UNIVERSITY OF SIERRA LEONE

FACULTY OF PURE AND APPLIED SCIENCES

DEPARTMENT OF CHEMISTRY

Introduction to Physical Analytical Chemistry

COURSE CODE: CHEM 212

FOURAH BAY COLLEGE
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COURSE BLUB

Introduction to Physical Analytical Chemistry

Welcome all to Introduction to Physical Analytical Chemistry ! In this course, we will explore the fundamental principles and concepts of Spectroscopy- an analytical technique that is used for the structural elucidation of organic molecules.

Physical Analytical Chemistry is a fascinating field that combines aspects of Mathematics, Physics and Chemistry. The study enables us to determine the chemical structures of simple organic molecules. However, its application can also be extended to biomolecules, such as proteins, carbohydrates, lipids, and nucleic acids.

Credit Units: **2 Units**

Course Status: **Core**

Semester: **First**

Course Duration: **15 weeks**

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INTRODUCTION

Welcome to the Introduction to Physical Analytical Chemistry. In this course, we will explore the fundamental principles and concepts of spectroscopy, the branch of science that investigates the interaction of light with matter.

Physical Analytical Chemistry is a fascinating field that combines aspects of Mathematics, Physics and Chemistry. The study enables us to determine the chemical structures of simple organic molecules. However, its application can also be extended to biomolecules, such as proteins, carbohydrates, lipids, and nucleic acids. I can assure you will enjoy studying the course. This course guide is a general overview of the course. It provides you with useful information about the structure of the course.

CHM 212 – Physical Analytical Chemistry is a 2-credit unit course meant to be taken in the second semester, at the BSc degree level. The course is available to all second-year students offering Chemistry and Biology, who have registered for degree programme at Open Distance Learning ODL of Sierra Leone. It is the first part of the two credit unit courses planned for an entire year. The materials have been developed to suit the distance learning mode.

WHAT YOU WILL LEARN IN THIS COURSE

The ultimate goal in this course is for students to be able to use spectroscopic data for the structural elucidation of organic compounds.

COURSE AIMS

CHEM 212 has specific aim which relates to giving you an understanding of the basic principles and foundational knowledge of spectroscopy with the ultimate goal of using spectroscopic data for the structural elucidation of organic compounds. The aim will be achieved by mastery of key concepts, providing working examples, conceptual checkpoints and end of unit assessments.

COURSE OBJECTIVES

To achieve the aims set out above, each unit in CHEM 212 sets out specific objectives. The unit objectives are always included at the beginning of every unit. I advise you to read them before you start working through the unit. You may want to refer to them during your study of the unit to check your progress. Set out below are the wider objectives for the course, as a whole. By meeting the objectives, you can count yourself as having met the aim of the course. On successful completion of the course, you should be able to use Spectroscopic data to completely elucidate the structure of simple organic molecules.

WORKING THROUGH THIS COURSE

To complete the course, you are required to read the study units and read sets of books and other relevant materials that you may lay your hands on. You will also need other materials that will be listed later in this course guide. At the end of each unit, you will be required to work on assignments for assessment purposes. At the end of the course, there will be a final examination. The course length is about 15 weeks.

COURSE MATERIALS

The major materials you will need for this course are listed below.

1. Course guide
2. Study Units
3. Assignment
4. Relevant textbooks
5. Presentation schedule

STUDY UNITS:

The course is broken down into units. Every unit has reference materials and prescribed text to be used for further studies by students. They also have aims, objectives, pre and post-tests.

TEXTBOOKS AND REFERENCES

At the end of every unit, you will find a list of books and other such materials that will enable you have a firm grasp of the course. The books required to aid your understanding of this course are by no means exhaustive here. You are, therefore, expected to consult as many materials as possible. This will enable you to deepen your understanding of the course.

THE PRESENTATION SCHEDULE

The dates for submission of all assignments will be communicated to you in due course. To be communicated to you are dates of completing the study units and dates for examinations.

THE ASSESSMENT FILE

The assessment file will be made available to you. In this file, you will find details of the work you must submit to your tutor for marking. The marks you obtain in this course will count towards your final marks.

ASSESSMENT

The course has three types of exercises or questions you are expected to tackle. The first is the Self-Assessment Exercises (SAEs) which you are expected to solve, but not to be submitted, at the end of the study. The second is the Tutor-Marked Assignment (TMAs) which you must solve and submit in an assignment file, in partial fulfilment of the requirements for the successful completion of the course. The third is the practical works undertaken by you. The TMA accounts for 30% of your total score for the course. Every unit has a Tutor-Marked Assignment, which is a compulsory question that must be answered and submitted at the end of the course. You will minimize your chance of doing well in the course if you fail to submit answers to all the Tutor-Marked Assignments and Laboratory work book, as required.

FINAL EXAMINATION AND GRADING

The final examination for CHM 311 will take certain duration. The examination itself will carry 70%. It will consist of questions that reflect the self-assessment exercises, as well as the tutor-marked assignments. You are expected to spend quality time to read the entire course units, and all the SAEs and TMAs for the final examination.

COURSE MARKING SCHEME

The table below shows how actual course marking scheme is broken down.

Table 1: Course Marking Scheme

Assessments	**Marks**
Assignments	These will count as 10% of course mark.
Tests	These will count as 20% of course mark.
Final examination	70% of overall course mark
Total	100% of course marks

FACILITATORS/TUTORS AND TUTORIALS

A number of tutorial hours have been provided for in this course to enable the students and their tutors to meet and examine the contents of the course at intervals. You will be informed of the dates, time, and venue for these tutorials and practical works, along with the name and particulars of your tutor as soon as one is assigned to your group. Your tutor will grade and comment on your assignments, monitor your progress and provide answers to your questions during tutorials. You must submit your assignments and practical books in good time to enable your tutor to read them well and to make appropriate comments. Do not play with your tutorials or hesitate to consult your tutor when the need arises. Tutorials afford you opportunity to meet and discuss with your tutor face to face and they help you to get immediate answers for troubling questions. Apart from tutorials, you may consult your tutor when:

- you do not understand any part of the study units
- you have difficulty understanding self-assessment exercises or tutor-marked Assignment
- When you have problems with the tutor's comments on your assignments or their grading.

To gain maximally from the tutorials, you ought to prepare list of questions before attending them and you must endeavour to participate, actively, in discussions during tutorials.

SUMMARY

The course guide is designed to familiarize you to an overview of what to expect in CHM 212 – Physical Analytical Chemistry. I wish you success as you go through the course.

MODULE 1

UNIT 1

INTRODUCTION TO PHYSICAL ANALYTICAL CHEMISTRY

1.0 INTRODUCTION : Importance of Determining the Structures of Organic Compounds

Whenever an interesting compound is isolated from a natural source, there is need for its structure to be completely determined before a synthesis can begin. Whenever we run a reaction, we must determine whether the product has the desired structure or whether unwanted side reactions have taken place. Traditionally the structures of organic molecules were determined by chemical means. These involve the following:

• Finding the molecular formula by analyzing the elemental composition and determining the molecular weight.
• Determining & comparing physical properties such as melting point, boiling point, refractive index etc with published values.
• Determining the various functional groups and narrowing down to a range of possible structures.

However, all of the aforementioned procedures are destructive and require a lot of test samples before a result can be correctly obtained. Spectroscopic techniques on the other hand are non-destructive; that is, the sample is not destroyed. Many different kinds of spectra can be measured with little or no loss of sample. In this course, we'll be looking at the various spectroscopic techniques that enables the structural determination of organic molecules.

1.1 OBJECTIVES

At the end of this unit, students will be able to:

1. Define spectroscopy and understand the importance of spectroscopy over chemical means
2. List the various regions of the Electromagnetic Spectrum
3. Understand the relationship between energy, wavelength and frequency
4. List the molecular effects of the various regions of the electromagnetic spectrum

1.2 MAIN CONTENT

Definition of Spectroscopy and the Electromagnetic Spectrum

Spectroscopy is the study of how light interacts with matter, and by light we are refering to the various regions of the electromagnetic spectrum (shown in Figure 1) which include radio waves, microwaves, infrared radiation, visible, near UV, X rays and gamma rays. The electromagnetic spectrum is defined by wavelength, frequency and energy. The relationship between wavelength, frequency and energy is given by the equation E=hν, where E is the energy, h is the plank's constant and ν is the frequency. Notice that form Figure 1, the energy and frequency are directly propotional while the wavelength and energy are inversely related. Each region of the electromagnetic spectrum imparts a molecular effect ranging from nuclear spin transitions to ionization of covalent bonds.

