ENGINEERING CHEMISTRY

Department of Science and Humanities

Class content:

- ***The allowed rotational energies of a rigid diatomic molecule***
- ***Selection rule***
- ***Rotational spectrum***

The energy expressed in spectroscopic units(cm^{-1}) is given by :

$$\varepsilon_J = \frac{h}{8\pi^2 Ic} J(J+1) cm^{-1}$$

which can be written as

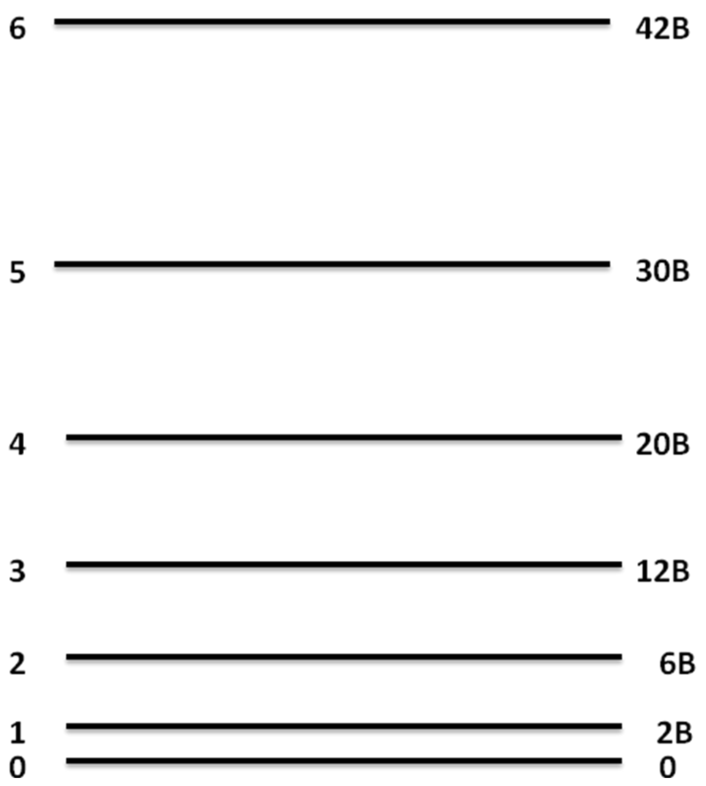
$$\varepsilon_J = BJ(J+1) cm^{-1}$$

where $B = \frac{h}{8\pi^2 Ic} cm^{-1}$

B is known as the **rotational constant**

Substituting for values of J = 0,1,2,3..., we can get the energies for the rotational levels

J	ε_J
0	0
1	2B
2	6B
3	12B



Source:Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

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The **selection rules** for rigid rotor model obtained after solving Schrodinger equation is :

- **Gross selection rule – molecule should possess permanent dipole moment**
- **Δ J = ± 1**

Since $\varepsilon_J = BJ(J+1)cm^{-1}$

For rotational transition of a molecule from level J → J +1 , the energy absorbed is given by $\Delta\varepsilon_{J\rightarrow(J+1)} = \bar{\upsilon} = 2B(J+1)cm^{-1}$

Substituting for values for J = 0,1,2,3....

J	$\Delta\varepsilon_{(J\rightarrow J+1)}$
0	$2B\ cm^{-1}$
1	$4B\ cm^{-1}$
2	$6B\ cm^{-1}$

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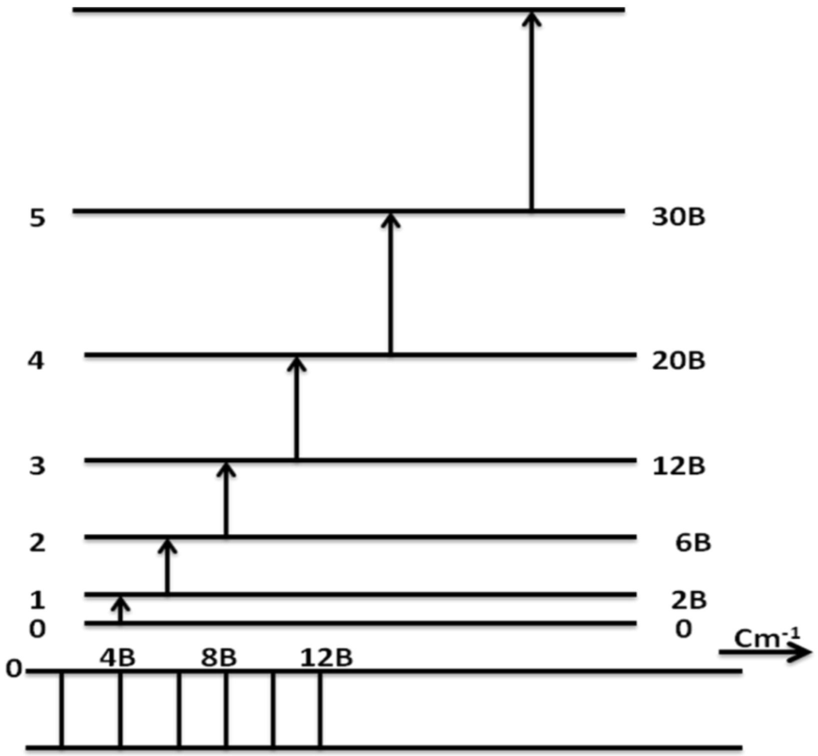
Rotational energy levels and spectrum

J	$\Delta\varepsilon_{(J\rightarrow J+1)}$
0	2B cm^{-1}
1	4B cm^{-1}
2	6B cm^{-1}
3	8B cm^{-1}
4	10B cm^{-1}



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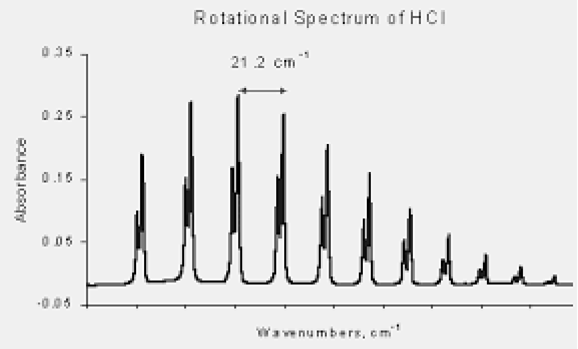
Information obtained from the rotational spectrum



Source:http://www.physics.dcu.ie/~be/Ps415/Rotational1.pdf

- The **first line in the spectrum** appears at 2B cm^{-1} and the **distance between any two consecutive lines** is constant and is equal to 2B cm^{-1} . We can get value of 'B' from the spectrum and calculate ,I, the moment of inertia using the expression

$$B = \frac{h}{8\pi^2 Ic} cm^{-1}$$

Since $\mathbf{I = \mu r_o^2}$, r_o can be determined ; $r_o = \sqrt{\frac{I}{\mu}}$

$\mathbf{r_o}$ is the **bond length** of the molecule

- The spectrum also reveals that **some higher rotational levels are also populated at room temperature**

THANK YOU

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