Rotational Spectroscopy

Recommended Reading:

1. Banwell and McCash: Chapter 2

2. Atkins: Chapter 16, sections 4 - 8

Aims

In this section you will be introduced to

1) Rotational Energy Levels (term values) for diatomic molecules and linear polyatomic molecules

2) The rigid rotor approximation

3) The effects of centrifugal distortion on the energy levels

4) The Principle Moments of Inertia of a molecule.

5) Definitions of symmetric , spherical and asymmetric top molecules.

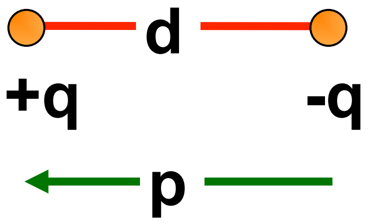
6) Experimental methods for measuring the pure rotational spectrum of a molecule

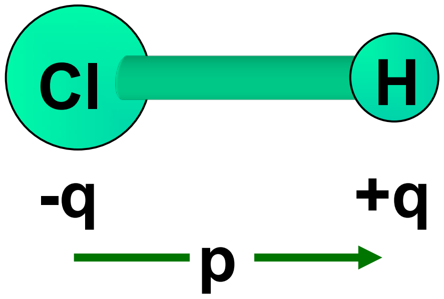
Microwave Spectroscopy - Rotation of Molecules

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

Definition

Electric Dipole: $p = q.d$





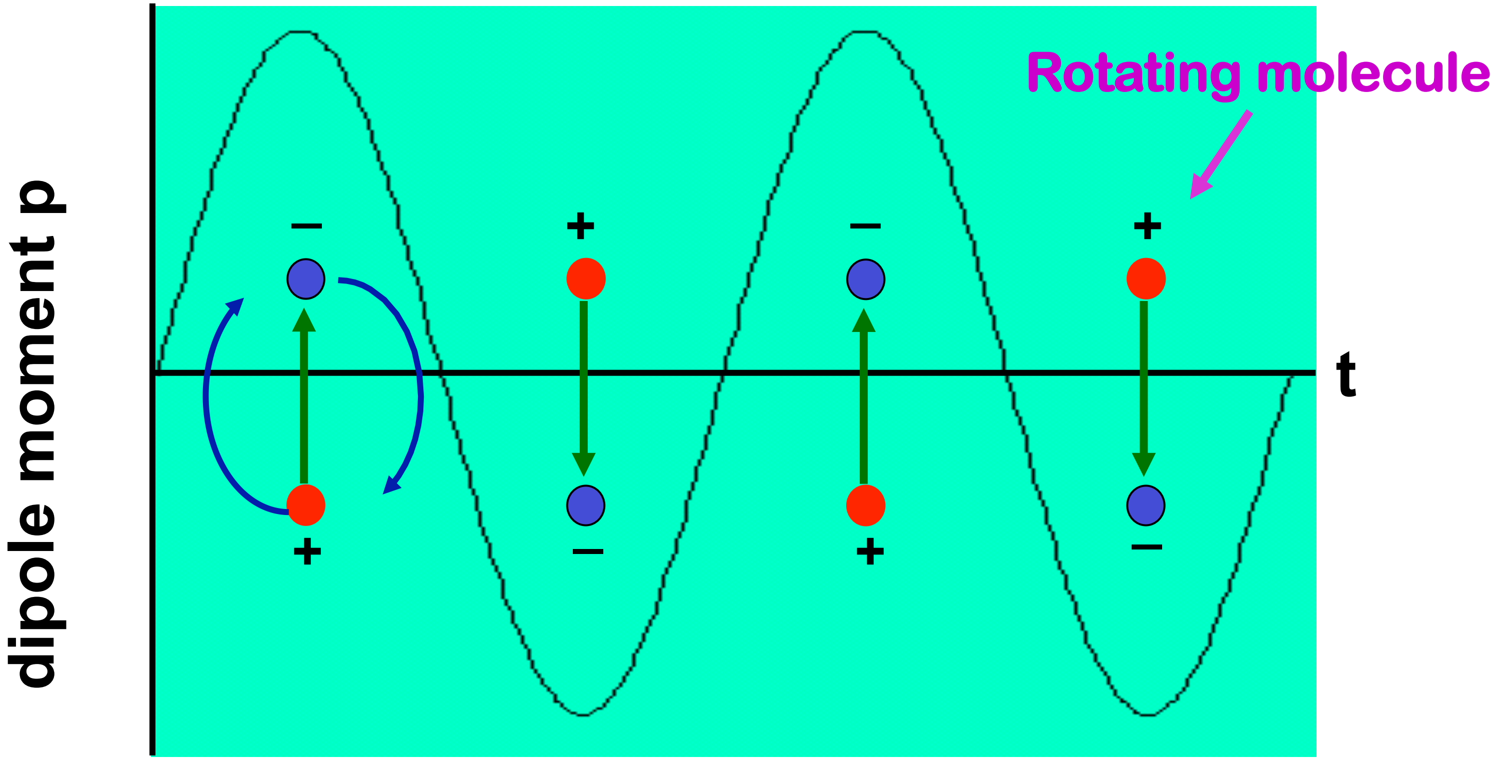
Most heteronuclear molecules possess a permanent dipole moment

e.g HCl, NO, CO, H_2O...

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.

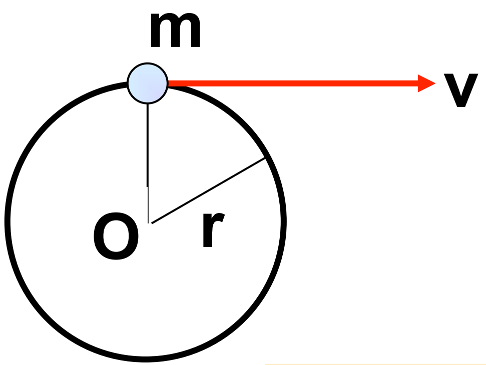


Homonuclear molecules (e.g. O_2, H_2, Cl_2, Br_2…. do not have a permanent dipole moment and therefore do not have a microwave spectrum!

General features of rotating systems

Linear velocity

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



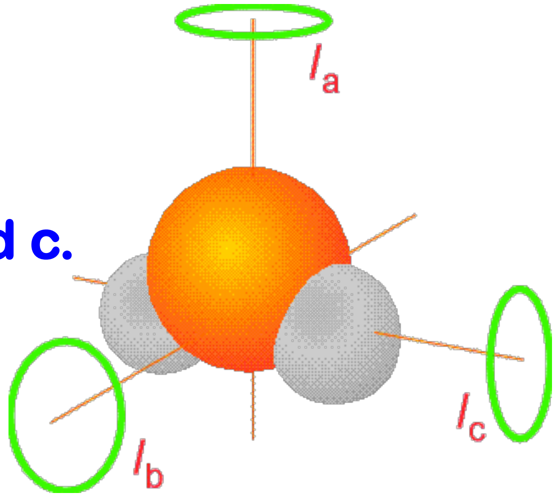
angular velocity

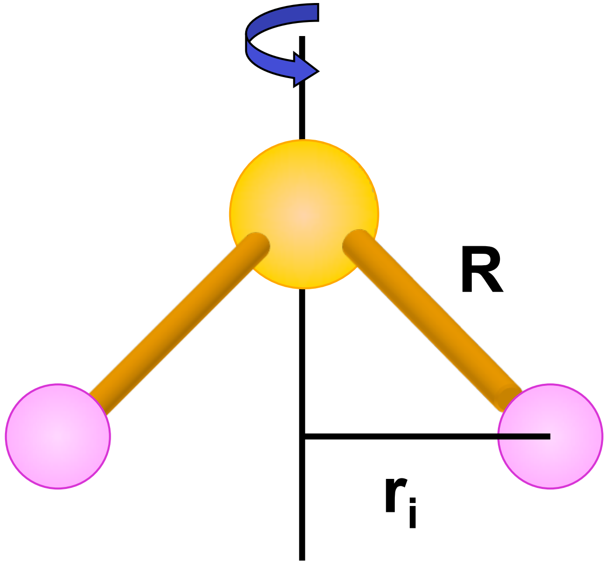
$$\omega = \frac{\text{radians}}{\text{time}}$$

$$v = \omega \times r$$

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.

