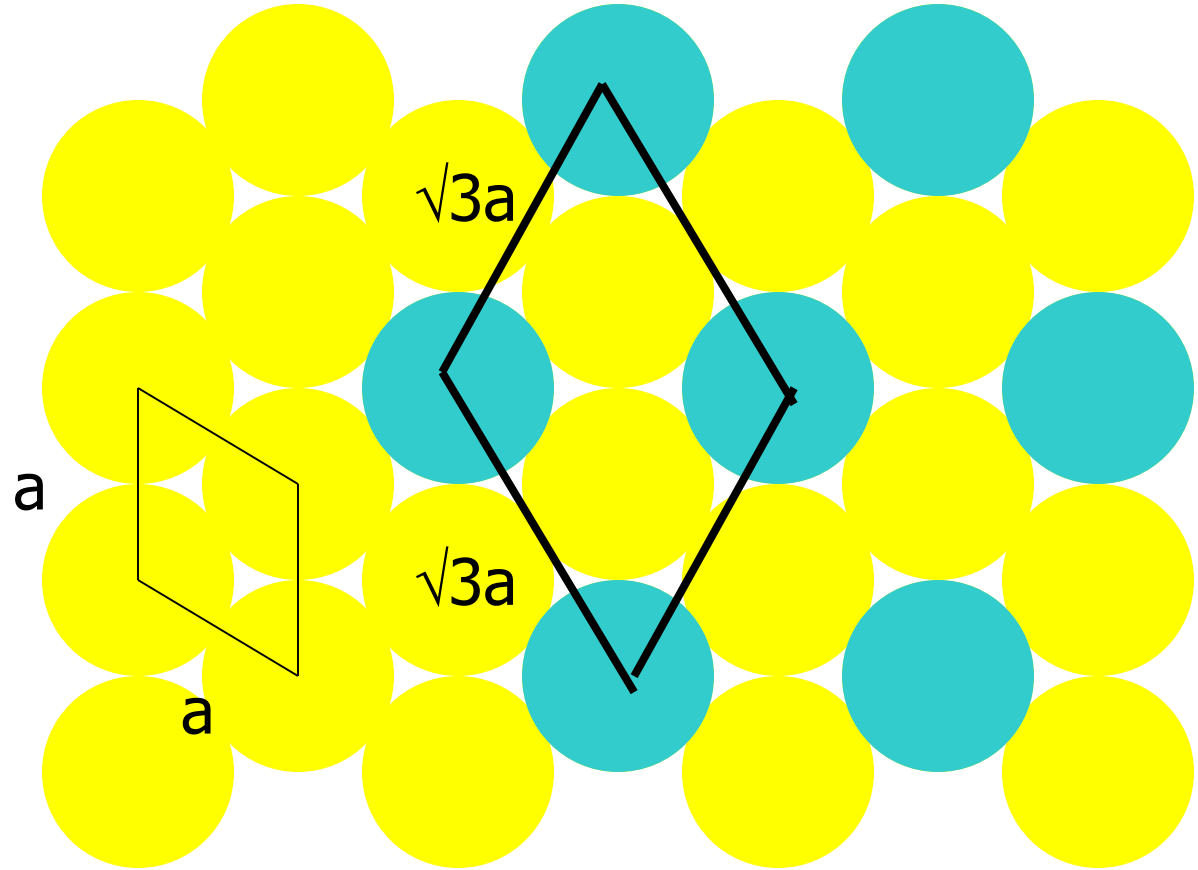


A B C

Binding sites on the 111 surface

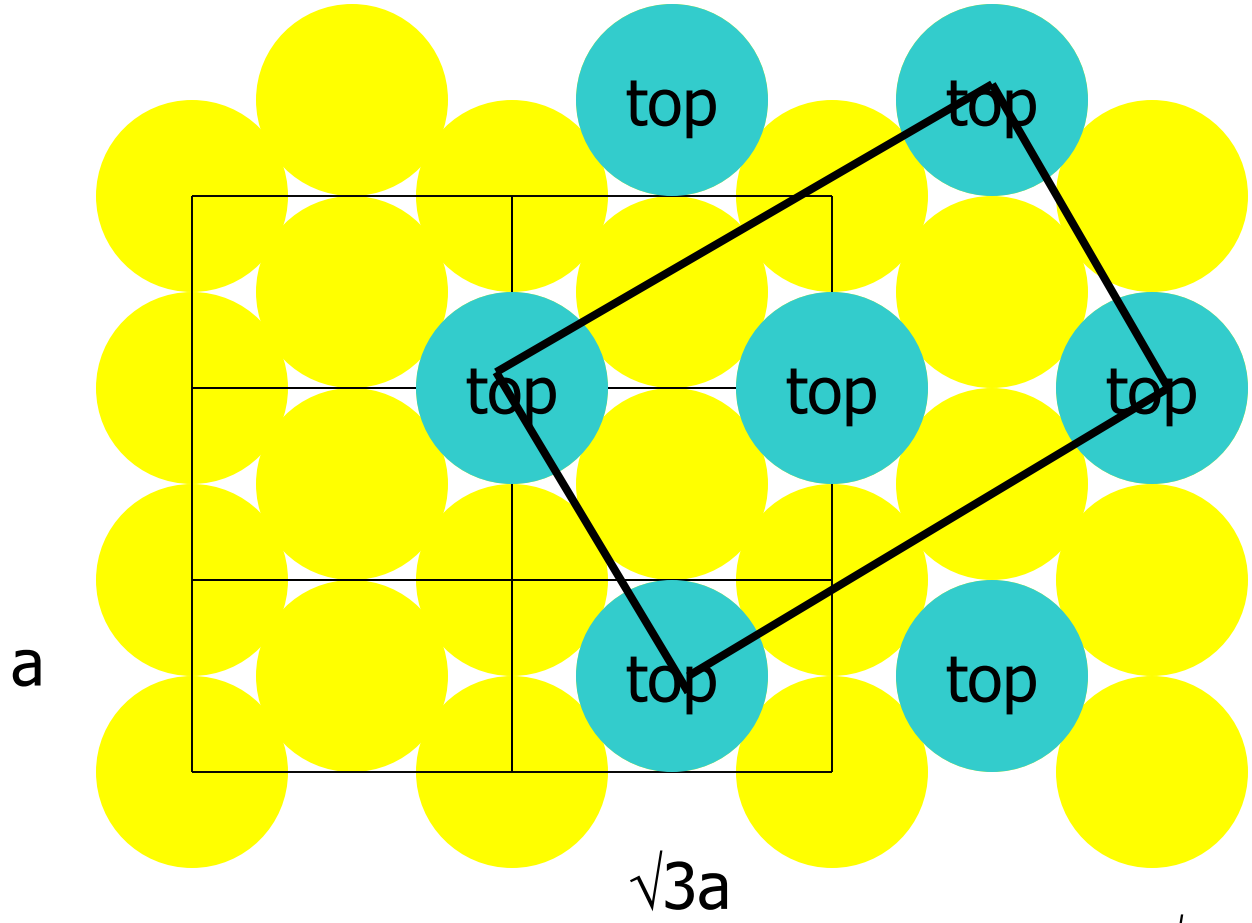


Hexagonal unit cells on the 111 surface



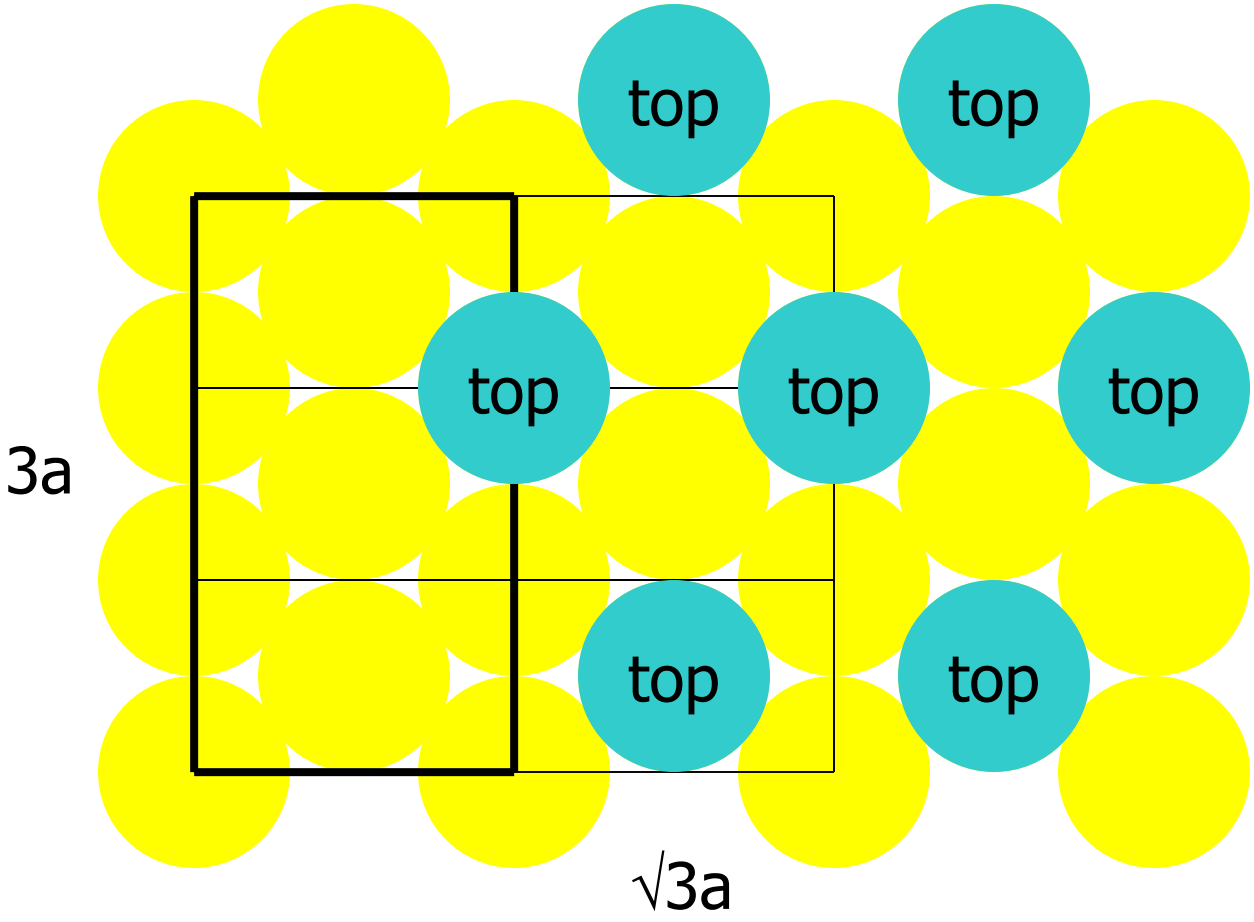
(√3 x √3 R30°)

Orthorhombic unit cells on the 111 surface

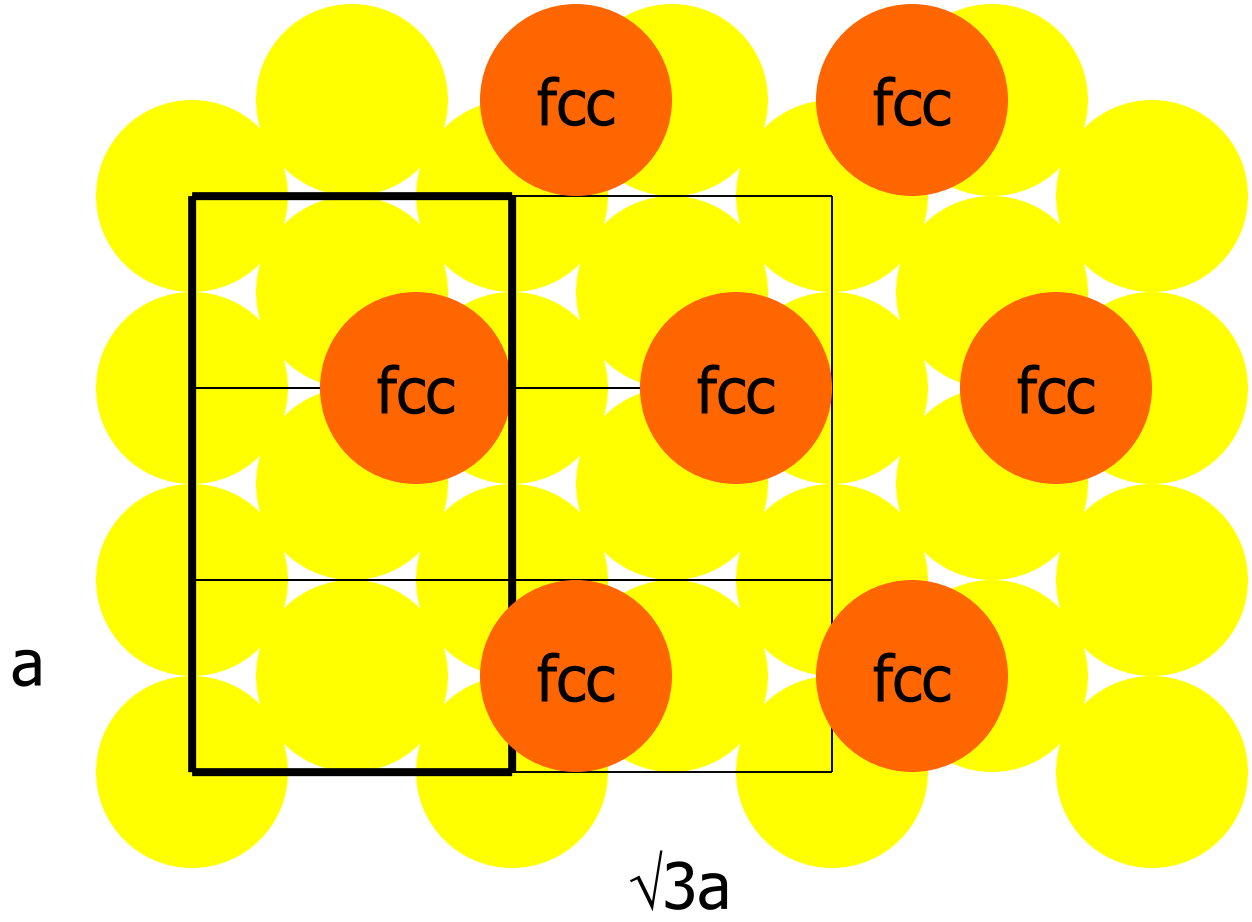


(√3 x 3 R30°)

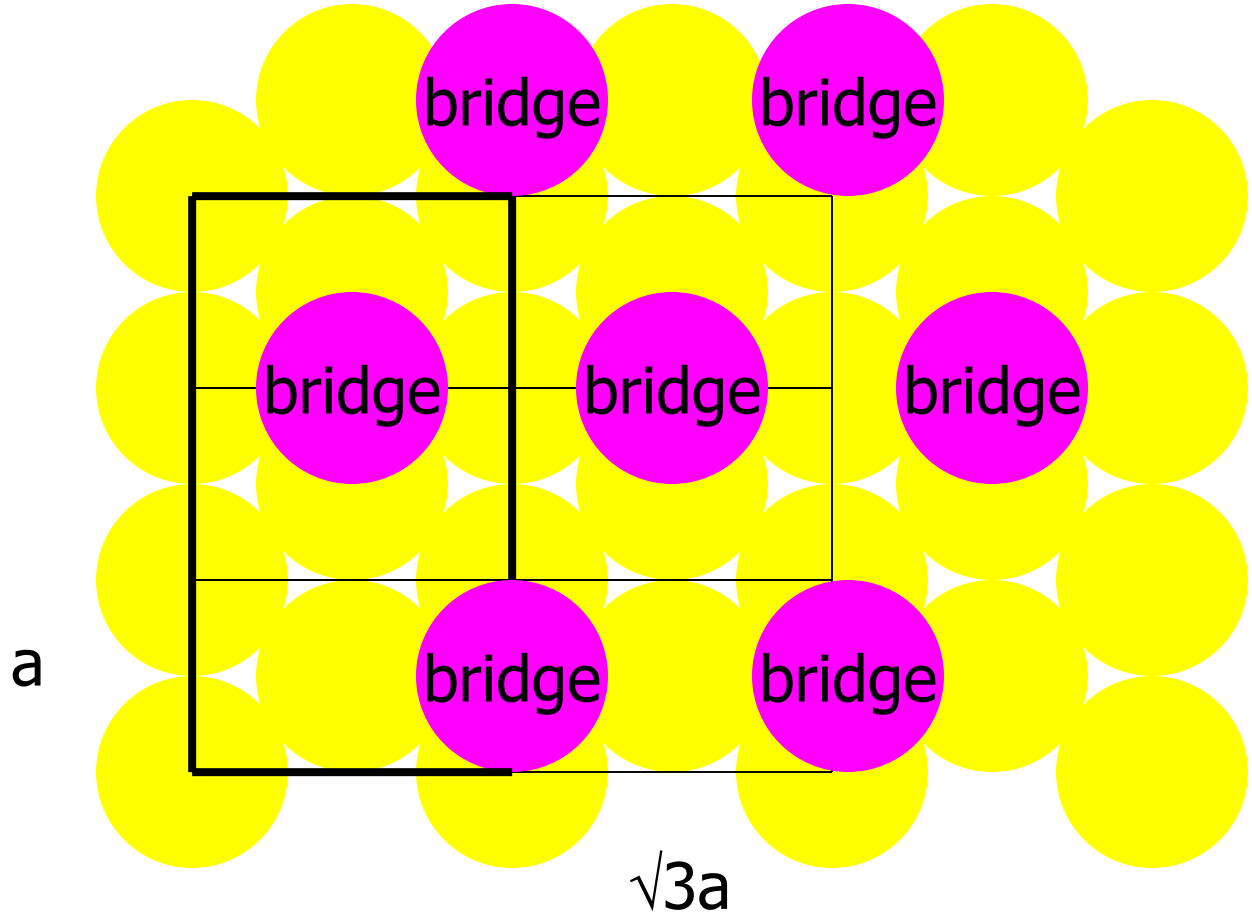
Unit cells on the 111 surface
top binding site



