Rotational Spectroscopy

The Intensities of Spectral Lines

We want now to consider briefly the relative intensities of the spectral line of the Equation $B = h^2/8\pi^2 Ic$; for this a prime requirement is plainly a knowledge of the relative probabilities of transition between the various energy levels. Does, for instance, a molecule have more or less chance of making the transition $J=0 \rightarrow J=1$ than the transition $J=1 \rightarrow J=2$? But we already know that a change of $\Delta J = \pm 2, \pm 3$, etc, is forbidden —in other words, the transitions probability for all these changes is zero. Precisely similar calculations show that the probability of all changes with $\Delta J = \pm 1$ is almost the same—all, to a good approximation, are equally likely to occur.

This does not mean, however, that all spectral lines will be equally intense. Although the intrinsic probability that a single molecule moving from $J=1$ to $J=2$, in an assemblage of molecules, such as in a normal gas sample, there will be different numbers of molecules in each level to begin with, and therefore different total numbers of molecules will carry out transitions between the various levels. In fact, since the intrinsic probabilities are identical, the line intensities will be directly proportional to the initial numbers of molecules in each level.

The first factor governing the population of 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 are given by:

$$N_J/N_0 = \exp(-E_J/kT) = \exp\left[-BhcJ(J+1)/kT\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(13)$$

Where, we must remember, c is the velocity of light in cm s^{-1} when B is in cm^{-1}.

A very simple calculation shows how N_J varies with J; for example, taking a typical value of B $=2$cm^{-1}, and room temperature (say T=300K), the relative population in the $j=1$ state is :

$$N_J/N_0 = \exp\left(-\frac{2 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} \times 1 \times 2}{1.38 \times 10^{-23} \times 300}\right)$$

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

and we see there are almost as many molecules in the $J=1$ state, at equilibrium, as in the $J=0$. In a similar way the two graph of Figure 6 have been calculated, showing the more rapid decrease of N_J/N_0 with increasing J and with larger B.]
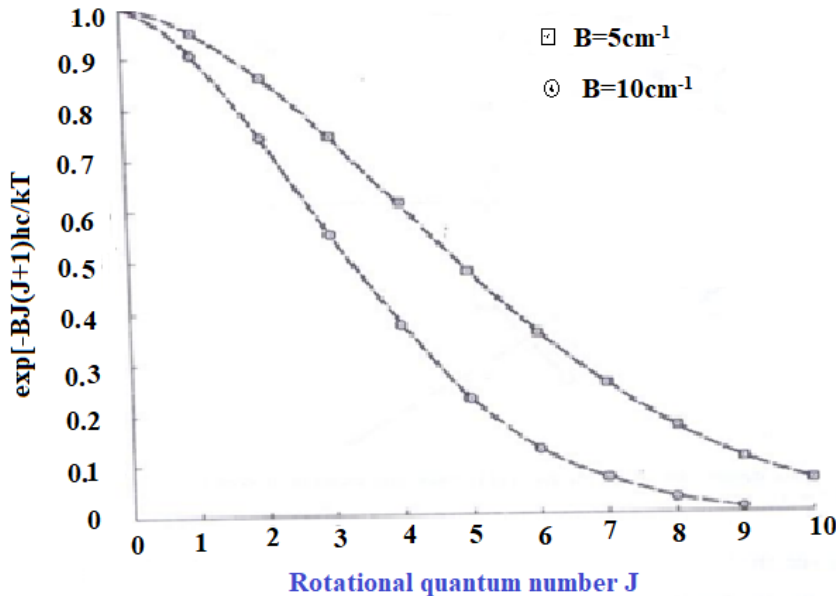
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Figure 6: The Boltzmann populations of the rotational energy levels of 4. The diagram has been drawn taking values B=5 and 10 cm^{-1} and T=300 K in Eq.13.

A second factor is also required — the possibility of degeneracy in the energy states. Degeneracy is the existence of two or more energy state which have exactly the same energy. In the case of diatomic rotator we may approach the problem in terms of its angular momentum.

The defining equation for the energy and angular momentum of a rotator are:

$$E = \frac{1}{2} I w^2$$

$$P = I\omega$$

Where I is the moment of inertia, ω the rotational frequency (in radians per second), and **P** is the angular momentum. Rearrangement of these gives:

$$P = \sqrt{2EI}$$

The energy level expression of Eq.(5), Can be rewritten:

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

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

Where J=0,1,2,………

Dr.Sandip Kumar Rajak|Dumkal College

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and hence

$$P = \sqrt{J(J+1)}\ \frac{h}{4\pi} = \sqrt{J(J+1)}\ \text{units}$$

...................(14)

Where, following conversion, we take $h/2\pi$ as the fundamental unit of angular momentum. Thus we see that **P,** like E, is quantized.

