Module 3 : Molecular Spectroscopy

Lecture 14 : Magnetic Resonance Spectroscopy

Objectives

After studying this lecture, you will be able to

- calculate the magnetic moments of nuclei, given the values of I and g.

- Calculate the population differences between nuclear and electron spin energy levels.

- Define chemical shift and shielding constant.

- Calculate Larmor frequency.

- Identify functional groups from the chemical shift data.

- Predict the number of lines and their relative intensities in the multiplets of the spectra.

- Distinguish between the features of NMR and ESR.

14.1 Introduction

Nuclei of several atoms and all electrons possess an intrinsic quantum number which is referred to as the spin quantum number, s. For electrons, s = ½ while for nuclei, s (denoted by I for nuclei) can be ½, 1, 1 ½, and so on. While you may have seen diagrams showing electrons rotating clockwise or anticlockwise, electron spin and nuclear spin are quantum mechanical features which have no classical counterparts. In the absence of a magnetic field, the spin levels are degenerate. When these nuclei or electrons are placed in a magnetic field, the degeneracy is removed and transitions are possible between the spin energy levels. Proton nuclear magnetic resonance (NMR) spectroscopy was developed first. Even in the presence of an external magnetic field, different protons absorb the radiofrequency radiation at different wavelengths because the local fields at the protons can be different from the external field. The local fields at a proton are created by the electrons surrounding it and also due to the presence of other additional electron clouds such as those in acetylene or benzene in its vicinity. The characteristic frequencies of protons in different environments can be used to identify different protons in unknown/newly synthesized molecules. NMR has become a very powerful analytical technique. Magnetic resonance imaging (MRI) has become a very useful tool in medicine which enables one to differentiate between normal tissues/organs from the abnormal ones. Electron spin resonance deals with transitions observed in free radicals. The nuclear spins and electron spins interact among themselves as well as with each other producing multiplets in spectral lines.

14.2 Spin and the Magnetic field

The magnitude of the angular momentum associated with a nuclear spin quantum number I is

$$\sqrt{\{I\ (I\ +\ 1)\}}\,\hbar \tag{14.1}$$

The projection of the angular momentum vector on the z axis can take on all the integral (for integral spins) and half integral (for half integral spins) starting from + I to − I. A "spinning" charge produces a magnetic moment. The magnetic moment (strength of the magnet, which is dipolar) associated with this angular momentum is given by

$$\mu\ =\ \frac{q}{2m}\{I\ (I\ +\ 1)\ \}^{1/2}\ \frac{h}{2\pi}\ =\ \frac{qh}{4\pi m}\ \sqrt{I\ (I+1)} \tag{14.2}$$

Here, q is the charge and m the mass of the nucleus.   The above equation is for point charges. Since the nuclei are not point charges, a factor g_I is associated with them and the magnetic moment becomes

$$\mu = \frac{qh}{4\pi m} \frac{g_I}{} \left[I \left(I + 1 \right) \right]^{1/2}, \quad \text{J/T} \qquad (14.3)$$

The standard MKS unit for μ is J/T, where T refers to Tesla, the magnetic field strength. For a proton of charge $e = 1.6 \times 10^{-19}$ Coulomb and mass $m_p = 1.67265 \times 10^{-27}$ kg. The nuclear magneton $eh/4\pi m_p$ is

$$\beta_N = \frac{eh}{4\pi m} = 5.05 \times 10^{-27} \quad J/T \qquad (14.4)$$

The g_I values for a few nuclei are H (5.586), ^{2}H (0.857), ^{13}C (1.405), ^{14}N (0.404). When a magnetic field B is applied, the interaction energy between the field and the magnetic moment is

$$E = -\mu \cdot B \qquad (14.5)$$

For the proton, spin ½ is aligned in the direction of the field and spin -½ is aligned in a direction opposite to the field. The difference in the energy between the two levels is

