EINSTEIN COEFFICIENTS & THEIR RELATIONS

Introduction:

- Einstein Coefficients are mathematical quantities that describe the probability of a photon being absorbed or emitted by an electron (or atom or molecule).
- They are named after Albert Einstein, who proposed them in 1916.

Interaction of Light (Radiation) with Matter:



- Let us consider that as light passes through the medium M, three quantum processes will occur, namely Induced Absorption, Spontaneous Emission and Stimulated Emission.
- Let N₁ and N₂ be the no. of electrons per unit volume, with the energies E₁ and E₂ respectively, in ground and excited states. And E_v be the energy density of incident photons at frequency v.

Induced Absorption:

- During this absorption, electrons in the ground state are raised to the excited state due to the absorption of an incident photon by an atom.
- The rate of induced absorption depends on the number of electrons in the ground state (N₁) and the energy density of the incident photon (E_ν).
- Rate of induced absorption $\propto N_1$ and Rate of induced absorption $\propto E_{\nu}$
- Hence Rate of induced absorption $\propto N_1 E_{\nu}$
- Therefore, the Rate of induced absorption = $B_{12}N_1E_{\nu}$ ------(1)
- where: B₁₂ is the Einstein coefficient of induced absorption constant.

Spontaneous Emission:

- During this emission, an electron in the excited state returns to its ground state by emitting a photon of energy E, without any external agency.
- Therefore the rate of spontaneous emission depends only on the number of electrons in the excited state (N₂).
- Rate of spontaneous emission $\propto N_2$

- Therefore, the Rate of spontaneous emission = $A_{21}N_2$ ------(2)
- where: A₂₁ = Einstein coefficient of spontaneous emission constant

Stimulated Emission:

- During this emission, all the electrons in the excited state are transferred to the ground state and emit photon energy by the interaction of radiation or photon or light.
- Therefore, the rate of stimulated emission depends on the number of electrons in the metastable state (N₂) and also on the energy density of the incident photon.
- Rate of stimulated emission $\propto N_2 E_{\nu}$
- Therefore, the Rate of stimulated emission = B₂₁ N₂ E_ν ------ (3)
- where: B₂₁ = Einstein coefficient of stimulated emission constant

At Thermal Equilibrium:

- Rate of induced absorption = Rate of spontaneous emission + Rate of stimulated emission.
- Equations:

 $B_{12} N_1 E_{\nu} = A_{21} N_2 + B_{21} N_2 E_{\nu}$

 $B_{12} N_1 E_{\nu} - B_{21} N_2 E_{\nu} = A_{21} N_2$

 $[B_{12} N_1 - B_{21} N_2] E_{\nu} = A_{21} N_2$

$$E_{\nu} = A_{21}N_2 / (B_{12}N_1 - B_{21}N_2)$$

=
$$(A_{21}N_2/B_{21}N_2)/[B_{12}N_1/B_{21}N_2-1]$$

$$E_{\nu} = (A_{21} / B_{21}) / [B_{12}N_1 / B_{21}N_2 - 1]$$

OR

$$E_{\nu} = (A_{21} / B_{21}) / [(B_{12} / B_{21}) (N_1 / N_2) - 1] ------ (4)$$

From Boltzmann's Law: $N = N_0 e^{E/kT}$

 $N_1 = N_o e^{E1/kT}$ and $N2 = No e^{E2/kT}$

$$N_{1} / N_{2} = N_{o} e^{E1/kT} / No e^{E2/kT}$$
$$= e^{E1/kT} / e^{E2/kT}$$
$$= e^{E1/kT - E2/kT} = e^{(E1 - E2)/kT}$$
$$N_{1} / N_{2} = e^{h\nu/kT} - \dots (5) \text{ (since } E_{1} - E_{2} = h\nu)$$

This equation is as called Boltzmann factor

From (4) & (5)

$$E_{\nu} = (A_{21} / B_{21}) / [(B_{12} / B_{21}) e^{h\nu/kT} - 1]$$

$$E_{\nu} = (A_{21} / B_{21}) \{ 1 / [(B_{12} / B_{21}) (e^{h\nu/kT} - 1)] \} ------(6)$$

From Planck's radiation law, the energy density

$$E_{\nu} = 8\pi h \nu^3 / C^3 [1 / 1. (e^{h\nu/kT} - 1)]$$
 ------ (7)

Comparison of Equations (6) & (7)

$$A_{21} / B_{21} = 8\pi h v^3 / C^3 \Rightarrow A_{21} / B_{21} \propto v^3$$
 ------(8)

$$B_{12}/B_{21} = 1 \implies B_{12} = B_{21}$$
 ----- (9)

Conclusions:

- From Equation (8): The ratio of coefficients of spontaneous to stimulated emission is proportional to the third power of the frequency of radiation.
- **From Equation (9):** When an electron with two energy levels is placed in a radiation field, the probability of an upward transition (absorption) is equal to the probability of a downward transition (stimulated emission).

Observations:

- The probability of spontaneous emission rapidly increases with frequency.
- This makes it difficult to achieve laser action in higher frequency ranges, such as X-rays.