

Anglo-Chinese School (Independent)

Year 6 (2023) IBDP Chemistry HL



TOPIC 11 MEASUREMENT AND DATA PROCESSING (Part 2)

(IBDP syllabus Topic 11)

11.3 Spectroscopic Identification of Organic Compounds

- Essential Idea: Analytical techniques can be used to determine the structure of a compound, analyse the composition of a substance or determine the purity of a compound. Spectroscopic techniques are used in the structural identification of organic and inorganic compounds.

(IBDP syllabus Topic 21)

21.1 Spectroscopic Identification of Organic Compounds

- Essential Idea: Although spectroscopic characterization techniques form the backbone of structural identification of compounds, typically no one technique results in a full structural identification of a molecule.

Solution Nature of science:

Improvements in instrumentation—mass spectrometry, proton nuclear magnetic resonance and infrared spectroscopy have made identification and structural determination of compounds routine. (1.8)

Models are developed to explain certain phenomena that may not be observable—for example, spectra are based on the bond vibration model. (1.10)

Understandings:

- The degree of unsaturation or index of hydrogen deficiency (IHD) can be used to determine from a molecular formula the number of rings or multiple bonds in a molecule.
- Mass spectrometry (MS), proton nuclear magnetic resonance spectroscopy (¹H NMR) and infrared spectroscopy (IR) are techniques that can be used to help identify compounds and to determine their structure.

Applications and skills:

- Deduction of the oxidation states of an atom in an ion or a compound. Determination of the IHD from a molecular formula.
- Deduction of information about the structural features of a compound from percentage composition data, MS, ¹H NMR or IR.

Guidance:

- The electromagnetic spectrum (EMS) is given in the data booklet in section 3. The regions employed for each technique should be understood.
- The operating principles are not required for any of these methods.
- The data booklet contains characteristic ranges for IR absorptions (section 26), ¹H NMR data (section 27) and specific MS fragments (section 28). For ¹H NMR, only the ability to deduce the number of different hydrogen (proton) environments and the relative numbers of hydrogen atoms in each environment is required. Integration traces should be covered but splitting patterns are not required.

21.1 Spectroscopic Identification of Organic Compounds

ØNature of science:

Improvements in modern instrumentation—advances in spectroscopic techniques (IR, ¹H NMR and MS) have resulted in detailed knowledge of the structure of compounds. (1.8)

Understandings:

- Structural identification of compounds involves several different analytical techniques including IR, 1H NMR and MS.
- In a high resolution ¹H NMR spectrum, single peaks present in low resolution can split into further clusters of peaks.
- The structural technique of single crystal X–ray crystallography can be used to identify the bond lengths and bond angles of crystalline compounds.

Applications and skills:

- Explanation of the use of tetramethylsilane (TMS) as the reference standard.
- Deduction of the structure of a compound given information from a range of analytical characterization techniques (X-ray crystallography, IR, ¹H NMR and MS).

Guidance:

- Students should be able to interpret the following from 1H NMR spectra: number of peaks, area under each peak, chemical shift and splitting patterns. Treatment of spin-spin coupling constants will not be assessed but students should be familiar with singlets, doublets, triplets and quartets.
- High resolution 1H NMR should be covered.
- The precise details of single crystal X-ray crystallography need not be known in detail, but students should be aware of the existence of this structural technique in the wider context of structural identification of both inorganic and organic compounds.
- The operating principles are not required for any of these methods.

11.3 Spectroscopic Identification of Organic Compounds

Nature of science

"Improvements in modern instrumentation – advances in spectroscopic techniques (IR, ¹H NMR and MS) have resulted in detailed knowledge of the structure of compounds. (1.8)."

Scientists are constantly innovating to improve not just their research methodologies, but also the instruments that assist them in their research so as to obtain more precise and accurate data. An example is the infrared spectrometer. Since its invention in 1957, for more than 20 years, each dispersive infrared spectrometer had to scan the reference and sample at every wavelength of the infrared spectrum. The process was tedious and very time–consuming. In the 1980's, Fourier–transformation infrared spectrometers (FTIR) started to appear in many research laboratories. These spectrometers are built with Fourier transformation functions in their software to allow all wavelengths to be used simultaneously and the process is completed in a fraction of the original time. Improvements in instrumentation also allow scientists to observe phenomenon that are not possible in the past. One example is the use of the NMR as body scanners on July 3, 1977. It was modified to provide a non–intrusive scan of the inside of the human body in 3–dimensions. Today, the technique, called magnetic resonance imaging (MRI), is commonly found in many hospitals.

"Models are developed to explain certain phenomena that may not be observable – for example, spectra are based on the bond vibration model. (1.10)"

The key objective of acquiring scientific knowledge and understanding is to make accurate predictions. The scientists will make repeated observations on a phenomenon to increase precision, design a model to explain the phenomenon, and apply it in a new situation to test the model. Models provides prediction to the outcome, and in so doing, scientists do make a lot of assumptions as models are supposed to be simple. In many cases, the models yield a set of close approximations to the actual phenomenon. One example is the ideal gas model, which firstly, requires us to imagine or visualize since molecules cannot be seen with our naked eyes and secondly, ideal gases do not exist. Thus, the model collapses when the molecules become too large and heavy. And so, scientists have developed more sophisticated models to consider other factors like the space occupied by the gas particles and the intermolecular attractive forces to provide more accurate predictions.

In this chapter, there will be many models which require visualization, such as how IR interacts with the atoms and causes vibrations in the form of bond stretching and bending, fragmentation of molecules and how they accelerate between charged plates and deflect in a magnetic field in MS, and how an external magnetic field affects the spin states of protons in NMR and their relaxation to the ground state emits radio frequencies that can be detected. Finally, Bragg's law will be introduced in X-ray crystallography to determine the distance between the planes of atoms or molecules and hence, the distance between the atoms or molecules in a solid crystal.

11.3.1 Difference between Spectroscopy and Spectrometry

The two terms, spectroscopy and spectrometry, are often used synonymously by many students and authors. However, there is a subtle difference between the two terms.

