

SPECTROSCOPY

Recommended Text

Fundamentals of University Physics. Vol III.

09/02/1999

Optical Spectroscopy

This is a simple process. EM radiation shines onto a sample of matter (in any particular phase). Two things can happen, the radiation is absorbed, and is re-emitted with a lower energy, or the radiation can be reemitted at a different wavelength. So this gives us information about the electronic structure of the sample. Within the sample there are quantized energy levels. Imagine there are so many atoms in the upper level and so many in the lower level. When there is incident EM radiation, the atoms are redistributed in terms of their energy whenever the energy $h\nu$ corresponds to dE (the Bohr frequency rule), the energy gap between the distribution of energy levels. Over different states this gives rise to absorption or emission.

The Hydrogen atom

The hydrogen atom is the simplest of all the atoms. There is one proton orbited by a single valence electron. They actually both orbit their mutual centre of gravity. The potential that holds them together can be expressed as,

$$V(r) = -e^2 / 4\pi\epsilon_0 r$$

From the solution of the Schrödinger equation we can state the energy level values as,

$$E_n = (-\mu e^4 / 8E_0^2 h^2) \cdot (1/n^2)$$

Where n is an integer and μ is the *reduced mass*,

$$\begin{aligned} \mu &= m_p m_e / (m_p + m_e) = m_e \\ (\text{approx, } m_p &= 1836 m_e) \\ \mu &= 0.9995 m_e \end{aligned}$$

We now define the Rydberg constant,

$$\begin{aligned} R_{\text{inf}} &= m_e e^4 / 8E_0^2 h^3 c \\ &= 1.097 \cdot 10^7 \text{ m}^{-1} \end{aligned}$$

Therefore,

$$\begin{aligned} E_n &= -(\mu/m_e) \cdot R_{\text{inf}} h c \cdot (1/n^2) \\ &= -R \cdot h c \cdot (1/n^2) \end{aligned}$$

Where $R = (\mu/m_e) \cdot R_{\text{inf}} = 1.98 \cdot 10^7 \text{ m}^{-1}$.

Therefore,

$$E_n = -2.186 \cdot 10^{18} \cdot (1/n^2) \\ = -13.6 \cdot (1/n^2) \text{ eV}$$

Hence for lowest allowed energy here (for $n=1$) is -13.6 eV.

fig 1

(See fig 1 for information on the Lyman, Balmer and Paschen series)

The **selection rule** states that Δn the change in energy levels can be anything.

Now if we look at the wavelength of a photon between two energy levels. Consider a system with two energy levels, E_2 and E_1

$$E_2 - E_1 = -Rhc \cdot ((1/n_1^2) - (1/n_2^2))$$

Photon energy is therefore

$$h\nu = E_2 - E_1 = hc/\lambda = Rhc \cdot ((1/n_1^2) - (1/n_2^2)) \\ 1/\lambda = R \cdot ((1/n_1^2) - (1/n_2^2))$$

In the Balmer series, $n_1=2$ and the series limit is $n_2=\infty$. Therefore,

$$1/\lambda = R \cdot 1/4 \\ \lambda = 3645 \text{ \AA}$$

For the first line $n_2=3$,

$$1/\lambda = R \cdot ((1/4) - (1/9)) \\ \lambda = 6561 \text{ \AA}$$

fig 2

16/02/1999

Orbital Quantisation

The density of the electron cloud, in Hydrogen say, is proportional to the modulus of the squared wave function. The density drops off with increasing radius from the nucleus. We define a new quantity called the radial probability where we have the relation,

$$4\pi r^2 dr \cdot |\Psi|^2$$

From the solution of the wave equation we find that for a given value of n , there are n different charge distributions, each associated with a different amount of angular momentum. Classically the angular momentum is expressed as,

$$L = mvr$$

Using quantum mechanics however we have,

$$L^2=l(l+1).\hbar^2$$

Where l is the orbital angular momentum quantum number, with a value of $(n-1)$ to zero. For example if $n=3$ then l can be 2, 1, 0 ie three electron clouds but all with the same energy.

