Raman Spectroscopy: Introductory Tutorial

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Goal of the tutorial is to answer the questions,

"What is Raman spectroscopy and can the new Raman microscope at NTUF help with my sample?"

Raman Spectroscopy: Some Sources

General Principles and Instrumentation:

Principles of Instrumental Analysis, by Douglas A. Skoog, F. James Holler, Timothy A. Nieman

Inorganic:

Infrared and Raman Spectra of Inorganic and Coordination Compounds : Theory and Applications in Inorganic Chemistry (Volume A) by Kazuo Nakamoto

Infrared and Raman Spectra of Inorganic and Coordination Compounds : Applications in Coordination, Organometallic, and Bioinorganic Chemistry (Volume B) by Kazuo Nakamoto

Organic:

The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules
by Daimay Lin-Vien, et al

Raman Spectroscopy: Overview

- A vibrational spectroscopy

  - IR and Raman are the most common vibrational spectroscopies for assessing molecular motion and fingerprinting species

  - Based on **inelastic** scattering of a monochromatic excitation source

  - Routine energy range: 200 - 4000 cm^{-1}

- Complementary selection rules to IR spectroscopy

  - Selection rules dictate which molecular vibrations are probed

  - Some vibrational modes are both IR and Raman active

- Great for many real-world samples

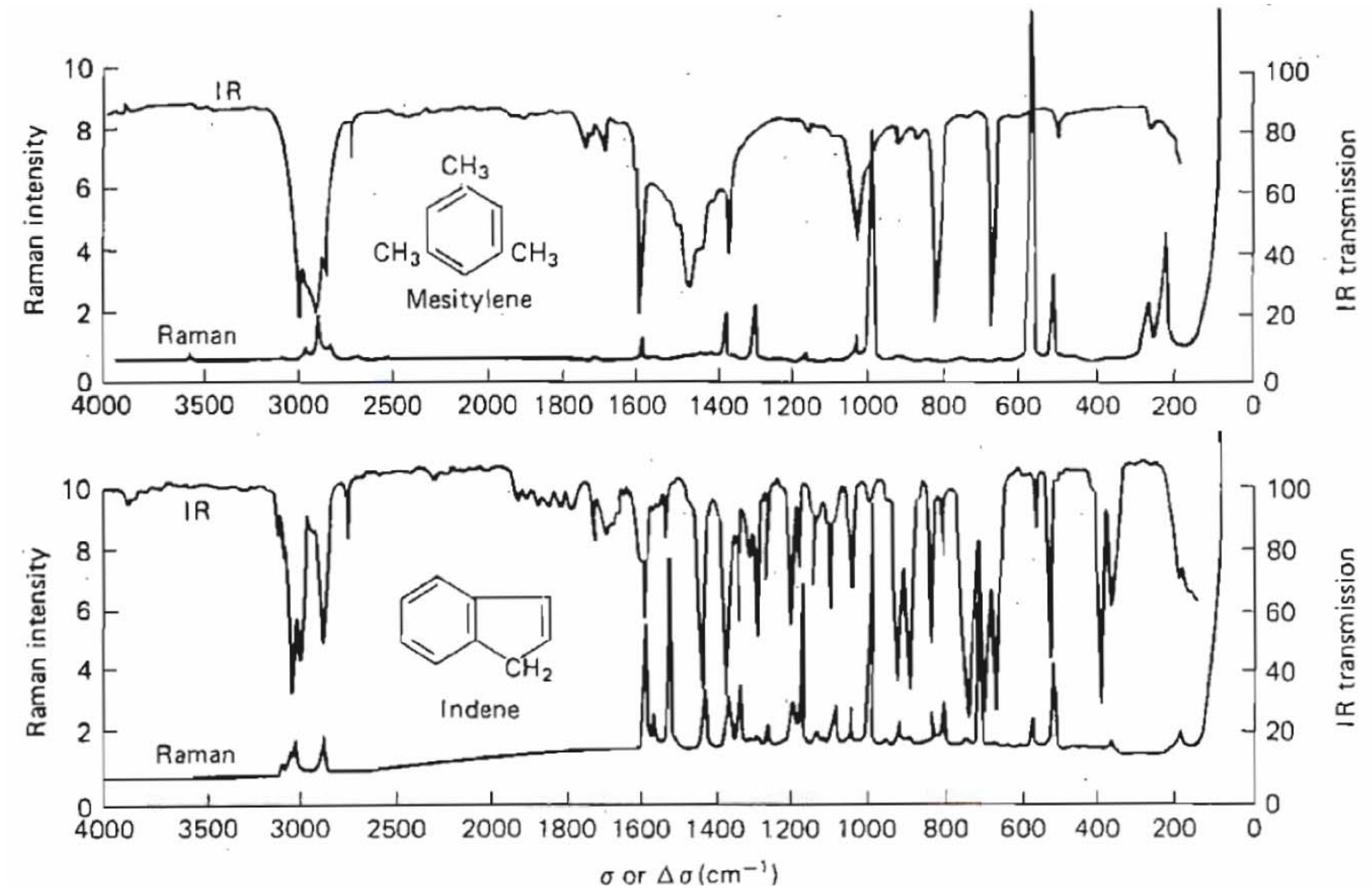
  - Minimal sample preparation (gas, liquid, solid)

