84.514
Advanced Analytical Chemistry

Part II
Molecular Spectroscopy

Important Websites

http://faculty.uml.edu/David_Ryan/84.514
http://cord.org/step_online/introduction/contents.htm
Spectroscopy = methods based on the interaction of electromagnetic radiation (EM) and matter

Electromagnetic Radiation = form of energy with both wave and particle properties

EM moves through space as a wave

Most interactions of EM with matter are best understood in terms of electric vector
Relationship between various wave properties

\[ \nu \lambda_i = \frac{C}{\eta_i} \]

Where \( \nu \) = frequency in cycles/s or Hz
\( \lambda_i \) = wavelength in medium \( i \)
\( \eta_i \) = refractive index of medium \( i \)
\( C \) = speed of light in vacuum (2.99 x 10^{10} \text{ cm/s})

EM slows down in media other than vacuum because electric vector interacts with electric fields in the medium (matter) \( \rightarrow \) this effect is greatest in solids & liquids, in gases (air) velocity similar to vacuum
A Typical Dispersion Curve showing $\eta$ as a function of frequency $\nu$. 

- **Normal dispersion**
- **Anomalous dispersion**

Graph showing refractive index ($\eta$) as a function of frequency ($\nu$) from infrared to ultraviolet.
Normally $\eta$ increases with $\nu$ and this is referred to as “Normal Dispersion”

When absorption occurs, the nature of the interaction changes

$\eta$ is a measure of the extent to which the electric vector interacts with the medium & slows down

For a given frequency and medium, a larger $\eta$ means more interaction with electric field & the medium is said to have greater polarizability i.e., is more able to follow the electric vector
A Typical Dispersion Curve

Three trends can be seen:
1) an overall decrease in $\eta$ as $\nu$ increases.

This reflects the inability of the electric fields in the material to keep up with the oscillations of the EM. 

Diagram:
- Normal dispersion
- Anomalous dispersion

Axes:
- Refractive index ($\eta$)
- Frequency, Hz
- Infrared: $10^{13}$
- Ultraviolet: $10^{15}$
A Typical Dispersion Curve

2) regions where \( \eta \) increases with \( \nu \) prior to an absorption band

This is referred to as normal dispersion
A Typical Dispersion Curve

3) regions where \( \eta \) decreases with \( \nu \) very sharply at absorption bands.

This is referred to as anomalous dispersion because the nature of the interaction changes.
Variation in the Refractive index ($\eta$) with wavelength ($\lambda$) for several types of glass
Refractive indices ($\eta$) for various substances at 589 nm (the sodium D line)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>1.00027</td>
</tr>
<tr>
<td>water, 20 °C</td>
<td>1.33336</td>
</tr>
<tr>
<td>NaCl crystal</td>
<td>1.544</td>
</tr>
<tr>
<td>benzene</td>
<td>1.501</td>
</tr>
<tr>
<td>quartz (fused)</td>
<td>1.46</td>
</tr>
<tr>
<td>glass (crown)</td>
<td>1.52</td>
</tr>
<tr>
<td>ethyl alcohol</td>
<td>1.36</td>
</tr>
<tr>
<td>carbon disulfide</td>
<td>1.63</td>
</tr>
</tbody>
</table>
**Refraction** = change in velocity of EM as it goes from one medium to another

Medium 1 (air)
Velocity larger $\eta = 1.00$

Medium 2 (glass)
Velocity smaller $\eta = 1.50$

Ray bent toward normal
Equation for Refraction

\[
\frac{\sin \Phi_1}{\sin \Phi_2} = \frac{v_1}{v_2} = \frac{\eta_2}{\eta_1} = \eta_2 \quad \text{if medium 1 is air } \eta_1 = 1.0
\]

Magnitude of the direction change (i.e., size of the angle depends on wavelength (shown in equation as } v) this is how a prism works

Direction of bending depends on relative values of } \eta for each medium. Going from low } \eta to higher, the ray bends toward the normal. Going from higher } \eta to lower the ray bends away from the normal.
Critical Angle $(\Phi_c)$

At $90^\circ$ incidence $\sin \Phi_1 = 1.0$

$$\sin \Phi_c = \frac{\eta_1}{\eta_2}$$

- Incident ray is $90^\circ$ to normal.
- This is called grazing incidence.
- Maximum value of $\Phi_2 = \Phi_c$.

