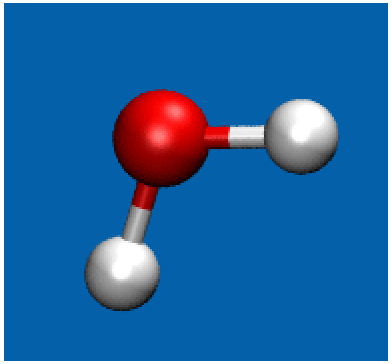
Rotational spectroscopy



- Involve transitions between rotational states of the molecules (gaseous state!)

- Energy difference between rotational levels of molecules has the same order of magnitude with microwave energy

- Rotational spectroscopy is called **pure rotational spectroscopy**, to distinguish it from roto-vibrational spectroscopy (the molecule changes its state of vibration and rotation simultaneously) and vibronic spectroscopy (the molecule changes its electronic state and vibrational state simultaneously)

Molecules do not rotate around an arbitrary axis!
Generally, the rotation is around the mass center of the molecule.

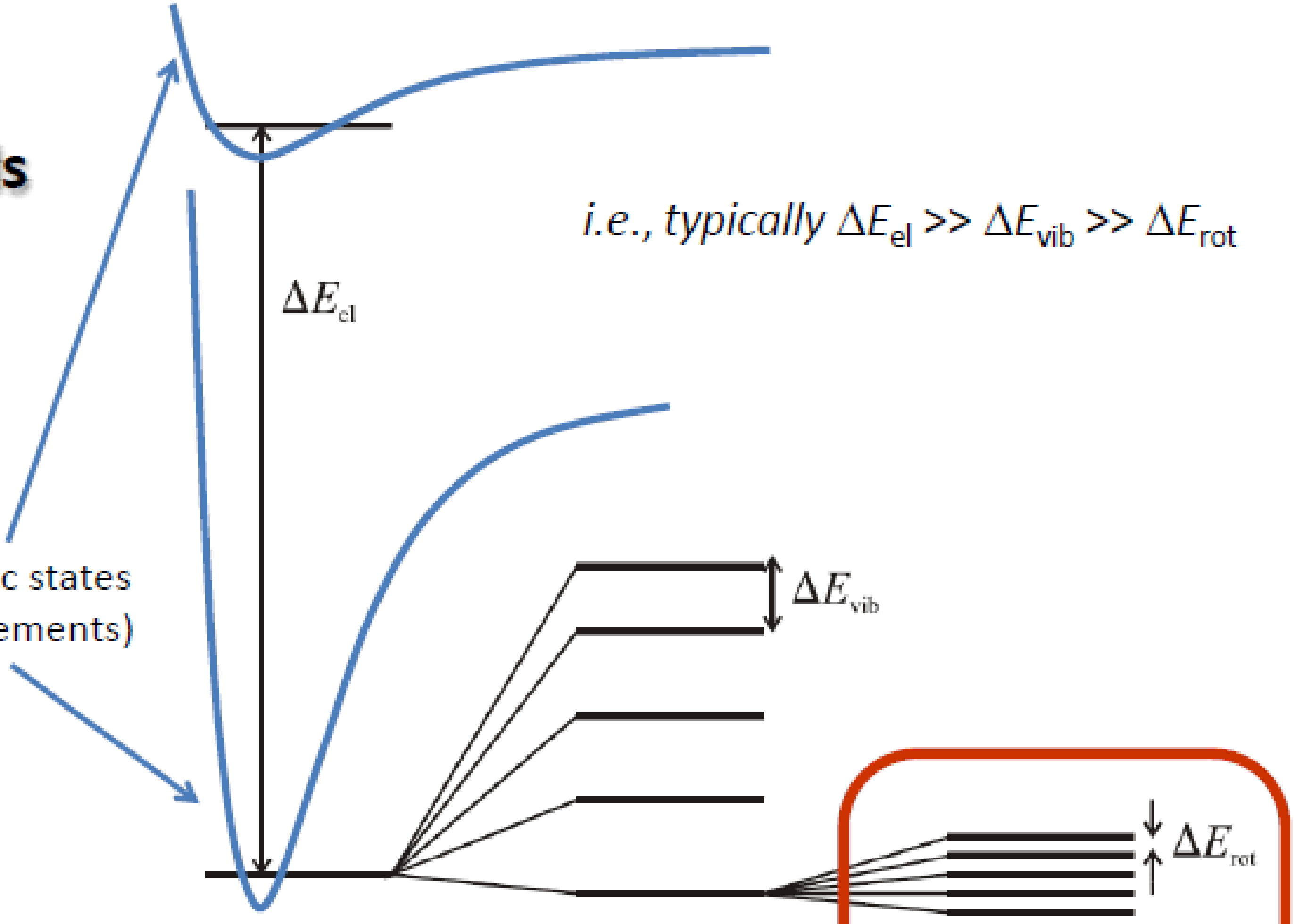
The rotational axis must allow the conservation of kinetic angular momentum.

$$\vec{M} = \sum_{\alpha} \vec{R}_{\alpha} \times \vec{p}_{\alpha} = \mathrm{const}$$

Molecular Energy Levels

i.e., typically $\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot}$

Different electronic states
(electronic arrangements)



	Electronic	Vibrational	Rotational
$\Delta E \approx$	$2 \times 10^4 – 10^6$ cm^{-1}	$10^2 – 5 \times 10^3$ cm^{-1}	3 – 300 GHz (0.1 – 10 cm^{-1})
Transitions at $\lambda \approx$	500 – 100 nm	1 cm – 2 µm	10 cm – 1 mm
	Vis – UV	infrared	microwave

Rotational spectroscopy

>130 molecules / ions have been identified in interstellar space by their rotational emission spectra (*rf*-astronomy)

H_2
AlF
AlCl
C_2
CH
CH+
CN
CO
CO^+
CP
CSi
HCl
KCl
NH
NO
NS

C_3
C_2H
C2O
C2S
CH2
HCN
HCO
HCO^+
HCS+
HOC+
H_2O
H_2S
HNC
HNO
MgCN
MgNC

$c\text{-}C_3H$
l-C3H
C_3N
C_3O
C_3S
C_2H_2
CH_2D+
HCCN
HCNH+
HNCO
HNCS
HOCO+
H_2CO
H2CN
H_2CS
H_3O^+

C_5
C4H
C4Si
l-C3H2
c-C3H2
CH2CN
CH_4
HC_3N
HC2NC
HCOOH
H2CHN
H_2C_2O
H2NCN
HNC3
SiH_4
H_2COH^+

C_5H
$l\text{-}H_2C_4$
C2H4
CH_3CN
CH_3NC
CH_3OH
CH_3SH
HC_3NH+
HC2CHO
NH_2CHO
C_5N
HC_4N

C_6H
CH_2CHCN
CH3C2H
HC5N
HCOCH3
NH2CH3
$c\text{-}C_2H_4O$
CH_2CHOH

CH_3C_3N
$HCOOCH_3$
$CH_3COOH?$
C7H
H_2C_6
CH_2OHCO
CH_2CHCHO

CH_3C_4H
CH_3CH_2CN
$(CH3)_2O$
CH_3CH_2OH
HC7N
C8H

$CH_3C_5N?$
$(CH3)_2CO$
NH_2CH_2COOH
CH_3CH_2CHO

HC_9N

$CH_3OC_2H_5$

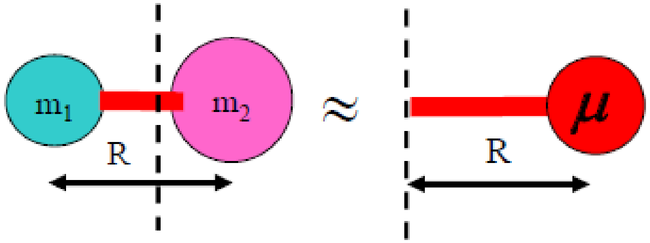
$HC_{11}N$

NIST & National Radio Astronomy Lab.

Rotation of diatomic molecule - Classical description

Diatomic molecule = a system formed by 2 different masses linked together with a rigid connector (rigid rotor = the bond length is assumed to be fixed!).

The system rotation around the mass center is equivalent with the rotation of a particle with the mass μ (reduced mass) around the center of mass.



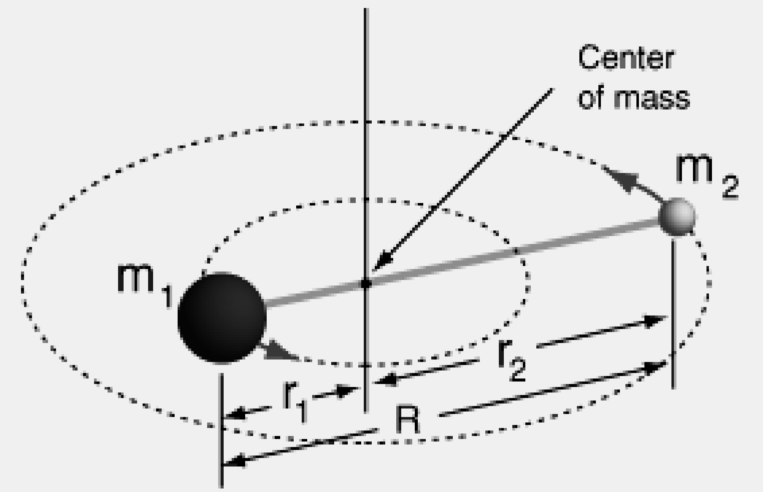
The moment of inertia: $\mathbf{I} = \sum_i m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2 = \mu R^2 = \frac{m_1 m_2}{m_1 + m_2} R^2$

Moment of inertia (I) is the rotational equivalent of mass (m).
Angular velocity (ω) is the equivalent of linear velocity (v).

E_r → rotational kinetic energy

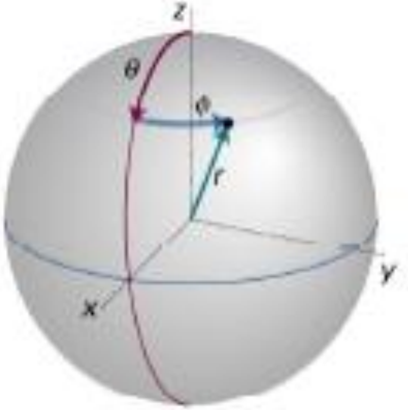
L = Iω → angular momentum

$$E_c = \frac{mv^2}{2} = \frac{p^2}{2m} \quad \leftrightarrow \quad \boxed{E_r = \frac{I\omega^2}{2} = \frac{L^2}{2I}}$$



Quantum rotation: The diatomic rigid rotor

The rigid rotor represents the quantum mechanical "particle on a sphere" problem:



Rotational energy is purely kinetic energy (no potential):

$$\hat{H}\psi = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}) \qquad \hat{p} = -i\hbar\nabla \qquad \nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$ nabla

Schrodinger equation: $$\hat{H}\psi = -\frac{\hbar^2}{2\mu}\nabla^2\Psi = E\Psi$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ Laplacian operator in cartesian coordinate

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$ spherical coordonate

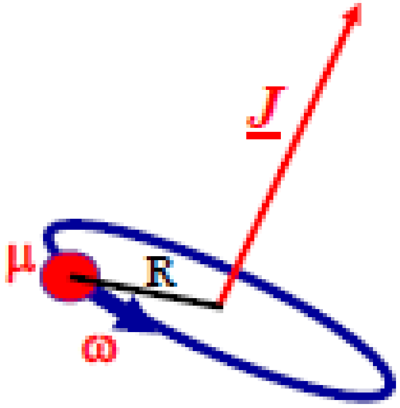
For **r = constant** ($\frac{\partial}{\partial r} = 0$), Schrodinger equation simplifies to:

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) = EY(\theta,\phi)$$

The solutions resemble those of the "particle on a ring":

$$Y_{lm_l}(\theta\phi) = \Theta_{lm_l}(\theta)\Psi_{m_l}(\phi)$$ → separation of variable

$$\Psi(\phi+2\pi) = \Psi(\phi)$$ → *cyclic boundary conditions*

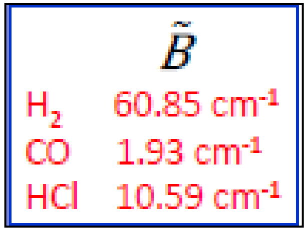


$$\begin{cases} \Psi_{m_J}(\phi) = \dfrac{e^{im_J\phi}}{\sqrt{2\pi}} & \rightarrow \text{ wavefunctions (rotational)} \\ E_{rot}(J,m_J) = J(J+1)\dfrac{\hbar^2}{2I} & \rightarrow \text{ eigenvalues (energy)} \end{cases}$$

J = 0, 1, 2, 3....(rotational quantum number)
m_J = 0, ±1, ±2, ... ±*J* (projection of J)

$$\boxed{E_{rotJ} = hcBJ(J+1)}$$ → the rotational energy of a molecule

$$\boxed{B = \frac{h}{8\pi^2 c\cdot I} = \frac{h}{8\pi^2 c\cdot \mu R^2}}$$ → *rotational constant* (in cm^{-1})



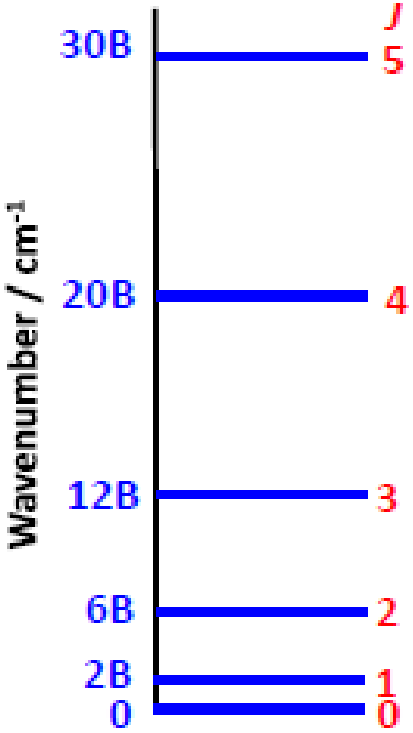
	$\tilde{B}$
H_2	60.85 cm^{-1}
CO	1.93 cm^{-1}
HCl	10.59 cm^{-1}

Obs:

→ Rotational energy levels get more widely space with increasing *J!*

$$\boxed{E_{rotJ} = hcBJ(J+1)}$$

$$\boxed{\begin{aligned} E_{rot5} &= hc\cdot 30B \\ E_{rot4} &= hc\cdot 20B \\ E_{rot3} &= hc\cdot 12B \\ E_{rot2} &= hc\cdot 6B \\ E_{rot1} &= hc\cdot 2B \\ E_{rot0} &= 0 \end{aligned}}$$



$\boldsymbol{E_{rot0} = 0}$

→ There is no zero point energy associated with rotation!

Obs:

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

→ For large molecules (μ): - the moment of inertia (I) is high,
- the rotational constant (B) is small

For large molecules the rotational levels are closer than for small molecules.

→ From rotational spectra we can obtain some information about geometrical structure of molecule (r):

For diatomic molecule we can calculate the length of bond!

→ Diatomic molecules rotations can partial apply to linear polyatomic molecules.

→ An isotopic effect could be observed: $B \sim 1/(\mu R^2)$

$$\frac{\tilde{B}_{H^{35}Cl}}{\tilde{B}_{H^{37}Cl}} = \frac{\mu_{H^{37}Cl}}{\mu_{H^{35}Cl}} = \frac{37u.u}{38u} . \frac{36u}{35u.u} = 1.0015$$

Rotational wavefunctions

General solution:

$$\Psi_{m_J}(\phi) = \frac{e^{i m_J \phi}}{\sqrt{2\pi}}$$

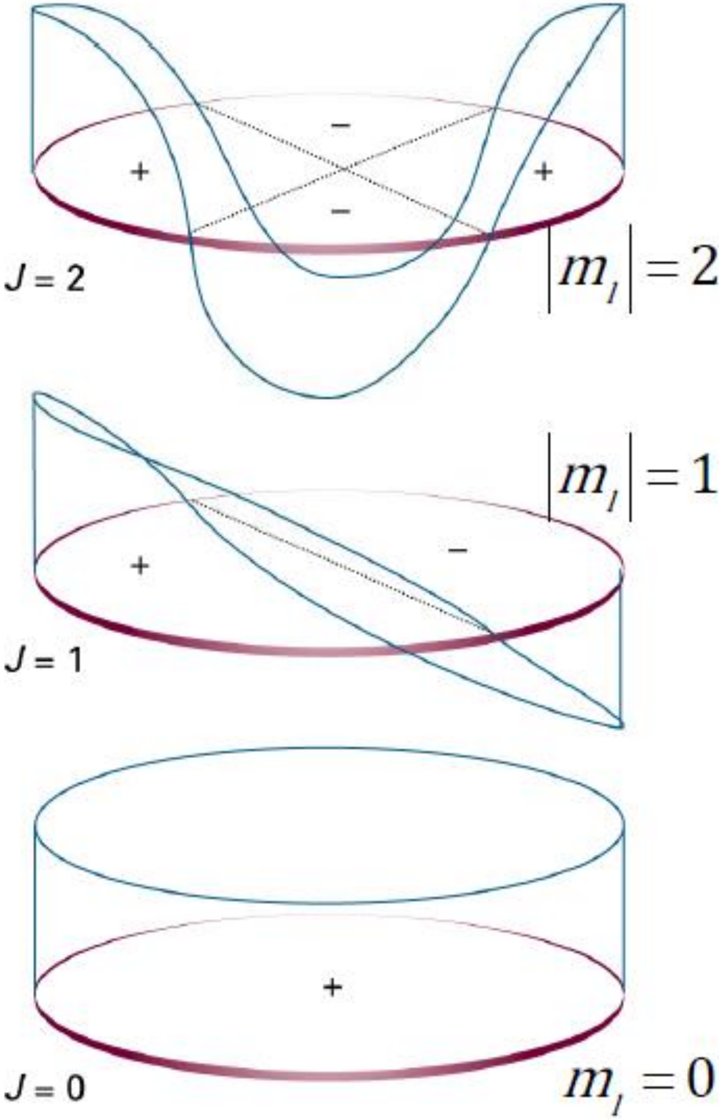
m_J = 0, ±1, ±2, ±3 .. when imposing cyclic boundary conditions:

$$\Psi(\phi+2\pi) = \Psi(\phi)$$

Rotational wavefunctions are imaginary functions!