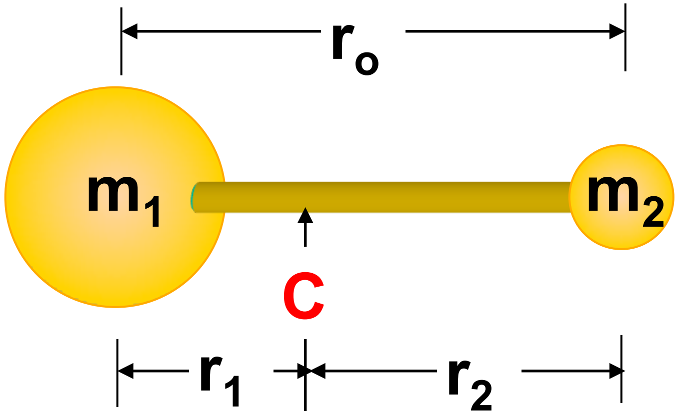




$$I = \sum_i m_i r_i^2$$

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

Rigid Diatomic Rotors



$I_B = I_c$, and $I_A = 0$.

C = centre of gravity.

Express I in terms of m_1, m_2 and r_0.

from

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

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

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

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

Derive this expression

NOTE:

Units of I = kg.m^2.

μ = reduced or effective mass of the molecule

Energy and Angular Momentum

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

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

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

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

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

And a total angular momentum given by

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

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:

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

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

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

Units: Joules

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

= 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

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

cm^{-1}

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

$$\boxed{\varepsilon_J = B \cdot J(J+1)}$$

where

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

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

$$\boxed{\mathrm{F(J)} \equiv \varepsilon_{\mathrm{J}} = \frac{\Delta E}{hc} = B \cdot J\left(J+1\right)}$$

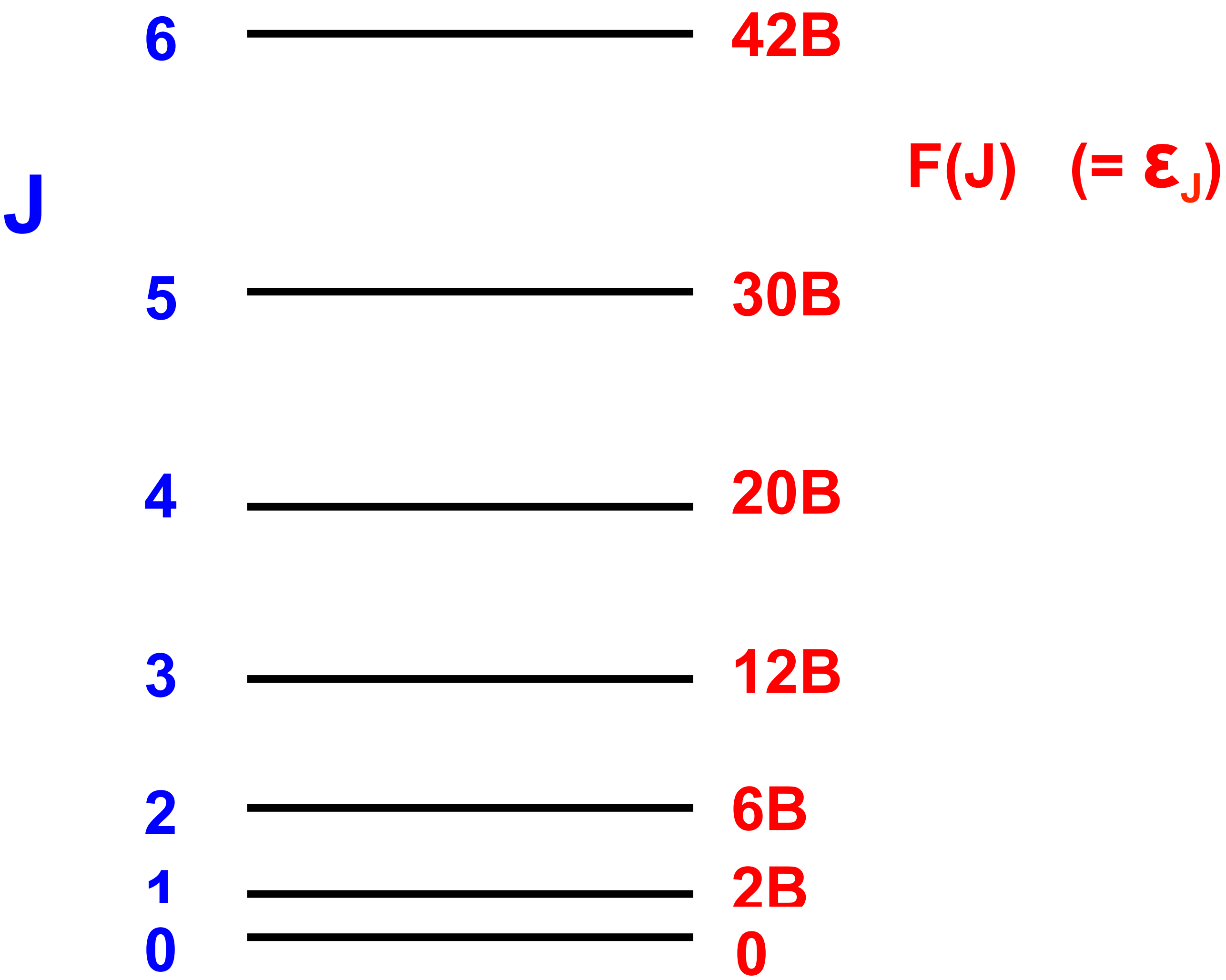
Ritz Combination Principle

The **wavenumber of any spectral line is the difference between two terms.** Two terms T1 and T2 combine to produce a spectral line of wavenumber.

$$\boxed{\tilde{\nu} = \mathrm{T}_1 - \mathrm{T}_2 = \frac{\Delta \mathrm{E}}{\mathrm{hc}}}$$

Energy Levels of a Rigid Diatomic Rotor

$$\varepsilon_J = B \cdot J(J+1) \qquad J = 0,\ 1,\ 2,\ 3\ldots..$$



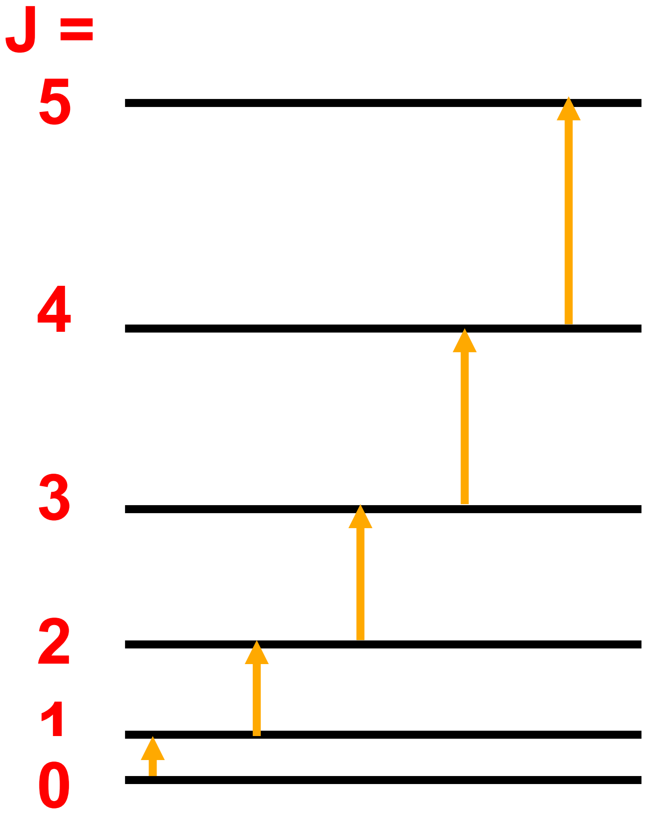
J	F(J) (= ε_J)
6	42B
5	30B
4	20B
3	12B
2	6B
1	2B
0	0

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. ΔJ = ± 1 +1 = adsorption of photon,
   -1 = emission of photon.



