

Inorganic Compounds Spectroscopy

329 CHEM

(Part 1)

Resources:

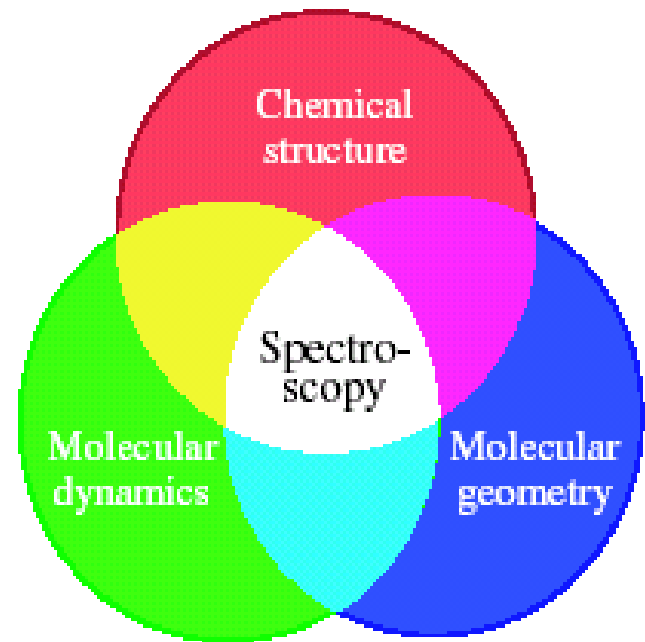
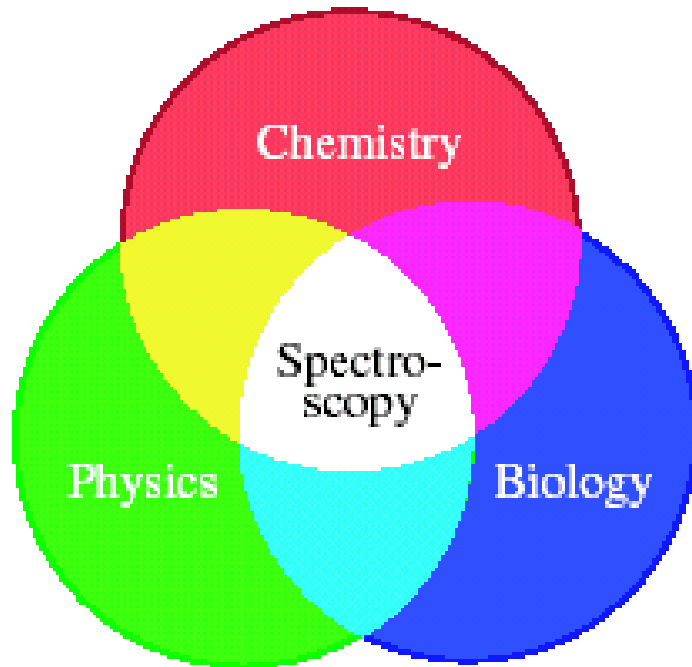
1. Textbook

