



CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture-13, 09-02-2018

Summary: L-10 (Extra Class)



Orbital angular momentum:

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$$

$$M_L = L, L - 1, \dots, 0, \dots, -L \{2L+1\}$$

Spin angular momentum:

$$S = s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|$$

$$M_S = S, S - 1, \dots, 0, \dots, -S \{2S+1\}$$

Total angular momentum:

$$J = L + S, L + S - 1, \dots, |L - S|$$

$$M_J = J, J - 1, \dots, 0, \dots, -J \{2J+1\}$$

Summary: L-10 (Extra Class)



Ground state term: Hund's rule

- The term with the greatest multiplicity lies lowest in energy.

The ground state therefore possesses the most unpaired spins because this gives the minimum electrostatic repulsion.

So one of the terms 3D , 3P , 3S arising from $[\text{He}]2s^22p^13p^1$ configuration lies lowest.

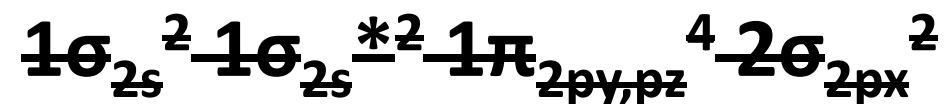
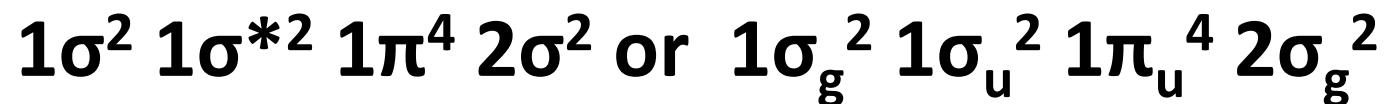
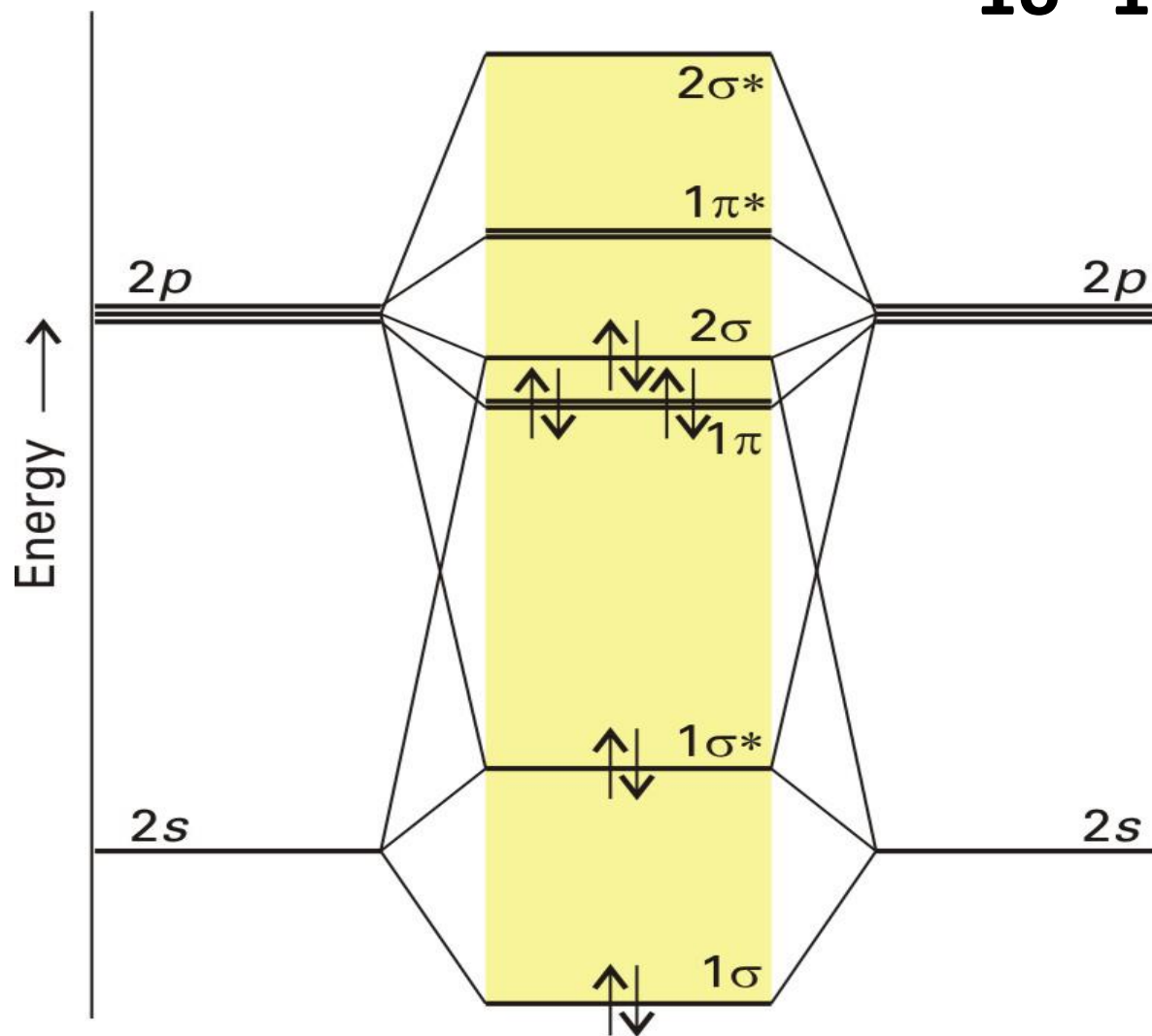
- The term with the greatest orbital angular momentum lies lowest in energy.

So 3D term mentioned above will lie lowest of all the terms.

- The level with lowest J lies lowest in energy if the subshell is less than half filled.

The level with highest J lies lowest in energy if the subshell is more than half filled. This rule is not applicable for excited configurations.

