

Rotational Spectroscopy

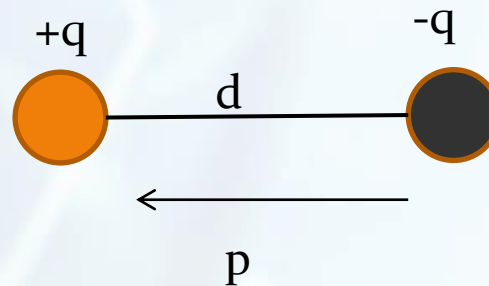
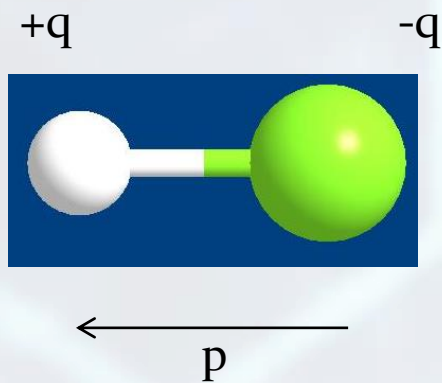
PG Sem. 3

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Introduction

- Rotational spectroscopy is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase.
- It is a uniquely precise tool for the determination of molecular structure in gas phase molecules.
- Pure rotational transitions in a molecule can be induced by radiation in the far infrared and microwave regions of the spectrum.
- Two requirements that restrict the microwave studies are : 1) the spectrum must be obtained in the gaseous state. 2) the molecule must have permanent dipole moment in the ground state in order to absorb microwave radiation.

- Electric dipole, $p = q \cdot d$ where q is the charge and d is the distance between the charges. (HCl molecule)

