

VIVEKANANDA COLLEGE
THAKURPUKUR
KOLKATA-700063
NAAC ACCREDITED 'A' GRADE



Topic: Microwave/Rotational Spectroscopy

Course Title: Chemistry (Gen.)

Paper: GE-4/CC-4

Semester: 4(Gen.)

Name of the Teacher: Prabal Giri

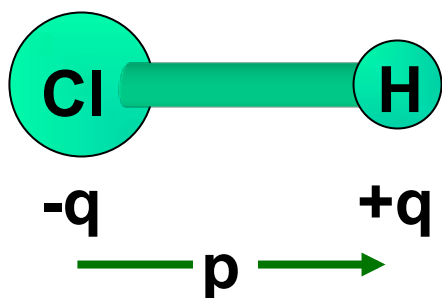
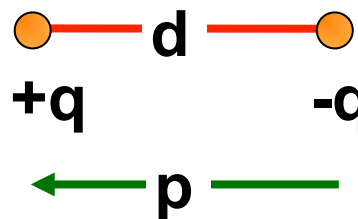
Name of the Department: Chemistry

Microwave Spectroscopy - Rotation of Molecules

Microwave Spectroscopy is concerned with transitions between **rotational energy levels** in molecules.

Definition

Electric Dipole: $p = q \cdot d$



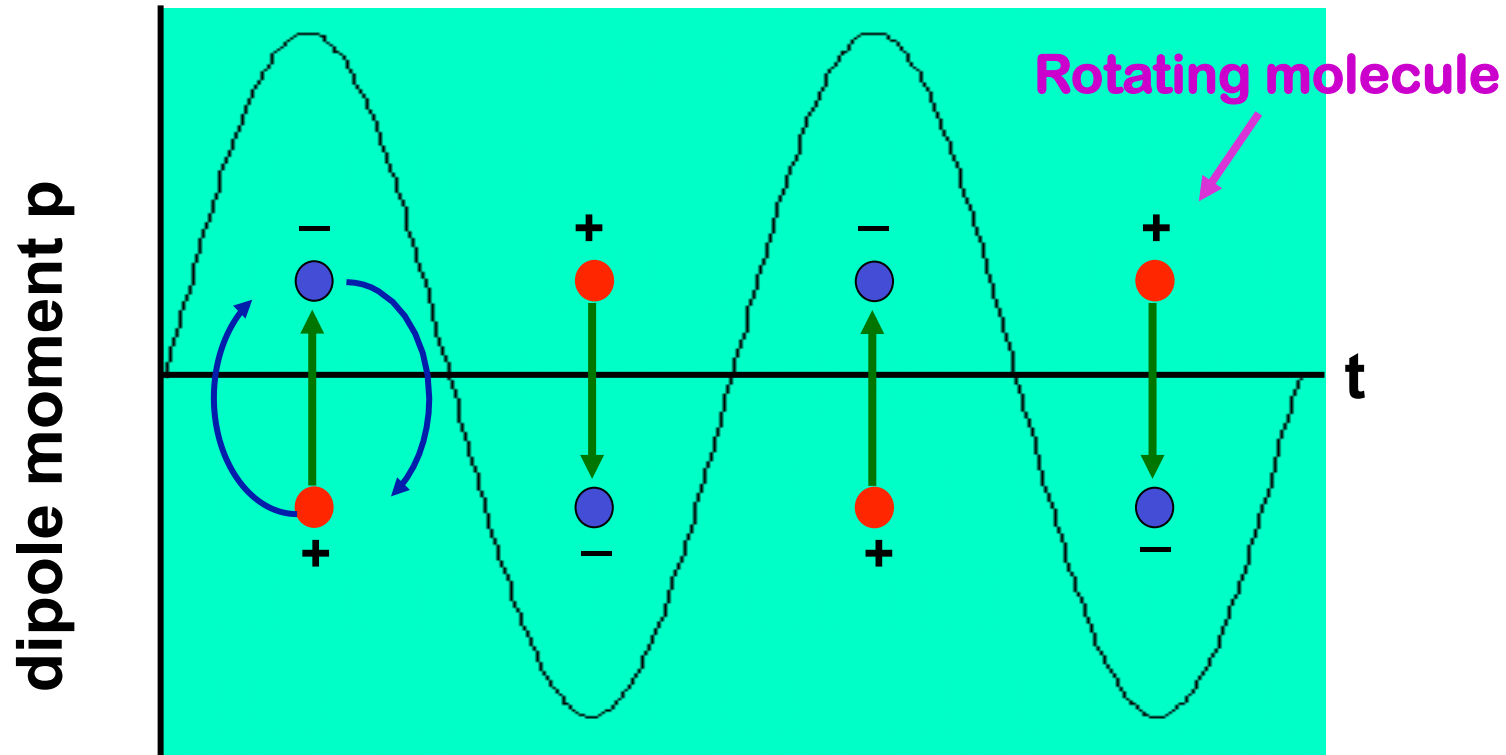
Most **heteronuclear** molecules possess a **permanent dipole moment**

e.g HCl, NO, CO, H₂O...

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**.

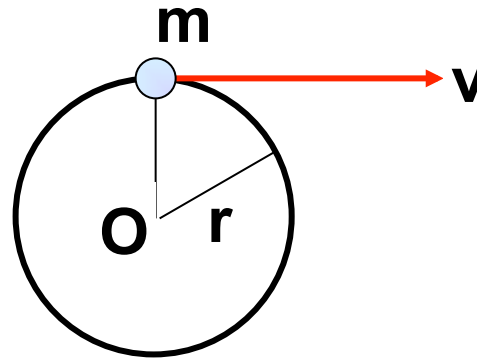


Homonuclear molecules (e.g. O_2 , H_2 , Cl_2 , Br_2 do not have a **permanent dipole moment** and therefore do not have a microwave spectrum!

