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Einstein Coefficients

Let, us Consider an assembly of atoms which is in thermal equilibrium with radiation of frequency ν and spectral energy density $u(\nu)^*$ at temperature T. Let, N_1 and N_2 be the number of atoms per unit volume in energy states 1 and 2 with energies E_1 and E_2 respectively, at any instant. An atom in the lower energy state, E_1 Can absorb radiation and get excited to the state E_2.

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The probability rate of occurrence of the absorption transition $1 \rightarrow 2$ would be proportional to N_1 and also to $u(\nu)$. Thus, the number of absorption transitions per unit time per unit volume Can be written as;

$$N_1 B_{12} u(\nu)$$

The proportionality Constant B_{12} is a characteristic of energy states 1, and 2, and is known as Einstein's 'B' Coefficient of absorption of radiation.

Let us now consider the emission transitions at frequency ν when an atom de-excites from energy state E_2 to E_1.

The probability rate of spontaneous emission $2 \rightarrow 1$ is determined only by the properties of the states 2 and 1, and is proportional to the number of atoms N_2 in the energy state 2. Thus, the no. of spontaneous emission transitions per unit time, per unit volume can be written as,

$$N_2 A_{21}$$

Again, the proportionality constant A_{21}, depends on the properties of energy states 2 and 1, and is known as Einstein's 'A' coefficient of spontaneous emission of radiation.

Finally the probability rate of stimulated emission transition $2 \rightarrow 1$ is proportional to the energy density $u(\nu)$ of the stimulating radiation. Thus, the number of stimulated emission transitions per unit time per unit valume can be written as,

$$N_2 B_{21} u(\nu)$$

where, B_{21} is 'Einstein's 'B' Coefficient of stimulated emission of radiation.

At thermal equilibrium the number of upward transitions $1 \to 2$ should be equal to the number of downward transitions $2 \to 1$ i.e.

$$N_1 B_{12} u(\nu) = N_2 [A_{21} + B_{21} u(\nu)] \quad \text{—— (1)}$$

or,
$$u(\nu) = \frac{N_2 \cdot A_{21}}{N_1 \cdot B_{12} - N_2 \cdot B_{21}}$$

$$u(\nu) = \frac{A_{21}}{B_{21}} \cdot \frac{1}{\frac{N_1}{N_2}\left(\frac{B_{12}}{B_{21}}\right) - 1} \quad \text{—— (2)}$$

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The equilibrium distribution of atoms among different energy states at temperature T is given by Boltzmann's law,

$$\frac{N_2}{N_1} = \frac{e^{-E_2/KT}}{e^{-E_1/KT}}$$

or,
$$\frac{N_1}{N_2} = e^{(E_2 - E_1)/KT} = e^{h\nu/KT}$$

because, $\nu = \frac{E_2 - E_1}{h}$, K is Boltzmann's const.

Using eqⁿ (2),

$$u(\nu) = \frac{A_{21}}{B_{21}} \cdot \frac{1}{e^{h\nu/kT}\left(\frac{B_{12}}{B_{21}}\right) - 1} \quad \text{--- (3)}$$

This is a formula for the spectral energy density of radiation, It must be consistent with black body radiation. Hence, comparing it with Planck radiation formula,

$$u(\nu) = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1}$$

We get,

$$\boxed{\frac{B_{12}}{B_{21}} = 1} \quad \text{--- (4)}$$

and,

$$\boxed{\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}} \quad \text{--- (5)}$$

These, results were obtained by Einstein in 1917, and that is why the coefficients A_{21}, B_{12} and B_{21}

are called Einstein's A and B Coefficients.

from eq^n (4), we conclude, In presence of electromagnetic radiation the probabilities of stimulated absorption and stimulated emission in atom are equal

from eq^n (5) we see that ~~the~~ larger the energy difference between the two states ($E_2 - E_1 = h\nu$), the much more likely is spontaneous emission compared to stimulated emission.