Transitions observed in absorption spectrum.

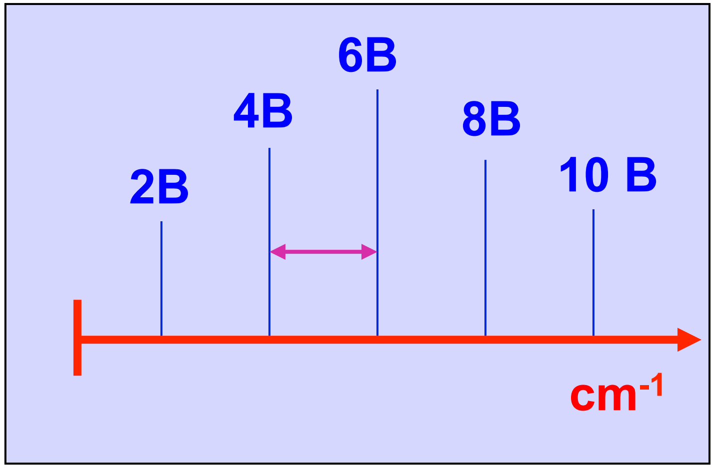
J = 0 ➔ J = 1

$$\boxed{\tilde{\nu} = \Delta\varepsilon_J = \varepsilon_{J=1} - \varepsilon_{J=0} = 2B - 0 = 2B\,\text{cm}^{-1}}$$

J = 1 ➔ J = 2

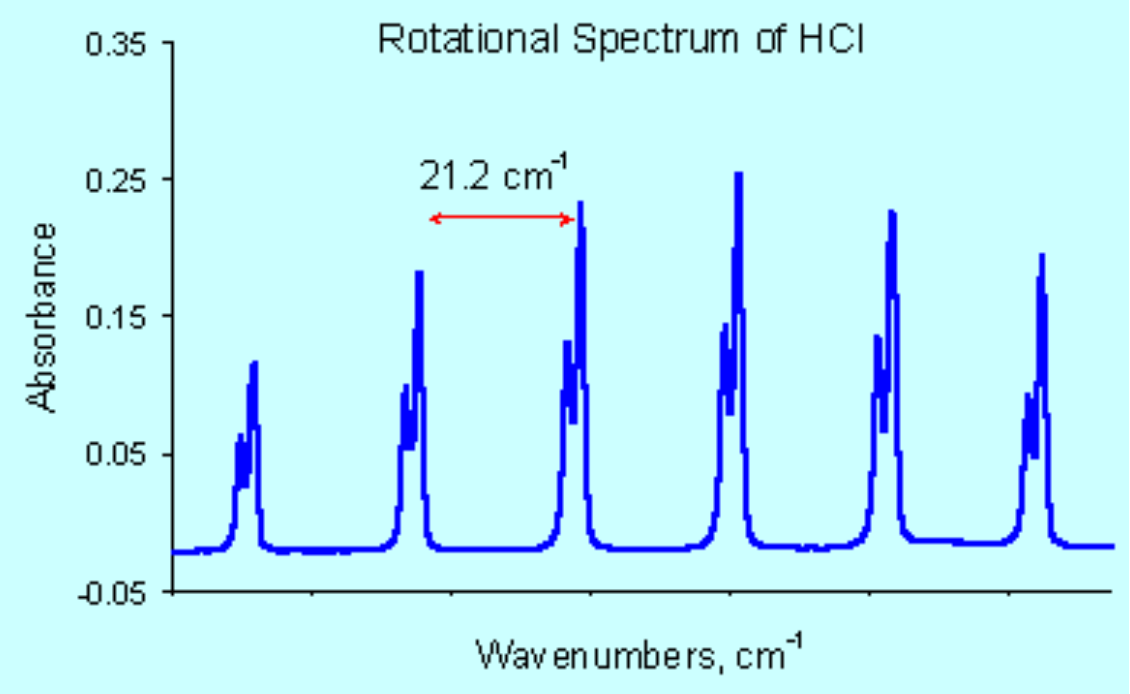
$$\boxed{\tilde{\nu} = \Delta\varepsilon_J = \varepsilon_{J=2} - \varepsilon_{J=1} = 6B - 2B = 4B\,\text{cm}^{-1}}$$

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



Spacing between lines in spectrum = 2B

Rotational Spectra of Rigid Diatomic Molecules



Line separation in the rotational spectrum of HCl is ≈ 21.2 cm^{-1} ➔ **B = 10.6 cm^{-1}**; I_{HCl} can be found from

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

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

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

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

$$\boxed{I = \sum_i m_i r_i^2}$$

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

3. Energy Levels of a rigid diatomic rotor

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

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

J = 0, 1, 2, ….; B = 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 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:

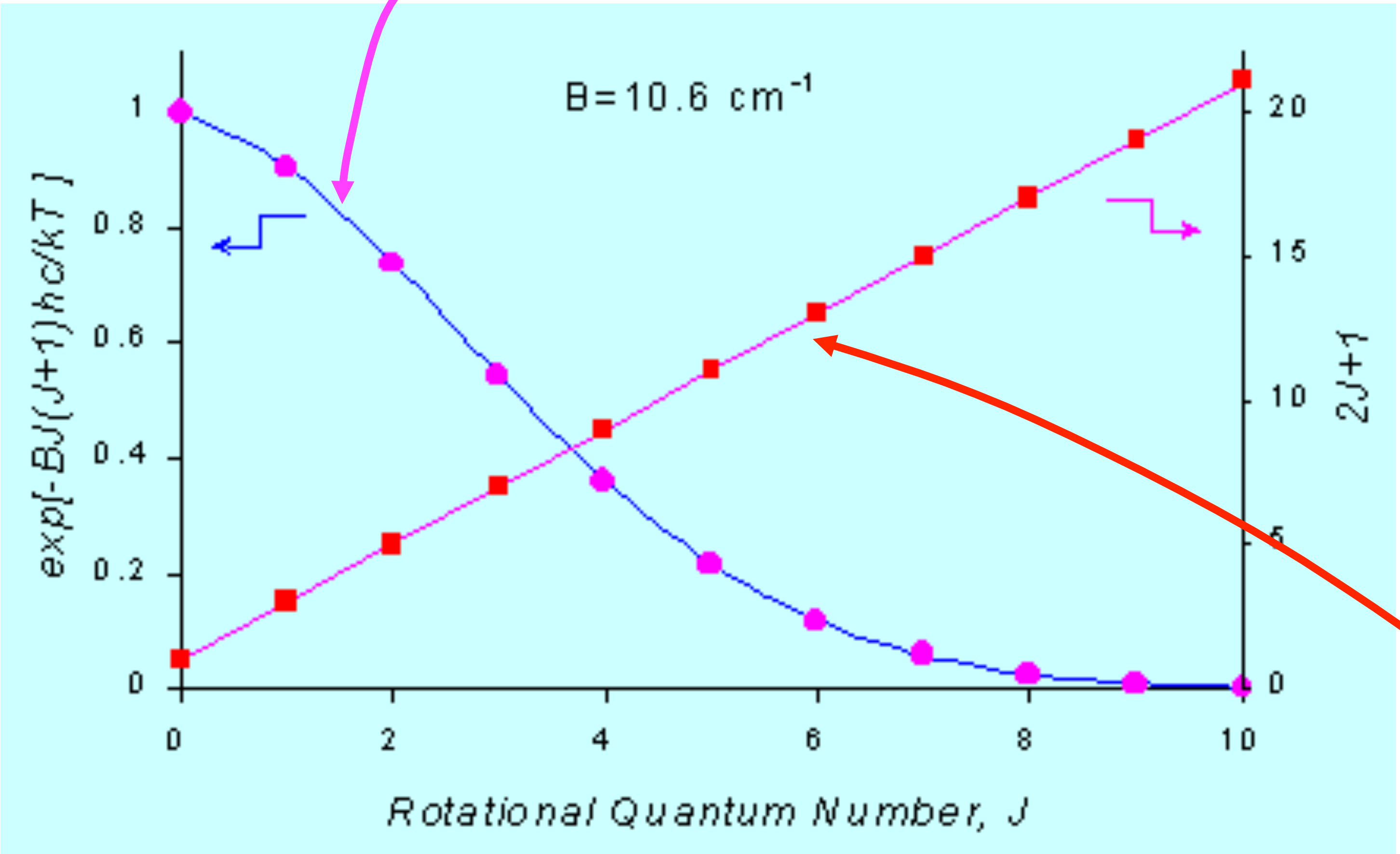
H_2, OH, SO, SiO, SiS, NO, NS,
HCl, PN, NH, CH^+, CH, CN, CO,
CS, C_2.

S.Taylor, D. Williams, Chemistry in Britain, 1993 pg 680 - 683

Population of Rotational Energy Levels

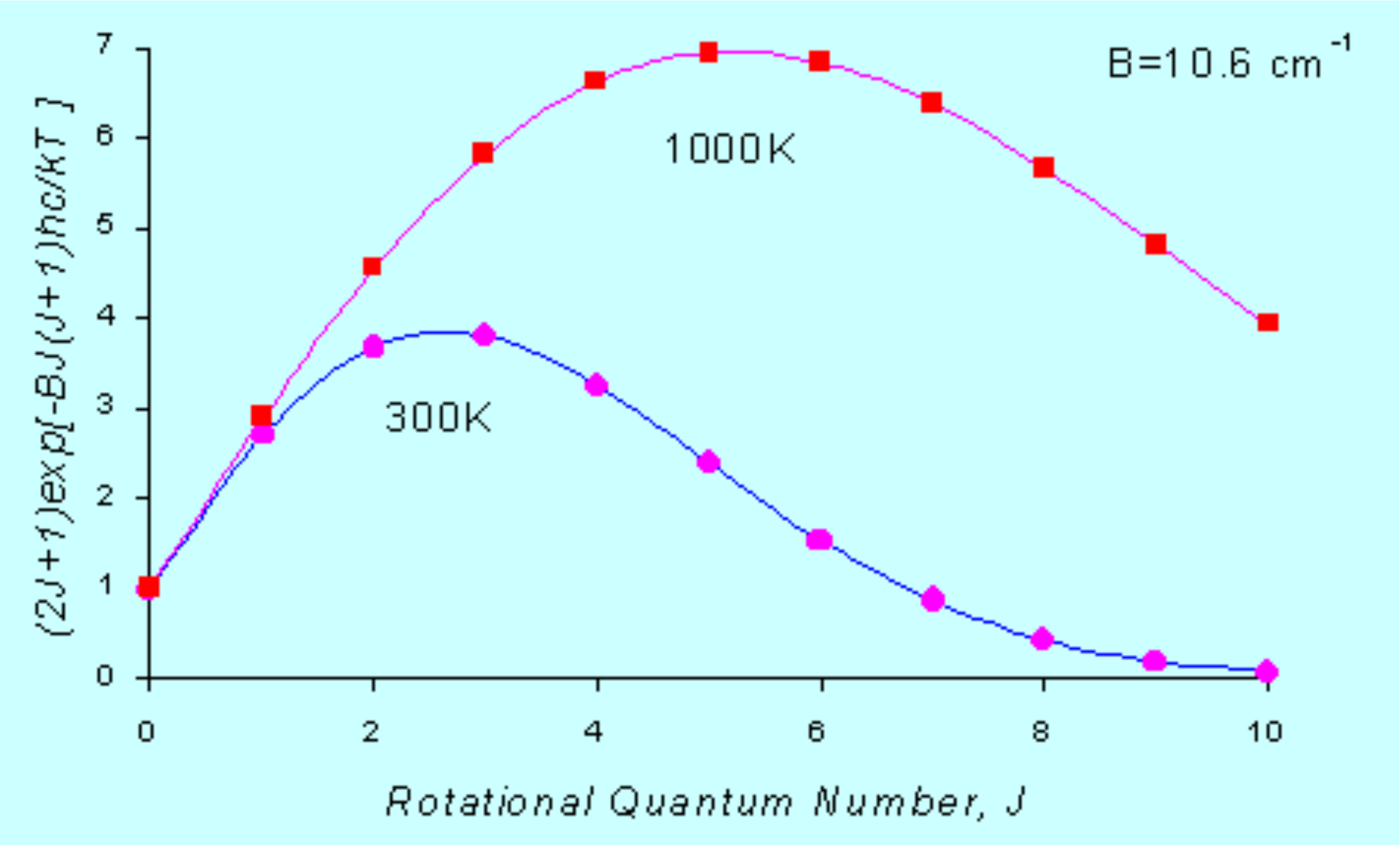
Boltzmann distribution:

$$\frac{N_{J+1}}{N_{J=0}} = \exp\left(-\frac{\Delta E}{\mathrm{k}T}\right) = \exp\left(-\frac{\varepsilon_J \mathrm{hc}}{\mathrm{k}T}\right)$$



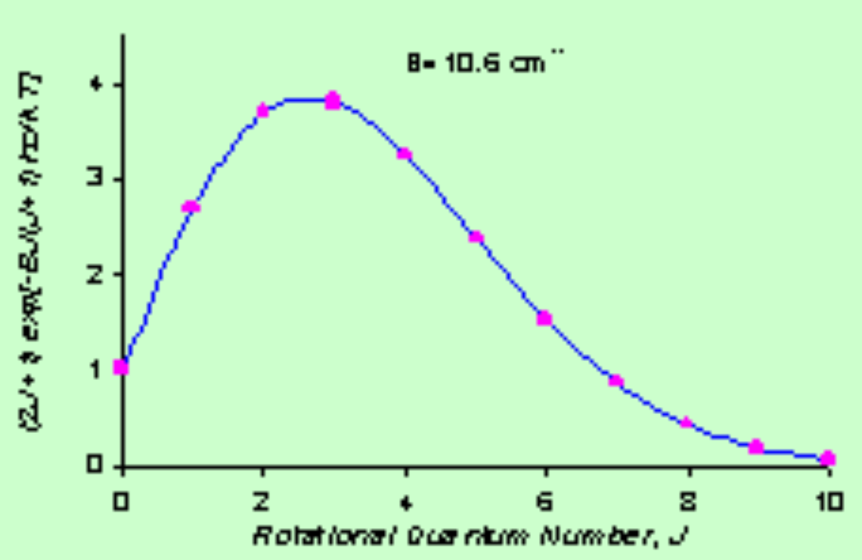
Orientation of the angular momentum L is quantised. This results in a **(2J+1) degeneracy** of the energy level

