

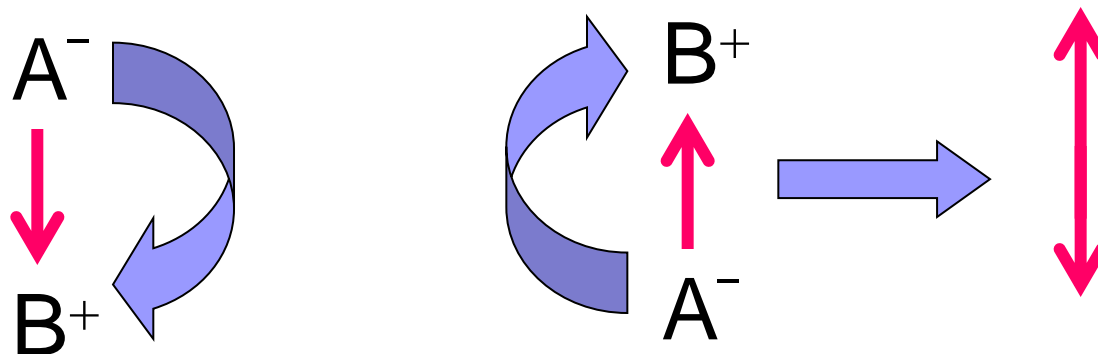


Microwave (Rotational) Spectroscopy

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Microwave Spectroscopy

It is concerned with transitions between rotational energy levels in the molecules, the molecule gives a rotational spectrum only if it has a permanent dipole moment.



A rotating molecule

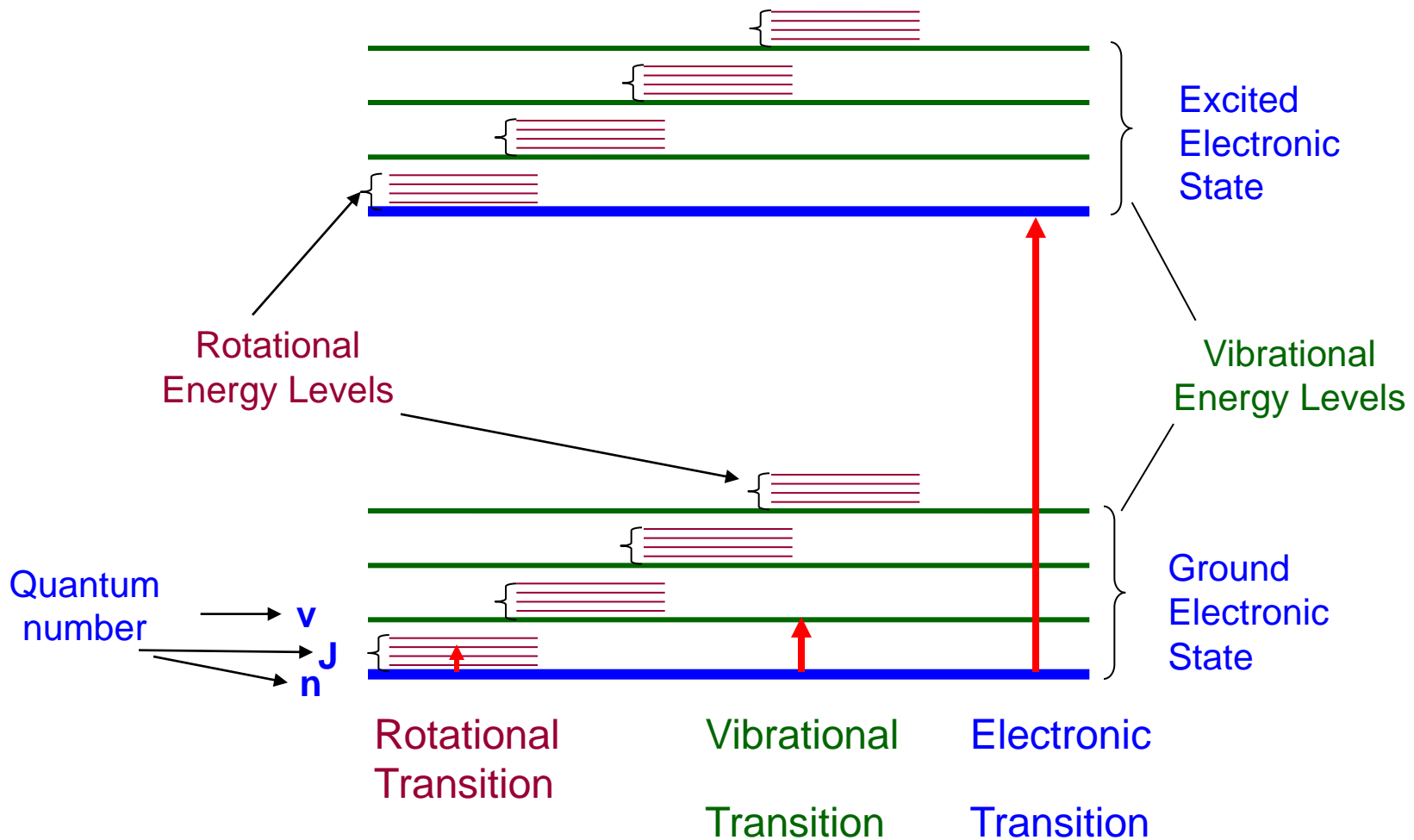
- H-Cl, and C=O give rotational spectrum (are microwave active).
- H-H and Cl-Cl don't give rotational spectrum (microwave inactive).

Rotational spectroscopy is really practical only in the gas phase where the rotational motion is quantized. In solids or liquids the rotational motion is usually quenched (restricted) due to collisions between their molecules.

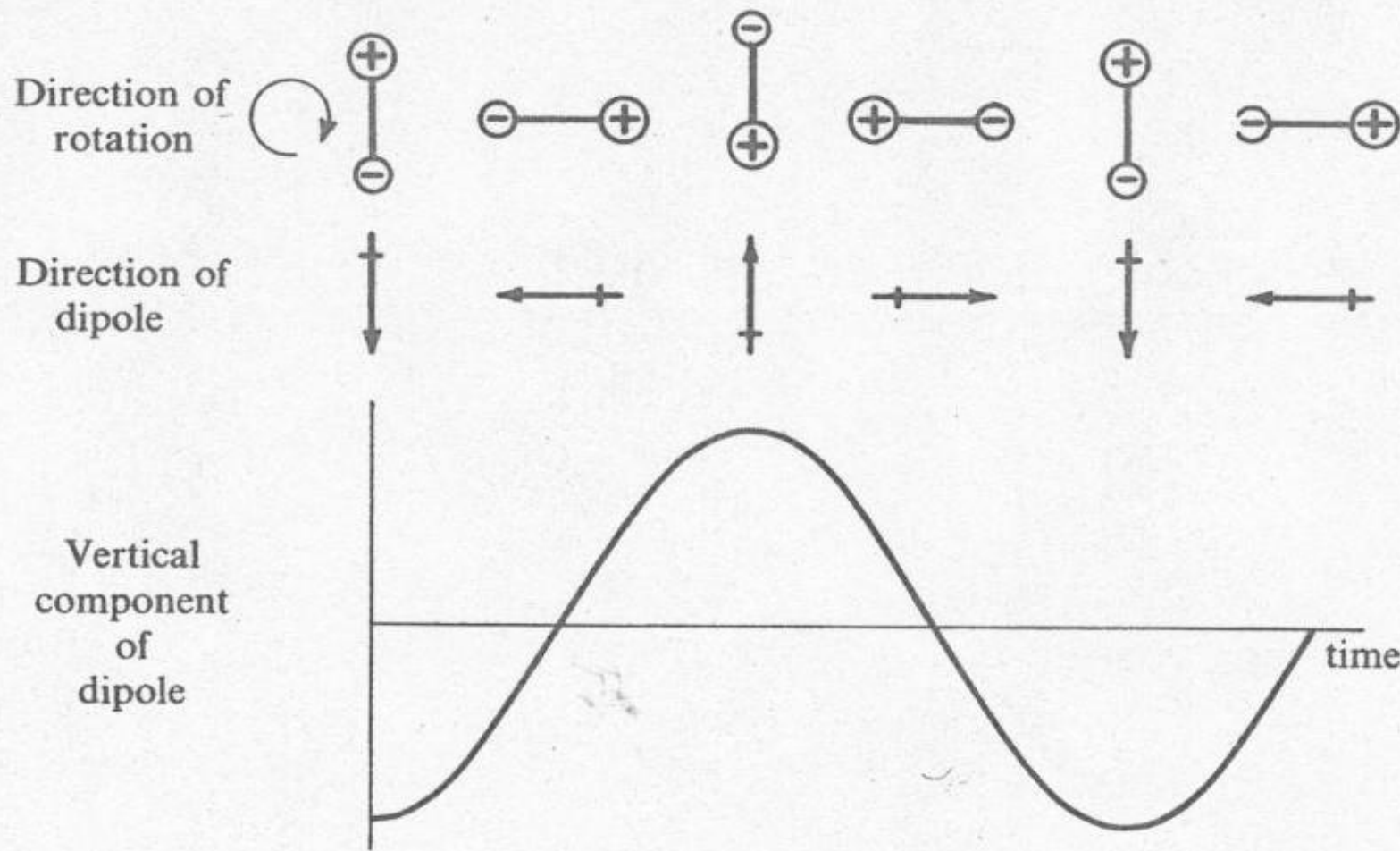
Which of the following molecules would show rotational spectrum: Br_2 , HBr, NO and CS_2 ? Why?

Molecular Energy Levels and interactions between light and matter

Radiations can be absorbed or emitted if the molecule changes any of its energy states



Rotational energy of a diatomic molecule, like HCl



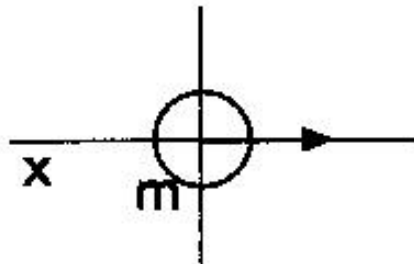
The rotation of a diatomic molecule, HCl, showing the fluctuation in the dipole moment measured in a particular direction.

General features of the rotating system:

1- Rotational motion in classical mechanics

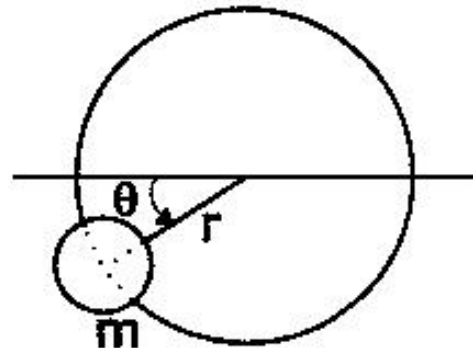
Rigid Rotors: molecules in which bonds don't distort under the stress of rotation, i. e bond length is fixed.