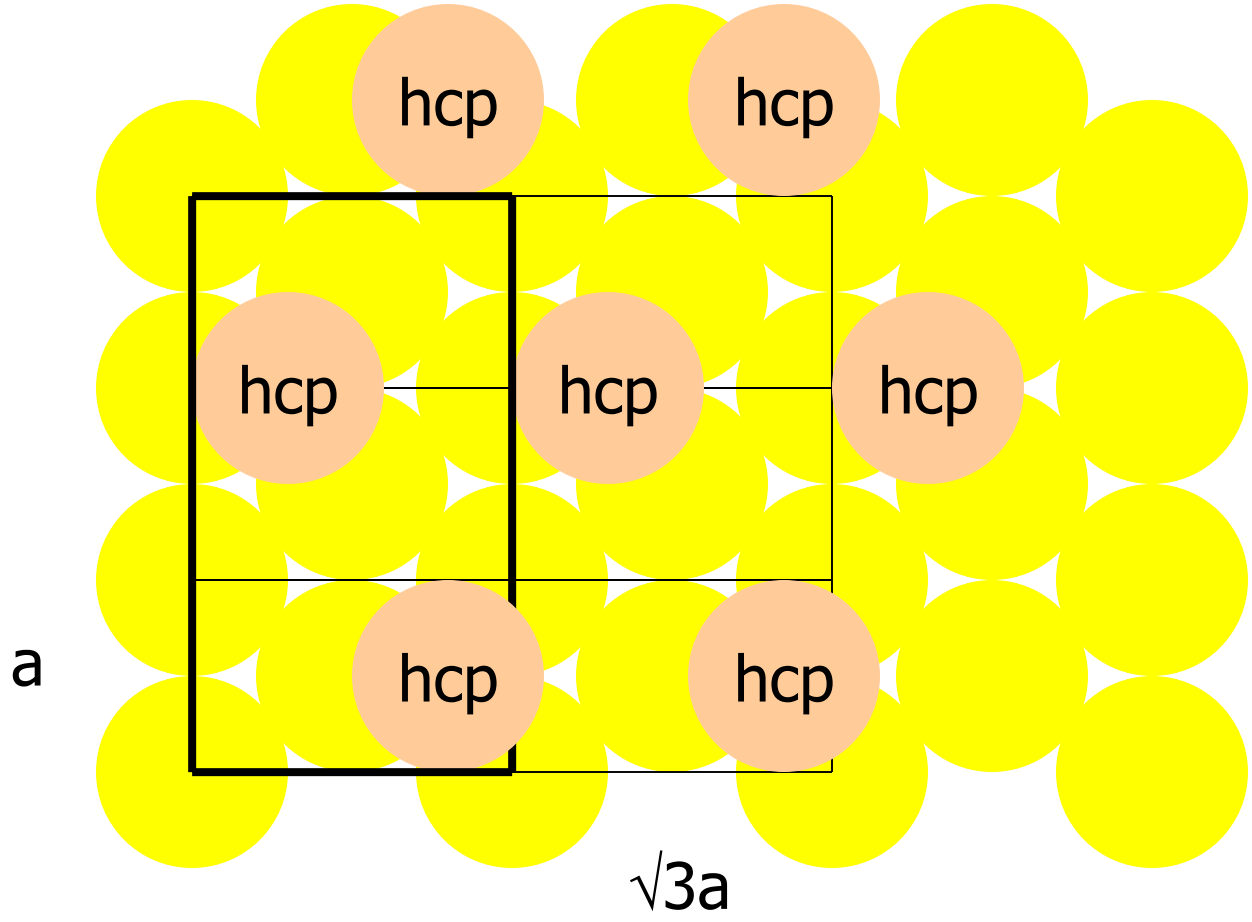
Unit cells on the 111 surface
fcc binding site



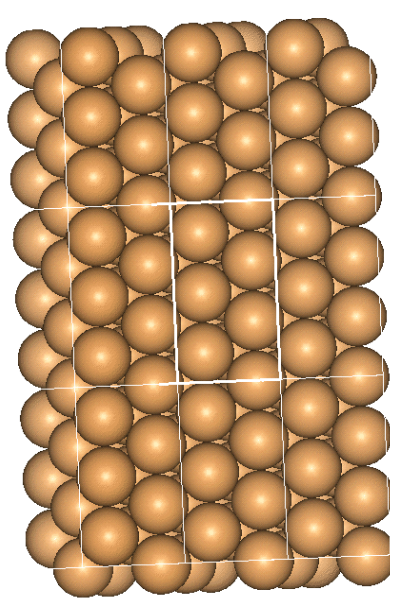
Unit cells on the 111 surface bridge binding site



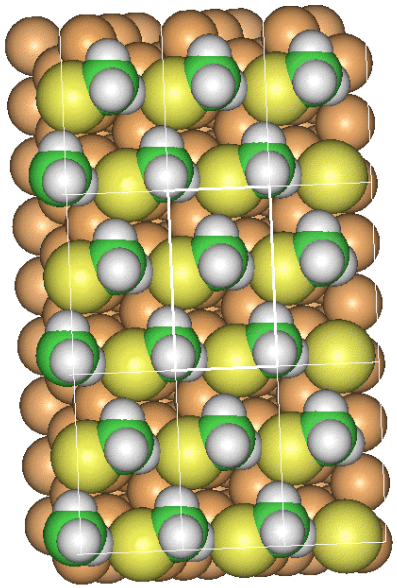
Unit cells on the 111 surface
hcp binding site



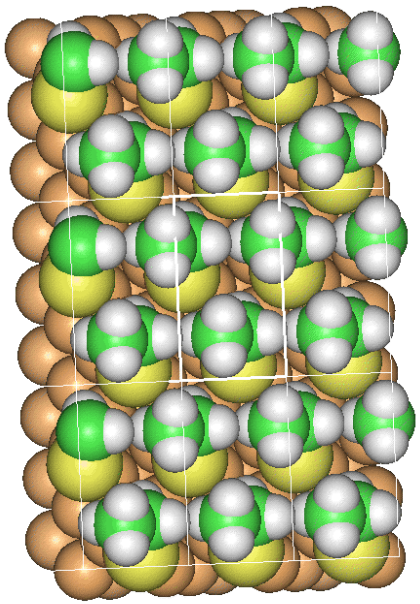
Comparing different chain lengths on Au(111)



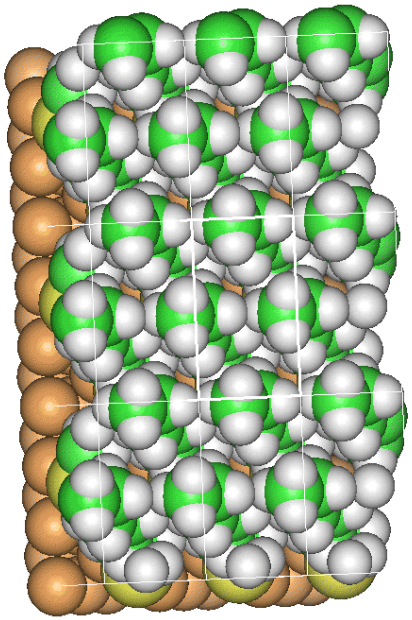
Au(111)



SCH_3 on Au(111)



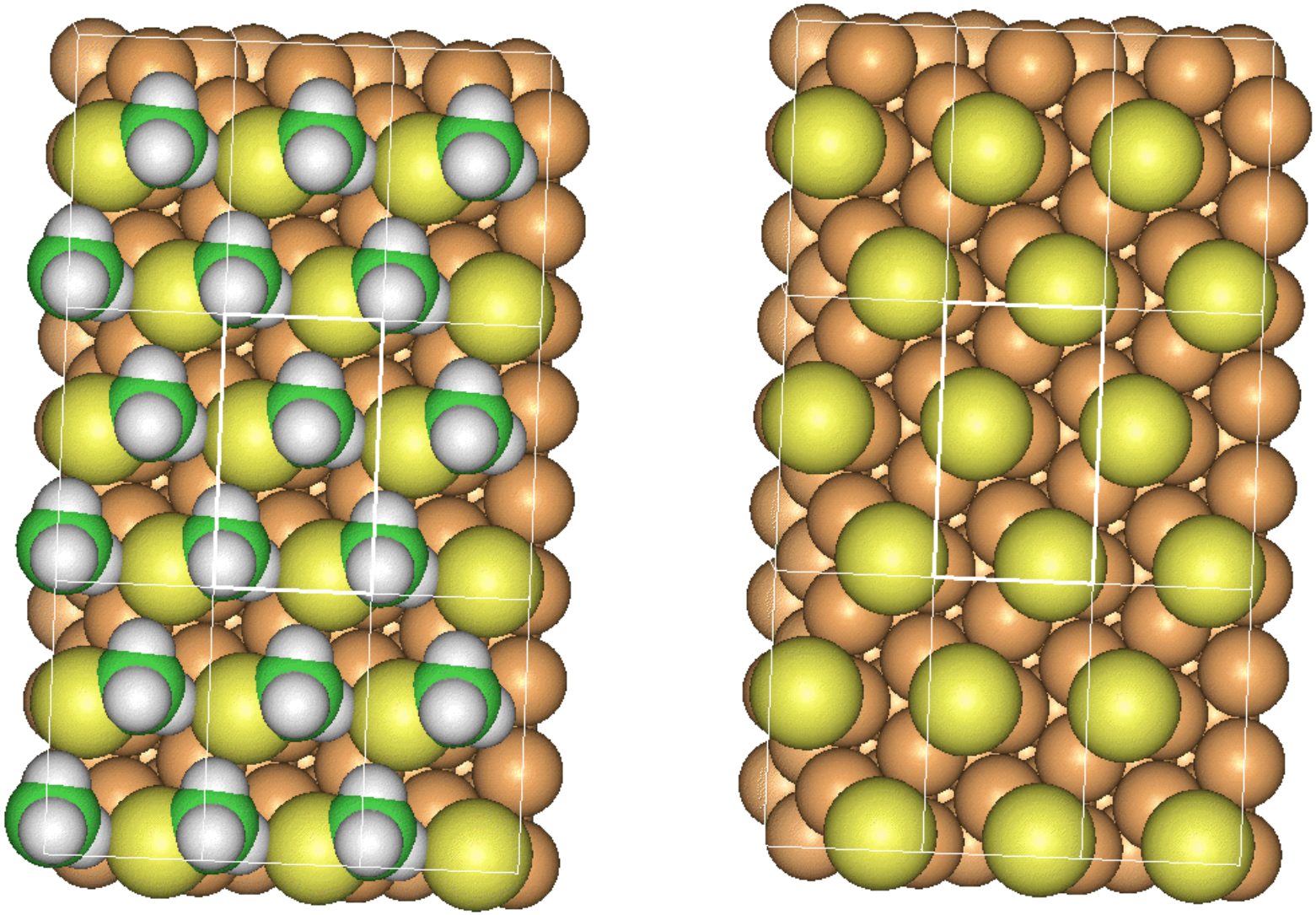
SC_2H_5 on Au(111)



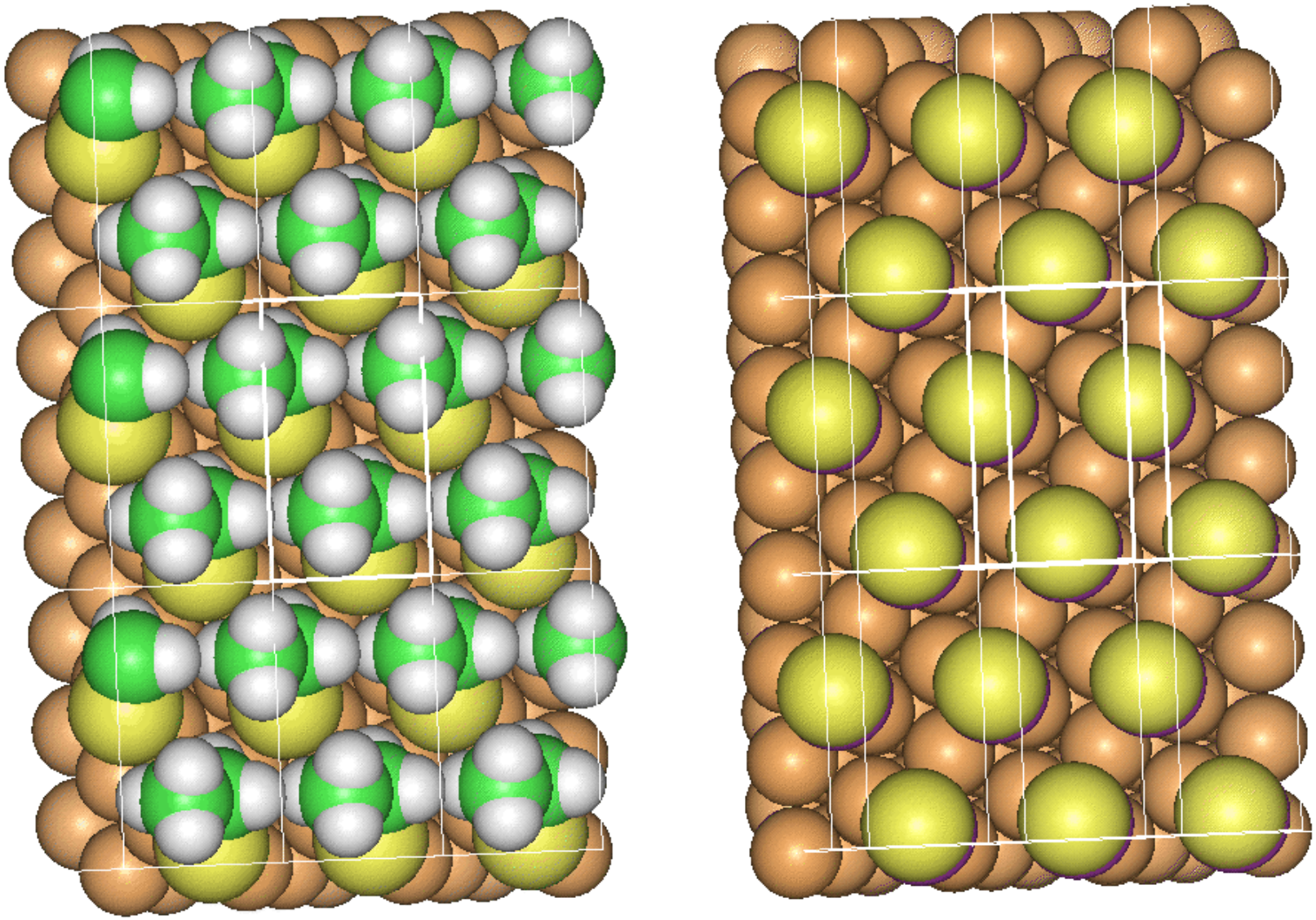
SC_6H_{13} on Au(111)

- Geometry optimize surface adlayer (fixed Au)
- Create models for fcc, top and bridge
- Calculate potential energy surface

