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Rotational Spectroscopy:

Introduction:

1. Free atoms do not rotate or vibrate.
2. For an Oscillatory or a rotational motion of a pendulum, one end has to be tied or fixed to some point.
3. In molecules such a fixed point is the center of mass.
4. The atoms in a molecule are held together by Chemical bonds.
5. The rotational and vibrational energies are usually much smaller than the energies required to break Chemical bonds.
6. The rotational energies correspond to the microwave region of electromagnetic radiation (3×10^{10} to 3×10^{12} Hz; energy range around 10 to 100 J/mol)
7. The vibrational energies are in the infrared region (3×10^{12} to 3×10^{14} Hz; energy range around 10 kJ/mol)
8. For rigid rotors (no vibration during rotation) and harmonic oscillator (where in there are equal displacement of atoms on either side of the center of ~~mass~~ mass), there are simple formulae characterizing the molecular energy level.
9. In real life, molecules rotate and vibrate simultaneously and high speed rotations affect vibration and vice versa.

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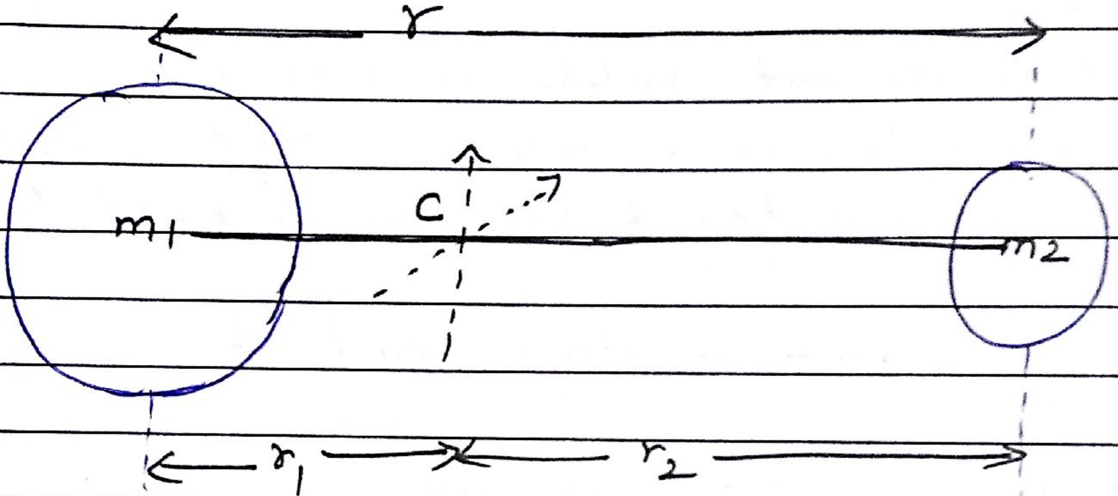
Rotational spectra of diatomics:



A rigid diatomic with masses m_1 and m_2 joined by a thin rod of length $r = r_1 + r_2$. The center of mass is at C.

* The two independent rotations of this molecule are with respect to the two axes which pass through C and are perpendicular to the bond length r.
* (The rotation with respect to the bond axis is possible only for 'classical' objects with large masses.
* For quantum objects a 'rotation' with respect to the molecular axis does not correspond to any change in the molecule as the new configuration is indistinguishable from the old one.)

Resistance of a rotational body for its own rotational motion

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The centre of mass is defined by equating the moments on both segments of the molecular axis

$$m_1 r_1 = m_2 r_2 \quad \text{--- (1)}$$

The moment of inertia is defined by

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

$$= m_1 r_1 \cdot r_1 + m_2 r_2 \cdot r_2$$

$$I = m_2 r_2 \cdot r_1 + m_1 r_1 \cdot r_2$$

$$I = (m_1 + m_2) r_1 r_2 \quad \text{--- (2)}$$

Since $m_1 r_1 = m_2 r_2$ and $r = r_1 + r_2$

$(r_2 = r - r_1)$

$$m_1 r_1 = m_2 (r - r_1)$$

$r_1 = r - r_2$

$$m_1 r_1 = m_2 r - m_2 r_1$$

$m_1 r_1 = m_2 r_2$

$$m_1 r_1 + m_2 r_1 = m_2 r$$

$$(m_1 + m_2) r_1 = m_2 r$$

$$\therefore \boxed{r_1 = \frac{m_2 r}{m_1 + m_2}} \quad \text{--- (3)}$$

Similarly,

$$r_2 = \frac{m_1 r}{m_1 + m_2} \quad \text{--- (3)}$$

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Substituting r_1 and r_2 in eqn (2)

$$I = r_1 r_2 (m_1 + m_2)$$

$$= \frac{m_2 r}{(m_1 + m_2)} \times \frac{m_1 r}{(m_1 + m_2)} \times (m_1 + m_2)$$

$$I = \frac{m_1 m_2 r^2}{(m_1 + m_2)}$$

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

μ is the reduced mass and is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

The rotation of a diatomic is equivalent to a rotation of a mass μ at a distance of r from the origin C.

