

Unit 6.4 Spin resonance spectroscopy (Marks 10)

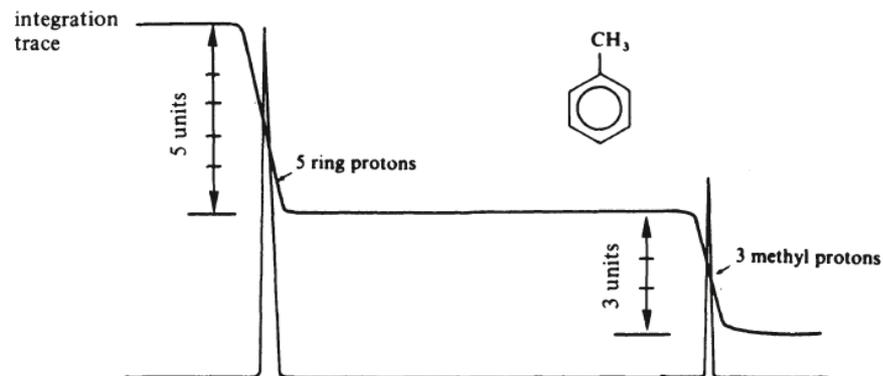
Interaction between spin and magnetic field – Nuclear spin – Nuclear magnetic resonance spectroscopy – ^1H NMR – presentation of the spectrum - chemical shift and its unit – chemical shifts for simple organic molecules (alkane, alkene, alkyne, arenes, aldehydes, carboxylic acids and esters). Spin-spin coupling and high resolution ^1H NMR spectra of ethanol, ethyl benzoate, 2-iodopropane, cyanohydrin.

Basic concept of electron spin resonance spectroscopy – presentation of the spectrum – hyperfine structure – esr of H- atom , deuterium atom.

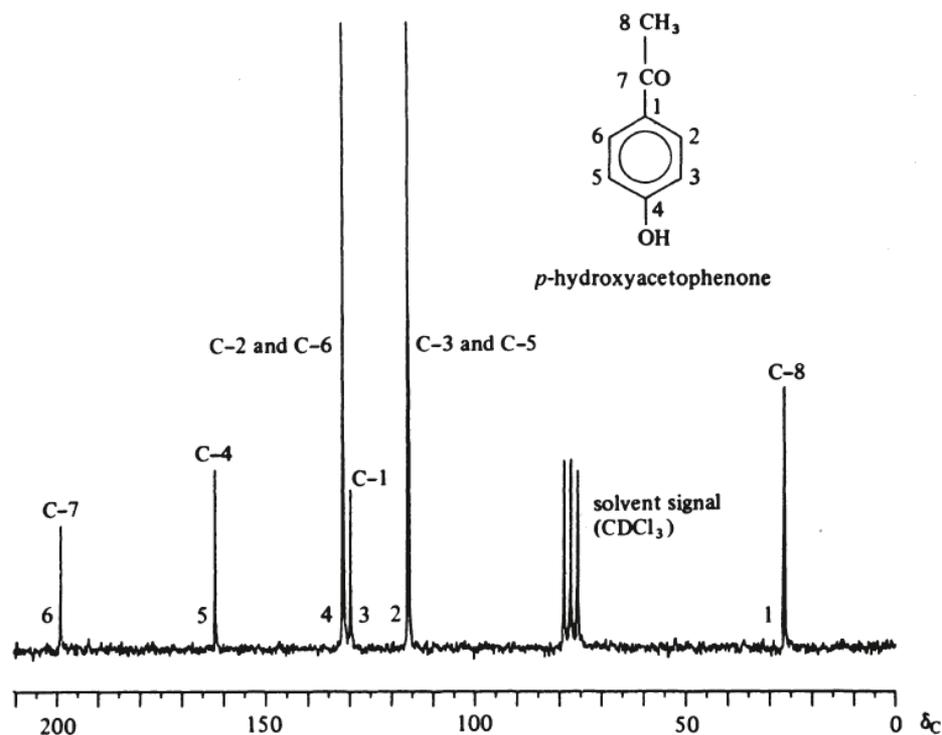
What is NMR Spectroscopy ?