Spectroscopy is the study of the **interaction between matter and energy**. The energy is usually electromagnetic radiation but it can also be a high energy beam of electrons, such as Auger electron spectroscopy (not required to learn) and X–ray spectroscopy and mass spectroscopy.

Spectrometry is the application of spectroscopy to **acquire quantitative data**, usually in the form of a spectrum. To understand spectroscopy or spectrometry well, it is important to understand the electromagnetic spectrum since most of these techniques, involves the use of electromagnetic radiations.

11.3.2 Electromagnetic Spectrum



The electromagnetic spectrum is given in the Data Booklet in Section 3. It is a continuum but arbitrarily broken into 7 bands according to the wavelength or the frequency of the radiation. Each electromagnetic wave is a photon (commonly called a "light particle" erroneously) that has dual property; electrical and magnetic, as its name implies. High frequency waves have higher amount of energies and lower wavelengths and vice versa. The relationship between energy, E, its wavelength, λ , and its frequency, v, is given in the following equations,

The frequency of the radiation can be determined using the equation:

 $c = \lambda v$, where c is the speed of light = 3.00 × 10⁸ m s⁻¹

A photon is characterised by either wavelength, denoted by λ or energy, by *E*. The inverse relationship between the energy of a photon (*E*) and the wavelength of the light (λ) is shown in the equation:

$$E = \frac{hc}{\lambda}$$
, where h is the Planck's constant = 6.63 × 10⁻³⁴ J s

The inverse relationship means that light consisting of high energy photons has a short wavelength. Light consisting of low energy photons has a long wavelength.

As
$$c = v\lambda$$
, the equation $E = \frac{hc}{\lambda}$ can also be written as:
 $E = hv$

How many times more energy does a photon of blue light of 350 nm have compared to a photon of red light of 700 nm?

The different energies of the electromagnetic radiations will produce different effects on matter. Higher energy waves such as ultraviolet, X–rays and γ –rays will cause electronic transitions or nuclear reconfiguration while the lower energy waves can only cause molecular or atomic vibrations such as bonds bending or stretching and flipping of electron and proton spins. The table below summarises the spectroscopic methods based on the type of electromagnetic radiations.

Type of electromagnetic radiation	Wavelength	Spectroscopic technique (application) that you need to know	Spectroscopic effect			
γ– r ay	Less than 0.1 nm					
X–ray	0.1 to 10 nm	X–ray crystallography	Diffraction of X–rays by particles (ions, atoms or molecules) in the crystal			
Ultraviolet	10 to 400 nm	UV-visible	Electron transition from			
Visible	400 to 700 nm	spectrometry	higher energy d–orbital in d– block metals, or π to π^* in conjugated molecules.			
Infrared	700 to 10 000 nm	IR spectrometry (IR)	Absorption of IR due to dipole moment change caused by bonds bending and bonds stretching			
Microwave	0.01 mm to 100 cm					
Radiowave	Greater than 100 cm	Nuclear magnetic resonance (NMR)	Changing spin states of protons in nucleus			

1. A student wrote the statement in his test, "*The energy of infrared radiation is 0.120 kJ, which is a hundred fold lower than light which has 12.0 kJ of energy.*"

What are the inadequacies a scientist will find in the statement?

2. The following table was taken from the internet. If you were a scientist, what would you modify in the table to present it to the scientific world?

Spectral region	VHF	UHF	Microwave	Infrared	Visible Ultraviolet		X-rays	γ-rays
Common usage	NMR	EPR	rotational tra nsitions	vibrational transitions	electronic transitions		ionisation	nuclear effe cts
Frequency (Hz)	5 x 10 ⁸	3 x 10 ¹⁰	3 x 10 ¹¹	3 x 10 ¹³	6 x 10 ¹⁴	1.2 x 1015	3.0 x 1017	1.5 x 10 ¹⁹
Wavelength	0.6 m	1 cm	1 mm	10 µm	500 nm	250 nm	1 nm	20 pm
Wavenumber (cm ⁻¹)	0.017	1.0	10.0	1000	20,000	40,000	1.0 x 10 ⁷	5.0 x 10 ⁸
Single photon energy (eV)	2.07 x 10 ⁻⁶	1,24 x 10 ⁻⁴	1.24 x 10 ⁻³	1.24 x 10-1	2,5	5.0	1.24 x 10 ³	6.2 x 104
Photon energy (kJ mol ⁻)	2.03 x 10 ⁻⁴	1.20 x 10 ⁻²	1.20 x 10-1	12.0	239	479	1.2 x 10 ⁵	6 x 10 ⁶

11.3.3 Degree of Unsaturation or Index of Hydrogen Deficiency (IHD)

The degree of unsaturation or index of hydrogen deficiency (IHD) is used to indicate the number of rings or multiple (double or triple) bonds in an organic molecule. In other words, the degree of unsaturation of IHD is the number of H_2 molecules required for a molecule to become non–cyclic and saturated. IHD provides some information to assist the scientist to make an inference on the molecular structure of a compound.

For the case of hydrocarbons, the most saturated homologous series is the alkanes with the general formula C_nH_{2n+2} . Thus, a molecule with *n* number of carbon atoms is expected to have 2n+2 number of hydrogen atoms. So the degree of unsaturation or IHD is zero.

If we consider alkenes with the general formula of C_nH_{2n} , the number of hydrogen atoms in the molecule is 2n, which is (2n+2)-2n hydrogen atoms short of the saturated alkane C_nH_{2n+2} . So, IHD is 1 as the alkene has one H_2 molecule fewer than its corresponding alkane.

There are two ways to determine the IHD of a molecule. The first is to add the number of rings, r, and π -bonds, π . So,

The second method is to determine the number of H_2 molecules required for a molecule to become saturated. Thus

$$HD = \frac{(\text{number of H atoms if the molecule is saturated}) - (\text{number of H atoms})}{2}$$
$$= \frac{(2n + 2) - (\text{number of H atoms})}{2}$$

Determine the degree of unsaturation or IHD for benzene, C_6H_6 .

