

Quantum Chemistry

Lecture 27

Calculation of Molecular Properties
Frequencies
Potential Energy Surfaces (PES)
Electrostatic Properties

NC State University

Calculation of vibrational frequencies

Vibrational frequencies are obtained from a classical calculation using the force constant matrix. Actually, the force constant matrix is derived from the Hessian matrix described in the previous section since the harmonic oscillator force constant is equal to the second derivative of the potential energy surface at the minimum of the nuclear geometry. Practical methods for the calculation of vibrational frequencies depend on the calculation of an accurate force constant matrix. There are two main methods used.

Calculation of derivatives

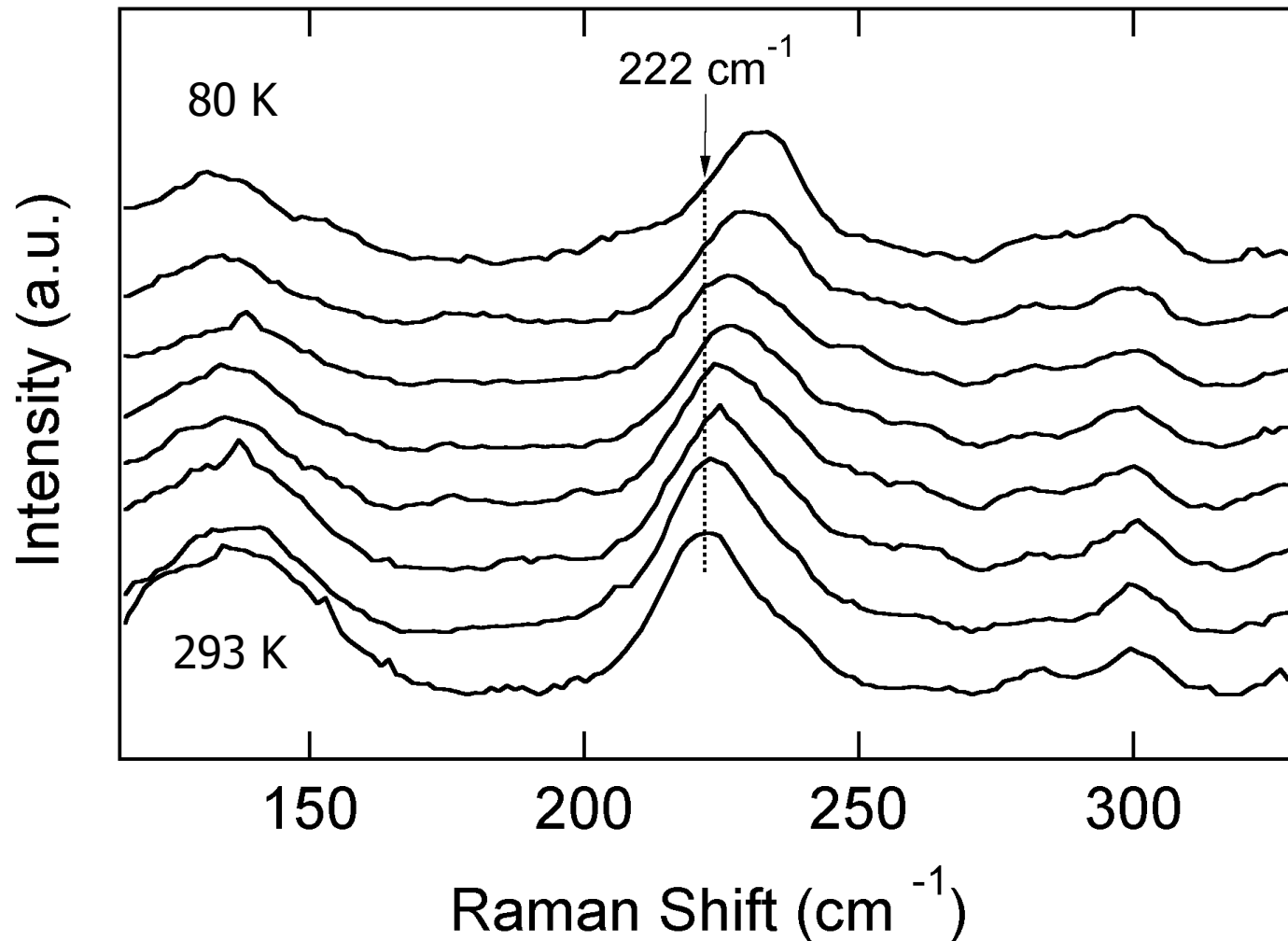
First, one can use analytic derivatives of the energy in terms of the nuclear coordinates at the minimum of the potential energy surface. However, this is only possible for analytic basis sets. Since Gaussian functions provide an analytic basis set, the Gaussian code uses analytic derivatives. A second method is based on finite difference calculation of the force constant matrix. Finite difference is a numerical approach that depends on an accurate energy calculation as the nuclei are displaced by small amounts away from their equilibrium positions. Once obtained the force constant matrix can be used along with the masses to calculate vibrational frequencies

Analytic vs. Numerical Derivatives

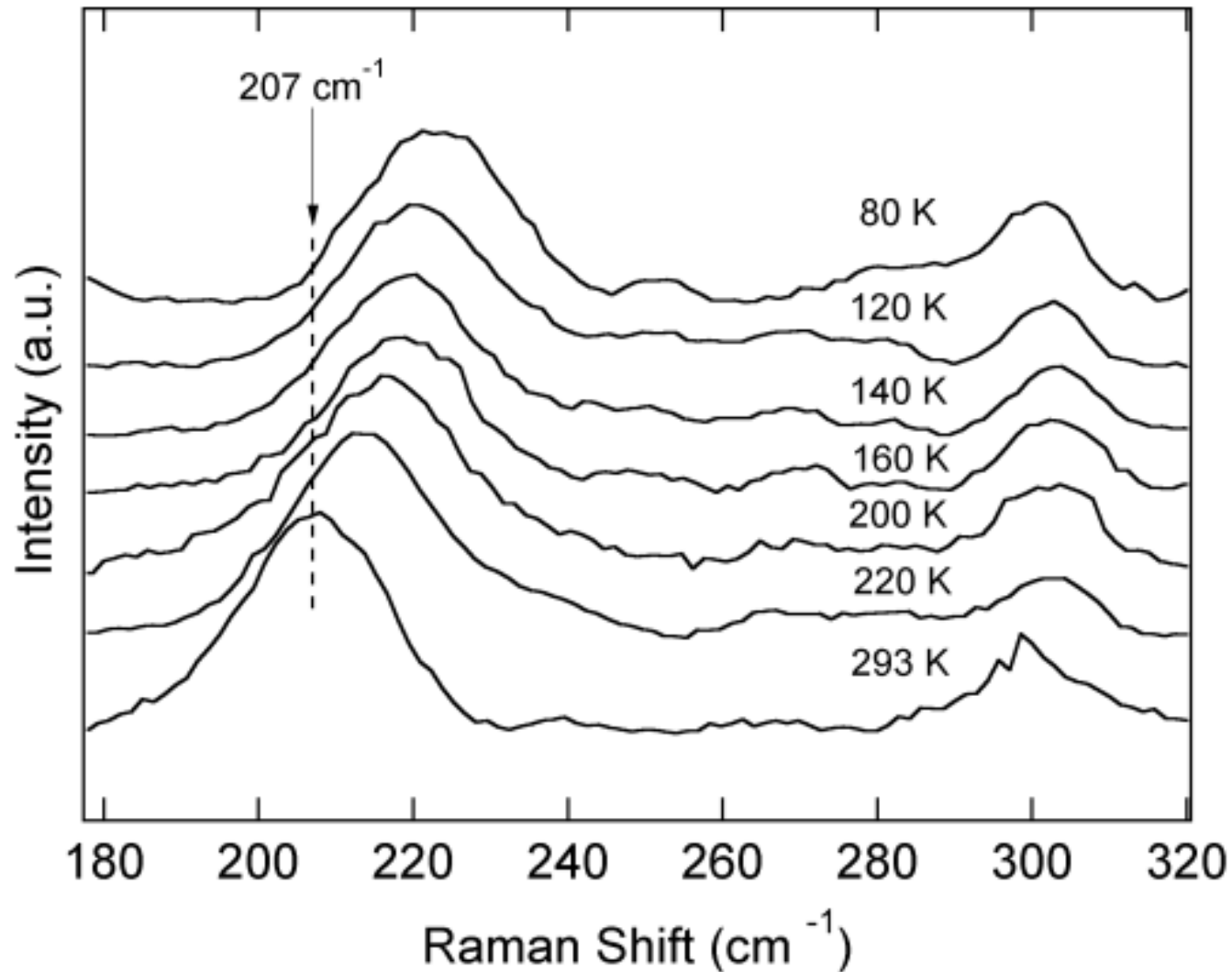
The Gaussian code can support higher derivatives than the second derivative at the energy minimum or optimized geometry. These higher order derivatives provide a method to estimate the corrections to the harmonic approximation. This can be seen in the expansion of the potential energy in terms of nuclear coordinate. Numerical methods do not provide such a simple way to approach anharmonic corrections to the potential energy surface. We have already shown that perturbation theory is a cumbersome way to approach this.

Perhaps the best way to approach anharmonicity is through explicit calculation of the potential energy surface (PES).

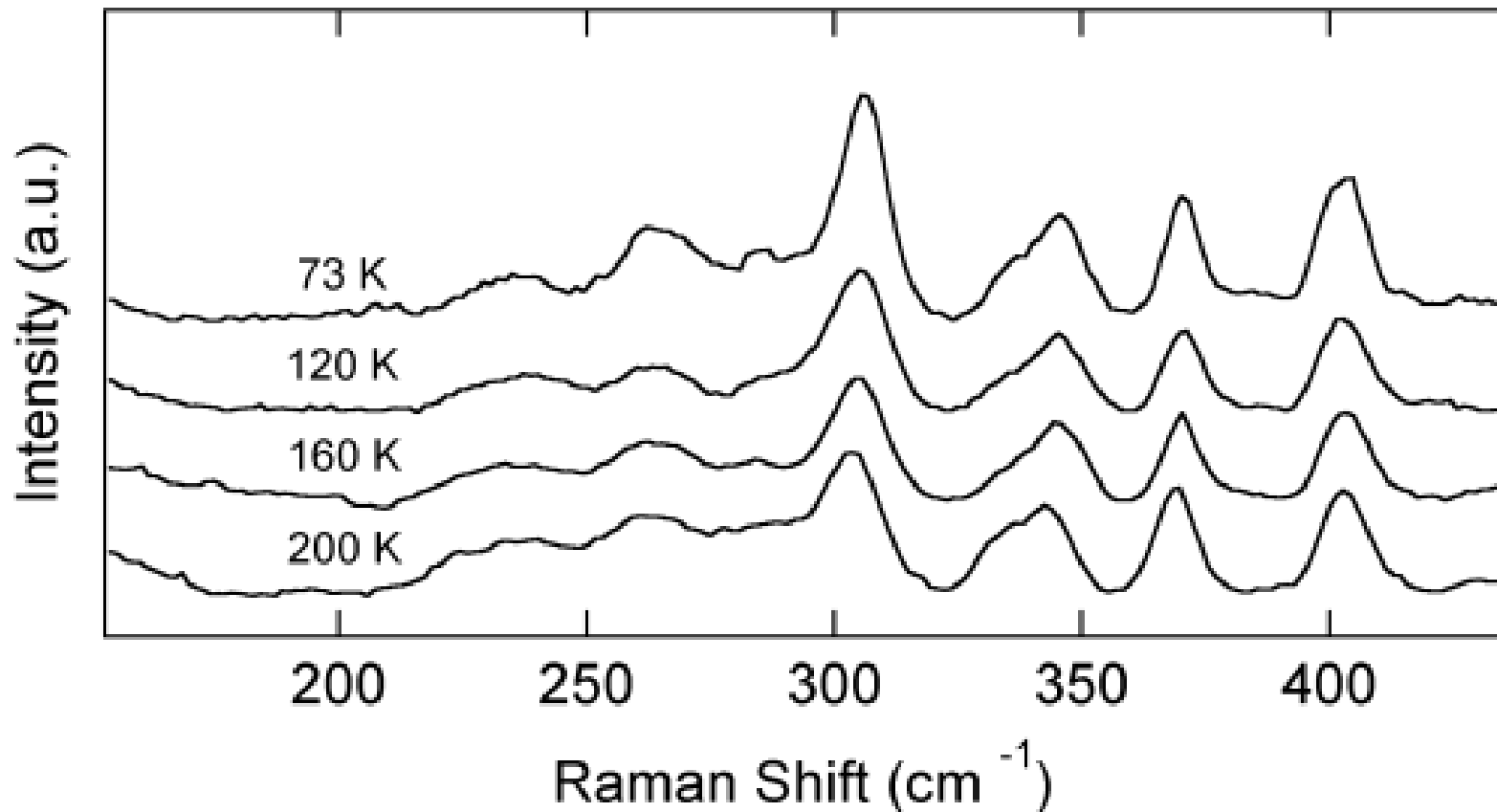
Temperature dependence of the H93G(Im) axial mode



Temperature dependence of the H93G(2-Me Im) axial mode



Temperature dependence of the H93G(H₂O) axial mode

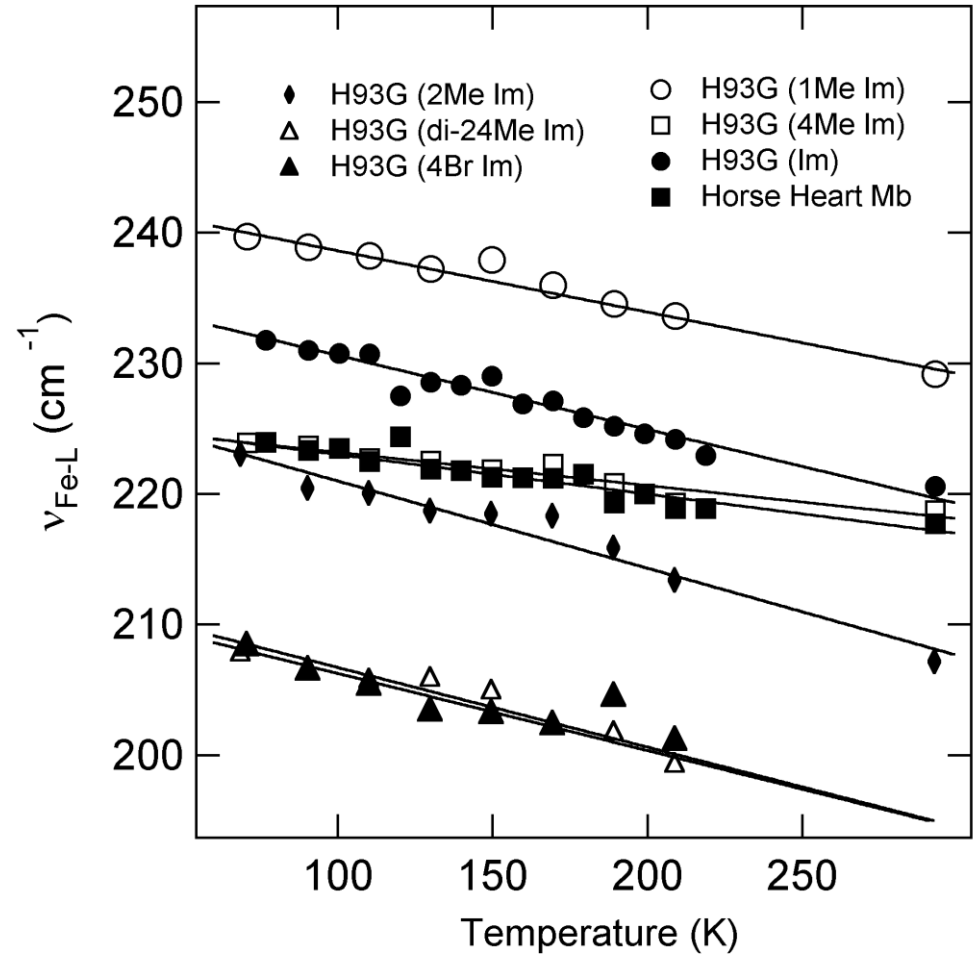


Differences in anharmonicity for axial ligands

Experimental approach shows that axial ligands differ.

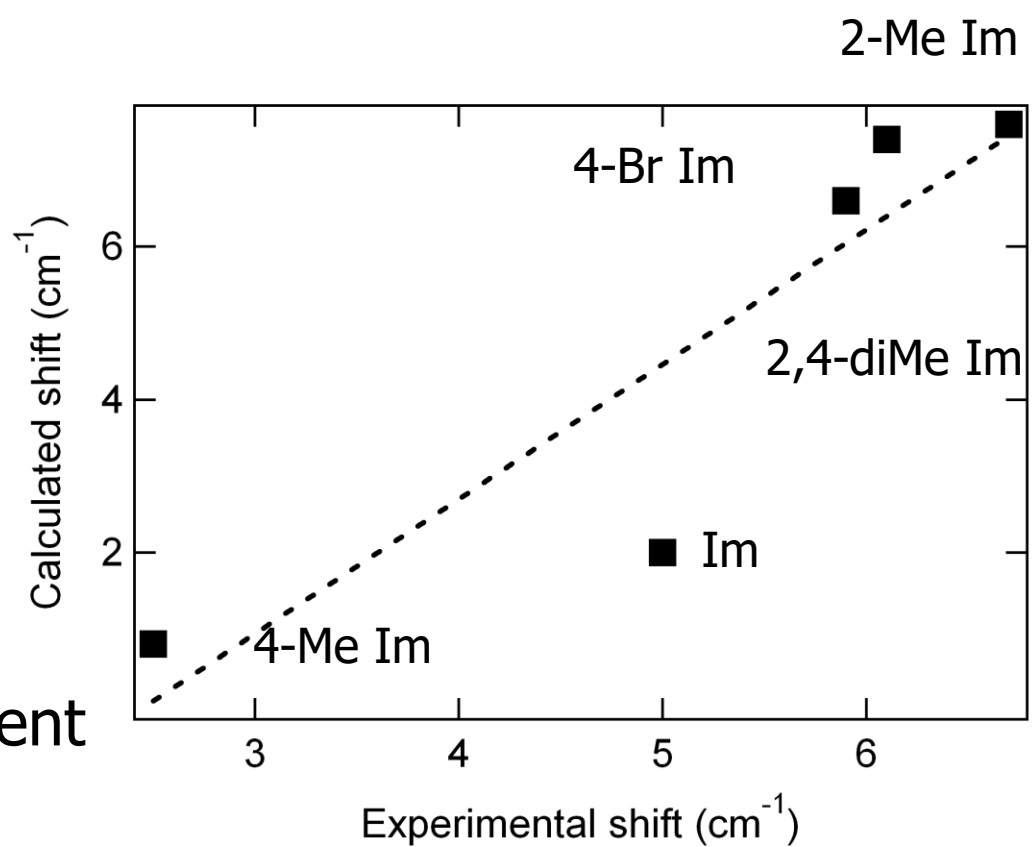
Horse heart is closest to H93G(4-Me Im).

H93G(2-Me Im) is the most anharmonic.



DFT calculated mode-mode anharmonic coupling

Comparison with experiment

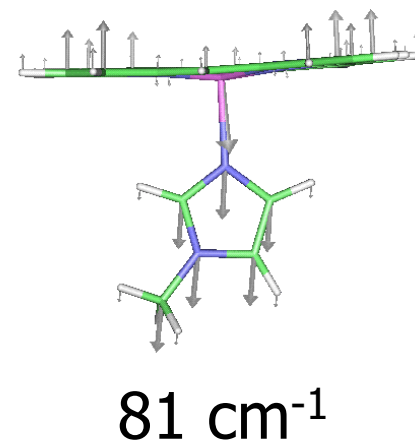
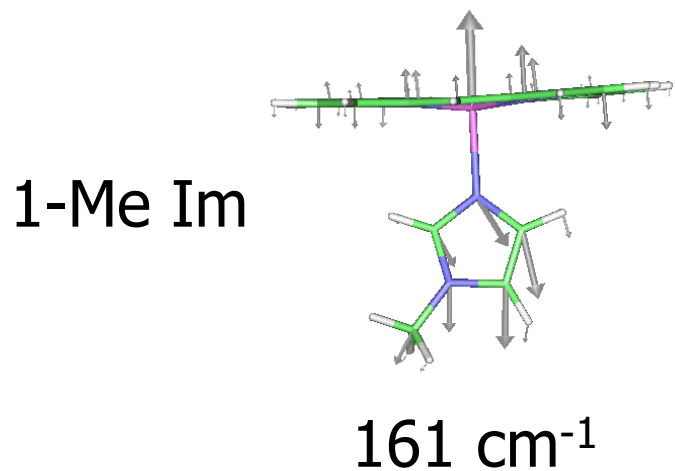
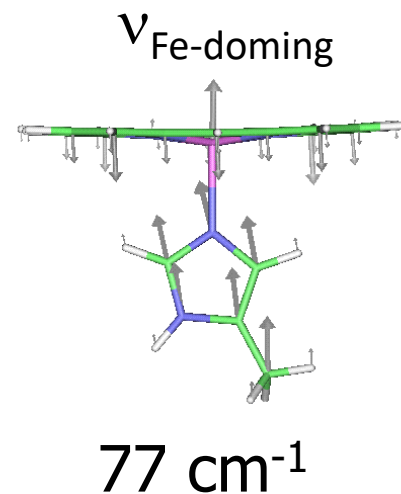
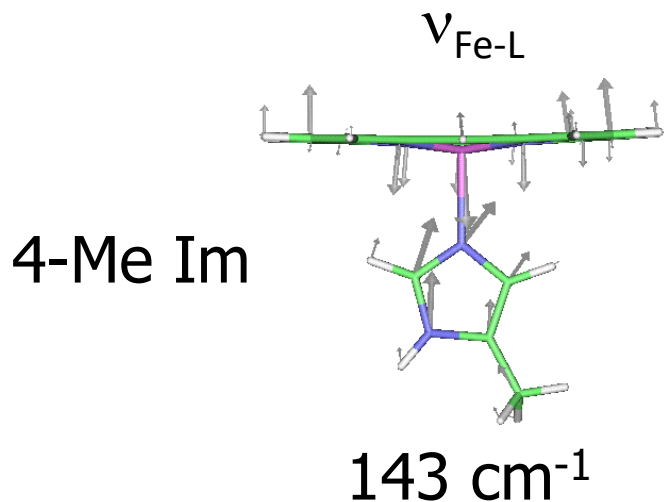


Frequency shift of axial-ligand mode calculated for displacement of iron doming mode.

Only H93G(1-Me Im) excluded because of Fermi resonance.



Iron-ligand stretching and doming modes

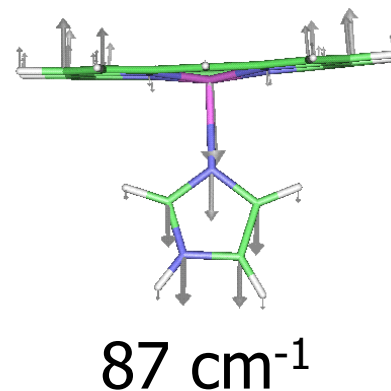
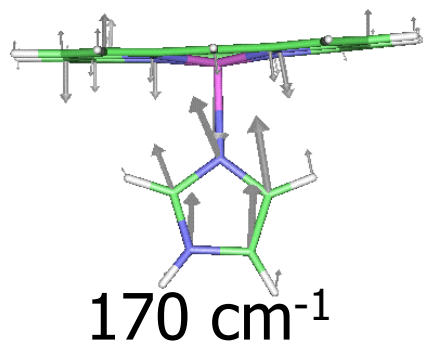


Iron-ligand stretching and doming modes

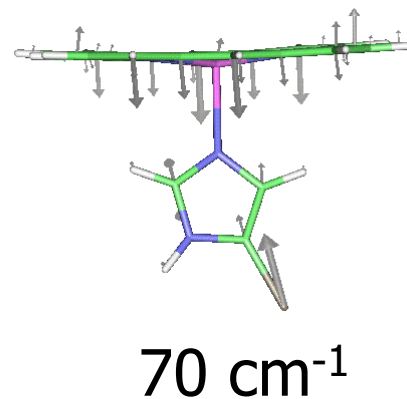
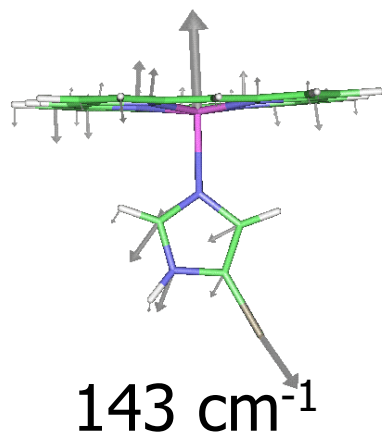
$\nu_{\text{Fe-L}}$

$\nu_{\text{Fe-doming}}$

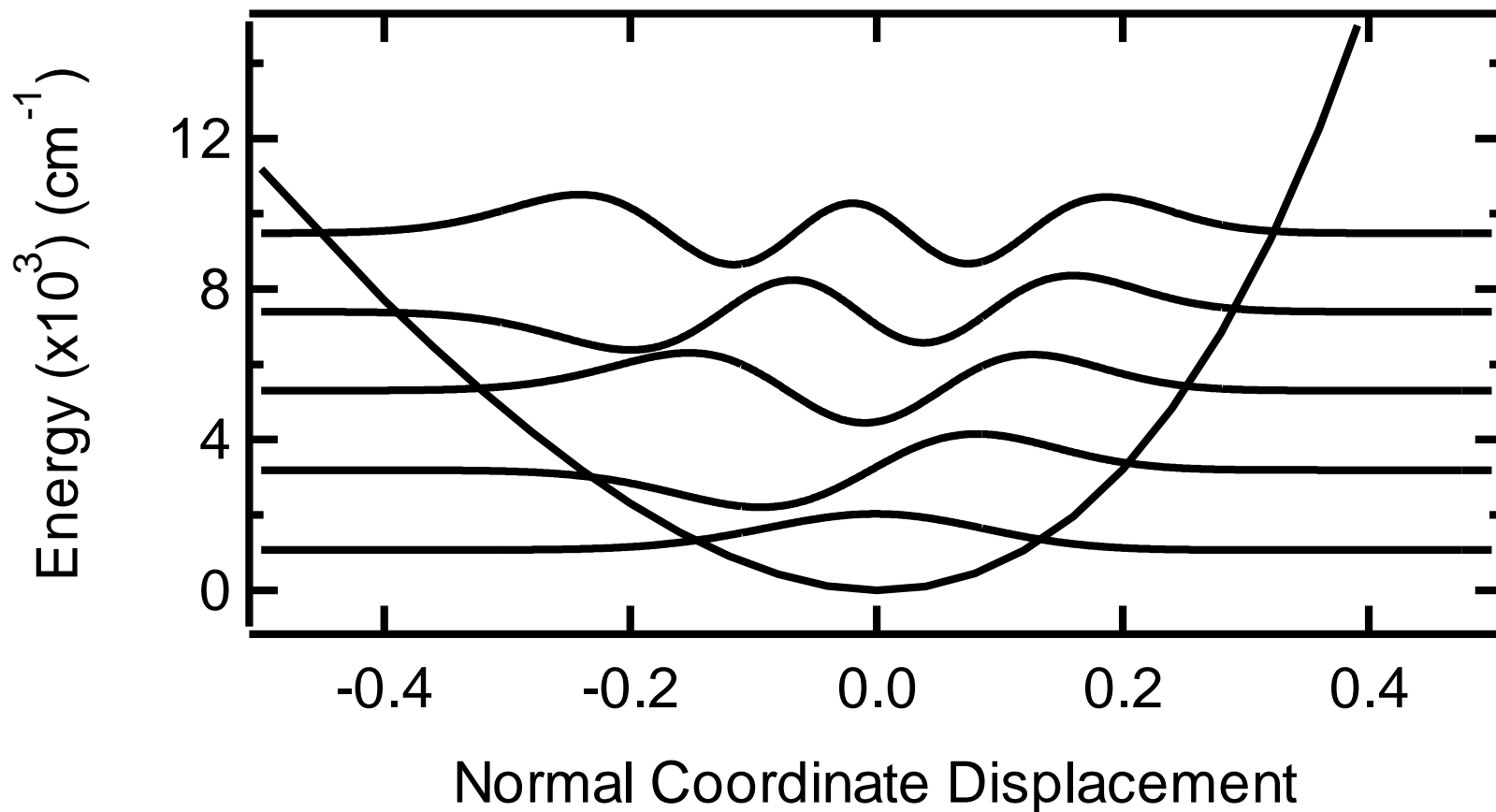
Im



4-Br Im

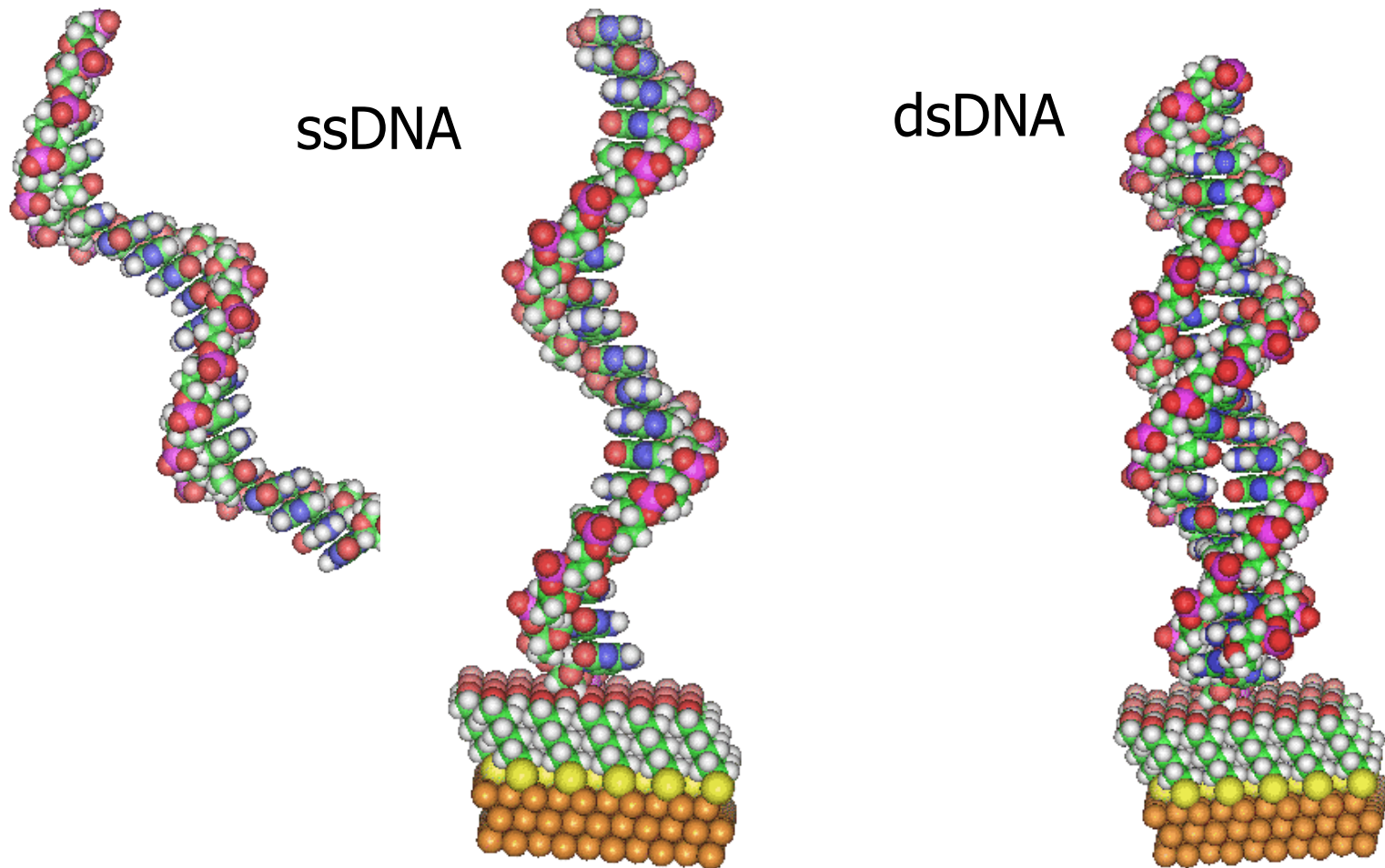


Anharmonic wavefunctions



Use Cooley-Numerov Algorithm to obtain eigenvalues and eigenfunctions for a polynomial model of PES

