People's Democratic Republic of Algeria

Ministry of Higher Education and Scientific Research

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وزارة التعليم العالي و البحث العلمي

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كلية العوم الدقيقة

قسم علوم المادة

Physico-chemical analysis technique

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ACADEMIC YEAR 2024-2025

Preface

This worksheet course that I present, in the framework of my habilitation (HDR) is addressed not only to students of the trunk-common Sciences of matter (SM: chemistry and physics), engineering Sciences (ST)..... but also to all those who need to know the basics of this science.

With this material the student will discover the techniques of physico-chemical analysis using spectrophotometers atomic absorption spectrometers infrared spectroscopes NMR and mass spectrometers. This document is intended for students of the training cycle of degrees and master's degrees in chemistry.

The concepts which are the most modern in the field of structure of matter have been more detailed in this course.

This reproduction includes seven chapters :

Chapter I refers to the concepts of spectroscopy (definition and general information on the spectra, electromagnetic).

Chapter II presents the absorption spectroscopy of the ultra-violet (principle. Different areas of absorption. Different chromophores. Application in quantitative analysis).
The chapter III concerns the spectrométsorts atomic absorption (Principle and theory. Instrumentation. Characteristics of a flame. Furnace atomization. Interference. Applications).

Chapter IV is dedicated to the vibrational spectroscopy in the infrared (Presentation of the spectrum of the mid-infrared. Origin of the absorptions in the mid-infrared. Bands of vibration-rotation of the mid-infrared. Simplified model of interactions vibrational. Features bands of organic compounds. Instrumentation. Comparison of the spectra).

Chapter V discusses the spectroscopy of rethere sonance magnetic familyé'vere-pro -ton NMR^{1}H (Generalities. Interaction spin/magnetic field for a kernel. The nuclei that can be studied by NMR. Theory of Bloch for a kernel I=1/2. The principle of obtaining the spectrum of NMRH^{1}. The chemical shift. Cores shielded and déblindés. Hyperfine Structure. Coupling spin-spin).

Chapter VI is consacre to the spectroscopy of rethere sonance magnetic familyeIre, from carbon-13 NMRC^{13}.

The last chapter is reserved for the spectrométrie mass (Principle of the method. Deviation of the ion – spectrum of Bainbridge. Performance mass spectrometers. The different analyzers).

I hope that this book will be appreciated by my colleagues and students and I will be happy to receive their opinions and suggestions to improve it.

SUMMARY

CHAPTER I : CONCEPTS OF SPECTROSCOPY

CHAPTER II : ABSORPTION SPECTROSCOPY OF The ULTRA-VIOLET

Chapter III : SPECTROMETRY ATOMIC ABSORPTION

Chapter IV: VIBRATIONAL SPECTROSCOPY IN The IR

Chapter V : SPECTROSCOPY OF RESONANCE MAGNETIC NUCLEAR energy OF the PROTON (NMR^{1}H)

CHAPTER VI : SPECTROSCOPY OF RESONANCE MAGNETIC NUCLEAR NMR ^{13}C

Chapter VII : MASS SPECTOMETRY

CHAPTER I: NOTIONS OF SPECTROSCOPY

1. Introduction

The identification of the nature of a compound and the determination of its geometric and electronic structures are of great interest.

They make it possible to know the products of a reaction, to follow the different stages of their synthesis, and to verify their purity.

Spectroscopic methods are based on light–matter interactions, they are widely used to identify compounds present in natural substances and to discover the active ingredients of medicines contained in plants.

2. Definition

Spectroscopy is the study of electromagnetic radiation emitted, absorbed or diffused by atoms or molecules. It provides information on the identity, structure and energy levels of atoms and molecules through the analysis of the interaction of electromagnetic radiation with matter.

3. Fields Of Application Of Spectroscopy

Spectroscopy makes it possible to explain a large number of phenomena that constantly surround us: the color of our clothes, the color of the sky ... In laboratories, it allows :

- the identification of molecules

-the determination of the structures

-the study of reaction kinetics

-the determination of the reaction mechanisms

-the dosages

Medical analyzes (MRI, scintigraphy, mammography ...) It also knows important applications in astrochemistry.

4. Electromagnetic radiation

Electromagnetic radiation is characterized by its relative frequency (expressed in Hertz (HZ)).

In a given medium, it can also be characterized by its maximum wavelength (nm) or by its maximum wave number ν (cm^{-1}) :

In the void :

$$\lambda = \frac{c}{\nu} \quad \text{and} \quad \nu = \frac{1}{\lambda} = \frac{\nu}{c}, \text{ with } c = 3{,}0.10^{8}\ m.s^{-1}$$

The energy E of the photon is therefore expressed, in the form :

$$E = h\,\nu = \mathrm{h}\frac{c}{\lambda} = \mathrm{hc}.\nu$$

Or h denotes the plank constant :

$$h = 6{,}62.10^{-34} j.s$$

For one mole of photon, $E = N_A.h.\nu$

N_A: Avogadro's Constant

This energy is usually expressed in $kj.mol^{-1}$

It can be calculated from the wavelength, expressed in nanometers :

$$E = N_A.\frac{h.c}{\lambda} = \frac{6.023.10^{23} \times 6.62.10^{-34} \times 3.10^{8(m)}}{\lambda.10^{-9}(m)} 10^{-3}(kj)$$

Or E is expressed in $kj.mol^{-1}$

We have: :

$$1nm = 10^{-7}cm = 10^{-9}m = 10A°$$

$$1e.v = 1.6.10^{-19}J$$

$$1\ cal = 4.18J$$

Four processes are the basis of spectroscopic phenomena: absorption, spontaneous emission, stimulated emission (case of lasers) and diffusion.

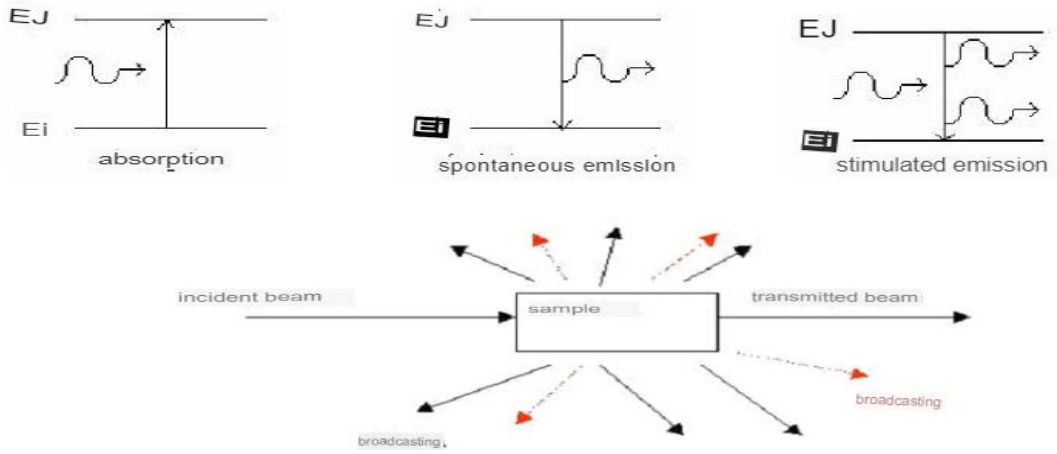


Fig01: spectroscopic phenomena

Following the exchange of energy, electromagnetic radiation leads to a disturbance of the internal molecular movement. There is a transition from one energy level to another energy level depending on the movement caused.

Energy level of a molecule

Energy of a molecule :

A molecule has its own energy E which comprises :

For the movement of atoms :

Rotational energy (Er): associated with the rotational movements about an axis passing through the center of inertia.

A vibration energy (Ev): associated with the movements of the atoms around their equilibrium position without there being any overall movement of the molecule.

For the electrons :

An electronic energy (Ee): associated with electronic transitions, the transitions are generally between a binding orbital (or single doublet) and an anti-binding orbital (or vacant non-binding).

The clean energy of the molecule can be expressed in the form: $E= Er+Ev+Ee$

Arrangement of energy levels :

The energy difference between two levels e (ΔEe), between two levels of vibrational (ΔEv) or between two levels of rotational mixing (ΔEr) is not of the same order of magnitude : $\Delta Er \ll \Delta Ev \ll \Delta Ee$

It can be considered that to each electronic energy level E_e correspond several vibrational energy levels V, and that to each vibrational energy level correspond several rotational energy levels Er.

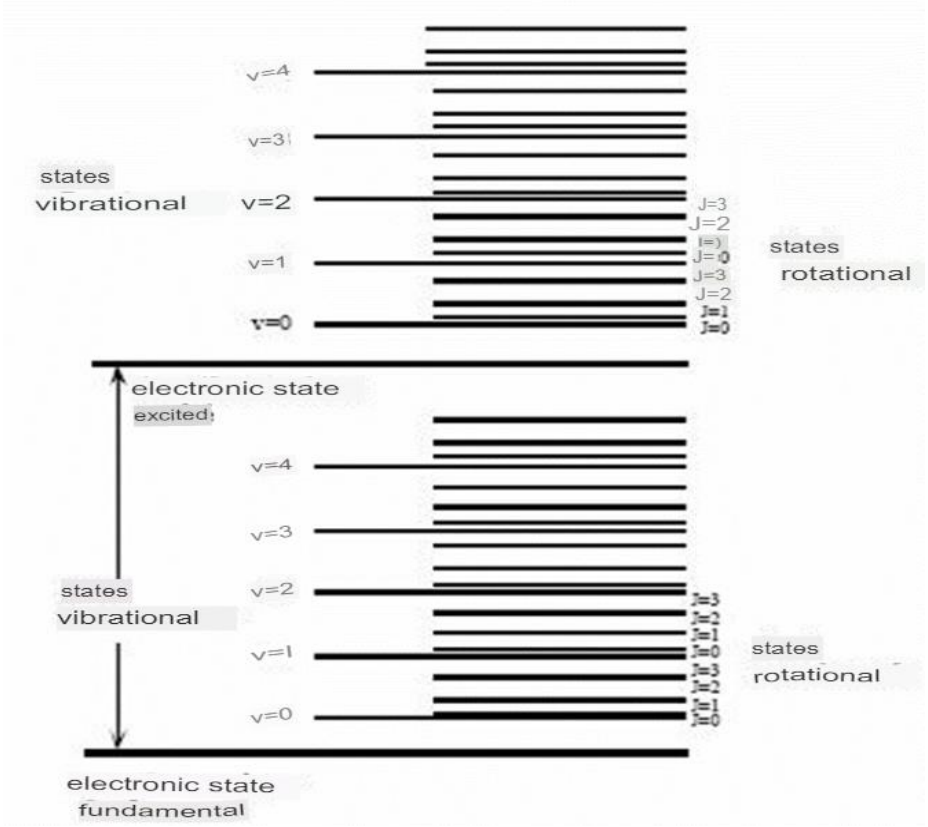


Fig 2: Relative arrangement of the energy levels

Each elementary particle (atom, ion or molecule) has a unique set of energy states. The particle can end up in one or the other of these states.

6. Electromagnetic spectrum of radiation

The spacing of the different levels is such that the radiation emitted or absorbed by the molecule is located in very diverse regions of the electromagnetic spectrum.

CHAPTER II: ABSORPTION SPECTROSCOPY OF THE ULTRA-VIOLET

I. Introduction

The spectrophotometry technique is based on the property of matter, and more particularly of certain molecules, to absorb certain wavelengths of the UV-visible spectrum.

The ultraviolet of organic compounds is associated with transitions between levels of electronic energy

The total absorption wavelength is in this case an absorption measurement of the energy levels of the orbitals.

II. Field of UV

The domain extends from the near ultraviolet to the very near infrared, called the UV-visible, i.e. between 200-1000 nm.

The spectral domain is subdivided into three ranges called near UV (200-400nm), visible (400-800nm) and very near infrared (800-1000) nm.

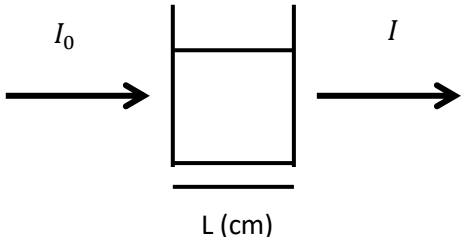
The unit of measurement is the nanometer (nm) (1nm= 10-7cm= 10A°)

III. Beer-Lambert Law

When a monochromatic radiation of medium wavelength passes through a tank with parallel faces containing a homogeneous medium, a more or less significant attenuation of the intensity of the beam is noted, there is an absorption of part of the light.

The absorbance A of a solution is defined :

$$A_\lambda = log\frac{I_0}{I} = log\frac{I}{T}$$



A is therefore an always positive or zero number ($I_0 \geq I$), without dimension (unit).

For a totally transparent solution $I_0=I$ so $A=0$

For a totally opaque solution, I=0, so the beam is totally absorbed.

T: the transmittance.