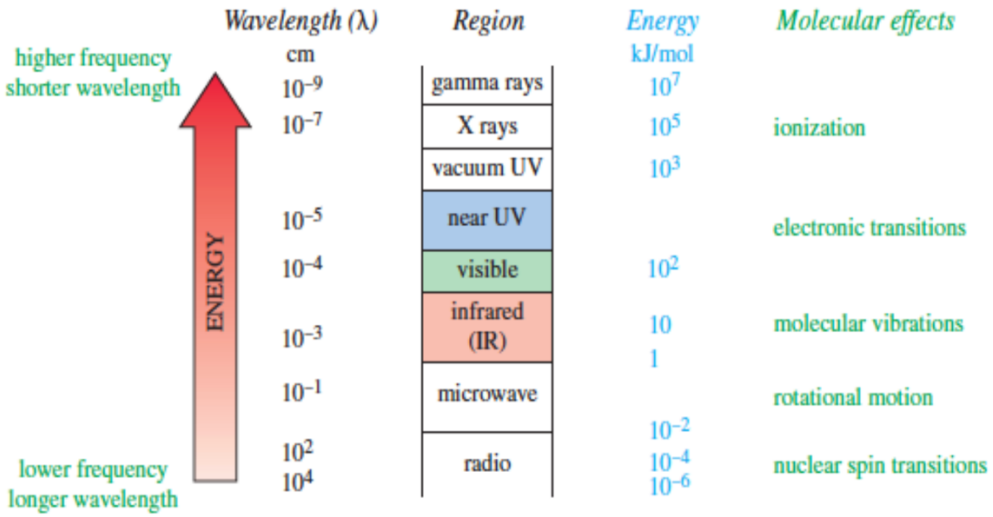


Figure 1. The Electromagnetic Spectrum

In this unit, we'll be looking at the radio region of the electromagnetic spectrum and its associated molecular effect - nuclear spin transitions; a spectroscopic technique referred to as Nuclear Magnetic Resonance Spectroscopy.

Nuclear Magnetic Spectroscopy also known as NMR is the most powerful tool available for the structural determination of organic structures. It is advantageous because it is a technique that requires with a very small sample and it does not harm the sample. Furthermore, it provides a great deal of information about the number and types of atoms in a molecule including 1H, 13C, 15N, 19F, and 31P NMR. Furthermore, it provides substantial information about the connectivity of the atom and can allow for etermining the structure of a molecule with no additional information

Theory Behind Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear Magnetic Spectroscopy (NMR) is based on two general principles and these are

1. Any nucleus with an odd atomic number or an odd mass number has a property referred to as Nuclear Spin with allowed values of +1/2 and -1/2.
2. Secondly, a moving charge has an associated Magnetic Field.

Hence, a proton (a hydrogen) can be considered as the simplest nucleus. Since it has an odd atomic umber of 1, it implies that it also has a nuclear spin. Furthermore, a proton can be visualized as a rotating sphere of positive charge whose rotating movement results in the formation of a magnetic field. The resulting magnetic field is referred to as the magnetic moment and resembles that of a bar magnet as shown in Figure 2.

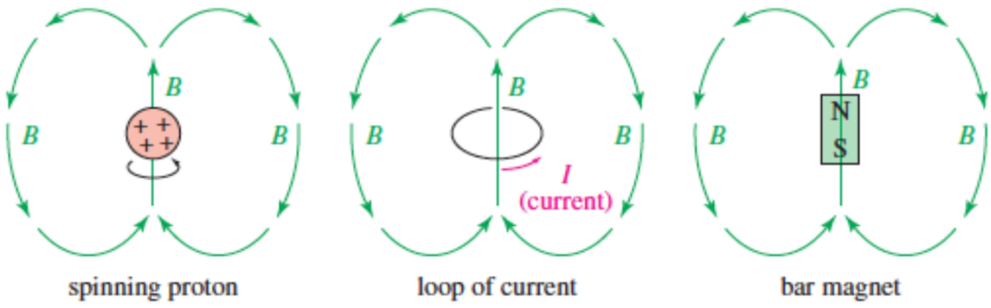


Figure 2. A spinning proton generates a magnetic field, called its magnetic moment. This magnetic field (B) resembles that of a small loop of current or bar magnet.

What happens when a Bar Magnet is placed in an external magnetic field ?

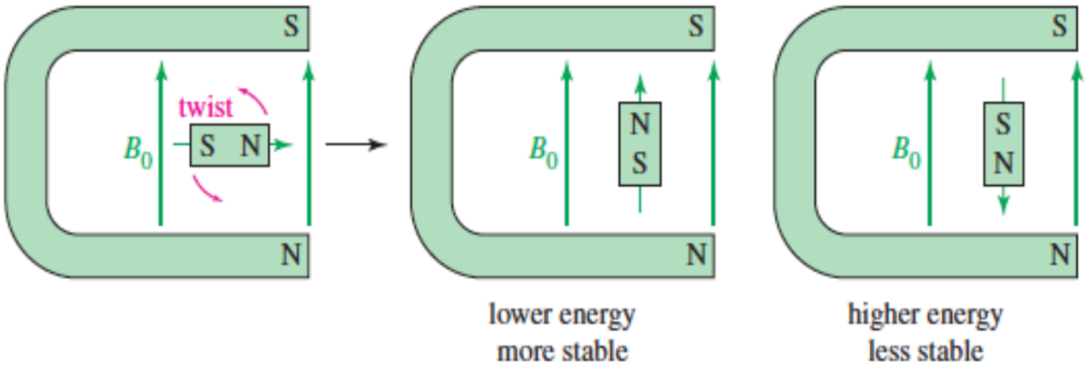


Figure 3. An external magnetic field applies a force to a small bar magnet, twisting the bar magnet to align it with the external field. This alignment results in the formation of two different orientations with different energy stability

When a bar magnetic is placed in an external magnetic field two orientations/states are observed: One whereby the bar magnet aligns with the field of the larger magnet and thus resulting in a lower energy arrangement and another whereby the bar magnet aligns against the field of the larger magnet resulting in a higher energy arrangement as shown in Figure 3.

What happens when a Proton is placed in an external magnetic field ?

However, it is worth mentioning that since a proton also behaves like a bar magnet, a proton (its magnetic field) will also align in two different orientations- aligning with the field of the larger magnet resulting in a lower energy arrangement referred to as α-spin state (+1/2) as well as aligning against the field of the larger magnet resulting in a higher energy arrangement referred to as β-spin state (-1/2). Figure 4.

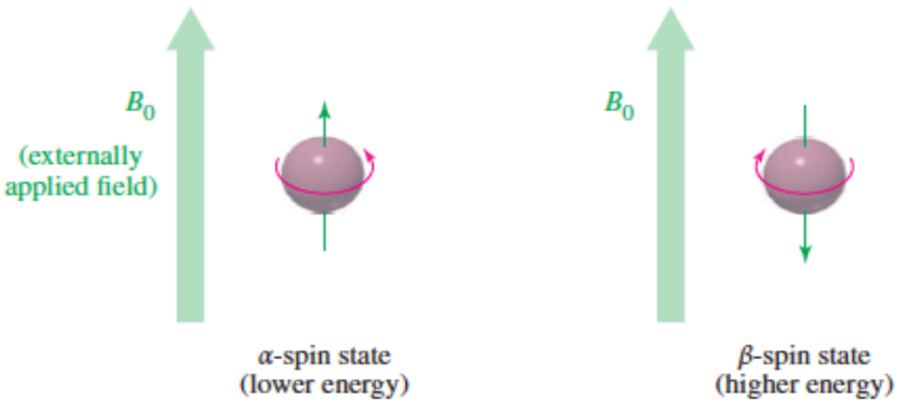


Figure 4. An external magnetic field applies a force to a proton, twisting its magnetic moment to align it with the external field. This alignment results in the formation of two different orientations with different energy stability.

