

# 300(5) (292(5)) : Calculation of Emission Coefficient

Consider the density of states :

$$\rho(\omega) = \frac{1}{V} \frac{dU}{d\omega} \quad - (1)$$

where  $U$  is the energy of electromagnetic radiation in a volume  $V$  and  $\omega$  denotes angular frequency. The intensity for polychromatic radiation is defined as

$$I = c\rho \quad - (2)$$

in joules per square metre. From note 300(4):

$$\frac{d\rho}{dt} = \frac{dI}{dl} \quad - (3)$$

where  $l$  is the path length or distance traversed by the radiation in a given sample of material.

For absorption :

$$\frac{dI}{dl} = - \frac{n(\omega)}{V} \frac{h\omega}{c} B_{if} I \quad - (4)$$

so

$$\frac{dI}{I} = - \alpha dl \quad - (5)$$

which is the Beer Lambert law for absorption.

Here, the absorption coefficient is :

$$\alpha(\omega) = \left( \frac{n(\omega)}{V} \right) \left( \frac{h\omega}{c} \right) B_{if} \quad - (6)$$

2) In the definition of the power absorption coefficient, the number of molecules per unit volume able to absorb light in the range  $\omega$  to  $\omega + d\omega$  is  $n(\omega)d\omega/V$ , and the total number of absorbing molecules in a volume  $V$  is:

$$\frac{N}{V} = \int \frac{n(\omega)}{V} d\omega \quad (7)$$

so  $N = \int n(\omega) d\omega \quad (8)$   
 and  $n(\omega)$  has the units of inverse frequency or  $\text{time}^{-1}$ . Each photon in the beam of light traversing the sample has an energy  $\hbar\omega$ . The rate at which a molecule absorbs a photon (in inverse seconds or  $\text{s}^{-1}$ ) is:

$$W_{if} = B_{if} \rho \quad (9)$$

where  $W_{if}$  is Einstein's coefficient of stimulated absorption. For absorption the rate of change of energy density per unit volume in the range  $\omega$  to  $\omega + d\omega$  is:

$$\frac{1}{V} \frac{dU}{dt} = -\hbar\omega W_{if} \frac{n(\omega)}{V} d\omega \quad (10)$$

so

$$\frac{d\rho}{dt} = -\frac{n(\omega)}{V} \hbar\omega B_{if} \rho \quad (11)$$

Eqs. (3) and (11) lead to eq. (4).

3) However for emission, the sign of eq. (11) is changed because in emission, nucleus emits photons.  
Stimulated emission is defined by:

$$W_{ji} = B_{ji} \rho \quad (12)$$

where:

$$B_{ij} = B_{ji} \quad (13)$$

However, thermal equilibrium between radiation and matter requires consideration of spontaneous emission, defined by:

$$W_{ji} = A_{ji} \quad (14)$$

where  $A_{ji}$  is the Einstein A coefficient. The total rate of emission is:

$$W_{ji} = B_{ji} \rho + A_{ji} \quad (15)$$

Consider a system of molecules in thermal equilibrium with radiation. There are  $N_i$  molecules in state  $|i\rangle$  and  $N_j$  molecules in state  $|j\rangle$ . The total rate of absorption by all molecules is  $N_i W_{ij}$ , and the total rate of emission by all molecules is  $N_j W_{ji}$ . At equilibrium these rates are equal:

$$N_j (A_{ji} + B_{ji} \rho) = N_i B_{ij} \rho \quad (16)$$

4) At thermal equilibrium at temperature  $T$ :

$$\frac{N_i}{N_g} = \exp\left(\frac{\epsilon_{gi}}{kT}\right) \quad (17)$$

which is the Boltzmann distribution, where  $k$  is Boltzmann's constant. So:

$$\frac{A_{gi}}{B_{gi}} = \left(\exp\left(\frac{\epsilon_{gi}}{kT}\right) - 1\right) \rho \quad (18)$$

and:

$$\rho = \left(\frac{A_{gi}}{B_{gi}}\right) \left(\exp\left(\frac{\epsilon_{gi}}{kT}\right) - 1\right)^{-1} \quad (19)$$

However, it is an uncorrected Planck distribution:

$$\rho = \frac{\hbar \omega^3}{\pi^2 c^3} \left(\exp\left(\frac{\hbar \omega}{kT}\right) - 1\right)^{-1} \quad (20)$$

The result (20) is derived from assuming that:

$$\frac{dN}{V} = \frac{\omega^2}{\pi^2 c^3} d\omega \quad (21)$$

and

$$\frac{dU}{V} = \langle E \rangle \frac{dN}{V} \quad (22)$$

where

$$\langle E \rangle = \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{kT}\right) - 1} \quad (23)$$

is the mean energy of a Planck oscillator.