The relationship between I and I_0 depends on the length of the optical path, i.e. the width of the tank and the concentration c of the absorbent solution

Beer Lambert's law puts this relationship into equation :

$$A\_c=\varepsilon.l.c$$

L: optical path (width of the tank) expressed in cm.

C: concentration of the substance in solution expressed in $mol.l^{-1}$

formula : Molar extinction coefficient of the substance, to be expressed in $mol^{-1}.L.cm^{-1}$

($M^{-1}.cm^{-1}$).

This law is verified on condition of having very diluted solutions (c□ 10^{-2} mol. L^{-1})

IV. Choice of solvent

The solvents used must not absorb in the UV zone for example, we use: hexane, cyclohexane, ethanol, …

V. Nature of transitions

V.1. Electrons engaged in a sigma bond :

- **Transition $\sigma \longrightarrow \sigma^*$:**

The monovalent bonds of saturated hydrocarbons are of the liquid type and are highly stable.

The energy required to excite them is only available in the far UV (around 130 nm).

Example : hexane : max brightness= 135nm.

V.2. Electrons engaged in a non-binding bond :

- **Transition $n \longrightarrow \sigma^*$:**

The transfer of an electron from a free pair (n doublet) of the atoms: O, N, S, X at a** level is observed for alcohols at around 180 nm, for amines at around 220 nm, for ether at around 10 nm as well as for halogenated derivatives.

- **Transition $n \longrightarrow \pi^*$:**

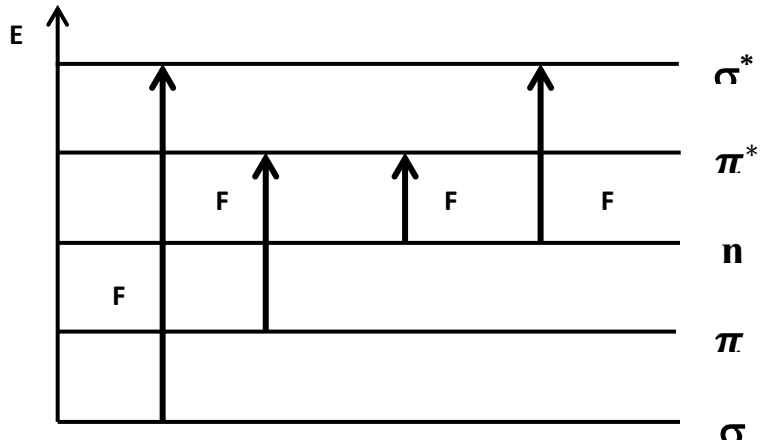
This transition results from the passage of an electron from a non-binding OM (n) to an anti-binding OM π* orbital. This type of transition is encountered in the case of molecules comprising a heteroatom carrying e-free doublets belonging to an unsaturated system. The best known is that which corresponds to the carbonyl band located between 270 and 280 nm.

V.3. Electrons engaged in a Pi bond :

- **Transition** $\pi \longrightarrow \pi^*$

The compounds which possess an isolated ethylene double bond lead to a strong absorption band around 170 nm.

Summary :



VI. Studies of the different chromophores :

a. Chromophore :

The word chromophore is used to describe the system containing the electrons responsible for the absorption in question.

b. Bathochrome effect :

A displacement of a maximum absorption towards the highest wavelength. It can be produced by a polar solvent which has the effect of stabilizing the excited form which favors the transition.

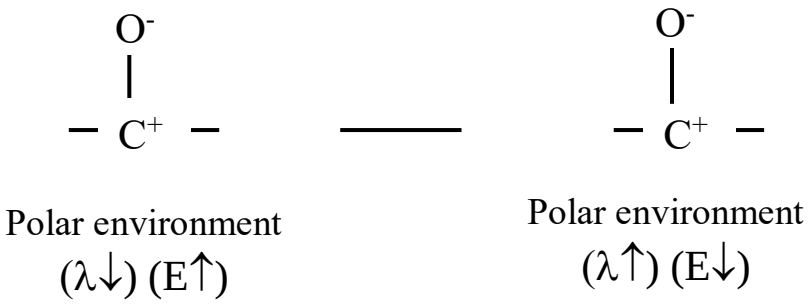
c. Auxochrome effect :

The chromophore decreases the absorption intensity (ε).

d. Hypsochromic effect :

It is a displacement towards the lowest wavelength, and which can be caused by a change in the medium and also by the elimination of the conjugation.

For example the n $\longrightarrow \pi^*$ transition of the carbonyl of the ketones in solution :



Polar environment
(λ↓) (E↑)

Polar environment
(λ↑) (E↓)

e. Hyperchrome effect

The chromophore increases the absorption intensity (ε): -max: wavelength of maximum absorption.

VII. Structural determination by UV spectrophotometry

Current rules for predicting the absorption of open chain or six-chain cycles were first established by Wood Ward in 1941. Since that time they have been modified by Fischer and Scott (see table of incrementation systems (Appendices page 50)).

From a table gathering, in the form of increments, the various factors and structural particularities to be taken into account, it is possible to predict the position of the absorption band of these particular conjugated systems. The agreement is good between the calculated values and the experimental positions.

Example :

max range=217+4□5=237nm max range=215+12=227nm

VIII - Units, Conversions And Usual Constants

VIII.1 - Units

For convenience, we use to characterize the wave :

IR: the wave number (cm^{-1}).

UV-visible: the wavelength (nm nanometer).

VIII.2 - Conversion factors for energy units used in spectroscopy

Unité	kJ.mole^{-1}	eV	Hz	cm^{-1}
1 kJ.mole^{-1}	1	0,18	$4{,}39.10^{13}$	$1{,}68.10^{3}$
1 eV	96,56	1	$2{,}42.10^{14}$	$8{,}07.10^{3}$
1 Hz	$3{,}98.10^{-13}$	$4{,}13.10^{-15}$	1	$3{,}33.10^{-11}$
1 cm^{-1}	$1{,}19.10^{-2}$	$1{,}24.10^{-4}$	3.1010	1

VIII.3 - Usual constants

Electron charge	$e = 1{,}6021773.10^{-19}$ C
Mass of the electron at rest	$m_e = 9{,}1093898.10^{-31}$ kg
Mass of the proton	$m_p = 1{,}6726231.10^{-27}$ kg
Number of Avogadro	$N = 6{,}0221367.10^{23}$ molécules.mole^{-1}
Planck's constant	$h = 6{,}6260755.10^{-34}$ J.s^{-1}
Speed of light in a vacuum	$c = 2{,}9979246.10^{8}$ m.s^{-1}
Boltzmann constant	$k = 1{,}3806581.10^{-23}$ J.K^{-1}

Chapter III

ATOMIC ABSORPTION SPECTROMETRY

I - Introduction

Atomic absorption spectrometry (AAS) is a technique described for the 1st time by Walsh (1955).

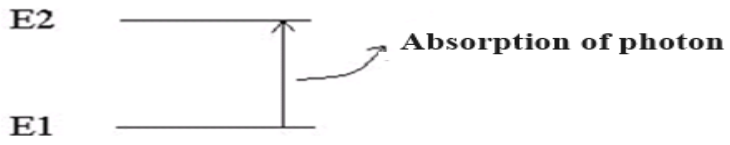
AAS studies the light absorptions by the free atom. It is one of the main techniques involving atomic spectroscopy in the UV-visible range used in chemical analysis. It makes it possible to dose about sixty chemical elements (metals and non-metals). The applications are numerous given that concentrations below mg/L (ppm) are commonly reached.

II - Principle

The atomic absorption of flame is a method that makes it possible to essentially dose the metals in solution.

This elementary analysis method requires that the measurement be made from an analyte (element to be assayed) transformed into the state of free atoms. The sample is heated to a temperature of 2000 to 3000 degrees so that the chemical combinations in which the elements are engaged are destroyed.

Atomic absorption spectrometry is based on the theory of the quantification of the energy of the atom. This one sees its energy vary during a passage of one of its electrons from one electronic orbit to another: where E=h, where h is the Planck constant and F is the frequency of the absorbed photon. Generally only the outer electrons of the atom are concerned.



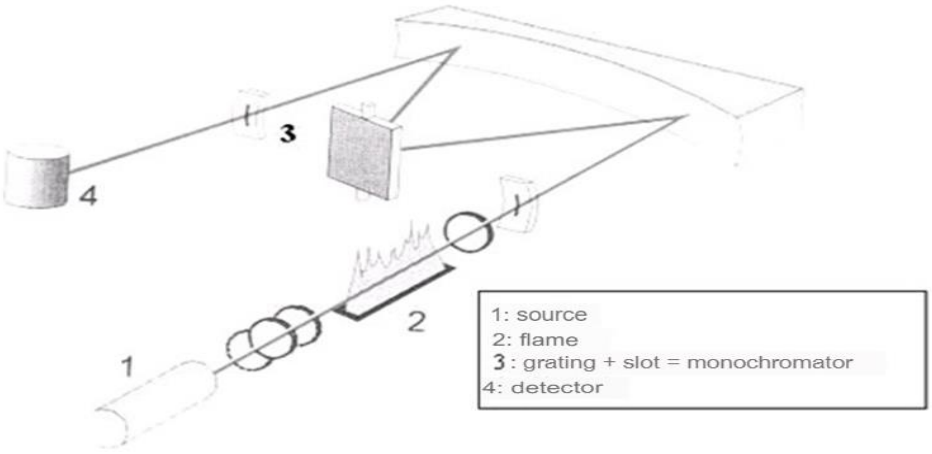
Since the absorbed photons are characteristic of the absorbing elements, and their quantity is proportional to the number of atoms of the absorbing element according to Boltzmann's law of distribution, absorption makes it possible to measure the concentrations of the elements to be assayed.

The atomic absorption analysis uses the Beer-Lambert law.

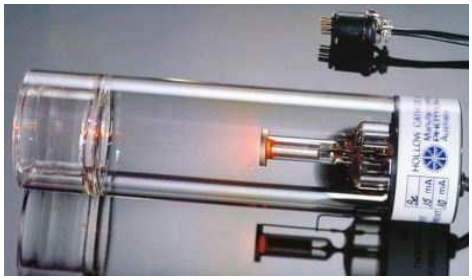
If there are several elements to be measured, this manipulation is carried out for each element of the sample by positioning itself at a fixed wavelength. It is therefore necessary for each manipulation to choose a suitable source to illuminate the element that we are trying to excite.

III - Basic instrumentation

The experimental device used in atomic absorption consists of a source, the hollow cathode lamp, a burner and a nebulizer, a monochromator and a detector connected to an amplifier and an acquisition device.



The hollow cathode lamp



The hollow cathode lamp consists of a sealed glass envelope and provided with a glass or quartz window containing a cylindrical hollow cathode and an anode. The cathode consists of the element which it is desired to dose. A high vacuum is created inside the bulb which is then filled with a rare gas (argon or neon) under a pressure of a few mm of Hg.

When a potential difference of a few hundred volts is applied between the two electrodes, a discharge is established. The rare gas is then ionized and these ions then bombard the cathode, tearing atoms from it. These atoms are therefore free and are excited by shocks: there is atomic

emission of the element constituting the hollow cathode. The particularity of the radiation thus emitted is that it consists of very intense and very fine lines.

The nebulizer

The sample to be analyzed is in solution. This is sucked by means of a capillary by the nebulizer. At the orifice of the nebulizer, due to the ejection of a gas at high speed, a vacuum is created (Venturi effect). The analysis solution is then sucked into the capillary and at the outlet, it is sprayed into an aerosol consisting of fine droplets. This aerosol then enters the nebulization chamber, the role of which is to burst the droplets and eliminate the larger ones. This homogeneous mist then penetrates into the burner.

The flame - atomization

The aerosol enters the burner and then into the flame. After a certain distance at the flame threshold, the solvent of the droplet is eliminated, the salts or solid particles remain which are then melted, vaporized and then atomized.

The acetylene air flame is the most widespread and makes it possible to carry out the dosage of many elements. Its temperature is approximately 2500°C.

Instead of a flame, a cylindrical graphite furnace can also be used to atomize the sample.

The light that leaves the source is not monochromatic. We obtain a spectrum of lines containing:

- the lines of the element to be dosed,

- the lines of the filling gas in the source,

- the lines of any impurities,

- the lines of the atomizer (flame).

The role of the monochromator consists in eliminating all the light, whatever its origin, having a wavelength different from that at which we are working.

The detector

The beam then arrives on the detector. The latter measures the light intensities necessary for the calculation of the absorbances. It is connected to an amplifier and an acquisition device. We determine :

Specific absorbance = Total absorbance – Non-specific absorbance

The specific absorption is due to the element to be measured (on a line). Nonspecific absorption is due to the continuous absorption of the matrix.

Measures allow the correction of non-specific absorptions.

IV - Physical And Chemical Disturbances

An element is dosed by absorption of its most intense line. However, several factors can affect the position of the lines and therefore lead to inaccurate dosages.

The interferences disturbing the analysis are of four types :

Chemical Composition.

ionization effect.