Orientation of Spin States in the Presence and Absence of an External Magnetic Field

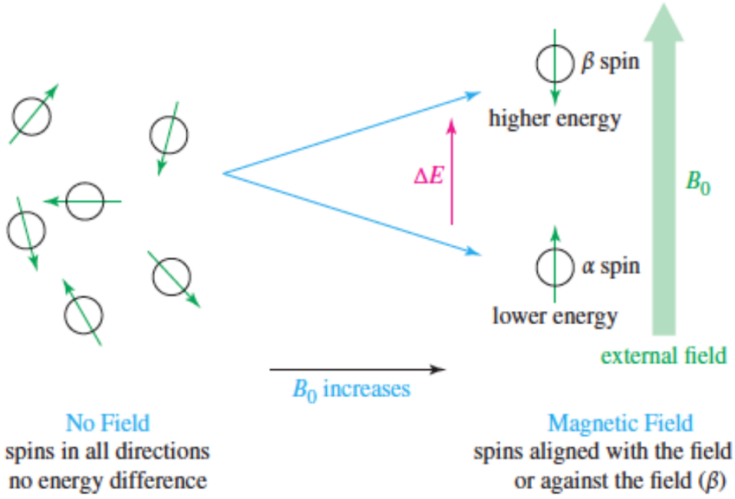


Figure 5. Spin orientation in the presence and absence of an external magnetic field (B_0)

In the absence of an external magnetic field (B_0), a proton's magnetic moments have random orientations as shown in Figure. In the presence of an external magnetic field (B_0), a proton's magnetic moments will align in two different orientations as already mentioned above. The difference in energy (ΔE) between nuclear spin states for a given nucleus is proportional to the strength of the magnetic field (B_0) experienced by that nucleus as shown in Figure 6.

Energy Difference (ΔE) between Spin States and the concept of Resonance

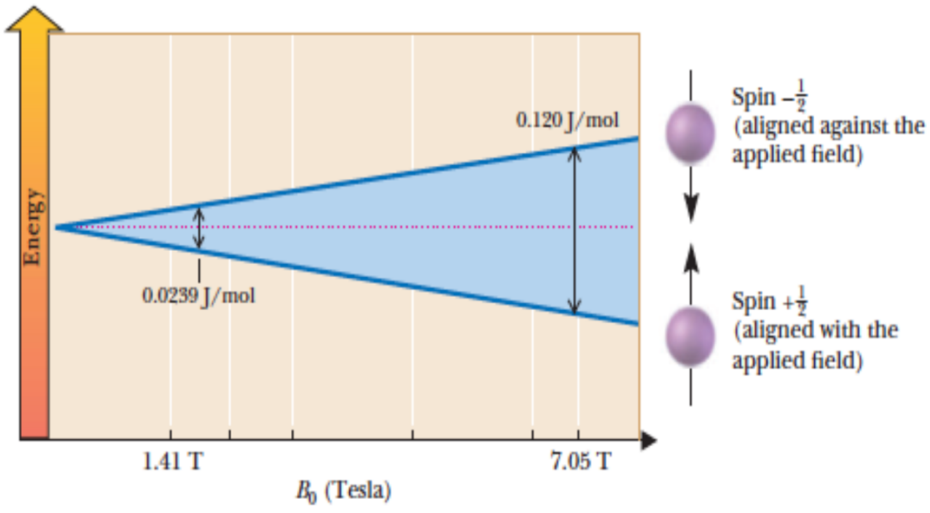


Figure 6. The energy difference between the allowed nuclear spin states increases linearly with applied field strength. The stronger the external field the greater the energy difference between the two spin states.

What is the meaning of "Resonance" in Nuclear Magnetic Resonance ?

When a proton interacts with a photon with just the right amount of electromagnetic energy (ΔE), they absorb the energy and nuclear spins flip from the lower energy state (α-spin state) to the higher energy state (β -spin state) as shown in Figure 7.

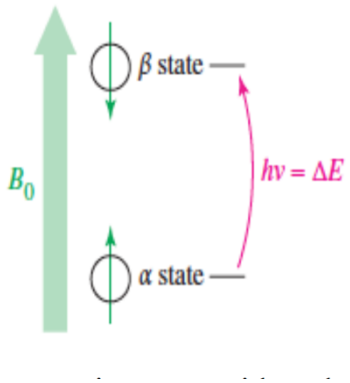


Figure 7. Illustration of the concept of resonance in NMR.

Concept of Chemical Shift

An applied magnetic field induces the electron density in a molecule to circulate. A key physical principle for NMR is that circulating electrons induce a magnetic field. The spin states of underlying nuclei are, in turn, influenced to a small but measurable degree by the magnetic field created by the induced electron density circulation. The circulation of electron density in a molecule in an applied magnetic field is called a diamagnetic current.

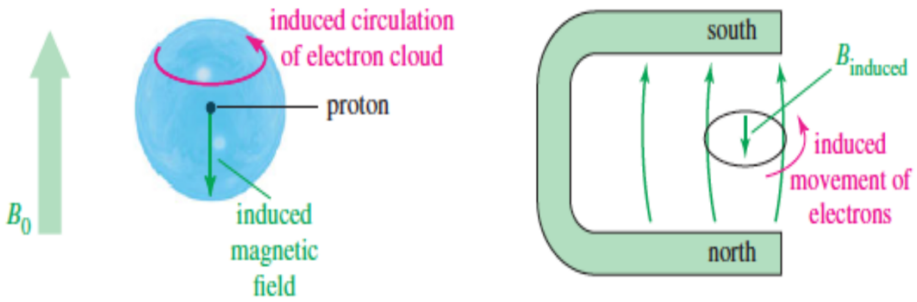
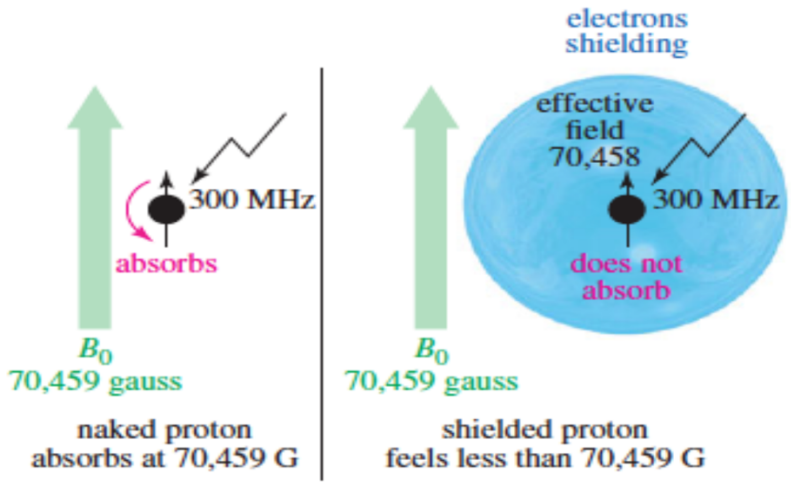


Figure 8. Circulating electrons induce a magnetic field which acts in the opposite direction of the applied magnetic field.

The magnetic field created by the induced electron density circulation opposes the applied magnetic field. As a result, the nuclei within the circulating electron density experience a magnetic field that is slightly smaller than the actual applied field. In other words, nuclei underneath the circulating electron density are "**shielded**" to a small degree from the applied magnetic field. This nuclear shielding is called **diamagnetic shielding**. As the shielding becomes greater, the net magnetic field present at a nucleus becomes smaller so the energy of electromagnetic radiation required to bring that nucleus into resonance (i.e., "flip its spin") also



decreases.

Figure 9. Concept of electron shielding

Energy is proportional to electromagnetic radiation frequency, and resonance frequencies are plotted on an NMR spectrum. Putting all of these ideas together, we see that a nucleus that is more shielded will come into resonance at lower frequency than a nucleus that is less shielded. "**Deshielding**" is the term commonly used to express the concept of less shielding. The relationship of greater shielding leading to resonance at lower frequency is fundamental to understanding NMR spectra. The difference in resonance frequencies caused by differing amounts of shielding is called **Chemical shift.**