"SPEC1" (sheet)

Fig1

Looking at the energy diagram in fig 1. The $n=1$ level is called the **1s** level and so on (see diagram). By the selection rules Δn can be anything and Δl can be ± 1 . So the Lyman series can be produced by transition the p terms to the 1s level. The Balmer series is formed from any transition from 2s upto 5s across to 2p upto 5p. Simillary we get the Pachen series from transitions from the d terms to the p terms.

Space Quantisation

Space quantisation gives us restricted orbits with respect to a magnetic field direction.

Fig 2

The restriction is such that the component $L_z = m_l \hbar$. Where m_l is the orbital magnetic quantum number. This number can have values as shown,

$$m_l=0,\pm 1,\pm 2,\dots,\pm l$$

Spin quantisation

As an electron orbits it has angular momentum about the atomic nuclei, but it also has additional angular momentum by spinning on it's own axis. S is the spin angular momentum, it is expressed as,

$$S^2=s(s+1).\hbar^2$$

Where $s=\frac{1}{2}$

Also, there is space quantisation of spin,

fig 3

From fig 3, $m_s=\pm\frac{1}{2}$

Summary,

n : Energy

l : Angular Momentum

m_l : orbital component of angular momentum

S : Spin

m_s : Spin component of angular momentum.

23/02/1999

One electron atoms

These are group one elements that have one valence electron.

See sheet SPEC3

We measure wave lengths in relation to corresponding energies. We can write

$$\mathbf{dE = h\nu = hc / \lambda = hc \bar{\nu}}$$

$\bar{\nu}$ is the wave number,

$$\mathbf{dE = 6.625 \cdot 10^{-34} \cdot 2.998 \cdot 10^8 \cdot \bar{\nu}}$$

Therefore,

$$\mathbf{1 \text{ J} = (1/1.98) \cdot 10^8 \text{ m}^{-1}} \\ \mathbf{= 5.034 \cdot 10^4 \text{ m}^{-1}}$$

$$\mathbf{1 \text{ J} = 5.034 \cdot 10^6 \text{ cm}^{-1}}$$

Also,

$$\mathbf{1 \text{ eV} = 1.602 \cdot 10^{-19} \cdot 5.034 \cdot 10^6} \\ \mathbf{= 8066 \text{ cm}^{-1}}$$

Now let us consider a specific series,

The Sodium spectrum

Sodium has eleven electrons, ten of them being in closed shells and the remaining electron in the valence shell. The ten electrons are tightly bound to the nucleus. For optical spectra they are inactive. It is the single valence electron that gives the optical spectra of the atom. Comparing to the energy levels of the hydrogen atom (see SPEC3 sheet again) because of the similarity of having one valence electron.

- 1) The levels for a given value of principal quantum number (n) are low.
- 2) The degeneracy on L is lifted. i.e., the 3s and 3p levels have different energies.
- 3) For a given value of n, the s level is decreased more than the p level. The p level is decreased more than the d level also.

Then: selection rules predict the emission lines. $\Delta n = \text{anything}$ & $\Delta l = \pm 1$. The **principal series** is formed from transitions from any p level to the 3s level. These are the strongest lines. The first line of the principal series is the 3p to 3s transition. The **diffuse series** is formed from 3d-6d transitions to the 3p level. The **sharp series** is formed from 6s-4s transitions to 3p level. The first letter of each series

historically determined the origin of the letters which denote energy terms.

To explain features of the energy level diagram;

- 1) Lifting the degeneracy on l . Each shell screens out nuclear charge to outer electrons. The effective nuclear charge is called Z_{eff} . The electron energy (like hydrogen atom) can be written as,

$$E_n = -(\mu Z_{\text{eff}}^2 e^4 / 8 E_0^2 h^2) (1/n^2)$$

As Z_{eff} increases (which happens when the coulombic screening is not complete) E_n decreases.

The screening depends on the electronic wave function.

fig 1

For $l=2$, the energy is of the order of the Hydrogen atom ($Z_{\text{eff}}=1$). As l decreases, Z_{eff} increases and E_n decreases. Therefore $l=0$ gives the lowest energy.

