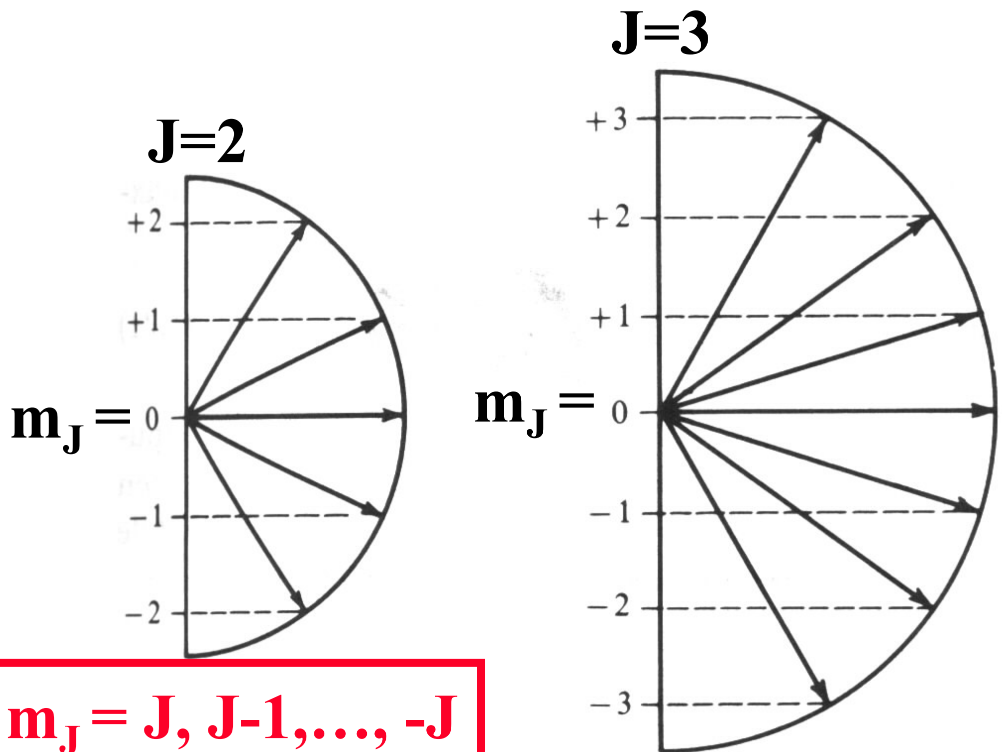
Degeneracy



$m_J = J, J\text{-}1, \ldots, \text{-}J$

Energy only determined by J