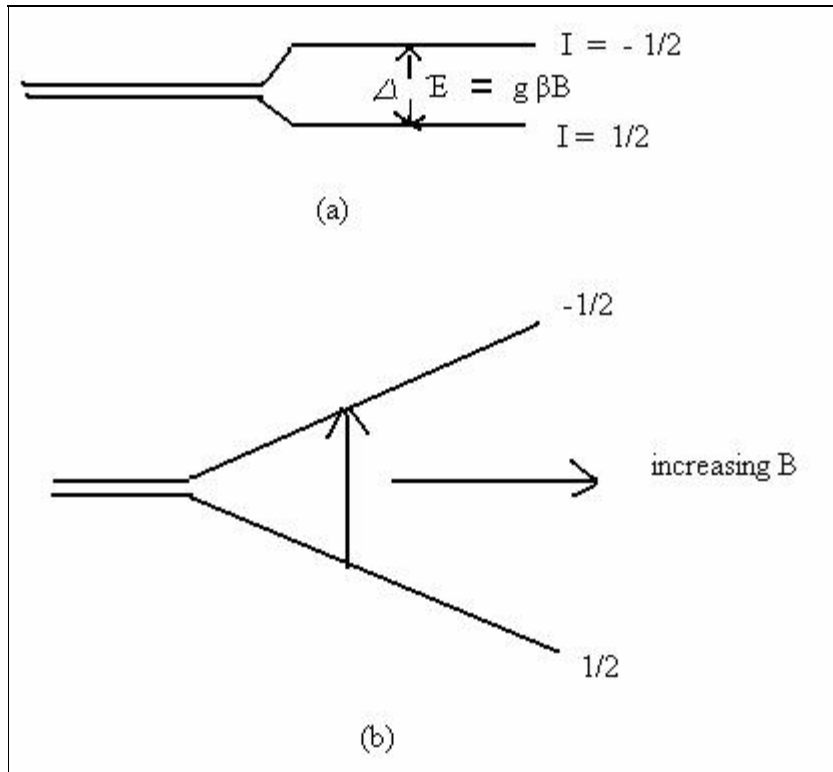$$\Delta E = E_{-1/2} - E_{1/2} = - \; g_I \, \beta_N \, B \left(-1/2 \right) - (-) \, g_I \, \beta_N B \left(1/2 \right))$$

$$= g_I \, \beta_N \, B \qquad (14.6)$$

If a radiation of frequency ν such that,

$$\Delta E = h\nu = g_I \, \beta_N \, B \qquad (14.7)$$

then, this frequency is absorbed by the nucleus.

14.2 Spin and the Magnetic field

Figure 14.1. (a) Energy levels of protons in a magnetic field. (b) Energy levels with increasing field.

The splitting of nuclear spin energy levels, the energy gap and the increase in the difference between the upper and lower levels are shown in Fig. 14.1.

One of the beautiful features of spins in a magnetic field is that they can not be aligned exactly in the field direction but precess in a cone around the field axis as shown in Fig. 14.2.
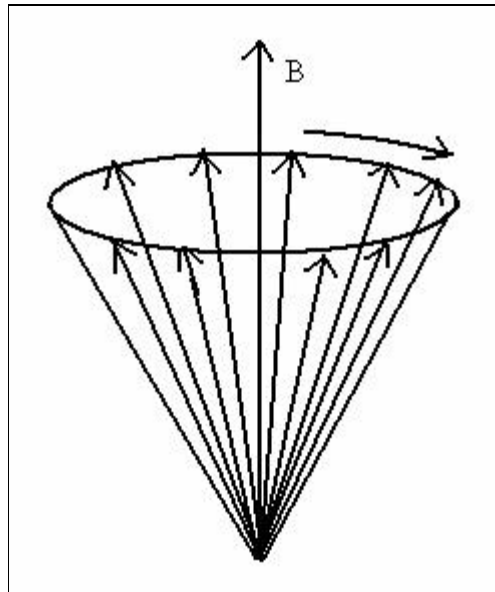
Fig. 14.2 The Larmor precession of nuclei. The arrows represent spins with respect to B. The nuclei precess in the cone. By giving appropriate pulses of radio frequency radiation, the precessing cone can be flipped, the spins can be bunched together or fanned out! The Larmor precession on frequency is given by

$$\omega = \frac{magnetic\ moment}{angular momentum} \quad x \quad B \ , \quad radians\ /\ sec.$$

(14.8)

$$= \frac{\mu B}{2\pi I} = \frac{g_I \beta_N B}{h} \quad Hz$$ Since the energy levels become more widely separated by increasing the field,

it can be readily seen (from $h n = g \beta B$) that a magnetic field of 2.3487 T requires a frequency of 100 MHz for the NMR transition of a bare proton. This frequency is in the radiofrequency range.

The differences between the energy levels of protons and electrons in a magnetic field are very small as ΔE is very small.

14.2 Spin and the Magnetic field

Example 14.1

Calculate N_{upper} / N_{lower} for protons (at 2.3487T) and electrons (at 0.34T) at 300 K.

Solution $\Delta E_p = g_p\beta_N \times 2.3487 = 7 \times 10^{-26}$ J

$\Delta E_e = g_e\beta_e \times 0.34$ T $= 6 \times 10^{-24}$J

The value of kT at 300 K is $1.38 \times 10^{-23} \times 300 = 4.2 \times 10^{-21}$ J

Therefore N_{upper} /N_{lower} for protons $\approx e^{-0.00001} = 0.99999$

For electrons, the value is 0.999. The value of g_e for electrons is 2.0023. An implication is that soon after absorbing light, the population of the lower and upper levels becomes equal (ie, the system is saturated) and then there is no more absorption. This feature, rather than becoming a bottleneck, is exploited greatly in pulsed and Fourier transform NMR. In these methods, the nuclei absorb radiation and relax to the lower levels several times in the given pulse sequence of an experiment.

