1. Rotational (microwave) spectra:

❖ These spectra result from the transition between the rotational energy levels of gaseous molecules on the absorption of radiations falling in the microwave region

❖ These spectra are shown by molecules possessing a permanent dipole moment, e.g., HCl, CO, H_2O vapour etc.

❖ Homonuclear diatomic molecules such as H_2, N_2, etc. and linear polyatomic molecules such as CO_2, which do not possess a dipole moment, do not show microwave spectra

❖ Microwave spectra occur in the spectral range of 1-100 cm^{-1}

2. **Vibrational and Vibrational-rotation (Infrared) spectra:**

❖ These spectra originate from transitions between the vibrational energy levels of a molecule on the absorption of radiation belonging to infrared region

❖ These spectra are shown by molecules when vibrational motion is accompanied by a change in the dipole moment of the molecule

❖ These spectra occur in the range of 500-4000 cm^{-1}

3. Electronic spectra:

❖ These spectra arise from electronic transitions in a molecule by absorption of radiations falling in the visible and ultraviolet regions

❖ Electronic spectra in the visible region: 12,500-25,000 cm^{-1}
In the ultraviolet region: 25,000-70,000 cm^{-1}

Energy level diagram of rigid rotor
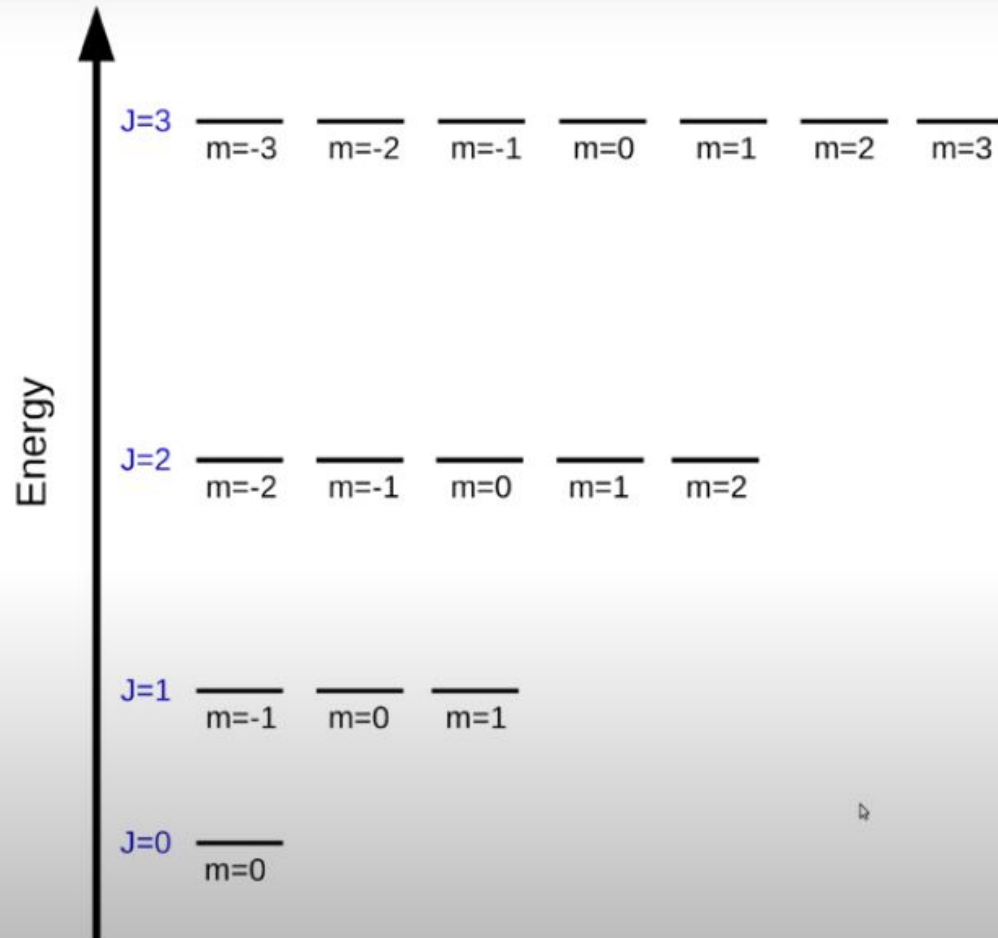
Energy levels

$$\tilde{E}_J = \tilde{B}J(J+1)$$

$$J = 0, 1, 2, \cdots$$
$$m = 0, \pm 1, \cdots, \pm J$$

- $(2J + 1)$-fold degeneracy

- Spacing between energy levels increases with J

Rotational Spectrum

$$E = Bj(j + 1)$$

Rigid Rotor Energy Levels

Energy

J=3 ——— E=12B

J=2 ——— E=6B

J=1 ——— E=2B

J=0 ——— E=0

Selection Rules

- $\Delta J = \pm 1$
- Molecule must have permanent dipole moment.