  - Compatible with wet samples and normal ambient

  - Achilles Heal is sample fluorescence

Raman Spectroscopy: General

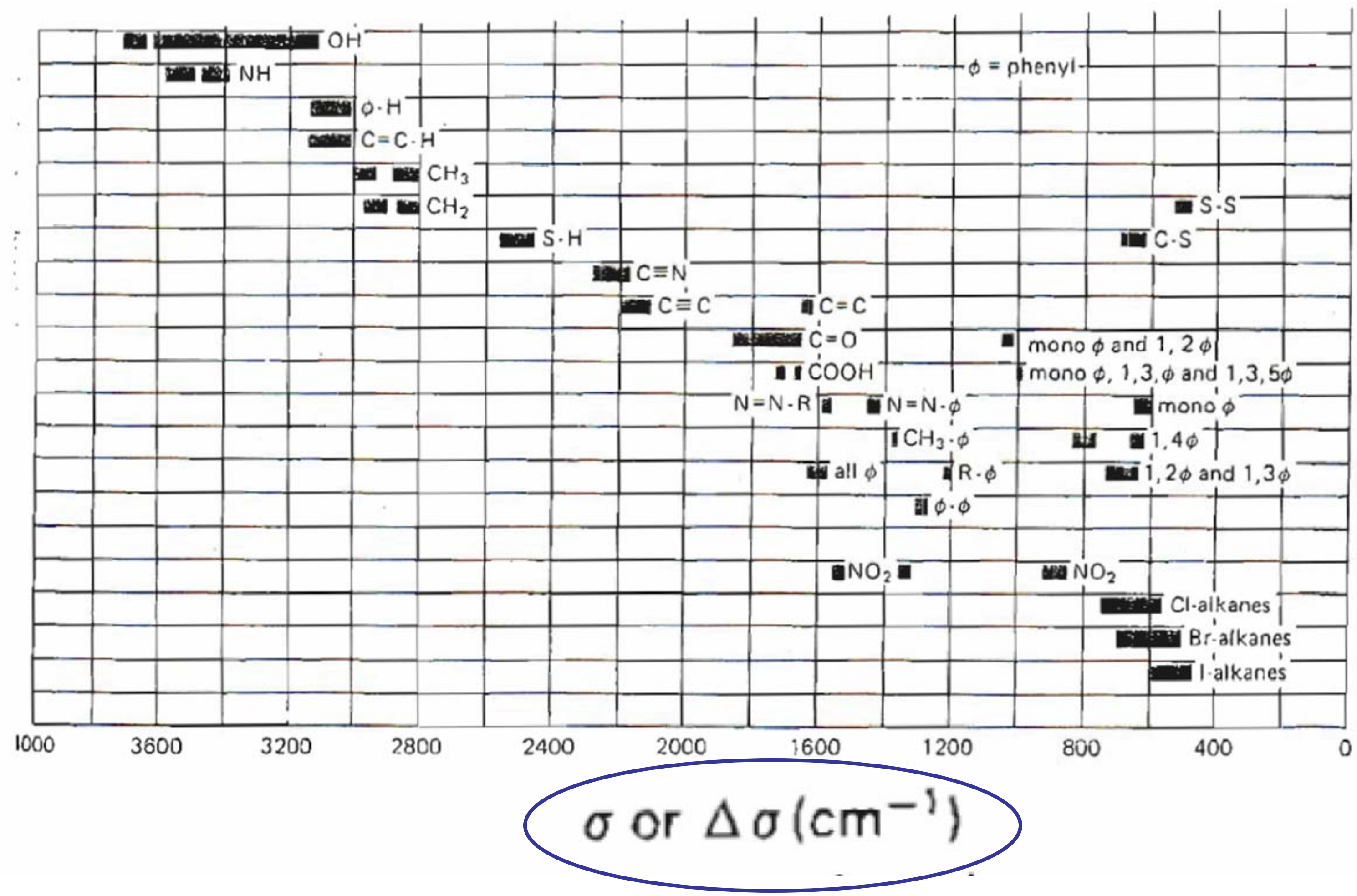
- IR and Raman are both useful for Fingerprinting



- Symmetry dictates which are active in Raman and IR

Raman Spectroscopy: General

- Group assignments identify characteristic vibrational energy



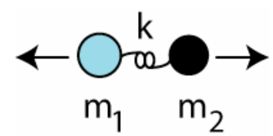
Raman Spectroscopy: Classical Treatment

- Number of peaks related to degrees of freedom

DoF = 3N - 6 (bent) or 3N - 5 (linear) for N atoms

- Energy related to harmonic oscillator

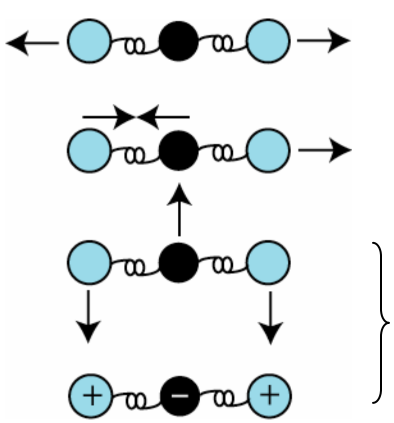
$$\sigma \ \ or \ \ \Delta\sigma \ = \ \frac{c}{2\pi}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$

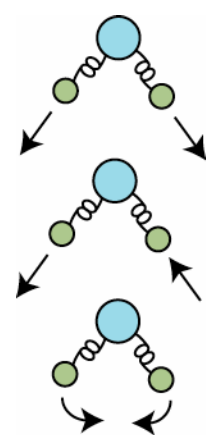


- Selection rules related to symmetry

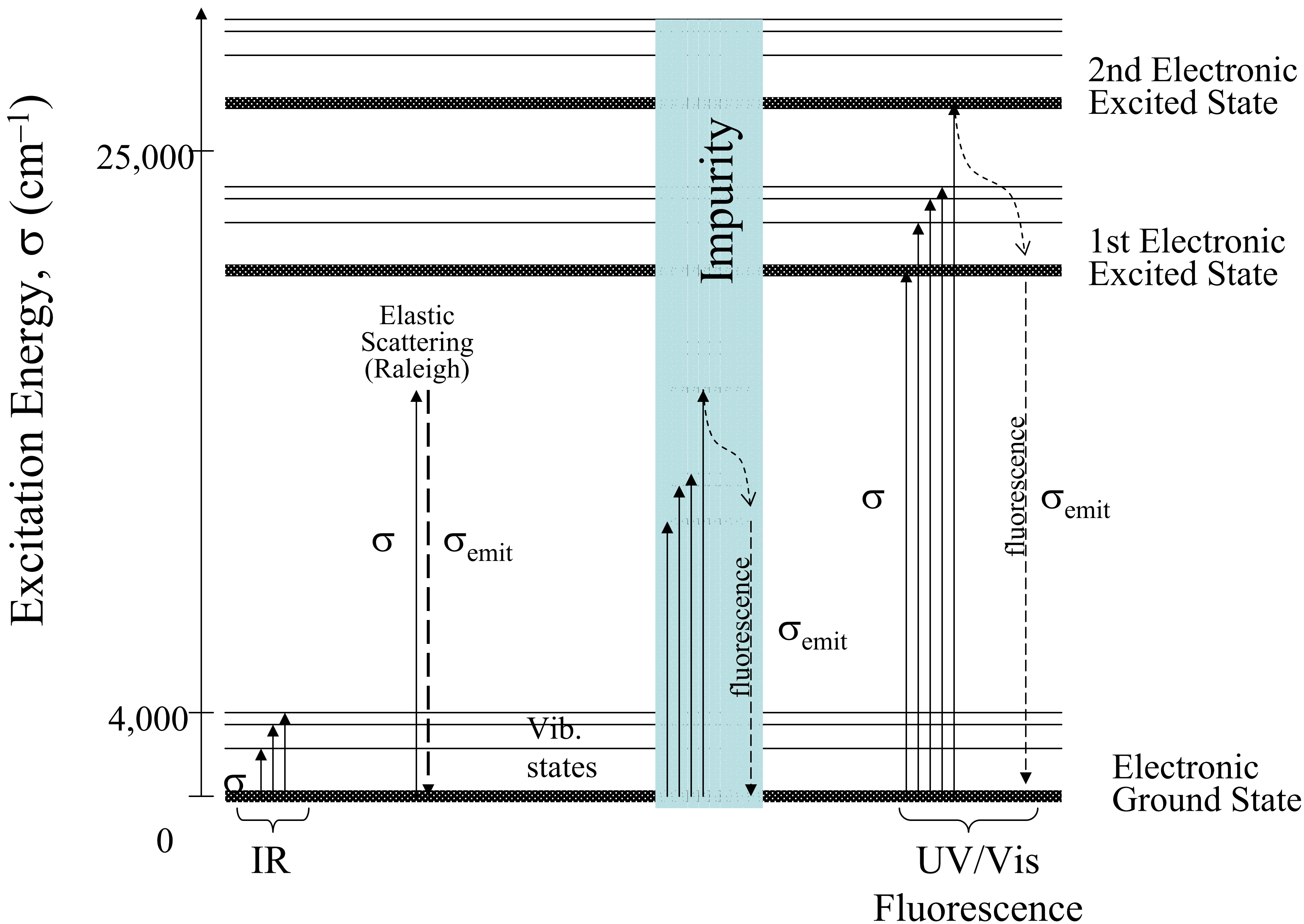
Rule of thumb: symmetric=Raman active, asymmetric=IR active