The kinetic energy of this rotational motion is

$$K.E = \frac{L^2}{2I}$$

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Where L is the angular momentum,
I is the angular velocity (rotational) in radian/sec.

The quantized rotational energy levels for the diatomic

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

The energy differences between any two rotational levels is usually expressed in cm^{-1}.
The wave number corresponding to a given ΔE is given by

$$\bar{\nu} = \frac{\Delta E}{hc} \; cm^{-1}$$

The energy levels in cm^{-1} are therefore

$$E_J = B J(J+1)$$

where $B = \dfrac{h}{8\pi^2 I c}$

The selection rule for a rotational transition is

$$\Delta J = \pm 1$$

The molecule has to possess dipole moment. Molecules such as HCl and CO will show rotational spectra while homonuclear diatomic H_2, Cl_2 and CO_2 will not.

$E_J = BJ(J+1)$

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$J=1, \; E_J = 1(1+1)\,B$

$= 2B$

$J=2, \; E_J = 2(2+1)\,B$

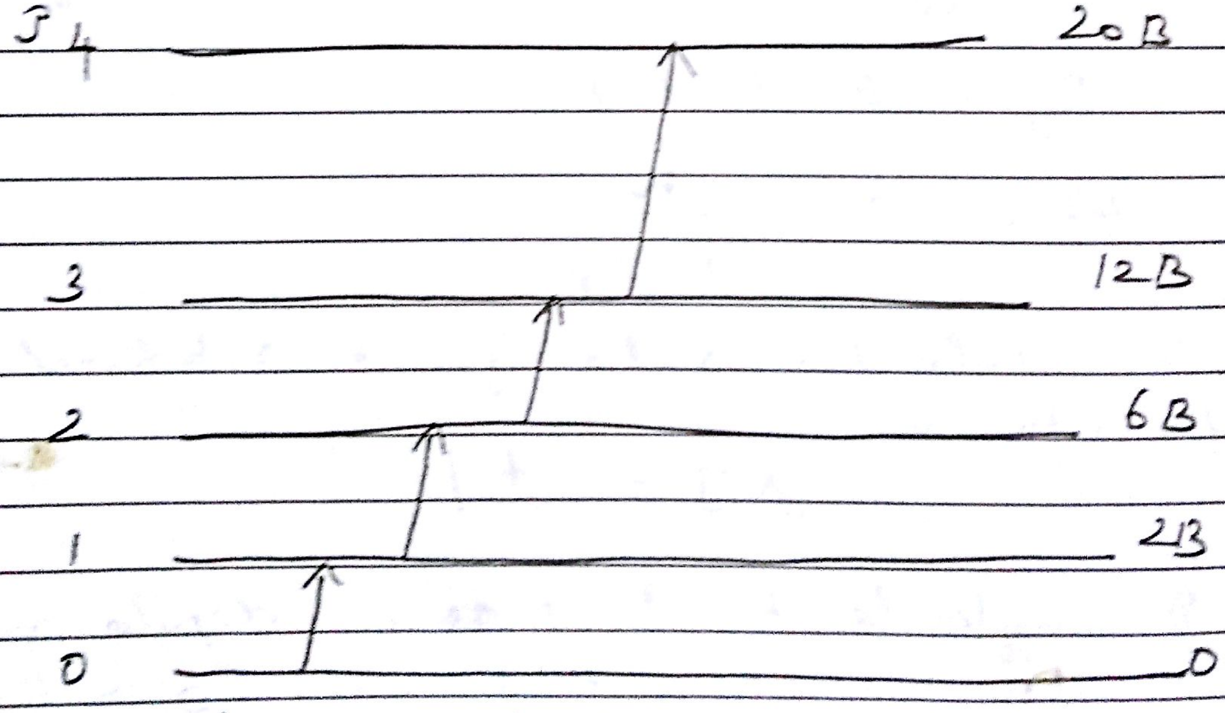
$= 6B$

$J=3, \; E_J = 3(3+1)\,B$

$= 12B$

$J=4, \; E_J = 4(4+1)\,B$

$= 20B.$



Rotational energy levels of a rigid diatomic molecule and the allowed transitions.