

308(3) : Exams / Maxis Shifts and Splittings in  
the Rotational Spectrum of a Diatomic Molecule.

Consider the solution of the Schrodinger equation  
 for a rotating diatomic molecule:



Its moment of inertia is:

$$I = \mu R^2 \quad - (1)$$

where  $\mu$  is reduced mass is:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad - (2)$$

The Schrodinger equation is:

$$H\psi = E\psi \quad - (3)$$

also

$$H\psi = -\frac{\hbar^2}{2\mu} \nabla^2 \psi \quad - (4)$$

In spherical polar coordinates:

$$\nabla^2 = \frac{1}{r^2} \left( \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) \quad - (5)$$

For a coordinate system centred at one of the atoms:  
 $r = R \quad - (6)$

so the Schrodinger equation is:

$$2) \quad -\frac{\hbar^2}{2I} \left( \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) \psi = E\psi \quad (7)$$

$$= -\frac{\hbar^2}{2I} \Lambda^2 \psi$$

where  $\Lambda^2$  Legendrian is defined by:

$$\Lambda^2 = \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \quad (8)$$

The spherical harmonics are defined by: (9)

$$\Lambda^2 Y_{lm}(\theta, \phi) = -l(l+1) Y_{lm}(\theta, \phi)$$

Therefore:

$$-\frac{\hbar^2}{2I} \Lambda^2 Y_{lm}(\theta, \phi) = E Y_{lm}(\theta, \phi) \quad (10)$$

$$= \frac{\hbar^2}{2I} l(l+1) Y_{lm}(\theta, \phi)$$

So the energy levels of the rotating diatomic molecule are:

$$E = \frac{\hbar^2}{2I} l(l+1) \quad (11)$$

In the absence of any other consideration there are  $(2l+1)$  degenerate, because:

$$m = -l, \dots, l \quad (12)$$

3) Therefore for  $l = 0$  there is one rotational energy level because  $m$  has only one value, 0. For  $l = 1$  there are three energy levels because  $m = -1, 0, 1$ , all at the same energy, and so on. Therefore for  $l = 12$  there are 25 rotational energy levels all at the same energy, i.e. 25 fold degenerate.

The selection rule between rotational energy levels is:

$$\Delta l = \pm 1, \Delta m = 0, \pm 1 \quad (13)$$

The energy levels do not depend on  $m$  and are the transition is defined by:

$$E(l+1) - E(l) = \frac{h^2}{2I} ((l+1)(l+2) - l(l+1)) \quad (14)$$

$$= \frac{h^2}{2I} (l+1)$$

usually this is denoted in wavenumbers by:

$$\bar{\nu} = 2B(J+1) \quad (15)$$

The rotational spectrum consists of equally spaced absorptions and occurs in the far infra-red or microwave.

For a linear diatomic there is one electric dipole moment and in spherical polar coordinates this is:

$$4) \quad \mu_z = e r \cos \theta \quad - (16)$$

$$= e R \cos \theta$$

The transition dipole moment between a state 1 and a state 2 is:

$$\mu_{ij} = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \psi^*(2) \mu_z \psi(1) \sin \theta d\theta d\phi \quad - (17)$$

For eqs (16) and (17):

$$\mu_{12} = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} e R \psi^*(2) \cos \theta \sin \theta \psi(1) d\theta d\phi \quad - (18)$$

In the microwave and far infra-red the use of the Planck distribution is the Beer (under law) produces, in the low frequency approximation:

$$\omega = \omega_0 \exp \left( -\frac{A\tau}{2} \right) \quad - (19)$$

where

$$A = \left( \frac{N}{V} \right) \frac{|\mu_{ij}|^2}{6\epsilon_0 c h} \quad - (20)$$

The initial angular frequency is:

$$\omega_0 = 2\pi \tilde{\nu} c = 4\pi c B(J+1) \quad - (21)$$

and

$$5) |\mu_{if}|^2 = \mu_{if} \mu_{if}^* \quad - (22)$$

Example

For the transition from  $l=0$  to  $l=1$ , the lower level is characterized by:

$$l=0, m=0 \quad - (23)$$

and the higher level by:

$$l=1, m=-1, 0, 1 \quad - (24)$$

So there are three possible transition dipole moments:

$$a) \mu_{01}(0) = eR \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} Y_{10}^* \cos\theta \sin\theta Y_{00} d\phi d\theta \quad - (25)$$

$$b) \mu_{01}(1) = eR \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} Y_{11}^* \cos\theta \sin\theta Y_{00} d\phi d\theta \quad - (26)$$

$$c) \mu_{01}(-1) = eR \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} Y_{1-1}^* \cos\theta \sin\theta Y_{00} d\phi d\theta \quad - (27)$$

The relevant spherical harmonics are:

$$Y_{00} = \frac{1}{2\pi}^{1/2} \quad - (28)$$

$$Y_{10} = \frac{1}{2} \left( \frac{3}{\pi} \right)^{1/2} \cos\theta \quad - (29)$$

$$Y_{11} = -\frac{1}{2} \left( \frac{3}{2\pi} \right)^{1/2} \sin\theta \exp(i\phi) \quad - (30)$$

$$6) \quad Y_{1-1} = \frac{1}{2} \left( \frac{3}{2\pi} \right)^{1/2} \sin\theta \exp(-i\phi) \quad - (31)$$

So the degeneracy of the  $l=0$  to  $l=1$  transition is lifted, and the initial  $\omega_0$  rotational absorption angular frequency is split into three frequencies and shifted to the red.

This is named "the rotational Evans-Morris shift".

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