Eqⁿ (7) is usually abbreviated to
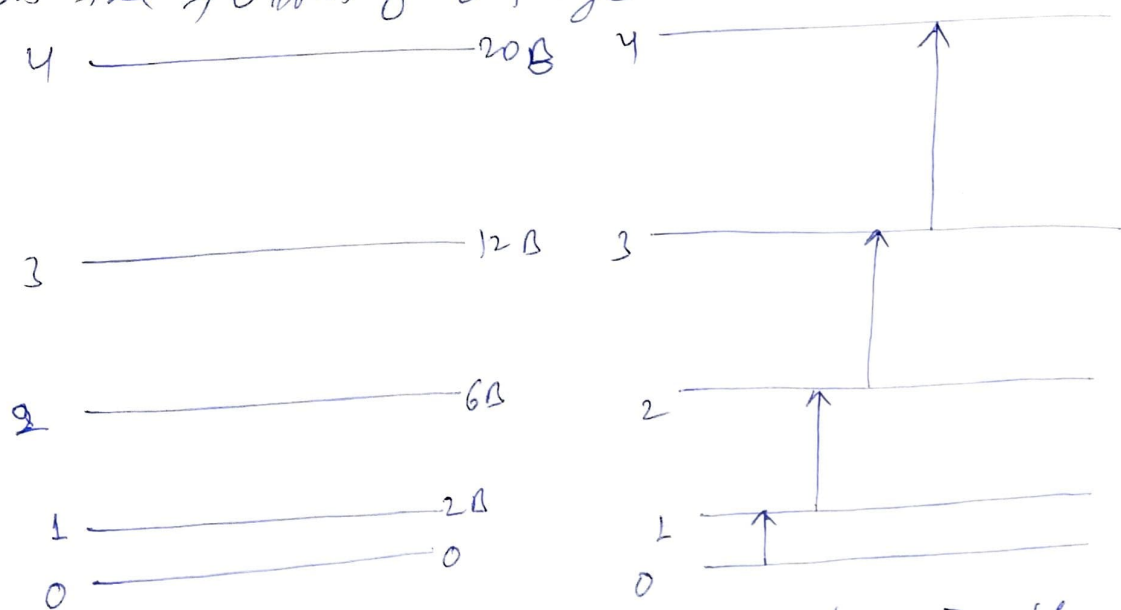
$$\varepsilon_J = BJ(J+1) \text{ cm}^{-1} \qquad —(8)$$

$$(J = 0, 1, 2 \dots)$$

B → rotational constant, is given by

$$B = \frac{h}{8\pi^2 I C} \text{ cm}^{-1} \qquad —(9)$$

From eqⁿ (8), we show the allowed energy levels in the following diagram

If we imagine the molecule to be in the J=0 state (ground rotational state, no rotation occurs), we can let the incident radiation be absorbed to raise it to the J=1 state, the energy absorbed will be

$$\varepsilon_{J=1} - \varepsilon_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

$$\bar{\nu}_{J=0 \to J=1} = 2B \text{ cm}^{-1} \qquad —(10)$$

Absorption line will appear at 2B cm⁻¹.

Similarly

$$\bar{\nu}_{J=1 \to J=2} = \varepsilon_{J=2} - \varepsilon_{J=1}$$

$$= 6B - 2B = 4B \text{ cm}^{-1} \qquad —(11)$$

In general, to raise the molecule from the state J to state J +1

$$\bar{\nu}_{J \to J+1} = B(J+1)(J+2) - BJ(J+1)$$

$$= B[J^2 + 3J + 2 - (J^2 + J)]$$

$$\bar{\nu}_{J \to J+1} = 2B(J+1) \, cm^{-1} \quad —(12)$$

An absorption spectrum consisting of lines at $2B, 4B, 6B$ ---, cm^{-1}, similar lowering would result in an identical emission spectrum.

We have not considered the sequence of transitions $J = 0 \to J = 2 \to J = 4$ ---, In fact, a rather sophisticated application of the Schrödinger wave eq^n shows that, for this molecule, we need only consider transitions in which J changes by one unit → all other transitions being spectroscopically forbidden. So selection rule for the rigid diatomic rotator may be stated as;

$$\Delta J = \pm 1 \quad —(13)$$

Only molecule is asymmetric (heteronuclear), this spectrum will be observed, since if it is homonuclear there will be no dipole component change during the rotation → no interaction with radiation.

We apply eq^n (3) to an observed spectrum to determine the moment of inertia and hence the bond length.

The first line ($J=0$) in the rotation spectrum of Carbon monooxide, measured as $3.84235 \, cm^{-1}$.