$\Downarrow$

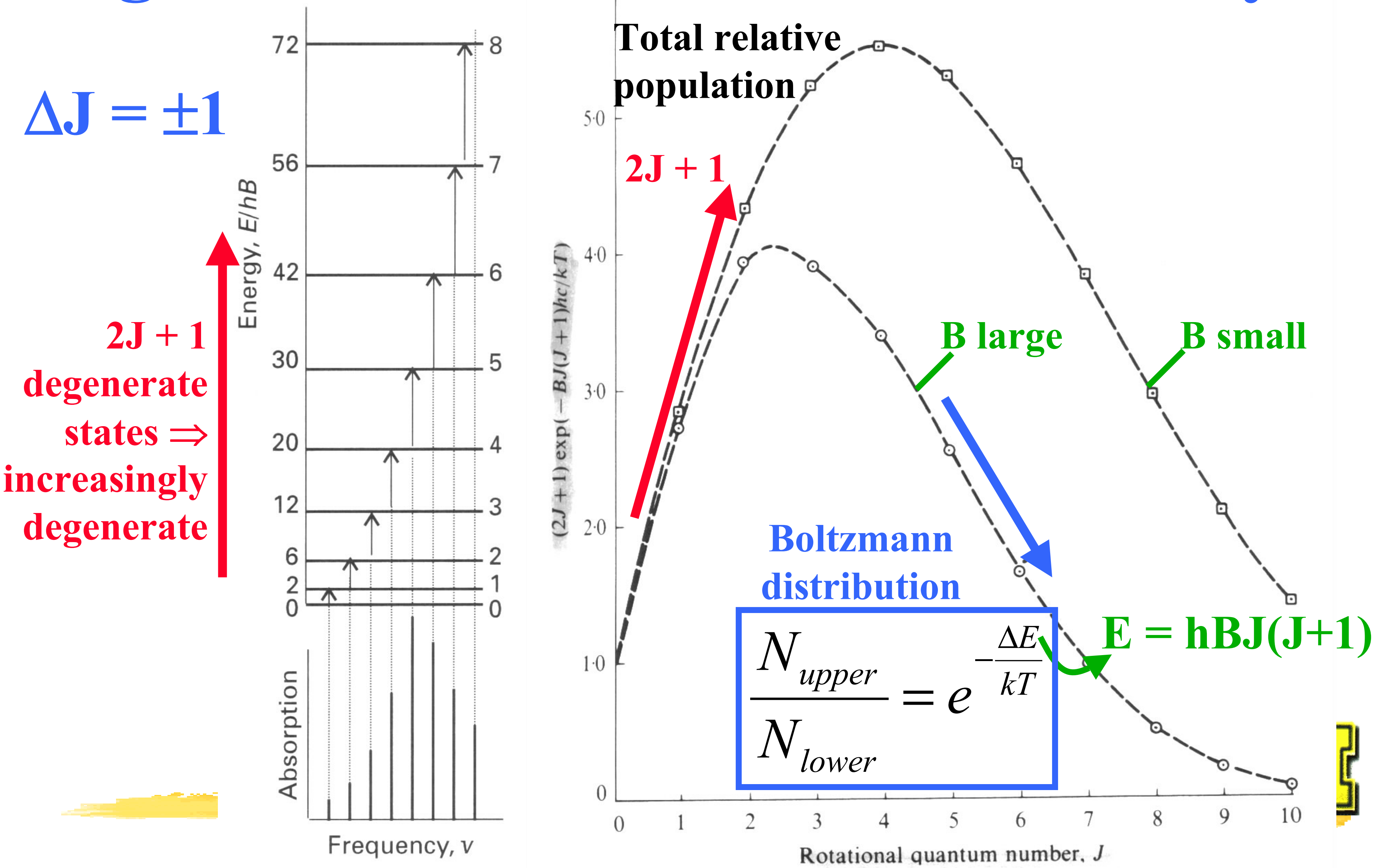
all $m_J = -J, \ldots, +J$ share the same energy