General features of rotating systems

Linear velocity

$$v = \frac{\text{distance}}{\text{time}}$$



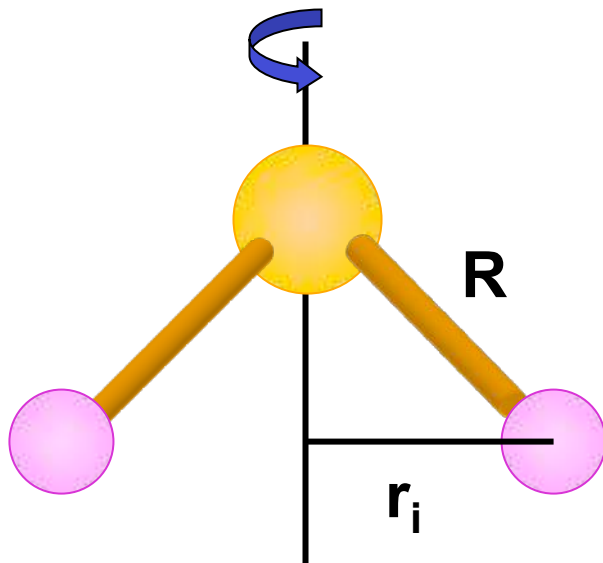
angular velocity

$$\omega = \frac{\text{radians}}{\text{time}}$$

$$v = \omega \times r$$

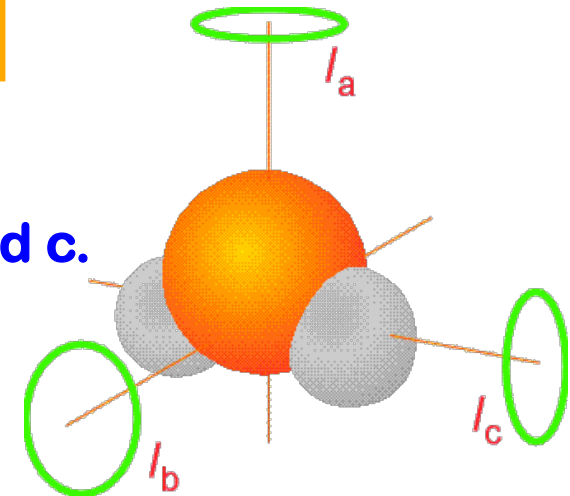
Moment of Inertia $I = mr^2$.

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

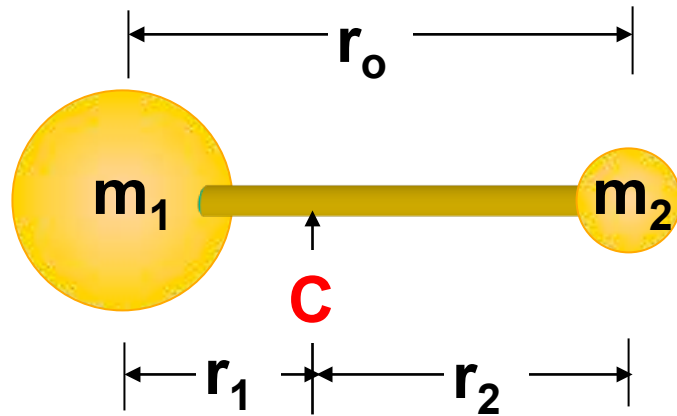


$$I = \sum_i m_i r_i^2$$

Note how r_i is defined, it is the perpendicular distance from axis of rotation



Rigid Diatomic Rotors



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

C = centre of gravity.

Express I in terms of m_1 , m_2 and r_0 .

from

$$r_1 + r_2 = r_0 \quad (1)$$

$$m_1 \cdot r_1 = m_2 \cdot r_2 \quad (2)$$

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



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

Derive this expression

NOTE:

Units of I = $\text{kg} \cdot \text{m}^2$.

μ = reduced or effective mass of the molecule

Energy and Angular Momentum

Angular momentum about axis a is $J_A = I_A \omega_A$

Energy of a body rotating about an axis 'a' with constant angular velo

$$E_a = \frac{1}{2} I_A \omega_A^2$$

A body free to rotate about all three axes has a total rotational energy

$$E = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2$$

And a total angular momentum given by

$$\begin{aligned} J^2 &= J_A^2 + J_B^2 + J_C^2 \\ &= (I_A \omega_A)^2 + (I_B \omega_B)^2 + (I_C \omega_C)^2 \end{aligned}$$

Recall that J is a vector

Energy Levels of a Rigid Diatomic Rotor

For diatomic molecule $I_B = I_C = I$ and $I_A = 0$ so:

$$E = \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 = \frac{J_B^2}{2I_B} + \frac{J_C^2}{2I_C} = \frac{J^2}{2I}$$

Can find quantum energy levels using **Correspondence Principle**:

$$J^2 \rightarrow J(J+1) \cdot \hbar^2 = \frac{J(J+1) \cdot h^2}{4\pi^2}$$

1. Rotational energy for a rigid diatomic rotor is quantised

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

Units: **Joules**

$J = 0, 1, 2, 3, \dots$

= rotational quantum number

Energy Levels of a Rigid Diatomic Rotor

2. Rotational energy is usually expressed in units of cm^{-1} .

Recall $E = h\nu = h \cdot c \cdot \tilde{\nu}$ therefore $\tilde{\nu} = \varepsilon = \frac{E}{h \cdot c}$ then

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

B - Rotational Constant, units cm^{-1}

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

where

$$B = \frac{h}{8\pi^2 Ic} = \frac{\hbar}{4\pi Ic}$$

ε_J gives the allowed energy levels of the rigid rotor (in cm^{-1}).