An NMR Spectrometer

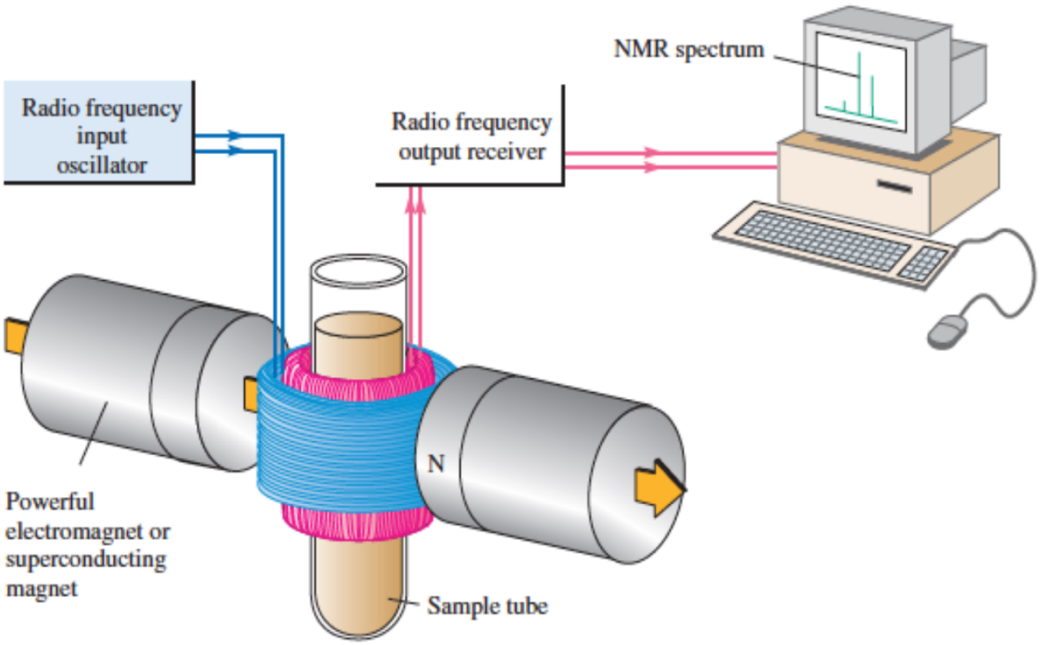


Figure 10. Schematic diagram of a nuclear magnetic resonance spectrometer

An NMR Spectrometer is made of the following: A Powerful Electromagnet or superconducting magnet, a radio frequency input oscillator, a sample tube in which the sample to be analyzed is placed, a radio frequency output receiver and a desktop computer for data processing.

NMR Spectrum

Figure 11 below shows a 300 MHz ^{1}H-NMR spectrum of methyl acetate. The lower axis is δ, in parts per million. The small signal at δ 0 is caused by the hydrogens of the TMS reference, a small amount of which was added to the sample. The remainder of the spectrum consists of two signals: one for the three hydrogens on the methyl adjacent to oxygen and one for the three hydrogens on the methyl adjacent to the carbonyl group. For now, we won't determine which hydrogens give rise to which signal, but only to recognize the form in which an NMR spectrum is recorded.

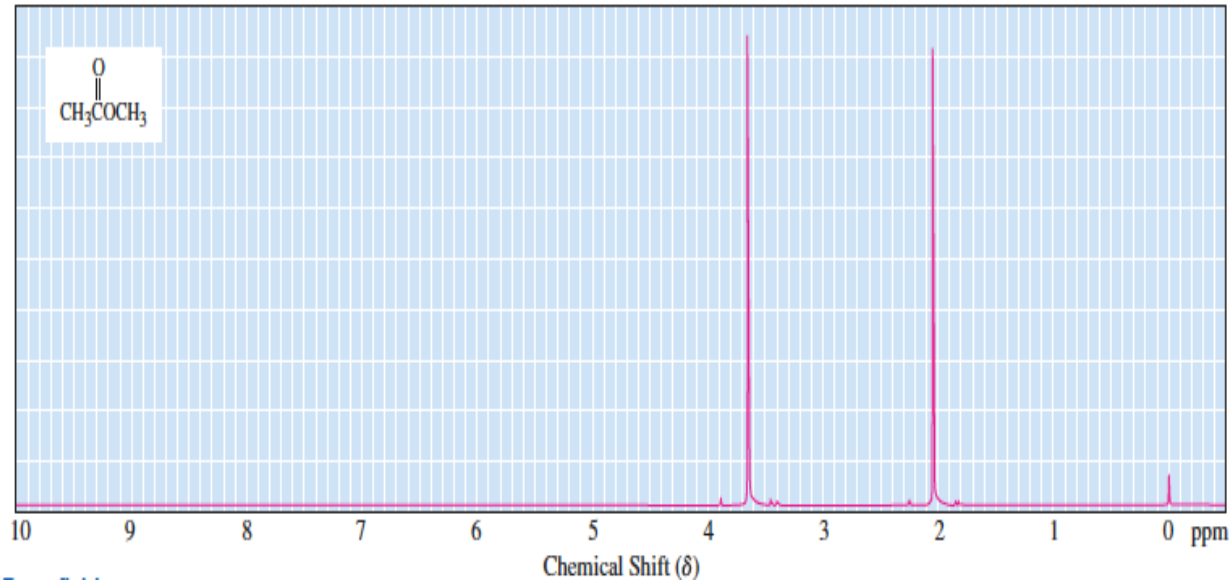


Figure 11. ^{1}H-NMR spectrum of methyl acetate

NMR Spectra Terminology

In NMR, if a signal is shifted toward the left on the chart paper (larger chemical shift), we say that it is shifted **Downfield**. A downfield shift corresponds to decreased shielding around a nucleus (i.e., deshielding). If a signal is shifted toward the right (smaller chemical shift), we say that it is shifted **Upfield** and therefore corresponds to increased shielding around a nucleus.

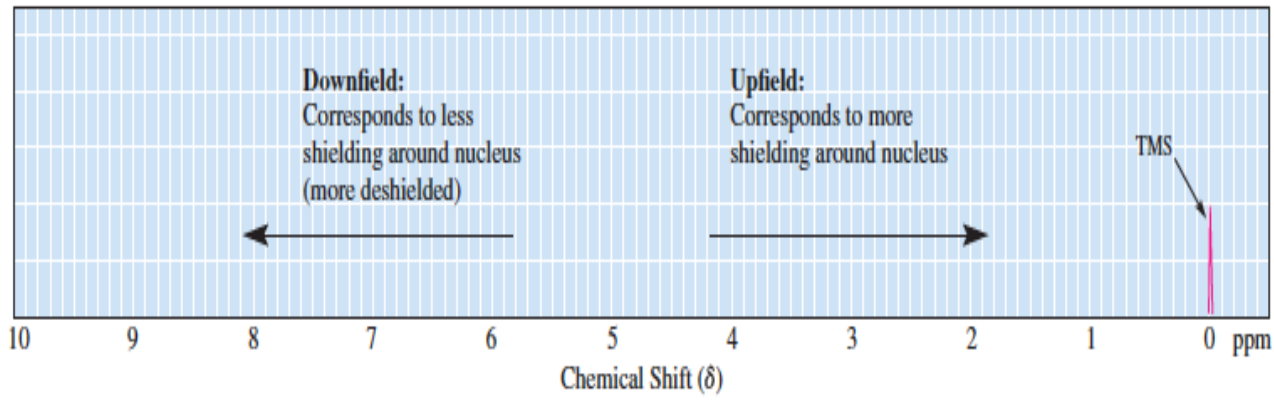


Figure 12. Terminology on Downfield and Upfield

Key Information obtained from an ^{1}H-NMR Spectrum

1. The amount of shielding shown by these absorptions implies the electronic structure of the molecule close to each type of proton. This is denoted by the concept of chemical shifts.

2. The number of different absorptions (also called signals or peaks) implies how many different types of protons are present.

3. The intensities of the signals imply how many protons of each type are present.

4. The splitting of the signals gives information about other nearby protons.

Characteristic Values of Chemical Shifts

The chemical shift of a proton is determined particularly by its environment. A short table of approximately approximate chemical shifts for many types of compound/ functional groups are given below.

Table 1. Typical Values of Chemical Shifts

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-CH_3$) methyl	0.9	$>C=C<$ allylic CH_3	1.7
alkane ($-CH_2-$) methylene	1.3	Ph—H aromatic	7.2
alkane ($-CH<$) methine	1.4	Ph—CH_3 benzylic	2.3
$-C(=O)-CH_3$ methyl ketone	2.1	$R-C(=O)-H$ aldehyde	9–10
$-C\equiv C-H$ acetylenic	2.5	$R-C(=O)-OH$ acid	10–12
$R-CH_2-X$ (X = halogen, O)	3–4	R—OH alcohol	variable, about 2–5
		Ar—OH phenol	variable, about 4–7
$>C=C<$ vinyl H	5–6	$R-NH_2$ amine	variable, about 1.5–4

As an example, Figure 13 below shows the NMR spectrum of toluene (methylbenzene). The aromatic protons absorb around δ 7.2. The methyl protons are deshielded by a smaller amount, absorbing at δ 2.3.

