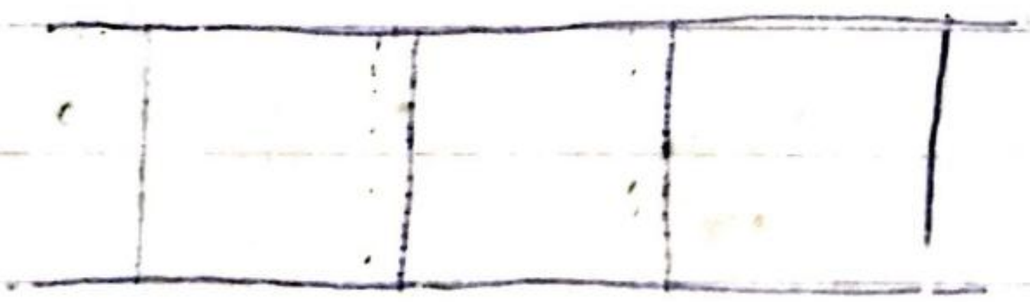
P.G. Sem. III rd
core course X

Unit-I; Effect of Isotopic Substitution

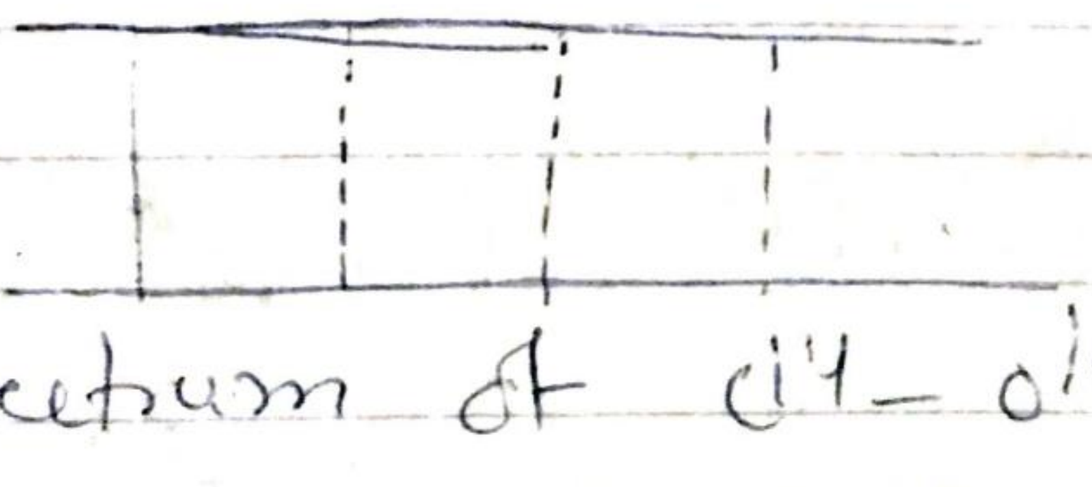
In case of heavier species reduced mass (μ) increases and therefore rotational constant $\overline{B}$ decreases.

$$\overline{B} = \frac{h}{8\pi^2 I c} = \frac{h}{8\pi^2 \mu r^2 c}$$

Thus, the spectrum of heavier species e.g., C^{14} — O^{16} shows a smaller separation between the lines than the separation of lighter species e.g., C^{12} — O^{16}. This decrease in separation between the lines can be used to calculate exact atomic weight



Spectrum of $C^{12} - O^{16}$



Spectrum of $C^{14} - O^{16}$.

Intensities of Spectral lines :-

- Factors determining the intensities of — Spectral lines are —

(1) ΔJ value → Since probability of all transitions between rotational energy levels is the same, the line intensities is independent of this factor.