It is useful to **plot the real part** to see their symmetries: odd and even J levels have opposite parity.

Rotational wave functions parity = $(-1)^J$



Degeneracy of Rotational Levels

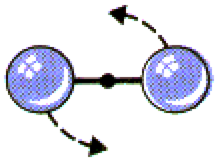
In the absence of external fields energy of rotational levels only determined by J (all $m_J = -J, \ldots +J$) share the same energy. Therefore, rotational levels exhibits (2J+1) fold degeneracy (arising from the projection quantum number m_J).

Both the magnitude and direction (projection) of rotational angular momentum is quantized. This is reflected in the **two quantum numbers:**

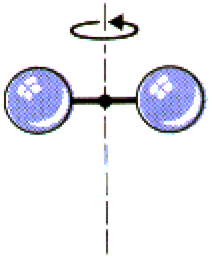
J (magnitude)

$\mathbf{m_J}$ (direction/projection).

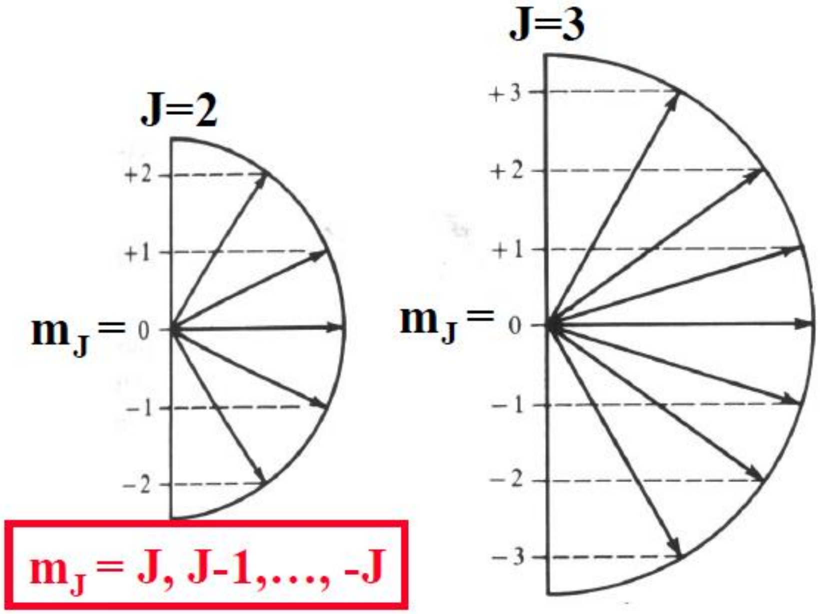
Taking the surface normal as the quantization axis, $m_J = 0$ corresponds to out of-plane rotation and $m_J = J$ corresponds to in-plane rotation.



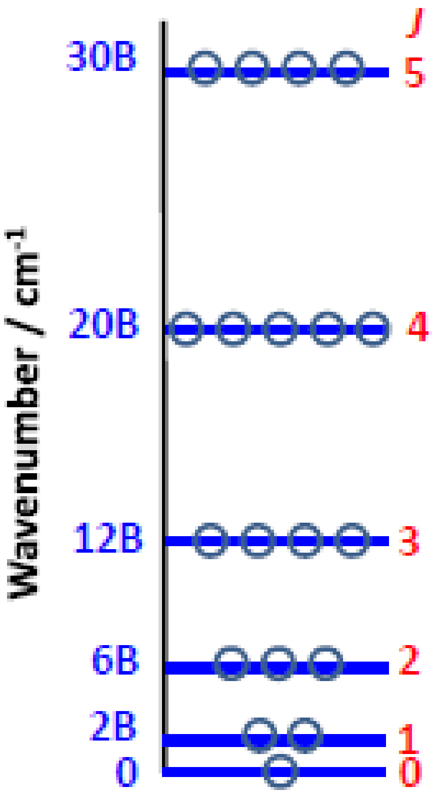
Rotation in the
plane of the paper



Rotation out of the
plane of the paper.



$$m_J = J, J\text{-}1, \ldots, \text{-}J$$



Populations of rotational levels

$$N_j = N_0 g_j \exp\left(-\frac{E_J}{kT}\right)$$ Boltzmann distribution

$$g_J = 2J+1$$ degeneracy

$$E_{rotJ} = hcBJ(J+1)$$ rotational energy

$$\boxed{N_j = N_0(2J+1)\exp\left(-\frac{hcBJ(J+1)}{kT}\right)}$$

The most populated level occurs for: $\frac{dN_J}{dJ} = 0$

$$\frac{dN_J}{dJ} = N_0\left[2-(2J+1)^2\frac{hcB}{kT}\right]\exp\left(-\frac{hcBJ(J+1)}{kT}\right) = 0$$

$$2-(2J_{max}+1)^2\frac{hcB}{kT} = 0$$

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

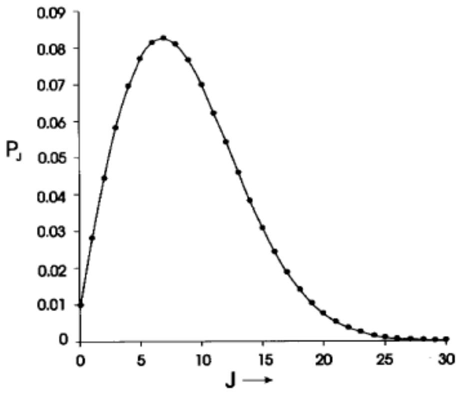


Figure 6.16. Distribution of population among rotational states of CO at room temperature.

Rotational spectroscopy (*Microwave spectroscopy*)

Molecules can absorb energy from microwave range in order to ***change theirs rotational state*** ($h\nu = \Delta E_{rot} = E_{rot(sup)} - E_{rot(inf)}$).

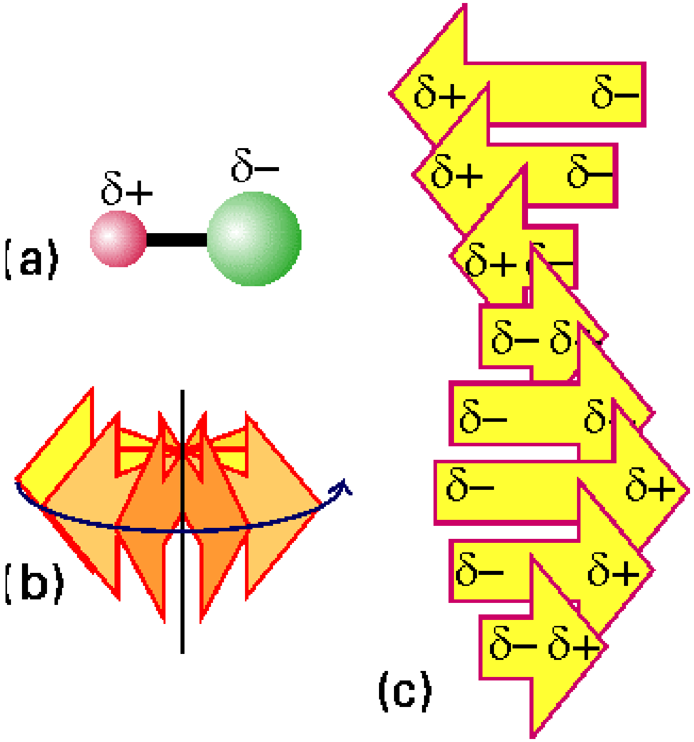
Gross Selection Rule:

For a molecule to exhibit a pure rotational spectrum it must posses a **permanent dipole moment.** (otherwise the photon has no means of interacting “nothing to grab hold of”)

→ a **molecule must be polar** to be able to interact with microwave.

→ a polar rotor appears to have an oscillating electric dipole.

Homonuclear diatomic molecules such as O_2, H_2, do not have a dipole moment and, hence, no pure rotational spectrum!



Specific Selection Rule: $\boxed{\Delta J = \pm 1 \quad \Delta m_J = 0, \pm 1}$

Only for diatomic molecules (linear molecules)!

The specific selection rule derive from conservation of angular momentum.

But need to change parity (see rotational wavefunctions)!

Schrödinger equation explains the specific selection rule ($\Delta J = \pm 1$):

$$\mu_{\mathrm{r}} = \int \Psi_{\mathrm{f}} \mu \Psi_{\mathrm{i}}$$

f - final state, i initial state

μ_r - transition dipol moment

The molecule absorbed microwave radiation (change its rotational state) only if integral is non-zero (**$\Delta J = \pm 1$**): the rotational transition is allowed!

If the integral is zero, the transition is forbidden!

Rotational transitions

$$\bar{\nu}_{r(J_1 \rightarrow J_2)} = \frac{\Delta E_{rotJ}}{hc} = \frac{E_{rotJ_2} - E_{rotJ_1}}{hc}$$

$$\boxed{E_{rot\,J} = hcBJ(J+1)}$$

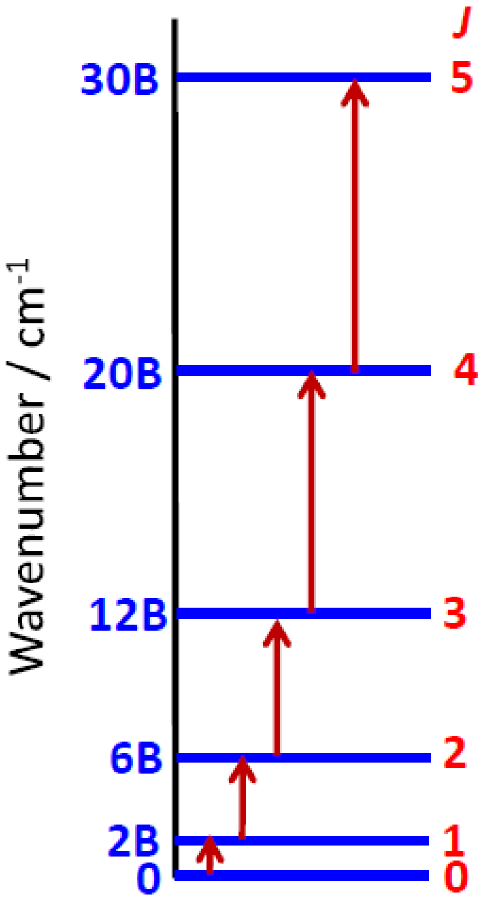
$$\bar{\nu}_{r(J_1 \rightarrow J_2)} = BJ_2(J_2+1) - BJ_1(J_1+1)$$

$$\bar{\nu}_{r(J_1 \rightarrow J_2)} = B \cdot \left(J_2{}^2 + J_2 - J_1{}^2 - J_1\right)$$

$$J_2 = J_1 + 1$$

$$\bar{\nu}_{r(J_1 \rightarrow J_1+1)} = B\left(1 + 2J_1 + J_1{}^2 + 1 + J_1 - J_1{}^2 - J_1\right)$$

$$\boxed{\bar{\nu}_{r(J_1 \rightarrow J_1+1)} = 2B \cdot (J_1 + 1)}$$



$\bar{\nu}_r$ rotational transition wavenumber

J_1 rotational quantum number of inferior state

J_2 rotational quantum number of superior state

$$\bar{\nu}_{r(J_2-1 \rightarrow J_2)} = 2B \cdot J_2$$

Rotational spectra have a lot of peaks ($\bar{\nu}_r$) spaced by 2B ($\Delta\bar{\nu}_r$).

$$\boxed{\bar{\nu}_{r(0\rightarrow1)} = 2B}$$

$$\Delta\bar{\nu}_r = 2B$$

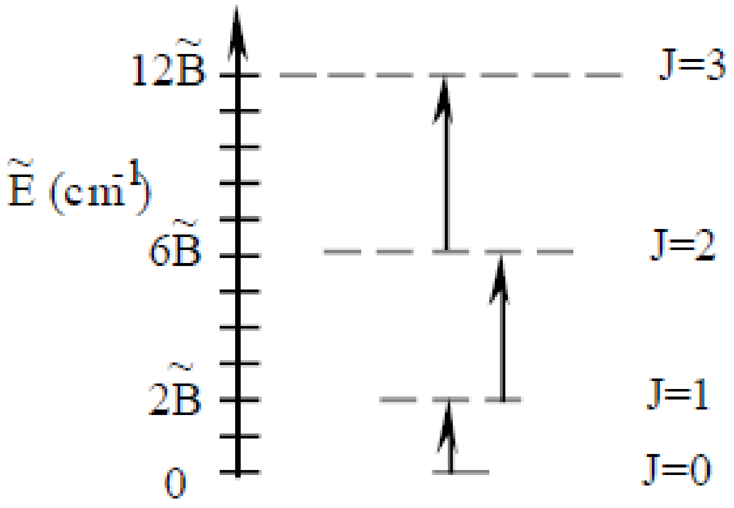
$$\boxed{\bar{\nu}_{r(1\rightarrow2)} = 4B}$$

$$\Delta\bar{\nu}_r = 2B$$

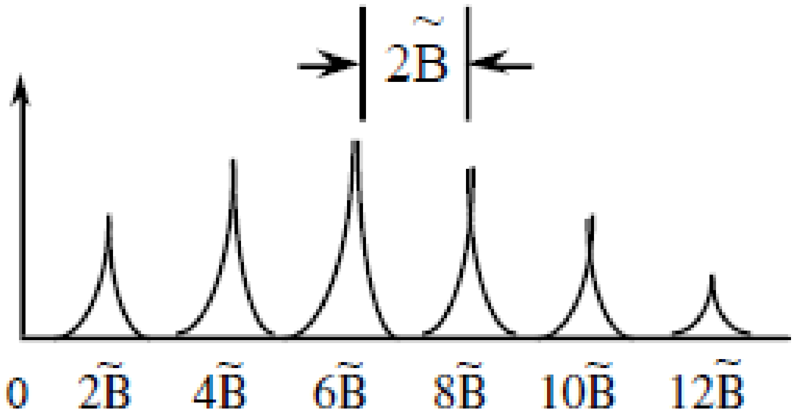
$$\boxed{\bar{\nu}_{r(2\rightarrow3)} = 6B}$$