02/03/1999

Fine Structure

We find that the sharp and the principal series are split into doublets. The diffuse series and the fundamental series are split into triplets.

fig 1

This is explained in the following section.

Spin-Orbit coupling

This splits all the levels except the s levels. When we have a charge carrier traveling in a circle and we have a magnetic field which is in the same direction as the angular momentum. We can formulate the following from fig 2

fig 2

$$\mu_L = iA = (e/T)A = (e\omega/2\pi) \cdot \pi r^2$$

But,

$$\underline{L} = mvr = m\omega r^2 = m_e (2\pi \mu_L / e)$$

Therefore,

$$\begin{aligned} \mu_L &= -(e2m_e)\underline{L} = -(e \cdot \hbar / 2m_e) \cdot (\underline{L} / \hbar) \\ &= -(\mu_B / \hbar) \underline{L} \end{aligned}$$

μ_B is known as the Bohr magneton (J/T),

$$\mu_B = e\hbar/2m$$

The (additional) electron magnetic moment due the electron spinning on it's own axis is,

$$\mu_s = -2(\mu_B/\hbar) \mathbf{S}$$

fig 3

The "2" is called the "Electron g-factor"

fig 4

μ_L and μ_s interact in the following way. The electron sees a positively charged nucleus circulating it.

fig 5

To determine the energy of μ_s in B_{int} ,

$$\mathbf{E} = -\mu_s \cdot \mathbf{B}_{int} \\ \propto \mathbf{S} \cdot \mathbf{L}$$

This is the orbit interaction energy. To calculate $\mathbf{S} \cdot \mathbf{L}$ by vector addition to give the total angular momentum of the atom, \mathbf{J} .

fig 6

(diagrammatic vector summation of J)

where,

$$\mathbf{L}^2 = l(l+1)\hbar^2 \\ \mathbf{S}^2 = s(s+1)\hbar^2 \\ \mathbf{J}^2 = j(j+1)\hbar^2$$

j is a new quantity to us, it is the total angular momentum quantum number. j has values $l+s \dots l-s$. Since $s=1/2$, $j=1+1/2 \dots 1-1/2$. There are rules for adding angular momentums in quantum mechanics. From the triangle in fig 6,

$$\mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L} \cdot \mathbf{S}$$

Therefore,

$$\mathbf{L} \cdot \mathbf{S} = 1/2(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) \\ = 1/2\hbar^2(j(j+1) - l(l+1) - s(s+1))$$

Therefore,

$$\mathbf{E}_{so} \propto \mathbf{L} \cdot \mathbf{S} = A[j(j+1) - l(l+1) - s(s+1)]$$

E_{so} is the spin orbit energy and A is the "spin-orbit interaction".

For the p level, $l=1$, $s=1/2$, therefore $j=3/2, 1/2$

fig 7

Therefore,

$$\begin{aligned} E_{s_0}(j=3/2) &= A[(3/2) \cdot (5/2) - 1 \cdot 2^{-1/2} \cdot (3/2)] = A \\ E_{s_0}(j=1/2) &= A[1/2 \cdot (3/2) - 1 \cdot 2^{-1/2} \cdot (3/2)] = -2A \end{aligned}$$

The energy difference between the transitions in figure seven (from both 3p levels to the s level) is **3A**.

For the s levels, $l=0$, $s=1/2$ and $j=1/2$ hence,

$$dE = A'[1/2(3/2) - 0 \cdot 1^{-1/2}(3/2)] = 0$$

This means there is no energy splitting.

09/02/1999

(Continued)

$$dE_{s_0} = A[j(j+1) - l(l+1) - s(s+1)]$$

fig 1

For the d state, $l=2$, $s=1/2$, $j=3/2, 5/2$

$$\begin{aligned} dE_{s_0} &= A'[5/2 \cdot 3/2 - 2 \cdot 3 - 1/2 \cdot 3/2] = 2A' \\ dE_{s_0} &= A'[3/2 \cdot 5/2 - 2 \cdot 3 - 1/2 \cdot 3/2] = -3A' \end{aligned}$$

The selection rule states that $\Delta j = \pm 1$

fig 2

Zeeman Effect

fig 3

fig 4

When a magnetic field is applied to atoms we get further splitting of the energy levels, for sodium see figures 3 and 4.

