

308(5): From Morse Red Shift in Vibrational Spectra.

The Lorentzian is again:

$$\frac{I}{I_0} = \left(\frac{\omega}{\omega_0} \right)^3 \left(\frac{e^{y_0} - 1}{e^y - 1} \right) = \exp(-\alpha Z) \quad (1)$$

where $y_0 = \frac{\hbar \omega_0}{kT}$, $y = \frac{\hbar \omega}{kT}$. - (2)

The power absorption coefficient α is integrated to give

$$A = \left(\frac{N}{V} \right) \frac{|\mu_{ij}|^2}{6 \epsilon_0 v \hbar} \quad (3)$$

Vibrational spectra occur at high frequencies so $\hbar \omega \gg kT$, $\hbar \omega_0 \gg kT$ - (4)

and to an excellent approximation:

$$\omega = \omega_0 \exp\left(-\frac{AZ}{3}\right) \quad (5)$$

The simplest case of Harmonic Oscillator can be used to model the vibration. The Hamiltonian is:

$$H = -\frac{\hbar^2}{2m} \nabla^2 + \frac{1}{2} k r^2 \quad (6)$$

and $H\psi = E\psi$. - (7)

The energy levels are:

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad (8)$$

where $n = 0, 1, 2, 3, \dots$ - (9)

and the wavefunctions are:

$$\psi_n = \left(\frac{1}{2^n n! \pi^{1/2}} \right)^{1/2} H_n(y) \exp\left(-\frac{y^2}{2}\right) \quad - (10)$$

where $y = \left(\frac{m\omega}{\hbar} \right)^{1/2} r$ - (11)

where $H_n(y)$ are the Hermite polynomials. The energy levels are given by:

$$E_{n+1} - E_n = \hbar\omega \quad - (12)$$

Therefore the transition dipole moment must be computed with the wavefunctions (10). The first few Hermite polynomials are:

$$H_0(y) = 1 \quad - (13)$$

$$H_1(y) = 2y$$

$$H_2(y) = 4y^2 - 2$$

$$H_3(y) = 8y^3 - 12y$$

$$H_4(y) = 16y^4 - 48y^2 + 12$$

$$H_5(y) = 32y^5 - 160y^3 + 120y$$

$$H_6(y) = 64y^6 - 480y^4 + 720y^2 - 120$$

$$H_7(y) = 128y^7 - 1344y^5 + 3360y^3 - 1680y$$

$$H_8(y) = 256y^8 - 3584y^6 + 13440y^4 - 13440y^2 + 1680$$

3) The x , y and z components of the transition dipole moment are given by:

$$\mu_x = \mu \sin\theta \cos\phi \quad - (14)$$

$$\mu_y = \mu \sin\theta \sin\phi \quad - (15)$$

$$\mu_z = \mu \cos\theta \quad - (16)$$

where

$$\mu = e r \quad - (17)$$

therefore:

$$\langle \mu_z \rangle = \int_{r=0}^{\infty} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \psi^* \mu_z \psi r^2 \sin\theta dr d\theta d\phi \quad - (18)$$

and similarly for μ_x and μ_y . The wave functions are real valued so:

$$\psi = \psi^* \quad - (19)$$

The selection rule is:

$$\Delta n = 1 \quad - (20)$$

so there is no degeneracy in the energy levels.

Therefore for the harmonic oscillator there is an even / Morse red shift but no splitting.

The extent of the shift can be calculated

4) from the above equations

Note a Rotational Transition Dipole Moments

The previous note case were evaluated for

μ_z :

$$\begin{aligned}\langle \mu_z \rangle &= \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} Y^*(2) \mu_z Y(1) \sin \theta d\theta d\phi \\ &= \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} e r Y^*(2) \cos \theta \sin \theta Y(1) d\theta d\phi\end{aligned} \quad -(21)$$

but can also be evaluated for μ_x and μ_y .
using eqs. (14) and (15).

Conclusion

It is clear that Eq. (1) can be applied to any type of absorption spectrum: rotational, vibrational or electronic, so the red shifts and splittings exist in any type of absorption spectrum.