

## 165(2): The R Spectra of Raman Scattering.

Here we found from eq. (86) of UFT 162:

$$R = \frac{1}{2ah^2c^2} \left( -b \pm (b^2 - 4ac)^{1/2} \right) \quad (1)$$

where

$$\begin{aligned} a &= 1 - \cos^2 \theta, \\ b &= (E_i^2 + E_f^2) \cos^2 \theta - 2A, \\ c' &= A^2 - E_i^2 E_f^2 \cos^2 \theta, \\ A &= E_i E_f - h^2 \omega \omega' (1 - \cos \theta). \end{aligned}$$

Here we found from:

$$h\omega + E_i = h\omega' + E_f \quad (2)$$

Here  $\omega$  is the incident angular frequency in Raman scattering, usually a laser frequency. Therefore  $\omega'$  is the scattered angular frequency in the Raman spectrum, and  $\theta$  is the angle of scatter used in the Raman spectrometer. The initial energy level of the electron in the star molecule is  $E_i$  and the final energy level is  $E_f$ .

For example in rotational Raman scattering the Stokes lines appear at:

$$\left. \begin{aligned} \bar{\nu} &= \bar{\nu}_0 - 4B(J + 3/2), \\ \Delta J &= 2, \\ J &= 0, 1, \dots \end{aligned} \right\} (3)$$

2) So the energy levels  $E_j$  and  $E_i$  may be found from the spectrum. In a textbook such as that by Atkins, the energy levels are given by his eq. (11.3.2) of the second edition:

$$\frac{E}{hc} = B J(J+1) - D J^2(J+1)^2 \dots \quad (4)$$

In molecules with permanent electric dipole moments the absorption spectrum is given by a series of equally spaced lines in the far infra-red:

$$\begin{aligned} \bar{\nu} &= (E_{J+1} - E_J) / (hc) \quad (5) \\ &= 2B(J+1) \end{aligned}$$

$$J = 0, 1, 2, \dots$$

Therefore in eq. (4) for Raman scattering:

$$E = E_f - E_i \quad (6)$$

and  $E_i = h\nu_i, E_f = h\nu_f \quad (7)$

In eq. (2), a photon  $h\nu$  collides with an electron in energy level  $E_i$  of an atom or molecule. The energy of the electron is increased to  $E_f$  of a higher energy orbital, and the photon loses energy to  $h\nu'$ . The photon is scattered out of the molecule with the energy  $h\nu'$ . Raman scattering depends on the induced electric dipole moment:

3)

$$\underline{\mu} = d \underline{E} \quad - (8)$$

In general  $d$  is a tensor and is anisotropic, in the simplest theory is given by Athias on his page 288:

$$d = d_0 + \Delta d \cos \omega' t \quad - (9)$$

where  $\omega'$  is a vibrational or rotational frequency of the molecule. The electric field is the component of the electromagnetic field at frequency  $\omega$ :

$$|\underline{E}| = E_0 \cos \omega t \quad - (10)$$

so

$$\begin{aligned} \mu(t) &= (d_0 + \Delta d \cos \omega' t) E_0 \cos \omega t \\ &= d_0 E_0 \cos \omega t + \frac{1}{2} \Delta d E_0 (\cos(\omega + \omega') t + \cos(\omega - \omega') t) \end{aligned} \quad - (11)$$

The unshifted frequency is the Rayleigh radiation, the anti-Stokes lines are  $\omega + \omega'$ . The Stokes lines are  $\omega - \omega'$ .

Eqs. (3) to (7) are non-relativistic quantum, and eqs (1) to (11) are non-relativistic classical.

The R spectra are found from a relativistic theory which conservation of momentum is correctly considered. Therefore the R spectra give new information not found in the standard theory of Raman scattering. The conservation of energy is eq. (2)

is:

$$4) \quad \hbar(\omega - \omega') = E_f - E_i \quad - (12)$$

and the conservation of linear momentum is:

$$\hbar(\underline{k} - \underline{k}') = \underline{p}_f - \underline{p}_i \quad - (13)$$

In the Rayleigh elastic scattering process:

$$\omega = \omega' \quad - (14)$$

$$\underline{k}^2 = \underline{k}'^2 \quad - (15)$$

Conservation of linear momentum is not considered in the standard theory of absorption and scattering.

The R spectrum for elastic Rayleigh scattering is given by eq. (43) of UFT 163:

$$m = \frac{\hbar\omega}{c^2}, \quad R = \left(\frac{mc}{\hbar}\right)^2 \quad - (16)$$

so

$$\boxed{R = \left(\frac{\omega}{c}\right)^2} \quad - (17)$$

Although this is a simple result, it is the result of general relativity. Therefore for the first time, general relativity has been incorporated into absorption and Rayleigh and Raman scattering.