Linear Motion



$$\text{Linear velocity (v)} = \frac{\text{Distance}}{\text{Time}}$$

Angular Motion



$$\text{Angular velocity (}\omega\text{)} = \frac{\text{Radians}}{\text{Time}}$$

Linear momentum (P) = m . v

Angular momentum (J) = I . ω

Then; I = m . r₂

Where; the moment of inertia for a molecule (I) =
= $\sum_i m_i . r_i^2$

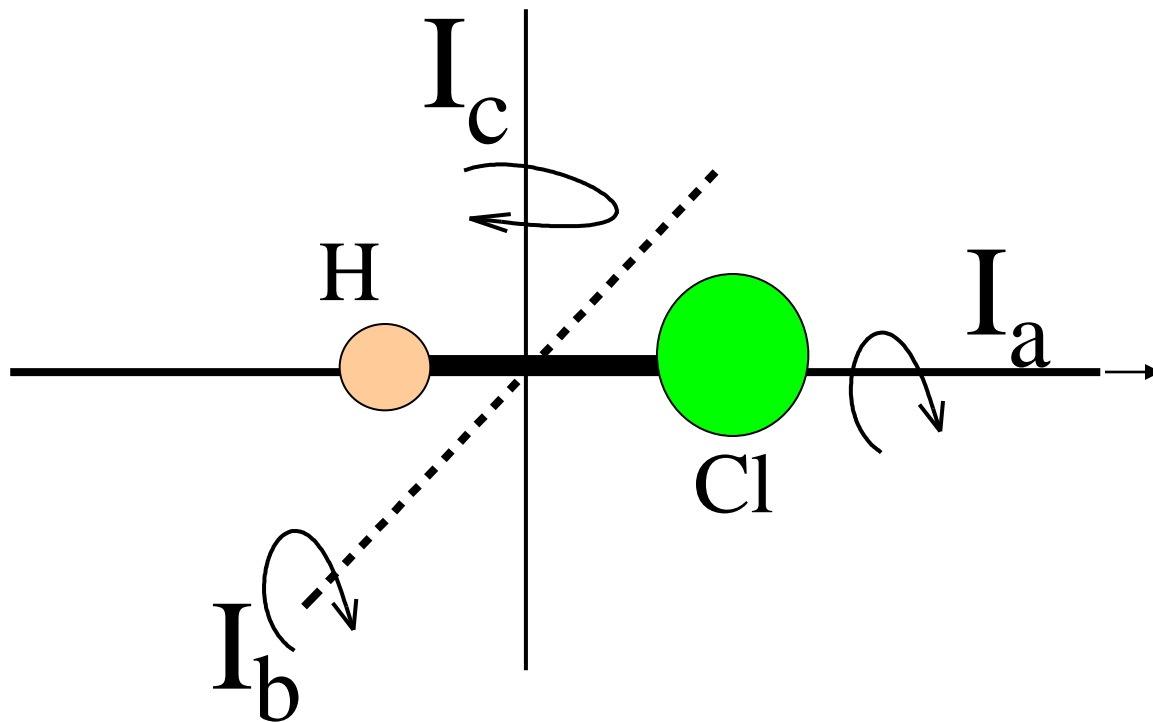
Where: r_i is the perpendicular distance of the atom i from the axis of rotation (**bond length**).

Moment of inertia (I), also called mass moment of inertia which is a measure of an object's resistance to changes in its rotation rate. It is the rotational analog of mass.

The Rotation of Molecules

- The rotation of a three-dimensional body is convenient to resolve it into rotational components about three mutually perpendicular directions (the principal axes of rotation) through the center of gravity.
- The body has three principal moments of inertia, one about each axis, usually designated I_a , I_b and I_c .
- Molecules may be classified into groups according to the relative values of their moments of inertia

A molecule can have three different moments of inertia I_a , I_b and I_c , according to the axis of rotation.



In HCl, $I_a = 0$, $I_b = I_c$.

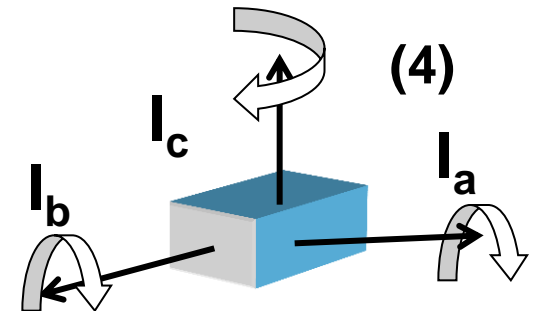
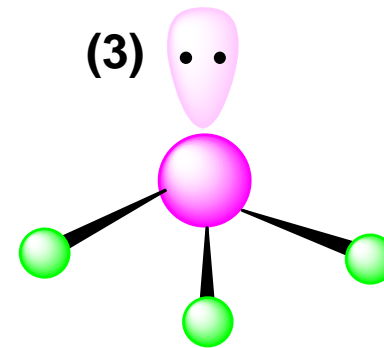
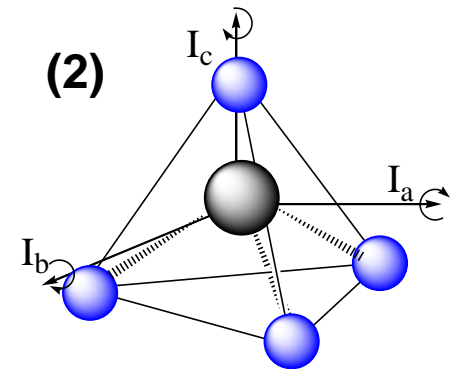
Rigid rotors are classified into four groups:

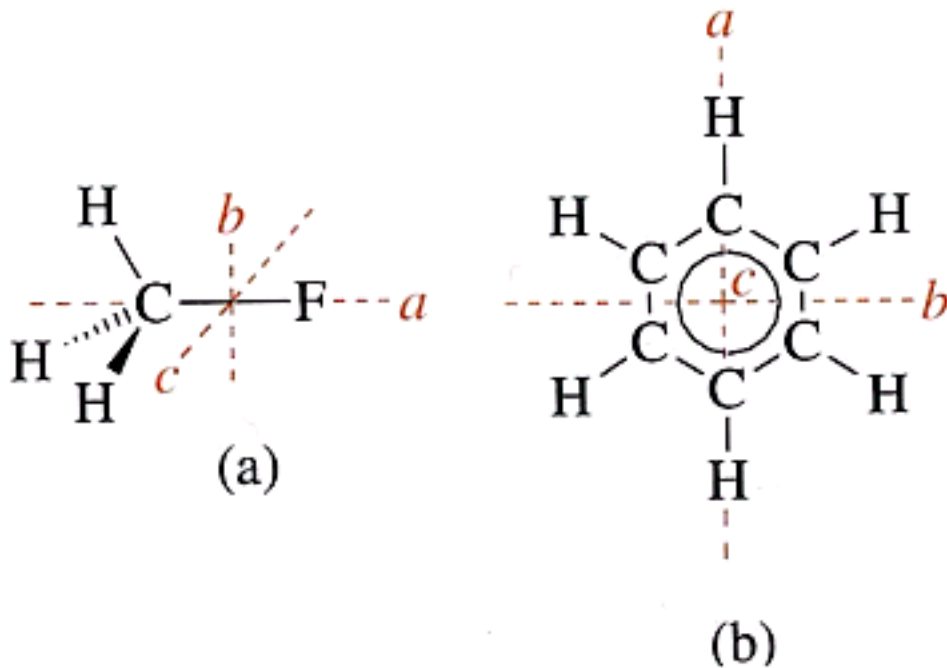
1- Linear rotors: such as diatomic or linear molecules, as H-Cl, O=C=S, acetylene and O=C=O, have; $I_a=0$ and $I_b=I_c$.

2- Spherical tops rotors: e.g. CH₄, SiH₄ and SF₆ have three equal moments of inertia.. $I_a=I_b=I_c$.

3- Symmetric tops rotors: e.g. NH₃, CH₃CN and CH₃Cl, have two equal moments of inertia. , $I_a=I_b \neq I_c$.

4- Asymmetric tops rotors: e.g. H₂O, CH₃OH, vinyl chloride CH₂=CHCl and formaldehyde, have three different moments of inertia. $I_a \neq I_b \neq I_c$.





Symmetric top molecules are classified into:

(a) Prolate as methyl fluoride, $I_a < I_b = I_c$

(a) Oblate as benzene and boron trichloride, $I_a = I_b < I_c$

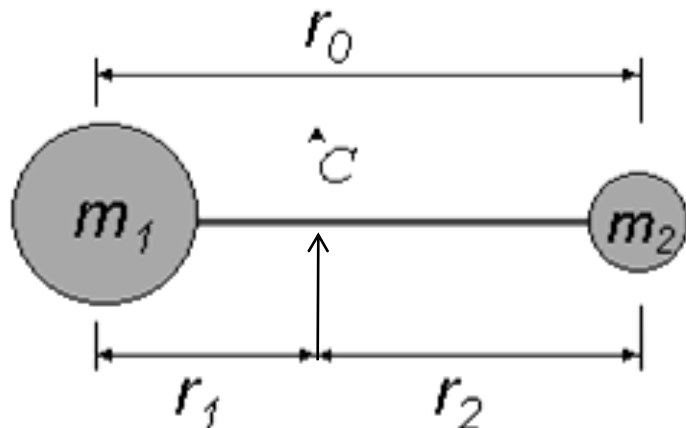
Classes of Rotating Molecules

- Molecules can be classified into five main groups depending on their moments of inertia.

1.	$I_C = I_B, I_A = 0$	Linear molecules
2.	$I_C = I_B = I_A$	Spherical top
3.	$I_C = I_B > I_A$	Symmetric top
5.	$I_C > I_B > I_A$	Asymmetric top

- ❖ **Homonuclear diatomic molecules (such as H₂, O₂, N₂, Cl₂) – have zero dipole (non polar) - have zero change of dipole during the rotation, hence NO interaction with radiation - hence homonuclear diatomic molecules are microwave inactive**
- ❖ **Heteronuclear diatomic molecules (such as HCl, HF, CO) – have permanent dipole moment (polar compound) - change of dipole occurs during the rotation – hence interaction with radiation takes place – Therefore, heteronuclear diatomic molecules are microwave active.**

For linear diatomic molecules, the moment of inertia can be calculated as follows;



$$I_B = I_C \text{ and } I_A = 0$$

C – centre of gravity

express I via m_1 , m_2 and r_0

$$m_1 r_1 = m_2 r_2 \quad (1)$$

from $r_1 + r_2 = r_0 \quad (2)$

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (3)$$

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

μ - reduced or effective mass

units: $\text{kg} \cdot \text{m}^2 = \text{kg} \cdot \text{m}^2$

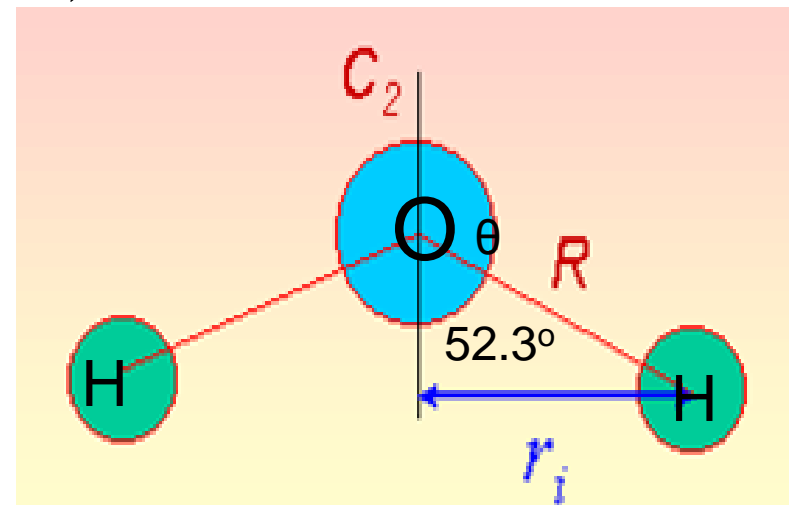
From the moment of inertia one can calculate the bond length as well as the atomic masses

- Calculate the moment of inertia of water molecule around the axis defined by the bisector of HOH bond. bond angle (HOH) = 104.5° and bond length (OH) = 95.7 pm ? (H = 1.0079, Atomic mass unit = 1.6606×10^{-27} kg).

$$I = \sum_i m_i r_i^2 = m_H r_H^2 + 0 + m_H r_H^2 = 2 m r^2 \sin^2 \theta$$

$$= 2 \times (1.67 \times 10^{-27} \text{ kg}) \times (95.7 \times 10^{-12})^2 \times \text{Sin}^2 52.3$$

