

### 304(2): Development of the Absorption and Emission Coefficients.

The Evans/Morris red shifts are given by:

$$\left(\frac{\omega}{\omega_0}\right)^3 \left(\frac{e^{y_0} - 1}{e^y - 1}\right) = \exp(-\alpha l) = \exp(-\alpha_a l)$$

where  $\omega_0$  is the incident frequency and  $\omega$  is the shifted frequency. Here:

$$y_0 = \frac{h\omega_0}{kT}, \quad y = \frac{h\omega}{kT} \quad - (2)$$

where  $k$  is Boltzmann's constant and  $T$  the temperature, and  $h$  the reduced Planck constant. The sample path length  $l$  is assumed is standard theory to be:

$$l = ct \quad - (3)$$

where  $c$  is the speed of light. However, in an absorbing medium:

$$l = vt \quad - (4)$$

where  $v$  is the phase velocity of light in the medium:

$$v = \frac{c}{n_0} \quad - (5)$$

where  $n_0$  is the refractive index.

The power absorption coefficient is defined by:

$$\alpha_a(\omega) = \frac{n(\omega)}{V} \left( \frac{h\omega}{c} \right) B_{if} \quad - (6)$$

in which

$$\int \frac{n(\omega)}{V} d\omega = \frac{N}{V} \quad - (7)$$

2) where  $N$  is the number of molecules in a volume  $V$ .  
 The momentum magnitude of a photon propagating at an assumed speed of light  $c$  is:

$$p = \hbar k = \hbar \frac{\omega}{c} \quad - (8)$$

and  $B_{ij}$  is the Einstein B coefficient for stimulated absorption.

The rate of absorption of a photon by a molecule is:

$$W_{ij} = \rho B_{ij} \quad - (9)$$

where  $\rho$  is the energy density of states.

At thermodynamic equilibrium:

$$N_i W_{ij} = N_g W_{ji} \quad - (10)$$

where  $W_{ji}$  is the rate of <sup>stimulated</sup> emission of a photon by a molecule.  
 Here  $N_i$  is the number of molecules in state  $i$  and  $N_g$  the number in state  $g$ . The Boltzmann distribution is:

$$\frac{N_i}{N_g} = \exp\left(\frac{\hbar \omega}{kT}\right) \quad - (11)$$

The total rate of emission is:

$$W_{ji} = \rho B_{ji} + A_{ji} \quad - (12)$$

where  $A$  is the Einstein coefficient of spontaneous emission.

As it is  $h\nu \gg kT$  it follows that the emission coefficient is:

$$3) \quad \alpha_e(\omega) = \frac{n(\omega)}{V} \left( \frac{\hbar \omega}{c} \right) (\rho B_{gi} + A_{gi}) \quad - (13)$$

Also: 
$$W_{gi} = \exp\left(\frac{\hbar \omega}{kT}\right) W_{ig} \quad - (14)$$

and: 
$$\alpha_e(\omega) = \exp\left(\frac{\hbar \omega}{kT}\right) \alpha_a(\omega) \quad - (15)$$

The rate of absorption of a photon by a molecule is given by the Fermi golden rule:

$$W_{ig} = 2\pi \hbar |H_{gi}^{(1)}|^2 \rho_N(\bar{E}_g) \quad - (16)$$

$$= \frac{1}{\hbar^2} |H_{ig}^{(1)}|^2 \rho_N(\omega_{gi})$$

where  $\rho_N$  is the number of molecules per unit volume in the range  $\omega$  to  $\omega + d\omega$ , and where  $|H_{ig}^{(1)}|^2$  is the square of the modulus of the perturbation Hamiltonian.

For electric dipole transitions:

$$H^{(1)}(t) = -\mu_z E(t) \quad - (17)$$

where  $\mu_z$  is the transition dipole moment and  $E(t)$  the magnitude of the electric component of the electromagnetic field:

$$E(t) = 2E^{(0)} \cos \omega t \quad - (18)$$

Therefore:

$$W_{ij} = \left(\frac{E}{\hbar}\right)^2 |\mu_{zji}|^2 \rho(\omega_{ji}) - (19)$$

In a liquid the mean transition dipole moment is:

$$\langle |\mu_{zji}|^2 \rangle = \frac{1}{3} |\mu_{zji}|^2 - (20)$$

In a solid  $\mu_{zji}$  is a single component of the transition dipole moment in the molecular axis system.

