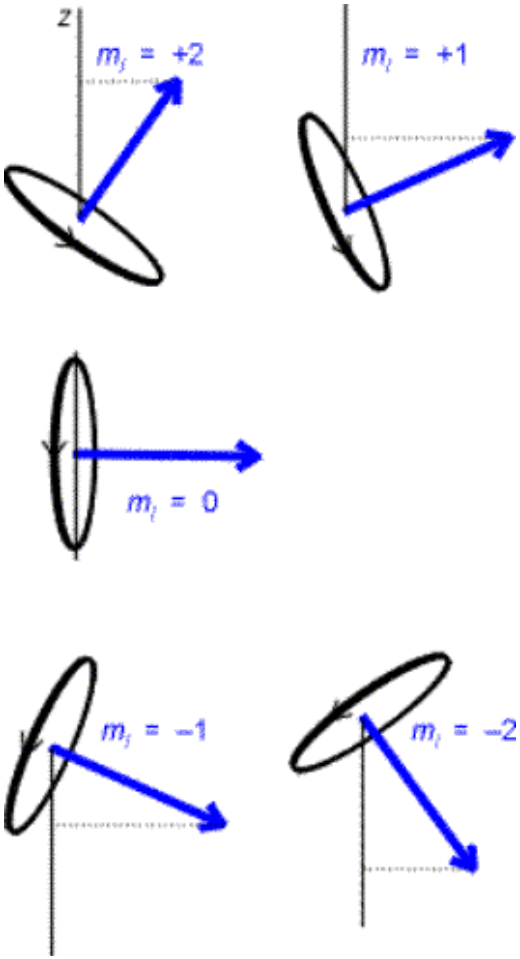
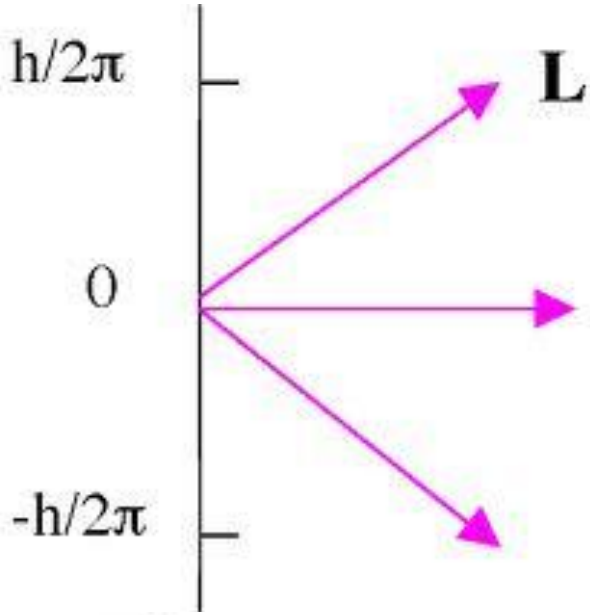
Intensity of spectral lines

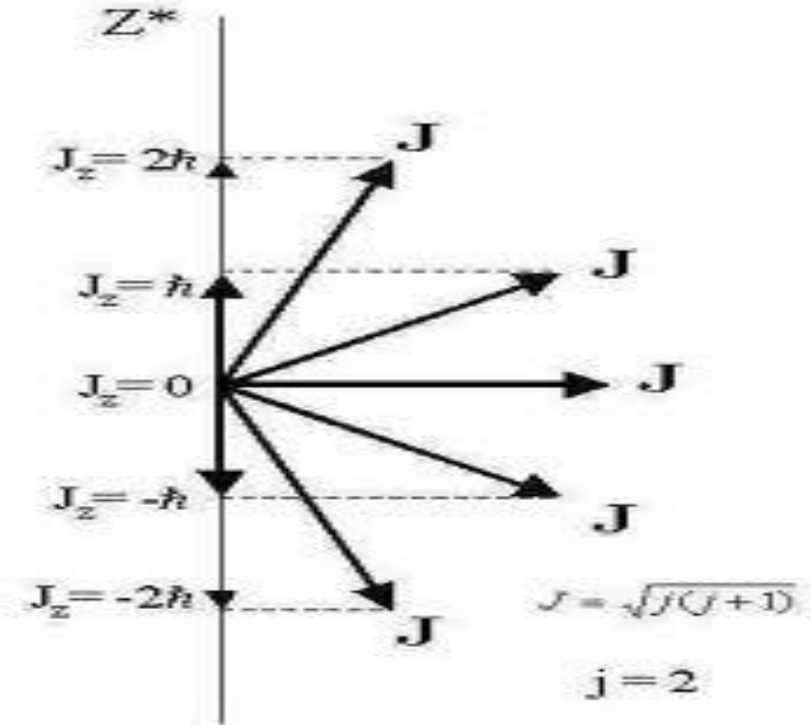
- Degeneracy of States
- Population of the states