$\Downarrow$

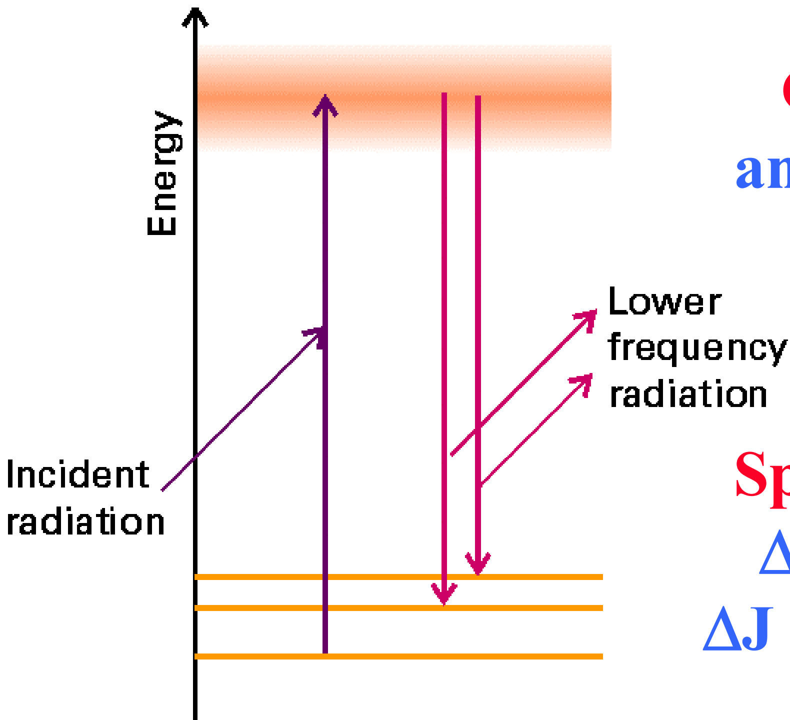
2J+1 degeneracy

Selection rule: $\Delta m_J = 0, \pm 1$

The allowed rotational transitions of a rigid linear rotor and their intensity

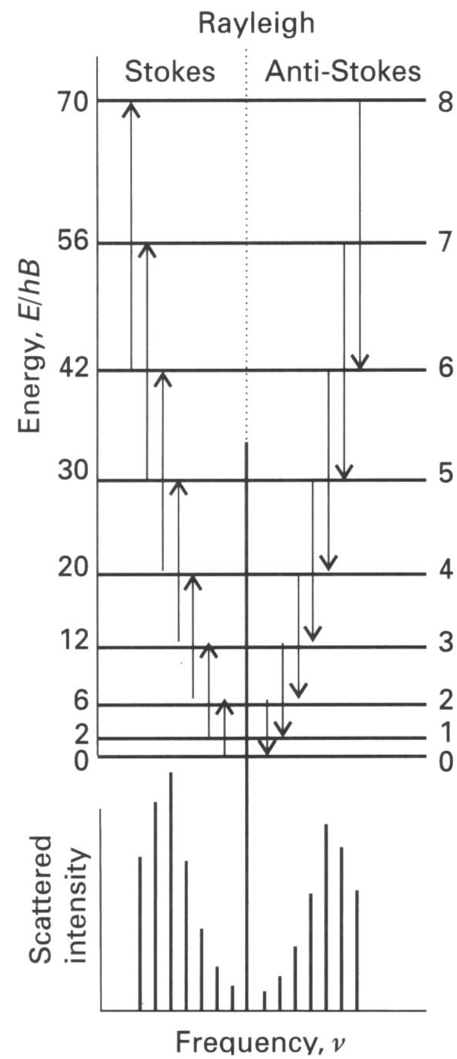


Rotational Raman spectroscopy

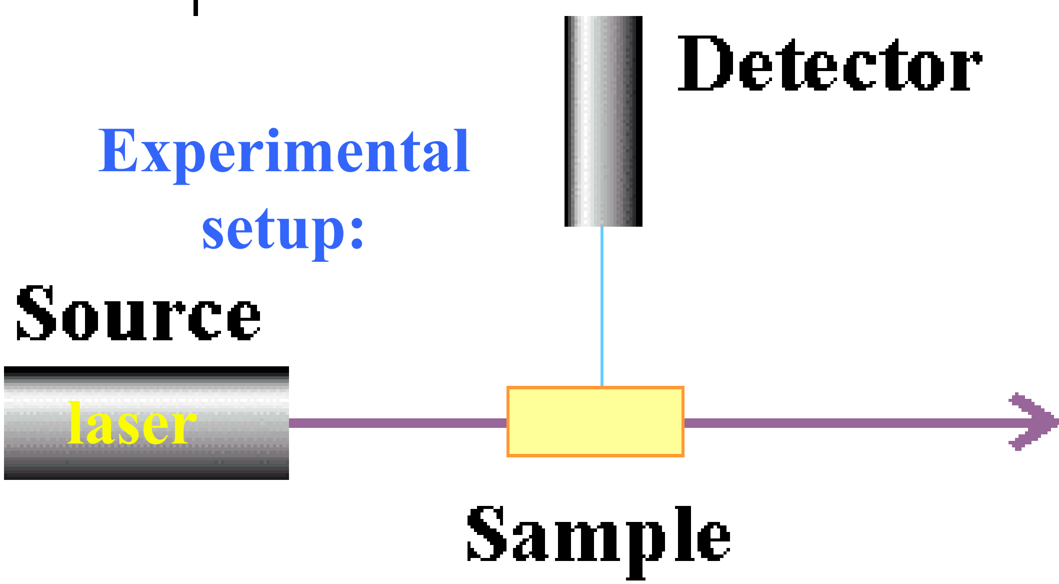


Gross selection rule:
anisotropic polarization (example: H-H!)