14.3 NMR of Protons

If all protons in a molecule absorbed at the same frequency in the presence of an external field, NMR will be of little use. Fortunately, this is not the case because local fields on different nuclei are different from the applied external field (B_o). The electrons around the nuclei shield the nuclei by inducing an opposing field (diamagnetic interaction) to the applied field. The induced fields and the effective fields are

$B_{induced} = \sigma B_{applied} = \sigma B_o$ (14.8)
s

$$B_{effective} = B_{applied} - B_{induced} \tag{14.9}$$

$$= B_o (1 - \sigma) \tag{14.10}$$

σ is called the shielding constant.   Different environments have different shielding constants because the electron densities at different protons (such as a methyl proton, an acetylenic proton, a hydroxyl proton, etc) are different. This feature may be expressed as

$$B_i = B_o (1 - \sigma_i) \tag{14.11}$$

$$B_{CH} = B_o (1 - \sigma_{CH}) \tag{14.12}$$

$$B_{RH} = B_o (1 - \sigma_{RH}) \tag{14.13}$$

When R is a functional group such as C_6H_5, CH_3O and so on.

Let us rationalize the meaning of the shielding constant and its effect on absorption frequencies. Consider the protons in C – H and O – H. Oxygen is more electronegative, draws more charge towards it leaving less charge on the connected hydrogen. The magnetic field experienced by H in O – H is greater than for the C – H hydrogen and thus O – H protons will have a larger Larmour precession frequency. Conversely, at a fixed radiofrequency, a C – H hydrogen requires a greater applied field for absorption than the O – H hydrogen. The characteristic features of an NMR spectrum are the chemical shifts (protons absorbing at different fields) and the proportionality of spectral peak areas to the number of absorbing protons.

The difference in the fields where the above two protons absorb is 3.26 µT. This corresponds to Δv = 139 Hz.   Since the shielding constants are independent of the applied field, it is good to have measures of chemical shifts which are independent of the applied field. This is done by dividing the shift in the local field by the external field or by dividing Δn by n. The dimensionless chemical shift δ thus given by

$$\delta = \frac{\Delta (h\nu_i)}{h\nu} = \frac{\Delta E_i}{h\nu} = \frac{g\,\beta_N B_0 \left(\sigma_{CH} - \sigma_{OH}\right)}{h \; x \; 100\,MHz} \tag{14.14}$$

$$= 139 / (100 \; x \; 10^6) = 1.39 \; x \; 10^{-6} = 1.39 \; ppm$$

Note that the same value of δ is obtained from $\delta B / B_o$. The notation ppm refers to parts per million.

$$\delta = \frac{\delta B}{B_o} = 3.26 \; \mu T \; / \; 2.3487 \; T = 1.39 \; ppm \tag{14.15}$$

We considered above the difference in the chemical shift between -OH and -C-H. To develop a chemical shift scale, we need a reference compound. Tetramethyl silane (TMS, i.e., $Si(CH_3)_4$) which has 12 equivalent protons and has a sharp resonance at high field is used as a reference. It has a low boiling point (27^0C) and can be easily removed from the sample after use.   In aqueous solution, the sodium salt $(CH_3)_3Si CH_2 CH_2 SO_3 Na$ is added. Approximate proton chemical shifts are given in Table 14.1.

Table   14.1   Chemical Shifts (δ) of protons (ppm) in some common molecules and functional groups.

Molecule/Group	δ (approximate)	Molecule/Group	δ (approximate)
$Si(CH_3)_4$	0 (reference)	O – H	0.5 – 5.5
CH$_4$	0	N – CH R$_2$	2.2 – 4.4
		R$_2$CH X	2.2 – 6
NH$_3$	0.3	CH – O	3.1 – 5.5
RCCHR$_2$	05 – 1.8	- = CHR	5.5 – 7.5
PH$_3$	1.7	Ar – H	6.3 – 8.8
R$_2$C=C-CH R$_2$	1.5 – 2.5	AR –OH	4.5 – 10
R$_2$CH–C = 0	1.7 – 3	RHC = O	9.2 – 10.4
- C ≡ CH	1.8 – 3.1	ArCH = O	9.5 – 10.6
R$_2$CH - Ar	2.2 – 3.4	- COOH	8.7 – 12

In the table, Ar refers to C_6H_5 and R to CH_3, C_2H_5 and so on, and X to halogens. Benzene rings produce a "paramagnetic" circulation greatly deshielding the aromatic Hs. Therefore aromatic hydrogens have large chemical shifts. Aldehydic protons and protons connected to carboxylic groups are also severely deshielded.