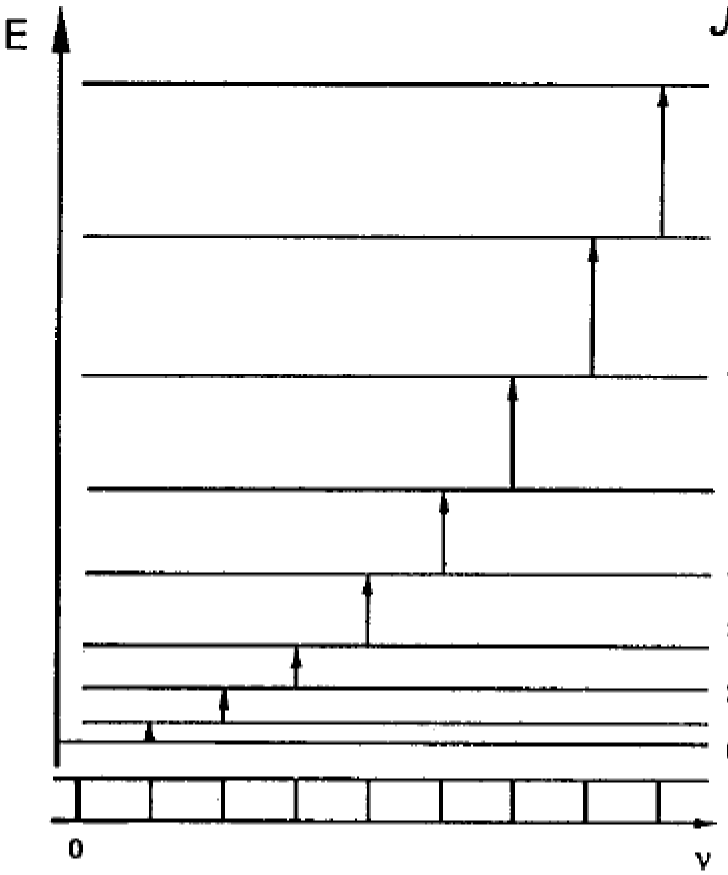
$$\Delta\bar{\nu}_r = 2B$$

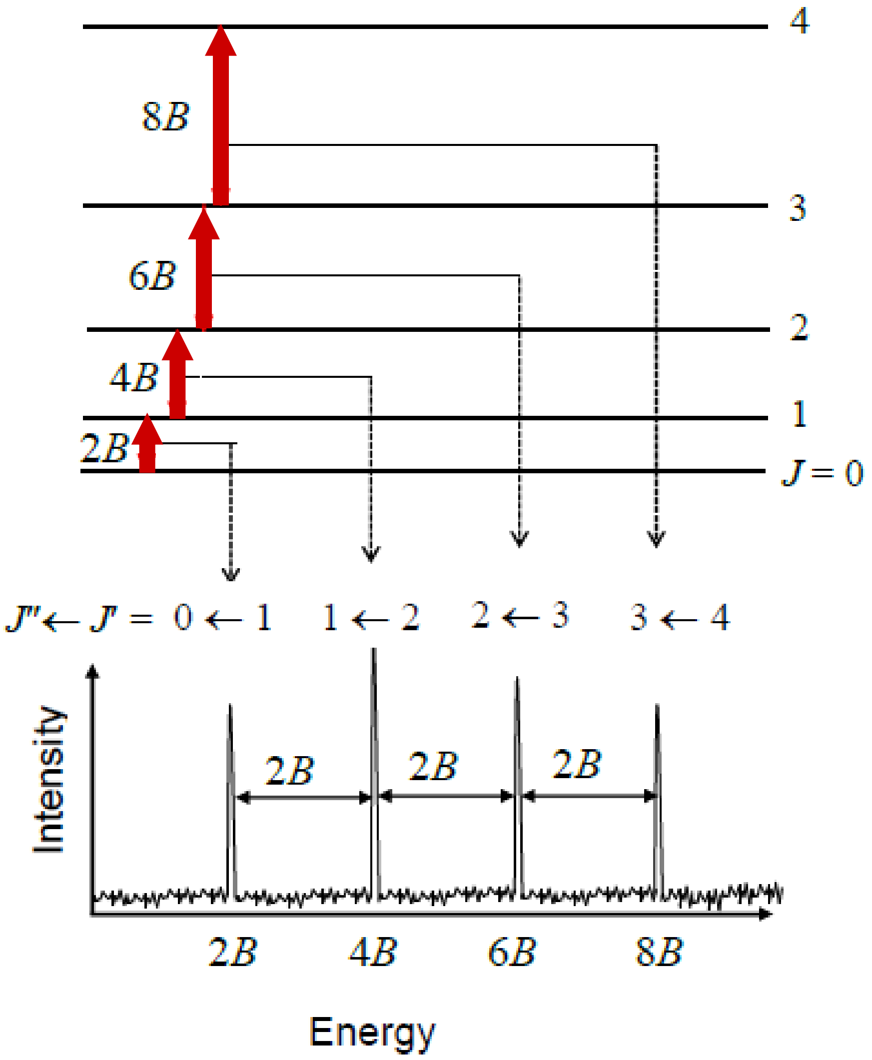
$$\boxed{\bar{\nu}_{r(3\rightarrow4)} = 8B}$$



J_1	E (cm^{-1})	$\bar{\nu}_r$ (cm^{-1})	$\Delta\bar{\nu}_r$ (cm^{-1})
0	0		
1	2B	2B	
2	6B	4B	2B
3	12B	6B	2B

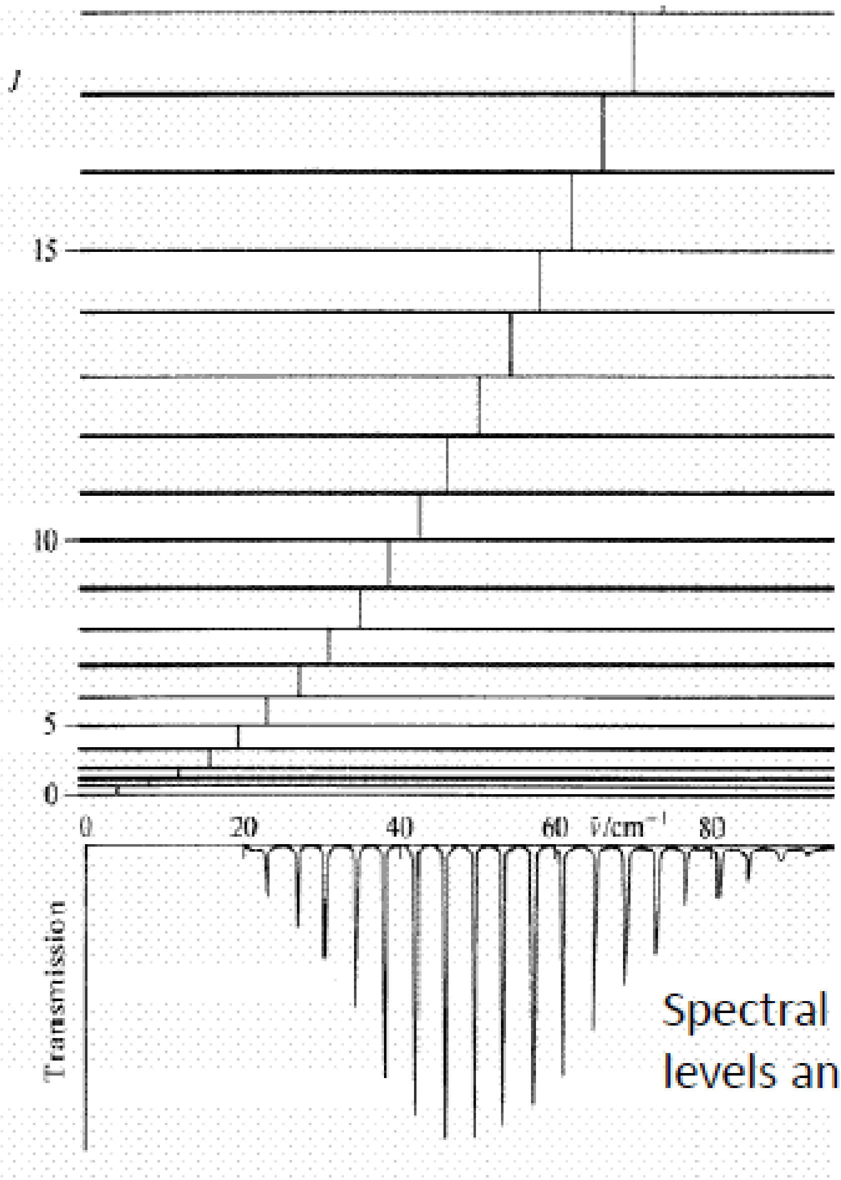






The rotational transitions are separated by 2*B* in the observed spectrum!

Rotational Spectrum of CO



Rotational spectrum of CO (300K)

$$\begin{aligned}\tilde{\nu} &= F_{J+1} - F_J \\ &= \tilde{B}(J+1)(J+2) - \tilde{B}J(J+1) \\ &= 2\tilde{B}(J+1)\end{aligned}$$

Transitions in the microwave region: 1-100 cm^{-1} (λ = 1 cm – 100 μm)

Lines *spaced* by $2\tilde{B}$

$F_J = E_J/hc$ rotational spectral terms

Spectral Profile governed by population of lower levels and *J* dependence of the transition strength.

Beyond the Rigid Rotor: **Centrifugal Distortion**

The rigid rotor model holds for rigid rotors.

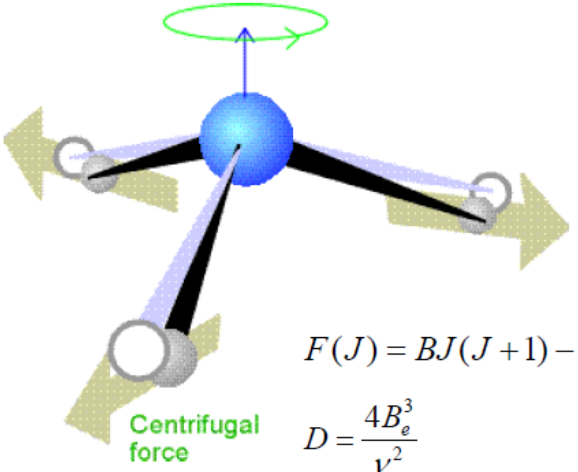
Molecules are *not* rigid rotors – their bonds stretch during rotation

As a result, the moment of inertia I change with J.

For real molecule, the rotational constant B depend on rotational quantum number J!

It is more convenient to treat centrifugal distortion as a perturbation to the rigid rotor terms.

In real rotational spectra the peaks are not perfectly equidistant: *centrifugal distortion* (D).



$$F(J) = BJ(J+1) - D\left[J(J+1)\right]^2$$

$$D = \frac{4B_e^3}{\nu_e^2}$$

- The effect of rotation on a molecule. The centrifugal force arising from rotation distorts the molecule, opening out bond angles and stretching bonds slightly. The effect is to increase the moment of inertia of the molecule and hence to decrease its rotational constant.

Centrifugal Distortion in diatomic molecules

When J increase (molecule rotates faster) the bond length increase → the moment of inertia increase → the rotational constant B decrease.

$$B' = B - D \cdot J(J+1)$$

The rotational energy becomes:

$$\boxed{E_{rot}(J) = hc \cdot [J(J+1) \cdot B - D \cdot J^2 (J+1)^2]}$$

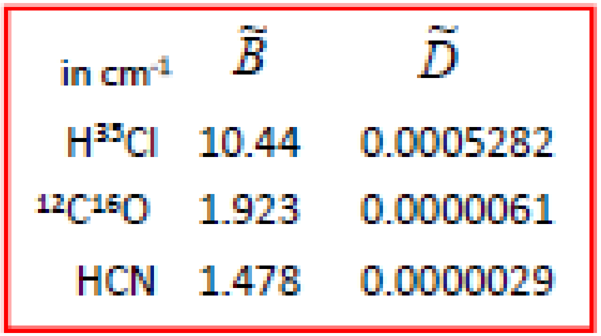
D*:* the centrifugal distortion constant (in cm^{-1})

$$\boxed{D = \frac{4 \cdot B^3}{\bar{\upsilon}_0^2} \quad (\mathrm{cm}^{-1})}$$

$\bar{\nu}_0$: the wavenumber of harmonic oscillator!

In this case, **the wavenumber of rotational transition** (J→J+1) is:

$$\boxed{\bar{\nu}_{rJ} = \frac{\Delta E}{hc} = 2B(J+1) - 4D(J+1)^3}$$

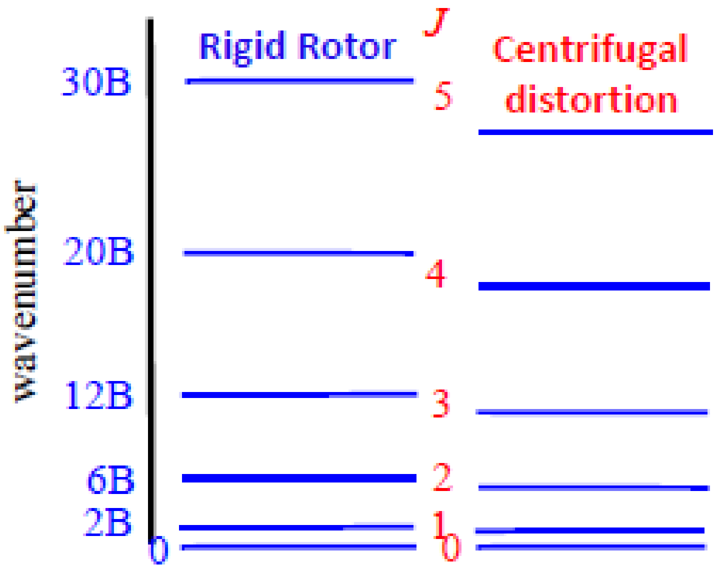


in cm^{-1}	$\tilde{B}$	$\tilde{D}$
$H^{35}Cl$	10.44	0.0005282
$^{12}C^{16}O$	1.923	0.0000061
HCN	1.478	0.0000029

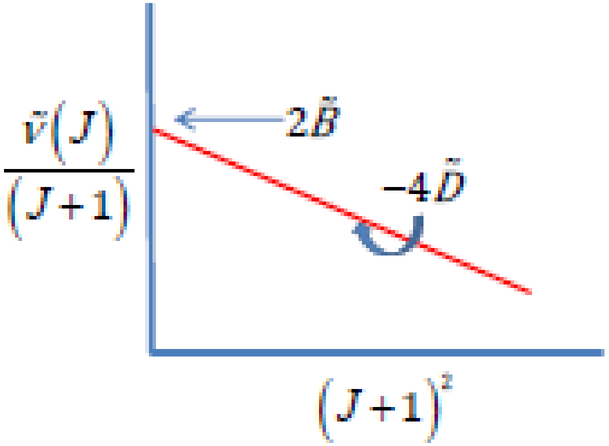
The centrifugal distortion constant D is much smaller than B!

The rotational energy levels of real molecule shrink together.

The peaks (rotational transitions) from rotational spectra of real molecule are not equidistant!



$$\boxed{\bar{\nu}_r = 2B(J+1) - 4D(J+1)^3}$$

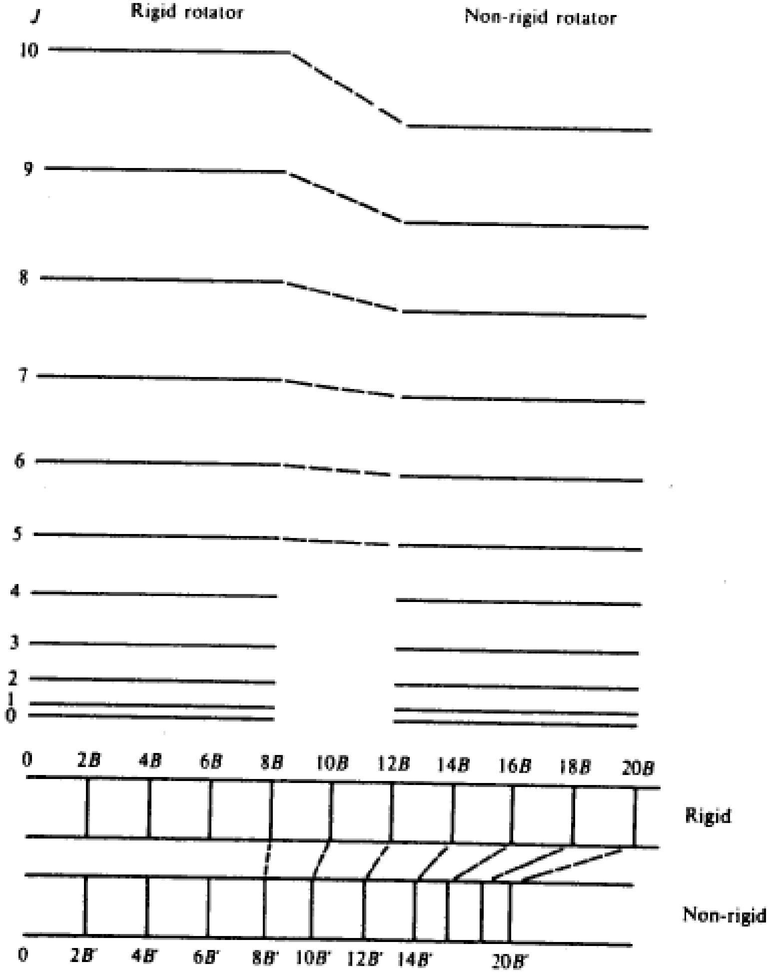


B and **D** constants can be calculated from the graph function: $\frac{\bar{\nu}_r}{(J+1)} = f(J+1)^2$

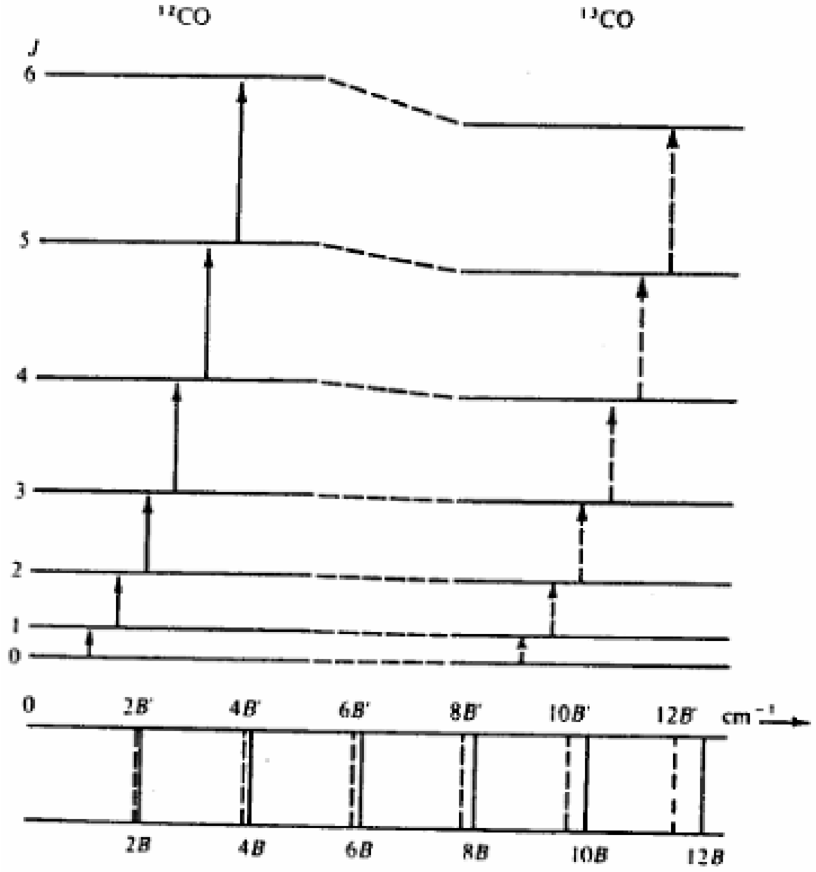
$$\frac{\bar{\nu}_r}{(J+1)} = 2B - 4D(J+1)^2 \quad \longrightarrow$$

slope = -4D; y intercept = 2B

$$E_{rot}(J) = hc \cdot [J(J+1) \cdot B - D_J J^2 (J+1)^2]$$



The change in rotational energy levels and spectrum when passing from a rigid to a non-rigid diatomic molecule. Energy levels on the right are calculated using $D = 10^{-3} B$.



