SPECTROSCOPY

- Interaction of electromagnetic radiation with atoms /molecules.

- Rotational and Vibrational Spectroscopy.

Suggested Books

- ***Atkins*, Physical Chemistry, 9th edition, 2009**
- ***Banwell & McCash*, Fundamentals of Molecular Spectroscopy, 4th edition, 1996**

What Is Spectroscopy?

Spectroscopy is the ***study*** of the **interaction of electromagnetic radiation with matter**.

The detection and analysis of the electromagnetic radiation absorbed or emitted by species.

What Is a Spectrum/spectra?

A spectrum is a plot of the intensity as a function of wavelength (or frequency or wave number, etc.) of the radiation emitted or absorbed by an atom or molecule.

Atomic spectroscopy

Electronic transition

Molecular spectroscopy

Electronic transition

Vibrational transition

Rotational transition

Discussed in this course

Molecular spectroscopy is more complex than atomic spectroscopy.

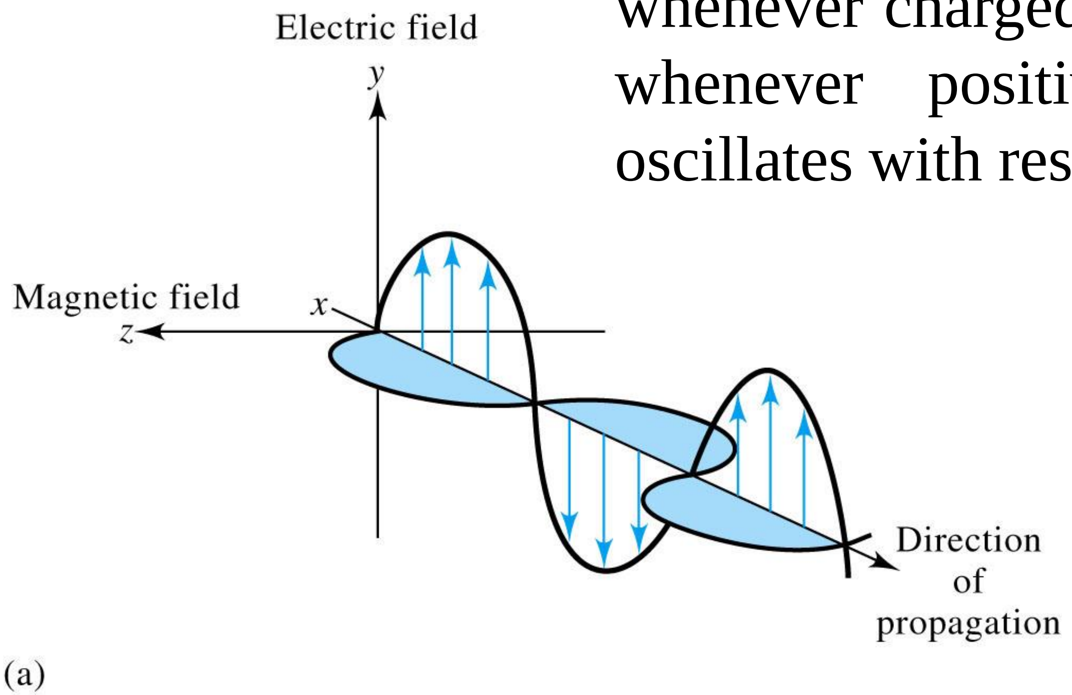
What Information Is Obtained?

- Atomic and molecular energy levels, bond strengths, bond angles, molecular shape, dipole moments etc.
- Often, spectra are used to identify the components of a sample (qualitative analysis). Spectra may also be used to measure the amount of material in a sample (quantitative analysis).
- Compared to chemical analysis, spectroscopic methods are faster and more accurate, require less sample, and are usually nondestructive.

What is electromagnetic radiation?

EMR consists of oscillating electric and magnetic fields directed perpendicular to the direction of propagation of the wave.

Electromagnetic waves are produced whenever charged particles are accelerated or whenever positive and negative charge oscillates with respect to each other.



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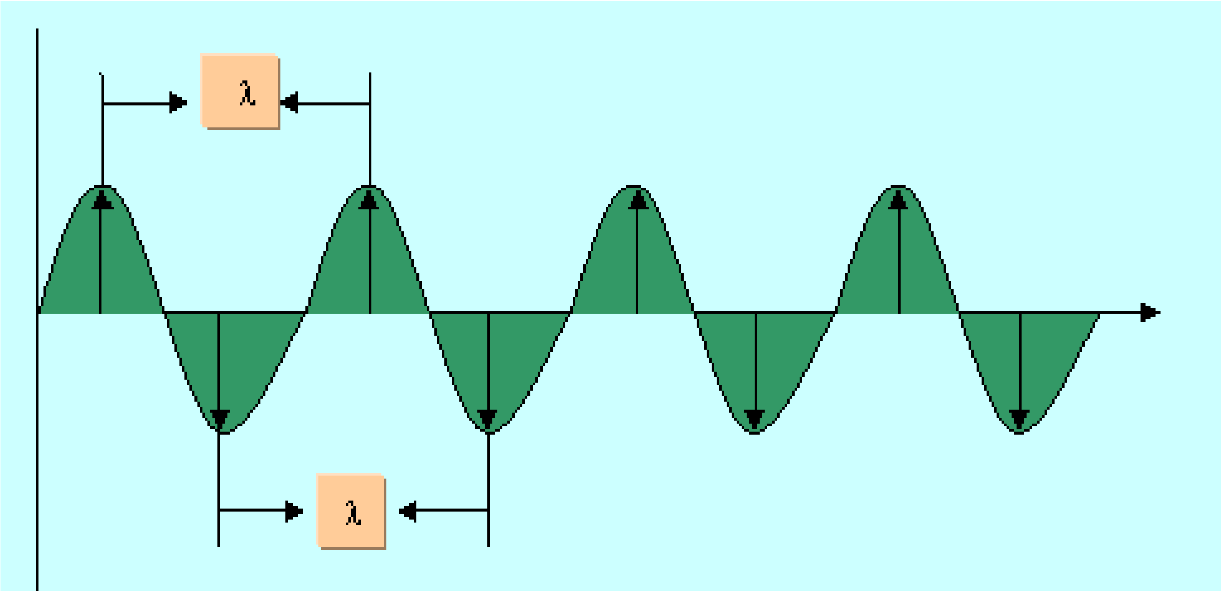
Ex: Radio waves, microwaves, IR, Visible light, UV light, X-rays and γ-rays

Electromagnetic radiation

The wave nature of an electromagnetic radiation is characterized by the following wave properties.

Wavelength (λ)

The wavelength of a wave is the distance between two consecutive maxima or two consecutive minima on the wave.



Time Period (T)

The time required for one wavelength to pass a fixed point in space.

It is expressed in seconds

Frequency (ν)

The number of wavelengths passing a fixed point in space per second.

$$\nu = 1/T$$

It is expressed in hertz (Hz), kilohertz(kHz), megahertz (MHz)
The frequency of the wave is directly proportional to the energy of the wave.

Wavenumber($\bar{\nu}$)

It is defined as the number of wavelengths which can be accommodated in 1 cm length along the direction of propagation. Hence

$$\bar{\nu} = \frac{1}{\lambda}$$

It is generally expressed in unit of cm^{-1} .

This is an important property especially in the study of infrared spectroscopy.

Wave-Particle duality of EMR

The classical wave model

- **The classical wave model describes electromagnetic radiation as waves that has a wavelength, frequency, velocity, and amplitude.**

- **These properties of electromagnetic radiation can explain classical characteristics of electromagnetic radiation like reflection, refraction, diffraction, interference, etc.**

- **However, the wave model can not explain the phenomena of absorption and emission of radiation by atomic or molecular species and necessitated the suggestion that radiation has a particle nature.**

Particle Model and Quantum Theory

- **To explain these phenomena, Max Plank (in 1900) developed a theory called Planck's quantum theory of radiation.**

- **According to this theory, EM radiation made up of discrete packets of energy, called quanta, which are shot out with the velocity of light.**

- **Thus energy changes take place only discontinuously and discretely, always as an integral multiple of small unit of energy, hν (i.e. photon).**

- **In 1905, Albert Einstein supplemented Planck's theory, EM waves can behave as a particle called a photon whose energy depends on the frequency of the waves.**

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

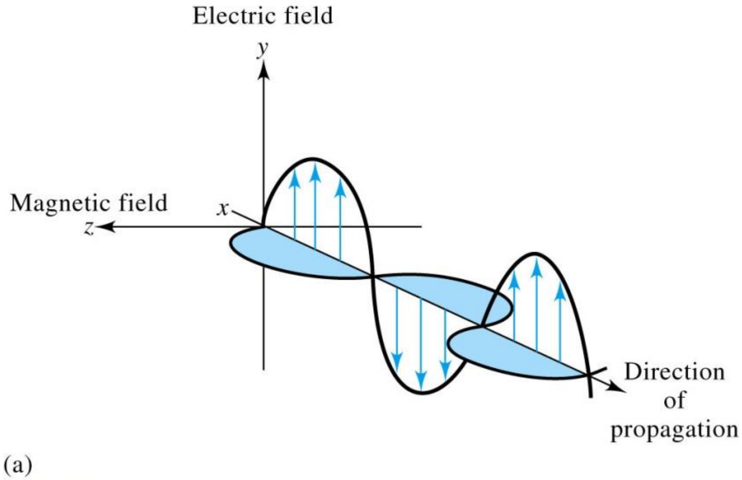
h is Planck's constant, which has a value of 6.626×10^{-34} J s.

Interaction of EMR with matter

The electromagnetic waves (radiation) are sine waves, composed of oscillating electric and magnetic fields **directed perpendicular to the direction of propagation of the wave**.

An electric field of the EMR interact with the induced electric field created by charge particles of matter (explain electronic, vibrational and rotational spectroscopy).

A magnetic field of the EMR interact with magnetic field created by electron and proton in nucleus (explain phenomena like NMR , EPR spectroscopy).



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Interaction of EMR with matter

- When e.m.r fall on an atom or a molecule, the electric field of the radiation tends to disturb the charge cloud around the atom or the molecule and generates a dipole in the particle in the direction of the electric vector of the field.

- The oscillating electric field of the EMR thus create an oscillating dipole in the matter with which it is interacting.

- The oscillating dipole (of the matter) now become a source of electromagnetic radiation of the same frequency as the frequency of incident radiation. This phenomena is called scattering.

- As long as the frequency of radiation (ν) is not equal to the frequency of atom or molecule as given by difference between its energy states (ν_o), the molecule will scatter radiation.

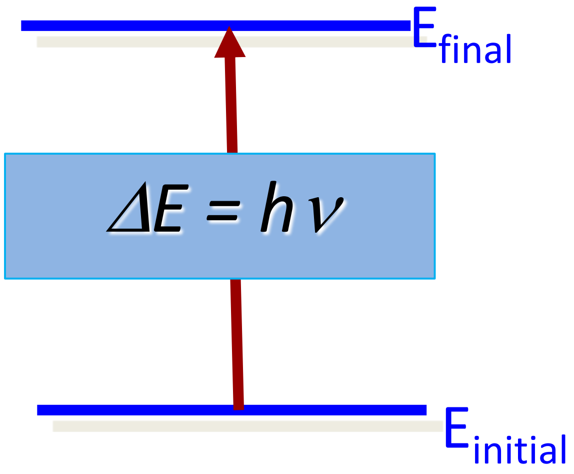
- When $\nu = \nu_o$, a quantum of radiation is absorbed by the atom or molecule and promoted to a higher energy state.

Interaction of EMR with matter

- Atoms, ions, and molecules can exist in certain discrete energy states only. Thus, Electromagnetic radiation is absorbed only when the energy of photon corresponds to difference in energy between two states and is related to the frequency of radiation absorbed or emitted by the relation:

$$E_{final} – E_{initial} = h\nu_o$$

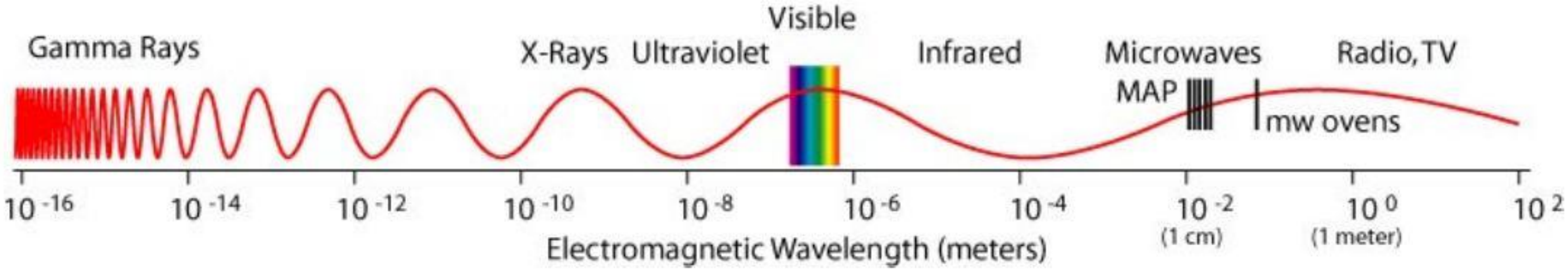
or $$DE = h\nu_o$$



Electromagnetic Spectrum

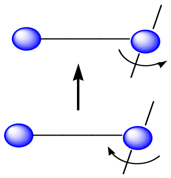
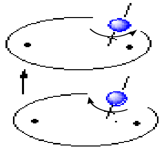
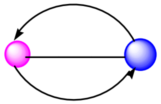
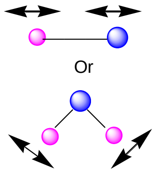
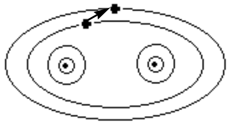
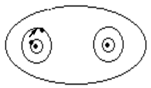
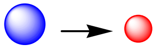
Arrangement of EM radiations in order of their wavelengths or frequencies

The Sun produces full spectrum of electromagnetic radiations



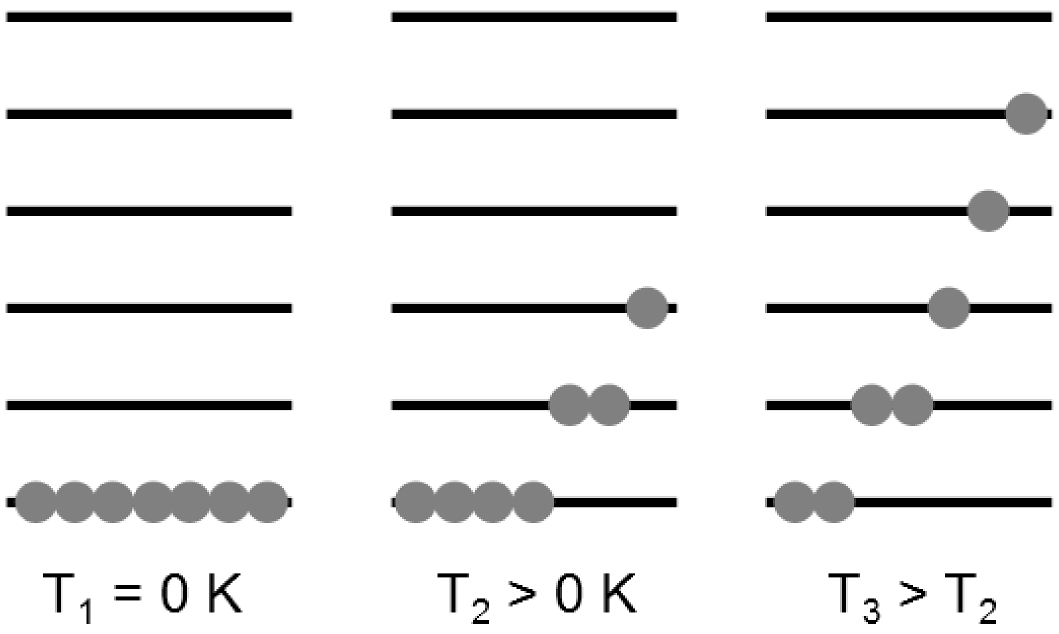
Interaction of EMR with matter

EMR is divided into different regions based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons.