Degeneracy of Rotational States

each energy level shows a degeneracy of $2J+1$


z
m_l = +2
m_l = +1
m_l = 0
m_l = –1
m_l = –2


h/2π
L
0
-h/2π


Z*
J
$J_z = 2\hbar$
$J_z = \hbar$
$J_z = 0$
$J_z = -\hbar$
$J_z = -2\hbar$
$J = \sqrt{j(j+1)}$
j = 2

The number of molecules in an excited state with quantum number J, relative to the number of molecules in the ground state, N_J/N_0 is given by the Boltzmann distribution

$$\frac{N_J}{N_0} = e^{-\frac{E_J}{kT}} = e^{-\frac{BhcJ(J+1)}{kT}}$$

The second factor is the degeneracy of the rotational state, which is equal to 2J+1

- To summarize: Total relative population at energy $E_J \alpha (2J+1) \exp(-E_J / kT)$ & maximum population occurs at nearest integral J value to :

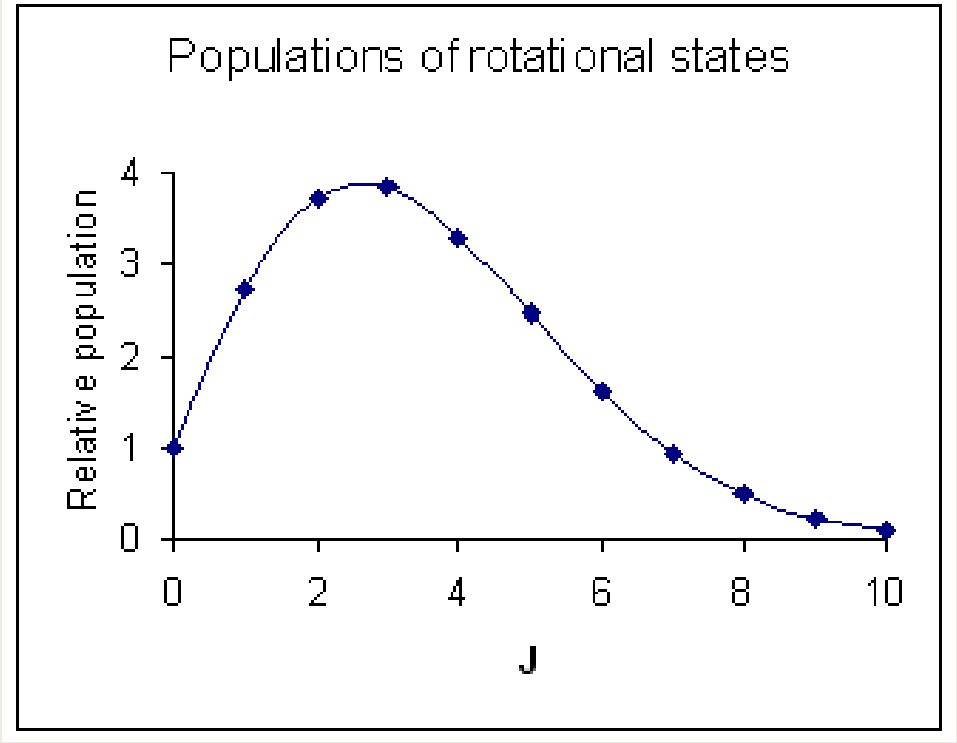
$$J = \sqrt{\frac{kT}{2hcB}} - 1/2$$

- **Since Jmax must be an integer, one takes the**
- **nearest integer value obtained from above Eq as the**
- **maximum.**

$$J = \sqrt{\frac{kT}{2hcB}} - 1/2$$

- One example from Kapoor Vol 4 page 449 for CO at 298K the value of J is equal to