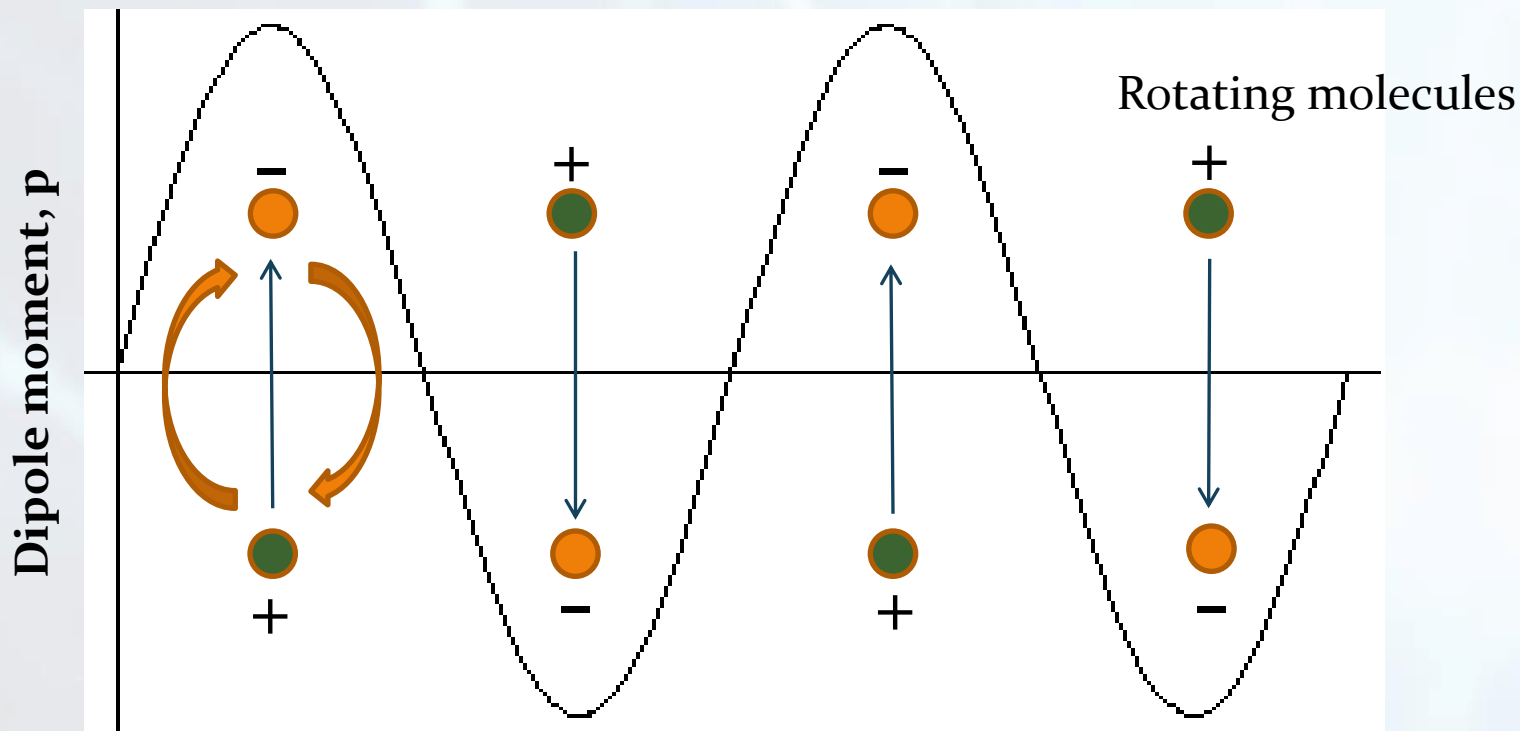


Most of the heteronuclear molecules such as HCl, H₂O, NH₃ etc. possess dipole moment and hence show rotational spectra.

Molecules can interact with electromagnetic radiation, absorbing or emitting a photon of frequency ω , if they possess an electric dipole moment p , oscillating at the same frequency

Gross Selection Rule:

A molecule has a rotational spectrum only if it has a permanent dipole moment.



Homonuclear molecules (e.g. O_2 , H_2 , Cl_2 , Br_2 do not have a permanent dipole moment and hence they do not have a microwave spectrum

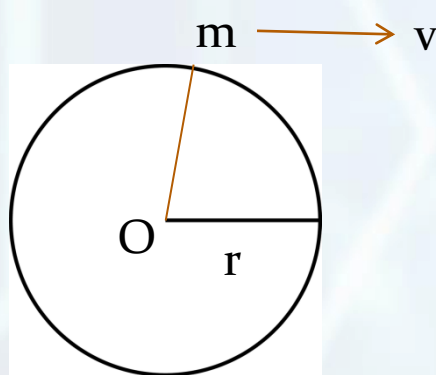
Rotating Systems

Linear velocity = distance/time

Angular velocity, ω = radians/time

$$I = \sum_i m_i r_i^2$$

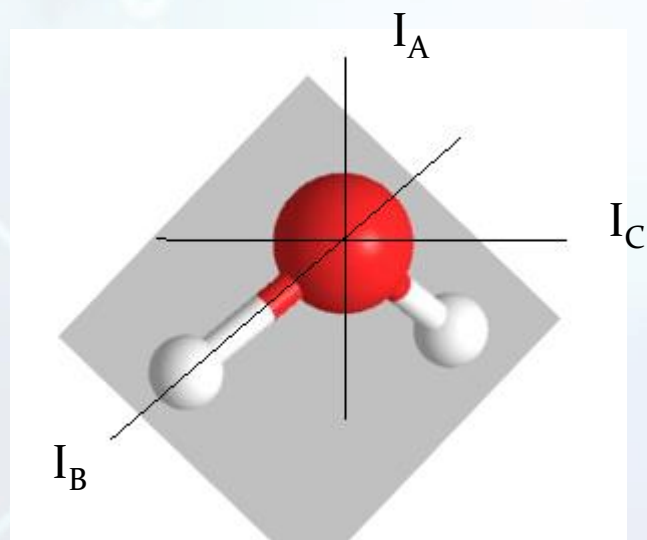
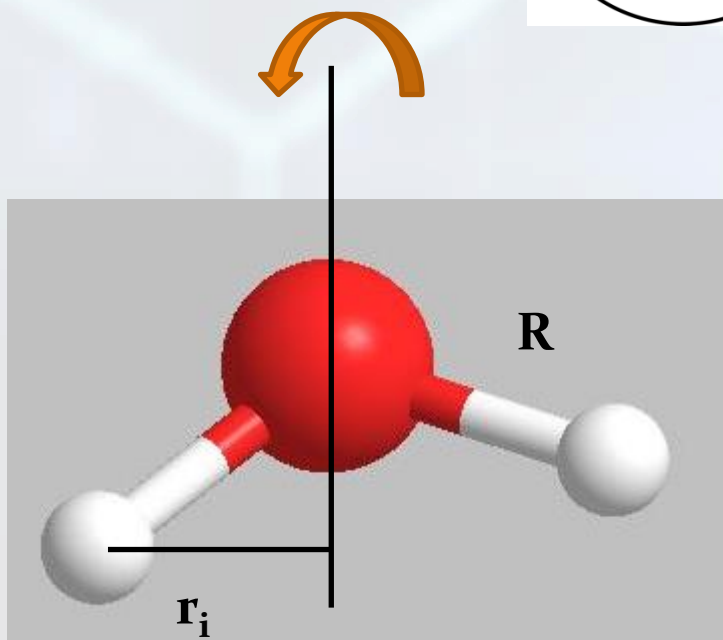
r_i stands for the distance perpendicular to the axis of rotation.