Fundamental of Molecular Spectroscopy, C. N. Banwell, 4th ed., 1995

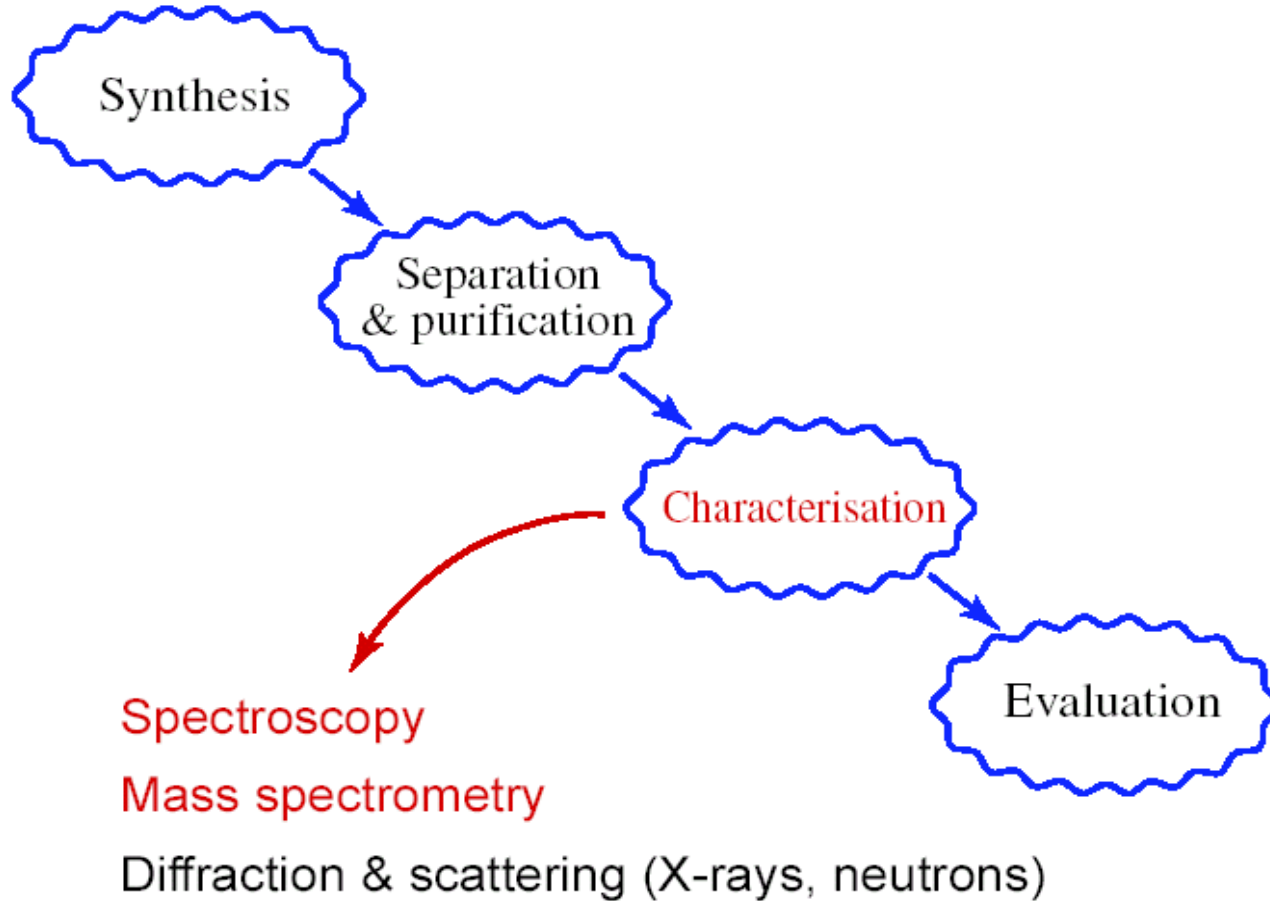
2. Internet website

www.hyperphysics.phy-astr.gsu.edu

Application of Spectroscopy

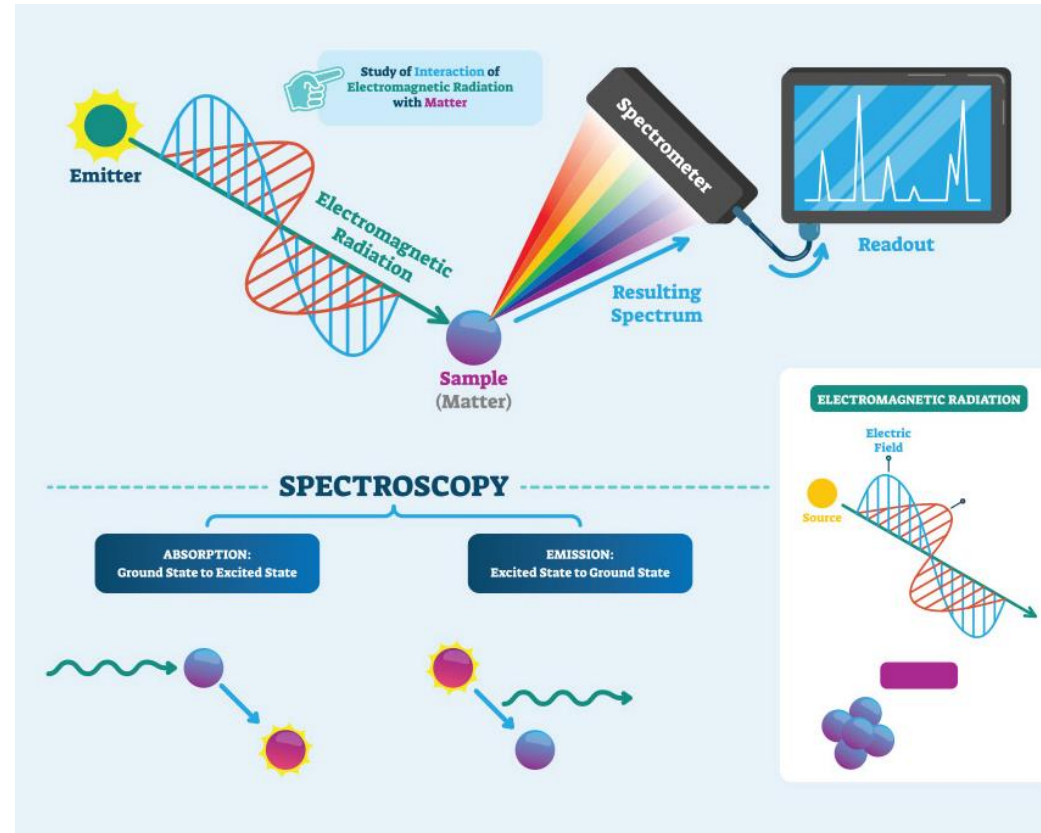


The Role of Spectroscopy



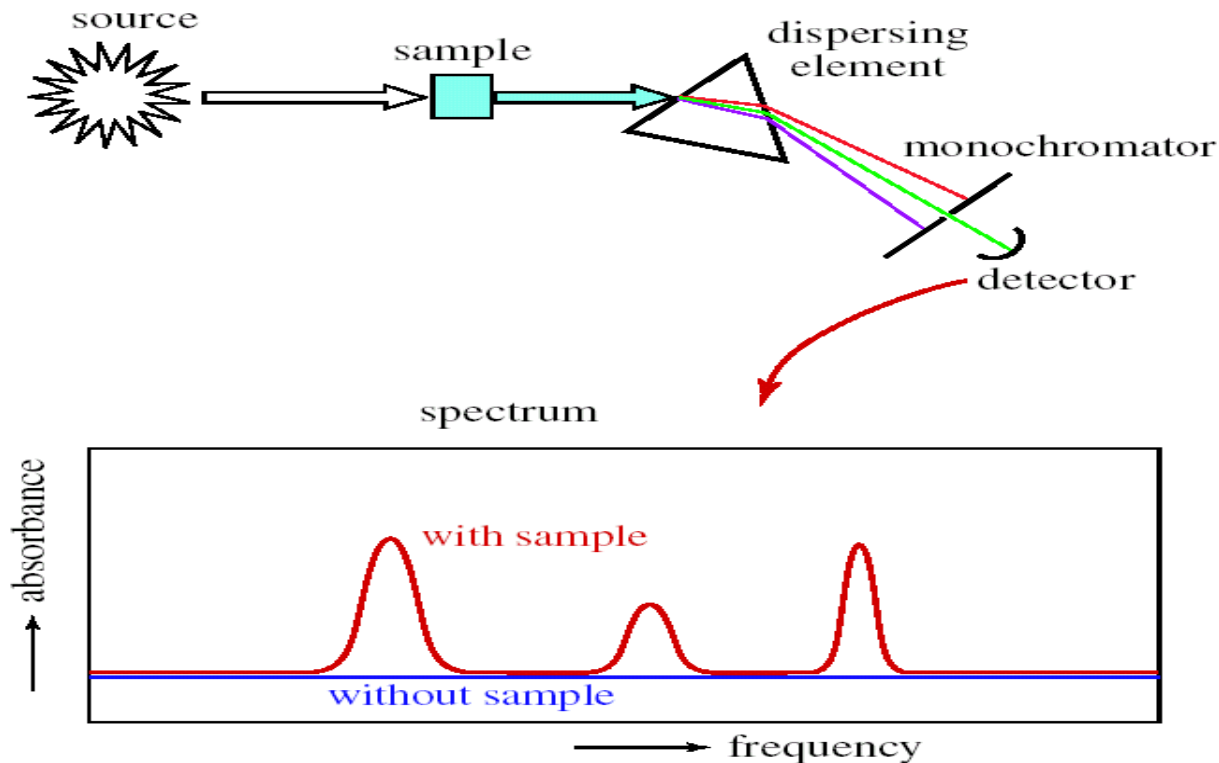
We Shall be Concerned With...

- What spectroscopy can tell us about the structure of matter ?
- Nature of electromagnetic radiation.