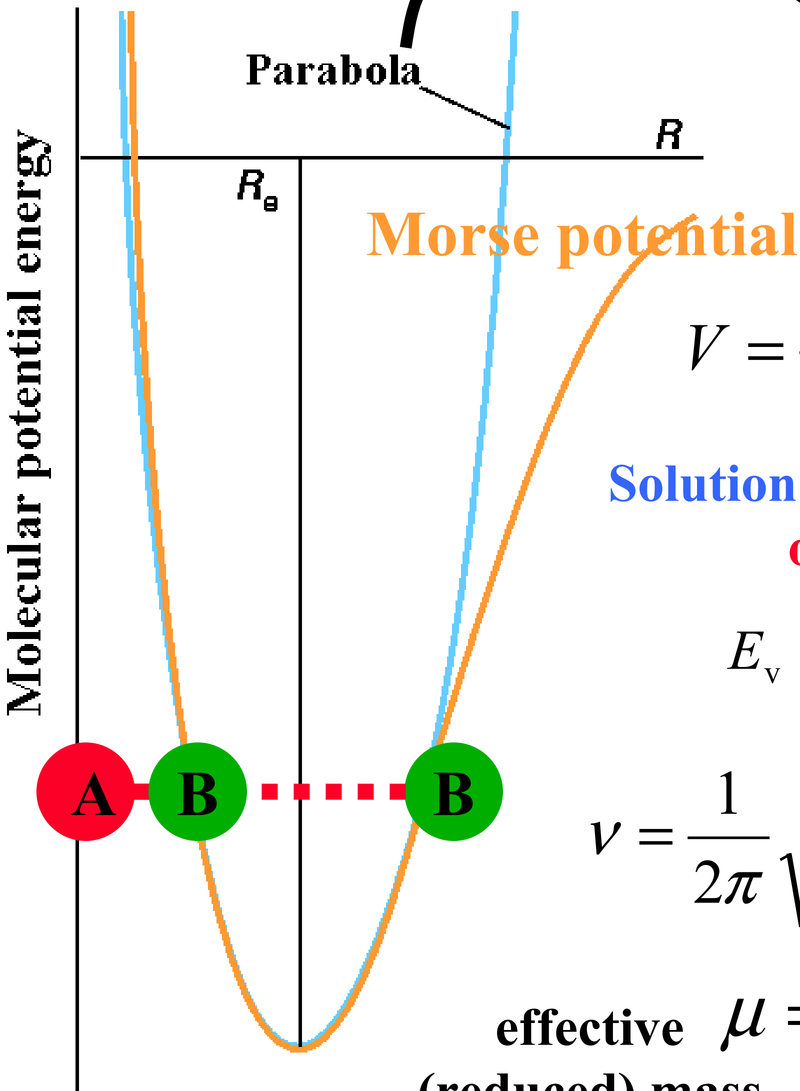
Specific selection rules:
ΔJ = +2 (Stokes lines)
ΔJ = -2 (anti-Stokes lines)



Experimental setup:



The vibration of molecules



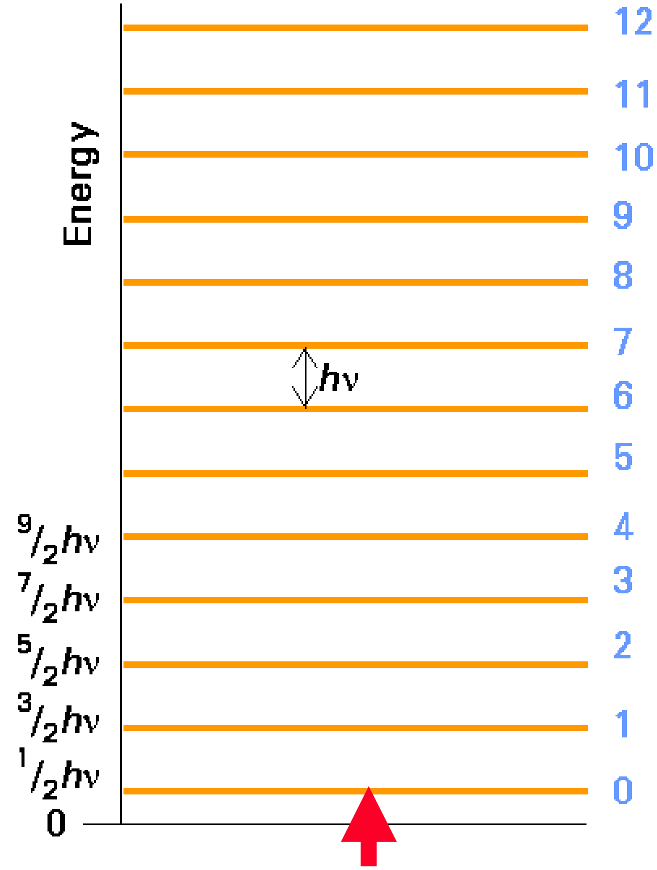
$$V = \frac{1}{2}k(R - R_e)^2$$

Solution for the harmonic oscillator:

$$E_v = \left(v + \frac{1}{2}\right)h\nu$$

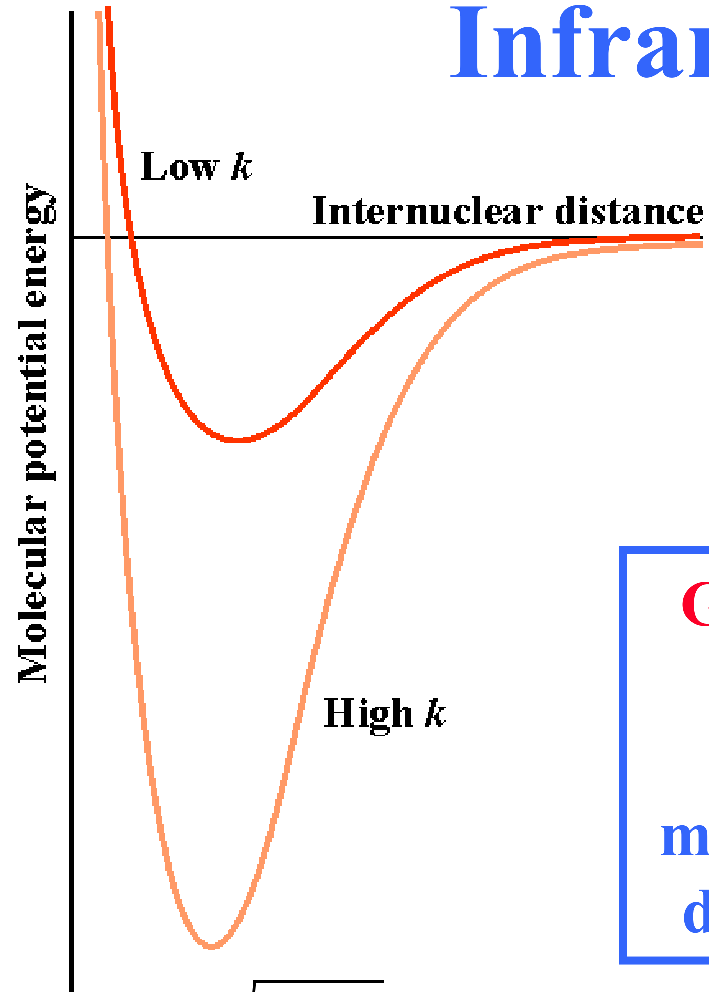
$$\nu = \frac{1}{2\pi}\sqrt{\left(\frac{k}{\mu}\right)}$$ ← **spring constant**

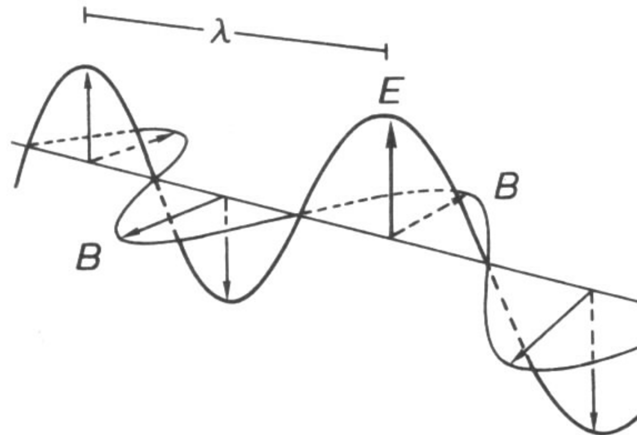
effective (reduced) mass $$\mu = \frac{m_A m_B}{m_A + m_B}$$