B can be determined experimentally by spectroscopy

Notation: Rotational Term F(J)

The energy of a rotational state is normally reported as the **Rotational Term, F(J)**, a wavenumber divided by hc

$$F(J) \equiv \varepsilon_J = \frac{\Delta E}{hc} = B \cdot J(J + 1)$$

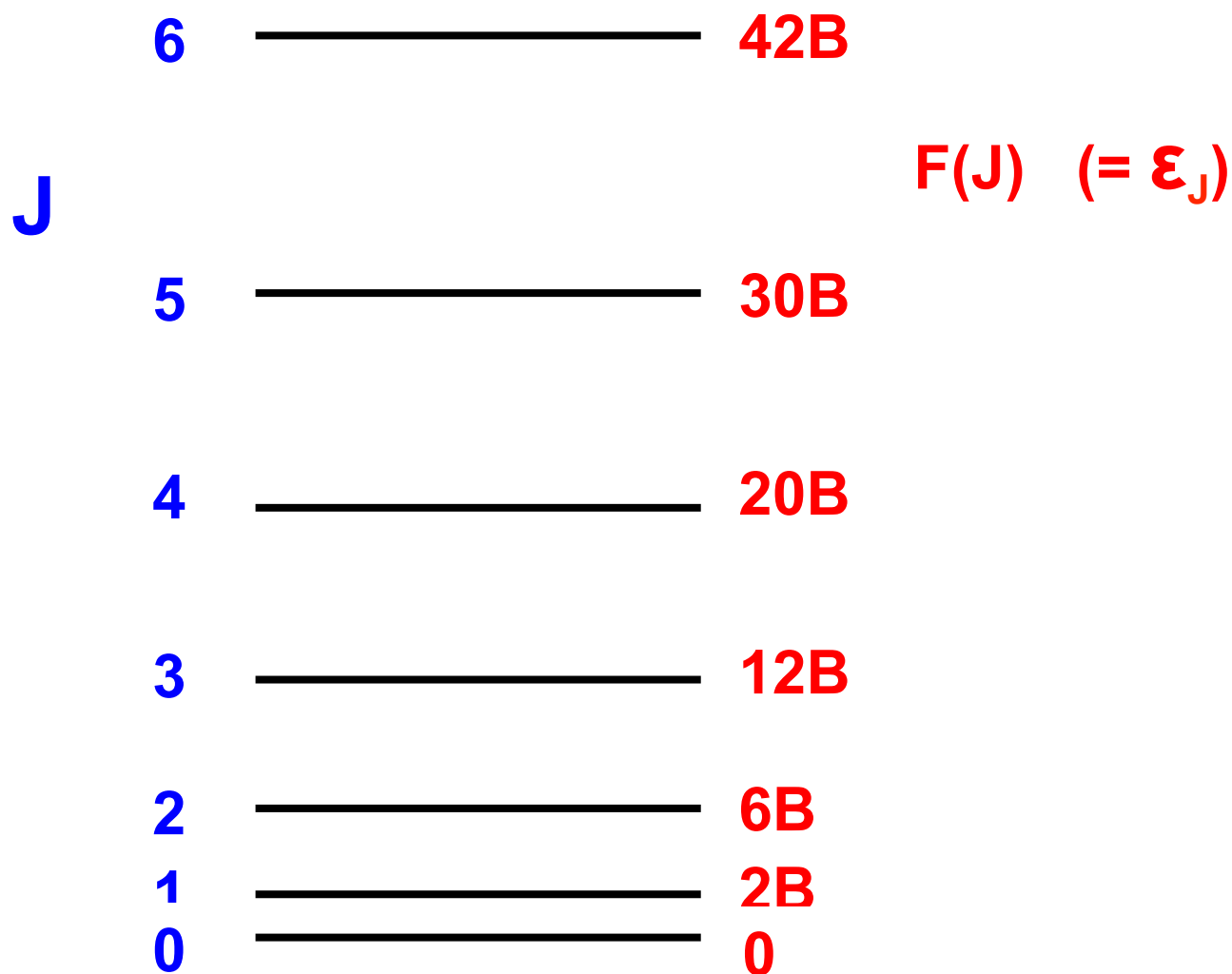
Ritz Combination Principle

The **wavenumber of any spectral line is the difference between two terms**. Two terms T_1 and T_2 combine to produce a spectral line of wavenumber.

$$\tilde{\nu} = T_1 - T_2 = \frac{\Delta E}{hc}$$

Energy Levels of a Rigid Diatomic Rotor

$$\varepsilon_J = B \cdot J(J+1) \quad J=0, 1, 2, 3, \dots$$



Can we predict nature of a microwave rotational spectrum?

Rotational Transitions in Rigid Diatomic Molecules

Selection Rules:

1. A molecule has a rotational spectrum only if it has a permanent dipole moment.
2. $\Delta J = \pm 1$ +1 = adsorption of photon,
 -1 = emission of photon.

