RED SHIFTS AND SPLITTING IN THE ROTATIONAL SPECTRA OF DIATOMIC MOLECULES.

by

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ABSTRACT

A new test of the quantum theory is proposed by equating the intensity ratio of the Planck distribution with that of the Bouguer Beer Lambert law. The power absorption coefficient of the latter is computed with transition dipole moments calculated from the wave functions for the rotational spectrum of a diatomic molecule. The wave functions are the spherical harmonics. It is shown that the quantum theory predicts a change in frequency to the red of probe radiation tuned to an absorption line, and that the initial probe frequency is split. These are the Evans / Morris shifts and splittings.

Keywords: ECE theory, Planck distribution, Bouguer Beer Lambert law, red shifts and splittings of the initial probe frequency.

4FT 308

1. INTRODUCTION.

In recent papers of this series {1 - 12} it has been shown that the probe frequency in any type of absorption process is shifted and split in a well defined way. This is a new optical phenomenon that emerged from the application of fundamental laws of optics to the Evans / Morris effects. These are colour changes that accompany the absorption of a laser by materials such as liquids and glasses, and they are described in comprehensive detail on the blog of www.aias.us. The quantum theory has been applied in a new way by equating the intensity ratio of the Beer Lambert law (first inferred by Bouguer in the early eighteenth century) to the same intensity ratio obtained from the Planck distribution. This procedure immediately shows that the frequency of the probe beam must be changed as it propagates through the sample. In an absorption process the frequency is progressively lowered. This process depends on the sample path length Z and on the transition dipole moment. The decrease in frequency occurs in a different way for each transition dipole moment. The result is that more than one red shifted frequency can emerge from the sample.

These emergent frequencies can be measured by a suitable experimental method such as interferometry. They can be predicted precisely by the quantum theory and this new effect is a test of the theory. The observations of G. J. Evans and T. Morris are reproducible and repeatable and can be explained by the quantum theory used in this way.

In immediately preceding papers the shifts and splittings were computed for the spectrum of atomic hydrogen, predicting an intricate pattern of splittings for each line. In Section 2 the red shifts and splittings are computed for the rotational spectrum of a diatomic molecule. This is well known to be a series of equally spaced lines in the microwave and far infra red, so a probe laser or microwave source can be tuned to each absorption line, and according to fundamental quantum theory the probe laser frequency is shifted progressively to the red as it propagates through the sample. The process depends on the transition dipole moment between wave functions that are known analytically, so the shifts and splittings can be computed precisely. As usual this paper should be read with its background notes. Notes 308(1) and 308(2) give more details of the shifts and splittings expected in atomic H. Section 2 is based mainly in Notes 308(3) and 308(4), which apply to the rotational spectrum of a diatomic, while Note 308(5) extends consideration to the harmonic oscillator which can be used to model the simplest type of vibrational spectrum. In each case there are characteristic patterns of shifts and splittings which can be computed precisely with the quantum theory.

2. RED SHIFTS AND SPLITTINGS IN THE ROTATIONAL SPECTRUM OF A DIATOMIC MOLECULE AND RED SHIFTS OF THE HARMONIC OSCILLATOR.

Consider the solution of the Schroedinger equation for a rotating diatomic molecule of reduced mass:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} . \quad -(1)$$

The moment of inertia of the molecule is:

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

where R is the distance between m_1 and m_2. The Schroedinger equation is:

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

where:

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

Here $\hbar$ is the reduced Planck constant and E the quantized total energy where ϕ is the wave function. In spherical polar coordinates the laplacian is well known to be:

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

It follows that the Schroedinger equation is:

$$-\frac{\hbar^2}{2I}\Lambda^2 = E\phi \quad -(6)$$

where the legendrian is given by:

$$\Lambda^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}. \quad -(7)$$

The spherical harmonics are defined by:

$$\Lambda^2 Y_{lm}(\theta,\phi) = -l(l+1)Y_{lm}(\theta,\phi) \quad -(8)$$

therefore:

$$-\frac{\hbar^2}{2I}Y_{lm}(\theta,\phi) = EY_{lm}(\theta,\phi) = \frac{\hbar^2}{2I}l(l+1)Y_{lm}(\theta,\phi). \quad -(9)$$

