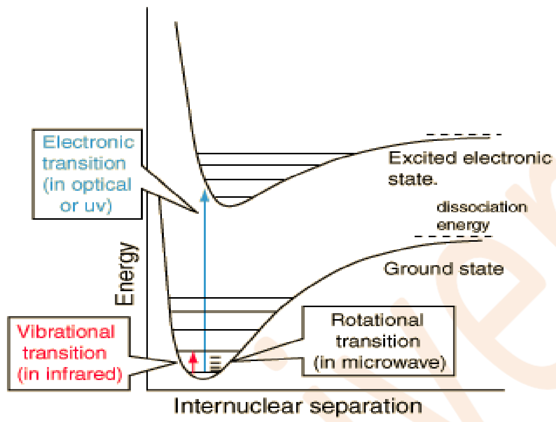
Question and Answers

1. State Born-Oppenheimer approximation. Draw energy level diagram of diatomic molecule which shows rotational, vibrational and electronic energy levels.

Answer: Born-Oppenheimer approximation: Total energy of a molecule is the sum of translational, rotational, vibrational and electronic energies, i.e.

$E = E_{trans} + E_{rot} + E_{vib} + E_{elec}$



2. What are hot bands?
Answer : In Anharmonic oscillator model, if the temperature is raised, transitions from v=1 to v=2 will be some 10 percent of those from v=0 to v=1. They are normally weak absorptions. Such weak absorptions are called hot bands since a high temperature is one condition for their occurrence.

3. State which of the following molecules are microwave active : HCl, H_2O, HI, OCS, N_2, H_2, HF.
Answer : HCl, H_2O, HI, OCS, HF molecules are IR active since they posses permanent dipole moment.

4. For HBr molecule:
i) The rotational spectrum shows the first line at 17.19 cm^{-1}. Calculate the bond length of HBr molecule(Use rigid rotor model)
ii) The vibrational spectrum shows fundamental and first overtone at 2559.08 cm^{-1} and 5027.54 cm^{-1} respectively. Calculate the anharmonicity constant for the molecule. (Use anharmonic oscillator model). (1 amu = 1.66×10^{-27} kg, h = 6.627×10^{-34} Js, c = $3 \times 10^{10} cms^{-1}$, N = 6.023×10^{23} mol^{-1}, Gram molar mass of H = 1.0 and Br = 79.9)

Answer : i) $2B = 17.19\ cm^{-1}$ $B = 8.595\ cm^{-1}$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(0.001/6.023\ X\ 10^{23})\ (0.0799\ X\ 6.023\ X\ 10^{23})}{(0.001/6.023\ X\ 10^{23}) + (0.0799\ X\ 6.023\ X\ 10^{23})} = 1.6395X\ 10^{-27}\ kg$$

$$B = \frac{h}{8\pi^2 Ic} = \frac{6.627\ X10^{-34}}{8X\,(3.14)^2\ X\ I\ X\ 3X10^{10}}$$

$$I = 3.2583X10^{-47}\ kgm^2$$

$$I = \mu r^2$$

$$r = \sqrt{I/\mu} = 0.141nm$$

ii) Fundamental absorption = $\bar{\nu}\,(1-2x_e) = 2559.08\,cm^{-1}$

First overtone = $2\bar{\nu}\,(1-3x_e) = 5027.54\,cm^{-1}$

$$\frac{2\bar{\nu}\,(1-3x_e)}{\bar{\nu}\,(1-2x_e)} = \frac{5027.54}{2559.08} = 1.9646$$

$$x_e = 0.0171$$

5. i) Why real molecules do not obey simple harmonic oscillator model?
   ii) The force constant of a HF is 970 N/m. Calculate reduced mass and the spacing between two consecutive levels. (Use simple harmonic oscillator model).
   (Given: Atomic masses of H = 1.008 and F = 18.99, Avagadro's number = 6.023 x 10^{23}, Speed of light = 3 x 10^{10} cm/s, 1 amu = 1.66 x 10^{-27} kg, Planck's constant = 6.627 x 10^{-34} Js, π = 3.14)