The effect of isotopic substitution on the energy levels and rotational spectrum of a dia
such as carbon monoxide.

$$\bar{\nu}_r = 2B(J+1) - 4D(J+1)^3$$

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

$$D = \frac{4 \cdot B^3}{\bar{\nu}_0^2}$$

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

Independent activity

a) The molecule $^{23}Na^{1}H$ (rigid rotor) is found to undergo a rotational transition from J = 0 to J = 1 when it absorbs a photon of frequency $2.94 \cdot 10^{11}$ Hz.

b) What is the equilibrium bond length of the molecule?

c) Calculate the wavenumber of the most intense rotational transition at room temperature.

d) Calculate the difference (in cm^{-1}) between energy of the fifth rotational level of NaH considering rigid rotor and non-rigid rotor ($D = 0.0003\ cm^{-1}$) approximations.

$$\bar{\nu}_r = 2B(J+1) - 4D(J+1)^3 \qquad B = \frac{h}{8\pi^2 c \cdot \mu R^2} \qquad J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

$$E_{rot}(J) = hc \cdot [J(J+1) \cdot B - D_J J^2 (J+1)^2]$$

$1\ u = 1.67 \cdot 10^{-27}$ kg $k = 1.38 \cdot 10^{-23}$ J/K $c = 3 \cdot 10^{8}$ m/s, $h = 6.626 \cdot 10^{-34}$ J·s

Rotation of polyatomic molecules

The moment of inertia I of a system about an axis passing through the center of mass is given by:

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

The **polyatomic molecules can be classified** on the basis of their moments of inertia about three mutually perpendicular axes through the center of mass (principal axes).

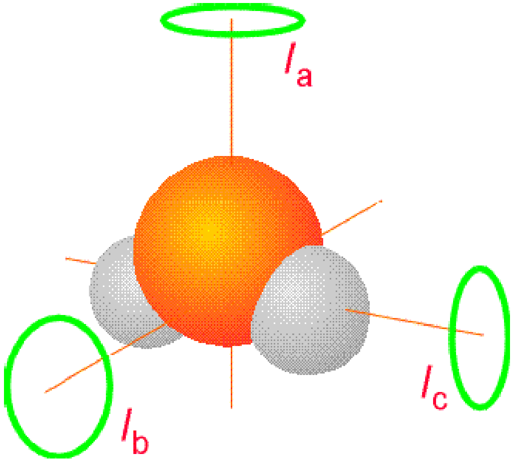
a, b, c: three axes

I_a, I_b, I_c: three moments of inertia

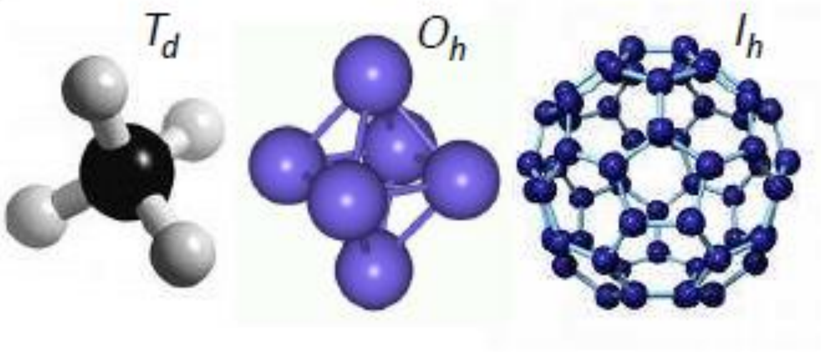
($I_c = I_{max}$)

$I_c > I_b > I_a$

- An asymmetric rotor has three different moments of inertia; all three rotation axes coincide at the centre of mass of the molecule.



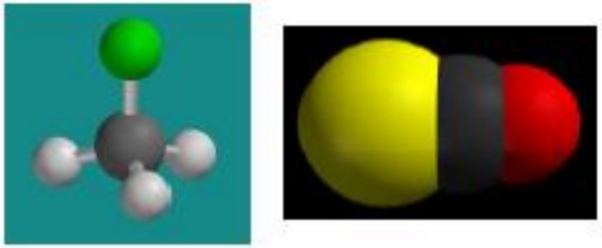
General Classification of Molecules



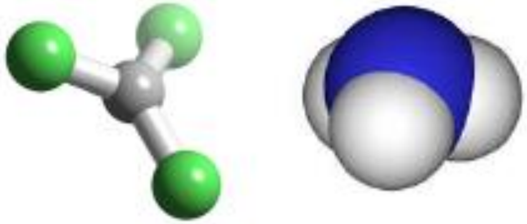
I. Spherical tops: $\boxed{I_a = I_b = I_c}$

Zero dipole moment
∴ no rotational spectrum

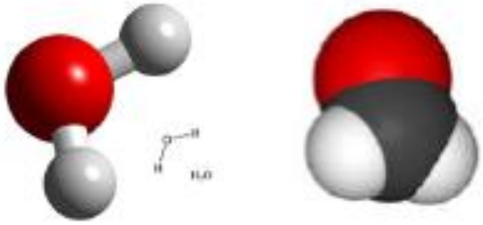
II. Symmetric tops: (two identical I_i)



a) Prolate tops: $\boxed{I_a < I_b = I_c}$



b) Oblate tops: $\boxed{I_a = I_b < I_c}$



III. Asymmetric tops: $\boxed{I_a < I_b < I_c}$

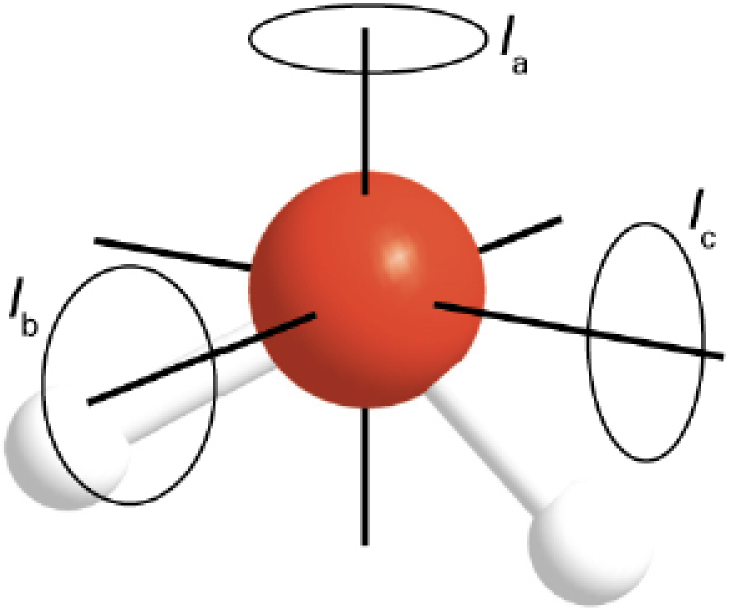
Rotational terms

For diatomics we defined a rotational constant $\tilde{B} \propto \frac{1}{I} = \frac{1}{\mu R^2}$

In general we require three such rotational constants:

as wavenumbers: $\boxed{\tilde{A} = \frac{h}{8\pi^2 c I_a}}$ $\boxed{\tilde{B} = \frac{h}{8\pi^2 c I_b}}$ $\boxed{\tilde{C} = \frac{h}{8\pi^2 c I_c}}$

$$\tilde{A} \geq \tilde{B} \geq \tilde{C}$$



H_2O molecule

$\tilde{A} = 27.9\ \text{cm}^{-1}$

$\tilde{B} = 14.5\ \text{cm}^{-1}$

$\tilde{C} = 9.3\ \text{cm}^{-1}$

But, we can no longer relate these constants explicitly to individual bond lengths within the molecule.

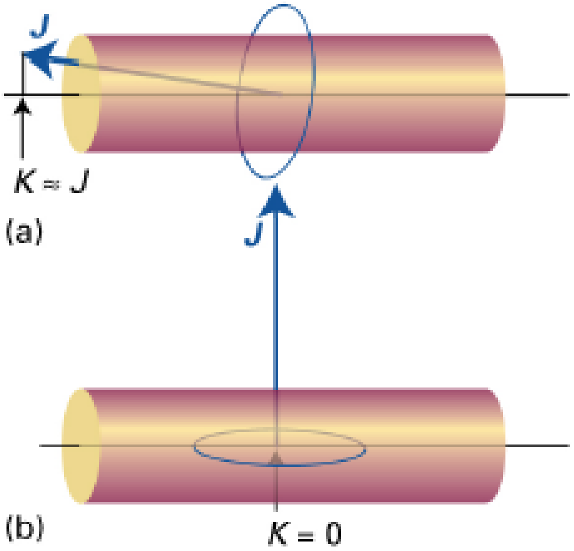
Prolate tops

$$\boxed{\begin{aligned} F_{J,K} &= \widetilde{B}J(J+1) + (\widetilde{A}-\widetilde{B})K^2 \\ J &= 0, 1, 2, 3, \ldots \\ K &= 0, \pm 1, \pm 2, \ldots \pm J \end{aligned}}$$

Levels labelled J_{Ka}

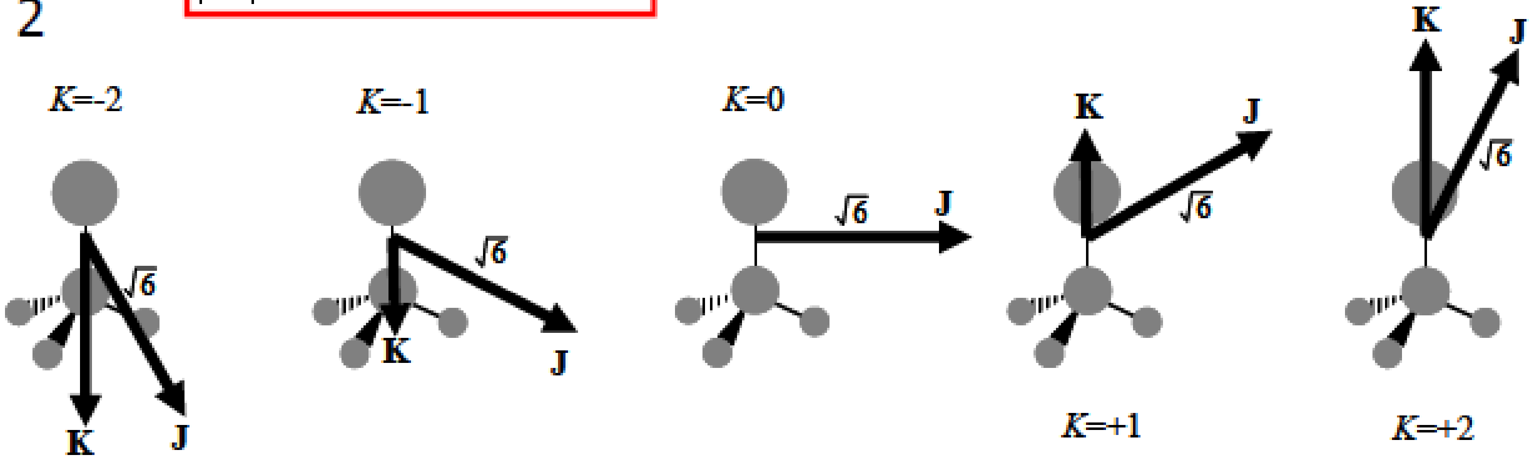
J is the *total angular momentum or rotational quantum number* and

K_a the *projection quantum number* (for projection on the unique, *a* axis).



$$\boxed{\left|\vec{J}\right| = \sqrt{J(J+1)}\,\hbar} \qquad \boxed{J_a = K\hbar}$$

$J = 2$

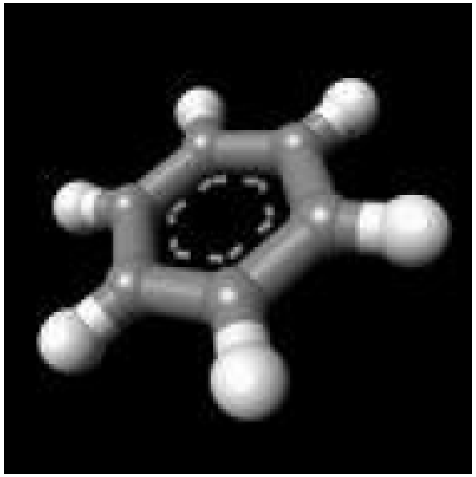


n.b., Each level has $2J+1$ degeneracy (arising from M_J)

In addition, each level $K > 0$ has extra two-fold degeneracy ($\pm K$)

Oblate tops

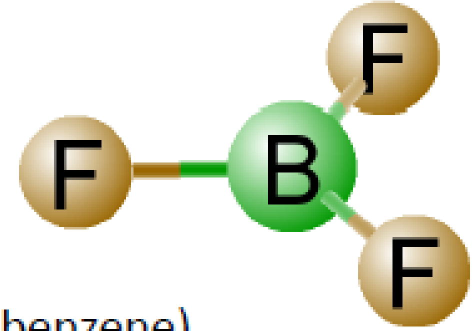
$$F_{J,K} = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2$$
$$J = 0, 1, 2, 3, \ldots$$
$$K = 0, \pm 1, \pm 2, \ldots \pm J$$



Levels labelled J_{Kc}

J is the *total angular momentum or rotational quantum number* and

K_c the *projection quantum number* (for projection on the unique, c axis).

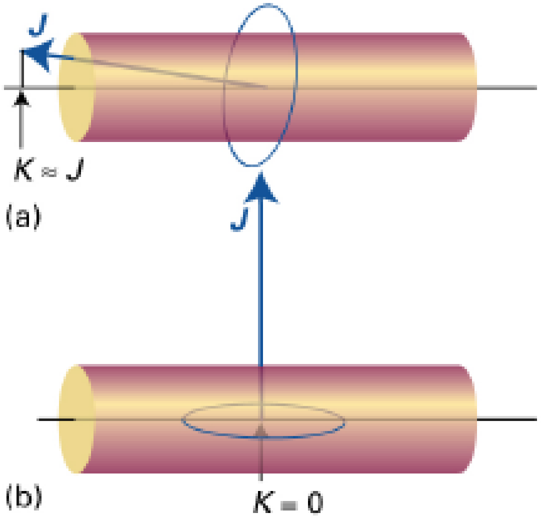


Oblate tops are typically flat "discus" – like molecules (e.g., benzene)

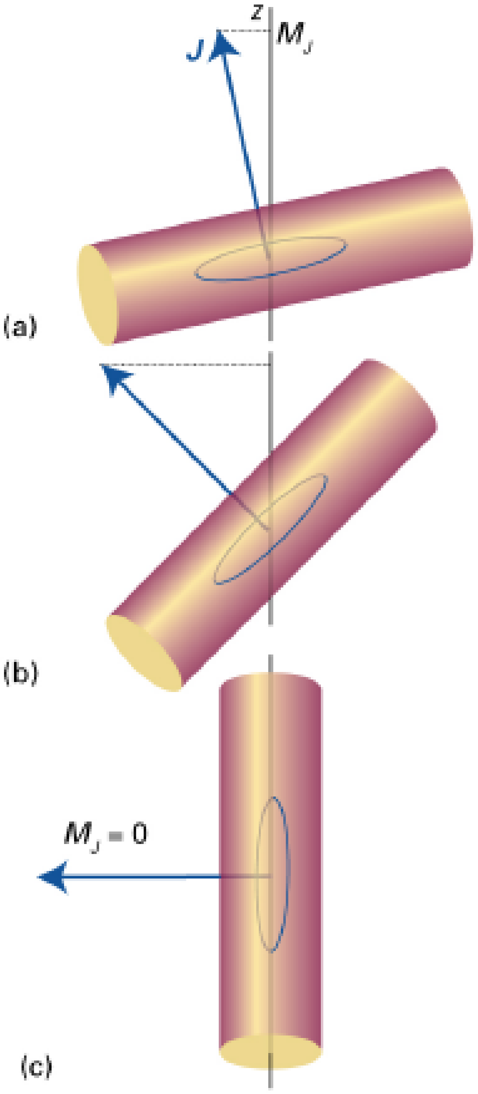
n.b., Each level has $2J+1$ degeneracy (arising from M_J)
In addition, each level $K > 0$ has extra two-fold degeneracy ($\pm K$)

Don’t confuse various projections

$$\boxed{\left|\vec{J}\right| = \sqrt{J(J+1)}\;\hbar}$$



K refers to a projection on a body-fixed axis (in this case, for a prolate top, the *a* axis)