So the energy levels of the rotating dipolar molecule are given by:

$$E = \frac{\hbar^2}{2I}l(l+1). \quad -(10)$$

In the absence of any other consideration these are (2l + 1) fold degenerate,

because:

$$m = -l, \ldots, l. \quad -(11)$$

Therefore for l = 0 there is one rotational energy level because m has only one value, 0. For l

= 1 there are three degenerate energy levels because m = -1, 0, and 1, and so on. Therefore for l = 12 for example there are 25 rotational energy levels all at the same energy, i. e. 25 fold degenerate. The selection rule between rotational energy levels is:

$$\Delta l = \pm 1, \quad \Delta m = 0, \pm 1. \quad -(12)$$

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

$$E(l+1) - E(l) = \frac{\hbar^2}{2I}\left((l+1)(l+2) - l(l+1)\right) = \frac{\hbar^2}{I}(l+1). \quad -(13)$$

Usually this is denoted in wave numbers by:

$$\bar{\nu} = 2B(J+1). \quad -(14)$$

The rotational absorption spectrum consists of equally spaced absorption lines and occurs in the microwave and far infra red. The envelope of the spectrum is the Boltzmann distribution.

The electric dipole moment of the linear diatomic in spherical polar coordinates is:

$$\mu_Z = er\cos\theta = eR\cos\theta \quad -(15)$$

so the transition dipole moment between wave functions 1 and 2 is:

$$\mu_{if} = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} Y^*(2)\,\mu_Z\,Y(1)\sin\theta\,d\theta\,d\phi. \quad -(16)$$

From Eqs. (15) and (16):

$$\mu_{12} = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} eRY^*(2)\cos\theta\sin\theta\,Y(1)\,d\theta\,d\phi. \quad -(17)$$

As in immediately preceding papers the use of the Planck distribution in the Beer Lambert law produces, in the low frequency approximation:

$$\omega = \omega_0 \exp\left(-\frac{AZ}{2}\right) \quad -(18)$$

where ω_0 is the incoming frequency of the probe laser and ω is its frequency after traversing a sample thickness Z. Here A is the integrated power absorption coefficient:

$$A = \left(\frac{N}{V}\right) \frac{|\mu_{if}|^2}{6\epsilon_0 v \hbar} \quad -(19)$$

where there are N molecules in a volume V, ϵ_0 is the S. I. vacuum permittivity and where v is the velocity of the electromagnetic probe radiation in the sample. In a sample of dilute gas the following approximation is sufficient:

$$v = c \quad -(20)$$

but in condensed matter this is no longer true (see immediately preceding papers of the UFT series on www.aias.us). The low frequency approximation is valid up to about 100 cm^{-1} in the far infra red.

For example, for the transition l = 0 to l = 1 the lower rotational energy level is characterized by:

$$l = 0, m = 0 \quad -(21)$$

and the higher by:

$$l = 1, m = -1, 0, 1 \quad -(22)$$

so there are three possible transition dipole moments:

1) $$\mu_{01}(0) = eR \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} Y_{10}^{*} \cos\theta \sin\theta \, Y_{00} \, d\phi \, d\theta \quad -(23)$$

2) $$\mu_{01}(1) = eR \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} Y_{11}^{*} \cos\theta \sin\theta \, Y_{00} \, d\phi \, d\theta \quad -(24)$$

3) $$\mu_{01}(-1) = eR \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} Y_{1-1}^{*} \cos\theta \sin\theta \, Y_{00} \, d\phi \, d\theta . \quad -(25)$$