- ❖ Nuclear magnetic resonance (or NMR) is concerned with the magnetic properties of certain atomic nuclei , notably the nucleus of the hydrogen atom-the proton (^1H) -and that of the carbon-13 (^{13}C) isotope of carbon, ^{31}P , ^{19}F , ^{11}B etc.
- ❖ NMR studies enable us to record differences in the magnetic properties of the various magnetic nuclei present, and to deduce in large measure what the positions of these nuclei are within the molecule.
- ❖ Deduce different kinds of environments there are in the molecule, and also which atoms are present in neighboring groups.
- ❖ Measure how many atoms are present in each of these environments.

NMR Spectrum



(a)



(b)

Figure 3.1 (a) Diagrammatic ¹H NMR spectrum of toluene, C₆H₅CH₃, showing two signals in the intensity ratio 5:3. (b) ¹³C NMR spectrum of *p*-hydroxyacetophenone, *p*-CH₃COC₆H₄OH, showing six signals corresponding to the six different carbon environments in the molecule. (20 MHz, in CDCl₃.)

Interaction between Spin and Magnetic Field

❖ **THE SPINNING NUCLEUS:** The nucleus of the hydrogen atom (the proton) behaves as a tiny spinning bar magnet, and it does so because it possesses both electric charge and mechanical spin; any spinning charged body will generate a magnetic field, and the nucleus of hydrogen is no exception.

❖ **THE EFFECT OF AN EXTERNAL MAGNETIC FIELD:** Like all bar magnets, the proton will respond to the influence of an external magnetic field, and will tend to align itself with that field, in the manner of a compass needle in the earth's magnetic field. Because of quantum restrictions which apply to nuclei but not to compass needles, the proton can only adopt two orientations with respect to an external magnetic field—either *aligned with the field (the lower energy state)* or *opposed to the field (the higher energy state)*. We can also describe these orientations as *parallel with or antiparallel with the applied field*.

Interaction between Spin and Magnetic Field

❖ **PRECESSIONAL MOTION:** Because the proton is behaving as a *spinning magnet*, *not only can it align* itself with or oppose an external magnetic field, but also it will move in a characteristic way under the influence of the external magnet. Consider the behavior of a spinning top: as well as describing its spinning motion, the top will (unless absolutely vertical) also perform a slower waltz-like motion, in which the spinning axis of the top moves slowly around the vertical. This is *precessional motion*, and the top is said to be *precessing around the vertical axis of the earth's gravitational field*. The precession arises from the interaction of spin-that is, gyroscopic motion-with the earth's gravity acting vertically downward. Only a spinning top will precess ; a static top will merely fall over.

As the proton is a spinning magnet, it will, like the top , precess around the axis of an applied external magnetic field, and can do so in two principal orientations, either aligned with the field (low energy) or opposed to the field (high energy). This is represented in figure 3.2, where B_0 is the external magnetic field.