From the above data, we can predict the locations of NMR lines of a few molecules. CH_3Cl will show one peak around δ of 3.5 ppm. The area under the proton absorption curve would correspond to three protons. CH_3-CH_2Cl will show two peaks, one for CH_3 ($\delta \sim 1$ ppm, area under the curve corresponding to three protons and another peak corresponding to an area for 2 protons at $\delta \sim 4$ ppm. In reality, the peaks are split into multiplets due to spin coupling (interactions).

Consider the spectrum of ethanol, CH_3-CH_2-OH. There are three distinct protons, the one in O-H, the two CH_2 protons and the three CH_3 protons. All 3 protons in CH_3 have an identical environment. The neighbouring two protons in CH_2 exert three different environments on the CH_3 protons. The spins on the two CH_2 protons have four possibilities, ↑↑, ↓↑, ↓↑, ↓↓. This causes the CH_3 peak to split into 3 peaks with intensity ration 1:2:1. The two up spins create an additional field in one direction on the methyl protons while the two down spins create an additional field in exactly the opposite direction. The field created by an up and a down spin is exactly in the middle. Calling this additional field due to two protons in one directions as δ_s, the methyl protons experience the three fields $B_o' + \delta_s$, B_o' and $B_o' - \delta_s$. B_o' is the local field on the methyl protons including the local effects of electrons in methyl hydrogens on the external field. The intensities of the middle line is twice the intensity of the extreme lines because the probability of a up-down spin configuration is twice that of the up-up or down-down configuration. Turning to the CH_2 group now, the eight possibilities of alignments of the three adjacent protons in the CH_3 group are ↑↑↑, ↑↑↓ , ↑↓↑, ↓↑↑, ↑↓↓ ↓↑↓, ↓↓↑, and ↓↓↓. Four distinct micro environments are created. The CH_2 peak splits into a quarlet with the intensity ratio of peaks being 1:3:3:1. The spectrum of ethanol is shown below.
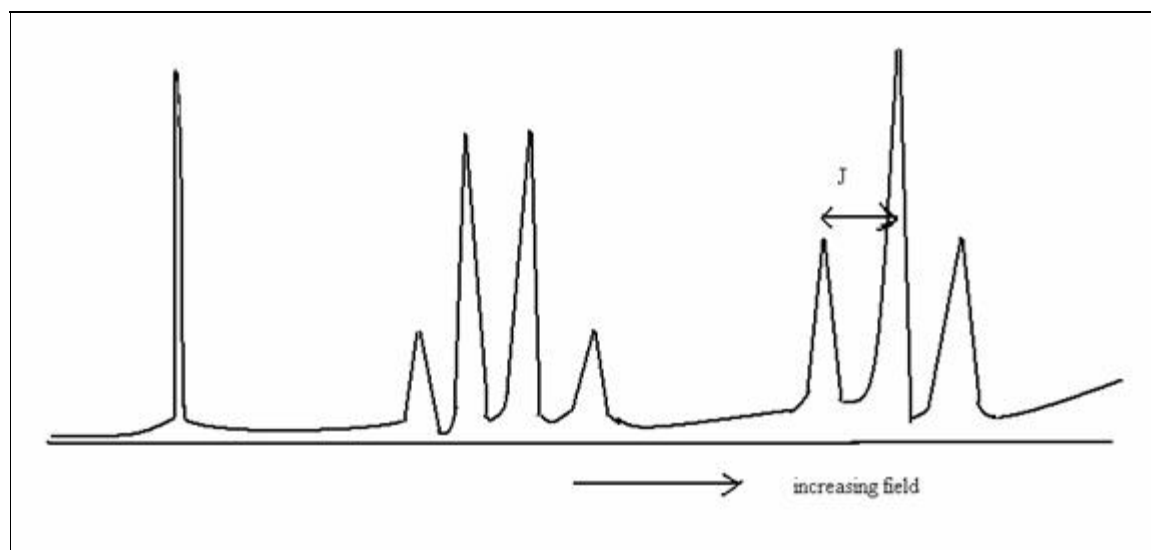

Fig. 14.3 NMR spectrum of ethanol.

The splitting between two adjacent lines is called the coupling constant J. The coupling constant is determined by the spatial interactions between the nuclear magnets. The same value of J results in the CH_3 and the CH_2 splittings. The –O-H protons do not show any effect because their spins have random orientations due to their continuous exchange with the solvent.

14.4 NMR of other Nuclei

Several nuclei have non zero nuclear spin. Some examples are ^{13}C, ^{19}F, ^{31}P, [29]Si, [195]Pt, [207]Pb (all these nuclei have spin ½), [14]N (spin 1), [27]Al (spin 3/2) and so on. [13]C is of great interest because it is a useful tool for the organic chemist. The main problem is that the ^{13}C isotope of carbon has only 1 % natural abundance leading to weak signals. The chemical shifts for these nuclei are much larger than those for hydrogen. The range of chemical shifts in ppm for some of these nuclei are [13]C (250), [31]P(400), [19]F (600) and [207]Pb (14000). A larger electron density at the nuclei and greater polarizability values lead to higher shielding constants and higher chemical shifts.