- How the interaction of electromagnetic and matter is occurred ?



What is Spectroscopy ?

- The Study of the interchange of energy between electromagnetic radiation and matter



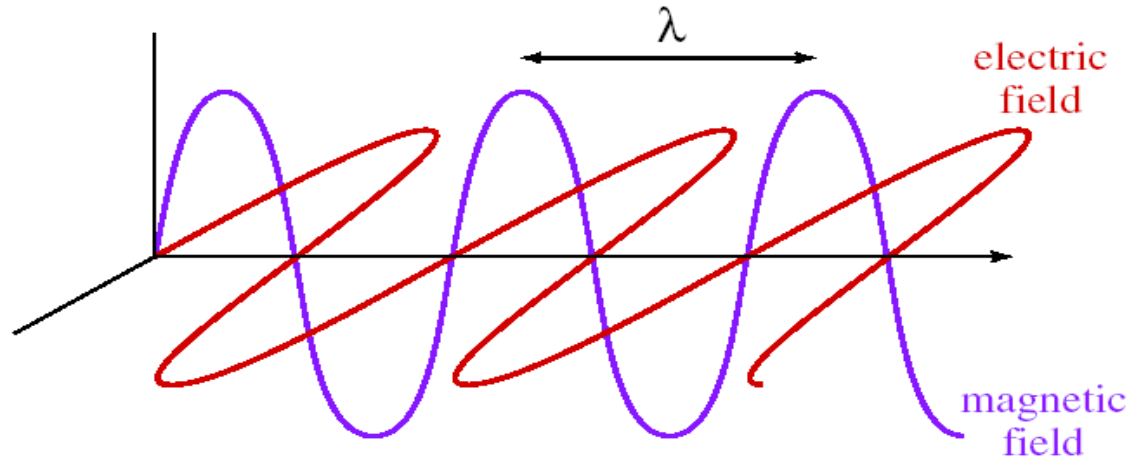
- Molecular spectroscopy** may be defined as the study of the interaction of electromagnetic **waves and matter**

Electromagnetic Radiation (e. m. r.)

- Light can be described in two complementary ways..