A complication arises in the use of the two methods highlighted earlier if there are elements from Groups 15 to 17 present, such as N, P, O, S, F, Cl etc. If we approach this with a clear conceptual understanding, the middle C atoms in any hydrocarbon is bonded to two carbon atoms and two hydrogen atoms if it is saturated. Thus, if a Group 15 element like N or P replaces a middle C atom, it will only have 3 covalent bonds instead of 4 (because there is a lone pair of unbonded electrons on N or P). Thus, in the determination of IHD, the number of hydrogen atoms will be reduced by one such that

 $\mathsf{IHD} = \frac{(2\mathsf{n} + 2) - (\mathsf{number of H atoms}) + (\mathsf{number of Group 15 atoms})}{2}$

Exercise 1

- 1. Deduce the IHD equation that encompasses atoms from Group 14 to Group 17 nonmetal atoms.
- 2. Determine the degree of unsaturation or index of hydrogen deficiency (IHD) of the following.
 - (a) C₄H₆
 - (b) C₅H₆O
 - (c) $C_5H_{10}O_2$
 - (d) $C_6H_4Cl(SiH_3)$
 - (e) C₃H₅NO
- **3.** Do all the isomers of $C_5H_6Cl_2$ have the same IHD? Explain your choice of answer.

11.3.4 Determination of Structure

In the past, the structure of an organic compound was determined from its empirical formula, its relative molecular mass, and any chemical analysis that might yield any clue to its functional groups. This process of determination is still being used today in combination with modern instrumental techniques.

Because information from only one technique is usually insufficient to determine and confirm a structure, modern and well-equipped laboratories today employ a combination of instrumental techniques, namely Mass Spectrometry, Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance (NMR).

11.3.5 Mass Spectrometry

11.3.5.1 Overview

When a specimen is bombarded with electrons in a mass spectrometer, it forms positive ions, the largest, molecular ion is M^+ , and can then further be split into smaller ions and neutral radicals. The positive ions will travel through an electric field and a magnetic field, where they will accelerate and deflect, and the magnitude of deflection depends on the mass of the ions and their charges. A schematic diagram of the processes involved in mass spectrometry is shown in the following page.

The deflection shows up as peaks on the detector and it is possible to identify or deduce what the fragments are, such as:

(m/z = 15) implies fragment is possibly CH_3^+ (m/z = 29) implies fragment is possibly $C_2H_5^+$ or CHO^+ (m/z = 31) implies fragment is possibly CH_3O^+ (m/z = 45) implies fragment is possibly $COOH^+$

More fragments and their m/z values can be found in Section 28 of the Data Booklet.

Subsequently, by piecing together the fragments and the molecular ion mass, the molecular structure of the compound M can be deduced but is not conclusive. One should always use a combination of techniques to confirm the structure of the organic molecule.



In the mass spectrum, the peak of highest abundance is assigned the name "**base peak**" and an arbitrary abundance of 100 %. All the other fragments are then represented as peaks with heights that give their **relative abundance** to the base peak (i.e., the summation of percentages of peaks will thus exceed 100 %).

Consider the compound butane, C₄H₁₀ whose mass spectrum is reproduced below.



Only those fragments with positive charge produce peaks in the mass spectrum. There are many peaks from m/z = 59 down to m/z = 15.

Peak at m/z = 58:

- Corresponds to the molecular ion C₄H₁₀⁺
- Not the largest peak as many of the butane molecules have broken down into a number of smaller fragments.

Peak at m/z = 43:

- Most common, and the most stable ion and is known as the base peak
- Accorded a relative abundance of 100% by convention, and all other peaks are expressed as a percentage of the base peak
- Due to the molecule losing a methyl group, •CH₃, forming the molecular ion, $C_3H_7^+$

Peak at m/z = 15:

- Corresponds to the molecular ion CH₃⁺
- Supports the presence of at least a methyl group in the molecule
- Smaller due to the low stability of CH₃+

$\begin{array}{l} C_4H_{10} \rightarrow \\ (m/z=58) \end{array}$	$C_{3}H_{7}^{+}$ + (m/z = 43)	•CH ₃ + (Mr = 15)	е
$\begin{array}{l} C_4H_{10} \rightarrow \\ (m/z=58) \end{array}$	CH ₃ + + (m/z = 15)	• $C_3H_7 + (Mr = 43)$	е

Another peak what we can expect comes from the fragment $C_2H_5^+$ and it occurs at m/z = 29.

 $\begin{array}{cccc} C_{4}H_{10} \ \rightarrow & C_{2}H_{5}{}^{+} \ + & \bullet C_{2}H_{5} \ + & e \\ (m/z = 29) \end{array}$

Mass spectrometers have become very accurate instruments for the determination of relative molecular masses of organic compounds (besides providing information on the isotopes present in elemental analysis). Together with accurate quantitative data about relative atomic masses, the mass to charge (m/z) ratio (usually given to four decimal places) of the molecular ion will enable the molecular formula of the compound to be determined. This is because there are limited combinations of relative atomic masses that can give us the obtained m/z ratio. However, in some cases the molecular ion is too unstable to be formed, making the molecular formula more difficult to be determined. In very rare cases, the molecular ion can undergo rearrangement (such as the McLafferty rearrangement, but that will not be dealt with at your level). The fragmentation pattern observed in the mass spectrum also helps us in determining the structure of the organic compound.

Mass spectrometry is usually not considered a spectroscopic technique because it does not involve the interaction of electromagnetic radiation (e.g. visible light) with matter. Since experimental data in mass spectrometry is presented in terms of increasing m/z ratio, it is analogous to spectroscopic techniques which present data in terms of increasing wavelengths or frequencies. Thus, we call it a "mass spectrum".

One disadvantage of mass spectrometry is that the sample must be appreciably volatile. It is difficult to analyse macromolecules unless their volatile derivatives can be obtained. For example, by methylating the amine groups of polypeptides, the hydrogen bonds can be negated and the boiling points lowered considerable enough for the macromolecule to be vapourised.



