Lectures in Spectroscopy

Rotational (Microwave) & Vibrational (Infra-Red) Spectroscopy

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My sincere acknowledgments to

- **Fundamentals of Molecular Spectroscopy**, 4th Ed., C.N. Banwell, McGraw-Hill, New York (2004).
- **Molecular Structure and Spectroscopy**, G. Aruldhas, Prentice Hall of India, New Delhi (2002).
- **Introduction to Atomic Spectra**, E. H. White, McGraw-Hill, New York (2005).
- **and many other free & copyright internet resources.**

Outline of Talk

1. Introduction
   - Spectroscopy
   - IR Spectroscopy
   - MW Spectroscopy
2. MW spectroscopy
   - Rigid Rotator
   - Non-Rigid Rotator
   - Linear Polyatomic Molecules
   - Symmetric Top Molecules
   - MW Spectrometer
3. IR spectroscopy
   - IR spectrometer
   - Vibration of Diatomic Molecule
   - Vibrating Diatomic Rotator
   - Vibrations of Polyatomic Molecules

Introduction to Spectroscopy

Spectroscopy

- **Method of “Seeing the Unseeable"!**

  USING

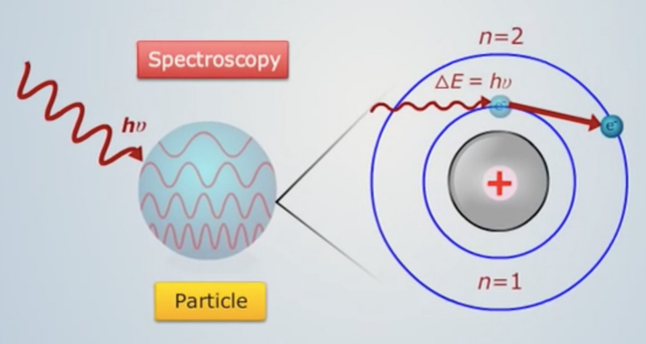
- **Electromagnetic radiation** to obtain information about atoms and molecules.

Spectroscopy

- **An instrumentally aided study of the interactions between matter and energy to obtain information about atoms and molecules.**
  Here **matter**: given sample.
  energy: supplied by any portion of the electromagnetic spectrum.

Spectroscopy

Interaction of electromagnetic radiation with matter!



Different types of Molecular Spectra

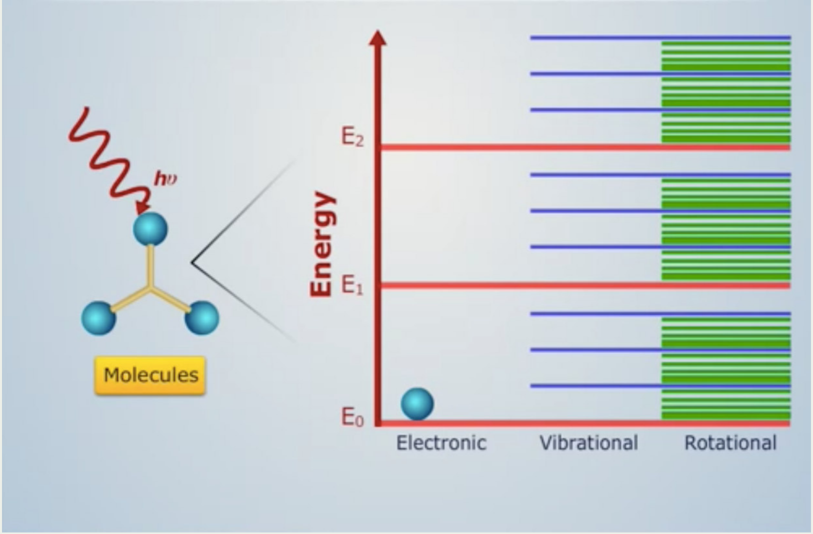
To understand the macroscopic thermodynamics, it is necessary to understand how energy distributed in microscopic molecular level.

Molecular Spectra

- **Rotational spectra**:
  Transition among several rotational levels.
- **Vibrational spectra**:
  Transition in different vibrational states & rotational levels.
- **Electronic spectra**:
  Transition in various electronic states and change in vibrational & rotational levels.

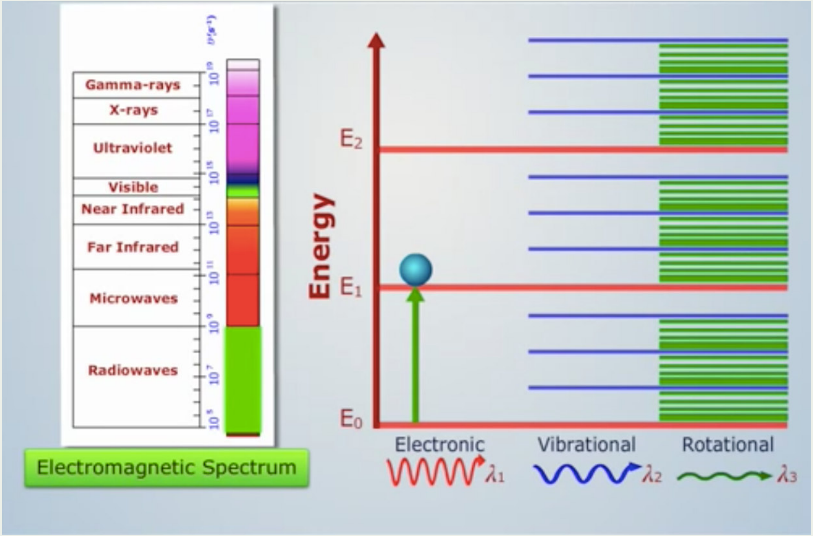
Spectroscopy

Three types of spectra in molecular transitions!



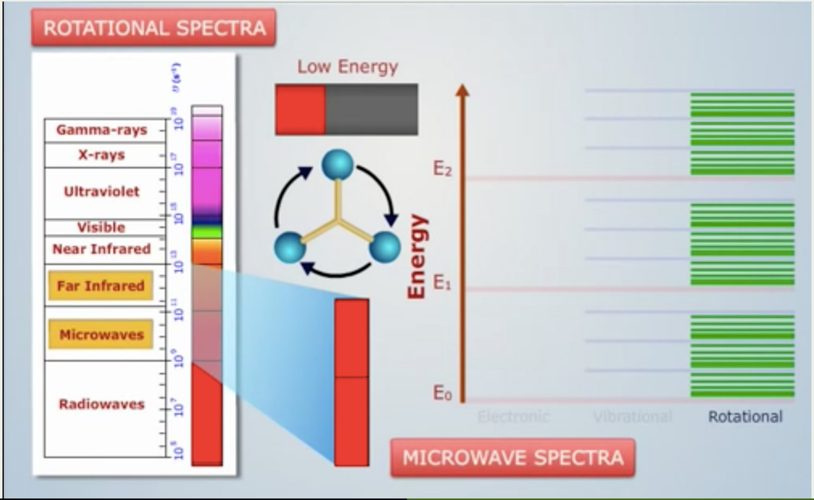
Spectroscopy...

Three types of spectra in molecular transitions!



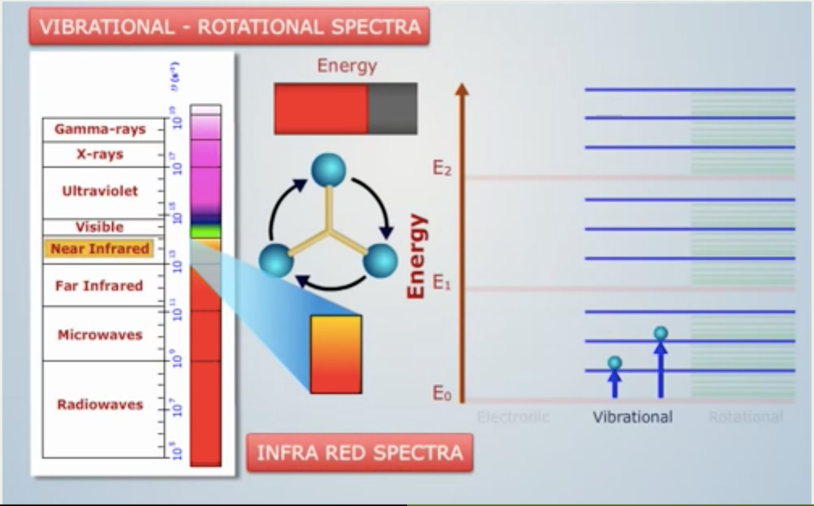
Rotational/MW Spectroscopy

Low energy EMR (MW/Far-IR) can change rotational levels only!