Transitions observed in absorption spectrum.

$$J = 0 \rightarrow J = 1$$

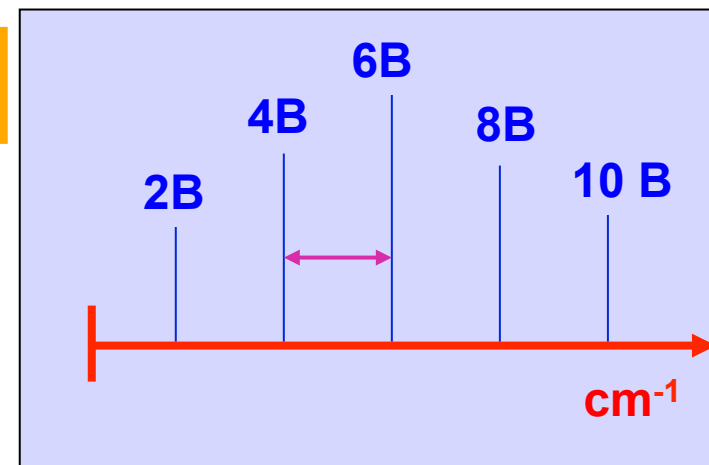
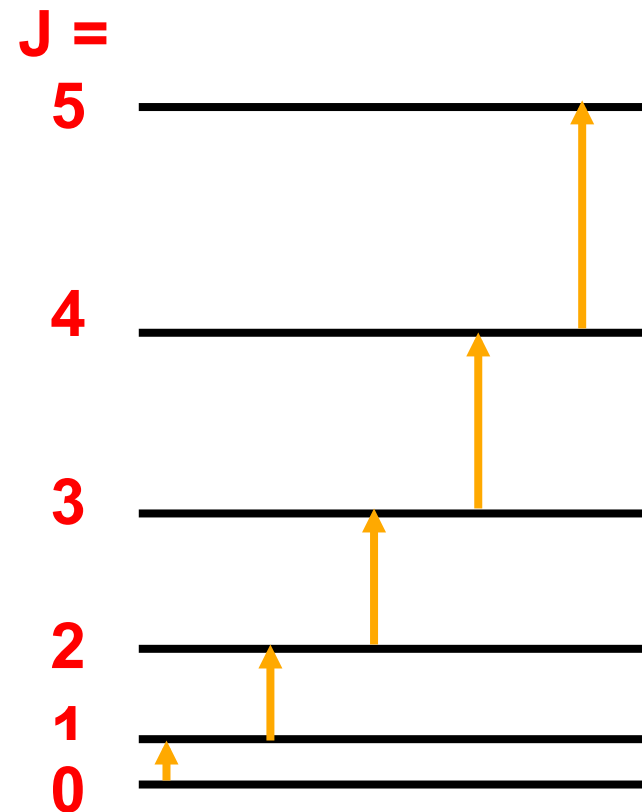
$$\tilde{\nu} = \Delta \epsilon_J = \epsilon_{J=1} - \epsilon_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

$$J = 1 \rightarrow J = 2$$

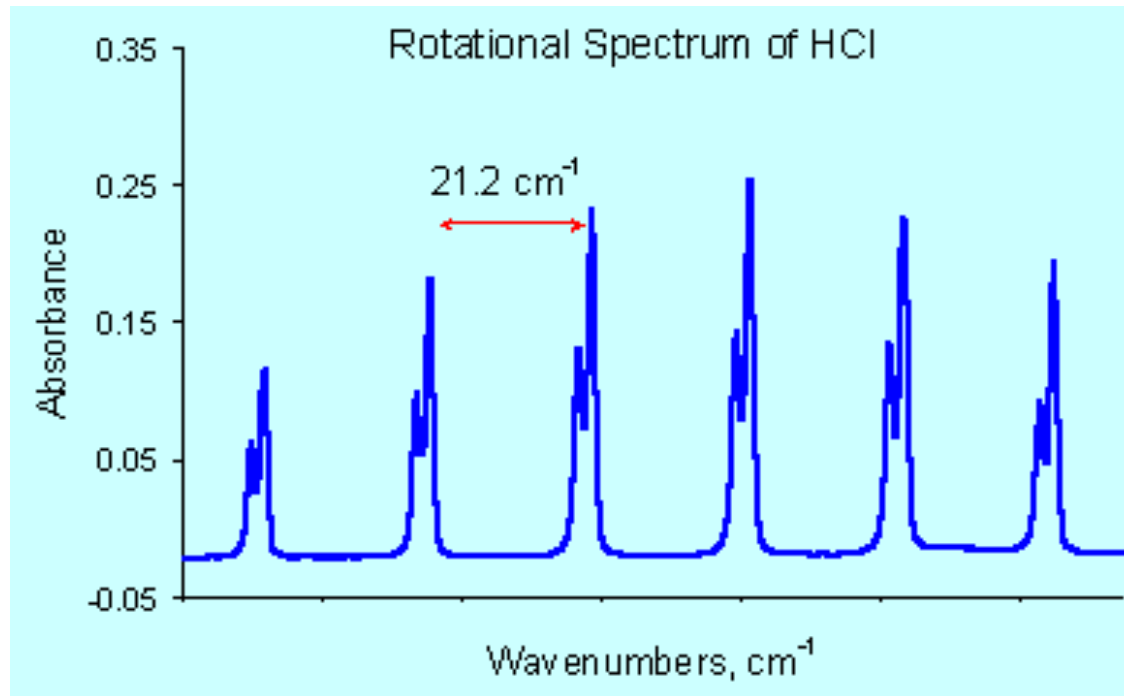
$$\tilde{\nu} = \Delta \epsilon_J = \epsilon_{J=2} - \epsilon_{J=1} = 6B - 2B = 4B \text{ cm}^{-1}$$

In general $\tilde{\nu}_{J \rightarrow J+1} = 2B(J+1) \text{ cm}^{-1}$

Spacing between lines in spectrum = 2B



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

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

Once I_{HCl} is known, then r_{HCl} (the bond length) can be determined from

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

Need to know m_{H} and m_{Cl} , but these are known and tabulated.