Wave picture:

Consists of oscillating electric and magnetic fields



$$c = \lambda \nu$$

c – velocity (m s^{-1})
 λ – wavelength (m)
 ν – frequency ($\text{Hz} \equiv \text{s}^{-1}$)

$$c_0 \text{ (vacuum)} = 2.99776 \times 10^8 \text{ m s}^{-1}$$

Particle picture: consists of “packets” of light, **photons**, each with energy $E = h\nu$

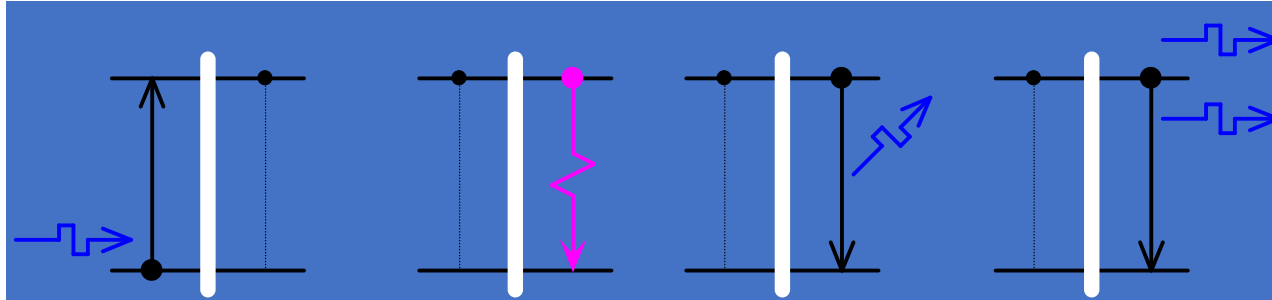
h – Planck's constant

Spectroscopy

- Microwave (Rotational)
- Infrared (Vibrational)
- Raman (Rotational & Vibrational)

Rotational vs Vibrational Spectroscopy		
More Information Online WWW.DIFFERENCEBETWEEN.COM		
	Rotational Spectroscopy	Vibrational Spectroscopy
DEFINITION	Rotational spectroscopy is the measurement of the energy of the transitions that take place between quantized rotational states of molecules in the gas phase	Vibrational spectroscopy is the measurement of the interaction of IR radiation with matter through absorption, emission, or reflection
ELECTRON TRANSITION TYPE	Rotational transitions	Vibrational transitions
PHASE OF MATTER	Occurs in gas phase molecules	Occurs in gas, solid or liquid matter

Fate of Molecule?



- Non-radiative transition: $M^* + M \rightarrow M + M + \text{heat}$
- Spontaneous emission: $M^* \rightarrow M + h\nu$ (very fast for large ΔE)
- Stimulated emission (opposite to stimulated absorption)

These factors contribute to *linewidth* & to lifetime of excited state.

Frequencies, Wavelengths and Energies

- **Frequencies** are always expressed in Hz (after Hertz) with the unit 1/second ("cycles" is derived from Hz and only used for cyclic movements. In one second how many cycle is travelled.
- **Wavelengths** are expressed in different units. (The distance travelled during a complete cycle) Å (Ångstrom, 10^{-10} m) is common for short wavelengths: g-rays, X-rays, up short wavelength UV ("vacuum UV") nm (10^{-9} m) is common for UV-Vis (350 nm - 800 nm) cm are used for microwave spectroscopy.
- **Energies** are expressed in different units. eV (electron volts) for atomic spectroscopy, photoelectron spectroscopy, mass spectroscopy, 1 eV is the energy that an electron acquires after passing through a voltage difference of one volt.

Wave numbers ($1/l$)

$$E = hn \text{ and } n = c/l$$

$$\sim\> E = hc/l$$

The Quantization of Energy

- The energy of an oscillator (absorbed or emitted) is not continuous and that any change in its energy can occur only by means of a jump between two distinct energy states i.e., it is quantized.

A molecule in space can have many sorts of energy:

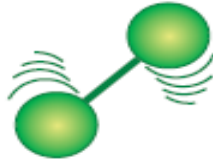
1. Rotational energy: by virtue of bodily rotation about its center of gravity.
 2. Vibrational energy: due to the periodic displacement of its atoms from their equilibrium positions.
 3. Electronic Energy: due to transfer of electrons associated with its atoms or bonds between available energy levels.
 4. Transitional Energy: due to free movement of the whole molecule in the space.
- All the above energies of the molecule are quantized except the Transitional Energy.

