304(3): Calculation of Electric Dipole Transition Moments.

It has been shown in previous papers that the Evans Morris shifts are given by:

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

where the integrated power absorption coefficient for a narrow band is given by:

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

Here ω_0 is the incident frequency, ω the shifted frequency,

$$y_0 = \exp\left(\frac{\hbar\omega_0}{kT}\right) \quad -(3)$$
$$y = \exp\left(\frac{\hbar\omega}{kT}\right), \quad -(4)$$

ℓ is the sample path length, v is the velocity of light in the sample and:

$$\ell = vt. \quad -(5)$$

Therefore t is the time:

$$t = \frac{\ell}{v} \quad -(6)$$

taken for a beam to traverse the sample length. This

2) can be measured with time resolved apparatus. Here are N molecules in a sample volume V. ϵ_0 is the vacuum permittivity and $\hbar$ is the reduced Planck constant.

The perturbation Hamiltonian is:

$$H^{(1)}(t) = -\underline{\mu} \cdot \underline{E}(t) \quad -(7)$$

where $\underline{\mu}$ is an electric dipole moment and $\underline{E}(t)$ is the electric component of the electromagnetic field. For a plane polarized beam in the Z axis:

$$H^{(1)} = -\mu_Z E(t) = -er\cos\theta . E(t) - (8)$$

The selection rules for an electric dipole transition are:

$$\Delta n \text{ unrestricted}, \; \Delta l = \pm 1, \; \Delta m_e = 0, \pm 1 \quad -(9)$$

For example to calculate the transition dipole moment for a 2s to $2p_Z$ transition using Slater orbitals:

$$\mu_Z = \int \phi_{2p_Z} \mu_Z \phi_{2s} \, d\tau \quad -(10)$$

Here:

$$\phi_{2s} = \left(\frac{Z^{*5}}{96\pi a_0^5}\right)^{1/2} r \exp\left(-\frac{Z^* r}{2a_0}\right), \quad -(11)$$

$$\phi_{2p_Z} = \left(\frac{Z^{*5}}{32\pi a_0^5}\right)^{1/2} r\cos\theta \exp\left(-\frac{Z^* r}{2a_0}\right) \quad -(12)$$

So:

3)

$$\mu_z = -\left(\frac{e}{\sqrt{3}}\right)\left(\frac{Z^{*5}}{32\pi a_0^5}\right)\int_0^{2\pi} d\phi \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta \int_0^{\infty} r^5 \exp\left(-\frac{Z_1^* r}{a_0}\right) dr$$

$$= -\left(\frac{5}{\sqrt{3} Z_1^*}\right) e a_0 \quad -(13)$$

Calculation for the Hydrogenic Wavefunctions

The calculation for the hydrogenic wave-functions proceeds by:

$$\mu_z = \int \psi_1 \, e r \cos\theta \, \psi_2 \, d\tau \quad -(14)$$

where

$$\mu = e r \cos\theta \quad -(15)$$

where ψ_1 and ψ_2 are different wavefunctions of the H atom with:

$$\Delta l = \pm 1, \ \Delta m_l = 0, \pm 1. \quad -(16)$$

Here..

$$\int f \, d\tau = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} f \, r^2 \sin\theta \, dr \, d\theta \, d\phi \quad -(17)$$

So the transition dipole moment is:

4)

$$\mu_z = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} \phi_1 e r \cos\theta \, \phi_2 \, r^2 \sin\theta \, dr \, d\theta \, d\phi \quad -(18)$$

and these can be calculated analytically for the H wave functions. The two wavefunctions ϕ_1 and ϕ_2 must satisfy the selection rules (16).

As a check on the calculation, μ_z should be zero if ϕ_1 and ϕ_2 do not satisfy the selection rules.

In the usual calculation of the integrated power absorption coefficient A, it is assumed that v is the speed of light. However in photon mass theory:

$$E = \hbar\omega = \gamma m c^2 \quad -(19)$$

$$\underline{p} = \hbar \underline{\kappa} = \gamma m \underline{v} \quad -(20)$$

and

$$\gamma = \left(1 - \frac{v^2}{c^2}\right)^{-1/2} \quad -(21)$$

where

In an absorbing sample the refractive index is frequency dependent and given by:

$$n(\omega) = \frac{c}{v} \quad -(22)$$

As in the next note, photon mass theory can be worked in to the above theory.