Summary so far:

1. Microwave spectroscopy is concerned with transitions between **rotational energy levels** of molecules
2. General features of rotational systems: **I , ω , μ**

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

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

3. Energy Levels of a rigid diatomic rotor

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

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

$$J = 0, 1, 2, \dots; \quad B = \text{rotational constant, units cm}^{-1}$$

4. Selection rules: (1) permanent dipole moment,
(2) $\Delta J = \pm 1$ only
5. Spacing between lines of in rotational spectra of rigid diatomic molecules is constant and equal to $2B \text{ cm}^{-1}$.

Why is Rotational Spectroscopy important?

From pure rotational spectra of molecules we can obtain:



1. bond lengths
2. atomic masses
3. isotopic abundances
4. temperature

Important in Astrophysics: Temperature and composition of interstellar medium

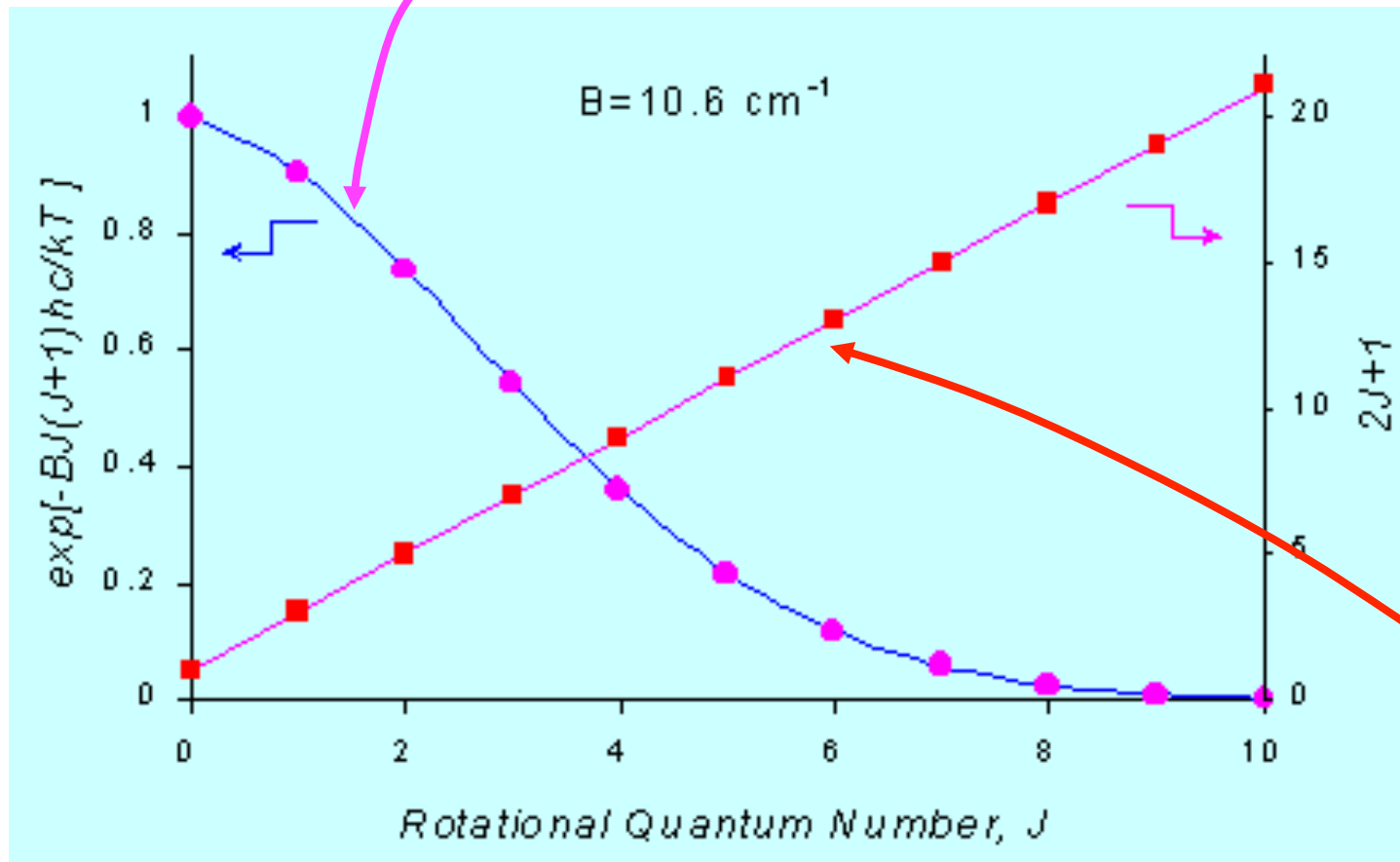
Diatomic molecules found in interstellar gas:

**H₂, OH, SO, SiO, SiS, NO, NS,
HCl, PN, NH, CH⁺, CH, CN, CO,
CS, C₂.**

Population of Rotational Energy Levels

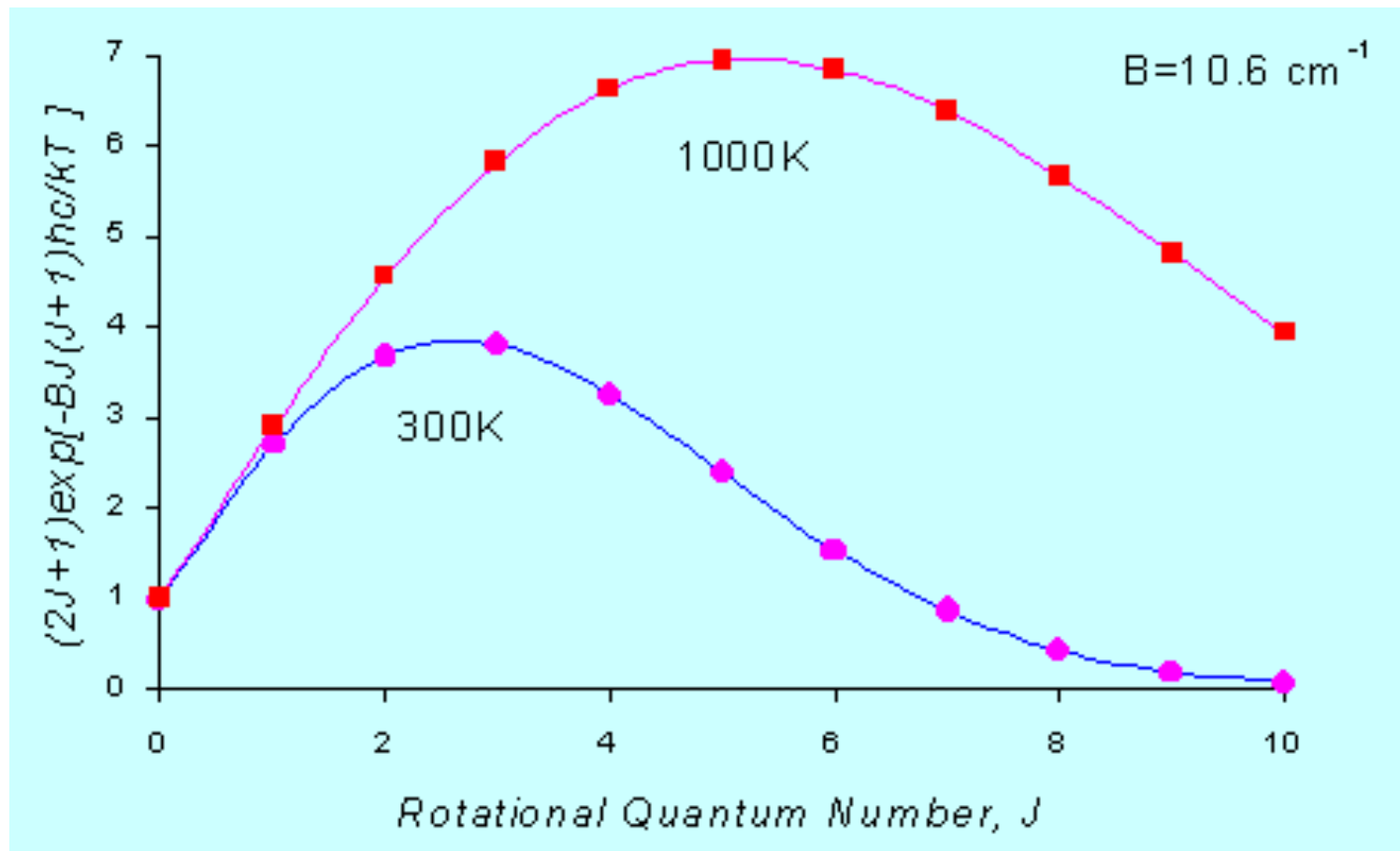
Boltzmann distribution:

$$\frac{N_{J+1}}{N_{J=0}} = \exp\left(-\frac{\Delta E}{kT}\right) = \exp\left(-\frac{\epsilon_J hc}{kT}\right)$$



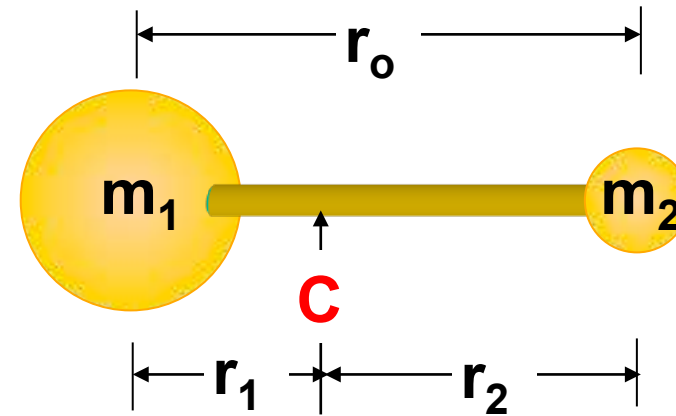
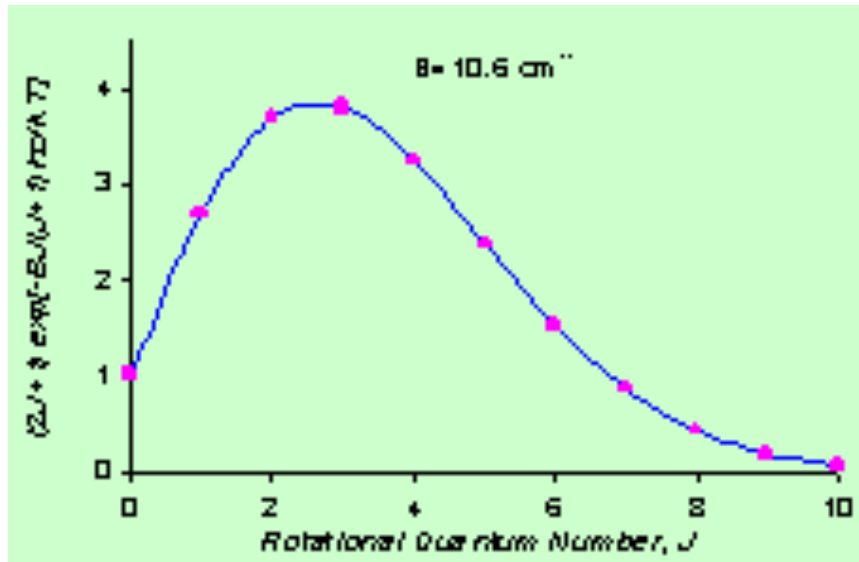
Orientation of the angular momentum L is quantised. This results in a **$(2J+1)$ degeneracy** of the energy level

