Lecture four

(Absorption)

1- Beer-Lambert Law

A fraction of the incident radiation is absorbed along the path of propagation in a Medium (here refer to the atmosphere). The Beer-Lambert law (also referred to as the Beer-Lambert-Bouguer law) governs the reduction in the radiation intensity I_λ at wavelength λ (Fig. below). If s stands for the medium thickness (oriented in the direction of propagation), the evolution of the radiation intensity is:

$$\frac{dI_\lambda}{ds} = -a_\lambda(s) I_\lambda \quad \dots\dots\dots\dots\dots\dots..(1)$$

Where $a_\lambda(s)$ is the absorption coefficient at wavelength λ (depending on the Medium). The unit of a_λ is, for instance, m^{-1} or cm^{-1}. Assuming that the medium is homogeneous, then a_λ has a constant value and:

$$I_\lambda(s) = I_\lambda(0) * \exp(-s a_\lambda) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(2)$$

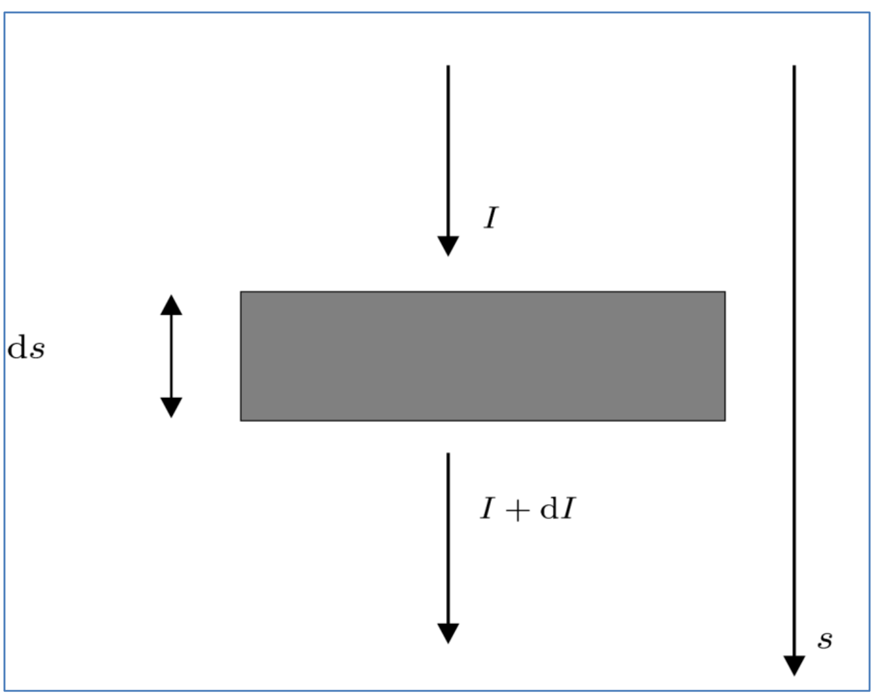

Fig. Absorption of an incident radiation traversing a medium (*gray box*)

Consider a medium composed of p absorbing species, with densities n_i $(i = 1, \ldots, p)$, expressed in (molecule cm^{-3}). The absorbing coefficient is then obtained by summing over all species. For a given species, the contribution depends on the density and on the so-called *absorption cross section* (the effective cross section resulting in absorption), $\sigma_i^a\,(\lambda, s)$, usually expressed in cm^2:

$$a_\lambda(s) = \sum_{i=1}^{p} n_i(s)\,\sigma_i^a\,(\lambda, s) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

A way to define the absorption cross section is to consider an incident flux of energy per surface, F (in Wcm^{-2}). The resulting absorbed energy is then:

$$F_a = \sigma_a \times F \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

(Expressed in Watt).

Another classical concept is the so-called *optical depth* τ_λ (unitless), defined for a monochromatic radiation by:

$$d\tau_\lambda = a_\lambda(s)ds \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

By substituted in equation (1) and Rewriting the Beer – Lambert law yields:

$$\frac{dI_\lambda}{d\tau_\lambda} = -I_\lambda \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Overall absorbance depend on two assumption:

1- Absorbance proportional with concentration of that medium. $a_\lambda \; \alpha \; c$

2- Absorbance directly proportional to length of light of path $a_\lambda \; \alpha \; s$

$$a_\lambda \; \alpha \; c.s \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where:

c = concentration

s = length or thickness

The proportionality in equation (7) can be converted to equality:

$$a_\lambda = \log\frac{I_0}{I} = \varepsilon\, c\, l \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

EXAMPLE 1: A Gas has a maximum absorbance of 275nm. ϵ_{275}=8400M^{-1}cm^{-1} and the path length is 1 cm. Using a spectrophotometer, you find the that A_{275}=0.70 .What is the concentration of gas?

SOLUTION

To solve this problem, you must use Beer's Law.

$$A = \epsilon l c$$

0.70 = (8400 M^{-1} cm^{-1})(1 cm)(c)

Next, divide both side by [(8400 M^{-1} cm^{-1})(1 cm)]

c = 8.33x10^{-5} mol/L

EXAMPLE 2: There is a substance in a solution (4 g/liter). The length of cuvette is 2 cm and only 50% of the certain light beam is transmitted. What is the extinction coefficient?

SOLUTION

Using Beer-Lambert Law, we can compute the absorption coefficient. Thus,

$$-log\left(\frac{It}{Io}\right) = -log\left(\frac{0.5}{1.0}\right) = A = 2 * 4\epsilon$$

Then we obtain that

$$\epsilon \ = \ 0.0376$$

2. Kirchhoff’s Law

For a given wavelength λ, the *absorptivity* A_λ is defined as the fraction of the incident radiation that is absorbed by the medium. Kirchhoff’s law (1859) connects the absorptivity and the emissivity of a medium at thermodynamic equilibrium, namely

$$\epsilon_\lambda \ = \ A_\lambda \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \ (6)$$

The absorption properties of a medium are therefore directly related to its emission properties. Note that A_λ can be derived from a_λ. For a medium supposed to be homogeneous, with a thickness *z* (typically a cloud), with an absorbing coefficient a_λ, the ratio of the absorbed intensity to the incident intensity is $A_\lambda = 1 - exp(-a_\lambda \Delta z)$. At thermodynamic equilibrium, when Taking into account absorption and emission, the evolution of the intensity is then

$$\frac{dI_\lambda}{ds} = -a_\lambda(s)(B_\lambda(T) - I_\lambda) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(7)$$

$B_\lambda(T)$: For a body at temperature T Maximum of emitted radiance at wavelength is given by the so-called Planck distribution,