Summary: L-12

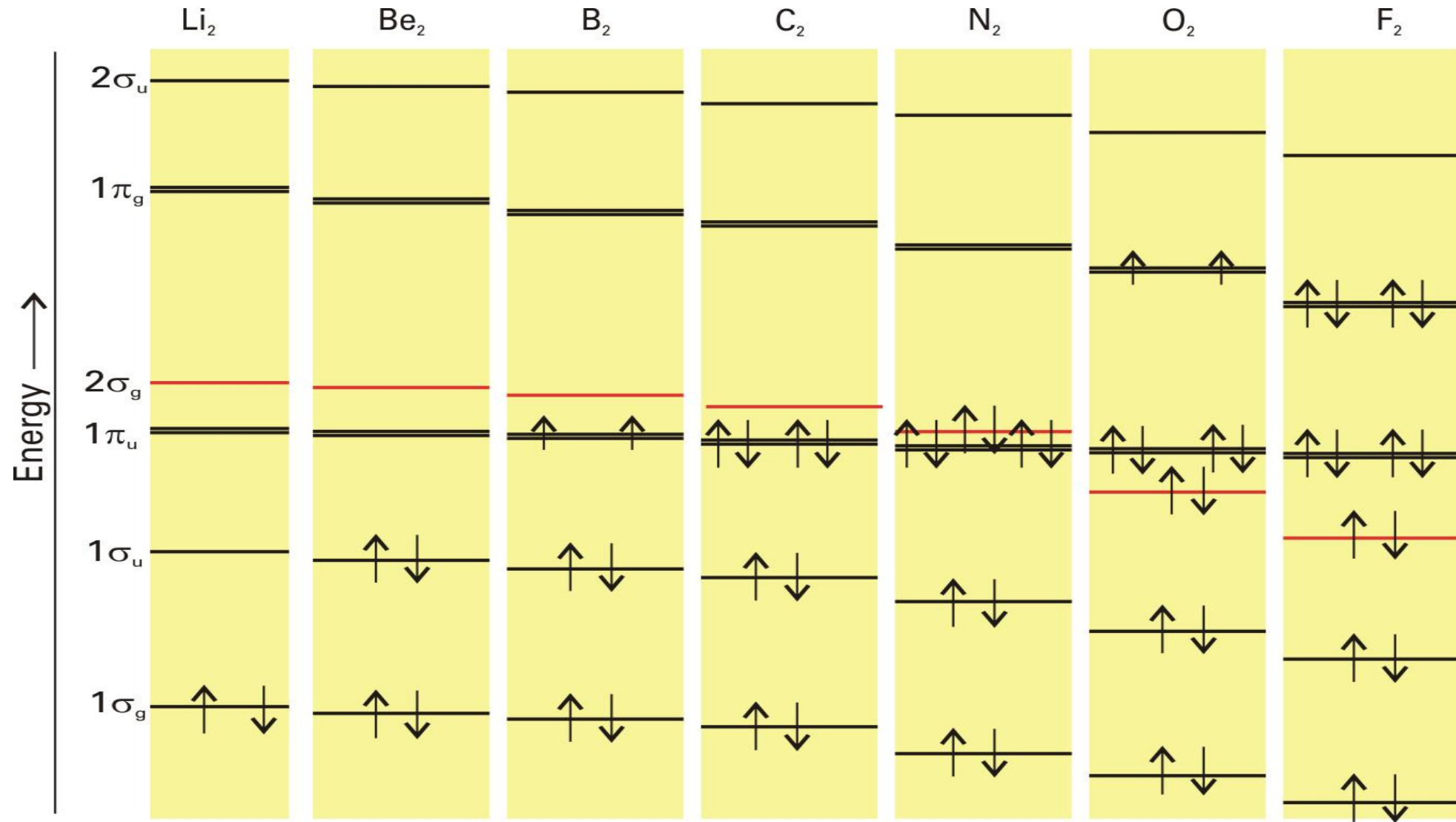


Bond order of $N_2 = 3$

Note σ and σ^* of mixed 2s and 2p character

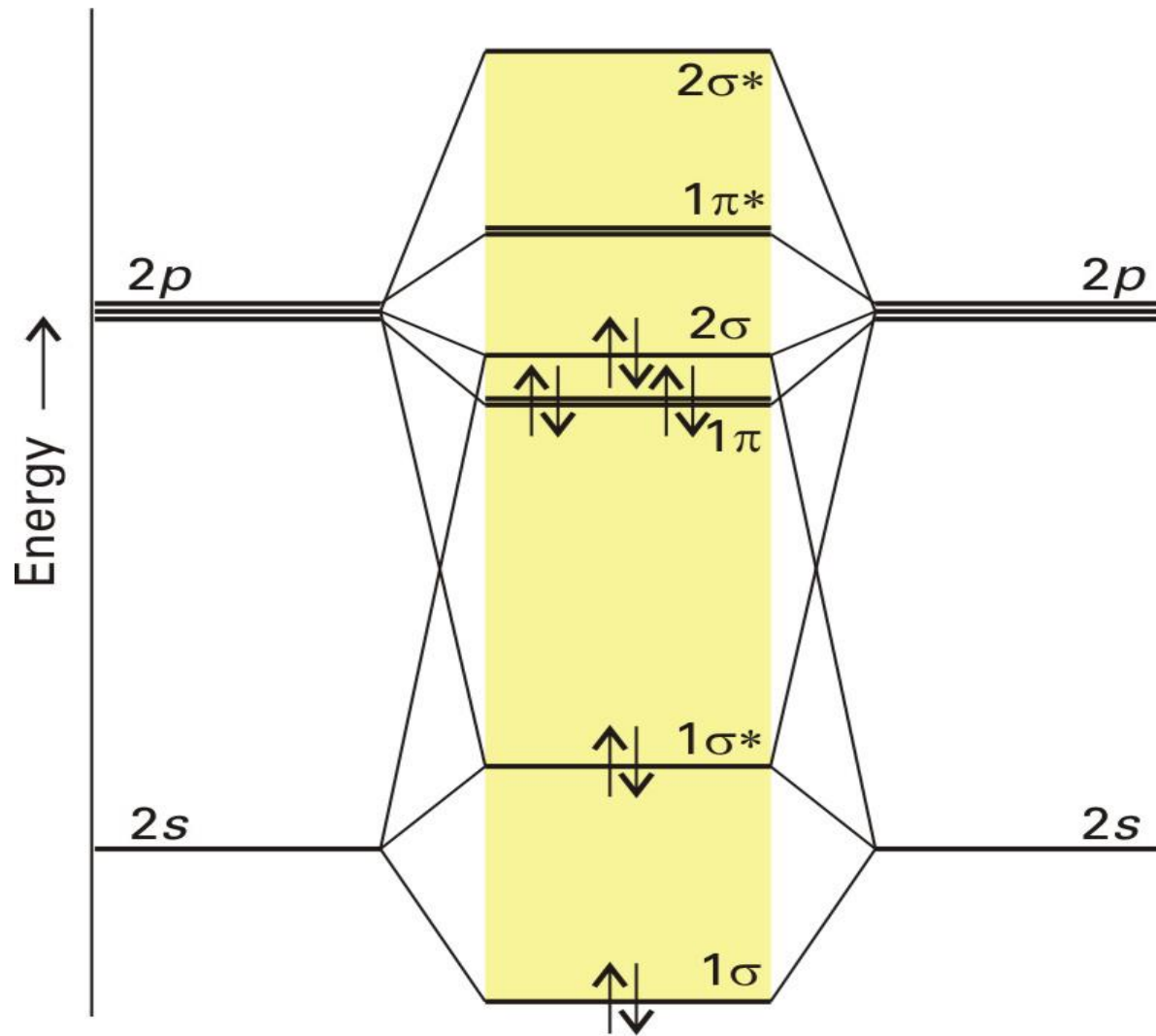
MO of N_2 molecule

Summary: L-12



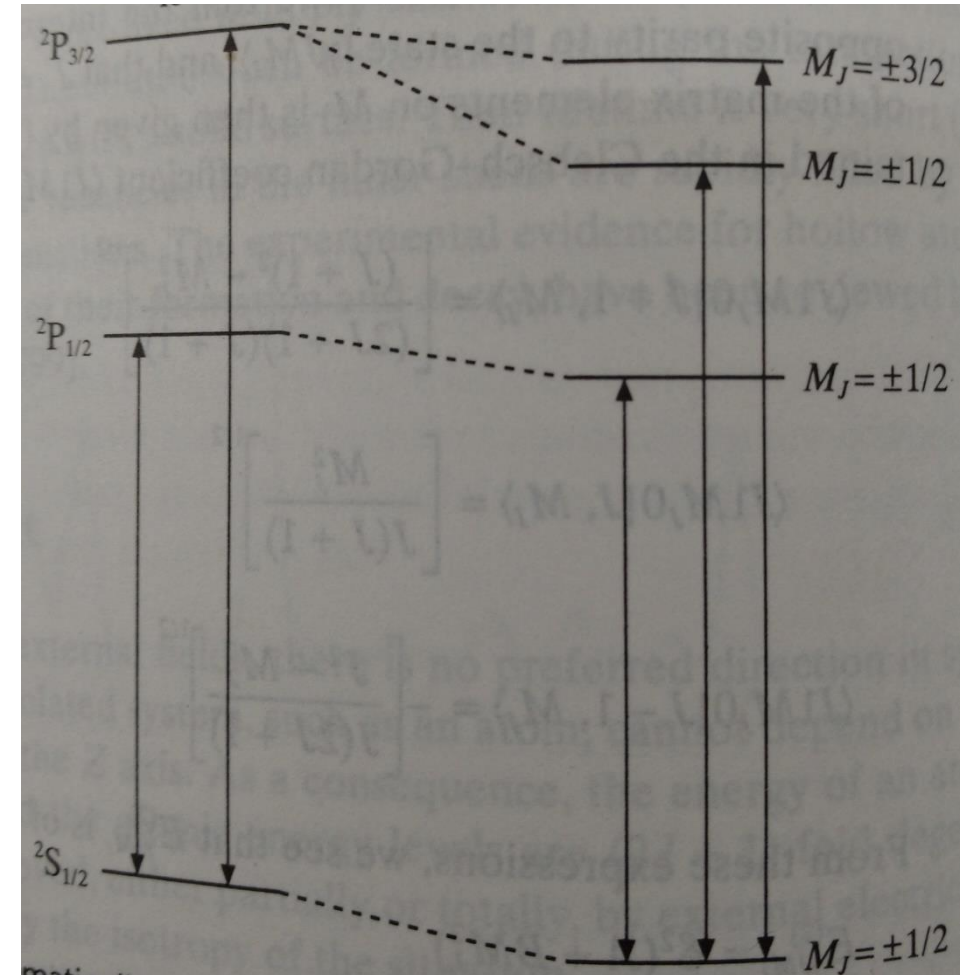
Variation of orbital energies

Energy states of a molecule

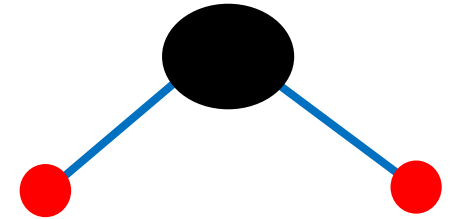
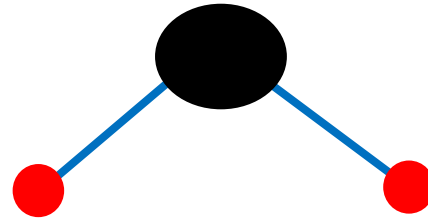
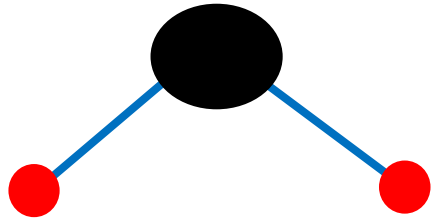
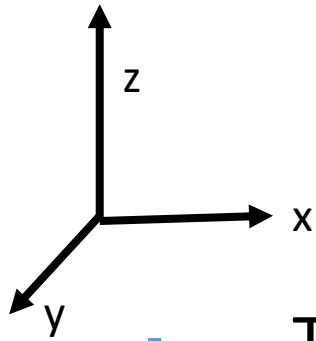


N_2 molecule

These are electronic energy states of the molecule as we have discussed in case of atoms



Various motion of a molecule



Translational motion will be like a free particle: KE will vary continuously

Molecule may rotate like a rigid rotor – weightless rod

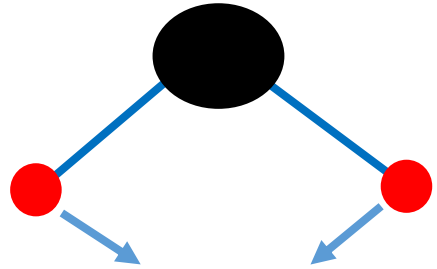
Classical expression of energy: $E = \frac{j^2}{2I}$;

j^2 : square of the magnitude of angular momentum
 $j^2 \rightarrow J(J + 1)\hbar^2, J = 0, 1, 2, \dots$ (*angular momentum quantum no.*)