Molecular Energies

Molecules can have many different types of energy



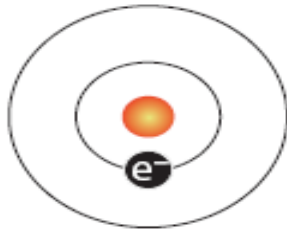
translation



rotation



vibration



electron orbital



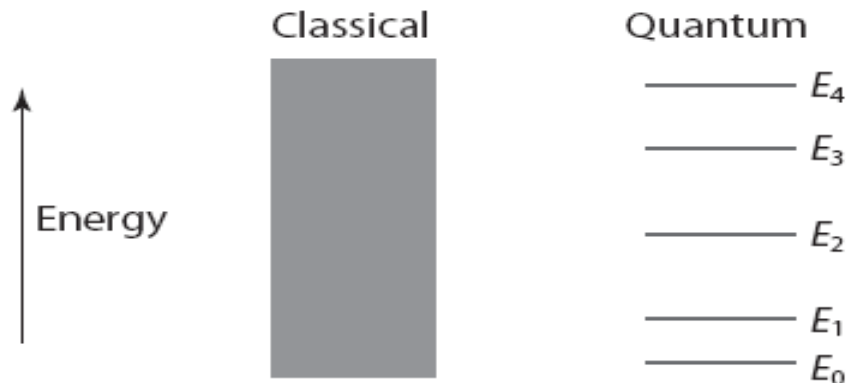
electron spin



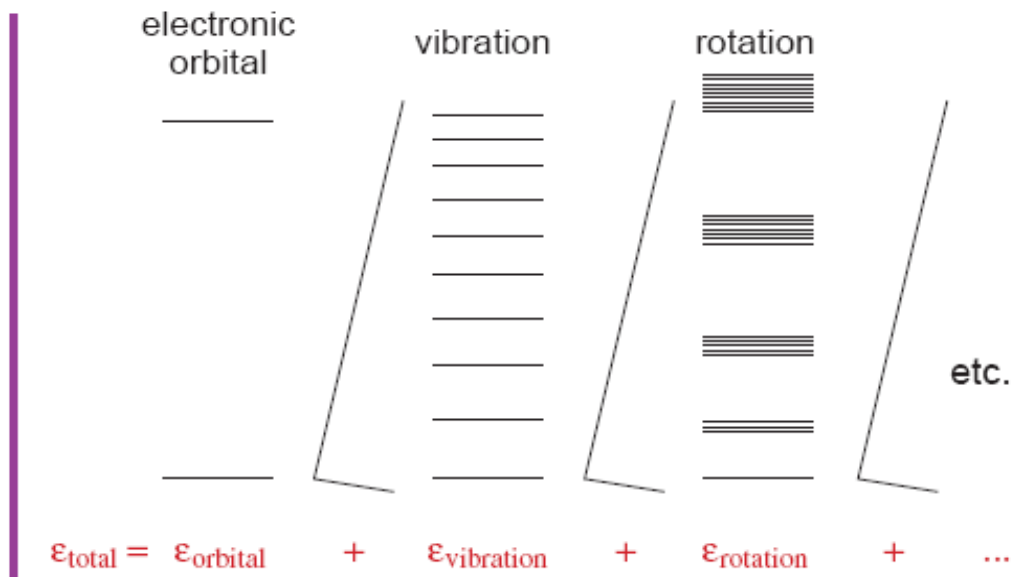
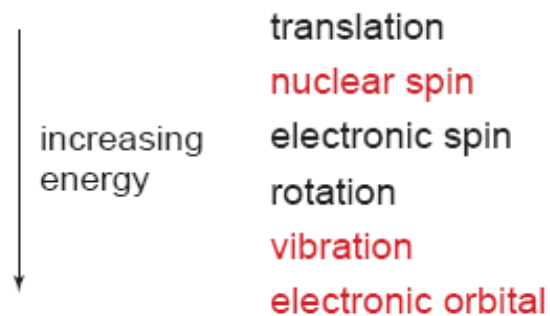
nuclear spin

$\Delta E = E_2 - E_1 = h \nu$
(joules) Where
 *ν is the frequency
of the light photon
absorbed*

These energies are **quantised**, giving a set of **energy levels**:



Molecular Energy Levels



The energy scales are very different and so are usually completely “decoupled” e.g. nuclear spin vs. vibration.

Dipole Moment

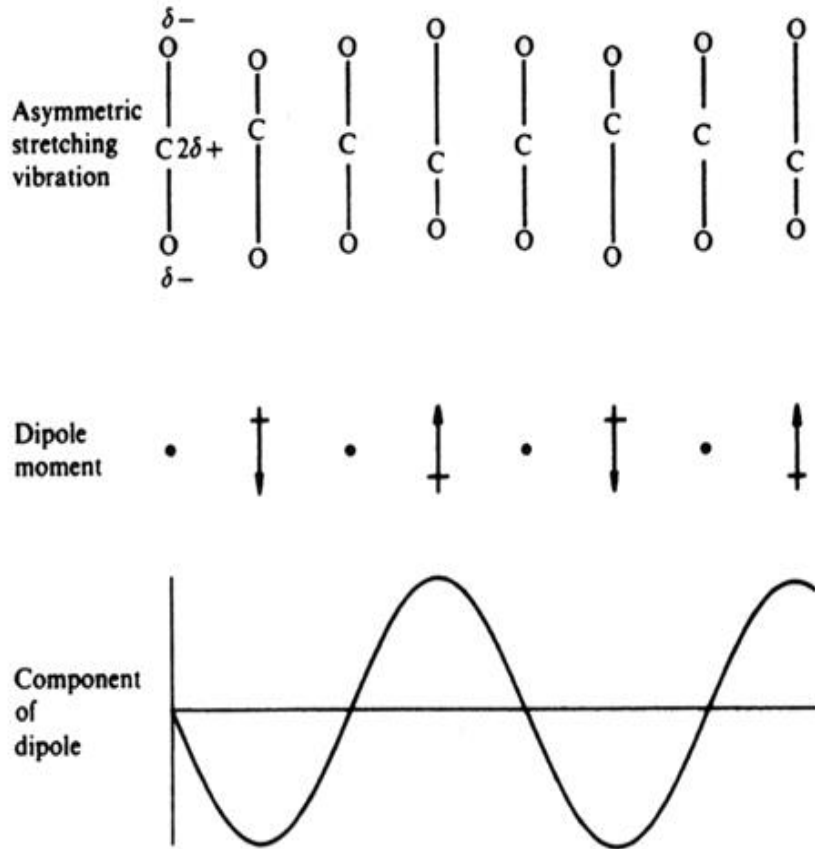


Figure 1.7 The asymmetric stretching vibration of the carbon dioxide molecule, showing the fluctuation in the dipole moment.