	Change of spin		Change of orientation	Change of configuration	Change of electron distribution		Change of nuclear configuration
	radiowave NMR	ESR	Microwave	Infra-red	Visible and UV	X-ray	γ- ray
							
$\bar{\nu}$ in cm^{-1}		10^{-2}	1	100	10^4	10^6	10^8
λ	10m	100cm	1cm	100µm	1µm	10nm	100pm
ν in Hz	3×10^6	3×10^8	3×10^{10}	3×10^{12}	3×10^{14}	3×10^{16}	3×10^{18}
E in J/mol	10^{-3}	10^{-1}	10	10^3	10^5	10^7	10^9

Population of energy states

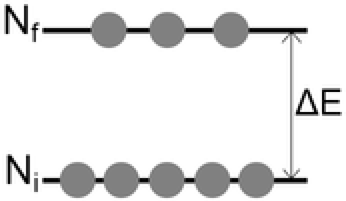
- At a given temperature various energy states of molecules are populated.
- Population of a state is the average number of molecules in a state at any given time.



Usually there is a higher population in a state of lower energy than in one of higher energy.

The Boltzmann distribution

The Boltzmann distribution defines the relative population of energy states (usually the ratio of excited states to ground state).



$$\frac{N_f}{N_i} = \exp\left(-\frac{\Delta E}{k_B T}\right)$$

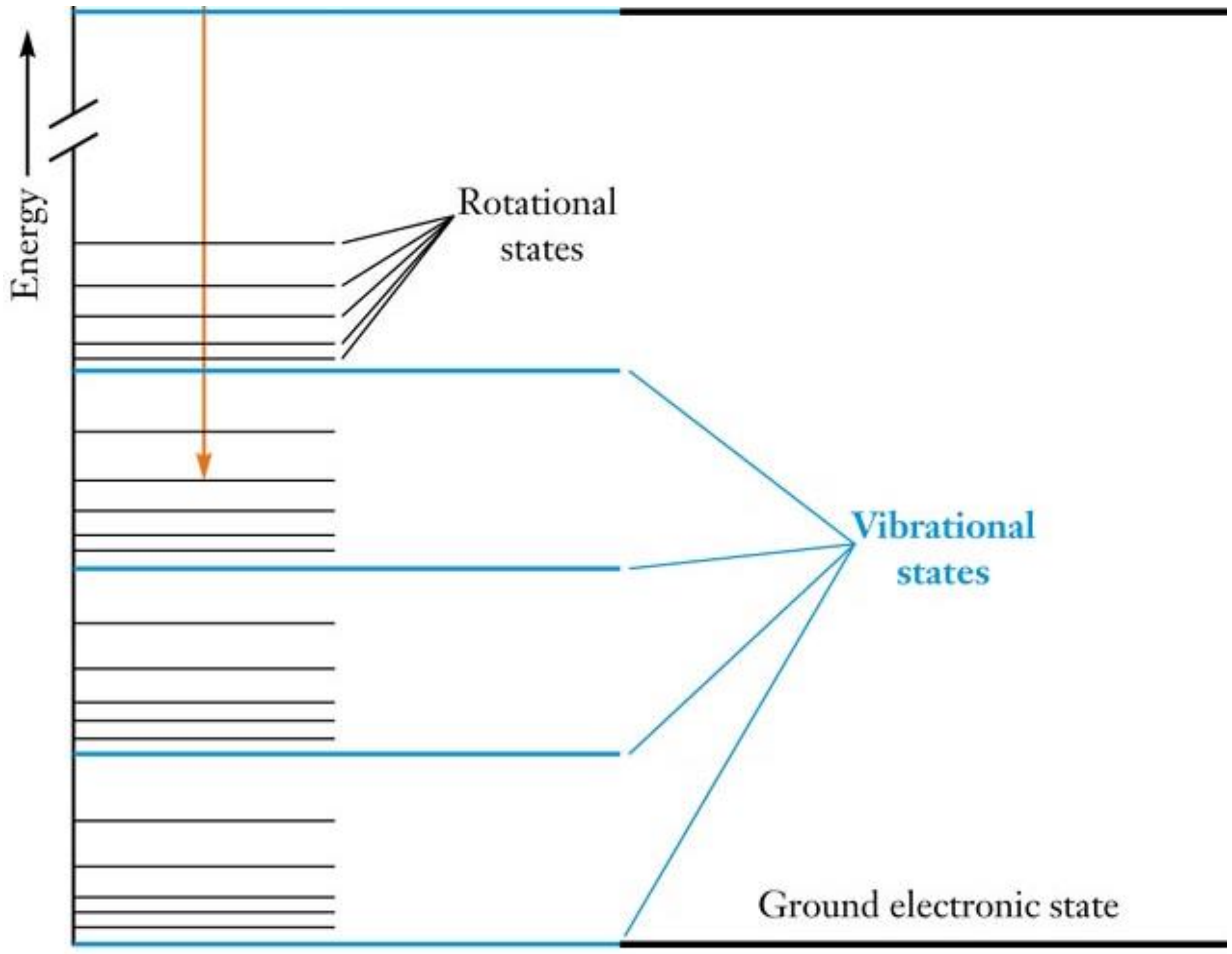
k_B = Boltzmann constant (= R / N_A) = $1.381\text{x}10^{-23}$ J K^{-1}
T = temperature (Kelvin)

Effect of temperature

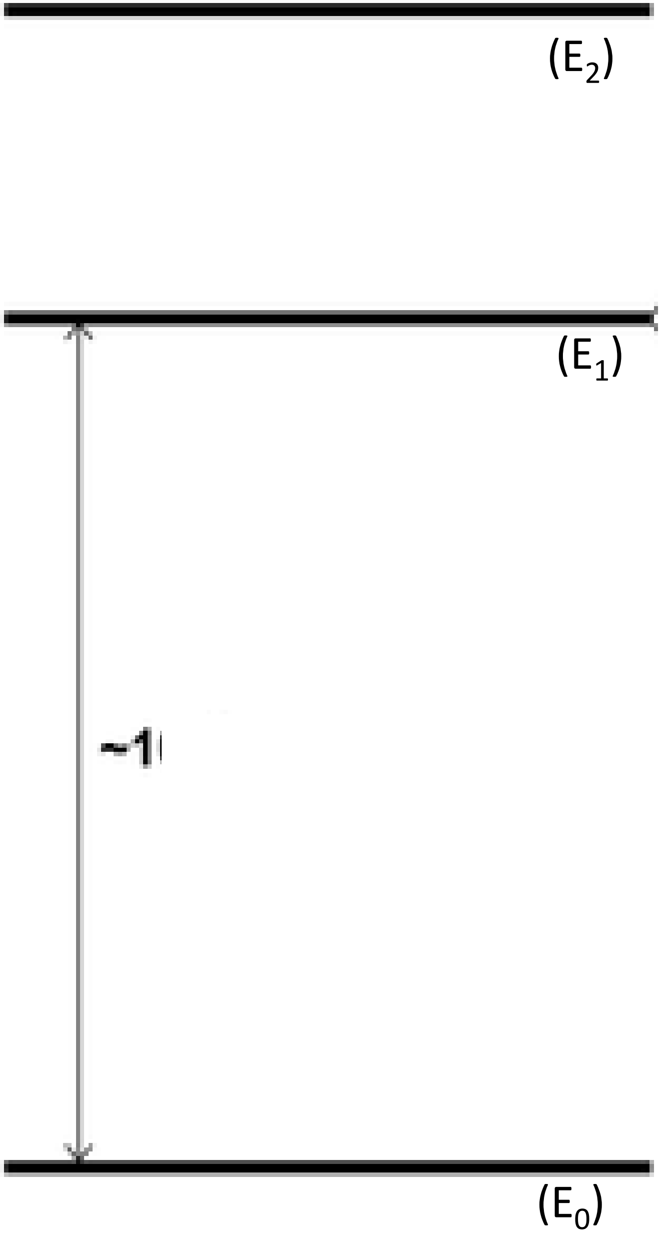
- At lower temperatures, the lower energy states are greatly populated.

- At higher temperatures, higher energy states are populated.

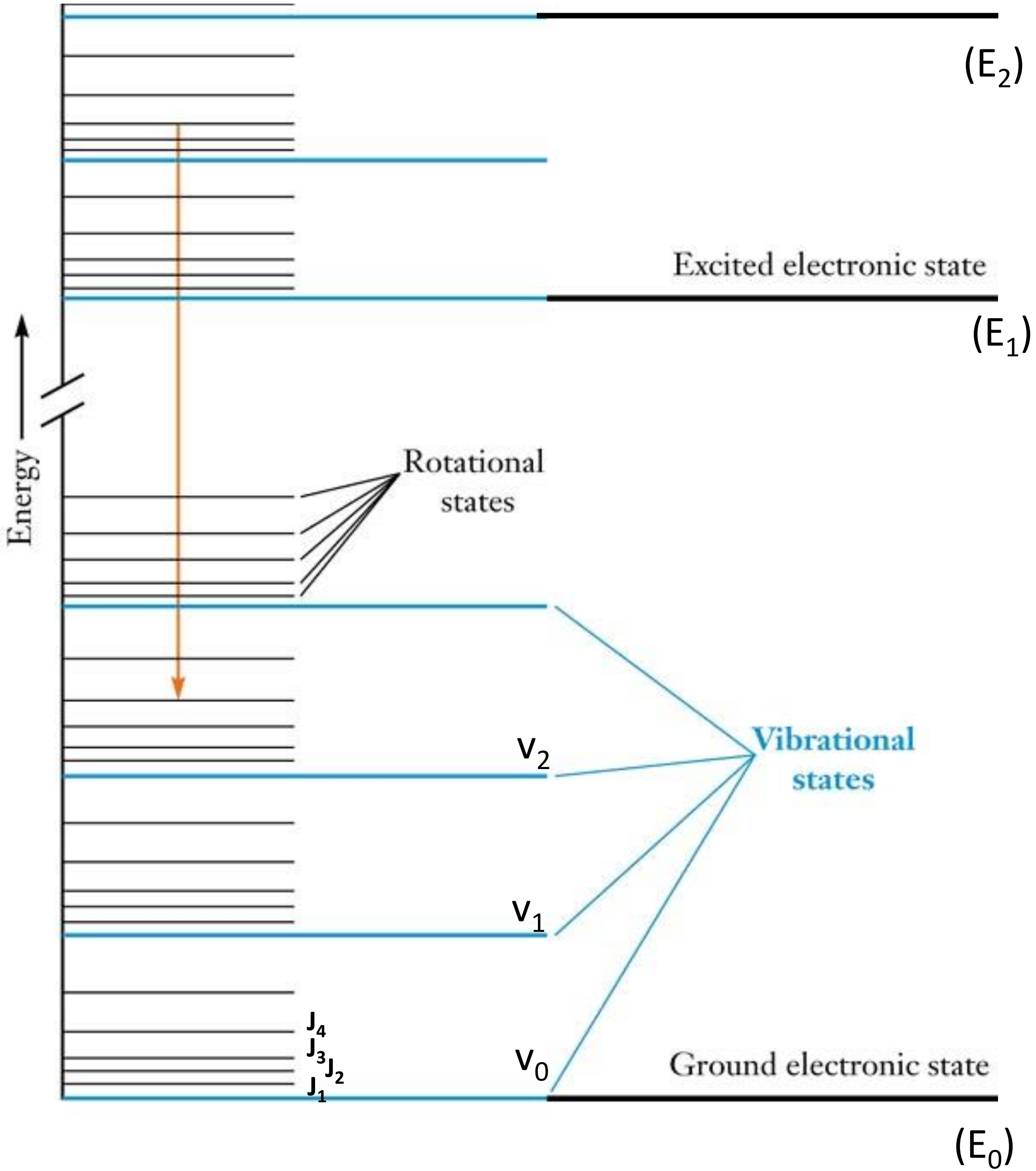
Electronic, Vibrational, and Rotational Energy Levels



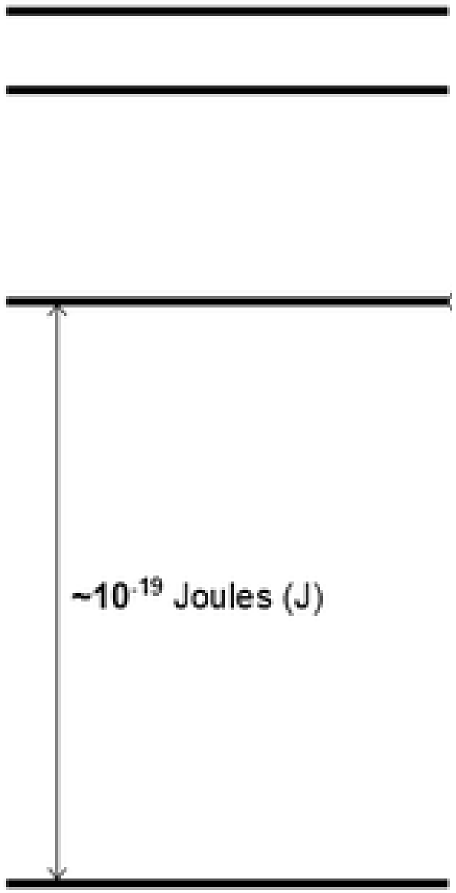
Electronic, Vibrational, and Rotational Energy Levels



Atom



Molecule



~10^{-19} Joules (J)

Electronic levels

$$\frac{N_f}{N_i} = \exp\left(-\frac{\Delta E}{k_B T}\right)$$

At 300 K. $k_B T$ ~ 2.5 kJ mol^{-1}

Electronic states ΔE = 120 kJ mol^{-1}

$$\frac{N_1}{N_0} = \exp\left(-\frac{120}{2.5}\right) \approx 1 \times 10^{-21} \approx 0$$

