ENGINEERING CHEMISTRY

Department of Science and Humanities

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Module I- Molecular Spectroscopy

PES UNIVERSITY

Class Content:

- ***Vibrational spectroscopy***
- ***Expression for vibrational energy levels (Harmonic oscillator)***
- ***Vibrational spectrum(Harmonic oscillator)***

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Vibrational Spectroscopy

- When a molecule undergoes vibrational changes it absorbs **IR radiation**
- For a molecule to be vibrationally active (IR active) the vibration of a molecule must be associated with **change in dipole moment**
- Vibrations of molecules can result in changes in electric dipoles that can interact with the **electrical component** of the electromagnetic radiation.

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- When the frequencies match, **resonance occurs** and the molecule absorbs energy and goes to the higher **vibrational levels** and exhibits **vibrational spectrum**

- Molecules such as **HCl ,CO and H_2O** will show vibrational spectra while **H_2, Cl_2** will not

- **CO_2** molecule does not possess permanent dipole moment but **is IR active** as when it vibrates asymmetrically or in bending mode ,there is change in dipole moment

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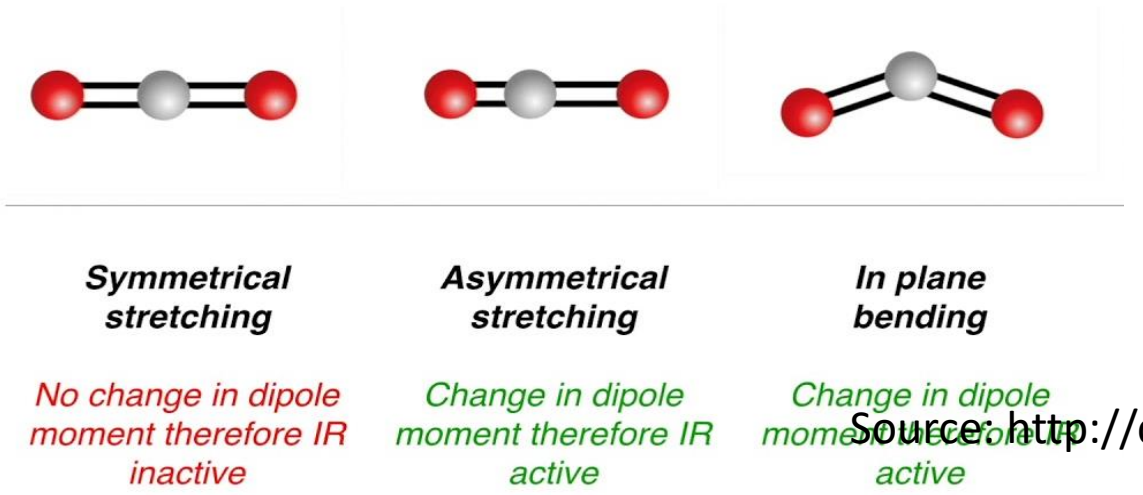
CO_2 molecule although does not possess permanent dipole moment is IR active because some of its vibrational modes are IR active:

CO_2 symmetric stretch is IR inactive as there is no change in dipole moment when molecule vibrates in this mode.

