

Chemistry 331

Lecture 37

Introduction to Spectroscopy

NC State University

Spectroscopy

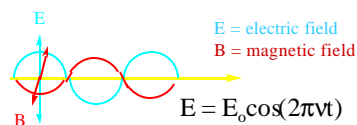
- Electromagnetic radiation
- Experimental techniques
- Intensities
- Dipole moment
- Transition moment
- Selection rules



The origin of spectral lines in molecular spectroscopy is the emission or absorption of a photon when the energy of a molecule changes.

Characteristics of electromagnetic radiation

Electromagnetic radiation can be described as a wave with an oscillating electric field. Light can be linearly polarized along the x, y, or z axes. The electric field vector is \perp to the direction of propagation.



Basic Phenomena

Emission spectroscopy - a molecule undergoes a transition from a state of high energy E_1 to a state of lower energy E_2 and emits the excess energy as a photon.

Absorption spectroscopy - the energy of an incident photon drives a polarization from the molecular ground state to the excited state. An absorbed photon has a frequency given by the Bohr relation:

$$h\nu = E_1 - E_2$$

Sources of Radiation

- Nerst filament = infrared
- Arc lamp (Xe) = UV-vis
- Tungsten-halogen = visible near-IR
- Lasers
 - Excimer
 - Ion
 - YAG
 - Ti:sapphire

Dispersion is essential

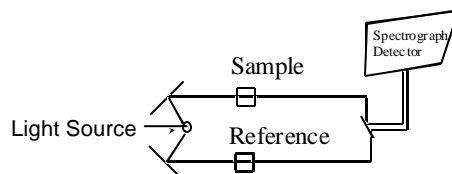
- A dispersing element separates different frequencies into different spatial directions.
- A prism separates different frequencies because of the optical beam using the variation of the index of refraction such that high-frequency radiation undergoes a greater deflection than low-frequency radiation.
- A diffraction grating consists of grooves cut ca. $1 \mu\text{m}$ apart. Interference from reflected waves gives rise to specific angles of propagation.

Detectors

- Thermistor bolometer, far ir
- Mercury Cadmium Telluride (MCT), ir
- Germanium, near ir
- Silicon, visible
- Photomultiplier tube. Amplification by dynodes generates current for each photon hit.
- CCD detector. Array of detectors on a chip. UV coatings, efficiency, ease of use.

Absorption Spectrometer

Dispersing element is in the spectrograph



Comparison of sample and reference is essential

Intensities of Spectral Lines

- Intensity of absorption for a sample that has thickness d is given by

$$\log \frac{I}{I_0} = -\epsilon cd$$

- ϵ is the molar absorption coefficient.
- c is the concentration.
- d is the pathlength.
- I is the transmitted intensity, I_0 is the incident intensity.

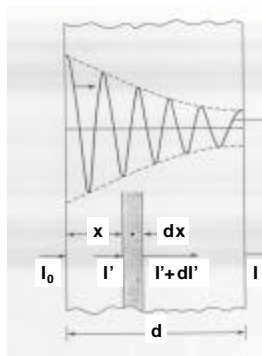
Beer-Lambert Law

$$I = I_0 10^{-A}$$

$$A = \epsilon(\nu) cd$$

A is the absorbance.
 d is the pathlength.
The exponential attenuation of the intensity is shown in the Figure.

The absorption cross section for an individual molecule is σ .
 $\sigma = h\nu k_{12}$ where k_{12} is the transition rate constant.



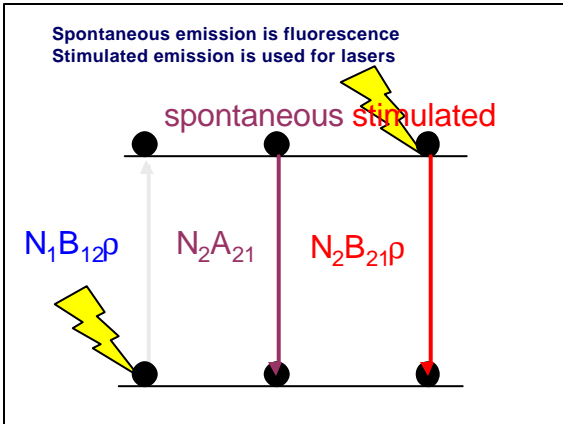
Absorbance and Transmittance

- The dimensionless product ϵcl is called absorbance, $A = \epsilon cl$.
- The ratio I/I_0 is called the transmittance, T .
- The relationship is $\log T = -A$
- The integrated absorption coefficient is proportional to the area under the band

$$A = \int \epsilon(\tilde{\nu}) d\tilde{\nu}$$

Theory of Absorption and Emission

- Stimulated absorption - low to high driven by absorption of a photon
- Stimulated emission - high to low driven by emission of a photon
- Spontaneous emission - high to low emission independent of photon field
- Einstein coefficients:
 - B_{12} - stimulated absorption
 - B_{21} - stimulated emission
 - A_{12} - spontaneous emission



Einstein's derivation of absorption and emission coefficients

- Absorption $w = B_{12}\rho$, Emission $w' = (A_{21} + B_{21}\rho)$ for individual molecules.
- The total rates of absorption and emission
 $W = N_1 w_{12}$ where N_1 is the number in the ground state
 $W' = N_2 w_{21}$ where N_2 is the number in the excited state
- Thermal equilibrium demands that
 $W = W'$ i.e. $N_1 B_{12}\rho = N_2 (A_{21} + B_{21}\rho)$
- The derivation consists of solving for ρ and noticing the similarity with Planck distribution.