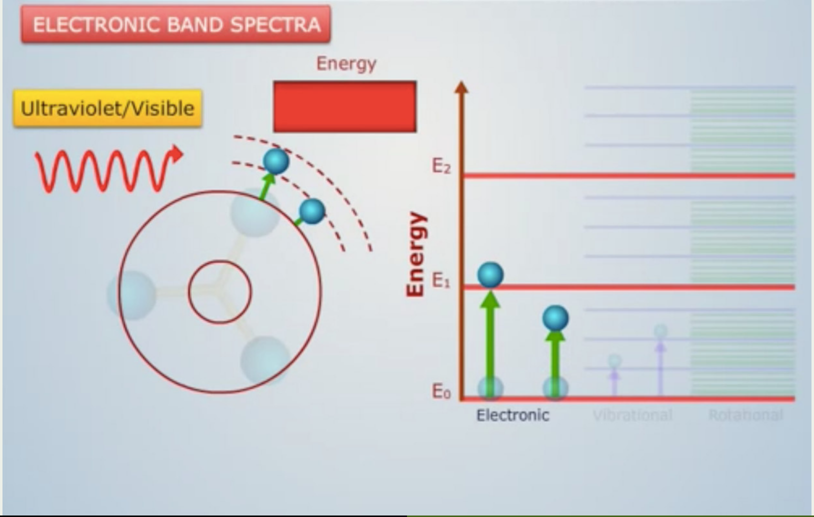
Vibrational/IR Spectroscopy

Medium energy EMR (Near-IR) can change vibrational levels and rotational sublevels!!



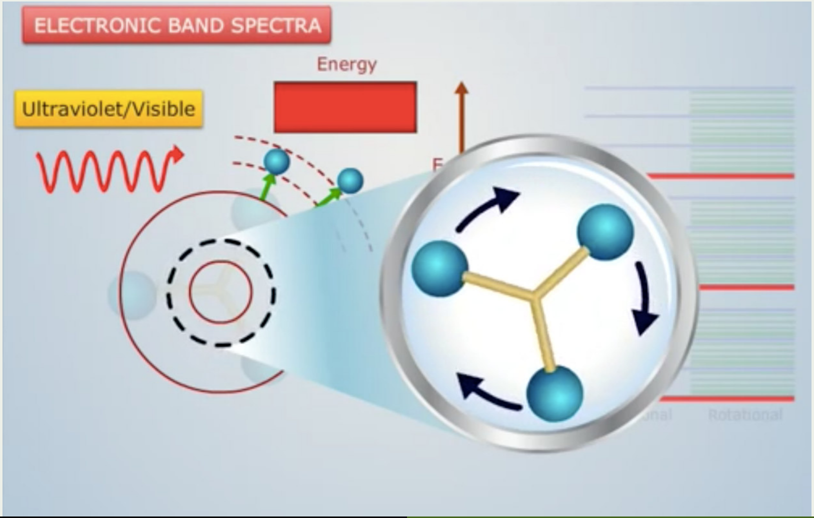
Electronic Spectroscopy

High energy EMR (UV/Vis) can change electronic levels along with vibrational and rotational sublevels!!!



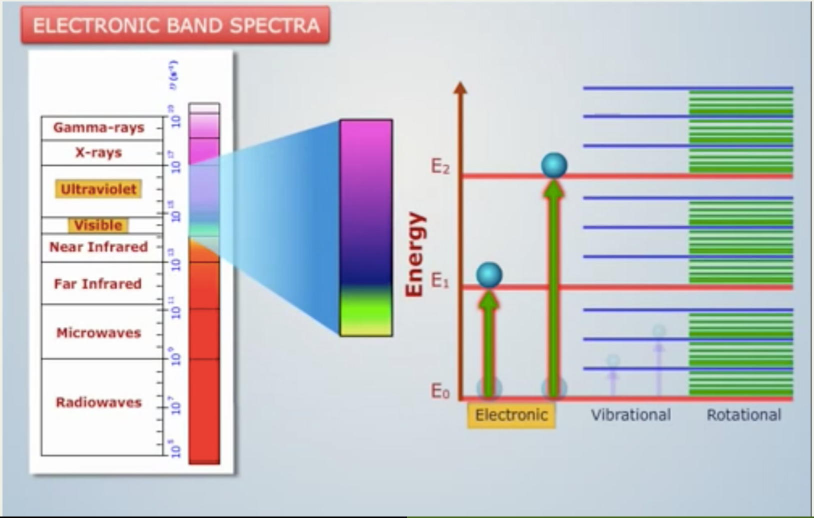
Electronic Spectroscopy...

High energy EMR (UV/Vis) can change electronic levels along with vibrational and rotational sublevels!!!

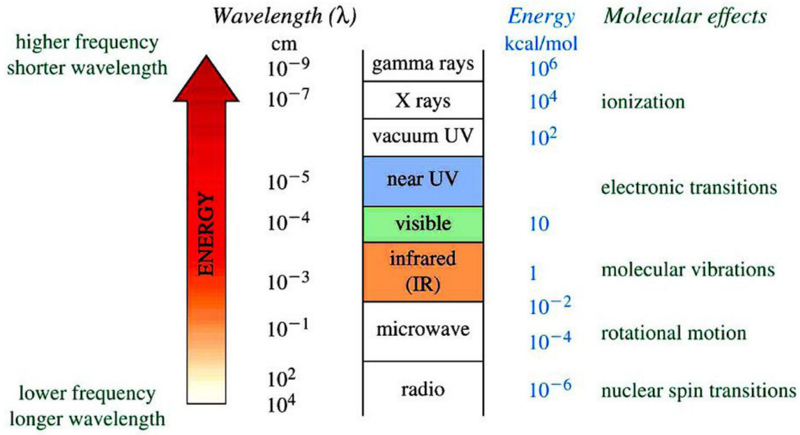


Electronic Spectroscopy...

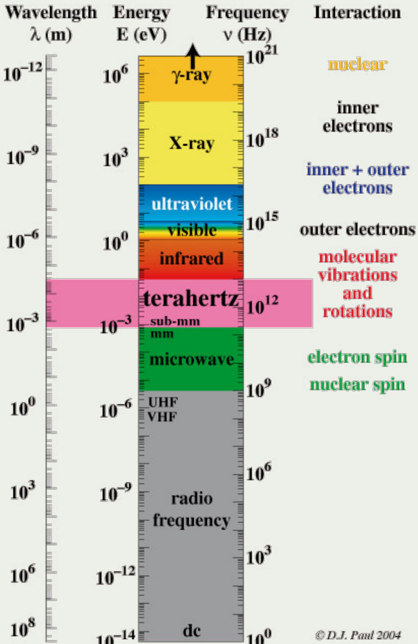
High energy EMR (UV/Vis) can change electronic levels along with vibrational and rotational sublevels!!!



Effect of EM Radiation on Molecules



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003


Wavelength λ (m)
Energy E (eV)
Frequency ν (Hz)
Interaction
10^{-12}
10^{-9}
10^{-6}
10^{-3}
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10^{3}
10^{0}
γ-ray
X-ray
ultraviolet
visible
infrared
terahertz
sub-mm
mm
microwave
UHF
VHF
radio frequency
dc
nuclear
inner electrons
inner + outer electrons
outer electrons
molecular vibrations and rotations
electron spin
nuclear spin
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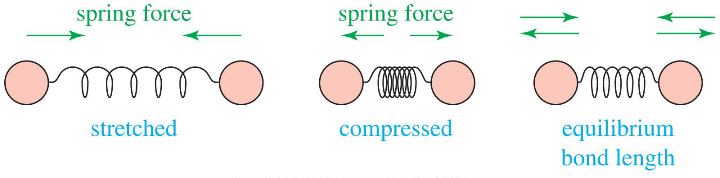
Different Spectroscopy Techniques w.r.t. EM Radiation

EM Radiation Nature of effect

- UV-Visible radiations ⇒ excitation of outer electrons ⇒ **UV-visible spectroscopy**.
- X-rays ⇒ excitation of inner electrons ⇒ **X-rays/Auger effect**.
- Radio frequency ⇒ nuclear spin transitions ⇒ **NMR spectrum**.
- MW/Radio frequency ⇒ electron spin transitions ⇒ **ESR/EPR/EMR spectrum**.
- IR radiations ⇒ molecular vibration changes ⇒ **IR spectroscopy**.
- MW radiations ⇒ changes in rotational levels ⇒ **MW spectroscopy**.