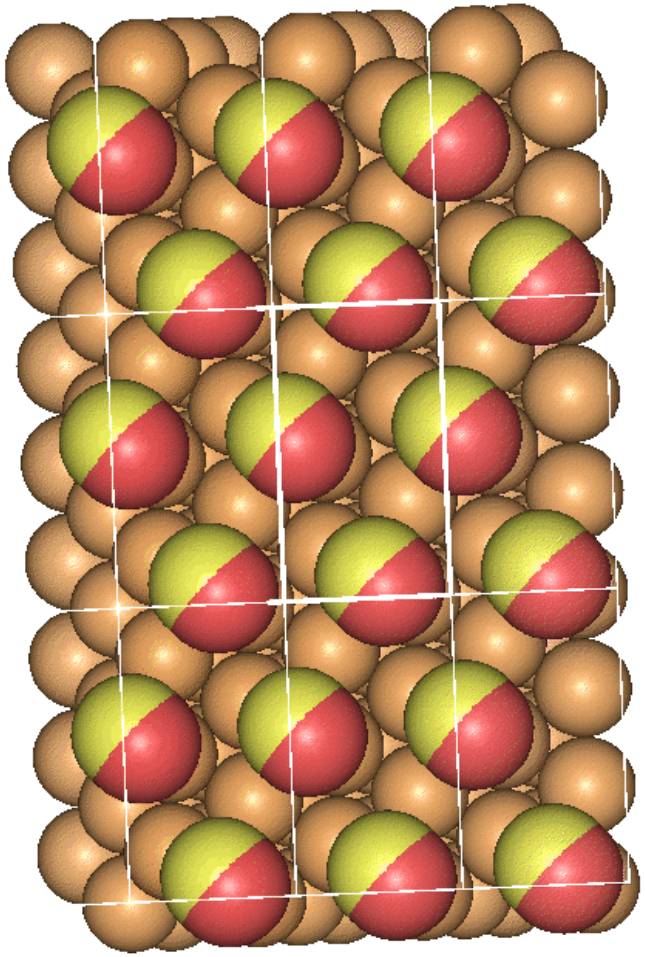
Methane thiol



Ethane thiol



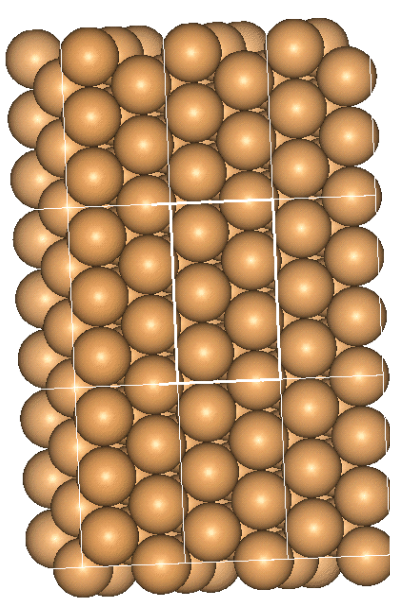
The difference between methane and ethane thiol



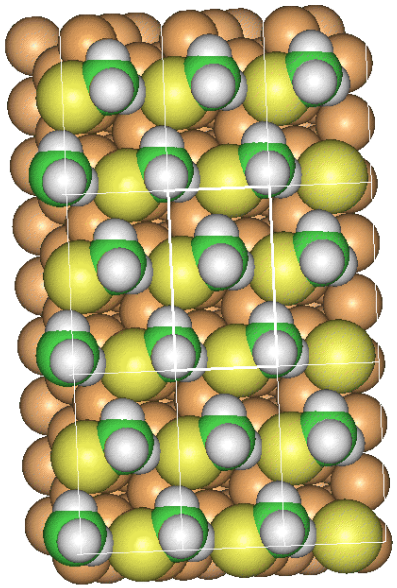
Ethane thiol
Fcc bridge site
Two au atoms

Methane thiol
Fcc hollow site
Three Au atoms

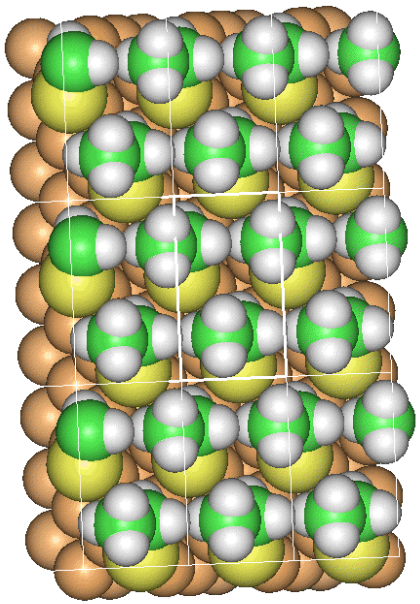
Comparing different chain lengths on Au(111)



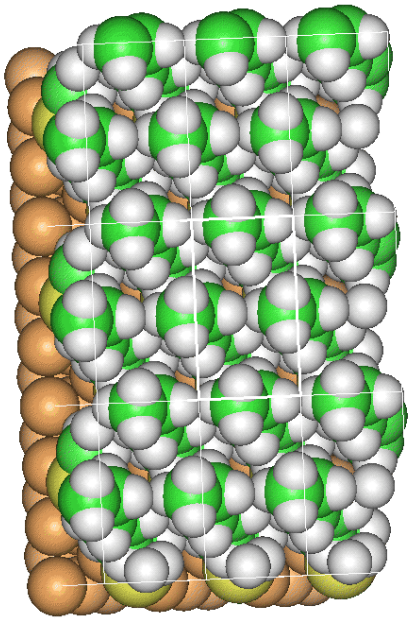
Au(111)



SCH_3 on Au(111)

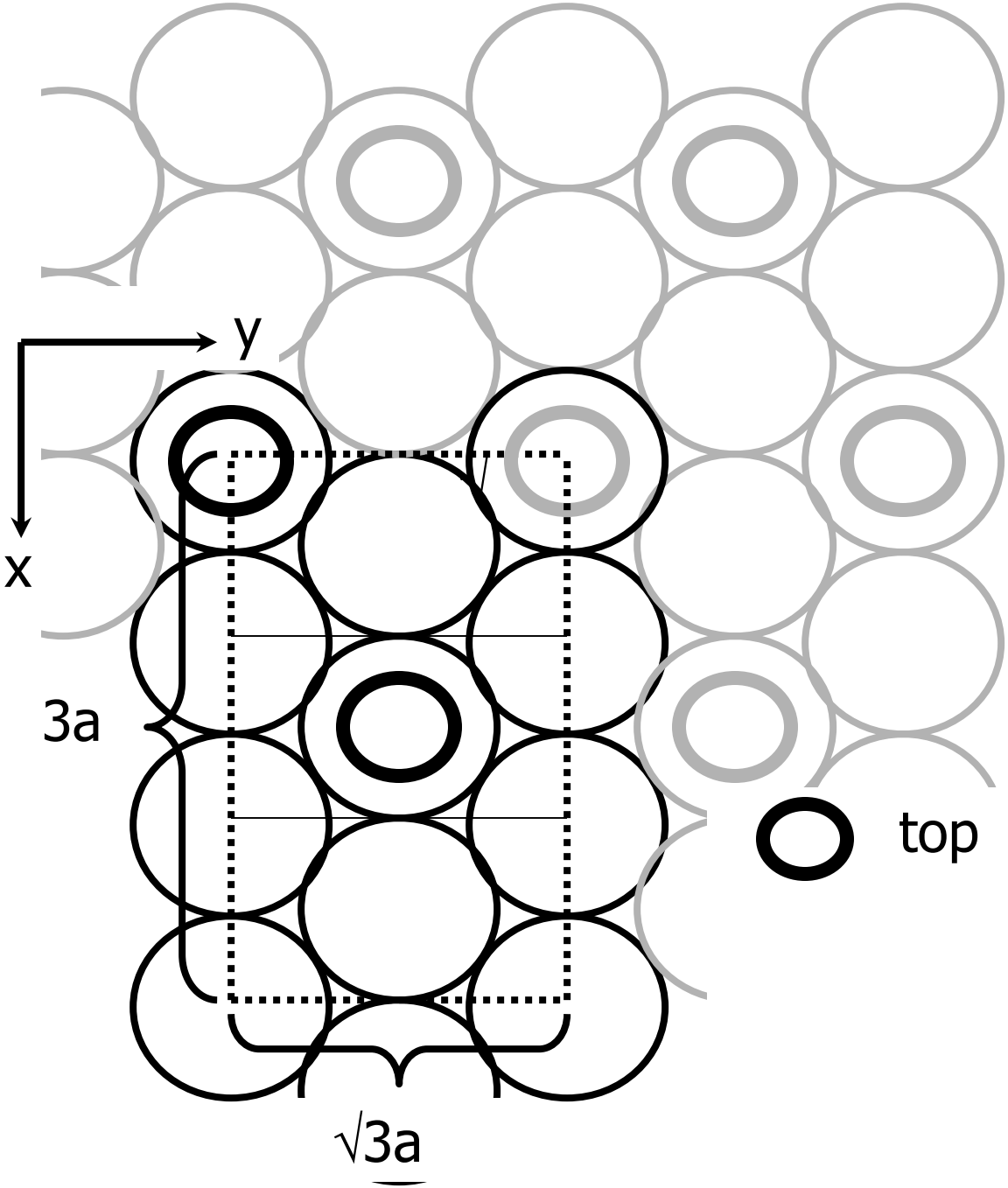


SC_2H_5 on Au(111)



SC_6H_{13} on Au(111)

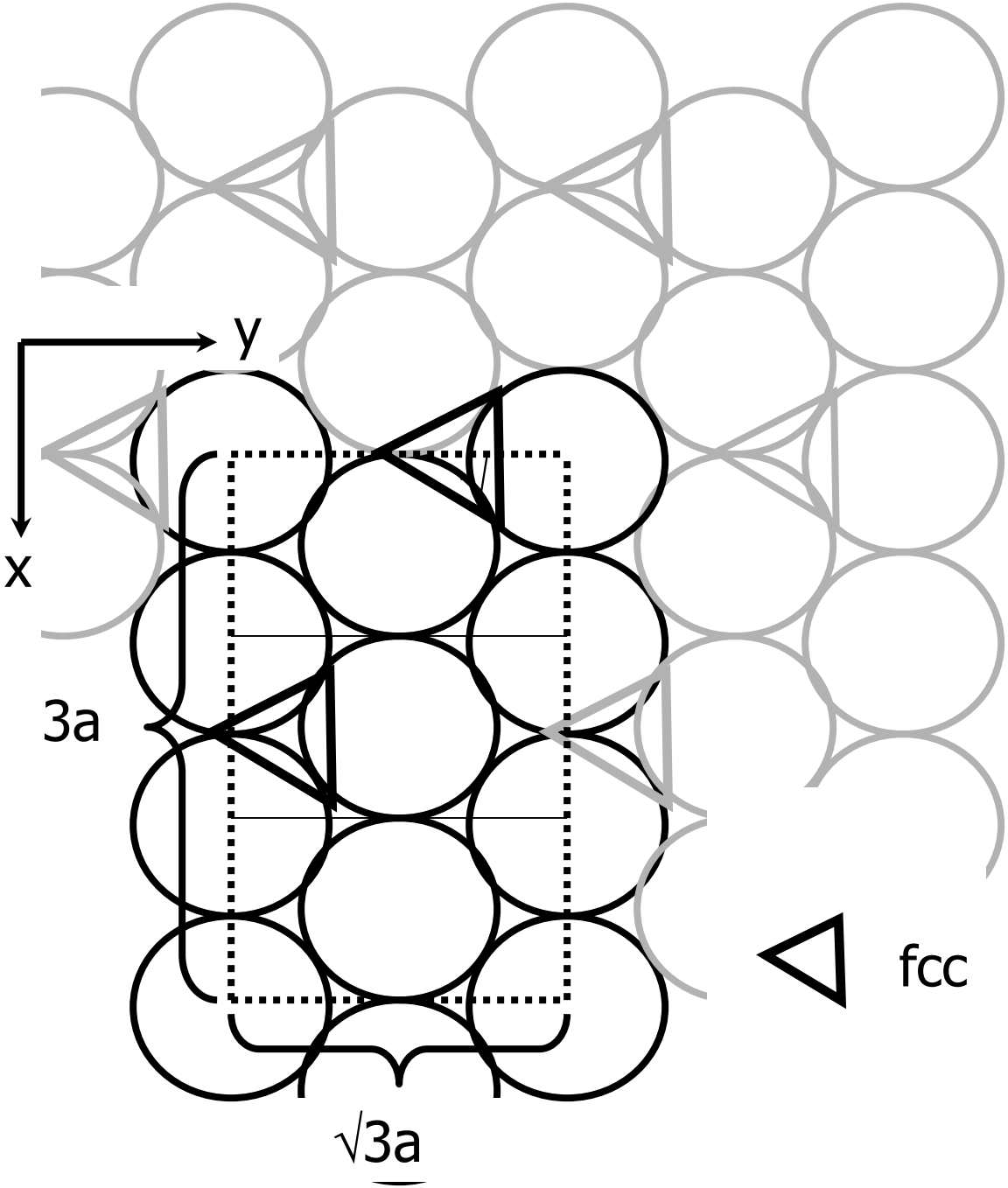
- Geometry optimize surface adlayer (fixed Au)
- Create models for fcc, top and bridge
- Calculate potential energy surface



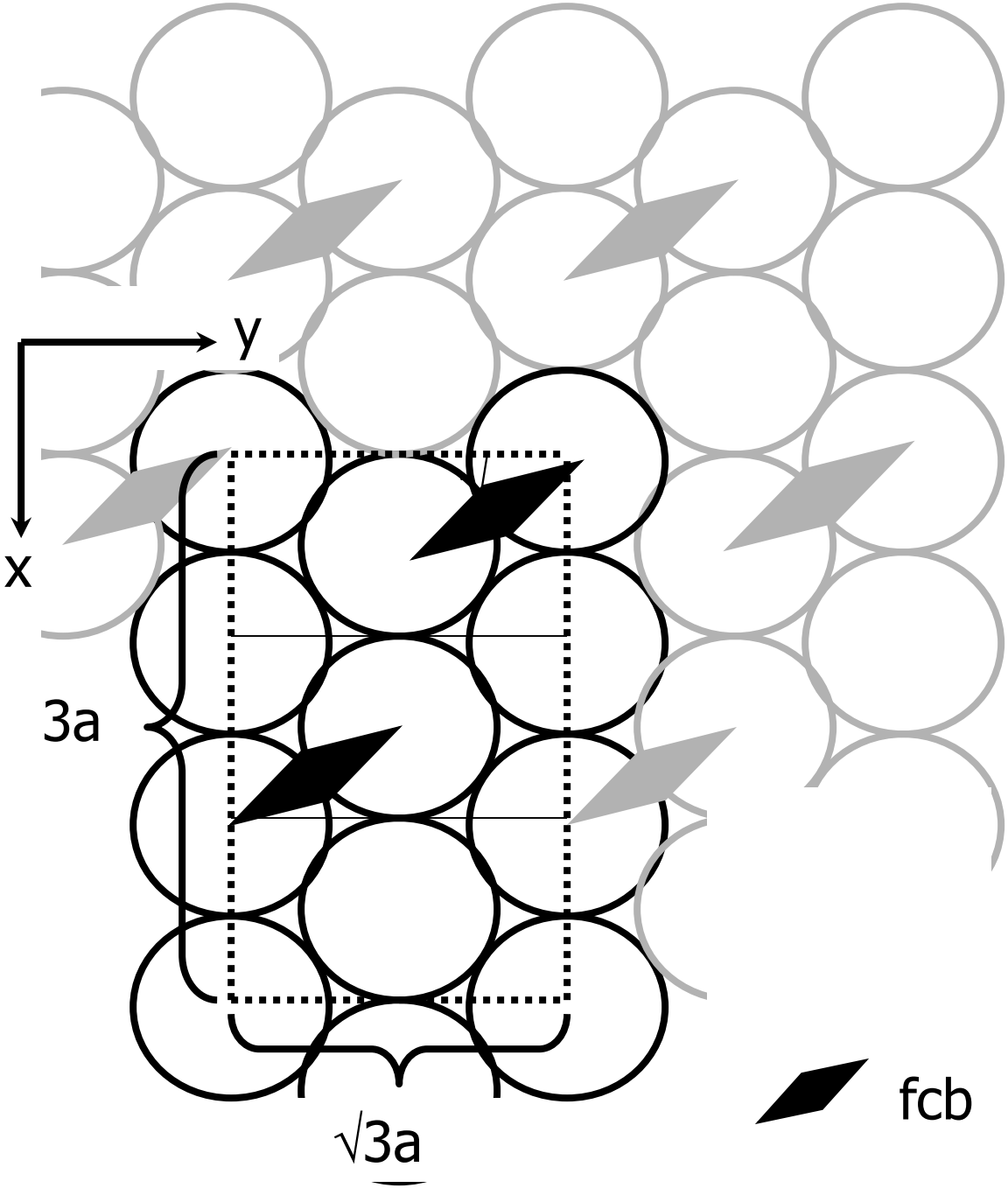
Binding sites on Au(111)

Unit cell consists of 18 Au atoms and two adsorbate molecules.