(2) Population and degeneracy

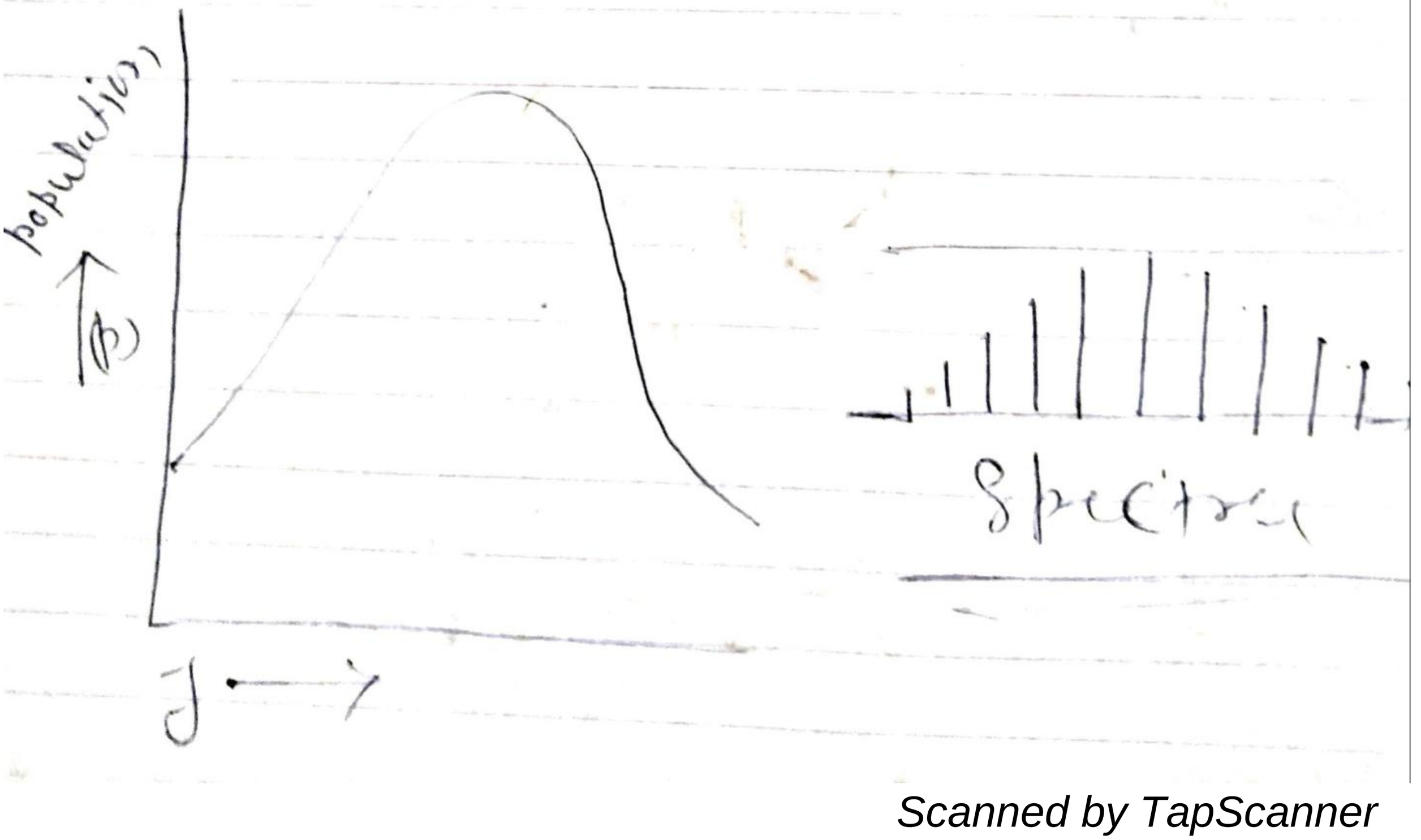
The molecular population of each rotational level decreases exponentially, number of degenerate rotational level $(2J+1)$ increases rapidly with J.

The population at any energy level is given by —

$$\text{population } (p) \propto (2J+1)\, e^{-E_J/kT}$$

$$\propto (2J+1)\, e^{-\frac{Bhc\,J(J+1)}{kT}}$$

- the exponential term decreases slowly and then much more rapidly as J increases. Thus, at smaller value of J, the (2J+1) predominates, and at higher value of J it is the exponential term which predominates. As a result, the population of rotational levels rises to a maximum and then diminishes. Therefore transition between levels with very low or very high J values will have small intensities while the intensity will be the maximum, somewhere else in the middle.



Q. Rotational lines in Cl_2 — O_2 are more closely spaced than in Cl^2 — O_2. Explain.

Ans. Separation of rotational spectral lines in TMI spectrum depends on rotational constant B.

$$\overline{B} = \frac{h}{8\pi^2 \mu r^2 c}$$

In case of heavier species reduced mass (μ) increases and therefore rotational constant B decreases.