Many different rotational states are populated at room temperature.
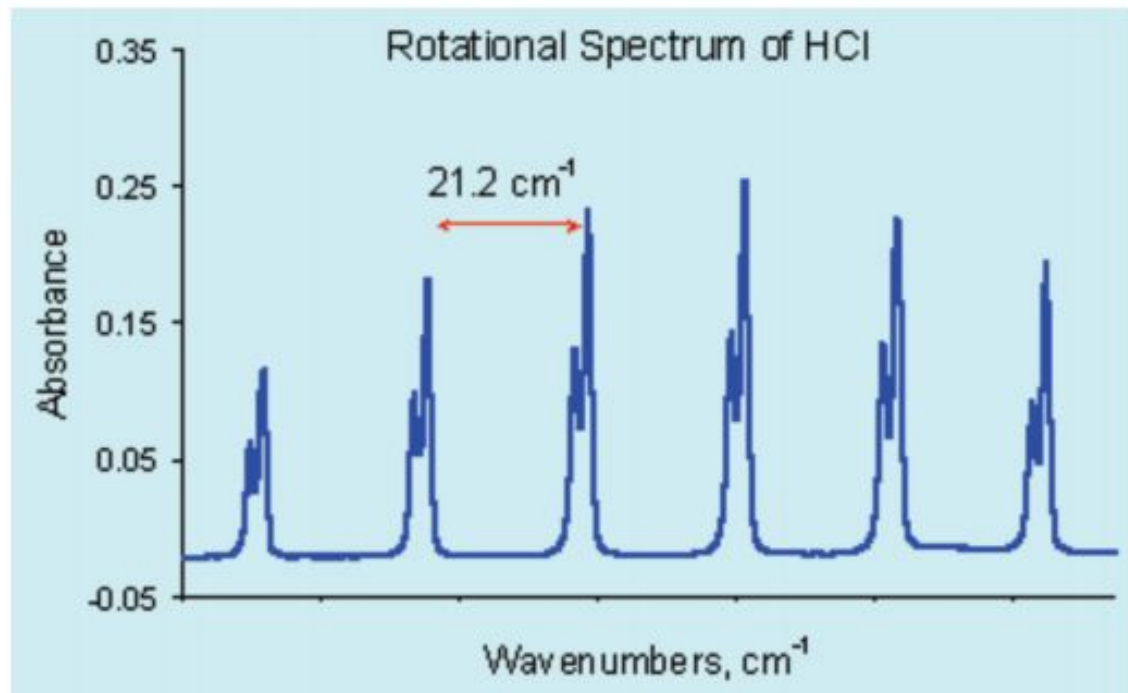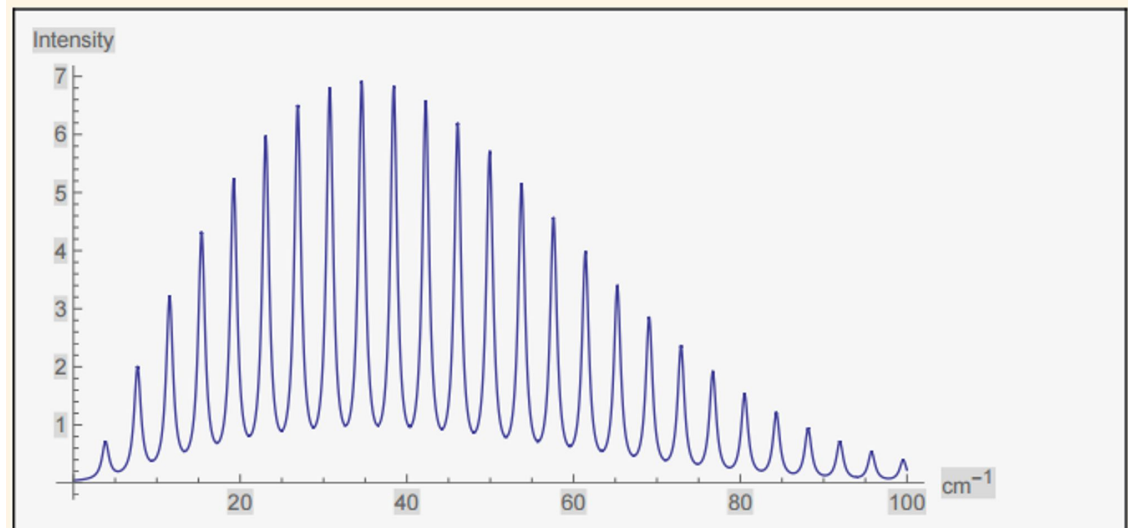
Rotational level population and spectral intensity

The intensity of rotational lines is proportional to the Boltzmann distribution of molecules in the rotational energy levels.

$$\frac{N_j}{N_0} = (2J + 1)\mathrm{e}^{-\frac{\Delta E_j}{kT}}$$

Degeneracy term

Energy term

Rotational Spectrum of HCl

21.2 cm⁻¹

Question: 1

The internuclear distance of CO is 1.13 Å. Calculate the energy and angular velocity of CO in the 1st excited rotational level?
Given: The atomic masses are: C: 1.99×10^{-26} kg, O: 2.66×10^{-26} kg