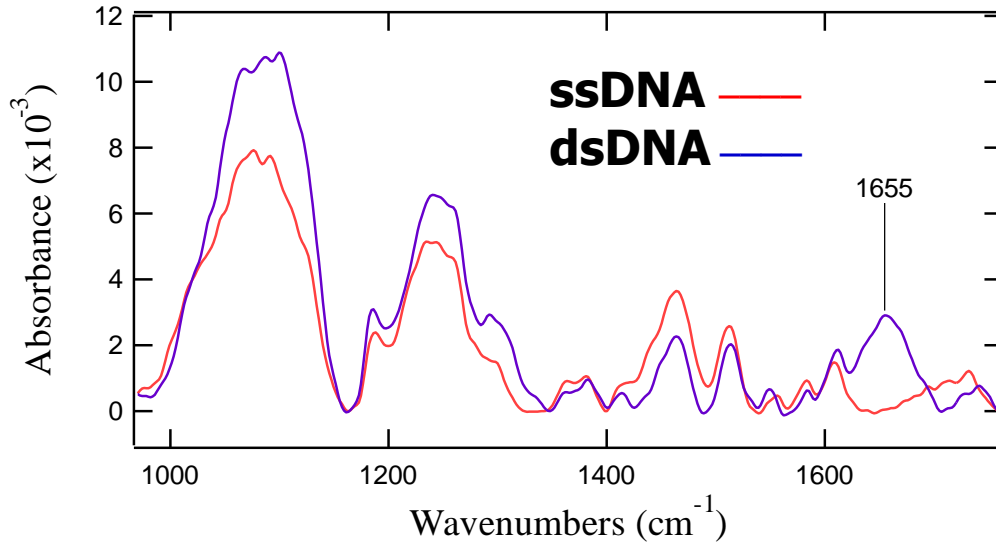
Mercaptohexanol and DNA on Au(111)



Atomically correct model for MD simulations

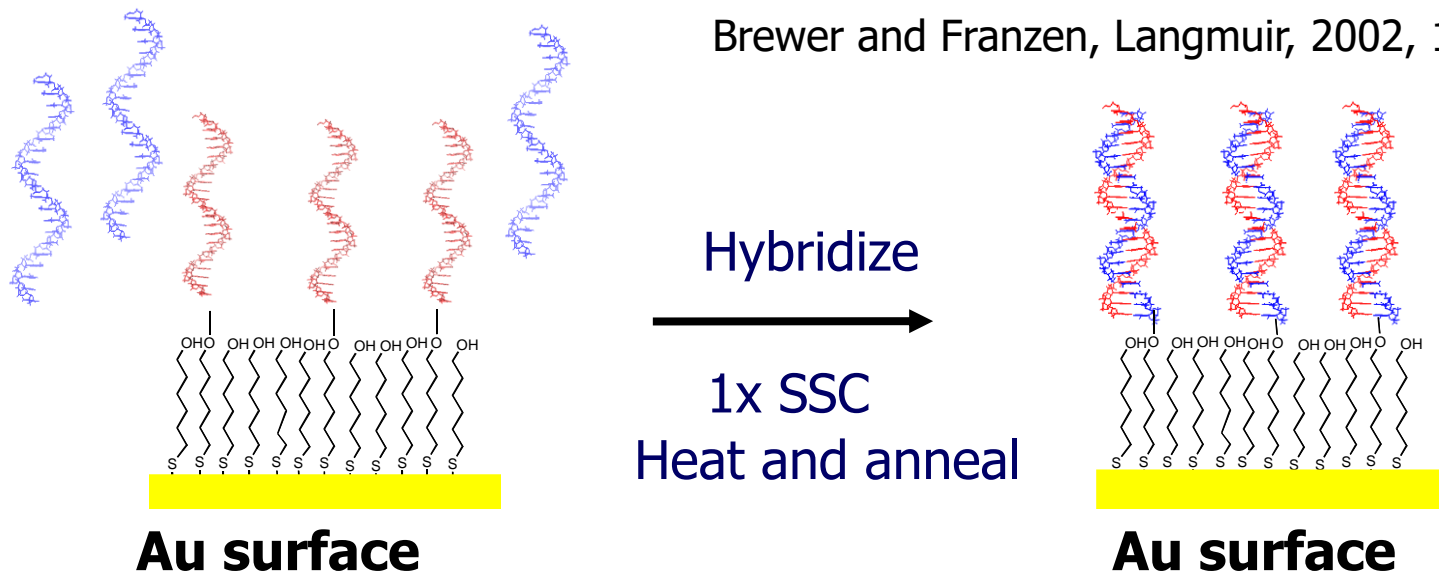
The structure of ssDNA and counterions require study

Detection of DNA hybridization by polarization modulation IR reflection-absorption spectroscopy

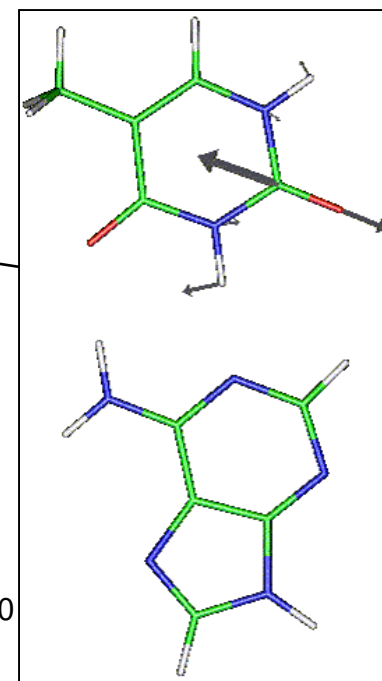
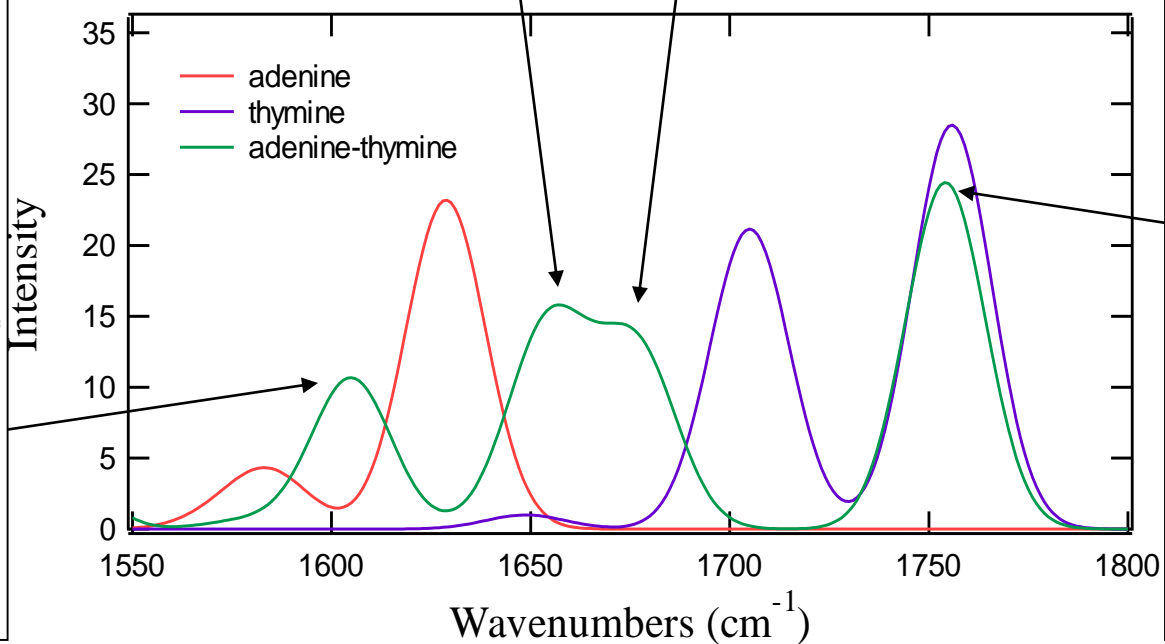
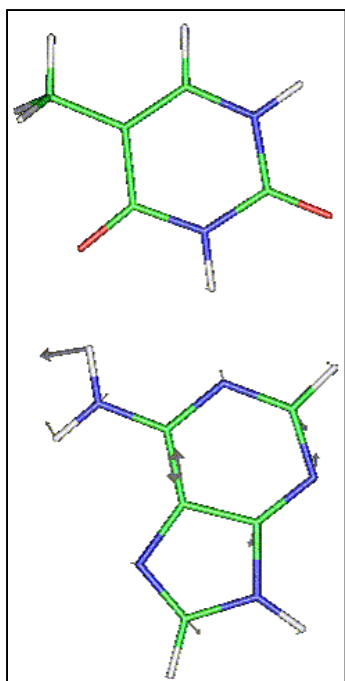
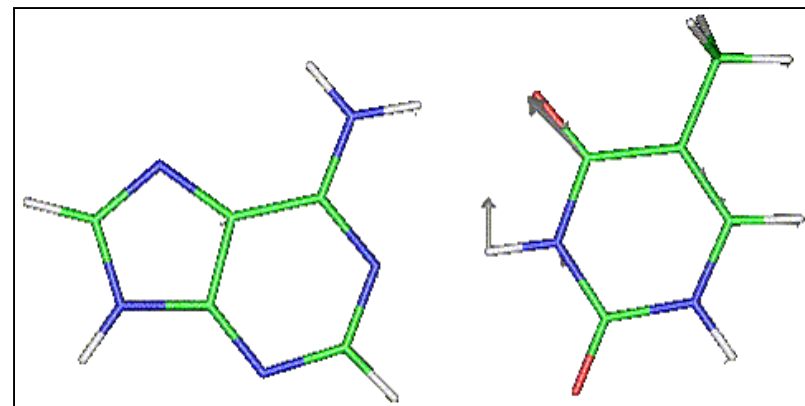
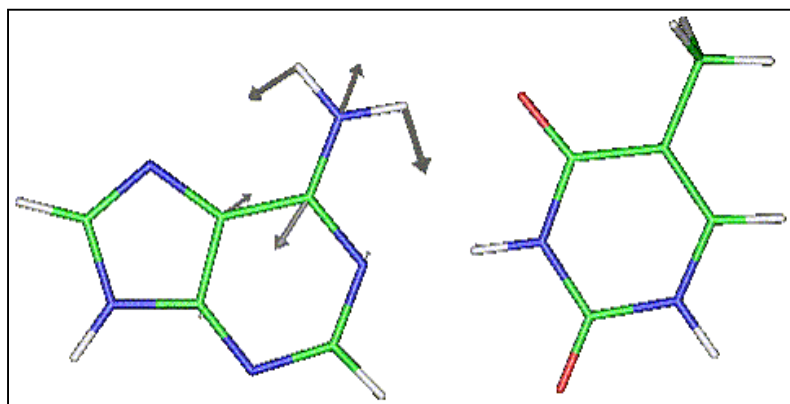


Signature of hybridization can be observed in the C=O stretching and NH_2 bending region between 1600 and 1750 cm^{-1}

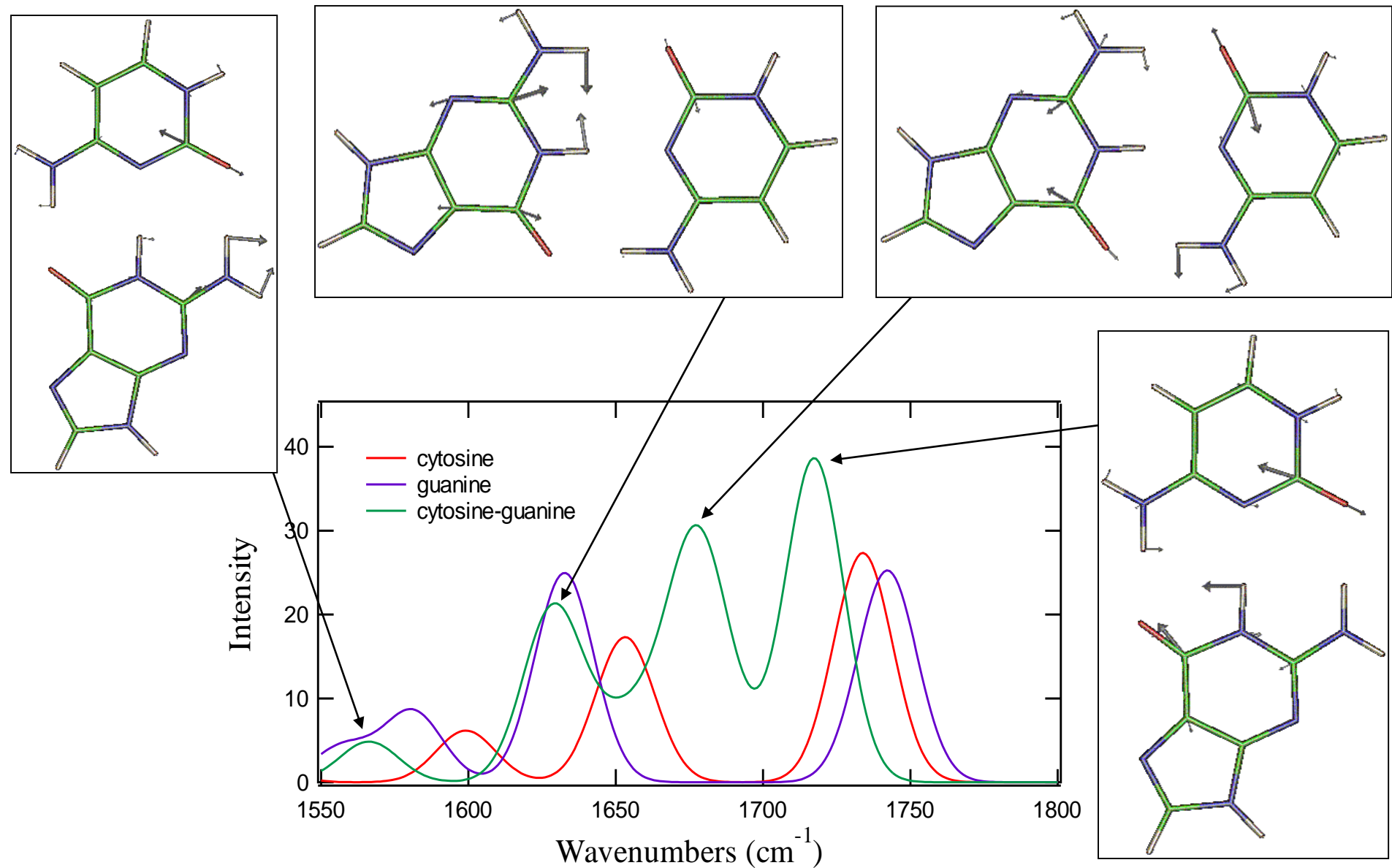
Brewer and Franzen, Langmuir, 2002, 18, 4460



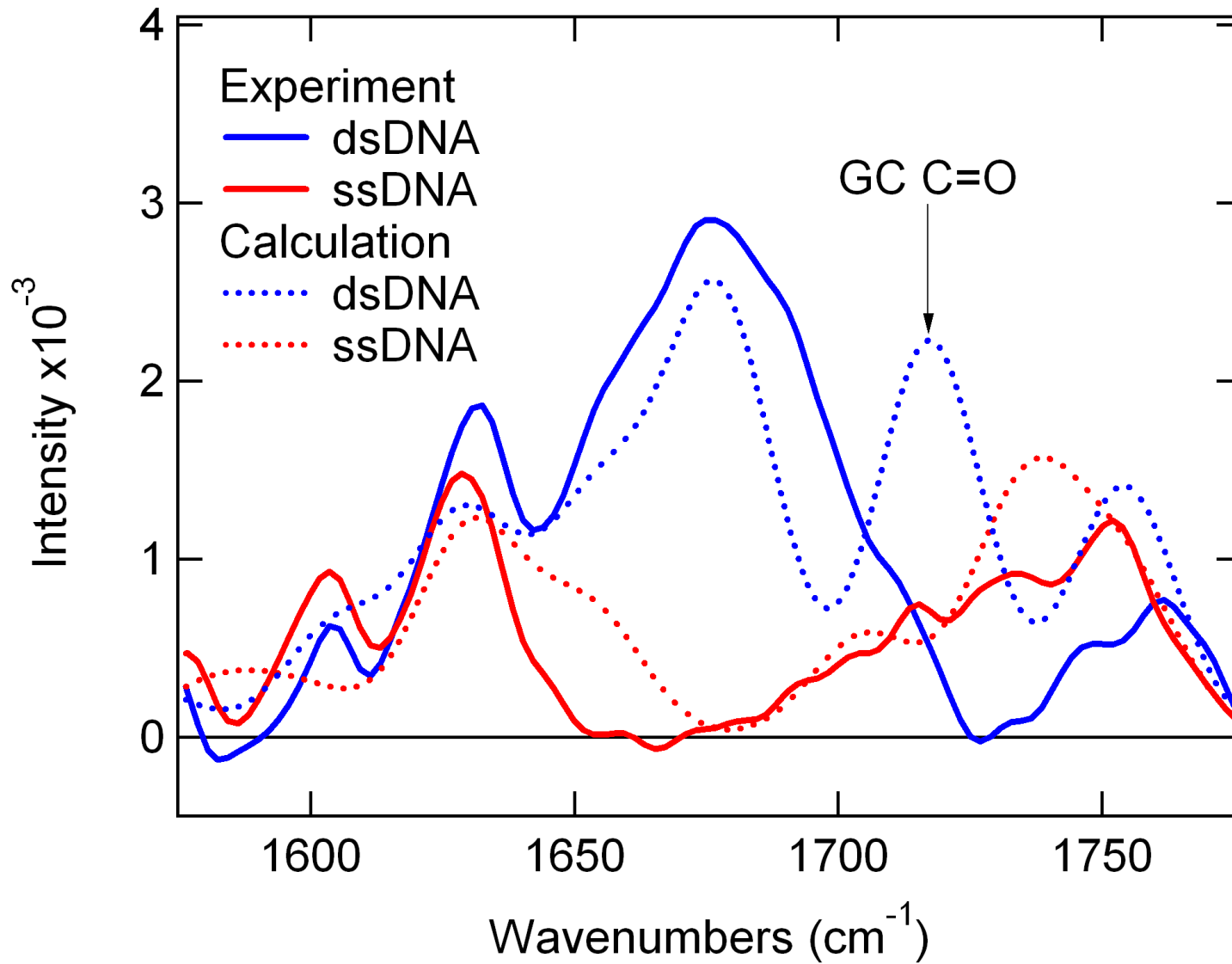
DFT Calculations - AT Base Pair



DFT Calculations - GC Base Pair



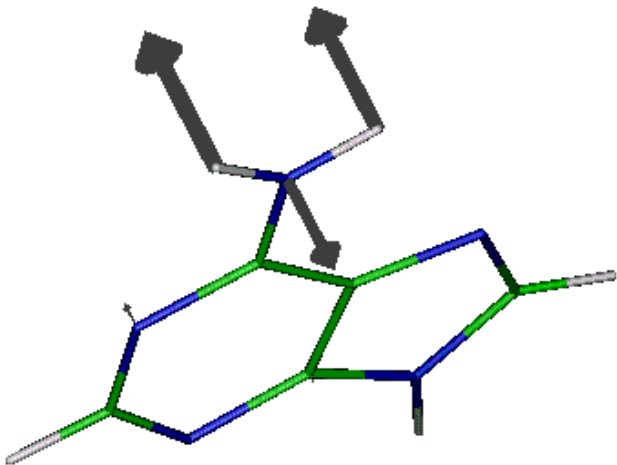
DFT Calculations - Model of 30-mer



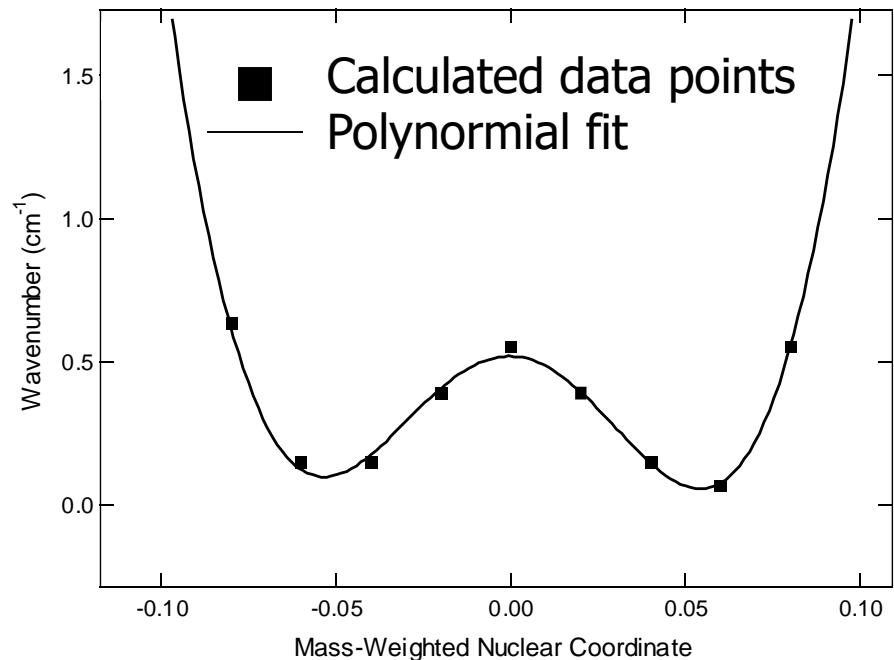
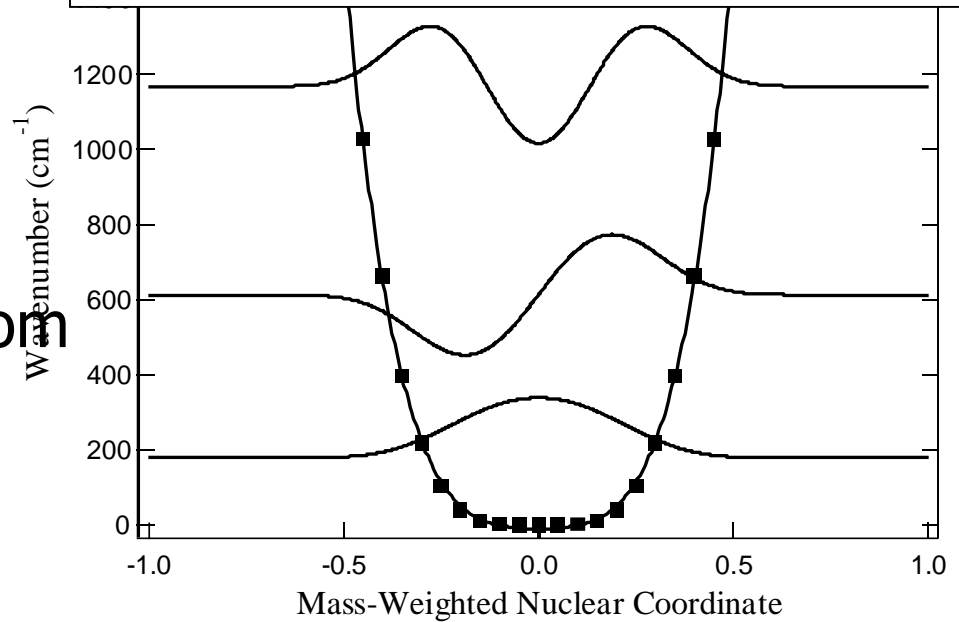
Anharmonic nature of amino pucker

Displacements obtained from normal mode projections.

Double well arises from projections out of plane.