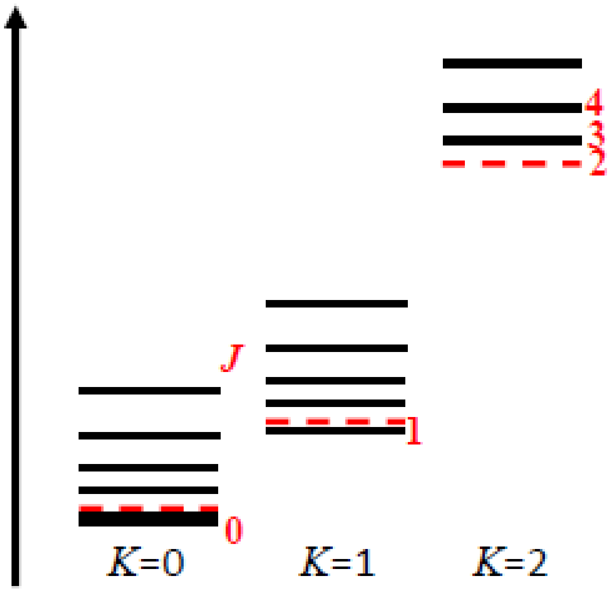


M_J refers to a projection on a space-fixed axis

Energy levels for Symmetric tops

Prolate top terms

$$F_{J,K} = \tilde{B}J(J+1)\underset{>0}{\boxed{+(\tilde{A}-\tilde{B})K^2}}$$

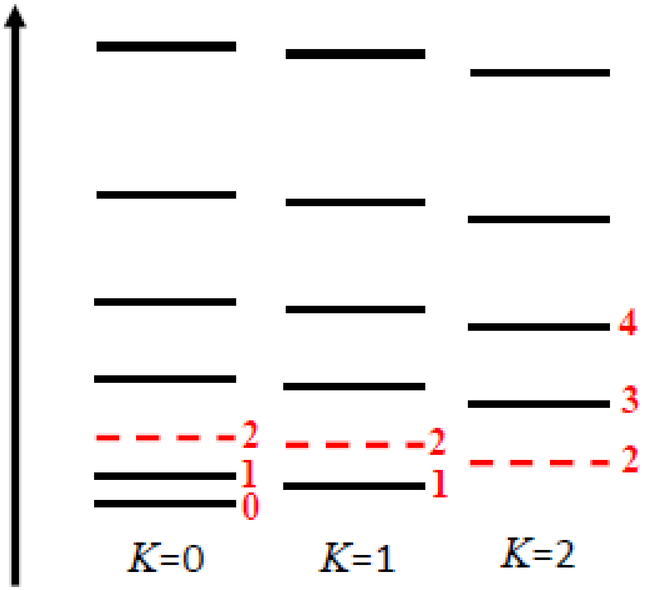


K - stacks

For a given *J*, energy increases with *K*

Oblate top terms

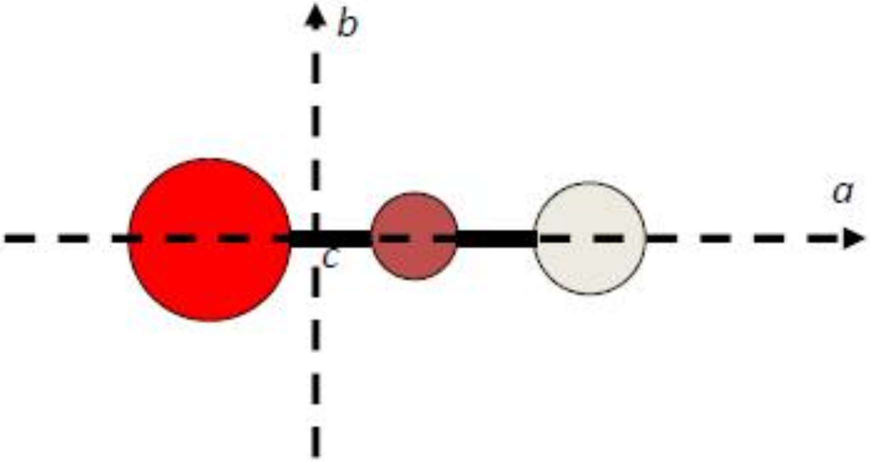
$$F_{J,K} = \tilde{B}J(J+1)\underset{<0}{\boxed{+(\tilde{C}-\tilde{B})K^2}}$$



K - stacks

For a given *J*, energy decreases with *K*

Linear Molecules ($C_{\infty v}$, $D_{\infty h}$)



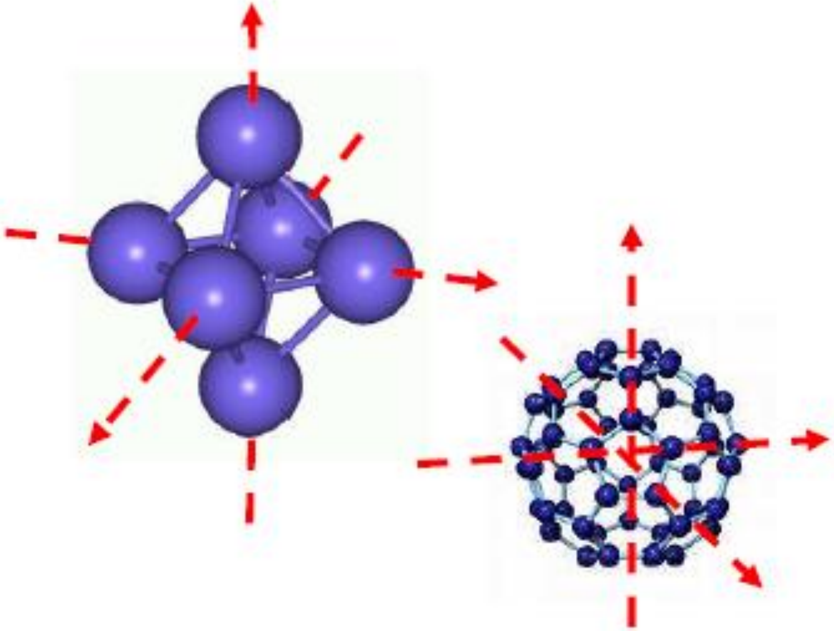
Special, limiting case of prolate top:

$$I_a = 0, \text{ hence } \quad \widetilde{A} = \infty$$

Only $K = 0$ exists, so

$$\boxed{F_J = \widetilde{B}J(J+1) \qquad J = 0, 1, 2, 3, \ldots}$$

Spherical Tops (T_d, O_h, I_h)



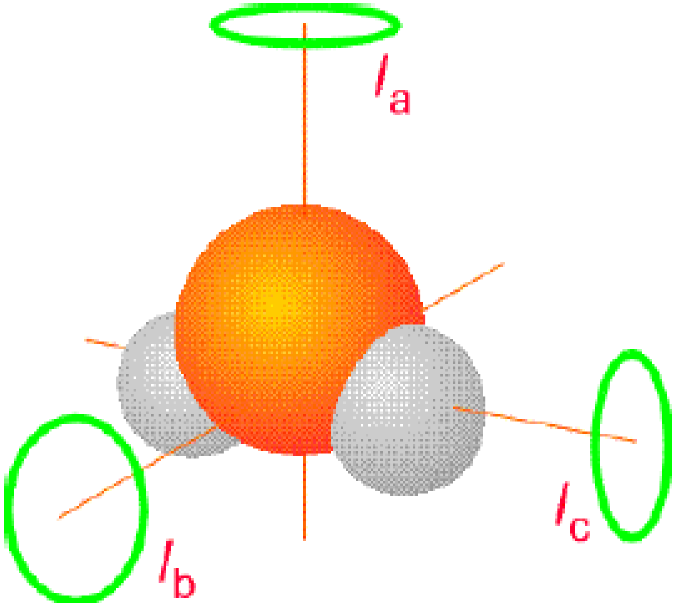
$$\widetilde{A} = \widetilde{B} = \widetilde{C}$$

$$\boxed{F_J = \widetilde{B}J(J+1) \qquad J = 0, 1, 2, 3, \ldots}$$

Degeneracy = $(2J+1)^2$

Asymmetric tops

Alas for the vast majority of molecules there is no simple general analytical form for the rotational levels. Some molecules are described as “near prolate” and “near oblate” tops. In general, terms can be derived by matrix diagonalisation.



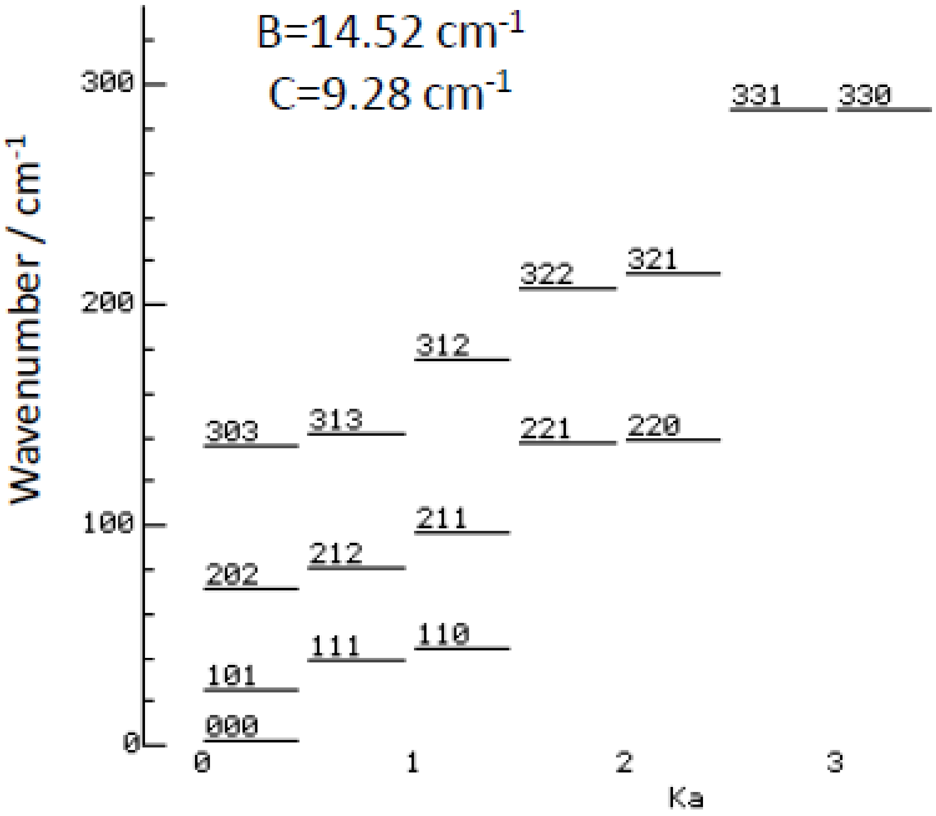
$$J_{Ka,Kc},\ e.g.,\ 2_{21}$$

H_2O

A=27.88 cm^{-1}

B=14.52 cm^{-1}

C=9.28 cm^{-1}



Rotational Spectroscopy

I. **Gross Selection rule:** To exhibit a pure rotational spectrum a molecule *must possess a permanent dipole moment*.

Homonuclear diatomic molecules such as O_2, H_2, etc. do not have a dipole moment and, hence, no pure rotational spectrum!

II. **Specific Selection Rule:** During a transition the allowed changes in the J, K quantum numbers are:

$$\boxed{\Delta J = \pm 1 \qquad \Delta K = 0}$$

(arises from quantum theory, but you ca think of this as a combination of conservation of angular momentum and parity)

Spectra of Symmetric tops

prolate **oblate**

Terms: $F_{J,K} = \widetilde{B}J(J+1) + (\widetilde{A} - \widetilde{B})K^2$ $F_{J,K} = \widetilde{B}J(J+1) + (\widetilde{C} - \widetilde{B})K^2$

Allowed transitions:

$$\widetilde{\nu} = F_{J+1,K} - F_{J,K}$$

$$\boxed{i.e., \quad \widetilde{\nu} = 2\widetilde{B}(J+1)}$$

Within the rigid rotor approximation spectra of prolate & oblate tops are the same as for linear molecules (and indeed spherical tops):

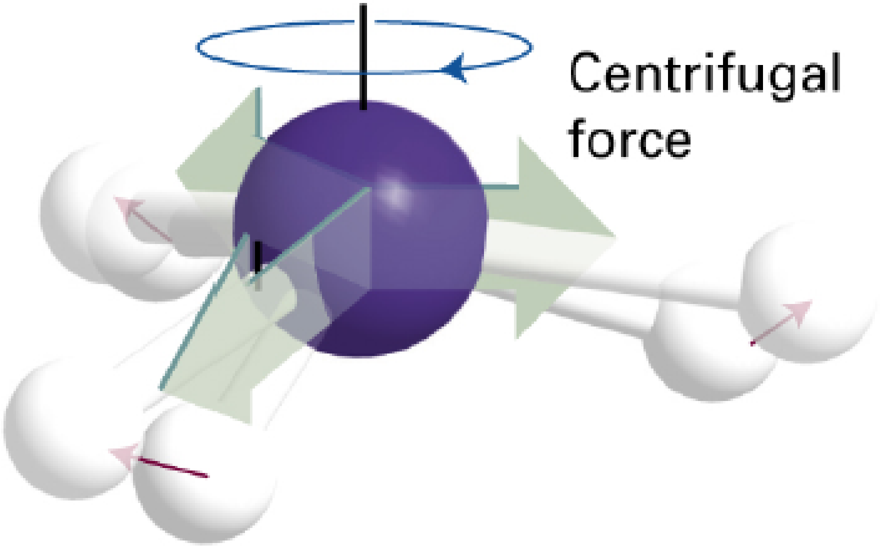
***i.e.*, Equally spaced lines with separation =** $2\tilde{B}$

We thus obtain no information on the unique axis (*a* for prolate, *c* for oblate) *i.e.*, nothing about the other rotational constants.

Beyond the Rigid Rotor: Centrifugal Distortion

The rigid rotor model holds for, well, rigid rotors.

Molecules, unfortunately, are *not* rigid rotors – their bonds stretch during rotation.



As a result, the various *I* (and thus rotational constants) *change* with *J*.

It is more convenient (*i.e.*, easier) to treat centrifugal distortion as a perturbation to the rigid rotor terms.

Centrifugal Distortion in symmetric tops

Prolate tops:

$$F(J,K)=\tilde{B}J(J+1)+(\tilde{A}-\tilde{B})K^2-\tilde{D}_J J^2(J+1)^2-\tilde{D}_{JK}J(J+1)K^2-\tilde{D}_K K^4,$$

Oblate tops:

$$F(J,K)=\tilde{B}J(J+1)+(\tilde{C}-\tilde{B})K^2-\tilde{D}_J J^2(J+1)^2-\tilde{D}_{JK}J(J+1)K^2-\tilde{D}_K K^4,$$

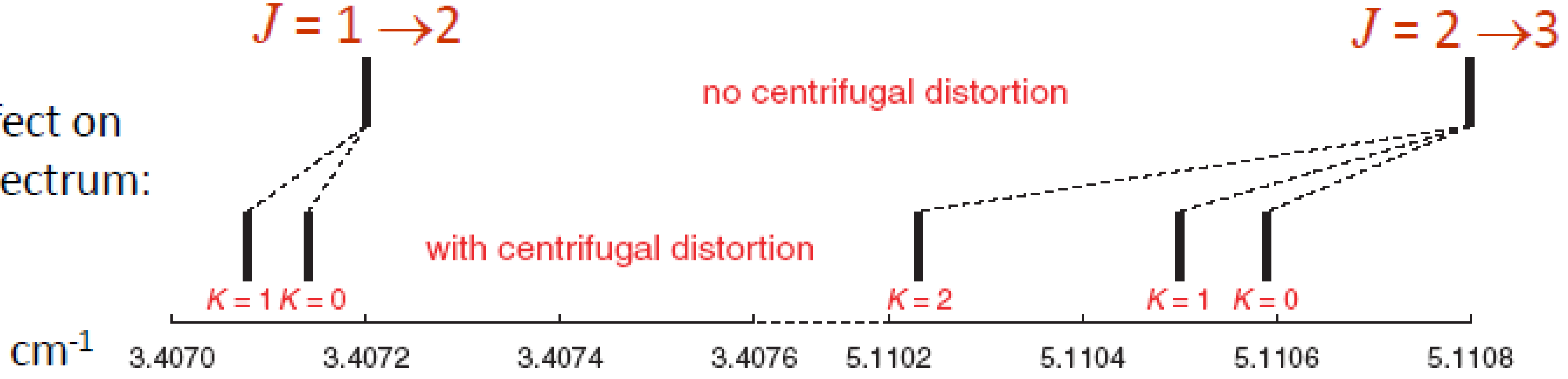
Rigid rotor terms **Centrifugal distortion terms**

i.e., three distortion constants!

$$\Delta J=\pm 1 \quad \Delta K=0$$

Transitions occur at:
$$\begin{aligned}\tilde{\nu}&=F(J+1,K)-F(J,K)\\&=2(\tilde{B}-\tilde{D}_{JK}K^2)(J+1)-4\tilde{D}_J(J+1)^3\end{aligned}$$

Effect on Spectrum:



Roto-vibrational IR spectroscopy

In the IR absorption spectra recorded at **high resolution**, the vibrational bands have a structure of lines due to rotational transitions ($J_1 \rightarrow J_2$) that occur *simultaneously* with the vibrational transition ($v_1 \rightarrow v_2$).

At room temperature - only *the vibrational ground state* (v = 0) *is populated*.