The energy of the classical electromagnetic field is:

$$E_h = \frac{1}{2} \int \left( \epsilon_0 \langle E^2(t) \rangle + \frac{1}{\mu_0} \langle B^2(t) \rangle \right) dV - (21)$$

In  $E \cdot E$  term this should include the contribution given by the  $B^{(3)}$  field. For the transverse components:

$$\begin{aligned} \langle E^2(t) \rangle &= 4E^2 \int_0^{2\pi/\omega} \cos^2 \omega t dt / \int_0^{2\pi/\omega} dt \\ &= 2E^2 - (22) \end{aligned}$$

Another way of deriving this result is to assume that:

$$\langle E^2(t) \rangle = \underline{E}^{(1)} \cdot \underline{E}^{(2)} - (23)$$

where

$$\underline{E}^{(1)} = \underline{E}^{(2)*} = E^{(0)} (\underline{i} - i\underline{j}) e^{i\phi} - (24)$$

So:

$$5) \quad \underline{E}^{(1)} \cdot \underline{E}^{(2)} = E^{(0)^2} (\underline{i} - \underline{i}j) \cdot (\underline{i} + \underline{i}j) \\ = 2E^{(0)^2} - (25) \\ = \langle E^2(t) \rangle$$

(Note carefully that the complex circular series must be defined by:  $\underline{E}^{(1)} = \underline{E}^{(2)*} = \frac{E^{(0)}}{\sqrt{2}} (\underline{i} - \underline{i}j) e^{i\phi}$  - (26)  
 so the factor 2 in eq. (25) does appear. However the factor 2 does not affect the argument in the note.)

Similarly:

$$\langle B^2(t) \rangle = \underline{B}^{(1)} \cdot \underline{B}^{(2)} - (27) \\ = 2B^{(0)^2}$$

where:  $\underline{B}^{(1)} = \underline{B}^{(2)*} = \frac{B^{(0)}}{\sqrt{2}} (\underline{i}i + \underline{j}) e^{i\phi}$  - (28)

Therefore:  $\epsilon_0 \langle E^2(t) \rangle = \frac{1}{\mu_0} \langle B^2(t) \rangle$  - (29)

and  $E_h = 2\epsilon_0 E^2 V$  - (30)

In a liquid:

$$W_{ig} = \frac{|\mu_{gi}|^2 \rho(\omega)}{6\epsilon_0 \hbar^3} - (31)$$

6) where the energy density of states is:

$$\rho(\omega) = \rho_n E_n \quad - (32)$$

and where:

$$W_{ij} = \rho B_{ij} \quad - (33)$$

Therefore:

$$d_a(\omega) = \frac{n(\omega)}{V} \left( \frac{\hbar \omega}{c} \right) \frac{|\mu_{gi}|^2}{6 \epsilon_0 \hbar^2} \quad - (34)$$

and

$$d_e(\omega) = \exp\left(\frac{\hbar \omega}{kT}\right) \frac{n(\omega)}{V} \left( \frac{\hbar \omega}{c} \right) \frac{|\mu_{gi}|^2}{6 \epsilon_0 \hbar^2} \quad - (35)$$

The quantity  $|\mu_{gi}|^2$  must be calculated from quantum mechanics. This method will be developed in the next note.

Therefore the Evans / Morris effects are given by eqs. (1) and (34).

In order to simplify the calculation the integrated power absorption coefficient may be used as follows.

$$7) A = \int \alpha(\omega) d\omega = \int \frac{n(\omega)}{V} \frac{\hbar\omega}{c} \frac{|\mu_{gi}|^2}{6\epsilon_0 \hbar^2} d\omega \quad - (36)$$

The usual procedure in spectroscopy is to assume that  $\alpha$  is approximately constant across a narrow band, so:

$$A = \frac{\hbar\omega}{c} \frac{|\mu_{gi}|^2}{6\epsilon_0 \hbar^2} \int \frac{n(\omega)}{V} d\omega \quad - (37)$$

$$= \frac{N \hbar\omega |\mu_{gi}|^2}{6\epsilon_0 c \hbar^2 V} = \frac{N |\mu_{gi}|^2}{6\epsilon_0 c \hbar^2 V} \quad - (38)$$

The units of  $A$  are  $\text{cm}^{-1}$  in spectroscopy, or  $\text{m}^{-1}$  in S.I. units. So

$$A = \left( \frac{N}{V} \right) \frac{|\mu_{gi}|^2}{6\epsilon_0 c \hbar^2} \quad - (39)$$

The quantity  $N/V$  is related to Avogadro's number, the number of molecules in a mole of material

Using the integrated absorption coefficient the Evans Morris red shift is:

$$\left( \frac{\omega}{\omega_0} \right)^3 \left( \frac{e^{y_0} - 1}{e^y - 1} \right) = \exp(-A\ell) = \exp(-A\sqrt{t}) \quad - (40)$$