So :

$$\frac{dU}{V} = \frac{\hbar \omega^3 d\omega}{\pi^2 c^3 (e^y - 1)} \quad - (24)$$

where

$$y = \frac{\hbar \omega}{kT} \quad - (25)$$

Therefore :

$$P = \frac{1}{V} \frac{dU}{d\omega} = \frac{\hbar \omega^3}{\pi^2 c^3} (e^y - 1)^{-1} \quad - (26)$$

which is eq. (20).

However the correct eq. (21) is :

$$\begin{aligned} \frac{dN}{V} &= \frac{\omega^2}{\pi^2 c^3} d\omega + \frac{\omega}{\pi^2 c^3} (d\omega)^2 + \frac{(d\omega)^3}{3\pi^2 c^3} \quad - (27) \\ &= \frac{10}{3} \frac{\omega^2}{\pi^2 c^3} d\omega \end{aligned}$$

as shown in Note 29(1). So :

$$P = \frac{10 \hbar \omega^3}{3 \pi^2 c^3} (e^y - 1)^{-1} \quad - (28)$$

and :

$$A_{fi} = \left( \frac{10 \hbar \omega^3}{3 \pi^2 c^3} \right) B_{fi} \quad - (29)$$

The total rate of emission of photons is :

$$b) \quad \bar{W}_{g_i} = B_{g_i} \left( \rho + \frac{10 \hbar \omega^3}{3\pi^2 c^3} \right) - (30)$$

Therefore for emission eq. (ii) becomes :

$$\frac{d\rho}{dt} = \frac{n(\omega)}{\sqrt{V}} \hbar \omega B_{g_i} \left( \rho + \frac{10 \hbar \omega^3}{3\pi^2 c^3} \right) - (31)$$

From eq. (3) and (31):

$$\frac{dI}{d\ell} = \frac{n(\omega)}{\sqrt{V}} \hbar \omega B_{g_i} \left( \rho + \frac{10 \hbar \omega^3}{3\pi^2 c^3} \right) - (32)$$

From eqs. (28) and (32):

$$\frac{10 \hbar \omega^3}{3\pi^2 c^3} = \rho (e^y - 1) - (33)$$

$$\text{So } \frac{dI}{d\ell} = \frac{n(\omega)}{\sqrt{V}} \hbar \omega B_{g_i} \exp\left(\frac{\hbar \omega}{kT}\right) \rho - (34)$$

$$= \frac{n(\omega)}{\sqrt{V}} \frac{\hbar \omega}{c} B_{g_i} \exp\left(\frac{\hbar \omega}{kT}\right) I$$

and

$$\boxed{\frac{dI}{I} = d_e d\ell} - (35)$$

where

$$d_e = \frac{n(\omega)}{V} \frac{\hbar\omega - B_{gi}}{c} g_i \exp\left(\frac{\hbar\omega}{kT}\right) \quad - (36)$$

i) The power emission coefficient.

From eqs. (6), (13) and (36) :

$$d_e = \exp\left(\frac{\hbar\omega}{kT}\right) \alpha(\omega) \quad - (37)$$

From eqs (17) and (37) :

$$d_e = \left(\frac{N_i}{N_g}\right) \alpha(\omega) \quad - (38)$$

The Beer Lambert law for emission is :

$$\frac{I}{I_0} = \exp(-d_e l) \quad - (39)$$

From eqs. (2) and (39) :

$$\frac{I}{I_0} = \exp(-d_e l) \quad - (40)$$

i.e. from eq. (20) :

$$\left(\frac{\omega}{\omega_0}\right)^3 \left(\frac{e^{y_0} - 1}{e^y - 1}\right) = \exp(d_e l) - (41)$$

If

$$\hbar\omega \ll kT - (42)$$

$$\hbar\omega_0 \ll kT - (43)$$

and

then:

$$\left(\frac{\omega}{\omega_0}\right)^2 = \exp(d_e l) - (44)$$

i.e.

where

$$\begin{aligned} \frac{\omega}{\omega_0} &= \exp\left(\frac{d_e l}{2}\right) - (45) \\ d_e &= \exp\left(\frac{\hbar\omega}{kT}\right) d(\omega) - (46) \\ &= \left(\frac{N_i}{N_g}\right) d(\omega) \end{aligned}$$

These are the blue shifted Evans / Morris effects.

The redshifted Evans / Morris effects are:

$$\frac{\omega}{\omega_0} = \exp\left(-\frac{d(\omega)l}{2}\right) - (47)$$

so the two effects are closely related.