

### 509(3): Evans / Morri Type Shift in Raman Scattering

As shown in the previous note the energy flux density in watts per square metre of Rayleigh scattered radiation is:

$$\bar{I} = \left( \frac{\mu^2 \sin^2 \phi}{32\pi^2 c^3 \epsilon_0 R^2} \right) \omega_0^4 \quad - (1)$$

In Rayleigh scattering the dipole moment  $\mu$  is considered to be induced by:

$$\mu = \alpha E_0 \quad - (2)$$

where  $E_0$  is the electric field strength in volts per metre of an electromagnetic field that induces  $\mu$  through the polarizability  $\alpha$  of the atom or molecule under consideration. This induced dipole radiates the dipole radiation (1) therefore:

$$\bar{I} = \left( \frac{\alpha^2 E_0^2 \sin^2 \phi}{32\pi^2 c^3 \epsilon_0 R^2} \right) \omega_0^4 \quad - (3)$$

### Units Check

$$\alpha^2 E_0^2 = \text{C}^2 \text{m}^2; \quad \epsilon_0 = \text{J}^{-1} \text{C}^2 \text{m}^{-1}$$

$$\begin{aligned} \text{So: } \bar{I} &= \frac{\text{C}^2 \text{m}^2 \text{s}^{-4}}{\text{m}^3 \text{s}^{-3} \text{J}^{-1} \text{C}^2 \text{m}^{-1} \text{m}^2} \\ &= \text{J} \text{s}^{-1} \text{m}^{-2} = \text{Watt m}^{-2} \quad \checkmark \end{aligned}$$

In the classical treatment of Raman scattering

$$\mu = (d_0 + \Delta d \cos \omega t) E_0 \cos \omega_0 t \quad - (4)$$

here  $\omega$  is an internal frequency of the atom or molecule and  $\omega_0$  the electromagnetic field frequency. The polarizability change periodically with time as the molecule rotates or vibrates. It has a mean polarizability  $d_0$ . Therefore:

$$\mu = d_0 E_0 \cos \omega_0 t + \frac{1}{2} E_0 \Delta d \left( \cos((\omega_0 + \omega)t) + \cos((\omega_0 - \omega)t) \right) \quad - (5)$$

Rayleigh scattering is given by the first term in this sum, anti-Stokes scattering by the second term and Stokes scattering by the third. In Rayleigh scattering the light is scattered at the same frequency  $\omega_0$  as the incident frequency. The scattered energy flux density is given by eq. (3).

The classical theory of Raman scattering depends on an oscillating polarizability. It later must be anisotropic for rotational Raman spectra to occur. The quantum theory of Raman scattering is the relativistic scattering of a photon. The scattered photon has lost energy, so its frequency is different. Its initial energy is  $h\omega_0$  and its Stokes scattering is final energy is  $h(\omega_0 - \omega)$  because  $h\omega$  has been lost by absorption.

3) In Stokes scattering the induced dipole moment is:

$$\mu = \frac{1}{2} E_0 \Delta d \cos((\omega_0 - \omega)t) \quad - (6)$$

so the radiation is scattered at the frequency  $\omega_0 - \omega$ .  
The induced dipole moment is the real part of

$$\mu = \frac{1}{2} E_0 \Delta d \exp(i(\omega_0 - \omega)t) \quad - (7)$$

whose complex conjugate is:

$$\mu^* = \frac{1}{2} E_0 \Delta d \exp(-i(\omega_0 - \omega)t) \quad - (8)$$

Therefore  $\mu^2 = \mu \mu^* = \frac{1}{4} E_0^2 (\Delta d)^2 \quad - (9)$

Therefore for Stokes scattering:

$$\bar{\Phi}(\text{Stokes}) = \frac{1}{4} \left( \frac{E_0^2 (\Delta d)^2 \sin^2 \phi}{32 \pi^2 c^3 \epsilon_0 R^2} \right) (\omega_0 - \omega)^4 \quad - (10)$$

Similarly for anti-Stokes scattering:

$$\bar{\Phi}(\text{anti Stokes}) = \frac{1}{4} \left( \frac{E_0^2 (\Delta d)^2 \sin^2 \phi}{32 \pi^2 c^3 \epsilon_0 R^2} \right) (\omega_0 + \omega)^4 \quad - (11)$$

The initial flux density in the case is:

$$\bar{\Phi}_0 = \frac{1}{2} c \epsilon_0 E_0^2 \quad - (12)$$

Therefore:

$$4) \frac{\bar{\Phi}}{\bar{\Phi}_0} (\text{Stokes}) = \left( \frac{(\Delta d)^2 \sin^2 \phi}{64\pi^2 c^4 \epsilon_0^2 R^2} \right) (\omega_0 - \omega)^4$$

$$= \left( \frac{\Delta d \sin \phi}{8\pi \epsilon_0 c^2 R} \right)^2 (\omega_0 - \omega)^4 \quad - (13)$$

Similarly:

$$\frac{\bar{\Phi}}{\bar{\Phi}_0} (\text{anti-Stokes}) = \left( \frac{\Delta d \sin \phi}{8\pi \epsilon_0 c^2 R} \right)^2 (\omega_0 + \omega)^4 \quad - (14)$$

In both cases the ratio depends on the anisotropy of the polarizability  $\Delta d$ .