Physical Activity.

spectral analysis.

1.Spectral interference (non-specific absorptions)

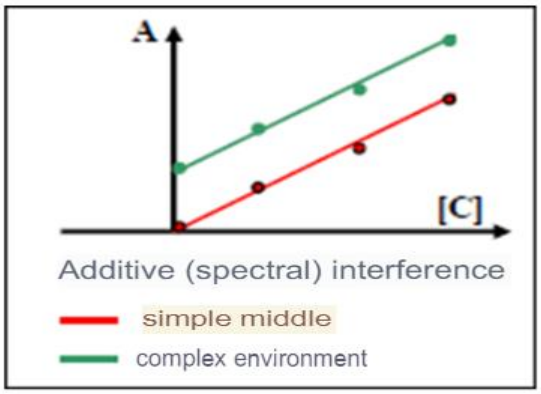
These phenomena have their seat in the atomization source and affect the spectral measurement of absorbance of the analyte :

- by superposition of lines: line of the element to be measured and line belonging to another element

- by superposition of absorbances from molecules

- by the diffusion of the incident light on solid or liquid particles present in the atomizer.

They often result in a **translation** of the calibration line established in a complex medium, relative to that obtained in a simple medium (additive interferences).



2.Correction of spectral interference

The role of the correctors is to automatically measure the non-specific absorbances due to interferents of all kinds in order to subtract them from the absorbance.

During the preliminary settings of the device (i.e.d. in the absence of a sample), it is necessary to adjust log I0/I = 0 if we want to obtain a correct measurement.

3.Chemical interference

They are due to the fact that certain metal salts are difficult to atomize, or that they form refractory oxides in the flame.

The anion that accompanies the cation that is dosed plays an important role in this context: Example: CaCl2 is easier to atomize, therefore easier to dose than Ca in the form of Ca3(PO4)2: tricalcium phosphate.

Therefore, phosphoric acid is never used as the acid to redissolve the samples after mineralization, because it forms phosphates that are difficult to atomize.

4.Correction of chemical interference

It will be necessary to do the calibration and the dosages in the same saline form; for example, if we dose Ca in CaCl2, we will take CaCl2 to make the calibration range.

5.Physical interference

They are generally linked to the physical properties of the solutions studied (change in viscosity between the standards and the samples).

If the solution in which a given metal is to be dosed contains one or more other ions in high concentration, when the solution is to be nebulized in a flame, these other metal salts become insoluble.

Sometimes there is formation of small particles that will physically cause disturbances, as they disperse the light.

This phenomenon is called the scattering effect: the effect of light scattering by particles that become insoluble in the flame.

6.Correction of physical interference

Then a measurement is made at the wavelength of the resonance line.

Then we have atomic absorption, and the scattering of light by particles.

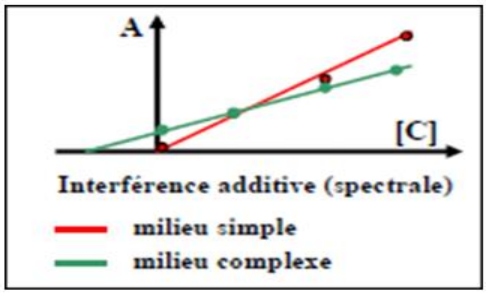
Then we are at a completely different wavelength from the resonance line :

But the metal no longer absorbs.

But there is always the diffusion of light by the insoluble particles.

Then we make the difference between the 2 measurements: hence the absorption of the metal that we want to dose.

Chemical and physical interferences lead to a change in the slope of the straight line relative to the calibration straight line established in a simple medium.



7.Ionization interference

Ionization interferences are encountered when the analyte is an easily ionizable element, because any atom that ionizes can no longer be dosed. Temperature conditions are therefore chosen which make it possible to avoid ionization.

However, it cannot always be avoided: the presence of another more easily ionizable element modifies the ionization equilibrium of the analyte. It can be added knowingly in order to reduce the ionization of the analyte (buffer effect) and therefore increase the absorbance.

8. Correction of ionization interference

-If we want to dose alkaline earth metals (e.g. Ca), to avoid ionization, elements that ionize more are added to the solution to be dosed (e.g. an alkaline)

- The AC is protected.

- To dose the alkalis, there is an element that ionizes more easily than them: a tantalum salt. But There is protection from alkali, because this salt supports ionization.

V- Determination By Atomic Absorption

The calibration curve is determined in two different ways :

- **Direct calibration** → simple matrix (only one element to be measured)

- **Method of dosed additions** → complex or unknown matrix

Remarks:

- Make sure of the similarity of composition (solvent, acid concentration, salt content...) between the calibration and sample solutions.

- Do not compare samples in organic solution with aqueous standards.

VI - Some Applications

Atomic absorption spectrophotometry is essentially a quantitative analysis method that is much more suitable for the determination of traces than for that of major components.

Atomic absorption spectrometry allows the determination of many inorganic materials (rocks and ores, metals and alloys...). It is therefore very suitable for the study of archaeological material. It also makes it possible to quantify the metallic elements in solutions (Waste management).

Let's cite some examples :

* the analysis of the major and minor constituents of archaeological ceramics

* the dosage of Ca, Sr, Zn in the bones

* the analysis of trace elements for identification of stones

* the degradation of the lenses

* determination of metal particles (Cu, Fe...) in the paper

* water analysis

* the analysis of plant and animal tissues, biological liquids

* food and beverage analysis,

* soil, fertilizer and sediment analysis

* the analysis of industrial products

Advantages: high sensitivity, high specificity, speed, low amount of substance required (1 mL of the solution may be sufficient) and ease of preparation of standard solutions.

Disadvantages: the need to use a characteristic source for each element to be assayed, destructive analysis technique, field of application limited almost exclusively to metals (Cu, Zn, Pb, Cr, Fe, Cd, etc ....), the need to have fairly low concentrations.

Chapter IV

INFRARED VIBRATION SPECTROSCOPY

I - Introduction

Infrared (IR) spectroscopy studies the vibrations of molecules when they are irradiated by an electromagnetic wave included in the infrared domain :

- Near-IR 0.8-2.5 µm 13300-4000 cm^{-1}

- Medium IR 2.5-25 µm 4000-400 cm^{-1}

- Far-IR 25-1000 µm 400-10 cm^{-1}

The range of wavenumbers generally used is 4000 cm^{-1} to 400 cm^{-1} (i.e. wavelengths from 2.5 µm to 25 µm).

Infrared spectroscopy is one of the most widely used spectroscopic tools for the characterization of molecules.

III- Molecular Vibrations

III.1 - Diatomic molecule

In a conventional way (and therefore a little false ...), we can equate the bond to a spring: two atoms A (mass m(A)) and B (mass(B)) connected to each other by a covalent bond are likely to vibrate around their equilibrium position.

The link A-B is therefore assimilated to a spring with a stiffness constant k. The wave number associated with the resonance frequency (in cm^{-1}) of this link is given by Hooke's law

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_A\, m_B}{m_A + m_B}$$

ν: frequency of the vibration

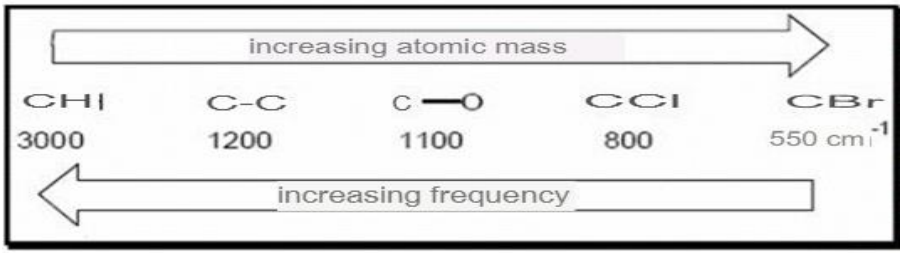
μ: reduced mass

k: bond strength constant

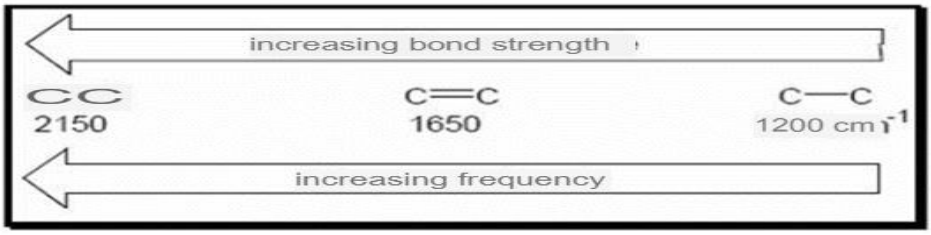
m_A and m_B: masses of atoms A and B respectively

This frequency depends on k and μ.

Effect of k: The vibration frequency is proportional to the force constant K.



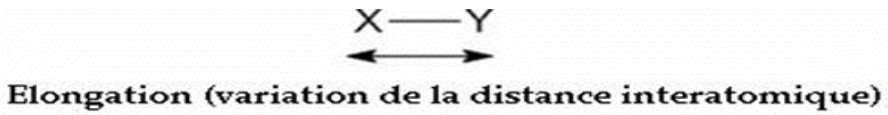
effect of μ: The vibration frequency is inversely proportional to the reduced mass μ.



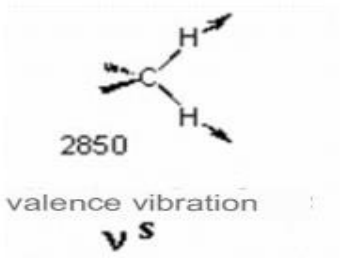
III.2 - Vibration movements

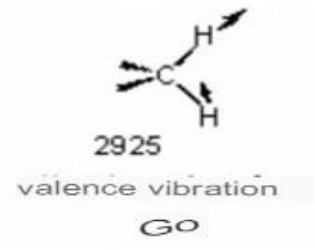
For a nonlinear (respectively linear) polyatomic molecule possessing n atoms, there are 3n-6 (respectively 3n-5) so-called fundamental vibrations. As a first approximation, these movements or vibration modes are classified according to two parameters :

- vibration mode which modifies the lengths of the bonds: valence vibration denoted vibration.

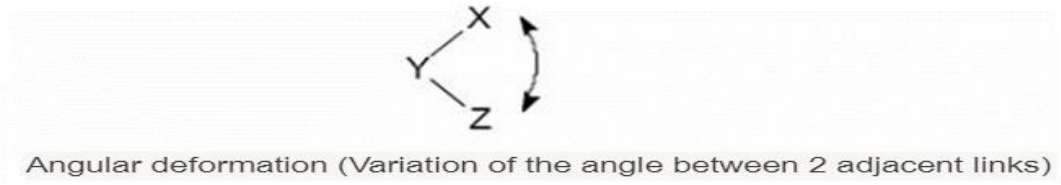


For groups formed by identical bonds (NH_2, CH_3, CH_2..), these links vibrate simultaneously. A vibration mode which preserves molecular symmetry is said to be symmetrical (index s). It is asymmetric or antisymmetric if it leads to the loss of one or more symmetry elements of the molecule (index a).





Deformation (bending): these are vibrations characterized by a modification of the angle of connection.



The vibrational deformation transitions are of lower energy than the vibrational elongation transitions. We distinguish :

Consider, for example, a nonlinear molecule with 3 atoms. 3n – 6 = 9 – 6 = 3

We have three degrees of freedom of vibration :

Symmetric valence vibration, (stretching) denoted vs

Asymmetric valence vibration, (stretching) denoted vas

Deformation vibration in the plane (bending) denoted δ

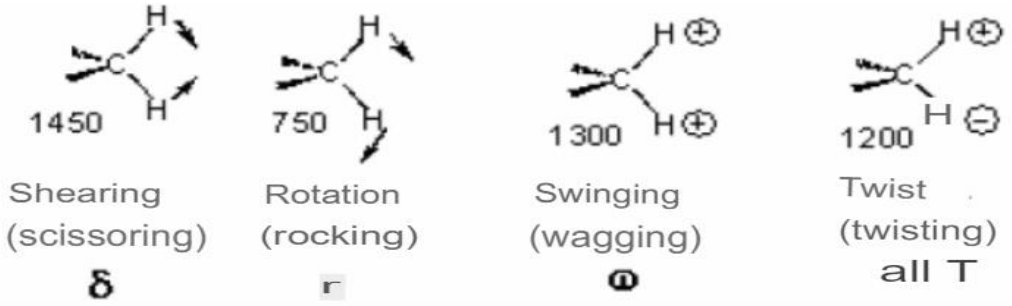
With 4 atoms the number of degrees of freedom is equal to 6. The molecule can then vibrate out of the plane formed by 3 of the 4 atoms.

Scissoring: (shearing) vibration in the opposite direction (on opposition). Of the two connections around an axis.

Rocking: (swinging) simultaneous vibration of the same direction of the two links around an axis.

Wagging: simultaneous vibration in the same direction causing the angles BAC and BAD to vary, out of the plane.