Molecular Spectroscopy

- **ROTATIONAL SPECTROSCOPY**

  (Microwave region)

Rotational Spectroscopy

- Rotational spectroscopy: ***caused by the change of rotational state of molecules. (Only observed in the gas phase)***

- Energy of microwave photons (0.00001-0.001 eV) matches the ranges of rotational states of molecules. Therefore it is also known as **Microwave Spectroscopy**

- Microwave region: $\nu = 3 \times 10^{10} - 3 \times 10^{12}$ Hz

$$\lambda = 1 \text{ cm} - 100\ \mu\text{m}$$

$$\bar{\nu} = 1 - 100\ \text{cm}^{-1}$$

Rotational Spectroscopy

Gross selection rule for observation of pure rotational spectrum:

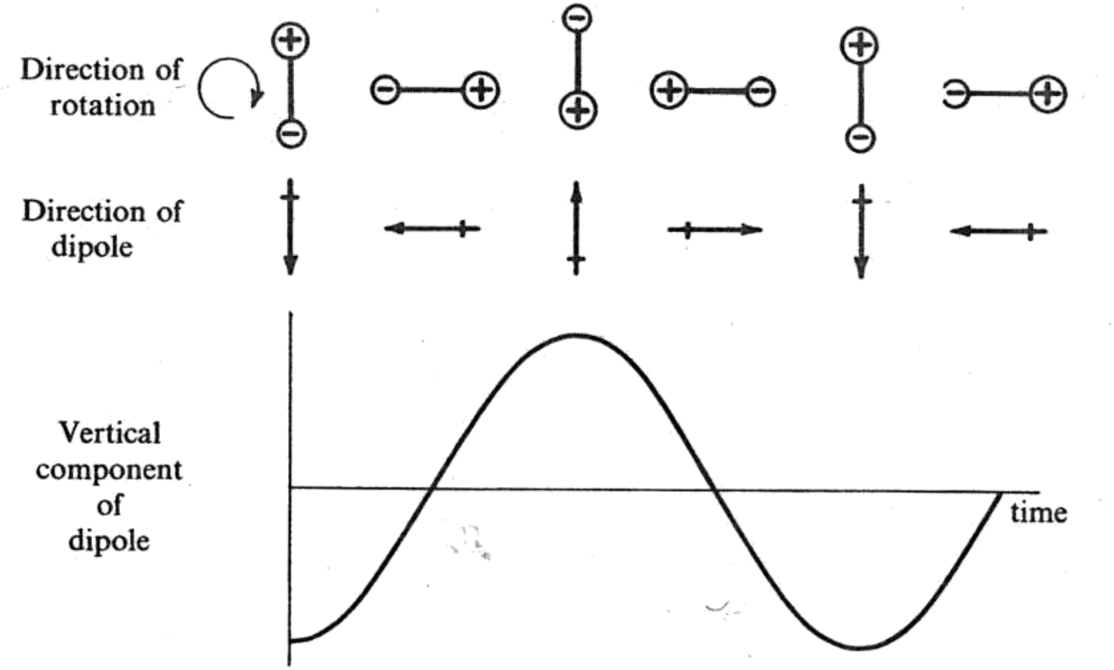
❖ Molecules having a **permanent dipole moment** (polar molecules) only show rotational spectra and are called "**microwave active**" : HCl, CO etc.

❖ Homonuclear molecules such as $\mathbf{H_2}$, $\mathbf{Cl_2}$, $\mathbf{N_2}$ etc. do not show rotational spectra and are called "**microwave inactive**"

Q. Which of the molecules N_2, CO_2, OCS, H_2O, $CH_2{=}CH_2$, C_6H_6 can have pure rotational spectrum?

Rotational Spectroscopy

❖ During the rotational motion of a polar molecule the component of dipole moment in a given direction fluctuates periodically, which is similar in form to the fluctuating electric field of radiation.



The rotation of a diatomic molecule, HCl, *showing the fluctuation in the dipole moment measured in a particular direction.*

❖When frequency of the electromagnetic radiation coincides with that of the frequency of oscillation of dipole, then absorption of light takes place and the molecule is excited to a higher rotational level.

Rotational properties of molecule

Rotational properties of any molecule can be expressed in terms of the **moments of inertia** about three perpendicular directions through the center of gravity.

$$I = \sum_i m_i r_i^2$$

r_i is the perpendicular distance of the atom *i* from the axis of rotation.
m_i is the mass of atom *i*.

❖ Thus a molecule has three principal moments of inertia, one about each axis, designated as I_A, I_B and I_C.

❖ Molecules are classified into groups according to the relative values of these three principal moment of inertia: depends mostly on their shapes

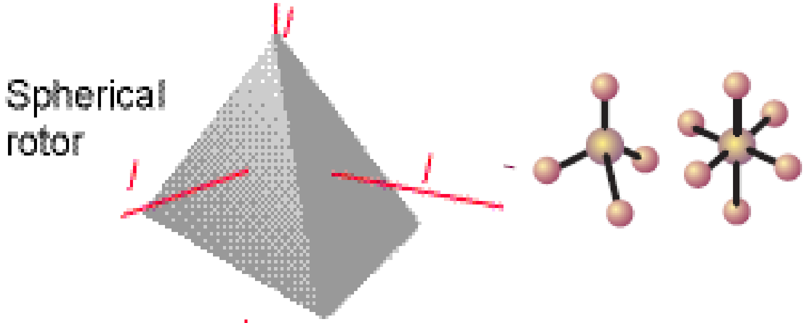
Q. Calculate the moment of inertia of an H_2O molecule around the axis defined by the bisector of the HOH angle. The HOH angle is 104.5° and the bond length is 0.957 Å. ($m_H = 1.67 \times 10^{-27}$ kg; $m_O = 13.36 \times 10^{-27}$ kg)

$$I = \sum_i m_i r_i^2$$

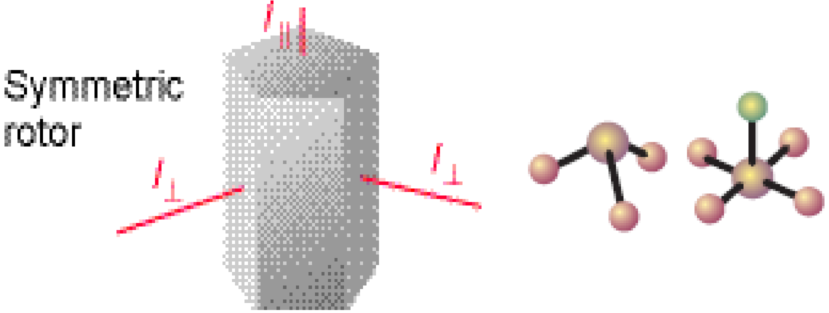
Ans. $I = 1.91 \times 10^{-47}$ kg.m^2

Rotational properties of molecule

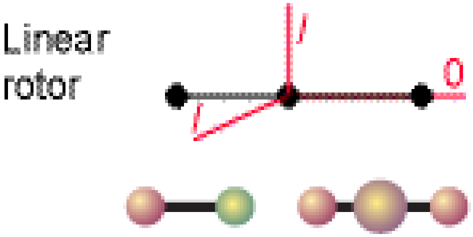
- **Spherical Rotors**: $I_B = I_C = I_A$ *e.g.* CH_4 **(Microwave inactive)**



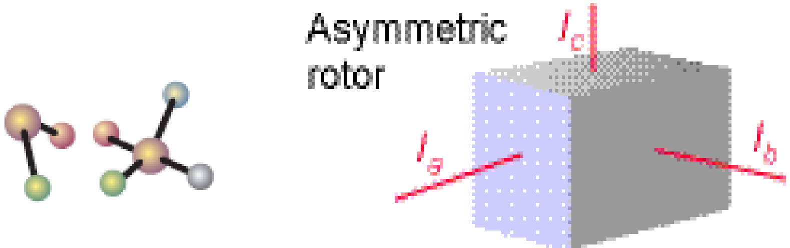
- **Symmetric Rotors**: $I_B = I_C \neq I_A$, $I_A \neq 0$ *e.g.* CH_3F, BCl_3, NH_3



- **Linear Rotor** (Linear Molecules): $I_B = I_C$, $I_A = 0$ (about the bond axis) *e.g.* HCl, OCS



- **Assymetric Rotors**: $I_B \neq I_C \neq I_A$ ***Majority of molecules belong to this class*** *e.g.* H_2O, $CH_2\text{-}CHCl$

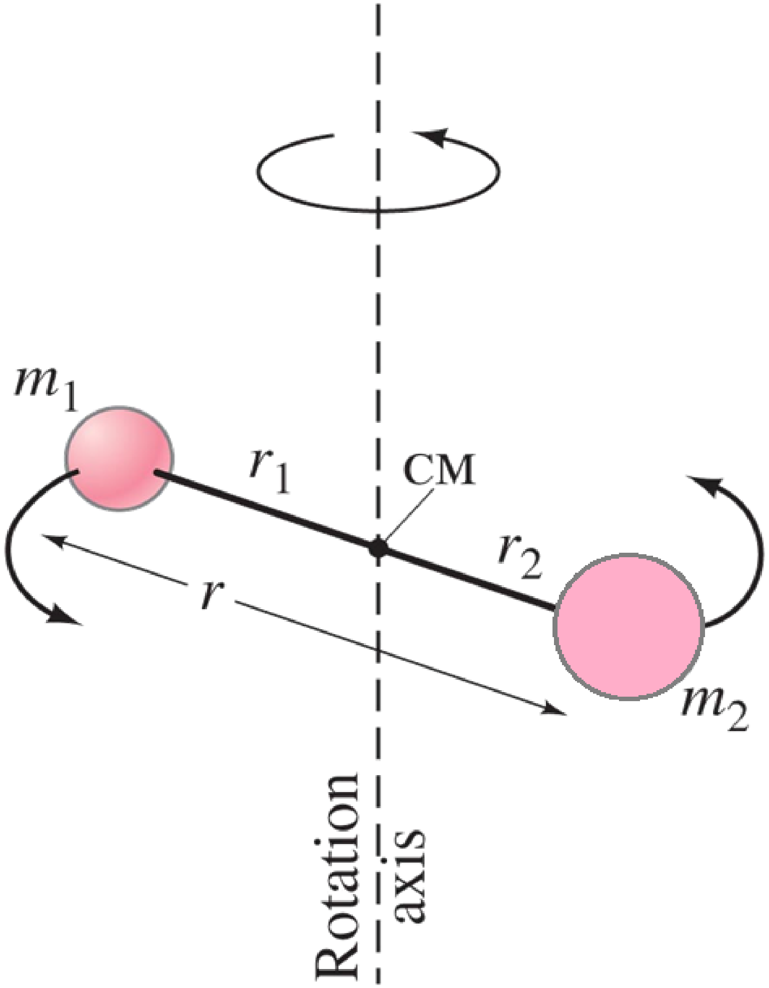


Rotational Spectra of Diatomic Molecules : Linear Rotors

Let’s consider molecules are **rigid rotor**, molecules that do not distort under stress of rotation.

Rigid Rotor Model for linear molecule

The molecule is supposed to consist of two atoms of masses m_1 and m_2 connected by a massless rigid rod of length r (bond length) and their distance from the center of mass are r_1 and r_2 , respectively



Rigid Rotor Model for Linear Molecule

The moment of inertia of the system about the center of mass (CM) is:

$$I = m_1 r_1^2 + m_2 r_2^2$$

As the system is balanced about its CM we can write $m_1 r_1 = m_2 r_2$

Also we know $r = r_1 + r_2$

On solving the equations we get $r_1 = \dfrac{m_2 r}{m_1 + m_2}$ $\qquad r_2 = \dfrac{m_1 r}{m_1 + m_2}$

$$\boxed{I = \frac{m_1 m_2 r^2}{m_1 + m_2} = \mu r^2}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \text{Reduced mass}$$

Rigid Rotor Model for Linear Molecule

Since the molecule is a rigid rotor, the potential energy is zero. And the energy of the molecule is given by

$$E_{rot} = \frac{1}{2} m_1 \mathrm{v}_1^2 + \frac{1}{2} m_2 \mathrm{v}_2^2$$

Where v_1 and v_2 are linear velocities of masses m_1 and m_2, respectively.
Since r_1 and r_2 are assumed to remain unchanged during rotation, the above equation can be written in terms of the angular velocity (ω)

$$\omega = \frac{\mathrm{v}}{r}$$

$$E_{rot} = \frac{1}{2} m_1 (\omega . r_1)^2 + \frac{1}{2} m_2 (\omega . r_2)^2$$

$$= \frac{1}{2} \omega^2 (m_1 r_1^2 + m_2 r_2^2) = \frac{1}{2} I\omega^2 = \frac{\mathrm{L}^2}{2I}$$

Where **L** is the angular momentum = Iω
L is a vector and has magnitude as well as direction. The direction of the angular momentum vector is conventionally taken to be along the axis about which rotation occurs.

$$\boxed{E = \frac{1}{2} I\omega^2 = \frac{L^2}{2I}}$$

We know that $L = \sqrt{J(J+1)}\,\hbar$ $(\hbar = h/2\pi)$

Putting this value in the previous equation,

$$\boxed{E_J = \frac{h^2}{8\pi^2 I} J(J+1) \ \text{joules}}$$

J = rotational quantum number = 0, 1, 2, ... (integral values)

I can be either I_B or I_C since both are equal.

The rotational energy is quantized, the molecule can have only certain permitted values of rotational energy.