Larger chemical shifts and a smaller chance for spin-spin coupling (due to small abundances) make the [13]C

NMR spectra a lot simpler than the ^{1}N NMR spectra. The chemical shifts in ppm for a few groups containing ^{13}C are, TMS (0, reference value), C-CH_3 (0 – 20), CH_2-C (20 – 40), CH_2-O- (40 – 70), CH-O- (60 – 85), -C≡C – (70 – 100), ›C = C‹ (100 – 150), aromatic C (0 – 130), H –C = 0 (180 – 200), R_2C = 0 (180 – 220).

The coupling of protons to the ^{13}Cs is more readily detected. E.g., J_{CH} (coupling constant) for an H directly bonded to an ^{13}C is 125 Hz. In ethylenic = C-H, J = 170 Hz and in acetylenic ≡ C-H, it is 250 Hz. The CH_2 carbon yields a 1:2:1 triplet and a CH_3 carbon yields a 1:3:3:1 quartet (as in the case of acetic acid). Since the spectral lines are weak, location of maxima could be difficult. This can be overcome by a technique called the double resonance. In double resonance, two radiofrequencies are simultaneously applied to the molecule. In CH_3CH_2OH, if and we use an additional frequency corresponding to the CH_2 absorption, both the Hs of CH_2 become equivalent (due to saturation) and these protons get decoupled from the CH_3 protons. The later will show only one line (sharply located) compared to the triplet. In ^{13}C spectra, the intensities of the lines are small to begin with. Double resonance leads to sharper lines.

14.5 Electron Spin Resonance (ESR) spectroscopy

Unpaired electrons spins interact with a magnetic field analogous to the proton spins. The splitting of the levels occurs at a lower external field because the electron Bohr magneton is much larger than the nuclear magneton, due to the smaller electron mass. The split levels are shown in Fig. 14.4.

Fig. 14.4   Electron spin energy levels.
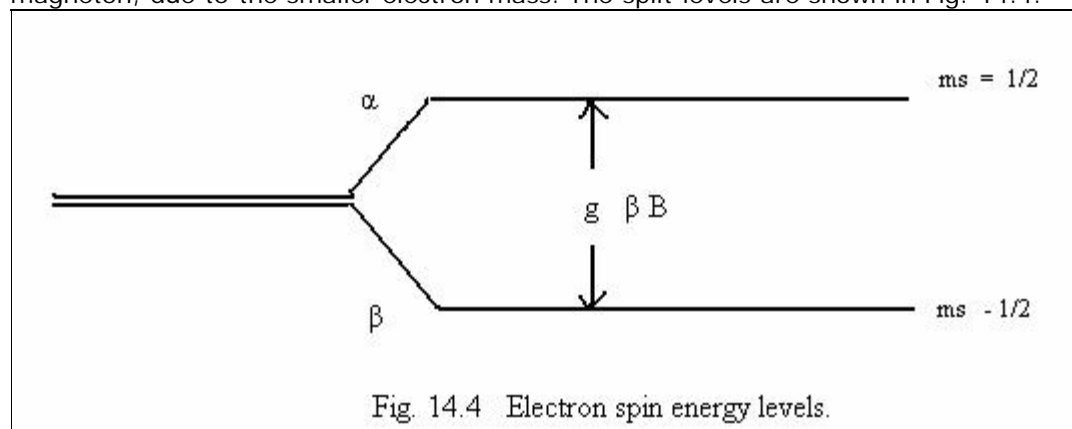
In case of the nuclei, the up spin (α) was lower in energy. But for electrons, the down spin (β) is lower in energy because of the negative charge on the electron. The energy levels and their differences are given below

$$E_{ms} = \quad g_e \; \beta_e \; m_s \; B \qquad\qquad\qquad (14.16)$$

$$\Delta E \;=\; g_e \,\beta_e\, B\,(1/\,2) \;-\; g_e\beta_e\, B\,(-1/\,2)$$

$$= \; g_e \,\beta_e\, B \qquad\qquad\qquad (14.17)$$

The resonance condition is

$$h\nu \;=\; g_e \,\beta_e\, B \qquad\qquad\qquad (14.18)$$

The g_e value for a free electron is 2.0023. In crystals, g_e values in the range of 0.2 to 8 have been observed.

Magnetic fields in the range of 0.3T require a microwave frequency of 10 GHz (10^{10} Hz). Similar to the case of NMR, the local field is different from the applied field and in place of B, we should be using B(1 – σ) as in Eq. (14.10). However, in ESR, it is customary to rewrite g_e (1 – σ) as g and the value of g can be obtained from the values of B and ν as follows:

$$g \;=\; \frac{h\nu}{\beta_e\, B} \qquad\qquad\qquad (14.19)$$

Example 14.2 Calculate the g value of electron in a methyl radical that absorbs at 9.468 GHz in a field of 0.3378T.

