

# CHEM 524-- Course Outline (Sect. 1)—update 2013

The hyperlinked version of this from 2005 might be linked here: [Notes 2005](#)

## I. Introduction -- Optical Spectroscopy in Analytical Chemistry

Review of [Syllabus materials](#), see handout

Obtain a class list with contact and interests

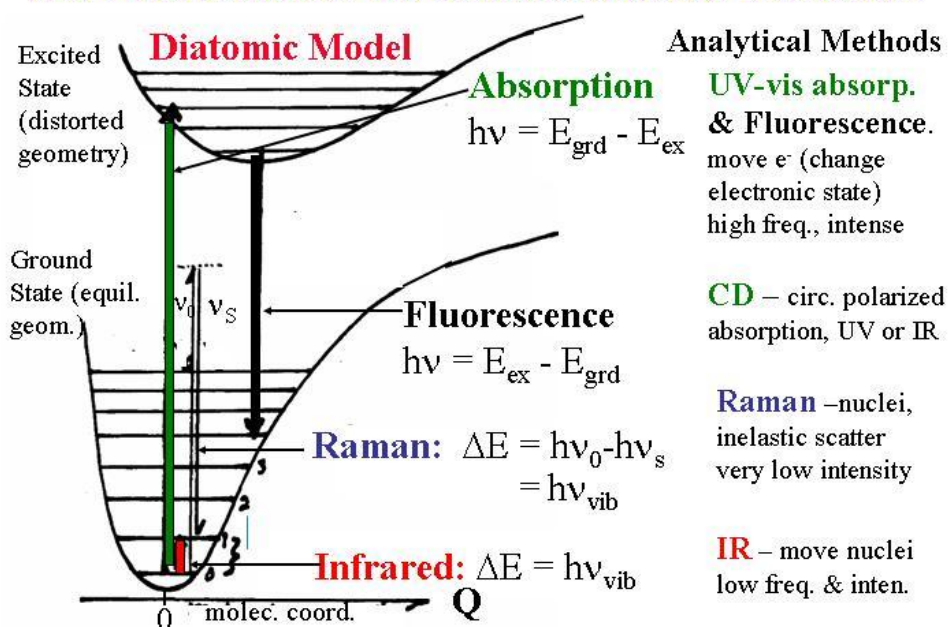
### A. Analytical uses of Spectroscopy

1. **Qualitative** -- "what is it?" → Property detection (characteristic of analyte)

[Spectral transitions](#) → [difference in E-levels](#) → molecular/material properties

**Molecular view:**

### Optical Spectroscopy - Processes Monitored UV/ Fluorescence/ IR/ Raman/ Circular Dichroism



**Types of transitions** -- spectral region studied ([ref. Text: Table 1-1](#))

Typical wavelength (cm)	Approximate energy (kcal mole <sup>-1</sup> )	Spectroscopic region	Techniques and Applications
10 <sup>-11</sup>	3 × 10 <sup>8</sup>	γ-ray	Mössbauer
10 <sup>-8</sup>	3 × 10 <sup>5</sup>	X-ray	x-ray diffraction, scattering
10 <sup>-5</sup>	3 × 10 <sup>2</sup>	Vacuum UV	Electronic Spectra
3 × 10 <sup>-5</sup>	10 <sup>2</sup>	Near UV	Electronic Spectra
6 × 10 <sup>-5</sup>	5 × 10 <sup>3</sup>	Visible	Electronic Spectra
10 <sup>-3</sup>	3 × 10 <sup>0</sup>	IR	Vibrational Spectra
10 <sup>-2</sup>	3 × 10 <sup>-1</sup>	Far IR	Vibrational Spectra
10 <sup>-1</sup>	3 × 10 <sup>-2</sup>	Microwave	Rotational Spectra
10 <sup>0</sup>	3 × 10 <sup>-3</sup>	Microwave	Electron paramagnetic resonance
10	3 × 10 <sup>-4</sup>	Radio frequency	Nuclear magnetic resonance

## 2. Quantitative --"how much is it?"→generally used to detect concentration

Optical Spectra --sensitive and widely useful, conc. to pM

--flexible and general, all states (gas, liq. sol.)

Calibrate by comparison to a standard (determine a linear range)

Simple/inexpensive-- many commercial instruments available

## B. Spectroscopy -- (*Assign: -- Read text: Chap 1 & 2, establish terms*)

### 1. Response of system to light -- as function of frequency /wavelength

--process is important to determine detectability, selectivity

--absorption, emission, excitation, scattering, ionization, etc.