Interaction between Spin and Magnetic Field

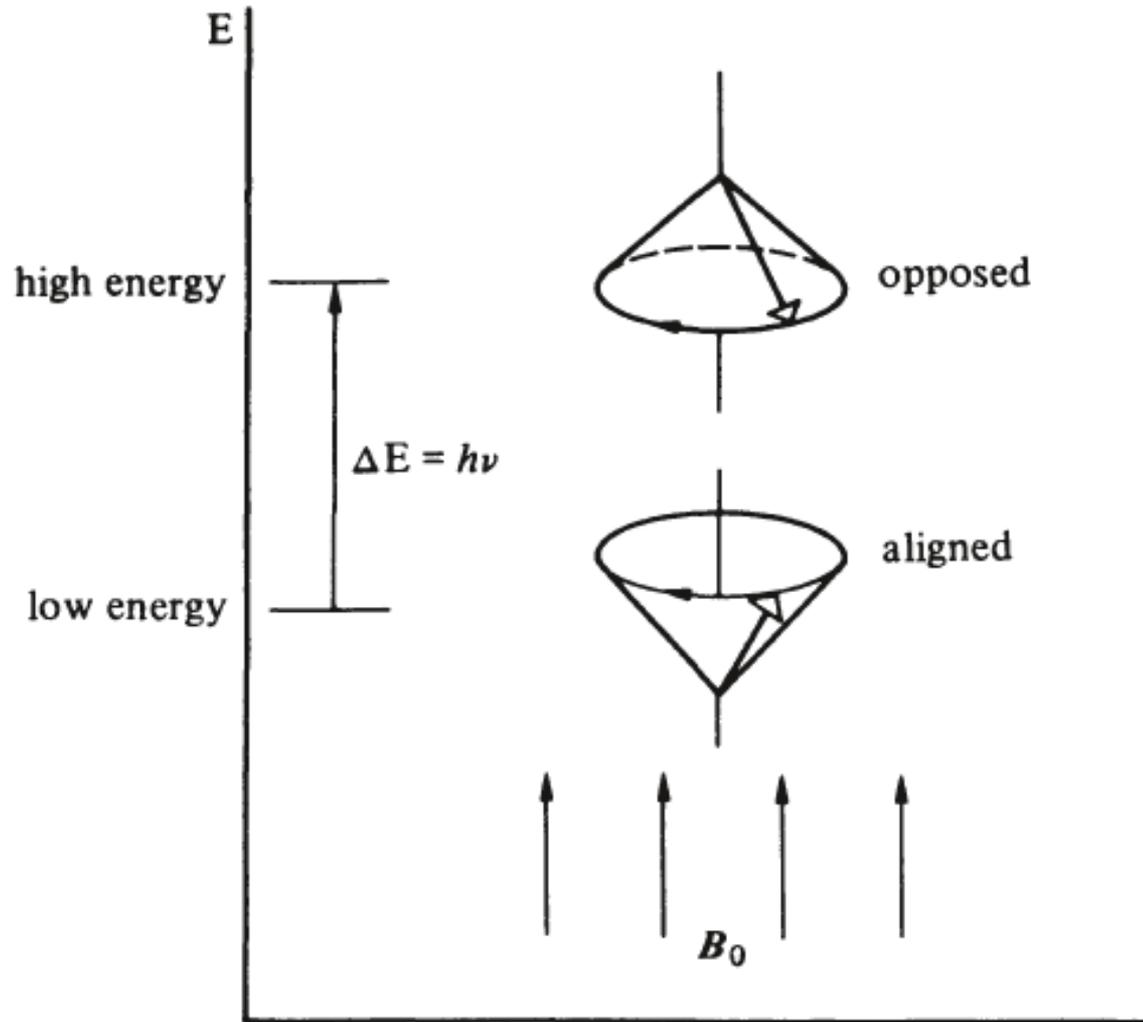


Figure 3.2 *Representation of precessing nuclei, and the ΔE transition between the aligned and opposed conditions.*

Interaction between Spin and Magnetic Field

❖ **PRECESSIONAL FREQUENCY:** The spinning frequency of the nucleus does not change, but the speed of precession does. The *precessional frequency, ν , is directly proportional to the strength of the external field, B_0* : that is,

$$\nu \propto B_0$$

❖ **ENERGY TRANSITIONS:** If a proton is precessing in the *aligned orientation, it can absorb energy and pass into the opposed orientation; subsequently it can lose this extra energy and relax back into the aligned position.* If we irradiate the precessing nuclei with a beam of radiofrequency energy of the correct frequency, the low-energy nuclei may absorb this energy and move to a higher energy state. The precessing proton will only absorb energy from the radiofrequency source if the precessing frequency is the same as the frequency of the radiofrequency beam; when this occurs, the nucleus and the radiofrequency beam are said to be *in resonance; hence the term nuclear magnetic resonance.*

Interaction between Spin and Magnetic Field

The simplest NMR experiment consists in exposing the protons in an organic molecule to a powerful external magnetic field; the protons will precess, although they may not all precess at the same frequency. We irradiate these precessing protons with radiofrequency energy of the appropriate frequencies, and promote protons from the low-energy (aligned) state to the high-energy (opposed) state. We record this absorption of energy in the form of an NMR spectrum.