Introduction to MW/IR Spectroscopy

- **Energy of molecule = Electronic energy+ Vibrational energy + Rotational energy**
- Electronic energy/transitions: X-rays/Compton effect, NMR, EMR, etc.
- **Vibrational energy: IR Spectroscopy.**
  It is concerned with the study of absorption of infrared radiation, which causes vibrational transition in molecules.
- So, it can be called as **Vibrational Spectroscopy**.
- IR spectra mainly used in structure analysis to determine the functional groups.
- **Rotational energy: Microwave Spectroscopy.**
  Deals the study of absorption of MW radiation giving rise to rotational transitions in molecules.



Principles of IR Spectroscopy

- **Molecules are made up of atoms linked by chemical bonds. The movement of atoms and the chemical bonds are like spring and balls (vibrations).**
- This characteristic vibration ⇒ *Natural Frequency* of vibration.

- **Applied energy (in the form of IR radiation) affects the vibrational motion (energy) of the molecules.**
- Vibration in a molecule: Any change in shape of the molecule due to stretching/bending of bonds or internal rotation around single bonds.

Principles of IR Spectroscopy

- If **Applied IR frequency = Natural Frequency of vibration ⇒ Absorption of IR radiation takes place**. We can observe a corresponding peak in the spectrum.

- Different functional groups possess different characteristic frequencies. So, they absorb their own matching frequencies of IR radiation. This produces different characteristic peaks in the spectrum.

- ⇒ **No two unique molecular structures produce the same infrared spectrum.**
- Therefore, IR spectrum of a chemical substance/sample is a **fingerprint of a molecular identification**.

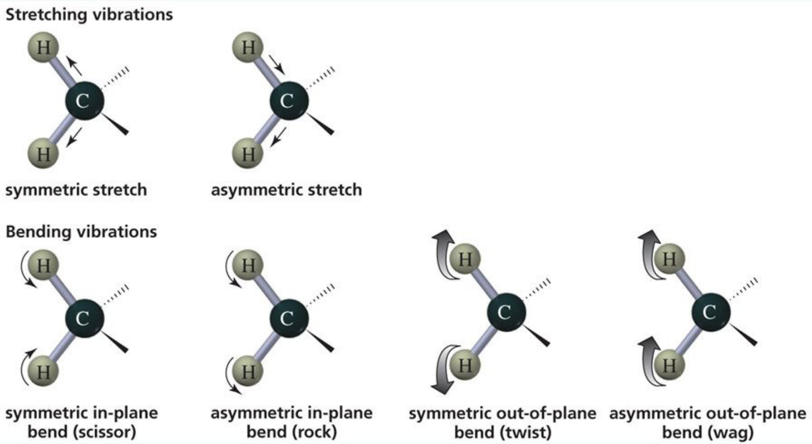
Different Types of Vibrations in Molecules

1. Fundamental Vibrations

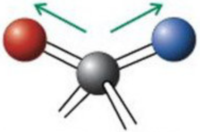
The transition of vibrational states 0 → 1 is fundamental.

- **Stretching Vibration**: **Change in the inter-atomic distance along the axis of the bond** b/w two atoms. It requires more energy and so appear at shorter wavelength.
    - SYMMETRIC: Inter-atomic distance b/w two atoms increases/decreases.
    - ASYMMETRIC: Inter-atomic distance b/w two atoms is alternate/opposite.
- **Bending vibrations**: **Change in the angle** b/w two bonds. Vibration or oscillation not along the line of bond. It requires less energy so appear at longer wavelength.
    - IN-PLANE: All the atoms are on same plane.
      (i) Scissoring (ii) Rocking
    - OUT-OF-PLANE: (Ex.) If two atoms are on same plane while the one atom is on opposite plane.
      (i) Wagging (ii) Twisting

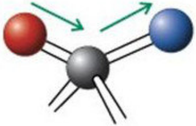
Stretching and Bending Vibrations



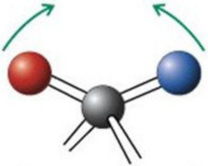
Vibrational modes leading to IR absorptions:



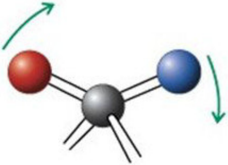
Symmetric stretching vibration (both outside atoms move away from or toward the center)



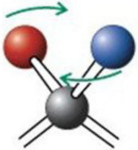
Asymmetric stretching vibration (as one atom moves toward the center, the other moves away)



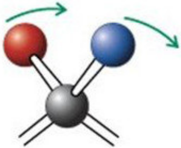
Symmetric bending vibration in a plane (scissoring)



Asymmetric bending vibration in a plane (rocking)



Symmetric bending vibration out of a plane (twisting)



Asymmetric bending vibration out of a plane (wagging)

Different Types of Vibrations in Molecules...

2. Non-Fundamental Vibrations

Secondary vibrations, caused due to the effects of Fundamental Vibrations & have lower intensities (3 types)

- **Overtones**: Transitions $0 \to n$ $(n > 1)$. Transitions $1 \to n$ $(n > 1)$ are called hot bands.
- **Combination tones**: When two or more fundamental vibrations are excited simultaneously.
- **Fermi Resonances**: Splitting of two vibrational bands that have nearly the same energy and symmetry.

Requirements for a Molecule to absorb IR radiation

- **Correct wavelength of radiation:** The natural frequency of vibrations of some part of a molecule should be same to the frequency of incident radiation.
- **Change in dipole moment:** Only when the IR radiation causes a change in electric dipole.

Microwave Spectroscopy

Microwave Spectroscopy

- Mainly used to get information about gas molecules, such as
  1. Accurate bond lengths and angles.
  2. Electric dipole moments.
  3. Centrifugal distortion constants.
- It can also be used to study relaxation times, dielectric constants, dipole moments in liquids and solutions, and potential energy barriers to rotation.
- In some cases, we can get information about the mechanism of chemical reactions (Ex.decomposition).

- The requirements to get a MW spectrum:
  1. Substance must have electric/magnetic dipole moment.
  2. Its vapour pressure $> 10^{-3}$ mmHg.

Microwave Spectroscopy...

Few Advantages of MW Spectroscopy

- It has a high resolving power.
- It analyses the WHOLE molecule (not like nmr, or ir spectra, which fingerprint selected parts).
- It also detects isotopic species, and conformational isomers.
- Requirements are very less.
- It is a non-destructive technique.
- Mainly, it can be used remotely, such as for interstellar analyses.
- Disadvantage: Similar to others, the spectra of large molecules are very complex.

Microwave Spectroscopy...

- Rotational energies of molecules are quantized.
  Ex. Energy $E = h\nu$. (ν: rotational frequency)
- The range of rotational frequencies: $8 \times 10^{10} - 4 \times 10^{11}$ Hz (or) wavelength range: $0.75 - 3.75\ mm \Rightarrow$ MWs

- Interaction of EM radiation of proper frequency (MWs) with rotating molecule results in rotational energy transitions.
- i.e. By **absorption** of MW radiation, **transitions** can occur **between rotational energy levels** of molecules.

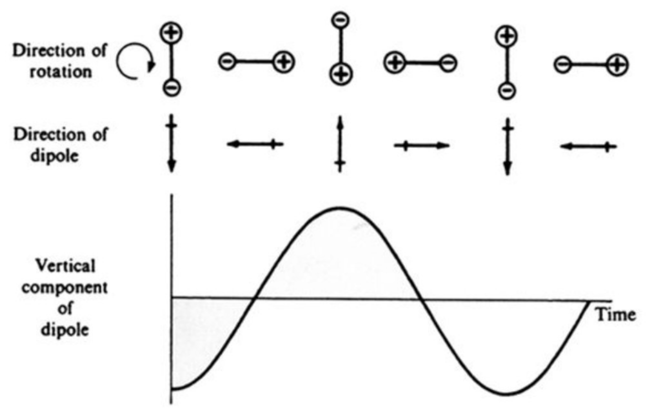
- The direction of dipole moment changes continuously. This fluctuating dipole interact with electric field of applied EM radiation gives rotational spectrum.
  (**Molecule must have permanent dipole moment**).

Microwave Spectroscopy...

