2.8 Einstein's A and B Coefficients (Derivation)

Einstein's theory of absorption and emission of light by an atom is based on Planck's theory of radiation. Also under thermal equilibrium, the population of energy levels obey the Boltzmann's distribution law.

Under thermal equilibrium,

$$\text{Rate of absorption} = \text{Rate of emission} \quad \ldots\ldots (1)$$

The rate of absorption R_{12} (SA) is proportional to the energy density of incident radiation (ρ) and number of atoms in the ground state (N_1)

$$R_{12}\,(SA) \quad \alpha \quad \rho N_1$$

$$R_{12}\,(SA) = B_{12}\,\rho\, N_1 \ \ldots\ldots\ldots (2)$$

Where, B_{12} is a constant which gives the probability of absorption transition per unit time.

The rate of spontaneous emission R_{21}(Sp.E) is proportional to the population of the higher energy level N_2. Therefore, we have,

$$R_{21}(Sp.E) = A_{21}N_2 \quad \ldots\ldots\ldots.(3)$$

Where, A_{21} is the proportionality constant known as the probability of spontaneous emission per unit time.

The rate of stimulated emission R_{21} (St.E) is proportional to the population of the higher energy level N_2 and energy density of incident radiation (ρ). Therefore, we have,

$$R_{21}\,(St.E) \quad \alpha \quad \rho N_2$$

$$R_{21}\,(St.E) = B_{21}\rho N_2 \ldots\ldots\ldots\ldots.(4)$$

Where, B_{21} is the proportionality constant known as the probability of stimulated emission of radiation per unit time.

The coefficients B_{12}, A_{21} and B_{21} in the expressions for the rate of absorption and emission are called the Einstein's coefficients.

Substitute equations (2), (3) and (4) in equation (1), we get,

$$B_{12}\,\rho N_1 = A_{21}N_2 + B_{21}\rho N_2$$

$$\rho\,[B_{12}N_1 - B_{21}N_2] = A_{21}N_2$$

$$\rho = \frac{A21N2}{B12N1 - B21N2}$$

(or)

$$\rho = \frac{A21}{B12\frac{N1}{N2} - B21} \text{----------------------(5)}$$

According to Boltzmann distribution law, the number of atoms N_1 in energy states E_1 and E_2 in thermal equilibrium at temperature T is given by,

$$N1 = N0\ e^{-E1/KBT}$$

$$N2 = N0\ e^{-E2/KBT}$$

$$\frac{N1}{N2} = e^{\frac{E2-E1}{KBT}}$$

since $E2 - E1 = h\nu$, we have

$$\frac{N1}{N2} = e^{\frac{h\nu}{KBT}} \text{----------------------(6)}$$

Substituting equation (6) in equation (5), we get

$$\rho = \frac{A21}{B12(e^{\frac{h\nu}{KBT}}) - B21}$$

(or)

$$\rho = \frac{A21}{B21} \frac{1}{\frac{B12}{B21}(e^{\frac{h\nu}{KBT}}) - 1} \text{---------------(7)}$$

According to Planck's theory of black body radiation is

$$\rho = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{KBT}} - 1} \text{----------------------(8)}$$

Comparing the equations (7) and (8)

$$B_{12} = B_{21} \text{---------------------(9)}$$

and

$$\frac{A21}{B21} = \frac{8\pi h v^3}{c^3} \text{-------------------------} (10)$$

Equation (10) shows that the Einstein's Coefficients A and B.

i) $B_{12} = B_{21}$, the probability of stimulated emission is the same as that of absorption.

ii) $A_{21}/B_{21} \propto v^3$, the ratio of spontaneous emission and stimulated emission is proportional to v^3. It means that the probability of spontaneous emission dominates over induced emission more and more as the energy difference between the two states increases.

ROHINI COLLEGE OF ENGINEERING AND TECHNOLOGY
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