CO_2 asymmetric stretch is IR active

CO_2 bending mode is IR active



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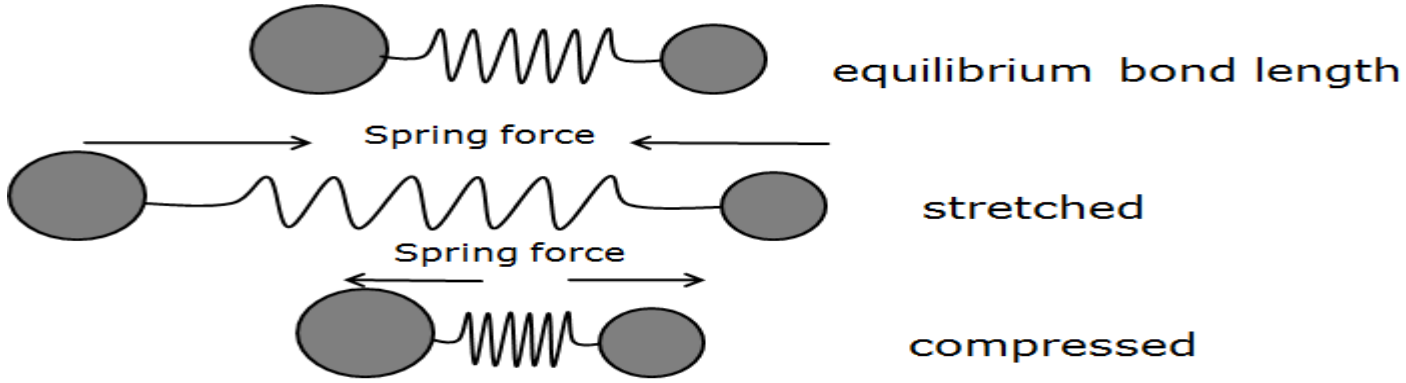
Vibrational spectroscopy of diatomic molecule: simple harmonic oscillator (SHO) model

- Every type of bond in a molecule has a unique natural **vibrational frequency**
- Therefore the IR spectrum of every molecule is **unique** as much as the finger print of human beings
- Bonds are not static but **vibrating in different ways**
- A vibrating bond can therefore be considered a spring with its ends tethered to two atoms as in the figure and obeys **Hooke's law**



Source : Ramasahayam, Swathi & Roy Chowdhury, Shubhajit. (2016). Non Invasive Estimation of Blood Urea Concentration using Near Infrared Spectroscopy. International Journal on Smart Sensing and Intelligent Systems. 9. 10.21307/ijssis-2017-878.

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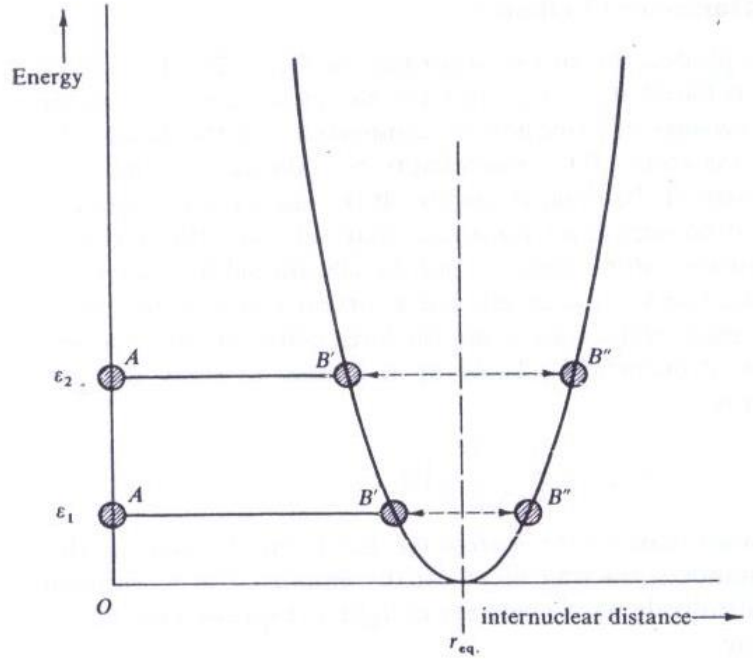
The vibrating bond obeys Hooke's law, **$F=-k(r-r_{eq})$**
where k is a force constant, r is the inter nuclear distance, r_{eq} is equilibrium inter nuclear distance or bond length.

Energy is given by $E=\frac{1}{2}k(r-r_{eq})^2$ Hence the energy curve is **parabolic**



Source: Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

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The **oscillation frequency** is given by,

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

where μ is **reduced mass**

Expressing frequency of oscillation in terms of wave number

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

Solving **Schrodinger equation for harmonic oscillator** shows vibrational energy levels are quantised and are given by the expression

$$E_V = (v+\frac{1}{2})h\nu_{osc}Joules$$

where **v= vibrational quantum number** which can take up values zero upwards; **v=0,1,2,3....**