Ans: r= 1.13 Å = 1.13 x $10^{-}10$ m

Reduced mass, $\mu = m_1m_2/m_1+m_2 = 1.14 \times 10^{-26}$ kg

$I = \mu r^2$

= 1.46 x 10^{-46} kg m2

For 1st excited state: J=1

$E_J = (h^2/8\pi^2 I)J (J+1)$

= 7.61x10^{-23} J

$E_J = \frac{1}{2} I \omega^2$
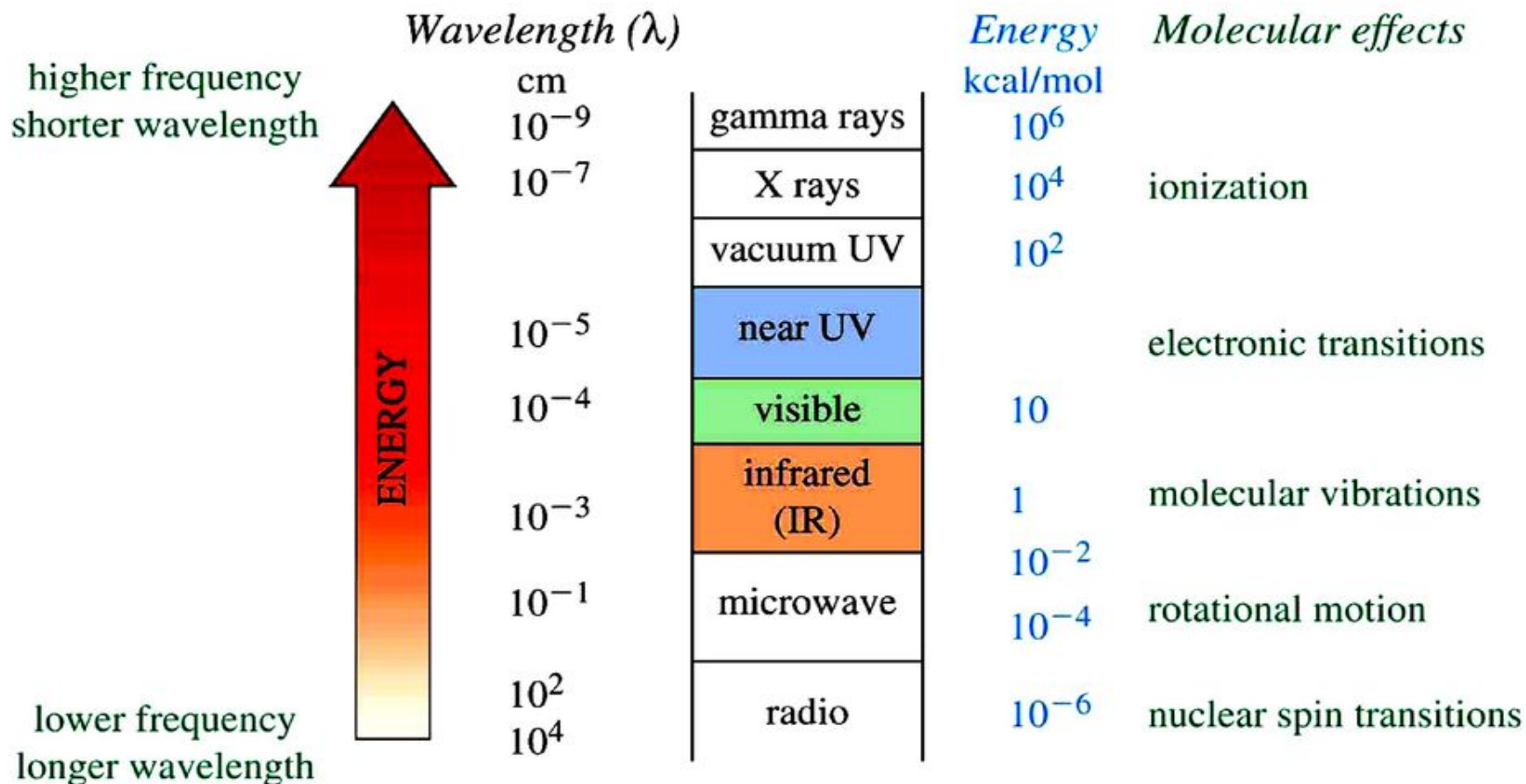
Or, $\omega = (2E_J/I)^{1/2}$

Or, $\omega = 3.23 \times 10^{11}$ radians s^{-1}

Vibrational Spectroscopy
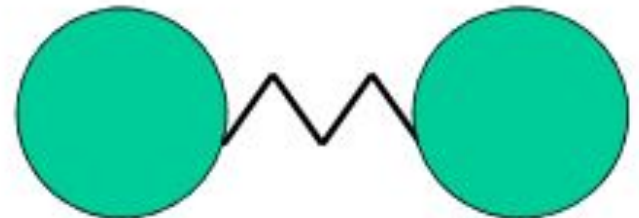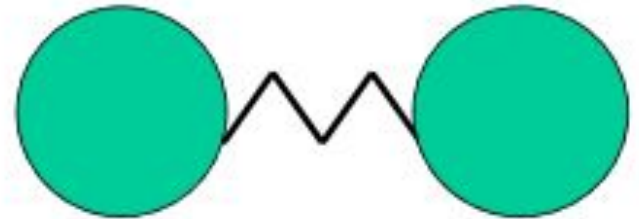
Module 2, Lecture S14

EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES

Diatomic molecules: Structure

Molecules can also vibrate at different frequencies.

But only specific discrete vibrational frequencies occur, corresponding to specific energies.

Vibrational energy levels

The vibrational energy states give a fine structure to the electronic states.

v=0 is the lowest vibrational frequency, then higher **v** numbers correspond to higher vibrational frequencies.

While the separation between electronic energy states is around 20000 cm^{-1}, the separation between vibrational energy states is on the order of 2000 cm^{-1}.