Solution : First calculate (h/β_e) = $(6.626 \times 10^{-26}$ Js / 9.273×10^{-24} J T^{-1}

$$= 7.14448 \times 10^{-11} Ts$$

$= 71.4448$ mT/GHz

Where we have used that 10^{-10} s = $(1$ GHz$)^{-1}$

The value of g can be calculated as

$$g = (\frac{h}{\beta_e})(\frac{\nu}{B}) = (\frac{71.4448mT}{GHz})(\frac{9.468GHz}{0.3378T}) = 2.0026$$

Just as nuclear spins interact with one another to give fine structure in NMR, the electron spins interact with nuclear spins to give a structure which is referred to as hyperfine structure. Consider the simplest case of an electron interacting with a single proton or a spin ½ nucleus. The field due to the nucleus can either enhance the external field or diminish it according to

$$B_{local} = B_o + am_I, \quad m_I = \pm \frac{1}{2} \qquad (14.20)$$

Where B_0 is the external field, m_I, the nuclear spin quantum number and a, the hyperfine coupling constant. The single absorption line splits into a doublet whose frequencies are given by

$$h\nu_1 = g_e \beta_e (B - \frac{1}{2}a), \quad h\nu_2 = g_e \beta_e (B + \frac{1}{2}a) \qquad (14.21)$$

The original peak splits into two peaks separated by a constant a. The intensities of each of these peaks are half of the original intensity.

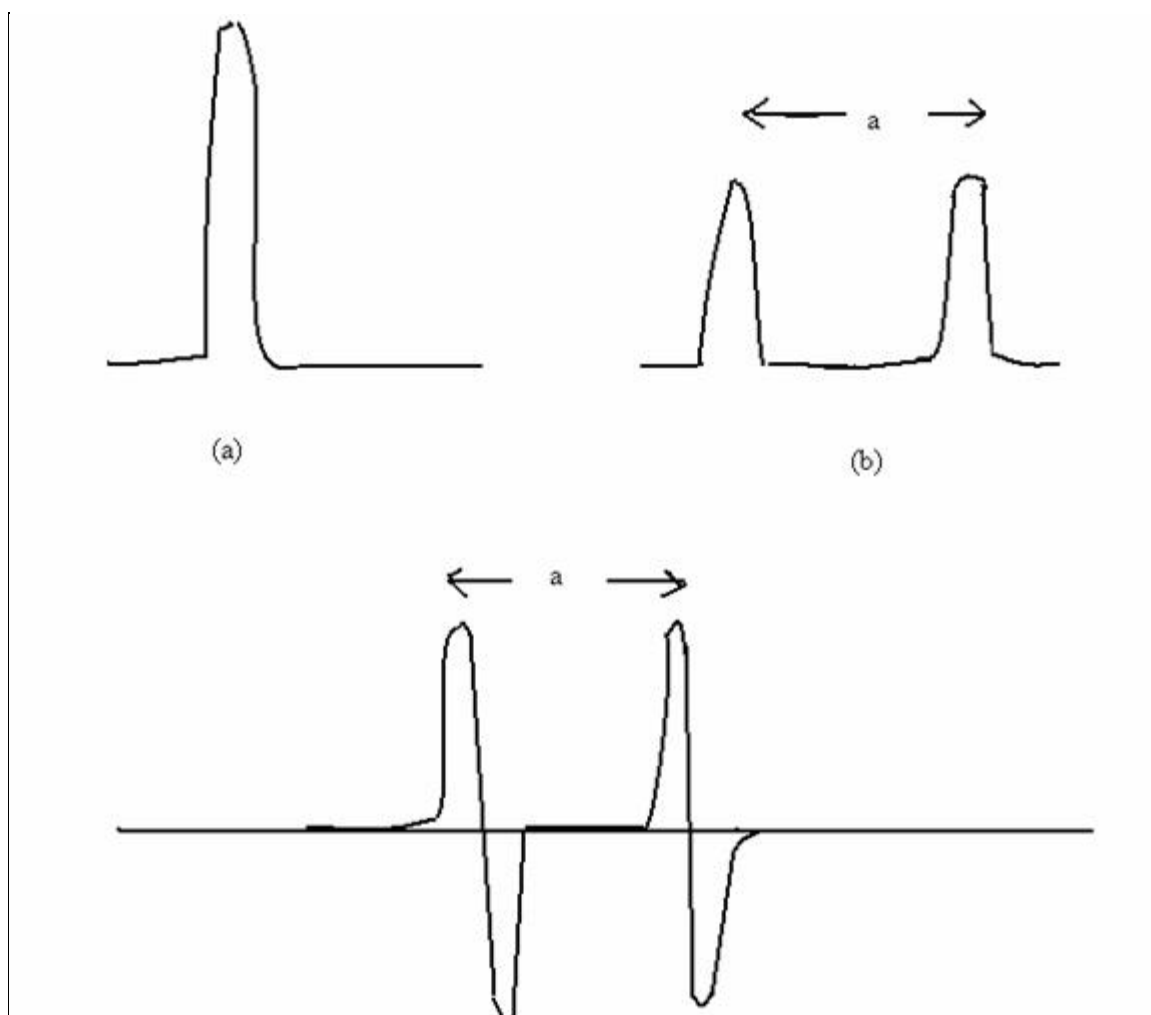## 14.5 Electron Spin Resonance (ESR) spectroscopy