Binding sites on Au(111)



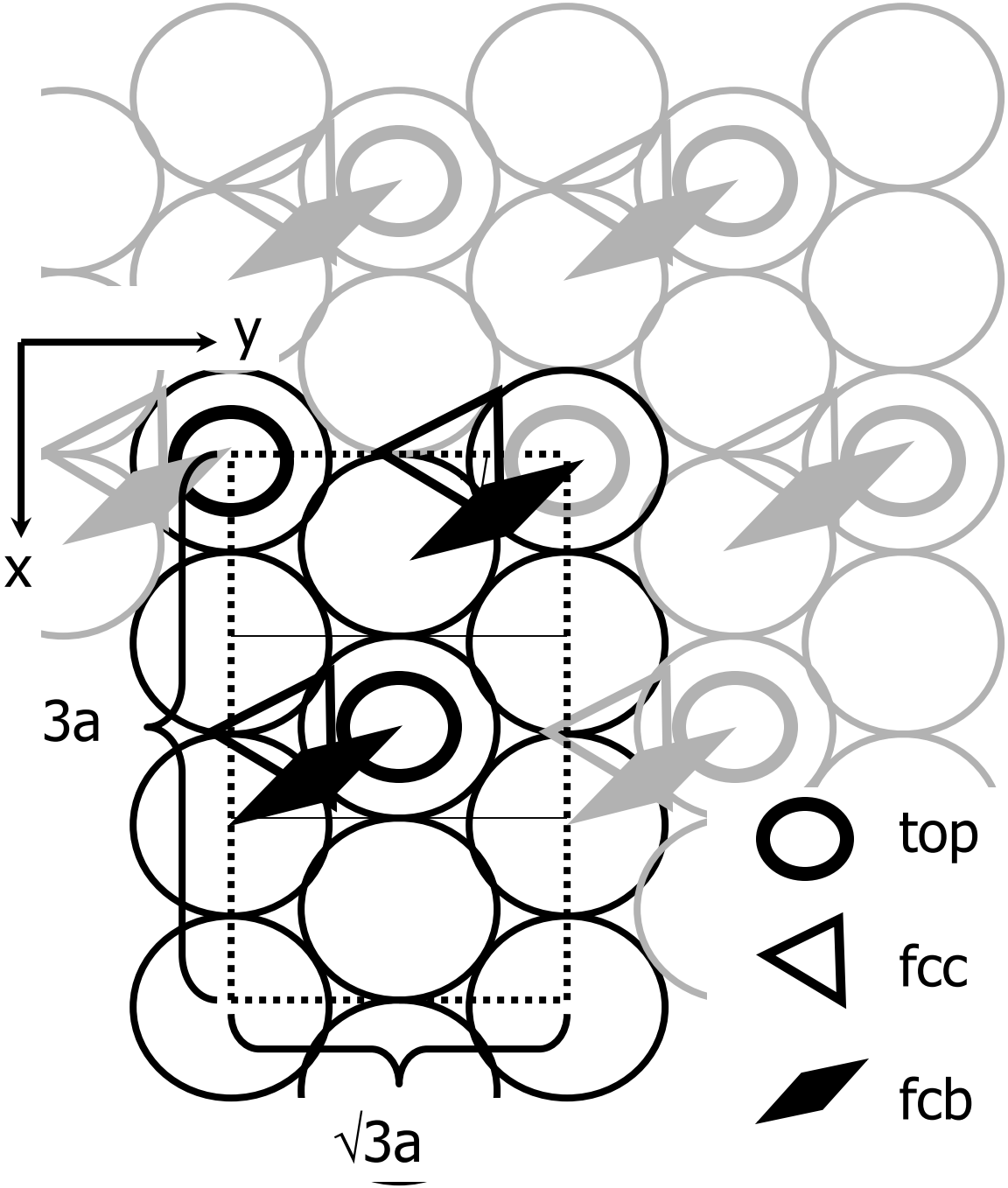
This calculation can be made tractable using effective core potentials (ecp).

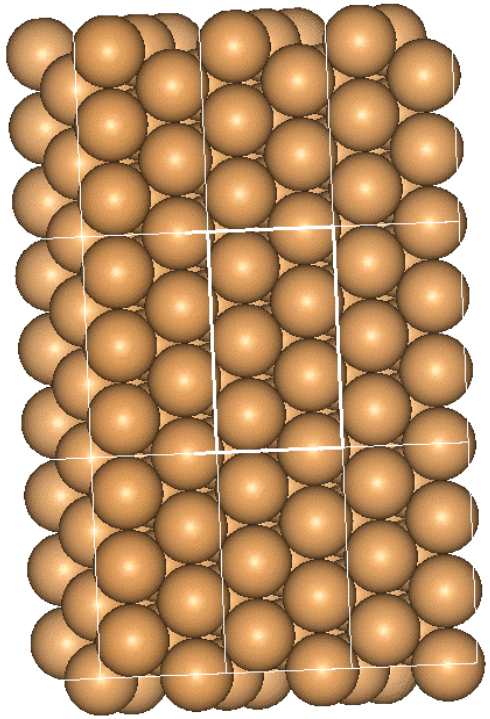


Binding sites on Au(111)

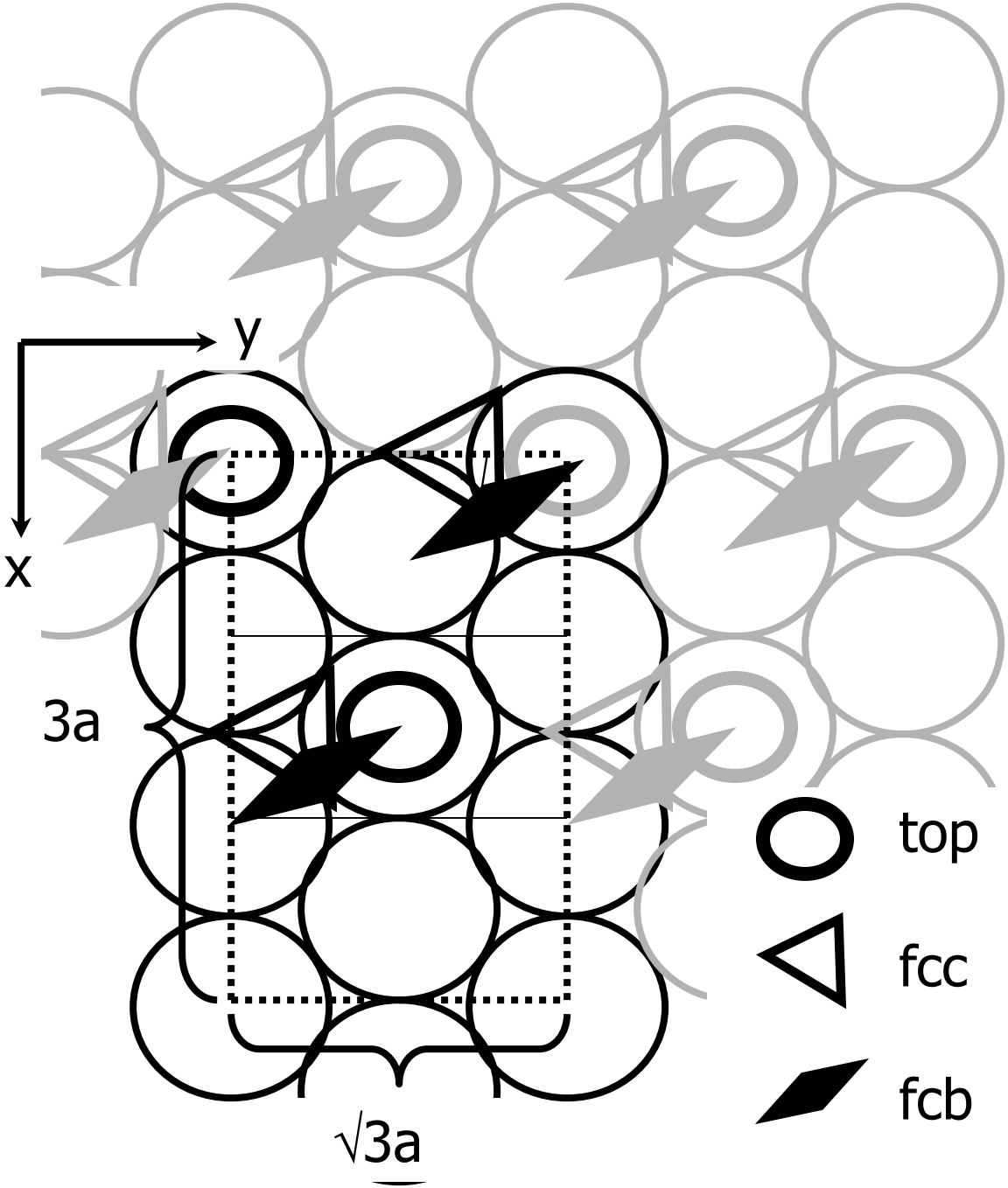
The Au atoms can be fixed in the optimization to save time.

Towards a chemical model of the surface

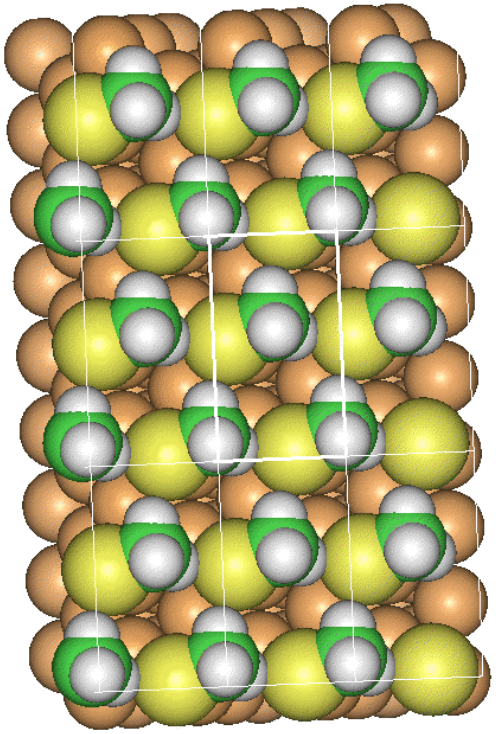




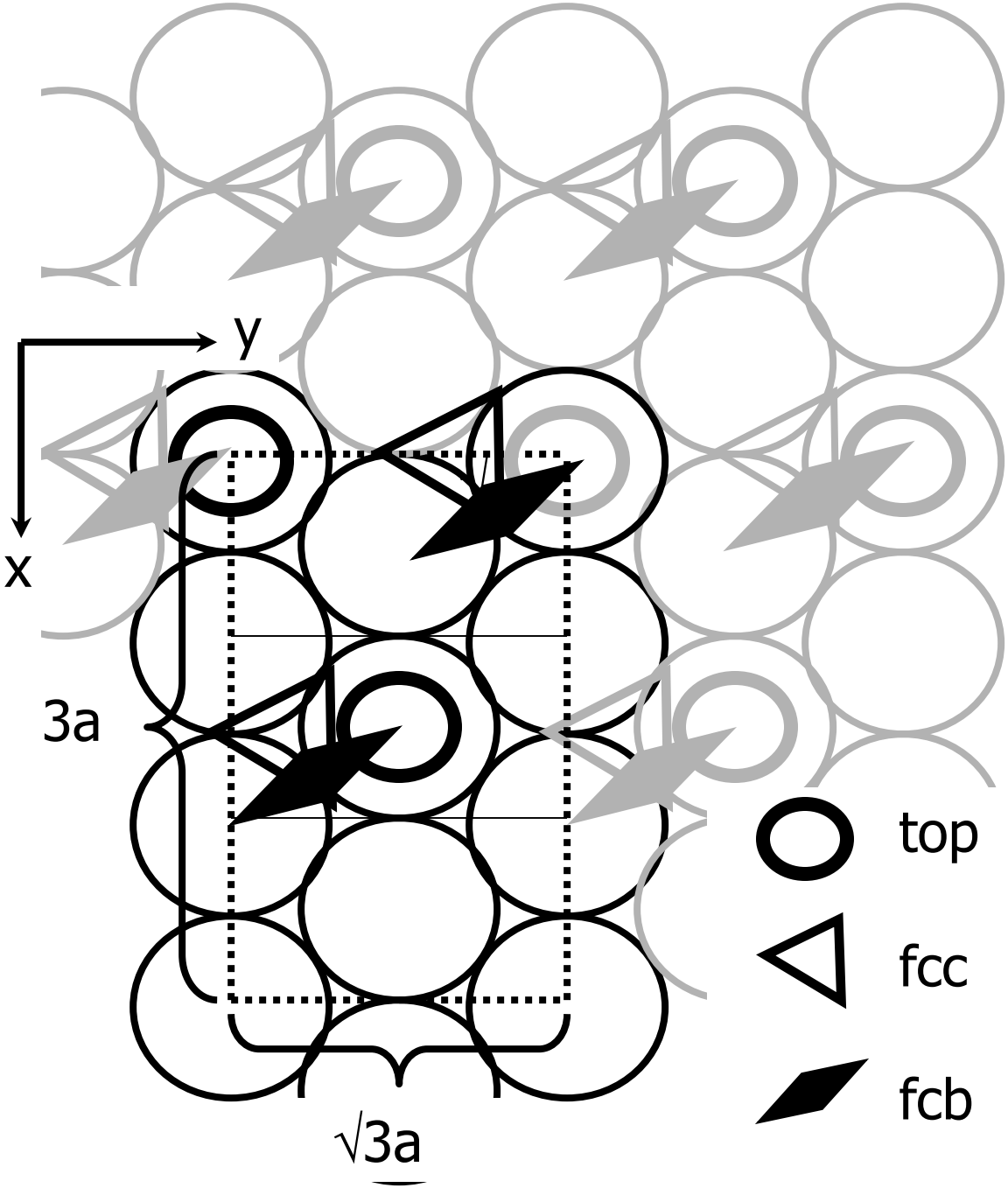
Au(111)



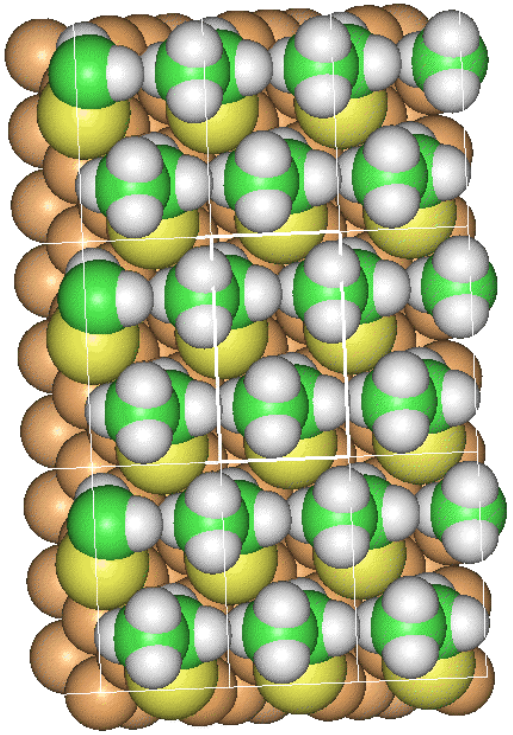
DFT calculations of self-assembled monolayers



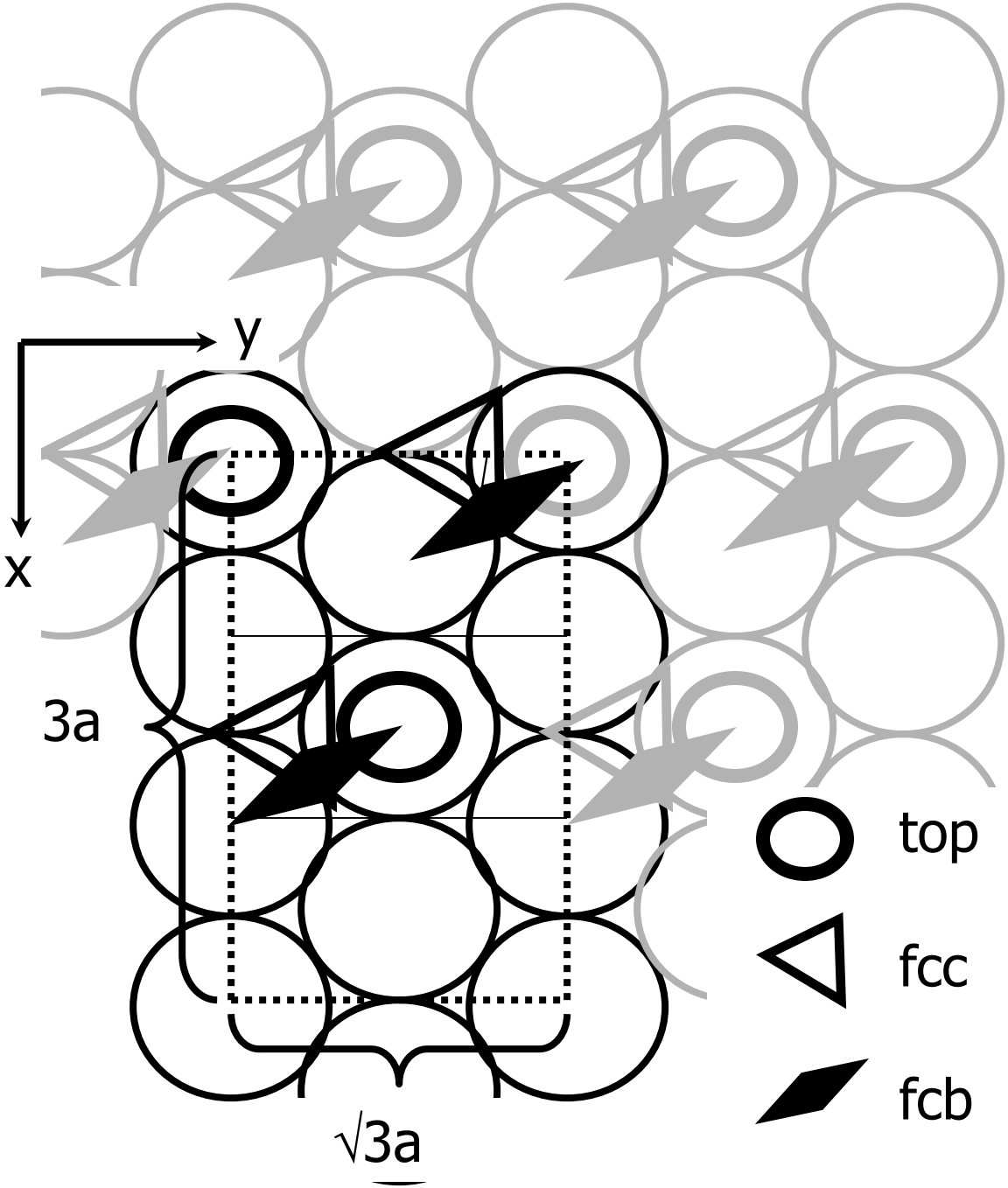
Methane thiol on Au(111)



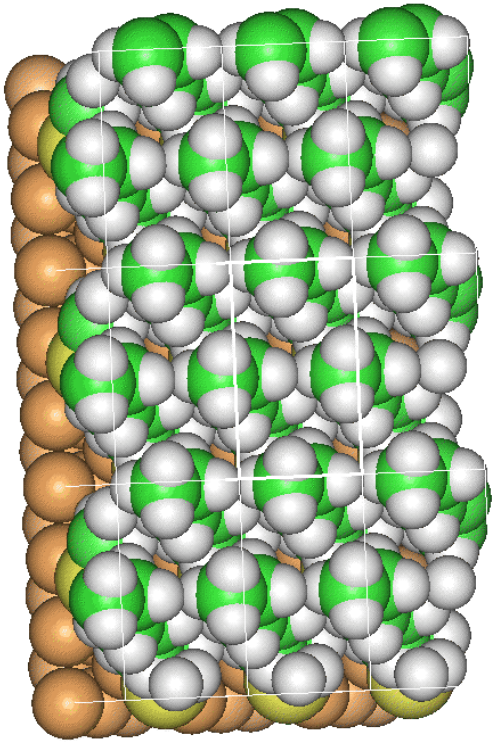
Model energetics and structure...