11.3.5.2 Determination of Structure from Mass Spectrum

Since the ionising electron beam in a mass spectrometer has enough energy (anything from 2000 to 6000 kJ mol⁻¹), the molecular ion formed by the loss of an electron (it is actually a radical-cation as it contains an odd number of electrons) will undergo bond fission, and molecular fragments are formed. Some of these will carry the positive charge, and therefore appear as further peaks in the mass spectrometer. Take propanone, CH_3COCH_3 as an example:



We therefore expect the mass spectrum of propanone to contain peaks at m/z = 15 and another at m/z = 43, as well as the molecular ion peak at m/z = 58.



Compare the previous spectrum of propanone with the following spectrum of propanal, CH_3CH_2CHO :



In the mass spectrum of propanal, there is no peak at m/z = 15, nor one at m/z = 43. Instead, there are peaks at m/z = 57 and several from m/z = 26 to m/z = 29. This is readily explained by the following fragmentations:



It should also be noted that there is usually a small peak which occurs 1 m/z unit after the molecular ion peak. This is usually due to the presence of ¹³C isotopes and is commonly known as the (M + 1) peak. ¹²C and ¹³C naturally occur in the ratio 99 : 1. Hence, one should expect to see a very short peak after the molecular ion peak for a carbon–based compound. Sometimes, this peak is so small that it is ignored and not reflected on a mass spectrum.

Interpretation of Mass Spectra

Keep in mind that:

- The peak with the highest abundance is due to the ion which is most easily formed
- M⁺ does not necessarily make part of the fragmentation pattern

Enrichment Reading: M+1 peak

It is also possible to determine the number of carbon atoms in an organic molecule using mass spectrometry.

The other peaks in the mass spectrum that may not have a clear indication of what the fragments are. They could be either due to the loss of •H atoms from some of these fragments, or due to the presence of the isotope; ¹³C, whose relative abundance is 1.1%. Invariably, one useful peak is the (M+1) peak. The ratio of the heights of the M : (M+1) peaks may be approximated to 1 : 0.011n where n represents the number of carbon atoms in the molecule. In the mass spectrum indicated in below, M : (M+1) = 12 : 0.5.



Some molecules also show M+2 peaks and they are usually due to the presence of chlorine isotopes (35 Cl and 37 Cl) (M : [M+2] = 3 : 1) and bromine isotopes (79 Br and 81 Br) (M : [M+2] = 1 : 1).

Exercise 2

1. Identify the main peaks (those with m/z values on them) within the simplified mass spectrums of methyl propanoate, CH₃CH₂COOCH₃.



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

2. IB 2004 Nov HL P3 G2

The mass spectra of halogenoalkanes show more than one line corresponding to the molecular ion. This is due to the presence of isotopes such as ³⁵Cl, ³⁷Cl, ⁷⁹Br and ⁸¹Br.

Analyse the following spectra of halogenoalkanes ${\bf P}$ and ${\bf Q}$ and deduce the formula of all the molecular ion species.



[Source: NIST Mass Spec Data Center, S E Stein, director, "IR and Mass Spectra" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P J Linstrom and W G Mallard, July 2001, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov)]

3. IB 2009 May HL TZ2 P3 A2

Mass spectrometry is a powerful analytical technique used in the identification of organic compounds. The mass spectrum of a compound with empirical formula CH_2O displays peaks at m/z 15, 45, 60.

(a) Determine the molecular formula of the compound.

(b) Identify the fragments responsible for the peaks at m/z 15 and 45.

(c) Identify a compound that could produce this spectrum.

Summary

- Mass spectrometry is very useful in providing some clues on the structural formula of the compound or the type of isotopes present. However, in structural determination, it has to be combined with other techniques such as Infrared Spectrometry and Nuclear Magnetic Resonance.
- The ionizing electron beam in a mass spectrometer has enough energy to cause bonds in a molecule to cleave and form molecular ionic fragments as a result.
- Molecular ions which are formed in the mass spectrometer are positively charged as the ionizing electron beam knocks out electrons from the molecule.
- This results in multiple peaks appearing in the mass spectrometer readout at different m/z values. The amount of deflection is inversely proportional to m/z value.
- Oftentimes, the peak at the highest m/z value corresponds to the Mr of the molecular ion, but some anomalous cases may occur, especially in cases where the molecule can dimerise (two molecules bonding together into a larger molecule).

11.3.6 Proton Nuclear Magnetic Resonance (¹H NMR)

11.3.6.1 Enrichment Reading: Theoretical Foundations of NMR

In an applied magnetic field, spin states are not of equal energies because the nucleus is a charged particle, and any moving charge generates a magnetic field of its own. Thus, the nucleus has a magnetic moment, μ , generated by its charge and spin.

A hydrogen nucleus may have a clockwise $\left(+\frac{1}{2}\right)$ or counter-clockwise $\left(-\frac{1}{2}\right)$ spin, and the nuclear magnetic moments in the two cases are in opposite directions.

In an applied magnetic field, all protons have their magnetic moments either aligned with the field or opposed to it.

Hence, as an external magnetic field is applied, the degenerate spin states split into two states of unequal energy, as shown in the figure that follows.



Many atomic nuclei behave as if they spin on an axis of rotation

- Nuclei are positively charged
- These spinning nuclei generate tiny magnetic fields
- Tiny magnets interact with an external magnetic field, denoted B₀
- Proton (¹H) and carbon (¹³C) are the most important nuclear spins to organic chemists

Nuclear spins are oriented randomly in the absence of an external magnetic field but have a specific orientation in the presence of an external field, B_0 .





Absence of an external magnetic field

Presence of an external field

- Some nuclear spins are aligned parallel to the external field
 - o Lower energy orientation
 - o More likely
- Some nuclear spins are aligned anti-parallel to the external field
 - Higher energy orientation
 - o Less likely

When nuclei that are aligned parallel with an external magnetic field are irradiated with the specific frequency of electromagnetic radiation, the energy is absorbed and the nuclei "spin–flips" to the higher–energy anti–parallel alignment.

- Nuclei that undergo "spin–flips" in response to applied radiation are said to be in resonance with the applied radiation ⇒ nuclear magnetic resonance.
- The frequency necessary for resonance depends on strength of the external magnetic field and the identity of the nuclei.