Figure 14.5. ESR hyperfine interaction. (a) ESR spectrum before accounting for hyperfine interaction, (b) ESR spectrum including hyperfine interaction and (c) a derivative spectrum of (b). In ESR, derivatives of intensities are plotted against frequency so that line positions can be more clearly identified.

Example 14.3

Rationalise the ESR spectra of a methyl radical and a benzene radical ion ($C_6H_6^-$).

Solution :

In the methyl radical the electron interacts with three proton spins. The total nuclear spin quantum number is 3/2 and the four, i.e., ($2I + 1$) possible orientations of nuclear spins correspond to 3/2, 1/2, -1/2 and -3/2. To get a total spin of $-\frac{1}{2}$, there are three possibilities, ie. ↑↓↓, ↑↓↑ and ↓↑↑ and hence the intensities of the four lines are in the ratio 1:3:3:1. The hyperfine coupling constant can be either measured as δv or δB; the latter is more common. The value of the hyperfine coupling constant a for CH_3 is 2.3 mT.
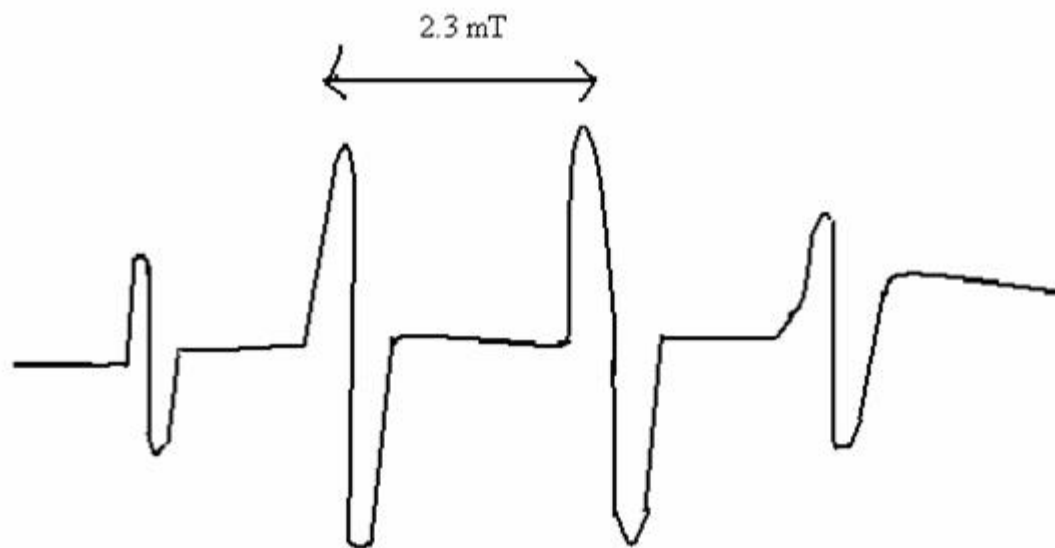
For the benzene radical anion, the electron interacts with six protons. The total spin is 3 and the number of levels into which the ESR line splits is $2I + 1 = 7$. The intensities of the lines can be calculated using binomial coefficients. E.g., the number of ways in which two spins can be in the 'up' state among 6 spins is given by $^6C_2 = 6!/(2!\ 4!) = 15$. The intensity radios of the lines in $C_6H_6^-$ are 1:6:15:20:15:6:1
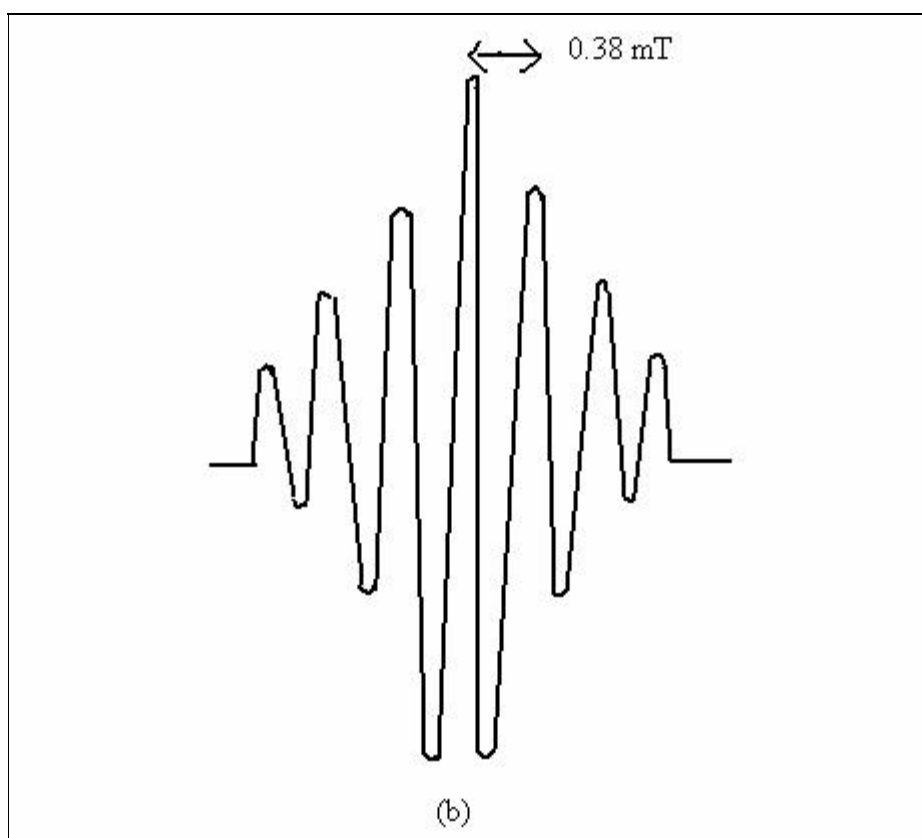
The spectra of CH_3 an $C_6H_6^-$ are shown below.