An atom has magnetic moments μ_l from orbital motion and μ_s from the electron spin. The two moments add together to give a total moment for the atom.

fig 5

fig 6

Where,

$$\underline{\mu}_L = -g_J(\underline{\mu}_B/\hbar)\underline{J}$$

Where g_J is the Landè g-factor.

fig 7

fig 8

Energy of $\underline{\mu}_B$ in the field B,

$$\begin{aligned} E &= -\underline{\mu}_J \cdot \underline{B} \\ &= +g_J(\underline{\mu}_B/\hbar)\underline{J} \cdot \underline{B} \end{aligned}$$

$$\begin{aligned} (\underline{J} \cdot \underline{B} &= JB\cos(\theta)) \\ E &= g_J(\underline{\mu}_B/\hbar)\underline{J} \cdot \underline{B} = g_J(\underline{\mu}_B/\hbar)m_J\hbar B \\ &= g_J\mu_B m_J B \end{aligned}$$

To find g_J, \dots

fig 9

$$\underline{\mu}_J = \mu_s \cos(\theta) \underline{J} + \mu_L \cos(\theta) \underline{L}$$

Where,

$$\begin{aligned} S^2 &= L^2 + J^2 - 2JL \cos(\theta) \\ \cos(\theta) &= (L^2 + J^2 - S^2)/(2JL) \end{aligned}$$

&

$$\begin{aligned} L^2 &= J^2 + S^2 - 2JS \cos(\theta) \\ \cos(\theta) &= (J^2 + S^2 - L^2)/(2JS) \end{aligned}$$

Now substitute for something

$$\begin{aligned} -g_J(\underline{\mu}_B/\hbar)\underline{J} &= -2(\underline{\mu}_B/\hbar) * (J^2 + S^2 - L^2)/(2JS) - ((\underline{\mu}_B/\hbar) * L) * ((L^2 + J^2 - S^2)/(2JL)) \\ g_J &= ((J^2 + S^2 - L^2)/(J^2)) + ((L^2 + J^2 - S^2)/(2J^2)) \\ &= (3J^2 + S^2 - L^2)/(2J^2) = 1 + (J^2 + S^2 - L^2)/2J^2 \\ &= 1 + ((j(j+1) - s(s+1) - l(l+1))/(2j(j+1))) \end{aligned}$$

(see sheet SPEC4)

16/03/1999

Splitting of the D₁ lines in a field of 1 Tesla

In a magnetic field the 2p level splits into two, where $j = \pm 1/2$ and the 2s level splits into two as well, also $j = \pm 1/2$. For the 2p level $g_j = 2/3$ and for the 2s level $g_j = 2$. Due to Zeeman splitting,

$$dE = g_J \mu_B m_J B$$

fig 1

From figure 1,

$$dE(1) = -(1+1/3)\mu_B B = -(4/3)\mu_B B$$

$$dE(2) = -(1-1/3)\mu_B B = -(2/3)\mu_B B$$

$$dE(3) = +(1-1/3)\mu_B B = +(2/3)\mu_B B$$

$$dE(4) = +(1+1/3)\mu_B B = +(4/3)\mu_B B$$

fig 2

We now calculate the shift of line 4 in a 1T field.

$$dE = 4/3 \times 9.27 \times 10^{-24} \text{ J/T} \times 1 \text{ T}$$

To find lambda,

$$E = hc/\lambda$$

$$dE/E = d\lambda/\lambda$$

Therefore,

$$d\lambda = \lambda \cdot (dE/E) = \lambda^2 \cdot (dE/hc)$$

$$= (5892 \times 10^{-10})^2 \cdot (4/3) \cdot 9.27 \times 10^{-24} / (6.626 \times 10^{-34} \cdot 3 \times 10^8)$$

$$= 0.22 \text{ \AA}$$

Multielectron atoms

Let us first consider a two electron atom. We first find all the terms, each term corresponding to a different energy level. When we say a *two electron atom* we mean two valence electrons.

