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, arenas, 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 (13C) isotope of carbon, 31P, 19F, 11B 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

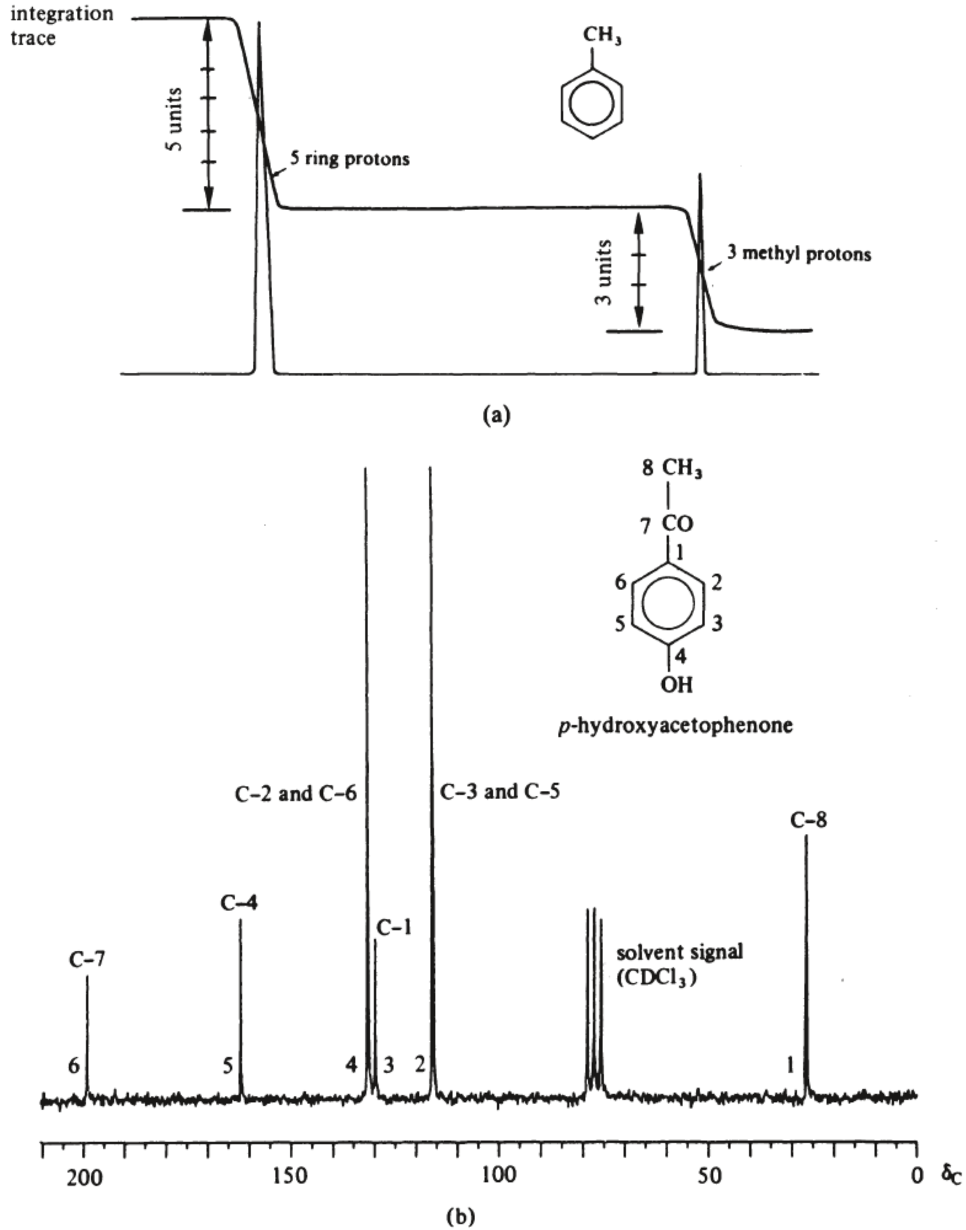

Figure 3.1 (a) *Diagrammatic* ^{1}H *NMR spectrum of toluene,* $C_6H_5CH_3$, *showing two signals in the intensity ratio 5:3.* (b) ^{13}C *NMR spectrum of p-hydroxyacetophenone, p-*$CH_3COC_6H_4OH$, *showing six signals corresponding to the six different carbon environments in the molecule.* (20 MHz, *in* $CDCl_3$.)

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 *Bo* is the external magnetic field.