Energy of rigid rotot: $E_J = J(J + 1) \frac{\hbar^2}{2I}; J = 0, 1, 2, \dots$

Various motion of a molecule




$$E_v = \left(V + \frac{1}{2} \right) h \nu, \quad V = 0, 1, 2, \dots$$

Consider a simple molecule: C=O

$$E_{J=1} - E_{J=0} = 4 \text{ cm}^{-1}$$

$$E_{V=1} - E_{V=2} = \sim 2000 \text{ cm}^{-1}$$

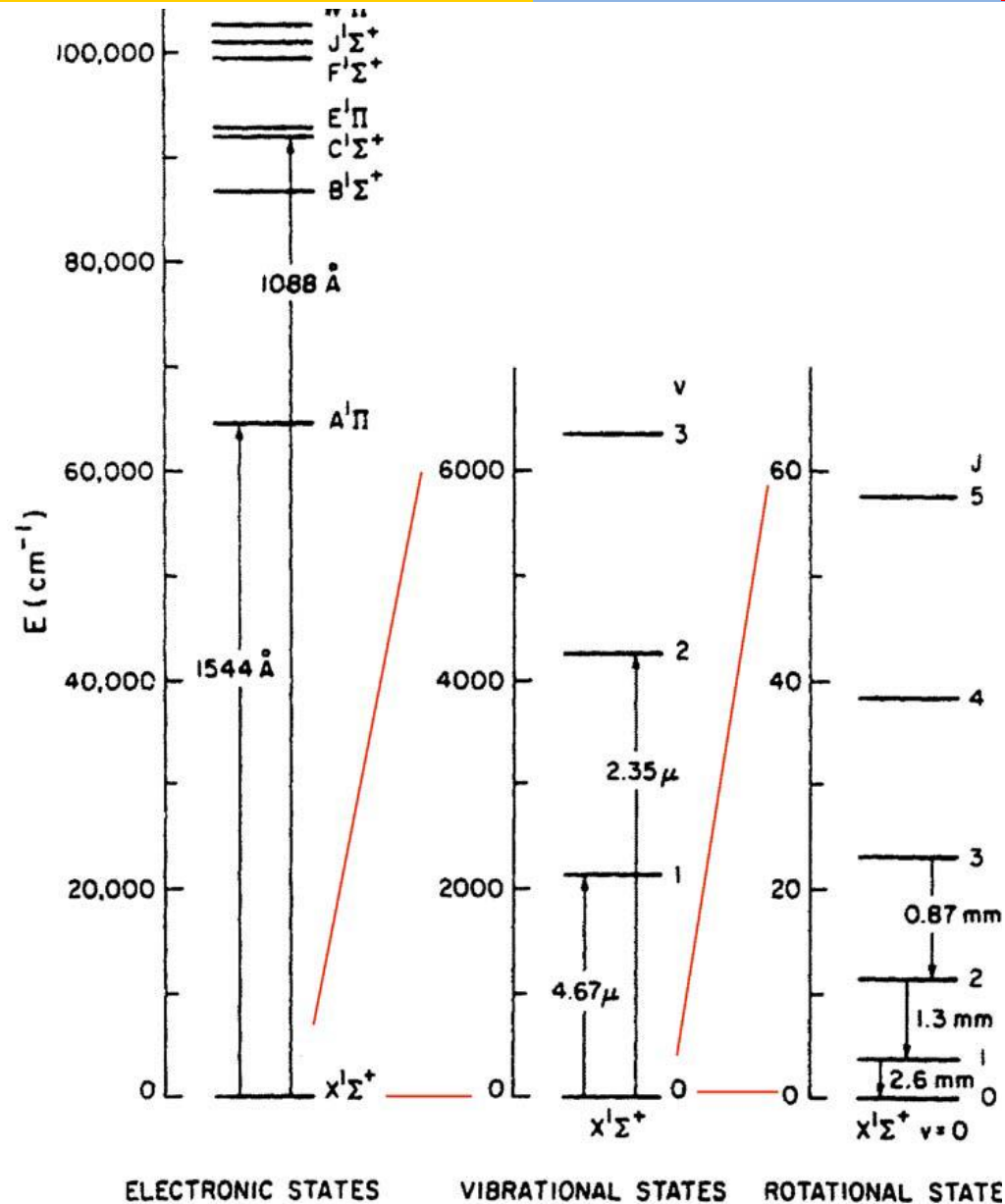
Wavenumber,

$$\bar{\nu} = 1/\lambda = \nu/c$$

Expected electronic transition in CO:

$$6.5 \times 10^5 \text{ cm}^{-1}$$

Relative energy states



Consider HCl molecule:

- Rotational energy states: $1 - 10 \text{ cm}^{-1}$
- Vibrational energy separation: 3000 cm^{-1}
- Energies of these states are too different – transitions will happen independently.
- **Born-Oppenheimer Approx:**
 $\Psi = \psi_e \psi_v \psi_r$ and $E = E_e + E_v + E_r$
- Combined transitions may only happen if the energy requirement is fulfilled.
- We'll consider very simple and ideal models to discuss Molecular Spectroscopy.