CO_2	H_2O
Raman: 1335 cm^{-1}	Raman + IR: 3657 cm^{-1}
IR: 2349 cm^{-1}	Raman + IR: 3756 cm^{-1}
IR: 667 cm^{-1}	Raman + IR: 1594 cm^{-1}

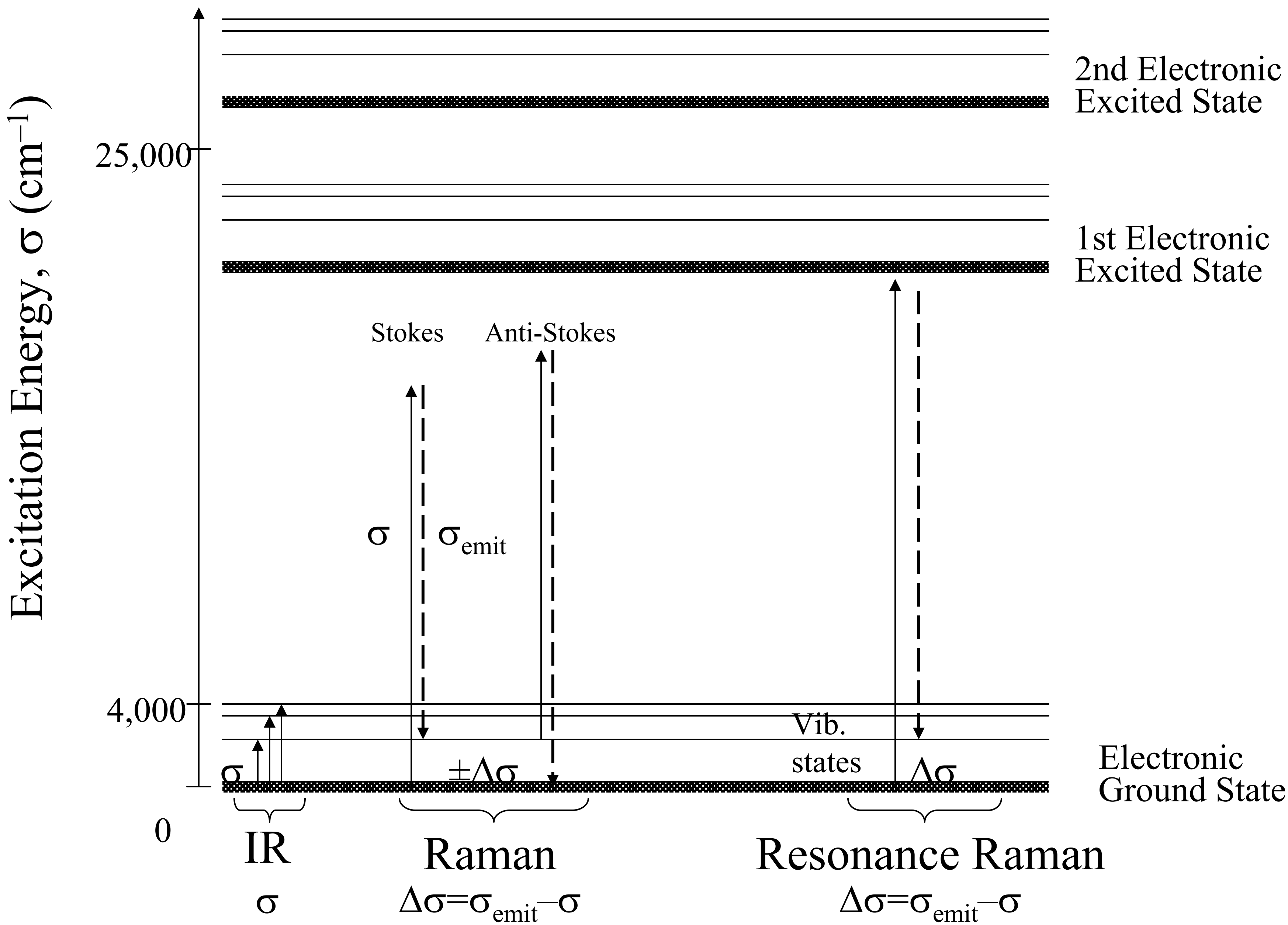