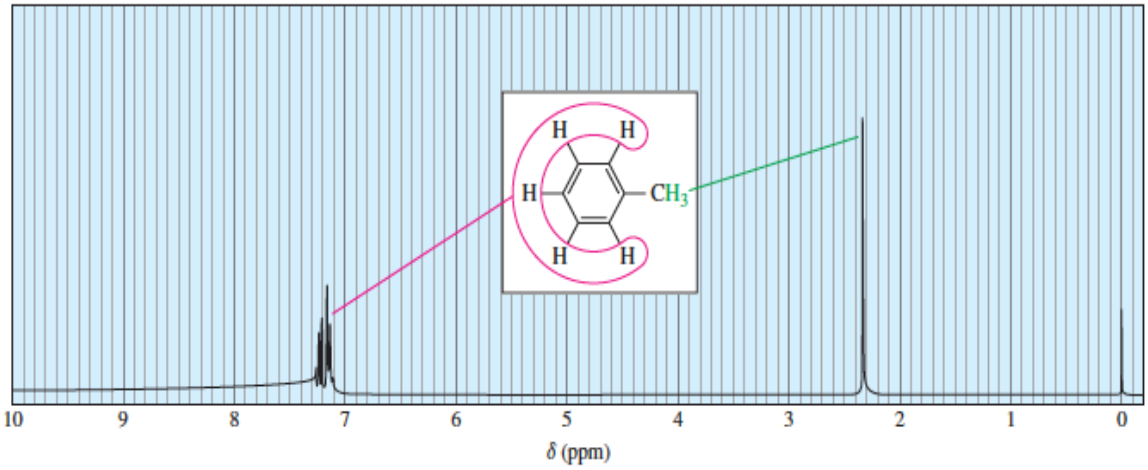


Figure 13. NMR spectrum of toluene (methylbenzene).

The Number of Signals: Chemical Equivalency

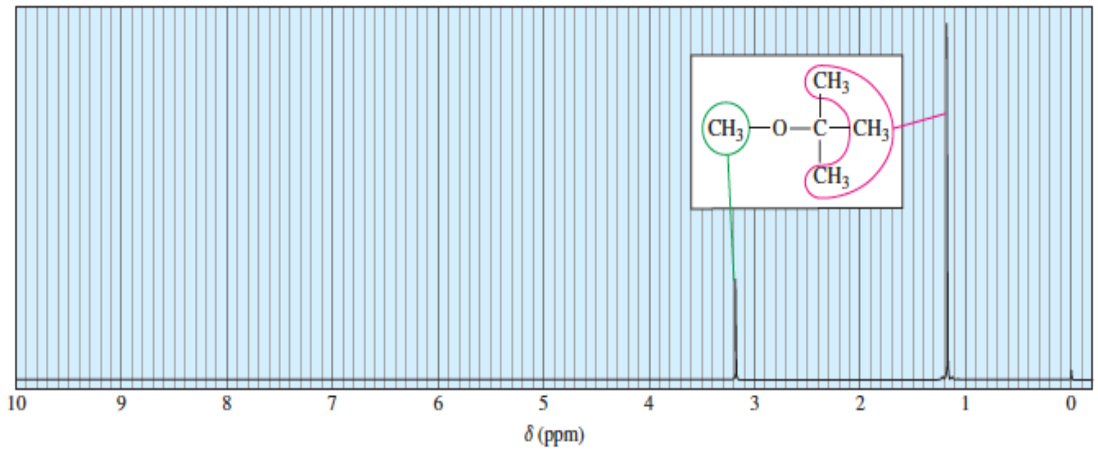
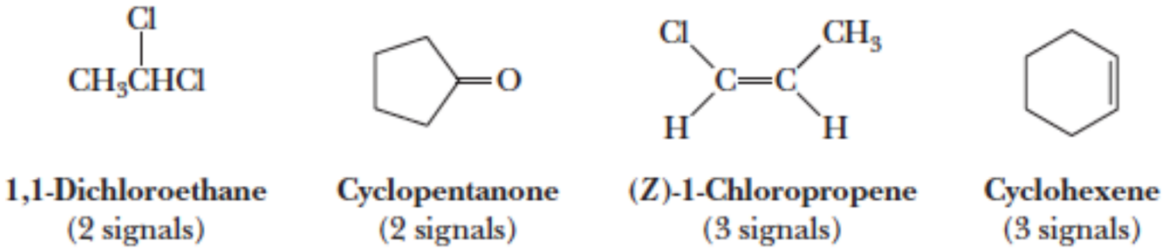


Figure 14. NMR spectrum of Methyl tert-butyl ether. Methyl tert-butyl ether has two types of protons, giving two NMR signals.

Protons in identical chemical environments with the same shielding have the same chemical shift. Such protons are said to be **chemically equivalent** as shown in Figure 14. **Equivalent hydrogens** have the same chemical environment. In methyl tert-butyl ether, the three methoxy protons are chemically equivalent, and the nine tert-butyl protons are chemically equivalent. Further examples regarding the concepts of chemical equivalency is given below:



1,1-Dichloroethane (2 signals) | **Cyclopentanone** (2 signals) | **(Z)-1-Chloropropene** (3 signals) | **Cyclohexene** (3 signals)

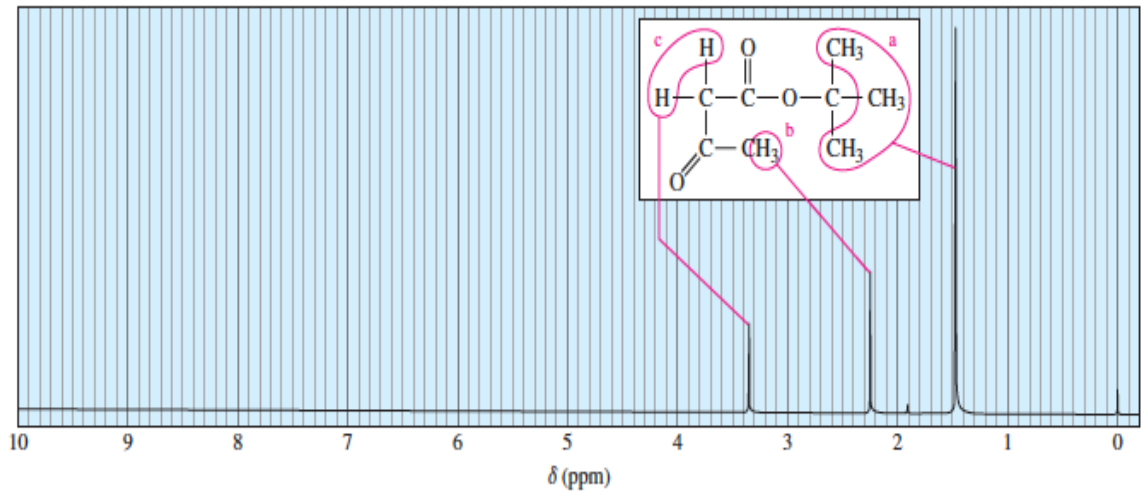


Figure 15. NMR spectrum of tert-Butyl acetoacetate. Tert-Butyl acetoacetate has three types of protons, giving three signals in the NMR spectrum.

The spectrum of tert-butyl acetoacetate shown in Figure 15 shows three types of protons: the tert-butyl protons (a), with a chemical shift of δ 1.5; the methyl protons (b), deshielded by an adjacent carbonyl group, with a chemical shift of δ 2.25; and the methylene protons (c), deshielded by two adjacent carbonyl groups, at δ 3.35.

Area of the peaks/e Signal Areas

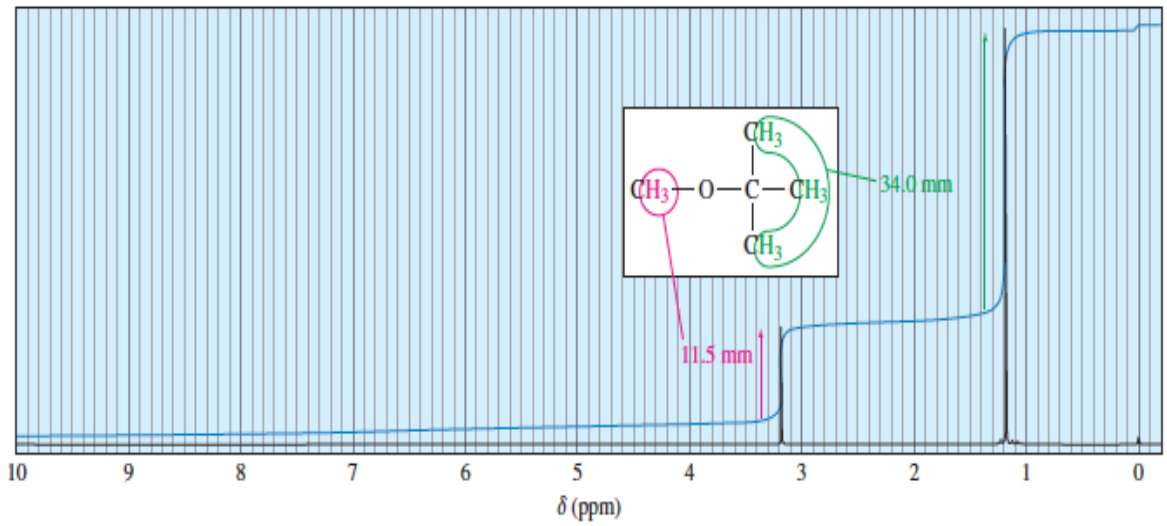


Figure 16. Integrated proton NMR spectrum of methyl tert-butyl ether. In going over a peak, the integrator trace (blue) rises by an amount that is proportional to the area under the peak.

