

7.5: Absorption Cross-Sections

The rate of absorption induced by a monochromatic electromagnetic field is

$$w_{k\ell}(\omega) = \frac{\pi}{2\hbar^2} |E_0(\omega)|^2 |\langle k|\hat{\epsilon} \cdot \bar{\mu}|\ell\rangle|^2 \delta(\omega_{k\ell} - \omega) \quad (7.5.1)$$

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 :

$$S = \epsilon_0 c^2 (\bar{E} \times \bar{B}) \quad (7.5.2)$$

$$I = \langle S \rangle = \frac{1}{2} \epsilon_0 c E_0^2 \quad (7.5.3)$$

Using this we can write

$$w_{k\ell} = \frac{4\pi}{3\epsilon_0 c \hbar^2} I(\omega) |\langle k|\bar{\mu}|\ell\rangle|^2 \delta(\omega_{k\ell} - \omega) \quad (7.5.4)$$

where I have also made use of the uniform distribution of polarizations applicable to an **isotropic** field:

$$|\bar{E}_0 \cdot \hat{x}| = |\bar{E}_0 \cdot \hat{y}| = |\bar{E}_0 \cdot \hat{z}| = \frac{1}{3} |E_0|^2. \quad (7.5.5)$$

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

$$\alpha = \frac{\text{total energy absorbed per unit time}}{\text{total incident intensity (energy/unit time/area)}} \quad (7.5.6)$$

$$= \frac{\hbar \omega w_{k\ell}}{I} \quad (7.5.7)$$

Note α has units of cm^2 . The golden rule rate for absorption also gives the same rate for stimulated emission. Given two levels $|m\rangle$ and $|n\rangle$,

$$w_{nm} = w_{mn} \quad (7.5.8)$$

$$\therefore (\alpha_A)_{nm} = (\alpha_{SE})_{mn} \quad (7.5.9)$$

We can now use a phenomenological approach to calculate the change in the intensity of incident light, I , due to absorption and stimulated emission passing through a sample of length L . 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 $|n\rangle$:

$$\frac{dI}{dx} = -N_n \alpha_A I + N_m \alpha_{SE} I \quad (7.5.10)$$

$$\frac{dI}{I} = -(N_n - N_m) \alpha dx \quad (7.5.11)$$

Here N_n and N_m are population of the upper and lower states, but expressed as population densities (cm^{-3}). Note that I and α are both functions of the frequency of the incident light. If N is the molecular density,

$$N_n = N \left(\frac{e^{-\beta E_n}}{Z} \right) \quad (7.5.12)$$

Integrating Equation 7.5.11 over a path length L , we have

$$T = \frac{I}{I_0} \quad (7.5.13)$$

$$= e^{-\Delta N \alpha L} \quad (7.5.14)$$

$$\approx e^{-N \alpha L} \quad (7.5.15)$$

We see that the transmission of light through the sample decays exponentially as a function of path length.

$$\Delta N = N_n - N_m \quad (7.5.16)$$

is the thermal population difference between states. The second expression in Equation 7.5.14 comes from the high-frequency approximation applicable to optical spectroscopy. Equation 7.5.14 can also be written in terms of the familiar [Beer–Lambert Law](#):

$$A = -\log \frac{I}{I_0} = \epsilon C L \quad (7.5.17)$$

where A is the absorbance and C is the sample concentration in mol L^{-1} , which is related to the number density via Avagadro's number N_A ,

$$C [\text{mol L}^{-1}] = \frac{N [\text{cm}^{-3}]}{N_A} \times 1,000 \quad (7.5.18)$$

In Equation 7.5.17, the characteristic molecular quantity that describes the sample's ability to absorb the light is ϵ , the **molar decadic extinction coefficient**, given in $\text{L mol}^{-1} \text{cm}^{-1}$. With these units, we see that we can equate ϵ with the cross section as

$$\epsilon = \frac{N_A \alpha}{2303} \quad (7.5.19)$$

In the context of sample absorption characteristics, our use of the variable α for cross section should not be confused with another use as an absorption coefficient with units of cm^{-1} that is equal to $N\alpha$ in Equation 7.5.14

These relationships also allow us to obtain the magnitude of the transition dipole matrix element from absorption spectra by integrating over the absorption line shape:

$$|\mu_{if}|^2 = \frac{6\epsilon_0 \hbar^2 2303c}{N_A n} \int \frac{\epsilon(v)}{v} dv \quad (7.5.20)$$

$$= (108.86 \text{ L mol}^{-1} \text{cm}^{-1} \text{D}^{-2})^{-1} \int \frac{\epsilon(v)}{v} dv \quad (7.5.21)$$

Here the absorption line shape is expressed in molar decadic units and the frequency in wavenumbers.

Readings

1. Herzberg, G., Molecular Spectra and Molecular Structure: Infrared and Raman of Polyatomic Molecules. Prentice-Hall: New York, 1939; Vol. II, p. 261.
2. McHale, J. L., Molecular Spectroscopy. 1st ed.; Prentice Hall: Upper Saddle River, NJ, 1999.

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