Symmetric stretching vibration:
The dipole moment remains zero
****infra-red inactive****

Antisymmetric stretch vibration:
there is a periodic alteration
in the dipole moment
****infra-red active****

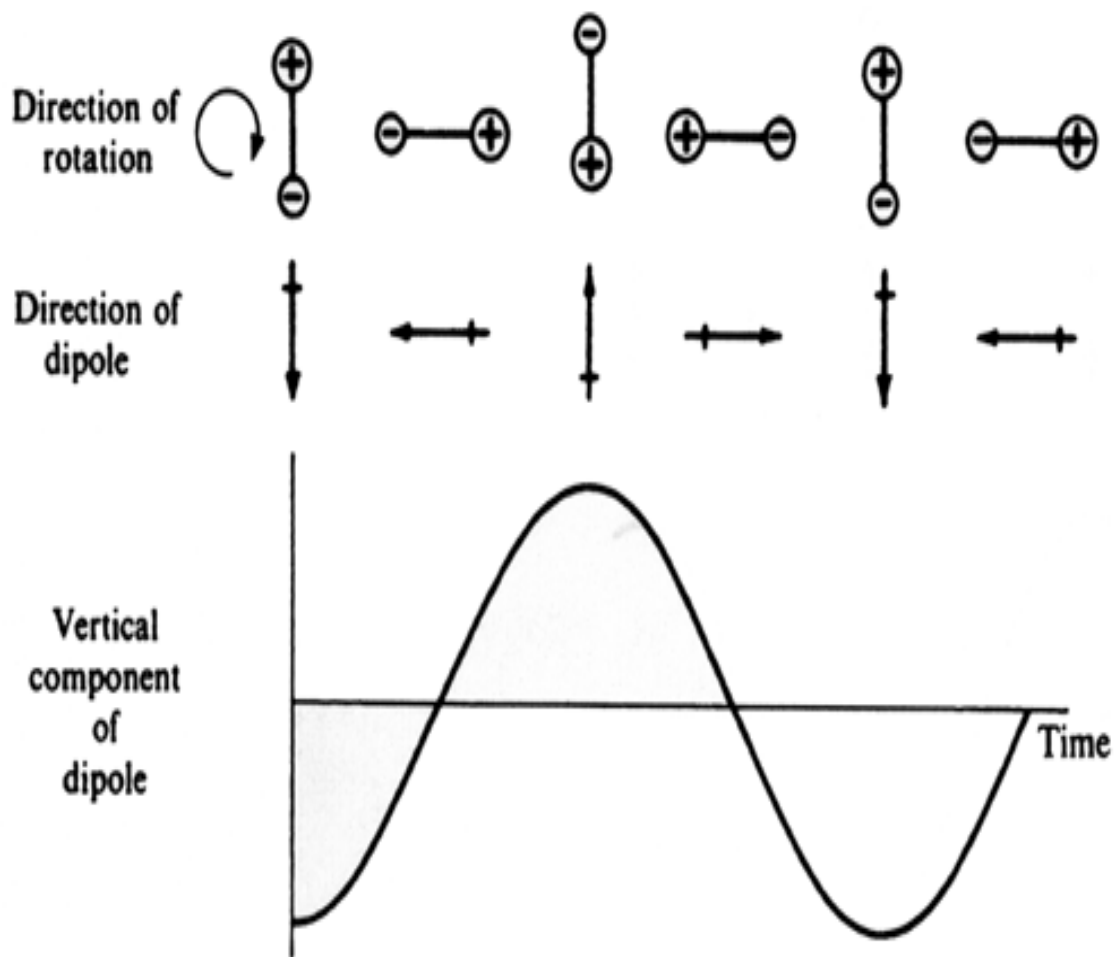
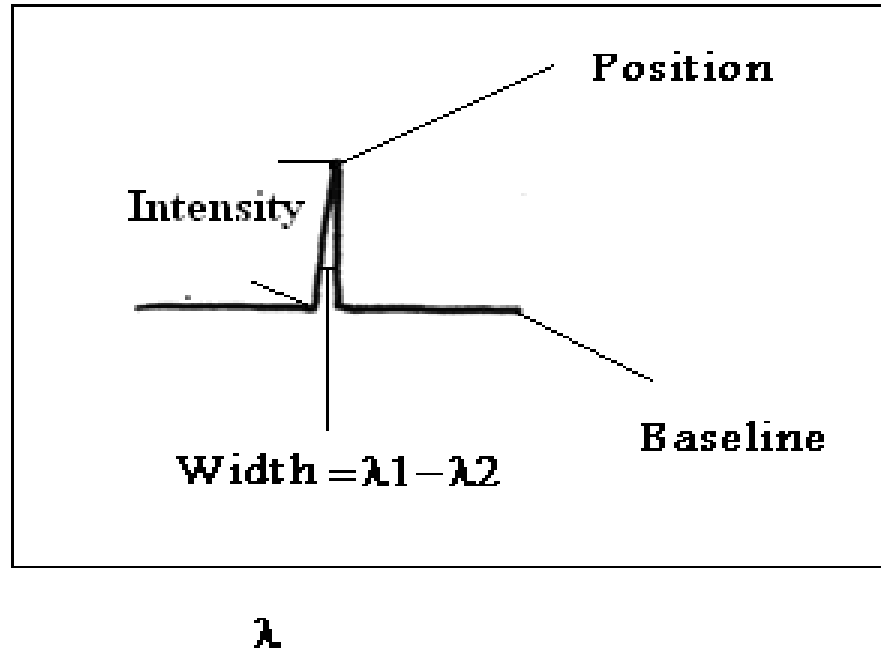