Ethane thiol on Au(111)

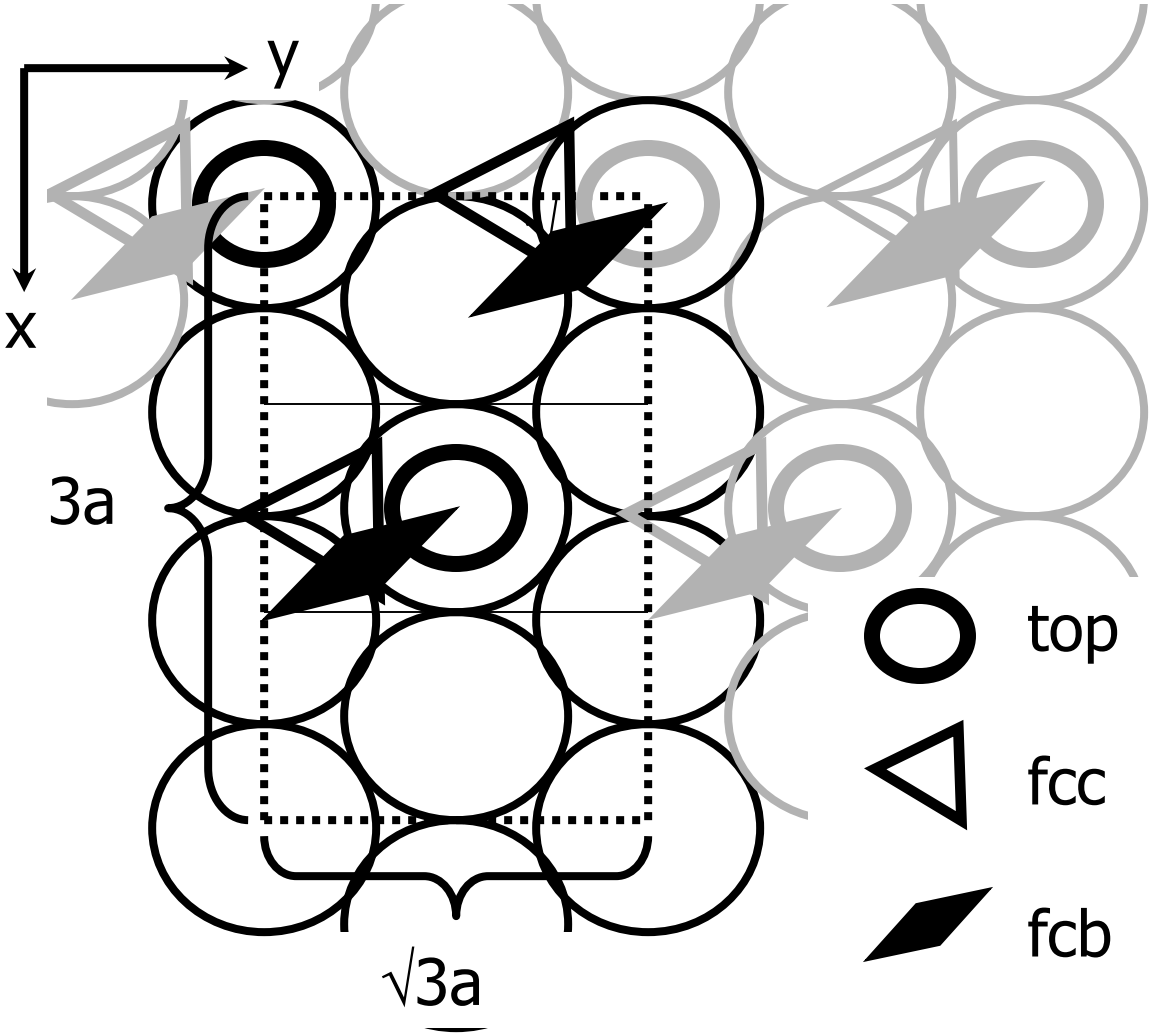


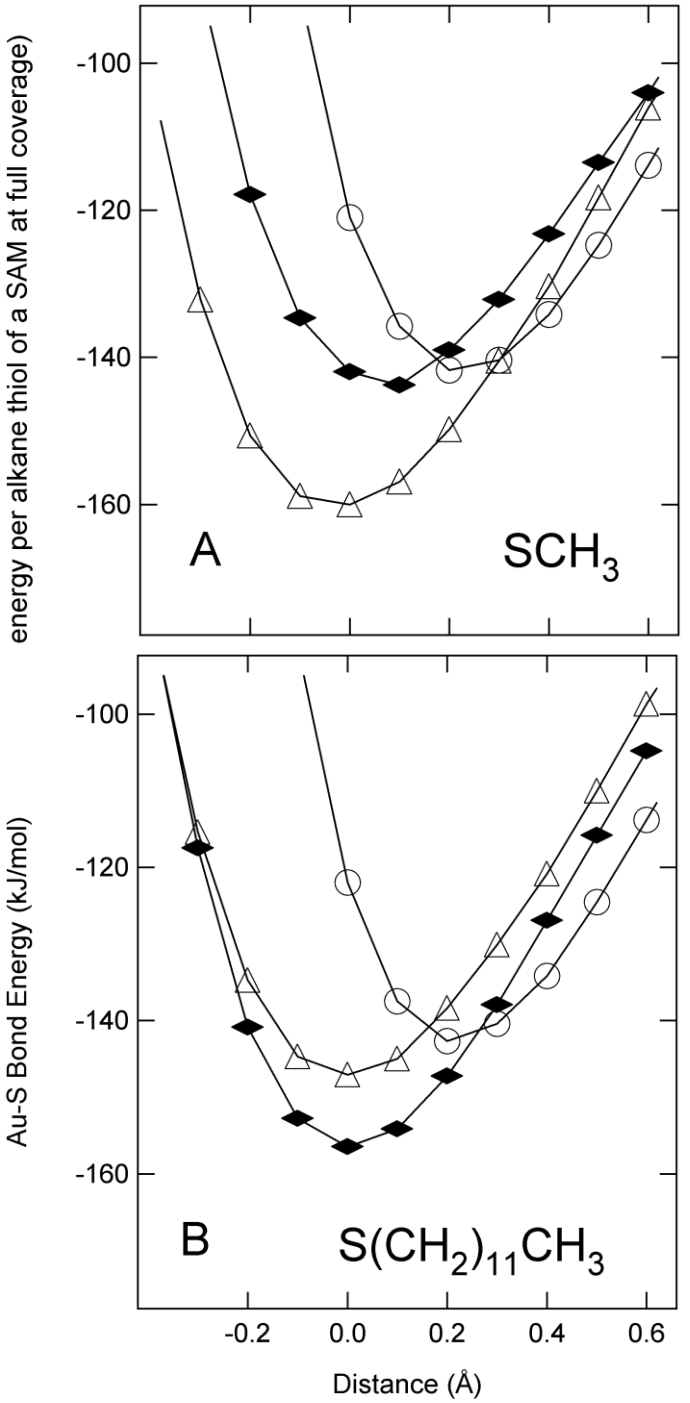
...as a function of chain length.



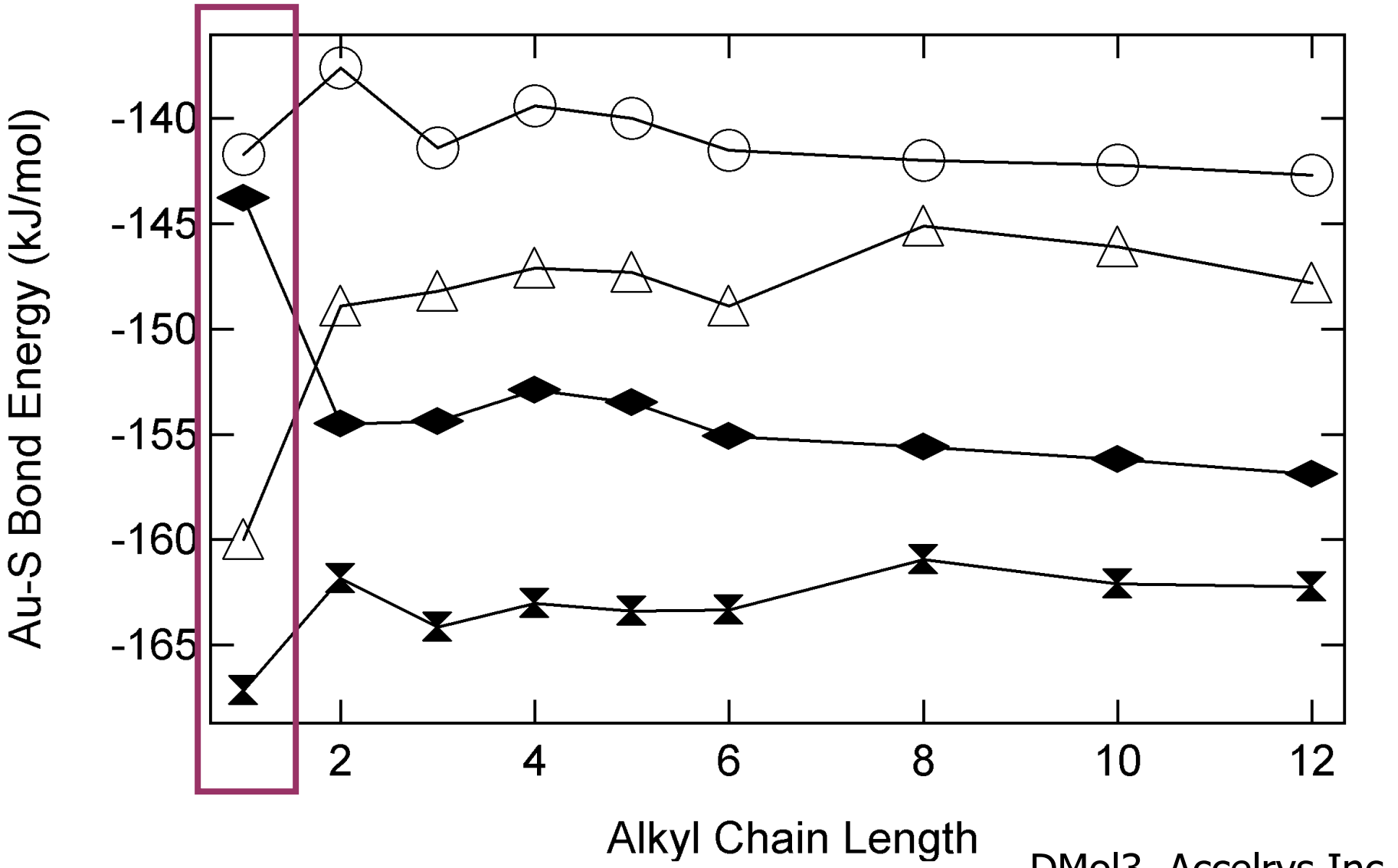
Hexane thiol on Au(111)