- the rotational levels with J > 0 are populated: the rotational level with maximum population have a rotational quantum number different from zero ($J_{max} \neq 0$)!

$$E_{tot} = E_{vibr} + E_{rot}$$

IR radiation : 300 – 4.000 cm^{-1}

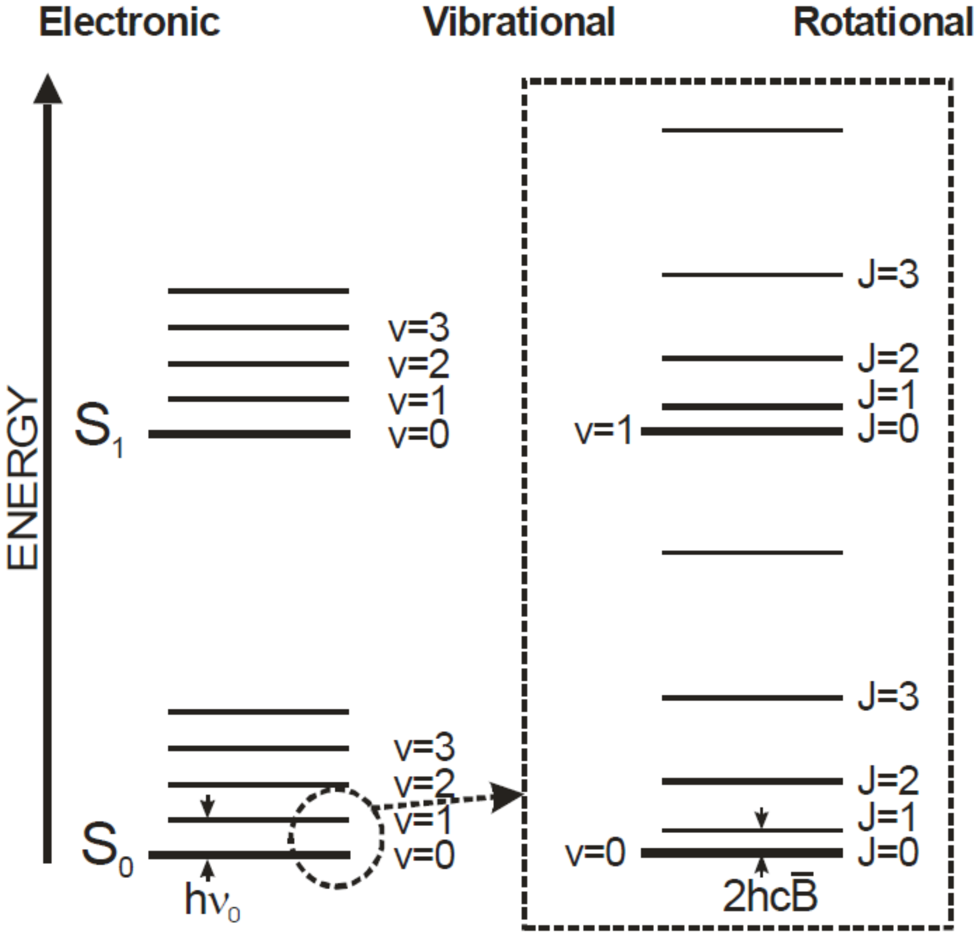
$$E_{tot} = h \cdot c \cdot \bar{\nu}_0 \left(v + \frac{1}{2} \right) + h \cdot c \cdot B \cdot J(J+1) + \ldots$$

$$\sim 1.000\,cm^{-1} \qquad \sim 1-10\,cm^{-1}$$

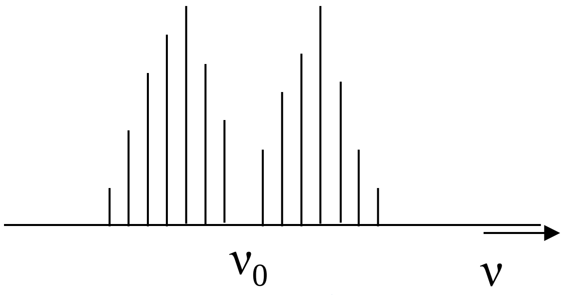
$$v = 0,1,2.... \qquad J = 0,1,2....$$

If the molecule (in vibrational ground state) *absorbed infrared radiation, it* will pass on an excited vibrational level ($\Delta v = +1$).

In the same time, the molecule can pass on another rotational level of excited vibration level (characterized by a *different rotational quantum number* than the initial) ($\Delta J = \pm 1$)



The spectrum consists of **lines** that appear at the **frequency** corresponding to **transitions**, having the *intensity proportional to the number of molecules that have made that transition*.



Pure vibrational spectrum: one line at ν_0.

Pure rotational spectrum: several lines separated by 2B.

Roto-vibrational spectrum : several lines separated by 2B, grouped into two branches (P and R), apart in ν_0 zone

(exception: for polyatomic molecule Q branch (ν_0) could appear!)

Roto-vibrational spectra of diatomic molecules

Consider the molecule as an harmonic oscillator and a rigid rotor.

The selection rules for roto-vibrational transition are: $\boxed{\Delta v = \pm 1 \qquad \Delta J = \pm 1}$

The energy absorbed by molecule is equal with the sum of vibrational and rotational energy changes.

$$E_{abs} = \Delta E_{vib} + \Delta E_{rot}$$

$$\boxed{E(v,J) = h \cdot c \cdot [\overline{\upsilon}_0\left(v + \frac{1}{2}\right) + B \cdot J(J+1)]}$$

$$h \cdot c \cdot \overline{\upsilon} = E_2 - E_1 = E(v_2, J_2) - E(v_1, J_1) \longrightarrow \text{absorbed energy}$$

$$\overline{\upsilon} = \frac{E_2 - E_1}{h \cdot c} = \left[\overline{\upsilon}_0\left(v_2 + \frac{1}{2}\right) + B \cdot J_2(J_2+1)\right] - \left[\overline{\upsilon}_0\left(v_1 + \frac{1}{2}\right) + B \cdot J_1(J_1+1)\right]$$

At room temperature: $v_1 = 0$ and **Δv = +1** so $v_2 = 1$

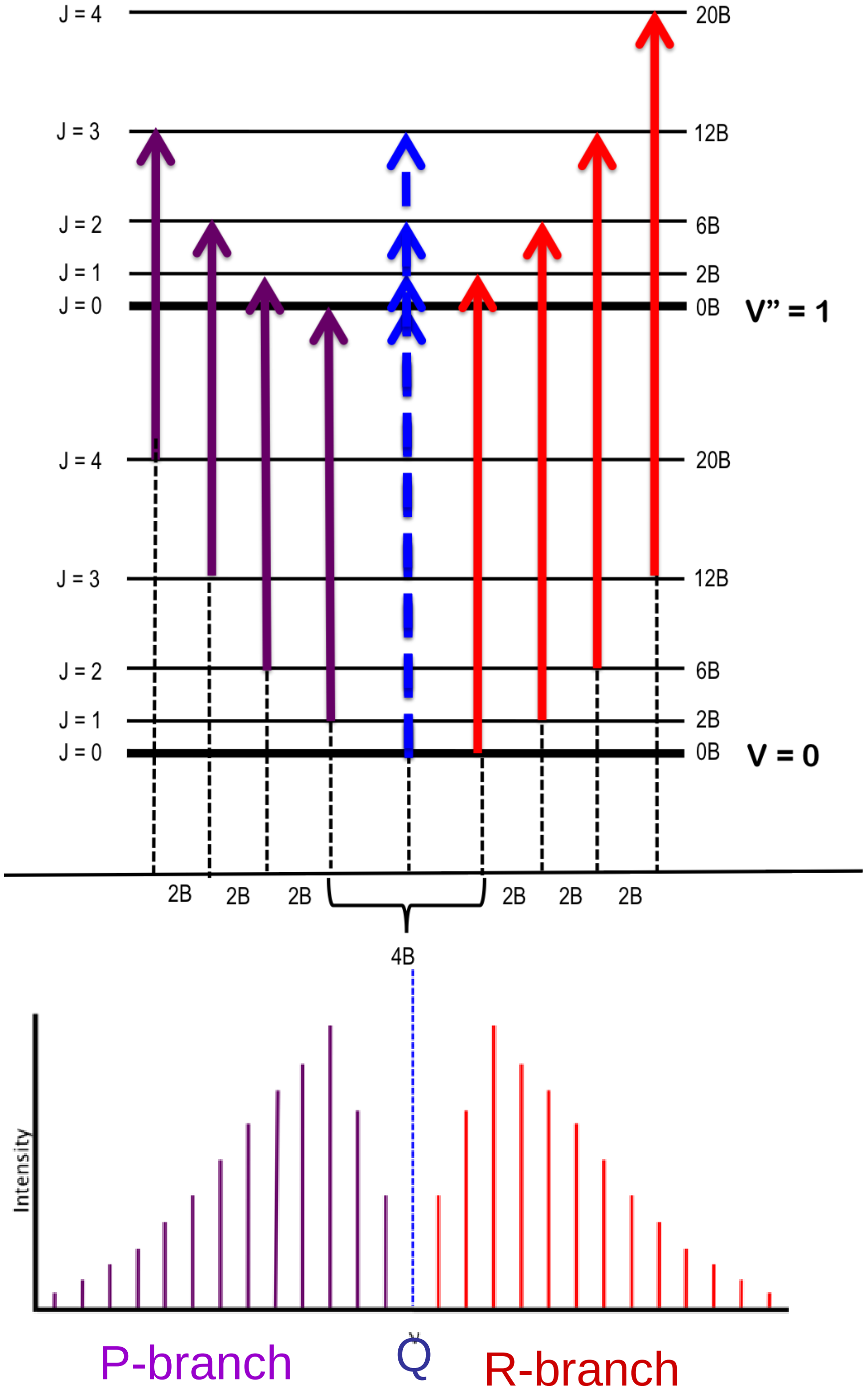
$$\boxed{\overline{\upsilon} = \overline{\upsilon}_0 + B \cdot \left[J_2(J_2+1) - J_1(J_1+1)\right]}$$

← wavenumber of roto-vibrational transition

The rotational levels with J ≠ 0 are populated, thus transitions with **ΔJ = 1** and **ΔJ = -1** may occur.

ΔJ = +1 → $J_2 = J_1 + 1$ $\boxed{\overline{\upsilon}_R = \overline{\upsilon}_0 + 2 \cdot B \cdot (J_1 + 1)}$ R branch (J_1 = 0, 1, 2, ...)

ΔJ = -1 → $J_2 = J_1 - 1$ $\boxed{\overline{\upsilon}_P = \overline{\upsilon}_0 - 2 \cdot B \cdot J_1}$ P branch (J_1 = 1, 2, 3, ...)



Selection rules: **ΔJ = 0, ±1**
Δv = 1

If ΔJ = +1 we obtained **R branch** (“rich”, the molecule gain rotational energy)

If ΔJ = -1 we obtained **P branch** (“poor”, the molecule lose rotational energy)

If ΔJ = 0 we obtained **Q branch** (for perpendicular vibrations in polyatomic molecules: *ex. NCN bend*)

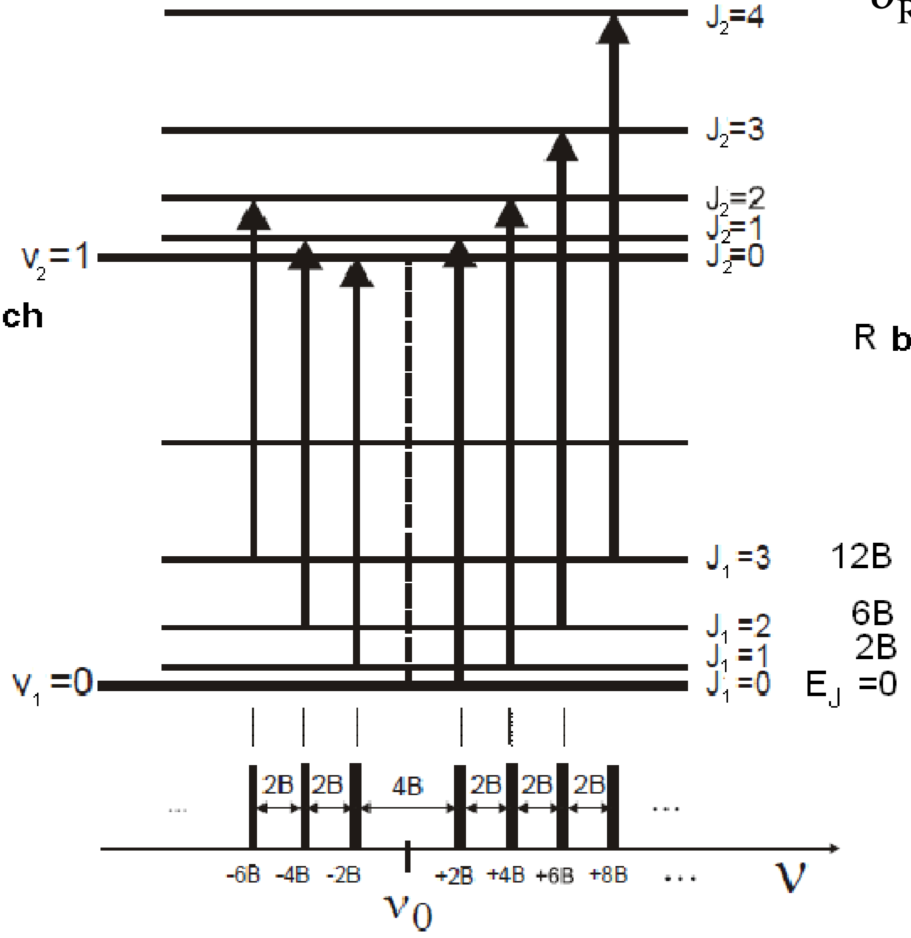
The lines of the P-branch (purple arrows) and R-branch (red arrows) are separated by 2B, thus the bond length can be deduced!

$$\bar{\upsilon}_{P,J} = \bar{\upsilon}_0 - 2\cdot B\cdot J$$

J = 1, 2, 3, ...

$$\bar{\upsilon}_{R,J} = \bar{\upsilon}_0 + 2\cdot B\cdot (J+1)$$

J = 0, 1, 2,



$$\bar{\upsilon}_{P,1} = \bar{\upsilon}_0 - 2\cdot B$$

$$\bar{\upsilon}_{P,2} = \bar{\upsilon}_0 - 4\cdot B$$

$$\bar{\upsilon}_{P,3} = \bar{\upsilon}_0 - 6\cdot B$$

$$\bar{\upsilon}_{P,4} = \bar{\upsilon}_0 - 8\cdot B$$

$$\bar{\upsilon}_{R,0} = \bar{\upsilon}_0 + 2\cdot B$$

$$\bar{\upsilon}_{R,1} = \bar{\upsilon}_0 + 4\cdot B$$

$$\bar{\upsilon}_{R,2} = \bar{\upsilon}_0 + 6\cdot B$$

$$\bar{\upsilon}_{R,3} = \bar{\upsilon}_0 + 8\cdot B$$

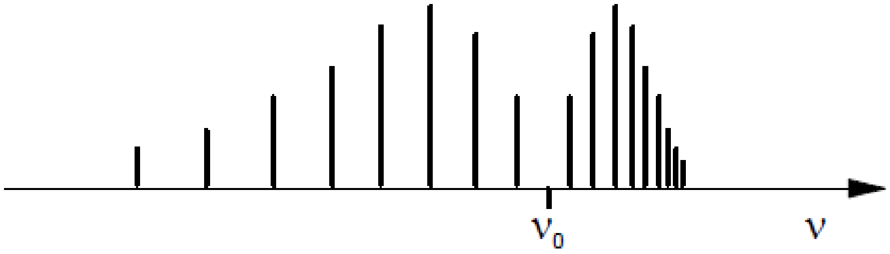
Q branch (ΔJ = 0) could appear in IR spectrum of polyatomic molecule!

Q tranzition (ΔJ = 0) is allowed only for vibrations that involved a perpendicular dipole moment change (to the symmetry axis of the molecule).

Q branch (ΔJ = 0): $\bar{\upsilon}_Q = \bar{\upsilon}_0$

For real molecule: vibration and rotation are not independent!

Two effects appear:



1) **roto-vibrational coupling**

Diatomic molecule: molecule vibrates → the bonds length (r) are changing → the moment of inertia changes → the rotational constant B changes

$$B_v = B_e - \alpha_e (v + \frac{1}{2})$$

α_e → roto-vibrational coupling constant
B_e → rotational constant for rigid and independent rotor

Each vibrational level have different rotational constant, so **$B_0 \neq B_1$!**

In this case the energy of roto-vibrational level is:

$$E(v,J) = h \cdot c \cdot [\overline{\upsilon}_0 \left(v + \frac{1}{2} \right) + B_v \cdot J(J+1)]$$

$$E(v,J) = h \cdot c \cdot [\overline{\upsilon}_0 \left(v + \frac{1}{2} \right) + B_e \cdot J(J+1) - \alpha_e (v + \frac{1}{2}) J(J+1)]$$

2) **centrifugal distorsion**

When the rotation velocity increase (J increase) → the bond lenght increase → the moment of inertia increase → the rotational constant B decrease

$$B_J = B_e - D \cdot J(J+1)$$

D → centrifugal distorsion constant

In this case the energy of roto-vibrational level is:

$$\boxed{\begin{aligned} E(v,J) &= h \cdot c \cdot [\bar{\upsilon}_0\left(v+\frac{1}{2}\right) + B_J \cdot J(J+1)] \\ E(v,J) &= h \cdot c \cdot [\bar{\upsilon}_0\left(v+\frac{1}{2}\right) + B_e \cdot J(J+1) - DJ^2(J+1)^2] \end{aligned}}$$

Considering both effects, the energy of a particular roto-vibrational level is:

$$\boxed{E_{v,J} = h \cdot c\left[\bar{\upsilon}_0\left(v+\frac{1}{2}\right) + B_e J \cdot (J+1) - \alpha_e\left(v+\frac{1}{2}\right) J \cdot (J+1) - D[J(J+1)]^2\right]}$$

$$E_{v,J} = h\cdot c\left[\bar{\upsilon}_0\left(v+\frac{1}{2}\right)+B_e J\cdot(J+1)-\alpha_e\left(v+\frac{1}{2}\right)J\cdot(J+1)-D[J(J+1)]^2\right]$$

We can consider: $E_{v,J} = hc\left[\bar{\nu}_0(v+1/2)+B_{v,J}J(J+1)\right]$

where: $B_{v,J} = B_e - \alpha(v+\frac{1}{2}) - DJ(J+1)$

P branch: (Δv = 1, ΔJ = -1) (v = 0 and J = 1, 2, 3 ...)