The area under a peak is proportional to the number of hydrogens contributing to that peak. For example, in the methyl tert-butyl ether spectrum (Figure 16), the absorption of the tert-butyl protons is larger and stronger than that of the methoxy protons because there are three times as many tert-butyl protons as methoxy protons.

NMR spectrometers have in-built softwares that compute the relative areas of peaks. The software draws a second trace (the integral trace) that rises when it goes over a peak. The amount the integral trace rises is proportional to the area of that peak. You can measure these integrals using a millimeter ruler. Newer instruments print out a number representing the area of each peak. These numbers correspond to the heights of the rises in the integral trace.

Neither an integral trace (shown in blue in Figure 16) nor a digital integral can specifically indicate that methyl tert-butyl ether has three methyl hydrogens and nine tert-butyl hydrogens. Each simply shows that about three times as many hydrogens are represented by the peak at δ 1.2 as are represented by the peak at δ 3.2. We must interpret what the 3:1 ratio means in terms of the structure

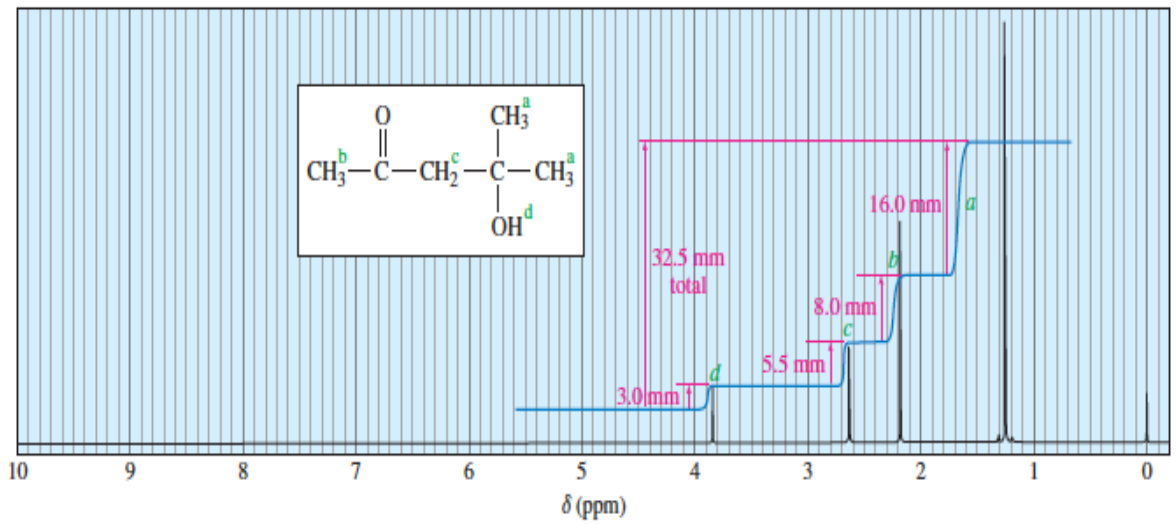
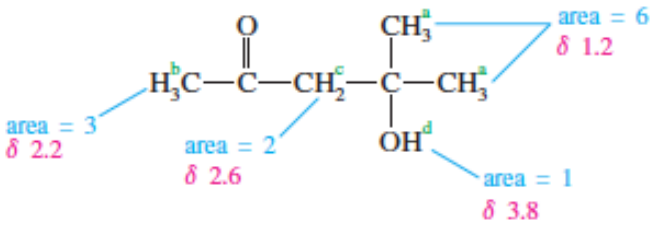


Figure 17. Proton NMR spectrum for a compound of molecular formula $C_6H_{12}O_2$.

Figure 17 above shows the integrated spectrum of a compound with molecular formula $C_6H_{12}O_2$. Because we know the molecular formula, we can use the integral trace to determine exactly how many protons are responsible for each peak. The integrator has moved a total of 32.5 mm vertically in integrating the 12 protons in the molecule. Each proton is represented by:

$$\frac{32.5 \text{ mm}}{12 \text{ hydrogens}} = \text{about 2.7 mm per hydrogen}$$

The signal at δ 3.8 has an integral of 3.0 mm, so it must represent one proton. At δ 2.6, the integrator moves 5.5 mm, corresponding to two protons. The signal at δ 2.2 has an integral of 8.0 mm, for three protons; and the signal at δ 1.2 (16.0 mm) corresponds to six protons. Considering the expected chemical shifts together with the information provided by the integrator leaves no doubt which protons are responsible for which signals in the spectrum.



Concept of Signal Splitting and the (n+1) Rule

If a signal is split by *n* neighboring equivalent protons, it will be split into n+1 peaks.

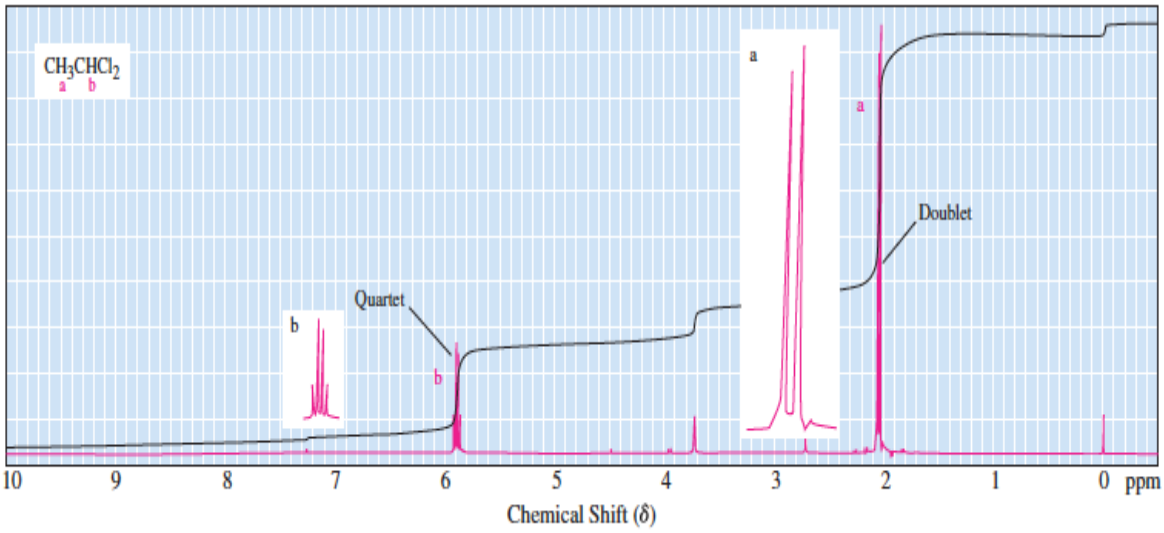


Figure 18. ^{1}H-NMR spectrum of 1,1-dichloroethane.

