309(5): A Simple Derivation of the Bouguer Beer Lambert Law (BBL Law) for Monochromatic Radiation.

For monochromatic radiation the electromagnetic flux density is defined by:

$$\Phi = c\frac{U}{V} = c\frac{N}{V}\langle\hbar\omega\rangle \quad -(1)$$

where U is the electromagnetic energy in a volume V, and N the number of Planck oscillators of mean energy

$$\langle\hbar\omega\rangle = \frac{\hbar\omega}{e^{y}-1} \quad -(2)$$

where

$$y = \frac{\hbar\omega}{kT}. \quad -(3)$$

From the Rayleigh theory for two polarizations:

$$\frac{N}{V} = \frac{1}{3}\frac{\omega^3}{c^3\pi^2}. \quad -(4)$$

Note carefully that the $\underline{B}^{(3)}$ field of ECE theory adds a contribution to eq. (4).

The energy density of states is:

$$\rho = \frac{U}{V} \quad -(5)$$

so

$$\Phi = c\rho \quad -(6)$$

The rate of transfer of energy to an atom or molecule in an absorption process is:

$$W_{if} = B_{if}\,\rho \quad -(7)$$

2) where B_{if} is the Einstein B coefficient. Therefore the rate at which the electromagnetic field loses energy in an absorption process is:

$$\frac{dU}{dt} = -W_{if} U \quad -(8)$$

Note carefully that this equation can also be used in a scattering process where electromagnetic energy is lost by scattering.

Now use:

$$v = \frac{dl}{dt} \quad -(9)$$

where v is the velocity of light in an absorber and l the sample path length. It follows that:

$$\frac{dU}{dl} = -\left(\frac{W_{if}}{v}\right) U \quad -(10)$$

Now generalize the definition (1) using v instead of c, so:

$$\Phi = v \frac{U}{V} \quad -(11)$$

It follows that:

$$\frac{d\Phi}{dl} = -\left(\frac{W_{if}}{v}\right) \Phi \quad -(12)$$

which is the Bouguer Beer Lambert law QED.

3) The power absorption coefficient is:

$$\alpha = \frac{W_{if}}{v} = \frac{B_{if}\rho}{v} \quad -(13)$$

In a dilute gas:

$$\alpha = \frac{W_{if}}{c} = \frac{B_{if}\rho}{c} \quad -(14)$$

but in the condensed state c is replaced by v.

Therefore:

$$\Phi = I_0 \exp(-\alpha \ell) \quad -(15)$$

and

$$\frac{\Phi}{\Phi_0} = \exp(-\alpha \ell) \quad -(16)$$

In the Planck theory of 1899 applied to mono-chromatic radiation:

$$\Phi = c\rho = c\frac{U}{V} = c\langle \hbar\omega \rangle \frac{N}{V} \quad -(17)$$

$$= \frac{\omega^3}{3c^2\pi^2}\langle \hbar\omega \rangle$$

and

$$\rho = \frac{\omega^3}{3c^3\pi^2}\langle \hbar\omega \rangle \quad -(18)$$

4) It follows that the power absorption coefficient is:

$$\alpha = B_{if}/c = \frac{\omega^3}{3c^4\pi^2}\langle \hbar\omega \rangle B_{if} \quad -(19)$$

Therefore for monochromatic radiation:

$$\boxed{\frac{\Phi}{\Phi_0} = \left(\frac{\omega}{\omega_0}\right)^4 \left(\frac{e^{y_0}-1}{e^{y}-1}\right) = \exp(-\alpha l) \quad -(20)}$$

in which:

$$\alpha = \frac{1}{l}\log_e \frac{\Phi_0}{\Phi} \quad -(21)$$

Note carefully that eq. (21) is valid for any type of process in which electromagnetic flux density is lost, i.e in which the initial flux density Φ_0 falls to Φ. So it is also valid for Rayleigh and Raman scattering, or any type of scattering such as Brillouin, Thompson or Compton scattering.

It is also valid for particle scattering if the photons are replaced by fermions and Fermi - Dirac statistics are used.

5) In the high frequency approximation:

$$\frac{e^{y_0}-1}{e^{y}-1} \sim \exp(y_0 - y) = \exp\left(\frac{\omega_0 - \omega}{kT}\right) \quad -(22)$$

So:

$$\frac{\Phi}{\Phi_0} = \left(\frac{\omega}{\omega_0}\right)^4 \exp\left(\frac{\omega_0 - \omega}{kT}\right) = \exp(-\alpha \ell) \quad -(23)$$

Therefore the Evans / Morris frequency shift is:

$$\left(\frac{\omega}{\omega_0}\right)^4 = \exp\left(-\alpha \ell - \frac{kT}{\omega_0 - \omega}\right) \quad -(24)$$

In the high frequency approximation:

$$\omega_0 - \omega \gg kT \quad -(25)$$

So

$$\boxed{\frac{\omega}{\omega_0} = \exp\left(-\frac{\alpha \ell}{4}\right)} \quad -(26)$$

for monochromatic radiation.

For polychromatic radiation as in previous work eq. (20) becomes:

$$\frac{I}{I_0} = \left(\frac{\omega}{\omega_0}\right)^3 \left(\frac{e^{y_0}-1}{e^{y}-1}\right) = \exp(-\alpha \ell) \quad -(27)$$

6) and the ratio of flux densities is replaced by the ratio of intensities. Therefore in the high frequency approximation for polychromatic radiation:

$$\frac{\omega}{\omega_0} = \exp\left(-\frac{\alpha l}{3}\right) \quad (28)$$

as in previous work. In polychromatic radiation the intensity is defined by:

$$I = \frac{d\Phi}{d\omega} \quad (29)$$

This definition cannot be used in monochromatic radiation because ω is a constant.

The theory of Rayleigh scattering considers a monochromatic beam which induces an electric dipole moment through the polarizability. So the Evans / Morris shift of Rayleigh scattering is given by eq. (26). If the scattered flux density is Φ and the initial flux density is Φ_0 then the power scattering coefficient is:

$$\alpha_s = \frac{1}{R} \log_e \frac{\Phi_0}{\Phi} \quad (30)$$

where R is the distance from the atom or molecule to the detector.

In a dilute gas the power scattering coefficient can be computed in terms of the

7) transition induced electric dipole moment. As in previous work the integrated scattering coefficient is:

$$A_s = \left(\frac{N}{V}\right)\frac{|\mu_{if}|^2}{6\epsilon_0 c\hbar} \quad -(31)$$

in a dilute gas. In condensed matter c is replaced by v. The expectation value is:

$$\langle \mu_{if} \rangle = \int \psi^* \mu_{if} \psi \, d\tau \quad -(32)$$

In Rayleigh and Raman scattering, restricting consideration to the Z direction:

$$\langle \mu_Z \rangle = \int \psi^* \alpha_{ZZ} E_Z \psi \, d\tau \quad -(33)$$

$$= E_Z \int \psi^* \alpha_{ZZ} \psi \, d\tau \quad -(34)$$

From perturbation theory:

$$\alpha_{ZZ} = -2 \sum_n{}' \left[\frac{\langle 0|\mu_Z|n\rangle\langle n|\mu_Z|0\rangle}{E_0 - E_n} \right]$$

So the Evans Morris shifts can be calculated exactly using eqs (26), (31), (33) and (34), i.e.

$$\frac{\omega}{\omega_0} = \exp\left(-\frac{A_s R}{4}\right) \quad -(35)$$