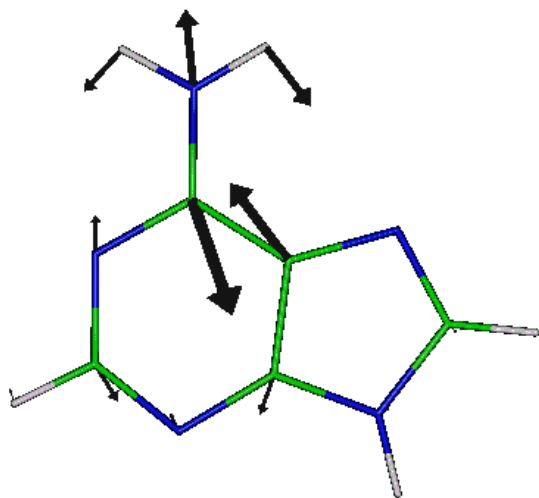


Numerov - Cooley wavefunctions

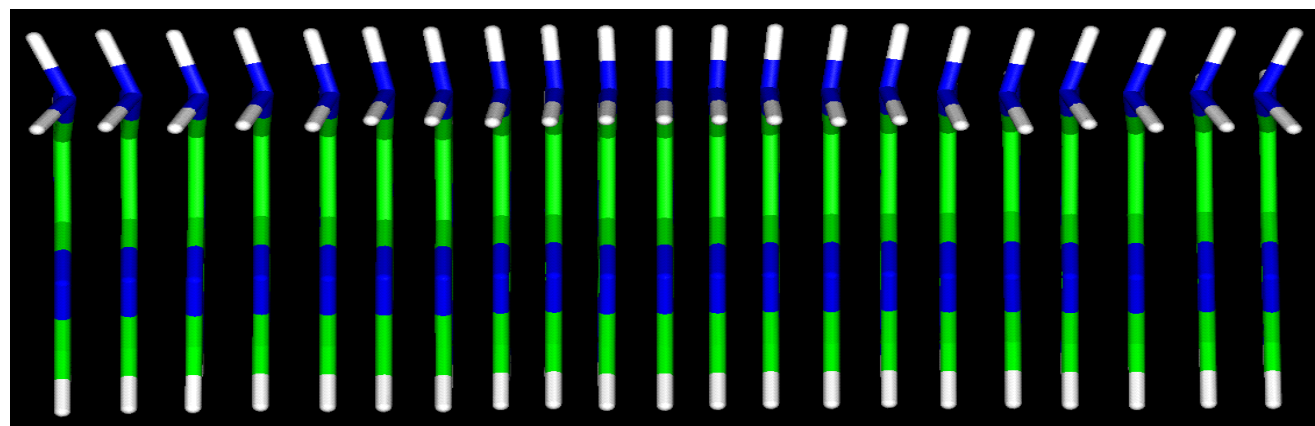
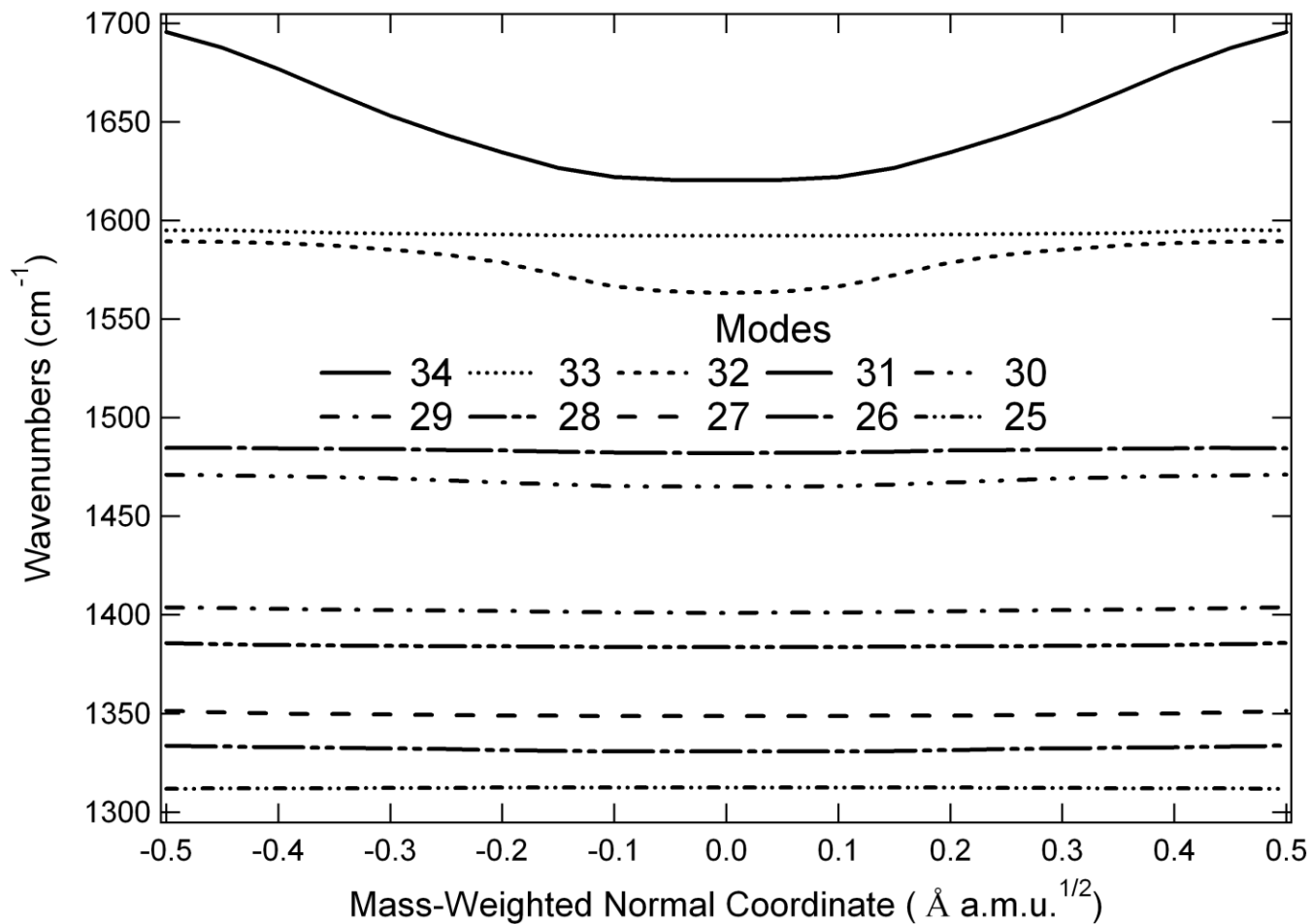


Harmonic shift analysis

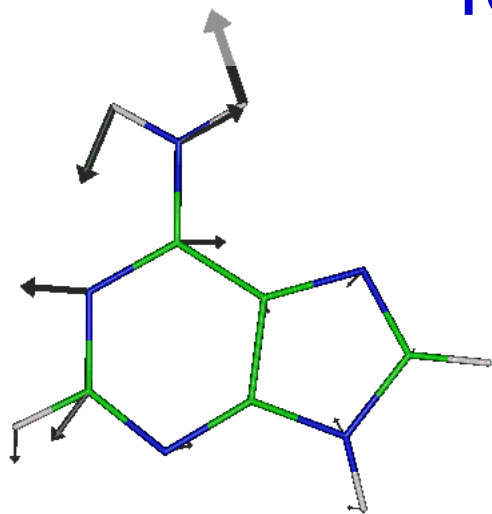
NH₂ puckering causes an upshift in NH₂ bending modes.



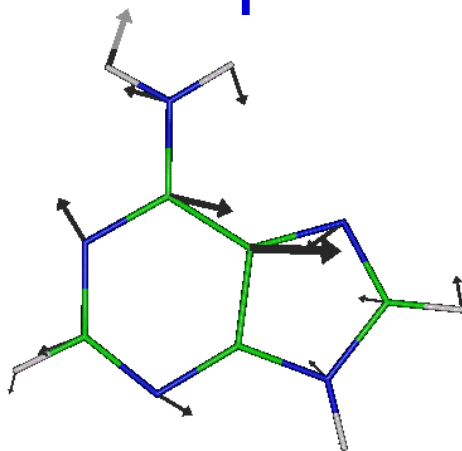
Mode 34



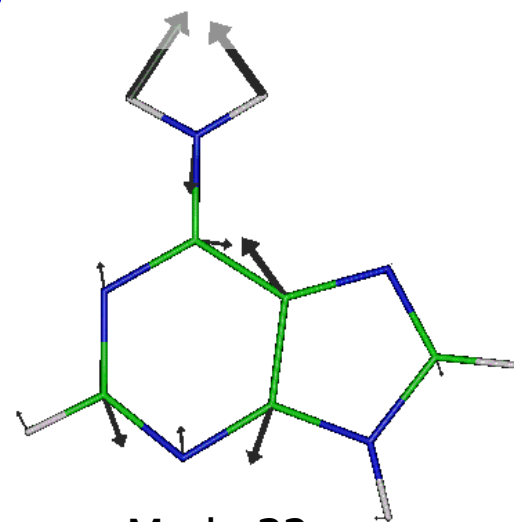
The exocyclic amino group vibrations form a coupled subsystem



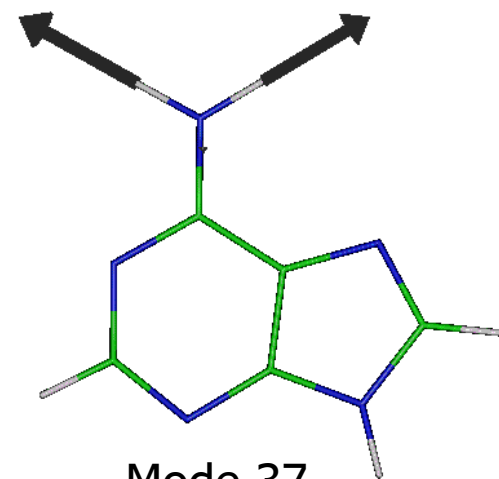
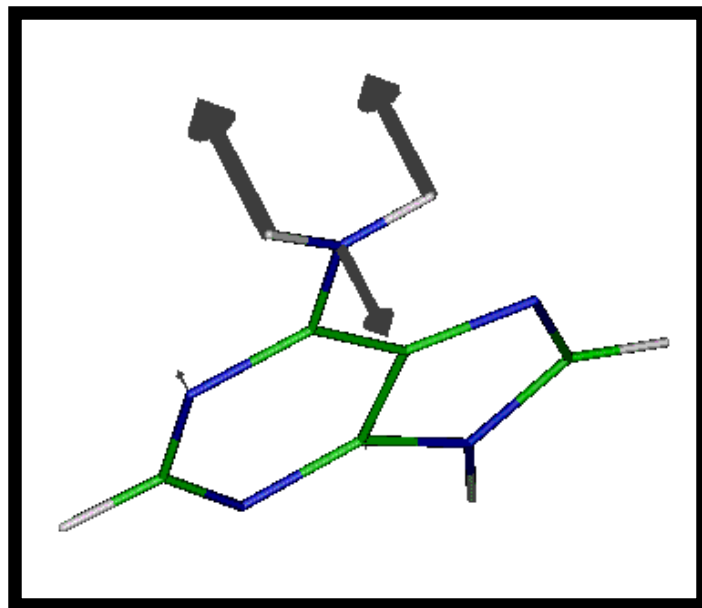
Mode 20



Mode 23



Mode 32



Mode 9

Mode 37

The Potential Energy Surface (PES)

Because of the Born-Oppenheimer approximation we solve for the electron density at a fixed nuclear position. We can find the lowest energy by means of minimization routines that alter the nuclear geometry after each energy calculation. Once we have found a local or global minimum we can consider the shape of the potential surface around that point. The reasons for doing this may be to understand chemical reactions, photochemical events, or properties of the molecule in terms of the vibrational normal modes. In spectroscopy the Franck-Condon factor depends on such a calculation. The anharmonic corrections can also be estimated using explicit calculation of the potential energy surface rather than using derivatives at the equilibrium geometry.

The diradical problem

We can envision potential surfaces that do not involve changes in spin state. Molecular complexes and certain metal (de)ligation reactions involve potential energy interactions on a single spin manifold (surface). However, most bond breaking or formation processes are inherently coupled to a change in spin state. For example, the H_2 molecule is a ground state singlet. If we pull the two H atoms apart to a great enough distance that the bonding energy is essentially zero and remain on the single state surface then both electrons would remain spin-paired in a $1s$ orbital on one of the two H atoms. This corresponds to a H^+ and H^- configuration. We know intuitively that the lowest energy configuration would consist of two H atoms each having a single electron. Thus, Hartree-Fock theory (MO theory) does not get the correct limit for the separated H atoms.

Spin-dependent PES

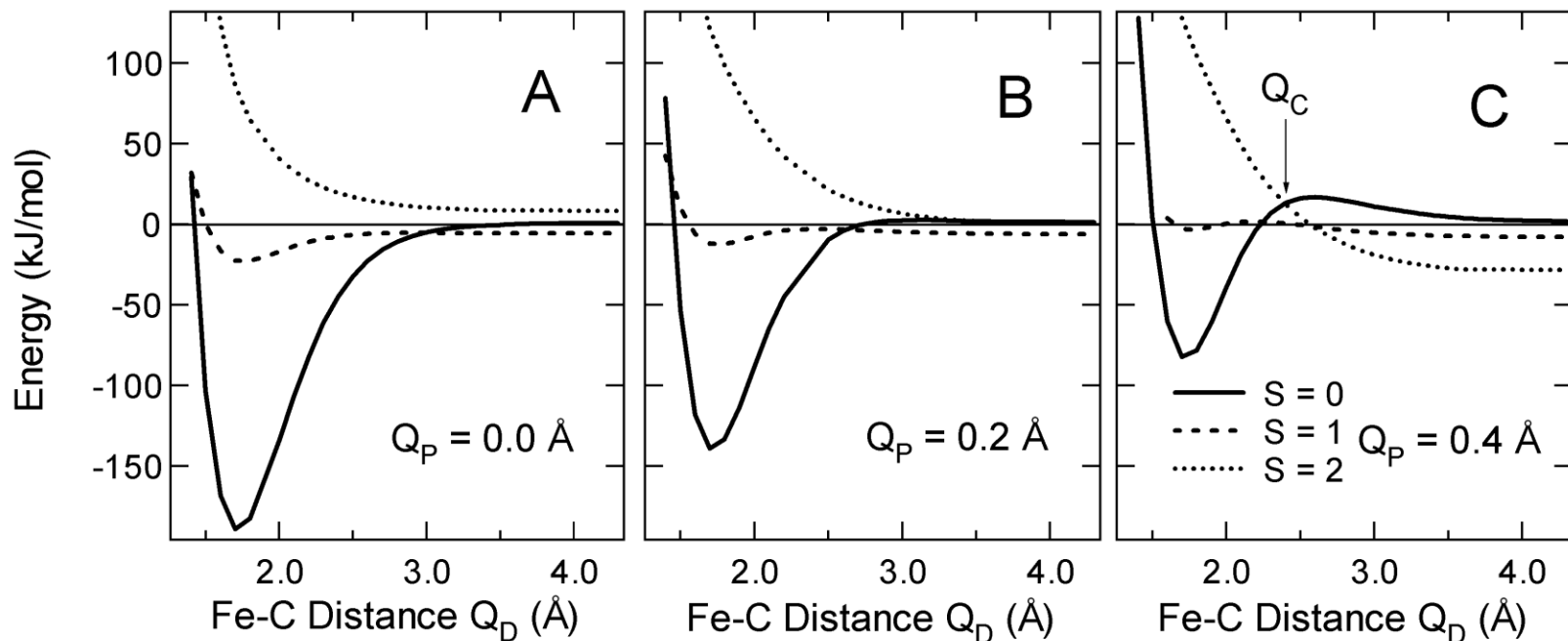
One solution to this problem is to consider the triplet state of excited H_2 and to examine the potential energy surface as the atoms are pulled apart long that state. Eventually, that state should cross the singlet state potential energy surface. In that case we can consider a curve crossing. Multireference configuration interaction is considered the best way to solve these types of problems.

PES in heme proteins

Another example is the breaking of an Fe-CO bond. In this case, there is no spin change required on the CO since it is a closed shell molecule bound to the Fe ion. However, often in such cases, the change in ligand field can lead to a spin change on the Fe atom. Thus, in such a case one would need to do two calculations, one high and one low spin. It may even be necessary to include more than two spin states.

When CO is dissociated from ferrous heme the central Fe²⁺ ion changes from low spin ($S = 0$) to high spin ($S = 2$). The change in spin state causes the Fe²⁺ ion is displaced axially out of the heme plane. This can be modeled by consideration of the potential energy surface with the inclusion of an Fe-out-of-plane coordinate. This type of coupled potential energy surface was described by Franzen for CO, NO and O₂ bound to heme.

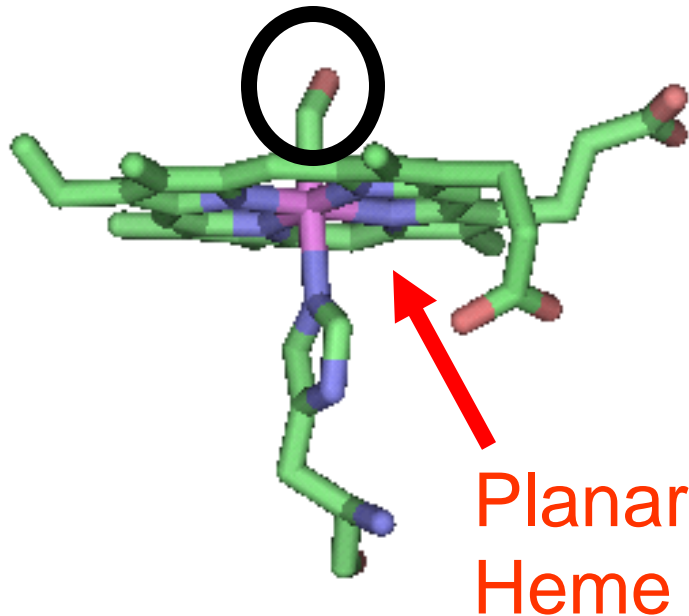
Spin-dependent CO recombination



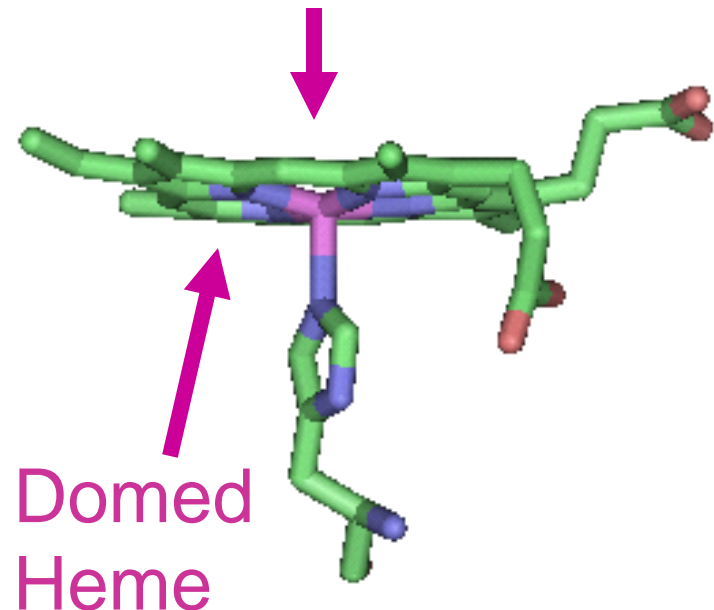
Potential energy surfaces for the spin-manifold-dependent dissociation of CO from the ferrous Fe of a porphine model for heme. Q_P is the out-of-plane coordinate for the heme Fe. Q_D is the dissociation coordinate for the CO from the Fe. Panels A, B and C correspond to Fe out-of-plane distances of $Q_P = 0.0, 0.2$ and 0.4

Application of numerical basis set: rebinding of diatomics in heme

CO is photolyzed



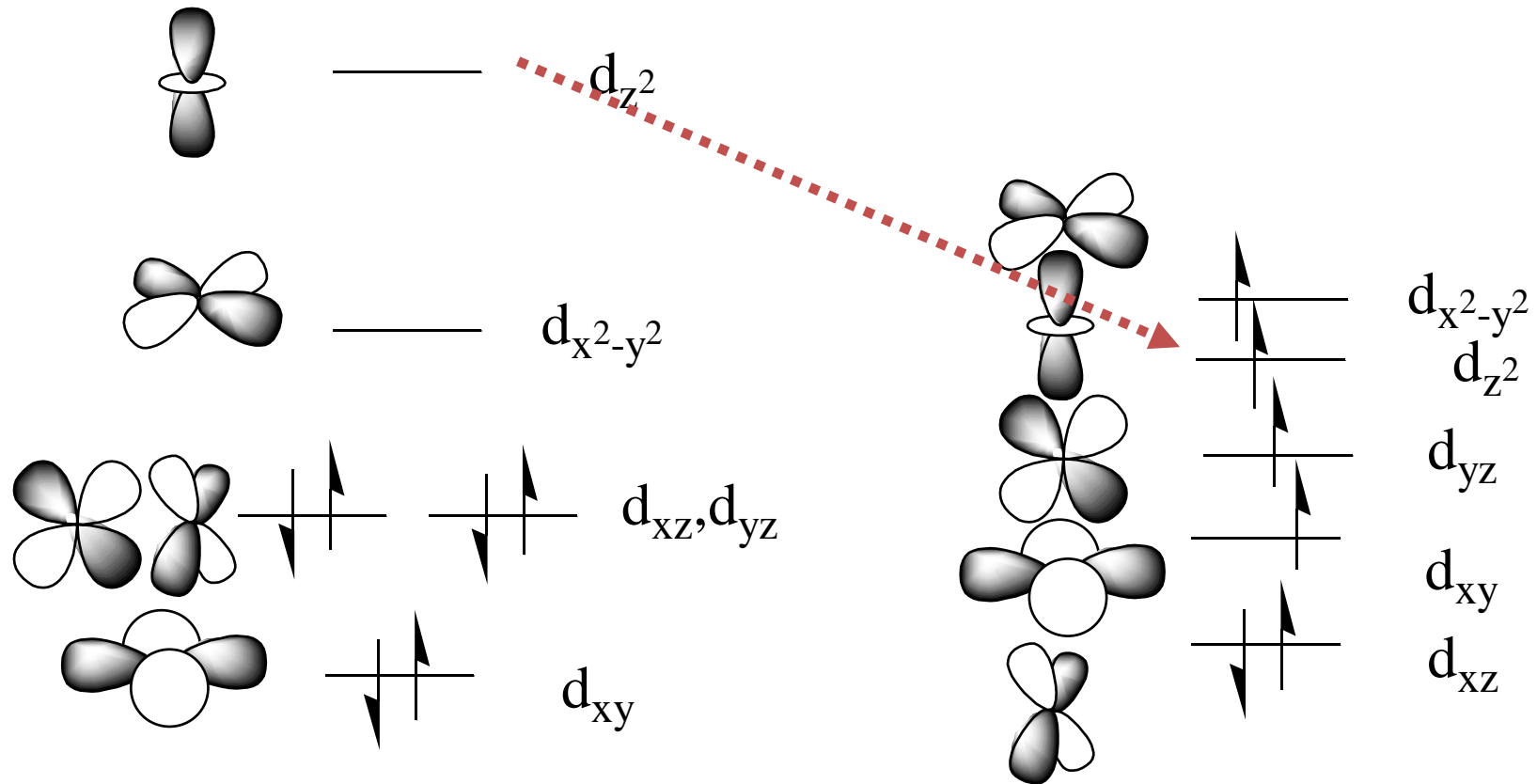
Fe displacement



The ligation of CO changes the spin state of the heme iron

$S = 0$

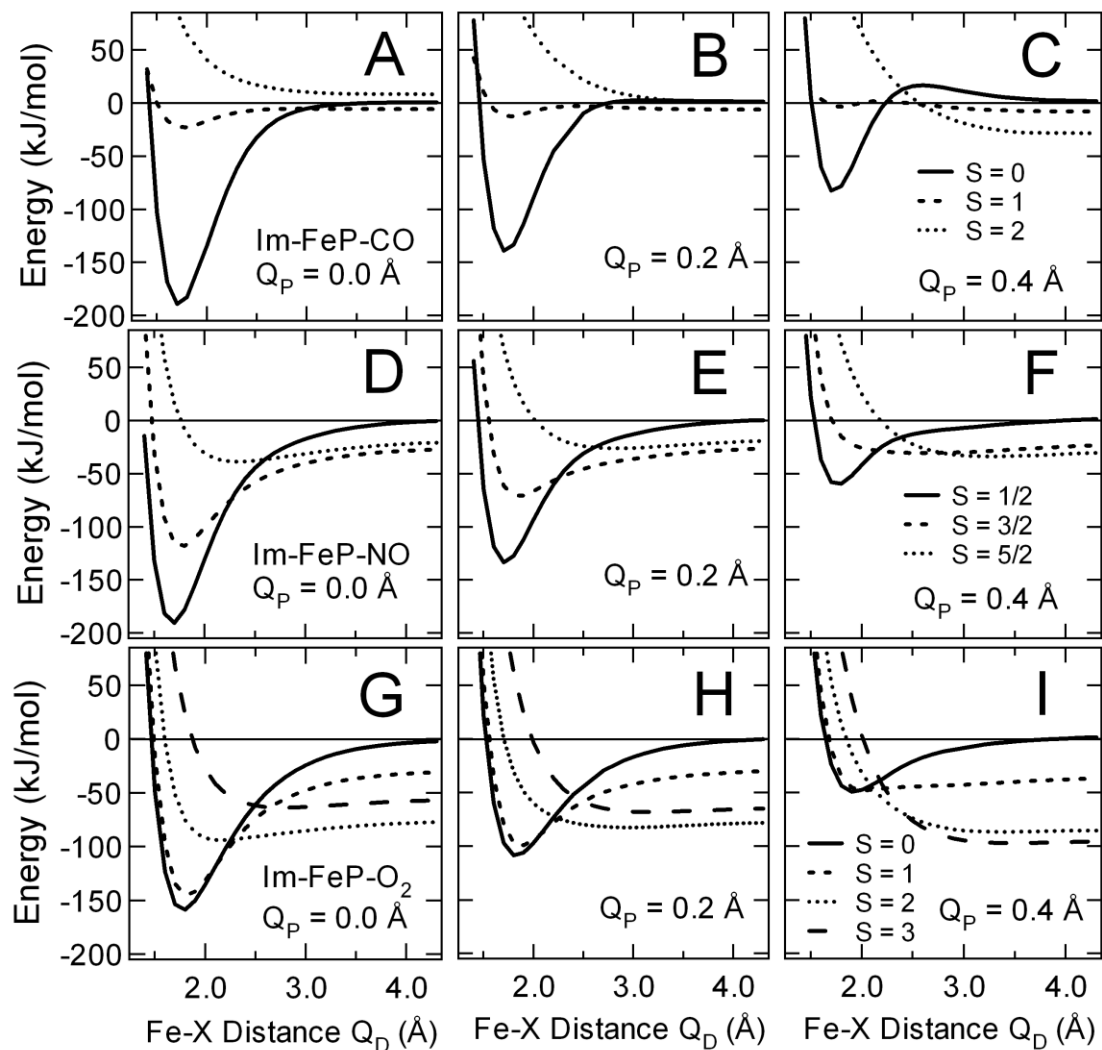
$S = 2$



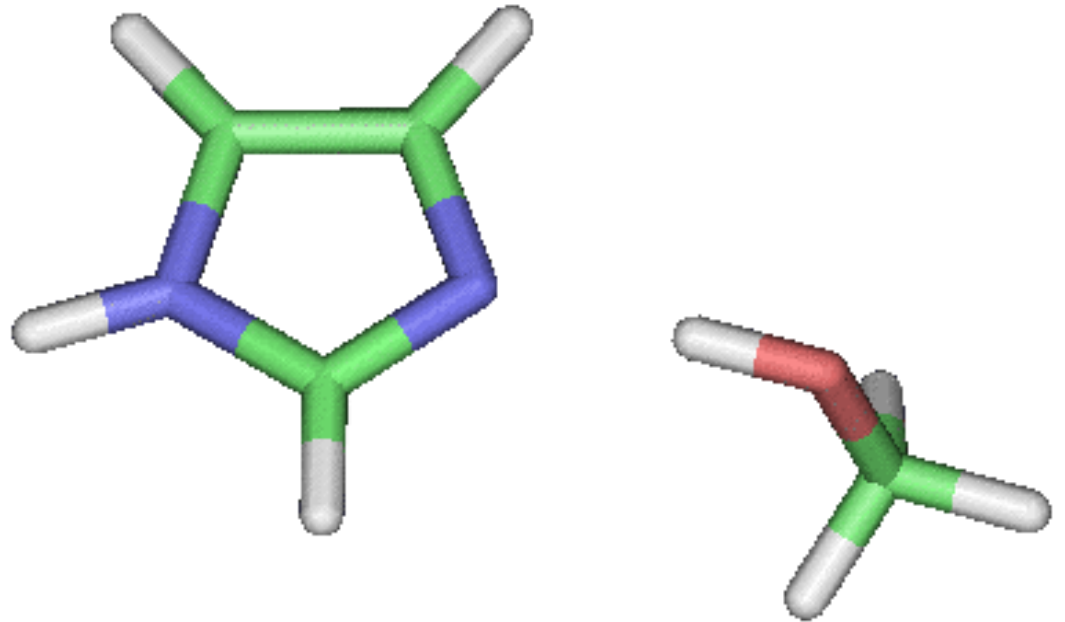
Low spin Fe(II)

High spin Fe(II)

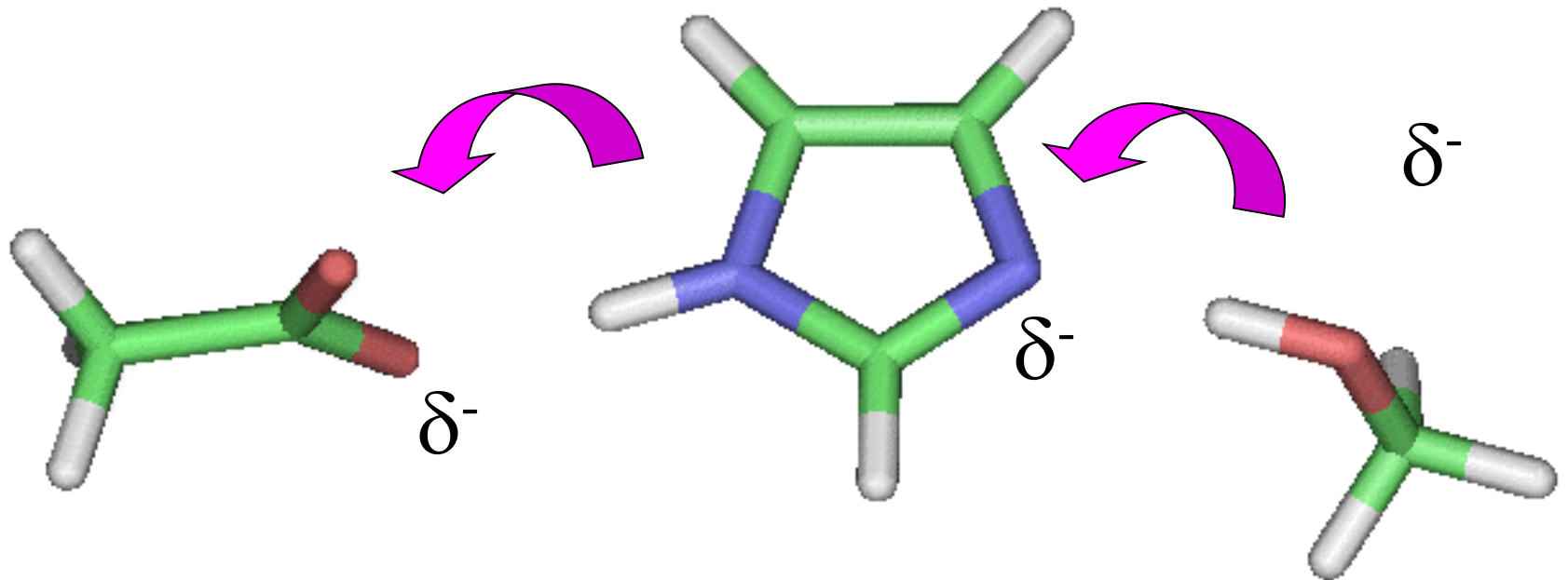
Refined basis set is needed to get spin-dependent recombination



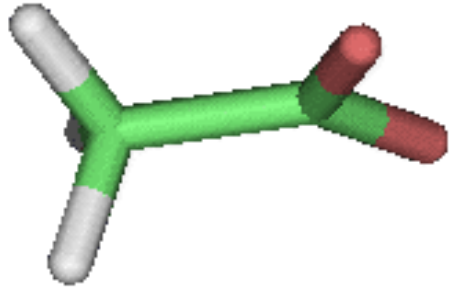
The Asp-His-Ser catalytic triad



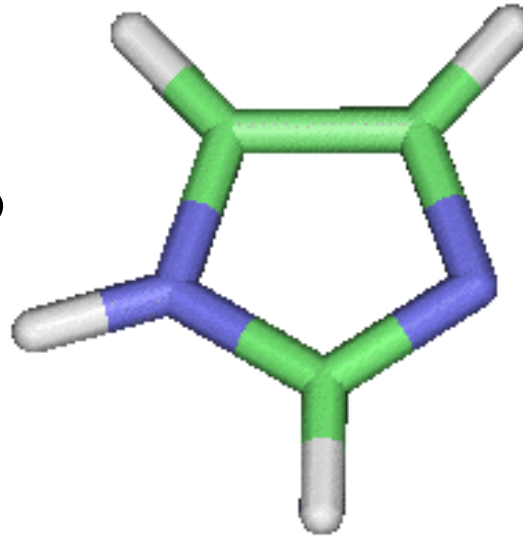
The Asp-His-Ser catalytic triad



Methoxide is a better nucleophile than methanol.
This is a model for the amino acid serine.