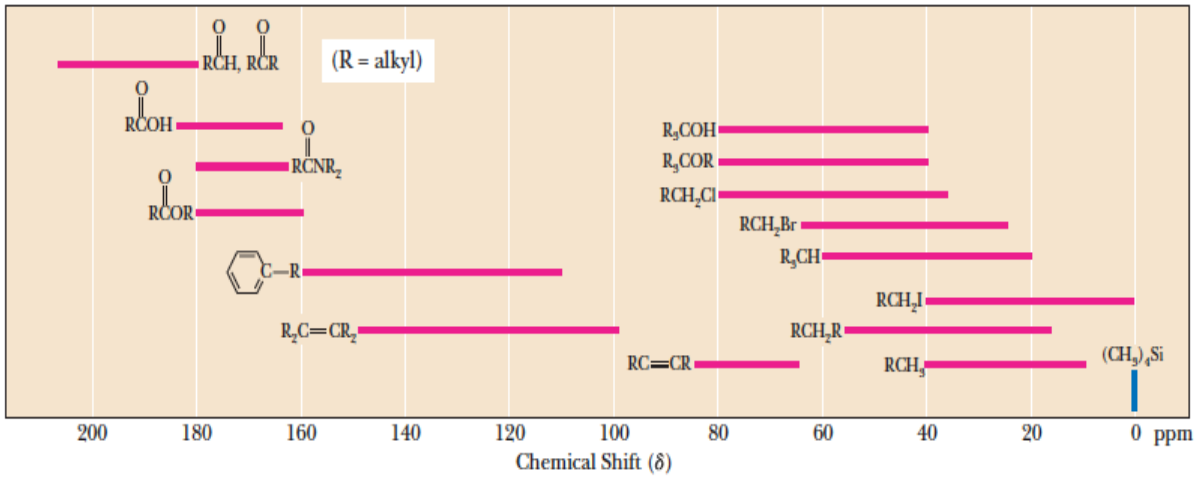
Consider, for example, the ^{1}H-NMR spectrum of 1,1-dichloroethane shown in Figure 18 above. This molecule contains two sets of equivalent hydrogens. According to what we have learned so far, we predict two signals with relative areas 3:1 corresponding to the three hydrogens of the $–CH_3$ group and the one hydrogen of the $–CHCl_2$ group, respectively. You see from the spectrum, however, that there are, in fact, six peaks. These peaks are named by how the signal is split: two peaks are a doublet, three peaks are a triplet, and so on. The grouping of two peaks at δ 2.0 is the signal for the three hydrogens of the $–CH_3$ group, and the grouping of four peaks at δ 5.9 is the signal for the single hydrogen of the $–CHCl_2$ group. We say that the CH_3 resonance at δ 2.1 is split into a doublet and that the –CH resonance at δ 5.9 is split into a quartet.

^{13}C-NMR

Carbon just like hydrogen has a nucleus with an odd atomic number and thus can be observed by NMR. The table below shows approximate chemical shifts for ^{13}C-NMR. Notice how much wider the range of chemical shifts is for 1^{13}C-NMR than for ^{1}H-NMR (Table 2). Most chemical shifts for ^{1}H-NMR fall within a rather narrow range of 0 to 10 ppm; however, those for ^{13}C-NMR cover 0 to 220 ppm.

Notice further that the chemical shift of carbonyl carbons is quite distinct from those of sp^3 hybridized carbons and of other types of sp^3 hybridized carbons. The presence or absence of a carbonyl carbon is quite easy to recognize in a ^{13}C-NMR spectrum. Note that signals from sp^2 hybridized carbons fall in a distinctive range of 100 to 160 ppm. A great advantage of ^{13}C-NMR spectroscopy is that it is possible to count the number of types of carbon atoms in a molecule.

Table 2. ^{13}C-NMR chemical shifts of representative groups.



1.3 CONCLUSION

By thoroughly analyzing the four key important information obtained from an ^{1}H NMR data, we can completely elucidate the structure of simple organic molecules.

1.4 SUMMARY

Knowledge of chemical shift values, number of signals/peaks, integration values and splitting patterns based on the n+1 rule are amongst the key important data that can be obtained from an NMR data and used for the complete elucidation of organic molecules.

1.5 SELF-ASSESSMENT QUESTIONS

1. Concept of NMR

(a) The two principles on which NMR is based

(b) The four key information that can be obtained for NMR data

(c) Relative range of chemical shift values for ^{13}C and ^{1}H NMR

1.6 TUTOR-MARKED ASSIGNMENT

1. Define what is meant by the concept Resonance?

2. List down the various components of an NMR Instrument.

3. Distinguish between upfield and downfield

4. Distinguish between between the structure of 1,3-dimethyl heptanal and toluene based on the four key information that can be obtained for NMR data

1.7 REFERENCES

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UNIT 2

INTRODUCTION TO MASS SPECTROMETRY

1.0 INTRODUCTION

Mass spectrometry is one of the primary analytical methods for molecular analysis available to organic chemist. It is a microanalytical technique requiring only a few nanomoles of the sample to obtain characteristic information pertaining to the structure and molecular weight of analyte. It is not concerned with non- destructive interaction between molecules and electromagnetic radiation. It involves the production and separation of ionized molecules and their ionic decomposition product and finally the measurement of the relative abundance of different ions produced. It is, thus a destructive technique in that the sample is consumed during analysis. In most cases, the nascent molecular ion of the analyte produced fragment ions by cleavage of the bond and the resulting fragmentation pattern constitutes the mass spectrum. Thus, the mass spectrum of each compound is unique and can be used as a "chemical fingerprint" to characterize the sample.

1.1 OBJECTIVES

1) To prove the identity of two compounds.
2) To establish the structure of a new a compound.

The mass spectrum of a compound helps to establish the structure of a new compound in several different ways:

1) It can give the exact molecular mass.
2) It can give a molecular formula or it can reveal the presence of certain structural units in a molecule.

1.2 MAIN CONTENT

Mass spectroscopy is the most accurate method for determining the molecular mass of the compound and its elemental composition. In this technique, molecules are bombarded with a beam of energetic electrons. The molecules are ionized and broken up into many fragments, some of which are positive ions.

Each kind of ion has a particular ratio of mass to charge, i.e. m/e ratio(value). For most ions, the charge is one and thus, m/e ratio is simply the molecular mass of the ion.

For a given charge, velocity and deflecting force, the deflection is less for a heavy particle as compared to that of a light one.

Thus, a number of beams each containing ions with the same m/z values are obtained.

These beams are then made to strike against a photographic plate where not only they appear as separate lines but the intensity of each peak is also recorded.

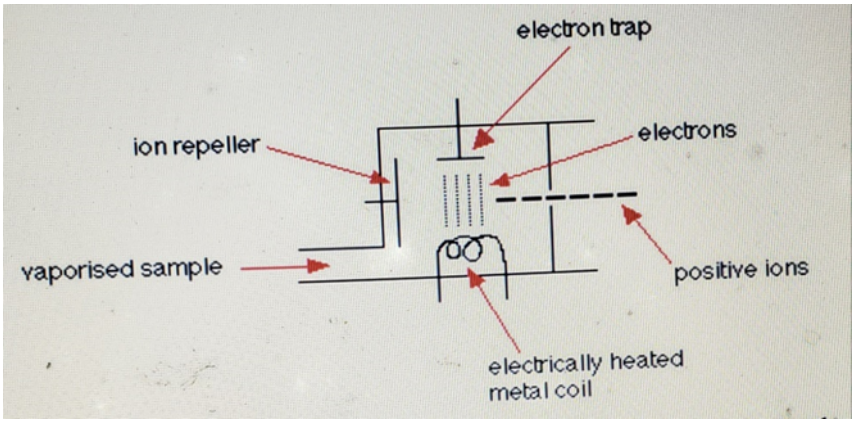
The clear visual presentation of a mass spectrum is usually obtain by plotting m/z value against relative abundance, assigning the most abundant ion (base peak)in the spectrum as 100 per cent.

Though organic mass spectrometry is routinely used along with IR, NMR and UV for structure determination, its basic theory is different from the others.

In mass spectrometry no characteristic selective absorption of radiation is involved as in the case of the other three methods, secondly, in the mass spectrometry, the compound undergoes irreversible chemical changes unlike in the others, where the changes are reversible physical changes.

The mass spectral reactions are much more drastic than usual chemical reactions.

1.3 Ionisation



The atom is ionised by knocking one or more electrons off to give a positive ion. (Mass spectrometers always work with positive ions).

The particles in the sample (atoms or molecules) are bombarded with a stream of electrons to knock one or more electrons out of the sample particles to make positive ions.

