290(1): Intensity Theory of the Evans / Morris Shifts and Frequency Shifts in Absorption

Consider refraction and reflection of a beam of intensity I in watts per square metre. Then:

$$I = I_1 + I_2 \quad -(1)$$

where I_1 is the refracted intensity and I_2 the reflected intensity. The number of oscillators of the beam in a volume of radiation V is given by note 281(1):

$$\frac{N}{V} = \frac{1}{6\pi^2}\left(\frac{\omega}{c}\right)^3 \quad -(2)$$

The average energy of the oscillator from the Planck theory is:

$$\langle E_n \rangle = \left(\frac{x}{1-x}\right)\hbar\omega \quad -(3)$$

where

$$x = \frac{\hbar\omega}{kT} \quad -(4)$$

Therefore the total energy of the beam per unit volume, the energy density, is:

$$E_n = \frac{\langle E_n \rangle}{6\pi^2}\left(\frac{\omega}{c}\right)^3 \quad -(5)$$

$$\boxed{E_n = \left(\frac{x}{1-x}\right)\frac{\hbar\omega^4}{c^3}} \quad -(6)$$

for a monochromatic beam of angular frequency ω.

2)

Units Check

The LHS of eq. (1) is $J m^{-3}$. The RHS is $\frac{J s s^{-4}}{m^3 s^{-3}}$

$= J m^{-3}$. ✓

The intensity of the beam is watts per square metre, i.e. $J s m^{-2}$, is:

$$I = c E_n \quad -(7)$$

so

$$\boxed{I = \left(\frac{x}{1-x}\right)\frac{\hbar\omega^4}{c^2}} \quad -(8)$$

From eqs. (1) and (8):

$$\left(\frac{x}{1-x}\right)\omega^4 = \left(\frac{x_1}{1-x_1}\right)\omega_1^4 + \left(\frac{x_2}{1-x_2}\right)\omega_2^4 \quad -(9)$$

where:

$$x_1 = \frac{\hbar\omega_1}{kT}, \quad -(10)$$

$$x_2 = \frac{\hbar\omega_2}{kT}. \quad -(11)$$

At thermodynamic equilibrium the temperatures of the three beams are the same, T.

In general:

$$I \neq I_1 \neq I_2 \quad -(12)$$

and the Evans Morris effects follow:

$$\boxed{\omega \neq \omega_1 \neq \omega_2} \quad - (13)$$

Let the mean wavenumber of the incoming beam be $\langle \underline{\kappa} \rangle$, that of the reflected beam $\langle \underline{\kappa}_1 \rangle$, and that of the refracted beam $\langle \underline{\kappa}_2 \rangle$. Then:

$$\langle \underline{\kappa} \rangle = \langle \underline{\kappa}_1 \rangle + \langle \underline{\kappa}_2 \rangle \quad - (14)$$

and:

$$\langle \kappa \rangle^2 = \langle \kappa_1 \rangle^2 + \langle \kappa_2 \rangle^2 + 2 \langle \kappa_1 \rangle \langle \kappa_2 \rangle \cos \theta_3 \quad - (15)$$

where:

$$\theta_3 = \pi - (\theta + \theta_1). \quad - (16)$$

By Snell's Laws:

$$\theta = \theta_2 \quad - (17)$$

$$n \sin \theta = n_1 \sin \theta_1 . \quad - (18)$$

Here θ is the angle of incidence, θ_2 the angle of reflection, θ_1 the angle of refraction, n the refractive index of the medium of incidence, n_1 the refractive index of the medium of refraction.

By note 289(7) the angle between $\underline{\kappa}$ and $\underline{\kappa}_1$ is defined as the least angle:

$$\underline{\kappa} \cdot \underline{\kappa}_1 = \kappa \kappa_1 \cos (\theta_1 - \theta) \quad - (19)$$

If the incoming medium is air, and the refracting medium has refractive index:

$$n = c / v \quad - (20)$$

) then eq. (15) gives:

$$\frac{\omega^2}{c^2}\left(\frac{x}{1-x}\right)^2 = \frac{\omega_1^2}{v^2}\left(\frac{x_1}{1-x_1}\right)^2 + \frac{\omega_2^2}{c^2}\left(\frac{x_2}{1-x_2}\right)^2 \quad -(21)$$

$$+ 2\,\frac{\omega_1\omega_2}{cv}\left(\frac{x_1}{1-x_1}\right)\left(\frac{x_2}{1-x_2}\right)\cos\theta_3$$

Eqs. (9) and (21) are solved to give ω_1 and ω_2 in terms of ω. The linear approximation of previous papers can be used.

The intensities I, I_1 and I_2 can be measured very easily, and in all cases:

$$I_1 < I, \quad I_2 < I \quad -(22)$$

by experiment.

I_1 the refracting medium:

$$I_1 = I_{10}\exp(-\alpha Z) \quad -(23)$$

by the Beer Lambert Law. Here α is the power absorption coefficient and Z the sample length. The power absorption coefficient is:

$$\alpha = \frac{\omega\epsilon''}{n'c} \quad -(24)$$

where ϵ'' is the dielectric loss and n' the real part of the refractive index as defined in previous

5) papers. However:

$$I_1 = \left(\frac{x_1}{1-x_1}\right)\frac{\hbar\omega_1^4}{c^2} \quad -(25)$$

so

$$\left(\frac{x_1}{1-x_1}\right)\frac{\hbar\omega_1^4}{c^2} = I_{10}\exp\left(-\alpha Z_1\right) \quad -(26)$$

Eq. (26) shows that frequency is shifted to the red by absorption. In Eq. (26):

$$I_{10} = \left(\frac{x_{10}}{1-x_{10}}\right)\frac{\hbar\omega_{10}^4}{c^2} \quad -(27)$$

so

$$\left(\frac{x_1}{1-x_1}\right)\omega_1^4 = \left(\frac{x_{10}}{1-x_{10}}\right)\omega_{10}^4\exp\left(-\alpha Z_1\right) \quad -(28)$$

where

$$x_1 = \exp\left(-\frac{\hbar\omega_1}{kT}\right) \quad -(29)$$

$$x_{10} = \exp\left(-\frac{\hbar\omega_{10}}{kT}\right) \quad -(30)$$

If

$$\hbar\omega_1 \ll kT \quad -(31)$$

and

$$\hbar\omega_{10} \ll kT \quad -(32)$$

then

$$\boxed{\omega_1^3 = \omega_{10}^3\exp\left(-\alpha Z_1\right)} \quad -(33)$$

where we have used:

$$\exp\left(\frac{\hbar\omega}{kT}\right) \sim 1 + \frac{\hbar\omega}{kT} \quad -(34)$$

Eq. (33) confirms the observations by Evans and Morris that colour or frequency changes as the beam propagates through a sample

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