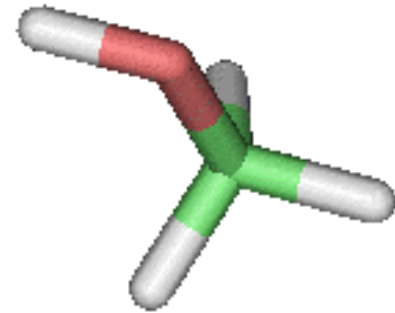


N_δ



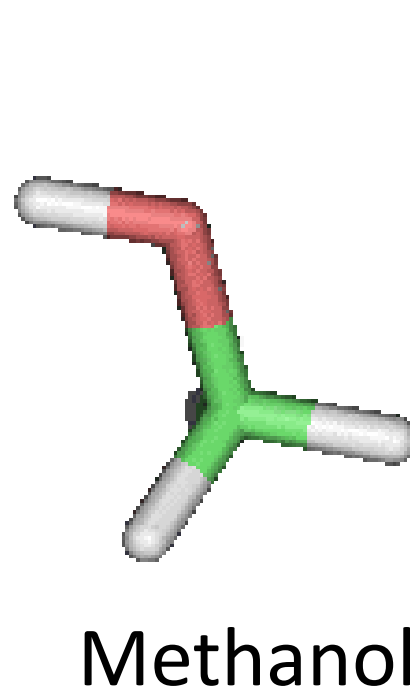
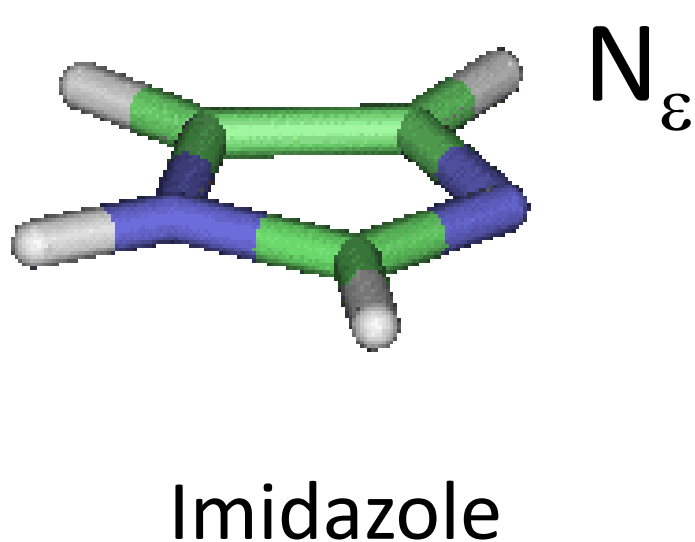
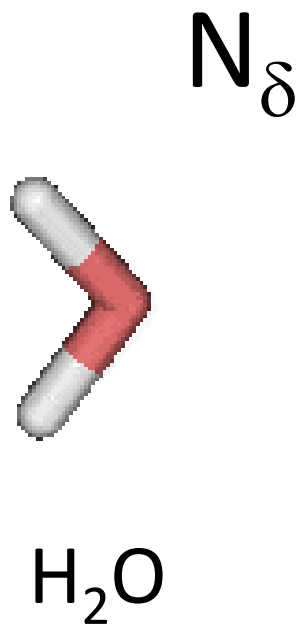
N_ϵ

Imidazole



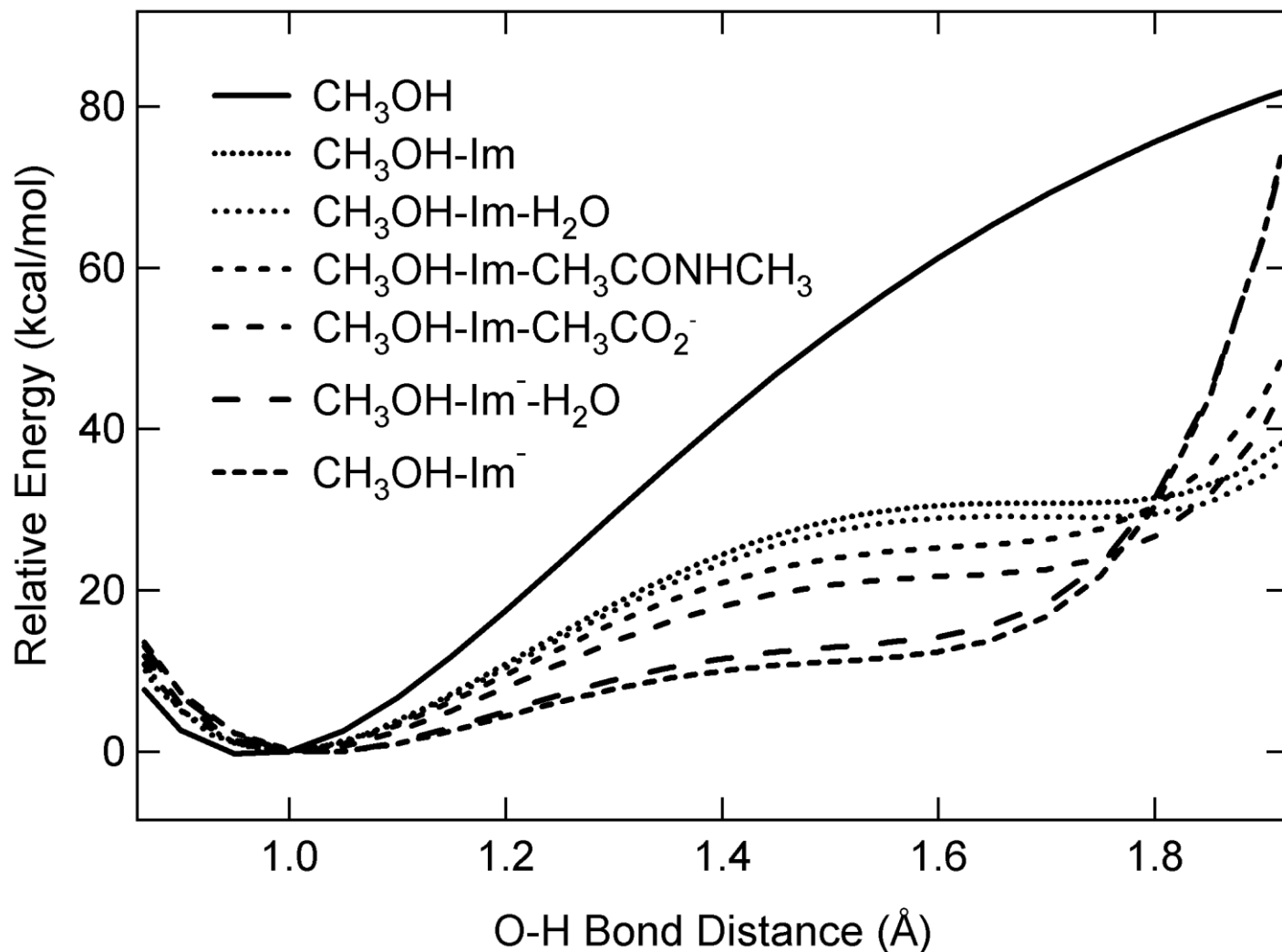
Methanol

An example of charge relay. The hydrogen bonding at N_δ affects the potential energy surface between N_ϵ and the methanol OH group. In biology the triad Asp-His-Ser plays a role in polarizing the -OH group of serine to make it a better nucleophile.



We can test the effect of the charge relay by replacing the the acetic acid by water (H_2O) or other hydrogen bonding groups.

The potential energy surface for O-H

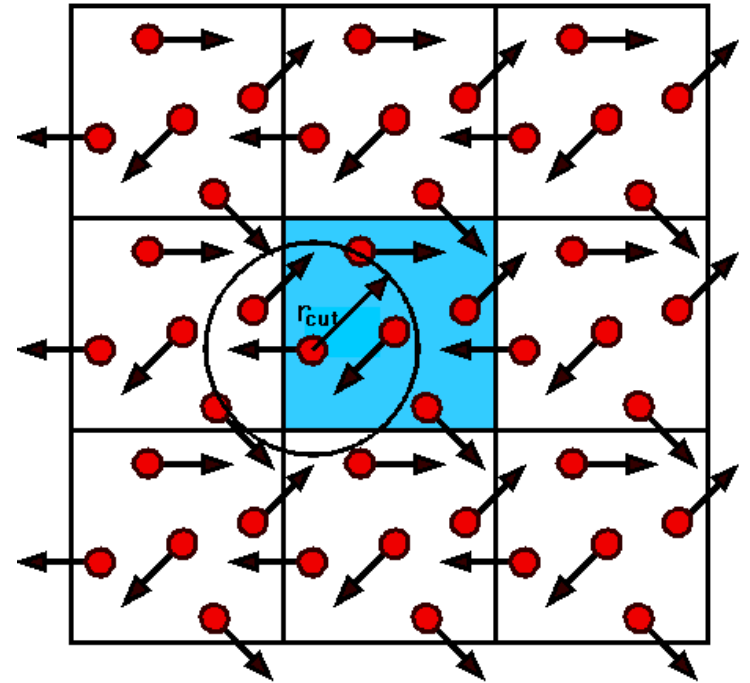


Computational modeling of the surface of Au(111)

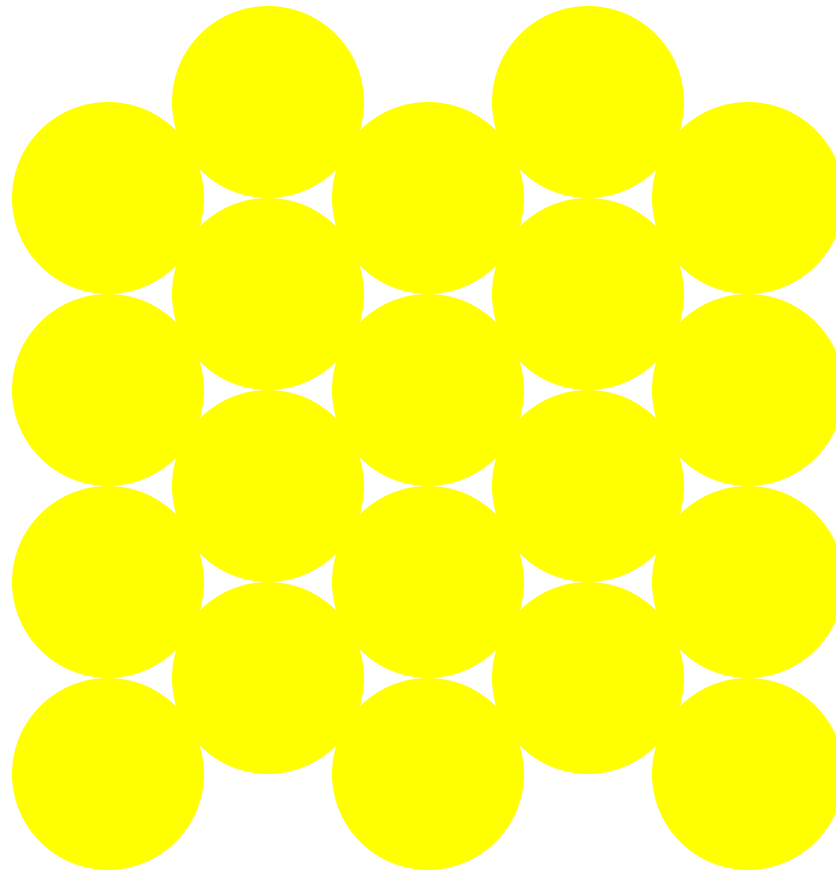
- Periodic boundary conditions
- Structure of the ($\sqrt{3} \times \sqrt{3}$ R30°) lattice
- Reconstruction of the Au(111) layer

Periodic boundary conditions

Periodic boundary conditions (PBC) define a unit cell or box of a geometry suitable for perfect three-dimensional tiling. In a dynamic simulation when an object passes through one face of the unit cell, it reappears on the opposite face with the same velocity. The simulation is of an infinite perfect replicate of the system. The tiled copies of the unit cell are called images. There are an infinite number of images. During the calculation, only the properties of the unit cell need be recorded since it accounts for all space. In the DFT calculation we need to include the dimensions in x , y and z of the box.