Twisting: vibration in the opposite direction causing the BAC and BAD angles to vary.



The IR is between 2 m and 50 m in wavelength, but in this domain the wavenumbers or spectral terms, denoted, expressed in cm^{-1}, are used. This is actually a simplification because this magnitude is directly related to the difference between two energy levels.

Example :

H_2O is not linear, it has 3 vibration modes. The spectrum obtained has in fact three bands :

Asymmetrical elongation up to 3756 cm^{-1}

Symmetrical elongation ν_s at 3652 cm^{-1}

Deformation δ at 1595 cm^{-1}

The water molecule therefore has three characteristic absorptions in its infrared spectrum.

The deformation vibrations have lower frequencies than the elongation vibrations and therefore correspond to lower energies.

(The asymmetric vibration corresponds to a greater energy than the symmetrical one, therefore to a higher frequency).

IV - Absorption spectrum in the IR

The IR spectrum is recorded in the medium IR between 2.5 µm and 25 µm. It represents for each wave number (or wavelength) the ratio of the transmitted intensities called transmittance **T**, which can be replaced by its percentage **%T** or by the absorbance **A.**

V - Characteristic Vibration Frequencies

Despite the apparent complexity of the IR spectra, due to the large number of absorption bands, there are absorptions with characteristic wave numbers that make it possible to identify the different groups of a molecule.

We can distinguish four main regions :

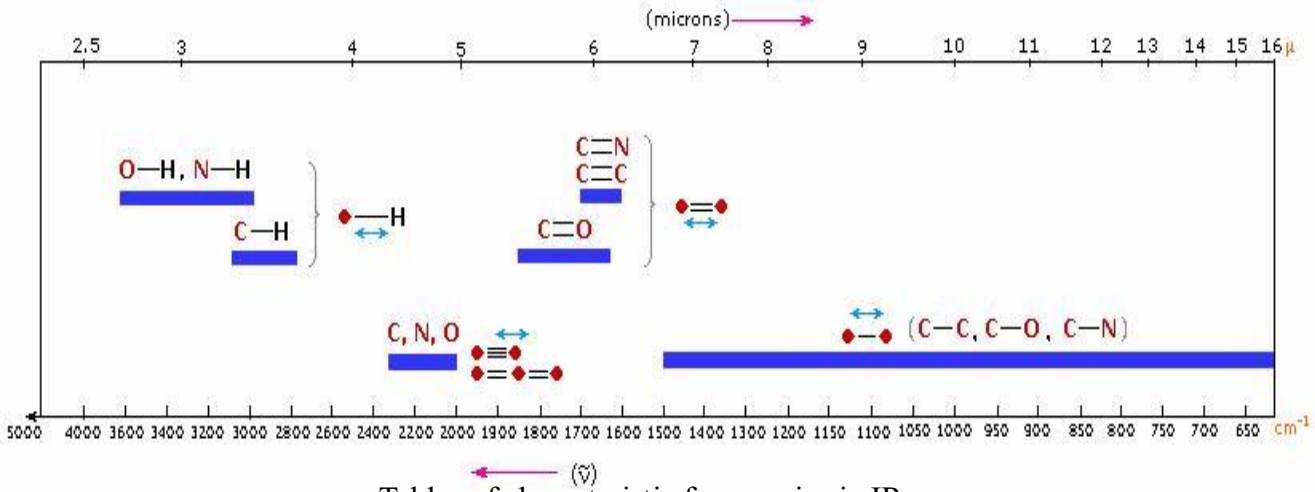
- 4000-2500 cm^{-1}: Elongations X-H (O-H, N-H, C-H)

- 2500-1900-cm^{-1}: Elongations of the triple bonds C≡C and C≡N and of the cumulative double bonds X=Y=Z (allenes, isocyanates....)

- 1900-1500 cm^{-1}: Elongations of the double bonds (C=O, C=N, C=C, NO_2)

- 1500-200 cm^{-1}: Single bond elongations (C-N (NO_2: strong at ≈ 1350 cm^{-1}) ;

C-O: strong between 1000 and 1300 cm^{-1}...). This area, called the fingerprint region, is used to identify a compound with certainty and attest to its purity.



Tables of characteristic frequencies in IR.

VI - Spectral Analysis Method

In principle, the procedure is as follows :

1.Examine the spectrum starting with the largest wave numbers.

2.Identify the most characteristic bands using the tables.

3.Determine the absence of bands in the characteristic regions.

4.Do not try to elucidate all the bands, especially in the region of the fingerprint (< 1500 cm^{-1}).

VII - Quantitative analysis

It is based on the Beer-Lambert law: **A = - log T = e l C**. Specialized devices for quantitative analysis are capable of accurate and fast dosages.

VIII - Instrumentation And Sampling

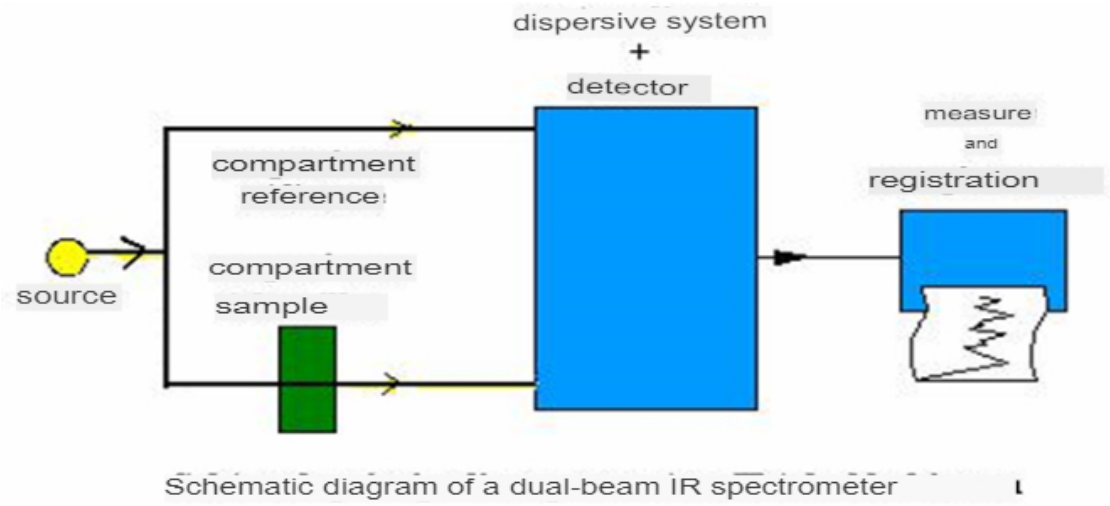
VIII.1 - Equipment

Two main techniques are used to obtain IR spectra :

- the first, and the oldest, is said to be scanning

- the second is called Fourier transform (Fourier's Transform or FT).

The main elements of an IR spectrometer are an infrared radiation source, a radiation separation system or dispersive system (monochromator), a signal detector and a recorder.



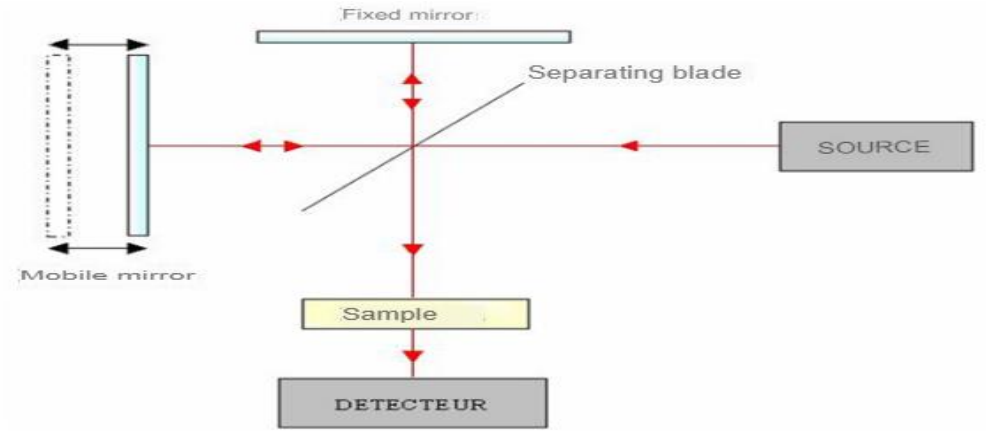
Schematic diagram of a dual-beam IR spectrometer

The source: It consists of a Globar (silicon carbide rod heated to 1300 ° C, maximum energy to 5300cm^{-1}, yttrium and thorium in a thin tube heated to 1900 ° C, maximum energy to 7100cm^{-1}).

The radiation separation system (monochromator): The sample is illuminated with polychromatic IR radiation.

For scanning spectrometers, prisms or diffraction gratings are used as dispersive system.

For Fourier transform spectrometers, an interferometer (Michelson interferometer) is used. The interferometer has three main components: a separator, a fixed mirror and a mobile mirror



The detector: Of the thermal type, the most commonly used detector is a pyroelectric detector. It is a triglycine phosphate crystal (TGS) doped with a temperature known as the "Curie point", the ferroelectric bodies, such as the TGS, show a strong spontaneous polarization between certain faces of the crystal. If such a crystal varies, for example under the action of IR radiation, its polarization varies. A voltage variation is thus obtained as a function of the temperature variation of the crystal.

Note: Scanning IR spectroscopy, which is relatively old, requires a significant amount of time. The advantages of FTIR are a significant time saving and a high precision on the frequency.

VIII.2 - Sampling

It is possible to make IR spectra of solid, liquid or gaseous compounds. Depending on the physical state of the sample, the techniques differ. For the cells, it is necessary to choose a material that does not absorb IR: often NaCl or KBr.

If the compound is liquid, a drop of it is deposited between the windows of the cell to constitute a liquid film.

If it is solid, it can either be dissolved in a solvent, or it can be mixed with anhydrous KBr, the powder obtained then being subjected to high pressure using a press to obtain a pellet. Finally, it can be placed in suspension in a liquid paraffin (nujol for example).

The gaseous compounds are studied in gas cells of large volume.

Chapter V

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF THE PROTON (1H NMR)

I. Introduction

In 1902, the physicist P. Leeman shared a noble prize for having discovered that the nuclei of certain atoms behave strangely when they are subjected to a powerful external magnetic field.

The principle of nuclear magnetic resonance spectroscopy is based on the study of molecular structures through the measurement of the interaction of an electromagnetic field oscillating at a radio frequency with a collection of nuclei immersed in a powerful external magnetic field.

II. The nuclear spin

The nucleus of an atom consists of a number (Z) of protons and a number N of neutrons, the atomic number Z determines the identity of the nucleus while the sum Z+N determines the atomic mass (A) of the nucleus.

The isotopes of a given element have the same value of Z and different values of N and A.

Each nucleus has a nuclear spin (I), and since the nuclei are positively charged this nuclear spin movement generates a magnetic moment U.

The nuclei that can be studied in NMR must have a non-zero spin I, i.e.d. they must have an odd atomic number (A) or an odd atomic number (Z) or both.

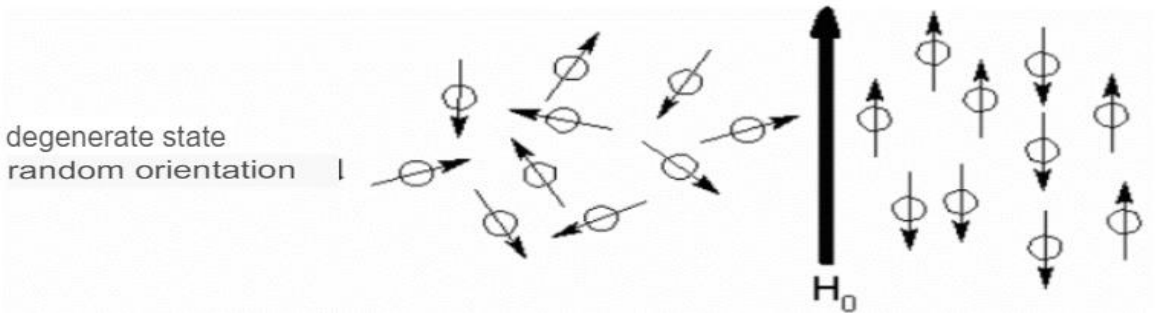
The most important among these nuclei are: ^{1}H, ^{13}C, ^{19}F and ^{31}P, they have a nuclear spin of I of ½. Deuterium and nitrogen have a nuclear spin of 1.