Molecular Spectroscopy



- Interaction of electromagnetic radiation with matter is in general come under the broad nomenclature of spectroscopy – here, we'll be dealing with molecules.
- Why we are interested in Molecular Spectroscopy?

Our primary goal, is to validate the theory that we have learnt so far.

Moreover, we'll utilize Molecular Spectroscopy to elucidate various chemical and physical phenomenon involve in chemistry.

Consequence of quantum mechanical treatment



Classical: Energy varies continuously.

Quantum: Energy is quantized.

Examples: PIB, Rotation in 2D, Rotation in 3D, Vibration,
H-Atom.

Application of spectroscopy:

- Fluorescence imaging,
- Magnetic Resonance Imaging (MRI),
- Analytical tool, and many more

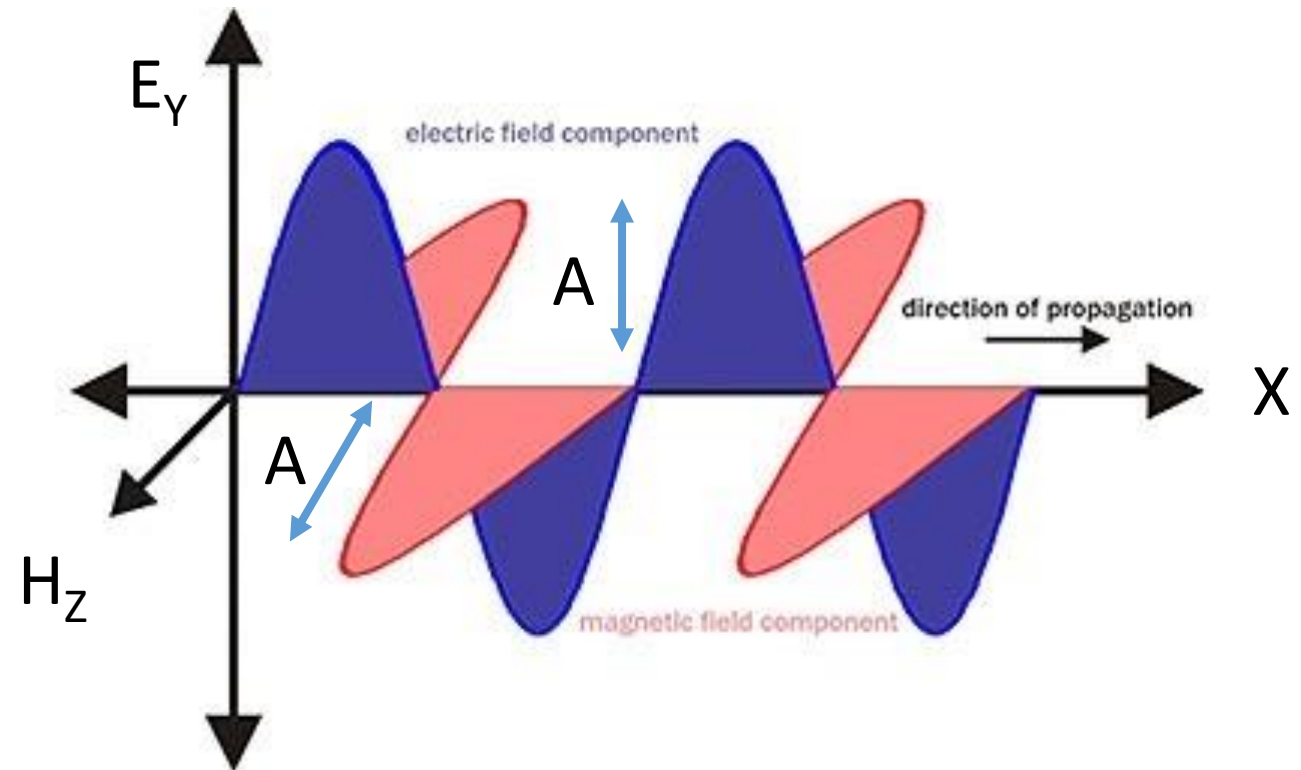
Electromagnetic radiation



- Electromagnetic radiation (EMR) includes, in addition to what we commonly refer to as “light”, radiation of longer and shorter wavelengths.
- EMR contains both an electric and magnetic component – plane polarized radiation.
- Electric field of strength of E.
- Magnetic field of strength of H