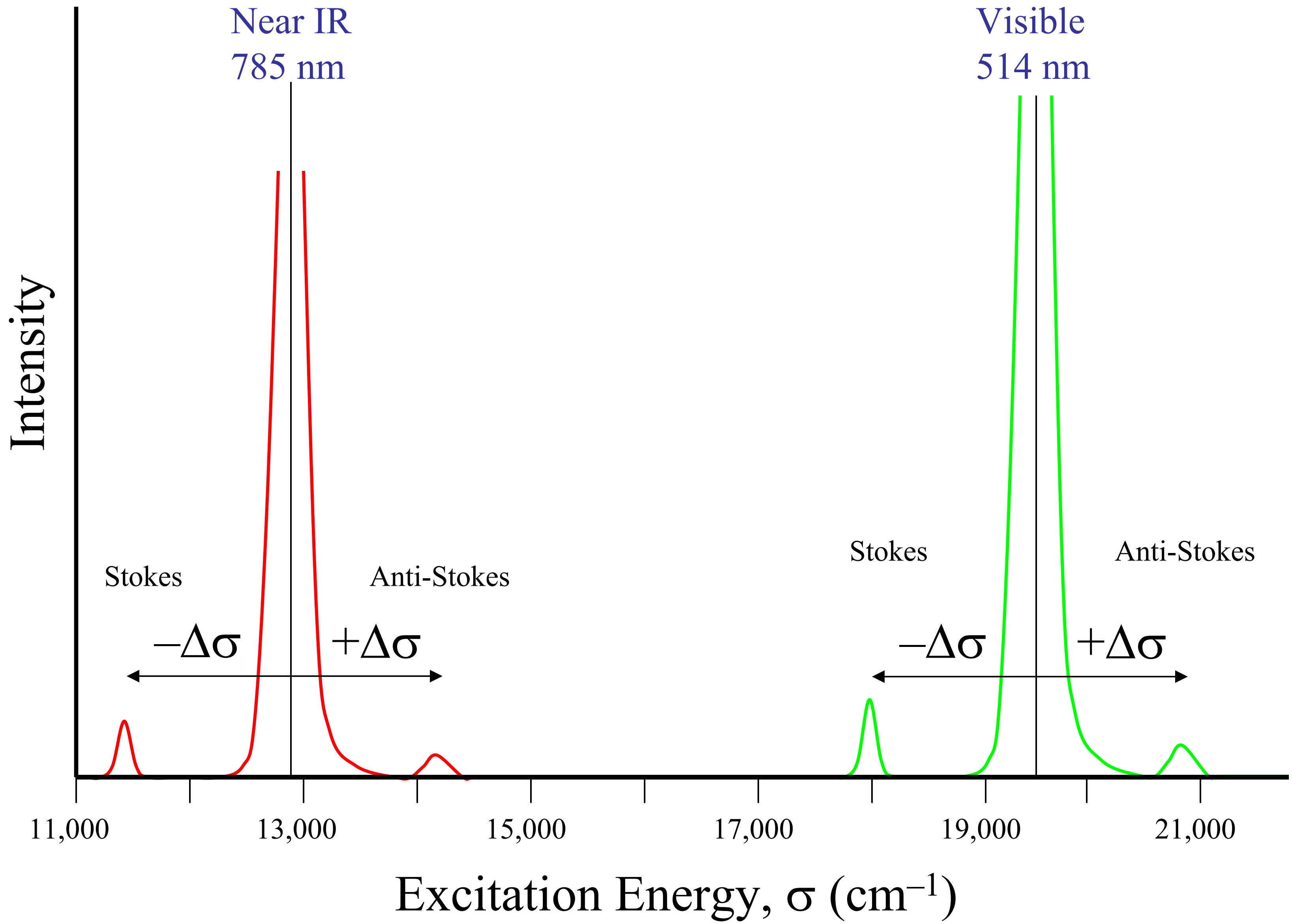
Main Optical Transitions: Absorption, Scattering, and Fluorescence



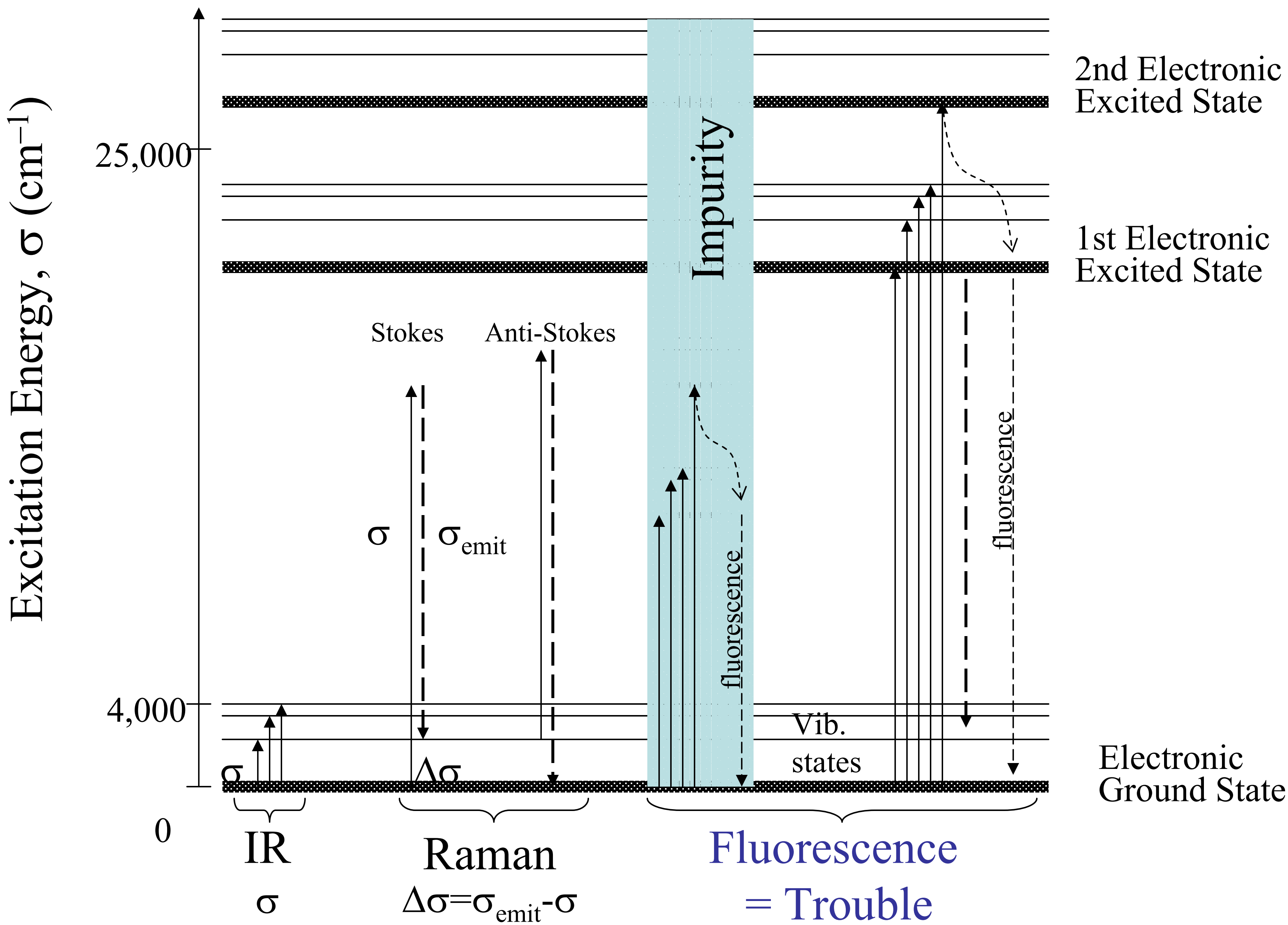
Raman Spectroscopy: Absorption, Scattering, and Fluorescence