Treatment of states in equilibrium

$$\rho = \frac{N_2 A_{21}}{N_1 B_{12} - N_2 B_{21}} = \left(\frac{A_{21}}{B_{12}} \right) \frac{1}{\left(\frac{N_1}{N_2} \right) - \left(\frac{B_{21}}{B_{12}} \right)}$$

$$\frac{N_2}{N_1} = e^{-hv/kT}$$

Comparison with Planck's blackbody distribution

The equation for the radiation density, r has the same form as the Planck distribution provided,

$$\frac{B_{12}}{B_{21}} = 1, \quad \frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}$$

The Planck distribution is:

$$r = \frac{8\pi h\nu^3}{c^3} \left(\frac{1}{e^{hv/kT} - 1} \right)$$

Interpretation of Einstein Coefficients

The intrinsic coefficient for absorption B_{12} is related to $k_{12} = N B_{12}\rho$, where ρ is the energy density:

$$I = c \int \rho(\nu) d\nu$$

Einstein showed that the rate of absorption and stimulated emission are equal. The spontaneous emission rate has a definite relation to the stimulated emission rate:

$$B_{21} = B_{12}$$

$$A_{21}^{spontaneous} = \frac{8\pi h\nu^3}{c^3} B_{21}$$

Connection with experiment

Beer's law states that

$$I = I_0 10^{-\epsilon(\nu)cd}$$

$\epsilon(\nu)$ is the molar extinction coefficient.
 c is the concentration.
 d is the pathlength.

In differential form this is written:

$$-dI = 2.303\epsilon(\nu)cl dx$$

A comparable expression in terms of the individual transition rates is given by

$$-dI = N h\nu k_{12} dx$$

Experimental determination of the transition moment by absorption spectroscopy

$$2.303\epsilon\{v\}cl = Nhv k_{12} = \frac{NhvI}{6c\epsilon_0 h^2} (\mu)^2 FC L\{v\}$$

$$2.303C \int_{band} \frac{\epsilon\{v\}}{v} dv = \frac{\pi N}{3c\epsilon_0 h} (\mu)^2 \int_{band} FC L\{v\} dv$$

$$(\mu)^2 = \frac{6909 c \epsilon_0 h}{\pi N_A} \int_{band} \frac{\epsilon\{v\}}{v} dv$$

The transition moment is related to the integrated extinction coefficient.

Definition of the Dipole Moment

The dipole moment operator is

$$\mu = e \sum_i z_i r_i$$

where ze is the electronic charge at a nucleus and r_i is a vector from an arbitrary origin. Along the x-direction

$$\mu = e \int_0^\infty Y^* x Y dx$$

Examples of ground state dipole moments

The ground state dipole moment of hydrogen halides can be calculated from the fractional charges

1 Debye = 3.33×10^{-30} Cm δ^+ δ^-

	δ^+	δ^-	R(pm)	$\mu(x 10^{-30} \text{ Cm})$
HF	0.42	0.42	91.7	6.37 \approx 1.9 D
HCl	0.16	0.16	127.5	3.44 \approx 1.0 D
HBr	0.11	0.11	141.4	2.64 \approx 0.8 D
HI	0.05	0.05	160.9	1.40 \approx 0.4 D

Definition of the transition dipole moment

The transition dipole moment results from the interaction of electromagnetic radiation with the molecule where $E = E_0 \cos(2\pi vt)$ and the hamiltonian for interaction is

$$H = -\mu_x E_{ox} \cos(2\pi vt)$$

where μ_x is the transition dipole moment

$$(\mu_x)_{ge} = e \int_0^\infty Y_g^* x Y_e dx$$

The transition probability is proportional to the square of the transition moment

The absorption of radiation involves time-dependence because the field is time-varying $E_0 \sin(2\pi vt)$. If we solve for the transition probability we find that it is proportional to the square of transition moment.

$$B = \frac{1}{6\epsilon_0 h^2} (\mu_x)_{g,e}^2$$

Selection Rules

A transition will be allowed only if the transition dipole moment integral is non-zero. The general rules are:

Electronic: $\Delta l = \pm 1, \Delta m = 0$

Rotational: $\Delta J = \pm 1, \Delta M = 0$

Vibrational: $\Delta v = \pm 1$

For mathematical description see the workshop on selection rules.