In the microwave region, rotational spectra are usually discussed in terms of wavenumber in cm^{-1}

$$\boxed{\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \ \text{cm}^{-1} \qquad (J = 0, 1, 2, \ldots)}$$

$$\boxed{\varepsilon_J = BJ(J+1)\ \text{cm}^{-1}} \quad (J = 0, 1, 2, \dots)$$

***B* is the rotational constant**

$$\boxed{B = \frac{h}{8\pi^2 Ic}\ \text{cm}^{-1}}$$

Energy of rotational level:

$J = 0$, $\varepsilon_{J=0} = 0$ (Molecule is not rotating)

$J = 1$, $\varepsilon_{J=1} = 2B$

$J = 2$, $\varepsilon_{J=2} = 6B$

$J = 3$, $\varepsilon_{J=3} = 12B$

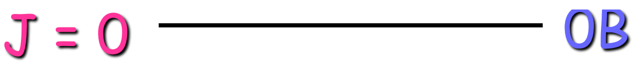
Energy difference between two rotational states

$$\varepsilon_{J=1} - \varepsilon_{J=0} = 2B\ \text{cm}^{-1}$$

$$\varepsilon_{J=2} - \varepsilon_{J=1} = 4B\ \text{cm}^{-1}$$

In general the energy difference between two rotational levels J and $(J+1)$ is

$$\boxed{\varepsilon_{J+1} - \varepsilon_J = \bar{\nu} = 2B\,(J+1)\ \text{cm}^{-1}}$$



Energy of rotational levels (Not equally spaced)

Rotational Spectrum of a Diatomic Rigid Rotor

Selection Rule

Transitions in which *J* changes by one unit are only possible, all other transitions are spectroscopically forbidden

$$\boxed{\begin{aligned}&\Delta j = \pm 1\\ &\Delta j = +1\ (absorption)\\ &\Delta j = -1\ (emission)\end{aligned}}$$

The wave numbers/energy associated with different transitions

$$\bar{\nu}_{J=1\rightarrow J=0} = 2B\ \text{cm}^{-1}$$ First spectral line

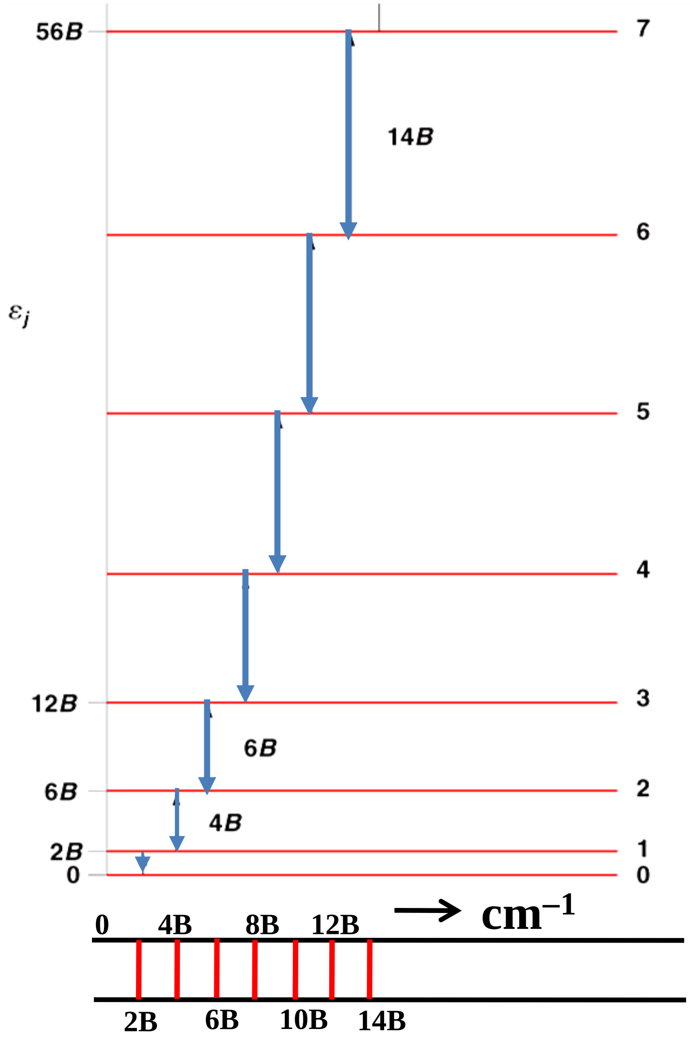
$$\bar{\nu}_{J=2\rightarrow J=1} = 4B\ \text{cm}^{-1}$$ Second spectral line

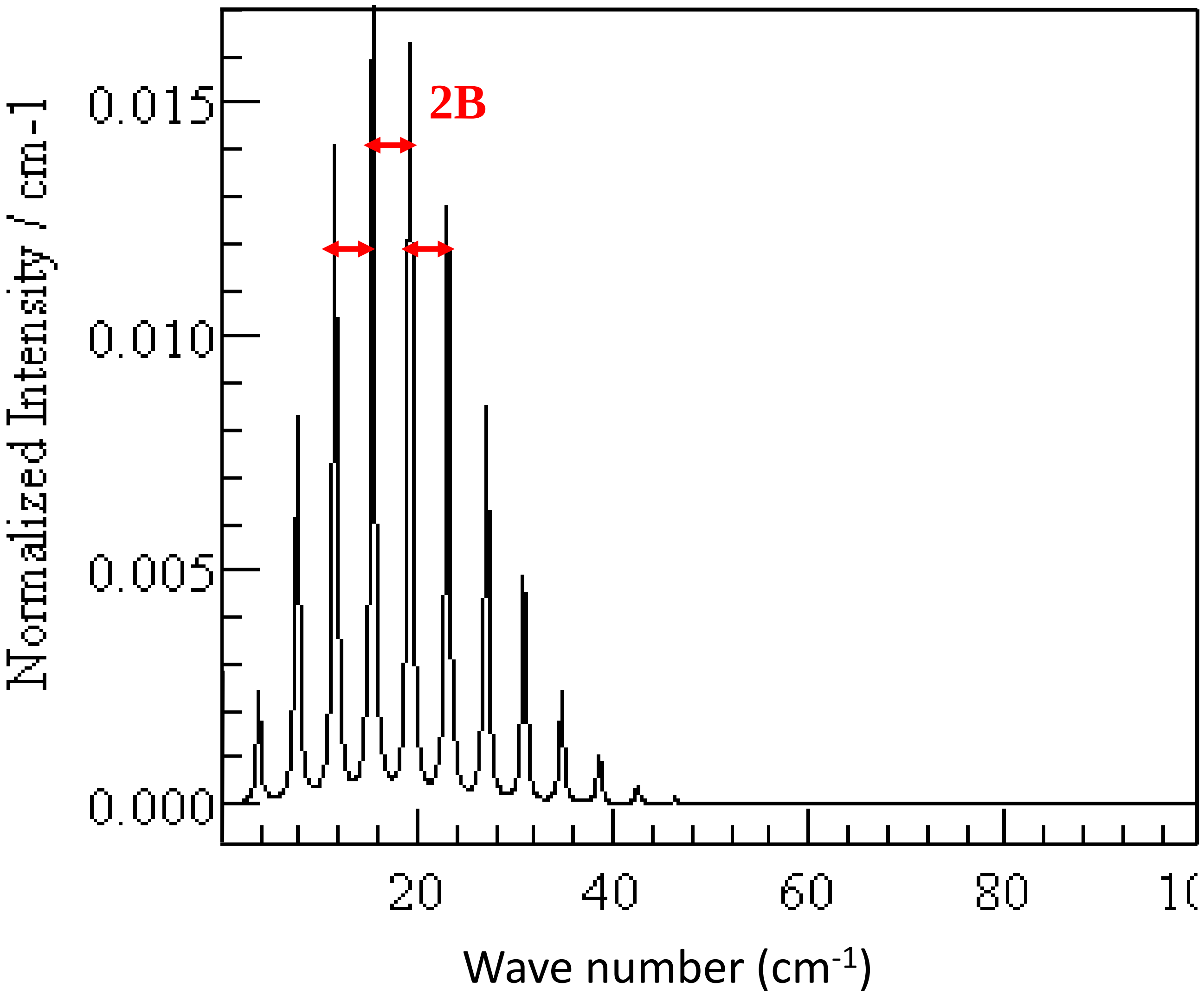
For a transition from *J* to (*J*+*1*)

$$\bar{\nu}_{J+1\rightarrow J} = B(J+1)\,(J+2) - BJ(J+1)\,\text{cm}^{-1}$$

$$\boxed{\bar{\nu}_{J\rightarrow J+1} = 2B(J+1)\,\text{cm}^{-1}}$$

Spectrum consists of equidistant (2*B*) lines




2B
Normalized Intensity / cm-1
0.015
0.010
0.005
0.000
20
40
60
80
1(
Wave number (cm^{-1})

Effect of Isotope Substitution on the Rotational Spectra

Diatomic molecules having different isotopes of the same element show different rotational spectra e.g. HCl and DCl; $^{12}C^{16}O$ and $^{13}C^{16}O$ etc.

Mass of the isotopic atoms are different ⇒ the reduced mass (μ), moment of inertia (I), rotational constant (B) are different

$$B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2 (\mu r^2) c}$$

Since there is no appreciable change in the internuclear distance (*r*) on isotopic substitution ⇒ $B \propto 1/\mu$

Spectrum of heavier species will show smaller value of *B* and hence smaller separation between the spectral lines.

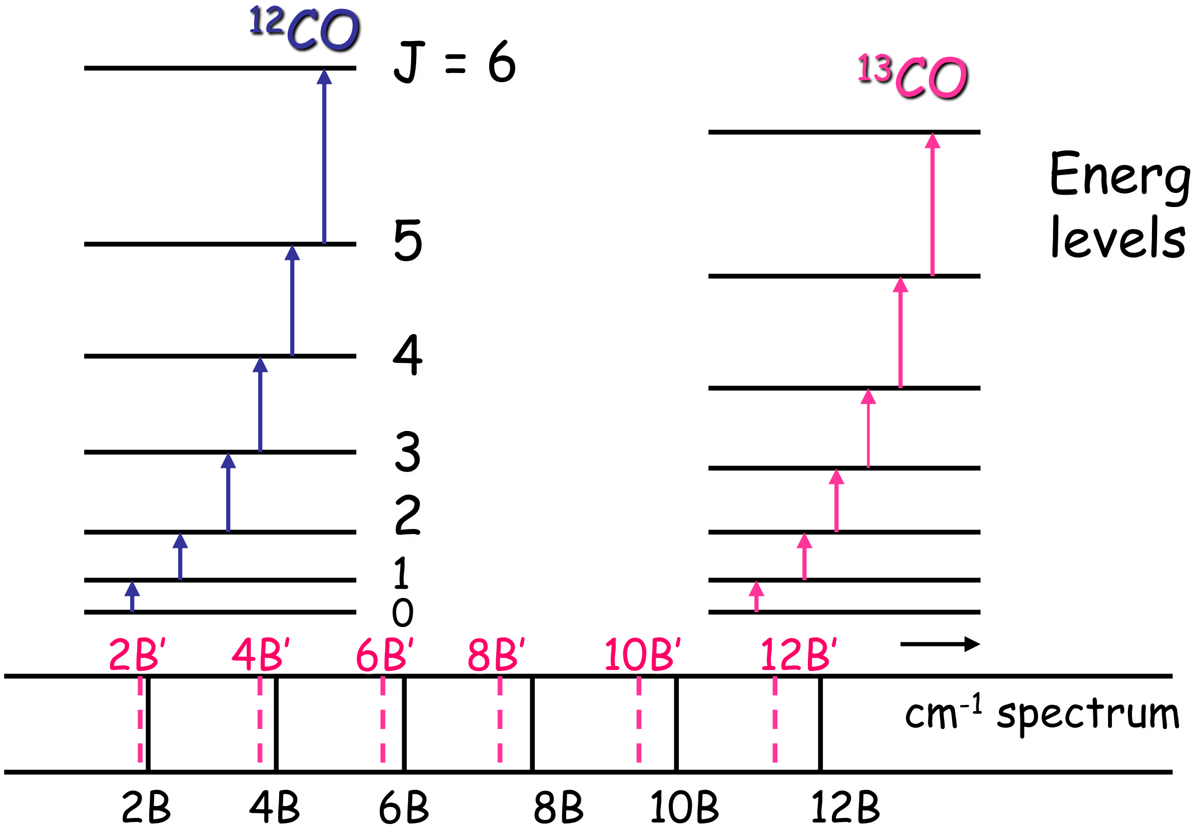
Comparison of rotational spectra of molecules with isotope substitution can determine:

(i) isotopic masses accurately, to within 0.02% of other methods for atoms in gaseous molecules

(ii) isotopic abundances from the absorption relative intensities.

Effect of isotopes

From $^{12}C^{16}O \rightarrow {}^{13}C^{16}O$, mass increases, B decreases ($\propto 1/I$), so energy levels lower and smaller separation between the spectral lines is observed



Application of Microwave Spectroscopy

- At lower energy levels of rotation the spectral lines are equidistant. This is utilized in the determination of the bond-distance in diatomic molecules.

- Is also useful in determining the moment of inertia and reduced mass of diatomic molecules.

- From two consecutive lines accurate values of B, and J can be determined.

- One fascinating area where microwave analysis is being used is in the chemical examination of interstellar space.

- Nearly 130 molecules/ions have been identified using rotational emission spectra.

Q1. Calculate the moment of inertia of a diatomic molecule, HCl, with H—Cl bond length is 1.27 Å. [1 a.m.u = 1.66×10^{-27} kg]

$I = \mu r^2$

Q2. Identify the molecules that exhibit rotational spectrum:

N_2, CO_2, SO_2, BF_3, NH_3, H_2O

Q3. Classify the following molecules as spherical, linear, symmetric or asymmetric tops.

SF_6, NH_3, NO_2, CS_2, CH_4, CF_3I, BH_3, BeH_2, SO_2, C_6H_6, XeF_6

Q4. Assume that $^{12}C^{16}O$ has the bond length of 113 pm. Calculate the value of its rotational constant in cm^{-1}. [1 a.m.u = 1.66×10^{-27} kg]

$$\mathbf{I = 1.456 \times 10^{-46}\ kg\ m^2}$$

$$\mathbf{B = 1921.18\ m^{-1} = 1.921\ cm^{-1}}$$

Q5. The rotational spectrum of BrF shows a series of equidistant lines of 0.71433 cm-1 apart. Calculate the rotational constant, B, and hence the moment of inertia and bond length of the molecule.

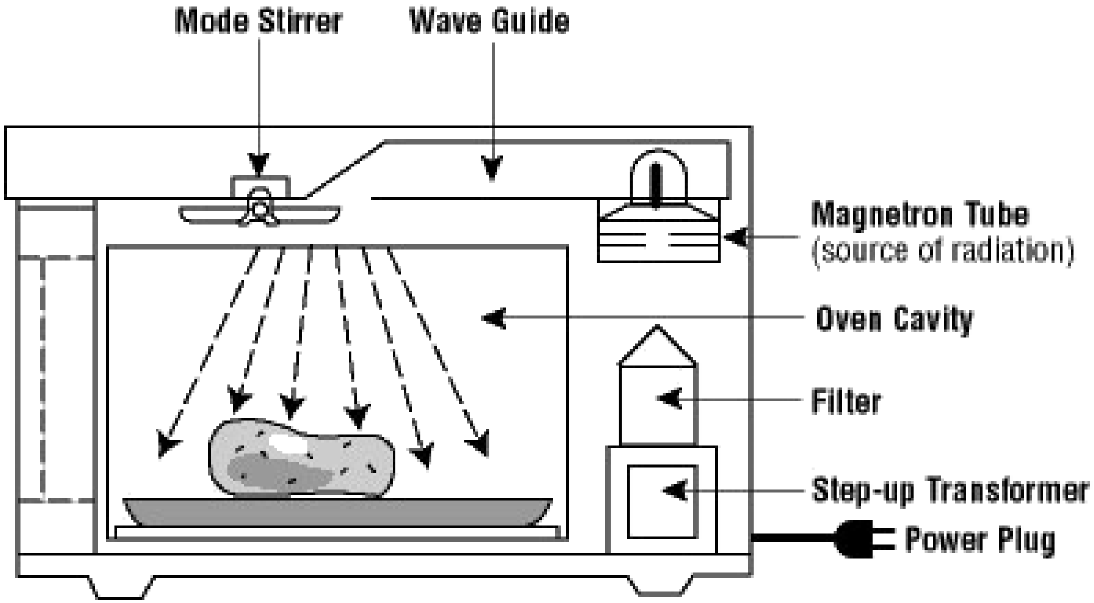
(m_{Br} = 133.4 x 10^{-27} kg; m_F = 31.73 x 10^{-27} kg]`

Ans. B = 0.35717 cm^{-1}; I = 7.837 x 10^{-46} kgm^2

r = 1.748 Å

Microwave Oven

Do you know what is the basic principle of cooking in a microwave oven !!



