April 8, 2005

- **Decision Time:**

  Monday or Tuesday Review Session for Exam #3

- **Problem Set #4 Solutions** – still coming soon!

Raman Properties

- ***Get vibrational spectrum***
  - ✓complementary with IR
  - ✓can use UV/Vis instrumentation
  - ✓aqueous solutions are accessible to study
- **Problems**
  - ✓Low efficiency of effect = poor sensitivity
  - ✓Competition from fluorescence for highly fluorescent species

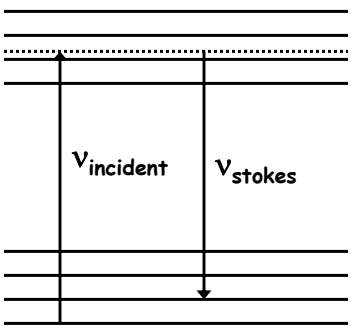
Solving Problems

- **Resonance Raman**
  - ✓ Selectivity and Detectability
- **Surface-Enhanced Raman**
  - ✓ Selectivity and Detectability
- **Multi-Channel Detection**
  - ✓ Detectability
- **Near-IR Excitation**
  - ✓ Fluorescence Rejection

Resonance Raman

- If $\lambda_{incident}$ corresponds to a strong absorption band, **I_{Raman} enhanced by 10^2 – 10^6 x**

• Enhancement only for vibrational modes associated with portion of molecule involved in electronic transition.



How does this differ from fluorescence?

Surface Enhanced Raman Spectroscopy (SERS)

- **Raman signal enhancement occurs if sample is on an "active metal" surface**
  - "active metal" = Ag, Au, Cu, and others
  - a generalizable phenomenon (SEIRA)
- **For ultimate in detectability (near unity "Raman Quantum Yield"), couple with:**
  - resonance enhancement
  - sample adsorbed onto metal nano-particles

Near-IR Excitation

- Can eliminate fluorescence background by using *low energy* excitation λ
  - use λ=1.06μm (Nd:YAG Laser)
- **Problem:** $I_{Raman} \propto \lambda^{-4}$
  - 16x decrease in signal from λ=500 nm

How can we enhance S/N to make measurement possible?

FT-Raman

- **Remember:** detector noise predominates, so ***multiplex advantage*** applies
- **How Implement?**
  - ✓CW **Nd:YAG** laser source
  - ✓**Michelson Interferometer** instead of monochromator
  - ✓**Filter Rayleigh scatter** (minimize *multiplex DISadvantage*)

FT-Raman Instrument

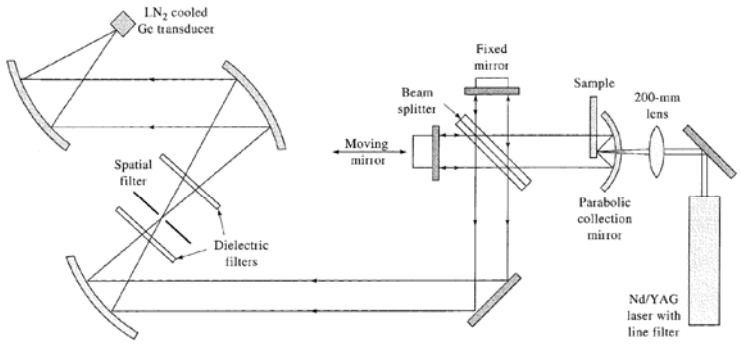


Figure 18-9 Optical diagram of an FT-Raman spectrometer (LN_2 = liquid nitrogen). *(From B. Chase, Anal. Chem., 1987, 59, 884A. With permission.)*

It works!

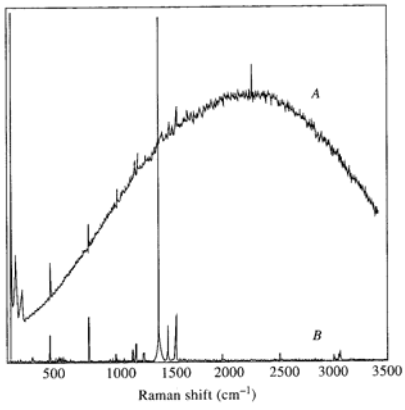


Figure 18-5 Spectra of anthracene. *A*: Conventional instrument, 5145 Å excitation. *B*: FT instrument, 1.064 μm excitation. *(From B. Chase,* Anal. Chem., ***1987,*** *59, 888A. With permission. Copyright 1987 American Chemical Society.)*

- **Outstanding fluorescence rejection**
  - ✓can get Raman spectra of PAH's, etc.
- **Precise λ-calibration**
  - ✓spectral subtraction
- **No S/N advantage**
  - ✓need to increase laser power to get same S/N
- **Can't do resonance Raman**