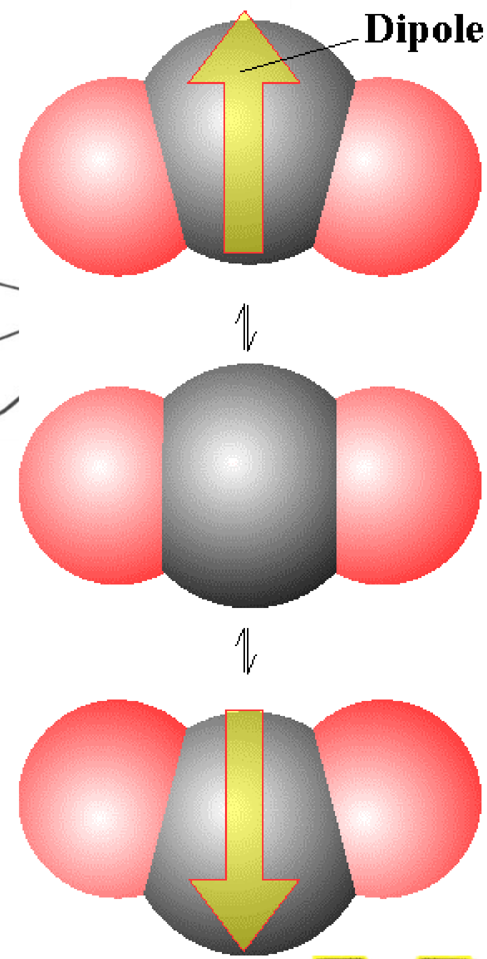


zero point energy

Vibrational transitions: Infrared spectroscopy





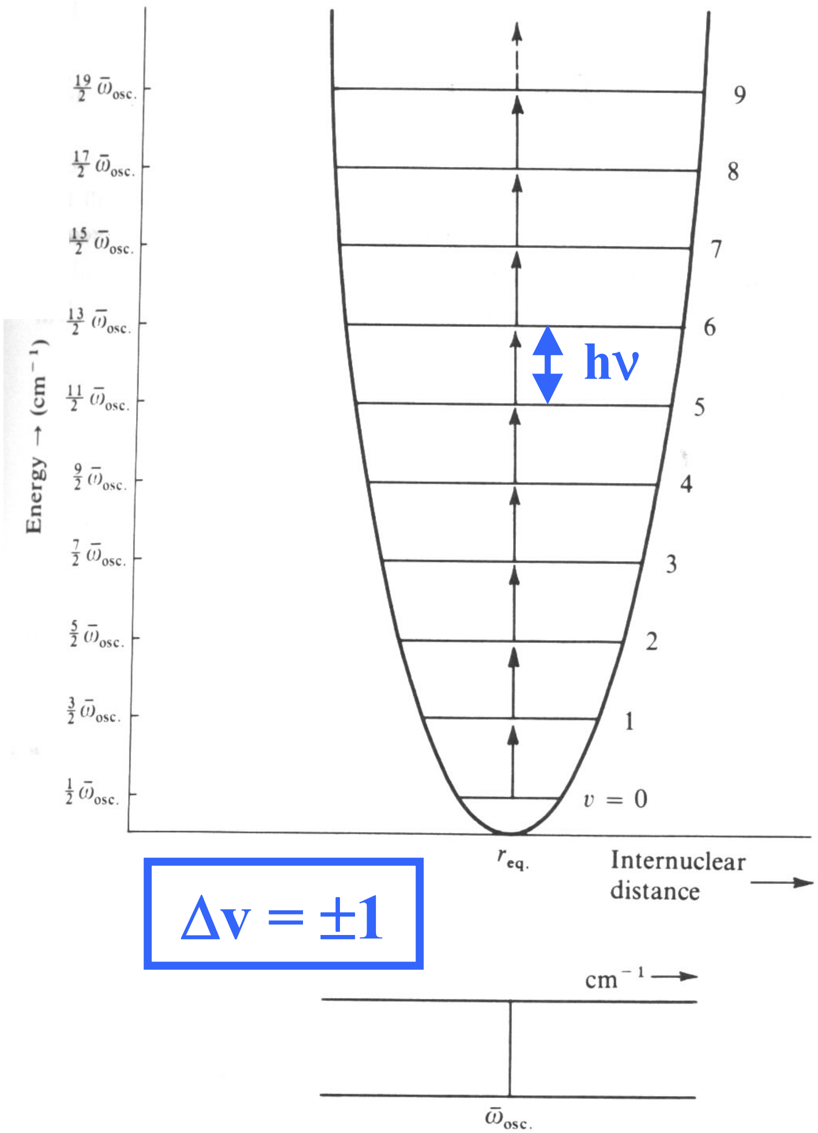


Gross selection rule:
the electric dipole moment of the molecule must change during the vibration

$$\nu = \frac{1}{2\pi}\sqrt{\left(\frac{k}{\mu}\right)} \Rightarrow 300\text{-}3000\ \text{cm}^{-1} = \text{Infrared}$$