Many nuclei exhibit NMR phenomenon

- All nuclei with odd number of protons
- All nuclei with odd number of neutrons
- Nuclei with even numbers of both protons and neutrons do not exhibit NMR phenomenon

Magnetic Nuclei	Non–magnetic Nuclei
¹ H	¹² C
¹³ C	¹⁰ C
² H	³² S
¹⁴ N	
¹⁹ F	
³¹ P	

In practice it is easier and cheaper to keep the frequency constant and gradually change the magnetic field strength, B_0 . The sample compound is dissolved in a proton–free solvent such as CCl₄ or DCCl₃ (Although deuterium is NMR active, it does not interfere because it does not absorb in the frequency range set in the instrument for ¹H.) If a more polar solvent is needed, dry (CD₃)S=O (perdeuterodimethyl sulfoxide) is used.

The solution is placed in a long thin glass tube which is spun in the magnetic field so that all the molecules are exposed to a uniform magnetic field. A small amount of a reference compound, tetramethylsilane, $(CH_3)_4Si$ is added to the sample. The spectrum is taken, and when the B₀ value is reached thus enabling the proton to be in resonance at the set frequency, a signal (peak) is traced on a calibrated chart paper that plots transmittance against B₀.



Scan me to see an animation of how the NMR Spectrometer works!



In an NMR spectrometer, the frequency of the oscillation is usually fixed (typically 60 MHz or 100 MHz). The magnetic field is then varied until the exact condition for resonance is attained, in which the nucleus absorbs energy as the nuclear spin 'flips' to align its magnetic moment against the applied field.

11.3.6.2 Chemical Equivalence

The NMR spectrum can distinguish between the types chemical environments of hydrogen atoms contained within the molecule.

If the hydrogen atoms within a molecule are chemically equivalent (or that all the protons are in the same chemical environment), then the NMR spectrum will only show one peak. Conversely, one should expect to see two absorption peaks if the hydrogen atoms are of two different chemical environments, and so forth. For example, the structure below shows that chloroethane has 2 different chemical equivalences for its hydrogen atoms.



The two hydrogen atoms bonded to the carbon on the left (circled) are in a different chemical environment from the three hydrogen atoms bonded to the carbon on the right (boxed). There are therefore two different chemical environments in the chloroethane molecule and we should therefore expect to see two absorption peaks.

However, if the chlorine atom were to be replaced by another hydrogen atom, then all the hydrogen atoms would be in exactly the same chemical environment, and we should only expect to see one absorption peak.

11.3.6.3 Integration Trace and Proton Counting

The area under each ¹H NMR peak is proportional to the number of protons causing that peak Integrating (electronically measuring) the area under each peak makes it possible to determine the relative number of each kind of proton in a molecule.

The ¹H NMR spectrum for methyl 2,2–dimethylpropanoate below shows an example of an integration trace.



Example 1

- 1. How will the number of different hydrogen environments in the following compounds and the number of hydrogen atoms in each environment differ in the following pairs of compounds?
 - (a) Propan-1-ol and propan-2-ol
 - (b) But–1–ene and but–2–ene
 - (c) Benzene and chlorobenzene
- **2.** The low resolution NMR spectrum of a compound with a molecular formula of $C_2H_3Cl_3$ is given below.



- (a) What does "low resolution" mean in NMR?
- (b) The two numbers shown above the peaks are relative numbers. What does the term "relative" mean and what do the two numbers refer to?
- (c) Deduce the structural formula of the compound.
- (d) Explain why the peaks are shifted downfield.

11.3.6.4 Tetramethylsilane (TMS) as a Standard (AHL)



One will find that in most NMR spectra, there is a peak at 0 ppm. This is due to the signal produced by the hydrogen atoms in tetramethylsilane - usually called TMS. Everything else is compared with this.

The purpose of using TMS is to identify the position where the chemical shift is zero. If TMS is not used, the instrument has to be calibrated often enough for the peaks in the spectrum to correspond to the correct chemical shifts.





Spectrum with no TMS peak

Spectrum with TMS peak at $\delta = 0$ ppm

There are many advantages of using TMS.

- There are 4 methyl groups bonded to the central silicon atom. Thus, there are 12 hydrogen atoms of the same chemical environment. This produces a strong single peak with very little TMS used.
- The TMS signal will not interfere with the spectrum. This is because silicon has a lower electronegativity than carbon, TMS absorbs radio waves in a different region from that absorbed by the hydrogen nuclei attached only to carbon.
- It is chemically inert and is soluble in most organic solvents.
- It can be easily removed from the sample as it has a low boiling point.

The net effect of this is that TMS produces a peak on the spectrum at the extreme right–hand side. Almost everything else produces peaks to the left of it.

It should also be noted that most ¹H NMR chemical shifts occur within the δ = 0 to 10 ppm range except for carboxylic acid O–H absorptions which usually occur within the 11–12 ppm range.

11.3.6.5 High Resolution ¹H NMR

If an experimenter were to employ high resolution ¹H NMR spectroscopy, some of the integral peaks in the NMR spectrum will show up as multiplets, or multiple peaks. The reason is due to spin–spin coupling and is explained in the following enrichment reading section (non–examinable).

Enrichment Reading: Origin of Spin–Spin Coupling

Multiple absorptions, called spin-spin coupling, are caused by the interaction (coupling) of the spins of nearby nuclei.

Tiny magnetic fields produced by one nucleus affects the magnetic field felt by neighbouring nuclei

- If protons align with the applied field the effective field felt by neighbouring protons is slightly larger
- If protons align against the applied field the effective field felt by neighbouring protons is slightly smaller



Take bromoethane for example. Each $-CH_2Br$ proton of CH_3CH_2Br has its own nuclear spin which can align either with or against the applied field, producing a small change in the effective field experienced by the $-CH_3$ protons.

Three possible spin states (combinations)

1.

- Both protons spin in alignment with applied field
 - Effective field felt by neighbouring –CH₃ protons is larger
 - Applied field necessary to cause resonance is reduced
- 2. One proton spin is aligned with and one proton spin is aligned against the applied field (two possible combinations)
 - No effect on neighbouring protons
- 3. Both proton spins align against applied field
 - Effective field felt by neighbouring –CH₃ is smaller
 - Applied field necessary to cause resonance is increased



The integral peaks in an NMR spectrum will be split according to the (n+1) rule.