$$\frac{\text{Population}_J}{\text{Population}_{J=0}} \propto (2J+1) \exp\left(-\frac{\Delta E}{kT}\right) = (2J+1) \exp\left(-\frac{BJ(J+1)hc}{kT}\right)$$

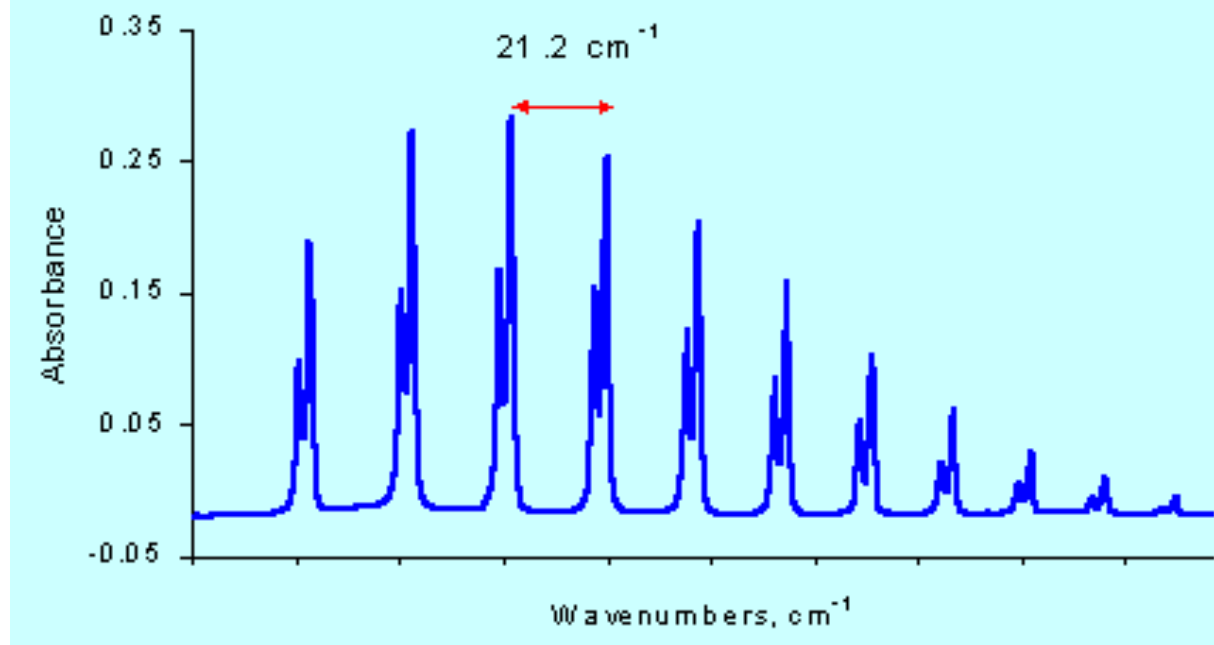


Spectral Line Intensity \propto Population

Example: Rotational Spectrum of HCl

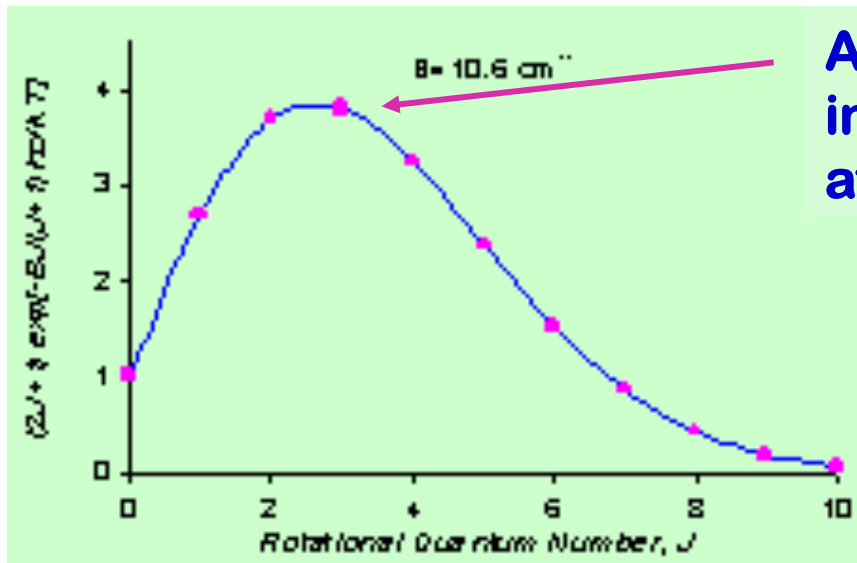


Rotational Spectrum of HCl



$B = 10.6 \text{ cm}^{-1}$,
 $T = 300\text{K}$

Maximum Value of J



At what value of J will the intensity be a maximum, at a given temperature?