Raman Spectroscopy: At NTUF, you pick the Laser Excitation



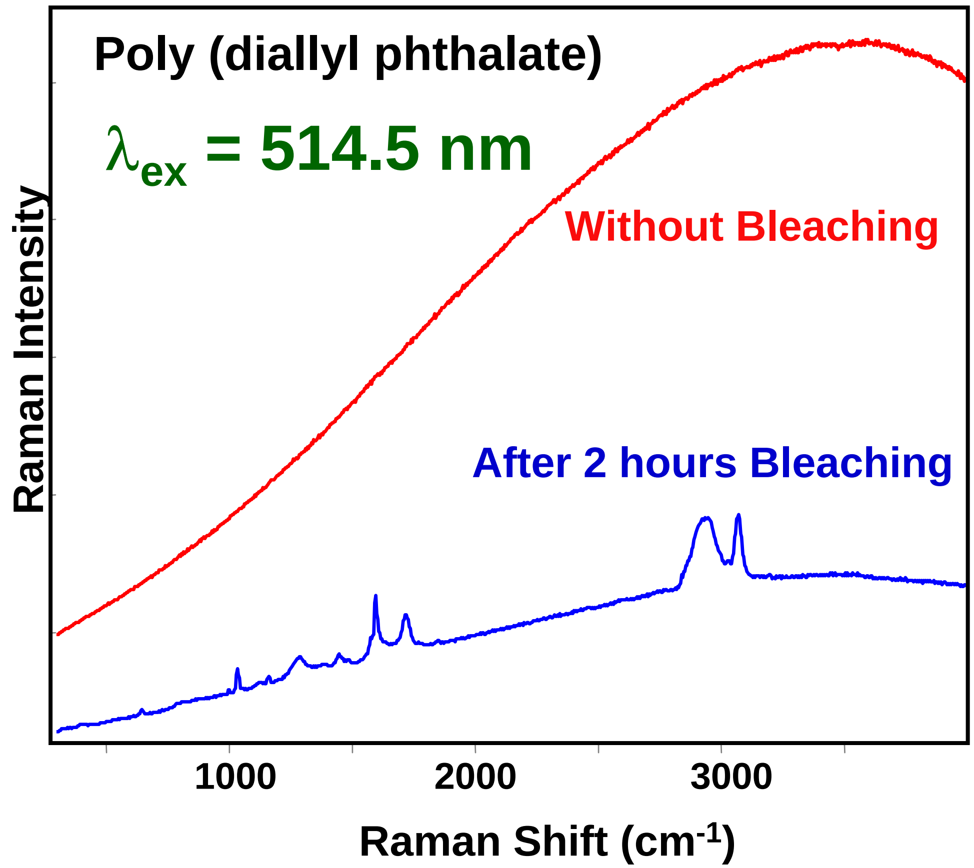
Raman Spectroscopy: Absorption, Scattering, and Fluorescence



Raman Spectroscopy: Coping w/ Fluorescence

1. Use NTUF 785 nm laser line (excites many fewer fluorophores)

2. Photobleach with long exposure laser irradiation.



Raman Spectroscopy: Summary

1. Raman is a vibrational spectroscopy akin to IR
   - Good for fingerprinting, probing molecular symmetry

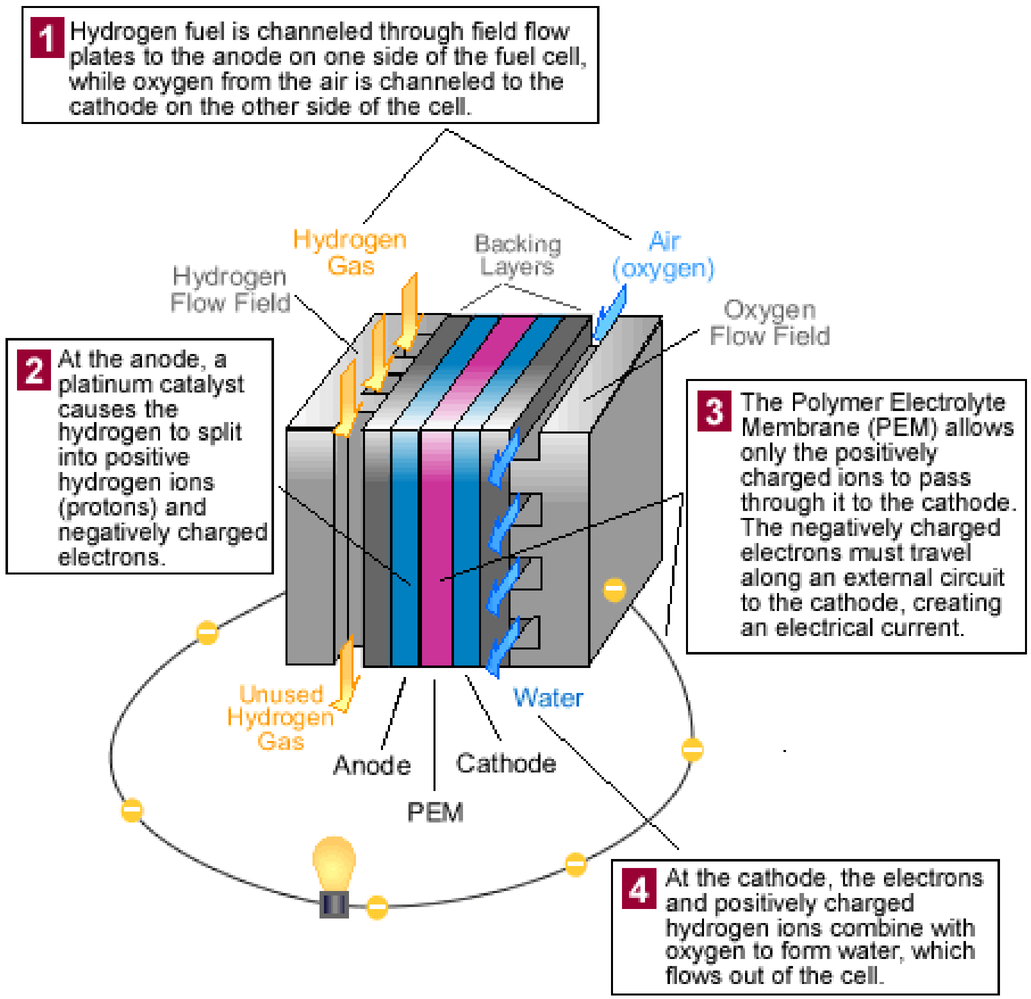
2. Scattering-based, not transmission/reflection
   - Means no need for fancy sample preparation…gas, liquid, or solid
   - Virtually always use anti-Stokes lines due to stronger signal