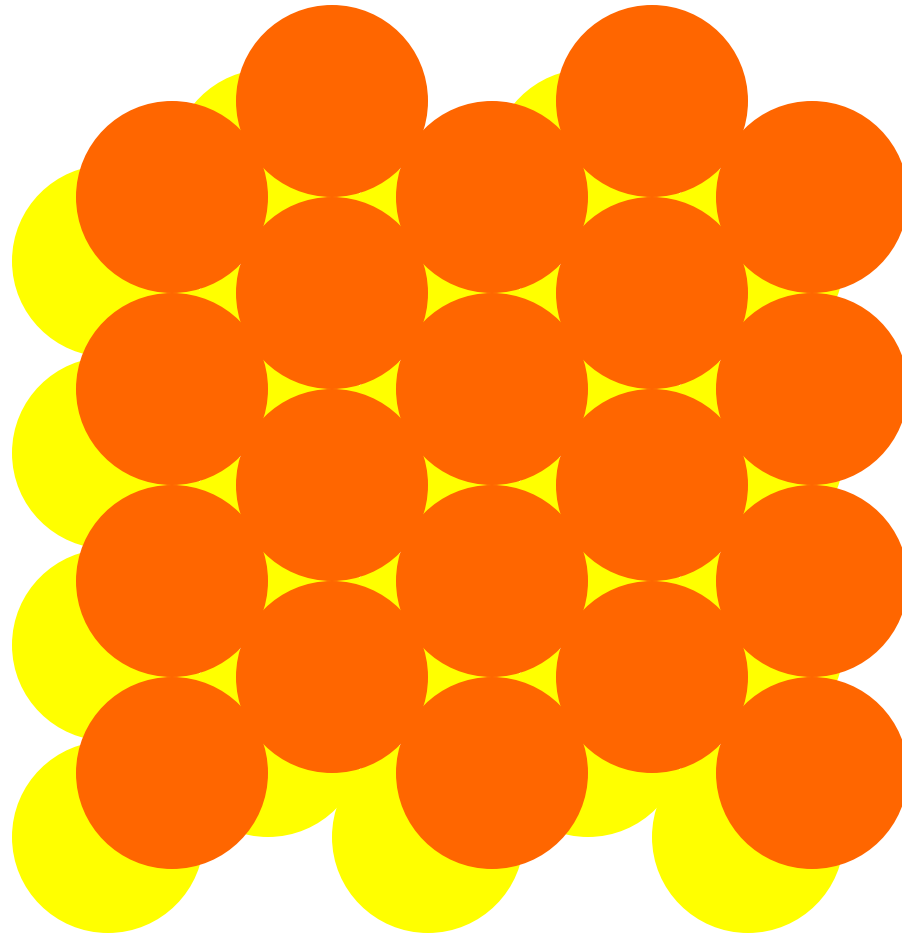


Top view of the Au(111) Surface



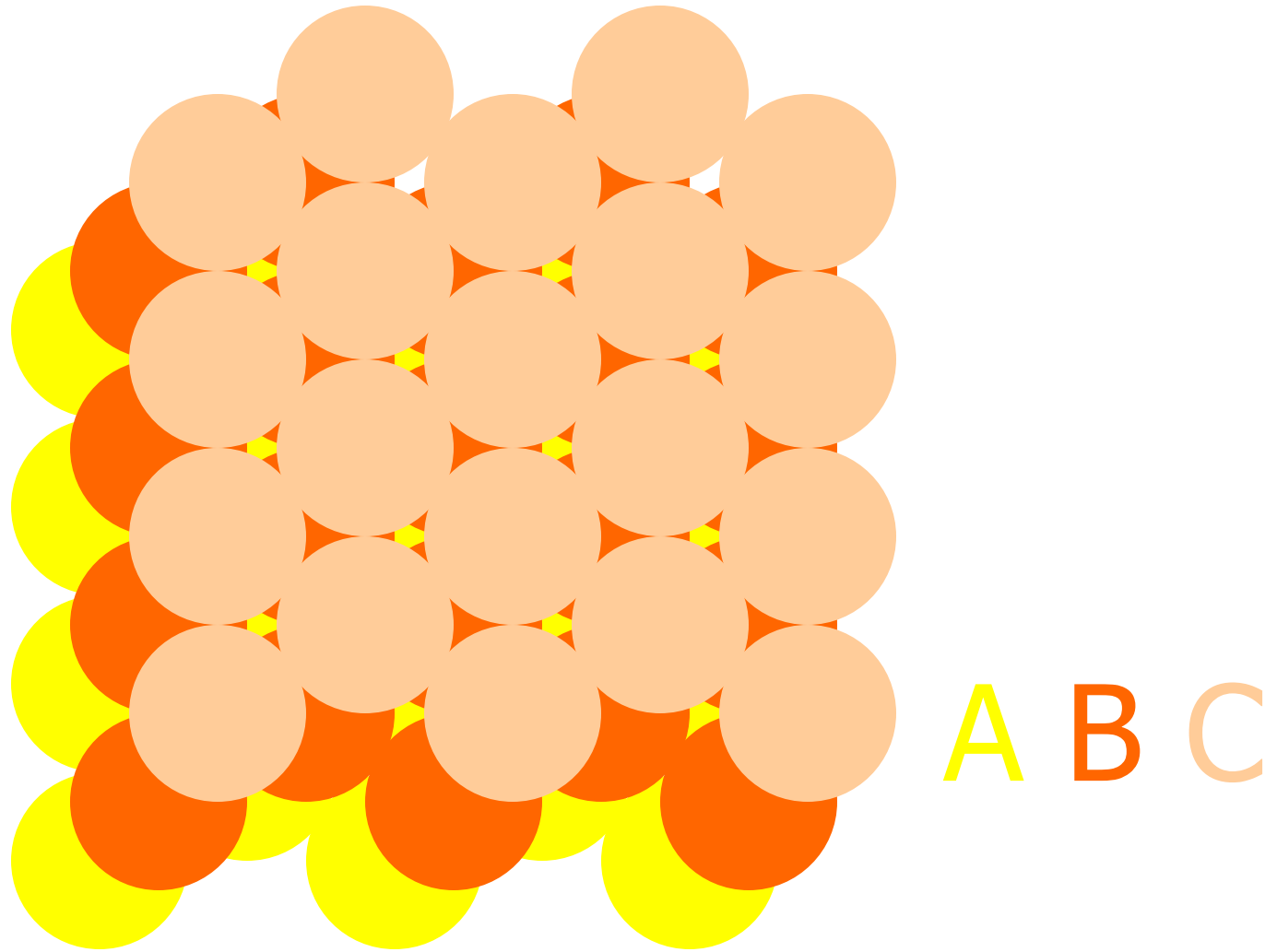
A

Face-centered cubic lattice is ABC

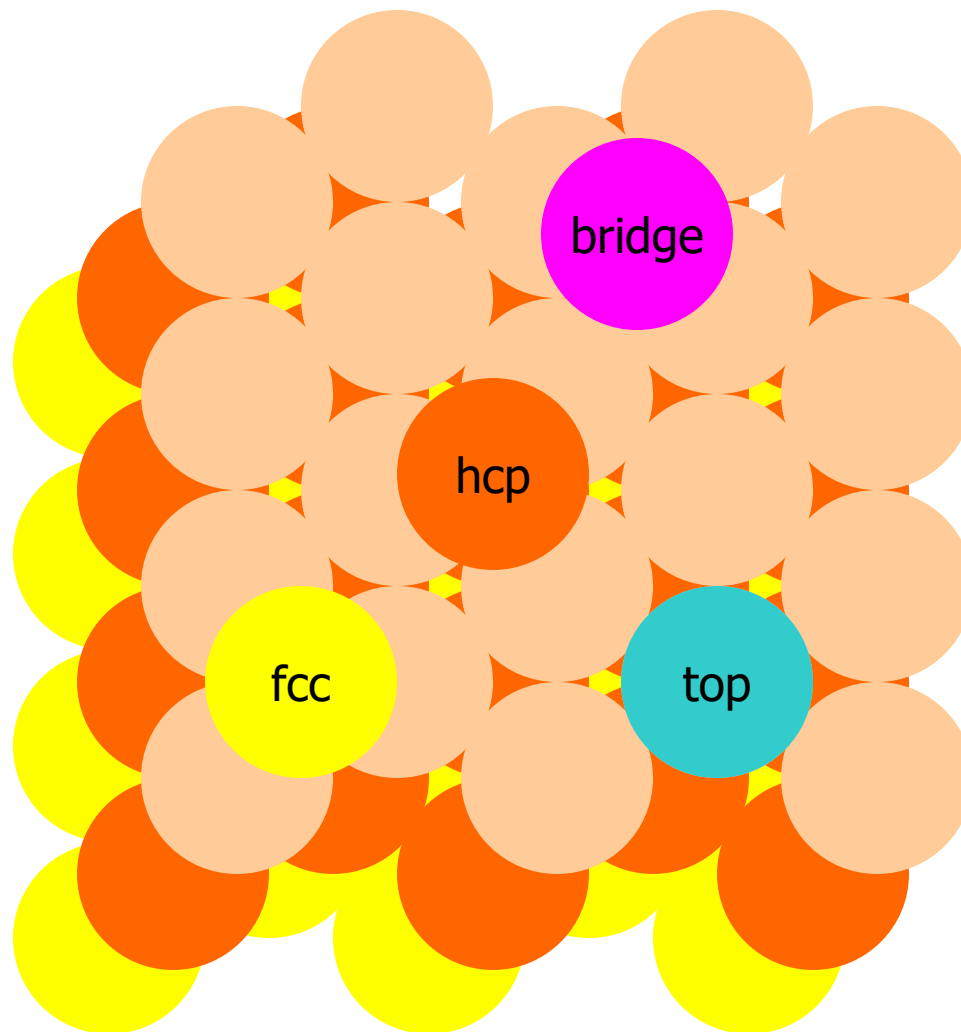


A B

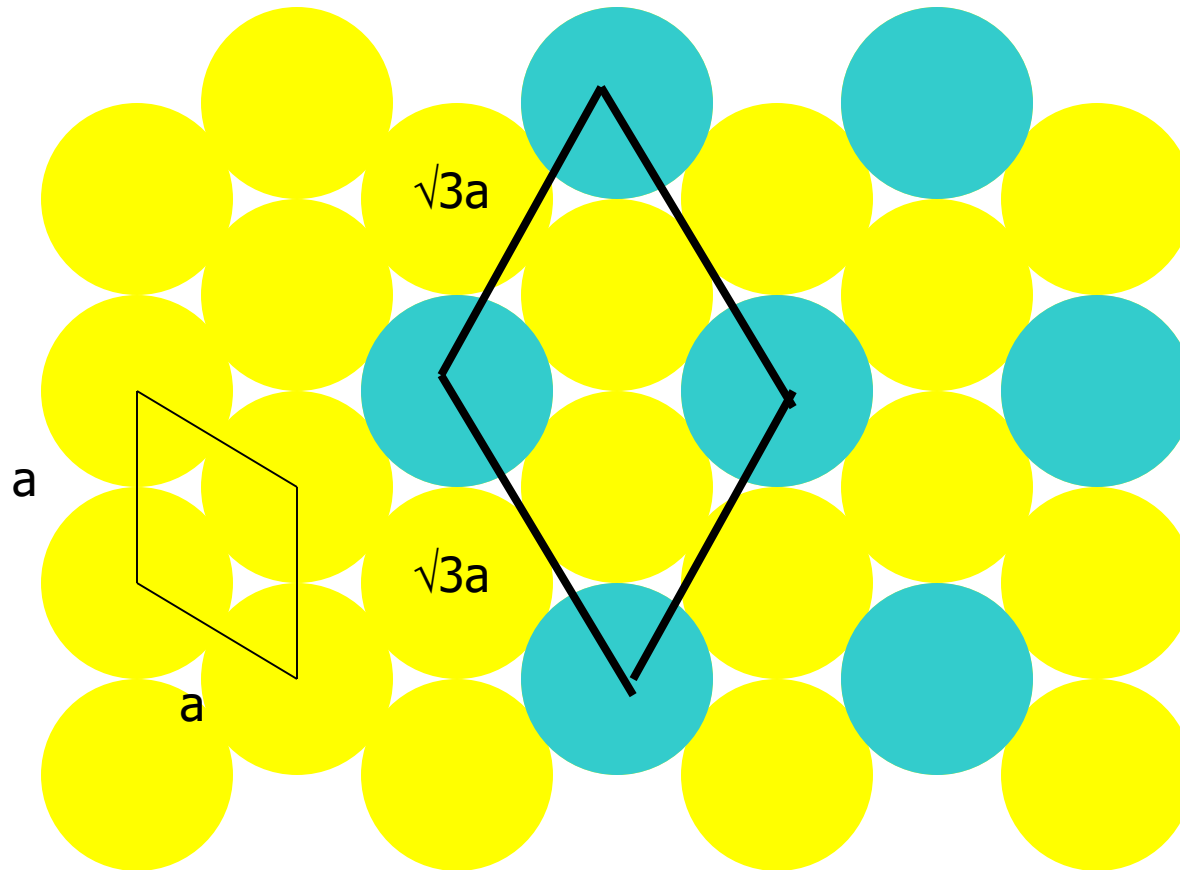
Face-centered cubic lattice is ABC



Binding sites on the 111 surface

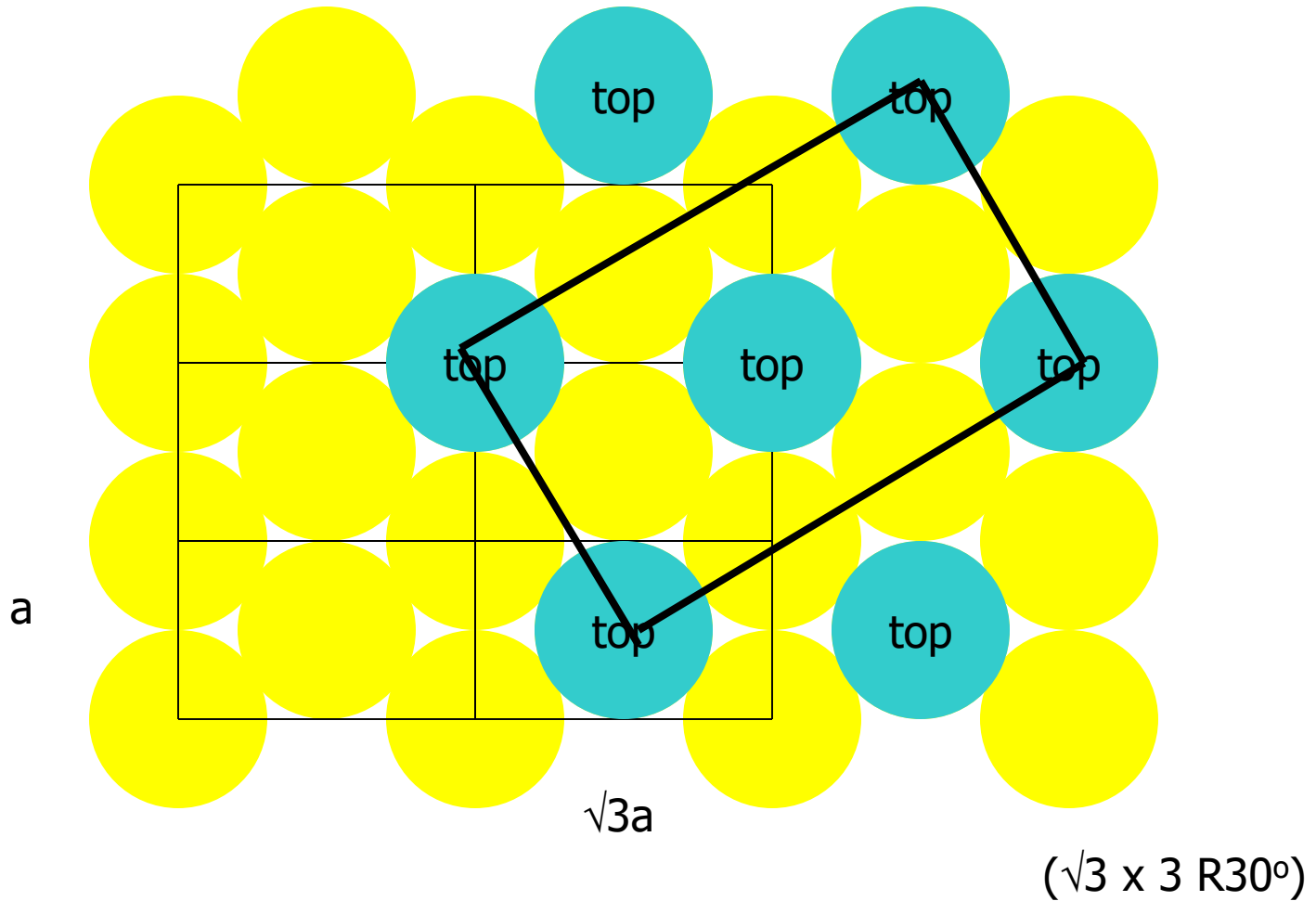


Hexagonal unit cells on the 111 surface

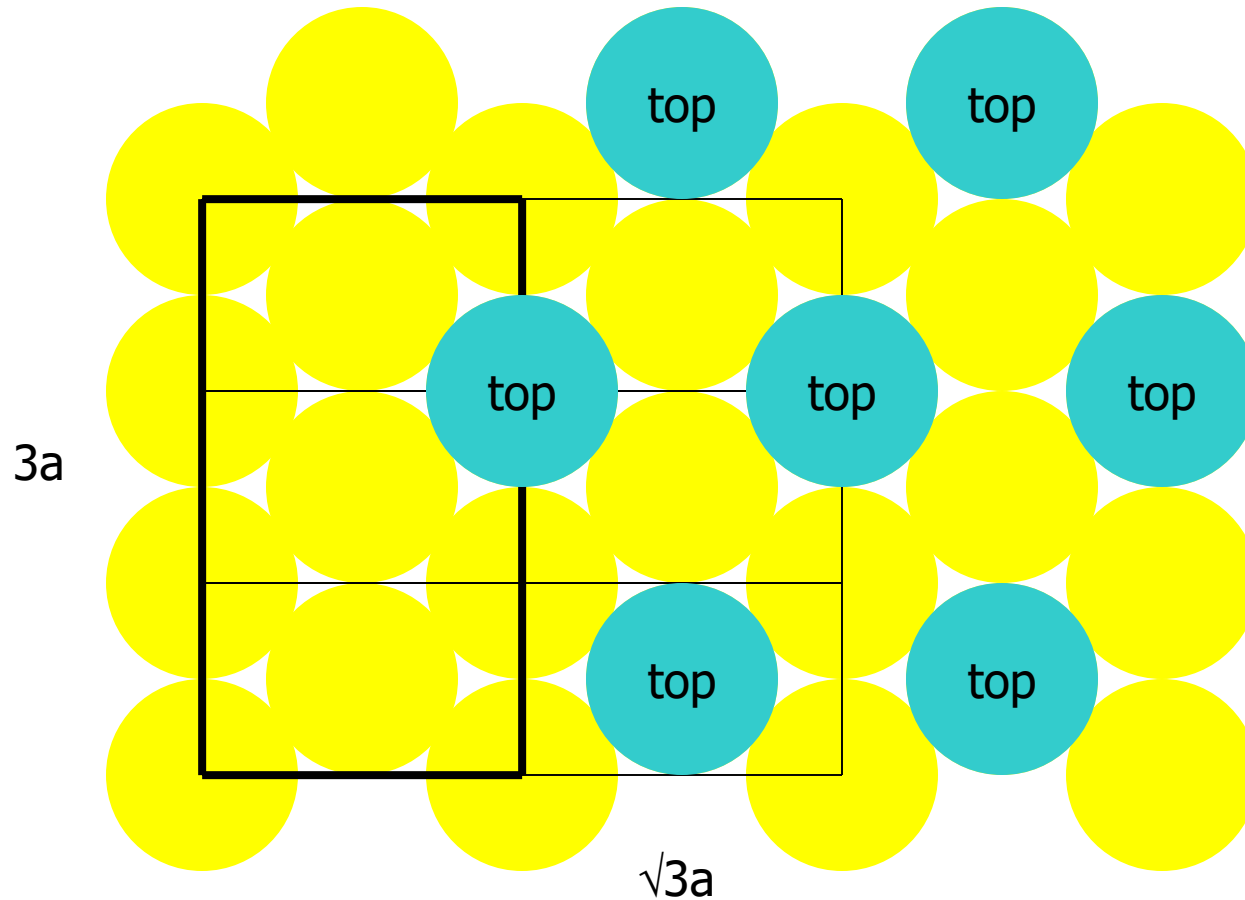


$$(\sqrt{3} \times \sqrt{3} \text{ R}30^\circ)$$

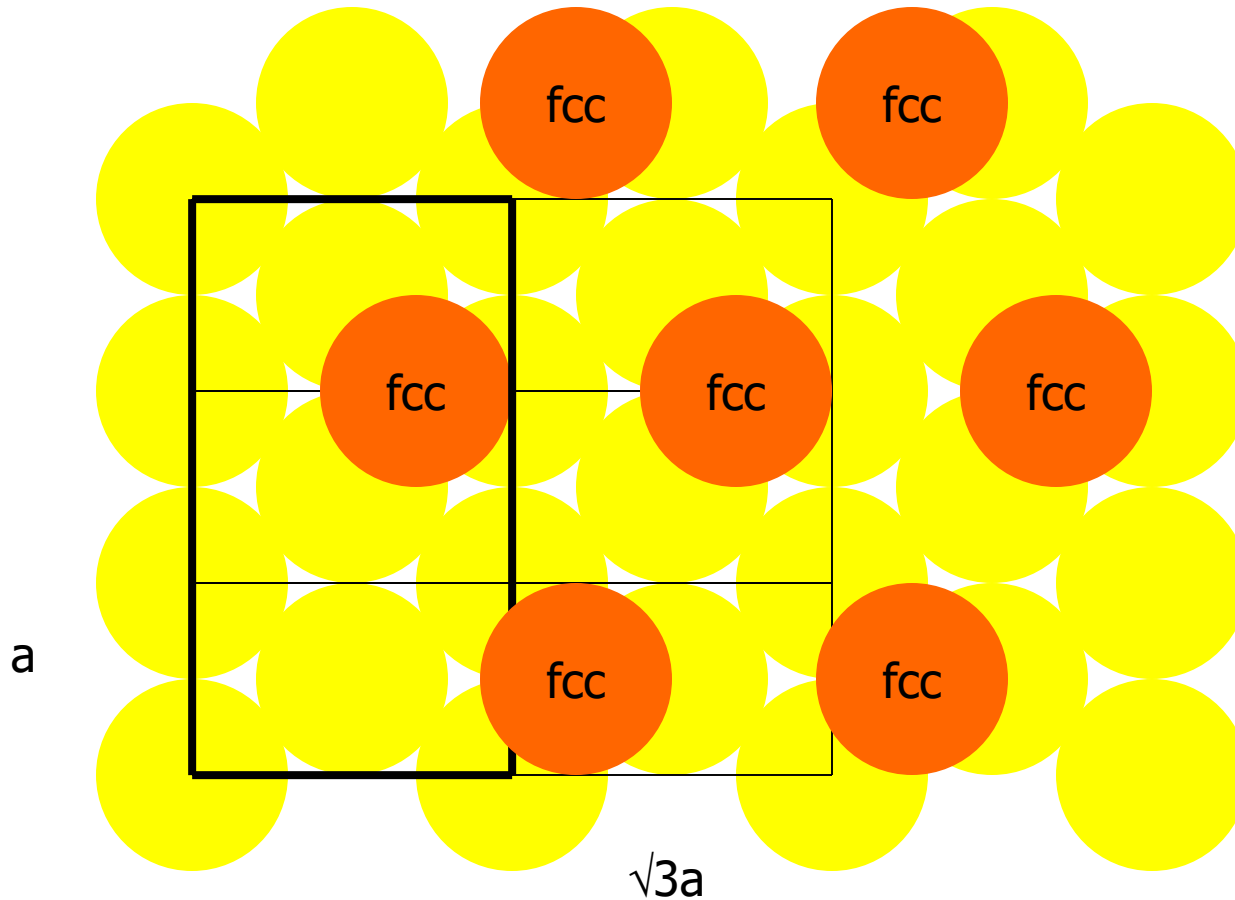
Orthorhombic unit cells on the 111 surface



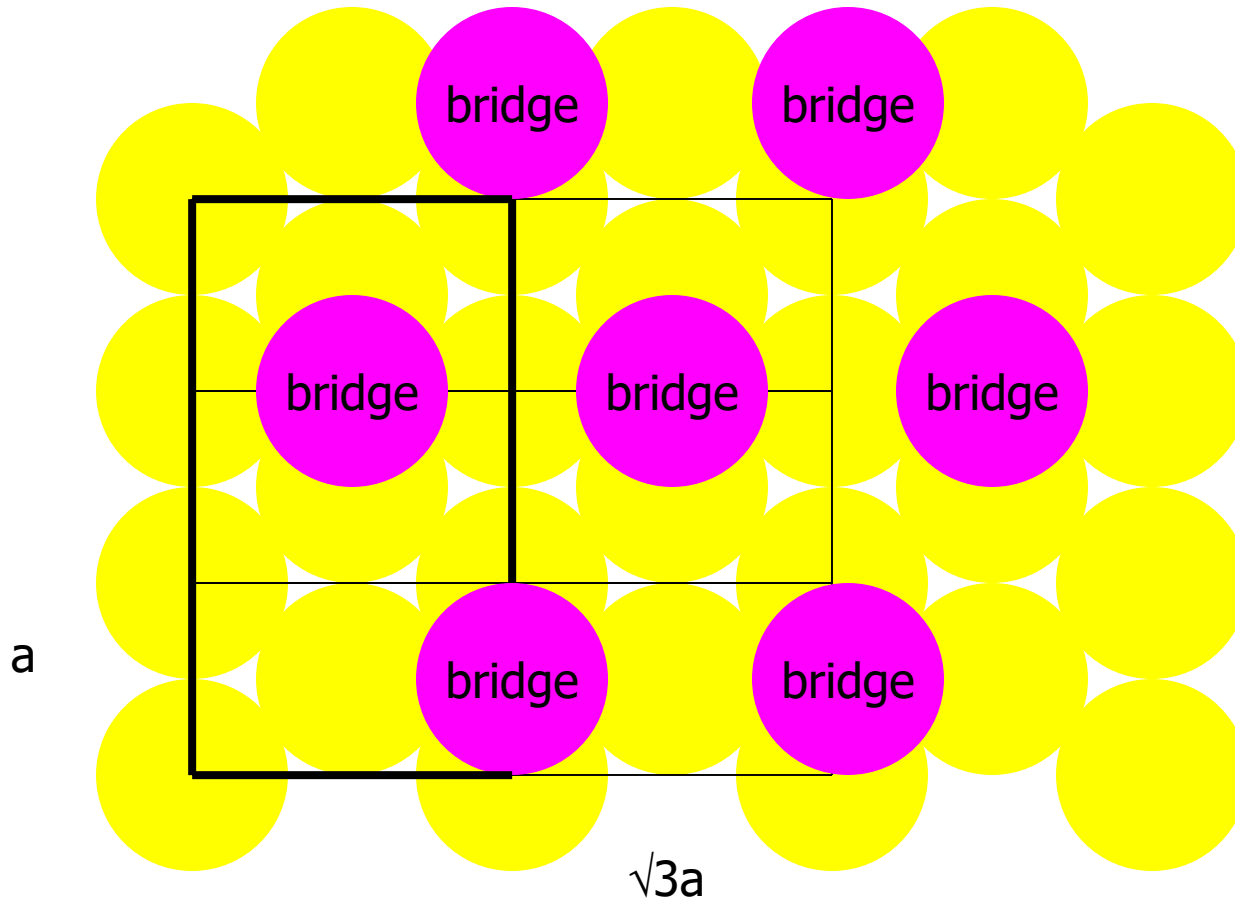
Unit cells on the 111 surface top binding site



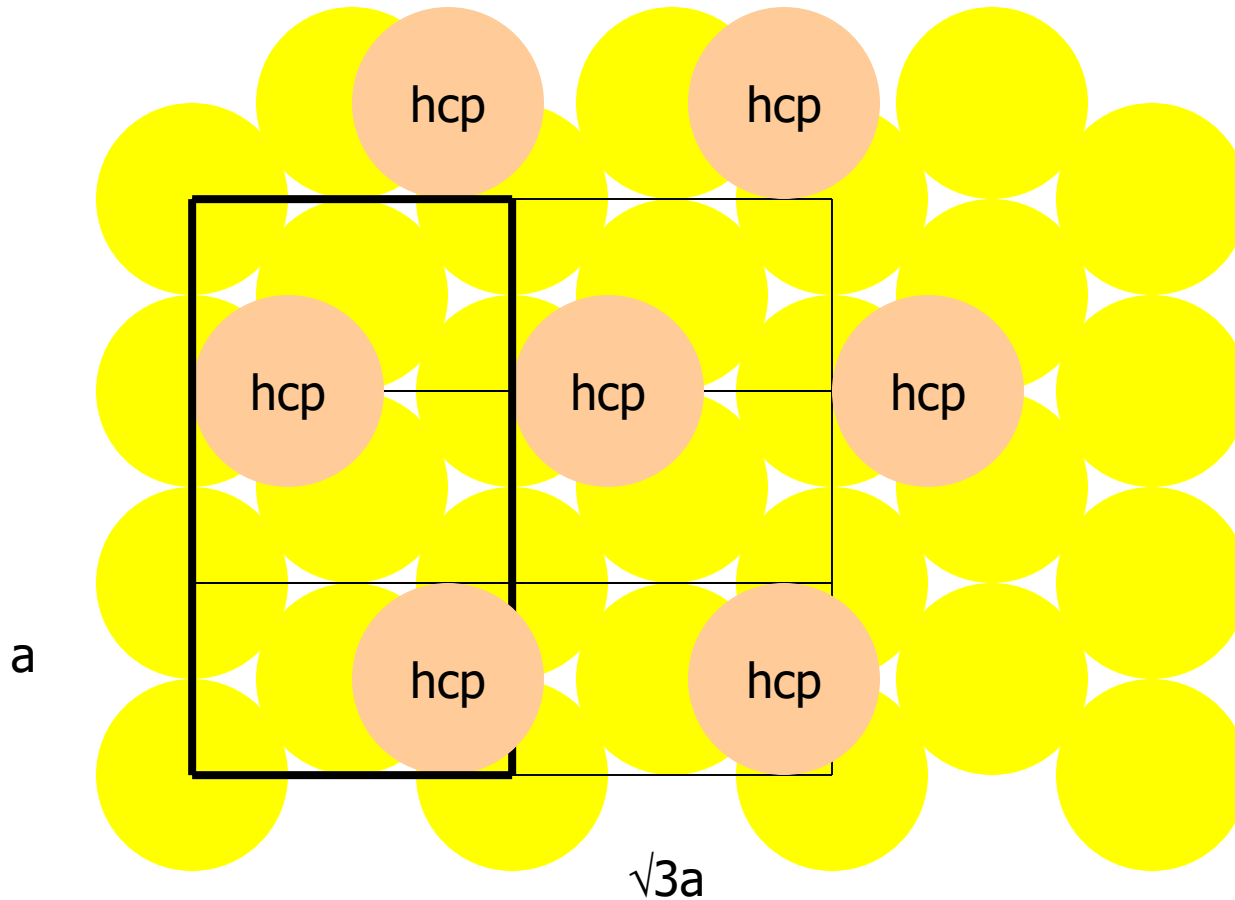
Unit cells on the 111 surface fcc binding site



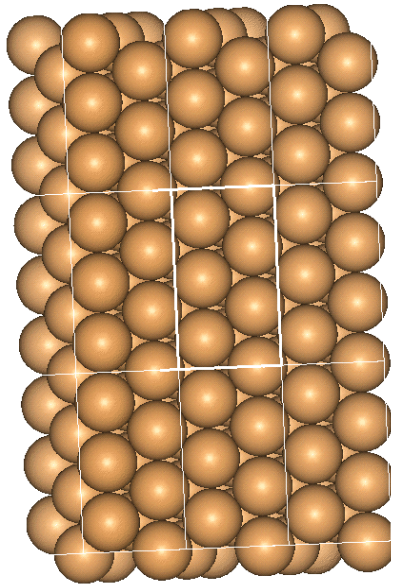
Unit cells on the 111 surface bridge binding site



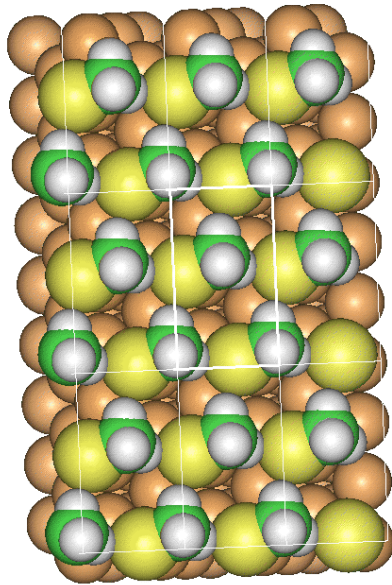
Unit cells on the 111 surface hcp binding site



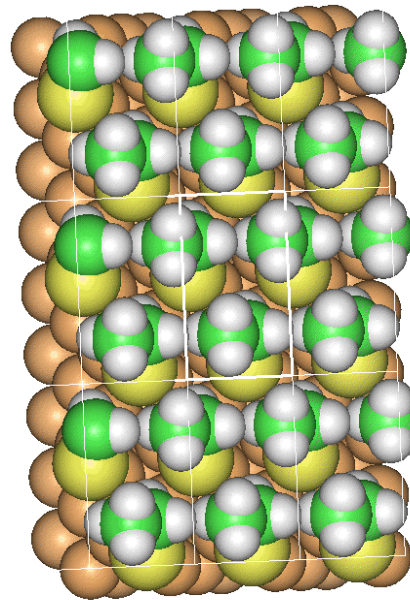
Comparing different chain lengths on Au(111)



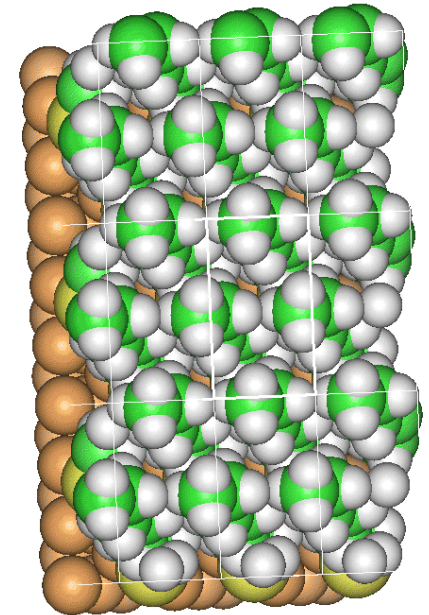
Au(111)



SCH_3
on Au(111)



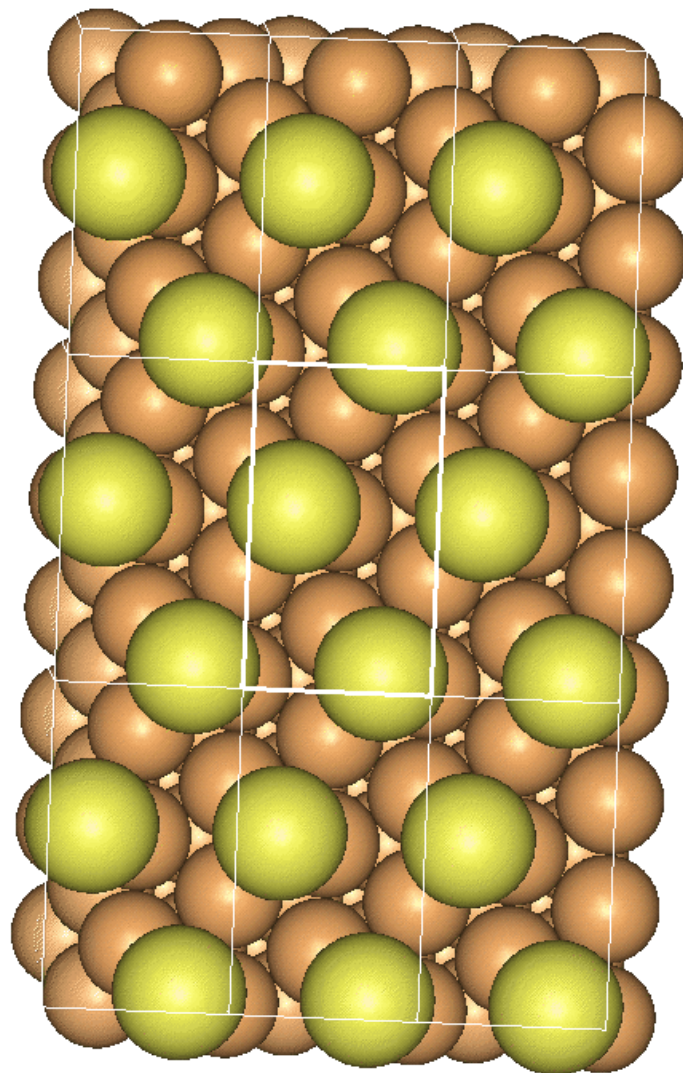
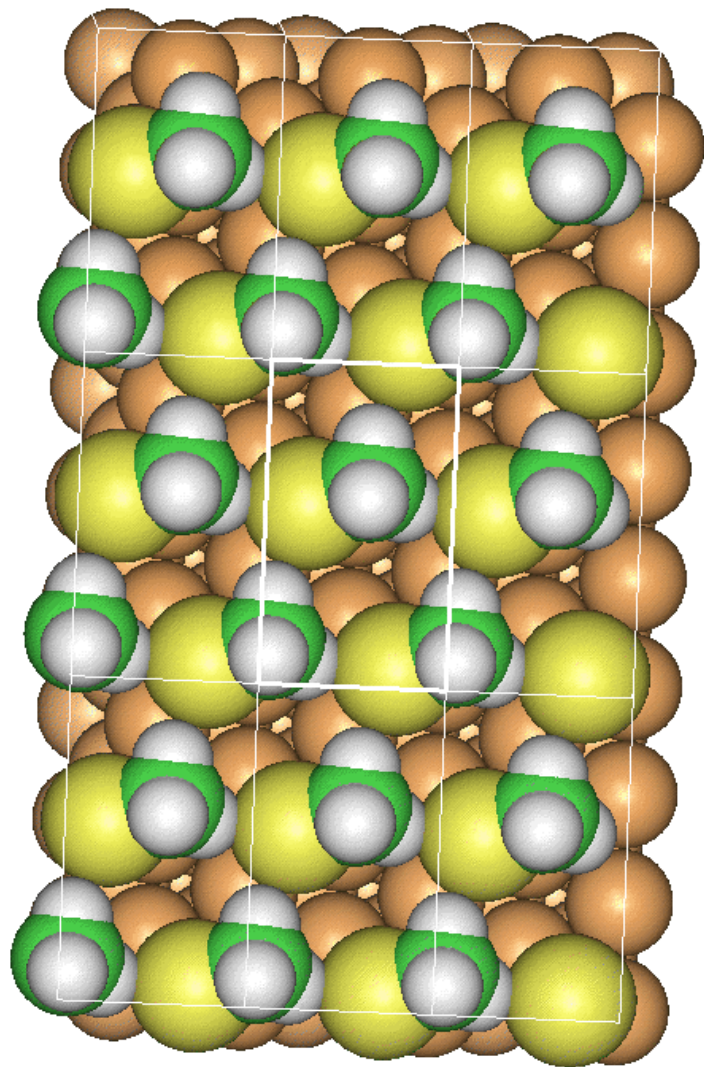
SC_2H_5
on Au(111)



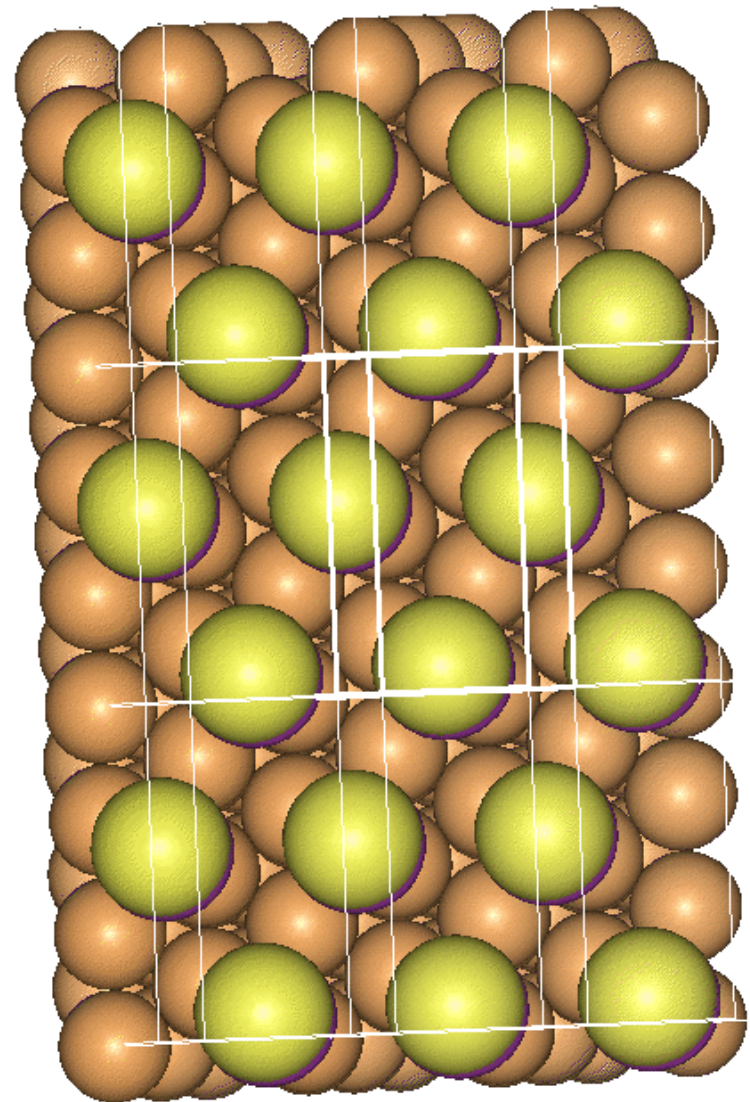
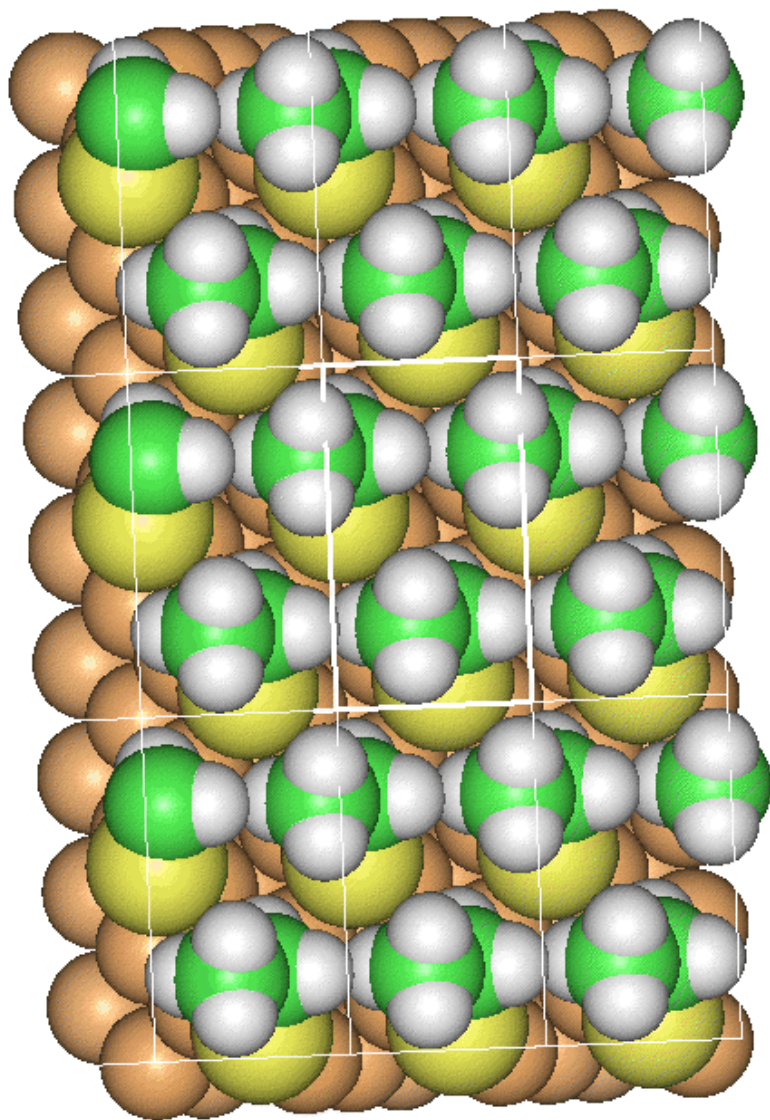
SC_6H_{13}
on Au(111)

