304(1): Time Dependent Beer-Lambert Law and Development of the Power Absorption Coefficient.

The usual form of the Beer-Lambert Law is:

$$\frac{dI}{dl} = -\alpha I \qquad - (1)$$

where

$$I = c\rho \qquad - (2)$$

Here I is the intensity, α is the power absorption coefficient in reper cm^{-1}, l the sample length, c the vacuum speed of light and ρ the density of states:

$$\rho(\omega) = \frac{1}{V}\frac{dU}{d\omega} \qquad - (3)$$

Therefore

$$I = \frac{c}{V}\frac{dU}{d\omega} \qquad - (4)$$

is joules per square metre. It follows from Eqn. (1) that

$$I = I_0 \, exp\left(-\alpha l\right) \qquad - (5)$$

i.e

$$\frac{I}{I_0} = exp\left(-\alpha l\right) \qquad - (6)$$

where I_0 is the initial intensity of the radiation. Therefore the intensity of the radiation decreases with path length. In absorption spectroscopy such as the far infra-red the power absorption coefficient is the

2) is measured as:

$$\alpha = \frac{1}{\ell} \cdot \log_e \frac{I_0}{I} \quad - (7)$$

From fundamental quantum theory the number density of states is calculated from:

$$\frac{dN}{V} = \frac{\omega^2}{\pi^2 c^3} d\omega + \frac{\omega}{\pi^2 c^3} (d\omega)^2 + \frac{(d\omega)^3}{3\pi^2 c^3} \quad - (8)$$

$$= \frac{10}{3} \frac{\omega^2}{\pi^2 c^3} d\omega$$

The energy density of states is calculated from:

$$\frac{dU}{V} = \langle E \rangle \frac{dN}{V} \quad - (9)$$

where $\langle E \rangle$ is the average energy of a Planck oscillator:

$$\langle E \rangle = \hbar \omega \left(\exp\left(\frac{\hbar\omega}{kT}\right) - 1 \right)^{-1} \quad - (10)$$

So:

$$\frac{dU}{V} = \frac{10}{3} \frac{\hbar}{\pi^2 c^3} \omega^3 \left(\exp\left(\frac{\hbar\omega}{kT}\right) - 1 \right)^{-1} d\omega \quad - (11)$$

and

$$\boxed{\rho = \left(\frac{10\hbar\omega}{3\pi^2 c^3}\right)\left(\frac{\omega^2}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}\right)} \quad - (12)$$

This equation can be expressed as:

$$\rho = a \hbar \omega \quad - (13)$$

3) we have

$$a = \frac{10}{3\pi^2 c^3} \left(\frac{\omega^2}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1} \right) \quad -(14)$$

The intensity of the beam is therefore:

$$I = ac\hbar\omega \quad -(15)$$

and is proportional to the energy of one photon, $\hbar\omega$. In deriving this, the theory it is assumed by Rayleigh that the speed of light is c, in the vacuum. This is equivalent to assuming a massless photon. This assumption works its way through it to the equation:

$$l = ct \quad -(16)$$

used in deriving the Beer Lambert law theoretically. So the Beer Lambert law can be expressed as:

$$\frac{I}{I_0} = \exp\left(-\alpha ct\right) \quad -(17)$$

so that I/I_0 decreases exponentially with time for a given α.

In these calculations:

$$\hbar = 1.05459 \times 10^{-34} \text{ Js} \quad -(18)$$

$$k = 1.38066 \times 10^{-23} \text{ JK}^{-1} \quad -(19)$$

and $\hbar/k = 7.638 \times 10^{-12} \text{ sK} \quad -(20)$

?) At a temperature of $300 K$:

$$\frac{\hbar}{kT} = 0.02546 \times 10^{-12} s$$

$$= 2.546 \times 10^{-14} s \qquad -(21)$$

In these equations:

$$\omega = 2\pi f \qquad -(22)$$

where f is the frequency in Hz (or s^{-1}). In the microwave

$$1 \, cm^{-1} = 30 \, GHz$$
$$= 3 \times 10^{10} \, Hz \qquad -(23)$$

So

$$1 \, cm^{-1} = 6\pi \times 10^{10} \quad \text{radians } s^{-1}$$

$$= 18.850 \times 10^{10} \, \text{radians } s^{-1} \qquad -(24)$$

$$1 \, cm^{-1} = 1.885 \times 10^{11} \, \text{radians } s^{-1}$$

Therefore in the microwave at $30 \, GHz$:

$$\hbar\omega \ll kT \qquad -(25)$$

In the far infra-red at $100 \, cm^{-1}$:

$$\omega = 1.885 \times 10^{13} \, \text{radians per second} \qquad -(26)$$

and in the mid infra-red at $1000 \, cm^{-1}$:

$$\omega = 1.885 \times 10^{14} \, \text{rad } s^{-1} \qquad -(27)$$

So

$$\hbar\omega / kT < 1 \qquad -(28)$$

5) However, in the near infra red at 10,000 cm^{-1} and at visible frequencies and higher at 300K:

$$\hbar\omega > kT. \quad -(29)$$

In general:

$$\frac{I}{I_0} = \left(\frac{\omega}{\omega_0}\right)^3 \left(\frac{e^{y_0}-1}{e^{y}-1}\right) \quad -(30)$$

where

$$y = \frac{\hbar\omega}{kT} \quad -(31)$$

and

$$y_0 = \frac{\hbar\omega_0}{kT} \quad -(32)$$

So

$$\boxed{\left(\frac{\omega}{\omega_0}\right)^3 \left(\frac{e^{y_0}-1}{e^{y}-1}\right) = \exp\left(-\alpha\ell\right) = \exp\left(-\alpha c t\right)} \quad -(33)$$

This equation must be used at visible frequencies at 300K. However at far infra-red frequencies it is well approximated by:

$$\left(\frac{\omega}{\omega_0}\right)^2 = \exp\left(-\alpha\ell\right) = \exp\left(-\alpha c t\right) \quad -(34)$$

6.) i.e

$$\omega = \omega_0 \exp\left(-\frac{\alpha \ell}{2}\right) \qquad -(35)$$

$$= \omega_0 \exp\left(-\frac{\alpha c t}{2}\right)$$

If a probe laser is tuned to α at a given initial frequency ω_0:

$$\alpha = \alpha(\omega_0) \qquad -(36)$$

then $\alpha(\omega_0)$ is a measurable constant at that frequency ω_0, so:

$$\omega = \omega_0 \exp\left(-\frac{t}{\tau}\right) \qquad -(37)$$

where

$$\tau = \frac{2}{c\,\alpha(\omega_0)} \qquad -(38)$$

so

$$\boxed{\frac{\omega}{\omega_0} = \exp\left(-\frac{t}{\tau}\right)} \qquad -(39)$$

Eq. (39) express the Evan Morris red shift as a time autocorrelation function of the type:

7)
$$\langle \mu(t)\mu(0)\rangle = \exp\left(-\frac{t}{\tau}\right), \quad -(40)$$

the orientational autocorrelation function of molecular dynamics theory.

The Fourier transform of ω/ω_0 is a Debye loss function:

$$F\left(\frac{\omega}{\omega_0}\right) \propto \frac{\omega\tau}{1+\omega^2\tau^2} \quad -(41)$$

If the photon propagates at v rather than c, the the relaxation time τ of eq. (38) is changed to:

$$\tau = \frac{2}{v\,d(\omega_0)} \quad -(42)$$

where v is the phase velocity of light in a medium in which absorption occurs. So the Evans/Morris relaxation time τ is changed from air to an absorbing medium.

Finally in photon mass theory:

$$E = \hbar\omega = \gamma m c^2 \quad -(43)$$

$$\underline{P} = \hbar\underline{\kappa} = \gamma m \underline{v} \quad -(44)$$

$$\gamma = \left(1-\frac{c^2}{v^2}\right)^{-1/2} \quad -(45)$$

where