3. You need to pick excitation energy (laser line)
   - 785 nm: Fluorescence less probable; Lower Raman signal
   - 514 nm: Fluorescence more probable; Resonance more likely; Higher signal

4. Other things not talked about
   - SERS: Surface Enhanced Raman Spectroscopy
   - Quantum origins of selection rules and scattering cross-section

Raman Spectroscopy: Dan’s trip to NTUF

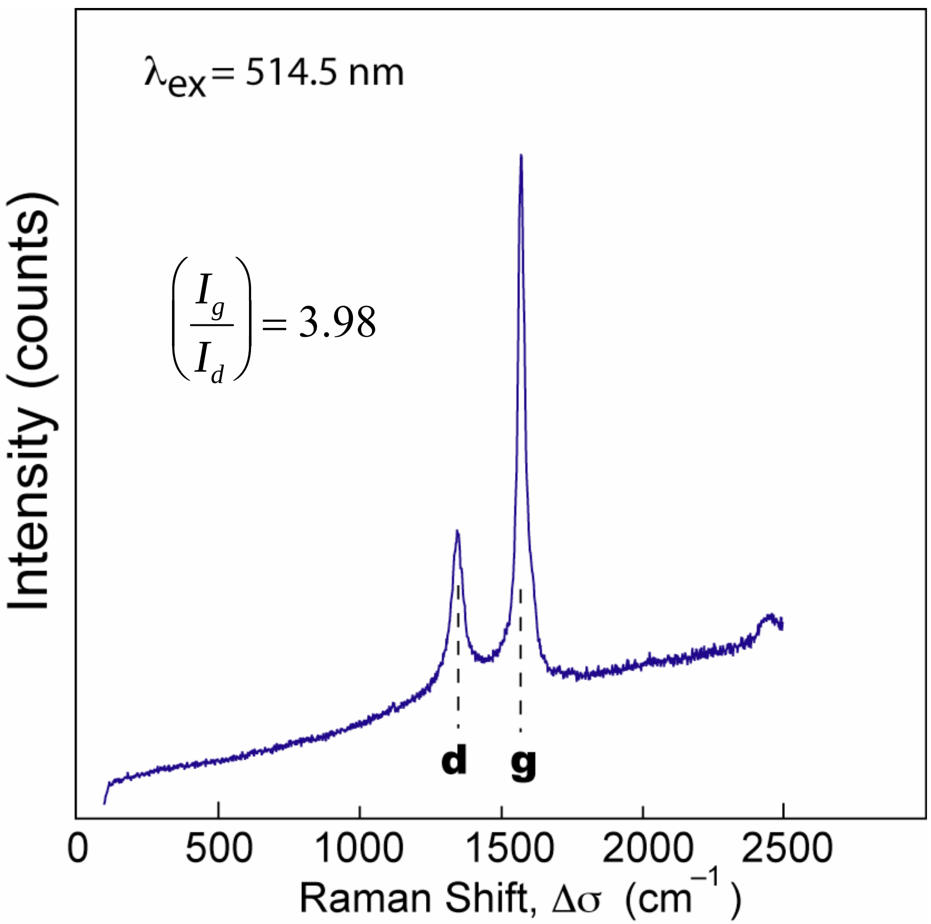
Fuel Cell Materials --- picked because I had little Raman experience with these materials

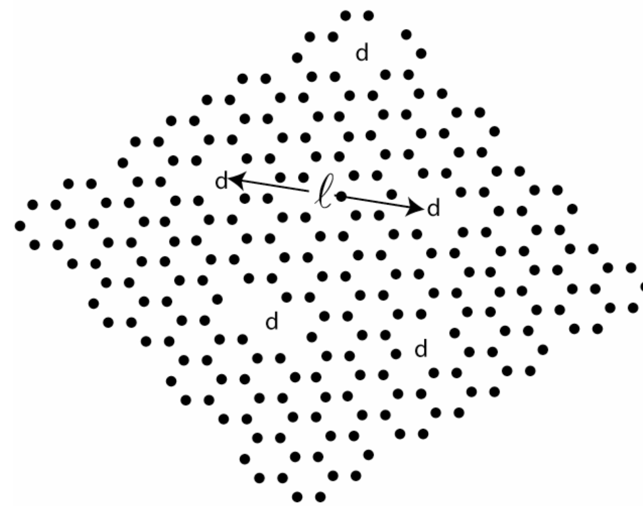


From http://www.fueleconomy.gov/feg/fc_pics/fuel_cell_still.gif

Raman Spectroscopy: Dan's trip to NTUF

Flow Field Plate - Graphite





Nanocrystalline graphite has graphitic (**g**) and disorder (**d**) peaks. The characteristic dimension of graphitic domains is given by:

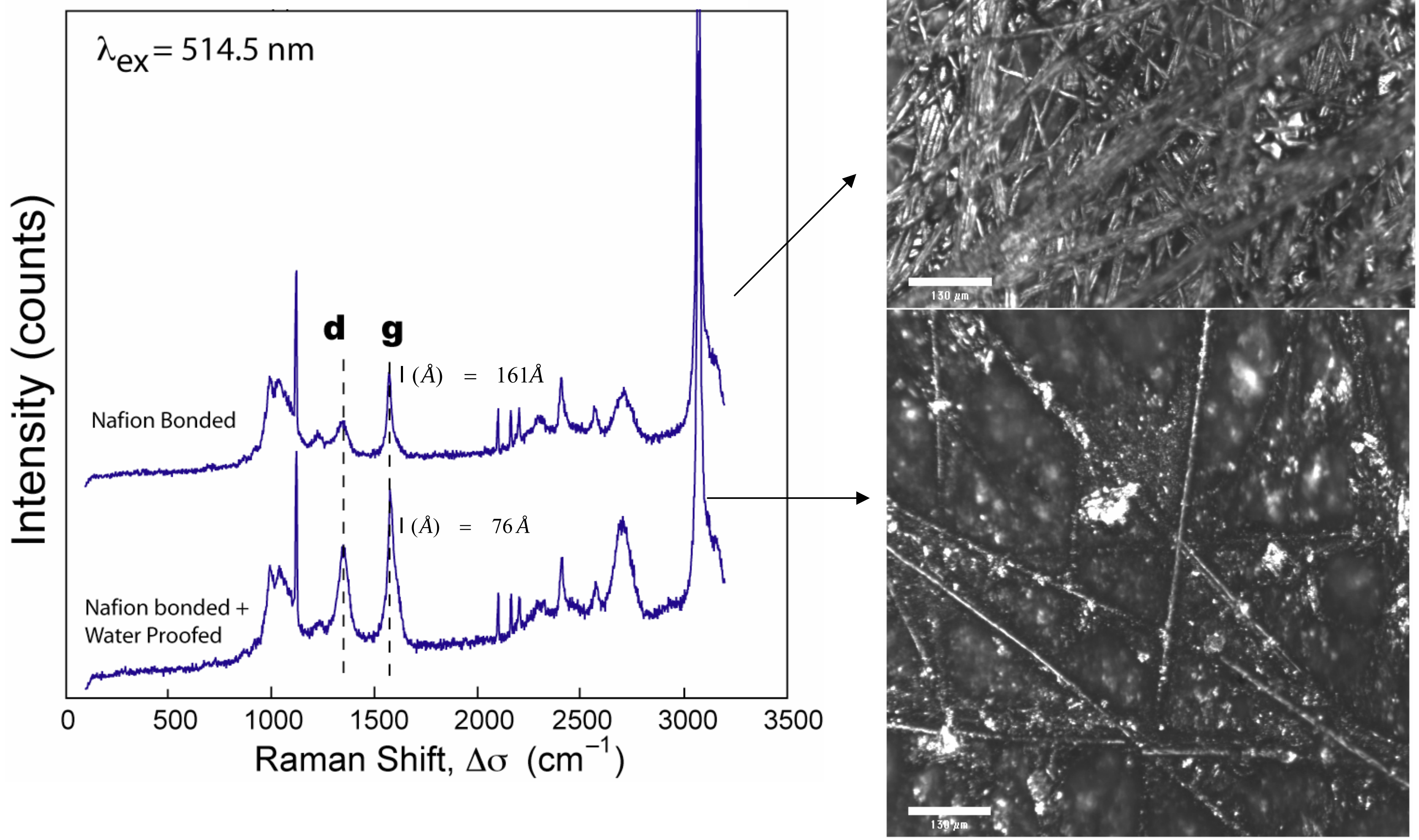
$$l\,(\mathring{A}) = 44\left(\frac{I_g}{I_d}\right)$$

$$= 175\mathring{A}$$

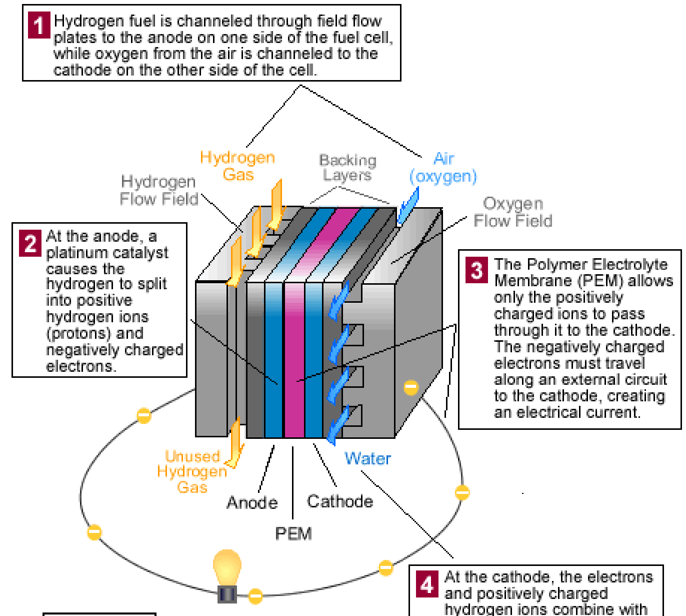
From early literature on graphitic materials
Tuinstra and Koenig, J. Chem Phys. 53, 1126 (1970).

Raman Spectroscopy: Dan's trip to NTUF

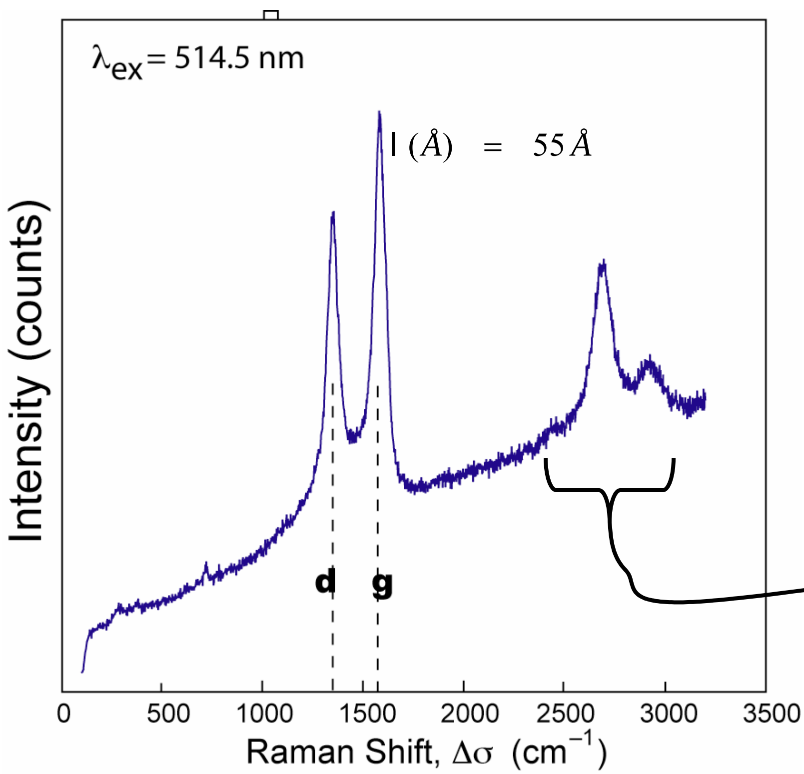
Gas Diffusion Layers
(graphite paper)