### 2. Needs: *Source* - depends on spectral regions (experiment requires light)

*Control light (optics)*--to maximize S/N, select property and sample

*Sampling*- vital for accuracy, - species/question dependent

*Detection*- spectral region and sensitivity dependent

*Analysis*--involves: standards/linearity/interference

### 3. Types of Spectrochemical Analyses:

Dispersion of response → Qualitative

Amount of response → Quantitative

Variables for control of analyses:

- **Light beam characteristics** - wavelength (frequency), intensity, polarization - determine types of transitions and information accessed.

- **Frequency** matches change in energy, type of motion

→  $E = h\nu$ , where  $\nu = c/\lambda$  (in  $\text{sec}^{-1}$ )

- **Intensity** increases the transition probability

- **Linear Polarization** aligns to direction of dipole change

→  $I \sim [\delta\mu/\delta Q]^2$  where Q is the coordinate of the motion

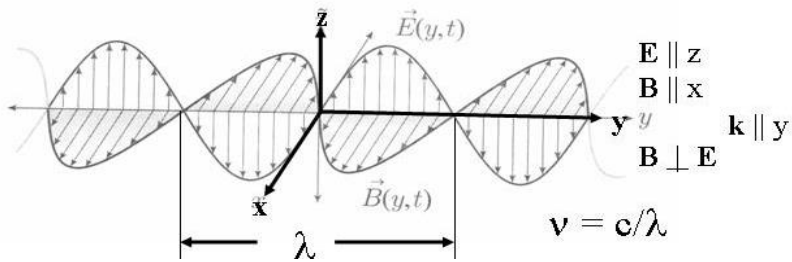
**Circular Polarization** results from an interference:

→  $I \propto \mu \cdot m$   $\mu$  and  $m$  are electric and magnetic dipole

#### 4. Basic Quantities

Wavelength/frequency -- (ref. Text: Table 1-1)

$$E_z = E_z^0 \cos(ky - \omega t) \quad B_x = B_x^0 \cos(ky - \omega t) \quad \mathbf{E}, \mathbf{B} \text{ in phase but perpendicular}$$



- **Light beam characteristics** - wavelength (frequency), intensity, polarization - determine types of transitions and information accessed
- Energy:  $Q$ ,  $\rightarrow$  Flux:  $\Phi = dQ/dt$ ;  $\rightarrow$  Intensity:  $I = d\Phi/d\Omega$
- Source radiance:  $B(l) = d^2\Phi / (d\Omega dA_s \cos\theta)$
- Irradiance on Detector:  $E = d\Phi/dA_{det}$

Measures of light strength: from source and onto detector

--(ref. Text: Table 2-1, Table 2-2)

**Definitions:** Energy (sum):  $Q \rightarrow$  Flux (rate):  $\Phi = \delta Q / \delta t \rightarrow$  Intensity:  $I = \delta \Phi / \delta \Omega$

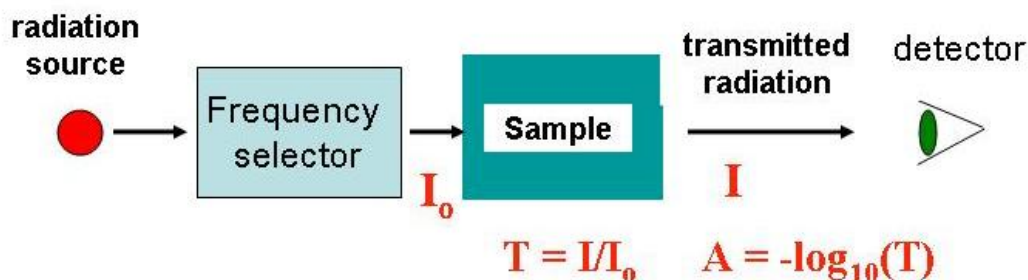
Source radiance:  $B(\lambda) = \delta^2 \Phi / \delta \Omega \delta (A_s \cos\theta) \rightarrow$  "from an area"

Irradiance on Detector:  $E = \delta \Phi / \delta A_{det} \rightarrow$  "to an area"