Non-Rigid Rotor Model

In reality, the molecules vibrate ⇒ can not be strictly rigid rotors

J is high ⇒ rotational energy high ⇒ a tendency for the bond to stretch because of the centrifugal distortion ⇒ moment of inertia increases ⇒ B decreases and the spectral line separation decreases

Therefore a better model for representing the rotations of the molecule:

Consider the diatomic molecule to consist of **two atoms connected by a massless spring** and this is known as **non-rigid rotor model**.

Solving the Schrodinger equation for a non-rigid rotor we can get

$$\boxed{\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 \ \ \mathrm{cm}^{-1}}$$

***D* is the centrifugal distortion constant.**

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc} = \frac{4B^3}{\overline{\omega}^2}\ \mathrm{cm}^{-1}$$

Where $\overline{\omega}$ is the vibrational frequency of the bond

k is the force constant = $4\pi^2\overline{\omega}^2 c^2 \mu$

The energy difference between two rotational levels *J* and (*J* +1) is

$$\varepsilon_{J+1} - \varepsilon_J = \bar{\nu} = 2B\,(J+1) - 4D\,(J+1)^3 \text{ cm}^{-1}$$

Selection remains same i.e. $\Delta J = \pm 1$

Wavenumber for a transition from *J* to (*J*+*1*) is given as

$$\boxed{\bar{\nu}_{J \to J+1} = 2B\,(J+1) - 4D(J+1)^3 \text{ cm}^{-1}} \qquad \text{(Absorption spectra)}$$

$$\bar{\nu}_{0 \to 1} = 2B\,(0+1) - 4D(0+1)^3 = (2B - 4D) \text{ cm}^{-1}$$

$$\bar{\nu}_{1 \to 2} = 2B\,(1+1) - 4D(1+1)^3 = (4B - 32D) \text{ cm}^{-1}$$

$$\bar{\nu}_{2 \to 3} = 2B\,(2+1) - 4D(2+1)^3 = (6B - 108D) \text{ cm}^{-1}$$

Separation between 1st and 2nd line = $(4B - 32D) - (2B - 4D) = (2B - 28D)$ cm^{-1}

Between 2nd and 3rd line = $(6B - 108D) - (4B - 32D) = (2B - 76D)$ cm^{-1}

- **The spectral lines are no longer equidistant.**
- **The separation decreases with increasing *J* value.**

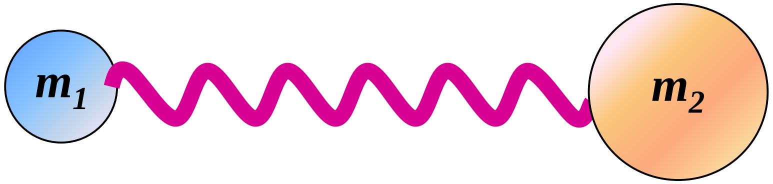
Molecular Spectroscopy

- **VIBRATIONAL SPECTROSCOPY**
  (IR region)

Vibrational Spectroscopy

Vibrational spectroscopy: caused by the change of vibrational state of molecule.

The bond between atoms is considered as a massless spring. The atoms are not static, they vibrate about the mean position



The appropriate frequencies for molecular vibrations are in the *Infrared* region of the electromagnetic spectrum therefore it is also known as **Infrared Spectroscopy**

Spectral Region	Frequency (Hz)	Wavenumber **(cm^{-1})**	Wavelength (μm)
Near IR (NIR)	3.8×10^{14} - 1.2×10^{14}	**12800 – 4000**	0.8 to 2.5
Mid IR	1.2×10^{14} - 6.0×10^{12}	**4000 - 400**	2.5 to 50
Far IR	6.0×10^{12} - 3.0×10^{11}	**400 - 100**	50 to 1000

Gross Selection Rule for Vibrational Spectroscopy

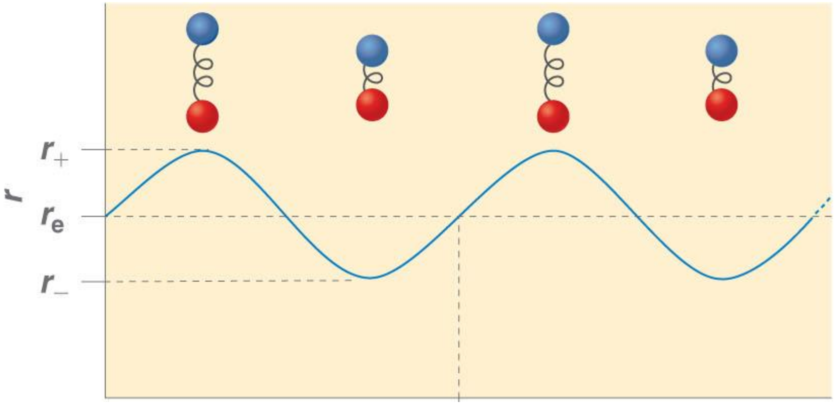
- The molecules, which undergo a change in dipole moment during vibration, show vibrational spectra. **Such vibrations are infrared active**.

- The electric dipole moment depends on the charge separation and the inter-nuclear distance. When a molecule (having permanent dipole moment) vibrates the dipole moment changes as the inter-nuclear separation changes.

- If no change in dipole moment occurs, when the molecule vibrates, there will be no interaction between the EMR and the molecule. Such a vibration is said to be IR-inactive.

- For diatomic molecule the molecule must be polar.

- Vibrational spectra are observed only in heteronuclear diatomic molecules (HCl, CO etc.) and they are called IR active. Homonuclear diatomic molecules are IR Inactive (H_2, O_2 etc.) .

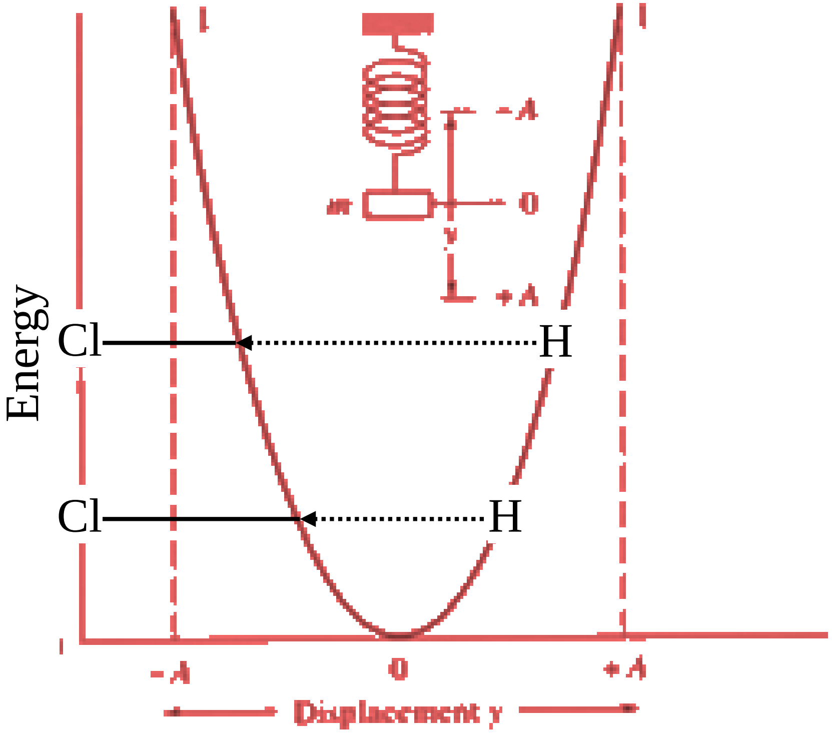


The Vibrating Diatomic Molecule

A vibrating diatomic molecule can be imagined as a

(1) Simple Harmonic Oscillator
(2) Anharmonic Oscillator

Simple Harmonic Oscillator : The atoms vibrate approximately like an harmonic oscillator (behaving like a perfectly elastic spring) and obeying **Hooke's Law**:



The oscillation frequency

$$\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \text{ Hz}$$

k = force constant

μ = reduced mass

Converting frequency into wave number

$$\overline{\omega}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

Vibrational Energy of Diatomic Molecules

Vibrational energy, like all other molecular energies, are quantized
By solving Schrodinger equation for vibrational motion we get

For derivation, see ATKINS 8th edition, page 291-297

Vibrational energy levels

$$\boxed{E_\mathrm{v} = (\mathrm{v}+\tfrac{1}{2})\, h\omega_{osc} \text{ joules} \qquad (\mathrm{v} = \text{vibrational quantum number} = 0, 1, 2, \ldots.)}$$

$$\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \text{ Hz} = \text{oscillation frequency}$$

k = force constant
μ = reduced mass

$$\boxed{\varepsilon_\mathrm{v} = \frac{E_\mathrm{v}}{hc} = (\mathrm{v}+\tfrac{1}{2})\, \bar{\omega}_{osc} \quad \mathrm{cm}^{-1}}$$

$$\bar{\omega}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

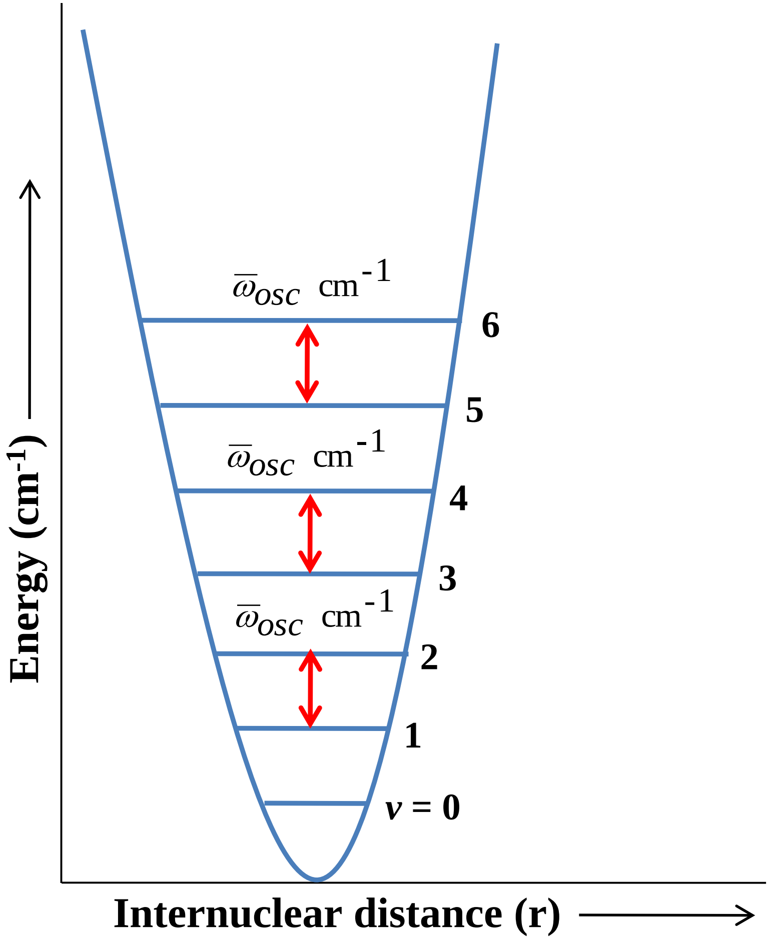
Vibrational Energy of Diatomic Molecules

When v = 0, the potential energy of the molecule:

$$\boxed{\varepsilon_0 = \frac{1}{2}\,\bar{\omega}_{osc}\ \text{cm}^{-1} \qquad (\text{v} = 0)}$$

Zero point energy

- Molecule can never have zero vibrational energy.
- Atoms can never be completely at rest relative to each other.
- Since the position of an atom is not completely uncertain, and therefore the momentum and hence the energy, can not be exactly zero.



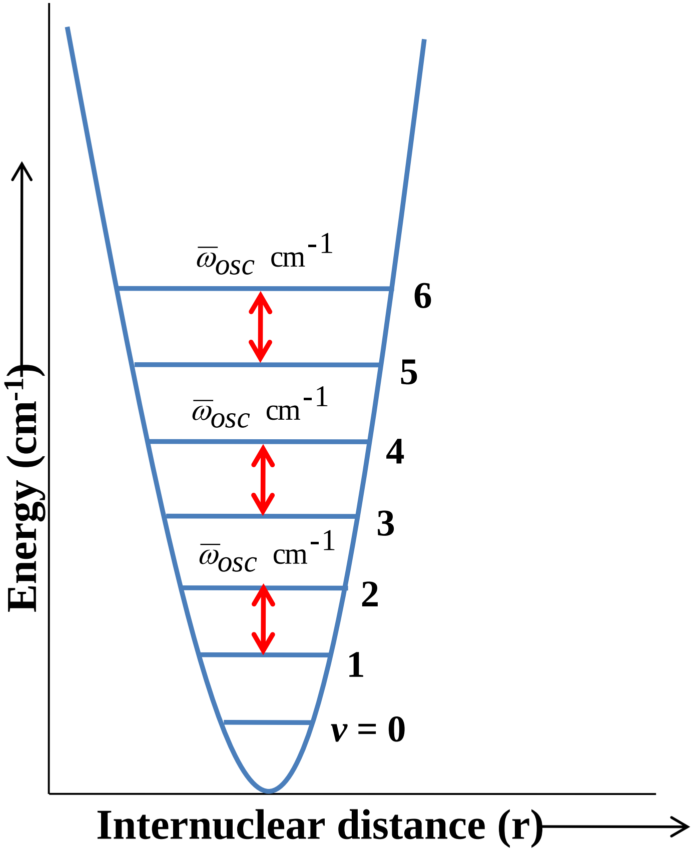
Vibrational Energy levels of Diatomic Molecules

$$\varepsilon_0 = \frac{1}{2}\,\bar{\omega}_{osc}\ \mathrm{cm}^{-1} \qquad (\mathrm{v}=0)$$

$$\varepsilon_1 = \frac{3}{2}\,\bar{\omega}_{osc}\ \mathrm{cm}^{-1} \qquad (\mathrm{v}=1)$$

$$\varepsilon_2 = \frac{5}{2}\,\bar{\omega}_{osc}\ \mathrm{cm}^{-1} \qquad (\mathrm{v}=2)$$

$$\varepsilon_4 = \frac{7}{2}\,\bar{\omega}_{osc}\ \mathrm{cm}^{-1} \qquad (\mathrm{v}=3)$$