Each electron has its own angular momentum. Let the respective orbital angular momenta be l_1 and l_2 .

The total orbital angular momentum is,

$$\underline{L^2} = L(L+1)\hbar^2$$

where,

$$L = \text{total orbital angular momentum quantum number}$$

$$L = (l_1 + l_2) \dots (l_1 - l_2)$$

The total spin angular momentum is,

$$\underline{S^2} = S(S+1)\hbar^2$$

where,

$$\mathbf{S} = \text{total spin angular momentum quantum number}$$

$$\mathbf{S} = (s_1 + s_2) \dots (s_1 - s_2)$$

So the total angular momentum is,

$$\mathbf{J}^2 = \mathbf{J}(\mathbf{J} + 1)\hbar^2$$

where,

$$\mathbf{J} = \text{total angular momentum quantum number}$$

$$\mathbf{J} = (\mathbf{L} + \mathbf{S}) \dots (\mathbf{L} - \mathbf{S})$$

This is known as *Russel Sanders coupling*. In general,

$L = S = J = 0$ for closed shells.

Terms for two electrons

fig 3

fig 4

From figure 3, there are two cases, $n_1 = n_2$ and $n_1 < n_2$.

1) $n_1 < n_2$, $l_1 = 0, l_2 = 0; L = 0$

$s_1 = 1/2, s_2 = 1/2; S = 1, 0$ (1 for parallel spins, 0 for opposite spins. Also

When $S = 1, J = 1$ and $S = 0$ and $J = 0$.

We get the terms, 3S_1 and 1S_0 , the former is a spin triplet and the latter is a spin singlet.

$n_1 = n_2, l_1 = 0, l_2 = 0, s_1 = 1/2, s_2 = 1/2$, from this 3S_1 is not allowed by the Pauli exclusion principal. We can only have the 1S_0 term.

2) $n_1 = n_2, l_1 = 1, l_2 = 0, L = 1$

$s_1 = 1/2, s_2 = 1/2, S = 1, 0$

For $S = 1$ we have, $^3P_{2,1,0}$ and for $S = 0$ we have 1P_1

This is applicable $n_1 = n_2$ and $n_1 < n_2$

L =	0	1	2	3
	S	P	D	F

3) $n_1 < n_2, l_1 = l_2 = 1, L = 2, 1, 0$

$s_1 = s_2 = 1/2, S = 1, 0$

The available terms are,

$^3D_{3,2,1}, ^1D_2, ^3P_{2,1,0}, ^1P_1, ^3S_1, ^1S_0$

The number of terms are restricted by the Pauli exclusion principal, however, this is unproved so far.

13/04/1999

Hund's rule tell us that the lowest energy state has the largest value of S, then if two states have the same value of S the lowest is the one with the higher L value.

fig 1

Figure one shows how this rule is applied when determining the values of sub levels.

The energy change due to spin orbit coupling is,

$$dE_{so}=(A/2)[J(J+1)-L(L+1)-S(S+1)]$$

This is the same as for single electron atoms, but J,L and S are for the atom as a whole.

Splitting between levels is given as follows. Suppose we have three levels, J+1, J and J-1. The difference between the J+1'th and J'th level is $dE_{so}(J+1 \rightarrow J)$.

$$\begin{aligned} dE_{so}(J+1 \rightarrow J) &= (A/2)[(J+1)(J+2)-L(L+1)-S(S+1)] \\ &= -(A/2)[J(J+1)-L(L+1)-S(S+1)] \\ &= A(J+1) \end{aligned}$$

i.e., splitting due to J value of the upper level. This is known as the *Landè interval rule*.

Say we have three levels 3P_2 , 3P_1 and 3P_0 the splitting between the first two is twice as wide as the second two, for example. Also three levels, 3D_3 , 3D_2 , 3D_1 the ratio between the first and second is 3 to 2.

The Helium atom

(see sheet)

In the ground state, we have;

$$\begin{aligned} n_1 &= n_2 = 1 \\ l_1 &= l_2 = 0, \quad L = 0 \\ s_1 &= s_2 = \frac{1}{2}, \quad S = 0, 1 \end{aligned}$$

However S=1 is forbidden by the Pauli exclusion principal.