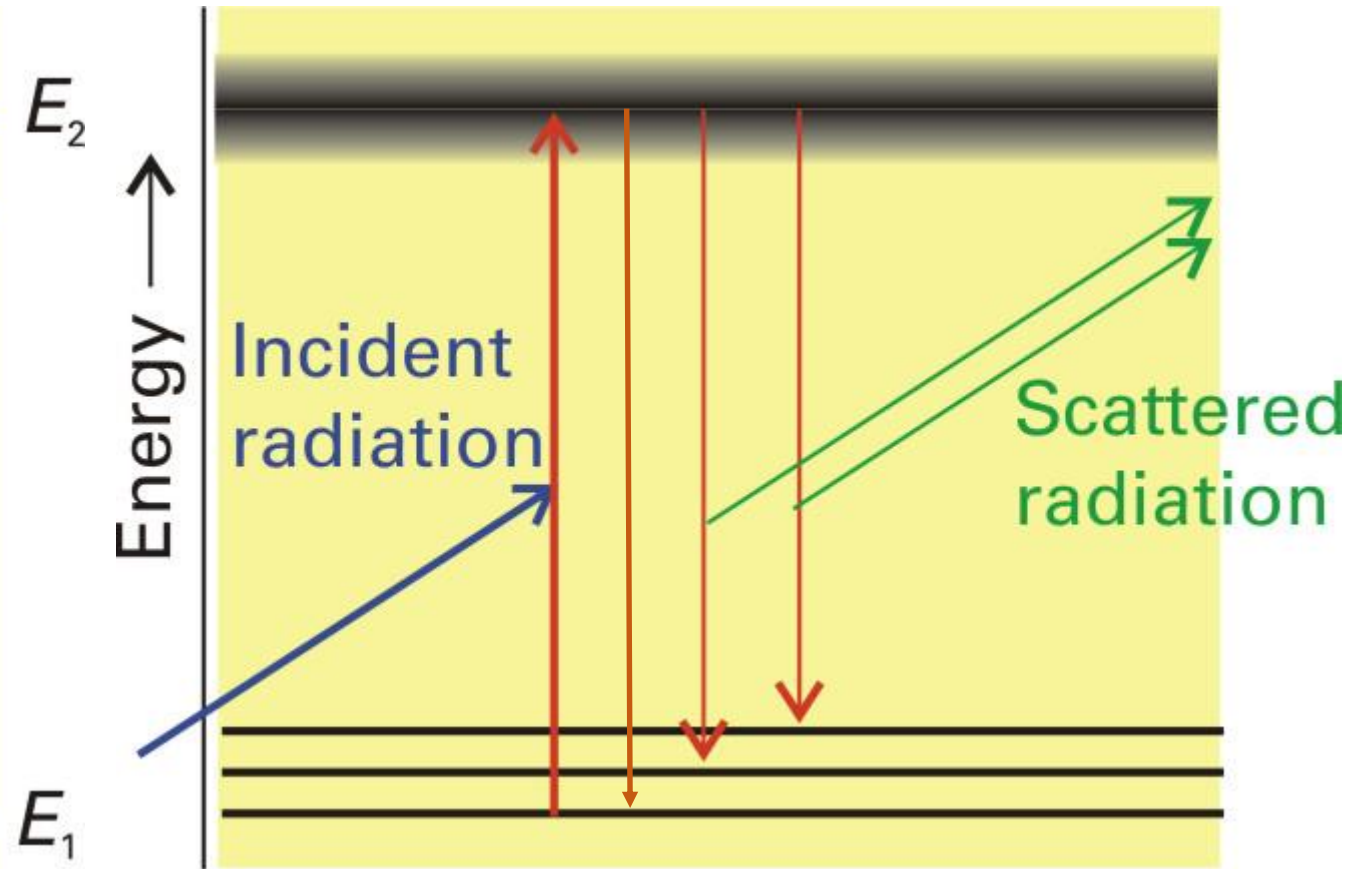
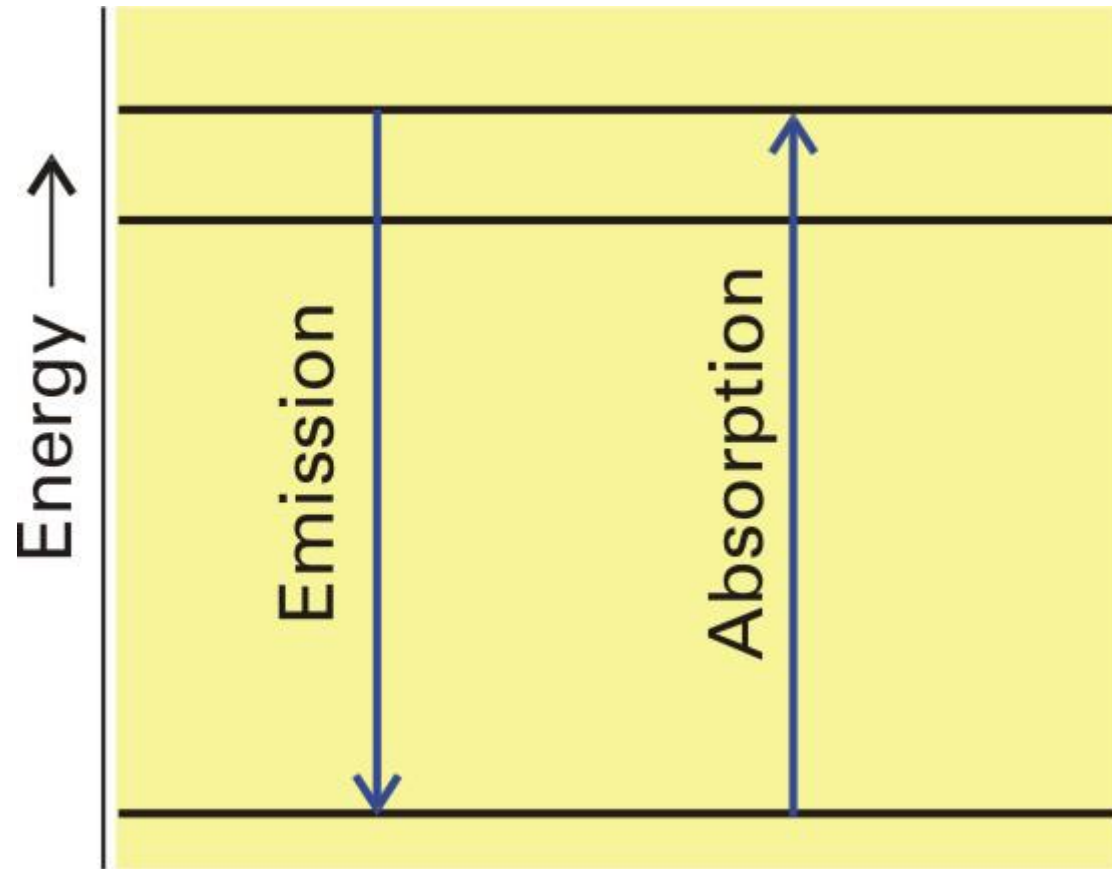
$$E_y = A \sin(2\pi\nu t - kx)$$

$$H_z = A \sin(2\pi\nu t - kx)$$



- Electric/magnetic component of EMR may interact with the molecule.
- How?
- Electric component may interact with the electric dipole moment of the molecule: Rotational-, vibrational-, and electronic- spectroscopy.
- Magnetic component may interact with the magnetic dipole moment of the molecule: NMR-, **EPR-** spectroscopy.