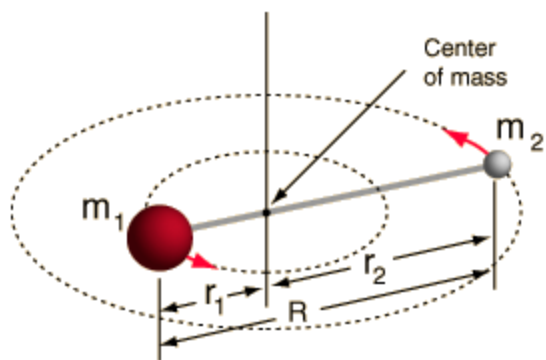
$$= 1.91 \times 10^{-47} \text{ kg m}^2$$



Rotational Spectra of Linear Rigid Rotators

Simplest Case: Diatomic or Linear Polyatomic molecules

Rigid Rotor Model: Two nuclei are joined by a weightless rod



From solution of Schrodinger equation;
The energy of any rotational level with
quantum number J is:

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

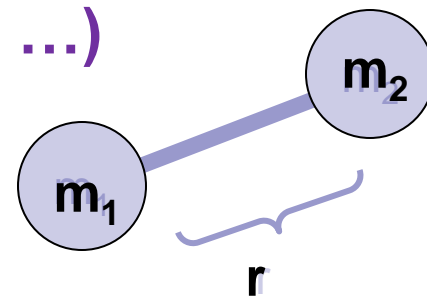
E_J = Rotational energy of rigid rotator (in Joules)

J = Rotational quantum number ($J = 0, 1, 2, \dots$)

I = Moment of inertia = μr^2

μ = Reduced mass = $m_1 m_2 / (m_1 + m_2)$

r = Internuclear distance (bond length)



Energy levels of a rigid diatomic rotor

1. Rotational energy for a rigid diatomic rotor E_J is quantized:

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

$J = 0; 1; 2; \dots$ - rotational quantum number

2. Rotational energy is normally expressed in cm^{-1}

recall: $E = h \cdot \nu = h \cdot c \cdot \tilde{\nu}$ therefore: $\tilde{\nu} \equiv \varepsilon = \frac{E}{h \cdot c}$

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h^2 J(J+1)}{4\pi^2 \cdot 2I \cdot hc} = \frac{h}{8\pi^2 I \cdot c} J(J+1)$$

B - rotational constant, units = cm^{-1}

$$\varepsilon_J = B \cdot J(J+1)$$

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

Note: units for c !

B can be determined from spectroscopic experiments

Example

From microwave spectroscopy, bond lengths can be determined with a correspondingly high precision, as illustrated in the following example.

* From the rotational microwave spectrum of $^1\text{H}^{35}\text{Cl}$, we find that $B = 10.59342 \text{ cm}^{-1}$. Given that the masses of ^1H and ^{35}Cl are 1.0078250 and 34.9688527 amu, respectively, determine the bond length of the $^1\text{H}^{35}\text{Cl}$ molecule. **We have;**

$$B = \frac{h}{8\pi^2 \mu c r_0^2}$$
$$r_0 = \sqrt{\frac{h}{8\pi^2 \mu c B}} = \sqrt{\frac{6.6260755 \times 10^{-34}}{8\pi^2 c \left(\frac{(1.0078250)(34.9688527)}{1.0078250 + 34.9688527} \right) (1.66054 \times 10^{-27}) (10.59342)}}$$
$$= 1.274553 \times 10^{-10} \text{ m}$$

Rotational transitions in rigid diatomic molecule.

Selection rules governing transition between rotational levels:

1- $\Delta \mu \neq 0$

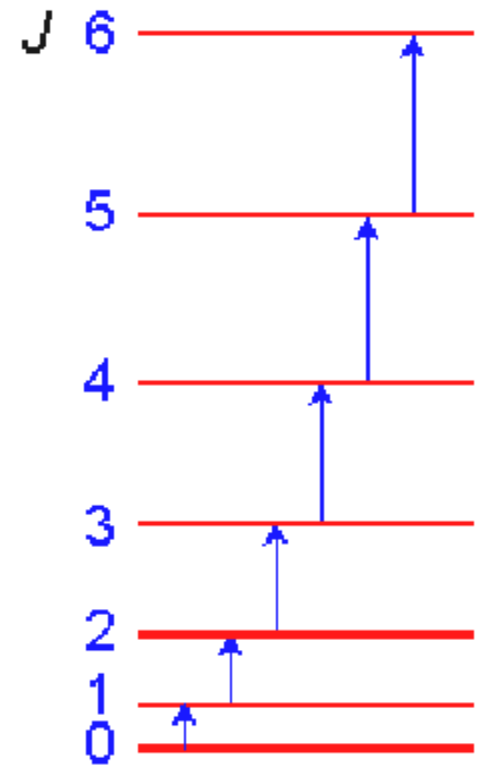
molecule gives a rotational spectrum only if it has a permanent change in dipole moment

2- $\Delta J = \pm 1$ where; +1 for absorption.
and -1 emission.

Separation between adjacent levels:

$$\Delta E_J = E(J) - E(J-1) = 2BJ$$

and B can be obtained from the spacing between rotational lines in the spectra of molecules.



Allowed transitions

Transitions observed in the rotational spectrum

* For the transition; $J = 0 \rightarrow J = 1$ **Since;** $E_J = \frac{h}{8\pi^2 I_C} J(J + 1)$

and; $B = h/8 \pi^2 I_C$

Then; $\Delta E_j = E_{j=1} - E_{j=0} = 2B - 0 = 2B \text{ cm}^{-1}$

= position of the first line in the spectrum = $\bar{\nu}_{j=0 \rightarrow j=1}$

* For the transition; $J = 1 \rightarrow J = 2$

$$\Delta E_j = E_{j=2} - E_{j=1} = 6B - 2B = 4B \text{ cm}^{-1}$$

= position of the second line in the spectrum = $\bar{\nu}_{j=1 \rightarrow j=2}$

* For the transition; $J = 2 \rightarrow J = 3$

$$\Delta E_j = E_{j=3} - E_{j=2} = 12B - 6B = 6B \text{ cm}^{-1}$$

= position of the third line in the spectrum = $\bar{\nu}_{j=2 \rightarrow j=3}$

Since, The allowed rotational energies are given by;

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

The wave numbers of the different rotational levels will be; **0, 2B, 6B, 12B, 20B, 30B (cm⁻¹),... and so on**

And for two adjacent rotational states, the energy difference is given by;

$$\Delta E_J = E_{J+1} - E_J = 2B(J + 1) \text{ cm}^{-1}$$

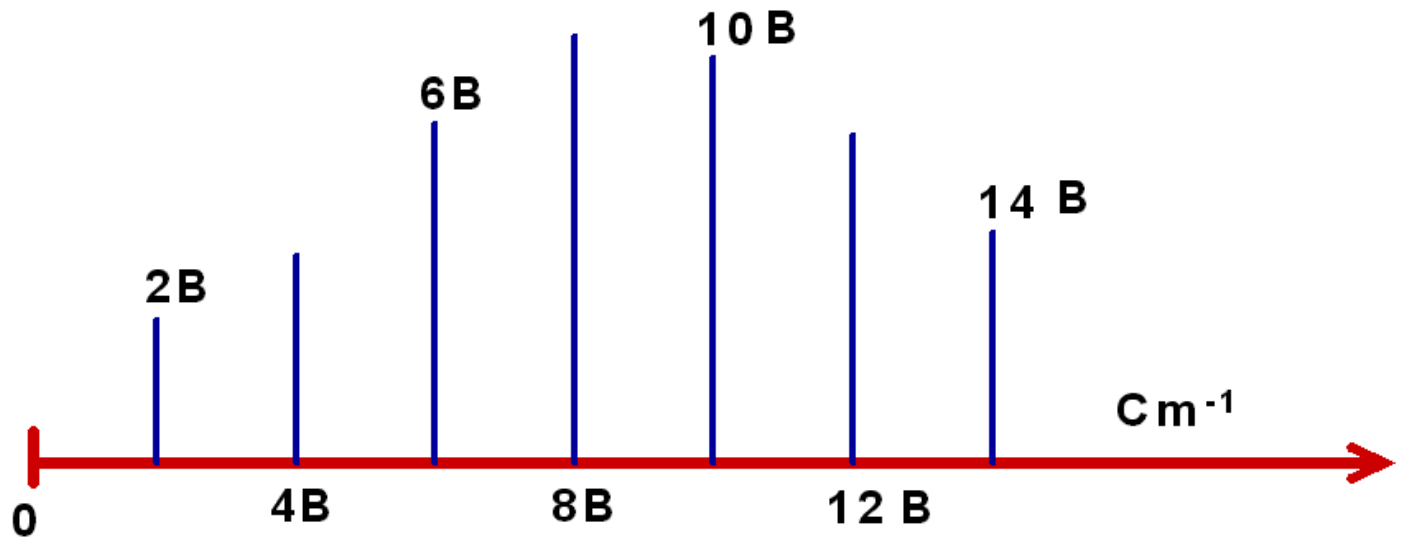
Hence, the wave number of the lines observed in the rotational spectrum will be; **2B, 4B, 6B, 8B (cm⁻¹), and so on.**

And the various lines in the rotational spectra will be equally spaced (separation between lines = 2B)..

Energy levels of a rigid diatomic rotor

$$\varepsilon_J = B \cdot J(J + 1) \quad J=0; 1; 2; \dots$$

J	6	_____	42B	ε_J
	5	_____	30B	
	4	_____	20B	
	3	_____	12B	
	2	_____	6B	
	1	_____	2B	
	0	_____	0	

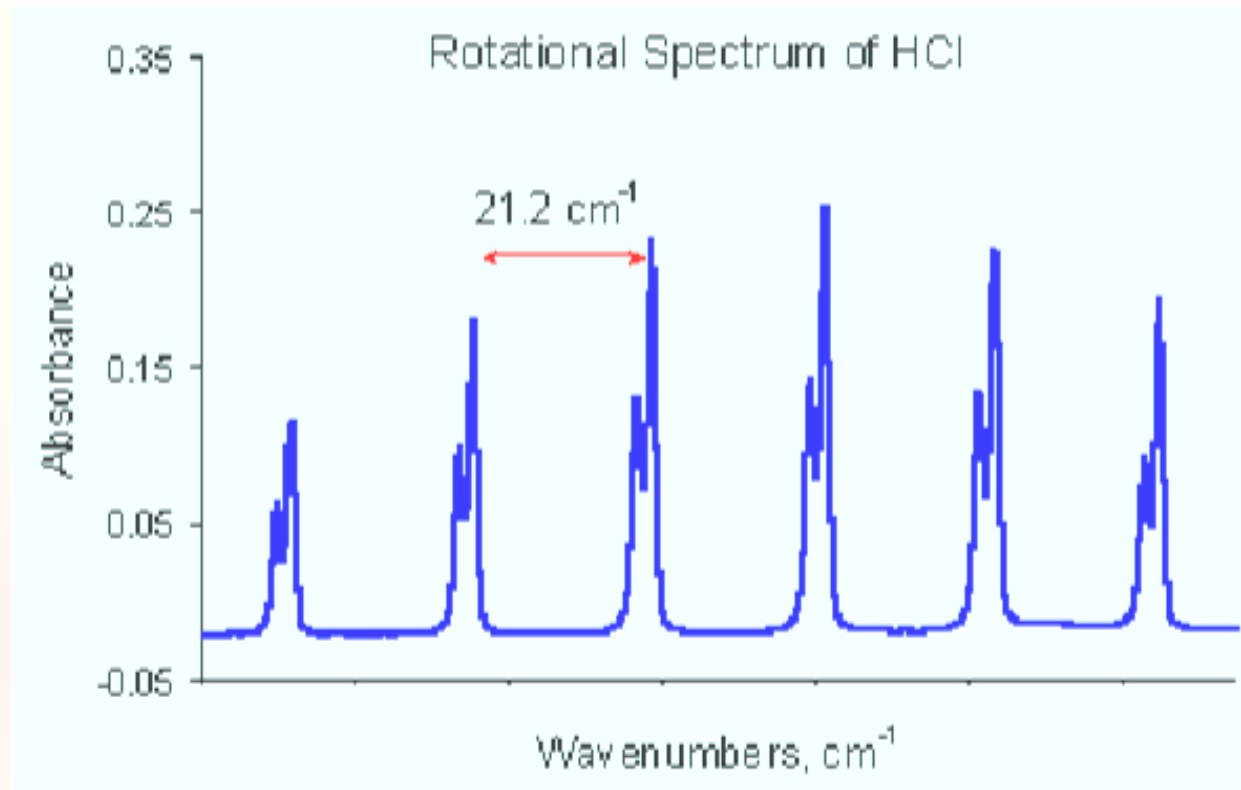


Microwave spectrum of rigid rotator

Separation between adjacent lines = $2B$

So, B can be obtained from the spacing between rotational lines.