For Rayleigh scattering:

$$\frac{\bar{\Phi}}{\bar{\Phi}_0} (\text{Rayleigh}) = \left( \frac{d_0 \sin \phi}{4\pi \epsilon_0 c^2 R} \right)^2 \omega_0^4 \quad - (15)$$

and the ratio depends on the mean polarizability  $d_0$ .

In all these cases the scattered flux density is given by dipole radiation theory:

$$\bar{\Phi} = \left( \frac{\mu^2 \sin^2 \phi}{32\pi^2 c^3 \epsilon_0 R^2} \right) \omega_s^4 \quad - (16)$$

where  $\omega_s$  is the scattered frequency.

5) clearly:

$$\left. \begin{aligned} \omega_s &= \omega_0 \quad (\text{Rayleigh scattering}) \\ \omega_s &= \omega_0 - \omega \quad (\text{Stokes scattering}) \\ \omega_s &= \omega_0 + \omega \quad (\text{anti Stokes scattering}) \end{aligned} \right\} - (17)$$

From Planck theory:

$$\bar{\Phi} = \frac{1}{3} \frac{\omega_s}{c^3 \pi^2} \langle h \omega_s \rangle - (18)$$

$$= \frac{1}{3} \frac{h \omega_s^4}{c^3 \pi^2} \left( \frac{1}{e^{y_s} - 1} \right) - (19)$$

where:

$$y_s = \frac{h \omega_s}{kT} - (20)$$

In all cases the initial flux density is

$$\bar{\Phi}_0 = \frac{1}{2} c \epsilon_0 E_0^2 - (21)$$

and from Planck theory:

$$\bar{\Phi}_0 = \frac{1}{3} \frac{\omega_0^2}{c^3 \pi^2} \langle h \omega_0 \rangle - (22)$$

$$= \frac{1}{3} \frac{h \omega_0^4}{c^3 \pi^2} \left( \frac{1}{e^{y_0} - 1} \right)$$

where

$$y_0 = \frac{h \omega_0}{kT} - (23)$$

b)  $\Gamma_L$  all cases:

$$\frac{\Phi}{\Phi_0} = \left( \frac{\mu^2 \sin^2 \phi}{32\pi^2 c^3 \epsilon_0 R^2} \right) \omega_s^4 \cdot \frac{2}{c \epsilon_0 E_0^2} \quad - (24)$$

$$= \left( \frac{\mu^2 \sin^2 \phi}{16\pi^2 c^4 \epsilon_0^2 R^2 E_0^2} \right) \omega_s^4 \quad - (24)$$

$$\boxed{\frac{\Phi}{\Phi_0} = \left( \frac{\mu \sin \phi}{16\pi c^2 \epsilon_0 R E_0} \right)^2 \omega_s^4} \quad - (25)$$

From Q. Planck theory:

$$\frac{\Phi}{\Phi_0} = \left( \frac{\omega_s}{\omega_0} \right)^4 \left( \frac{e^{\gamma_0} - 1}{e^{\gamma} - 1} \right) \quad - (26)$$

$$\sim \left( \frac{\omega_s}{\omega_0} \right)^4 \exp \left( -\frac{\hbar \left( \frac{\omega_s - \omega_0}{\hbar} \right)}{kT} \right)$$

is a high frequency approximation

Therefore:

$$\exp \left( -\frac{\hbar (\omega_s - \omega_0)}{kT} \right) = \left( \frac{\mu \sin \phi \omega_0^2}{16\pi c^2 \epsilon_0 R E_0} \right)^2 \quad - (27)$$

So

$$\omega_0 - \omega_s = \frac{kT}{\hbar} \log_e \left( \frac{\mu \sin \phi \omega_0^2}{16\pi c^2 \epsilon_0 R E_0} \right)^2 \quad - (28)$$

7) In the conventional theory of Rayleigh scattering:  
 $\omega_0 = \omega_s$  — (29)

in which case  $\frac{\Phi}{I_0} = ?$  — (30)

and there is a contradiction between the Rayleigh  
theory and the Planck distribution.

This contradiction is clearly seen from  
 eqs. (21) and (22): — (31)

$$\begin{aligned}\frac{\Phi}{I_0} &= \frac{1}{2} \epsilon_0 E_0^2 \\ &= \frac{\hbar \omega_0^4}{3 c^3 \pi^2} \left( \exp \left( \frac{\hbar \omega_0}{kT} \right) - 1 \right)^{-1}\end{aligned}$$

$$\text{So } E_0^2 = \frac{2 \hbar \omega_0^4}{3 c^4 \epsilon_0 \pi^2} \left( \exp \left( \frac{\hbar \omega_0}{kT} \right) - 1 \right)^{-1} \quad \text{— (32)}$$

and  $E_0^2$  cannot be frequency independent.  
 The consequences of this will be developed in the next  
 note.