Energy

v=2
v=1
v=0
} Excited Electronic state

v=2
v=1
v=0
} Ground Electronic state

0
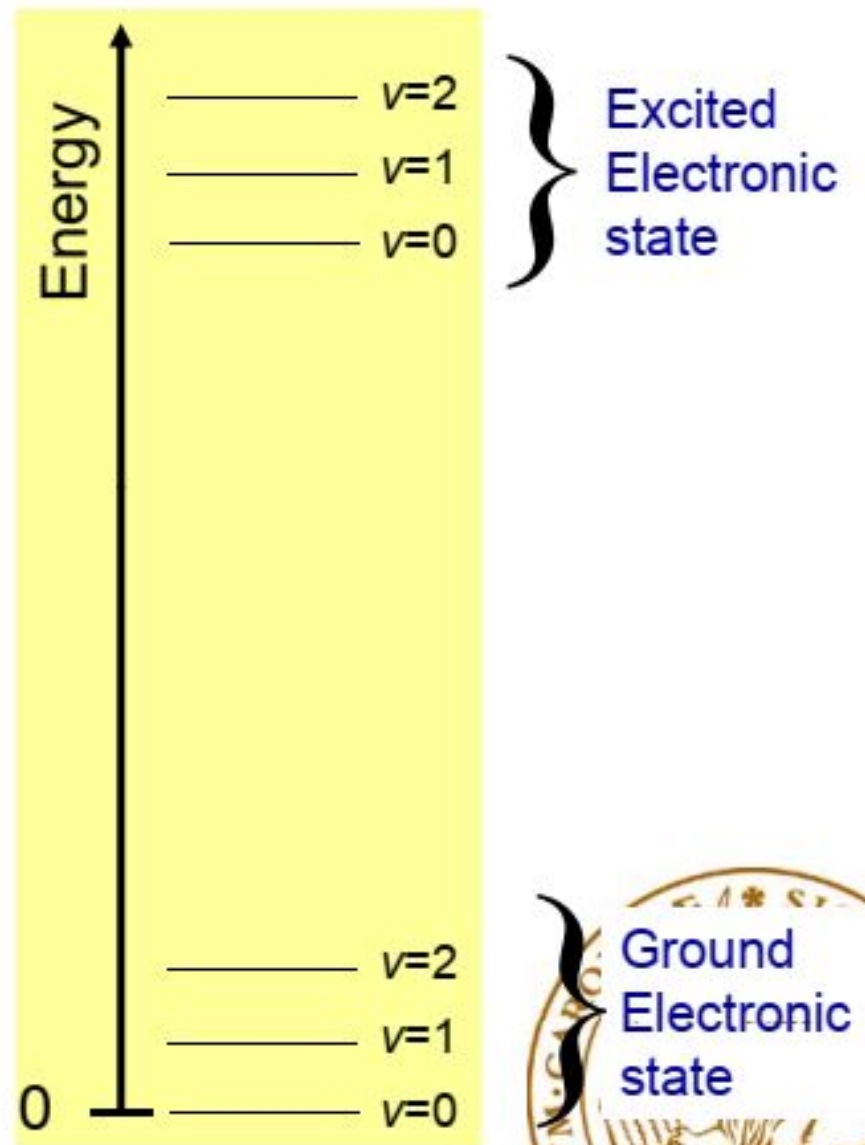
Energy of a vibrating diatomic molecule

Diatomic molecular vibration
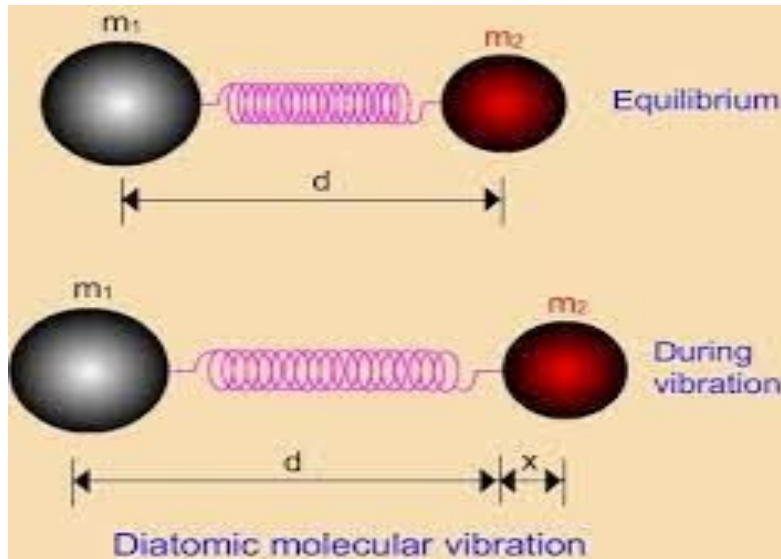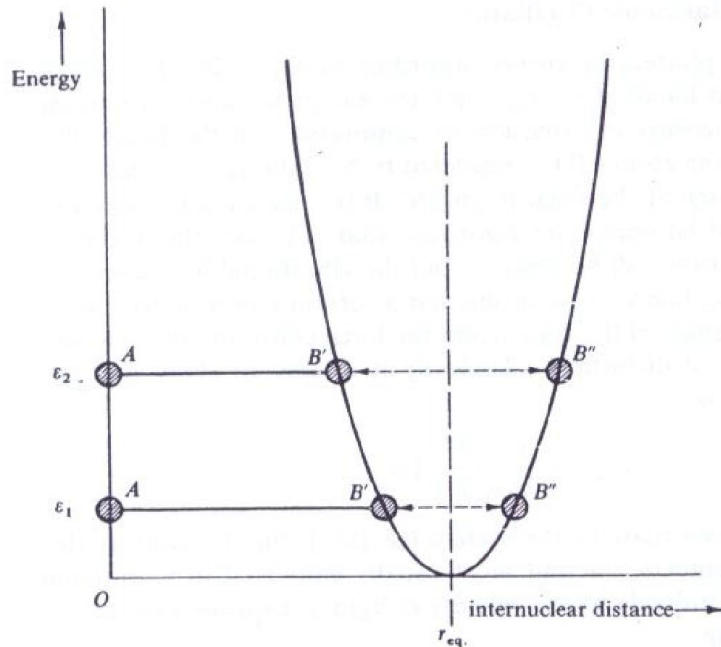
- The extension and compression of a bond may be likened to the behavior of a spring and obeys Hooke's law

⇩

$$f = -k(r - r_{eq})$$

Restoring force   force constant

$$V(x) = \frac{1}{2}k(r - r_{eq})^2$$

Simplified as $V(x) = \frac{1}{2}kx^2$

The Simple Harmonic Oscillator

- The model of S.H.O. forms as an excellent approximation as a starting point for the vibrational spectra