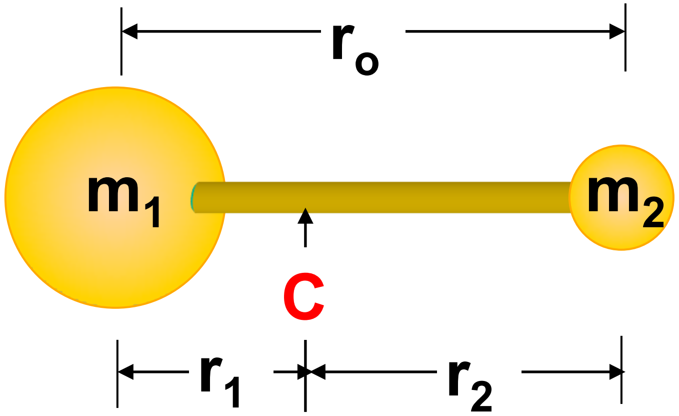
$$\frac{\text{Population}_J}{\text{Population}_{J=0}} \propto (2J+1)\exp\left(-\frac{\Delta E}{kT}\right) = (2J+1)\exp\left(-\frac{BJ(J+1)hc}{kT}\right)$$



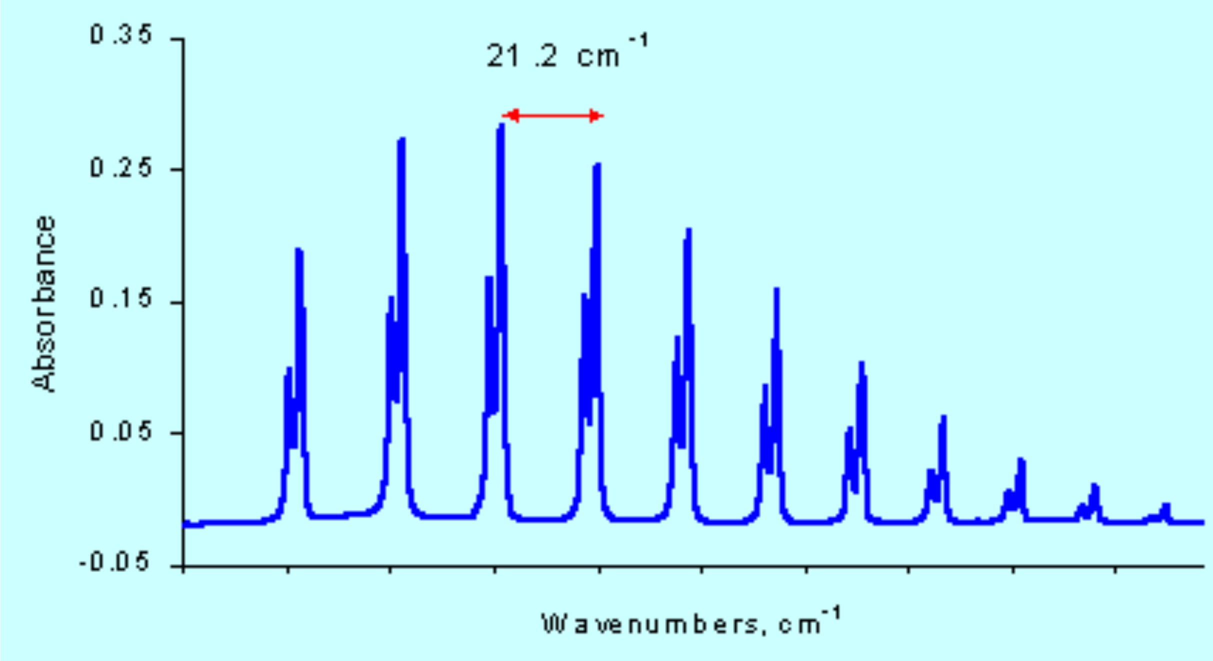
Spectral Line Intensity ∝ Population

Example: Rotational Spectrum of HCl





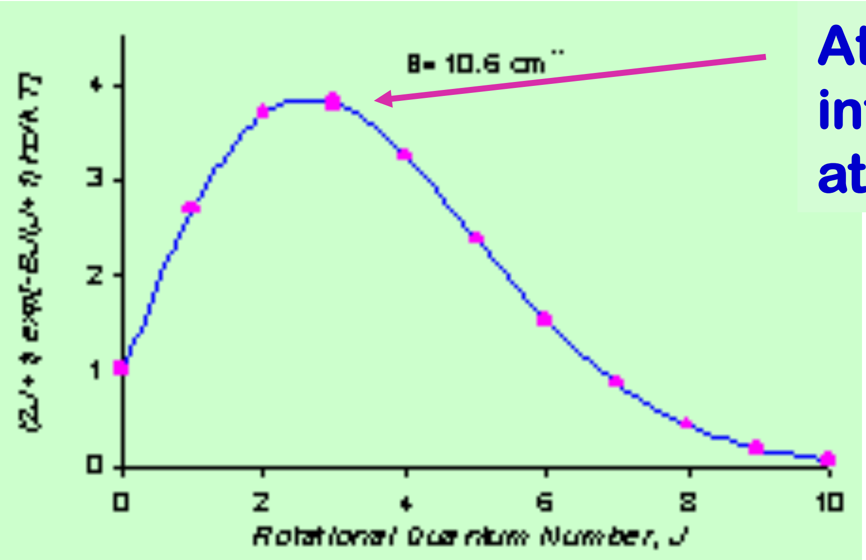
Rotational Spectrum of HCl



$B = 10.6\ cm^{-1}$,

$T = 300K$

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:

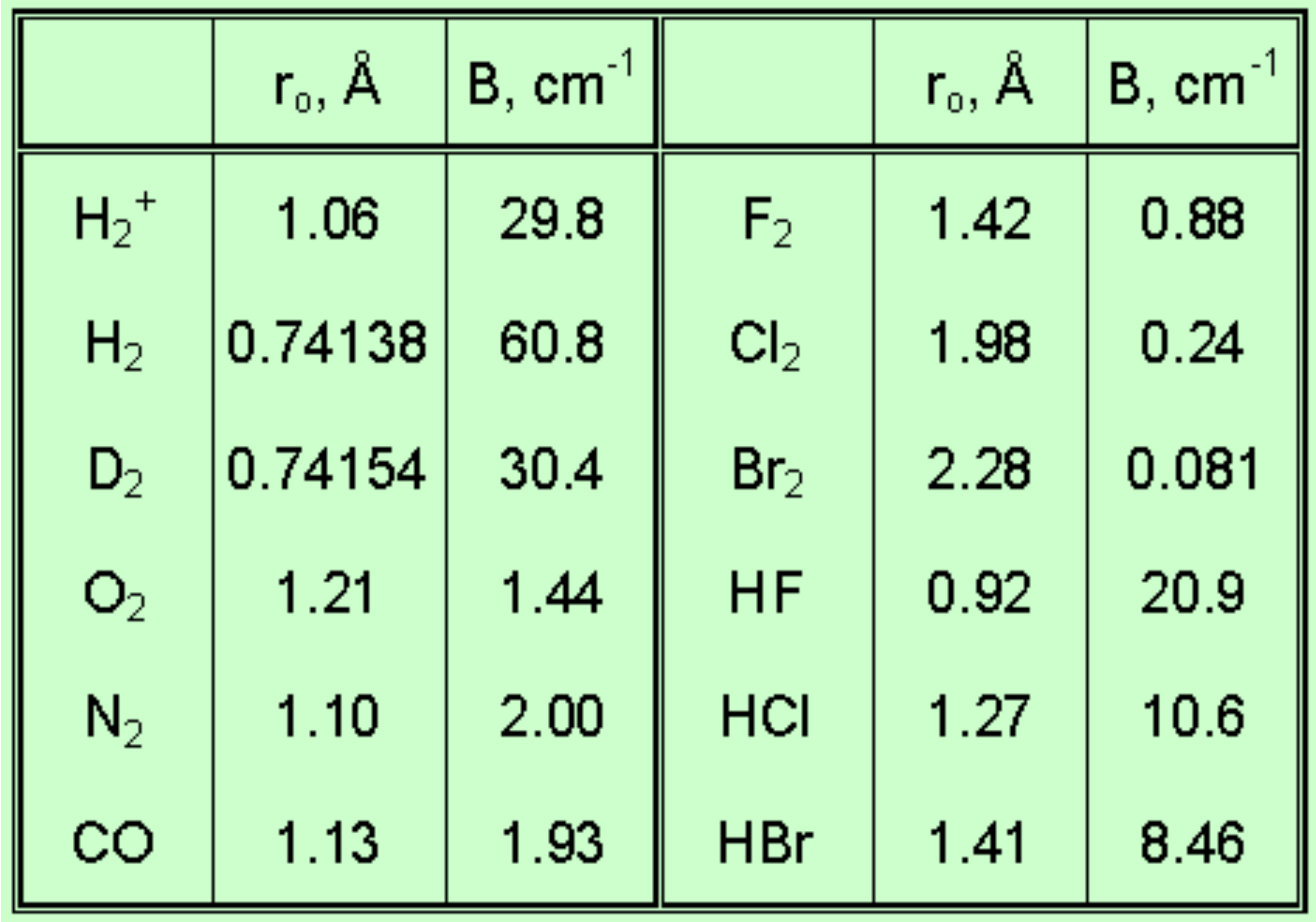
$$\text{Population} \propto (2J+1)\exp\left(-\frac{\Delta E}{kT}\right) = (2J+1)\exp\left(-\frac{BJ(J+1)hc}{kT}\right)$$

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

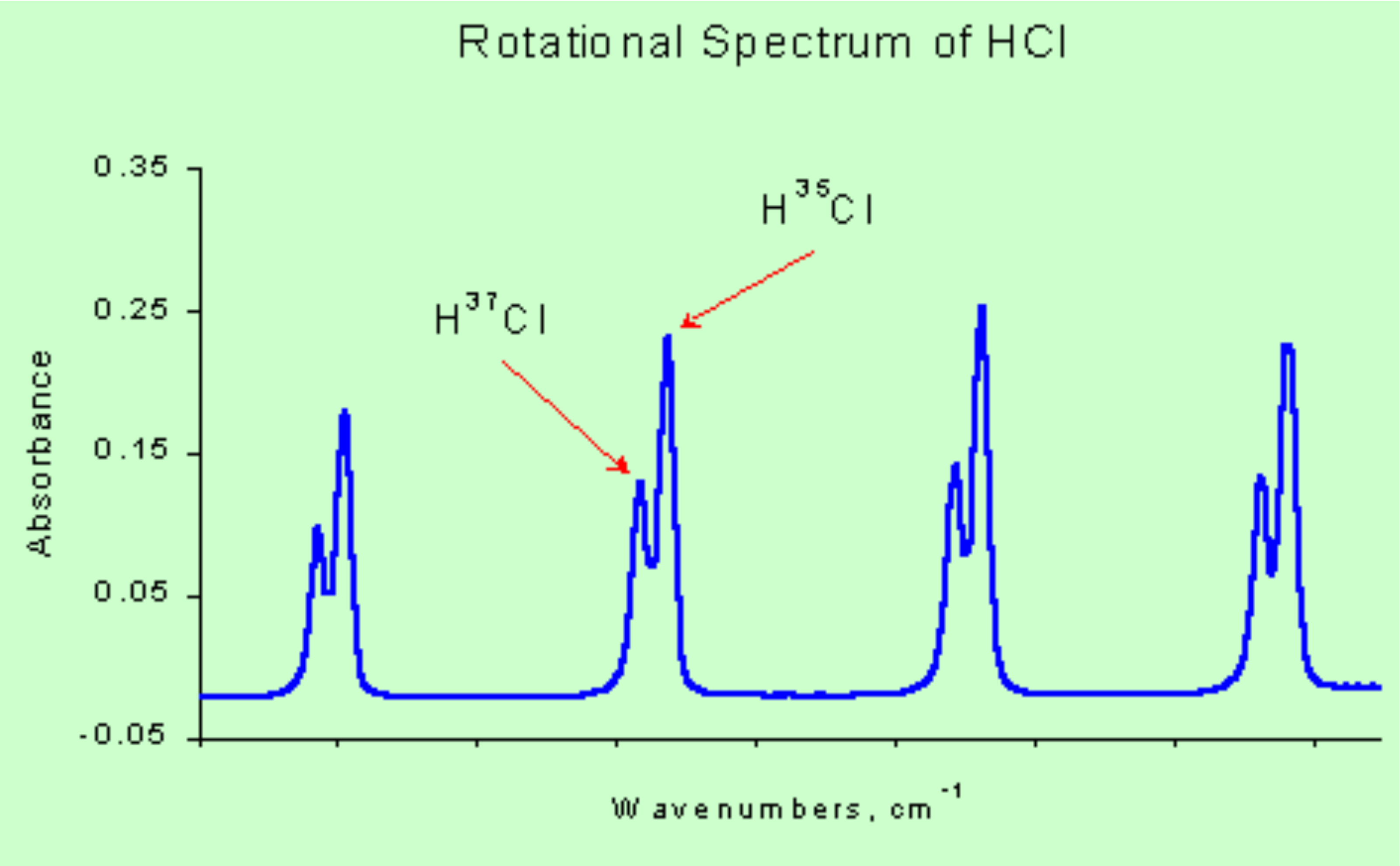


	r_0, Å	B, cm^{-1}		r_0, Å	B, cm^{-1}
H_2^+	1.06	29.8	F_2	1.42	0.88
H_2	0.74138	60.8	Cl_2	1.98	0.24
D_2	0.74154	30.4	Br_2	2.28	0.081
O_2	1.21	1.44	HF	0.92	20.9
N_2	1.10	2.00	HCl	1.27	10.6
CO	1.13	1.93	HBr	1.41	8.46