Calculation of Potential Energy of an Adsorbate on a Au(111) Surface



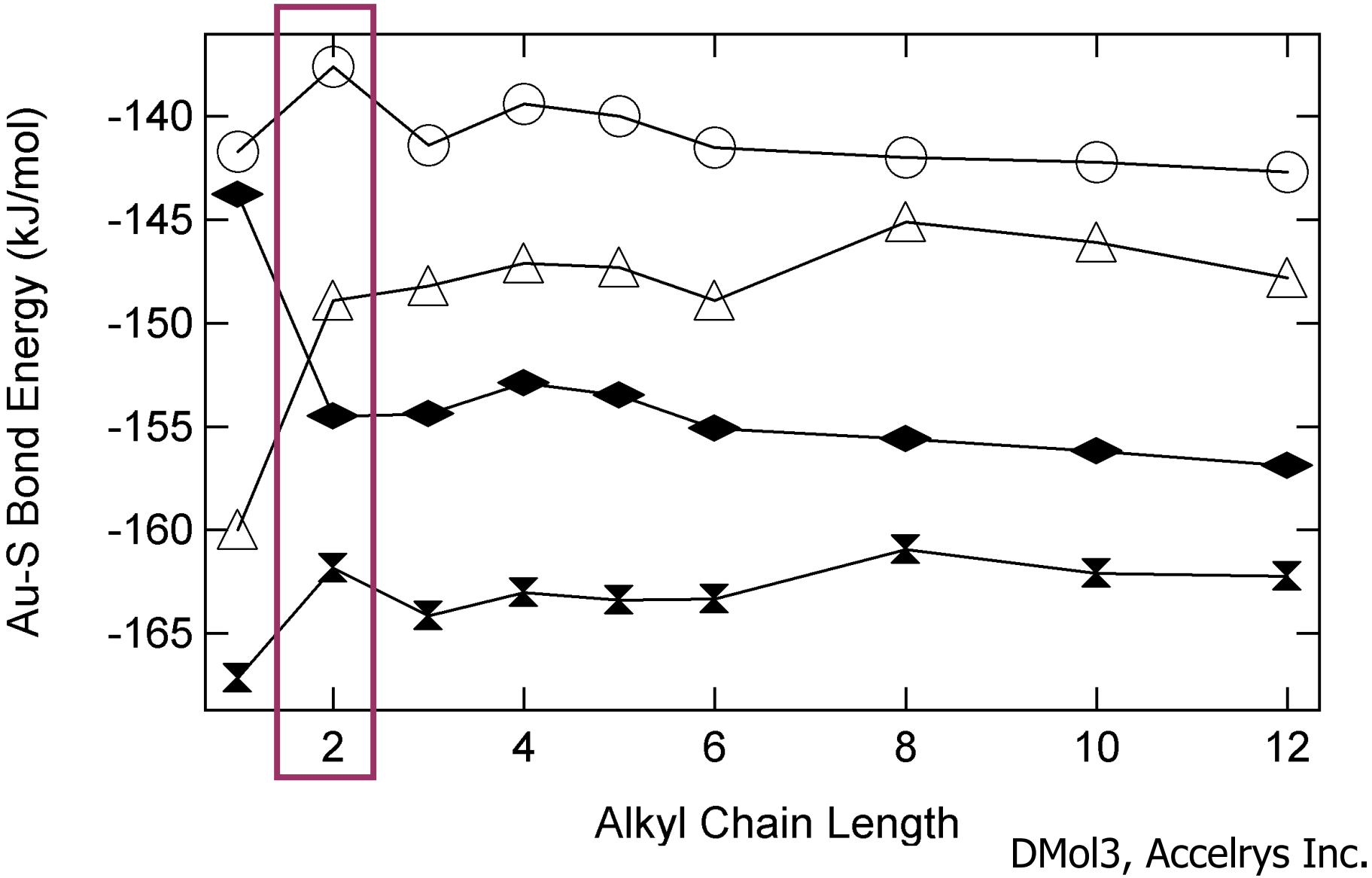


Methane thiol is anomalous



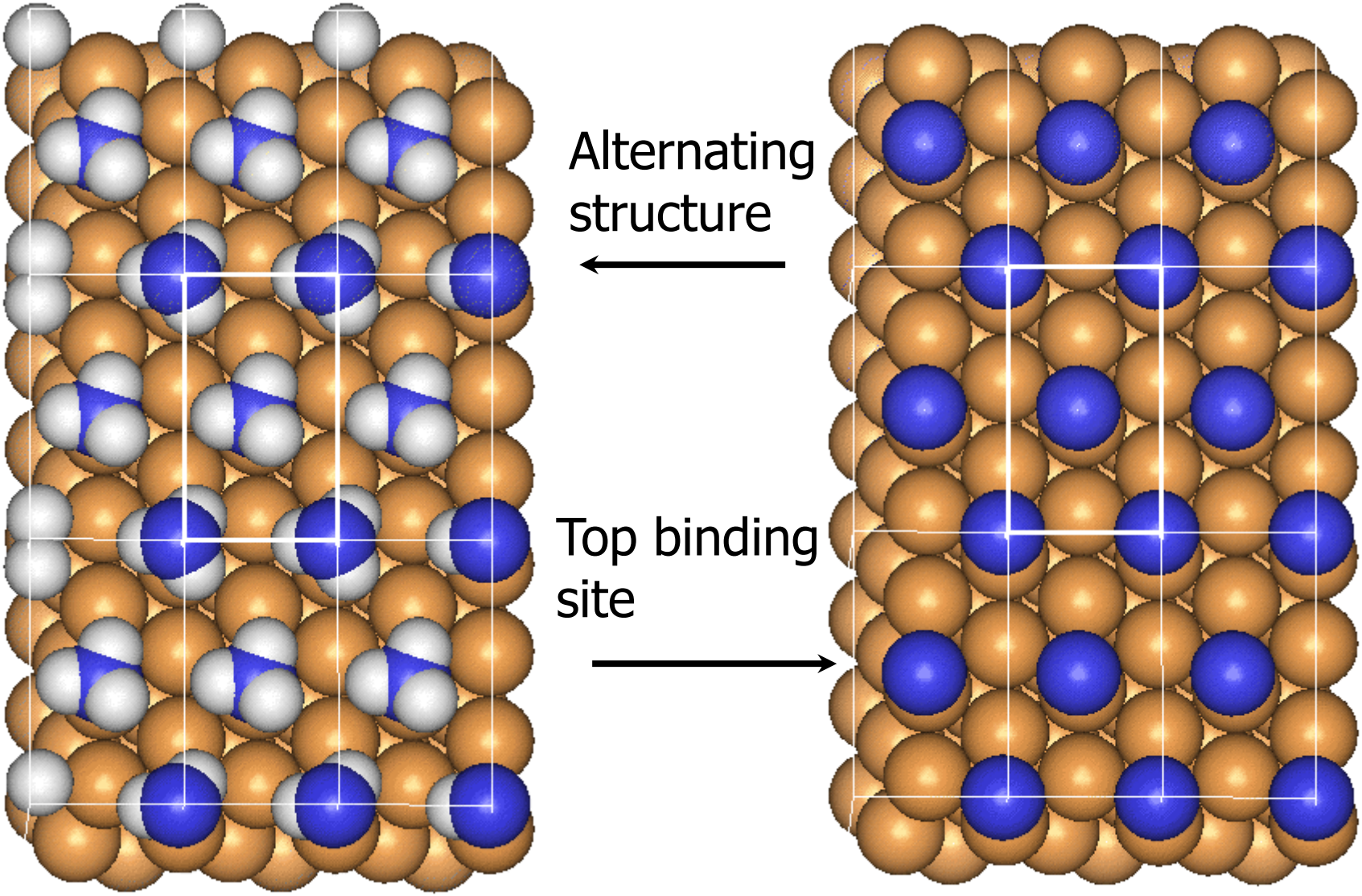
DMol3, Accelrys Inc.

Ethane thiol follows the trend

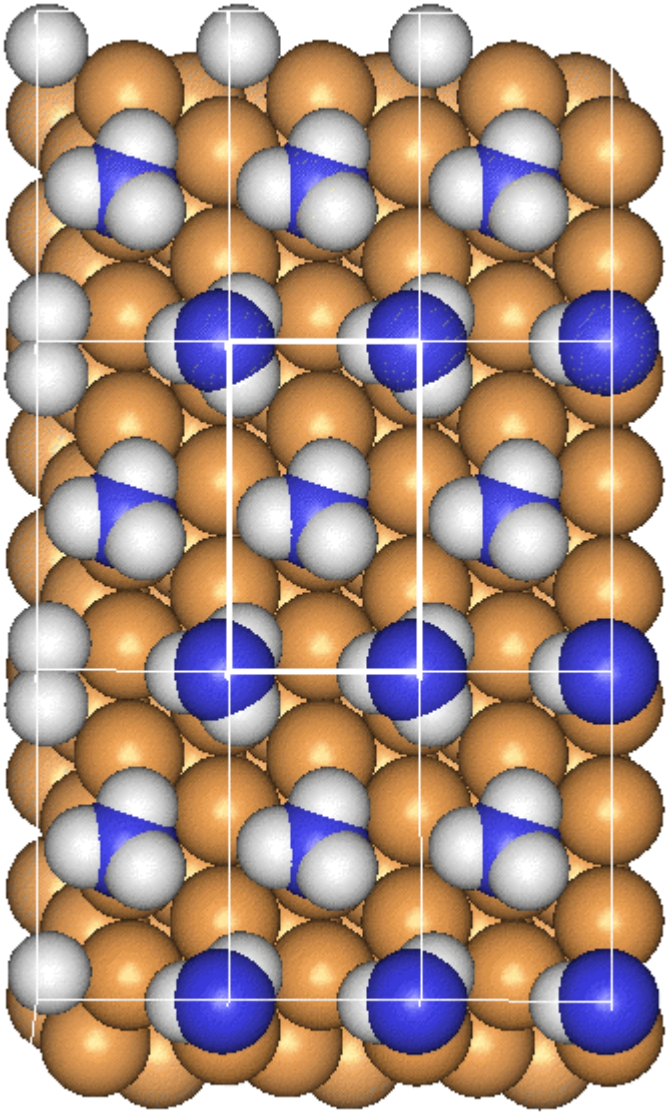


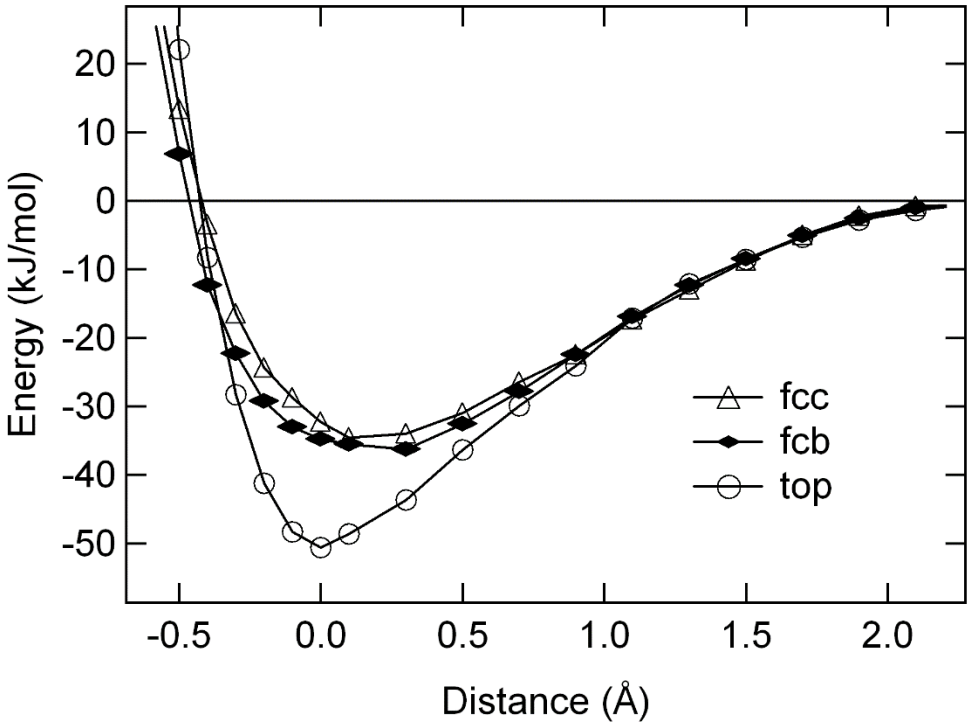
DMol3, Accelrys Inc.

Ammonia adlayer



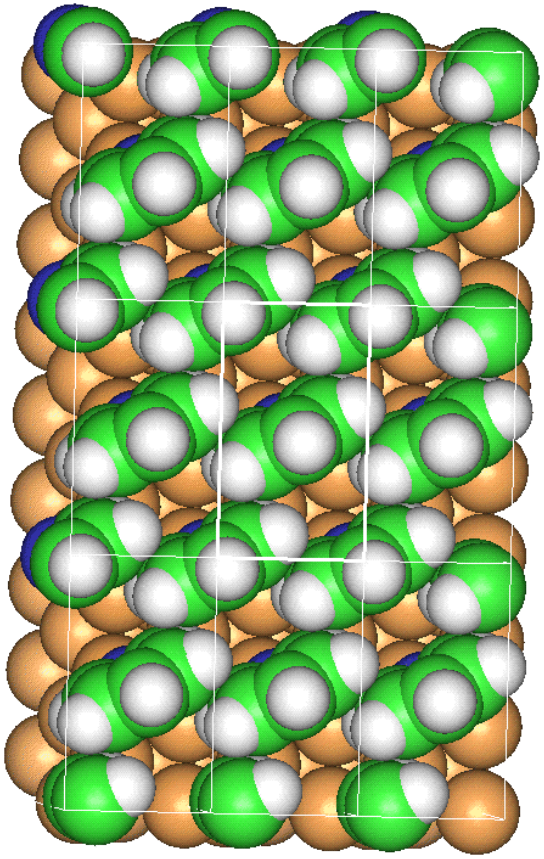
Ammonia adlayer

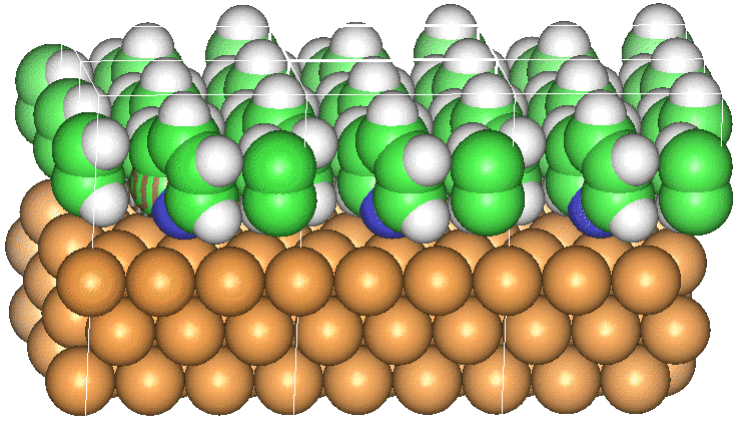


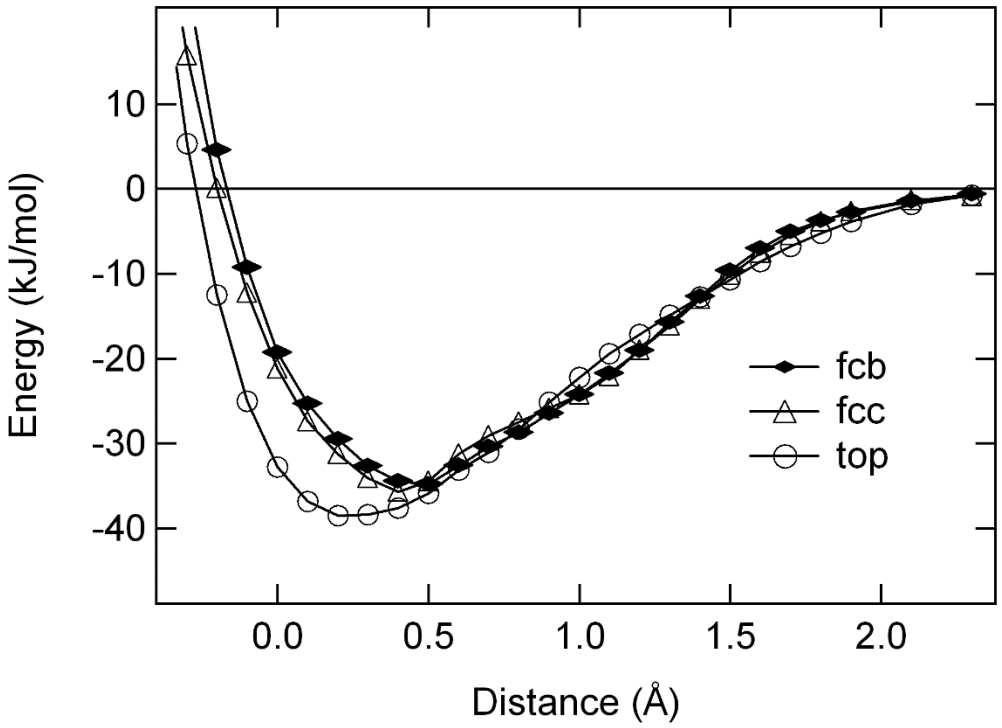


"Up facing" geometry used
Top binding site is favored
Binding is three times weaker than for alkane thiols

Pyridine adlayer

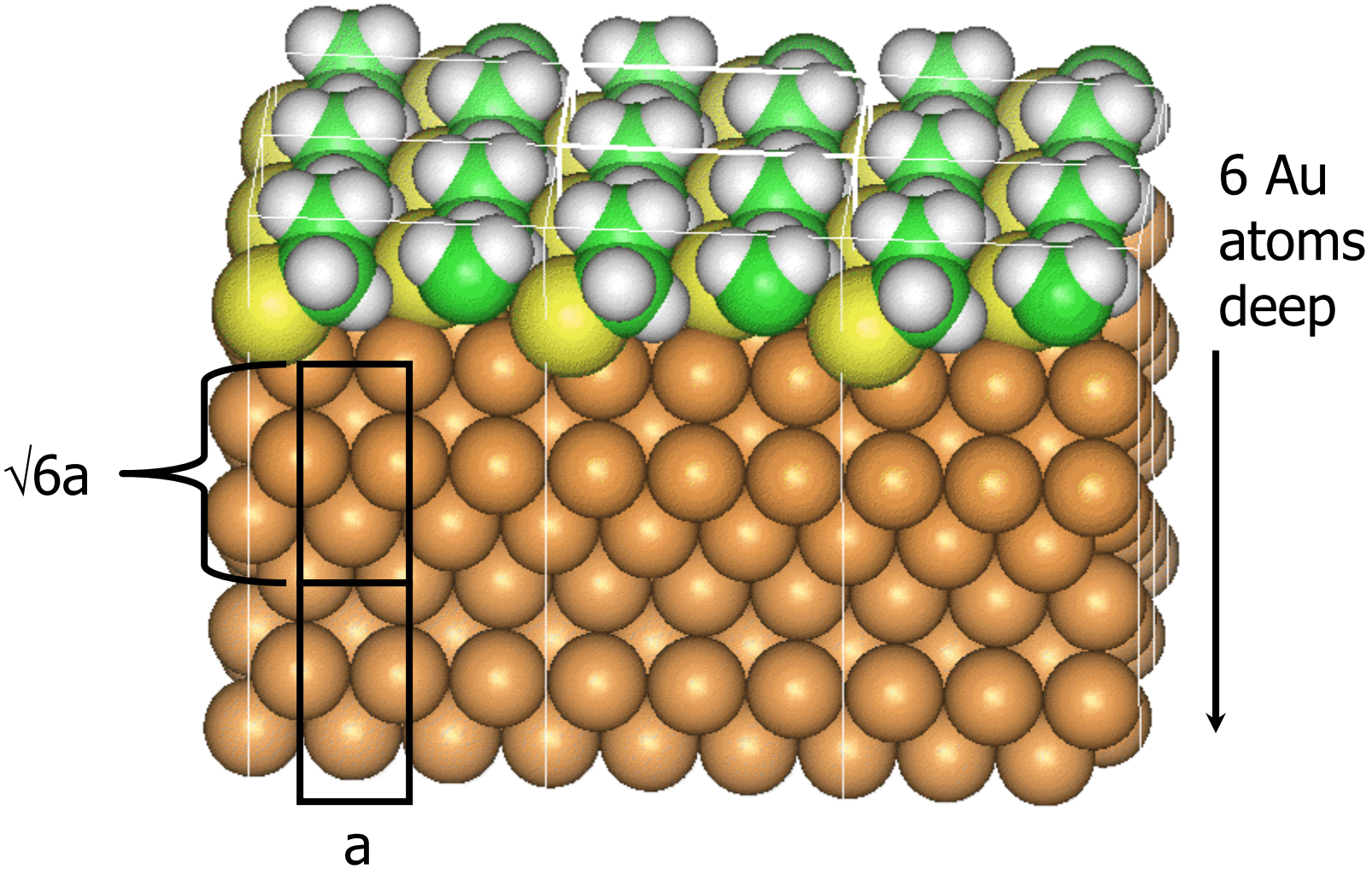






Top binding site is favored.
Binding is three times weaker than for alkane thiols.