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

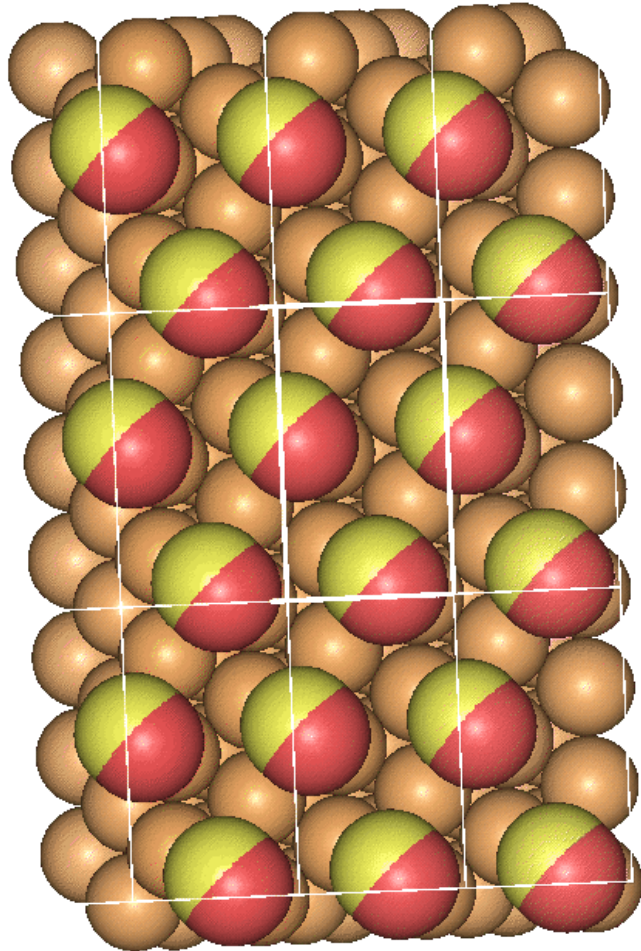
Methane thiol



Ethane thiol



The difference between methane and ethane thiol

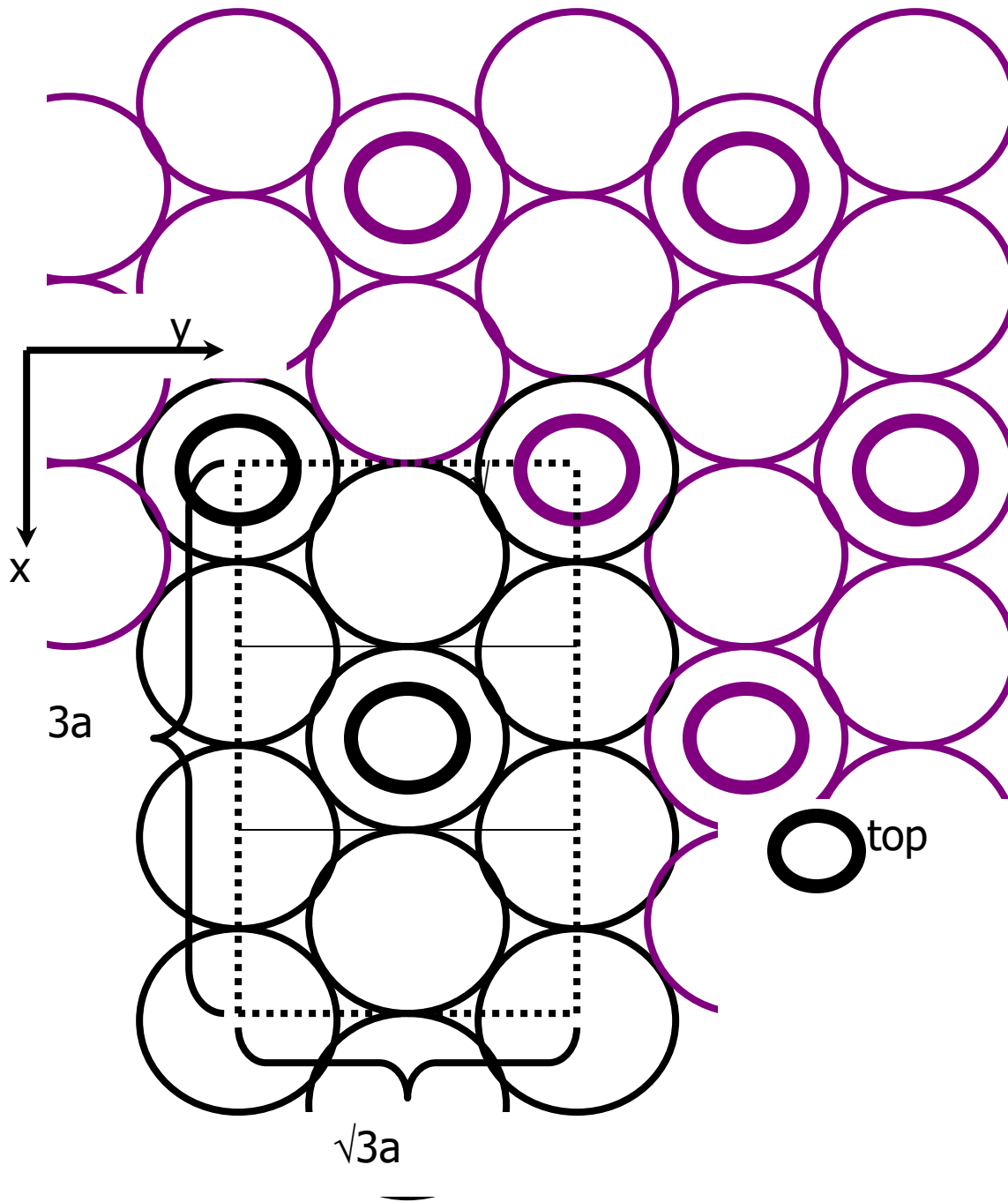


Ethane thiol
Fcc bridge site
Two au atoms

Methane thiol
Fcc hollow site
Three Au atoms

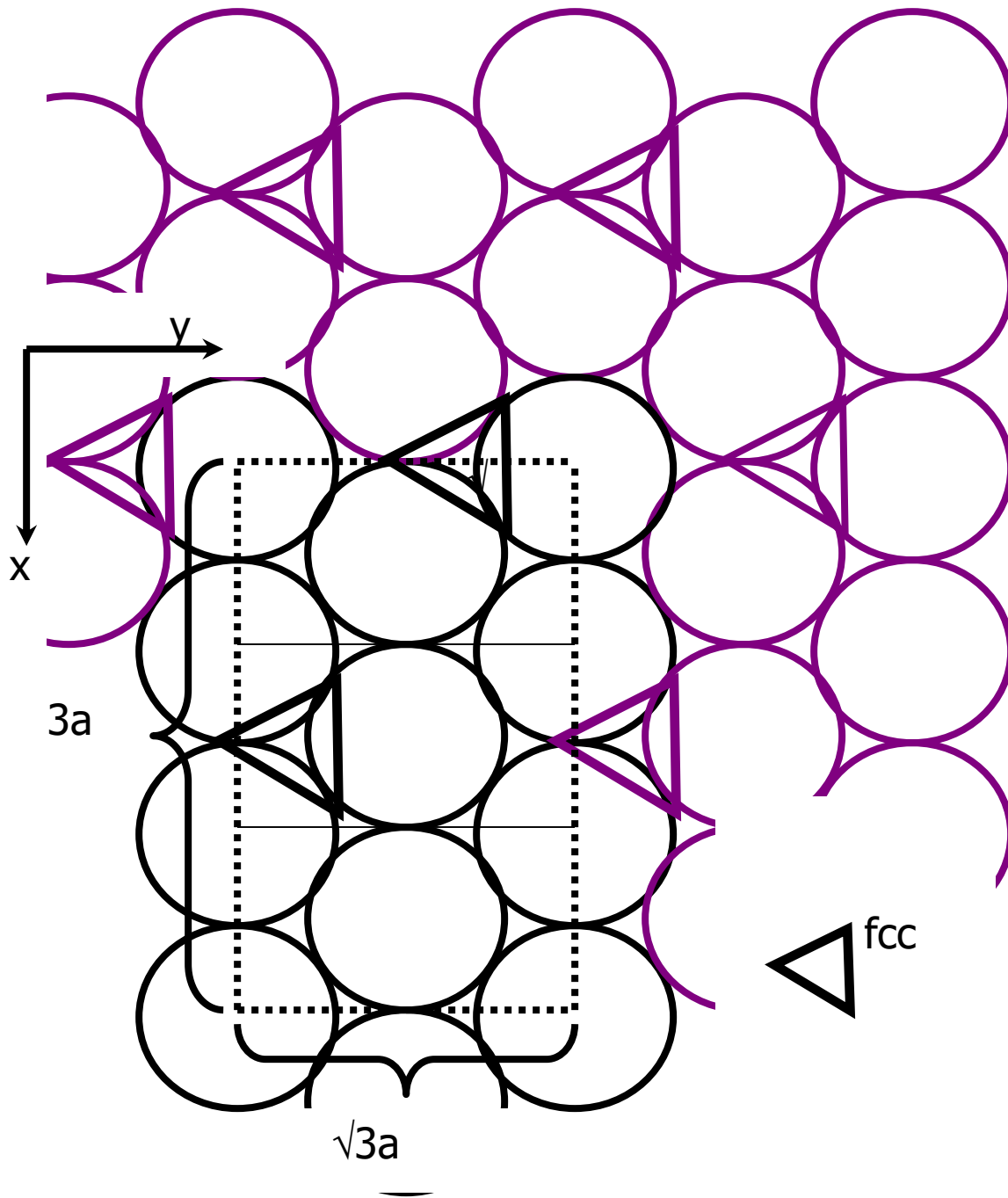
Binding sites on Au(111)

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



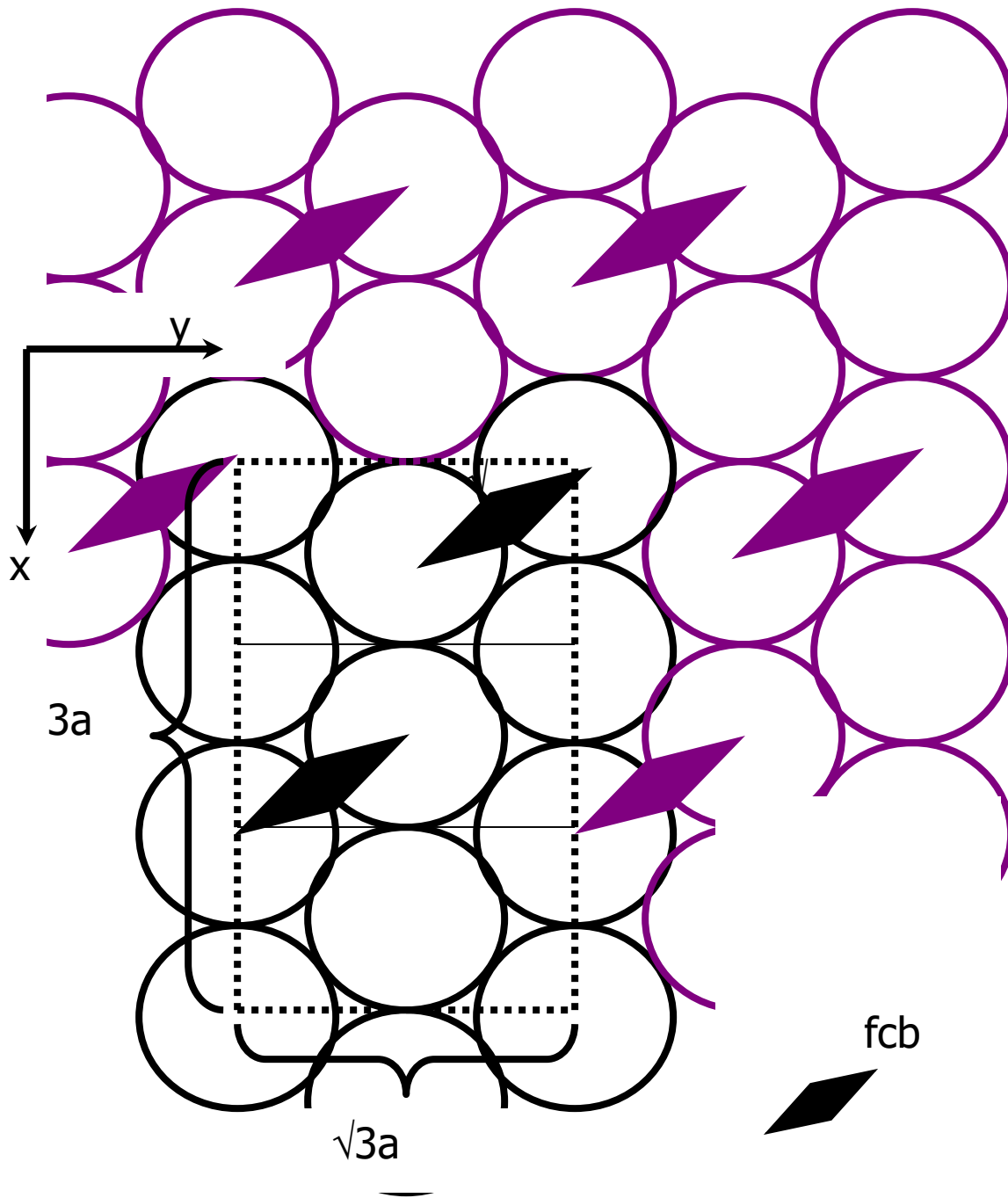
Binding sites on Au(111)

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

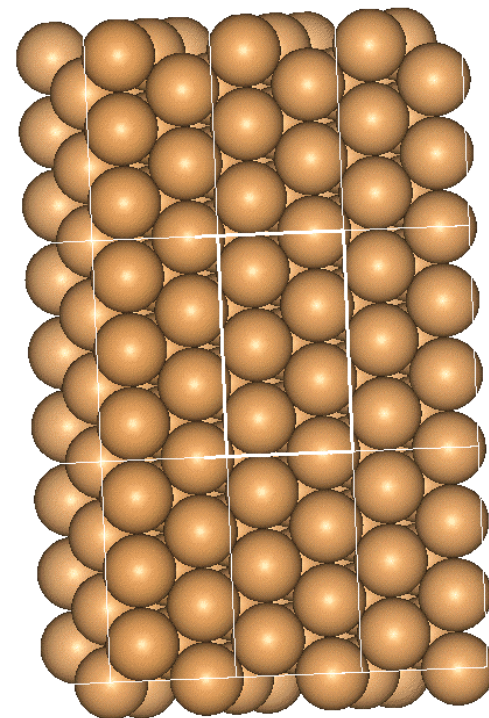
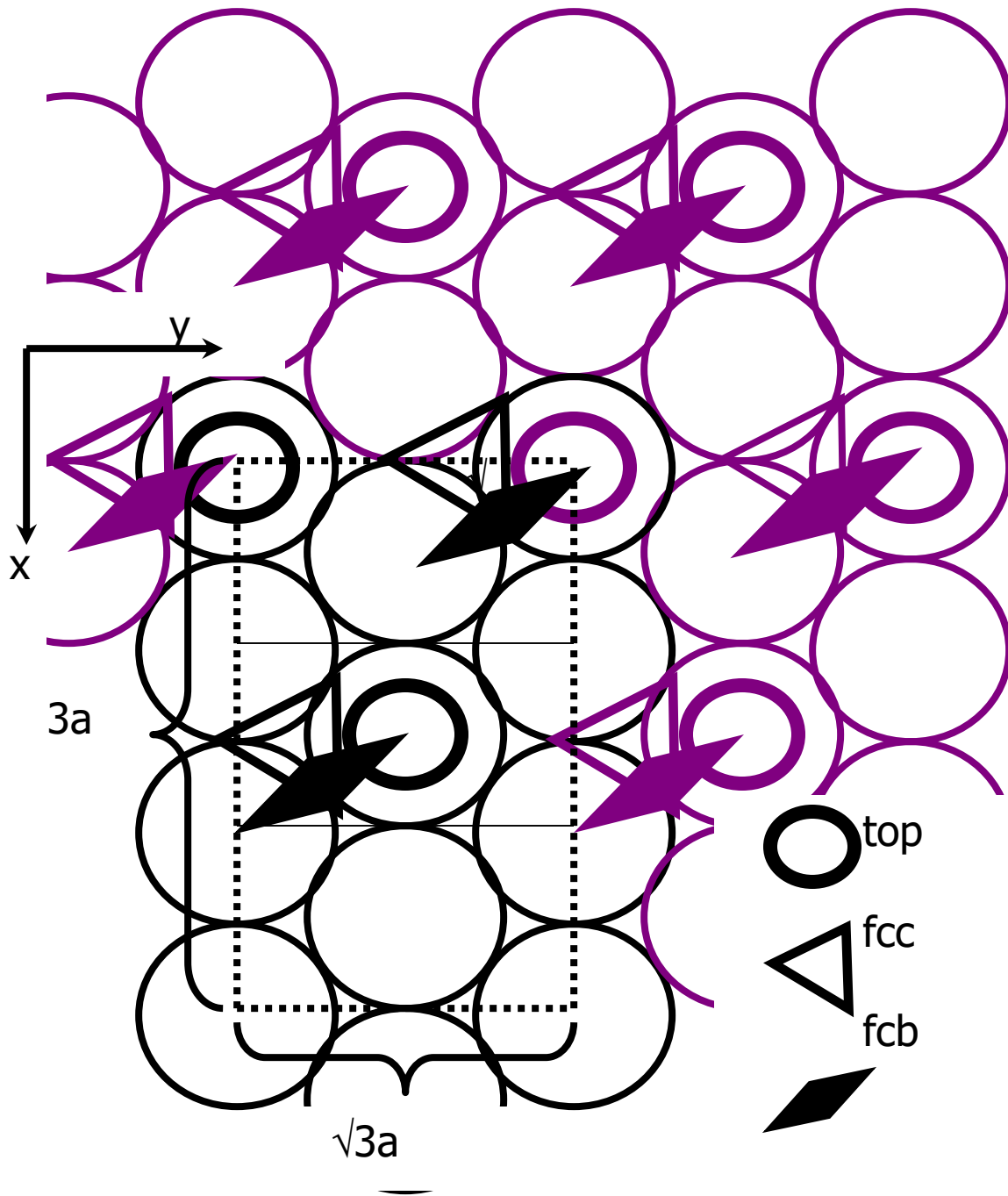


Binding sites on Au(111)

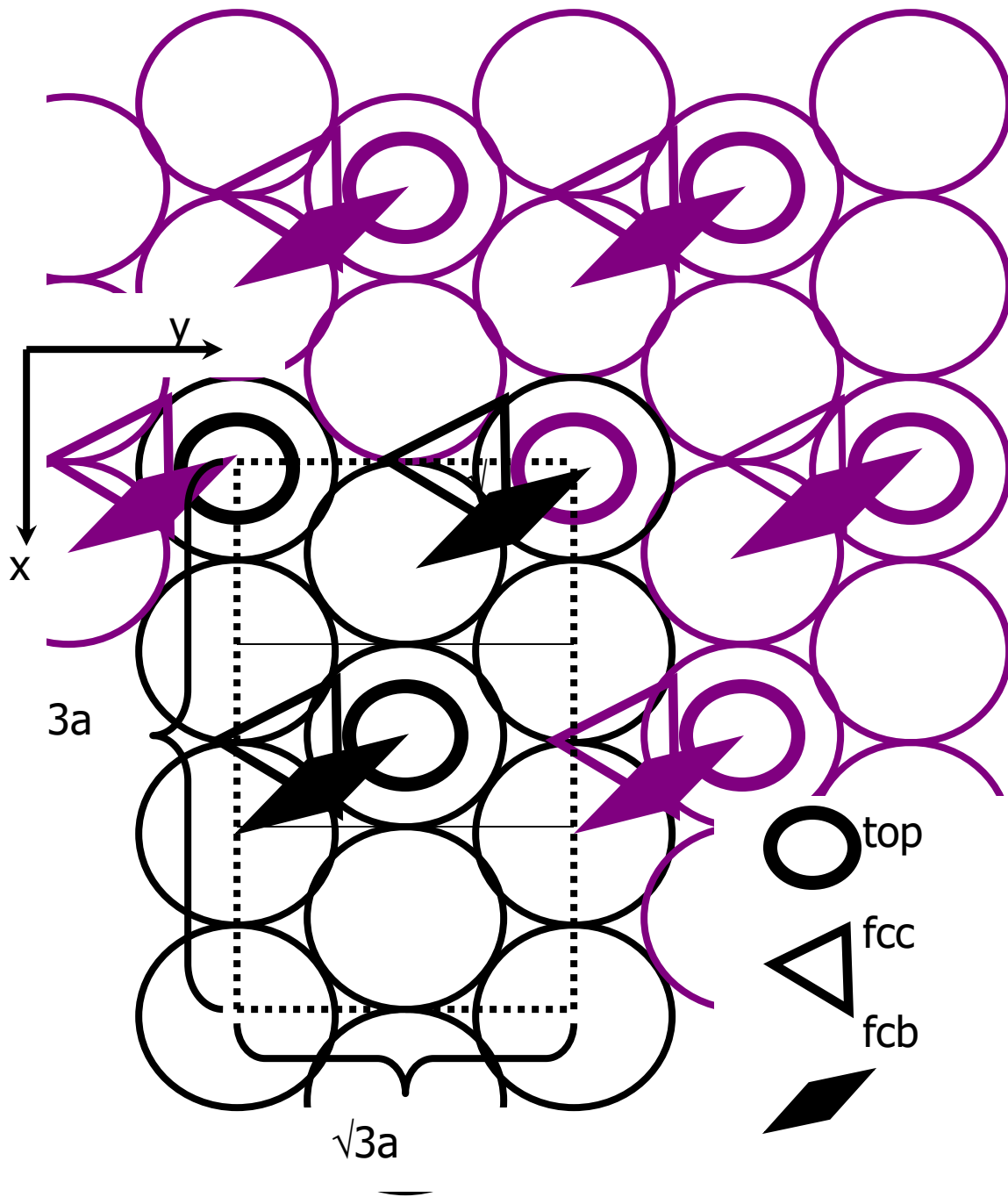
The Au atoms
can be fixed in
the optimization
to save time.



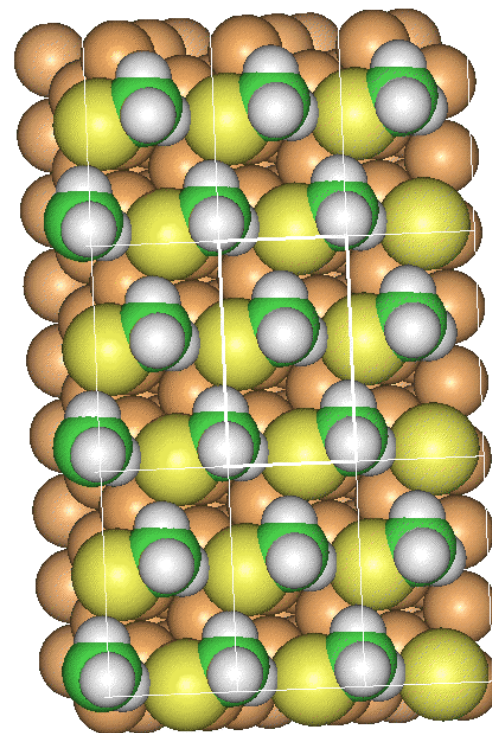
Towards a chemical model of the surface



Au(111)

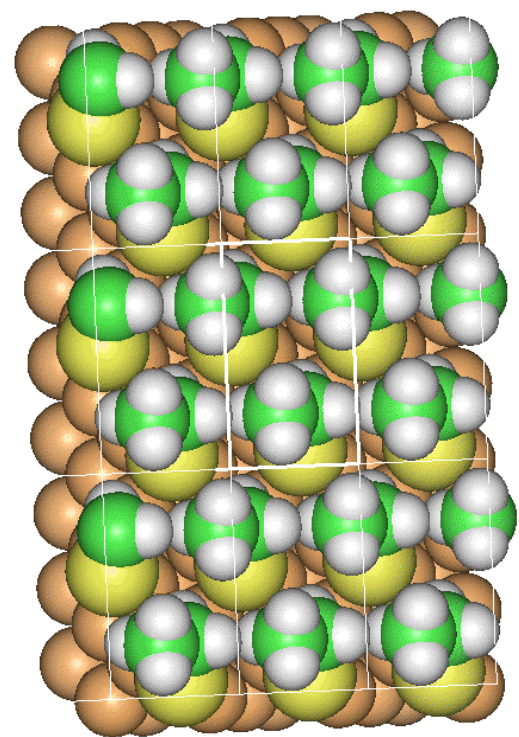
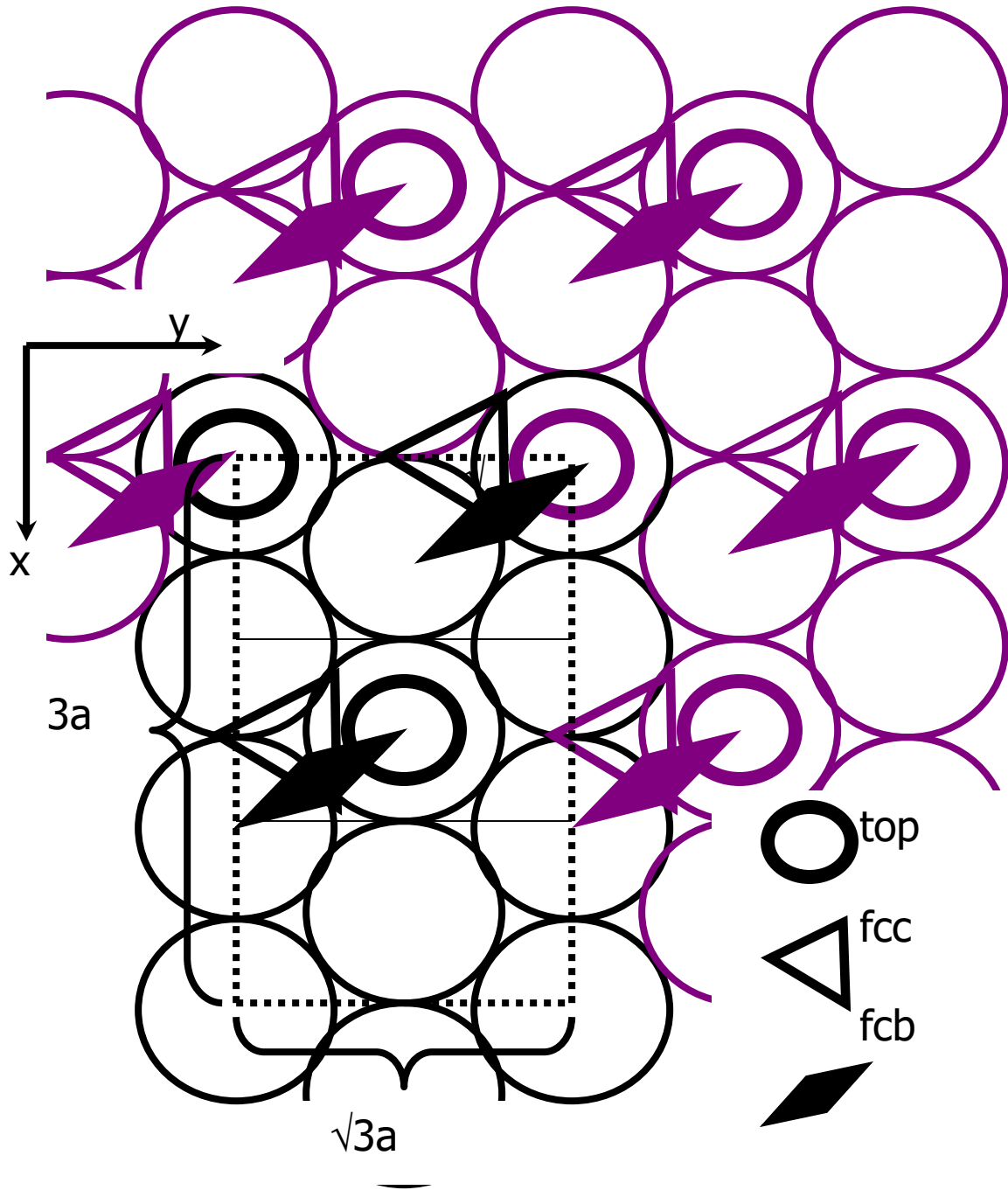