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

$I \propto r_0$ and m and $B \propto 1 / I$

Effect of Isotope Substitution



From spectra we can obtain:

bond length or atomic weights

and Isotopic Abundances

Effect of Isotope Substitution on Spectra

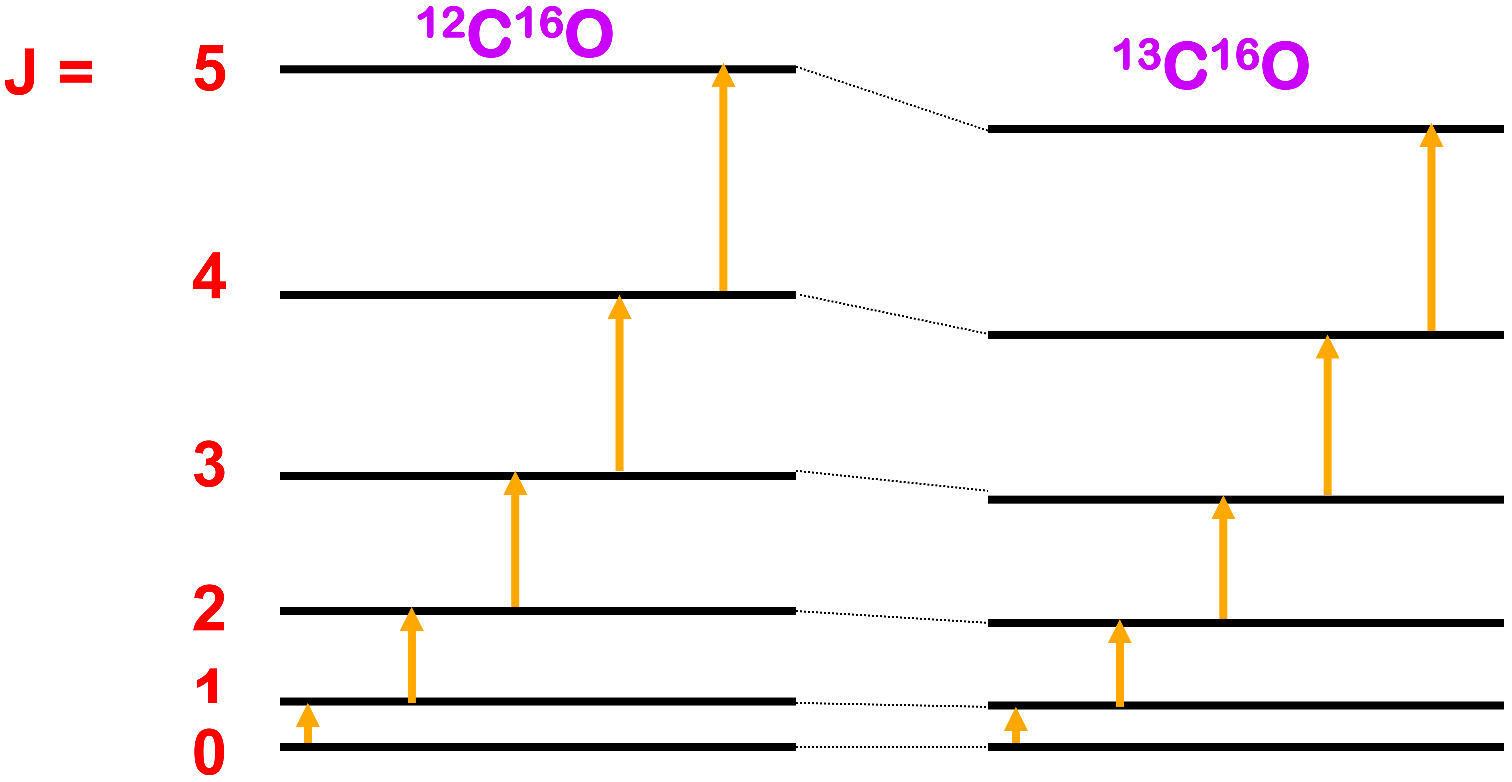
For $^{12}C^{16}O$ $B' = 1.92118\ cm^{-1}$.

$^{13}C^{16}O$ $B'' = 1.\ 83669\ cm^{-1}$.

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

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

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

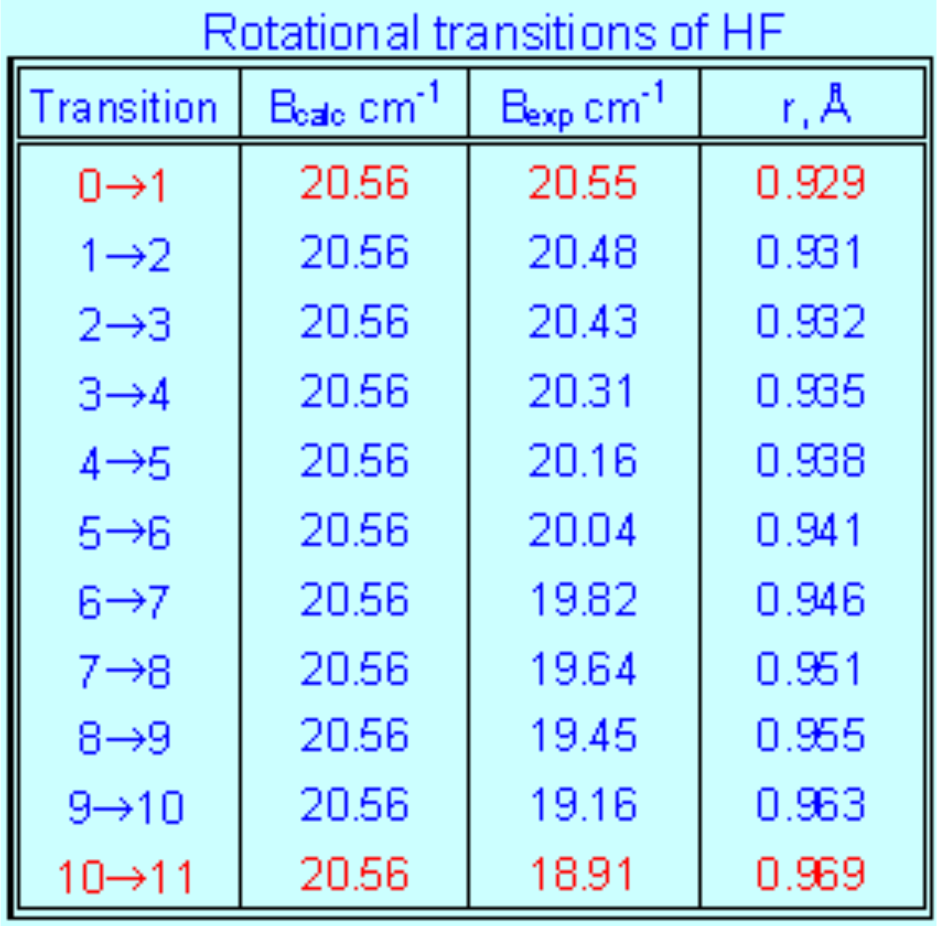


Non-Rigid Rotor

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

$$\boxed{B = \frac{h}{8\pi^2 Ic}} \Rightarrow \boxed{B \propto \frac{1}{r^2}} \Rightarrow$$

B decreases as J increases



Rotational transitions of HF

Transition	B_{calc} cm^{-1}	B_{exp} cm^{-1}	r, Å
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

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

D - Centrifugal Distortion constant
(stiffness constant)
units: cm^{-1}.