Examples of rotational spectra of rigid diatomic molecules



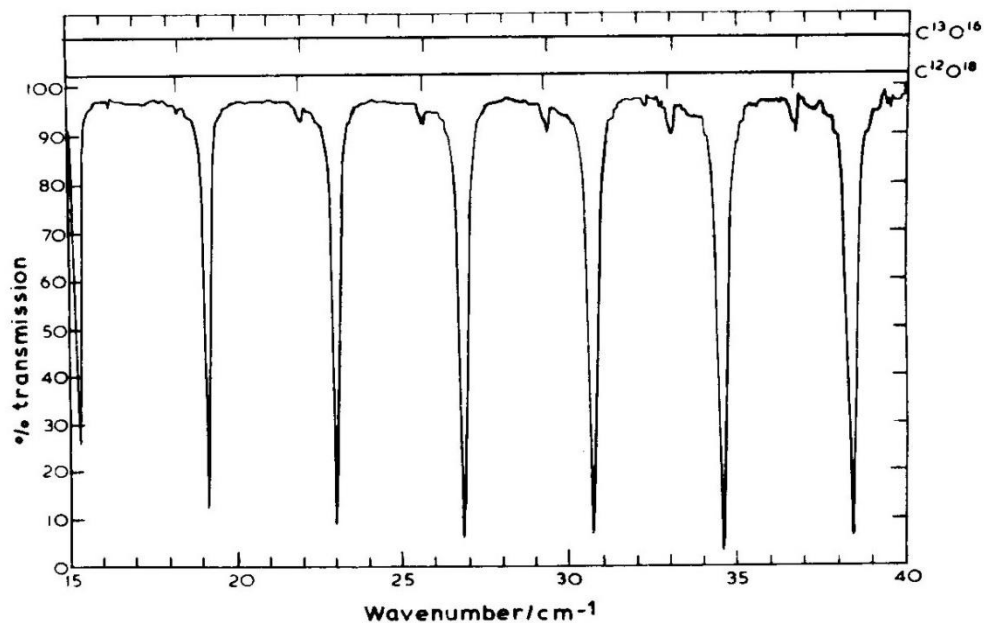
line separation in the rotational spectrum of HCl is $\approx 21.2 \text{ cm}^{-1} \Rightarrow B = 10.6 \text{ cm}^{-1}$; I_{HCl} can be found from:

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

next r_{HCl} can be obtained using
need to know m_1 and m_2

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

Rotational Spectrum of CO



$J'' \rightarrow J'$	$E(J') - E(J'')$	
3 → 4	2(1.91)(4)	15.3 cm ⁻¹
4 → 5	2(1.91)(5)	19.1 cm ⁻¹
5 → 6	2(1.91)(6)	22.9 cm ⁻¹
6 → 7	2(1.91)(7)	26.7 cm ⁻¹
7 → 8	2(1.91)(8)	30.6 cm ⁻¹
8 → 9	2(1.91)(9)	34.4 cm ⁻¹
9 → 10	2(1.91)(10)	38.2 cm ⁻¹

Example:

The first rotational line in the rotational spectrum of CO is observed at 3.84235 cm^{-1} . Calculate the rotational constant (B) and bond length of CO. The relative atomic weight C = 12.00 and O = 15.9994, the absolute mass of H = $1.67343 \times 10^{-27} \text{ kg}$.

$$\bar{\nu}_{0 \rightarrow 1} = 3.8425 = 2 B$$

$$B = 1.92118 \text{ cm}^{-1}$$

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

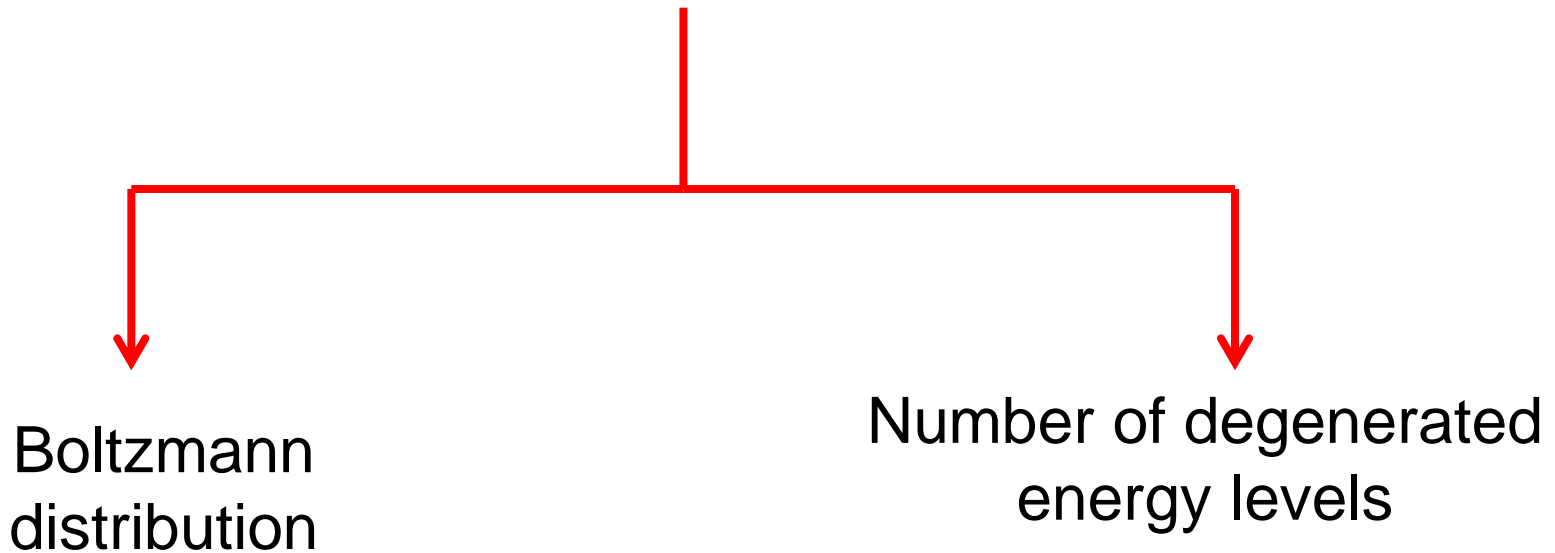
$$I_{CO} = \frac{6.626 \times 10^{-34}}{8 \pi^2 \times 2.99793 \times 10^{10} \times B}$$
$$= 14.5695 \times 10^{-47} \text{ kg} \cdot \text{m}^2$$

$$\mu = \frac{19.92168 \times 26.56136 \times 10^{-54}}{46.48303 \times 10^{-27}} = 11.38365 \text{ kg}$$

$$r^2 = \frac{I_{CO}}{\mu} = 1.2799 \times 10^{-20} \text{ m}^2$$

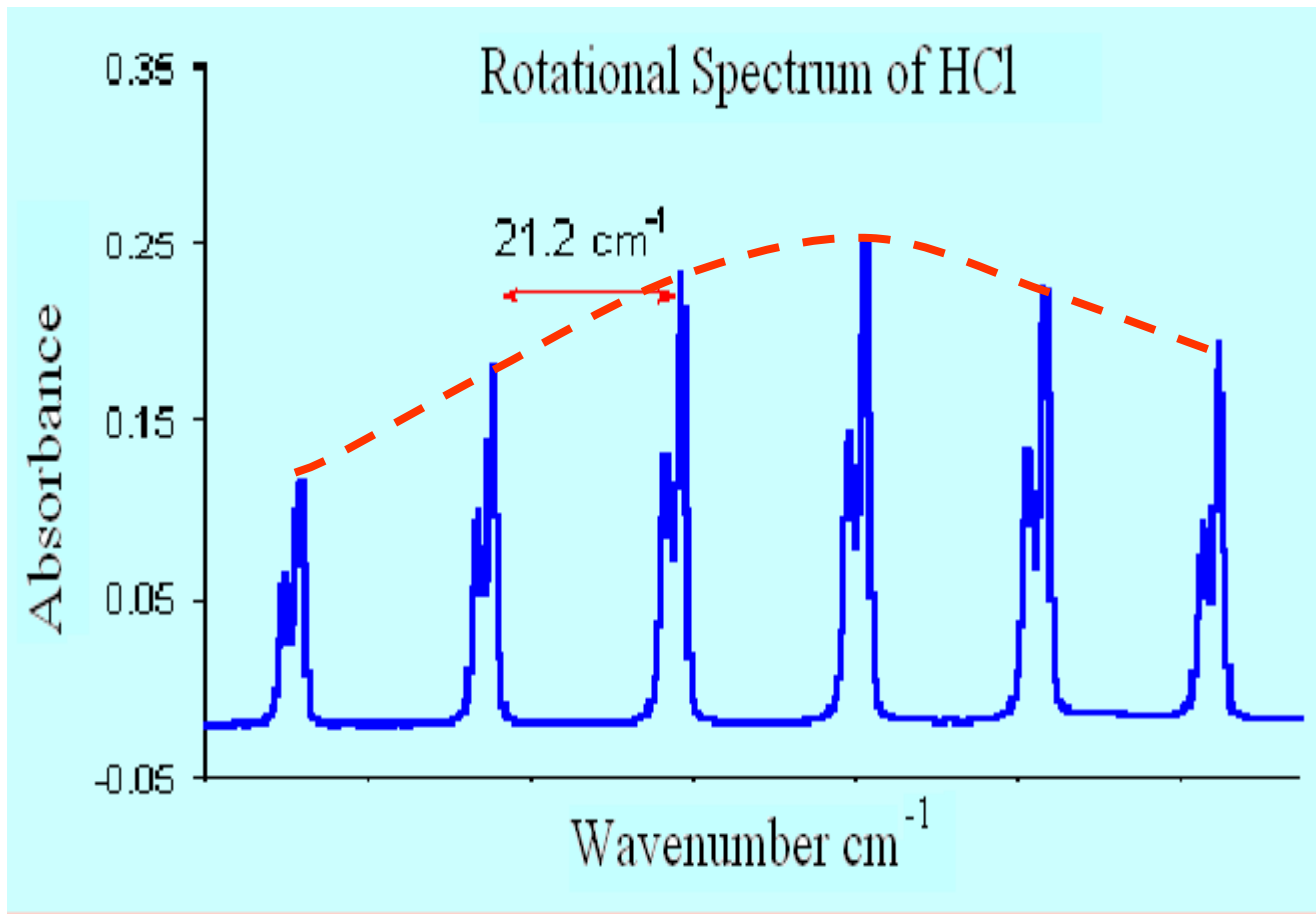
$$\text{So, } r_{CO} = 0.113 \text{ nm} = 1.131 \text{ \AA}$$

Intensity of rotational spectral lines (Population of energy levels)



Population of energy levels is affected by;

- 1- Boltzmann distribution**
- 2- Number of degenerated energy levels (levels which have the same energies)**



1-Boltzmann distribution

The number of molecules in the first state = N_o

The number of molecules in any higher state = N_j

$$\frac{N_j}{N_o} = e^{-E_J/kT} = e^{-(h\nu/kT)} = e^{-(hc\bar{\nu}/kT)}$$

$\epsilon_j = \bar{\nu} = B J(J + 1)$ **So,**

$$\frac{N_j}{N_o} = e^{-[BhcJ(J+1)]/kT} = e^{-BJ(J+1)hc/kT}$$

The population of the state decreases as the J –value increases.