DFT calculations of self-assembled monolayers



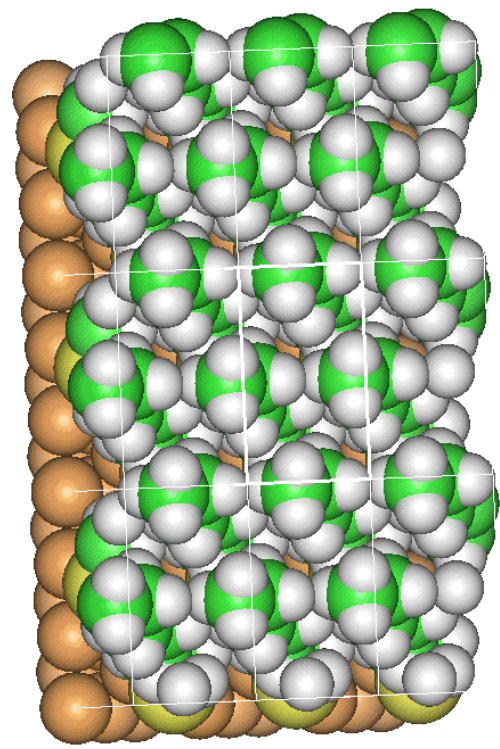
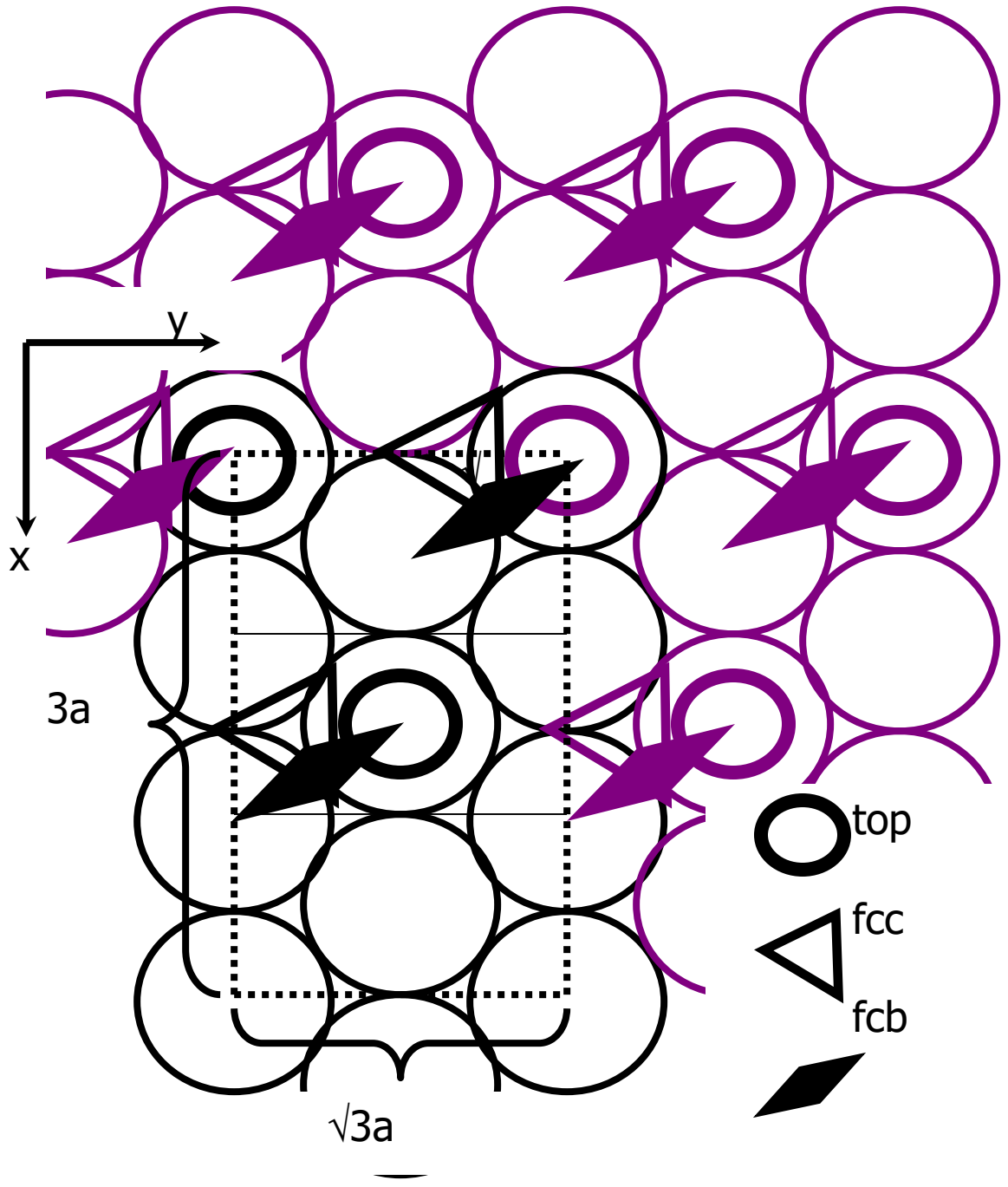
Methane thiol on Au(111)

Model energetics and structure...



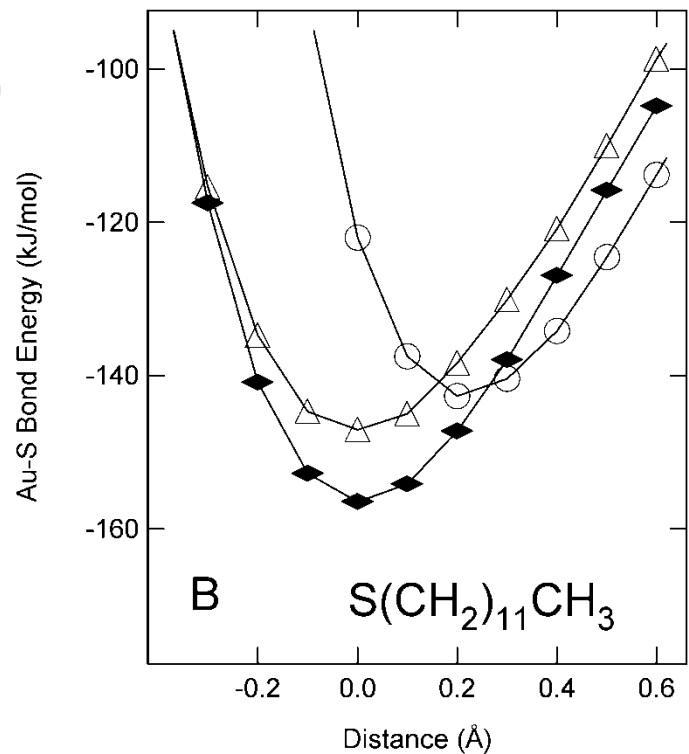
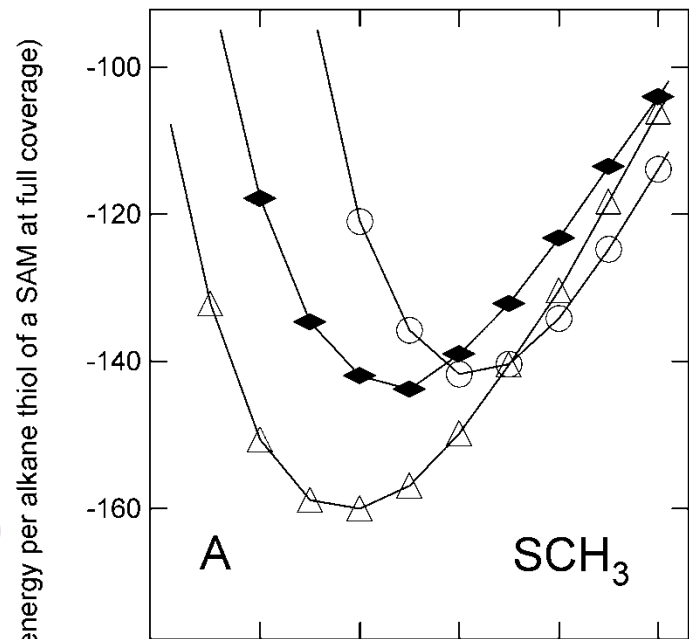
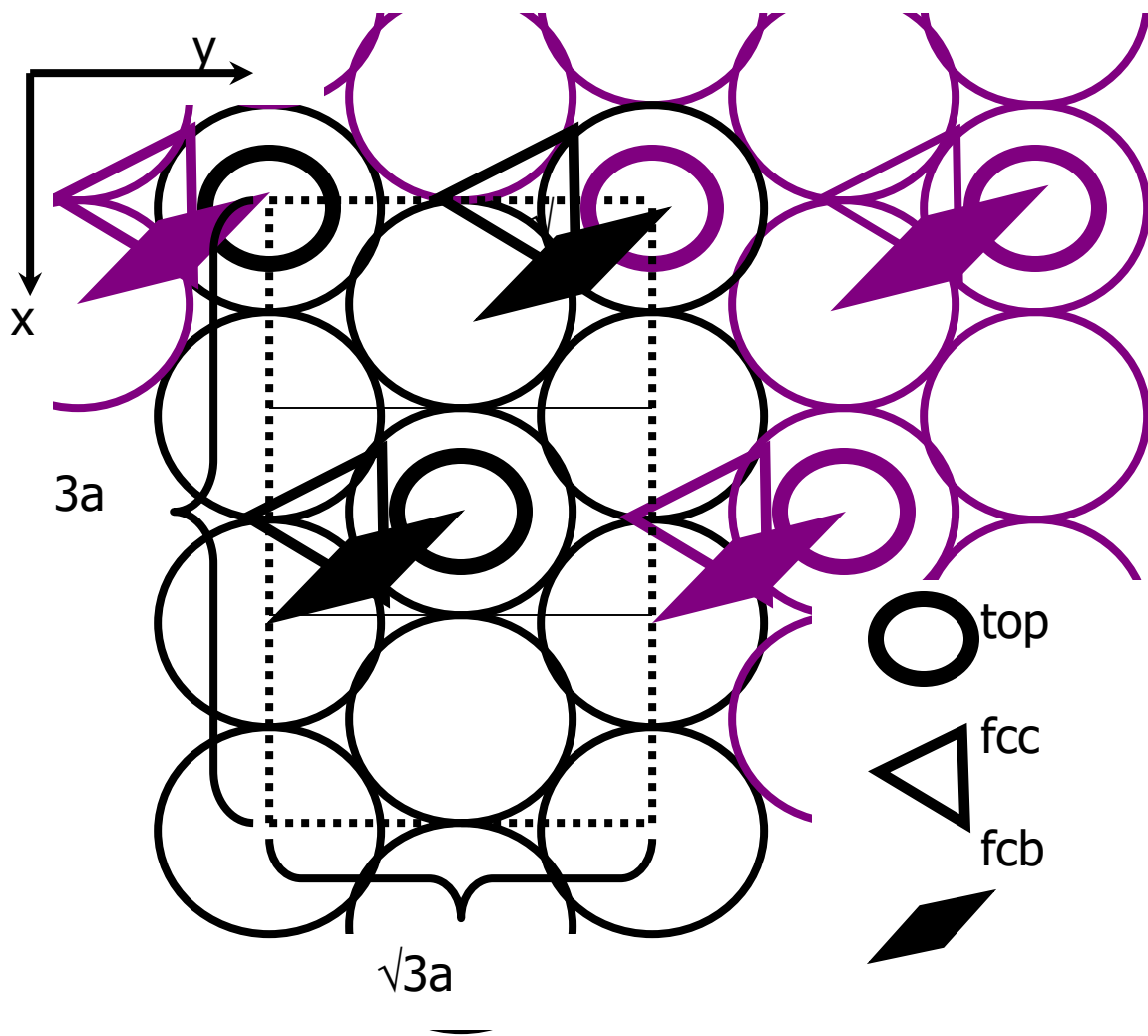
Ethane thiol on Au(111)

...as a function
of chain length.

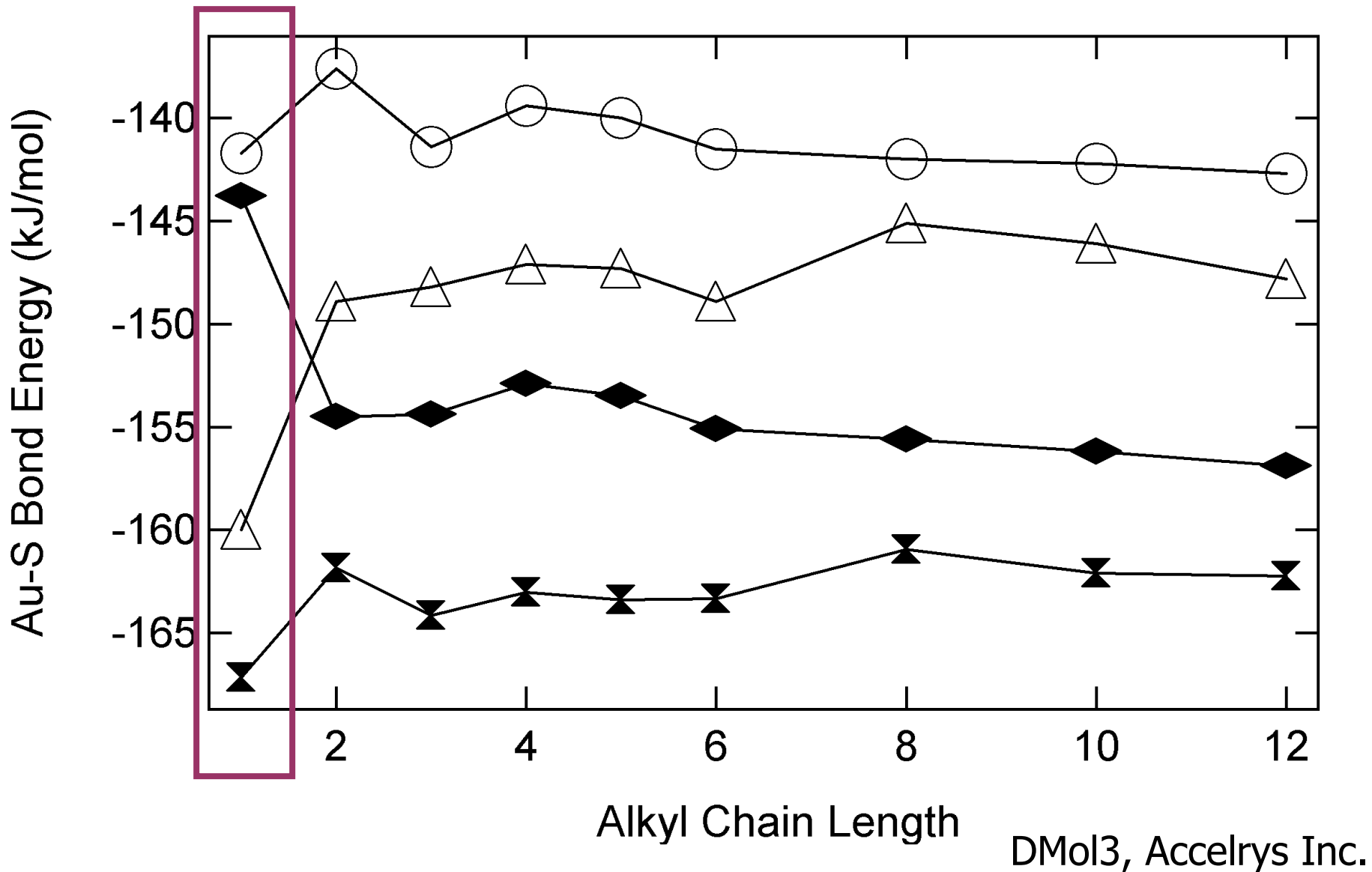


Hexane thiol
on Au(111)

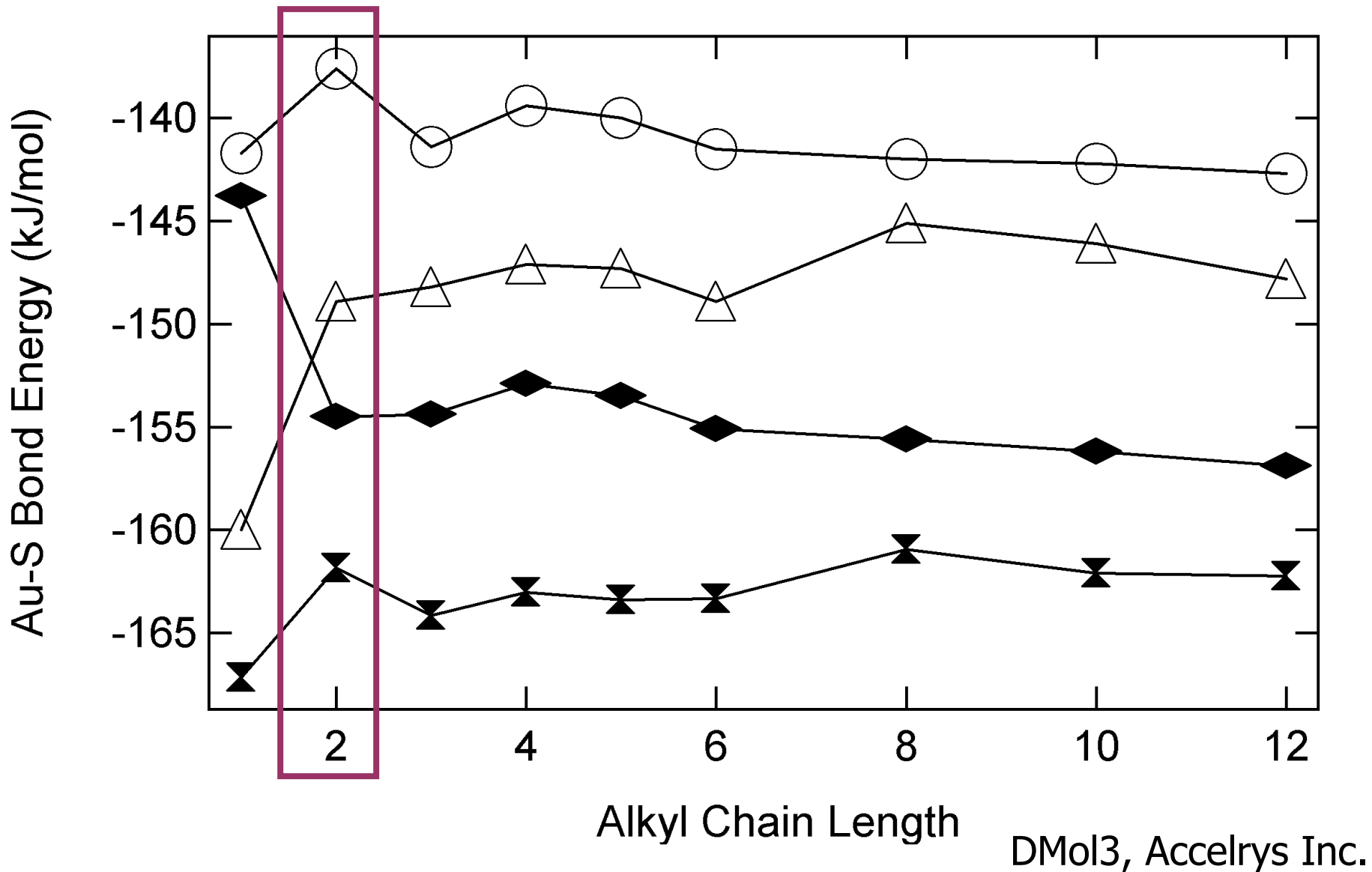
Calculation of Potential Energy of an Adsorbate on a Au(111) Surface



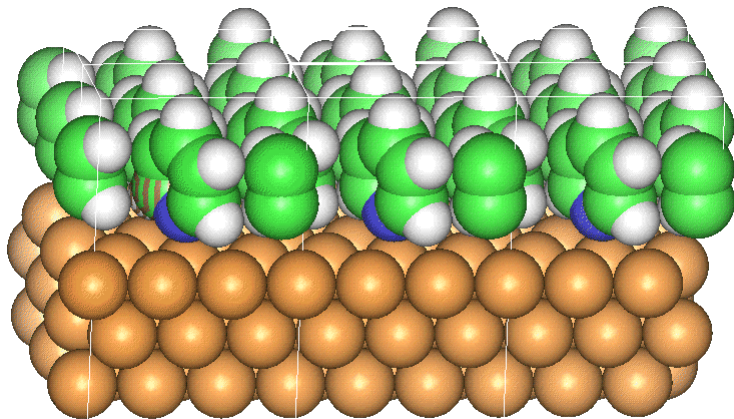
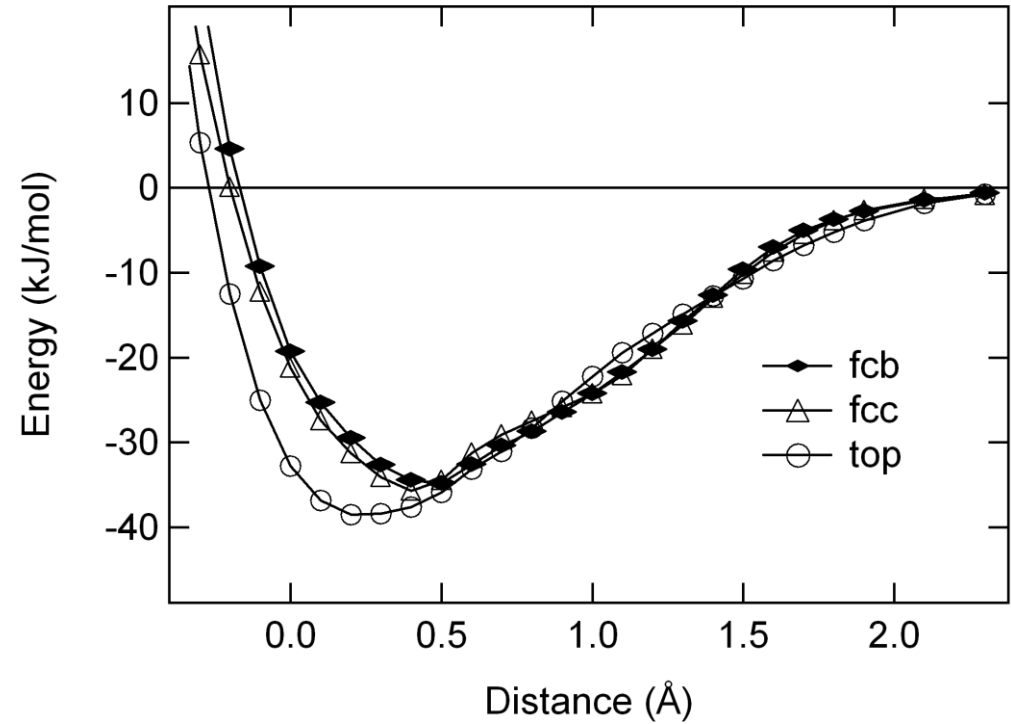
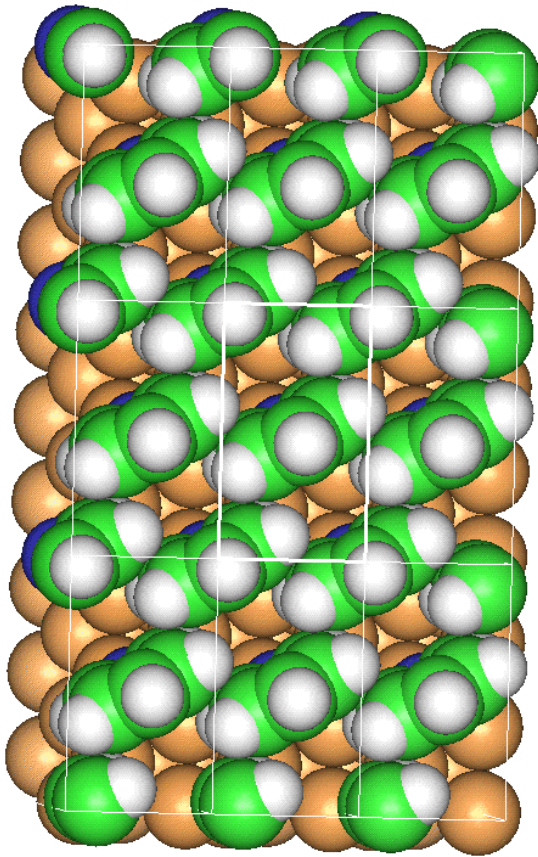
Methane thiol is anomalous



Ethane thiol follows the trend



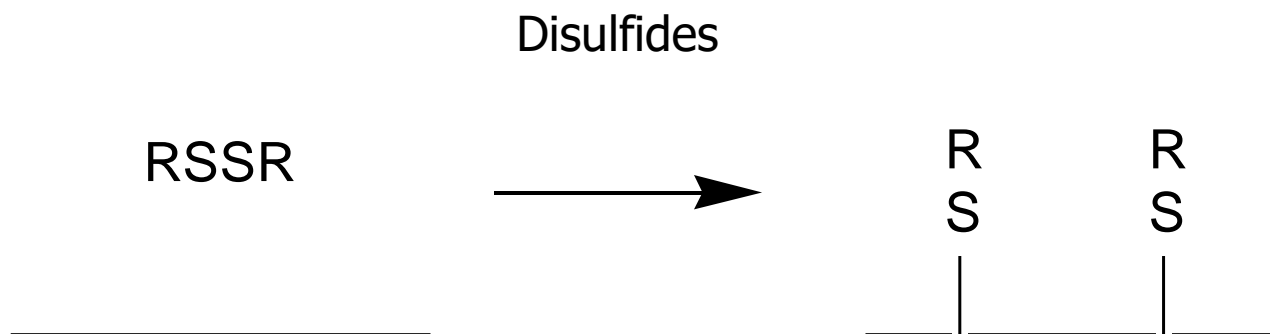
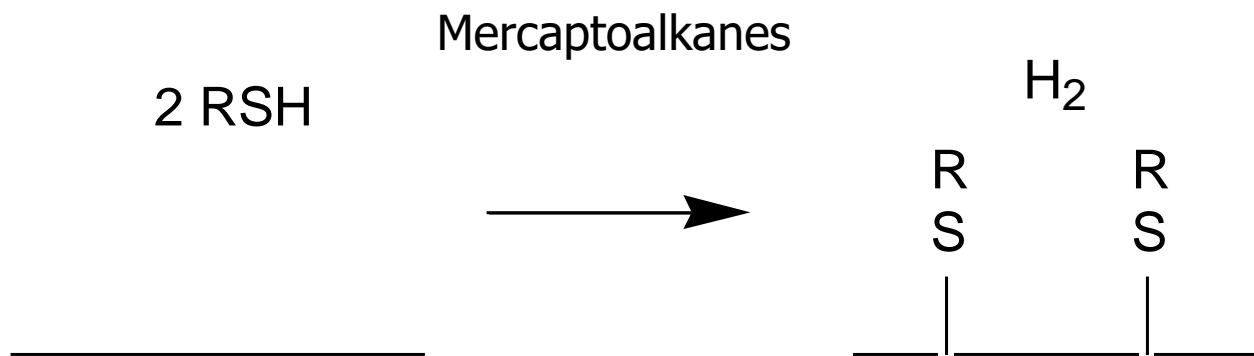
Pyridine adlayer



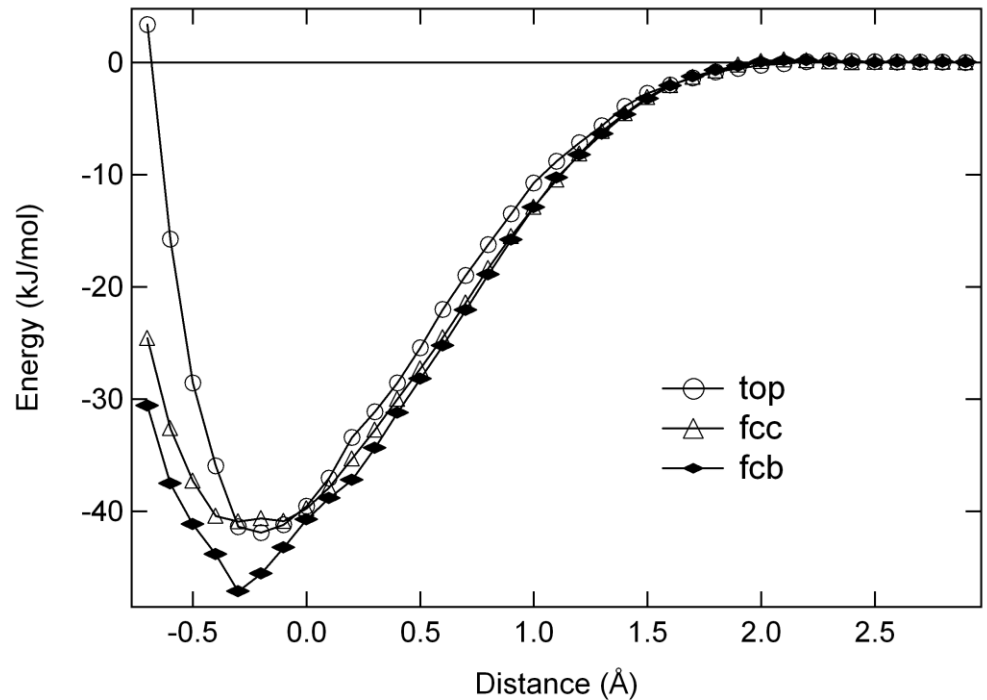
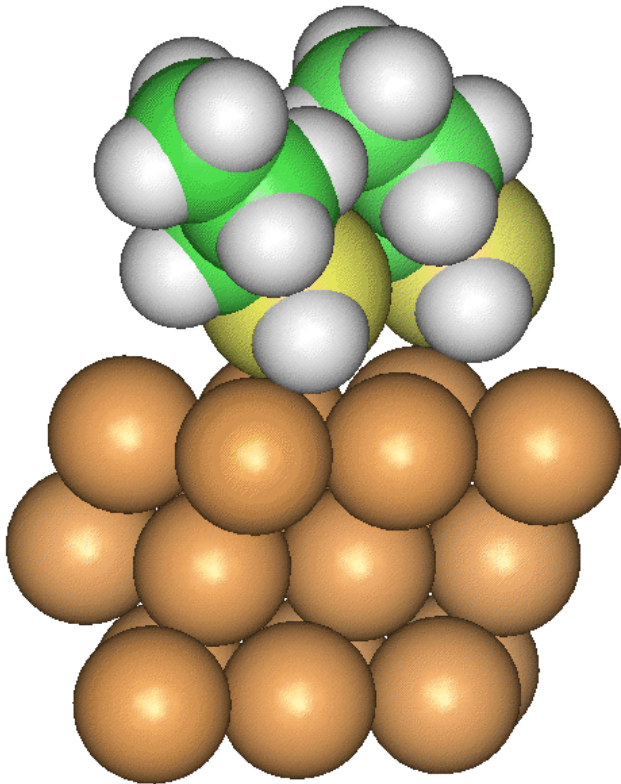
Top binding site is favored.
Binding is three times weaker
than for alkane thiols.