Interaction of EMR – molecule: Processes

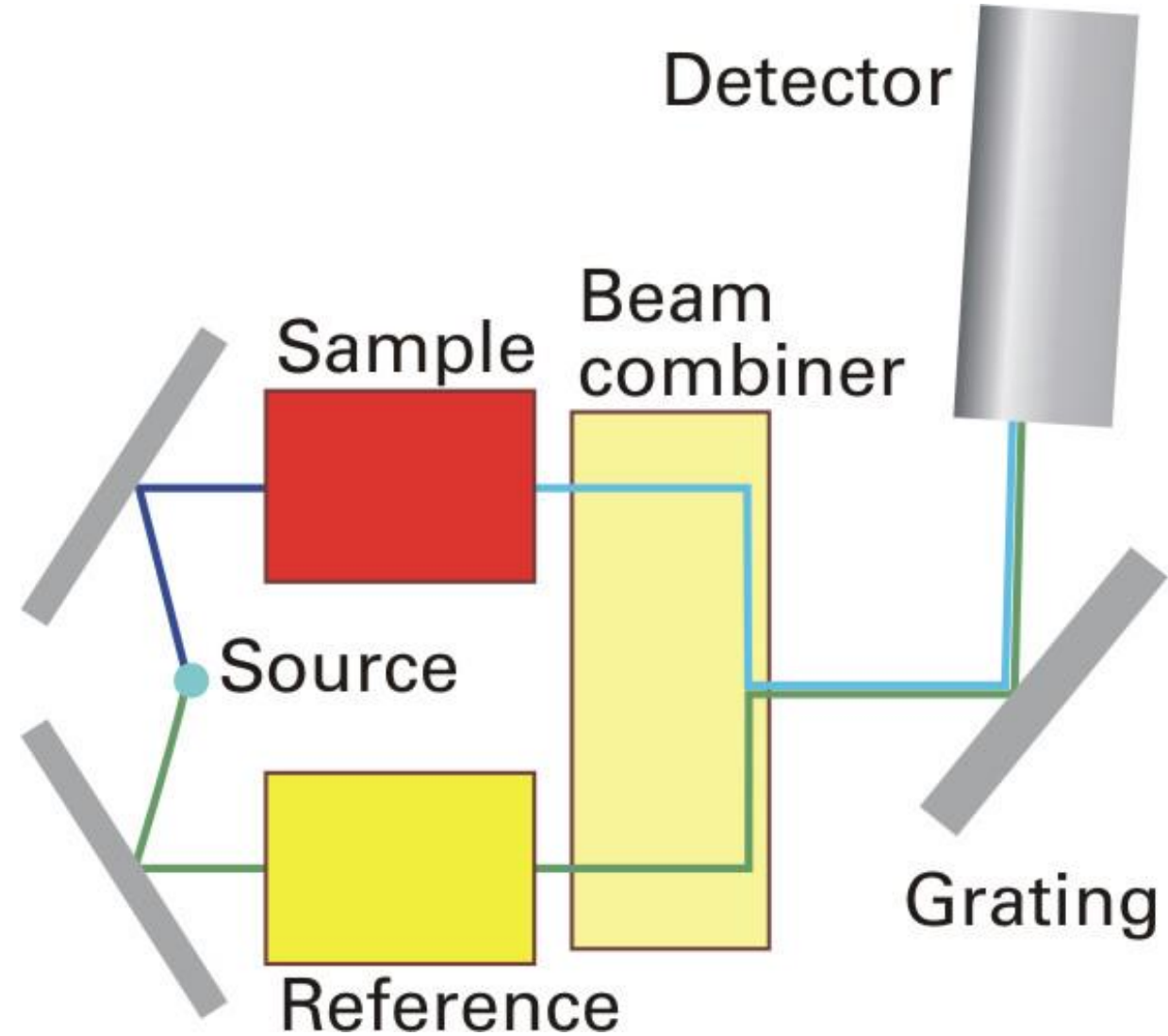
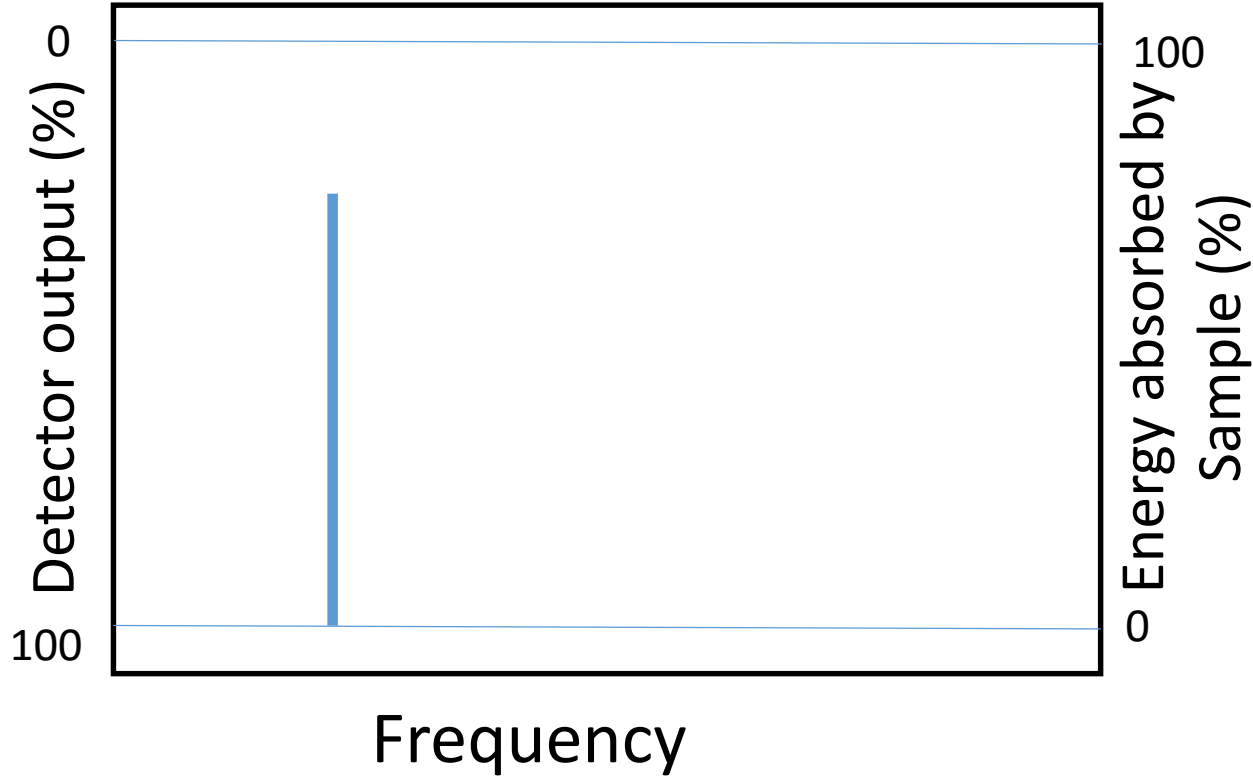


Molecular Spectroscopy



- Analysis of electromagnetic radiation absorbed, emitted, or scattered by molecules.
- In molecules, transitions between electronic/ vibrational/ rotational energy levels.
- Information regarding energy levels, geometry (bond lengths, bond angles), and bond strengths
- Useful in qualitative and quantitative analysis, including kinetics
- Bohr frequency condition $h\nu = |E_2 - E_1|$
- Wavelength $\lambda = c/\nu$, Wavenumber, $\nu = 1/\lambda = \nu/c$