**Example; For HCl, $2B = 21.2 \rightarrow B = 10.6$, $T=300$ K,
 $h=6.626 \times 10^{-34}$ J.s, $k=1.38 \times 10^{-23}$ J/K, $c = 3 \times 10^{10}$ cm/s**

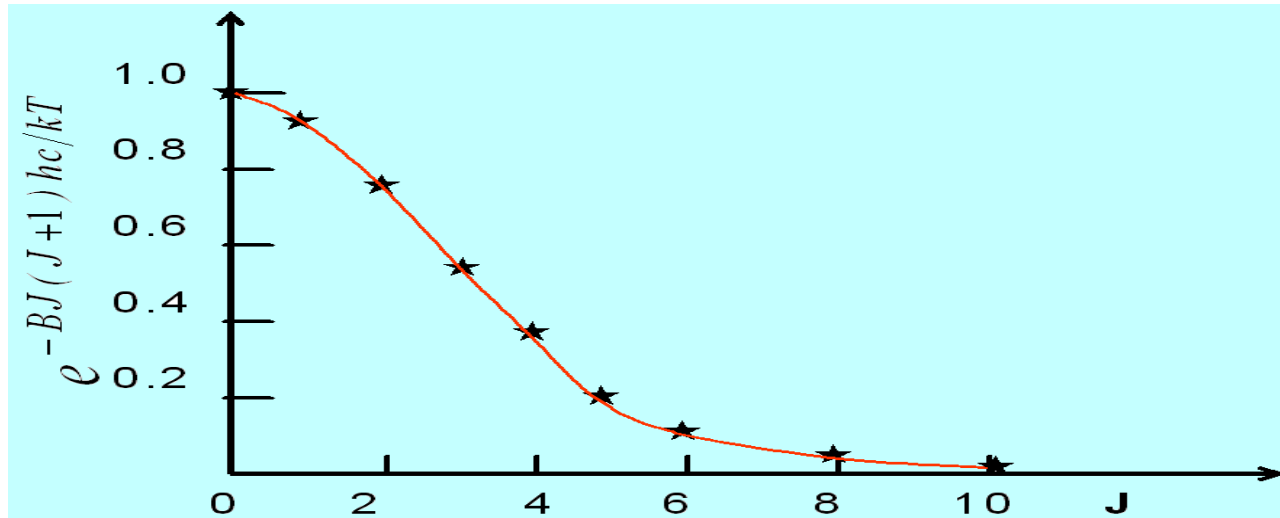
$$J = 0, \rightarrow \frac{N_0}{N_o} = e^0 = 1$$

$$J = 1, \rightarrow \frac{N_1}{N_o} = e^{-\frac{10.6 \times 6.63 \times 10^{-34} \times 3 \times 10^{10}}{1.38 \times 10^{-23} \times 300} (J(J+1))}$$
$$= e^{-0.0509J(J+)} = 0.903$$

$$J = 2, \rightarrow \frac{N_2}{N_o} = e^{-0.0509J(J+)} = 0.7367$$

2- Make another calculations with $B = 5$

$\frac{N_J}{N_0}$ decreases with increasing J
and with higher B



The Boltzmann distribution alone does not fit the shape of the spectra so, degeneracy of the states is required.

2-Degeneracy

The existence of more than two energy states having the same energy.

Kinetic energy (K.E) in rotational motion = $\frac{1}{2} I \omega^2$
and since, angular momentum (P) = $I \omega$ then;

$$E = \frac{I \times I \omega^2}{2I} = \frac{I^2 \omega^2}{2I} = \frac{P^2}{2I} \quad \rightarrow \quad P = \sqrt{2 E I}$$

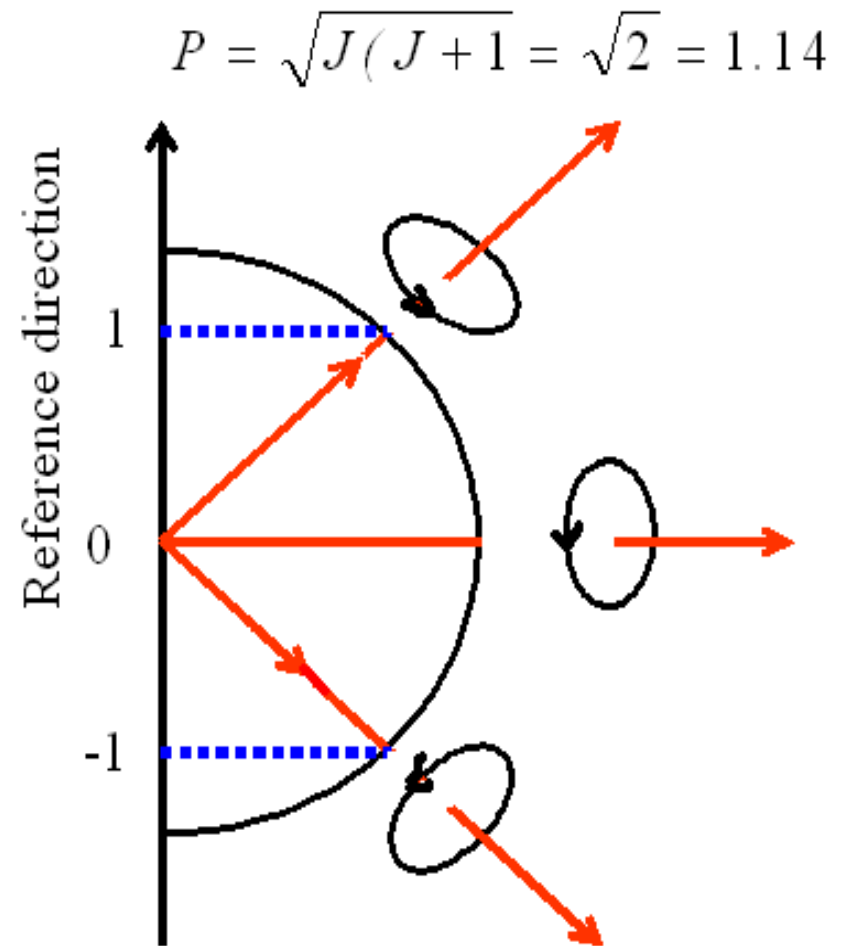
$$E = \frac{h^2}{4\pi^2} \frac{J(J+1)}{2I} \quad \rightarrow \quad 2 E I = \frac{h^2}{4\pi^2} J(J+1) = P^2$$

$$P = \sqrt{J(J+1)} \times \frac{h}{2\pi} = \sqrt{J(J+1)} \text{ unit.}$$

$\frac{h}{2\pi}$ is the fundamental angular momentum unit.

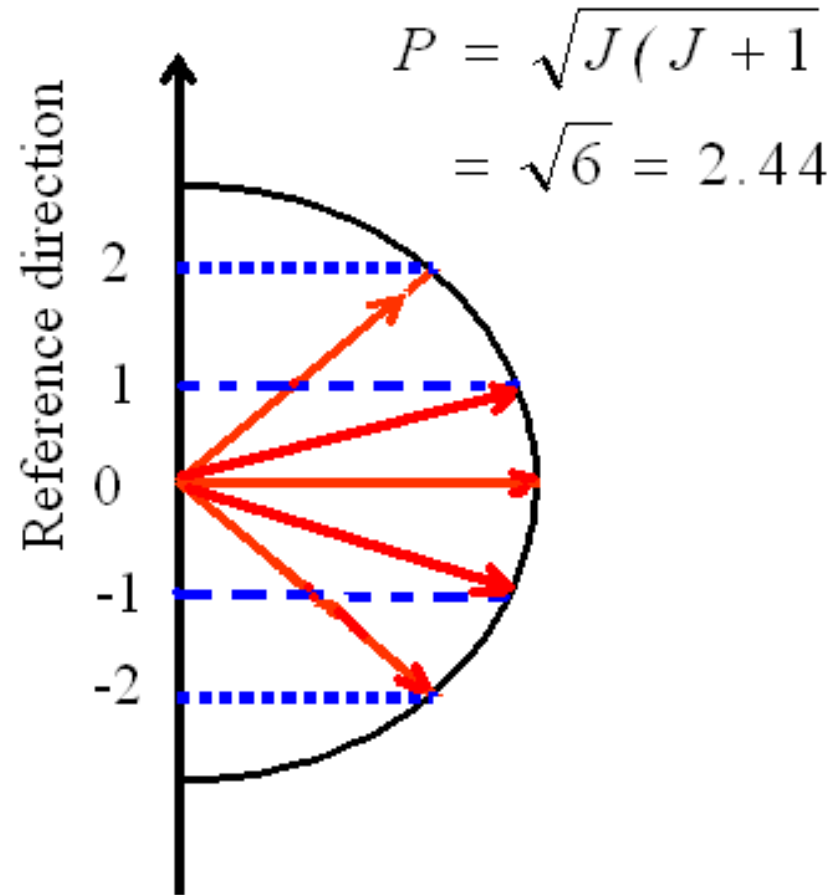
For $J = 1$

- P is quantized, so it takes a directions such that the value of P along the reference direction are $(-1, 0, +1)$.
- Number of degeneracy is $2J + 1 = 3$



