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5.74 Introductory Quantum Mechanics II
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4.3. EINSTEIN B COEFFICIENT AND ABSORPTION CROSS-SECTION

The rate of absorption induced by the field is

$$w_{k\ell}(\omega) = \frac{\pi}{2\hbar^2} |E_0(\omega)|^2 |\langle k | \hat{\epsilon} \cdot \bar{\mu} | \ell \rangle|^2 \delta(\omega_{k\ell} - \omega) \quad (4.56)$$

The rate is clearly dependent on the strength of the field. The variable that you can most easily measure is the intensity I , the energy flux through a unit area, which is the time-averaged value of the Poynting vector, S

$$S = \frac{c}{4\pi} (\bar{E} \times \bar{B}) \quad (4.57)$$

$$I = \langle S \rangle = \frac{c}{4\pi} \langle \bar{E}^2 \rangle = \frac{c}{8\pi} E_0^2. \quad (4.58)$$

(Note, I've rather abruptly switched units to cgs). Using this we can write

$$w_{k\ell} = \frac{4\pi^2}{3c\hbar^2} I(\omega) |\langle k | \hat{\epsilon} \cdot \bar{\mu} | \ell \rangle|^2 \delta(\omega_{k\ell} - \omega), \quad (4.59)$$

where I have also made use of the uniform distribution of polarizations applicable to an isotropic field: $|\bar{E}_0 \cdot \hat{x}| = |\bar{E}_0 \cdot \hat{y}| = |\bar{E}_0 \cdot \hat{z}| = \frac{1}{3} |E_0|^2$. An equivalent representation of the amplitude of a monochromatic field is the energy density

$$U = \frac{I}{c} = \frac{1}{8\pi} E_0^2. \quad (4.60)$$

which allows the rates of transition to be written as

$$w_{k\ell} = B_{k\ell} U(\omega_{k\ell}) \quad (4.61)$$

The first factor contains the terms in the matter that dictate the absorption rate. B is independent of the properties of the field and is called the Einstein B coefficient

$$B_{k\ell} = \frac{4\pi^2}{3\hbar^2} |\mu_{k\ell}|^2. \quad (4.62)$$

You may see this written elsewhere as $B_{k\ell} = (2\pi/3\hbar^2) |\mu_{k\ell}|^2$, which holds when the energy density of a wave is expressed in Hz instead of angular frequency.

If we associate the energy density with a number of photons N , then U can also be written in a quantum form

$$N\hbar\omega = \frac{E_0^2}{8\pi} \quad U = N \frac{\hbar\omega^3}{\pi^2 c^3}. \quad (4.63)$$

Now let's relate the rates of absorption to a quantity that is directly measured, an absorption cross-section α :

$$\begin{aligned} \alpha &= \frac{\text{total energy absorbed / unit time}}{\text{total incident intensity (energy / unit time / area)}} \\ &= \frac{\hbar\omega \cdot w_{k\ell}}{I} = \frac{\hbar\omega \cdot B_{k\ell} U(\omega_{k\ell})}{cU(\omega_{k\ell})} \\ &= \frac{4\pi^2}{\hbar c} |\mu_{k\ell}|^2 = \frac{\hbar\omega}{c} B_{k\ell} \end{aligned} \quad (4.64)$$

More generally, you may have a frequency-dependent absorption coefficient $\alpha(\omega) \propto B_{k\ell}(\omega) = B_{k\ell} g(\omega)$ where $g(\omega)$ is a unit normalized lineshape function. The golden rule rate for absorption also gives the same rate for stimulated emission. Given two levels $|m\rangle$ and $|n\rangle$:

$$\begin{aligned} w_{nm} &= w_{mn} \\ B_{nm} U(\omega_{nm}) &= B_{mn} U(\omega_{mn}) \quad \text{since } U(\omega_{nm}) = U(\omega_{mn}) \end{aligned} \quad (4.65)$$

$$B_{nm} = B_{mn}$$

The absorption probability per unit time equals the stimulated emission probability per unit time.

Also, the cross-section for absorption is equal to an equivalent cross-section for stimulated emission, $(\alpha_A)_{nm} = (\alpha_{SE})_{mn}$.

We can now use a phenomenological approach to calculate the change in the intensity of incident light, due to absorption and stimulated emission passing through a sample of length L where the levels are thermally populated. Given that we have a thermal distribution of identical non-interacting particles, with quantum states such that the level $|m\rangle$ is higher in energy than $|n\rangle$:

\bar{k}

$$\frac{dI}{I} = -N_n \alpha_A dx + N_m \alpha_{SE} dx \quad (4.66)$$

$$\frac{dI}{I} = -(N_n - N_m) \alpha dx \quad (4.67)$$

Here N_n and N_m are population of the upper and lower states, but expressed as a population densities. If N is the molecule density,

$$N_n = N \left(\frac{e^{-\beta E_n}}{Z} \right) \quad (4.68)$$

Integrating (4.67) over a pathlength L we have

$$T = \frac{I}{I_0} = e^{-\Delta N \alpha L} \quad (4.69)$$

$$\approx e^{-N \alpha L} \quad N : \text{cm}^{-3} \quad \alpha : \text{cm}^2 \quad L : \text{cm}$$

We see that the transmission of light through the sample decays exponentially as a function of path length. $\Delta N = N_n - N_m$ is the thermal population difference between states. The second expression comes from the high frequency approximation applicable to optical spectroscopy, but certainly not for magnetic resonance: $\Delta N \approx N$. Written as the familiar Beer-Lambert Law:

$$A = -\log \frac{I}{I_0} = \epsilon CL. \quad (4.70)$$

$$C : \text{mol / liter} \quad \epsilon : \text{liter / mol cm} \\ \epsilon = 2303 N \alpha$$