Nanoparticles & Raman
Surface Enhancement?

Lycurgis Cup (324 A.D)
dichroic glass?

Lit from inside or behind
Lit from outside

http://www.britishmuseum.org/explore/highlights/highlight_objects/pe_mla/t/the_lycurgus_cup.aspx
Nanoparticles (1-100 nm)

What were the nanoparticles used *last quarter*?

What are some properties of nanoparticles?

What about gold nanoparticles?

How many moles of each reagent is added? What is the mole ratio b/w reagents? What is the limiting reagent?

- 20 mL of 1 mM HAuCl₄•3H₂O(aq)

- 2 mL of 1% w/w Na₃C₆H₅O₇(aq)
Colloids

- **Solution:**
- **Colloid:**
- **Tyndall effect:**

http://www.chimicamo.org/chimica-generale/i-colloidi.html
Aggregation of solutes in colloids can result in suspension formation.

Aggregation:

Suspension:
Solution, Colloid, Suspensions

http://pixgood.com/suspensions-examples-chemistry.html.png
Capping w/ Citrate

Controlling Aggregation: “capping”

http://www.chemistry.unsw.edu.au/research/research-groups/gooding-group/nanoparticles
Possible Half-Rxns:

- \( \text{Au}^{3+}(aq) + 3\text{e}^- \rightarrow \text{Au}(s) \)
- \( \text{C}_6\text{H}_5\text{O}_7^{3-}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{C}_5\text{H}_4\text{O}_4^{2-}(aq) + \text{CO}_2(g) + \text{H}_3\text{O}^+(aq) + 2\text{e}^- \)

**What is the mole ratio of \( \text{Au}^{3+} \) to citrate?** *(Balance the redox rxn!)*

**Point of the experiment:**

*What happens to the NP once \( \cdot\text{SCN} \) is added?*
Spectroscopy of Nanoparticles

- Instrumentation needed to “see” nanoparticles.
- Electronic (Visible) Spectroscopy can be used to measure amount of aggregation.
- Vibrational Spectroscopy can be used to measure “types” of bonds present.
What is the relationship between the fluorescence and absorption spectra of the same chemical?

What causes Stoke’s shift?
Infrared (IR) radiation ($\lambda = 700$ to 1000 nm) is less energetic (longer $\lambda$) than visible radiation.

Absorption or emission of IR changes a molecule’s vibrational levels resulting in the wiggling of bond lengths & angles (How do we experience this?).

Measured spectroscopically: IR radiation absorbed or emitted can be detected & spectra can be created.
IR & Raman Spectra

Absorbance

Emission
2 Types of Vibrational Spectroscopy

**Infrared (IR)**

- Measurement of IR Radiation Absorbed
- IR signal when stretch or bend of bonds causes a dipole moment
- Water can't be present

**Raman**

- Measurement of IR Radiation Emitted (scattered)
- Raman active vibration with polarizability
- Water can be present
Visible Excitation & Emission

Raman Excitation & Emission

HOMO
Ground Electronic State

LUMO
Excited Electronic State

hν

HOMO
Ground Electronic State

LUMO
Excited Electronic State

hν
What are the possible Raman excitation transitions?

Which is responsible for most peaks in a Raman spectrum?

What is $2\pi \nu$? **RESONANCE**

frequency at which the chemical species can vibrate.....
where $\nu = c/\lambda$, and $\lambda$ is 785 nm (excitation $\lambda$).

→ peak on Raman spectrum at that frequency (wavelength)
Bulk vs. Nanoparticle Gold

**Bulk Gold**
- Gold is a metal (a conductor) w/ delocalized valence e⁻
- Valence e⁻s = e⁻ cloud w/ a certain $\lambda$. *Remember wave-particle duality?*
- If that certain $\lambda$ ($\geq 750$ nm), is absorbed by Au & all other $\lambda$s are reflected off e⁻ cloud, gold appear yellow.

**Nanoparticles**
- Much larger surface area to volume ratio
- NP size changes e⁻ cloud size, so “certain” $\lambda$ changes w/ size.
Surface Plasmon Resonance

Surface Plasmons: valence e⁻s oscillate at a “certain” $\lambda$ or $\nu$:

Resonance: the tendency of a system to absorb more energy when exposed to a frequency ($\nu$) matching its own

http://www.kristoflodewijks.be/?page_id=175
When excitation energy ($h\nu_{\text{exc}}$) is resonant (has the same frequency as) the NP’s plasmon, the intensity of the Raman scattering ($h\nu_s$) increases.

The electromagnetic (EM) field is enhanced where 2 nanoparticles meet.

This causes an enormous enhancement of the Raman scattering of the molecules adsorbed at the junction of a Au nanoaggregate.
What does SERS stand for?

How is the Raman spectrum of SCN\(^-\) effected by binding to the NP?

Explain what is meant by “single molecule spectroscopy”?
**Model:** Predict what will happen in the experiment.

- Macroscopic: What do you expect to observe?
- Microscopic: Sketch/Explain what you think the molecular level looks like and what the spectra will look like... you can’t be wrong!

**Observe:** Follow the procedures and make observations

**Reflect:** What do your observations mean? Look for connections in qualitative observations. Compare & contrast different spectra.

**Explain:** Explain your results. In other words, create a better model.