Nuclear Spin and NMR Theory

The spin quantum number, I , of a nucleus is a fixed characteristic property of a nucleus and is either an integer or a half-integer. A nucleus with spin quantum number I has the following properties:

1. An angular momentum of magnitude $\{I(I + 1)\}^{1/2}\hbar$.
2. A component of angular momentum $m_I\hbar$ on a specified axis ('the z-axis'), where $m_I = I, I - 1, \dots, -I$.
3. If $I > 0$, a magnetic moment with a constant magnitude and an orientation that is determined by the value of m_I .

According to the second property, the spin, and hence the magnetic moment, of the nucleus may lie in $2I + 1$ different orientations relative to an axis. A proton has $I = \frac{1}{2}$ and its spin may adopt either of two orientations; a ^{14}N nucleus has $I = 1$ and its spin may adopt any of three orientations; both ^{12}C and ^{16}O have $I = 0$ and hence zero magnetic moment.

Nuclear Spin and NMR Theory

The only nuclei that exhibit the NMR phenomenon are those for which the spin quantum number I is greater than 0: the spin quantum number I is associated with the mass number and atomic number of the nuclei as follows:

Number of protons	Number of neutrons	I
even	even	0
odd	odd	integer (1, 2, 3, ...)
even	odd	half-integer ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$)
odd	even	half-integer ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$)

* The spin of a nucleus may be different if it is in an excited state; throughout this chapter we deal only with the ground state of nuclei.

The nucleus of ^1H , the proton, has $I = \frac{1}{2}$, whereas ^{12}C and ^{16}O have $I = 0$ and are therefore nonmagnetic. If ^{12}C and ^{16}O had been magnetic, the NMR spectra of organic molecules would have been much more complex.

Nuclear Spin and NMR Theory

Under the influence of an external magnetic field, a magnetic nucleus can take up different orientations with respect to that field ; the number of possible orientations is given by $(2I + 1)$, so that for nuclei with spin $\frac{1}{2}$ (^1H , ^{13}C , ^{19}F , etc .) only two orientations are allowed. Deuterium and ^{14}N have $I = 1$ and so can take up three orientations: these nuclei do not simply possess magnetic *dipoles*, *but rather possess electric quadrupoles* . *Nuclei* possessing electric quadrupoles can interact with both magnetic and electric field gradients, the relative importance of the two effects being related to their magnetic moments and electric quadrupole moments, respectively .

Nuclear Spin and NMR Theory

In an applied magnetic field, magnetic nuclei like the proton precess at a frequency ν , which is proportional to the strength of the applied field. The exact frequency is given by

$$\nu = \frac{\gamma B_0}{2\pi}$$

where B_0 = strength of the applied external field experienced by the proton,

γ = magnetogyric ratio, being the ratio between the nuclear magnetic moment, μ , and the nuclear angular momentum, I :
 γ is also called the gyromagnetic ratio.

Nuclear Spin and NMR Theory

Table 3.1 Precessional frequencies (in MHz) as a function of increasing field strength

B_0 /tesla	1.4	1.9	2.3	4.7	7.1	11.7	14.1
<i>Nucleus</i>							
^1H	60	80	100	200	300	500	600
^2H	9.2	12.3	15.3	30.6	46.0	76.8	92
^{11}B	19.2	25.6	32.0	64.2	96.9	159.8	192
^{13}C	15.1	20.1	25.1	50.3	75.5	125.7	151
^{14}N	4.3	5.7	7.2	14.5	21.7	36.1	43
^{15}N	6.1	8.1	10.1	20.3	30.4	50.7	61
^{17}O	8.1	10.8	13.6	27.1	40.7	67.8	81
^{19}F	56.5	75.3	94.1	188.2	288.2	470.5	565
^{31}P	24.3	32.4	40.5	81.0	121.5	202.4	243
(Free electron)	3.9×10^4						

Nuclear Spin and NMR Theory

The strength of the signal, and , hence, the sensitivity of the NMR experiment for a particular nucleus, are related to the magnitude of the magnetic moment, μ . The magnetic moments of ^1H and ^{19}F are relatively large, and detection of NMR with these nuclei is fairly sensitive . The magnetic moment for ^{13}C is about one-quarter that of ^1H , and that of ^2H is roughly one-third the moment of ^1H ; these nuclei are less sensitively detected in NMR.