   Answer : i) Real molecules do not obey exactly the laws of simple harmonic motion. Although real bonds are elastic, they are not homogeneous to obey Hook's law. If the bond between atoms is stretched, bond breaks. The molecule dissociates into atoms.

   ii)

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.008\ X\ 18.99\ X\ 1.66\ X\ 10^{-27}}{1.008 + 18.99} = 1.5889\ X\ 10^{-27}\ kg$$

$$\bar{\nu} = \frac{1}{2\pi}\sqrt{k/\mu} = \frac{1}{2\ X\ 3.14}\sqrt{970/1.5889\ X\ 10^{-27}} = 4147\,cm^{-1}$$

6. The rotational constant of $^{127}ICl^{35}$ is 0.1142 cm^{-1}. Calculate the ICl bond length,
   (Given: Atomic masses of I = 126.9amu and Cl = 34.9688 amu, Avogadro's number = 6.023 x 10^{23}, Speed of light = 3 x 10^{10} cm/s, π = 3.14, Planck's constant = 6.627 x 10^{-34} Js, 1 amu = 1.66 x 10^{-27} kg)
   Answer : $\mu = m_1m_2/m_1+m_2 = 45.5 \times 10^{-27}$ kg
   $I = h/8\pi^2Bc = 0.244 \times 10^{-44}$ kgm^2
   $I = \mu r^2$ = 231.5 ppm

7. The force constant of a HI is 294 N/m. Calculate reduced mass and the spacing between two consecutive levels. (Use simple harmonic oscillator model). (Given: Atomic masses of H = 1.008 and I = 126.9, Avogadro's number = 6.023×10^{23}, Speed of light = 3×10^{10} cm/s, 1 amu = 1.66×10^{-27} kg, Planck's constant = 6.627×10^{-34} Js, π = 3.14)

Answer: $\mu = \frac{m1m2}{m1+m2}$

= 1.66×10^{-27} kg

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

= 2333 cm^{-1}

8. The internuclear distance (bond length) of carbon monoxide molecule is 1.13 Å. Calculate the reduced mass, moment of inertia and energy (in cm^{-1}) of this molecule in the first excited rotational energy level (J = 1). (Given : The atomic masses of $^{12}C = 1.99 \times 10^{-26}$ kg and $^{16}O = 2.66 \times 10^{-26}$ kg, Speed of light = 3×10^{10} cm/s, π = 3.14, Planck's constant = 6.626×10^{-34} Js)

Ans : r = 1.13 Å = 1.13×10^{-10} m

$$\mu = \frac{m1m2}{m1+m2} = \frac{(1.99 \times 10^{-26})(2.66 \times 10^{-26})}{(1.99 \times 10^{-26} + 2.66 \times 10^{-26})} = 1.1383 \times 10^{-26} \text{ kg}$$

$$I = \mu r^2 = 1.1383 \times 10^{-26} \text{ kg} \times (1.13 \text{ x } 10^{-10} \text{ m})^2 = 1.4534 \text{ x } 10^{-46} \text{kgm}^2$$

$$\varepsilon_J = \frac{h}{8\pi^2 Ic} J(J+1) \text{ (1M)}$$

$$\varepsilon_J = \frac{6.626 \times 10^{-34}}{8 \text{ x } 3.14^2 \times 1.4534 \text{ x } 10^{-46} \times 3 \text{ x } 10^{10}} 1(1+1) = 3.853 \text{ cm}^{-1}$$

9. What is zero point energy ? Calculate the zero point energy of KCl molecule if $v\bar{v} = 378\, cm^{-1}$.

Answer : Vibrating diatomic molecule can never have zero vibrational energy.
ε_o is called zero point energy

$$\text{Zero point energy} = \frac{1}{2}\tilde{\nu} = \frac{1}{2} \times 378 \text{ cm}^{-1} = 189 \text{ cm}^{-1}$$