Figure 1.5 The rotation of a polar diatomic molecule, showing the fluctuation in the dipole moment measured in a

Representation of Spectra

- Generally, the spectral band is characterized by position, width, and intensity.



- The position of the spectral bands, or the frequencies at which the molecule absorb, depends on its structural features (Functional group) as well as on its environment.

The two most important features of spectral lines are:

1. their height (\sim intensity)
2. and their width (Δn).



Ideal spectra



Real Spectra

I- Width

There are two factors cause the **width broadening**

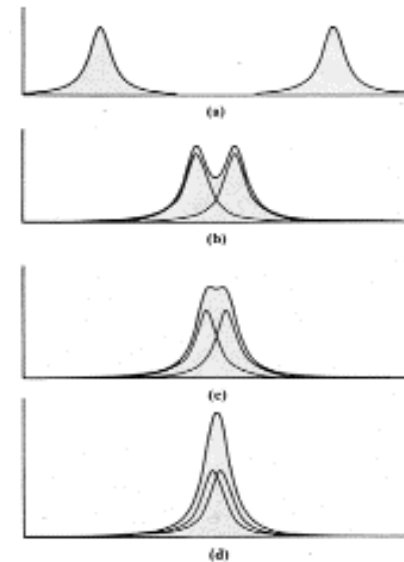
1- Factors related to an instrumental defect

a) Signal to noise ratio S/N (4/1)

In order to detect the real sample signal from the instrument noise, the intensity of this signal should be Four times that of noise.

b) Shape and Resolution

A crucial question that arises with any spectroscopic technique is the question of how well we will be able to resolve two different spectral lines



(a) Two well-resolved lines. (b)–(d) Two overlapping lines. From (b) through (d), the observed line shape is the sum of the two overlapping lines.

From R. Chang
"Physical Chemistry"
2nd ed. Macmillan
p 508

2- Natural Broadening (Deformation of molecular orbitals)

a) Collision Broadening

- 1- The collision of molecules causes the excited state to revert to the ground state
- 2- Collisions thus shorten the lifetimes of excited states and lead to the broadening of the associated spectral lines.

a) Doppler Broadening

The frequency that an object emits is modified by its speed relative to the observer (detector). It is possible to eliminate Doppler broadening by investigating a molecular beam of the atoms / molecules and placing the detector at a 90 deg angle to the direction of the beam.

a) Heisenberg Uncertainty Principle

$$(\Delta E \cdot \Delta t > h / 4 \pi \cdot 10^{-34} \text{ J} \cdot \text{s})$$

II- Intensity

1. Transition Probability:

The precise calculation of transition probabilities is involved and requires quantum mechanics. However, it is often possible to predict if a transition is symmetry allowed or forbidden. We will discuss the respective **Selection Rules** for each spectroscopic technique individually.

2. Population of States:

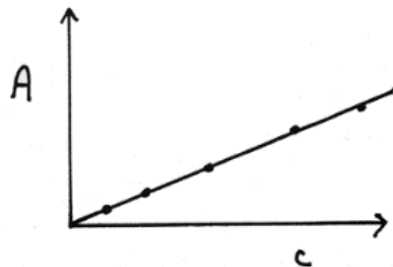
For thermal equilibrium, the probability of a state in thermal equilibrium is given by the Boltzmann Distribution

$$N_{\text{upper}} / N_{\text{lower}} = \exp(-\Delta E/kT)$$

3. The Concentration or path length of the sample

(Lambert-Beer's Law)