Chemical Shift

Nuclear magnetic moments interact with the *local magnetic field*. The *local field* may differ from the applied field because the latter induces electronic orbital angular momentum (that is, the circulation of electronic currents) which gives rise to a small additional magnetic field δB at the nuclei. This additional field is proportional to the applied field, and it is conventional to write

$$\delta B = -\sigma B_0 \dots\dots\dots(15.15)$$

where the dimensionless quantity σ is called the **shielding constant of the nucleus** (σ is usually positive but may be negative). The ability of the applied field to induce an electronic current in the molecule, and hence affect the strength of the resulting local magnetic field experienced by the nucleus, depends on the details of the electronic structure near the magnetic nucleus of interest, so nuclei in different chemical groups have different shielding constants. The calculation of reliable values of the shielding constant is very difficult, but trends in it are quite well understood and we concentrate on them.

Chemical Shift

Because the total local field is

$$\mathcal{B}_{\text{loc}} = \mathcal{B}_0 + \delta\mathcal{B} = (1 - \sigma)\mathcal{B}_0 \quad (15.16)$$

the nuclear Larmor frequency is

$$\nu_{\text{L}} = \frac{\gamma\mathcal{B}_{\text{loc}}}{2\pi} = (1 - \sigma)\frac{\gamma\mathcal{B}_0}{2\pi} \quad (15.17)$$

This frequency is different for nuclei in different environments. Hence, different nuclei, even of the same element, come into resonance at different frequencies. It is conventional to express the resonance frequencies in terms of an empirical quantity called the **chemical shift**, which is related to the difference between the resonance frequency, ν , of the nucleus in question and that of a reference standard, ν° :

$$\delta = \frac{\nu - \nu^\circ}{\nu^\circ} \times 10^6 \quad [15.18]$$

Chemical Shift

The standard for protons is the proton resonance in tetramethylsilane ($\text{Si}(\text{CH}_3)_4$, commonly referred to as TMS), which bristles with protons and dissolves without reaction in many liquids. Other references are used for other nuclei. For ^{13}C , the reference frequency is the ^{13}C resonance in TMS; for ^{31}P it is the ^{31}P resonance in 85 per cent $\text{H}_3\text{PO}_4(\text{aq})$. The advantage of the δ -scale is that shifts reported on it are independent of the applied field (because both numerator and denominator are proportional to the applied field). The relation between δ and σ is obtained by substituting eqn 15.17 into eqn 15.18:

$$\delta = \frac{(1 - \sigma)\mathcal{B}_0 - (1 - \sigma^0)\mathcal{B}_0}{(1 - \sigma^0)\mathcal{B}_0} \times 10^6 = \frac{\sigma^0 - \sigma}{1 - \sigma^0} \times 10^6 \approx (\sigma^0 - \sigma) \times 10^6 \quad (15.19)$$

Chemical Shift

As the shielding, σ , gets smaller, δ increases. Therefore, we speak of nuclei with large chemical shift as being strongly **deshielded**. **Some typical chemical shifts are given in Fig. 15.5.** As can be seen from the illustration, the nuclei of different elements have very different ranges of chemical shifts. The ranges exhibit the variety of electronic environments of the nuclei in molecules: the heavier the element, the greater the number of electrons around the nucleus and hence the greater the range of shieldings. By convention, NMR spectra are plotted with δ increasing from right to left. Consequently, in a given applied magnetic field the Larmor frequency also increases from right to left. In the original continuous wave (CW) spectrometers, in which the radiofrequency was held constant and the magnetic field varied (a 'field sweep experiment'), the spectrum was displayed with the applied magnetic field increasing from left to right: a nucleus with a small chemical shift experiences a relatively low local magnetic field, so it needs a higher applied magnetic field to bring it into resonance with the radiofrequency field. Consequently, the right-hand (low chemical shift) end of the spectrum became known as the 'high field end' of the spectrum.