The relevant spherical harmonics are:

$$Y_{00} = 1 / \left(2\pi^{1/2}\right) \quad -(26)$$

$$Y_{10} = \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2} \cos\theta \quad -(27)$$

$$Y_{11} = -\frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2} \sin\theta \exp(i\phi) \quad -(28)$$

$$Y_{1-1} = \frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2} \sin\theta \exp(-i\phi). \quad -(29)$$

So as the probe laser propagates through a gas made up of rotating diatomic molecules the energy degeneracy of the l =0 to l = 1 transition is lifted, and the initial probe frequency is shifted to the red in three different ways. Therefore the radiation emerging from a sample cell of thickness Z will contain three different frequencies. So the initial ω_0 is split into three. This is the direct result of fundamental quantum theory and the three emergent frequencies can be predicted precisely with this fundamental quantum theory. Therefore they can be investigated experimentally, giving a new test of the quantum theory.

These are named the Evans / Morris red shifts and splittings.

In general the wave number of the pure rotational spectrum is:

$$\tilde{\nu} = \left(E_{\ell+1} - E_{\ell}\right) / (hc) = 2B(\ell+1), \quad \ell = 0, 1, 2, \ldots \quad -(30)$$

and the transition dipole moments are:

$$\langle \mu_Z \rangle = \int Y_{l'm'} \, \mu_Z \, Y_{lm} \, d\tau \quad -(31)$$

Two examples can be considered as follows.

1) For l = 0 the transition wave number is

$$\bar{\nu} = 2B = (E_1 - E_0)/(\hbar c) \quad -(32)$$

and the selection rule is:

$$\Delta l = 1. \quad -(33)$$

The absorption line occurs at this transition wave number. There are three possible values of m for l =1:

$$m = -1, 0, 1 \quad -(34)$$

and so there are three possible transitions:

$$Y_{00} \rightarrow Y_{11}, \; Y_{00} \rightarrow Y_{10}, \; Y_{00} \rightarrow Y_{1-1}. \quad -(35)$$

The three selection rules for m are:

$$\left.\begin{array}{ll} \Delta m = 1 & \text{(left circularly polarized probe)} \\ \Delta m = 0 & \text{(linearly polarized probe)} \\ \Delta m = -1 & \text{(right circularly polarized probe)} \end{array}\right\} -(36).$$

Therefore:

$$\left.\begin{array}{ll} Y_{00} \rightarrow Y_{11} & \text{(left CP)} \\ Y_{00} \rightarrow Y_{01} & \text{(linear)} \\ Y_{00} \rightarrow Y_{1-1} & \text{(right CP)} \end{array}\right\} -(37)$$

and there is one transition dipole moment possible in each sense of polarization of the probe laser.

2) For l = 1 the transition wave number is:

$$\tilde{\nu} = 4B = (E_2 - E_1)/(\hbar c) \quad -(38)$$

and the number of possible transition dipole moments is given by:

$$Y_{11}, Y_{10}, Y_{1-1} \rightarrow Y_{22}, Y_{21}, Y_{20}, Y_{2-1}, Y_{2-2}. \quad -(39)$$

Therefore:

$$\left.\begin{array}{l} Y_{11} \rightarrow Y_{22} \\ Y_{10} \rightarrow Y_{21} \\ Y_{1-1} \rightarrow Y_{20} \end{array}\right] \text{left CP}, \ \Delta l = 1, \ \Delta n = 1 \quad -(40)$$

Similarly:

$$\left.\begin{array}{l} Y_{11} \rightarrow Y_{21} \\ Y_{10} \rightarrow Y_{20} \\ Y_{1-1} \rightarrow Y_{2-1} \end{array}\right] \text{linear}, \ \Delta l = 1, \ \Delta n = 0 \quad -(41)$$

and

$$\left.\begin{array}{l} Y_{11} \rightarrow Y_{20} \\ Y_{10} \rightarrow Y_{2-1} \\ Y_{1-1} \rightarrow Y_{2-2} \end{array}\right] \text{right CP}, \ \Delta l = 1, \ \Delta n = -1 \quad -(42)$$

Therefore there are three transition dipoel moments for each sense of polarization of the probe laser.