III. Nuclear spin interaction magnetic fields

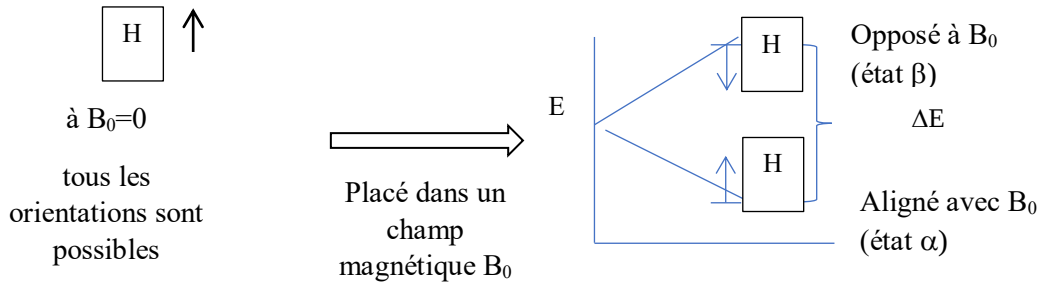
In the absence of a magnetic field, there is no particular orientation of $\vec{U}$ but in the presence of a magnetic field

$\overrightarrow{B_0}$ fort strong, certain orientations of $\vec{U}$ are allowed.

In the case of the proton and the 13C, the spin quantum number I=1/2, so there are (2I+1) =2 possible orientations.



These orientations relate to the direction of the applied field, an orientation in the direction of B0 with an energy and an orientation in the opposite direction of B0 with a higher energy.



énergie des états de spin de l'atome d'hydrogéné dans un

The difference in energy (energy E) between the two states is given by the following relation :

$$\Delta E = \frac{\delta . h . B_0}{2\pi}$$

δ: characteristic gyromagnetic ratio to each core.

h: Planck's constant

IV. Principle of NMR

Like any spectroscopy, NMR is based on transitions between two different energy levels to induce this transition, an oscillatory magnetic field $\vec{B}$ perpendicular to $(\overrightarrow{B_0})$ is used, associated with an electromagnetic wave of frequency V.

the frequency V_0 of the photons which allows the protons to resonate is deduced from the relation

$$\Delta E = h . V_0 \rightarrow V_0 = \frac{\gamma B_0}{2\pi}$$

V_0 is called Larmor frequency.

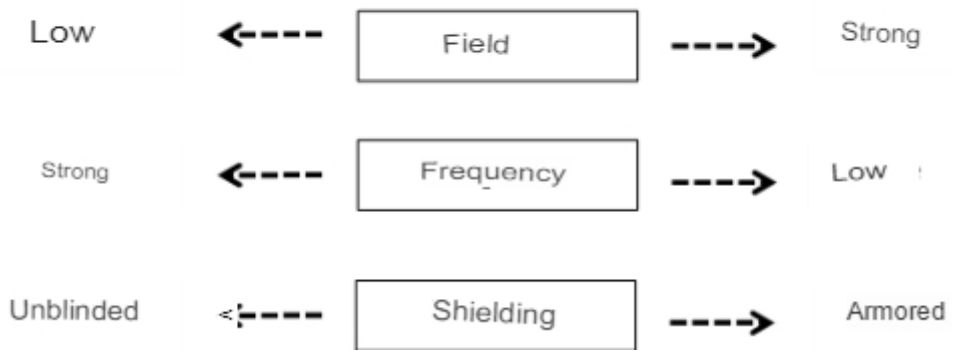
The absorption of the emitted photon results in a displacement of the nuclear spin of the α state towards the β state:

The B_0 field induces an electronic current at the level of the binding electrons located around the nucleus, which in turn generates a local magnetic field affixed to B0, this effect is reflected on the relative position of the NMR spectrum.

The local magnetic field decreases the frequency necessary to cause resonance.

A shift to stronger fields means that the signal appears further to the right (shielding phenomenon).

If the local magnetic field increases the extreme field B0 (for strongly electronegative atoms), we observe a displacement towards the weaker fields (left). It is said that the atom undergoes a de-shielding.



V. Experimental techniques

V.1 - Equipment

There are 2 types of spectrometers, the scanning spectrometer or continuous-wave (cw), and the Fourier transform spectrometer (FT-NMR).

The following elements are essential to constitute a spectrometer :

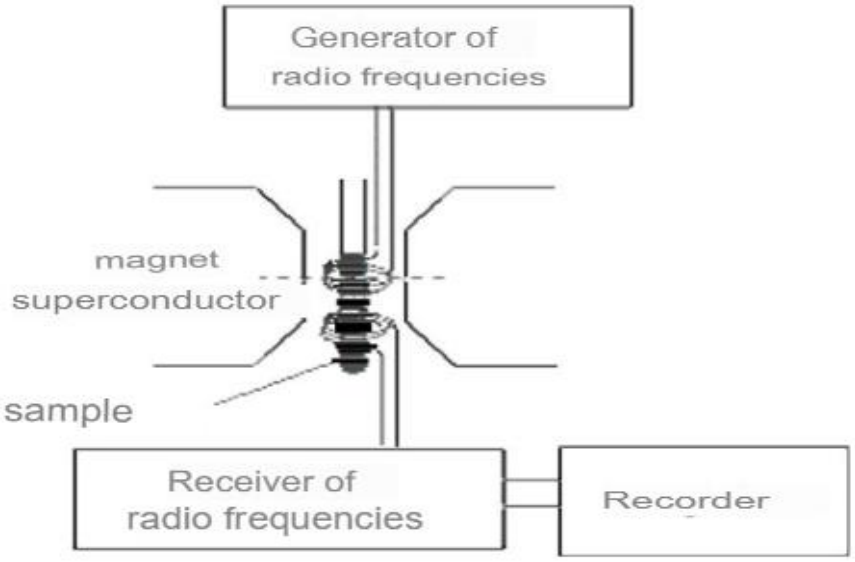
A magnet to produce the static field H_0.

A source of electromagnetic radiation of appropriate frequency (generator).

A frequency scanning unit in the entire field of absorptions.

A cell containing the sample.

A detector (radio frequency receiver) that measures the amount of radiation absorbed by the cell. A recorder that tracks the energy absorbed according to the frequency.



V.2 - Sampling

For the solution study, the sample is dissolved in a solvent. The amount of product required for proton NMR is from 10 to 50 mg. The sample is placed in a glass tube rotated in the center of a magnetic coil.

The solvent chosen must be free of hydrogens. Indeed, the protons of the solvent must not mask the protons of the sample examined.

VI. The nuclear magnetic resonance of the proton

1. The chemical displacement of the proton

Instead of identifying each proton by its resonance frequency, it is preferred to do so with respect to an internal frequency, introduced into the sample studied.

A chemical displacement measurement is obtained defined according to :

$$\delta = \frac{V_x - V_R}{V_0} \cdot 10^6$$

V_x: the resonance frequency of the proton studied.

V_R:the resonance frequency of the protons of the reference.

$V_0 = \frac{B_0 \gamma}{2\pi}$, operating frequency of the spectrometer used.

The chemical shift is expressed in HZ/MHZ, one part per million.

The chemical displacement of the not exceeding 12 to 15 ppm.

2. Choice of the reference :

The most commonly chosen reference compound is tetramethyl silane (TMS) $Si(CH_3)_4$ If, in the protons are strongly shielded δ_{TMS} = O ppm

3. Choice of solvent

The solvents used are the following :

CCl_4, $CDCl_3$, DMSO, D_2O.

The choice of solvent is determined by the solubility of the compound.

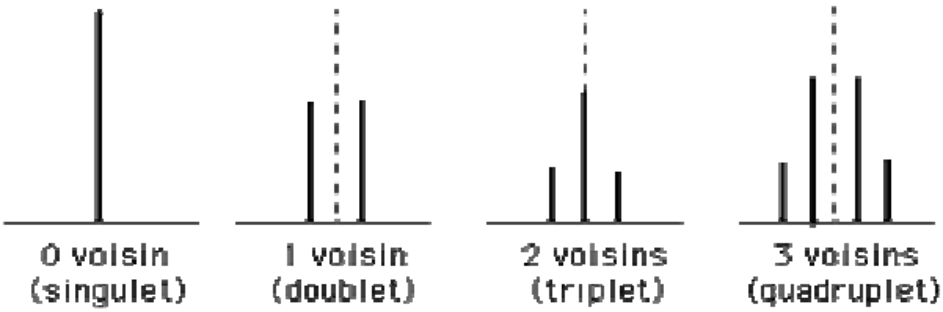
4. Multiplicity of a signal

For protons that are in the vicinity of other hydrogen atoms, the influence of each neighbor must be taken into account :

Rule of n+1: if a proton H_A is coupled with n equivalent protons, carried by one or more carbon atoms immediately adjacent to the one carrying the proton H_A studied, its signal is a multiplet comprising (n+1) peaks.

The intensities of the peaks are proportional to the coefficients of the newton binomial, given by the pascal triangle :

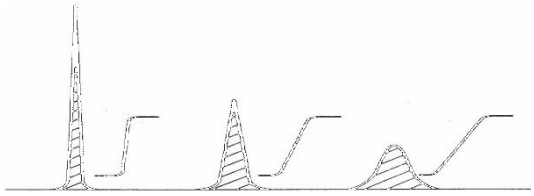
number of neighbors	number of peaks and relative intensity	Name of the signal
0	1	singulet
1	1 -1	doublet
2	1 - 2 - 1	triplet
3	1 - 3 -3 - 1	quadruplet
4	1 - 4 - 6 - 4 - 1	quintuplet
5	1 - 5 - 10 - 10 - 5 - 1	sextuplet
6	1 - 6 - 15 - 20 - 15 - 6 - 1	septuplet



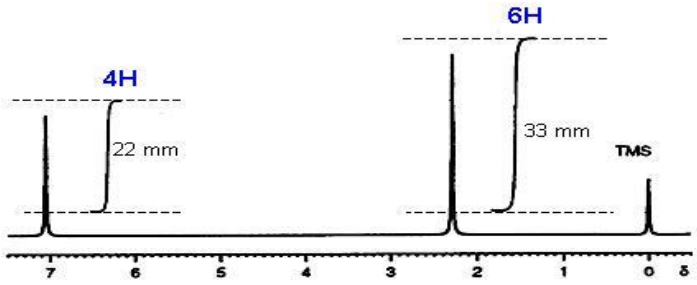
5. Integration curve

In an NMR spectrum, the intensity of a signal is measured by its surface. The integration of the signal surfaces takes the form of a series of bearings.

The height of each landing is proportional to the number of corresponding H's.



Example: ^{1}H NMR spectrum of p-xylene



6. The regions of the proton NMR spectrum

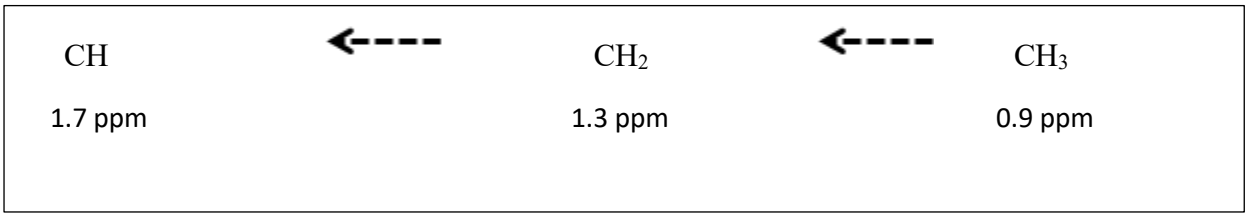
10.5 ppm	**8.5 ppm**	**6.5 ppm**	**4.5 ppm**	**3 ppm** **0**
Proton on carbon introduced next to oxygen aldehydes	Proton on unsaturated carbons, aromatic hydrocarbons	Proton on carbons, unsaturated alkenes	H on saturated carbon next to oxygen	Saturated hydrogens (CH3, CH2, CH) Not next to oxygen

7. Proton on saturated carbon

The chemical displacements of protons on saturated carbons are intimately linked to the electronegativity of the substituents.