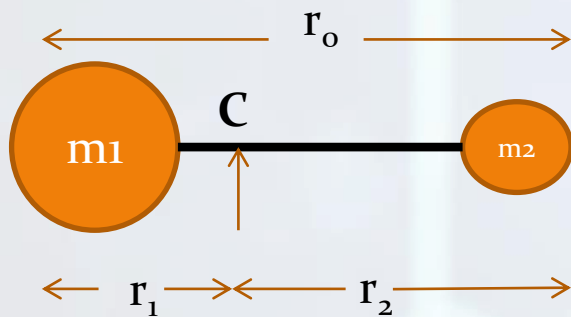
$$v = \omega \times r$$

Moment of inertia, $I = mr^2$

A molecule can have three different moments of inertia I_A , I_B and I_C about orthogonal axes a, b and c.



Rigid Diatomic Rotors



C stands for centre of gravity

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

$$I = \mu r_0^2$$

Where μ stands for reduced mass or the effective mass of the molecule and is given by the equation

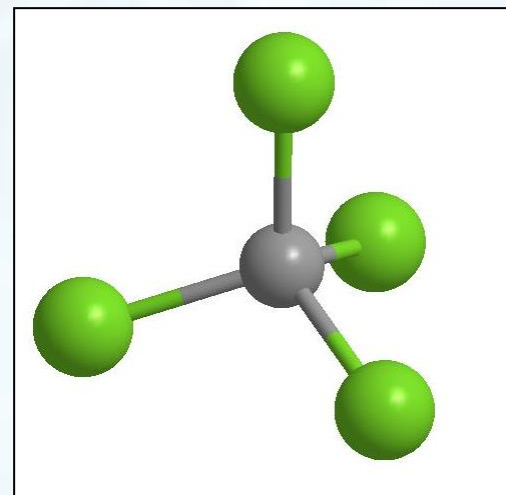
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The rotations of a diatomic molecule can be modeled as a rigid rotor. This rigid rotor model has two masses attached to each other with a fixed distance between the two masses.

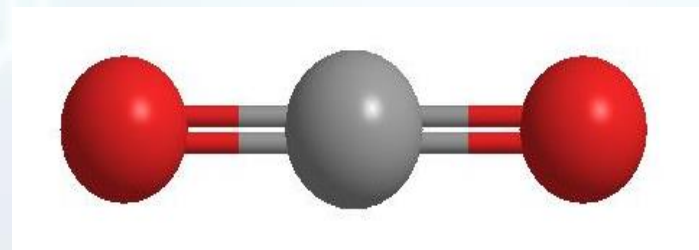
Classification of molecular rotors

- The particular pattern of energy levels (and, hence, of transitions in the rotational spectrum) for a molecule is determined by its symmetry. A convenient way to look at the molecules is to divide them into four different classes, based on the symmetry of their structure.
- I_A denotes the axis A which is the axis of rotation for highest order. The general convention, used in this article, is to define the axes such that with axis $I_A \leq I_B \leq I_C$ with axis A, corresponding to the smallest moment of inertia.
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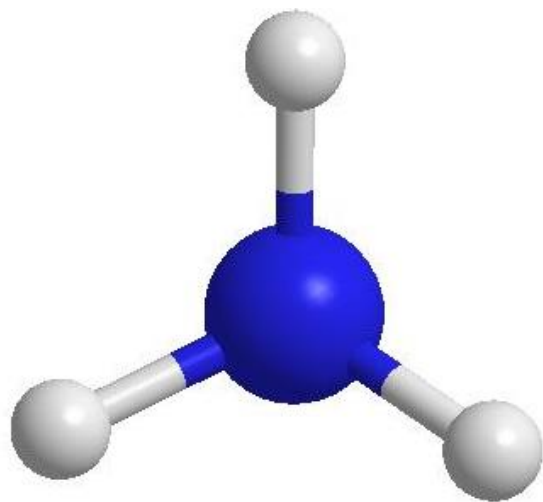
Spherical tops (spherical rotors): All three moments of inertia are equal to each other i.e. $I_A = I_B = I_C$. Molecules with tetrahedral or octahedral symmetry mostly come in this zone eg. CH_4 , CCl_4 , SF_6 .