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1.4 Fragmentation process

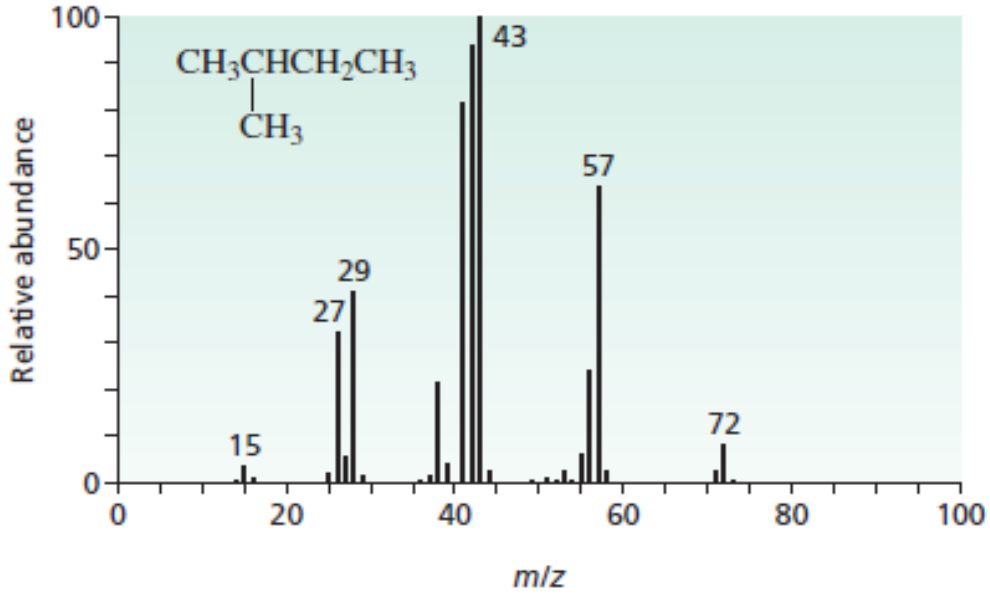
Bombardment of molecules by an electron beam with energy between 10-15ev usually results in the ionization of molecules by removal of one electron (Molecular ion formation).

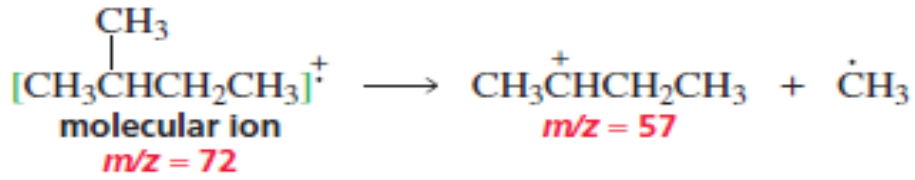
When the energy of electron beam is increased between 50-70ev, these molecular ions acquire a high excitation resulting in their break down into various fragments. This process is called — Fragmentation process.

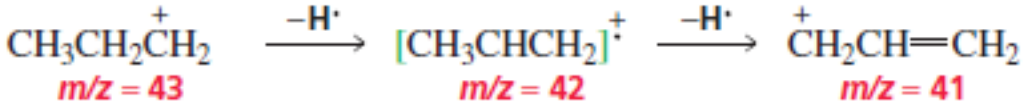
1.5 Types of Ions

1. Molecular ion or Parent ion.
2. Fragment ions.
3. Rearrangement ions.
4. Multicharged ions.
5. Negative ions.
6. Metastable ion.

1.6 **MS of Isopentane**







1.7 CONCLUSION

MS can provide confirmatory drug testing that laboratories can be confident in reporting. The methodology accomplishes this by combining necessary sensitivity with necessary selectivity and specificity, which is currently unachievable by other platforms.

1.8 SUMMARY

Mass spectrometry is an analytical tool useful for measuring the mass-to-charge ratio (m/z) of one or more molecules present in a sample. These measurements can often be used to calculate the exact molecular weight of the sample components as well.

1.9 **SELF-ASSESSMENT QUESTIONS**

1. Using thermochemical data, find the energy required to remove an electron from the following species: H , Na, C, CH , and Fe. Express this energy in kJ/mole and eV (per 2 4 atom).

2. Which mass analyzer would be appropriate for the following analysis:

3. Routine analysis of drug testing samples. A quadrupole mass analyzer would provide the necessary mass range and resolution. It is also fast enough for use with high resolution chromatography.

TUTOR-MARKED ASSIGNMENT

1. Give a combination of carbon, nitrogen and hydrogen to account for the m/z value of 29?

2. Give a combination of carbon, nitrogen and hydrogen to account for the m/z value of 57?

3. Why can an atom with an m/z value of 31 not be C 2 H 7 + ?

4. Give a combination of atoms to account for the m/z value of 31?

5. Give the molecular formula of hydrocarbon cation with an m/z value of 28.

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UNIT 3

INTRODUCTION TO UV-VIS SPECTROSCOPY

3.0 INTRODUTION

UV-vis spectroscopy is a cost-effective, simple, versatile, non-destructive, analytical technique suitable for a large spectrum of organic compounds and some inorganic species. As a function of wavelength, UV-vis spectrophotometers measure the absorption or transmission of light that passes through a medium.

3.1 OBJECTIVES

At the end of this unit, students will be able to:

1. Students will be able to define and derive Beer-Lambert Law
2. Understands the different transitions
3. Define Chromphore, Auxchrome
4. Understands Woodward Fieser Rules

3.2 MAIN CONTENT

UV- Visible Spectroscopy is concerned with the study of UV or Visible radiation whose wavelength ranges from 200-800nm.

Colorimetry or Visible spectroscopy is concerned with the study of absorption of visible radiation whose wavelength ranges from 400-800nm.

Any coloured substance will absorb radiation in this wavelength region.

Ultraviolet spectroscopy is concerned with the study of absorption of UV radiation which ranges from 200-400nm.

Compounds which are colorless absorb radiation in the UV region.

In both UV as well as visible spectroscopy, only the valence electrons absorb the energy there by the molecule undergoes transition from the ground state to the excited state.

This absorption is characteristic and depends on the nature of electrons present.

Region from 200 to 380nm → Near or Quartz

UV region Region from 10 to 200nm → Far or Vacuum UV region

Ultraviolet-Visible spectroscopy is a technique that examines the absorption of a photon of certain frequency or wave length or energy by materials or molecules to cause excitation of an electron on the Highest Occupied Molecular Orbital (HOMO) which may be bonding or non-bonding depending on the number of electrons and molecular orbitals to Lowest Unoccupied Molecular Orbital (LUMO) which is on an anti-bonding or non-bonding orbital.

3.3 Types of transitions in organic molecules

Energy absorbed in the ultraviolet region by complex organic molecules causes transitions of valence electrons in the molecules.

These transitions are σ-σ^*, n-σ^*, π-π^*, n-π^*.

3.4 CHROMOPHORE

The term 'Chromophore' may be define as any group which exhibits absorption of electromagnetic radiations in the visible or ultraviolet region.

It may or may not impart any colour to the compound. The colour usually appears if a compound contains certain unsaturated groups.

The compound containing a chromophore is chromogen

3.5 AUXOCHROME

An auxochrome is a colour enhancing group which does not itself act as a chromophore but whose presence bring about a shift of the absorption band towards longer wavelength along with an increase in the intensity of absorption

The absorption at longer wavelength is due to the combination of a chromophore and an auxochrome to give rise to another chromophore. An auxochromic group is also known as colour enhancing group.

The effect of the auxochrome is due to its ability to extend the conjugation of a chromophore by the sharing of non-bonding electrons

Thus a new chromophore results which has a different value of the absorption maximum as well as the extinction coefficient.

Some auxochromic groups are –OH, -OR, -Cl, -Br etc. for example, benzene shows absorption maximum as well as extinction coefficient at 255nm and 203nm whereas aniline absorbs at 280nm, whereas aniline absorbs at 280nm with extinction coefficient at 1430. Hence -NH2 group acts as an auxochrome.

3.6 Beer-Lambert Law

Beer's-Lambert Law is a combination of Beer's law and Lambert's law.

This law associates the intensity of absorbed light with the thickness of the absorbing medium and the concentration of the solution.

This law was first enacted by Pierre Bouguer before 1729. According to the attribution to Johann Heinrich Lambert, the law included path length as an extinction-affecting variable.

Finally, in 1852, beer extended the law to include the concentration of the solution, which was called Beer-Lambert's law.

3.7 CONCLUSION

UV–Vis spectroscopy is a cost-effective, simple, versatile, non-destructive, and analytical technique, which is suitable for a large spectrum of organic compounds and some inorganic species.

3.8 SUMMARY

Ultraviolet–visible (UV–Vis) spectroscopy is a simple, rapid, and low-cost technique routinely used in analytical chemistry for the quantitative determination of different analytes in solutions, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules.

3.9 SELF-ASSESSMENT QUESTIONS

What is UV visible spectroscopy?

What is the wavelength range of the UV spectrum?

The λ of σ to σ^* transitions lies in the ?

4.0 TUTOR-MARKED ASSIGNMENT

1. What are the limitations of beer lambert law?

2. Monochromatic radiation is incident on a solution of 0.5 molar concentration of an absorbing substance. The radiation intensity is reduced to one-fourth of the initial value after passing through the 10 cm length of the solution. Calculate the molar extinction coefficient of the substance.

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