For $J = 2$

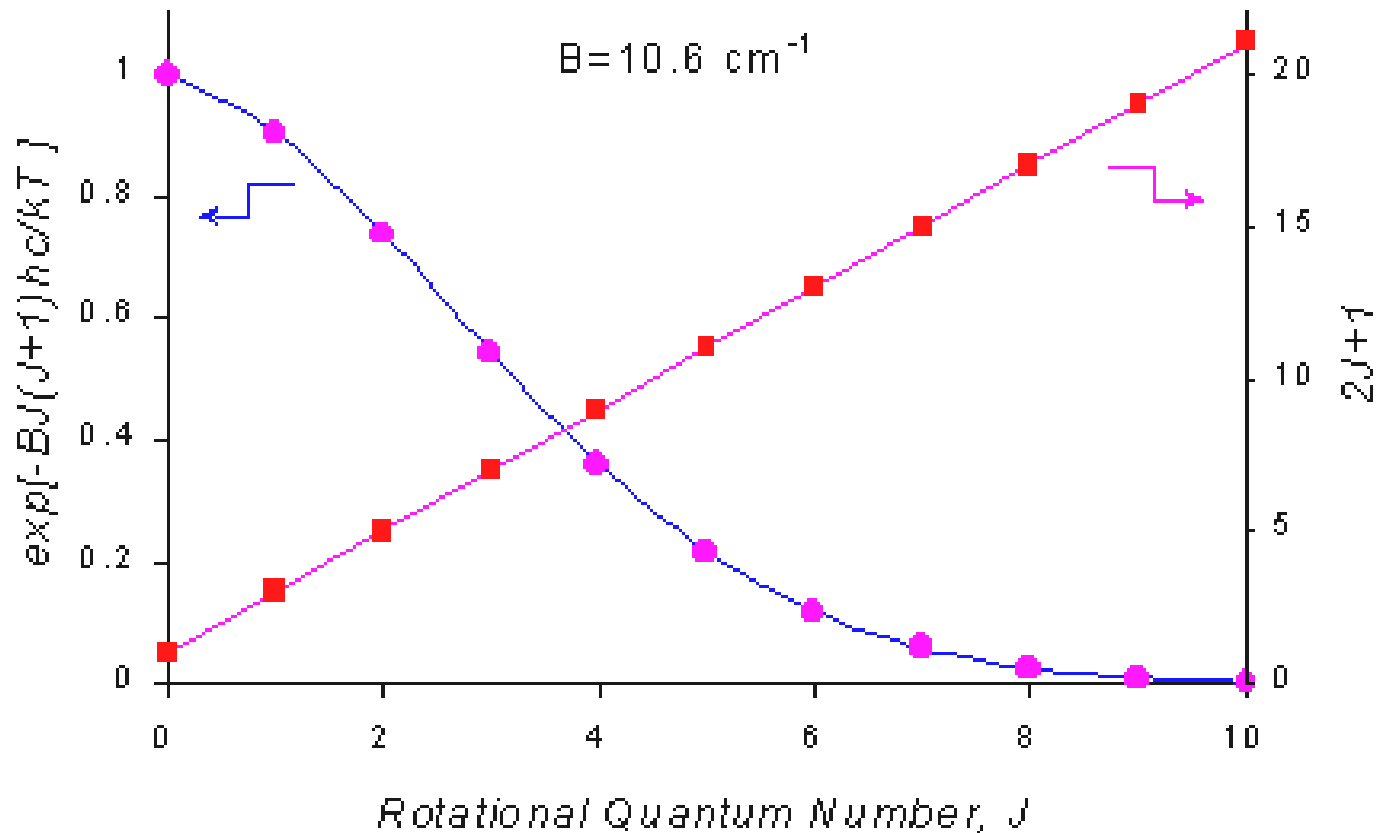
- $(-2, -1, 0, 1, 2)$ degeneracy.
- Number of degeneracy is $2J + 1 = 2 \times 2 + 1 = 5$



Population of Rotational Energy Levels

Boltzmann distribution

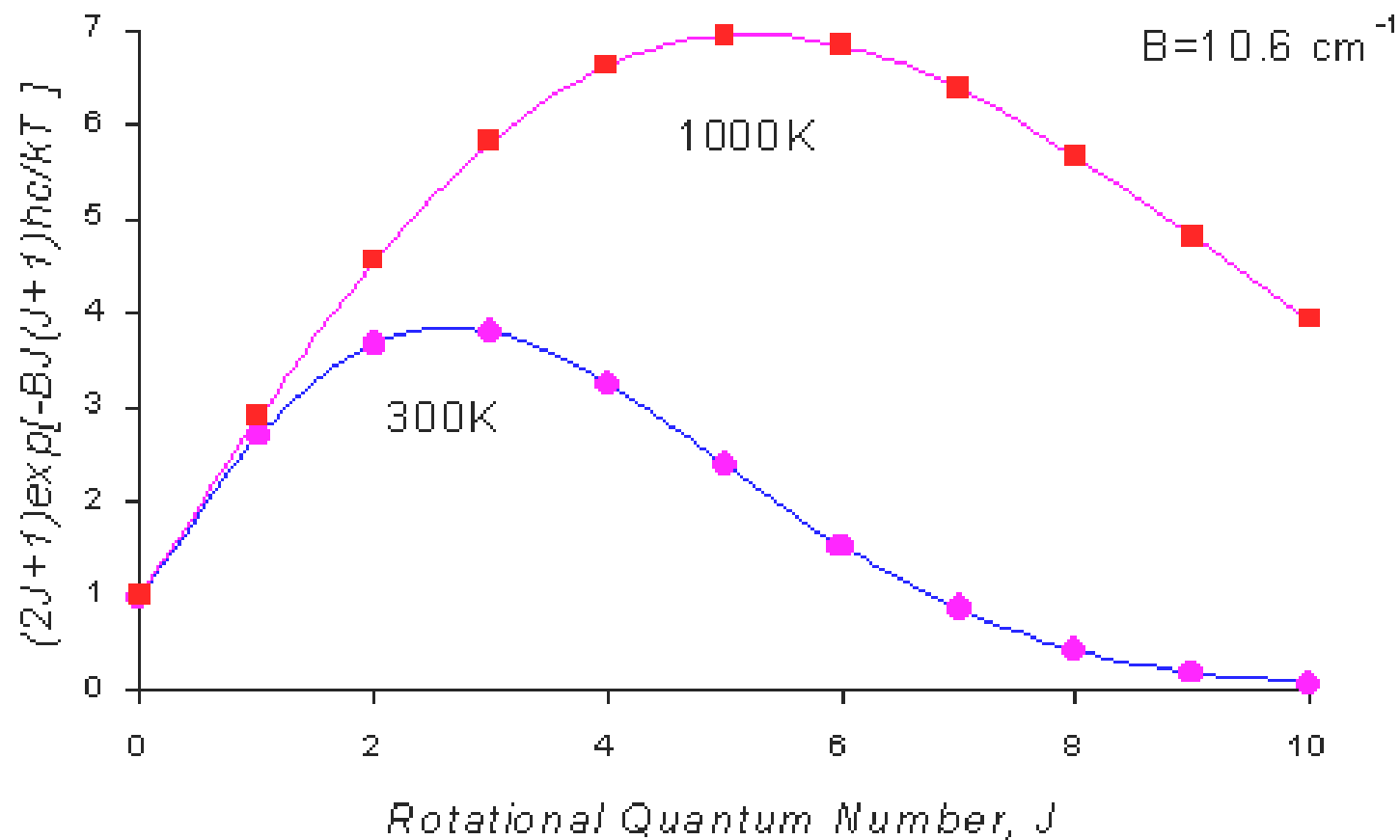
$$\frac{N_2}{N_1} = e^{-(\Delta E/kT)} = e^{-(hc\mathcal{V}/kT)}$$



Orientation of the angular momentum, \mathbf{P} , is quantized. This results in $(2J+1)$ -fold degeneracy of the energy levels.

Population $\propto (2J + 1) \cdot e^{-(\Delta E / kT)}$

where $\Delta E = hc\varepsilon_j = hc \cdot B J(J+1)$



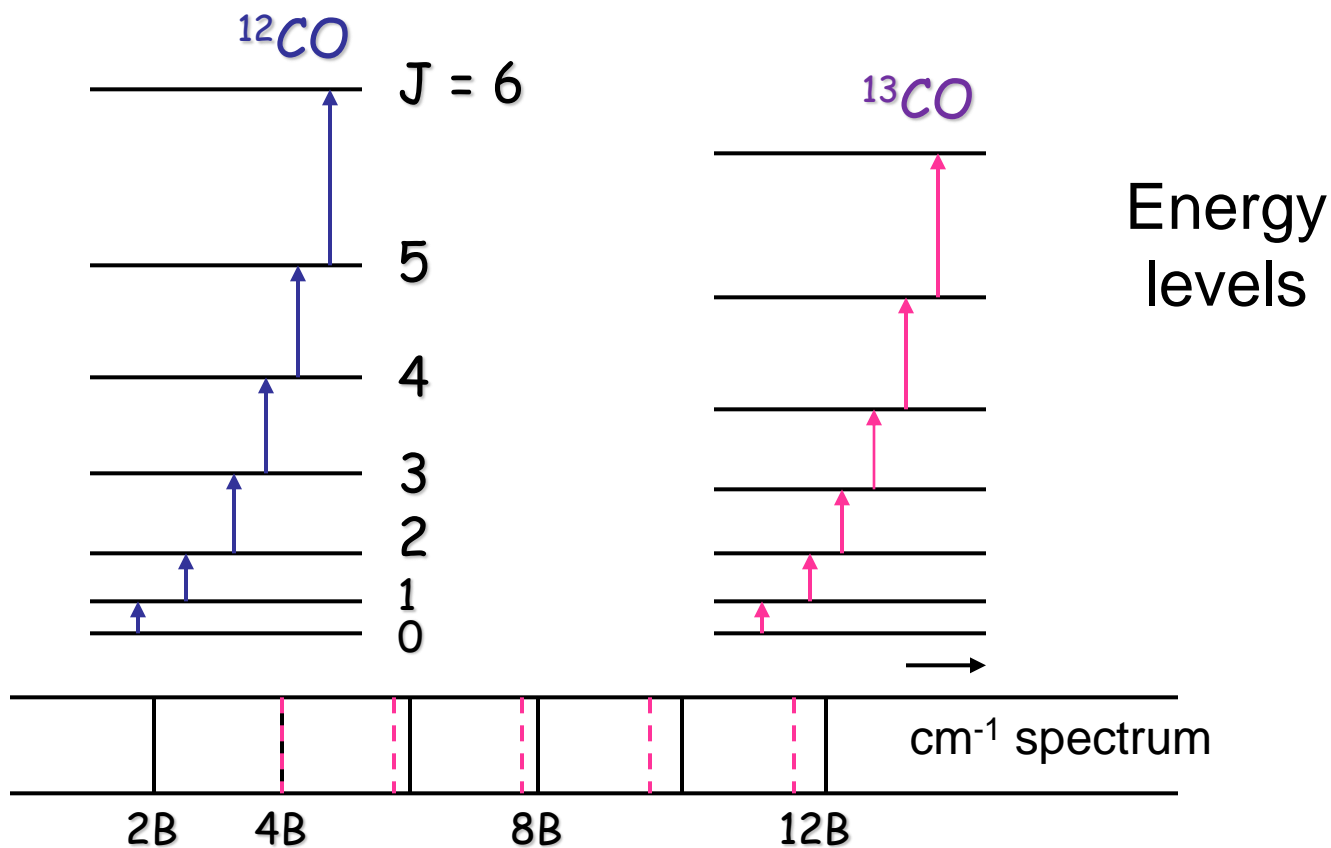
Bond Length and Rotational Constants of Diatomic Molecules

	$r_0, \text{\AA}$	B, cm^{-1}		$r_0, \text{\AA}$	B, cm^{-1}
H_2^+	1.06	29.8	F_2	1.42	0.88
H_2	0.74138	60.8	Cl_2	1.98	0.24
D_2	0.74154	30.4	Br_2	2.28	0.081
O_2	1.21	1.44	HF	0.92	20.9
N_2	1.10	2.00	HCl	1.27	10.6
CO	1.13	1.93	HBr	1.41	8.46

*What is \AA ? What is MO configuration of H_2^+ ?
Note effect of r_0 and m on the rotational constant*

Effect of isotopic substitution

On changing from $^{12}\text{C}^{16}\text{O} \rightarrow ^{13}\text{C}^{16}\text{O}$, atomic mass increases, so, B decreases (since $B \propto 1/I$), so the energy of rotational levels becomes lower.



Since,

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



$$\frac{B'}{B''} = \frac{h}{8\pi^2 I' \cdot c} \cdot \frac{8\pi^2 I'' \cdot c}{h} = \frac{I''}{I'} = \frac{\mu''}{\mu'}$$

From comparison of rotational energy levels of ^{12}CO and ^{13}CO

We can determine:

- (i) isotopic masses accurately, to within 0.02% of other methods for atoms in gaseous molecules;
- (ii) isotopic abundances from the absorption relative intensities.

