Microspectroscopy, Rigid Rotor Model, Quantum Mechanical Expression (rotational)

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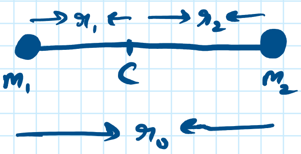
MICROSPECTROSCOPY

- Studying of rotational transitions
- Homodiatomic molecules like H_2, N_2, O_2 ....
  - Microwave inactive = rotationally inactive
    WHY?
    Dipole moment = $M = 0$
- Heterodiatomic molecules like HCl, HBr, HI ...
  - Microactive active = rotationally active
    WHY?
    Dipole moment = $M \neq 0$

Heterodiatomic molecule (rigid rotor model)

no vibration during rotation of molecule; pure rotatory transition

Masses are m_1, m_2 joined by a rigid bar of length:



$$r_0 = r_1 + r_2$$

$$r_2 = r_0 - r_1 \quad \text{—— (1)}$$

Balancing equation:

$$m_1 r_1 = m_2 r_2 \quad \text{—— (2)}$$

End-over-end rotation about point "C"

Moment of inertia I

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{—— (3)}$$

Compare eqn. (2) & (3)

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

$$I = r_1 r_2 (m_1 + m_2) \quad \text{—— (4)}$$

Substitute eqn (2) values into eqn. (1)

$$m_1 r_1 = m_2 r_2$$

$$m_1 r_1 = m_2 (r_0 - r_1) \qquad [\because r_2 = r_0 - r_1]$$

$$m_1 r_1 = m_2 r_0 - m_2 r_1$$

$$m_1 r_1 + m_2 r_1 = m_2 r_0$$

$$\Rightarrow r_1(m_1+m_2) = m_2 r_0$$

$$\left.\begin{aligned} r_1 &= \frac{m_2 r_0}{m_1+m_2} \\ r_2 &= \frac{m_1 r_0}{m_1+m_2} \end{aligned}\right] \quad (5)$$

Substitute eqn. (5) in eqn. (4)

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

$$I = \left(\frac{m_2 r_0}{m_1+m_2}\right)\left(\frac{m_1 r_0}{\cancel{m_1+m_2}}\right)\cancel{(m_1+m_2)}$$

$$I = \frac{m_1 m_2 r_0^2}{m_1+m_2}$$

reduced mass $= \mu = \dfrac{m_1 m_2}{m_1+m_2}$

$$\boxed{I = \mu r_0^2}$$

Quantum Mechanical Expression (rotational)

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

Moment of inertia

Planck's constant $= 6.6\times10^{-34}$

Rotational quantum number

w.k.t

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

Substituting E,

$$\bar{\nu} = \frac{\frac{h^{\cancel{2}}}{8\pi^2 I}(J)(J+1)}{\cancel{h}c}$$

$$\boxed{\varepsilon_J = \bar{\nu} = \frac{h}{8\pi^2 Ic}(J)(J+1) \text{ cm}^{-1}}$$

$$\boxed{\varepsilon_J = \bar{\nu} = (B)(J)(J+1) \quad \text{cm}^{-1}}$$

$$\boxed{\varepsilon_J = \nu = \underbrace{(B)}_{\text{Rotational constant}}(J)(J+1) \ \text{cm}^{-1}}$$

Rotational constant

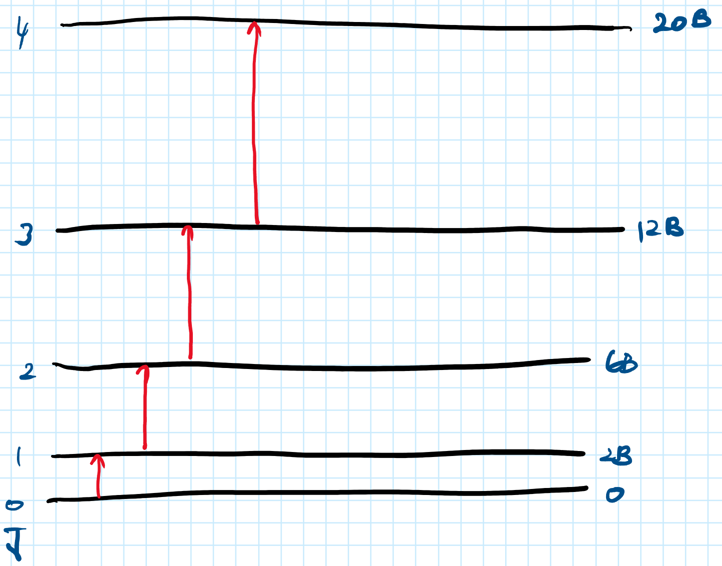
$$\boxed{B = \frac{h}{8\pi^2 I c}}$$

Selection Rule (rotational transitions, rigid rotor)

$$\boxed{\Delta J = \pm 1}$$

Allowed Rotational Energy Level Diagram

J	$\varepsilon_J = \bar{\nu} = BJ(J+1)\ \text{cm}^{-1}$
0	0
1	$2B$
2	$6B$
3	$12B$
4	$20B$

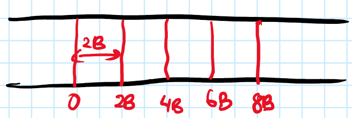


$J = 0, 1, 2, 3, 4, 5$

energy $= 0,\ 2B,\ 6B,\ 12B,\ 20B$

energy difference $= \underbrace{2B,\ 4B}_{2B},\ \underbrace{4B,\ 6B}_{2B},\ \underbrace{6B,\ 8B}_{2B}$

Spectrum



FORMULAE

① $M = \dfrac{m_1 m_2}{m_1 + m_2}$

② $I = M r_0^2$

③ $r_0^2 = \frac{I}{M} \Rightarrow r_0 = \sqrt{\frac{I}{M}}$

④ $E_J = \frac{h^2}{8\pi^2 I} J(J+1)$ Joules

⑤ $\varepsilon_J = \bar{\nu} = \frac{h}{8\pi^2 Ic} J(J+1)$ cm^{-1}

⑥ $B = \frac{h}{8\pi^2 Ic}$

⑦ $I = \frac{h}{8\pi^2 Bc}$

NUMERICALS

① Calculate the rotational energy of NO molecule corresponding to J = 1 in Joule and cm^{-1}, assuming it to be rigid rotor. The atomic masses of N and O are 14.004 amu, 15.994 amu respectively, and bond length is 115 pm.
[1 pm $= 10^{-12}$ m, $c = 3\times10^{8}$ m/s, 1 amu $= 1.66\times10^{-27}$ kg, $h = 6.6\times10^{-34}$ J/kg?
$N = 6.023\times10^{23}$]

Soln: $M = \frac{m_1 m_2}{m_1+m_2}$

$= \frac{14.004\times1.66\times10^{-27}\times15.994\times1.66\times10^{-27}}{14.004\times1.66\times10^{-27}+15.994\times1.66\times10^{-27}}$

$= 1.239\times10^{-26}$ kg

$I = Mr_0^2$

$= 1.239\times10^{-26}\times115\times115\times10^{-24}$

$= 1.638\times10^{-46}$ Kg m^2

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

$= \frac{(6.6\times10^{-34})^2}{\cancel{4}8\pi^2(1.638\times10^{-46})}(1)(\cancel{2})$

$= 6.736\times10^{-23}$ J

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

$$= \frac{6.736 \times 10^{-23}}{6.6 \times 10^{-34} \times \underline{3 \times 10^{10}}} = \underline{\underline{3.402 \ cm^{-1}}}$$

cm^{-1}; not m^{-1}