We can find the value of J_{\max} by finding the value of J that maximises the population:

$$\text{Population} \propto (2J+1) \exp\left(-\frac{\Delta E}{kT}\right) = (2J+1) \exp\left(-\frac{BJ(J+1)hc}{kT}\right)$$

Differentiate w.r.t. J and set equal to zero for a maximum. This gives

$$J_{\max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

must round this value to the nearest integer (J can only be an integer)

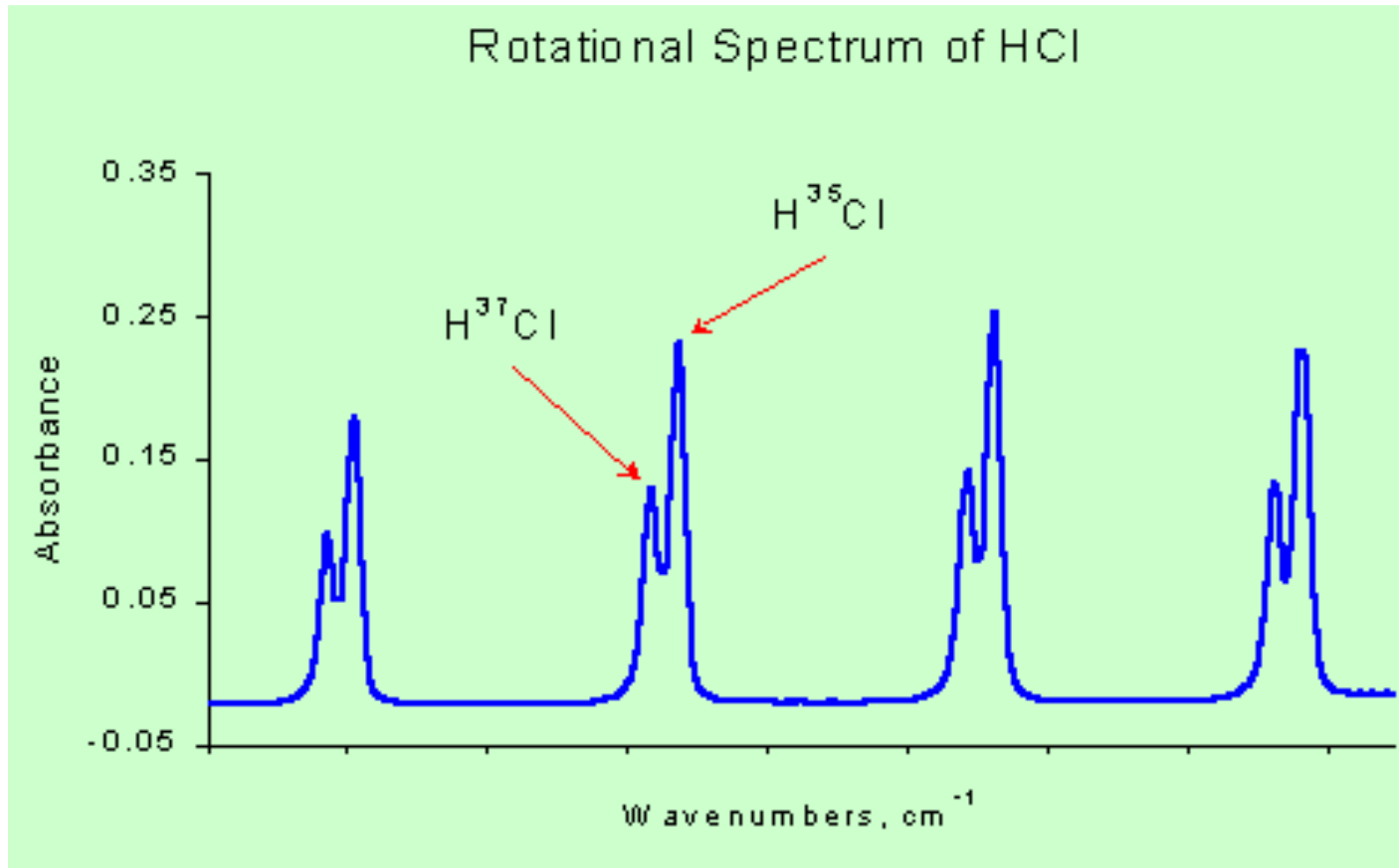
Bond lengths and Rotational Constants of some Diatomic Molecules

| | $r_0, \text{\AA}$ | 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 |

Note effect of r_0 and m on the rotational constant B .

$$I \propto r_0^2 \text{ and } m \quad \text{and} \quad B \propto 1 / I$$

Effect of Isotope Substitution



From spectra we can obtain:

**bond length or atomic weights
and Isotopic Abundances**

Effect of Isotope Substitution on Spectra

For $^{12}\text{C}^{16}\text{O}$

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

$^{13}\text{C}^{16}\text{O}$

$$B'' = 1.83669 \text{ cm}^{-1}$$

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

$$\frac{B'}{B''} = \frac{h}{8\pi^2 I' c} \frac{8\pi^2 I'' c}{h} = \frac{I''}{I'} = \frac{\mu''}{\mu'} = 1.046001$$

Atomic weight $^{12}\text{C} = 12.0000$, $^{16}\text{O} = 15.9994$ \longrightarrow $^{13}\text{C} = 13.0007$,

