CHEM 524 -- Course Outline (Sect. 1)

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

   Types of transitions -- spectral region studied (ref. Text: Table 1-1)

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

   Control light (optics)--to maximize S/N

   Sampling - vital for accuracy, - species/question dependent

   Detection - spectral region and sensitivity dependent

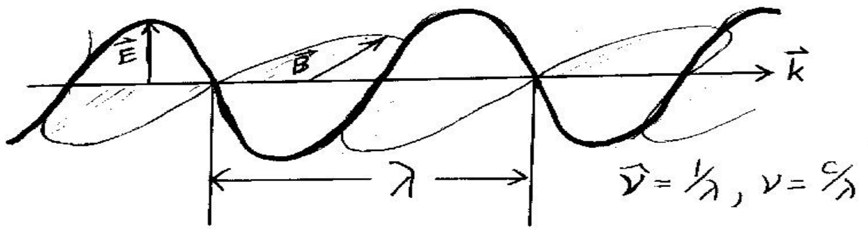
   Analysis--involves: standards/linearity/interference

3. Types of Analyses:

   Dispersion of response ⇓ Qualitative

   Amount of response ⇓ Quantitative

E – M Radiation



$\vec{E} = \vec{E}_o \cos(\omega t - \hat{k}\bar{x})$ $\quad \bar{E} \perp \bar{B}$

$\vec{B} = \vec{B}_o \cos(\omega t - \hat{k}\bar{x})$ $\quad$ (in phase)

Approximate Spectral Regions

VUV –	$\lambda < 200$ nm	
UV –	$200 < \lambda < 400$ nm	$50000 > \tilde{\nu} > 25000$ c
Vis –	$400 < \lambda < 700$ nm	$25000 > \tilde{\nu} > 14000$ c
near IR –	$700 < \lambda < 2500$ nm	
IR(vib) –	$2500 < \lambda < 50000$ nm $2.5 < \lambda < 50\mu$	$4000 > \tilde{\nu} > 200\ cm^{-1}$
far IR –	$25\mu < \lambda < 1000\mu$	$400 > \tilde{\nu} > 10\ cm^{-1}$

4. Basic Quantities

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

Measures of light strength: from source and onto detector

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

Energy: Q, → Flux: $\Phi = \delta Q/\delta t$; → Intensity: $I = \delta\Phi/\delta\Omega$

Source radiance: $B(\lambda) = \delta^2\Phi/\delta\Omega\delta A_s \cos\theta$

Irradiance on Detector: $E = \delta\Phi/\delta A_{det}$

5. Methods -- all analyte population dependent

Absorbance/transmittance (figure I-1):

$T = \Phi/\Phi_o$ $\Rightarrow$ $A = -\log_{10}(T)$ -- derive $d\Phi = -k(c)\,\Phi(z)\,dz$

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

Concentration dependence has a linear regime (λ and instr. dep.)

Cross-section: σ—$[cm^2]$, $A = 0.434\,\sigma\, b\, n$, n – conc. in number $[\#/cm^3]$
Note: Need 2 measurements for absorption, Φ and Φ_o,

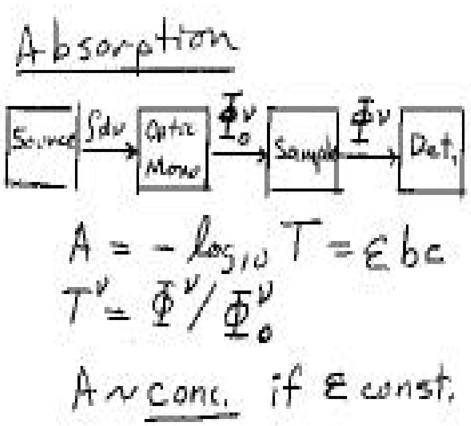
Optional design, double beam, done simultaneously

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

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



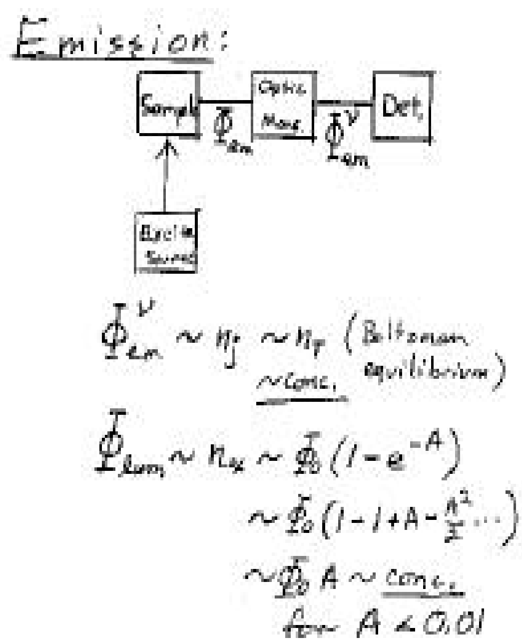


Figure 1. Absorption schematic

Figure 2. Emission schematic

Read on your own: ***Chap. 2-4*** Selection of information (we will do in - Sect. 4&5)
Chap. 2-5 Analytical signal – Sorting out various contributions to the signal measured from background, etc. – This topic will recur and be tested. (also Sect. 7-10)

Homework: (For discussion only: Chap. 1—3, 4, 6, 10,
Chap 2-1, good model test question)
To hand in: Chap. 2 – 7, 11, 1 & Calculate population of molecular states for vibrations at 600, 2500 cm^{-1} and electronic state at 30000 cm^{-1} for T=300K