If N is the number of red shifted frequencies emerging from a sample of path length Z the number of red shifted frequencies is:

$$N = 2l + 1 \quad -(43)$$

and is the same as the energy degeneracy of each line.

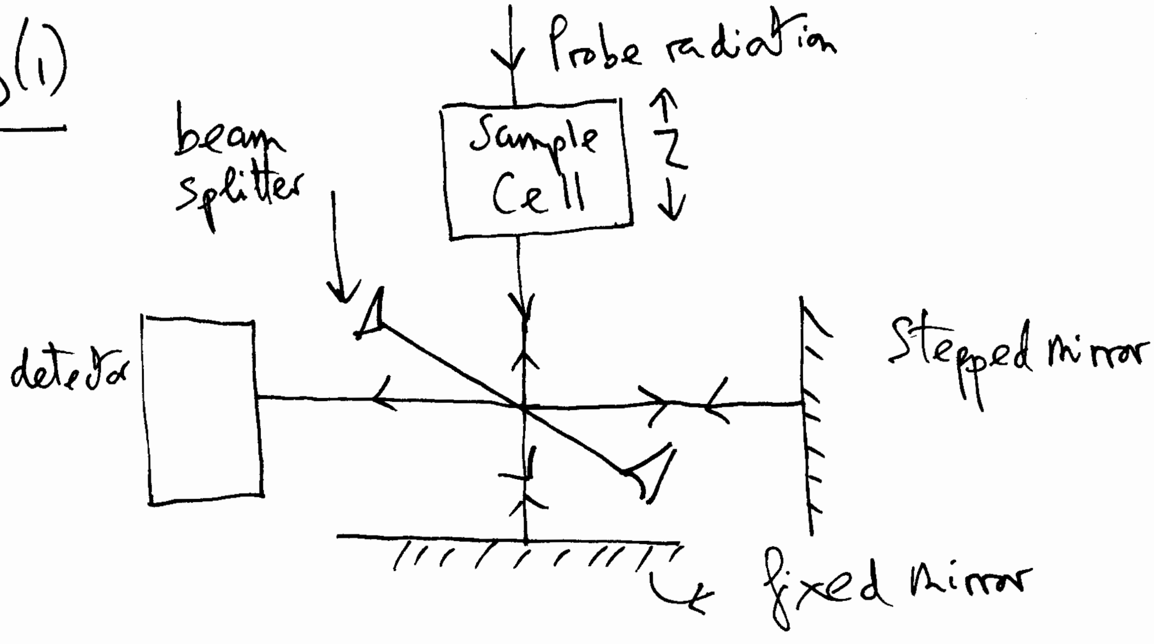
The initial angular frequency is:

$$\omega_0 = 2\pi \overline{\sim}_0 c \quad -(44)$$

in radians per second where $\overline{\sim}_0$ is the initial wavenumber. For l = 0 this is 2B; for l = 1 it is 4B; for l = 2 it is 6B; and for l = x it is 2B(x + 1). For example, if the initial probe laser frequency is tuned to $\overline{\sim}_0$ = 4B, three red shifted frequencies emerge from the sample cell according to fundamental quantum theory. If the initial probe laser is tuned to 16B, fifteen red shifted frequencies emerge from the sample cell, and so on.

In order to observe these frequencies a fully computerized far infra red Fourier transform Michelson interferometer can be used as in the following sketch:

Fig(1)



Finally in this Section a synopsis is given of Note 308(5) accompanying UFT308 on www.aias.us , a note that deals with the harmonic oscillator and the simplest type of vibrational spectrum.