Spacing between adjacent vibrational sates:

$$\boxed{\Delta\varepsilon_{\mathrm{v}} = \bar{\omega}_{osc}\ \ \mathrm{cm}^{-1}\ \ \text{for any v}}$$

$$\bar{\omega}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\ \ \mathrm{cm}^{-1}$$

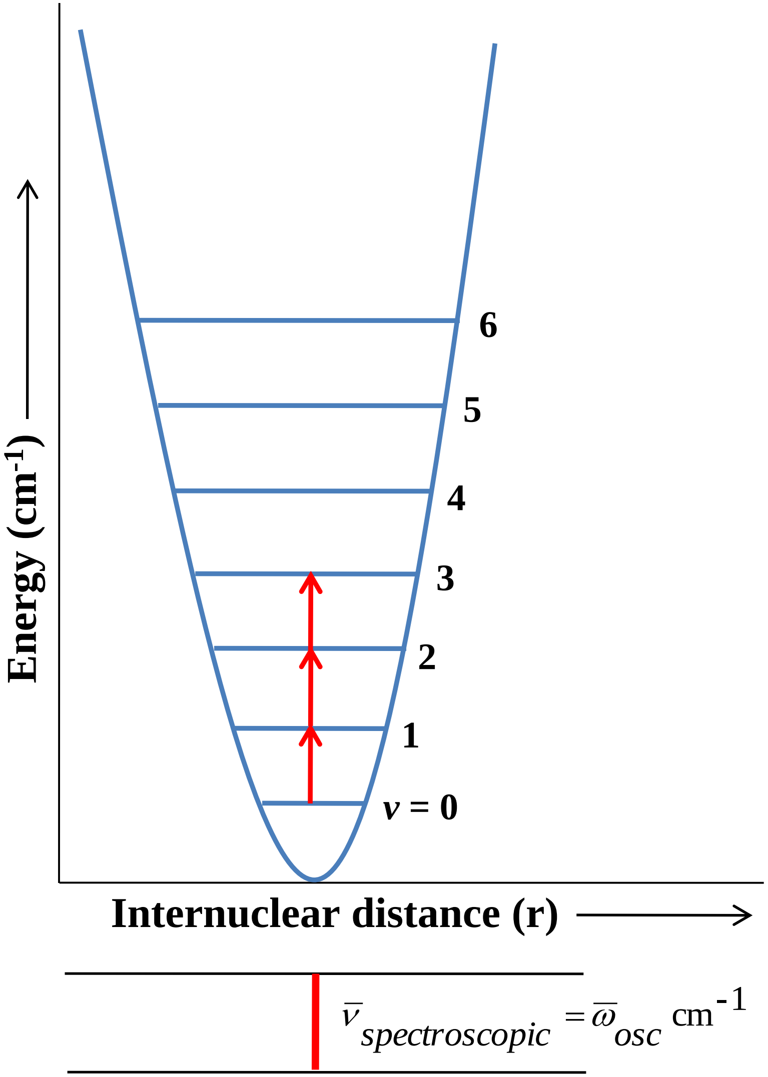
The vibrational levels of simple harmonic oscillator are equidistant.

Specific Selection Rule for a Harmonic Oscillator

$$\boxed{\begin{aligned}&\Delta v = \pm 1\\&\Delta v = +1 \text{ (absorption)}\\&\Delta v = -1 \text{ (emission)}\end{aligned}}$$

$$\varepsilon_{v \rightarrow v+1} = \bar{\omega}_{osc} \ \text{cm}^{-1}$$

$$\boxed{\bar{\nu}_{spectroscopic} = \bar{\omega}_{osc} \ \text{cm}^{-1}}$$



✓ Since all the vibrational levels are equally spaced, transition between any two neighboring states will give rise to the same energy change.

✓ Thus only one vibrational peak is observed in the IR spectrum of a diatomic simple harmonic oscillator.

Q1. Which of the following vibrational transitions will be observed for a diatomic molecule (treated as a harmonic oscillator):
v = 1 to v = 3; v = 2 to v = 3; v = 5 to v = 4.

Q2. Calculate the force constant in N/m unit for $^{1}H^{35}Cl$ that has equilibrium oscillation frequency of 2990 cm^{-1}

Ans. $$\overline{\omega}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \ \mathrm{cm}^{-1}$$

Force constant $k = (2\pi c\overline{\omega}_{osc})^2\mu = 516\ Nm^{-1}$

Q3. Arrange in the increasing order of the stretching frequencies: C-Br, C-F, C-Cl and explain the trend.

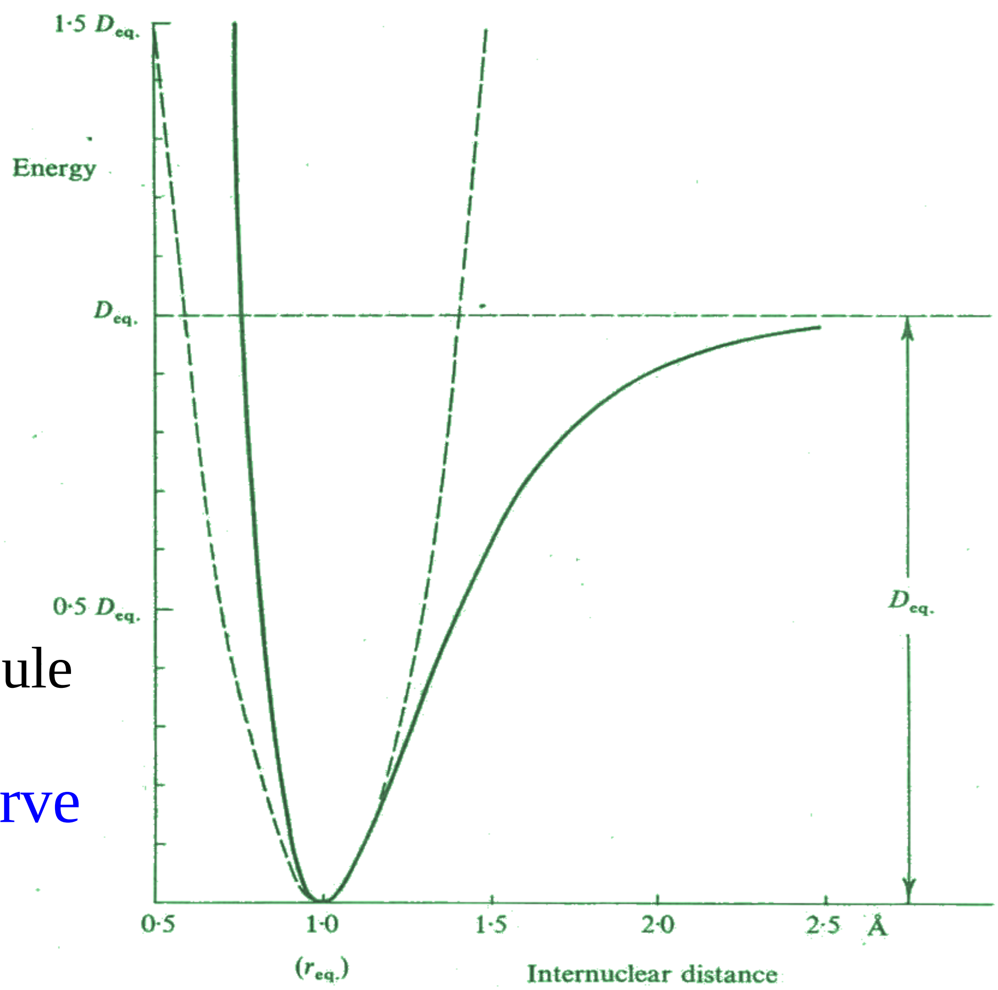
Ans. Increasing order of stretching frequency: lighter terminal atom has higher frequency

C-Br < C-Cl < C-F

Anharmonic Oscillator Model

Real bonds, although elastic, do not exactly obey Hook's law especially at higher vibrational levels.

If the bond between atoms is stretched there comes a point at which it will break – the molecule will dissociate into atoms



An empirical expression for this curve was derived by P. M. Morse and is called the Morse function

$$E_{Morse} = D_{eq}(1 - e^{-a(r-r_e)})^2$$

D_{eq} is the dissociation energy
a is a constant for a particular molecule

The curve is called the Morse Curve

By solving Schrodinger equation for an anharmonic oscillator we get the allowed vibrational energy levels:

$$\boxed{\varepsilon_v = (v+\frac{1}{2})\,\bar{\omega}_e - (v+\frac{1}{2})^2\,\bar{\omega}_e x_e \quad \mathrm{cm}^{-1}} \qquad (v = 0, 1, 2, \ldots.)$$

$\bar{\omega}_e$ = equilibrium oscillation frequency of the anharmonic system

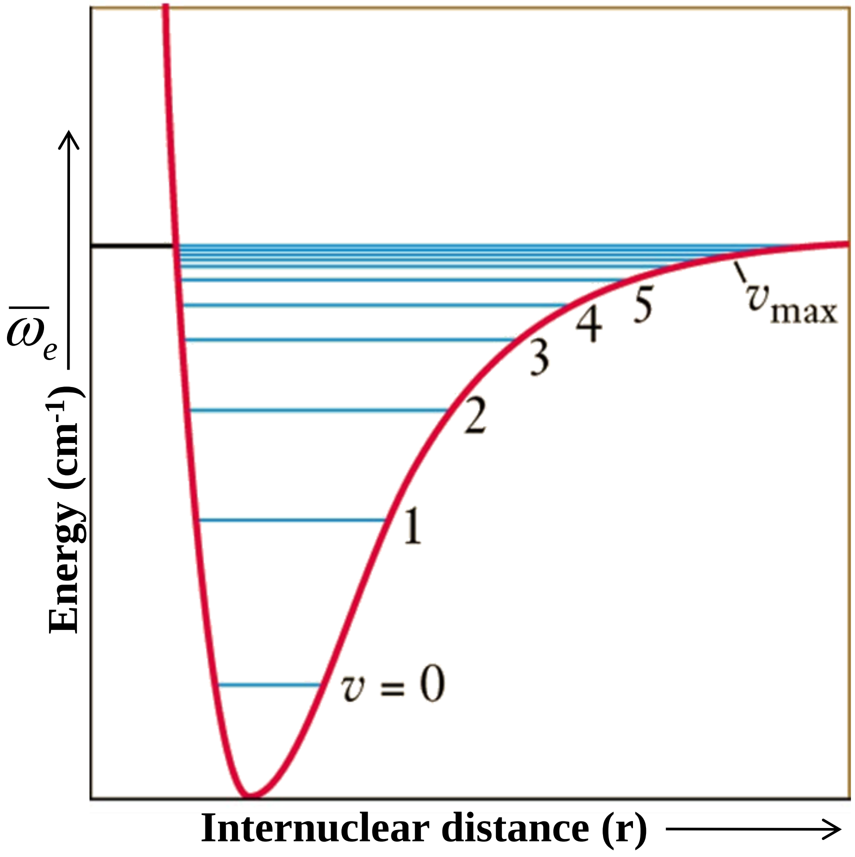
x_e = anharmonicity constant. It has small positive magnitude

$$\varepsilon_{v=0} = \tfrac{1}{2}\,\bar{\omega}_e - \tfrac{1}{4}\,\bar{\omega}_e x_e$$

$$\varepsilon_{v=1} = 3/2\,\bar{\omega}_e - 9/4\,\bar{\omega}_e x_e$$

$$\varepsilon_{v=2} = 5/2\,\bar{\omega}_e - 25/4\,\bar{\omega}_e x_e$$

The vibrational levels crowd more closely together with increasing v.



Selection rule for the anharmonic oscillator

Δv = ± 1, ± 2, ± 3, …
Δv = + 1, + 2, + 3… (absorption)
Δv = –1, –2, –3 … (emission)

Boltzmann distribution says the population of the v =1 state is around 1% of the ground state population.

Consider only the transitions from v=0 state

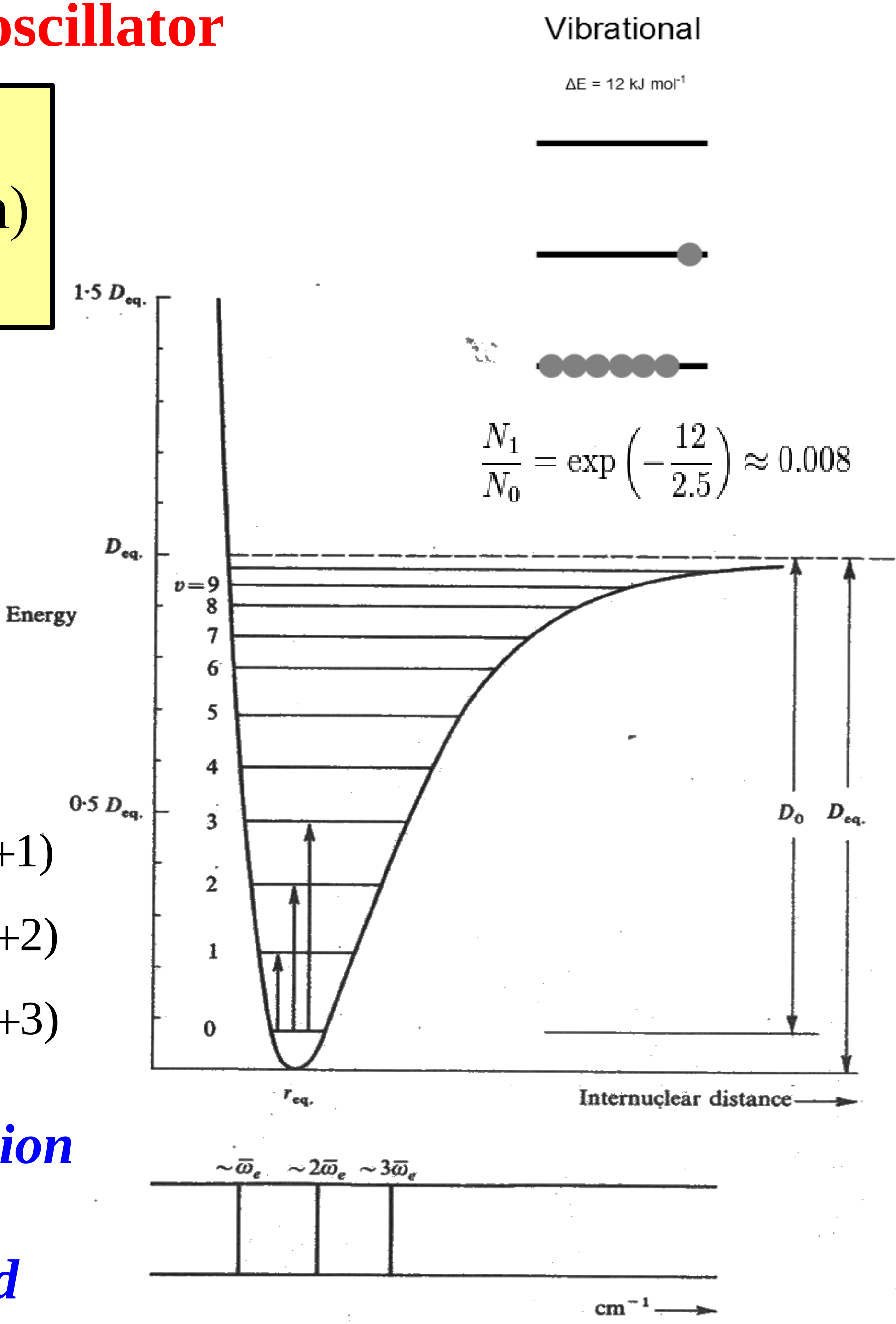
Only the lines of Δv = ± 1, ± 2, ± 3 have observable intensity; transition probability rapidly diminishes for higher jumps

