Einstein A & B Coefficients

The Einstein relations

Einstein showed that the A and B coefficients are related.

In equilibrium, the rate of change of upper and lower populations must be 0, i.e.

$$\frac{dN_2}{dt} = \frac{dN_1}{dt} = 0$$

$$\frac{dN_2}{dt}$$ = spontaneous emission 'flow'
+ stimulated emission 'flow'
- stimulated absorption 'flow'

$$\frac{dN_2}{dt} = A_2 N_2 + B_{21}\, \rho_\nu N_2 - B_{12}\, \rho_\nu N_1 = 0$$

likewise,

$$\frac{dN_1}{dt} = - A_2 N_2 - B_{21} \rho_\nu N_2 + B_{12} \rho_\nu N_1 = 0 \qquad [2]$$

From [1]:

$$B_{12} \rho_\nu N_1 = A_2 N_2 + B_{21} \rho_\nu N_2$$

Re-arrange for ρ_ν

$$\rho_\nu = \frac{A_2 N_2}{B_{12} N_1 - B_{21} N_2}$$

or

$$\rho_\nu = \frac{\frac{A_2}{B_{21}}}{\frac{B_{12}}{B_{21}} \frac{N_1}{N_2} - 1} \qquad [3]$$

However, in thermal equilibrium, Boltzmann statistics will tell us the relative population of state 1 and state 2

$$\frac{N_1}{N_2} = \frac{g_1}{g_2} \exp((E_2 - E_1)/kT)$$

where

g_1 = degeneracy of state 1
g_2 = degeneracy of state 2
k = Boltzmann's constant
T = temperature in Kelvin

In our case

$$h\nu = E_2 - E_1$$

Therefore

$$\frac{N_1}{N_2} = \frac{g_1}{g_2} \exp(-h\nu/kT) \qquad [4]$$

sub into equ. [3]

$$\rho_\nu = \frac{\frac{A_2}{B_{21}}}{\left(\frac{g_1 B_{12}}{g_2 B_{21}} \exp(h\nu/kT)\right) - 1} \qquad [5]$$

Since our system is in thermal equilibrium, ρ_ν must be identical the black body emission , i.e.

$$\rho_\nu = \frac{8\pi n^3 h\nu^3}{c^3} \left(\frac{1}{\exp(h\nu/kT) - 1}\right) \qquad [6]$$

Equating equs. [5] and [6] we get the Einstein relations:

$$g_1 B_{12} = g_2 B_{21} \qquad [7]$$

and

$$\frac{A_2}{B_{21}} = \frac{8\pi n^3 h\nu^3}{c^3} \qquad [8]$$

The ratio of the spontaneous to stimulated emission is given by:

$$\text{Ratio} = \frac{\text{spont.}}{\text{stim.}} = \frac{A_2}{\rho_\nu B_{21}} \qquad [9]$$

Re-arranging equ. [7], to get:

$$\text{Ratio} = \left(\frac{g_1B_{12}}{g_2B_{21}}\exp(h\nu/kT)\right) - 1)$$

but $g_1B_{12} = g_2B_{21}$, therefore:

$$\text{Ratio} = \exp(h\nu/kT) - 1$$

e.g. electric light bulb, $T = 2000K$, $\nu = 5 \times 10^{14}$ Hz

$$\text{Ratio} = 1.5 \times 10^{5}$$