For excited states we have,

$$\begin{aligned} n_1 &= 1 & l_1 &= 0 & s_1 &= \frac{1}{2} \\ n_2 &= \text{anything} & l_2 &= \text{determined by } n_2 \end{aligned}$$

Therefore, $L = l_1 + l_2 = l_2$ and $S = s_1 + s_2 = 0$ (up,down), 1(up,up). Both singlet and triplet stages.

Screening effect

This causes the energy levels to be different with the same value of n.

fig 2

The energy for this is expressed as

$$E = -(\mu Z_{\text{eff}}^2 e^4 / 8 E_0^2 h^2) (1/n^2)$$

For $l_2=1$, complete screening, $Z_{\text{eff}}=1$. $l_2=0$, incomplete screening, $Z_{\text{eff}}>1$, which means the energy is decreased.

20/04/1999

Fine Structure (see last sheet)

For a singlet state (parallel), no fine structure. For the red line, 6680 Å. At the $^3P_{2,1,0}$ level we have a triplet with spacing in the ratio of two to one. Transitions from the upper 3S_1 (QN J) we get three transitions to each 3P triplet. Fine structure is found on all the triplet (parallel) states.

The energy difference between the singlet and triplet states.

fig 1

The total energy of the electrons in the atom is,

$$= E(1) + E(2) + e^2 / 4\pi\epsilon_0 r_{12} \pm \\ = (\mu 2p^2 e^4 / 8\pi\epsilon_0^2 h^2) (1/n^2) + e^2 / 4\pi\epsilon_0 r_{12} \pm dE$$

These are known as the single particle energies. The $\pm dE$ is known as the exchange energy, + for anti-parallel orbits and - for parallel orbits.

Molecular Spectroscopy

The energy associated with rotations and vibrations of the molecule is much less than that with electronic transitions. Measurement of these are made as shown in fig 4.

fig 4

For higher energy absorptions, vibrational electron states absorb at near infrared and lower energy transition we have electron rotation states at the far infrared to μ -wave.

Rotation energy of molecules

fig 5

The energy of rotation is,

$$E_{\text{rot}} = \frac{1}{2} I \omega^2$$

where,

$$I = M_A x^2 + M_B (R-x)^2$$

but,

$$M_A x = M_B (R-x)$$

Therefore,

$$\begin{aligned} x &= M_B R / (M_A + M_B) \\ R-x &= (M_A / M_B) (M_B R / (M_A + M_B)) = R M_A / (M_A + M_B) \end{aligned}$$

Therefore,

$$\begin{aligned} I &= (M_A M_B^2 R^2 / (M_A + M_B)^2) + (M_A^2 M_B R^2 / (M_A + M_B)^2) \\ &= (M_A M_B R^2 / (M_A + M_B)^2) (M_A + M_B) \\ &= \mu R^2 \end{aligned}$$

$$\mu = M_A M_B / (M_A + M_B)$$

Also, the angular momentum,

$$L = (J(J+1))^{1/2} \hbar$$

Where J is the rotational quantum number. Also classically,

$$L = I \omega$$

Therefore,

$$\omega = (1/I) (J(J+1))^{1/2} \hbar$$

Therefore,

$$\begin{aligned} E_{\text{rot}} &= \frac{1}{2} I \left(\frac{1}{I^2} (J(J+1)) \hbar^2 \right) \\ &= (\hbar^2 / 2I) J(J+1) \\ &= B J(J+1) \end{aligned}$$

Where,

$$B = \hbar^2 / 2I$$

This is called the rotational constant.

fig 6

The selection rule says that J changes by one, or $dJ = \pm 1$.