Important for:
1) Refractometers
2) Fiber Optics
Wave Interaction - interaction between waves
- waves must have similar $\nu$ but can be out of phase (i.e., they start in different places)
Principle of superposition = vectors add
- wave $y_1 + y_2$ formed by adding $y_1$ & $y_2$ by vector addition
Wave Equation

\[ y = A \sin (\omega t + \alpha) \]

Where

- \( A \) = amplitude
- \( \omega \) = angular frequency
- \( \alpha \) = phase angle
- \( t \) = time

For a collection of waves the resulting position \( y \) at a given \( t \) can be calculated by

\[ y = A_1 \sin (\omega_1 t + \alpha_1) + A_2 \sin (\omega_2 t + \alpha_2) + \ldots \]
**Interference** - amplitude of the resulting wave depends on phase difference $\alpha_1 - \alpha_2$

Constructive Interference $\Rightarrow$ waves add

Destructive Interference $\Rightarrow$ waves cancel
At $\alpha_1 - \alpha_2 = 0^o$ adding of waves gives Maximum Constructive Interference.

Wave 1

Wave 2

Resultant wave

Phase angle difference between Wave 1 & Wave 2 is zero $\alpha_1 - \alpha_2 = 0^o$
Also at $\alpha_1 - \alpha_2 = 360^\circ$ adding of waves gives Maximum Constructive Interference

Phase angle difference between Wave 1 & Wave 2 is $360^\circ$ ($\alpha_1 - \alpha_2 = 360^\circ$)
When $\alpha_1 - \alpha_2 = 180^\circ$ or $540^\circ$ adding of waves gives **Maximum Destructive Interference**

Phase angle difference between Wave 1 & Wave 2 is $180^\circ$ ($\alpha_1 - \alpha_2 = 180^\circ$)
Fourier Analysis – mathematical process of resolving a combination of waves of various frequencies into their individual frequencies. This requires a Fourier integral and is important in all Fourier Transform (FT) methods like FTIR and FT NMR. Requires complex mathematics and a computer to figure out amplitudes of various component frequencies.
Diffraction = EM going past an edge or through a slit (2 edges) tends to spread

The combination of diffraction effects & interference effects are important in spectroscopy for

1) diffraction gratings
2) slit width considerations
Scattering  =  EM interacts with matter and changes direction, usually without changing energy

This can be described using both the wave or particle nature of light:

1) Wave – EM induces oscillations in electrical charge of matter  ⇒  resulting in oscillating dipoles which in turn radiate secondary waves in all directions = scattered radiation

2) Particle (or Quantum) – EM interacts with matter to form a virtual state (lifetime $10^{-14}$ s) which reemits in all directions.

Raman effect = when some molecules return to a different state  ⇒  change in frequency
Many types of scattering exist depending on several parameters characterizing the system, we will be concerned with: Rayleigh Scattering and Large Particle Scattering.
Rayleigh Scattering – scattering by particles whose longest dimension is < 5 % to 10 % of $\lambda$ with no change in observed frequency

$$I_s = \frac{8 \pi^4 \alpha^2}{\lambda^4 r^2} (1 + \cos^2 \theta) I_o$$

scattering intensity \hspace{2cm} polarizability \hspace{2cm} angle between incident beam & scattered beam

wavelength \hspace{2cm} distance from scattering center to detector \hspace{2cm} incident beam intensity

Notice the fourth power dependence on wavelength meaning short wavelengths are scattered more efficiently ⇒ sky is blue
Polarizability ($\alpha$) is a measure of how well a given frequency induces a dipole in a substance. 

$\alpha$ tends to be large for large molecules (e.g., proteins).

Large Particle Scattering – particle dimensions < 10% $\lambda$ to 1.5 $\lambda$

- Applies in techniques like turbidimetry and nephelometry.
- Large particles do not act as a point source & give rise to various interference phenomena.
- Forward scatter becomes greater than back scatter.