- **Molecules with zero dipole moment show no rotational spectrum**.
- Ex.: Homonuclear diatomic molecules $H_2,\ N_2,\ O_2$, etc.
  Heteronuclear molecules $CO_2,\ CS_2$, etc.
  Spherical top molecules.
- Addition/mixing of isotopes also becomes MW inactive (only it changes the mass).
- To a static observer, it appears like a change in dipole moment along a direction/axis (say z) when the molecule rotates. (Due to these rotations radiation is absorbed).
- In QM notation, transition moment corresponding to a transition from state i to j: $\mu_{ij} = \int \psi_i^* \mu \psi_j d\tau$
- Selection rule: Rotational transitions are allowed only between adjacent rotational levels ($\Delta J = \pm 1$).

Microwave Spectroscopy...

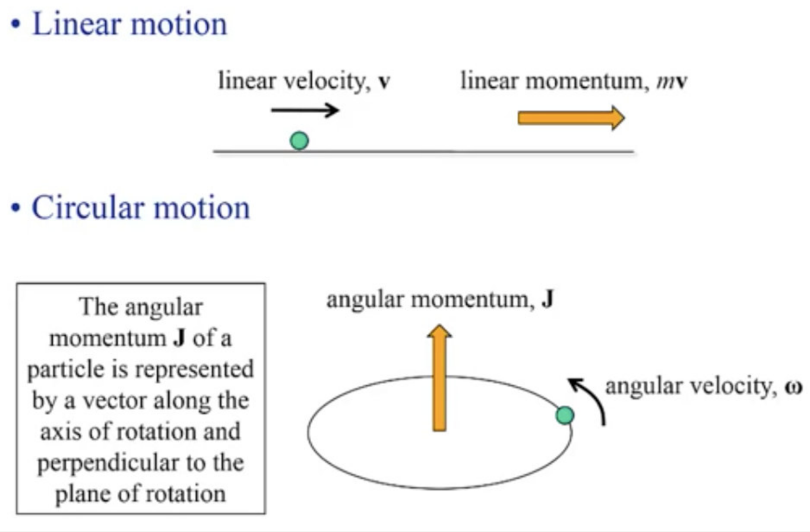
Transitions between different rotational levels within the same vibrational level give rise to pure rotational spectra in MW.



- For example, consider a diatomic molecule
  Moment of inertia $I = \sum_i^2 m_i r_i^2$.
  r = distance of i-th atom from rotation axis.
- Angular momentum = $I\omega$. ($\omega = 2\pi\nu$: angular frequency)

Angular Velocity & Angular Momentum

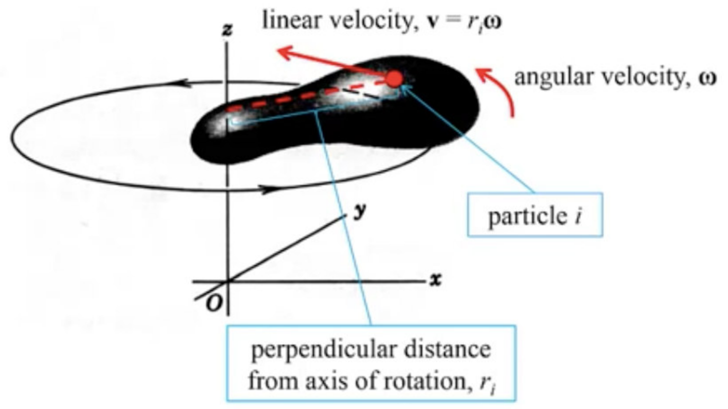
Difference between linear motion and angular motion.
Kinetic energy of particle in linear motion $T = \frac{1}{2}mv^2$.



- Linear motion
- Circular motion

The angular momentum **J** of a particle is represented by a vector along the axis of rotation and perpendicular to the plane of rotation

Moment of Inertia (MoI)



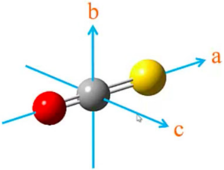
Kinetic Energy of each rotating i-th particle
$= \frac{1}{2}m_i v_i^2 \Rightarrow \frac{1}{2}m_i r_i^2\omega^2$.
$\therefore$ Total Kinetic Energy of all rotating particles
.
$$T = \sum \frac{1}{2}m_i r_i^2\omega^2 \Rightarrow \sum \frac{1}{2}I\omega^2.$$
$\because$ Moment of Inertia $I = m_i r_i^2$.

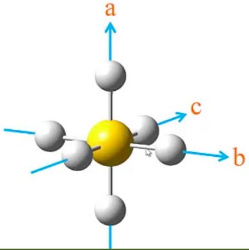
Classification of Molecules based on 'MoI'

Molecules can be classified into four types based on the rotations by using three principal MoI I_a, I_b & I_c with $I_a < I_b < I_c$.

1. Linear Molecules

All atoms arranged in a straight line. All nuclei are in axis a, so moment of inertia $I_a = 0$. End-to-end rotation along b & c axes are same $\Rightarrow$ $I_b = I_c$. Ex: HCl, CO_2, OCS, HCN, etc.





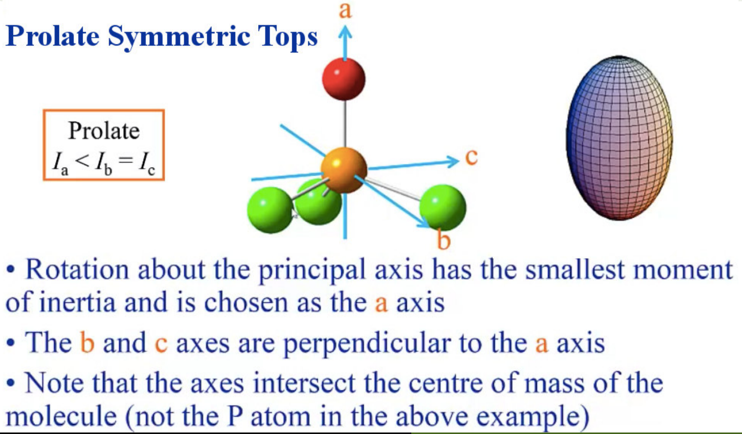
2. Spherical Tops

All the three principal MoI are same $I_a = I_b = I_c$.
Ex: CH_4, OsO_4, SF_6, CCl_4, etc.

Classification of Molecules based on ‘MoI’...

3. Symmetric Tops

All the three principal MoI are non-zero and two are same.
Spinning about a axis.
Prolate ($I_a < I_b = I_c$) and Ablate ($I_a = I_b < I_c$)

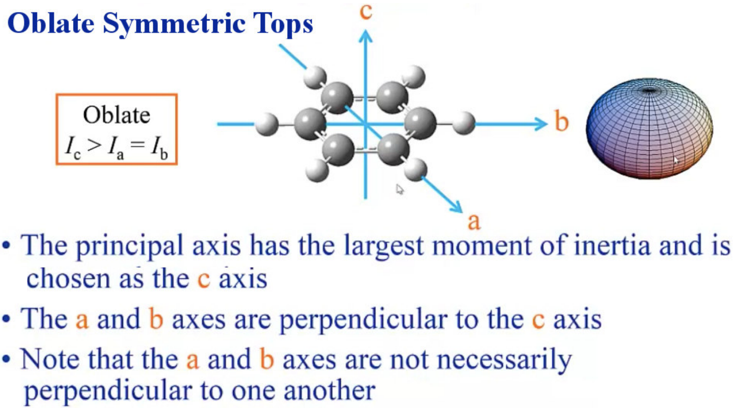


Prolate Symmetric Tops

Prolate
$I_a < I_b = I_c$

- Rotation about the principal axis has the smallest moment of inertia and is chosen as the a axis
- The b and c axes are perpendicular to the a axis
- Note that the axes intersect the centre of mass of the molecule (not the P atom in the above example)

Classification of Molecules based on ‘MoI’...



Oblate Symmetric Tops

Oblate
$I_c > I_a = I_b$

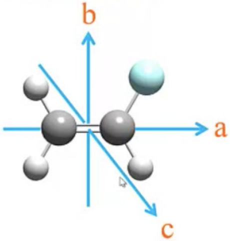
- The principal axis has the largest moment of inertia and is chosen as the c axis
- The a and b axes are perpendicular to the c axis
- Note that the a and b axes are not necessarily perpendicular to one another

Classification of Molecules based on 'MoI'...