6.82 and closest integer is 7



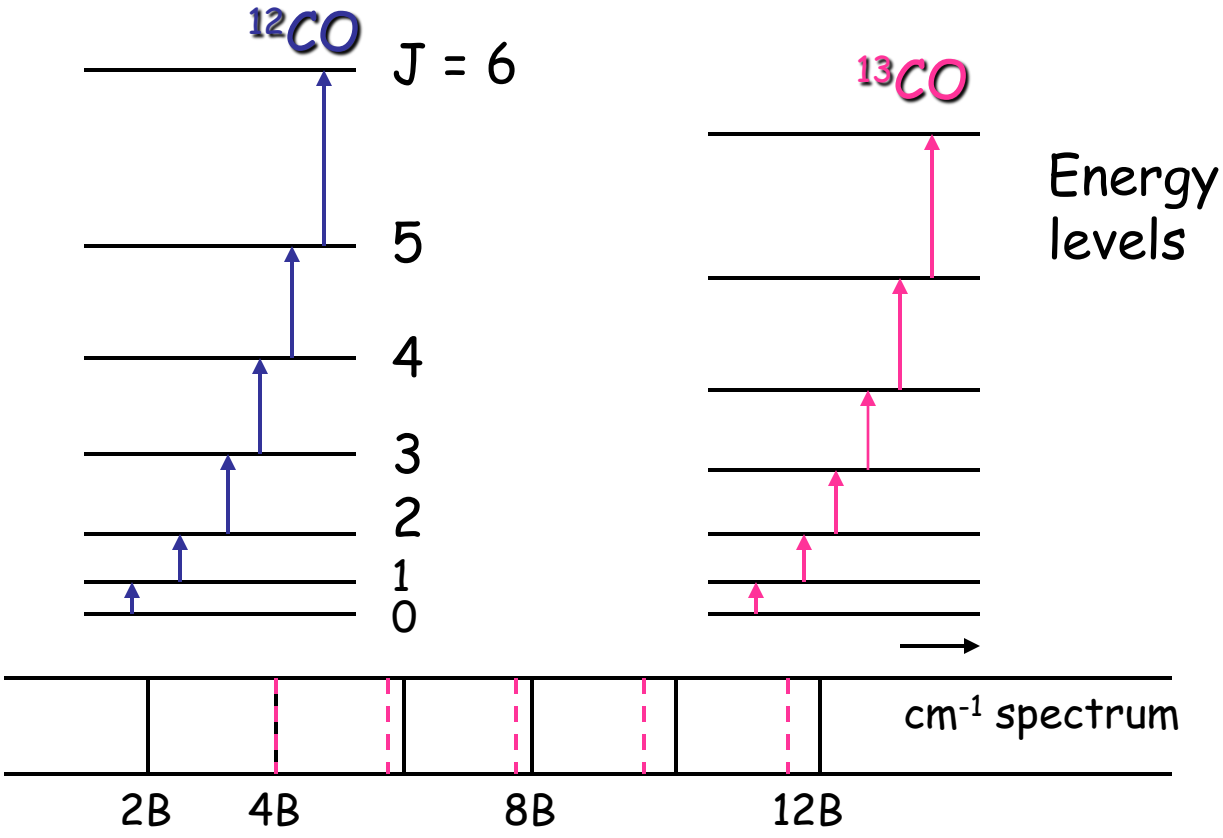
As J increases

Multiciplity factor increases

Exponential factor decreases

Effect of isotopes

From $^{12}C^{16}O \rightarrow {}^{13}C^{16}O$, mass increases, B decreases ($\propto 1/I$), so energy levels lower.



Comparison of rotational energy levels of ^{12}CO and ^{13}CO

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 $J=0 \rightarrow J=1$ at 3.84235 cm^{-1}

for ^{13}CO 3.67337 cm^{-1}

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

THANK YOU

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BCC