A typical vibrational spectrum occurs in the high frequency approximation:

$$\omega = \omega_0 \exp\left(-\frac{AZ}{3}\right) \quad -(45)$$

The hamiltonian of the harmonic oscillator is:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}kr^2 \quad -(46)$$

and its energy levels are well known to be:

$$E(n) = \left(n + \frac{1}{2}\right)\hbar\omega \quad -(47)$$

where

$$n = 0, 1, 2, 3, \ldots \quad -(48)$$

The wave functions of the harmonic oscillator are:

$$\psi(n) = \left(\frac{1}{2^n n! \pi^{1/2}}\right)^{1/2} H_n(y) \exp\left(\frac{-y^2}{2}\right) \quad -(49)$$

where:

$$y = \left(\frac{m\omega}{\hbar}\right)^{1/2} r \quad -(50)$$

and where $H_n(y)$ are the Hermite polynomials. There is only one quantum number n and the selection rule is:

$$\Delta n = 1 \quad -(51)$$

between energy levels:

$$E(n+1) - E(n) = \hbar\omega. \quad -(52)$$

Therefore the transition dipole moments must be computed with the wave functions (49). The well known Hermite polynomials are real valued and the first eight are given in Note 308(5). The X, Y and Z components of the transition dipole moment are given in spherical polar coordinates by:

$$\mu_x = \mu \sin\theta \cos\phi \qquad (53)$$

$$\mu_Y = \mu \sin\theta \sin\phi \qquad (54)$$

$$\mu_Z = \mu \cos\theta \qquad (55)$$

where:

$$\mu = er. \qquad (56)$$

Therefore the transition dipole moment is:

$$\langle \mu_Z \rangle = \int \psi^* \mu_Z \psi \, d\tau \qquad (57)$$

and similarly for μ_x and μ_Y. There is no degeneracy in the energy levels.

Therefore for the harmonic oscillator and a simple vibrational spectrum there is an Evans / Morris red shift for each vibrational absorption line, but no splitting. The extent of the red shift is given by the transition dipole moment, and the red shift is observable with the experimental set up sketched in Figure 1. This is another critical test of the quantum theory.

3. COMPUTATION OF ENERGY LEVELS AND DISCUSSION

Section by Dr. Horst Eckardt

Red shifts and splitting in the rotational spectra of diatomic molecules

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3 Computation of energy levels and discussion

The dipole transition matrix elements of the spherical harmonics have been calculated for the lowest angular momenta. As explained in section 2, the transition rules are

$$\Delta l = \pm 1,\ \Delta m = 0,\ \pm 1. \tag{58}$$

The cartesian dipole components, translated to spherical coordinates, are

$$\mu_X = e\,R\,\sin(\theta)\,\cos(\phi), \tag{59}$$

$$\mu_Y = e\,R\,\sin(\theta)\,\sin(\phi), \tag{60}$$

$$\mu_Z = e\,R\,\cos(\theta). \tag{61}$$

The corresponding matrix elements of the spherical harmonics are

$$\mu_{K\ l,l',m,m'} = \int Y^*_{l'm'}\ \mu_K\ Y_{lm}\ d\tau \tag{62}$$

for K=X,Y,Z, where the common factor eR has been omitted. Only the matrix elements obeying the transition rules (58) are non-zero. The results are listed in Table 1. Obviously the rule $\Delta m = 0$ belongs to the Z component of μ while the rules $\Delta m = \pm 1$ belong to the X and Y components. The Y components are the same as the X components but imaginary and partially with a sign change. These differences are not relevant because only the modulus of the transition element occurs in physical laws. They show a kind of parity difference between left- and right-circular polarization.