Representation of spectra



Spectrometer components

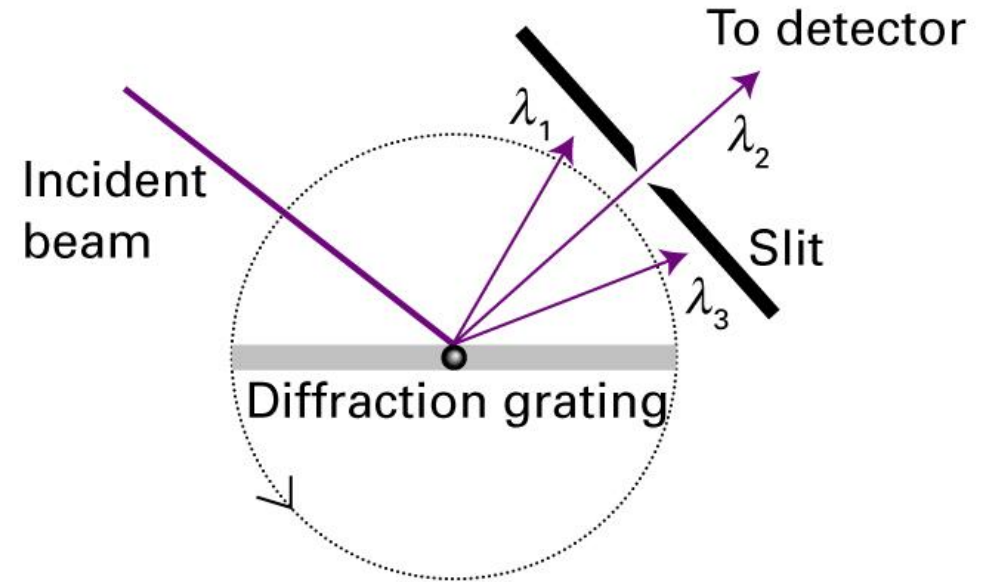


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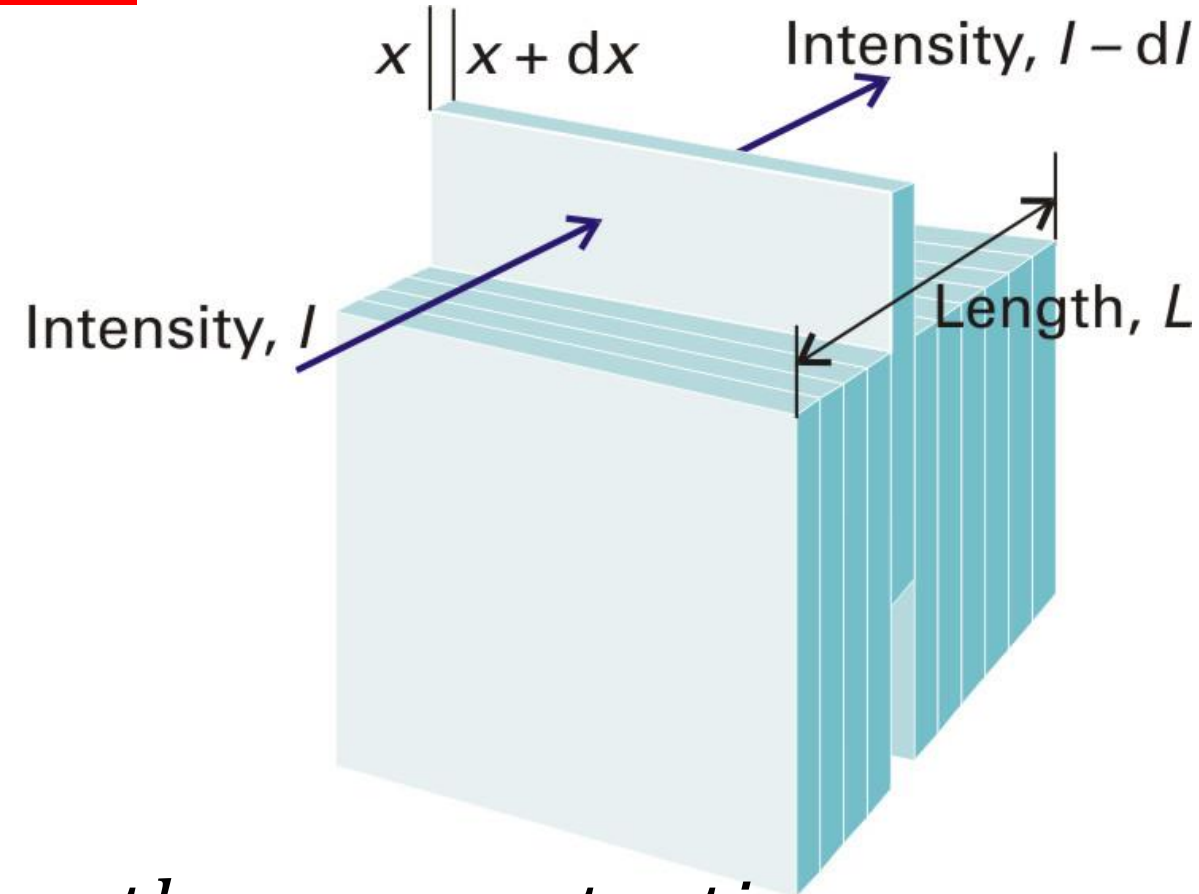
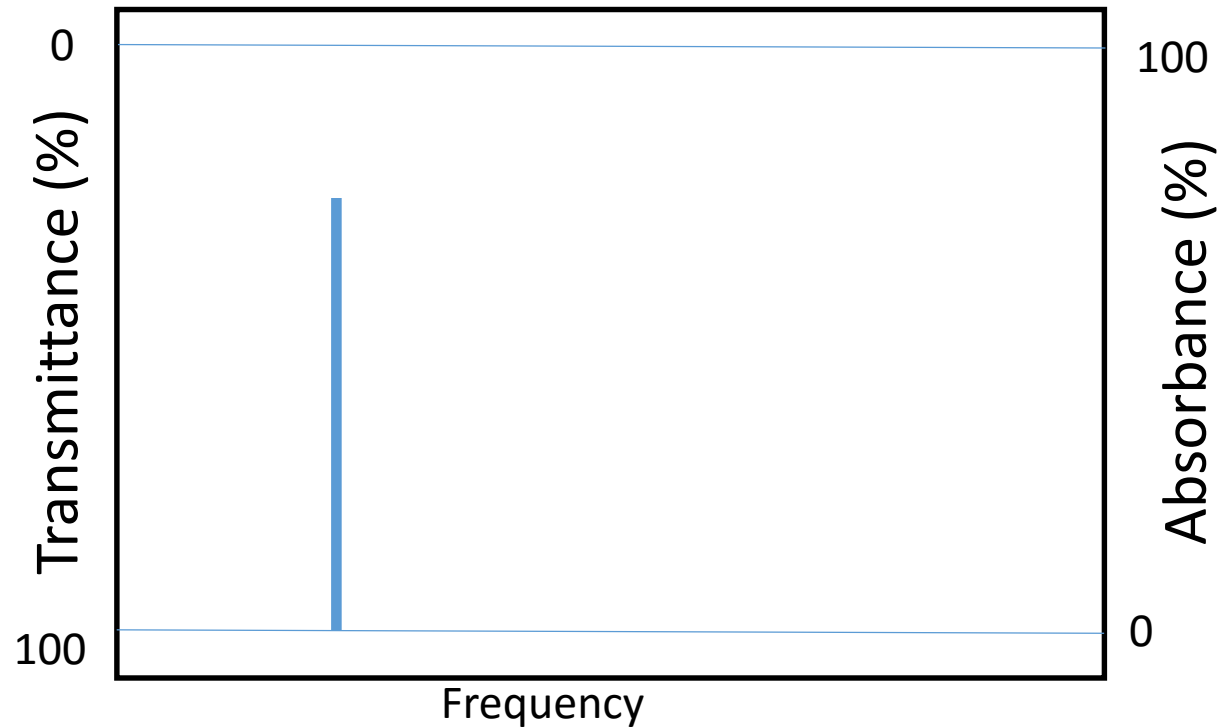
Xenon or Deuterium arc lamp (uv)
Tungsten lamp (visible)
Nernst filament (ir)
Mercury arc in quartz envelope (far ir)
Gunn diode or Klystron (mw)

Dispersing element: Grating or Prism

Detector: Device that converts radiation to electrical current/voltage signal, eg., photodiode. Can be a single device or an array (used with a polychromator).



Representation of spectra



Beer-Lambert Law:

Absorbance $A = \log \frac{I_0}{I} = \epsilon [C] l$; l : length, c : concentration, ϵ :

Transmittance $T = \frac{I}{I_0}$

$A = -\log T$

molar absorption coefficient
Unit: $1/(\text{conc.}) (\text{length})$

Some more terminologies in spectroscopy



- **Resolution:** Smallest observable separation between bands – in terms of wavelength or frequency.
- **Fourier transform techniques:** Used in IR and Raman spectroscopy – do not need to use any dispersion element – total signal is recorded and analyzed for the component frequencies.
- Fourier transform techniques offer greater sensitivity and speed.
- **Sensitivity:** Related to the detector response.

Spectral characteristics



Transitions induced by electric dipole are governed by transition moment

integral: $R^{nm} \propto \int \Psi_n^* \hat{\mu} \Psi_m d\tau, \hat{\mu} = \sum q_i r_i$

R^{nm} can be thought of as the oscillating electric dipole moment due to the transition and are related to the wave functions Ψ_m and Ψ_n . A transition induced from state m to state n through the interaction with the electric component of radiation.