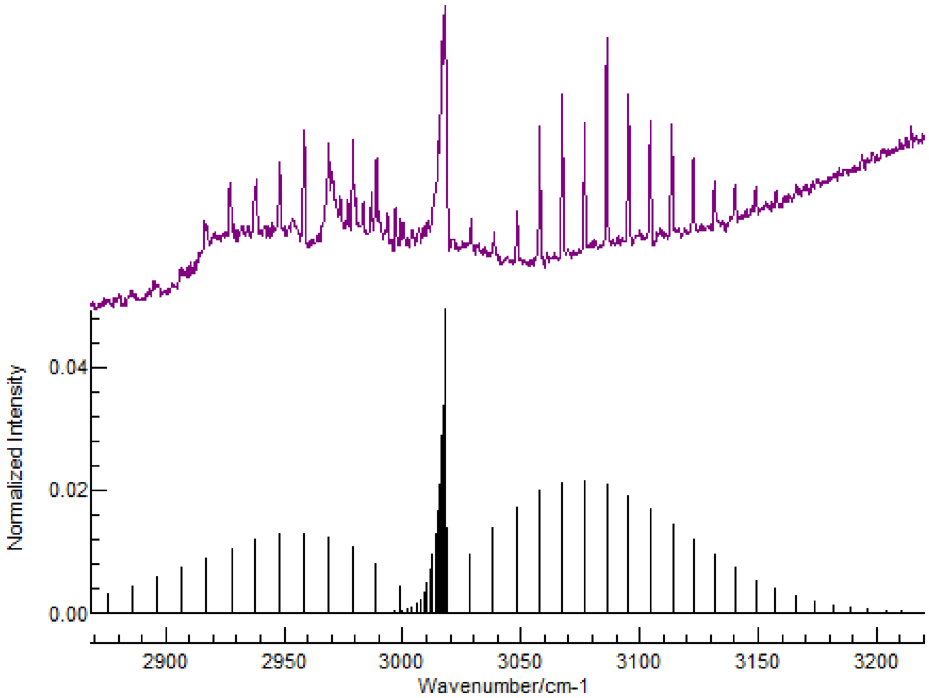
$$\bar{\nu}_{P,J} = \frac{1}{hc}(E_{(1,J-1)} - E_{(0,J)}) = \bar{\nu}_0 + (B_1 - B_0)J^2 - (B_1 + B_0)J$$

Q branch : (Δv = 1, ΔJ = 0) (v = 0 şi J = 1, 2, 3 ...) (if observable)

$$\bar{\nu}_{Q,J} = \frac{1}{hc}(E_{(v+1,J)} - E_{(v,J)}) = \bar{\nu}_0 + (B_1 - B_0)J(J+1)$$

R branch: (Δv = 1, ΔJ = +1) (v = 0 şi J = 0, 1, 2, 3 ...)

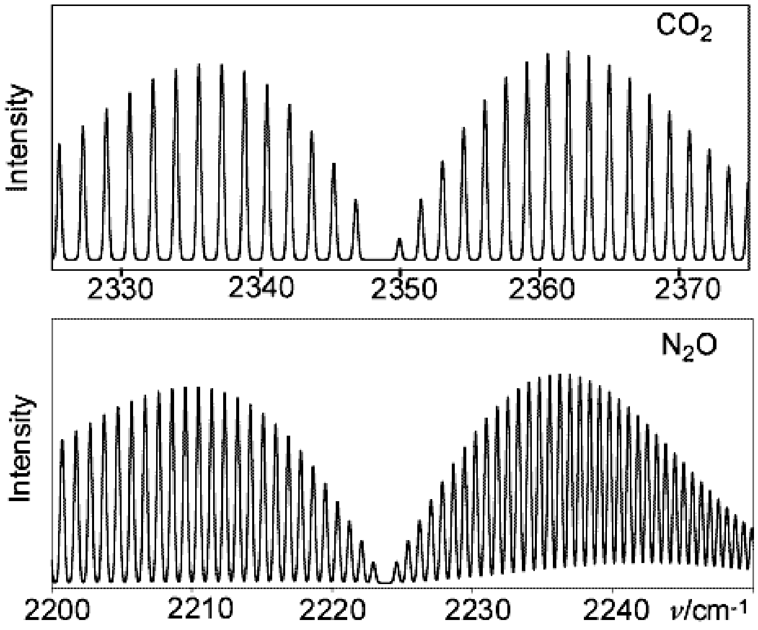
$$\bar{\nu}_{R,J} = \frac{1}{hc}(E_{(1,J+1)} - E_{(0,J)}) = \bar{\nu}_0 + (B_1 - B_0)(J+1)^2 + (B_1 + B_0)(J+1)$$

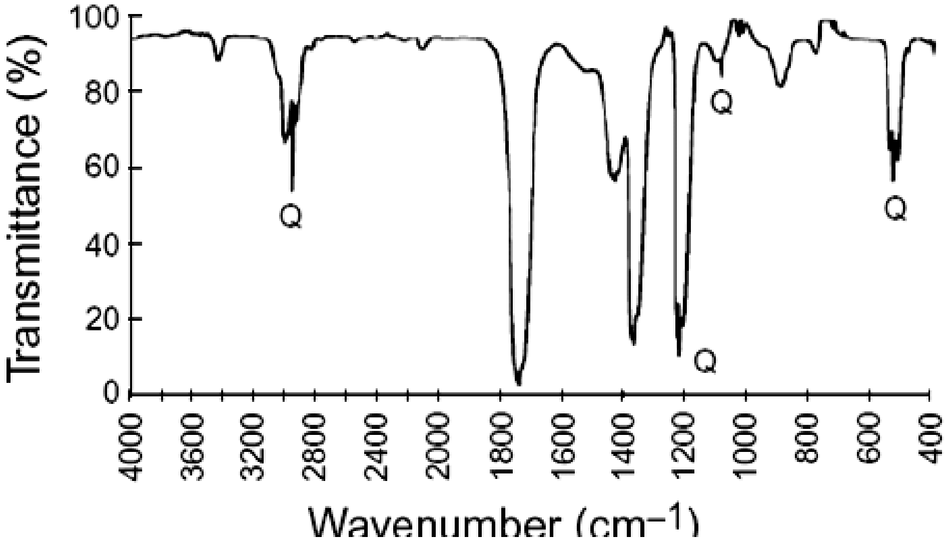


Part of the rotational-vibrational spectrum of methane (CH_4) gas (from FTIR), showing the presence of P-, Q- and R- branches (purple, top)

A simulation ot the rotational-vibrational spectrum of methane (CH_4) . Frequency is on the x-axis, and transmittance on the y-axis (black, down).

Interference from the absorption band of water can be seen > 3150cm^{-1}.





Roto-vibrational coupling effect is higher than centrifugal distorsion!

Because of anharmonicity, the bond length is higher in v = 1 state than in v = 0 state ($r_1 > r_0$), so $\mathbf{B_1 < B_0}$ (with 1-2%).

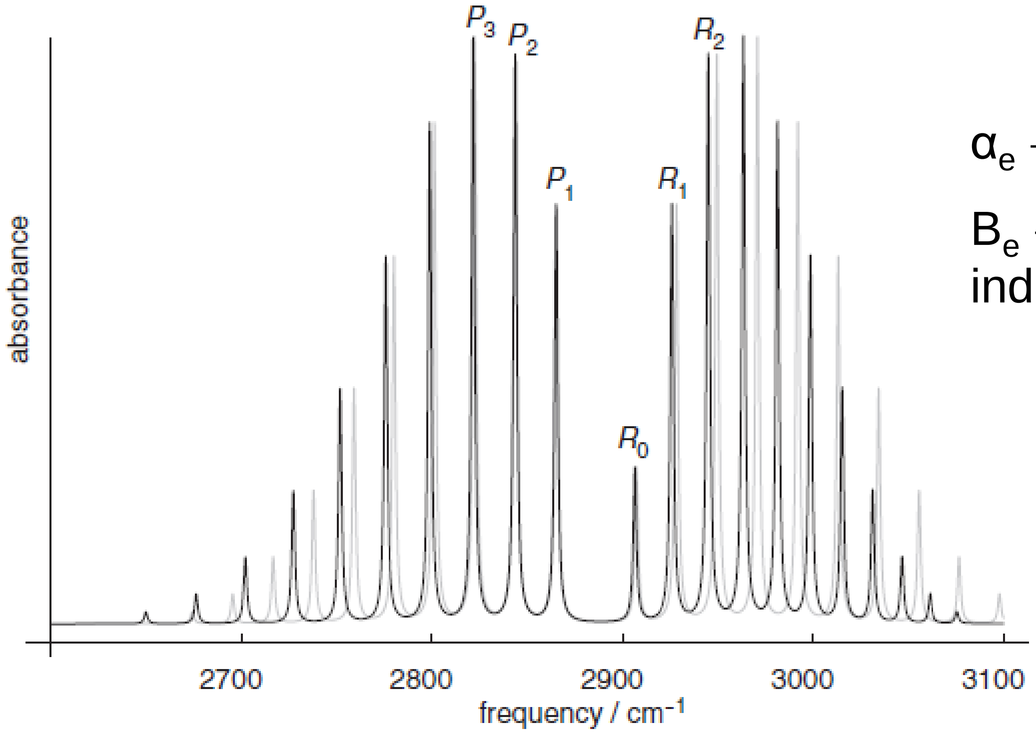
In R branch the distances between lines decrease (when J increase).

In P branch the distances between lines increase (when J increase).

$$B_v = B_e - \alpha_e (v + \frac{1}{2})$$

α_e → roto-vibrational coupling constant

B_e → rotational constant for rigid and independent rotor



$$B_0 = B_e - \frac{1}{2}\alpha_e$$

$$B_1 = B_e - \frac{3}{2}\alpha_e$$

$$\boxed{\alpha_e = B_0 - B_1}$$

gray - calculated spectrum (supposed $B_0 = B_1$)
black - experimental spectrum (real molecule!)

$$E_{v,J} = hc\left[\bar{\nu}_0\left(v+1/2\right)+B_eJ\left(J+1\right)\right]$$

Rigid rotor: $B_0 = B_1 = B_e$

P branch: **ΔJ=-1**

$$E_{(v=1,J=0)} - E_{(v=0,J=1)} = hc[\bar{\nu}_0 + B_e(0) - B_e(2)] = hc[\bar{\nu}_0 - 2\,B_e] = hc\bar{\nu}_{P1}$$
$$E_{(v=1,J=1)} - E_{(v=0,J=2)} = hc[\bar{\nu}_0 + B_e(2) - B_e(6)] = hc[\bar{\nu}_0 - 4\,B_e] = hc\bar{\nu}_{P2}$$
$$E_{(v=1,J=2)} - E_{(v=0,J=3)} = hc[\bar{\nu}_0 + B_e(6) - B_e(12)] = hc[\bar{\nu}_0 - 6\,B_e] = hc\bar{\nu}_{P3}$$

R branch: **ΔJ=+1**

$$E_{(v=1,J=1)} - E_{(v=0,J=0)} = hc[\bar{\nu}_0 + B_e(2) - B_e(0)] = hc[\bar{\nu}_0 + 2\,B_e] = hc\bar{\nu}_{R0}$$
$$E_{(v=1,J=2)} - E_{(v=0,J=1)} = hc[\bar{\nu}_0 + B_e(6) - B_e(2)] = hc[\bar{\nu}_0 + 4B_e] = hc\bar{\nu}_{R1}$$
$$E_{(v=1,J=3)} - E_{(v=0,J=2)} = hc[\bar{\nu}_0 + B_e(12) - B_e(6)] = hc[\bar{\nu}_0 + 6B_e] = hc\bar{\nu}_{R2}$$

$$E_{v,J} = hc\left[\bar{\nu}_0\left(v+1/2\right)+B_vJ\left(J+1\right)\right]$$

Non-rigid rotor: $B_0 \neq B_1$ ($B_0 > B_1$)

P branch: **ΔJ=-1**

$$E_{(v=1,J=0)} - E_{(v=0,J=1)} = hc[\bar{\nu}_0 + B_1(0) - B_0(2)] = hc[\bar{\nu}_0 - 2B_0] = hc\bar{\nu}_{P1}$$
$$E_{(v=1,J=1)} - E_{(v=0,J=2)} = hc[\bar{\nu}_0 + B_1(2) - B_0(6)] = hc[\bar{\nu}_0 + 2B_1 - 6B_0] = hc\bar{\nu}_{P2}$$
$$E_{(v=1,J=2)} - E_{(v=0,J=3)} = hc[\bar{\nu}_0 + B_1(6) - B_0(12)] = hc[\bar{\nu}_0 + 6\,B_1 - 12B_0] = hc\bar{\nu}_{P3}$$

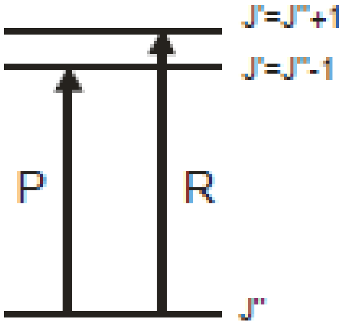
R branch: **ΔJ=+1**

$$E_{(v=1,J=1)} - E_{(v=0,J=0)} = hc[\bar{\nu}_0 + B_1(2) - B_0(0)] = hc[\bar{\nu}_0 + 2B_1] = hc\bar{\nu}_{R0}$$
$$E_{(v=1,J=2)} - E_{(v=0,J=1)} = hc[\bar{\nu}_0 + B_1(6) - B_0(2)] = hc[\bar{\nu}_0 + 6B_1 - 2B_0] = hc\bar{\nu}_{R1}$$
$$E_{(v=1,J=3)} - E_{(v=0,J=2)} = hc[\bar{\nu}_0 + B_1(12) - B_0(6)] = hc[\bar{\nu}_0 + 12B_1 - 6B_0] = hc\bar{\nu}_{R2}$$

The lab analysis of roto-vibrational spectra

Difference combination method is based on the determination of difference between wavenumbers of two transitions with a common energy level (initial or final)

Same (J”) initial level



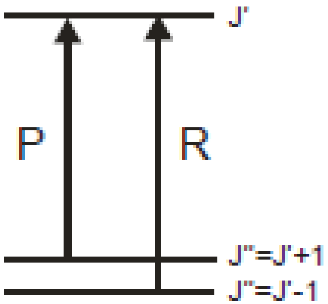
$$\bar{\nu}_{RJ} - \bar{\nu}_{PJ} = B_1(4J+2)$$

$$\boxed{B_1 = \frac{\bar{\nu}_{RJ} - \bar{\nu}_{PJ}}{(4J+2)}}$$

$$B_1 = B_e - \frac{3}{2}\alpha_e$$

B_1 rotation constant of superior vibrational level (B')

Same (J’) final level



$$\bar{\nu}_{R(J-1)} - \bar{\nu}_{P(J+1)} = B_0(4J+2)$$

$$\boxed{B_0 = \frac{\bar{\nu}_{R(J-1)} - \bar{\nu}_{P(J+1)}}{(4J+2)}}$$

$$B_0 = B_e - \frac{1}{2}\alpha_e$$

B_0 rotation constant of inferior vibrational level (B")

$$\boxed{\alpha_e = B_0 - B_1}$$

$$\boxed{B_e = \frac{3B_0 - B_1}{2}}$$

Only the gaseous molecules have rotational fine structure!