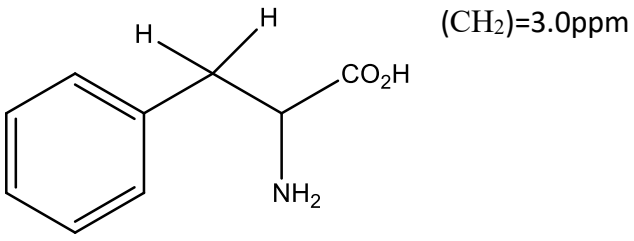
Atom	Electronegativity	Composed	δ (ppm)
Li	1.0	CH_3- Li	-1.94
Si	1.9	CH_3- Si Me $_3$	00
N	3.0	CH_3- NH_2	2.41
O	3.4	CH_3- OH	3.50
F	4.0	CH_3- F	4.27

The chemical displacements of the protons on CH, CH_2, CH_3 nearby electron effect group are:

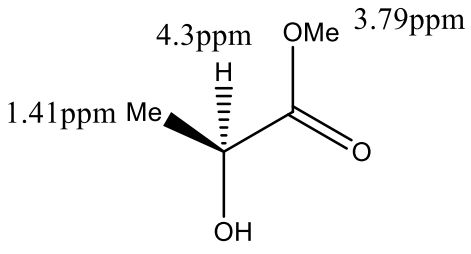


These chemical shifts vary according to the environment of each group

Example :

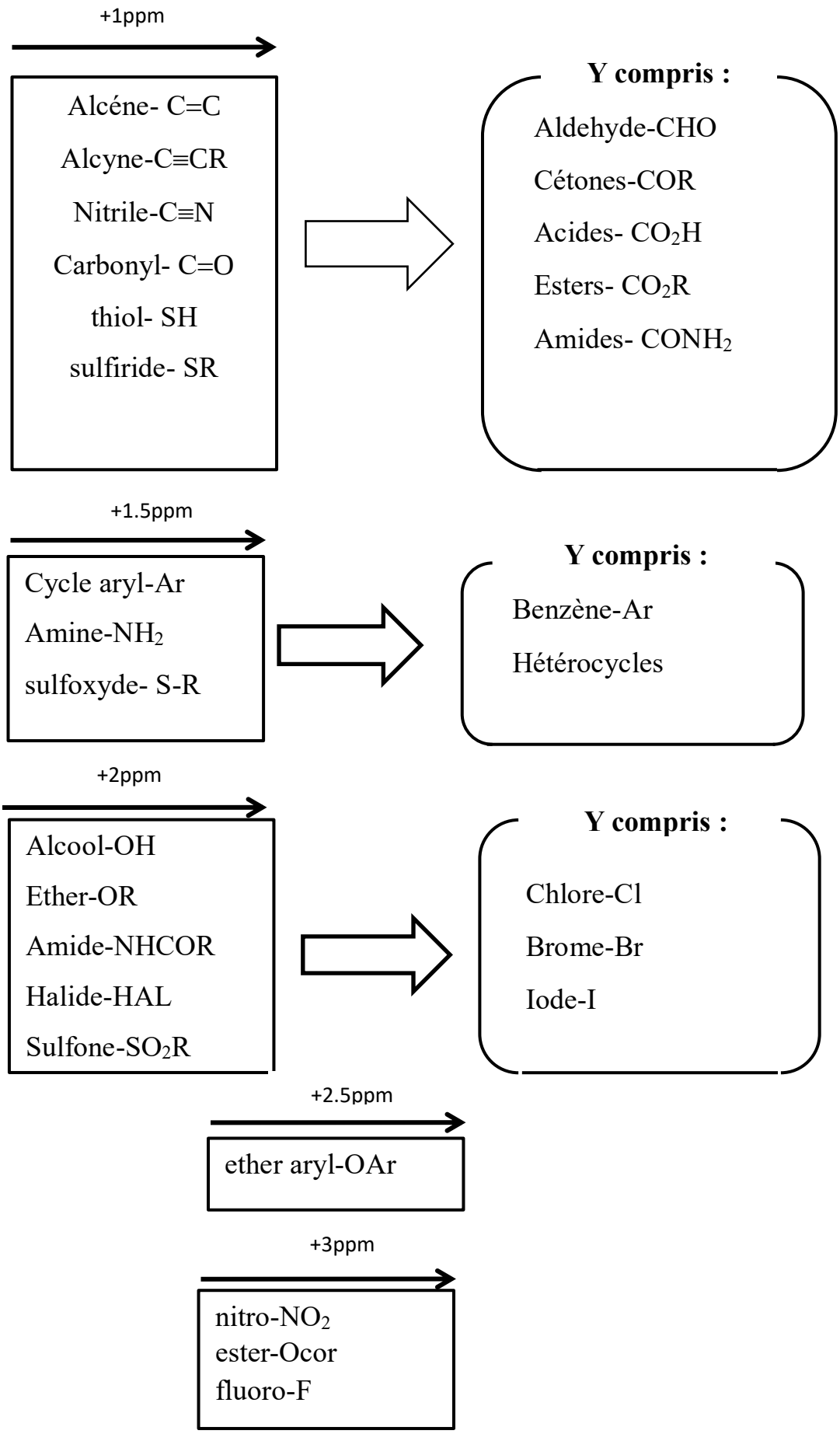


(CH2)=3.0ppm

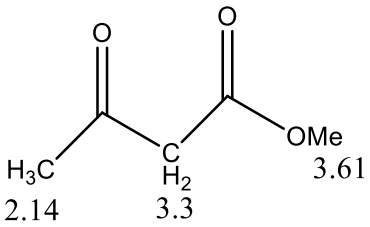


The chemical displacements of the groups CH_3, CH_2, CH or neighborhood of functional groups can be calculated, giving approximate values :

• Values to be added to 0.9 ppm for CH_3, 1.3 for CH_2 and 1.7 for CH :


+1ppm
Alcéne- C=C
Alcyne-C≡CR
Nitrile-C≡N
Carbonyl- C=O
thiol- SH
sulfiride- SR
Y compris :
Aldehyde-CHO
Cétones-COR
Acides- CO_2H
Esters- CO_2R
Amides- $CONH_2$
+1.5ppm
Cycle aryl-Ar
Amine-NH_2
sulfoxyde- S-R
Y compris :
Benzène-Ar
Hétérocycles
+2ppm
Alcool-OH
Ether-OR
Amide-NHCOR
Halide-HAL
Sulfone-SO_2R
Y compris :
Chlore-Cl
Brome-Br
Iode-I
+2.5ppm
ether aryl-OAr
+3ppm
nitro-NO_2
ester-Ocor
fluoro-F

Example :



1. The region of alkenes and benzene :

There are some chemical shifts, which cannot be predicted solely by electronegative effects, such as alkenes and alkynes.

Example:

$H_3C\text{-}CH_3$ $H_2C{=}CH_2$ $HC{\equiv}CH$

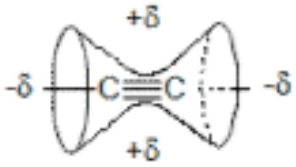
δ= 0.9ppm δ= 5.0ppm δ= 2.3ppm

We attributed this anomaly to the anisotropy of the bonds.

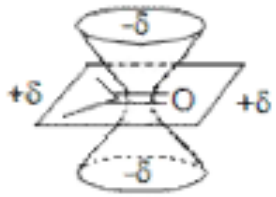
In a molecule having a double bond, a carbonyl group or a benzene ring, the electrons are widely localized in certain regions of space.

The applied magnetic field causes the circulation of these electrons, which can be favored rather in one plane than in the other.

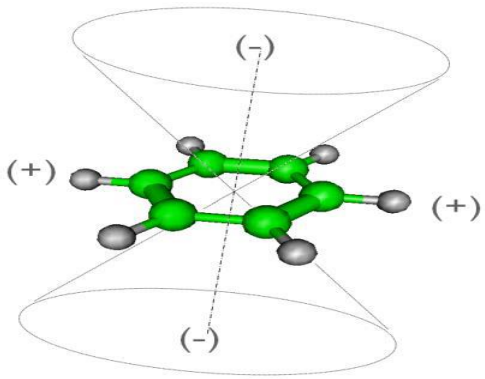
In the case of acetylene, the two pairs of bonds, perpendicular, form a cylinder around which the electrons can move and consequently cause the shielding of the acetylene protons.



This anisotropic phenomenon is also perceived in the aldehyde group where we see the great unblinding of the proton of the aldehyde.



In the aromatic cycles, we find that a cyclic current is established. And that the aromatic protons do not extend inside the shielding surface but rather on the side of the unblinding.

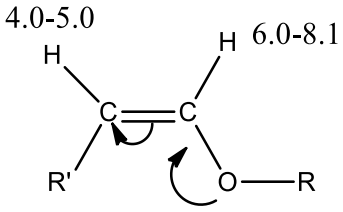


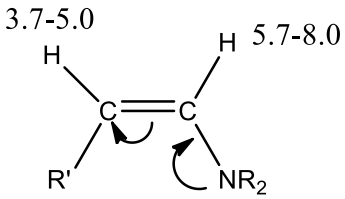
This is also observed for olefinic protons.

2.Effect of electroattaractor or donor substituents

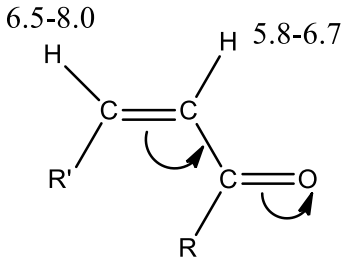
The protons in the intermediate position of the enomers or enemins are relatively shielded compared to the protons placed in parallel. This is due to the electronegativity of the hetero atom.

Example :





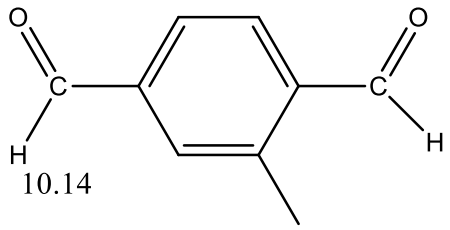
The reverse polrization of the fatty ketones, especially unsaturated ones, causes a contrary effect. The anisotropies of the C=C and C=O double bonds are qualitatively similar.



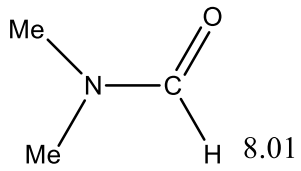
The anisotropy effects decrease rapidly as protons become further away from the bond.

8-a. The aldehyde region :

The aldehyde proton is unique, it is directly linked to a carbonyl group, so it is completely unbound when it is conjugated with an Oxygen or nitrogen atom (DMF , formate).

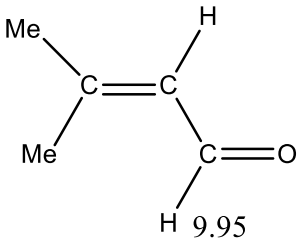


Aldehyde aromatique



DMF

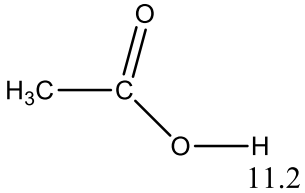
A conjugaision with sexual persuasion causes an opposite effect (unblinding of the CHO).

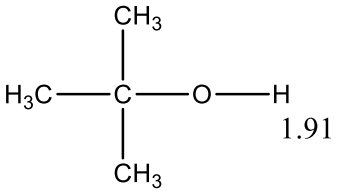


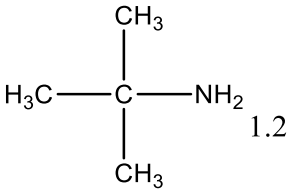
8-b. Region of protons carried on heteroatoms :

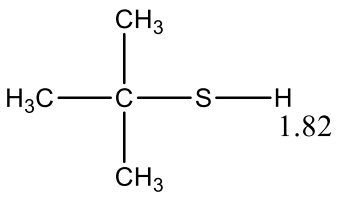
The protons carried on heteroatoms are very variable compared to the protons carried on carbon, this is related to the acidity of the protons.

The more acidic the proton is (its departure is easy) the more the X-H bond is polarized vars the heteroatoms the proton is therefore very unblinded.









3.The spin-spin coupling in proton NMR

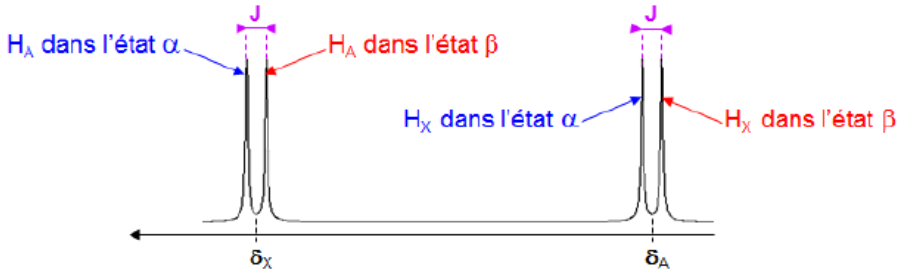
a- Origin of the phenomenon

We know that two magnets placed in the vicinity of each other interact for the nuclei, this interaction exists and is called spin-spin coupling, which translates into the appearance of groups of signals.

$$A_2CH–HCX_2$$

For the protons HA, which are located in the vicinity of a proton Hx (of configuration α and β), they undergo a local field $H= H_0 \pm \mu_{HB}$

the peak is therefore split into a doublet.

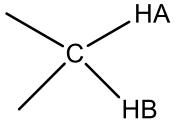


The center of the doublet corresponds to the chemical displacement of the HA protons. And the distance between the two lines of the doublet (expressed in HZ) is called the coupling constant designated by (J).

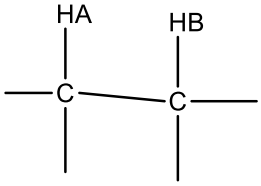
b- The types of coupling

This is particularly the case for hydrogen atoms carried :

1- Let pr be the same carbon atom, we then speak of geminate coupling, denoted J^2 :



2- Either by two adjacent atoms: this is then a vicious coupling, denoted J^3 :

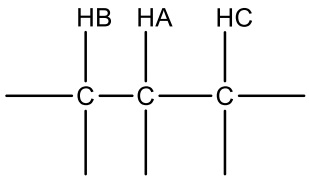


When the number of bonds separating the protons concerned increases, the couplings unite very quickly.

