Consider the following two-level system:

$\bar{E}_1$ ..... N_1

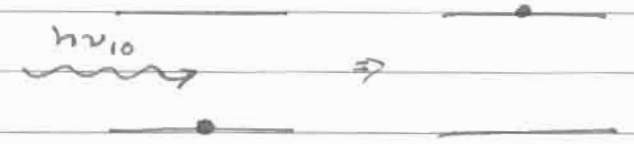
$\bar{E}_0$ ..... N_0

$\bar{E}_1$ is the energy of the upper level
$\bar{E}_0$ is the energy of the lower level
N_1 is the number of particles in the upper level.
N_0 is the number of particles in the lower level.

There are three possible processes:

① Absorption

$h\nu_{10} = \bar{E}_1 - \bar{E}_0 = \Delta\bar{E}$



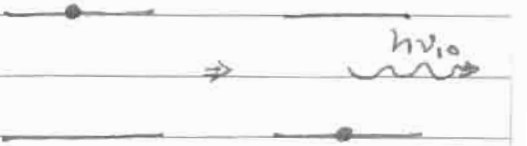
The rate at which the molecules are being excited to the level 1 is given by:

$$\frac{dN_1}{dt} = B_{1\leftarrow 0}\, \rho_\nu(\nu_{10})\, N_0$$

$B_{1\leftarrow 0}$ is a rate constant and known as Einstein absorption coefficient.
$\rho_\nu(\nu_{10})$ is the spectral radiation density.

② Spontaneous Emission

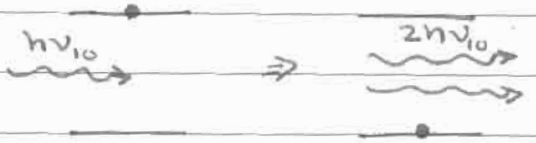
$h\nu_{10} = \bar{E}_1 - \bar{E}_0 = \Delta\bar{E}$



$$\frac{dN_1}{dt} = -A_{1\to 0}\, N_1$$

$A_{1\to 0}$ is the Einstein coefficient for spontaneous emission

③ Stimulated Emisson



A photon of $E = h\nu_{10}$ can induce the system to undergo an emisson process.

$$\frac{dN_1}{dt} = -B_{1\to 0}\, \rho_\nu(\nu_{10})\, N_1$$

This process is very common in laser techniques.

The population when the system is at thermal equilibrium at given temperature is described by Boltzmann distribution law:

$$\frac{N_1}{N_0} = e^{-h\nu_{10}/k_B T} = e^{-\Delta E/k_B T}$$

where k_B is Boltzmann constant.

It is clear from Boltzmann expression that as the energy difference increases, the equilibrium population decreases. Also as the temperature increases, the population will be increasing.

It can also be shown that stimulated (induced) absorption and emission constant are equal:

$$B_{1\to 0} = B_{1\leftarrow 0}$$

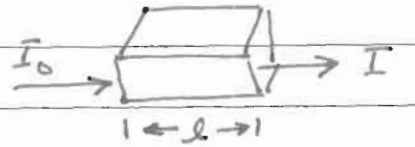
Moreover, the spontaneous emission can be determined from the absorption coefficient:

$$A_{1\to 0} = \frac{8\pi h \nu_{10}^2}{c^3} B_{1\leftarrow 0}$$

Since $\frac{8\pi h}{c^2}$ is constant, the factor ν_{10}^3 plays an important role in determing the importance of the spontaneous emission or induced emission.

→ Beer's Law

Consider a simple absorption experiment, in which a radiation of intensity I_0 of a continuous range of wavelengths passes through a cell of length l containing a sample with a concentration c.



The sample is considered to absorb the incident radiation over a range of wavenumbers $\bar{\nu}_1$ to $\bar{\nu}_2$.

After the absorption of the passing light takes place, the intensity of the exiting light becomes I.

Beer's law can be derived by relating the flux of incident photons F_0 to the intensity I_0, and one can get:

$$I = I_0 10^{-\varepsilon c l}$$

where ε is the molar absorption coefficient.

$$\frac{I}{I_0} = 10^{-\varepsilon c l}$$

$$\log_{10}(I/I_0) = -\varepsilon c l$$

$$\log_{10}(I_0/I) = \varepsilon(\bar{\nu}) c l = \text{Absorbance } (A)$$

Since A is unitless, ε has a unit of $\frac{1}{\text{conc.} \times \text{length}}$ or $\frac{L}{\text{mol.} m}$. ε is also a function of the wavenumber.

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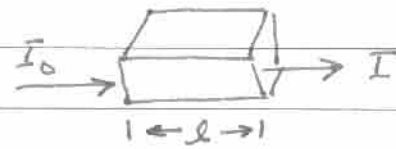

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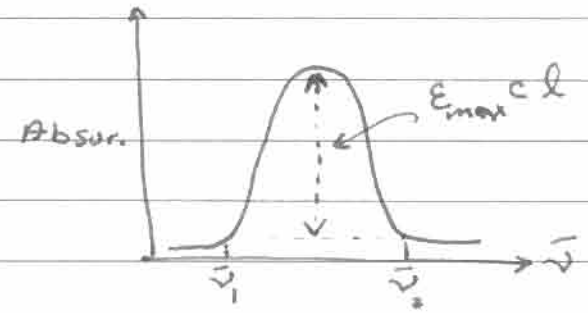
Since A is unitless, ε has a unit of $\frac{1}{\text{conc.} \times \text{length}}$ or $\frac{L}{\text{mol.} \cdot m}$. ε is also a function of the wavenumber.

The absorption spectrum can be obtained by plotting A against $\bar{\nu}$, where ε_{max} can be determined.

ε_{max} will be the same regardless the width of the absorption band.



Thus, a more accurate way to measure the intensity is the area under the absorption curve which is given by $\int_{\bar{\nu}_1}^{\bar{\nu}_2} \varepsilon(\bar{\nu})\, d\bar{\nu}$

Here consider a case (which represents mostly liquid sample with electronic transition) with two energy states that are separated by energy difference enough for N_1 to be very much less than N_0, then stimulated emission will be negligible compared with absorption. In this case, the area under the absorption curve is related to $B_{1\leftarrow 0}$ (the absorption coefficient) by:

$$\int_{\bar{\nu}_1}^{\bar{\nu}_2} \varepsilon(\bar{\nu})\, d\bar{\nu} = N_A h \bar{\nu}_{10} B_{1\leftarrow 0} / 2.303$$

where $\bar{\nu}_{10}$ is the average wavenumber of the transition and N_A is the Avogadro's constant.