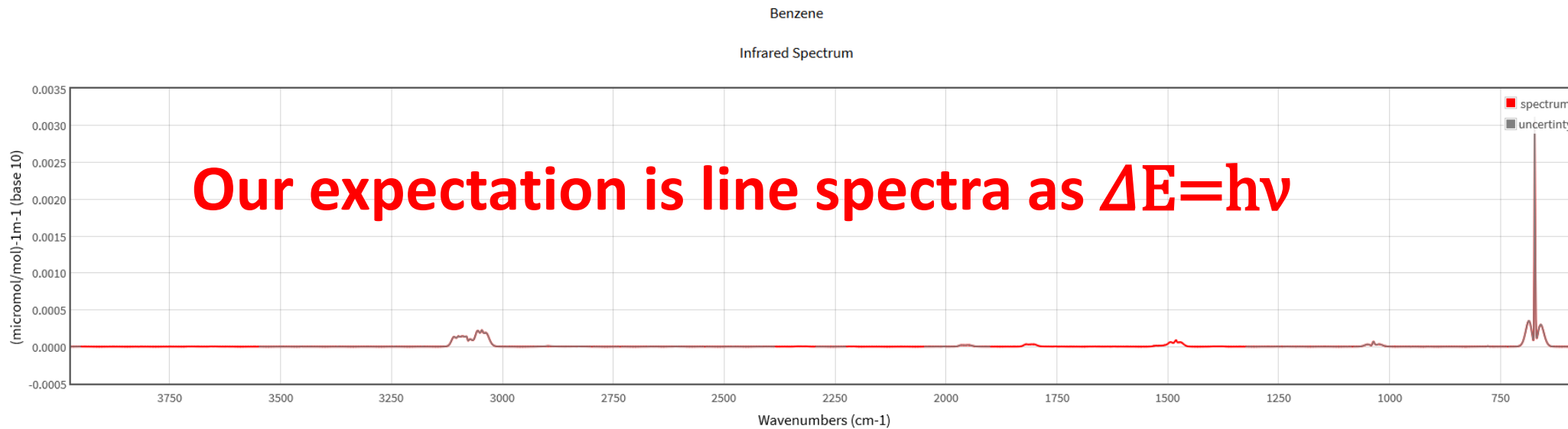
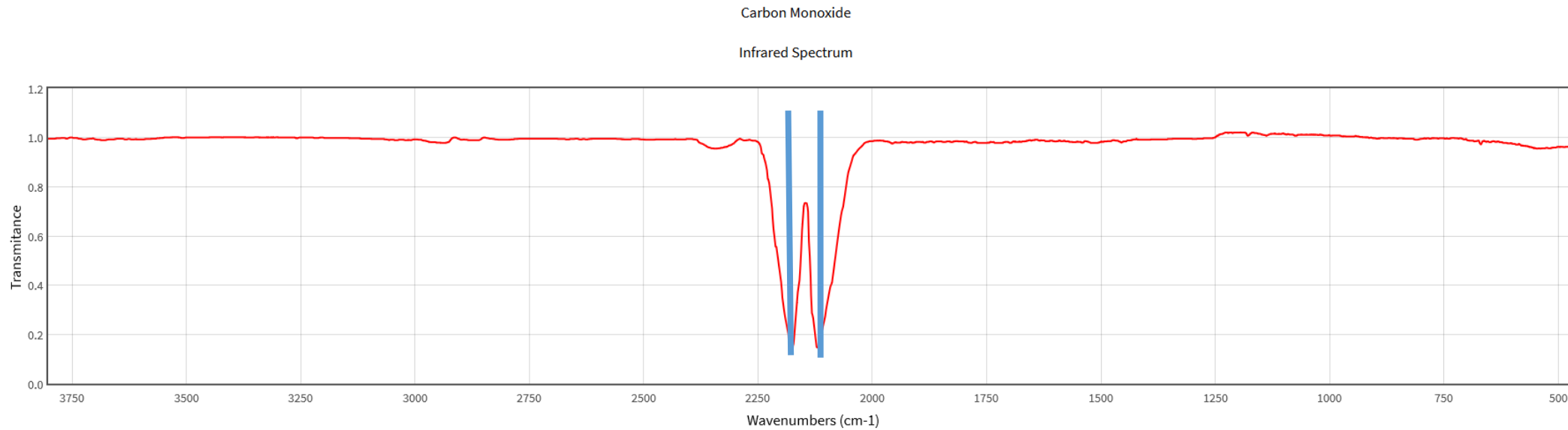
Transition probability $\propto \left| \int \Psi_n^* \hat{\mu} \Psi_m d\tau \right|^2$

$R^{nm} = 0 \Rightarrow$ Transition probability = 0 \Rightarrow transition may not happen

Transitions are forbidden

$R^{nm} \neq 0$ transitions are allowed

Spectral characteristics



NIST Chemistry
Web Book

Spectral characteristics



Selection rules:

Gross – gross feature that molecule must possess – some molecular properties those can be measured

Specific – which specific transitions are allowed or forbidden

Spectral linewidth – spread of wavelength/frequency

Doppler broadening

If a molecule is travelling towards the detector with a velocity V_a , then the frequency ν_a at which the transition is observed is related to the actual transition frequency of ν of a stationary molecule by

$$\nu_a = \nu \left(1 - \frac{V_a}{c} \right)^{-1}$$

Lifetime broadening, Thermal Broadening

Rotational Spectroscopy



- Transitions between rotational energy levels.
- Frequency $\nu \sim 10$ GHz corresponding to wavelengths in the range 0.1 – 1 cm.
- Also known as microwave spectroscopy.
- Long path lengths required.

Rotational energy levels – rigid rotor



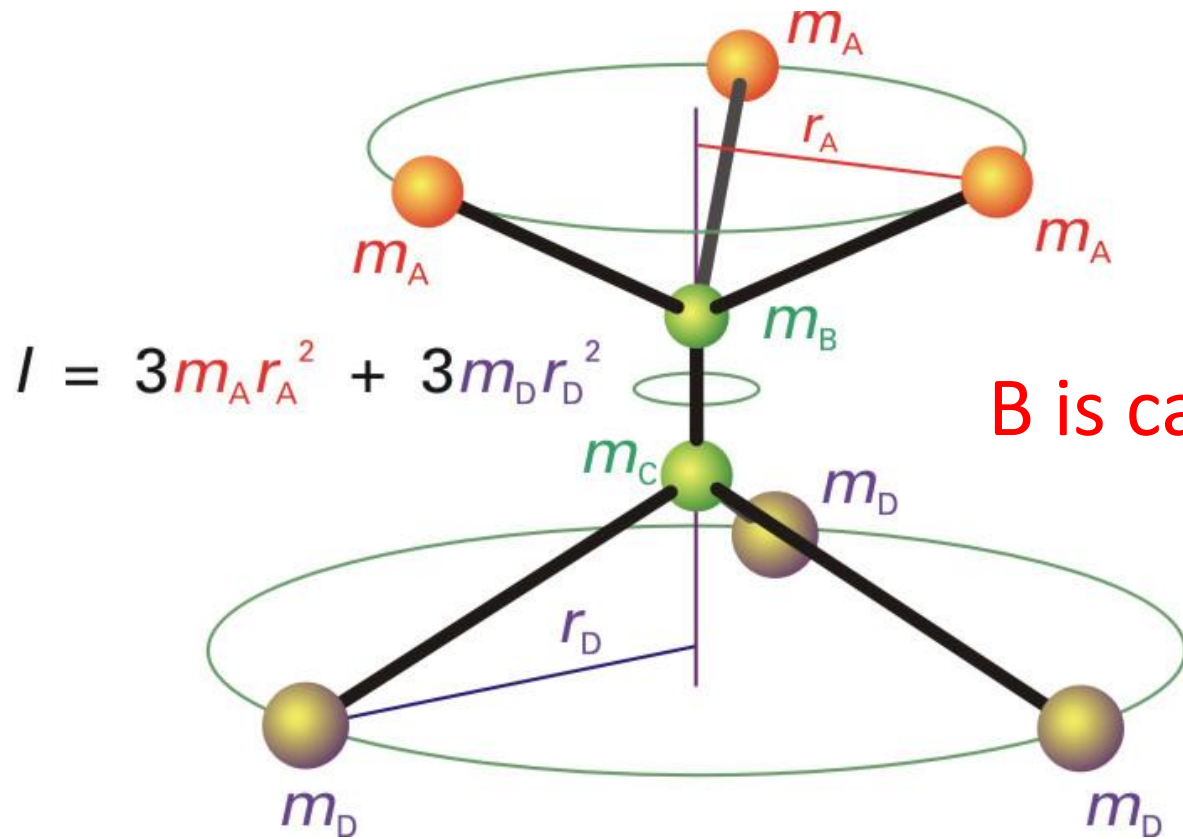
Energy of rigid rotot: $E_J = J(J + 1) \frac{\hbar^2}{2I}; J = 0, 1, 2, \dots$

$$= J(J + 1) \frac{h^2}{8\pi^2 I} \text{ Joules}; I = \mu r_0^2$$
$$= B J(J + 1) \text{ cm}^{-1}; B = \frac{h}{8\pi^2 I c}$$

B is called the rotational constant

M_J does not appear in energy expression

Thus in absence of an electric or magnetic field each rotational energy level is (2J+1) fold degenerate.



$$I = 3m_A r_A^2 + 3m_D r_D^2$$
$$E_J = hBJ(J + 1) \text{ Joules; where } B = \frac{h}{8\pi^2 I} \text{ in Hz}$$

Rotational energy levels – rigid rotor



Using the energy expression for energy of a rigid rotor calculate the rotational energy levels, in Joules, for $J = 0, 1, \& 2$ states for $^{12}\text{C}^{16}\text{O}$. Convert these energy values in cm^{-1} . Determine degeneracy for each state. Assume $r_{\text{C-O}} = 1.1283 \text{ \AA}$. # Attention: Consider unit very carefully.