$\varepsilon_{0\rightarrow1} = \bar{\omega}_e (1 - 2x_e)$ cm^{-1} v=0 → v = 1 (Δv=+1)

$\varepsilon_{0\rightarrow2} = 2\bar{\omega}_e (1 - 3x_e)$ cm^{-1} v=0 → v = 2 (Δv=+2)

$\varepsilon_{0\rightarrow3} = 3\bar{\omega}_e (1 - 4x_e)$ cm^{-1} v=0 → v = 3 (Δv=+3)

v =0 → v = +1 : *fundamental absorption*
v =0 → v = +2 : *first overtone band*
v =0 → v = +3 : *second overtone band*



$$\frac{N_1}{N_0} = \exp\left(-\frac{12}{2.5}\right) \approx 0.008$$

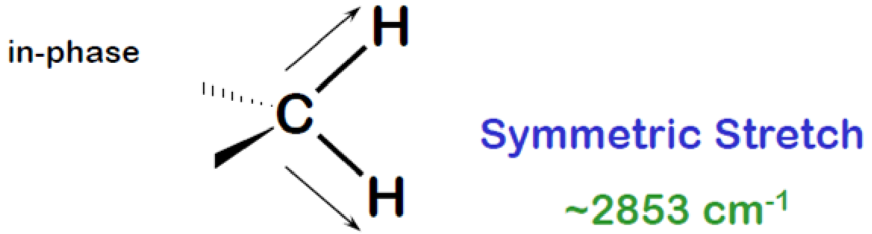
Vibrations of Polyatomic Molecules

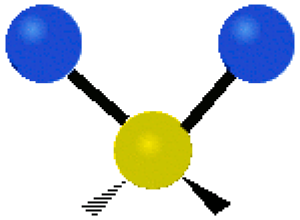
There are many possible vibrational modes giving rise to complicated spectra with many peaks

The fundamental vibrations of a molecule are

1. Stretching vibration: The stretching vibration in which the distance between two atoms around a bond varies with time.

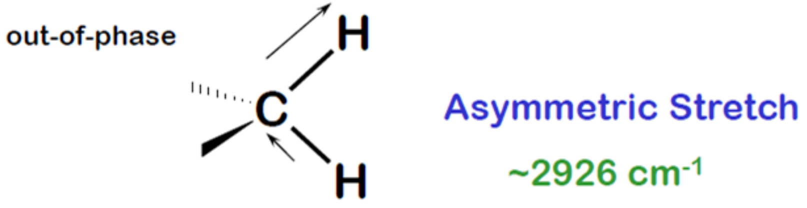
❖ *Symmetrical stretching* : the side atoms move away from the central atom along the molecular axis and move back toward the central atom.

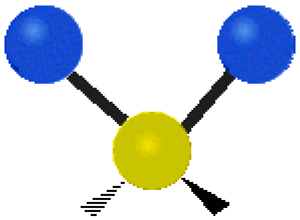




Methylene Group Stretching Vibrations

❖*Asymmetrical stretching*: one side atom approaches the central atom while the other move away from the central atom.

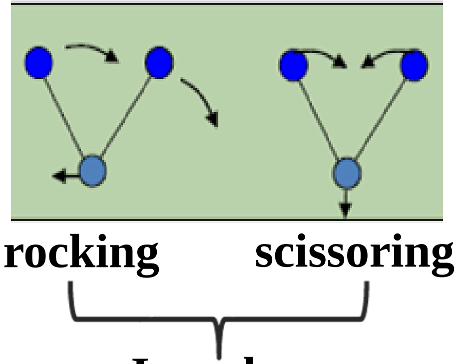




Vibrations of Polyatomic Molecules

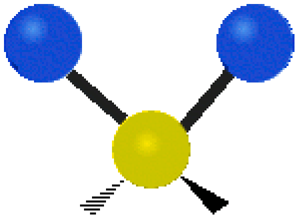
2. Bending vibrations: The angle between two atoms w.r.t central atom varies with time.

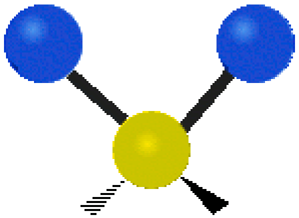
Rocking: the structural unit rotates about the bond which joins it to the rest of the molecule.


rocking **scissoring**

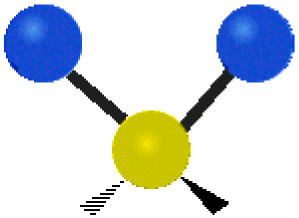
In - plane

Scissoring: scissor like movement.

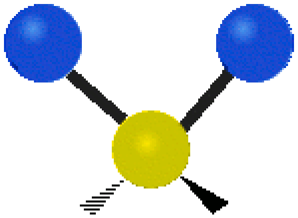


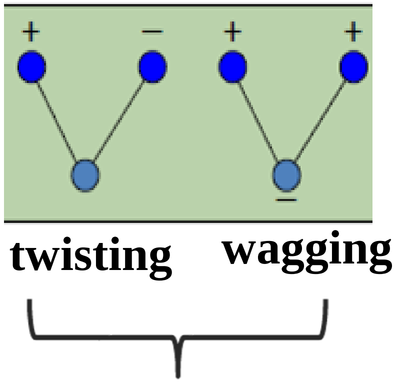


Wagging: the structural unit swings back and forth.



Twisting: the structural unit swings back and forth out of the plane of the molecule





twisting **wagging**

Out -of - plane

Normal vibrational modes of a molecule containing N atoms

- Total **degrees of freedom**: 3N *(N = No. of atoms in a molecule)*

Number of parameters of a system that may vary independently.

Each atom can be specified using three coordinates (e.g. x, y, and z)

- Translational motion uses 3 degrees of freedom.

- Rotation of nonlinear molecule can occur along three axial direction, which counts 3 degrees of freedom.

- For nonlinear molecule the remaining degrees of freedom, 3N−6, is due to internal vibration.

For nonlinear N atomic molecule: 3N – 6 fundamental vibrations.

Vibrations of Polyatomic Molecules

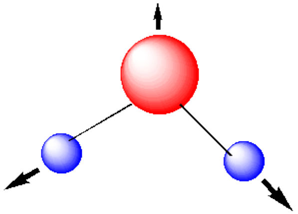
- A linear molecule there is no rotation about the bond axis.
- So, only 2 rotational degrees of freedom (and 3 translational degrees of freedom).
- Hence there are **3N – 5** degrees of vibrational freedom for linear molecule.

All fundamental vibrations are not necessarily give vibrational spectrum or active in IR region.

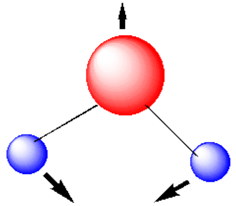
Vibrational modes of H_2O and CO_2 Molecules

H_2O (nonlinear molecule)

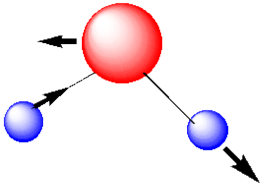
Number of vibration modes: $3N-6 = 3$



Symmetric Stretch
3657 cm^{-1}



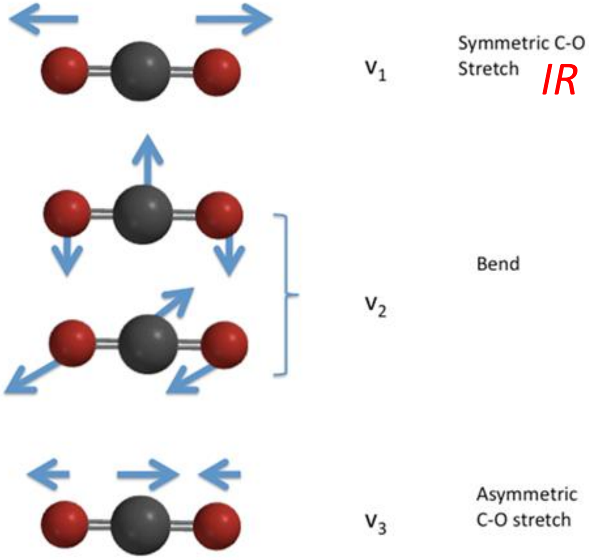
Bend 1595 cm^{-1}



Asymmetric Stretch
3756 cm^{-1}

CO_2 (linear molecule)

Number of vibration modes: $3N-5 = 4$



IR inactive mode

- Occasionally *more absorption bands than would be predicted are* found.

The number of observed absorption bands may be increased by the presence of bands which are not fundamentals but combination bands, overtones, or difference bands.

More often *fewer absorption bands are identified*.

- It may happen to have frequencies of some vibrations so nearly alike that they are not separated by the spectrometer
- Some fundamental bands may be so weak that they are not observed or are overlooked.

IR Spectrum of Complex Organic Molecules

Two types of vibrational modes are possible:

1. Skeletal vibrations where all the atoms in the molecule move about to some extent.
   These vibrations give rise to absorption peaks in the range 400 – 1600 cm^{-1} which is called the fingerprint region.

1600 $cm^{-1} \Rightarrow$ 400 cm^{-1}: "***fingerprint***" region.

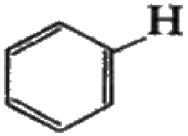
Many bands of mixed origin. Some prominent bands are reliable.

2. Functional group vibrations in which only the atoms in that functional group vibrate appreciably.
   Each functional group gives rise to an absorption peak at a characteristic frequency, no matter what the rest of the molecule contains. These peaks can be used to identify the functional groups present in the molecules.

4000 $cm^{-1} \Rightarrow$ 1600 cm^{-1}: "***functional group***" region.

Most of the stretching bands, specific functional groups (specific atom pairs).

Characteristic Stretching Frequencies of some Molecular Groups

Group	*Approximate Frequency* (cm^{-1})
$-OH$	3600
$-NH_2$	3400
$\equiv CH$	3300
	3060
$=CH_2$	3030
$-CH_3$	2970 (asym. stretch) 2870 (sym. stretch) 1460 (asym. deform.) 1375 (sym. deform.)
$-CH_2-$	2930 (asym. stretch) 2860 (sym. stretch) 1470 (deformation)
$-SH$	2580
$-C\equiv N$	2250
$-C\equiv C-$	2220

Group	*Approximate Frequency* (cm^{-1})
$>C=O$	1750–1600
$>C=C<$	1650
$>C=N\backslash$	1600
$>C-C<$	1200–1000
$>C-N<$	
$>C-O\backslash$	
$>C=S$	1100
$>C-F$	1050
$>C-Cl$	725
$>C-Br$	650
$>C-I$	550

Four Primary Regions of IR Spectrum

Bonds to H	Triple bonds	Double bonds	Single Bonds
O-H single bond N-H single bond C-H single bond	C≡C C≡N	C=O C=N C=C	C-C C-N C-O Fingerprint Region

4000 cm^{-1} 2700 cm^{-1} 2000 cm^{-1} 1600 cm^{-1} 400 cm^{-1}

$$\bar{\nu}_{spectroscopic} = \bar{\omega}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \ \text{cm}^{-1}$$

Larger *k* ⇒ higher frequency

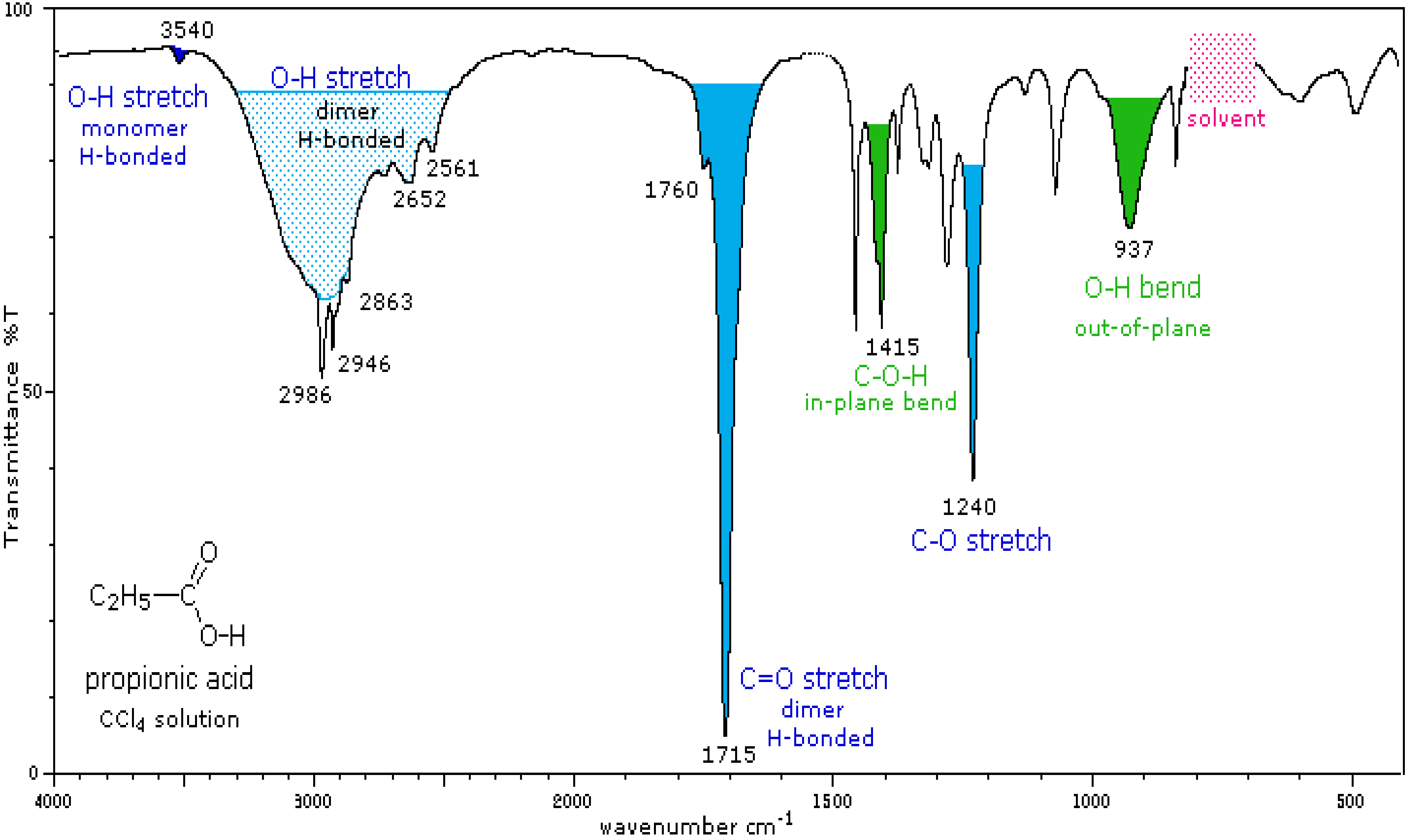
increasing K ←

C≡C	>	C=C	>	C-C
2150		1650		1200

Larger μ (large atomic mass)
⇒ lower frequency

increasing μ →

C-H	>	C-C	>	C-O	>	C-Cl	>	C-Br
3000		1200		1100		750		650



The x-axis of the IR spectrum is in units of wavenumbers (cm^{-1}):

directly proportional to the energy of transition being observed

The y-axis on an IR spectrum is in % transmittance

APPENDIX

NOT REQUIRED FOR EXAMINATION POINT OF VIEW

Intensities of Spectral Lines

All spectral lines are not equally intense.

