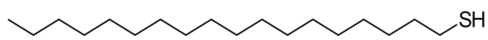
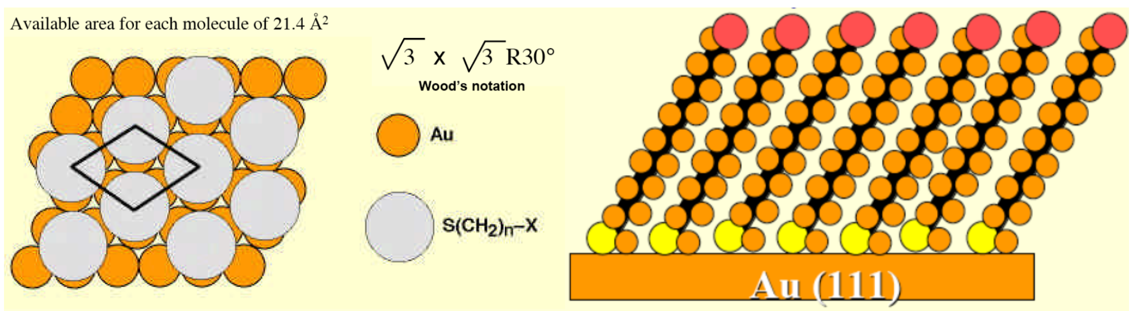
Surface Chemistry and Nanoscience

We learned in today's class that alkanethiol molecules can assemble to form ordered self-assembled monolayers (SAMs). Let's do some problems to understand better how many molecules a SAM consists of and how the properties can be changed based on functional groups.

1. When octadecanethiol forms a SAM on a gold (111) surface, the molecules adopt a $\sqrt{3} \times \sqrt{3}R30°$ arrangement. This means the following:
   - The molecular adsorption lattice is expanded by $\sqrt{3}$ relative to the atomic lattice of gold (111), which has a nearest-neighbor spacing of 0.288 nm
   - The resulting center-to-center distance of the molecules is $a = \sqrt{3} \times 0.288\, nm$



Octadecanethiol



Based on this information, please calculate the following:

a) Derive the center-to-center distance a of the SAM based on $\sqrt{3} \times \sqrt{3}R30°$ arrangement.

b) Calculate the area per molecule in the SAM assuming a hexagonal lattice.

c) Calculate the SAM packing density in molecules per square nanometer.

d) Calculate the total number of molecules in the SAM on a 1 cm^2 gold surface assuming a 90% coverage due to defect sites.

Gold nanoparticles (AuNPs) are widely used in biological and material science applications. When aggregated, their optical properties, such as plasmon resonance, and their interaction with light change significantly, which is useful in biosensing, imaging, and diagnostics. Let's work on a few problems that help us to understand AuNPs and plasmon resonance better.

2. Gold nanoparticles typically have a work function (Φ) that can vary with size. For small gold nanoparticles of approximately 10 nm, the work function is typically found to be around **5.1 eV**.

   a) Calculate the energy required to remove an electron from a gold nanoparticle (using the work function) and express this in Joules.
   *Note 1 eV = 1.602 x 10^{-19} J

b) The work function (Φ) of bulk gold is approximately **5.47 eV**. How does the energy required to remove an electron from a gold nanoparticle compare to that of bulk gold, and what accounts for this difference?

3. The surface plasmon resonance (SPR) wavelength of gold nanoparticles depends on the size of the nanoparticle and the dielectric properties of the surrounding medium. Assume that the plasmon resonance wavelength (λ_{SPR}) for a spherical gold nanoparticle with a diameter of **20 nm** is **530 nm** in water.

a) Calculate the frequency of light corresponding to this plasmon resonance wavelength (λ_{SPR}=530 nm)

b) Using the frequency calculated in part (a), determine the energy of the photon at this frequency. Recall the equation for energy of a photon:

$$E_{\text{photon}} = h \text{ x } f$$

where h is Planck's constant = 6.626×10^{-34} J s
and f is the frequency of light

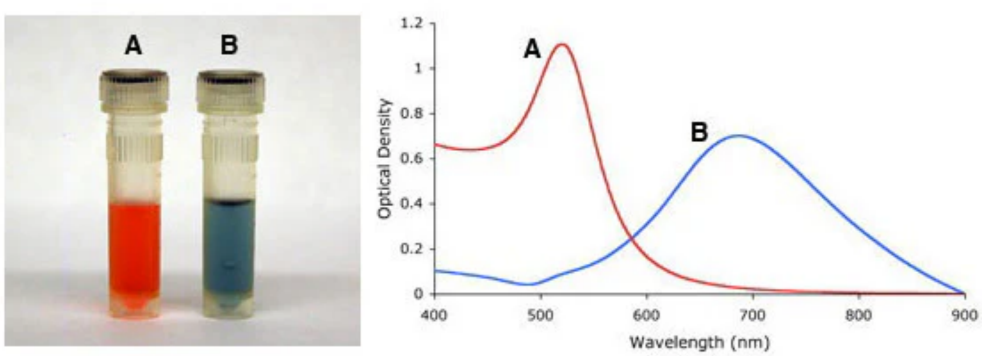
c) The plasmon resonance of gold nanoparticles shifts when they aggregate. This shift depends on the degree of aggregation, and the change in the plasmon resonance wavelength can be observed as a color change. Given that for isolated gold nanoparticles the plasmon resonance is at 530 nm, and when aggregated, it shifts to **600 nm**, calculate the fractional change in the plasmon resonance wavelength ($\Delta\lambda/\lambda_{\text{initial}}$). What is the relevance of this value (*i.e.,* what could it be useful for?).

d) What is the shift in the photon energy (in eV) corresponding to this change in plasmon resonance wavelength (from 530 nm to 600 nm)? Use the energy-wavelength relation:

$$E = \frac{h \cdot c}{\lambda}$$

where h is Planck's constant = 6.626×10^{-34} J s
and c = $3.0 \text{ x } 10^{8}$ m/s

What is the relevance of this value that you calculated?



Key Takeaways from this Exercise:

- The hexagonal lattice arrangement of molecules on a gold (111) surface provides optimal packing and reflects the underlying surface structure of the substrate.
- Calculating the packing density and total number of molecules demonstrates how molecular-scale properties translate to macroscopic surface properties.
- By calculating photon energy, see how gold nanoparticles interact with light at specific wavelengths and that the energy of light required to excite surface electrons correlates with their optical response.
- How nanoparticle aggregation can cause significant shifts in the plasmon resonance wavelength, which can be used for various applications such as biosensing