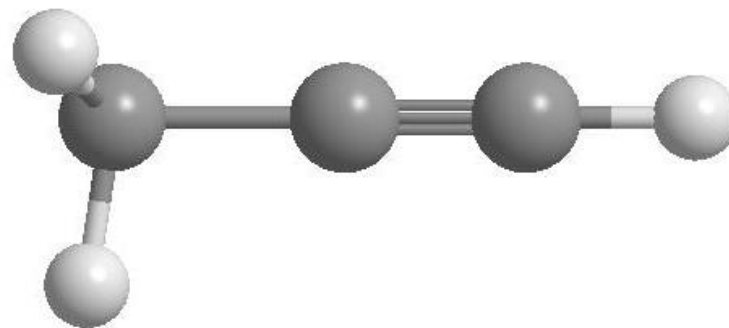
Linear molecules: For a linear molecule the moments of inertia are related by $I_A \ll I_B = I_C$. The value of I_A mostly stands zero in this case. Molecules with $C_{\infty h}$ and $D_{\infty h}$ symmetry comes in the category. Eg. Carbondioxide, HCN, Acetylene, CO etc.



Symmetric tops (symmetric rotors) A symmetric top is a molecule in which two moments of inertia are the same, i.e. $I_A = I_B$ or $I_B = I_C$. By definition a symmetric top must have a 3-fold or higher order rotation axis. They are further categorized into two types : Prolate ($I_A < I_B = I_C$) for the molecules such as Propyne and chloromethane and Oblate ($I_A > I_B = I_C$) for the molecules such as benzene and ammonia.



Oblate symmetry in Ammonia



Prolate symmetry in Propyne

Degrees of Freedom

Translational: It entails the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.

Rotational: The rotations around the center of mass of the molecule and they are also described by three orthogonal vectors i.e. it contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.

Vibrational: $3N - 6$ degrees of vibrational freedom for a nonlinear molecule and $3N - 5$ for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

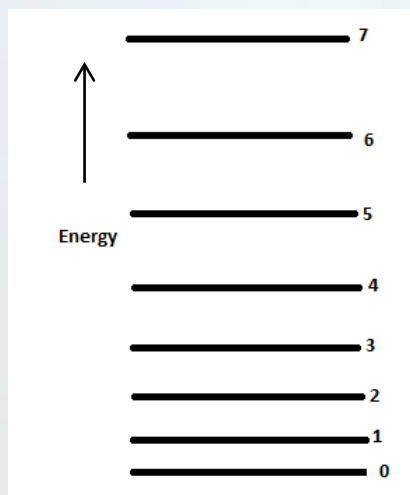
The quantum expression for angular momentum in a rigid rotor is given as:

$$P_J = [J(J + 1)]^{\frac{1}{2}} \frac{h}{2\pi}$$

According to Schrödinger equation for a rigid rotor :

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

Where J stands for rotational energy level and its value is always an integer 0,1,2,3,4....



Selection Rules of Rotational Spectroscopy

There are three rules for rotational spectra out of which two holds very firm role:

1. The molecule must have a permanent dipole moment i.e. $\mu \neq 0$.
2. $\Delta J = \pm 1$
3. $\Delta M_J = 0, \pm 1$ this rule only holds for the cases when the molecules is in electric or magnetic field.

Structure of rotational spectra

Spherical top molecules have no net dipole moment. A pure rotational spectrum cannot be observed by absorption or emission spectroscopy because there is no permanent dipole moment whose rotation can be accelerated by the electric field of an incident photon.