Intensity depends on

population in each state.
transition probability.
concentration/ path length of sample.

Population of a state is governed by two factors

(a) Boltzmann distribution, (b) degeneracy

Boltzmann distribution

$$\frac{N_J}{N_0} = \exp\left(-\frac{E_J}{kT}\right) = \exp\left(-\frac{Bhc\,J(J+1)}{kT}\right)$$

$$\frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1)$$

$$\frac{E_J}{hc} = BJ(J+1)$$

The population thus depends upon *J* and temperature T and B.

Population is smaller for higher J states. Population in higher J states will be more at higher temperature.

Rapid decrease of population for higher J with larger *B* value.

Greater initial state population gives stronger (intense) spectral lines

Degeneracy in the energy states

Degeneracy : existence of two or more energy states having exactly the same energy

Each level *J* is (2*J*+1) degenerate ⇒ population is greater for higher *J* states

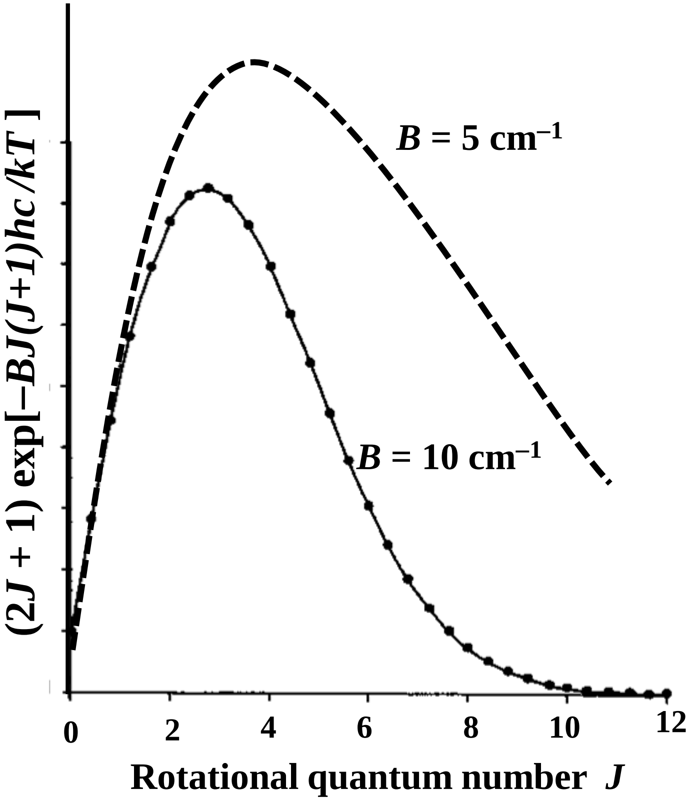
Boltzmann distribution suggests an **exponential decrease** in the molecular population in each level. However, the number of degenerate levels available **increases rapidly** with *J*.

The total relative population at an energy E_J

$$\propto (2J + 1)\exp(-E_J/kT)$$

The population rises to a maximum and then diminishes.

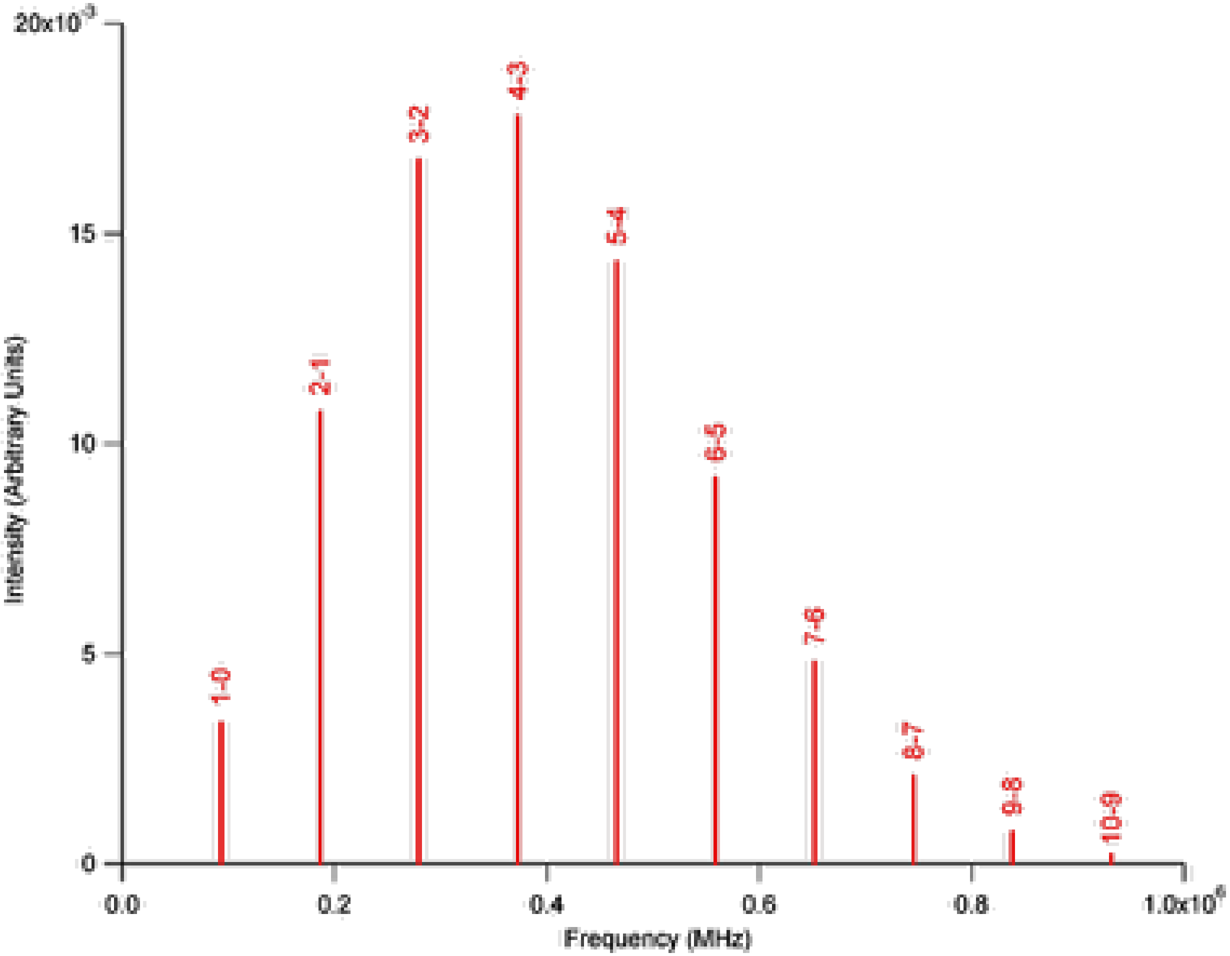
Maximum population: $J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$



The line intensities are directly proportional to the population

Transition between levels with very low and very high J values will have small intensities while

The intensity will be maximum near the J value where population is maximum



Emission spectra of transition in rotational levels

Effect of Isotope Substitution on the Rotational Spectra

Diatomic molecules having different isotopes of the same element show different rotational spectra e.g. HCl and DCl; $^{12}C^{16}O$ and $^{13}C^{16}O$ etc.

Mass of the isotopic atoms are different ⇒ the reduced mass (μ), moment of inertia (I), rotational constant (B) are different

$$B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2(\mu r^2)c}$$

Since there is no appreciable change in the internuclear distance (*r*) on isotopic substitution ⇒ $\boldsymbol{B \propto 1/\mu}$

Spectrum of heavier species will show smaller value of *B* and hence smaller separation between the spectral lines.

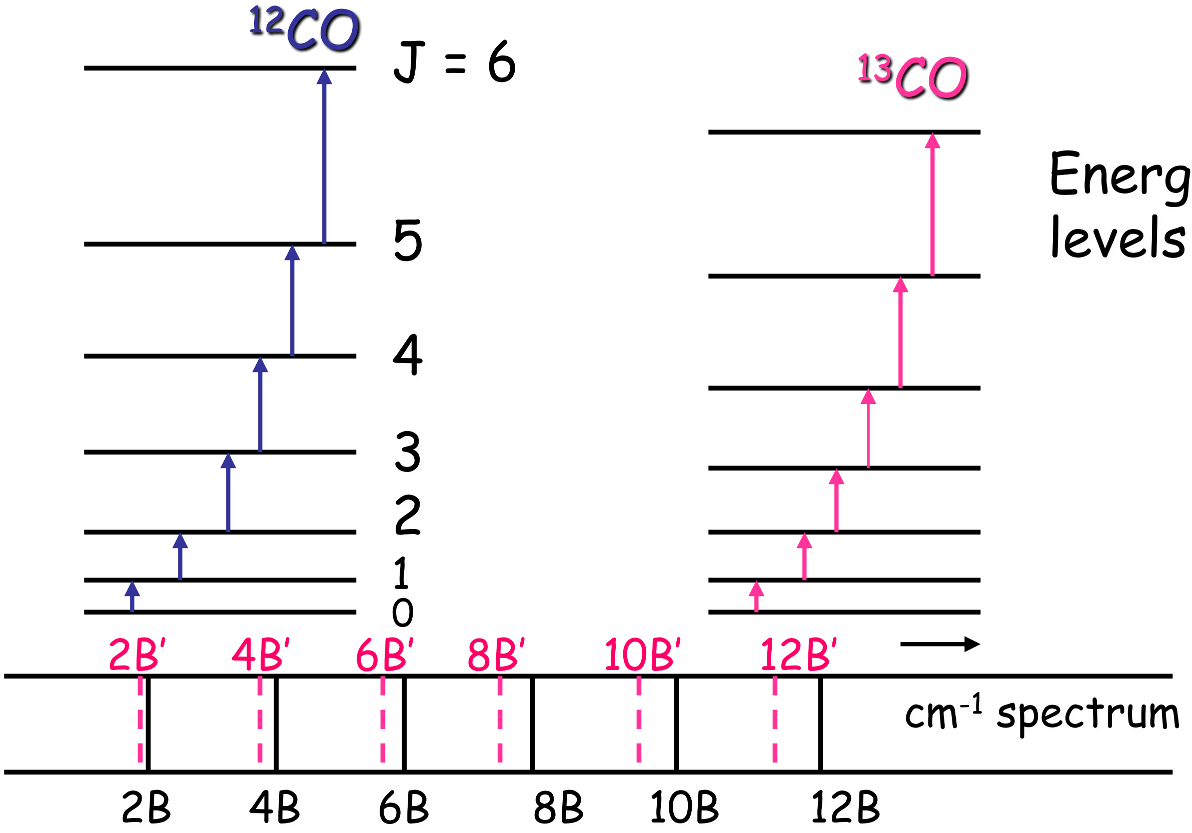
Comparison of rotational spectra of molecules with isotope substitution can determine:

(i) isotopic masses accurately, to within 0.02% of other methods for atoms in gaseous molecules

(ii) isotopic abundances from the absorption relative intensities.

Effect of isotopes

From $^{12}C^{16}O \rightarrow {}^{13}C^{16}O$, mass increases, B decreases ($\propto 1/I$), so energy levels lower and smaller separation between the spectral lines is observed



Non-Rigid Rotor Model

In reality, the molecules vibrate ⇒ can not be strictly rigid rotors

J is high ⇒ rotational energy high ⇒ a tendency for the bond to stretch because of the centrifugal distortion ⇒ moment of inertia increases ⇒ B decreases and the spectral line separation decreases

Therefore a better model for representing the rotations of the molecule:

Consider the diatomic molecule to consist of **two atoms connected by a massless spring** and this is known as **non-rigid rotor model**.

Solving the Schrodinger equation for a non-rigid rotor we can get

$$\boxed{\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 \ \ \mathrm{cm}^{-1}}$$

***D* is the centrifugal distortion constant.**

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc} = \frac{4B^3}{\overline{\omega}^2}\ \mathrm{cm}^{-1}$$

Where $\overline{\omega}$ is the vibrational frequency of the bond

k is the force constant = $4\pi^2\overline{\omega}^2c^2\mu$

The energy difference between two rotational levels J and $(J+1)$ is

$$\varepsilon_{J+1} - \varepsilon_J = \bar{\nu} = 2B\,(J+1) - 4D\,(J+1)^3 \text{ cm}^{-1}$$

Selection remains same i.e. $\Delta J = \pm 1$

Wavenumber for a transition from J to $(J+1)$ is given as

$$\boxed{\bar{\nu}_{J \rightarrow J+1} = 2B\,(J+1) - 4D(J+1)^3 \text{ cm}^{-1}}$$ (Absorption spectra)

$$\bar{\nu}_{0 \rightarrow 1} = 2B\,(0+1) - 4D(0+1)^3 = (2B - 4D) \text{ cm}^{-1}$$

$$\bar{\nu}_{1 \rightarrow 2} = 2B\,(1+1) - 4D(1+1)^3 = (4B - 32D) \text{ cm}^{-1}$$

$$\bar{\nu}_{2 \rightarrow 3} = 2B\,(2+1) - 4D(2+1)^3 = (6B - 108D) \text{ cm}^{-1}$$

Separation between 1st and 2nd line = $(4B - 32D) - (2B - 4D) = (2B - 28D)$ cm^{-1}

Between 2nd and 3rd line = $(6B - 108D) - (4B - 32D) = (2B - 76D)$ cm^{-1}

- **The spectral lines are no longer equidistant.**
- **The separation decreases with increasing *J* value.**