4. Asymmetric Tops

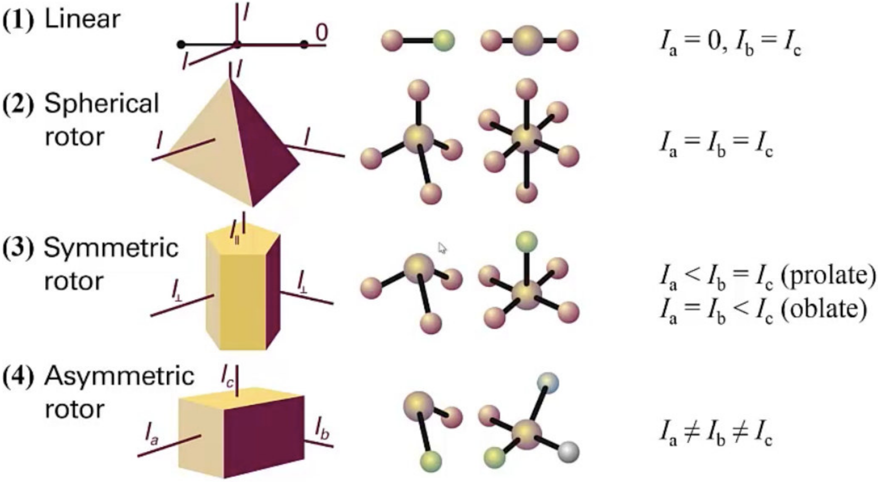
All the three principal MoI are different $I_a \neq I_b \neq I_c$.
Ex: H_2O, CH_3OH, CH_2CHCl, etc.

- For example: H_2O, C_2H_3Cl, H_2O_2



- The axis with the smallest moment of inertia is chosen as the a axis, the axis with the largest moment of inertia is chosen as the c axis

Classification of Molecules based on 'MoI'...



(1) Linear $I_a = 0,\ I_b = I_c$

(2) Spherical rotor $I_a = I_b = I_c$

(3) Symmetric rotor $I_a < I_b = I_c$ (prolate)
$I_a = I_b < I_c$ (oblate)

(4) Asymmetric rotor $I_a \neq I_b \neq I_c$

Energy of a molecule

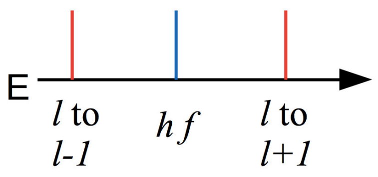
- **When an atom is a molecule moves, its associated energy changes. (or) When energy is supplied to a molecule the associated atoms absorb it and move.**

- If these energy change is large, an electron in the molecule make a transition to higher energy level (quantum state).

- Total energy = (Electronic+Vibrational+Rotational) energies.
- Vibrational energy $E = hf(v + 1/2)$,
  f frequency of vibration, v vibrational quantum no.
  For a transition b/w v and $v+1$ state: $\Delta E = hf$.
- Rotational energy $E = \frac{\hbar^2}{2I}l(l+1)$.
  For a transition b/w l and $l-1$ state: $\Delta E = \frac{-\hbar^2 l}{I}$.

Energy of a molecule...

- Total energy change: $\Delta E_{tot} = hf - \frac{\hbar^2\ l}{I}$. $\Delta l = -1$
- Total energy change: $\Delta E_{tot} = hf + \frac{\hbar^2\ l}{I}$. $\Delta l = +1$ (from l to $l+1$)
- So, three spectral lines with different energies corresponding to $\Delta l = -1$, hf and $\Delta l = +1$.



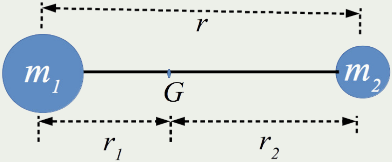
Rotational (MW) spectroscopy

Rigid Diatomic Molecule

Rigid Rotator: Diatomic molecule

Rotations of a diatomic molecule = Rigid rotor model

- Consider two atomic masses (m_1 and m_2) connected by rigid bond r and rotation perpendicular to molecular axis.



- Rotational energy $E_J = \frac{\hbar^2}{2I} J(J+1)$ Joules, $J = 0, 1, 2, \cdots$
  J: Rotational quantum number.
- Moment of Inertia $I = m_1 r_1^2 + m_2 r_2^2$,
  $m_1 r_1 = m_2 r_2$ & $r = r_1 + r_2 \Rightarrow r_1 = \frac{m_2 r}{m_1+m_2}$, $r_2 = \frac{m_1 r}{m_1+m_2}$.
  $I = \frac{m_1 m_2}{m_1+m_2} r^2 \equiv \mu r^2$, $\because \mu = \frac{m_1 m_2}{m_1+m_2} \Rightarrow$ Reduced mass.

MoI is proportional to square of distance b/w atoms

Rigid Rotator: Diatomic molecule...

- Rotational energy (in wavenumber units) $\epsilon_{_J} = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1)$ cm^{-1} $\Rightarrow \epsilon_{_J} = BJ(J+1)$ cm^{-1}. Here $B = \frac{h}{8\pi^2 Ic}$ cm^{-1} (or)$B = \frac{h^2}{8\pi^2 I}$ (Rotational constant)
- Let us take there is a transition between two rotational energy levels (upper state $J^{'}$ and lower state $J^{''}$).
- $\therefore$ Change in the rotational energy: $\Delta\epsilon_{_J} = \epsilon_{_{J'}} - \epsilon_{_{J''}} = B[J^{'}(J^{'}+1) - J^{''}(J^{''}+1)]$.
- w.k.t. selection rule $\Delta J = \pm 1 \Rightarrow J^{'} - J^{''} = 1$ (absorption). Substituting $J^{'} = J^{''} + 1 \Rightarrow \Delta\epsilon_{_J} = 2B(J+1)$ cm^{-1} $= \nu_{_J}$.
- Here J represents lower rotational energy state.
- $\therefore$ Change in energy due to rotational transitions from different levels takes different values in magnitudes of B.

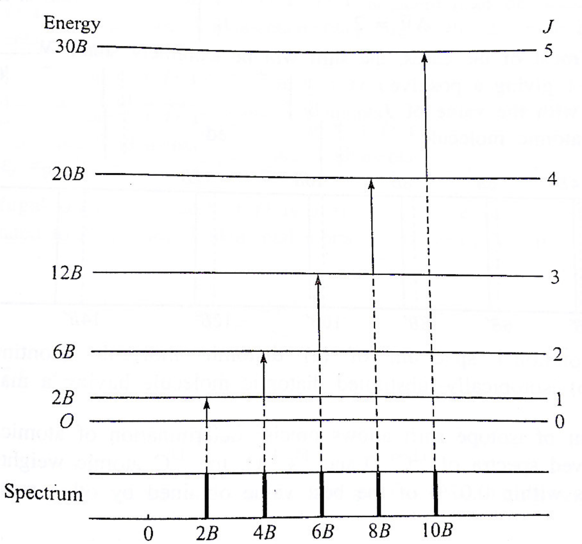


Figure: Transitions for a Diatomic (Rigid Rotator) Molecule.
($2B$ difference between two adjacent levels: 0, $2B$, $4B$, $6B$, ...)
Solid lines: Allowed transitions & Dashed lines: Forbidden

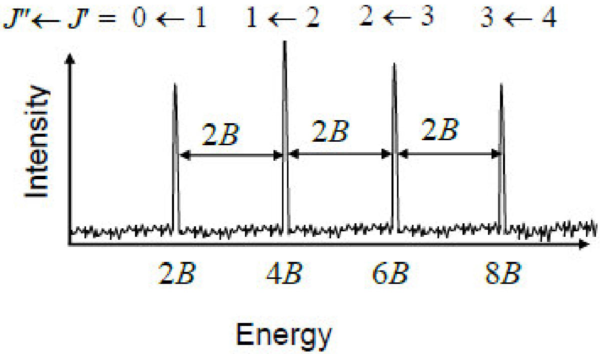


Figure: Rotational spectrum for Rigid Rotator.