#### 5. Methods -- all analyte population (concentration/extrinsic) dependent

### Techniques of Absorption Spectroscopy

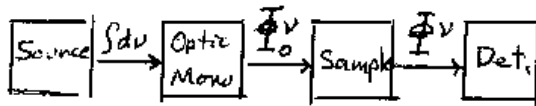
UV-vis and Infrared spectroscopy deals with **absorption of radiation**--detect attenuation of beam by sample at detector



**Dispersive** spectrometers measure transmission as a function of frequency (wavelength) - sequentially--same as typical CD

**Interferometric** spectrometers measure intensity as a function of mirror position, all frequencies simultaneously--Multiplex advantage

**Absorbance/transmittance** (figure I-1):



$$A = -\log_{10} T = \epsilon b c$$

$$T = \Phi / \Phi_0$$

$A \sim \text{conc.}$  if  $\epsilon$  const.

$T = \Phi / \Phi_0 \rightarrow A = -\log_{10}(T)$  – you can derive (Lambert):  $d\Phi = -k(c) \Phi(z) dz$

Beer Lambert Law:  $A = \epsilon(\lambda)bc$ ,  $\epsilon \sim [M^{-1}cm^{-1}]$ , const. over range of  $c$

Concentration dependence has a linear regime ( $\lambda$  and instr. dep.)

Cross-section:  $\sigma$ –[ $cm^2$ ],  $A = 0.434 \sigma b n$ ,  $n$  — conc. in number [ $\#/cm^3$ ]

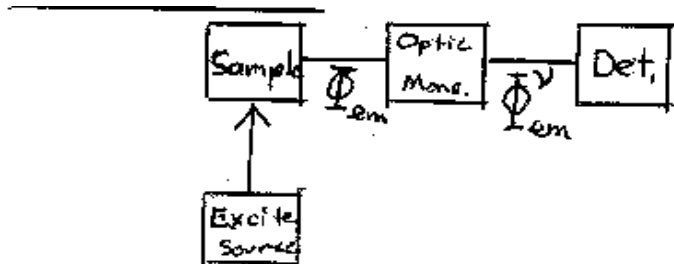
Note: Need **2 measurements** for absorption,  $\Phi$  and  $\Phi_0$ ,

Optional design, double beam, done simultaneously

**Emission** (figure I-2): – emitting states in equilibrium (thermal),  $n_j \sim n_t$

**Luminescence** – specific state excited (cool),  $n_j \sim n_t$

Works if low abs.  $\Phi_L = k\Phi_0(1-10^{-A})$  – expand, show  $\sim$  linear for  $A < 0.01$



$$\Phi_{em} \sim n_j \sim n_T \text{ (Boltzmann equilibrium)}$$

$$\sim \text{conc.}$$

$$\Phi_{lum} \sim n_{ex} \sim \Phi_0 (1 - e^{-A})$$

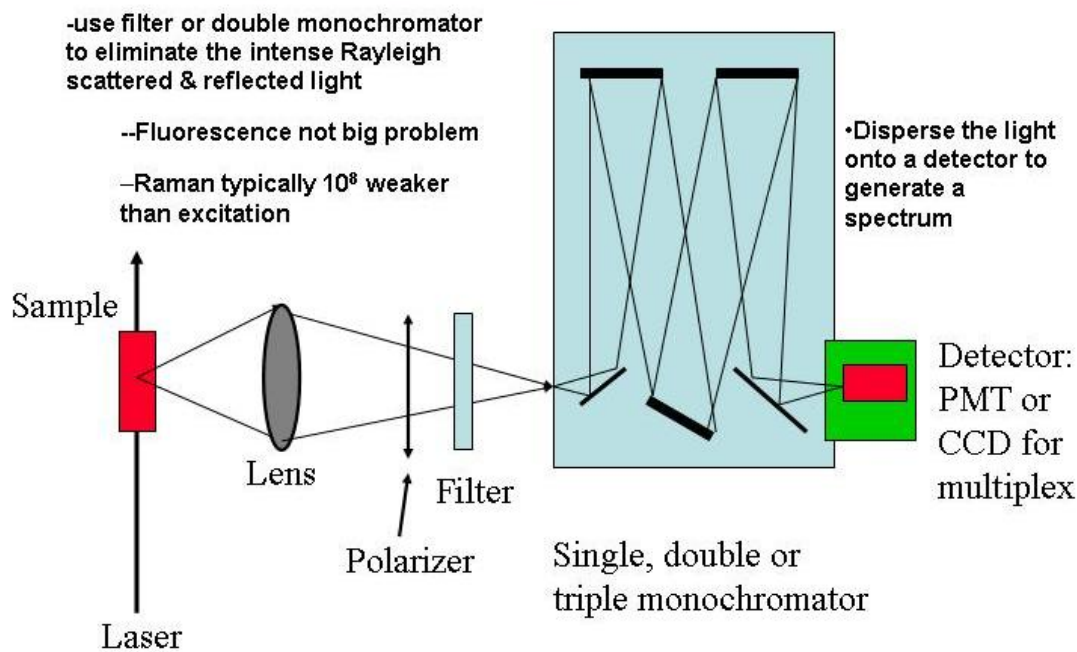
$$\sim \Phi_0 (1 - 1 + A - \frac{A^2}{2} \dots)$$

