EINSTEIN'S COEFFICIENTS

In the presence of radiation of appropriate frequency, in a system having a large number of atoms, all the three types of transitions- absorption, spontaneous emission and stimulated emission- occur simultaneously. For simplicity, let us consider a system having levels 1 and 2 as shown in the fig.6. Let their energies be E_1 and E_2 and E_2 - E_1 be hν.

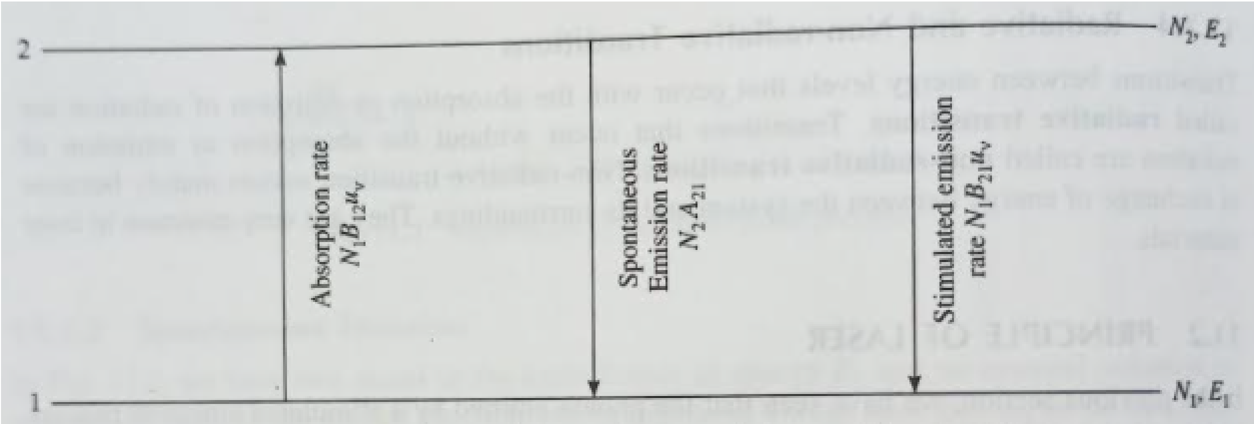

Fig.6 Emission and absorption rates between states 1 and 2

Let the total number of atoms be N_0. Under equilibrium conditions, let N_1 atoms be in state 1 and N_2 atoms be in the state. By Boltzman distribution, we get

$$N_1 = N_0\, e^{-\frac{E_1}{kT}} \quad \text{and} \quad N_2 = N_0\, e^{-\frac{E_2}{kT}} \qquad \text{(1)}$$

$$\frac{N_1}{N_2} = e^{\frac{(E_2-E_1)}{kT}} = e^{\frac{h\nu}{kT}} \qquad \text{(2)}$$

Let this system of atoms be in equilibrium with electromagnetic radiation of energy hν and energy density u_ν. The rate of absorption is proportional to the density of radiation u_ν and the number of atoms N_1 present in the lower state. That is, the

$$\text{Rate of absorption} = B_{12}\, N_1\, u_\nu \qquad \text{(3)}$$

where B_{12} is the constant of proportionality, called the Einstein's coefficient for absorption and it can be shown that B_{12} is simply the probability per unit time for absorption.

Next, let us consider transitions from state 2 to state 1. Atoms in state 2 can come to state 1 both by spontaneous and stimulated emissions. The spontaneous emission rate depends only on the number of atoms N_2 in state 2.

$$\text{Rate of spontaneous emission} = A_{21}\, N_2 \qquad \text{(4)}$$

Where the constant of proportionality A_{21}, called Einstein's coefficient for spontaneous emission represents the probability per unit time for spontaneous emission. The stimulated emission rate depends on the energy density u_ν of the radiation and the number of atoms N_2 in state 2. Hence,

$$\text{Rate of stimulated emission} = B_{21}\, N_2\, u_\nu \qquad \text{(5)}$$

where B_{21} is the Einstein's coefficient for stimulated emission.

When the system is in equilibrium, the rate of absorption from state 1 to 2 must be equal to the rate of emissions from state 2 to 1. That is,

$$B_{12}\, N_1\, u_\nu = B_{21}\, N_2\, u_\nu + A_{21}\, N_2 \qquad \text{(6)}$$

$$u_\nu B_{21} N_2 \left(\frac{B_{12} N_1}{B_{21} N_2} - 1 \right) = A_{21} N_2$$

$$u_\nu = \frac{A_{21}}{B_{21}\left(\frac{B_{12} N_1}{B_{21} N_2} - 1 \right)} \quad \text{——— (7)}$$

Substituting the value of N_1/N_2 from equation (2), we get

$$u_\nu = \frac{A_{21}}{B_{21}\left(\frac{B_{12}}{B_{21}} e^{\frac{h\nu}{kT}} - 1 \right)} \quad \text{——— (8)}$$

From Planck's radiation law, we have

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \quad \text{——— (9)}$$

Comparing equations (8) and (9), Einstein guessed that

$$B_{12} = B_{21} = B \quad \text{——— (10)}$$

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} \quad \text{——— (11)}$$

Equations (10) and (11) are called **Einstein's relations** and the coefficients are called **Einstein's A and B coefficients**. Equation (10) gives the important result that the probability for absorption from state 1 to 2 is equal to the probability for stimulated emission from state 2 to 1. From equation (11) it is evident that the ratio of spontaneous to stimulated radiation is proportional to v^3. It means that the probability of spontaneous emission becomes more and more dominant over stimulated emission as the energy difference between the two states increases.