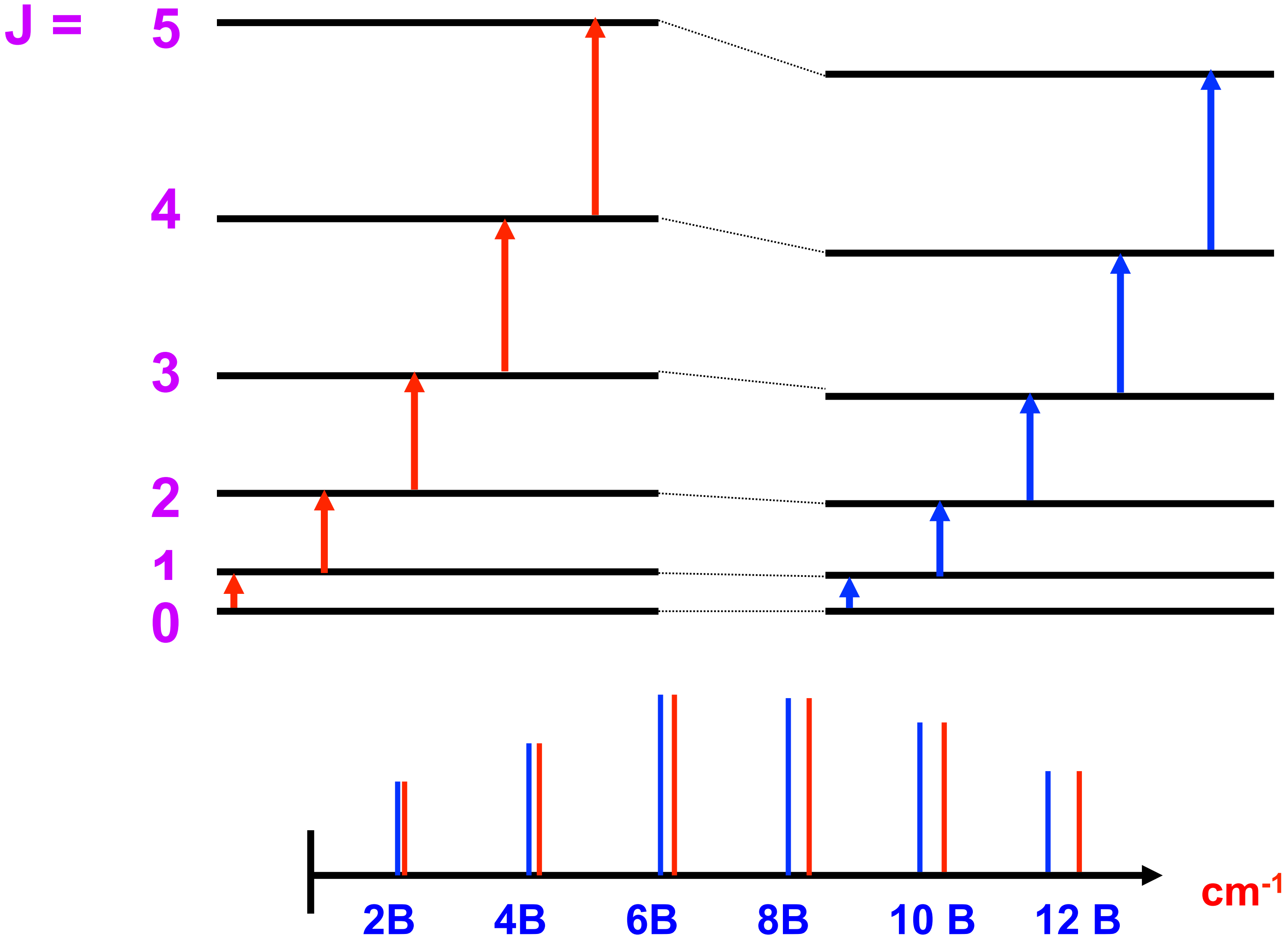
Like B, D depends on the molecule

rigid rotor

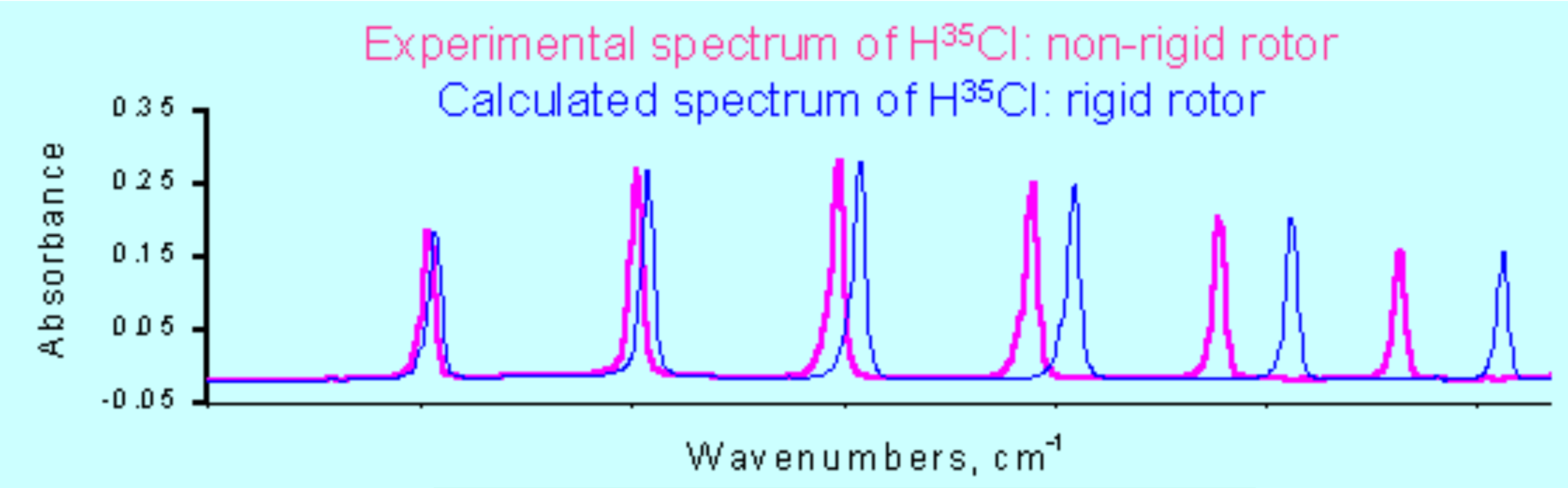
$$\varepsilon_J = B \cdot J(J+1)$$

non-rigid rotor

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



Non-Rigid Rotor



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

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

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

Typical values: B ~ 1 - 10 cm $^{-1}$ and D ~ 10^{-3} – 10^{-2} cm^{-1}.

D can be related to the
vibrational frequency of the molecule

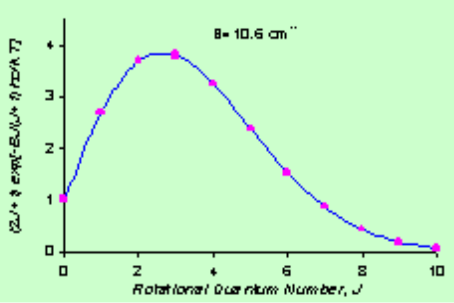
$$D = \frac{4B^3}{\tilde{\nu}_{vib}^2}$$

Summary

1. **Population of energy levels:**

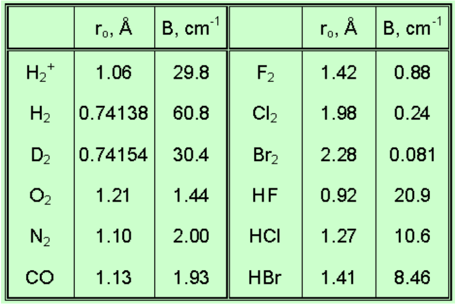
   Boltzmann Distribution

   degeneracy of rotational states



2. **Efect of bond length and mass**

   on rotational constant of diatomic molecule



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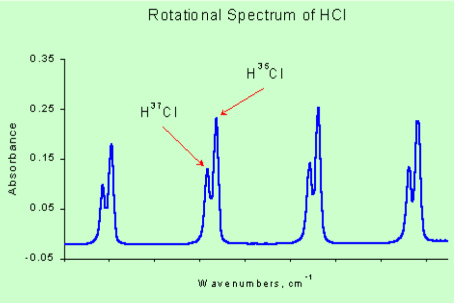
3. **Efect of isotopic substitution**

   atomic weights and

   isotopic abundances



4. **Non-rigid rotor**

   D - centrifugal distortion constant