Intensity of Rotational energy levels

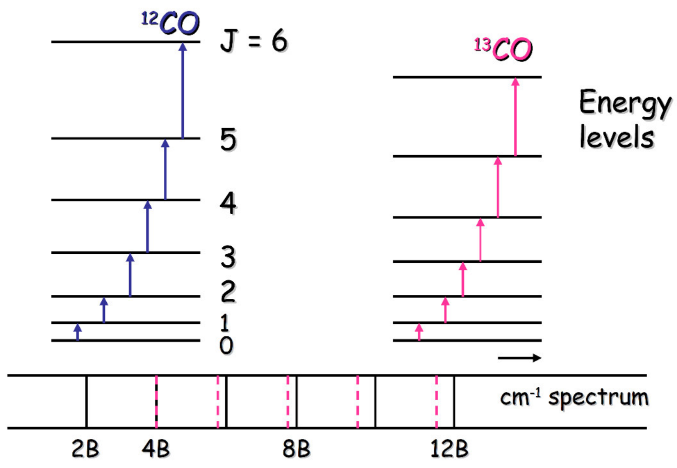
- Rotational spectra consist of transition between several levels (absorption or emission) with a linearly/equally spaced energy difference. Difference between two adjacent levels is $2B$: $0, 2B, 4B, 6B, ..$
- Apart from the energy difference, Number of molecules in each level is another important factor in rotational spectra.
- Number density (population): Boltzmann distribution.
- If we assume N_0 is number density in $J = 0$ state, the number of molecules in J-th state can be written as $N_J = N_0 \exp \frac{-E_J}{kT}. \Rightarrow N_0 \exp \left[\frac{-BhcJ(J+1)}{kT}\right]$.
- If we consider degeneracy of the level $(2J + 1)$, then actual no. of molecules: $N_J = N_0(2J + 1) \exp \left[\frac{-BhcJ(J+1)}{kT}\right]$
- Maximum population is possible when $\frac{dN_j}{dJ} = 0 \Rightarrow J = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$.

Effect of Isotopes: Diatomic (Rigid Rotator) Molecule

- Addition/mixing of isotope in a given MW inactive (zero-dipole moment) molecule also will not give any rotational spectra. Because, isotope changes the mass only.
- Replacement of one atom by its isotope alters the nuclear mass, but the dipole moment and bond length are intact.
- Mass change alters the moment of inertia: $I \rightarrow I^{'} = \mu^{'} r^2$. Let us take $\frac{I}{I^{'}} = \frac{\mu}{\mu^{'}} = \rho^2$.
- Corresponding energy-change becomes $\nu^{'} = 2B^{'}(J+1)$.
- So, alteration in energy-change becomes $\Delta\nu = \nu - \nu^{'} = 2(J+1)(B - B^{'}) \Rightarrow 2(J+1)\frac{h}{8\pi^2 Ic}\left(1 - \frac{I}{I^{'}}\right)$ $\Rightarrow \Delta\nu = 2B(J+1)(1-\rho^2)$.
- When atomic mass increase $\Delta\nu$ also increases. Transitional energy will be lesser by $\Delta\nu$ from the initial energy.

Effect of Cabon Isotopes: Rotational Spectra

Isotope substitution decreases the energy during rotational transition of molecules.



Energy variation in rotational spectra for $^{12}C^{16}O$ Vs $^{13}C^{16}O$.

Diatomic (Rigid Rotator) Molecule: Revisit

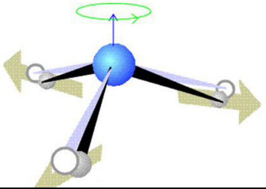
- Energy changes due to Rotational transitions between different levels ($\Delta J = \pm 1$).
- Different energy in the spectrum represents corresponding/different molecules.
- Exact identification of the molecule in given sample.

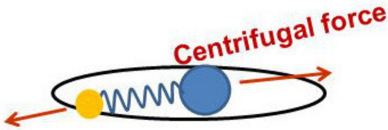
- Replacing with corresponding isotope shifts the change in energy due to rotational transitions ($\Delta \nu$).
- $\Delta \nu$ helps to find exact atomic mass of atoms. Ex. Isotope Molecules $^{12}C^{16}O$ and $^{13}C^{16}O$.

- In general, the chemical bonds (spring-like) are elastic. They are not always (mostly) constant and change.
- Energy loss due to these elastic bonds should be considered for correct analysis ⇒ **Non-Rigid Rotator**.

Non-Rigid Rotator

- **Assumption of rigid bond is only an approximation.**
- The separation between successive lines in the spectra (and hence the B value) decreases steadily with increasing J.
- **Rotation of atoms affects the rigid nature (length) of the chemical bonds and it increases the moment of inertia of a given molecule.**
- More faster the rotation of a diatomic molecule, the greater the centrifugal force tending to move the atoms apart. This results increase in the bond length ⇒ MoI also increases. **Increase in MoI reduces energy separation.**





Non-Rigid Rotator...

- In Rigid-Rotator: Rotational energy $\Delta\epsilon_J = B(J+1)$ cm^{-1}.
- **Non-Rigid Rotator**:
  Rotational energy decreases due to centrifugal force.
  $E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k}[J(J+1)]^2$ Joules, $J = 0, 1, 2,$
  (or)
  $\epsilon_J = \frac{E_J}{hc} \Rightarrow BJ(J+1) - DJ^2(J+1)^2$ cm^{-1}.
- B: Rotational constant ($B = \frac{h^2}{8\pi^2 I}$).
  D: Centrifugal distortion constant ($D = \frac{h^3}{32\pi^4 I^2 r^2 kc}$).
- Change in rotational energy $\Delta\epsilon_J = \epsilon_{J+1} - \epsilon_J = \nu_J$ (say).
  $\nu_J \Rightarrow 2B(J+1) - 4D(J+1)^3$ cm^{-1}, $j = 0, 1, 2, ...$
- **Transition energy decreases (lower shift) due to vibrations induced by rotations of atoms in a molecule.**

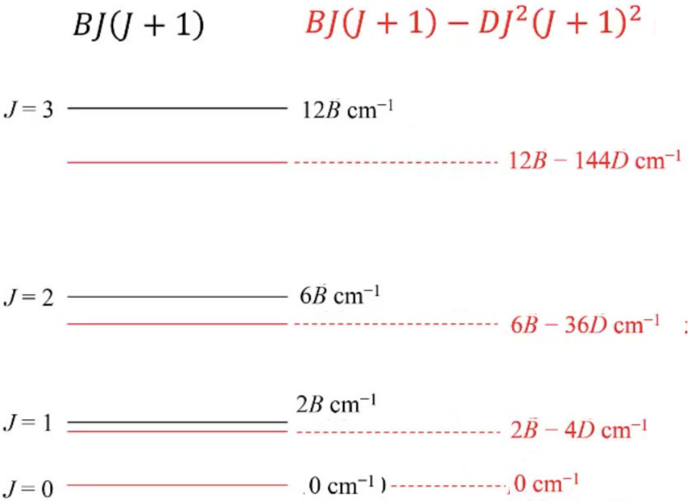


Figure: Rotational Energy levels for Rigid (black lines) & Non-Rigid (red dashed lines) in linear diatomic rotators. (Non-Rigid bonds decrease energies in rotational transitions).

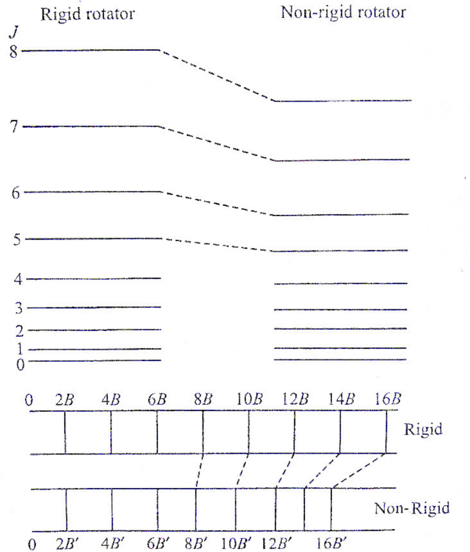


Figure: Rotational Transitions for Rigid (left) & Non-Rigid (right) Rotators (linear diatomic molecule).
(Non-Rigid bonds decrease energies in rotational transitions).

Non-Rigid Rotator...

- **For better analyses, in addition to the distortion effect due to centrifugal force, we should consider vibrations induced by such bond length variations.**
- Because, so far, we have taken MoI $I = \mu r^2$. (r: constant).

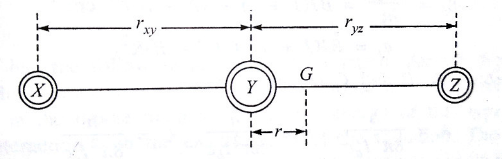
- But, when there is vibrations due to centrifugal force, the inter-atomic/nuclear distance keeps on changing.
  $\Rightarrow r$ changes continuously $\Rightarrow$ MoI I also not constant.