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

$$\overline{\omega_{osc.}} = \frac{1}{2\pi C}\sqrt{\frac{k}{\mu}}\ cm^{-1}$$

Quantized vibrational energies

- For the S.H.O., the Schrodinger equation gives

$$E_v = \left(v + \frac{1}{2}\right) h\omega_{osc.} \; joules \; (v = 0,1,2,3..)$$

$$\varepsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \bar{\omega}_{osc.} \; cm^{-1}$$

- Lowest vibrational energy

$$E_0 = \frac{1}{2} h\omega_{osc..} \; joules$$

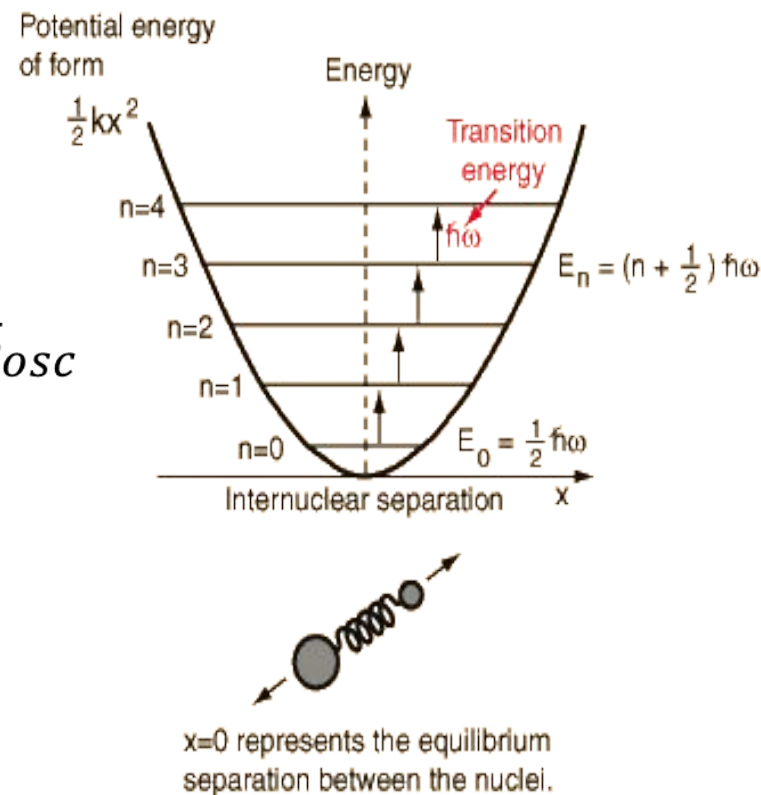$$\varepsilon_0 = \frac{1}{2} \bar{\omega}_{osc.} \; cm^{-1}$$

Allowed and Forbidden transitions

- The use of Schrodinger equation gives a simple selection rule for S.H.O. undergoing vibrational changes

$$\Delta v = \pm 1$$

- Applying selection rule we have

$$\varepsilon_{v+1 \to v} = \left(v + 1 + \frac{1}{2} \right) \bar{\omega}_{osc} - \left(v + \frac{1}{2} \right) \bar{\omega}_{osc}$$

$$= \bar{\omega}_{osc} \ cm^{-1}$$

Potential energy of form $\frac{1}{2}kx^2$

Energy

Transition energy

$\hbar\omega$

n=4

n=3 .... $E_n = (n + \frac{1}{2})\hbar\omega$

n=2

n=1

n=0 .... $E_0 = \frac{1}{2}\hbar\omega$

Internuclear separation   x

x=0 represents the equilibrium separation between the nuclei.

The anharmonic oscillator

- Real molecules do not obey the laws of simple harmonic motion and Hooke's law

- For example, if the bond between the atoms is stretched there comes a point at which it will break

- For longer amplitude of compression expansions – say greater than 10% of the bond length, a much more complicated behavior must be assumed