Protons that have n equivalent neighbouring protons show (n+1) peaks in their ¹H NMR spectrum.



In the ¹H NMR spectrum of 2–bromopropane, the $-CH_3$ proton signal at 1.71 ppm is split into a doublet, and the -CHBr proton signal at 4.28 ppm is split into a septet.

The intensity ratios of multiplets derived from the (n+1) rule follows the Pascal's triangle:

Number of equivalent adjacent protons	Multiplet	Ratio of intensities
0	Singlet	1
1	Doublet	1:1
2	Triplet	1:2:1
3	Quartet	1:3:3:1
4	Quintet	1:4:6:4:1
6	Septet	1:6:15:20:15:6:1

Some Common Spin Multiplicities

Using an ester, ethyl ethanoate, as an example, we will interpret the three features of a NMR spectrum and assigned (match) them to the different sets of equivalent protons on the ester molecule.





1. The following statement is found in an IB Study Guide for Chemistry.

"....one piece of evidence is that the high resolution ¹H NMR spectrum of benzene shows a single peak. This would not be the case if benzene had three alternate double bonds as the hydrogen atoms would be in different chemical environments."

Comment on the statement.

Exercise 3

1. IB 2005 May HL P3 G3

¹H NMR spectroscopy can be used to obtain information about the structure of molecules.

State the information that can be obtained from the

(a) number of peaks

(b) chemical shift

(c) ratio of peak areas

(d) splitting pattern

2. The ¹H NMR spectrum of a compound with the formula C₄H₈O₂ exhibits three major peaks with chemical shifts, areas and splitting patterns given below.

chemical shift / ppm	peak area	splitting pattern
0.9	3	triplet
2.0	2	quartet
4.1	3	singlet

(a) Using information from Section 27 in the Data Booklet, determine the types of proton present in the molecule.

chemical shift / ppm	peak area	splitting pattern	deduction
0.9	3	triplet	
2.0	2	quartet	
4.1	3	singlet	

(b) Deduce a structure consistent with the information indicated in (a). Explain your answer.

Summary

- Reading a basic NMR readout requires that one is conversant with three main concepts:
 - Chemical equivalence the presence of hydrogen atoms in different chemical environments.
 - Integration trace and proton counting where the height of the integral peak at a specific chemical shift value corresponds to the relative number of protons present in a specific chemical environment.
 - Chemical shift peaks arising at different chemical shift (δ) values due to a difference in shielding in different chemical environments.
- TMS (tetramethylsilane) is often used as a reference standard in the NMR. The peak produced by the TMS standard occurs at 0 ppm and all other peaks are measured with reference to it. The reason why TMS is used is that all the hydrogens in TMS are very shielded, hence allowing it to produce a very strong signal at 0 ppm.
- If high resolution ¹H NMR spectroscopy were to be employed, some of the integral peaks in the NMR spectrum will actually show up as multiplets, which can then be used to predict the relative number of hydrogen atoms in the carbon adjacent to that which is exhibiting magnetic resonance.

11.3.7 Infrared Spectroscopy (IR)

11.3.7.1 Overview

The absorption of radiation in the infrared (IR) region of the spectrum is usually associated with the vibrational energy levels within a molecule.

A molecule in the ground state is not stationary. Rather, it is constantly moving through space. In addition, the bonds are also stretching and bending as the atoms in the molecule interact with one another. Depending on the structure of the molecule, some are able to absorb IR radiation (IR active). If a molecule is IR active, when it absorbs a photon corresponding to the IR region of the electromagnetic spectrum, the bonds in the molecule will begin to stretch or bend more vigorously.

For diatomic molecules such as HCl there is only one mode of vibration, the stretching of the H–Cl bond. But for more complicated molecules, the number of vibrational modes quickly increases. In water, for example, the following modes are all possible:



For a molecule to be IR active, there must be a change in the dipole moment of the molecule when the vibration takes place.

For example, only two of the possible modes of vibration in the linear CO_2 molecule cause IR absorptions:

Ĵ.	€€	$\stackrel{\downarrow}{\bigcirc} \stackrel{\downarrow}{\longrightarrow} \stackrel{\downarrow}{\longrightarrow}$, C=O =⊋
symmetric stretch inactive As the molecule remains symmetrical, it has no change in dipole.	asymmetric stretch $\approx 2350 \text{ cm}^{-1}$ The molecule has a temporary dipole moment when the C= O bond lengths are of unequal length.	two symmetric bend The molecule has a t moment as it bends geometry. The two vi identical, except that of the page and the o plane of the page.	Is ≈ 670 cm ⁻¹ emporary dipole away from its linear ibrations are t one is in the plane other is out of the

The symmetrical stretching mode results in no change in overall dipole of the molecule, as the change in one $C^{\delta_+}-O^{\delta_-}$ bond dipole on stretching is exactly compensated by the change in the other $C^{\delta_+}-O^{\delta_-}$ bond dipole.



The bent SO₂ molecule, however, shows three IR absorptions, just like water (the O–S–O angle is 119° due to the lone pair of electrons on sulfur). Symmetrical diatomic molecules, such as H_2 and O_2 , also **do not absorb in the IR region** because there is no dipole moment change when IR is absorbed.



Absorptions in the IR region are relatively easy to understand, and it is possible to identify precisely each absorption, when considering diatomic or triatomic molecules. The complexity increases when the number of atoms within the molecule increases. Moreover, the same type of bond in two different compounds will not always have absorption at the same frequency because the two compounds produce different chemical environments. Hence, no two molecules will produce the same IR spectra as exemplified by the spectra of benzaldehyde and phenylethanone.



The **frequency of the IR radiation** is inversely proportional to the wavelength or **directly proportional to the wavenumber**. The **higher the wavenumber is, the stronger the bond**.

Bond stretching requires more energy than bond bending, and thus, bond stretching occurs at the higher wavenumber region.