Example:

for ^{12}CO the transition $J=0 \rightarrow J=1$ appears at 3.84235 cm^{-1}

for ^{13}CO the transition $J=0 \rightarrow J=1$ appears at 3.67337 cm^{-1}

Given : $^{12}\text{C} = 12.0000$; $\text{O} = 15.9994$ amu

What is isotopic mass of ^{13}C ?

$$B(^{12}\text{CO}) = 1.921175 \text{ cm}^{-1}$$

$$B(^{13}\text{CO}) = 1.836685 \text{ cm}^{-1}$$

Now

$$B \propto \frac{1}{I} \propto \frac{1}{\mu}$$

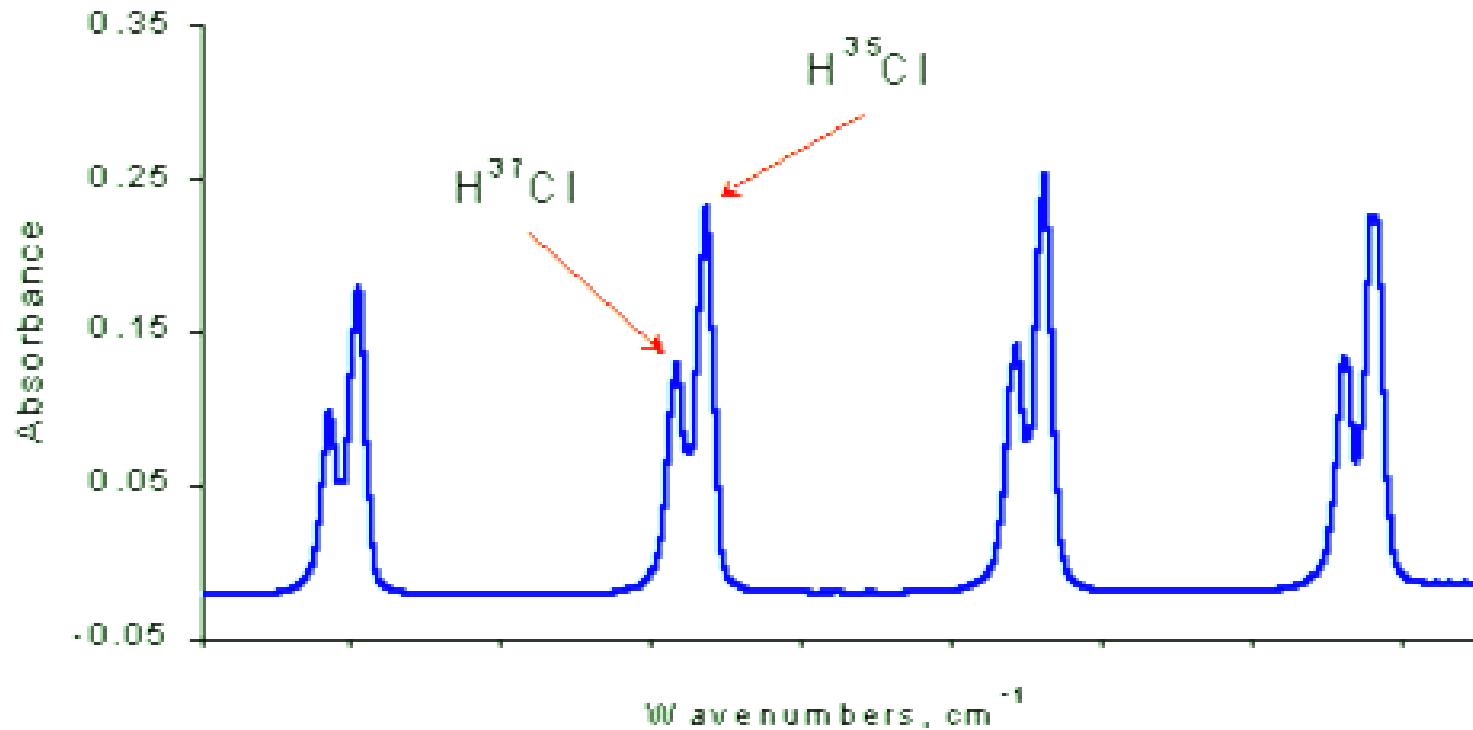
$$\Rightarrow \frac{\mu(^{13}\text{CO})}{\mu(^{12}\text{CO})} = \frac{1.921175}{1.836685} = 1.04600$$

$$\Rightarrow 1.046 = \frac{(^{13}\text{C}) \times 15.9994}{(^{13}\text{C}) + 15.9994} \times \frac{12 + 15.9994}{12 \times 15.9994}$$

$$\Rightarrow (^{13}\text{C}) = 13.0006 \text{ amu}$$

Effect of Isotopic Substitution

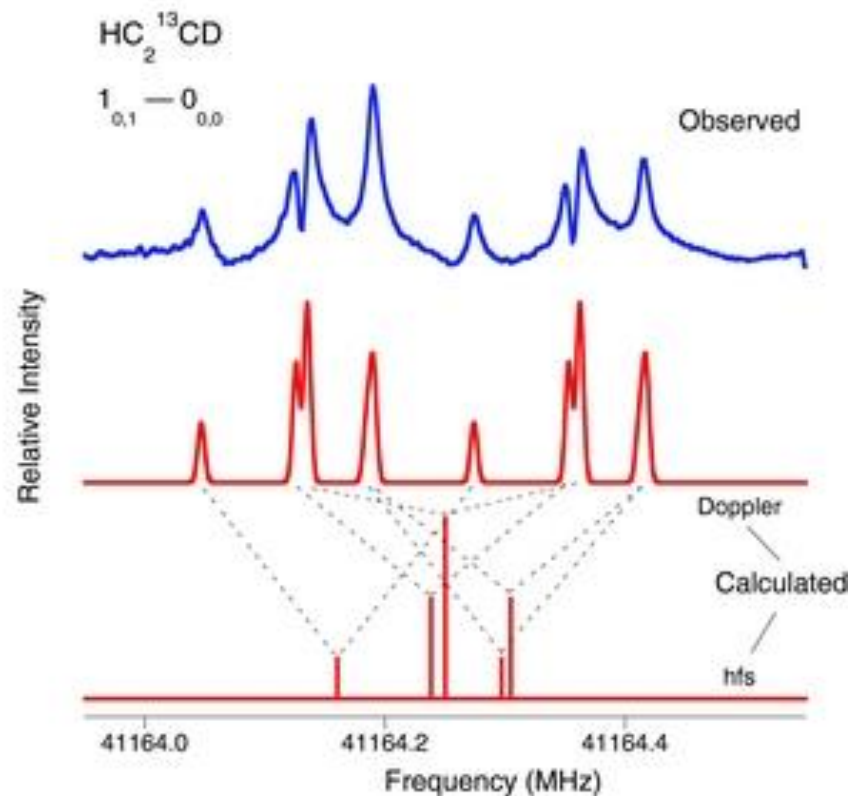
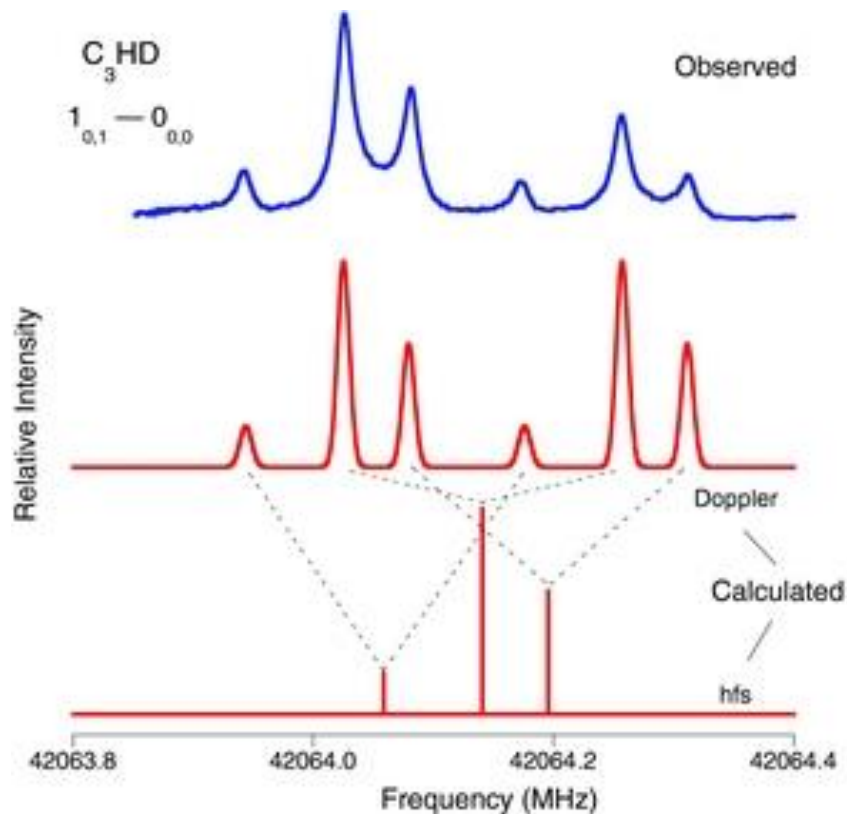
Rotational Spectrum of HCl



We can obtain; atomic masses, bond length or relative abundance of isotopes

Isotope splitting

■ $c\text{-C}_3\text{HD}$



Non-rigid Rotor

For a non-rigid rotor, the bond length increases as the angular velocity increases

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



$$B \propto \frac{1}{r^2}$$



B decreases with J

Rotational transitions of HF

Transition	$E_{\text{calc}} \text{ cm}^{-1}$	$E_{\text{exp}} \text{ cm}^{-1}$	$r, \text{ \AA}$
0→1	20.56	20.55	0.929
1→2	20.56	20.48	0.931
2→3	20.56	20.43	0.932
3→4	20.56	20.31	0.935
4→5	20.56	20.16	0.938
5→6	20.56	20.04	0.941
6→7	20.56	19.82	0.946
7→8	20.56	19.64	0.951
8→9	20.56	19.45	0.955
9→10	20.56	19.16	0.963
10→11	20.56	18.91	0.969