- MoI "$I \longrightarrow I_v$". (MoI depends on vibrational state also)
- If MoI is not constant, then rotational constant B also!
  $\Rightarrow \qquad B_v = \frac{h}{8\pi^2 I_v c}$.
- For a diatomic molecule: $B_v = B_e - \left(v + \frac{1}{2}\right) \frac{12B_e^2}{\bar{\nu}}$.
  B_e: rotational constant at equilibrium (fixed bond length).

Linear Polyatomic Molecules

Linear Polyatomic Molecules

- **Molecules with more than two atoms.**
- Rotational transitions are similar to Diatomic Molecules. Only one independent MoI $I_a = 0, \; I_b = I_c$.



- Analyses for polyatomic molecules ($n \geq 3$) are same to that of Diatomic molecule, but with one major change in MoI.
- Ex.: For a tri-atomic molecule given above MoI $I = \frac{m_x m_y r_{xy}^2 + m_y m_z r_{yz}^2 + m_x m_z (r_{xy} + r_{yz})^2}{m_x + m_y + m_z}$.
- So, change in energy during rotational transition: $\Delta\epsilon_{_J}$. $\nu_{_J} \Rightarrow 2B(J+1) - 4D(J+1)^3$ cm^{-1}, $j = 0, 1, 2, ...$

Linear Polyatomic Molecules...

MoI in Polyatomic Molecules

- MoI for $n \geq 3$ is greater than that of diatomic molecule. So, rotation constant B is less $\Rightarrow$ Energy shift $(\Delta\epsilon_J)$ is very short & spectral lines are closely spaced.

- For a tri-atomic molecule, distance from each atoms to center of mass G are different, $r_{xy} + r$, r and $r_{yz} - r$.
- Here $m_x(r_{xy} + r) + m_y r = m_z(r_{yz} - r) \Rightarrow r = \frac{m_z r_{yz} - m_x r_{xy}}{m_x + m_y + m_z}$.

- So, MoI $I = m_x(r_{xy} + r)^2 + m_y r^2 + m_z(r_{yz} - r)^2$,

  . $\Rightarrow m_x r_{xy}^2 + m_z r_{yz}^2 + (m_x + m_y + m_z)r^2$.

  (or) $I = \frac{m_x m_y r_{xy}^2 + m_y m_z r_{yz}^2 + m_x m_z (r_{xy} + r_{yz})^2}{m_x + m_y + m_z}$.

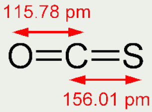
  (Here MoI is due to an end-over-end rotation. Ex. OCS)

Linear Polyatomic Molecules...

MoI in Polyatomic Molecules...

- MoI in polyatomic molecule is due to end-over-end rotation.
- Can not exactly find individual bond lengths between two atoms. Because, one MoI will not give different inter-atomic distances in a molecule.
- So, we need additional data by means of MoI for the corresponding molecule by substituting/replacing an atom with its isotope.
- Isotope of different atoms in a molecule can give different MoI (shifted spectral lines), from which one can obtain explicit bond length between given two atoms.

Ex.: Isotopic molecules (carbon oxysulphide) $^{16}O^{34}CS$ & $^{18}O^{34}CS$



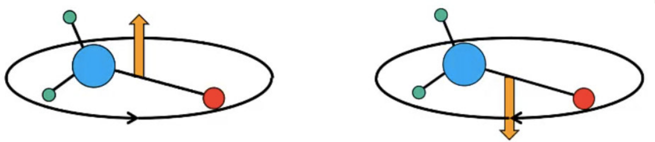
Symmetric Top Molecules

Symmetric Top Molecules

- (General) Rotational energy $E_R = \frac{J^2}{2I}$.
  I cumulative/same MoI along the three axes.
- For different MoI: $E_R = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z}$.
- Symmetric Top molecules: Two independent MoI
  $(I_x = I_y \neq I_z, \quad I_z \neq 0)$. (similar $I_b = I_c \neq I_a, \quad I_a \neq 0$)
  So, rotational KE $E_R = \frac{J_x^2+J_y^2}{2I_x} + \frac{J_z^2}{2I_z} \quad \because I_x = I_y$.
- Hamiltonian $H = \frac{\hat{J}_x^2+\hat{J}_y^2}{2I_x} + \frac{\hat{J}_z^2}{2I_z} \Rightarrow \frac{\hat{J}^2-\hat{J}_z^2}{2I_x} + \frac{\hat{J}_z^2}{2I_z}$
  ($\because$ operator relation: $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$)
- From Shcrödinger eqn.: $\hat{H}\psi = E\psi$,
  $\Rightarrow \hat{J}_z\psi = K\hbar\psi \quad$ and $\quad \hat{J}^2\psi = \hbar^2 J(J+1)\psi$.
  Here $K = -J, -J+1, \cdots, +J$: $(2J+1)$ eigenfunctions

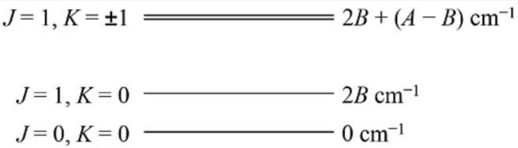
Symmetric Top Molecules...

- We can also write as
  $\Rightarrow \hat{J}_z\psi_{JK} = K\hbar\psi_{JK}$ and $\hat{J}^2\psi_{JK} = \hbar^2 J(J+1)\psi_{JK}$.
- So, $\hat{H}\psi_{JK} = \left(\frac{\hbar^2}{2I_x}[J(J+1) - K^2] + \frac{\hbar^2 K^2}{2I_z}\right)\psi_{JK}$.
- Energy $E_{JK} = \frac{\hbar^2}{2I_x}[J(J+1) - K^2] + \frac{\hbar^2 K^2}{2I_z}$.
  (or) $\epsilon_{JK} = \frac{E_{JK}}{hc} = BJ(J+1) + (A-B)K^2$ cm^{-1}(prolate).
  (or) $\epsilon_{JK} = \frac{E_{JK}}{hc} = BJ(J+1) + (C-B)K^2$ cm^{-1} (oblate).
- Here $B = \frac{h}{8\pi^2 cI_z}$, $A = \frac{h}{8\pi^2 cI_x}$ & $C = \frac{h}{8\pi^2 cI_y}$ are constants.
  $J = 0, 1, 2, \ldots$ & $K = 0, \pm1, \pm2, \ldots$ (projection of J).
- Sign of K denotes the direction of rotation.



Symmetric Top Molecules...

- Prolate ($I_x > I_z$): $A < B$ & Oblate ($I_x < I_z$): $A > B$.
- $k > 0$ Gives doublet states.

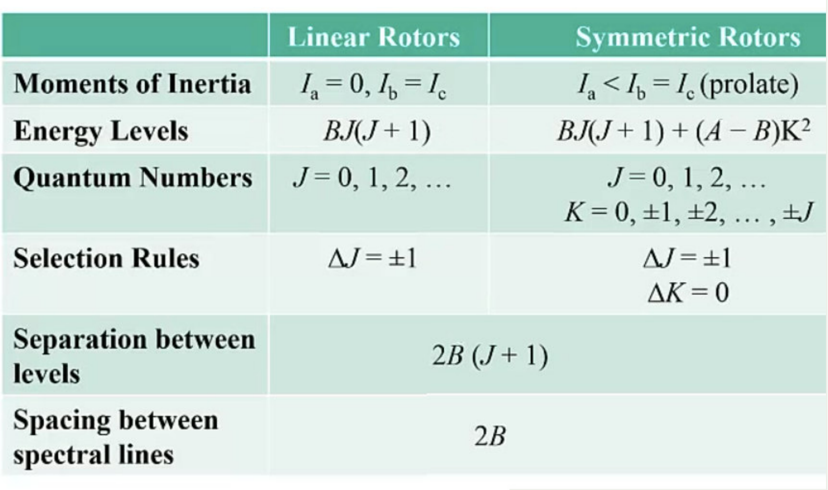


Transitions in Symmetric Top Molecules

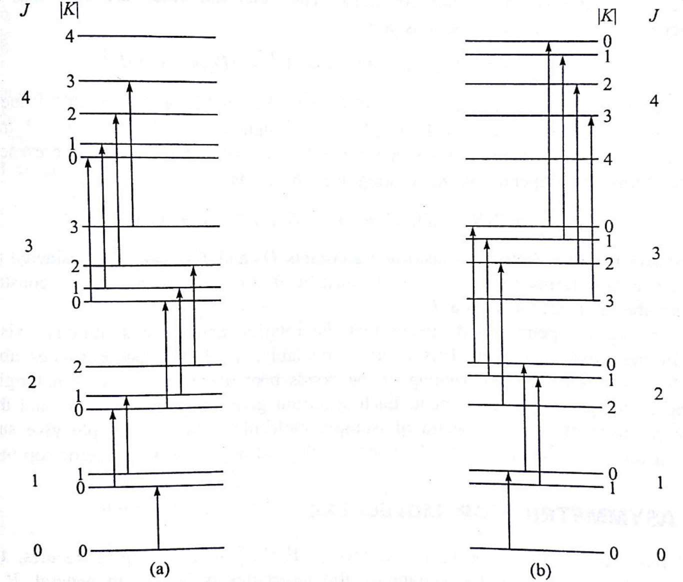
- Selection Rules $\Delta J = \pm 1$ and $\Delta K = 0$.
- Let us take a transition $J \to J + 1$:
  $\Delta\epsilon_{JK} = \epsilon_{J+1K} - \epsilon_{JK} = 2B(J + 1)$ cm^{-1} $= \nu$.
- So, change in rotational energy due to transition b/w states will depends B and J only. Spectrum is independent of K.
- Rotation about the symmetry axis does not affect dipole moment (& hence MoI) which already exist along that axis.
- *We can find only B from the spectrum* and not A.