Microwave spectroscopy**fig 7**

The absorption lines are all equally spaced (see fig 7). NOW we will determine why. The energy for each absorption is dE , which is the difference between the upper and lower level of the transition.

fig 8

$$\begin{aligned} dE &= BJ(J+1) - BJ(J-1) \\ &= 2BJ \end{aligned}$$

So the energy gap is simply integer multiples $2B$ that is why each gap is $2B$! To find the band length for CO, for which $2B = 3.83 \text{ cm}^{-1} = 7.66 \times 10^{-23} \text{ J}$

Therefore,

$$2B = 2 \cdot (\hbar^2 / 2I) = 7.66 \times 10^{-23} \text{ J}$$

Therefore,

$$I = 1.45 \times 10^{-46} \text{ Kg m}^2$$

but,

$$I = \mu R^2$$

Where,

$$\mu = \frac{M_A M_B}{(M_A + M_B)} = \frac{(12 \cdot 15.99)}{(12 + 15.99)} \cdot (1/N) \cdot 0.001$$

This converts from amu's to grams, then grams to kilograms!

Therefore,

$$R = 1.13 \times 10^{-10} \text{ m}$$

27/04/1999

Vibrational Spectra of diatomic molecules

First we consider the simplest molecule, two atoms. Between these two atoms there is a potential, which can be expressed as a function of the distance between them.

fig 1

In figure one, the repulsive force arises from the overlap of electron clouds and the attractive force can be covalent or coulombic forces. r_0 is the equilibrium position. An approximate expression for $V(r)$ is,

$$V(r) \sim (r-r_0)^2$$

ie the restoring force is proportional to the square of the displacement, just as a harmonic oscillator region. To find the total energy of the molecule (KE+PE) solve the Schrödinger equation.

$$-(\hbar^2/2\mu)(d^2\Psi/dr^2)(E-V(r))\Psi = 0$$

The solution of the equation is,

$$E_v = h\nu_{osc}(n+1/2)$$

Where n is used as the vibrational quantum number and ν_{osc} is the characteristic frequency of vibration. At the distance r_0 , $n=0$ and E_v is called the **zero point energy** (see quantum mechanics notes).

fig 2

This leads us to the field of infra red spectroscopy.

IR Specroscopy

For IR spectroscopy, we have an IR source, the IR beam is then passes through a *monochromator* the beam then passes through the sample, finally a detector senses what is transmitted from the sample. The seletion rules for molecular vibrations state that dn can be ± 1 , ± 2 , ± 3 and so on. However, ± 1 is the fundamental absorption, it is strong here. The other values for dn are called *overtones* are weaker than the fundamental. At room temperature however, all the molecules are in the ground state. Rarely seen transitions are from the $n=1$ level to higher levels, they are called **hot bands**. This is beacause the difference in energy values are greater than the kT value (recall the Boltzmann distrobution, $N=N_0 \exp(-dE/kT)$). The net effect is only ususally observed in the $n=0$ to the $n=1$ transition. Also, these are only then oberved if the molecule has a instantaneous electric dipole moment.

More complex molecules

How absorption lines do we expect to see for more complicated molecules ? It is found from counting the number of degrees of freedom of the molecule. For a single atom the number of degrees of freedom is equal to **3**, and these are all translational. For N atoms of the molecule, the number of degrees of freedom is simply **3N**, of which, 3 are translational (unless we have a linear molecule), the rest that remain are vibrational.

fig 3

Therefore, the number of modes of vibration is $(3N-6)$ or $(3N-5)$ if the molecule is linear).

Now let us consider the example of SO₂,

fig 4

The motions indicated by (1) are symmetrical stretches at a frequency, ν_1 . (2) is an Asymmetrical stretch, at ν_2 . (3) is a bending process at frequency ν_3 . We would hence observe three absorption lines. For SO₂ $\nu_1 = 7.35 \mu\text{m}$, $\nu_2 = 8.69 \mu\text{m}$ and $\nu_3 = 19.23 \mu\text{m}$.

Now let us consider the linear molecule, CO₂ (O-C-O). There should be four modes of vibration ($3N-5=4$) but we only observe two absorption lines at $4.25 \mu\text{m}$ and $14.99 \mu\text{m}$. An unobservable motion is a symmetrical stretch, this is because there is never a dipole moment, the molecule is always symmetrical. However the asymmetric stretch allows a dipole to occur, which gives us the $4.25 \mu\text{m}$ line. The bending motion gives us the $14.99 \mu\text{m}$ line, this bending is bending in the plane of the molecule. CO₂ has two modes of bending, both degenerate (same energy). The other bending motion is such that the carbon (or both oxygens) vibrate in and out of the molecular plane.