14.5 Electron Spin Resonance (ESR) spectroscopy

The spectra of CH_3 an $C_6H_6^-$ are shown below:

2.3 mT

(a)

0.38 mT

(b)

Figure 14.6. The ESR spectra of CH$_3$ radical (a) and the benzene radical anion (b). The hyperfine structures provide excellent finger prints to identify radicals present in solution. The hyperfine coupling constant depends on unpaired electron density experienced by the electron from the interacting nuclei. Greater the spin density, larger the value of a.

14.6 Problems

- A $^{27}Al^{3+}$ nucleus has a spin of 3/2. How many levels do we get in a magnetic field? How many transitions and distinct absorption frequencies are observed?

- In a 400 MHz NMR spectrometer, what is the range of the external magnetic field for proton NMR?

- Predict the NMR spectra of CH_3F and $CH_3CH_2CH_3$.

- Why are proton NMR spectra easier to observe than the ^{13}C NMR spectra?

- The ^{14}N nucleus has spin of 1 and a q_I value of 0.4036. At a field of 10 T, calculate the energy levels and thefrequency of absorption.

- In the ESR spectrum of H_2S^-, what are the numbers and intensities of lines due to hyperfine interaction?

- Predict the ESR spectra of $CF_2H^.$, $CF_2D^.$ and $CFD_2^.$

- The chemical shifts of the CH_3 proton and CHO proton in CH_3CHO are 2.2 ppm and 9.8 ppm respectively. If the external magnetic field is 5 T, what is the difference in the local magnetic field of these two protons?

- An ESR spectrometer uses 10 mm microwave radiation. At what field does the electron spin show ESR absorption?

- An ESR spectrometer can detect spins at a concentration of 10^{10} per cm^3 of sample. What is the molar concentration of spins?

Recap

In this lecture you have learnt the following

14.7 Summary

In this lecture, we have studied magnetic resonance spectroscopy. Nuclear and electrons spins have degenerate energy levels in the absence of an external magnetic field. In the presence of an external field, the degeneracy is lifted and transitions can be induced between the levels. The energy differences between the levels are $q_I\beta_N B$ (for nuclei) and $q_e\beta_e B$ (for electrons). These differences are quite small compared to energies in electronic/vibrational/rotational transitions and the populations between the upper and lower levels are quite small. In a magnetic field, the spins precess in a cone around the field direction. The local fields at protons are different from the external field because of the diamagnetic shielding of nuclei by the surrounding electrons. Differences in local fields lead to chemical shifts in the NMR peaks. The chemical shift data of protons can be used to identify the number and types of hydrogens present in molecules. Protons on adjacent groups interact with one another to give a fine structure in NMR. Nuclei other than protons which possess non zero spins also show NMR spectra. Since radiofrequency is less invasive to the human body than X rays and other high energy radiation, Magnetic Resonance Imaging (MRI) (which uses NMR principles) has been developed into a very advanced medical tool to detect anomalies in brain and other tissues.

Electron spins lead to ESR spectra. Interactions between nuclear spins and electron spins lead to hyperfine structure of the ESR lines. ESR is used widely for studying free radicals.