

April 6, 2005

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Spectroscopy: Raman Spectroscopy

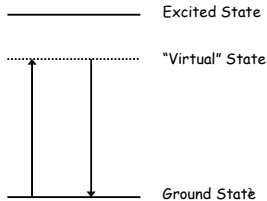
Chem 221
Instrumental Analysis
Spring 2005

Raman Scattering

➤ Discovered in 1928 by C.V. Raman (received Nobel Prize in 1930)

First, let's look at Elastic (Rayleigh) scattering (no change in energy of light):

EMR induces oscillating electric field in electron cloud around molecule - which is then re-emitted as a photon



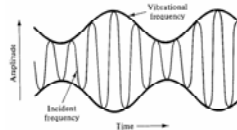
Inelastic Scattering

- If there is a *vibration* which results in a **change in the net polarizability** of the electron cloud:

Scattered photon will be at an energy either greater than or lower than the original energy by an amount equal to the energy of the vibration:

Inelastic Scattering

(Only about 1 molecule in $10^8 - 10^9$ will inelastically scatter photons)



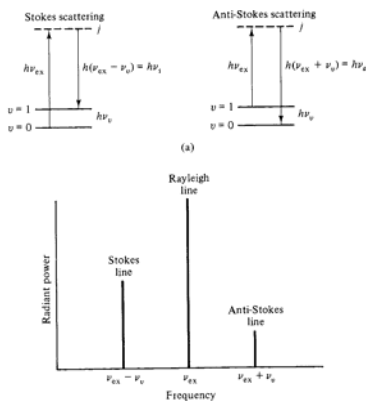
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Quantum View

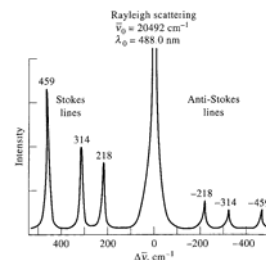
Stokes Lines:
longer wavelength
(more intense)

Anti-Stokes Lines:
shorter wavelength

$$\Delta\nu = \nu_{\text{Raman}}$$



Sample Spectrum: CCl_4



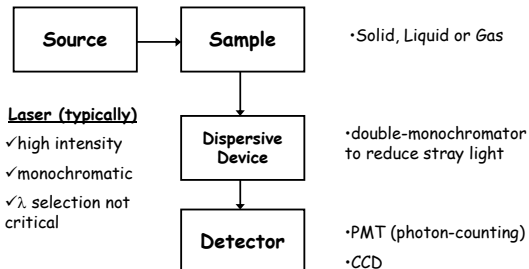
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Factors Affecting Raman Scatter Intensity

- **Concentration**
 - directly proportional
- **Source Intensity**
 - directly proportional
- **Source Wavelength**
 - $1/\lambda^4$ dependence

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Instrumentation



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Resolution?

Not straightforward - varies with source wavelength . . . why?

- $\Delta\lambda_{\text{eff}}$ is λ -independent, but $\Delta\bar{\nu}_{\text{eff}}$ varies with λ

For a 1-m monochromator, 1200 g/mm grating, and 100- μm slits: $\Delta\lambda_{\text{eff}} = 8 \text{ \AA}/\text{mm} \times 0.100 \text{ mm} = 0.8 \text{ \AA}$

So:

$$\lambda_{\text{source}} = 300 \text{ nm}; \text{ gives } \Delta\bar{\nu} = 8.9 \text{ cm}^{-1}$$

$$\lambda_{\text{source}} = 500 \text{ nm}; \text{ gives } \Delta\bar{\nu} = 3.2 \text{ cm}^{-1}$$

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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

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Solving Problems

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

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