Comparison: Linear & Symmetric Molecules

Without Centrifugal Distortion.



	Linear Rotors	Symmetric Rotors
Moments of Inertia	$I_a = 0, I_b = I_c$	$I_a < I_b = I_c$ (prolate)
Energy Levels	$BJ(J+1)$	$BJ(J+1) + (A - B)K^2$
Quantum Numbers	$J = 0, 1, 2, \ldots$	$J = 0, 1, 2, \ldots$ $K = 0, \pm 1, \pm 2, \ldots, \pm J$
Selection Rules	$\Delta J = \pm 1$	$\Delta J = \pm 1$ $\Delta K = 0$
Separation between levels	$2B(J+1)$	
Spacing between spectral lines	$2B$	



Energy levels for (a) Prolate and (b) Oblate type molecules.

Symmetric Top Molecules...

General case: With Centrifugal Distortion

- Energy $\epsilon_{JK} = BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$ cm^{-1}.
- Selection rules remain the same.
- Change in rotational energy transition $(J \to J+1)$: $\Delta\epsilon_{JK} = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2$ cm^{-1}. (or) $\nu = 2[B - 2D_J(J+1)^2 - D_{JK}K^2](J+1)$ cm^{-1}.
- Here the spectrum depends on K also.
- Centrifugal distortion acts as correction in rotational spectrum through a perturbation in MoI $I_x = I_y$.
- Each spectrum gives one MoI.
- Spectrum of isotopic molecules give data for finding bond lengths & bond angles.

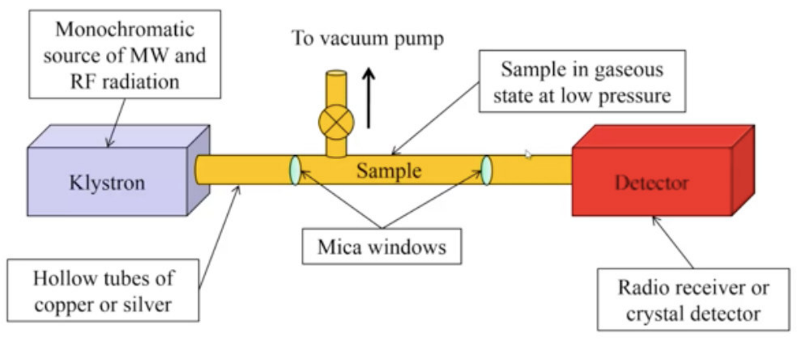
Asymmetric Top Molecules

- Most of the molecules are Asymmetric.
- Each bond (with different length & angle) give a complex form of MoI along the three axes ($I_x \neq I_y \neq I_z$).
- Difficult to derive exact energy expression.
- Analyses are only with approximation by comparing with symmetric top molecules.
- Near Prolate rotors: $I_z < I_y \approx I_x$.
  Near Oblate rotors: $I_x \approx I_y < I_z$.
- Perturbation theory: Hamiltonian for rotational state
  $H_r = H_p + H^{'} \qquad (or) \qquad H_r = H_o + H^{''}$
  $H_{p,o}$: Hamiltonian for prolate or oblate.
  $H^{'}$ & $H^{''}$: Hamiltonian when $I_x \neq I_y$.
- Breaking out from prolate/oblate symmetry to asymmetry.
  $\kappa = \frac{2B-A-C}{A-C}, \quad \kappa = -1$ (+1) for prolate (oblate).

Influence of external electric field !!! $\Rightarrow$ Stark effect

MW Spectrometer: Schematic-1

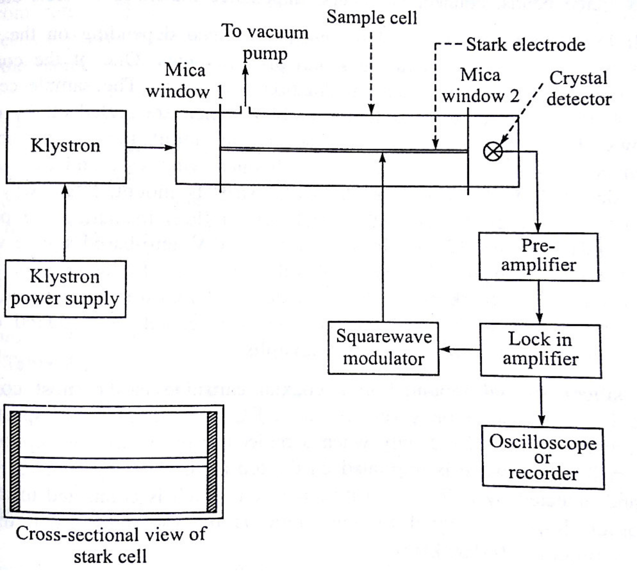
MW Absorption Spectrometer



Steps:

EMR source ⇒ Frequency tuning (MW) ⇒ waveguiding (Radiating towards substance) ⇒ sample cell ⇒ detector for outward radiation ⇒ spectrum analysis.

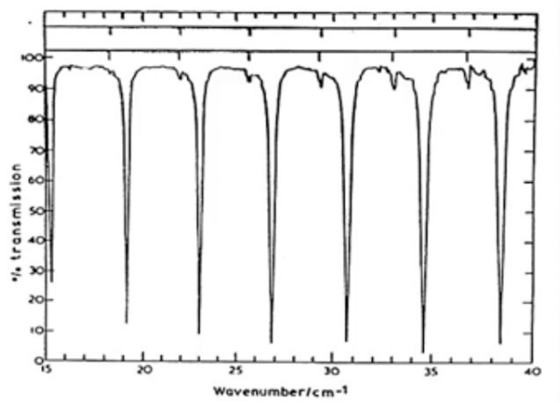
MW Spectrometer: Schematic-2

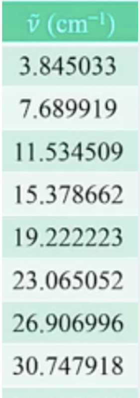


MW Spectrometer...

- **MW Source**: Gun diodes (wider frequency range, low input power $\approx 20V$, monochromatic, etc.) preferred over traditional Klystron tube/backward wave oscillator.
- **Frequency**: Measure using cavity wavemeter or frequency counters.
- **Waveguides**: Hollow metallic rectangular waveguides to direct the MW towards sample.
- **Sample cell**: Stark cell - Modulated by resonance frequency of molecule.
- **Detector**: Crystal detectors with oscilloscope or chart recorder.

MW Spectra: Linear molecule (CO)





$\tilde{\nu}$ (cm^{-1})
3.845033
7.689919
11.534509
15.378662
19.222223
23.065052
26.906996
30.747918

Spectral lines are with equal spacing and small change in intensities between two successive lines.

Applications of Rotational (MW) Spectroscopy

- With mathematical manipulation, we can find exact bond lengths & bond angles: molecular structure
- Determination of dipole moment.
- Atomic masses.
- Identification of different compounds.
- Quantity of a compound in the molecules: Intensity of spectrum
- Presence of different isotopes.

- Real-time applications:
  Detecting the chemical compounds in distant stars, space dust/particles, interstellar molecules, Antarctic ozone hole, molecules in the space/atmosphere, etc. (with advanced high resolution MW spectrometers).

Summary

From the present series of lectures, we have learned the principle, explicit description and detailed analyses on the transitions due to different types of vibrational and rotational characteristics of molecules by means of spectroscopy!