Chemical Shift

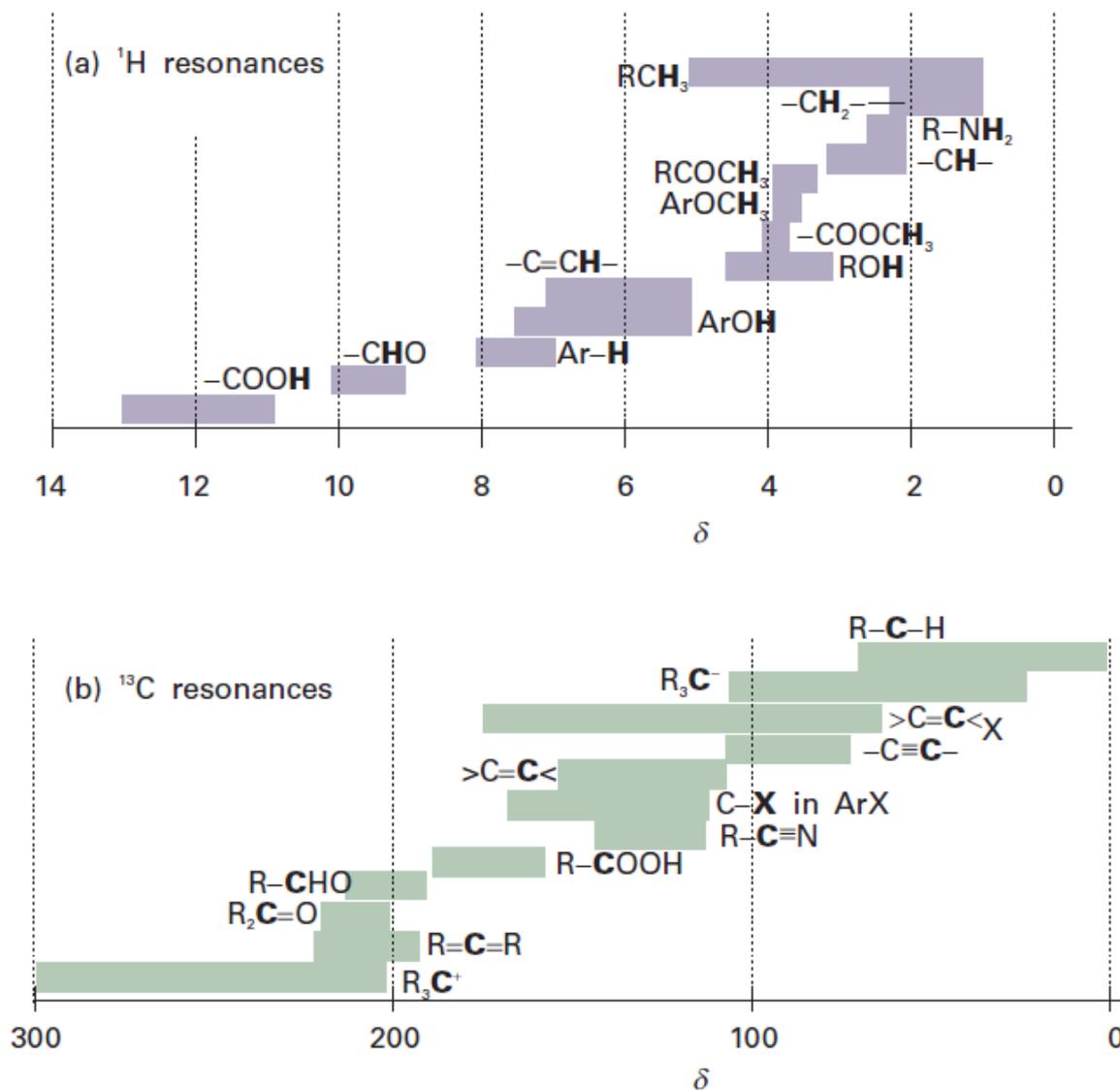


Fig. 15.5 The range of typical chemical shifts for (a) ^1H resonances and (b) ^{13}C resonances.