Thus, the spectrum of heavier species, e.g. Cl_2 — O_2 show a smaller separation between the lines than the separation of lighter species e.g., Cl^2 — O^2. This decreased in separation between the lines can be used to calculate the exact atomic weight.

Q Potational energy level of HCl are widely spaced compare to most other molecules. Explain

or

Potational transitions of HCl absorbs at higher frequency.

Question

Separation between successive rotational lines and hence B value decrease steadily with increasing J. Explain.

Ans As J increase, centrifugal force increases and bond is Stratched. Bond length. thus, increase and

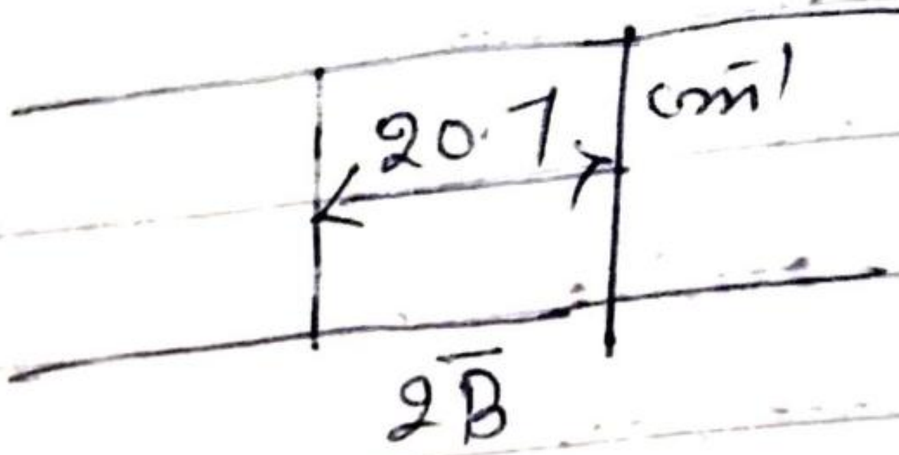
$$\overline{B} = \frac{h}{8\pi^2 \mu r^2 c}$$ decreases.

so that Separation between the lines $2\overline{B}$ decreases.

Sum

(1) Rotational lines of HCl are equally separated by 20.7 cm^{-1}. Calculate the internuclear bond length.

Soln



$$2\bar{B} = 20.7 \text{ cm}^{-1}$$

$$\therefore \bar{B} = \frac{20.7}{2} = 10.35 \text{ cm}^{-1}$$

$$I = \frac{h}{8\pi^2 \bar{B} C}$$

$$= \frac{6.625 \times 10^{-27} \text{ erg.sec}}{8 \times (3.14)^2 \times 10.35 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm}}$$

$$= 2.7 \times 10^{-40} \text{ gm cm}^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} / N$$

$$= \frac{1.008 \times 35.46}{(1.008 + 35.46) \times 6.023 \times 10^{23}}$$

$$= 1.627 \times 10^{-24} \text{ molecule}$$

$$\therefore r = \sqrt{I/\mu}$$

$$= \sqrt{\frac{2.7 \times 10^{-40}}{1.627 \times 10^{-24}}}$$

$$= 1.29 \times 10^{-8} \text{ cm}$$

$$= 1.29 \text{ A}^\circ$$

Q The first line of PMR spectra of CO occurs at frequency of 115271 megacycle second. calculate internuclear distance.

Sol

$$\nu = 115271 \text{ megacycle/sec}$$

$$= 115271 \times 10^6 \text{ cycle/sec}$$

$$\therefore 2B = 115271 \times 10^6 \text{ cycle/sec}$$

$$\therefore B = \frac{11597.1 \times 10^6}{2}$$

$$= 51635 \times 10^6$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} / N \text{ molecule}$$

$$= \frac{12 \times 16}{(12+16) \times 6.023 \times 10^{23}} \text{ molecule}$$

$$= 1.1385 \times 10^{-23} \text{ molecule}$$

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

$$= \frac{6.625 \times 10^{-27}}{8 \times (3.14)^2 \times 51635 \times 10^6}$$

$$= 14.57 \times 10^{-4} \text{ gm cm}^2$$

$$\therefore r = \sqrt{I/\mu}$$

$$= \sqrt{\frac{14.57}{1.1385 \times 10^{-23}}}$$

$$= 1.13 \text{ Å}$$