$$\sim \Phi_0 A \sim \text{conc.}$$

for  $A < 0.01$

**Scattering** --elastic ( $\omega_s = \omega_o$ ) and inelastic ( $\omega_s < \omega_o$ ),

## Dispersive Fluorescence or Raman



**Detect intensity,  $I$ , against zero background--ideal**

[Figure 1. Absorption schematic](#)

[Figure 2. Emission schematic](#)

*All of the above use sources, optics, detectors, electronics and processing – which we now discuss*

[Homework link to set #1](#)

**Read in Text:** this section covers: **Chapter1, Chapter 2-2, 2-3, 2-5**

**Study on your own:** **Chap.2-4** Selection of information (we will do later)

**Chap.2-5** Analytical signal — Sorting out various contributions to the signal measured from background, etc. — This topic will recur and be tested.

**Homework:** (For discussion only: Chap. 1: #3, 4, 6, 10, Chap. 2: #5, 10;

Chap2: #1, **good model test question**, previously on 1<sup>st</sup> exam)

You should already know how to solve/use: Chap 1: #1,12, Chap 2: #6,13, 14

**To eventually hand in:** Chap.2: # 4, 7, 11, 15, plus

- Consider  $H_2O$ , calculate the population of the  $v = 0$  and 1 molecular states for the vibrational states corresponding to  $\nu = 3600$  and  $1650\text{ cm}^{-1}$  for  $T = 1000\text{K}$  and  $300\text{K}$  (room temperature). Do the same for the  $J = 1, 2$  and 3 rotational states of  $HCl$ , assuming  $B$  is  $\sim 20\text{ cm}^{-1}$ .
- I have a glower in my IR spectrometer with a heated area roughly  $3 \times 5\text{ mm}$ . The lamp is rated at  $50\text{ W}$ . If its color temperature is  $1500\text{K}$ , calculate the wavelength of maximum intensity, assuming blackbody character, and then determine the radiance assuming that 70% of the power comes out as light and that you can use  $\lambda_{\text{max}}$  as an average wavelength/frequency mark.



[Link to slides used in class](#)

**Links to spectroscopy courses on line (Some may be out of service):**

**Brian Tissue Course** on several methods, giving an instrumental analysis level survey, (on a Korean server) may be incomplete, quite terse, some figures

<http://elchem.kaist.ac.kr/vt/chem-ed/analytic/ac-meths.htm>- spectroscopy

<http://elchem.kaist.ac.kr/vt/chem-ed/courses/spec/toc.htm>- intro

**MIT lab course** – links to pdf files – Phys Chem. Lab style—two versions:

<http://web.mit.edu/5.33/www/lectures.html>

**Iowa State course**, properties of light, (*might be temporarily down?*)

<http://avogadro.chem.iastate.edu/CHEM513/513-1.pdf>

physical optics

<http://avogadro.chem.iastate.edu/CHEM513/513-2.pdf>

<http://avogadro.chem.iastate.edu/CHEM513/513-3.pdf>

**Michigan State course**, the home of the textbook authors, this site by Simon J. Garrett

<http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/spectro.htm>- contnt

Introduction

<http://www.cem.msu.edu/~cem333/Week01.pdf>

<http://www.cem.msu.edu/~cem333/Week02.pdf>

Optical spectra tech--optics, sources detect

<http://www.cem.msu.edu/~cem333/Week03.pdf>

UV-vis abosrption

<http://www.cem.msu.edu/~cem333/Week04.pdf>

Luminescence

<http://www.cem.msu.edu/~cem333/Week05.pdf>

IR notes

<http://www.cem.msu.edu/~cem333/Week06.pdf>

Atomic spectra

<http://www.cem.msu.edu/~cem333/Week07.pdf>