

Moment of Inertia

The moment of inertia of a rotating object is defined as:

$$I = \int r^2 dm$$

m: mass

r: perpendicular distance of a point mass (could be an atom or nucleus) to the axis of rotation.

SI Unit for I is $\text{kg} \cdot \text{m}^2$

For a rigid body consisting of N point masses (m_i) with distances (r_i) to the rotation axis, the moment of inertia is given by:

$$I = \sum_{i=1}^N m_i r_i^2$$

Different axes of rotation will have different I 's about those axes. The moment of inertia tensor is a convenient way to summarize all moments of inertia of an object using matrix representation.

$$I = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix}$$

Here, I_{xx} denotes the moment of inertia w.r.t. the

x-axis when the molecule is rotated about the x-axis.

I_{xy} denotes the moment of inertia w.r.t. the y-axis

when the molecule is rotated about the x-axis.

The off diagonal elements are called products of inertia.

The matrix elements are given by:

$$I_{xx} = \sum_{i=1}^N m_i (y_i^2 + z_i^2) = \sum_{i=1}^N m_i r_{x,i}^2$$

$$I_{yy} = \sum_{i=1}^N m_i (x_i^2 + z_i^2) = \sum_{i=1}^N m_i r_{y,i}^2$$

$$I_{zz} = \sum_{i=1}^N m_i (x_i^2 + y_i^2) = \sum_{i=1}^N m_i r_{z,i}^2$$

The products of inertia are given by:

$$I_{xy} = I_{yx} = - \sum_{i=1}^N m_i (x_i y_i)$$

$$I_{xz} = I_{zx} = - \sum_{i=1}^N m_i (x_i z_i)$$

$$I_{yz} = I_{zy} = - \sum_{i=1}^N m_i (y_i z_i)$$

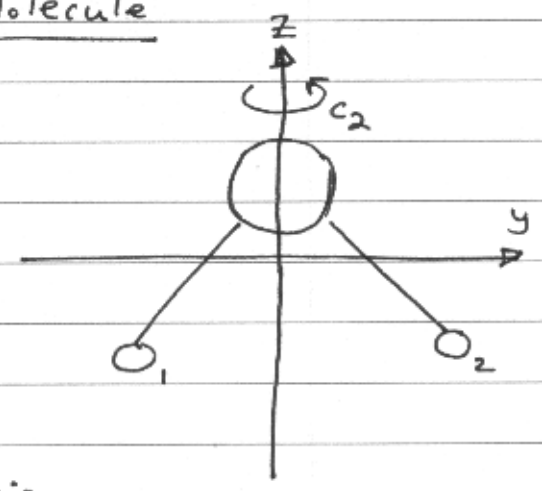
There are three principal axes of moment of inertia given by I_a , I_b and I_c

These principal axes must meet the following conditions:

- ① Axes of rotation (c) must coincide with principal axes.
- ② A reflection plane must contain two principal axes
- ③ The center of symmetry of the molecule must be at the origin.
- ④ The principal axes must go through the center of gravity and must be perpendicular to each other.

Moment of Inertia for H₂O molecule

H₂O molecule is an example of a planar molecule.



By convention, the highest order axis of rotation is always chosen to be the z-axis, while the out of plane axis is chosen to be the x-axis.

The figure shown in the PowerPoint slides for water is to be used. ($I = mr^2$)

$$I_z = m_H f^2 + m_H f^2 = 2m_H f^2$$

$$I_y = m_O h^2 + m_H g^2 + m_H g^2 = m_O h^2 + 2m_H g^2$$

For any planar molecule, the out of plane moment of inertia is equal to the sum of the two in-plane moments of inertia. Thus:

$$I_x = I_y + I_z = m_O h^2 + 2m_H g^2 + 2m_H f^2 = m_O h^2 + 2m_H (g^2 + f^2)$$

The cartesian axes can be labeled based on the magnitudes of the moments of inertia. The x, y and z-axes are labeled with a, b, and c such that:

$$I_c \geq I_b \geq I_a$$

From the center of mass definition:

$$\sum_{i=1}^N m_i r_i = 0 \quad ; \text{ and trigonometry,}$$

The moments of inertia can be obtained. (Details also next page)

$$\begin{aligned} I_z &= 1.148 \text{ uA}^2 && \rightarrow I_B \\ I_y &= 0.6115 \text{ uA}^2 && \rightarrow I_A \\ I_x &= 1.760 \text{ uA}^2 && \rightarrow I_c \end{aligned}$$

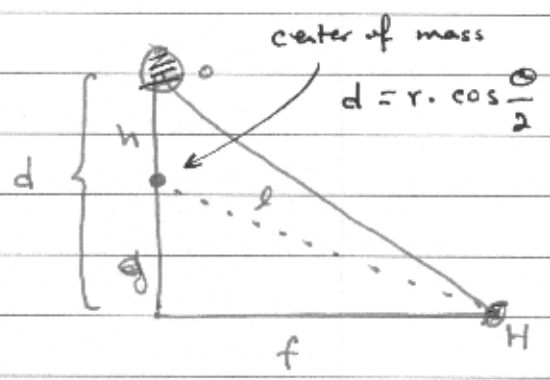
Details of how f, g and h distances could be obtained.