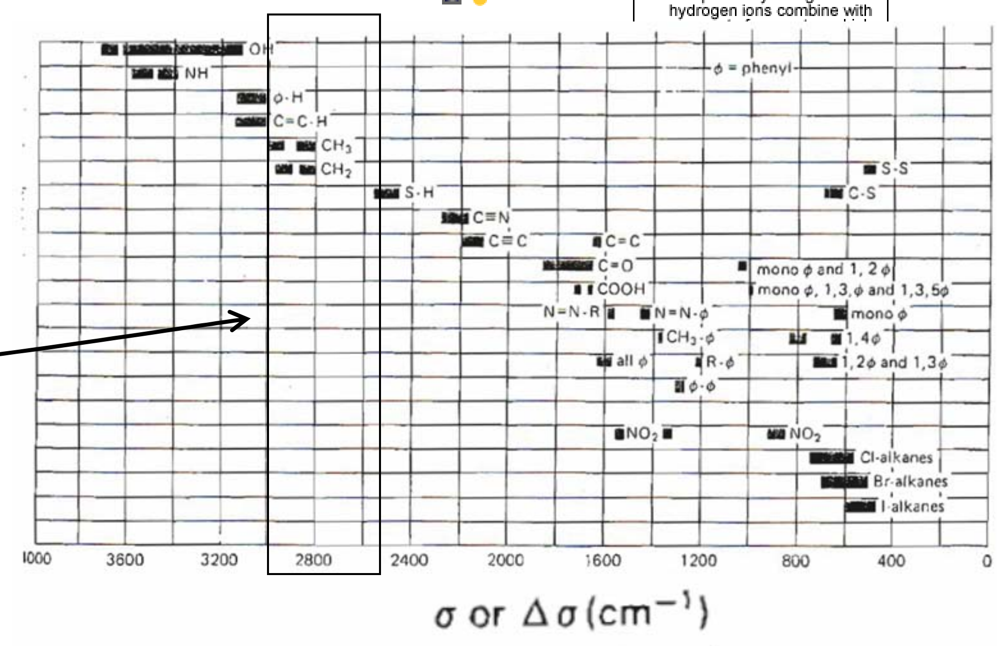


Raman Spectroscopy: Dan's trip to NTUF



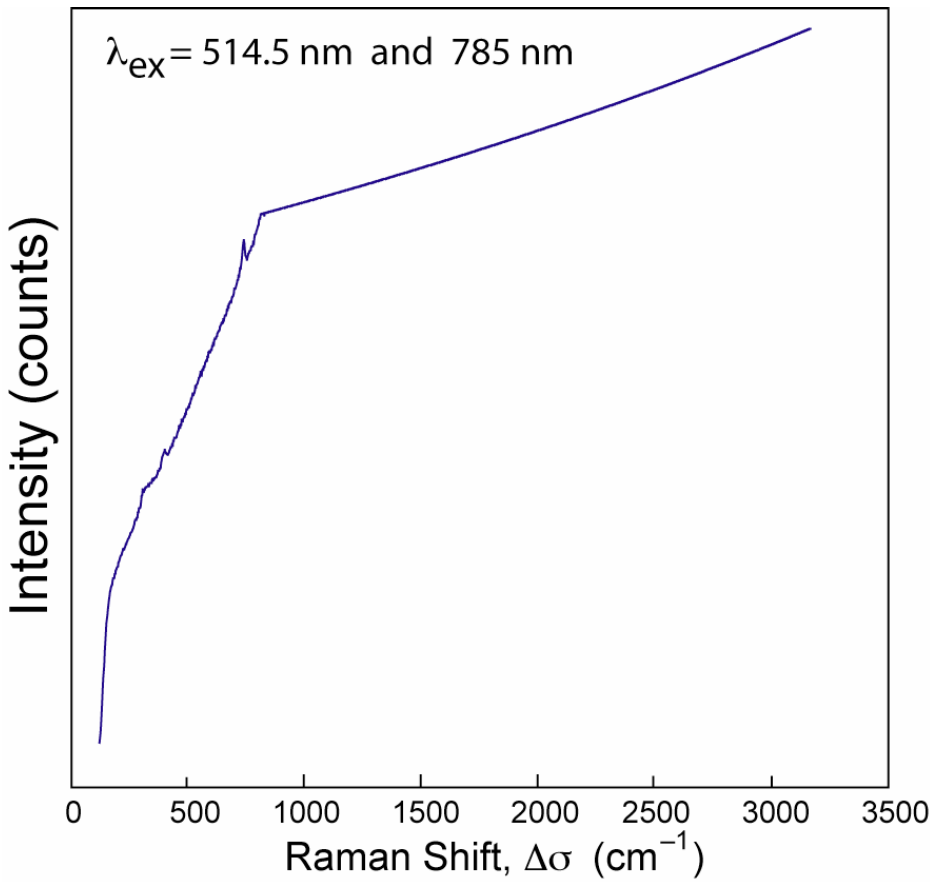
Gas Diffusion Layers (Woven Fibers)

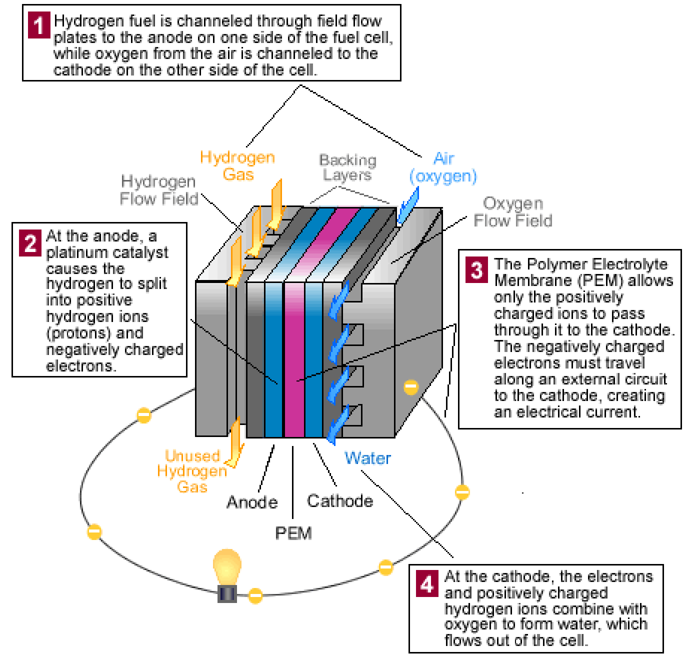




Raman Spectroscopy: Dan’s trip to NTUF

Nafion





Fluorescence problems! Maybe try photobleaching as next option.