Interaction between Spin and Magnetic Field

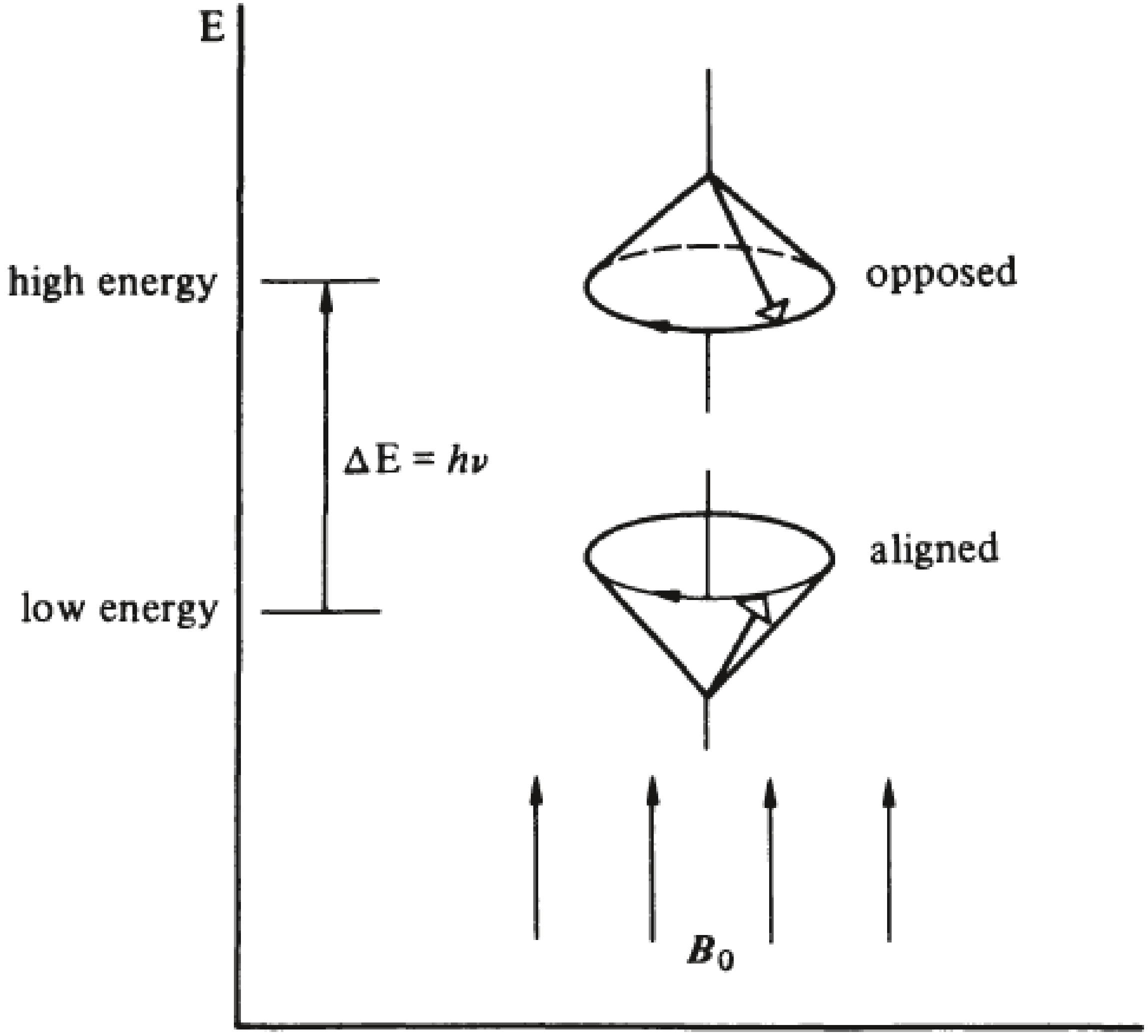

Figure 3.2 *Representation of precessing nuclei, and the ΔE transition between the aligned and opposed conditions.*

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, v, is directly proportional to* the strength of the external field, *Bo*: 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 $m_I = I, I - 1, \ldots, -I$.
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* $I = ½$ and its spin may adopt either of two orientations; a 14N nucleus has *I = 1 and its spin* may adopt any of three orientations; both 12C and 16O 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 ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$)
odd	even	half-integer ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$)

* 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 = ½ , whereas I2C and 16O have I = 0 and are therefore nonmagnetic. If I2C and 16O 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 ½ (1H, 13C, 19F, etc .) only two orientations are allowed. Deuterium and 14N 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 .