There is no coupling if the hydrogen atoms are magnetically equivalent, i.e. if they have the same chemical environment: they then present the same chemical displacement.

c- Coupling with non-equivalent protons :

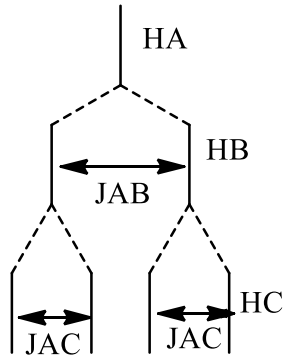
When protons are coupled to two sets of nonequivalent neighbors, the application of the (1+1) rule is more difficult.



The coupling of HA with HB gives a doublet of coupling constant JAB; the doublet is then split in two during the coupling of H_A with H_C (J_{AC}). Two cases can arise :

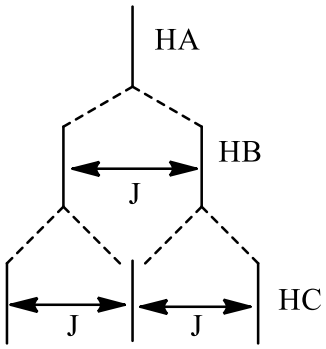
1st case: $J_{AB} \neq J_{Ac}$ with for example, , $J_{AB} > J_{Ac}$

The observed signal is a doublet of doublets, and m= 4



2nd case: $J_{AB} = J_{Ac} = J$

The signal has three peaks and m=3


HA
HB
J
J
J
HC

CHAPTER VI

C^{13} NMR NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

1- Introduction

Although proton NMR is among the most important techniques in NMR, there are other techniques with non-zero spin nuclei, and for an organic chemist, C^{13} NMR is also useful, since C^{13} has a spin number I=1/2.

The NMR of C^{13} differs from that of the proton in the following points :

1- H1 is the major isotope of hydrogen (99.85% natural abundance) while c13 is a minor isotope (1.1%).

2- The proton NMR is quantitative because it provides the number of hydrogenated nuclei (integration curve), which is not observed in the C^{13} NMR.

3- It is only rarely possible to have a coupling between the C^{13} nuclei while it is very common for the H1 nuclei.

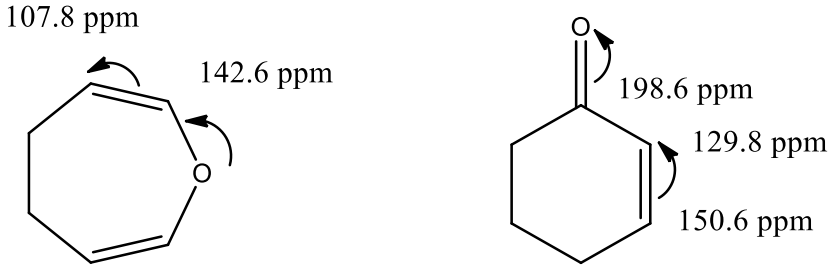
4- The scale of the chemical displacement for the proton is 10 ppm while for the C^{13} is 250 ppm. Because the change in the distribution of two electrons around a hydrogen nucleus is small compared to that of eight valence electrons around the C^{13} nucleus.

2- The chemical displacement

As in proton NMR, the chemical displacement scale can be divided into subregions for the resonances of aliphatic, olefinic and near oxygen carbon atoms.

The carbon atoms of the carbonyl are the most strongly unbound.

The charge densities due to the resonance structures can explain the chemical displacements.



3- Hybridization

The hybridization of carbon has a preponderant effect on the chemical shift.

Csp^3: the region is between 0-100 ppm.

Csp^2: for C=C: 100 – 150 ppm

For C=O and C=N: 150 – 250 ppm

Csp: for C≡C: 75 – 95 ppm

For C≡N: 115 – 125 ppm

4- Empirical correlations

a- alkanes

Empirical correlations are very useful for the analysis of c§ spectra!! the best known are the effects of substituents on alkanes.

The chemical displacement(s) of a carbon atom (i) in a hydrocarbon chain can be calculated from the following :

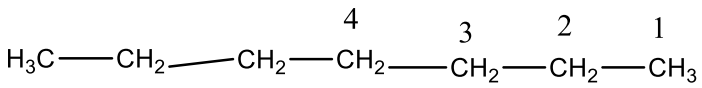
$$\delta_i = -2.1 + 9.1\, n\alpha + 9.4\, n\beta - 2.5\, n\gamma \text{ (ppm)}$$

With

n_α: the number of carbons directly linked to the i atom

n_β and n_γ: the number of bonds to the carbon atoms distant from carbon i and 3 carbon atoms distant from carbon i.

Example: heptane



$\delta_1 = -2,1 + 9,1 .1 + 9,4 .1 - 2,5 .1 = 13.9$ ppm

$\delta_2 = -2,1 + 9,1 .2 + 9,4 .1 - 2,5 .1 = 23.0$ ppm

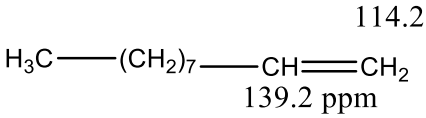
$\delta_3 = -2,1 + 9,1.2 + 9,4 .2 - 2,5 .1 = 32.4$ ppm

$\delta_4 = -2.1 + 9,1 .2 + 9,4 .2 - 2,5 .2 = 29.9$ ppm

b- Alkenes

Most alkenes have their peaks that appear in the range 100 -150 ppm.

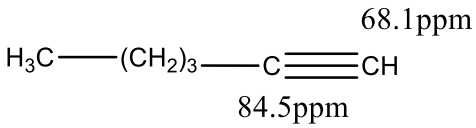
A terminal methylen generally has a lower displacement of about 24 ppm compared to its adjacent.



The conjugation has a lesser effect on the chemical displacements of the alkenes.

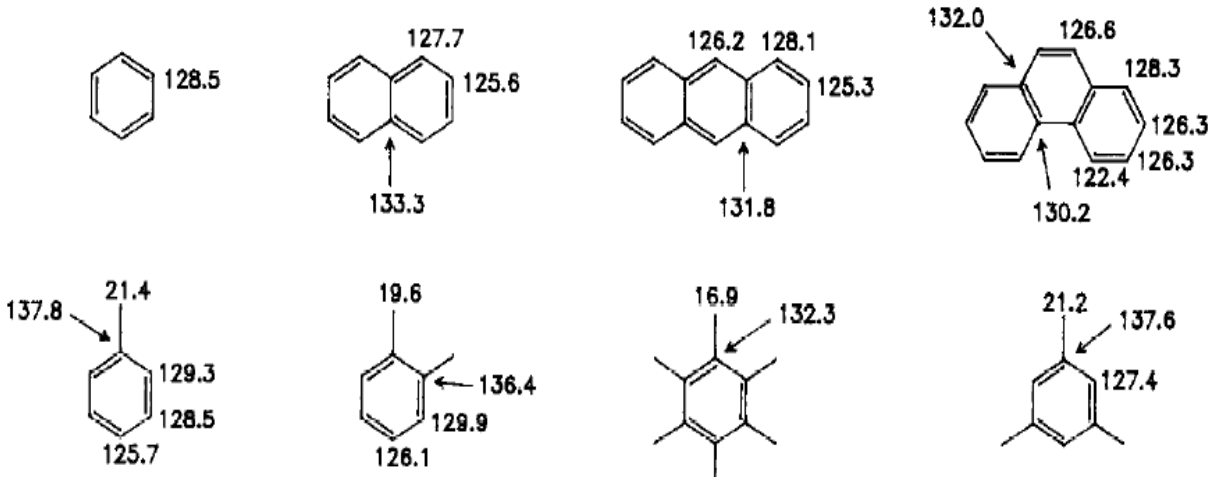
c- The alkynes

Alkynes have chemical shifts lying between those of alkanes and alkenes, and their range extends from 75 – 95 ppm.



a- The aromatic carbons

The chemical displacements of benzene carbons, substituted benzenes and other aromatic compounds are observed in the 120-140 ppm zone.

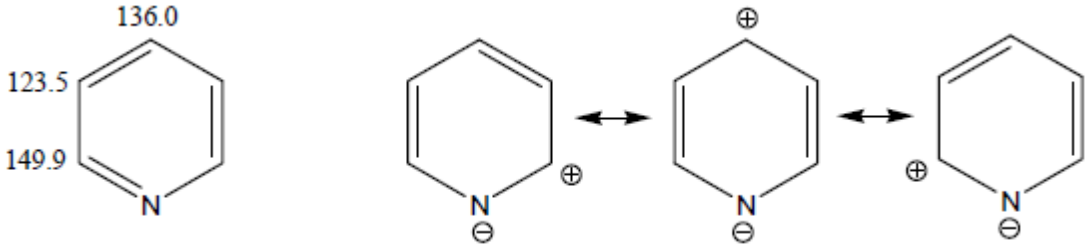


The introduction of substituents extends the range of chemical displacement and the signals of the substituted arenas can be observed in a wider spectral range of 100-150 ppm. Since the alkene signals are also located in this zone, the assignment of the carbon-13 signals is not immediate.

In these substituted compounds, the resonances most affected are those of the carbon directly attached to the substituent, then the ortho and para carbons. The meta resonances show very weak effects. The observed displacements depend on the inducing and mesomeric effects of the substituents. It is also necessary to consider the steric effects and those of magnetic anisotropy.

Note: Heteroaromatic nuclei

In aromatic heterocycles, the shielding of the nuclei of the aromatic ring is mainly determined by the heteroatom. Pyridine is an interesting example. In this case, the signals of the carbons at the top and bottom are slightly more shielded than in the open position. These observations can be explained qualitatively by taking into account the electron density of the boundary mesomeric forms.



Chapter VII

MASS SPECTROMETRY

I. Definition

Mass spectrometry makes it possible to transform molecules in their natural states into ions in the gaseous state and to obtain their molecular mass m by analyzing their mass, charge ratio, denoted m /z, where m is the mass of the compound and z its charge.

II. The mass spectrometer

A mass spectrometer is a device that makes it possible to measure the mass/charge ratio (m/z) of the formed from the analyzed sample. It always consists of the following parts

1.An ion source in which the gaseous phase of the sample to be analyzed takes place, the ionization of the molecules, but also the decomposition of the ions.

2.An analyzer that makes it possible to sort the ions according to their m/z ratio.

3.A detector that counts the ions in association with their m/z ratio.

4.A recorder for signal processing and spectrum visualization.

Two methods are used to convert neutral molecules into cations: by electronic impact and chemical ionization.

III. The principle of the SM technique

In the spectrometer, a beam of very energetic electrons hits the sample. An ionization of the molecules then occurs :

$M^{+\bullet}$ is a cation-radical, called a molecular ion. It corresponds to the molar mass of the compound. This molecular ion will be able to fragment and produce cations of lower masses, called fragment ions, and neutral fragments (radicals or molecules). The charged fragment ions are sorted according to their m/z ratio and measured according to their relative abundance.

This technique is based on the **analysis of molecular fragments obtained by ionization**.

The ions of charge z and velocity $\mathbf{v} \perp \mathbf{B}$, the magnetic field, undergo a magnetic force

$$F = zvB = m\frac{v^2}{r} \Rightarrow v = \frac{zBr}{m}$$

$$\frac{1}{2}mv^2 = zV \Rightarrow m/z = \frac{B^2r^2}{2V}$$

The mass spectrometer must perform the following operations:

1- Volatilize (Separate the molecules from each other): We go from the state of condensed matter to a gaseous state.

2- Ionize (Transform molecules into ions): Thanks to electric fields

3- Measure m/z ratios

The molecular mass is calculated from the mass-to-charge ratio (m/z).

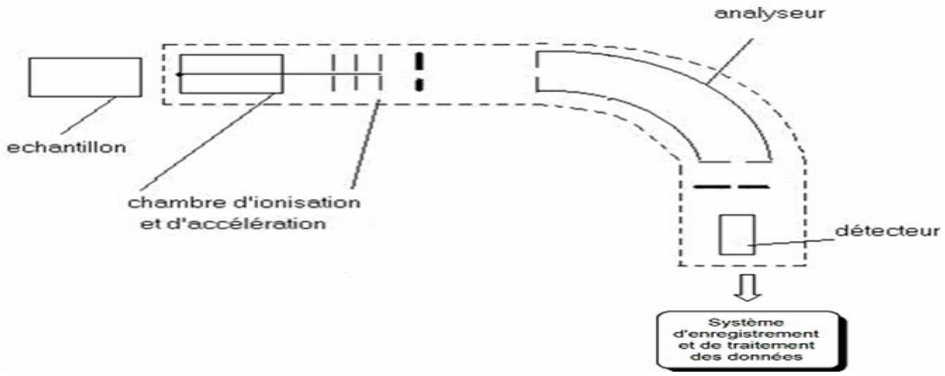


Figure 1: Mass Spectrometer

A mass spectrometer consists of at least

 A sample introduction system.