Hence from eqn (8)

$$\bar{\nu}_{0 \to 1} = 3.84235 = 2B \, cm^{-1}$$

or $\quad B = 1.92118 \, cm^{-1}$

Now $I = \dfrac{h}{8\pi^2 B c}$, we have

$$I_{CO} = \frac{6.62 \times 10^{-14}}{8\pi^2 \times 2.99793 \times 10^{0} \times B} = \frac{27.9902 \times 10^{-47}}{B} \, kg \, m^2$$

$$= 14.5695 \times 10^{-47} \, kg \, m^2$$

We express velocity of light in $Cm \, s^{-1}$, since B is in cm^{-1}. The reduced mass μ may be calculated as follows;

The mass of Carbon $\quad 19.92168 \times 10^{-27} \, kg$

" " Oxygen $\quad 26.5636 \times 10^{-27} \, kg$

$$\left[\begin{array}{l} knowing \ the \ relative \ atomic \ weights \ (H=1.0080) \ to \ be \\ C=12.0000, \ O=15.9994, \ and \ the \ absolute \ mass \ of \\ \qquad\qquad\qquad hydrogen \ atom / 1.67343 \times 10^{-27} kg \end{array} \right]$$

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

$$= 11.38365 \times 10^{-27} \, kg$$

$\Rightarrow \qquad \gamma^2 = \dfrac{I}{\mu} = 1.2755 \times 10^{-20} \, m^2$

$$\gamma_{CO} = 0.1131 \, nm \, \left(or \; 1.131 \, \text{Å} \right)$$

Intensities of Spectral lines: The line intensities will be directly proportional to the initial number of molecules in each level.

The first factor governing the population of the ⑨
levels is the Boltzmann distribution. Here we
know that the rotational energy in the lowest
level is zero, since $J=0$, So, if we have N_0
molecules in this state, the number in any
higher state is given by:

$$N_J/N_0 = \exp\left(- E_J/kT\right)$$

$$= \exp\left\{- BhcJ(J+1)/kT\right\}$$

$C \rightarrow$ velocity of light in $cm\ \color{red}{s^{-1}}$

$B \rightarrow cm^{-1}$

How N_J varies with J
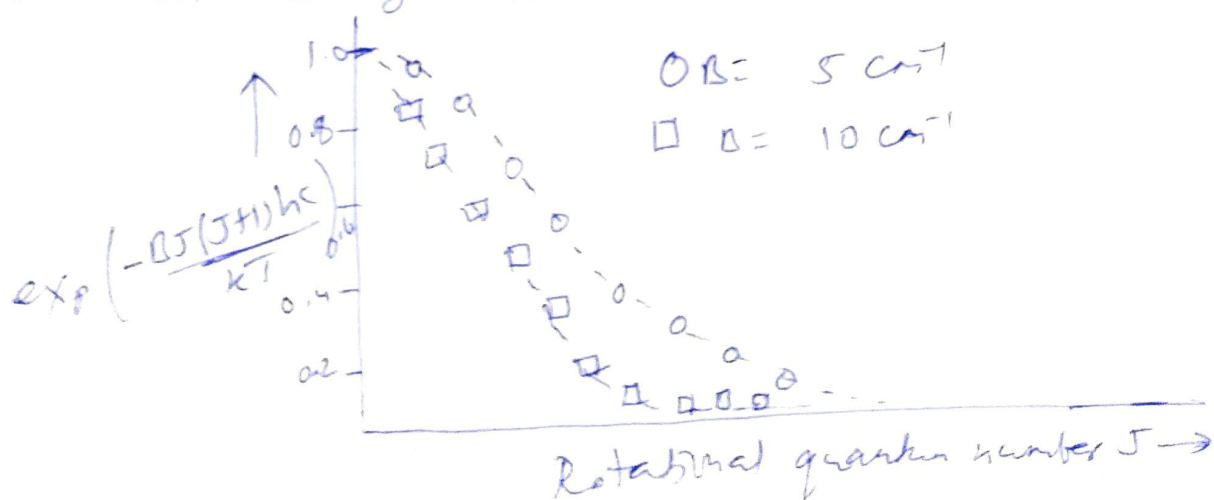
Example : $B = 2\ cm^{-1}$ at room temperature $(T=300K$

The relative population in the state $J=1$ is;

$$\frac{N_1}{N_0} = \exp\left\{- \frac{2 \times 6.63\times10^{-34} \times 3\times10^{10} \times 1 \times 2}{1.38\times10^{-23} \times 300}\right\}$$

$$= \exp(-0.019) \approx 0.98$$

There are as many molecules in the $J=1$ state, at
equilibrium, as in the $J=0$. Following graphs show
the more rapid decrease of N_J/N_0 with increasing
J and with larger B.

In general, it may readily be seen that each energy level is $2J+1$ fold degenerate.

The Effect of Isotopic Substitution

When a particular atom in a molecule is replaced by its isotope — there is a change in total mass and hence in the moment of inertia and B value for the molecule

Example $^{12}C^{16}O \rightarrow ^{13}C^{16}O$; there is mass increase and hence a decrease in the B value.

If we designate ^{13}C molecule with a prime we have $B > B'$. $\rightarrow$ This change will be reflected in the rotational energy levels of the molecule

The spectrum of the heavier species will show a smaller separations between the lines ($2B'$) than that of lighter one ($2B$)

12CO   13CO