From trigonometry:

$$\sin \frac{\theta}{2} = \frac{f}{r} \Rightarrow f = r \cdot \sin \frac{\theta}{2} = 0.7575 \text{ \AA}$$

From center-of-mass definition:

$$\begin{aligned} m_o r_o + 2 m_H r_H &= 0 \\ m_o h + 2 m_H l &= 0 \\ m_o h + 2 m_H \sqrt{g+f} &= 0 \\ m_o^2 h^2 + 4 m_H^2 (g+f) &= 0 \\ m_o^2 h^2 + 4 m_H^2 d - 4 m_H^2 h + 4 m_H^2 f &= 0 \\ m_o^2 h^2 - 4 m_H^2 h + 4 m_H^2 (d+f) &= 0 \end{aligned}$$



Solving for h gives $h = 0.0652 \text{ \AA}$

Since $d = h + g$; $g = 0.5213 \text{ \AA}$

Linear Molecules :

We showed that the selection rule for rotational transitions is $\Delta J = \pm 1$ and the transition wavenumber is given by:

$$\Delta \bar{E} = 2B(J+1)$$

Important points to be looked at:

- ① The separations between adjacent transitions in linear molecules are nearly equal to $2B$ as shown from the rigid rotor theory.

However, as J becomes higher a systematic decrease in the $2B$ value is observed and it is attributed to the "Centrifugal distortion".

- ② As the number of atoms increases in linear molecules, a smaller B value is observed. This is because polyatomic molecules have larger moments of inertia compared to diatomic molecules.

$$\begin{aligned} B(\text{Hz}) &= \frac{h}{8\pi^2 I} \\ \text{or} \\ B(\text{cm}^{-1}) &= \frac{h}{8\pi^2 c I} \end{aligned} \quad \left. \vphantom{\begin{aligned} B(\text{Hz}) \\ B(\text{cm}^{-1}) \end{aligned}} \right\} \bar{E} = h\nu = hc\bar{\nu}$$

Example:

<u>Molecules</u>	<u>$B(\text{GHz})$</u>
CO	~ 115.2
O=C=S	~ 12.2
H-C≡C-C≡C-C≡N	~ 1.331

As a result, one expects to see more rotational transitions of heavier molecules in the microwave and millimeter range of the spectrum.

Line Intensity in a Rotational Spectrum

The populations of rotational energy levels relative to $J=0$ are obtained from Boltzmann equation:

$$\frac{N_n}{N_m} = g_i e^{-\Delta E/kT}$$

This is rewritten for rotational levels as:

$$\textcircled{A} \rightarrow \frac{N_J}{N_{J=0}} = (2J+1) e^{-E_r/kT}$$

$2J+1$ is the degeneracy.

* Remember that M_J can take $2J+1$ values that represent space quantization of the rotational angular momentum in a diatomic molecule.

E_r is the rotational energy of level J .

$$* E_r = BJ(J+1)$$

It is clear that:

$$\frac{N_J}{N_0} \propto (2J+1) \propto \frac{1}{e^{-E_r/kT}}$$

$\frac{N_J}{N_0}$ increases as J increase to a certain level

and then it drops down afterwards.

See CO rotational spectra as an example.

The highest population can be obtained by :

$$\frac{d(N_J/N_0)}{dJ} = 0$$

that gives:

$$J_{\max} \approx \sqrt{\frac{kT}{2hB}} - \frac{1}{2} \quad B \text{ is given here in Hz}$$

At high temperature or for small B values (heavier molecules) many upper rotational levels will have significant populations.

However, the intensities (I_{obs}) of rotational transitions are proportional to the fraction of the total number of molecules (N) and not to the number of molecules in the $J=0$ level (N_0).

$$\text{That is } I_{\text{obs}} \propto \frac{N_J}{N}$$

Here the use of the statistical mechanics is essential.

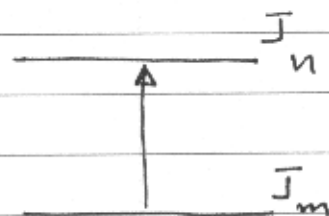
$$\frac{N_J}{N} = \frac{(2J+1)e^{-E_J/kT}}{q_r}$$

where q_r is the rotational partition function given by:

$$q_r = \sum_{J=0}^{\infty} (2J+1) e^{-E_J/kT}$$

$$q_r \approx \int_0^{\infty} (2J+1) e^{-E_J/kT} dJ = \frac{kT}{hB} \quad (B \text{ in Hz})$$

The intensity of absorption (I_{abs}) for a transition between a lower state m to a higher state n is a net result of stimulated absorption.



$$I_{nm} = \frac{N_{J_m}}{N} B_{nm} \rho(\nu_{nm}) h\nu_{nm}$$

B_{nm} : Einstein coefficient.

$\rho(\nu_{nm})$: Radiation density of frequency ν_{nm} .

$h\nu_{nm}$: Energy difference between states n and m .

Some derivation results in that:

$$\textcircled{B} \rightarrow I_{abs} \approx \rho(\nu_{J'J}) \frac{8\pi^3}{3(4\pi\epsilon_0)} \frac{hB}{kT} \mu^2 \nu_{J'J}^2 (J+1) e^{-\frac{E_r}{kT}}$$

↑
Permanent dipole moment

This results in that I_{abs} is a factor of ν^2 and of $(J+1)$ instead of $(2J+1)$ as was the case for $\frac{N_J}{N_0}$.

This has the effect of producing a maximum rotational line at $J > J_{max}$, where J_{max} corresponds to the highest population according to equation A.

Equation B tells that from intensity measurements of pure rotational spectrum, the magnitude of the dipole moment can be estimated.