$$V(x) = D_{eq.}[1 - e^{ax^2}]$$

$$\varepsilon_v = \left(v + \frac{1}{2}\right)\bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e x_e \, cm^{-1} \quad (v = 0,1,2\ldots)$$
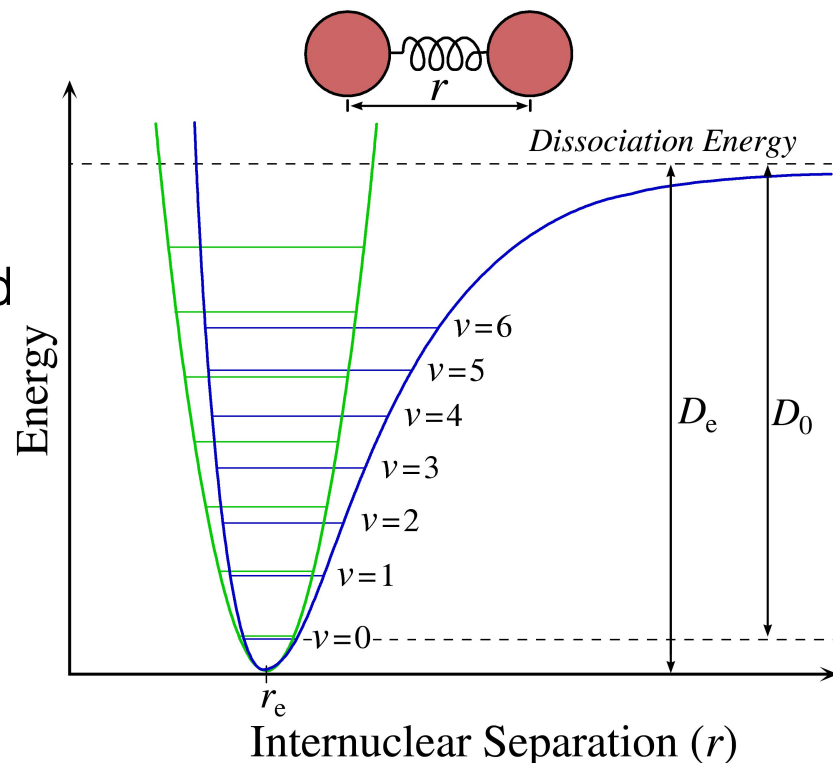
Morse curve
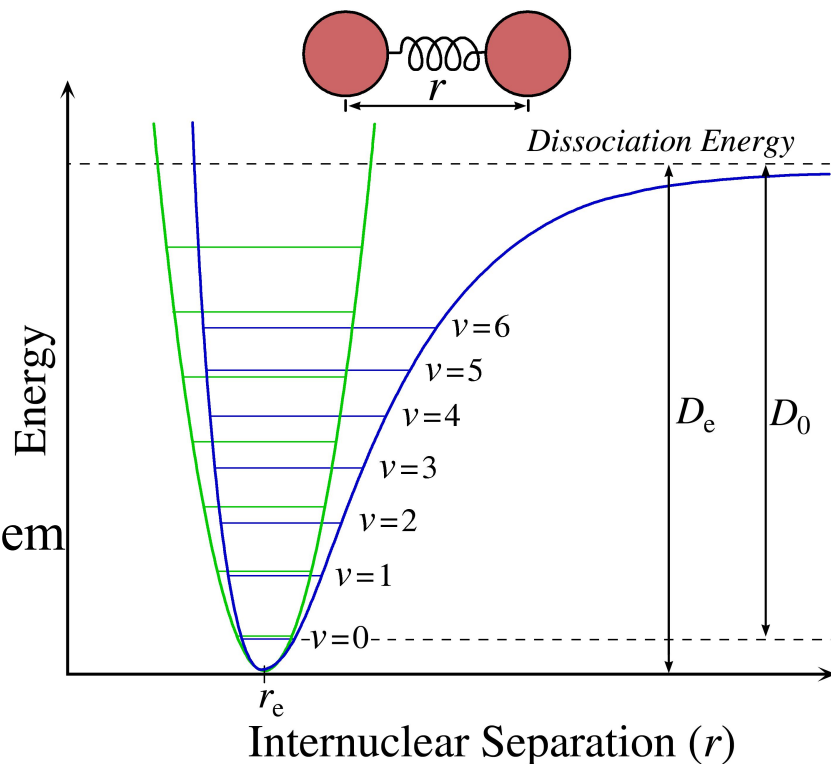
The anharmonic oscillator

When the Schrodinger Eq. for an anharmonic oscillator is solved using the Morse potential energy, the energy levels are given by,

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

where $\omega_e x_e$ is called anharmonicity constant.

$$\bar{\omega}_{osc.} = \bar{\omega}_e \left\{1 - x_e\left(v + \frac{1}{2}\right)\right\}$$

❖ The consequence of anharmonicity is that the vibrational energy levels of the S.H.O. are all slightly lowered and the spacing between them is no longer constant but goes on steadily decreasing with increase in the vibrational quantum number

Morse curve

The harmonic and anharmonic oscillator

• Frequency of oscillation

$$\overline{\omega}_{osc} \, cm^{-1}$$

$$\overline{\omega}_{osc.} = \overline{\omega}_e \left\{ 1 - x_e \left(v + \frac{1}{2} \right) \right\}$$

The anharmonic oscillator behaves like harmonic oscillator but with an oscillation frequency which decreases steadily with increasing 'v'

Because of anharmonicity, the selection rule is changed to:

$$\Delta v = \pm 1, \pm 2,$$

❖ The transitions corresponding to $\Delta v = \pm 2, \pm 3$ etc. are called the 1st overtone, 2nd overtone, respectively.

❖ Compared to the highly intense fundamental vibrational frequency, the overtones are very weak, i.e., of considerably low intensity

INFRARED ACTIVE BONDS

Not all covalent bonds display bands in the IR spectrum. **Only polar bonds do so. These are referred to as IR active**.

The intensity of the bands depends on the magnitude of the **dipole moment** associated with the bond in question:

- Strongly polar bonds such as carbonyl groups ($C=O$) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
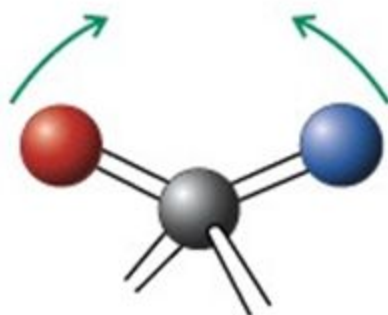- Weakly polar bond and symmetric bonds produce weak or non observable bands.

STRONG	MEDIUM	WEAK	NOT OBSERVABLE
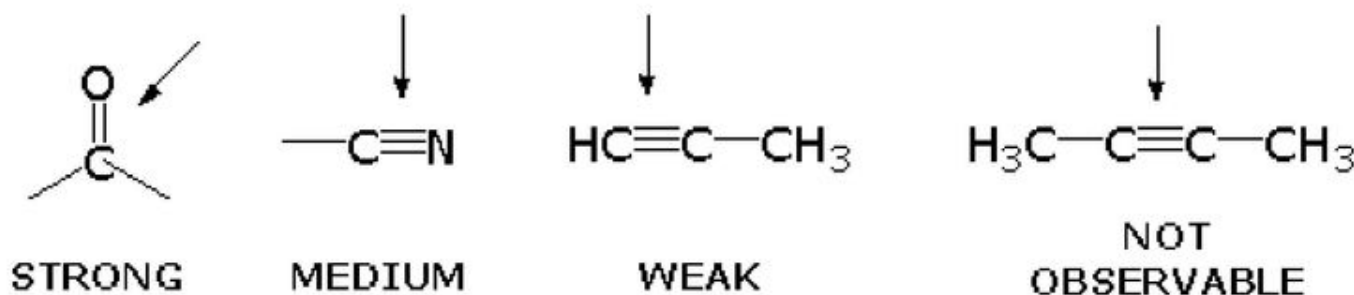
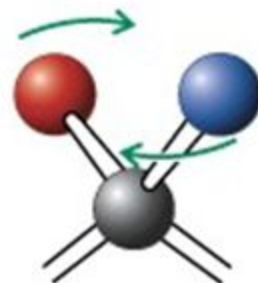# Many possible absorptions per molecule exist: stretching, bending,…