Fingerprint region: lower frequency part of the IR spectrum of a molecule that is completely unique and differs from that of any other molecule. It is usually from 1500 cm⁻¹ to 500 cm⁻¹.

Organic substances produce spectra which shows absorption in the range of wavelengths (2.5 μ m to 17 μ m) or wavenumbers (number of waves per cm) from 4000 cm⁻¹ to 400 cm⁻¹. Each peak in the spectrum is associated with a molecular vibration of combination of vibrations, and the complexity of the spectrum reflects the number of possible IR active vibrations. With more atoms and different types of bonds, the spectrum becomes more complex with absorptions frequently superimposed. It is also rarely possible to identify all the peaks in the IR spectrum as many of the smaller peaks are due to harmonics and overtones of the fundamental vibrations.

The figure below shows the IR spectrum of propan–1–ol, CH₃CH₂CH₂OH. Notice that this, like all IR spectra, is plotted as a graph of transmittance against wavenumber, with the base–line at the top of the graph, and the absorption "peaks" appearing as troughs in the transmittance.



In the spectrum above, there are 3 peaks that should be considered as they are very prominent. They are at 3350 cm⁻¹, 2900 cm⁻¹ and a couple at 1050 cm⁻¹ and 1400 cm⁻¹.

The absorbance "peak" at 3350 cm⁻¹ can be identified with the O–H bond vibration. The O–H absorptions in IR spectrums are often seen as broad peaks. (Reason: The hydrogen bonding between two molecules lengthens and weakens as the H atom of one molecule is drawn towards the O atom of another molecule. This results in a wide range of vibrational frequencies, hence a broader peak.)

The various peaks at around 2900 cm⁻¹ are associated with the different C–H vibrations in the molecule.

There are many peaks between 1050 cm⁻¹ and 1500 cm⁻¹. These are usually attributed to C–O stretch and in many IR spectrums, two of them will be evident with one of them at around 1050 cm⁻¹ to 1150 cm⁻¹. The peaks also occur in fingerprint region (1500 cm⁻¹ and 500 cm⁻¹) which is stored in many digital databases for matching with future samples and quick identification of compounds (provided the database has a record of the IR spectrum of the compound from previous runs).

To figure out which absorption peak corresponds to the wavenumber on the IR spectrum, one would have to refer Section 26 of the Data Booklet for this information.

The two IR spectrums below show how –OH groups are identified in simple compounds such as ethanoic acid and ethanol. The Data Booklet shows that the O–H stretch for carboxylic acid occurs from 2500 cm⁻¹ to 3000 cm⁻¹, while the O–H stretch for alcohols occurs from 3200 cm⁻¹ to 3600 cm⁻¹.



infra-red spectrum of ethanoic acid, CH3COOH

In summary, IR spectroscopy allows us to identify the type of bonds in an organic compound and hence, deduce the functional groups present. Sole dependency on IR information for a detailed analysis of a compound is not sufficient; we need information from the other analytical techniques (like NMR and Mass spectrometry) for a complete analysis of unknown compounds.

Enrichment Reading: How Double Beam IR Spectrometer Works

The double–beam IR spectrometer has a source of infrared light (hot coil of nichrome wire) that emits radiation over the whole of the frequency range of the detector. The incident beam is then split into two beams of equal intensity. One of the beams is passed through the sample, while the other functions as a reference beam.

Using a rotating disk, the beams are alternatingly passing through the sample and reference readers. The intensities of the two beams are then compared and the wavelength over which the comparison is made is calibrated and dispersed on the detector using a monochromator (e.g. prism).



Today's IR spectrometers do not scan the sample wave number by wave number. It uses all the wavelengths at one go and convert the signal to the spectrum using a mathematical function known as Fourier Transformation. The technique is commonly described as FTIR (Fournier Transformation Infrared).

Exercise 4

1. IB May 2009 HL TZ1 P3 A1(d)

Consider the IR spectra of the following three compounds.

 $A = CH_3(CH_2)_3COOH$ $\mathbf{B} = CH_3COOC(CH_3)_3$ $\mathbf{C} = (CH_3CH_2)_3COH$ 001 % Transmittance 0 % Transmittance 100 100 % Transmittance % Transmittance 50 50 0 0 0 1000 4000 3000 2000 4000 3000 2000 4000 3000 2000 1000 Wavenumber / cm⁻¹ Wavenumber / cm⁻¹ Wavenumber / cm⁻¹ I Π III

Determine which IR spectrum corresponds to each compound **A**, **B** and **C**. Explain your reasoning.

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Summary

- Absorption in the infrared (IR) region of the electromagnetic spectrum causes the bonds in a molecule to stretch or bend more vigorously.
- If there is a change in the dipole moment of the molecule in question when its bonds begin to stretch or bend more vigorously, then there will be a reading generated on the IR spectrometer. We can say that this molecule is IR active.
- Symmetrical diatomic molecules such as H₂ and O₂ do not absorb in the IR region. (IR inactive.)
- When reading the IR spectrum, the axes are presented as transmittance against wavenumber, which are the reciprocal functions of absorbance and wavelength respectively.
- The part of the spectrum between 500 cm⁻¹ and 1500 cm⁻¹ is called the fingerprint region and the peaks here cannot be associated with any particular bond in the molecule.
- Broad troughs in the IR spectrum correspond to the –OH group in either carboxylic acids or alcohols.
- IR spectroscopy only gives information on the type of bond present in the molecule. It does not give any information on molecular structure and hence must be used in tandem with other analytical techniques.

11.3.8 Structural Identification of Compounds Using IR, ¹H NMR and MS

Sole dependency on one method for detailed analysis of a compound will not yield sufficient data to infer what the compound is. Typically, analytical and organic chemists use a combination of analytical techniques like ¹H and ¹³C NMR, FTIR, Mass spectrometry, Raman spectroscopy and X–ray Crystallography for a complete analysis of unknown compounds.

In this section, a combination of techniques; ¹H NMR, IR and MS, will be used to identify organic compounds.

Exercise 5

1. IB 2010 Nov SL P3 A2(c)

The IR spectrum, mass spectrum and ¹H NMR spectrum of an unknown compound, **X**, of molecular formula $C_3H_6O_2$ are as follows.