Now let us consider the HCl molecule. See Sheet.

04/05/1999

We now consider the energy in the R branch (see sheet).

$$\begin{aligned} \text{Energy of R branch} &= h\nu_{\text{osc}} + BJ(J+1) - B(J-1)J \\ &= h\nu_{\text{osc}} + 2BJ \end{aligned}$$

where $J=1,2,\dots$

So the energy increases by an amount $2B$, this gives the regular increments across the spectra.

Intensity of the fine structure lines

fig 1

The intensity is proportional to the population of molecules in the latter lower vibrational state. Also,

$$I \propto g_i \cdot \exp(-dE/kT)$$

Where the first term is the degeneracy of the energy level and the second term is the Boltzmann distribution term. The degeneracy is calculated as,

$$\text{Degeneracy} = \text{No. of } m \text{ values}$$

$$=(2J+1)$$

Another feature is that each peak (which is spaced by $2B$) splits into two peaks in itself. This is due an isotopic effect. There are two common isotopes of Chlorine (remember we are talking about the spectra from HCl !), there is ^{35}Cl (75%) and ^{37}Cl (25%). This means that there are two different frequencies at which the molecules will vibrate at, one for each isotope.

Raman Spectroscopy

Consider sending photons at a molecule, the photons are usually reflected from the molecule. Suppose that the frequencies are changed so that we send in a frequency ν and we get frequencies away from the molecule of $\nu \pm d\nu$. By energy conservation we have,

$$h\nu + E_i = h\nu' + E_f$$

Where E_x are the initial and final energy of the molecule.

$$\nu - \nu' = (1/h)(E_f - E_i)$$

If $E_f = E_i$, then $\nu = \nu'$ (this is the case for Rayleigh scattering). If $E_f < E_i$ then $\nu < \nu'$, we then have a change of frequency, this is **Raman scattering**. The energy path for Raman scattering is as shown in fig 2.

fig 2

Fig 3 shows a plot of the Raman and Rayleigh lines.

fig 3

The selection rules for Raman spectroscopy are different to usual, in this case **$dJ = \pm 2$** . So we can determine the shift of energy lines (dE). The molecule gets excited and then ends in a final state (as in fig 2. The molecule goes to a virtual state and then rests at a final state, here the final state is the $J+2$ and the initial is J).

$$\begin{aligned} dE &= B(J+2)(J+3) - BJ(J+1) \\ &= B(4J+6) \end{aligned}$$

So the difference between all the lines is hence **$4B$** . That is to say that all the energy lines from Raman scattering are split by **$4B$** . This is however the rotational energy as seen by Raman spectra. We also observe Raman spectra from the vibrational states. Again we follow the path that molecule are excited from the $n=0$ level to a virtual level and then back down the the next level up ($n=1$). Again, plotting intensity against frequency gives us the Stokes and anti-Stokes line shifts again ($d\nu = dE/h$).

If we have rotational states also with the vibrational states we get the Rayleigh and Raman lines, but with lots of fine structure.

fig 4

Example of vibration spectra:

Consider SO_2 we have three absorption lines; (ν_1 , highest frequency) symmetrical stretch, (ν_2) anti-symmetrical stretch and (ν_3 , lowest frequency) bending. Figure 5 shows what Raman spectroscopy gives us for this system.

fig 5

Now consider CO_2 . We have two absorption lines (see earlier), the first is for the anti-symmetrical stretch (highest energy, ν_1) and the second is for the molecule bending (lowest energy, ν_2). For the symmetrical stretch we didn't see a absorption line because there was no dipole moment. For Raman spectroscopy however, we do see a line for the symmetrical stretch (ν_3) this is due to the **rule of mutual exclusion**.

The Rule of Mutual Exclusion (for vibrational states)

This applies for molecules with a centre of symmetry (of which linear molecule are). If such a molecule is Raman active then it is IR inactive. If it is Raman inactive then it is IR active.

Raman lines are always seen between rotational states.

The End !!! ;-D