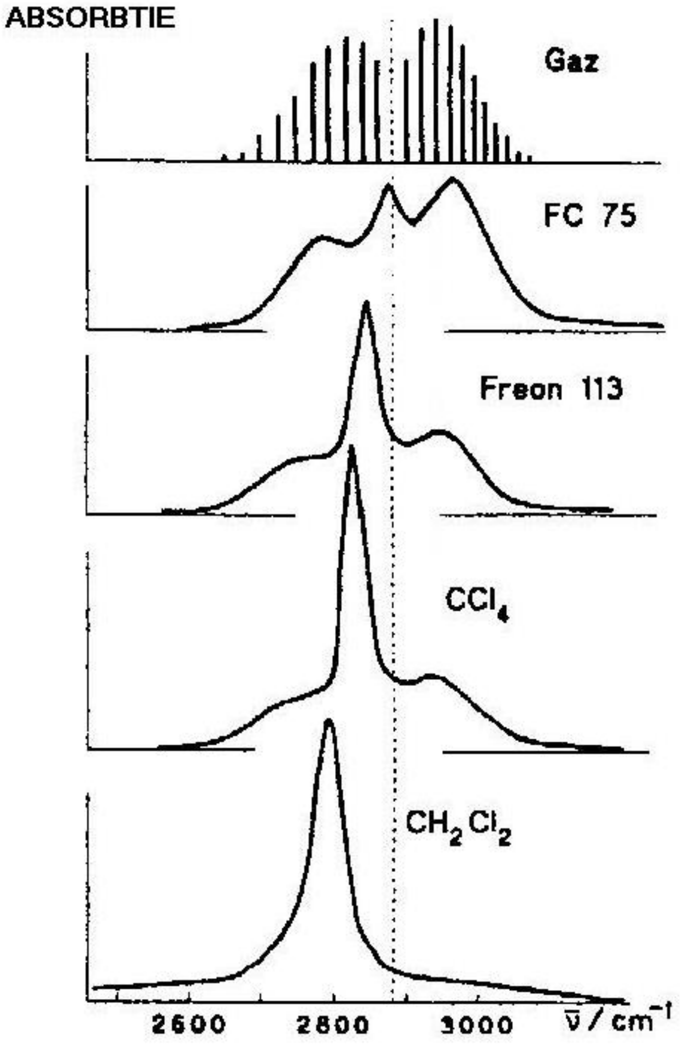
In lichid state the molecular rotations are partially blocked by molecular interactions → the rotational fine structure disappears or appears like an envelope of P, Q, R structure.

If the solvents are increasing polarity, we will obtain different spectra

-unpolar solvents (FC 75 ($C_8F_{16}O$) and Freon 113)
→ envelope of rotational bands

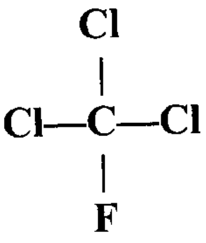
-polar solvents (dichlorhmetane: CH_2Cl_2)
→ the rotational bands disapper complete.

The H-Cl bond force constant decrease from unpolar solvents to polar solvents. *Therefore, the maximum of principal band shift to lower frecquencies.*



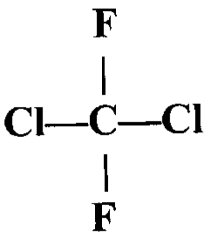
Rotational fine structure (HCl - gas)

Pure vibrational band (HCl in CH_2Cl_2 - liquid)



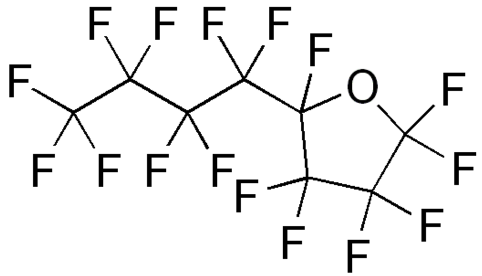
$$\begin{array}{c} Cl \\ | \\ Cl-C-Cl \\ | \\ F \end{array}$$

Freon-11

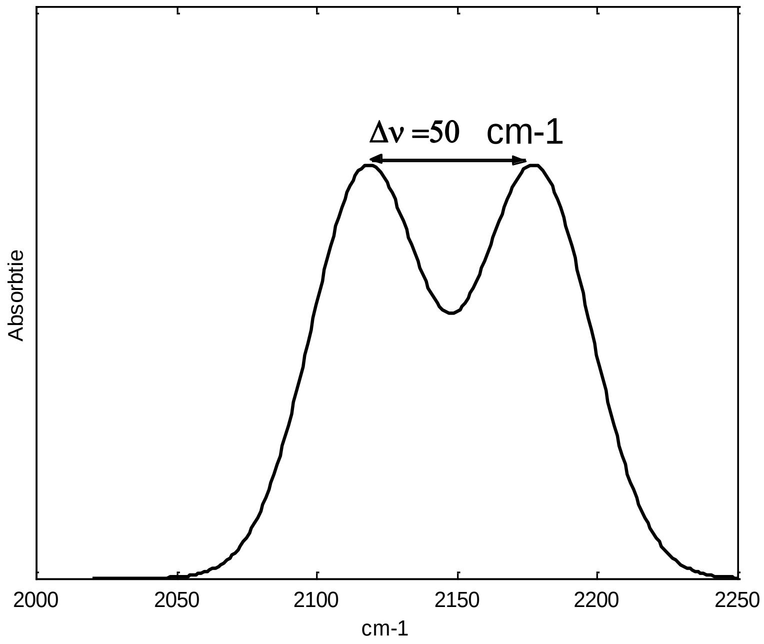


$$\begin{array}{c} F \\ | \\ Cl-C-Cl \\ | \\ F \end{array}$$

Freon-12



Lower resolution roto-vibrational spectrum → the rotational structure do not appear!



Still rotational constant B could be calculated with formula:

$$\boxed{\Delta\bar{\nu} = \sqrt{\frac{8kTB}{hc}}}$$

$\Delta\bar{\nu}$ = the distance between the 2 maxima (the envelopes of R and P branch).

Ex: For T = 300 K and $\Delta\nu$ = 50 cm^{-1} rotational constant is B = 1,51 cm^{-1}

Independent activity:

Calculate the distance (in wavenumbers) between the transitions ($\Delta J = \pm 1$) that start from the most populated rotational level of lower vibrational level (the two maxima from the figure). Consider the molecule as an harmonic oscillator and a rigid rotor:

$$E(v,J) = h \cdot c \cdot [\bar{\nu}_0\left(v + \frac{1}{2}\right) + B \cdot J(J+1)]$$

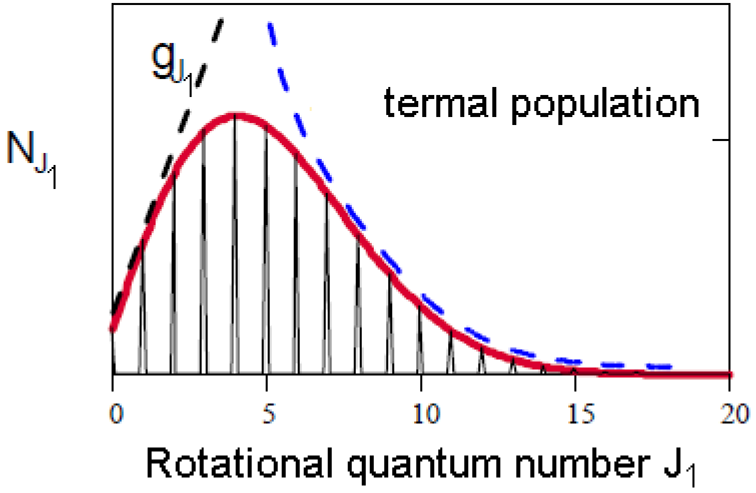
$$J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

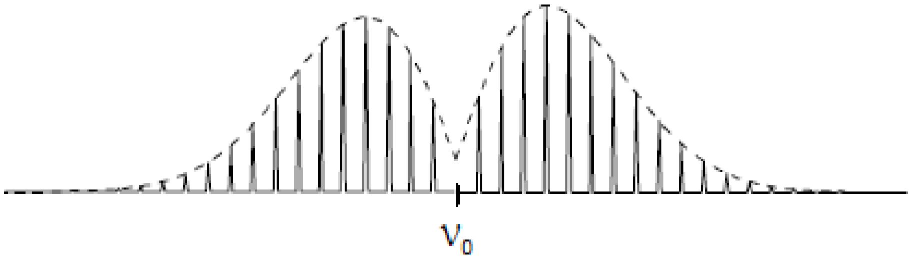
Usually superior level (v_2, J_2) is not populated, so *the roto-vibrational transitions intensity depends on the* ***lower level population*** **(v_1, J_1)** .

$$\Delta N = N\left(v_1, J_1\right) - N\left(v_2, J_2\right) \approx N\left(v_1, J_1\right)$$

$$N\left(v_1, J_1\right) = N_0 g\left(J_1\right) \exp\left(-\frac{E_{v_1} + E_{J_1}}{k \cdot T}\right)$$

$$N(v_1, J_1) = N_0\left(2J_1 + 1\right) \exp -\frac{hc}{kT}\left(\bar{v}_0 (v_1 + \frac{1}{2}) + B \cdot J_1 (J_1 + 1)\right)$$





Relative amplitude of roto-vibrational lines is related mainly to the population of rotational levels.

At room temperature:

- vibrational states 0 and 1:
  $N_1/N_0 = (1/1)\exp[-10^{-18} J/(1.38 \cdot 10^{-23} J/K \cdot 300K)] = 0$ (all the population is in the lower state)

- rotational states 0 and 1:
  $N_1/N_0 = (3/1)\exp[-10^{-21} J/(1.38 \cdot 10^{-23} J/K \cdot 300K)] = 2.4$ (two and a half larger population at state J = 1 than at state J = 0)

Determination of temperature through spectroscopy:

There are two types of temperature: one that can be measured through thermal equilibrium of the medium with a thermometer or a thermocouple, and one that is determined through spectroscopy.

To a first approximation, the height of the peaks in the roto-vibrational spectrum depends on the population of the state where the absorption/emission line is originated.

For rotational lines, the population is proportional to:

$$N_J = N_0 g(J) \exp\left(\frac{-E_J}{k \cdot T}\right) = N_0 (2J+1) \exp\left(\frac{-h \cdot c \cdot B_e}{k \cdot T} J(J+1)\right)$$

$$N_J = N_0 (2J+1) \exp\left(\frac{-h \cdot c \cdot B_e}{k \cdot T} (J^2 + J)\right)$$

(2J +1) comes from the *degeneracy of rotational states* and $E_J = B_e J(J+1)$

The rotational quantum number (J_{max}) corresponding to maximum intensity line can be calculated by taking the first derivative of the expression with respect to J and setting it to 0.

$$N_J = N_0(2J+1)\exp\left(\frac{-h\cdot c\cdot B_e}{k\cdot T}(J^2+J)\right)$$

$$\frac{dN_J}{dJ} = 2N_0\exp\left(\frac{-h\cdot c\cdot B_e}{k\cdot T}(J^2+J)\right) + N_0(2J+1)\left(\frac{-h\cdot c\cdot B_e}{k\cdot T}(2J+1)\right)\exp\left(\frac{-h\cdot c\cdot B_e}{k\cdot T}(J^2+J)\right)$$

$$\frac{dN_J}{dJ} = 0 \quad \Rightarrow \quad 2 + (2J+1)\left(\frac{-h\cdot c\cdot B_e}{k\cdot T}(2J+1)\right) = 0$$

$$2kT - hcB_e\cdot(4J^2+2J+1) = 0$$

$$4hcB_eJ^2 + 2hcB_eJ + (hcB_e - 2kT) = 0$$

$$J = -\frac{1}{2} \pm \sqrt{\frac{kT}{2hcB_e}}$$

Since J ≥ 0:

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

$$\boxed{J_{max} = -\frac{1}{2} + \sqrt{\frac{k_B T}{2B_e}}}$$

We can calculate which line will be the largest for a given temperature, or if we know which is the strongest line, we can calculate the temperature.

For the example of HCl absorption, the largest lines were the 4th of the R branch, and the 3rd of the P branch.

R branch, $\Delta J = +1$ $0 \rightarrow 1$
$1 \rightarrow 2$
$2 \rightarrow 3$
$3 \rightarrow 4$ originated in 3rd state

P branch, $\Delta J = -1$ $1 \rightarrow 0$
$2 \rightarrow 1$
$3 \rightarrow 2$ originated in 3rd state

Then: $$3 + \frac{1}{2} = \sqrt{\frac{k_B T}{2B_e}} = \sqrt{\frac{1.38\text{x}10^{-23}\,T}{2 \times 2\text{x}10^{-22}}}$$ T = 355K

Problems:

1. a) From the following wavenumbers of the P and R branches of the 0→1 infrared vibrational band of $^1H^{127}I$, obtain the values for the rotational constants B_0, B_1 and B_e (in cm^{-1}), the band center ν_0 (in cm^{-1}) and the vibration-rotation interaction constant α_e (in cm^{-1}).

Transition	Frequency (cm^{-1})	Transition	Frequency (cm^{-1})
R(0)	2242	P(1)	2217
R(1)	2254	P(2)	2204
R(2)	2265.5	P(3)	2190.5
R(3)	2276.5	P(4)	2176.5

b) What value results for the internuclear distance r_o (in A)?
How does the value for r_e compare with the value r_e=1.607775 A for $^2H^{127}I$?
How should it compare? Why?

c) What fraction of the HI molecules are in the v = 0; 1; 2 states at 300 K and at 1500 K?

2. Which of the following set of molecules, O_2, HF, CCl_4, H_2O and CO, would exhibit a microwave spectrum ?

A molecule requires a permanent dipole moment to exhibit a microwave spectrum. Thus HF, H_2O and CO would have such a spectrum, whilst O_2 and CCl_4 would not.

Will CO and O_2 give rotational fine structure in an infra-red spectrum ?

To give a line in an infra-red spectrum, the molecule must exhibit a change in dipole moment during a vibration.
To get rotational fine structure the molecule must also have a permanent dipole moment.

Thus the vibrational lines in the IR spectrum of CO will have rotational fine structure, but O_2 will not give an IR spectrum at all.

3. The rotational constant for the ground vibrational state (v = 0) for $^{12}C^{16}O$ is 1,9314 cm^{-1} In a microwave spectrum of $^{12}C^{16}O$, what will be the spacing between absorption lines? (used the rigid rotor approximation)

For the rigid rotor approximation, microwave absorption lines appear at 2B, 4B, 6B etc. giving the line separation = 2B.
Therefore, the absorption lines would be separated by $2 \cdot 1{,}9314 = 3{,}8628\ cm^{-1}$.

4. The rotational constant for the ground vibrational state (v = 0) for $^{12}C^{16}O$, denoted B_0, is 1,9314 cm^{-1}. Using the rigid rotor approximation, calculate the equilibrium internuclear distance.

For the rigid rotor approximation, the energy of a rotational level J is given by

$$E(J) = h \cdot c \cdot B\, J(J+1)$$

and the wavenumber of an absorption line as

$$\bar{\nu}_{J\rightarrow J+1} = \Delta E/h\cdot c = [E(J+1) - E(J)]/h\cdot c = 2\,B\,(J+1)$$

where the rotational constant $B = \frac{h}{8\pi^2 \cdot I \cdot c}$ cm^{-1} (c is in units of $cm\cdot s^{-1}$),

and the moment of inertia, $I = \mu\, r_e^2$. Thus, $r_e = \sqrt{\frac{h}{8\pi^2 c \mu B}}$

For $^{12}C^{16}O$, $\mu = [12\cdot 16/(12+16)] \cdot 1{,}6606\cdot 10^{-27} = 1{,}13850^{-26}$ kg

In its ground vibrational state (v=0), the rotational constant is given as $B = B_0 = 1{,}9314\ cm^{-1}$, thus,

$$r_e = \sqrt{\frac{6{,}6262\cdot 10^{-34}}{8\cdot \pi^2 \cdot 2{,}9979\cdot 10^{10}\cdot 1{,}1385\cdot 10^{-26}\cdot 1{,}9314}}$$

$r_e = 0{,}11283\cdot 10^{-9}$ m = **0,1128 nm**

5. For the first vibrationally excited state (v = 1) of $^{12}C^{16}O$, the rotational constant, denoted B_1, is 1,6116 cm^{-1}. Again using the rigid rotor approximation, calculate the equilibrium bond distance for this state.

Similar to question (4), except that in the first vibrational state (v=1), the rotational constant B = B_1 = 1,6116 cm^{-1}. Thus ,

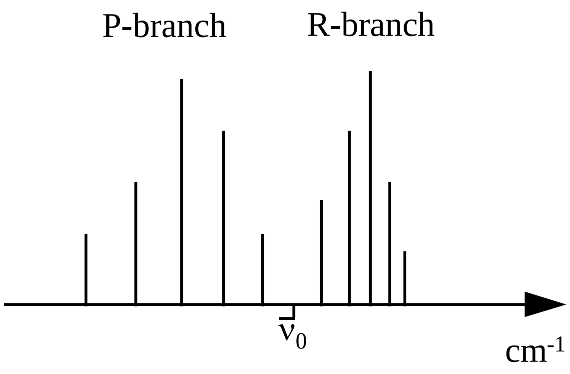
$$r_e = \sqrt{\frac{6{,}6262 \cdot 10^{-34}}{8 \cdot \pi^2 \cdot 2{,}9979 \cdot 10^{10} \cdot 1{,}1385 \cdot 10^{-26} \cdot 1{,}6116}}$$

r_e = 0,12352·10^{-9} m = **0,1235 nm**

6. How will manifest the change in the equilibrium internuclear distance (hence the change in rotational constant) in the rotational fine structure of the infra-red spectrum ?

When the molecule is in its lowest vibrational state (v=0), it has an equilibrium bond length of 0,1128 nm corresponding to a rotational constant, B_0 = 1,9314 cm^{-1}. When vibrationally excited to its first vibrational state (v = 1), it has an increased equilibrium bond length of 0,1235 nm, and a lower rotational constant, B_1 = 1,6116 cm^{-1}. This will be the observed in the rotational fine structure of the fundamental vibrational peak $\bar{\nu}_0$ = ΔG (v = 0→1) of the IR spectrum.

Since $B_0 > B_1$, we would observe lines getting wider spaced in the P-branch and closer in the R-branch, as depicted in the spectrum below.



http://rkt.chem.ox.ac.uk/tutorials/rotation/rot_spectra.html