Possible mechanisms for formation of alkane thiol self-assembled monolayers

Where do the hydrogens go?

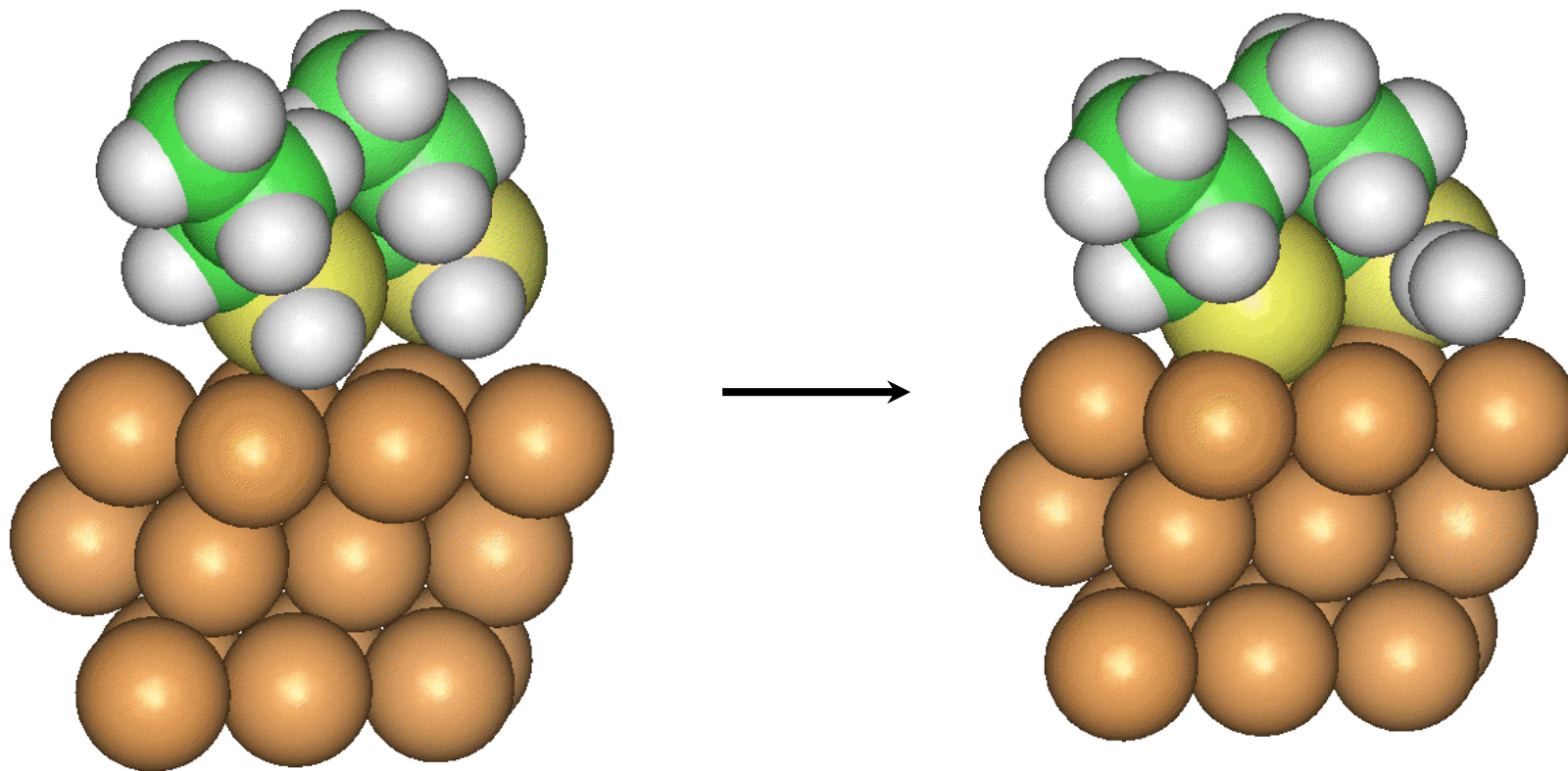


Propane mercaptan on Au(111)



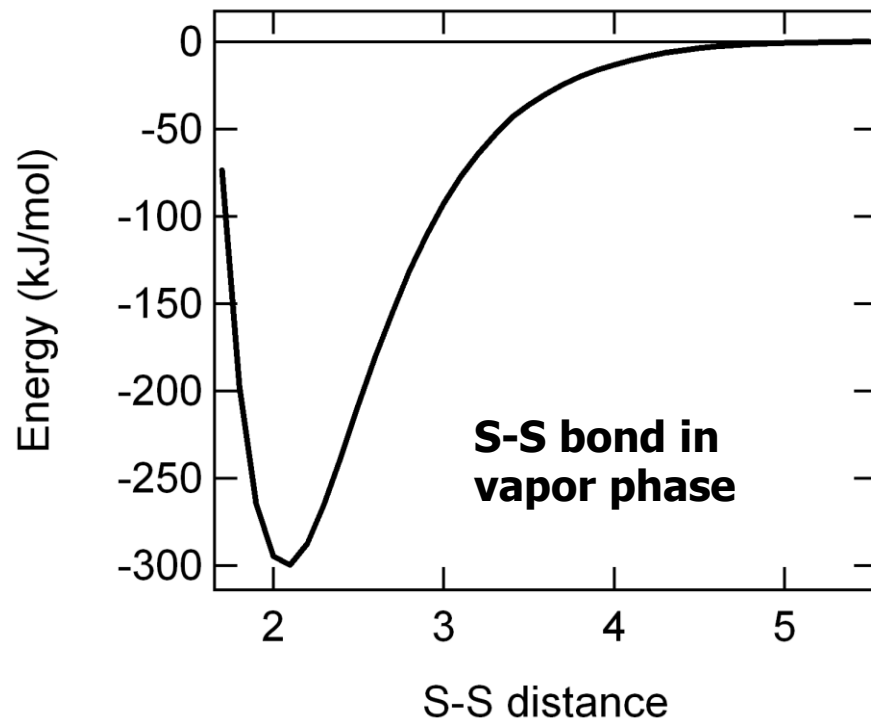
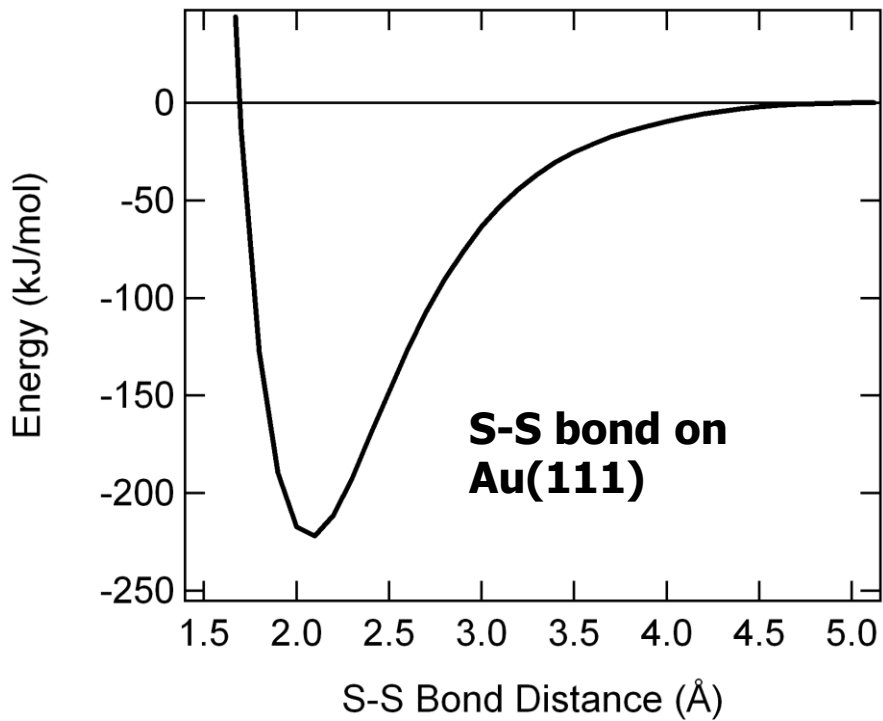
Binding strength is of the same order as that for ammonia or pyridine. However, the fcc bridge site is favored as observed for thiols.

Formation of H₂ on the Au(111) surface

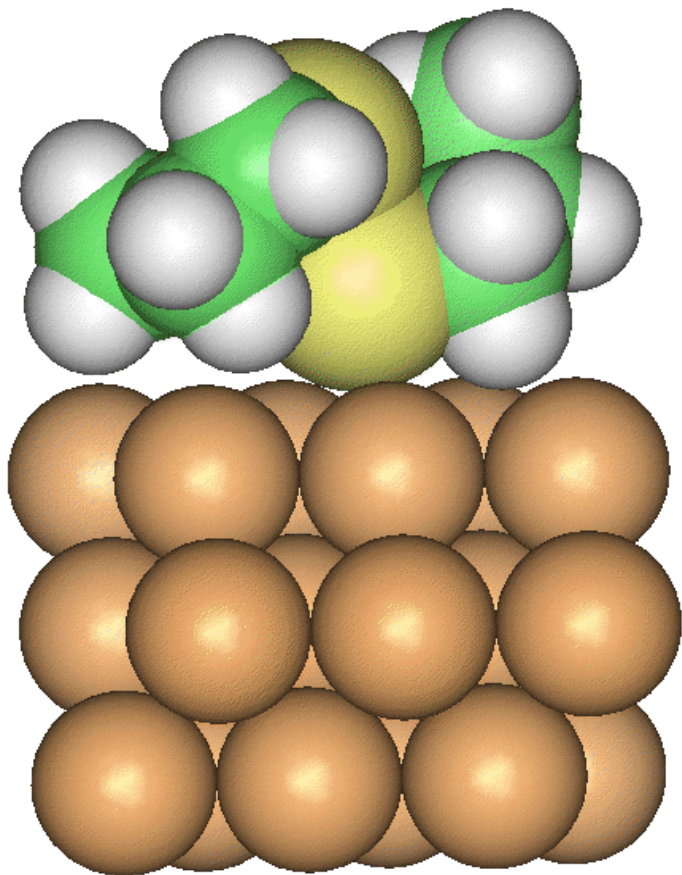


Mercaptan Reactant	Binding energy	Thiol Product	Binding energy	Reaction energy
2 MethylSH	-1611.8	2 MethaneS + H ₂	-1581.3	30.5
2 EthylSH	-4154.4	2 EthaneS + H ₂	-4136.3	18.1
2 PropylSH	-6653.1	2 PropaneS + H ₂	-6723.1	-70.0
2 ButylSH	-9325.7	2 ButaneS + H ₂	-9388.1	-62.4
2 PentylSH	-11847.2	2 PentaneS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

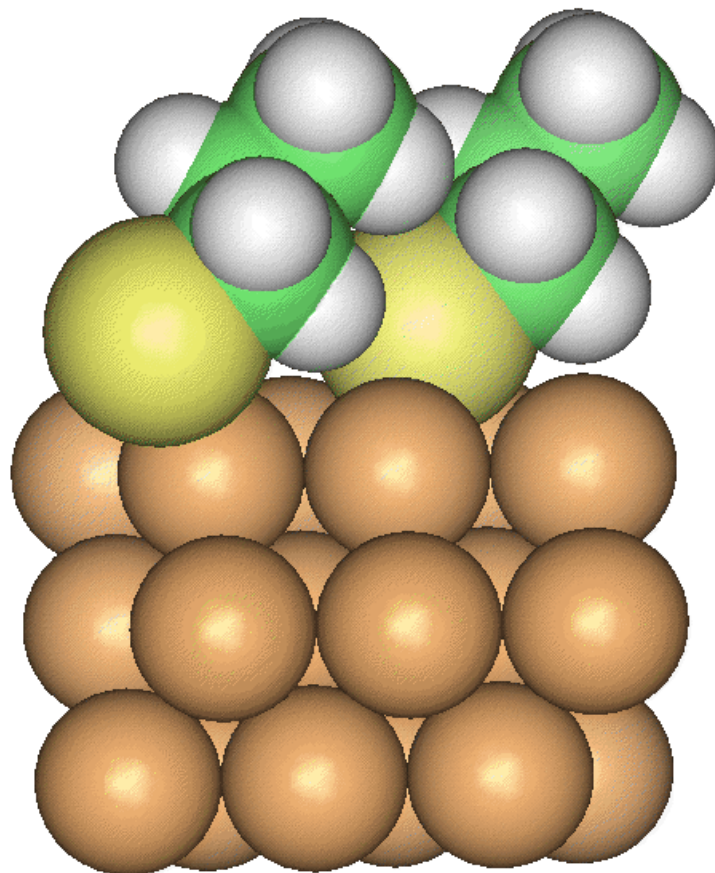
Disulfide bond strength



Propane disulfide and propane thiol on Au(111)

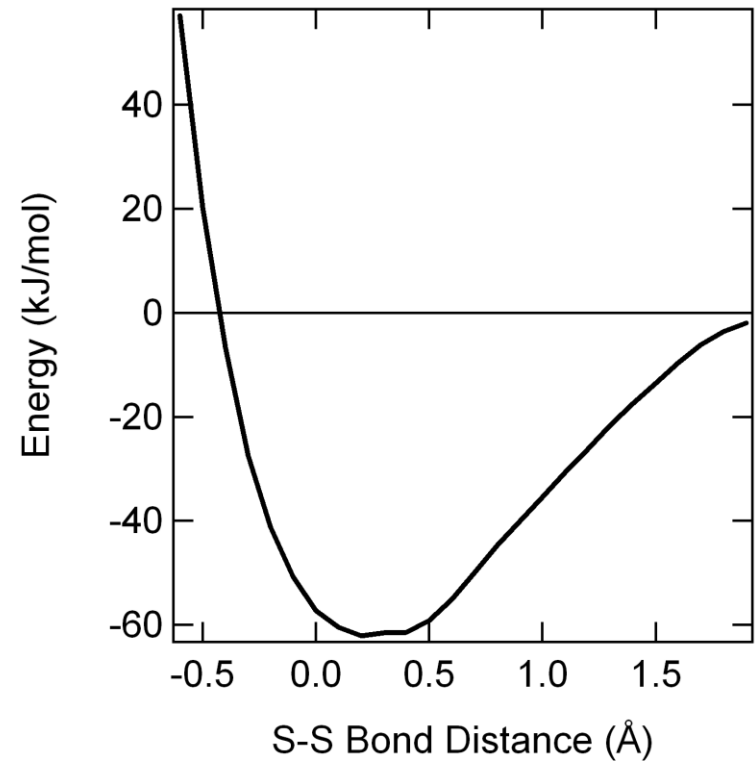
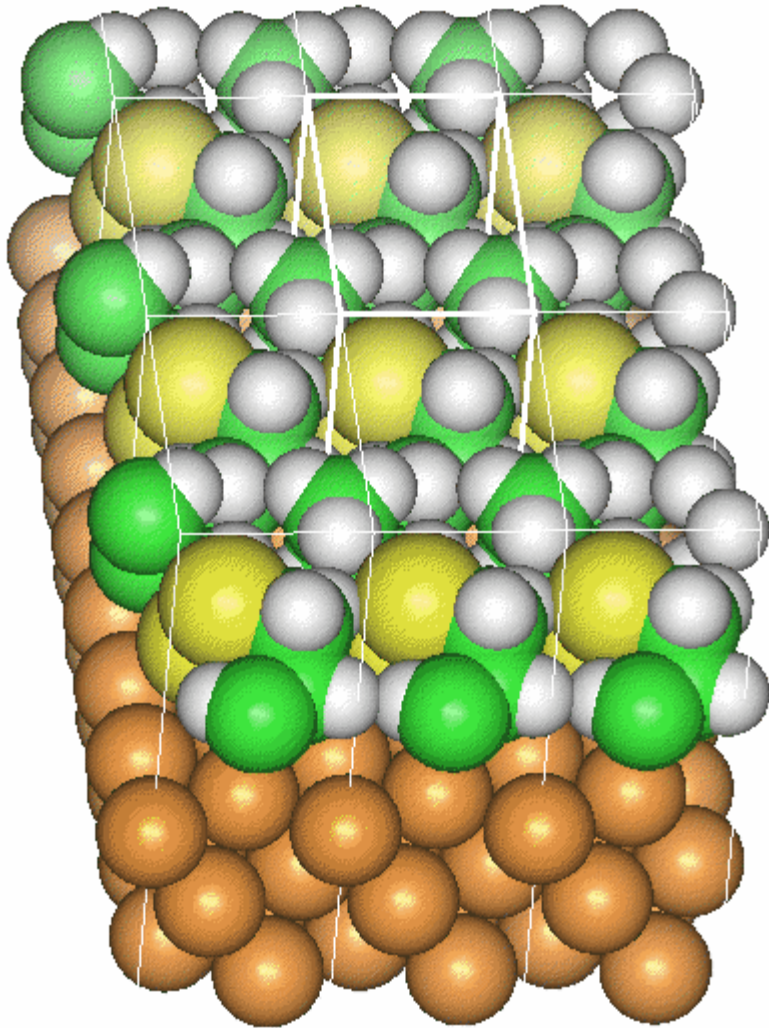


-6239.0 kJ/mol



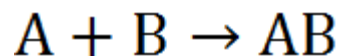
-6191.0 kJ/mol

Disulfide binding energy to the Au(111) surface



Basis set superposition error

We considering the approach of fragments of a molecule represented by a finite basis set, we must consider the effect of mixing of the two basis sets of two fragments. We can think of two fragments A and B that approach and eventually bond or strongly interact,

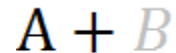


When the A fragment comes into contact with B the basis sets available to it include a large set than when A is far away from B. The same is true for B. The error in the energy due to this artifact is called basis set superposition error (BSSE).

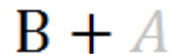
One solution to this problem would be to use a very large (infinite?) basis set. However, a large basis set is not practical for many system (and an infinite basis is never practical). The binding energy is always overestimated because of BSSE. The practical solution to the problem is known as the counterpoise correction.

Counterpoise Correction

In the counterpoise correction, the energy of isolated A is calculated with inclusion of the orbitals of B (but no actual atoms). The orbitals of B are present without the nuclei and are called ghost atoms. Thus, we represent A as



where the gray color represents that only the orbitals are on the B positions and no actual nuclei or electrons. The same procedure is carried out for B. The B system is



With these corrections one considers that the artifact of having a large total basis set in AB is corrected.

Electrostatic properties

The electron density is the fundamental observable obtained from an electronic structure calculation. There are a number of definitions of charge on individual atoms that can be derived from the electron density. We first consider these methods since charge is an important concept for applications of classical mechanics based on quantum chemical calculations. The charge is the first term in a multipole expansion that consists of dipole, quadrupole, octapole etc. In MKS units the electric multipole expansion is:

$$V = \frac{1}{4\pi\epsilon_0} \frac{1}{R^{n+1}} \sum_{n=1}^{\infty} \int r^n P_n(\cos\theta) \rho(r) d^3r$$

where V is the voltage, $P_n(\cos\theta)$ is the Legendre polynomial, and the vectors r and R are defined below.

Definition of vectors

The polar angle θ is defined such that

$$\cos\theta = \vec{r} \cdot \vec{R}$$

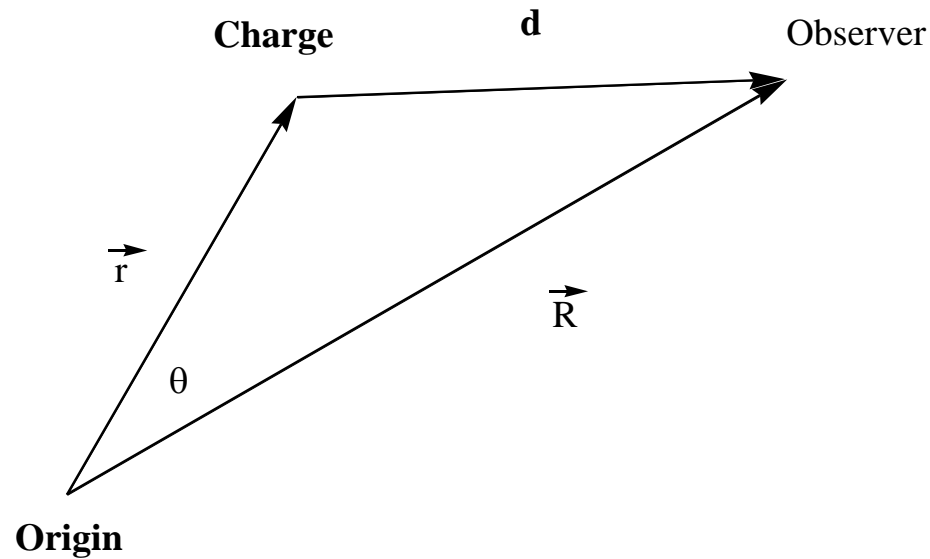


Diagram showing the relationship between the vector r from the origin to a charge in a distribution and the vector R from the origin to an observer.

Expansion of the potential

The expansion can also be written explicitly in terms of the charge, dipole and quadrupole etc.

$$V = \frac{1}{4\pi\epsilon_0} \left(\frac{q}{r} - \frac{\vec{\mu} \cdot \vec{r}}{r^3} + \frac{1}{2} \sum_{ij} \frac{r_i r_j}{r^5} \Theta_{ij} + \dots \right)$$

where each term is defined in terms of the potential

$$q = \int \rho(\mathbf{r}) d^3r \quad \text{Charge}$$

$$\mu = \int \rho(\mathbf{r}) \mathbf{r} d^3r \quad \text{Dipole}$$

$$\Theta_{ij} = \int \rho(\mathbf{r}) (3r_i r_j - \delta_{ij} r^2) d^3r \quad \text{Quadrupole}$$

Multipole expansion

The multipole field expansion is derived from the gradient of the potential

$$\vec{F} = -\nabla V = \frac{1}{4\pi\epsilon_0} \left(q \frac{\vec{d}}{|\mathbf{r} - \mathbf{R}|^2} + \frac{3\vec{d}(\vec{\mu} \cdot \vec{d}) - \vec{\mu}}{|\mathbf{r} - \mathbf{R}|^2} + \dots \right)$$

Where F is the electric field. Finally, we can calculate the energy

$$E = qV - \vec{\mu} \cdot \vec{F} - \frac{1}{6} \sum_{ij} \Theta_{ij} \frac{\partial \vec{F}_1}{\partial r_i} - \dots$$

The multipole expansion can be used in a method to calculate charge, dipole moment and so on.

Partial atomic charge

The partial atomic charge is an artificial way to represent the electrostatic potential in terms of point charges on each nucleus. The utility of this method is that it provides a way to estimate the effective charge on an atom for other types of calculations, such as molecular mechanics and molecular dynamics. It must be kept in mind that any partitioning of the electrostatic potential into partial atomic charges is subjective. There is not absolutely correct way to do this.

Mulliken charge is the contribution to the electron density from a given atom minus the nuclear charge of that atom.

Electrostatic Potential Fitting is a method based on a fit of the best charge distribution that matches the expansion of the electron density.

Mulliken charge

The most basic definition of partial atomic charge is that due to Mulliken. First, we define the Mulliken population matrix,

$$P_{\mu\nu} = 2 \sum_{i=1}^N c_{\mu i} c_{\nu i} S_{\mu\nu}$$

where $c_{\mu i}$ are the coefficients of the occupied molecular orbitals, i for atoms m and n and $S_{\mu\nu}$ is the overlap. For a given atom we can define the population, which is related to the electron density on that atom

$$P_{\mu\mu} = 2 \sum_{i=1}^N c_{\mu i}^2$$

The Mulliken charge is defined as:

$$q_{\mu} = Z_{\mu} - P_{\mu\mu}$$

where Z_{μ} is the nuclear charge on atom μ .

Electrostatic potential fitting

The method of electrostatic potential fitting is considered a more accurate estimate of the atomic charge for applications such as molecular dynamics simulations. The method is also known as CHELPG, which stands for CHarges from Electrostatic Potentials using a Grid based method. In this method one determines the multipole expansion based on the electrostatic potential and then uses a fitting method to determine the set of atomic charges that most accurately fits the multipole terms. If the molecule is flexible then it is best to conduct this calculation for a number of different molecular geometries in order to get an appropriate average value of the charge.

Dipole moment

A dipole moment is defined in terms of the amount of charge displaced through a given distance.

$$\mu = qr$$

For a diatomic molecule with defined partial atomic charges, the dipole moment is simply the partial charge times the bond length. However, calculation of dipole moment using such an approach is not at all accurate. In the first place, the definition of partial atomic charge is not unique. The classical approach to the dipole moment ignores the information present in the quantum chemical calculation.

State dipole moment

The quantum mechanical definition of the dipole moment is based on the expectation value. In general, a molecule has three dipole moments defined along each of the Cartesian coordinates. Therefore, we can write,

$$\vec{\mu}_\sigma = \int \psi_g^* \vec{\sigma} \psi_g d\tau = \langle \psi_g | \vec{\sigma} | \psi_g \rangle$$

where $\sigma = x, y$ or z and g denotes the ground state. In the quantum chemical approach we can also calculate a dipole moment for an excited state, e .

$$\vec{\mu}_\sigma = \int \psi_e^* \vec{\sigma} \psi_e d\tau = \langle \psi_e | \vec{\sigma} | \psi_e \rangle$$

Obviously, there is no way to obtain the excited state dipole moment by classical methods.

Transition dipole moment

Since unoccupied energy levels are typically not as determined as accurately as occupied energy levels, the calculation of excited state and transition dipole moments is less accurate than the calculation of the ground state dipole moment.

Finally, one can calculate a transition dipole moment. For the optically induced electronic transition from g to e we have,

$$\vec{\mu}_{\sigma} = \int \psi_g^* \vec{\sigma} \psi_e d\tau = \langle \psi_g | \vec{\sigma} | \psi_e \rangle$$

Molecular Polarizability

The polarizability is the propensity for an induced dipole to form in an electric field.

$$\vec{\mu}_\sigma = \alpha_{\rho\sigma} \vec{F}_\rho$$

The polarizability is a second-rank tensor so there are 9 different elements possible. The quantum mechanical polarizability is given by

$$\alpha_{\rho\sigma} = \sum_i \frac{\langle \psi_g | \rho | \psi_i \rangle \langle \psi_i | \sigma | \psi_g \rangle}{E_i - E_g}$$

where the terms in the numerator are the transition moments along ρ and σ . In this expression bracket notation is obviously much more economical in terms of space and it also improves the clarity.

Intrinsic inaccuracy in the molecular polarizability

From this expression we can see the polarizability can be viewed as the mixing of higher lying states into the ground state. Thus, an applied electric field slightly changes the character of the ground state by mixing the other states. The mixing terms along the directions ρ and σ are the transition dipole moments.

Since unoccupied energy levels are typically not as determined as accurately as occupied energy levels, the molecular polarizability is much more difficult to calculate accurately than other properties.