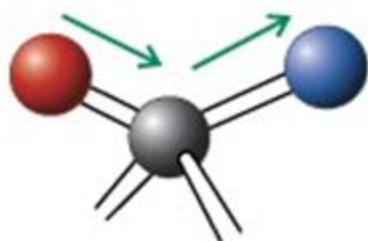Vibrational modes leading to IR absorptions:
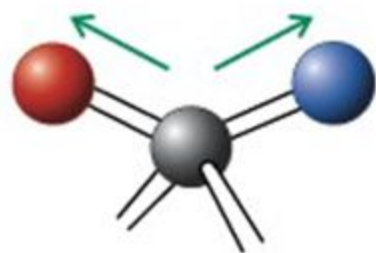
Symmetric stretching vibration (both outside atoms move away from or toward the center)
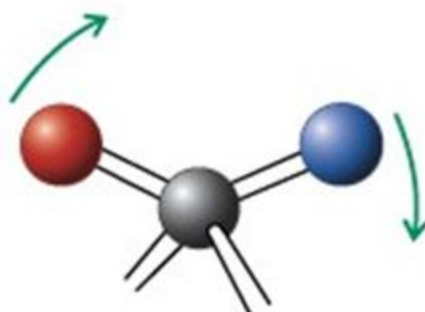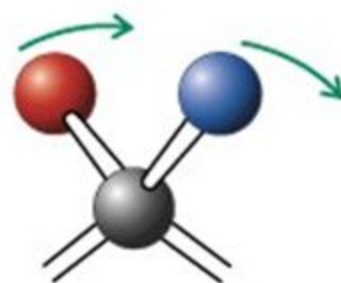
Symmetric bending vibration in a plane (scissoring)

Symmetric bending vibration out of a plane (twisting)

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

Asymmetric bending vibration in a plane (rocking)

Asymmetric bending vibration out of a plane (wagging)

INFORMATION OBTAINED FROM IR SPECTRA

- IR is most useful in providing information about the presence or absence of specific **functional groups**.

- IR can provide a **molecular fingerprint** that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.

- IR **does not** provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.

- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.

Question: The force constant of CO is 1840 Nm^{-1}. Calculate the vibrational frequency in cm^{-1} and the spacing between the vibrational energy levels in eV. Compare the spacing with the thermal energy at room temperature.

The atomic masses of C and O are 12C = 19.9 x 10^{-27} kg, 16O = 26.6x10^{-2}

Ans: The vibrational frequency can be given by,

$\bar{\upsilon}$ = 1/2πc) (k/μ)$^{1/2}$
Hence we need to evaluate the reduced mass (μ) of the molecule.
The reduced mass, μ can be calculated as,
μ = m$_1$m$_2$/m$_1$+m$_2$
 =11.4 x 10^{-27} kg

Now $\bar{\upsilon}$ = (1/2x3.1416x3x10^{10} cm s^{-1}) (1840 kg s^{-2}/11.4x10^{-27} kg)$^{1/2}$
 = 2140 cm^{-1}
The spacing between the energy levels in cm^{-1} is hυ/hc = $\bar{\upsilon}$ = 2140 cm^{-1}

As 1 eV = 8066 cm^{-1},
ΔE = 2140/8066 = 0.265 eV

Thermal energy = kT = (1.38x10^{-23}) 300/1.602x10^{-19}
= 0.026 eV

Note: As the value of ΔE > kT, hence the thermal energy is not sufficient for the excitation of molecules to the 1st excited vibrational state and most of the molecules are in the **ground state vibrational level** at room temperature.

Rotation-vibration spectra of diatomic molecules

The freely moving molecules in the gaseous state are almost rotating regardless of their vibrational state. Hence, molecules in the **gaseous state** show **rotation-vibration spectra**

As rotational energy <<< vibrational energy, the vibrational transition is associated with rotational transitions

The rotation and vibration are, to a first approximation, **independent** of each other.

The rotation-vibration term, S (v, J) for vibrating rotor is given by,

$$S (v, J) = F(J) + G (v)$$

$$= BJ(J+1) + (v+1/2)\, \omega_e - (v+1/2)^2\, \omega_e x_e \ cm^{-1}$$

The **selection rules** for combined vibrational and rotational transitions are

$\Delta v = \pm 1, \Delta J = \pm 1$

Using the above selection rule, we have the frequency of transition

$\Delta S (v, J) = \{BJ'(J'+1) + (v+1/2)\, \omega_e - (v+1/2)^2\, \omega_e x_e \} - \{BJ''(J''+1) + (v+1/2)\, \omega_e - (v+1/2)^2\, \omega_e x_e$

$= \{BJ'(J'+1) + (3/2)\omega_e - (9/4)\, \omega_e x_e \} - \{BJ''(J''+1) + (1/2)\, \omega_e - (1/4)\, \omega_e x_e\}$

$= \omega_e - 2\, \omega_e x_e + B\, (J'-J'')\, (J'+J''+1)\ cm^{-1}$

$= \omega_0 + B\, (J'-J'')\, (J'+J''+1)\ cm^{-1}\ \text{where}\ \omega_0 = \omega_e - 2\, \omega_e x_e$