$$-\log [I/I_0] = c \cdot \epsilon \cdot l$$

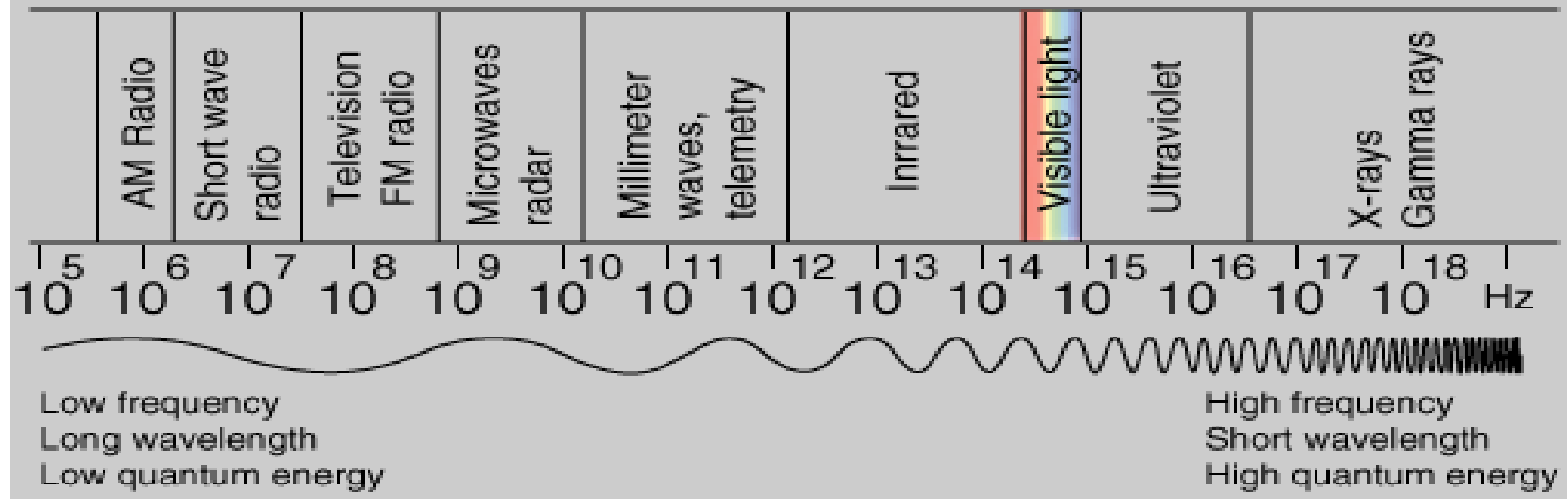
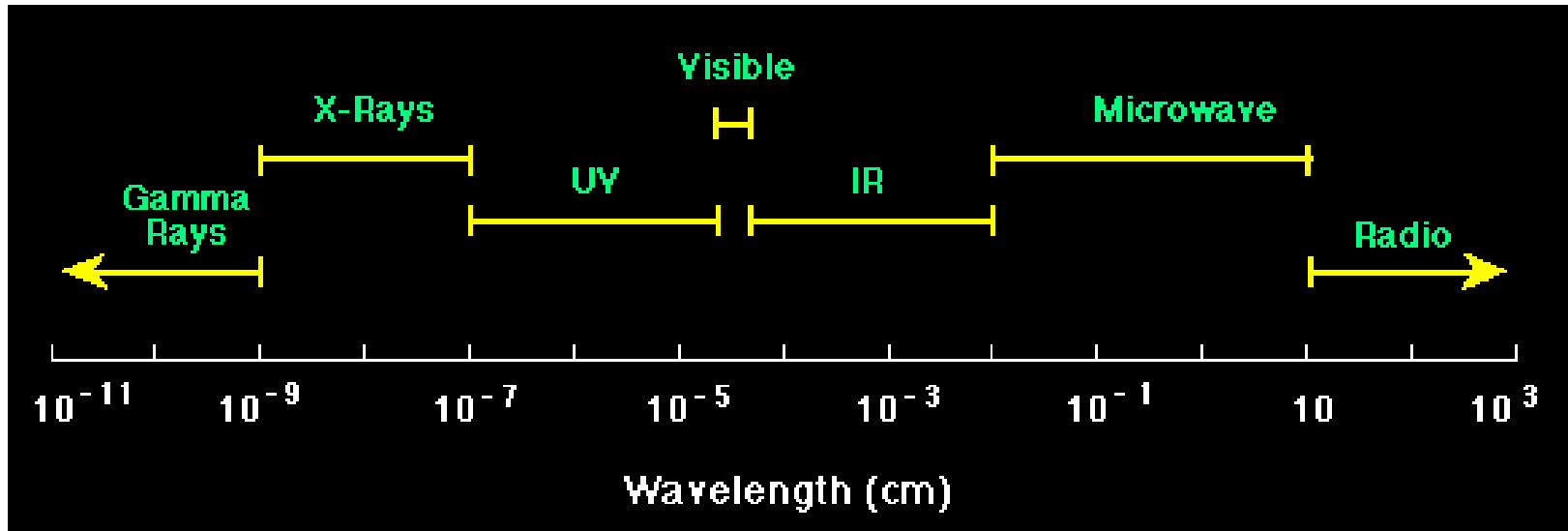


$$A = k'c \quad k' \text{ is slope of line}$$

Typical Energies

Region	Frequency/Hz	$N_A h\nu$	n_f / n_i
<i>RF</i>	10^7	4 mJ/mol	0.999998
<i>MCWE</i>	10^{11}	40 J/mol	0.984
<i>IR</i>	10^{13}	4 kJ/mol	0.202
<i>UV-VIS</i>	10^{15}	400 kJ/mol	3×10^{-70}
<i>X-RAY</i>	10^{18}	400 MJ/mol	$< 10^{-99}$

Wavelength vs Frequency vs Energy



Regions of The Electromagnetic Spectrum