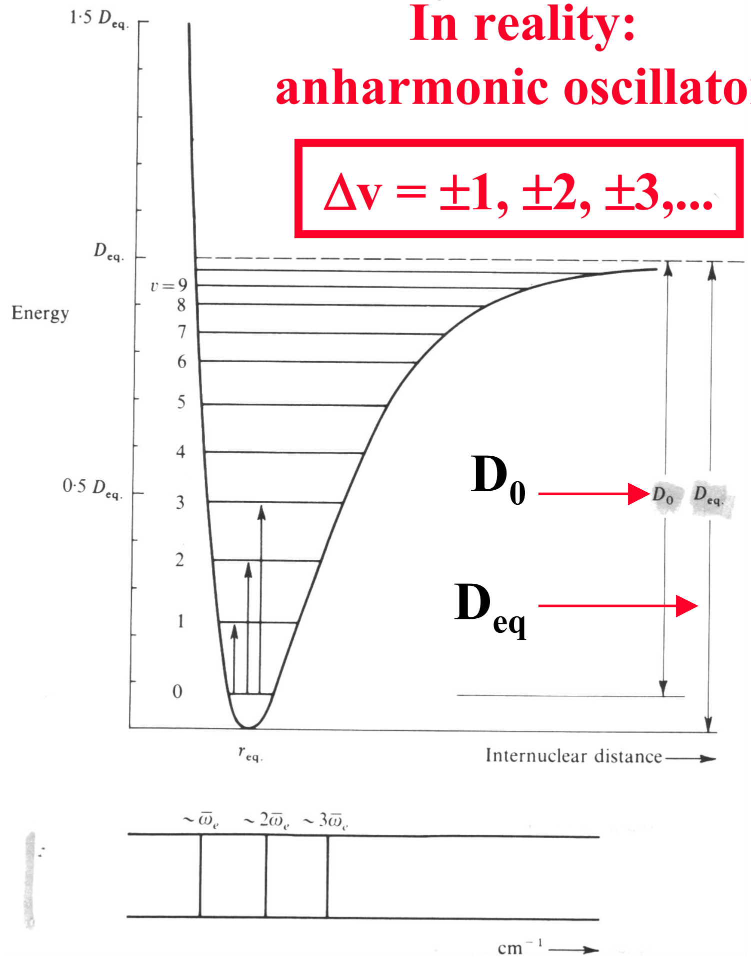
Specific selection rules

harmonic oscillator



$\Delta v = \pm 1$

In reality: anharmonic oscillator

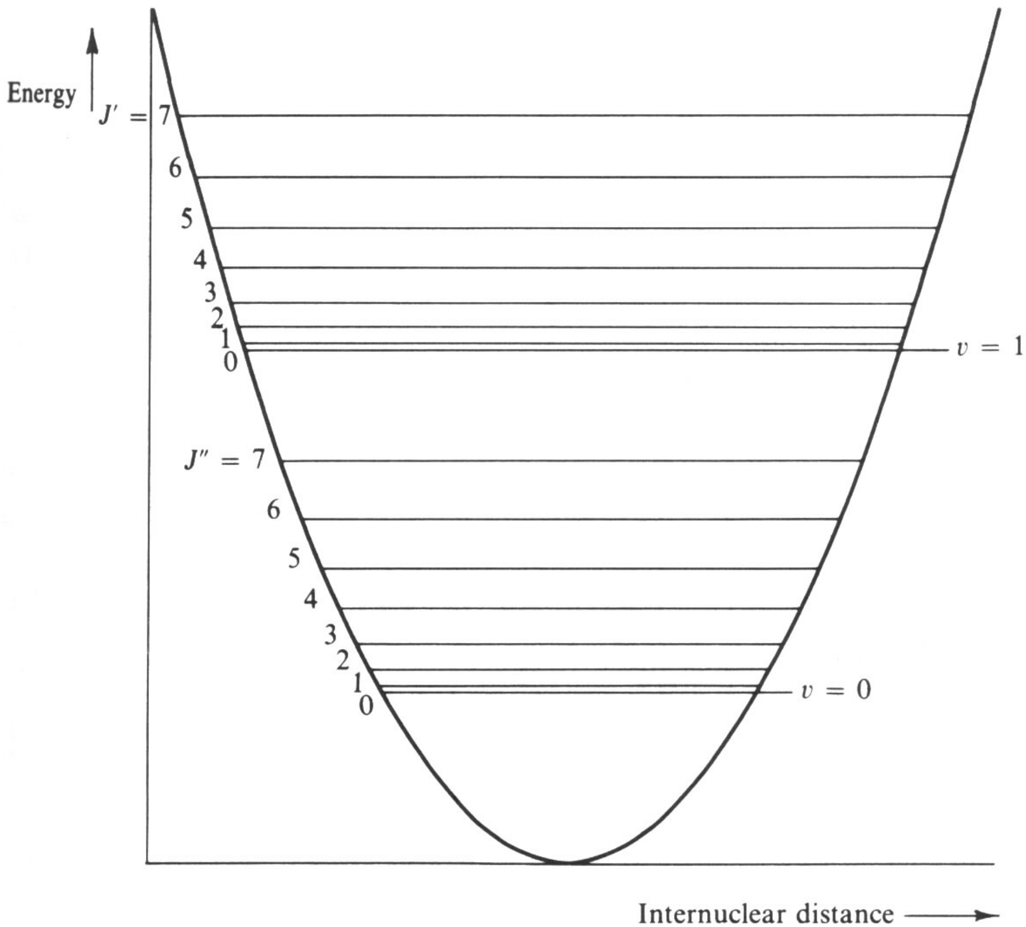


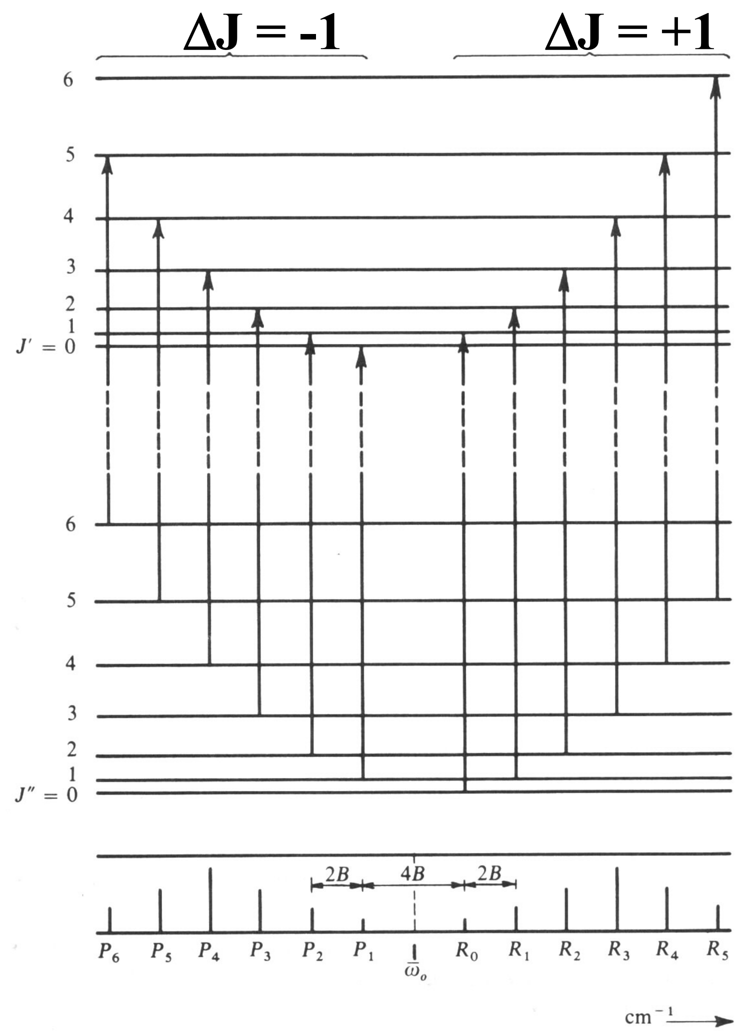
$\Delta v = \pm 1, \pm 2, \pm 3, \ldots$

x_e = anharmonicity constant

$$E_v = \left(v + \frac{1}{2}\right) h\nu - \left(v + \frac{1}{2}\right)^2 h\nu x_e$$

The vibrating rotor





Born-Oppenheimer approximation:

The energies of rotations and vibrations are so different that $E_{total} = E_{rot.} + E_{vib.}$

Vibrations of polyatomic molecules: How many are there?

Each atom can move along one of three axes:

⇒ 3N possible displacements (= degrees of freedom)

⇓

Three of these degrees of freedom correspond to translational motion:

⇒ 3N - 3 degrees of freedom left

⇓

Three (/two) degrees of freedom correspond to rotations:

⇒ 3N - 6 (3N - 5 for linear molecule) degrees of freedom left for vibrations