Since $B_{12} = B_{21}$ we can rewrite equation (8) as

$$\frac{A}{Bu_\nu} = e^{\frac{h\nu}{kT}} - 1 \quad \text{——— (12)}$$

From equations (4), (5) and (12), we have

$$\frac{\text{Spontaneous emission rate}}{\text{Stimulated emission rate}} = \frac{A}{Bu_\nu} = e^{\frac{h\nu}{kT}} - 1 \quad \text{——— (13)}$$

If hν >> kT, $e^{h\nu/kT} - 1$ will be very large and spontaneous emission far exceeds stimulated emission. At ordinary temperature this happens in the visible region. Stimulated emission becomes important when hν = kT and may dominate when hν<< kT, which happens in the microwave region.

POPULATION INVERSION

Let us consider an energy state E having N atoms per unit volume. This number N is called population and is given by Boltzman's equation

$$N = N_0\, e^{-E/k_B T}$$

Where N_0 is the population of ground state with E=0, k_B is the Boltzman's constant and T is the absolute temperature. From the above equation it is clear that the population is maximum in the ground state and decreases exponentially as we go to a higher energy state. If N_1 is the population in the energy state E_1 and N_2 is the population in energy state E_2, then

$$N_1 = N_0\, e^{-E_1/k_B T} \quad \text{and} \quad N_2 = N_0\, e^{-E_2/k_B T}$$

$$\frac{N_2}{N_1} = \frac{e^{-E_2/k_B T}}{e^{-E_1/k_B T}} \quad \text{— (1)} \qquad \text{or} \qquad N_2 = N_1\, e^{-(E_2-E_1)/k_B T} \quad \text{— (2)}$$

As $E_2 > E_1$; $N_2 < N_1$, therefore if an electromagnetic radiation is incident on the system at the thermal equilibrium condition, then there is net absorption of radiation. Usually population decreases with the increase of the energy of the state. But it is observed that for emission processes and for laser action, it is essential that the number of excited atoms must be more than the atoms in the ground state. In other words, the number of atoms in higher energy level, E_2 must be greater than the number of atoms in the lower energy state, E_1. The process by which this condition is achieved is known as the process of population inversion. From equation (2) it is clear that $N_2 > N_1$ only when T assumes negative value and that is why the state of population inversion is also known as the negative temperature state. Here it should be clearly understood that the negative temperature is not a physical quantity but it is a convenient mathematical expression signifying the non-equilibrium state of the system.

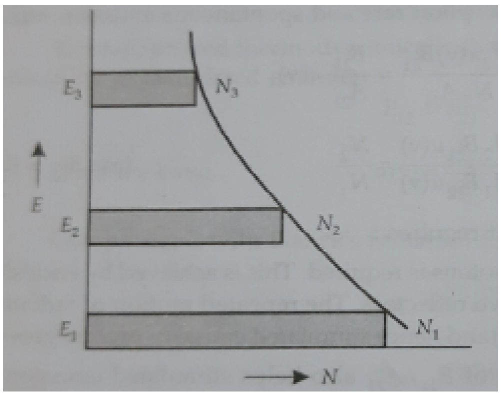

Fig.7 Normal population of a system (N_1>N_2)

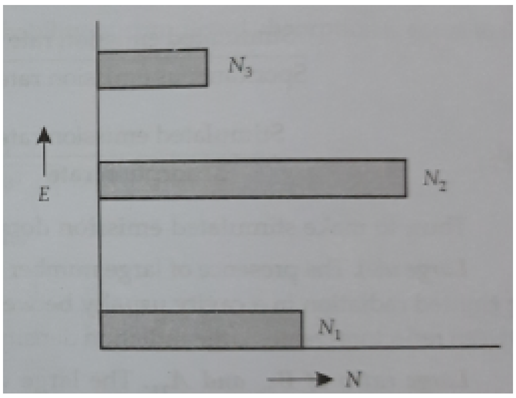

Fig.8 Inverted population of a system (N_2>N_1)

If N_1, N_2 and N_3 be the populations in energy states E_1, E_2 and E_3 respectively such that $E_1<E_2<E_3$, then N1>N2>N3. This situation is shown in Fig.7. If the process of stimulated emission dominates over the process of spontaneous emission, then it may possible that $N_2>N_1$. If this happens, the state is called the state of population inversion. To achieve population inversion the external energy is supplied to excite the atoms of the system and a system in which population inversion is achieved is called active system.