Throughout the above derivation **P** has been printed in bold face type to show that it is a vector— i.e it has direction as well as magnitude. The direction of the angular momentum vector is conventional taken to be along the axis about which rotation occurs and it is usually drawn as an arrow of length proportional to the magnitude of the momentum. The number of different directions which an angular momentum vector may take up is limited by a quantum mechanical law which may be stated:

For integral values of the rotational quantum number (in this case J), the angular momentum vector may only take up directions such that its component along a given reference direction is zero or an integral multiple of angular momentum units.

We can see the implication of this most easily by means of a diagram. In Figure 7 we show the case J=. Here $P = \sqrt{1 \times 2}\ \text{units} = \sqrt{2}$,and, as Figure 7 (a) shows, a vector of length $\sqrt{2}(=1.41)$ can have only three integral or zero components along a reference direction (here assumed to be from top to bottom in the plane of the paper): +1,0, and -1. Thus the angular
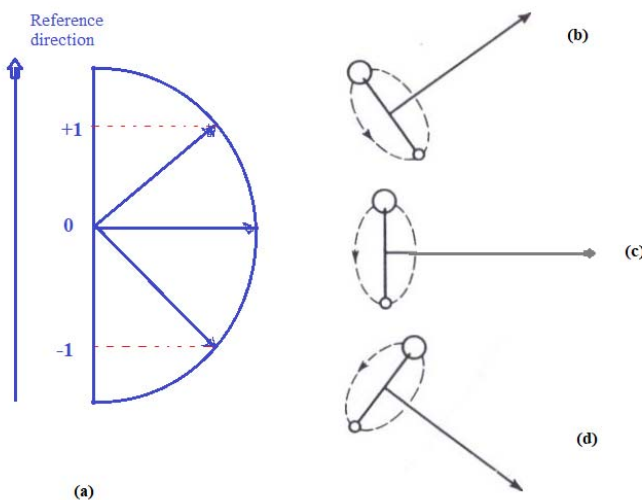
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Figure 7: The three degenerate orientations of the rotational angular momentum vector for a molecule with J=1
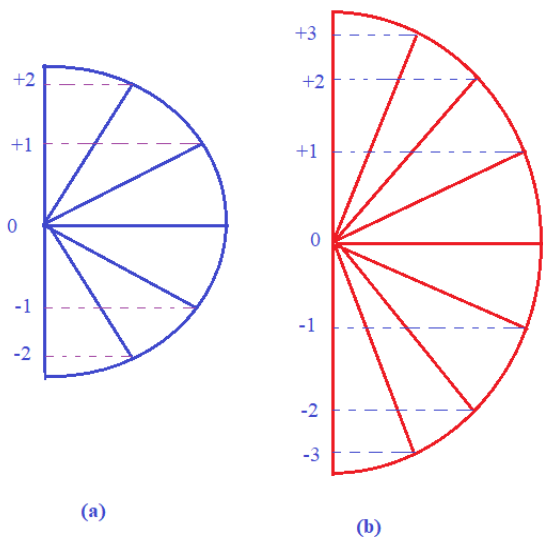

(a)   (b)

Figure 8: The five and seven degenerate rotational orientations for a molecule with J=2 and J=3, respectively.

Momentum vector in this instance can be oriented in only three different direction Figure 7 (b) to (d) with respect to the reference direction. All three rotational directions are, of course, associated with the same angular momentum and hence the same rotational energy: the J=1 level is thus threefold degenerate.

Figure 8 (a) and (b) shows the situation for J=2($P=\sqrt{6}$) and J=3($P2=2\sqrt{3}$) with fivefold and sevenfold degeneracy, respectively. In general it may readily be seen that each energy level is (2J+1) fold degenerate.