The harmonic oscillator in one dimension is defined by the Hermite polynomials. Different definitions of these functions exist, we used the "physicist's

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polynomials" whose first functions are given by

$$H_0\,(y) = 1 \tag{63}$$

$$H_1\,(y) = 2\,y \tag{64}$$

$$H_2\,(y) = 4\,y^2 - 2 \tag{65}$$

$$H_3\,(y) = 8\,y^3 - 12\,y \tag{66}$$

$$H_4\,(y) = 16\,y^4 - 48\,y^2 + 12 \tag{67}$$

$$H_5\,(y) = 32\,y^5 - 160\,y^3 + 120\,y \tag{68}$$

The normalized wave function of the harmonic oscillator is defined by

$$\psi\,(n, y) = \left(\frac{m\,\omega}{\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n\,n!\,\sqrt{\pi}}}\,H_n(y)\exp\left(\frac{-y^2}{2}\right) \tag{69}$$

with

$$y = \sqrt{\frac{m\,\omega}{\hbar}}\,x. \tag{70}$$

These represent an orthonormal set of functions:

$$\int_{-\infty}^{\infty} \psi(n_1, x)\,\psi(n_2, x)\;dx = \delta_{n_1 n_2}. \tag{71}$$

These orthogonality relations have been checked. The dipole transition matrix elements then read

$$\mu = \int_{-\infty}^{\infty} \psi(n_1, x)\,x\,\psi(n_2, x)\;dx \tag{72}$$

and have been tabulated in Table 2. One can see that the transition rule

$$\Delta n = 1 \tag{73}$$

of the harmonic oscillator is fulfilled.

transition			
$l, m \to l', m'$	μ_X	μ_Y	μ_Z
0, 0 → 1, -1	$-\frac{1}{\sqrt{2}\sqrt{3}}$	$\frac{i}{\sqrt{2}\sqrt{3}}$	
0, 0 → 1, 0			$\frac{1}{\sqrt{3}}$
0, 0 → 1, 1	$-\frac{1}{\sqrt{2}\sqrt{3}}$	$-\frac{i}{\sqrt{2}\sqrt{3}}$	
1, -1 → 2, -2	$-\frac{1}{\sqrt{5}}$	$\frac{i}{\sqrt{5}}$	
1, -1 → 2, -1			$\frac{1}{\sqrt{5}}$
1, -1 → 2, 0	$\frac{1}{\sqrt{2}\sqrt{3}\sqrt{5}}$	$\frac{i}{\sqrt{2}\sqrt{3}\sqrt{5}}$	
1, 0 → 2, -1	$-\frac{1}{\sqrt{2}\sqrt{5}}$	$\frac{i}{\sqrt{2}\sqrt{5}}$	
1, 0 → 2, 0			$\frac{2}{\sqrt{3}\sqrt{5}}$
1, 0 → 2, 1	$-\frac{1}{\sqrt{2}\sqrt{5}}$	$-\frac{i}{\sqrt{2}\sqrt{5}}$	
1, 1 → 2, 0	$\frac{1}{\sqrt{2}\sqrt{3}\sqrt{5}}$	$-\frac{i}{\sqrt{2}\sqrt{3}\sqrt{5}}$	
1, 1 → 2, 1			$\frac{1}{\sqrt{5}}$
1, 1 → 2, 2	$-\frac{1}{\sqrt{5}}$	$-\frac{i}{\sqrt{5}}$	

Table 1: Dipole matrix elements μ_{fi} of spherical harmonics.

transition	
$n_1 \to n_2$	μ
$0 \to 1$	$\frac{\sqrt{\hbar}}{\sqrt{2}\sqrt{m}\sqrt{\omega}}$
$1 \to 2$	$\frac{\sqrt{\hbar}}{\sqrt{m}\sqrt{\omega}}$
$2 \to 3$	$\frac{\sqrt{3}\sqrt{\hbar}}{\sqrt{2}\sqrt{m}\sqrt{\omega}}$
$3 \to 4$	$\frac{\sqrt{2}\sqrt{\hbar}}{\sqrt{m}\sqrt{\omega}}$
$4 \to 5$	$\frac{\sqrt{5}\sqrt{\hbar}}{\sqrt{2}\sqrt{m}\sqrt{\omega}}$

Table 2: Dipole matrix elements μ_{fi} of the harmonic oscillator.

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