for a non-rigid rotor

$$E_J = B \cdot J(J+1) - D \cdot J^2(J+1)^2$$

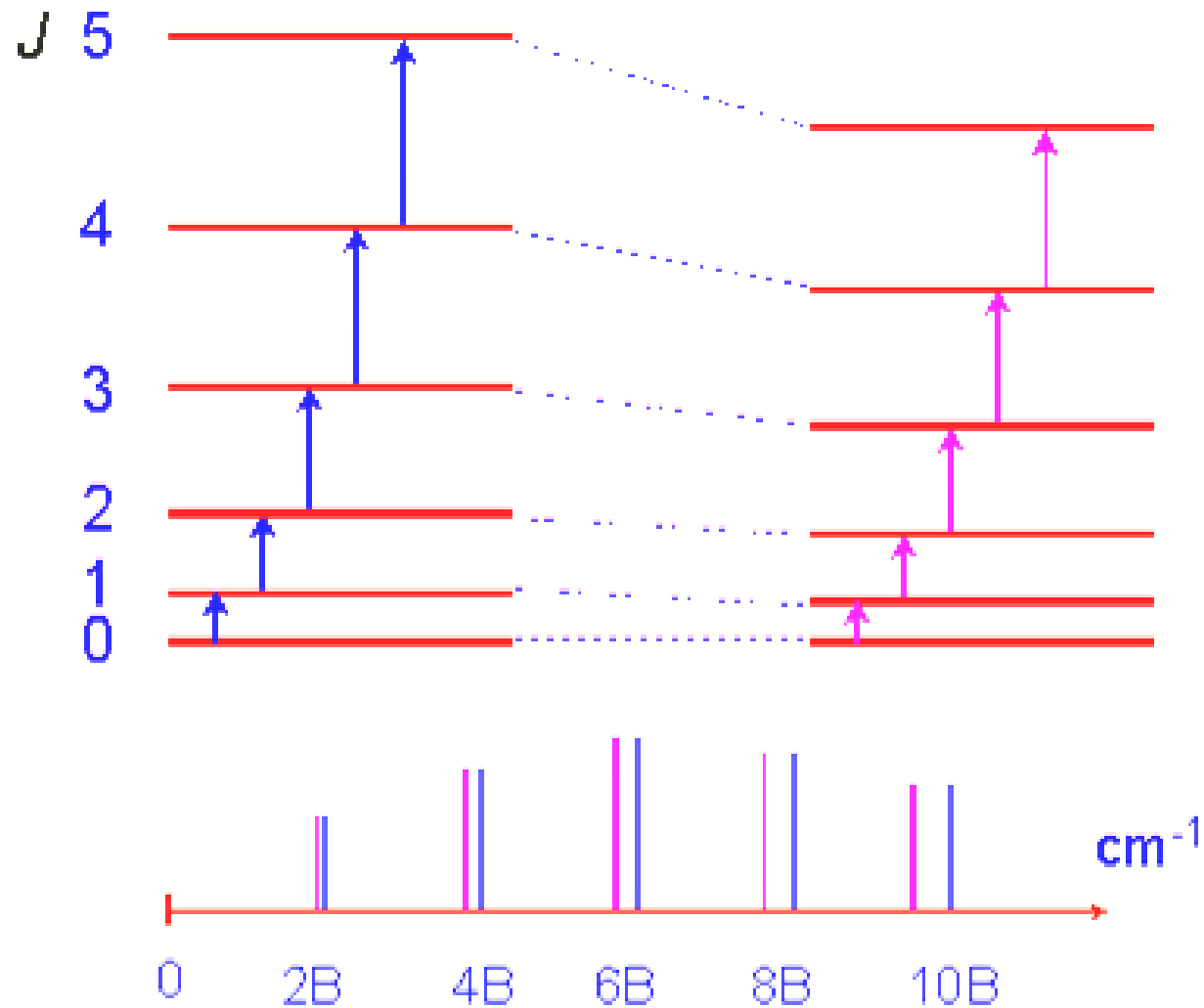
D – centrifugal distortion constant
(‘stiffness’ constant)
units: cm^{-1}

rigid rotor

$$\varepsilon_J = B \cdot J(J+1)$$

non-rigid rotor

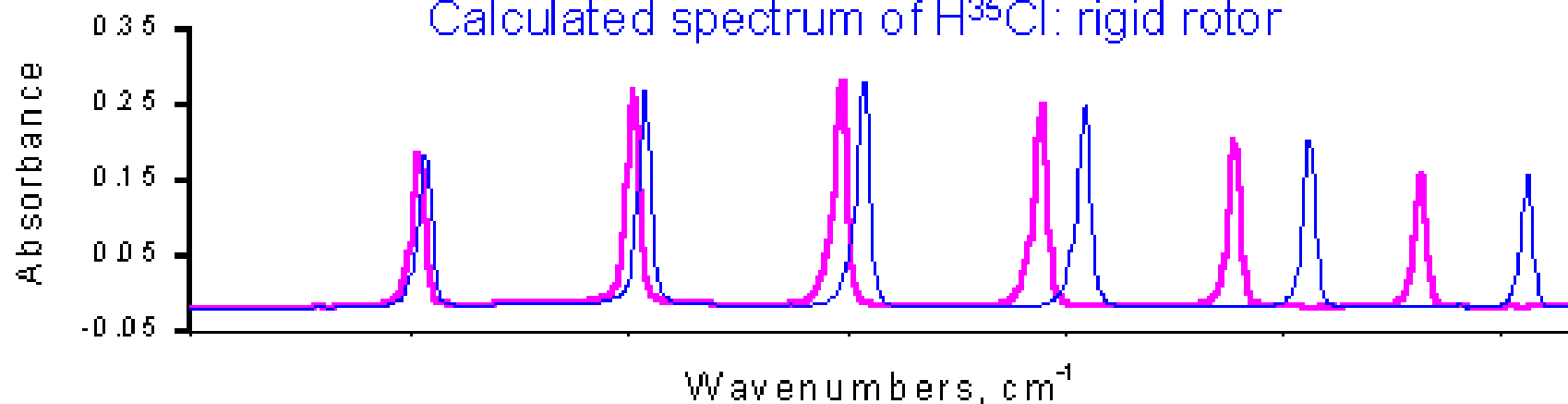
$$\varepsilon_J = B \cdot J(J+1) - D \cdot J^2 (J+1)^2$$



Non-rigid Rotor

Experimental spectrum of H³⁵Cl: non-rigid rotor

Calculated spectrum of H³⁵Cl: rigid rotor



$$\varepsilon_J = B \cdot J(J+1) - D \cdot J^2(J+1)^2$$

$$\tilde{\nu} = \varepsilon_{J+1} - \varepsilon_J = 2B(J+1) - 4D \cdot (J+1)^3$$

the rigid rotor selection rules apply, i.e. $\Delta J = \pm 1$

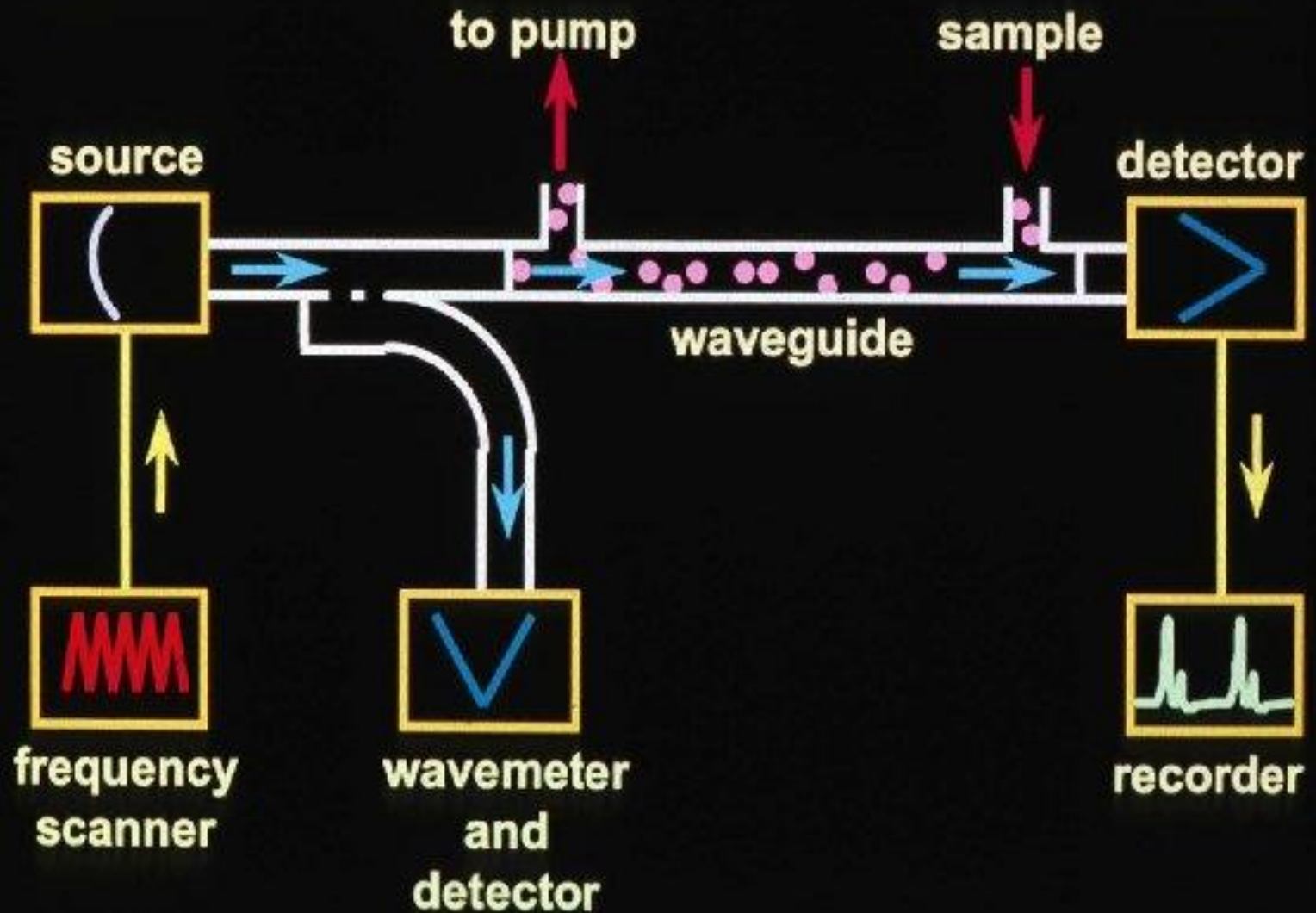
$$B \approx 1 \text{ to } 10 \text{ cm}^{-1}$$


$$D \approx 10^{-3} \text{ to } 10^{-2} \text{ cm}^{-1}$$

$$D = \frac{4B^3}{\tilde{\nu}^2}$$

$\tilde{\nu}$ is the bond vibrational frequency which is related to the force constant

Microwave spectrometer






In the conventional Stark-modulated spectrometer, the sample is contained in a long (1- to 3-meter, or 3.3- to 9.8-foot) section of a rectangular waveguide, sealed at each end with a microwave transmitting window (*e.g.*, mica or Mylar), and connected to a vacuum line for evacuation and sample introduction. The radiation from the source passes through a gaseous sample and is detected by a crystal diode detector that is followed by an amplifier and display system (chart recorder). In order to increase the sensitivity of the instrument, signal modulation by application of a high-voltage square wave across the sample is used.

Applications of microwave spectroscopy

Microwave spectroscopy has been used in monitoring and control of industrial processes. It is an ideal process analyzer as it is:

1. non-invasive: the measurement can be made outside of the reaction chamber, eliminates the need for sampling or physical removal of sample.
2. non-destructive.
3. can be used for solids, liquids, gases and suspensions .
4. can be used for dark coloured samples.
5. analyses large sample volumes, as microwaves diffuse out from the transmitter though the entire sample becomes lower.

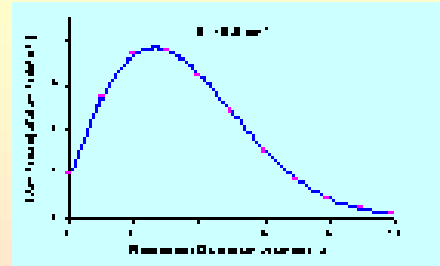


Microwave spectroscopy has been used in monitoring and control of industrial processes, such as;

1. materials with low dielectric constants, such as plastics, glass, ceramics and composite materials.
2. determination of moisture in various tobacco types.
3. Monitoring of a batch esterification reaction as in the esterification of butanol by acetic acid.
4. Monitoring of the drying process in industry as it is one that is hard to monitor. For example, huge cakes of wet material when dried in big vessels.
5. Astrophysical applications, radioastronomy: probe of the molecular universe (molecular clouds) using Telescope.

Summary

- Population of rotational energy levels:
Boltzmann distribution,
degenerate states
- Effect of bond length and mass
on rotational constants of
diatomic molecules
- Effect of isotopic substitution:
atomic weights and
abundance of isotopes
- Non-rigid rotor
 D - centrifugal distortion constant



	r_e , Å	B , cm^{-1}		r_e , Å	B , cm^{-1}
H_2^+	1.08	20.3	F_2	1.42	0.23
H_2	0.74128	60.8	Cl_2	1.98	0.24
D_2	0.74134	30.4	Br_2	2.28	0.091
O_2	1.21	1.64	HF	0.92	20.3
N_2	1.10	2.00	HCl	1.27	10.6
CO	1.13	1.93	HBr	1.41	8.48