Vibrational energy expressed in terms of wave number is given by,

$$\varepsilon_v = (v+\frac{1}{2})\bar{\nu}_{osc}cm^{-1}$$

The energy levels will appear at,

v	ε_v
0	$\varepsilon_0 = \frac{1}{2}\bar{\nu}_{osc} cm^{-1}$
1	$\varepsilon_1 = \frac{3}{2}\bar{\nu}_{osc} cm^{-1}$
2	$\varepsilon_2 = \frac{5}{2}\bar{\nu}_{osc} cm^{-1}$

ε_o is called **zero point energy**

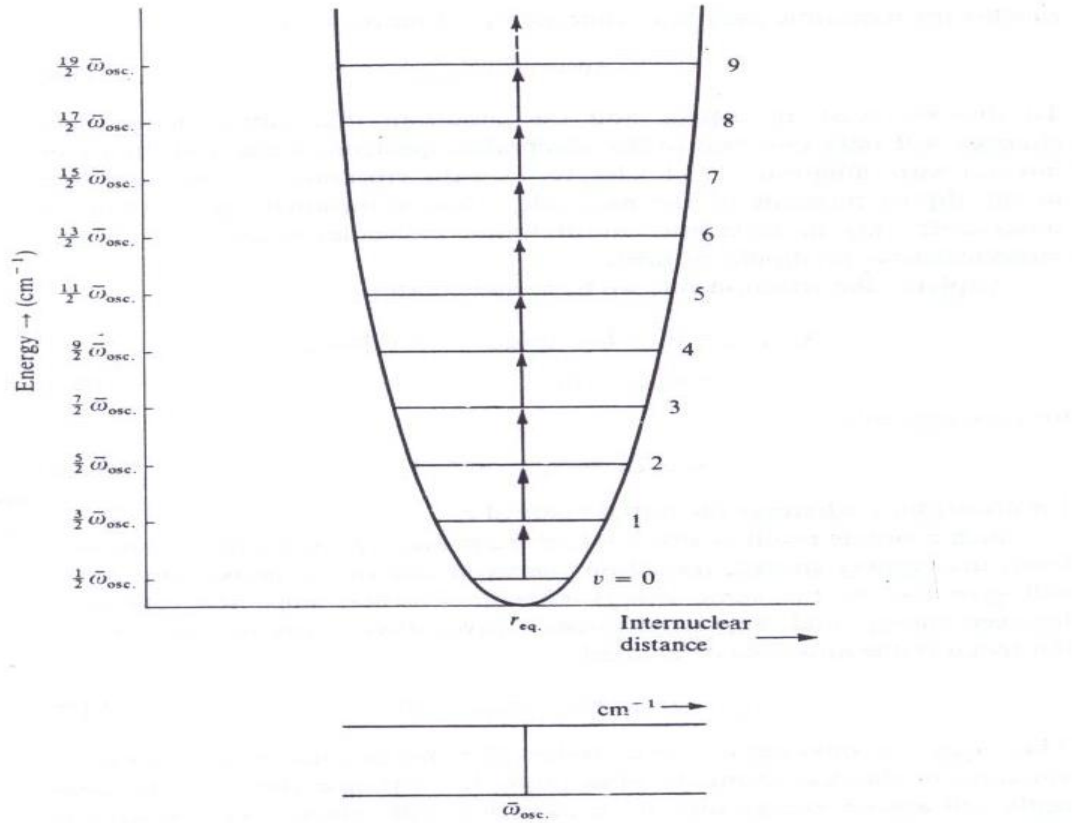
The **difference between any two consecutive energy levels** is equal to
Hence the energy levels are equally spaced.

The **selection rules** for vibrational transitions are

- **Gross selection rule :** When the molecule vibrates there should be a change in the dipole moment
- **Δv = ± 1**

Therefore transition between any two consecutive vibrational levels are allowed and only **one line** is observed in the vibrational spectrum at $\bar{\nu}_{osc} cm^{-1}$

Vibrational energy levels and resulting spectrum for a diatomic molecule executing simple harmonic motion



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From the spectrum $\bar{\nu}_{osc}$ can be obtained and using the expression

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

k can be determined which is the **bond strength (force constant)**of the molecule

THANK YOU

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