Test of the layer effect of Au(111)



The same results are obtained for 3 layers and 6 layers

Structural Results

- Methane thiol on a fixed Au(111) surface shows a preference for the fcc hollow site binding to three Au atoms.

- Ethane thiol and all higher alkane Thiols bind instead at the fcc bridge site to two Au atoms.

- Ethane thiol is the least expensive model for larger calculations.

- The top site is favored for ammonia and pyridine.

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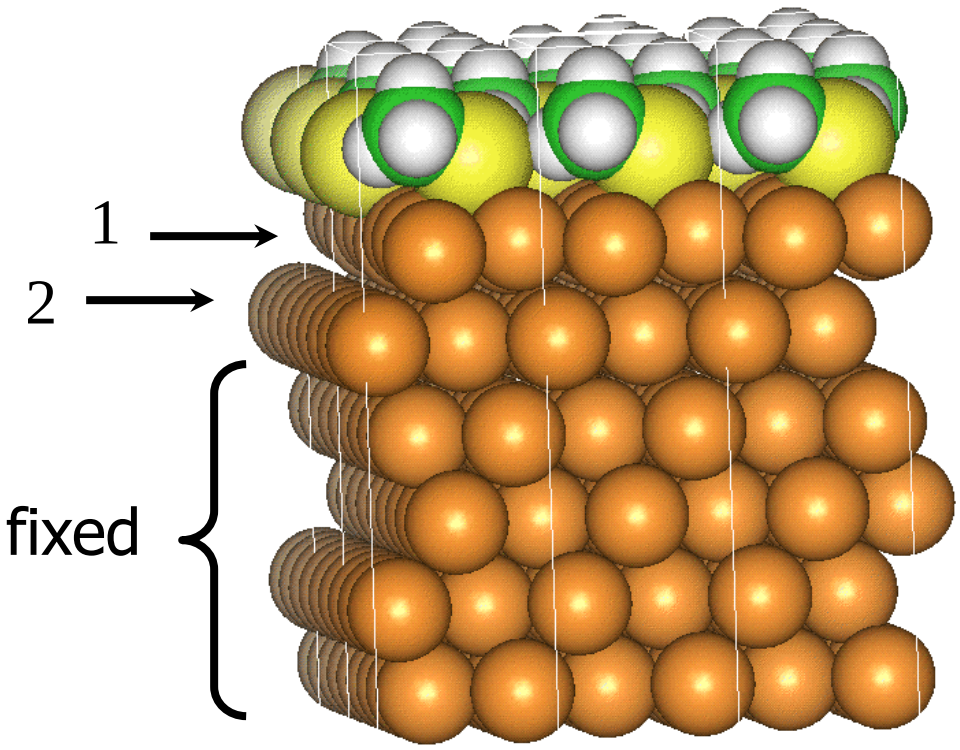
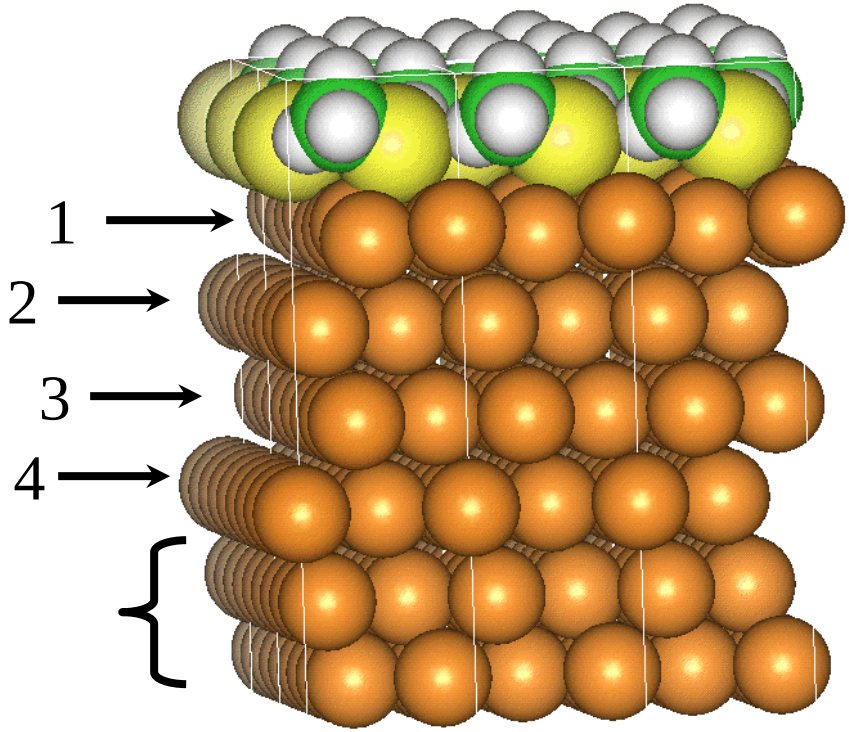
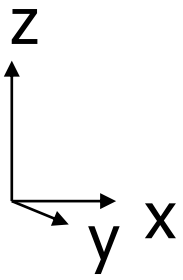
Methane thiol adlayer reconstruction

Model 1



Model 2





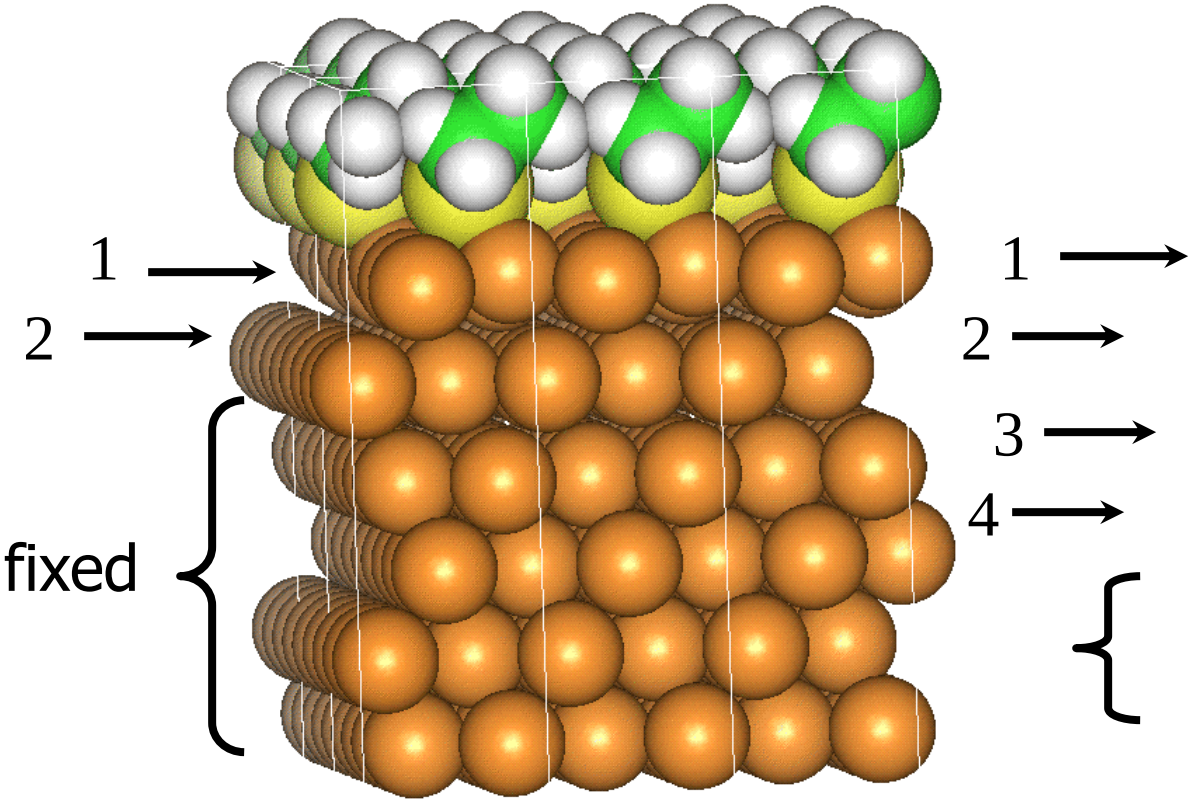
x	y	z
0.65	0.43	0.59
0.46	0.39	0.27

x	y	z
-0.10	0.07	1.30
0.04	-0.06	0.93
-0.01	-0.07	0.61
0.00	-0.04	0.30

Ethane thiol adlayer reconstruction

Model 1

Model 2



x y z

x y z

-

z

y x

Reconstruction results

Methane thiol causes a rearrangement of Au atoms to create a fcc bridge binding site. The difference in structure appears to be a subtle undulation in the Au atoms while maintaining their overall hexagonal packing. The net effect is create a less dense surface layer of the Au atoms. The Au adlayer is 1 Å higher than for the fixed gold calculation in the same unit cell. These conclusions also hold for ethane and hexane thiol.

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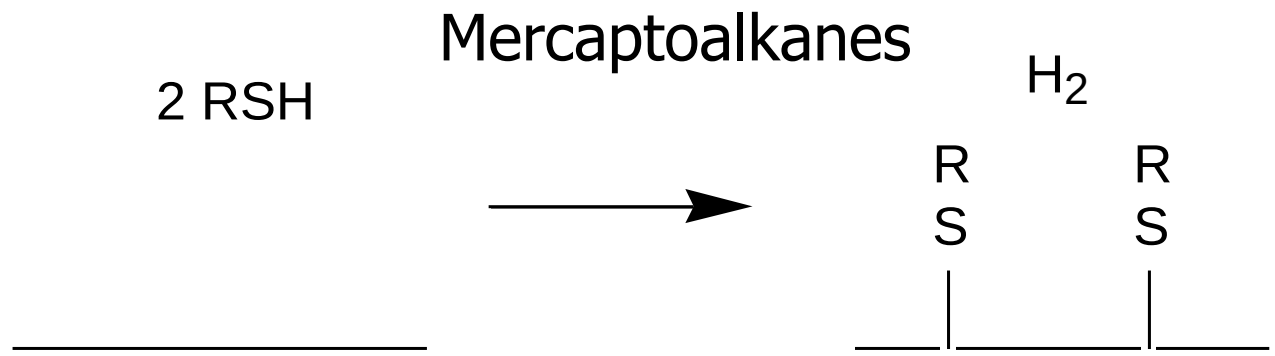
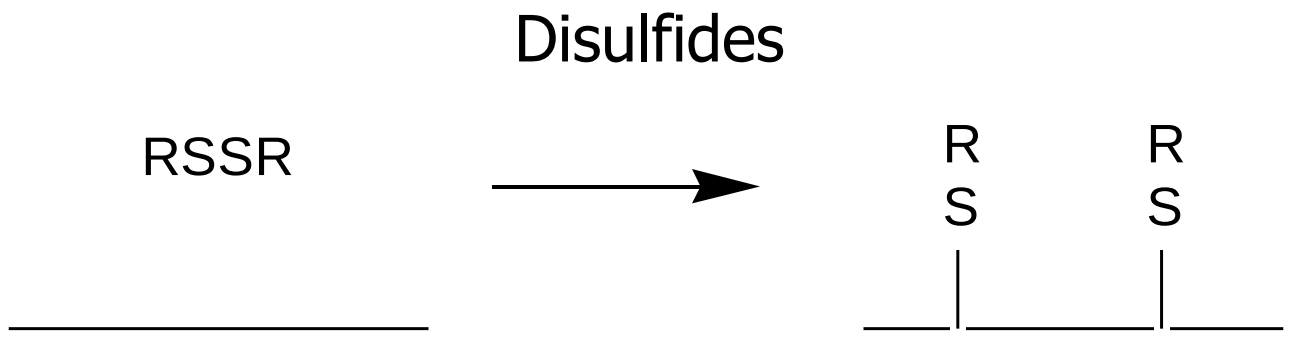
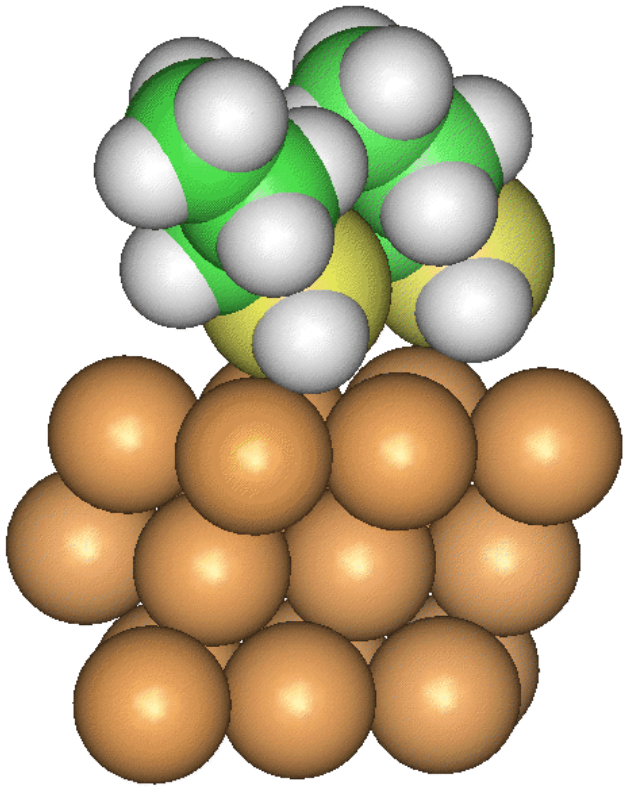
Possible mechanisms for formation of alkane thiol self-assembled monolayers

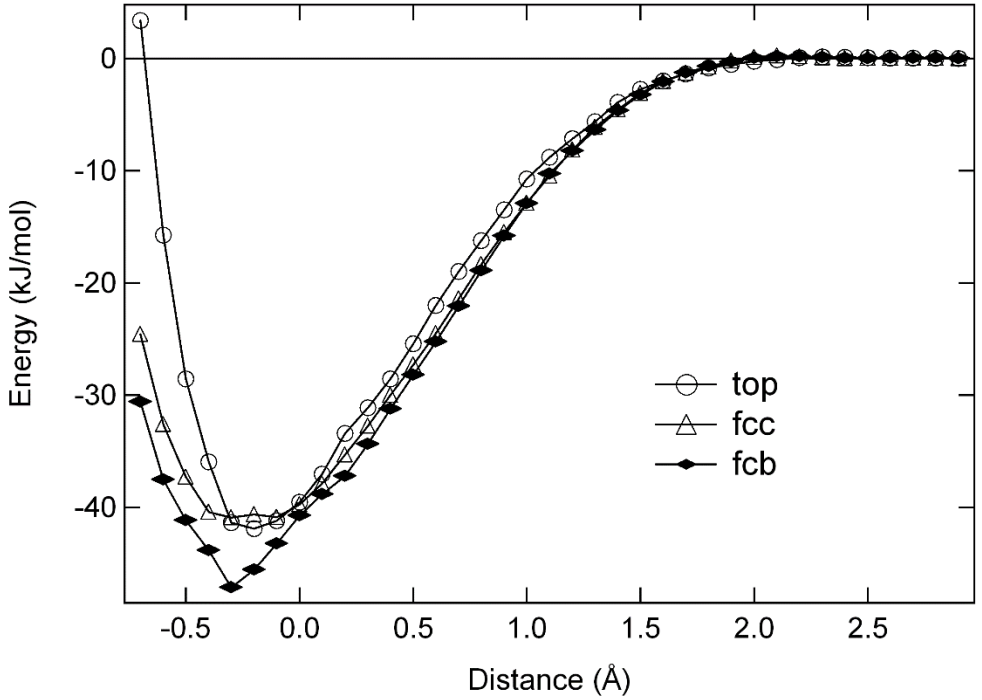
Where do the hydrogens go?