Thus we see that, although the molecule population in each level decreases exponentially (Eq.13 ,the number of degenerate levels available increases rapidly with J. The total relative population at an energy E_J will plainly be:

Population $\propto$ (2J+1)exp($-E_J$/kT)   …………………………………………………(15)

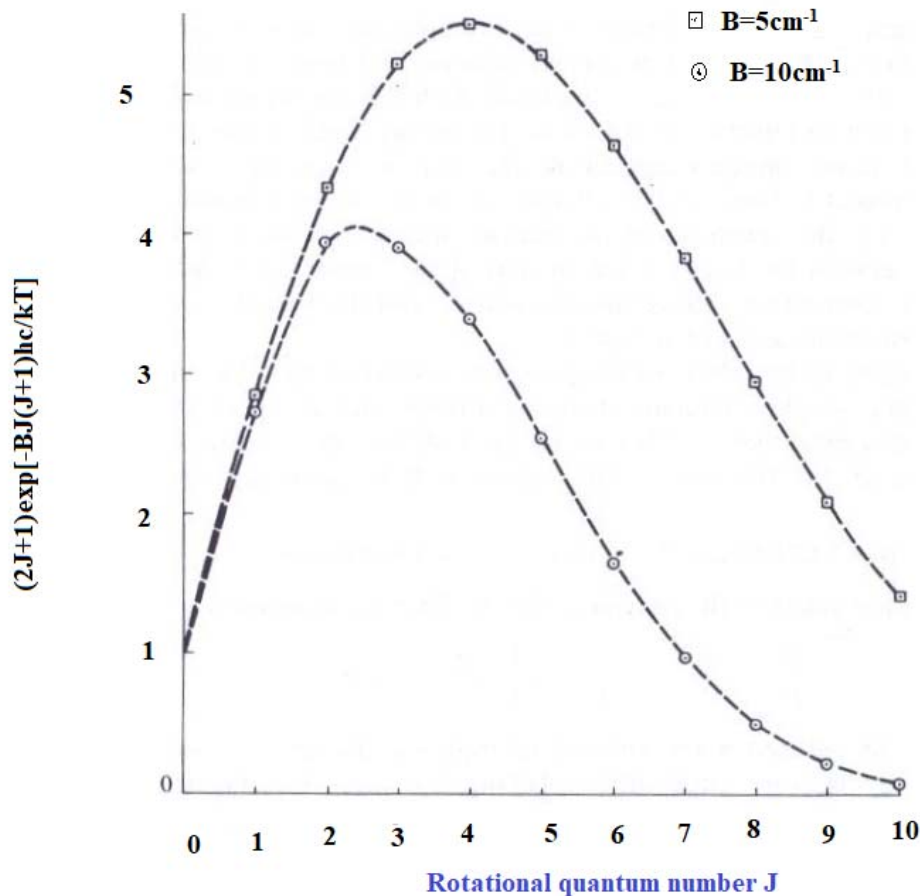# Rotational Spectroscopy

Figure 9: The relative populations, including degeneracy of the rotational energy levels of a diatomic molecule.

When this is plotted against J the points fall on a curve of the type shown in Figure 9, indicating that the population rises to maximum and then diminishes. Differentiation of Eq. (15) shows that the population is maximum at the nearest integral J value to :

Maximum population:

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$$\frac{d\,(\text{Population})}{dJ} = \frac{d}{dJ}\left\{A(2J+1)e^{\frac{-BhcJ(J+1)}{kT}}\right\}$$

$$= A.\,e^{\frac{-BhcJ(J+1)}{kT}}\,2 + A\,(2J+1)(-1)\frac{Bhc}{kT}\,e^{\frac{-BhcJ(J+1)}{kT}}\,(2J+1)$$

$$= A.\,e^{\frac{-BhcJ(J+1)}{kT}}\left\{2-(2J+1)^2\,\frac{Bhc}{kT}\right\}$$

At the maximum,

$$A.\,e^{\frac{-BhcJ(J+1)}{kT}}\left\{2-(2J+1)^2\,\frac{Bhc}{kT}\right\} = 0$$

$$\left\{2-(2J_{max}+1)^2\,\frac{Bhc}{kT}\right\} = 0$$

$$(2J_{max}+1)^2\,\frac{Bhc}{kT} = 2$$

$$(2J_{max}+1)^2 = \frac{2kT}{Bhc}$$

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

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

or, $$J_{max} = \sqrt{\frac{kT}{2\,Bhc}} - \frac{1}{2}$$

………………………………..(16)

We have seen that line intensities are directly proportional to the populations of the rotational level; hence it is plain that transitions between levels with very low or very high J values will have small intensities while the intensity will be a maximum at or near the J value by Eq.(16)

Dr.Sandip Kumar Rajak|Dumkal College