(a) Identify the bonds responsible for the peaks **A**, **B** and **C** in the IR spectrum of **X**.

(b) In the mass spectrum of **X**, deduce which ions the m/z values at 74, 45 and 29 correspond to.

(c) Identify the peak at 11.73 ppm in the ¹H NMR spectrum.

(d) Deduce the structure of **X**.

2. IB May 2008 TZ1 P3 G2

Use information from Section 26 in the Data Booklet to help answer this question.

There are several isomers with the molecular formula $C_4H_8O_2$. The structural formulae of some of them are shown below.



(a) (i) Identify two wavenumber ranges, other than 2840–3095 cm⁻¹, of absorptions that are present in the infrared spectra of all four isomers.

(ii) Identify one wavenumber range of an absorption that is present in the infrared spectrum of only one isomer.

(iii) Suggest a structural formula for another isomer of $C_4H_8O_2$ that has an absorption close to 1650 cm⁻¹.

- (b) The technique of ¹H NMR spectroscopy can also be used to distinguish between different organic compounds. State what information can be obtained from:
 - (i) The number of peaks
 - (ii) The ratio of areas under each peak
 - (iii) The splitting pattern
- (c) For isomers **B** and **C** deduce the ratio of peak areas and the splitting pattern.
 - (i) **B** ratio of peak areas
 - (ii) **B** splitting pattern
 - (iii) C ratio of peak areas
 - (iv) **C** splitting pattern
- (d) The ratio of the peak areas and the splitting pattern are the same for isomers C and D. State how their ¹H NMR spectra differ.
- (e) Suggest the structural formula of an isomer of $C_4H_8O_2$ that has the same ratio of peak areas and splitting pattern as isomer **B**.

11.3.9 X–Ray Crystallograhy

11.3.9.1 Overview

The discovery of X–rays in 1895 by Wilhelm Rontgen has enabled scientists to use the electromagnetic radiation to probe into the crystalline structure at the atomic level. This is because the wavelength of the X–rays is approximate equal to the size of the atoms (or more accurately, the distance between the atoms as it involves diffraction). The announcement of the X–ray crystallography was first made by Max von Laue in 1912. In 1913, Sir William Henry Bragg and his son Sir William Lawrence Bragg did the analysis of the diffraction patterns and explained how they were formed.

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X-ray diffraction pattern of a single crystal

Most X-ray crystallography is carried out on the powder form of the crystalline solid. Each compound has its unique diffraction pattern which may be used as a "fingerprint" for its identification. X-ray crystallography may also be used to determine how the atoms pack together in the crystal and the interatomic distances and bond angles. However, in your course, you are only required to apply the technique to single crystals and know that the structural technique of single crystal X-ray crystallography can be used to identify the bond lengths and bond angles of crystalline compounds.

The technique exploits on X–rays having a wavelength [approximately 10^{-10} m or 0.1 nm or 1 Å (angstrom)] similar to the sizes of atoms and a physical phenomenon, *diffraction*.



Diffraction is the slight bending of electromagnetic radiation as it passes around the edge of an object. The amount of diffraction depends on the wavelength of electromagnetic radiation to the size of the opening. If the wavelength and gap is very large, the diffraction is not noticeable. In X-ray crystallography, the wavelengths of X-rays and the gap between the two ions are very close or equal, and hence, the diffraction will be very significant (which is the reason why X-rays are chosen for use in the crystallography).

The X-rays are generated using a cathode ray tube in which high-energy electrons collide with copper or molybdenum atoms to generate electronically excited cations. In single crystal X-ray crystallography, molybdenum is more commonly used. When these ions relax back to their ground state, they emit two close wavelengths of electromagnetic radiation. One of the two X-rays is then directed onto a single crystal, which can be rotated to allow the experimenter to orientate the incidence ray according to one of the three crystallographic axes. While most of the X-ray waves pass through the crystal, a small but significant amount of it will be diffracted by the crystal, producing a diffraction pattern caused by constructive interference of monochromatic X-rays.

Bragg's Law

William Lawrence Bragg and William Henry Bragg first proposed Bragg's Law in 1913. The law relates the wavelength of electromagnetic radiation to the diffraction angle and the distance between the atoms in the crystal by the following equation:



where *n* is a positive integer, λ is the wavelength of the X—ray, *d* is the distance between the crystalline planes (between two atoms), and θ is the angle of diffraction.

The positions and arrangement of molecules or atoms are then reconstructed from the diffraction pattern.



Difference in the two X–ray paths is $2d \sin\theta$. If $n\lambda = 2d \sin\theta$, where *n* is an integer, then constructive interference occurs.



How angle of diffraction, θ , is determined from the diffractometer Source: SERC Media (2007). http://serc.carleton.edu/download/images/8400/IUCrimg69.v2.gif

Example 1

X–rays of wavelength 0.7107 Å are reflected off a crystal of sodium chloride. When the angle between the incidence beam and the face of the crystal is increased from zero, a strong reflected beam is detected when the angle becomes 7.2°. Calculate the distance between the ions.

This value derived from Example 1 above is the shortest distance from one Na⁺ ion to the next Na⁺ ion, or one Cl⁻ ion to the next Cl⁻ ion. Using the ionic radii from Section 9 of the Data Booklet, compare the ionic radii of Na⁺ ion and Cl⁻ ion with the value *d* and suggest a reason for the discrepancy.

Summary

- Only single crystal X-ray crystallography is required in your syllabus. The theory involved and working principles are not required.
- X-ray crystallography provides information on the structure of crystals, how the particles (atoms, molecules or ions) are arranged, the distances between the particles and the bond angles.
- The technique utilizes diffraction, which becomes more pronounced when the distances between the particles become narrower and the wavelength becomes smaller. That is the reason why X–rays are most suitable as its wavelengths are of the same order (0.1 nm or 1 x 10⁻¹⁰ m or 1 Å) to the sizes of the particles.
- The determination of the distances between the particles (more accurately the planes of particles) is through measurement of angle of deflection using a diffractometer and application of Bragg's law: $n\lambda = 2d \sin\theta$

Further reading

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