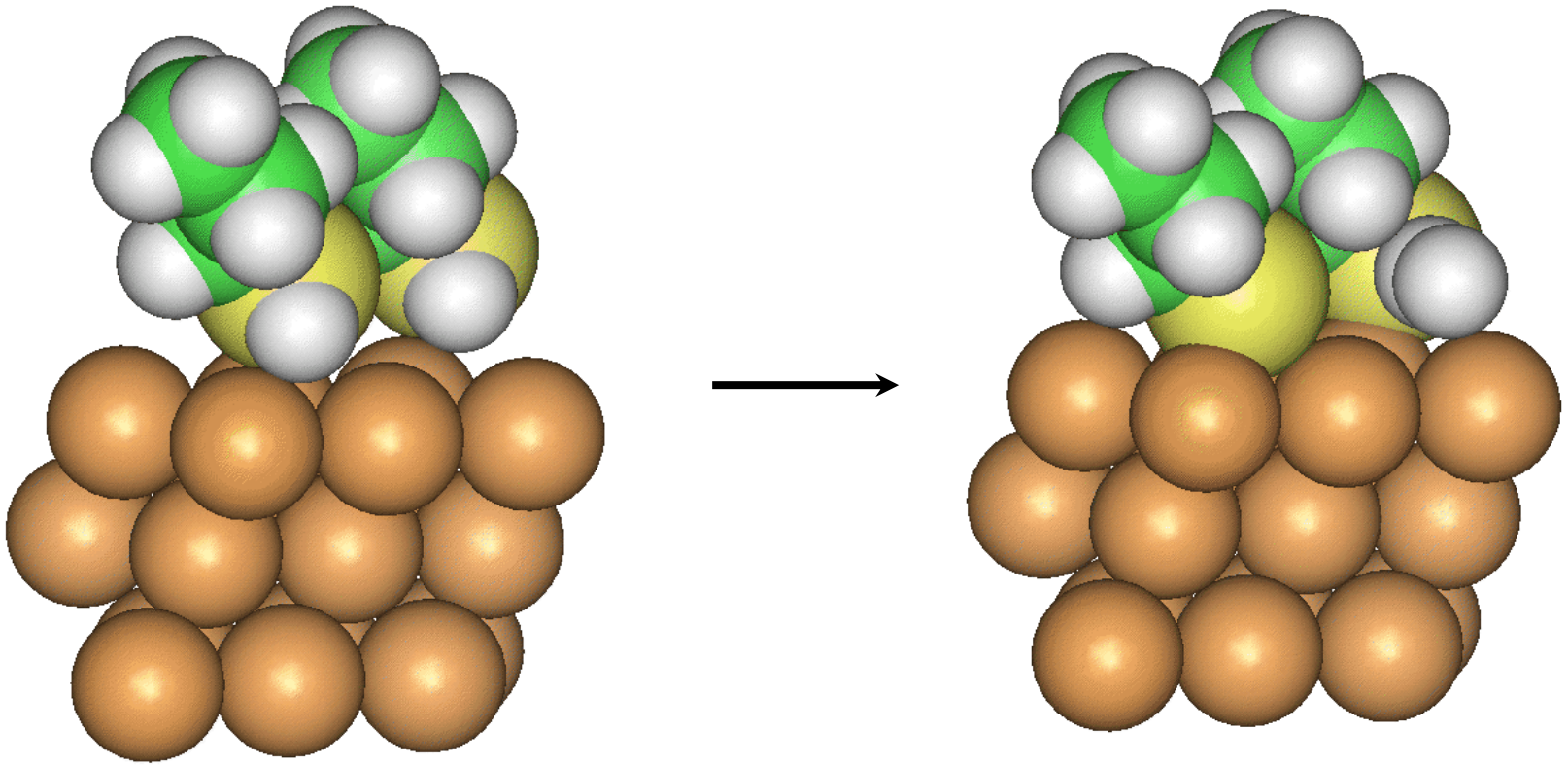
Propane mercaptan on Au(111)





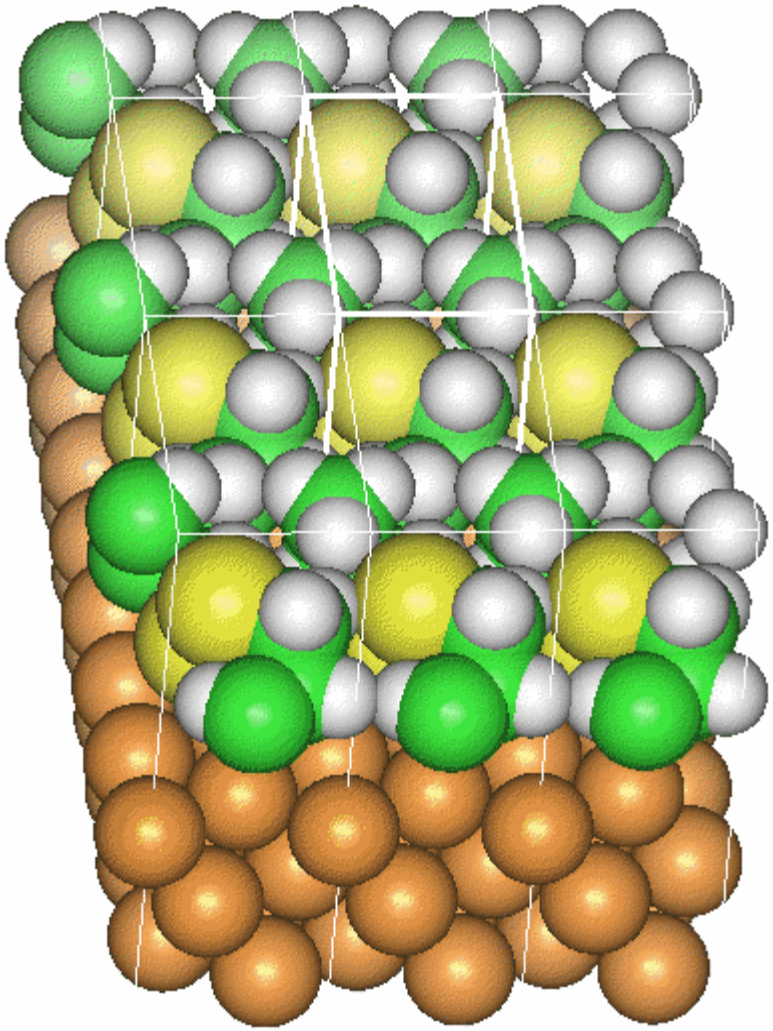
Binding strength is of the same order as that for ammonia or pyridine. However, the fcc bridge site is favored as observed for thiols.

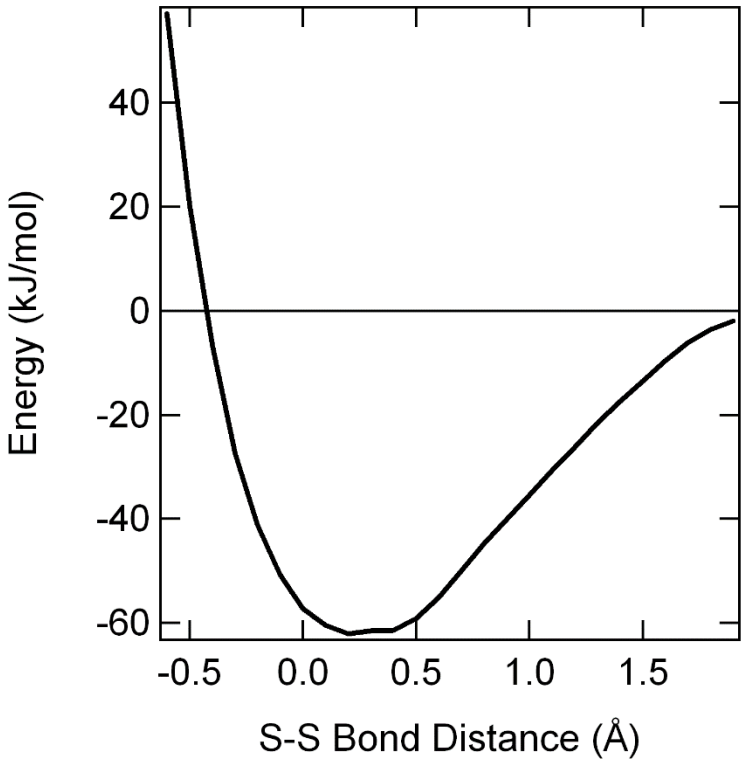
Formation of H_2 on the Au(111) surface



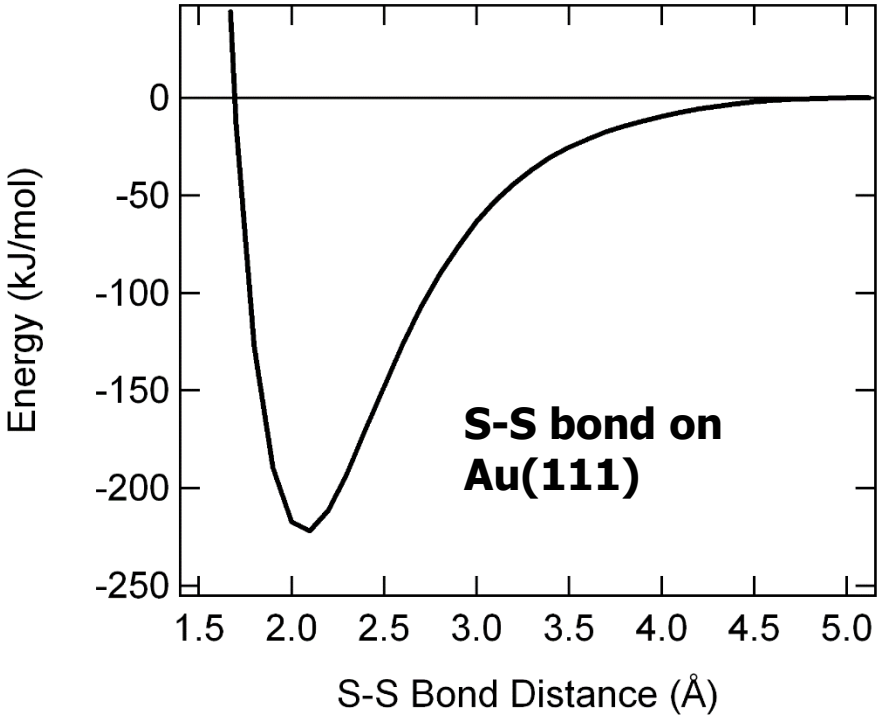
Mercaptan Reactant	Binding energy	Thiol Product	Binding energy	Reaction energy
2 MethylSH	-1611.8	2 MethaneS + H_2	-1581.3	30.5
2 EthylSH	-4154.4	2 EthaneS + H_2	-4136.3	18.1
2 PropylSH	-6653.1	2 PropaneS + H_2	-6723.1	-70.0
2 ButylSH	-9325.7	2 ButaneS + H_2	-9388.1	-62.4
2 PentylSH	-11847.2	2 PentaneS + H_2	-11917.2	-70.0
2 HexylSH	-14512.0	2 HexaneS + H_2	-14579.7	-67.7

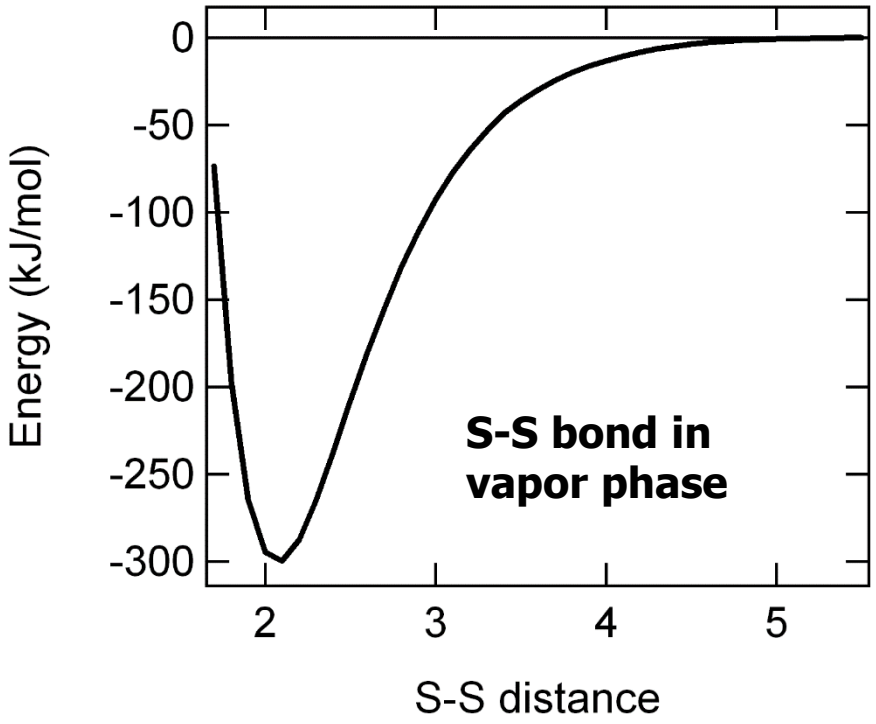
Disulfide binding energy to the Au(111) surface



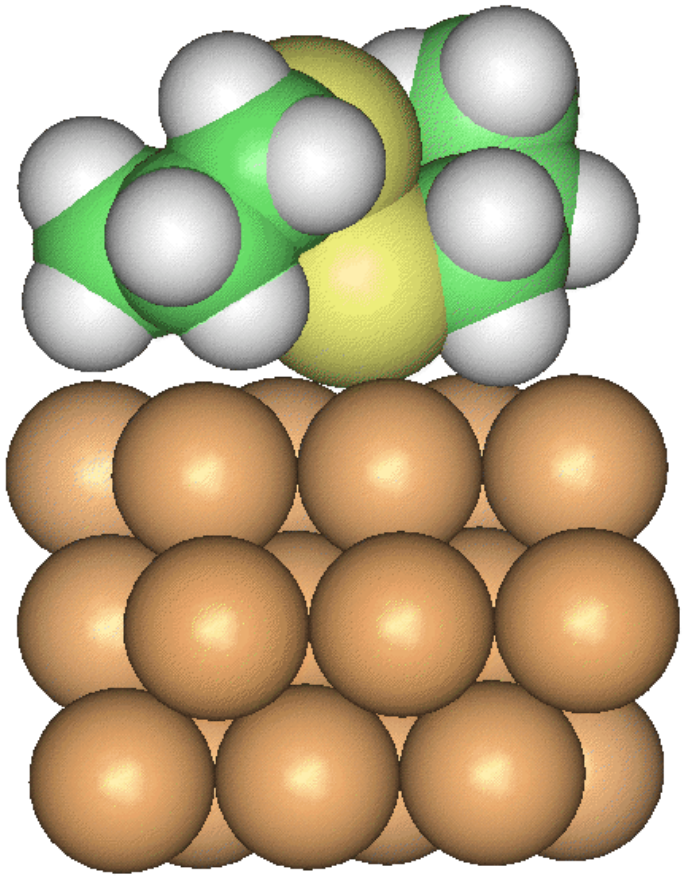


Disulfide bond strength

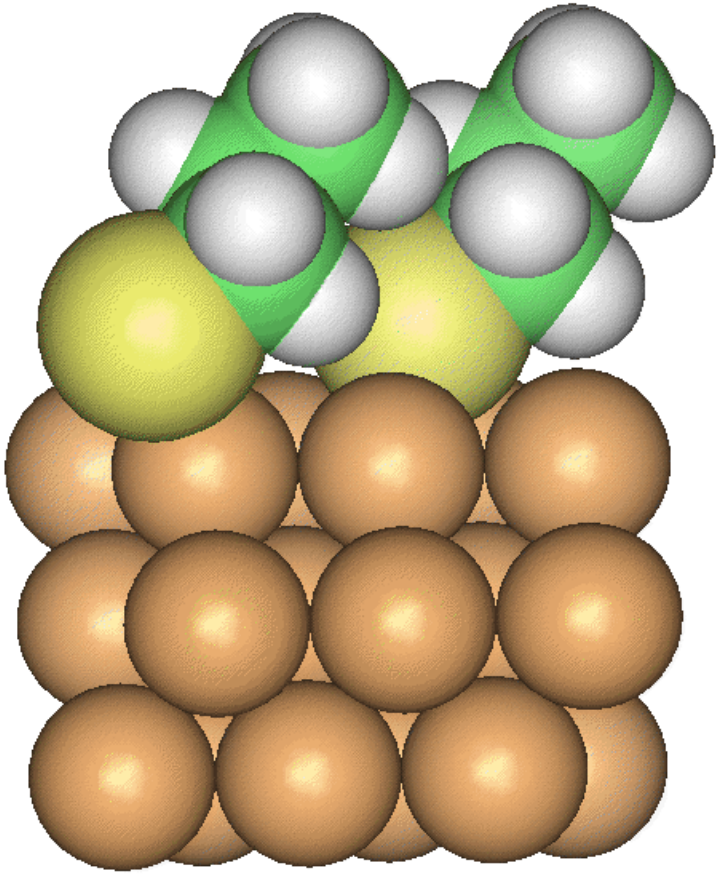




Propane disulfide and propane thiol on Au(111)



-6239.0 kJ/mol



-6191.0 kJ/mol

Computational modeling of the surface of Au(111)

- Structure of the ($\sqrt{3}$ x $\sqrt{3}$ R30^{o}) lattice
- Reconstruction of the Au(111) layer
- Studies of c(4x2) superlattice
- Mechanism of adlayer formation
- Modeling DNA adlayers
- Surface attachment of proteins
- Surface attachment of boronic acid biosensors