Under the rigid rotor model, the rotational energy levels, $F(J)$, of the molecule can be expressed as,

$$F(J) = BJ(J + 1)$$

where B is the rotational constant of the molecule and is related to the moment of inertia of the molecule and $J=0,1,2,3$ and the value of B is given by

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

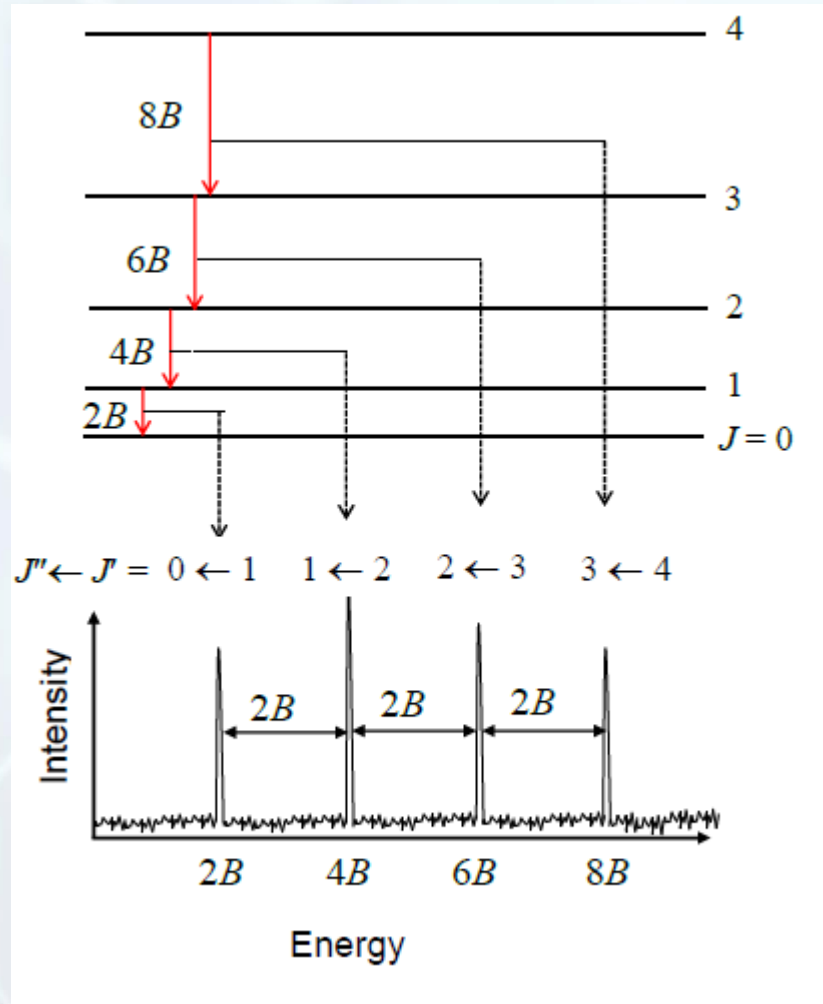


Image Source:
https://upload.wikimedia.org/wikipedia/commons/3/35/Rotational_spectrum_example.png

For $J=0$, $F(0) = BJ(J+1) = B \times 0(1) = 0$

For $J=1$, $F(1) = BJ(J+1) = B \times 1(1+1) = 2B$

For $J=2$, $F(2) = BJ(J+1) = B \times 2(2+1) = 6B$

For $J=3$, $F(3) = BJ(J+1) = B \times 3(3+1) = 12B$

Therefore for transition from $0 \rightarrow 1$ the difference is $2B$ and for transition from $1 \rightarrow 2$ the energy difference is $4B$. The above equation can be summarized as $\Delta F(J) = 2B(J+1)$

and for $J=0$, $\Delta F(0) = 2B$,

for $J=1$, $\Delta F(1) = 2B(J+1) = 4B$

$J=2$, $\Delta F(2) = 2B(J+1) = 6B$

$J=3$, $\Delta F(3) = 2B(J+1) = 8B$

Hence it be summarized that for every transition while the energy of transition increases the intensity of the transitions remains the same.

Rotational Raman spectroscopy

Molecular rotational transitions can also be observed by Raman spectroscopy. Rotational transitions are Raman-allowed for any molecule with an anisotropic polarizability which includes all molecules except for spherical tops. This means that rotational transitions of molecules with no permanent dipole moment, which cannot be observed in absorption or emission, can be observed, by scattering, in Raman spectroscopy.

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- Banwell, Colin N.; McCash, Elaine M. (1994). *Fundamentals of Molecular Spectroscopy* (4th ed.). McGraw-Hill. [ISBN 0-07-707976-0](#).
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