Since most of the molecules are in the ground vibrational state at room temperature, only the **v=0 to v=1** transition is of interest

Case-1: For $\Delta J=+1$
$J' = J'' + 1$, i.e., $J'- J'' = 1$ so that
$$\Delta S \ (v, J) = \omega_0 + B \ (J'- J'') \ (J'+J'' + 1) \ cm^{-1}$$
$$= \omega_0 + Bx1x(J'' + 1 +J'' + 1) \ cm^{-1}$$
$$= \omega_0 + 2B \ (J'' +1) \ cm^{-1}; \ J''= 0, 1, 2, 3\ldots\ldots \ (1)$$

Case-2: For $\Delta J=-1$
$J' = J''-1$, i.e., $J'- J'' = -1$ so that
$$\Delta S \ (v, J) = \omega_0 + B \ (J'- J'') \ (J'+J'' + 1) \ cm^{-1}$$
$$= \omega_0 + B \ (-1) \ (J'+(J'+1) +1) \ cm^{-1}$$

$$= \omega_0 - B \ (2(J'+1))$$
$$= \omega_0 - 2B \ (J'+1); \quad J'= 0, 1, 2, 3\ldots\ldots \quad (2)$$

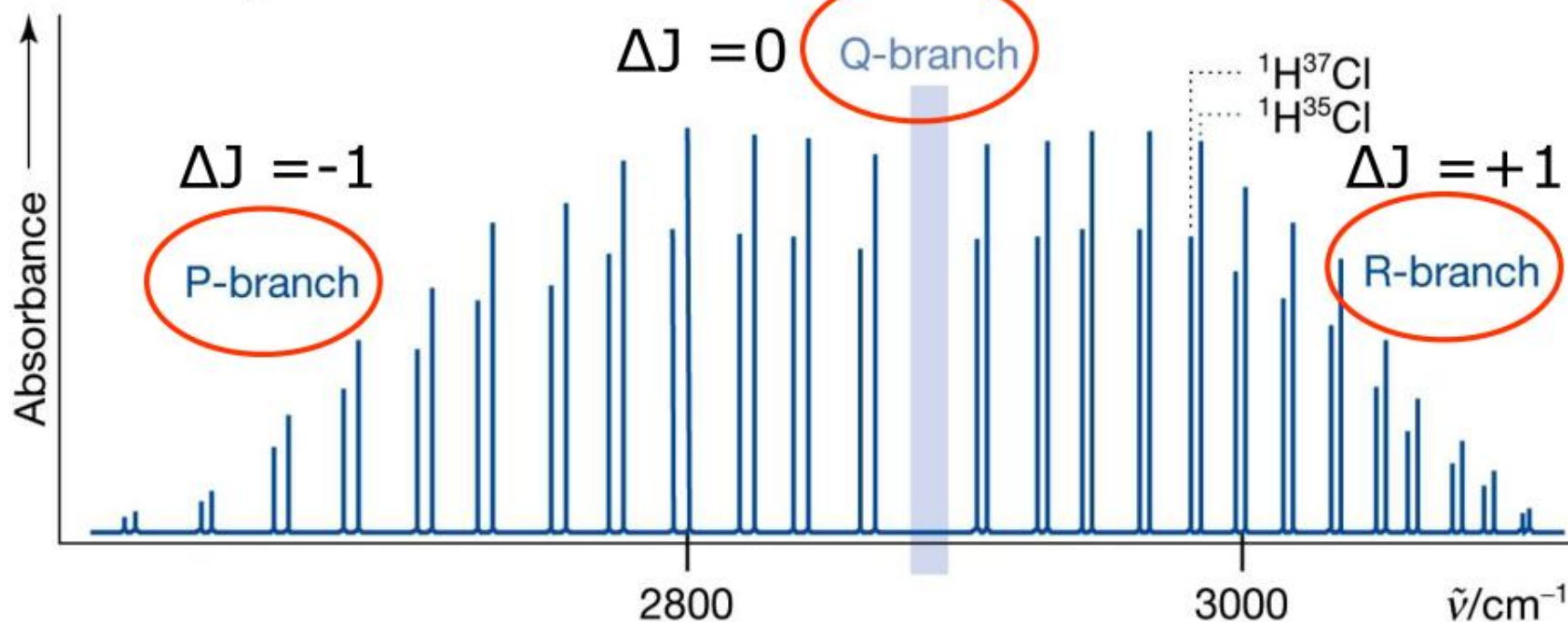Combining both expressions in Eq. 1 and 2,

$$\Delta S\,(v,\,J) = \omega_0 \pm 2Bm \text{ cm}^{-1}, \; m = \pm 1, \pm 2, \pm 3, \ldots.$$

The frequency ω_0 is called the **band centre**

The rotation-vibration spectrum consists of equally spaced lines with spacing equal to 2B on each side of the band centre

The lines corresponding to $\Delta J = -1$ are called the P branch, and the lines corresponding to $\Delta J = +1$ are called the R branch

Fig 13.34 High resolution vibration-rotation spectrum of HCl for a v + 1 ← v transition

$\Delta J = 0$ — Q-branch

$\Delta J = -1$

P-branch

$^1H^{37}Cl$
$^1H^{35}Cl$

$\Delta J = +1$

R-branch

Absorbance

2800   3000 $\tilde{v}/cm^{-1}$

Combined vib-rot terms, S:

$$S(v, J) = G(v) + F(J)$$

$$B = \frac{\hbar}{4\pi cI} \qquad I = \sum_i m_i r_i^2$$

$$= (v + \tfrac{1}{2})\, \tilde{v} + BJ(J+1)$$