Choose **a source** (ion production) where the ionization of the molecules and the fragmentation of the ions take place.

 An analyzer that separates the ions according to their mass and their charge.

 An ion collector or detector that detects the ions leaving the analyzer and expresses them according to their relative abundance.

 A system for recording and processing data.

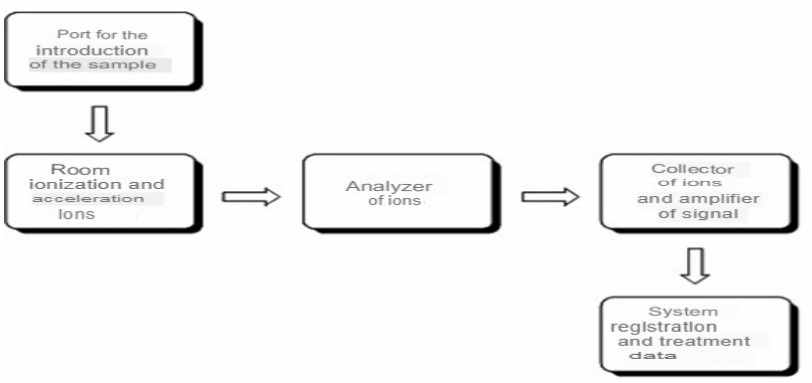


Fig. 2: Composition of a Mass Spectrometer.

IV. The ion source

The ionization of molecules is done by electronic impact (EI), chemical ionization (IC) or electrospray.

The source is a stainless steel chamber where a vacuum of about 6.10^{-7} mm Hg prevails. A rhenium filament emits electrons which will be accelerated under a voltage of 70 Volts. The collision of electrons at 70 eV and molecules is very energetic.

 Electron impact ionization (EI): Positively charged ions are formed

$$M+ e \rightarrow M+ + 2nd$$

Molecular ions tend to break up to form fragments.

 Chemical ionization (CI): Charged ions are formed by chemical reactions between molecules and ions. This ionization is less energetic than (EI).

 Ionization by bombardment with accelerated atoms (FAB): Charged ions are formed by bombardment with accelerated heavy atoms (for example, xenon at 6 keV).

 Electrospray ionization (ESI): The spraying of a solution of the analyte through an electric field (some kV) produces the ions.

 Ionization by matrix-assisted laser desorption (MALDI): the analyte is dissolved in a matrix, a small amount of the solution is introduced and bombarded by a laser pulse.

V. Spectral analysis

The interpretation of a mass spectrum can be broken down into two stages :

- Exploitation of the molecular ion (the molecular mass, the parity, the isotopes, the raw formula...)

- Exploitation of fragment ions which depend on the nature and structure of the molecule.

V-1. Mass of the molecular ion

Mass spectrometry makes it possible to know the molecular mass of an unknown substance from the molecular peak.

a-Parity of the molecular ion

A molecular ion gives a peak at an odd mass if it contains an odd number of trivalent elements (N, P...).

Example: Ammonia NH_3: molecular peak at m/z = 17.

b- Isotopic cluster

The table below shows the relative natural abundances of the isotopes of the current elements. The relative abundances are calculated by giving the value 100 to the majority isotope.

Élément	Isotope le plus abondant		Abondance naturelle relative des autres isotopes			
Carbone	^{12}C	100%	^{13}C	1.1%		
Hydrogène	^{1}H	100%	^{2}H	0.016%		
Azote	^{14}N	100%	^{15}N	0.38%		
Oxygène	^{16}O	100%	^{17}O	0.04%	^{18}O	0.20%
Fluor	^{19}F	100%				
Silicium	^{28}Si	100%	^{29}Si	5.10%	^{30}Si	3.35%
Phosphore	^{31}P	100%				
Soufre	^{32}S	100%	^{33}S	0.78%	^{34}S	4.40%
Chlore	^{35}Cl	100%			^{37}Cl	32.5%
Brome	^{79}Br	100%			^{81}Br	98.0%
Iode	^{127}I	100%				

The set of peaks due to different isotopes of an element constitutes **the isotopic cluster**.

In general, the number and the relative intensities of the peaks constituting the isotopic cluster are determined from the relationship: $\mathbf{(a+b)^n}$

a: relative abundance of the lightest isotope

b: relative abundance of the heaviest isotope taken equal to unity n: number of atoms of the element considered

Case of isotopes of considerable abundance (chlorine; bromine)

Chlorine or bromine atoms have an abundant heavy isotope (+2). In the case of an ion containing n halogens, the relation (a+b)n gives :

Example 1: CH_3Br

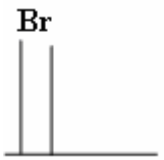
^{79}Br : 100% ^{81}Br : 98%

a = 1 b = 1 $(a+b)^1 = a + b$

1 1

M M+2

In the isotopic cluster, there are two peaks at M and M+2 of relative intensity 1:1.



Example 2 : CH_2Cl_2

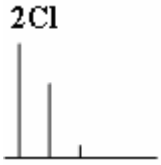
^{35}Cl : 100% ^{37}Cl : 32%

a = 3 b = 1 $(a+b)^2 = a^2 + 2ab + b^2$ 9

6 1

M M+2 M+4

Il y a 3 pics à M, M+2 et M+4 avec des intensités relatives 9:6:1.



c- Exploitation of fragment ions

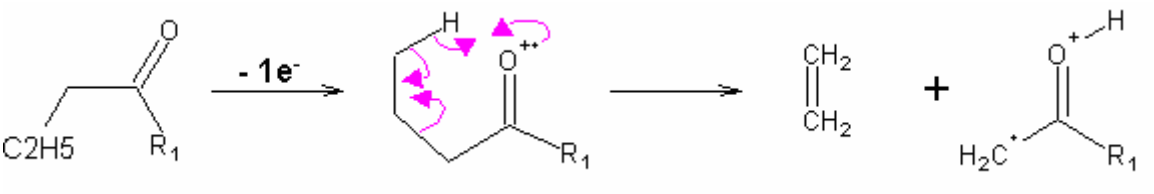
The factors influencing the fragmentation process are as follows :

- Weak bonds break more easily.

- Stable fragments tend to form more easily.

- Fragmentations with rearrangement are favored if the molecule has a transient state with 6 centers.

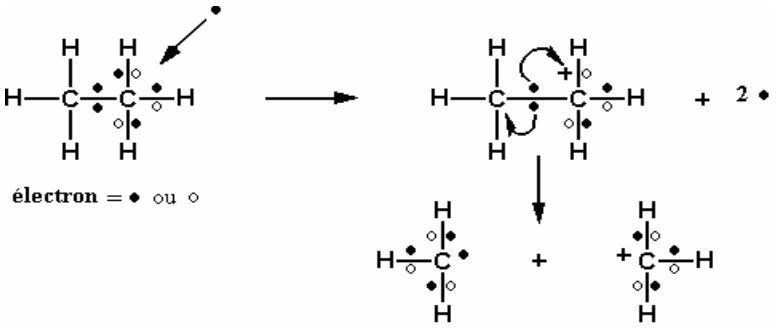
d-McLafferty rearrangement: H in γ of an unsaturation.



VI- Characteristic fragmentations of some chemical classes

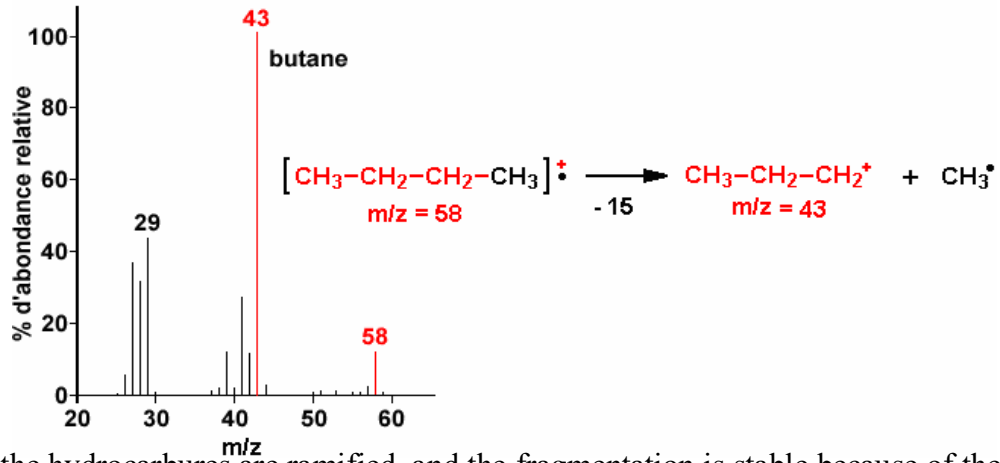
1. Aliphatic hydrocarbons

The fragmentation of the hydrocarbons takes place by homolytic cleavage.

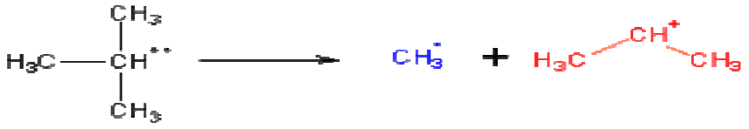


For all linear hydrocarbons, ions 43 and 57 are the most intense peaks of the spectrum because they correspond to the most stable cations.

Ion R+	CH_3^+	CH_3-CH_2^+	CH_3-CH_2-CH_2^+	CH_3-CH_2-CH_2-CH_2^+
m/z	15	29	43	57



In this case, the hydrocarbures are ramified, and the fragmentation is stable because of the sin à thunder, the carbocation is stable.



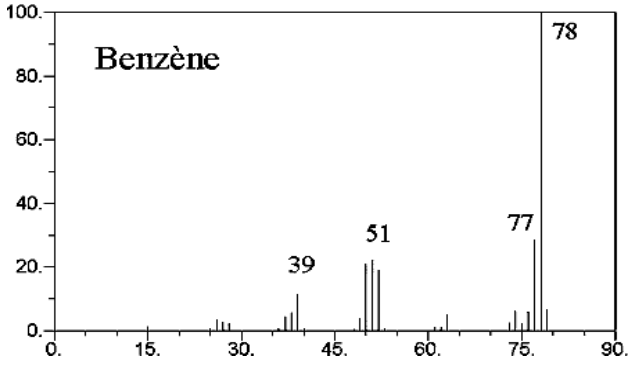
The isopropyl cation is more stable than the CH^{3+} cation.

Croissant : $CH_3^+ < RCH_2^+ < R_2CH^+ < R_3C^+$

2. Benzene

The goal is to interpret the mass design. The moulecular est toujours intensive car l'ion molecular est fortement stabilizes.

a-Le Benz below

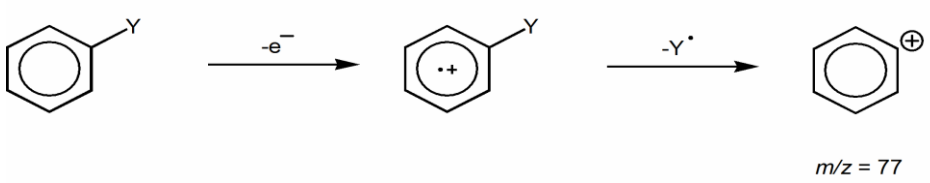


These fragmentations you Benz below produce of the ion caracteristics: m/z = 77 $[M-H]^+$, m/z = 51: $C_4H_3^+$ [77 – 26 (acetyl below)] m/z = 39: ion $C_3H_3^+$.

b - Monosubstituted benzenes

α Cleavage

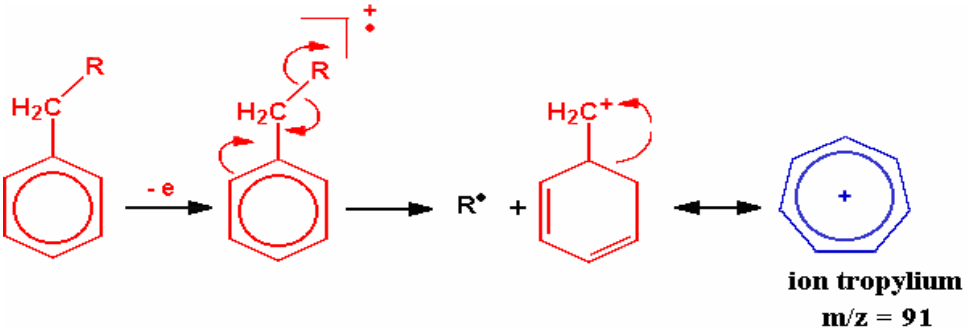
If the substituent is not an alkyl, the monosubstituted benzenes frequently lose their substituent to form the phenyl cation at m/z = 77.



β Cleavage

The benzenes substituted by an alkyl group have a predominant fragmentation: the β-rupture of the aromatic ring, called benzyl rupture.

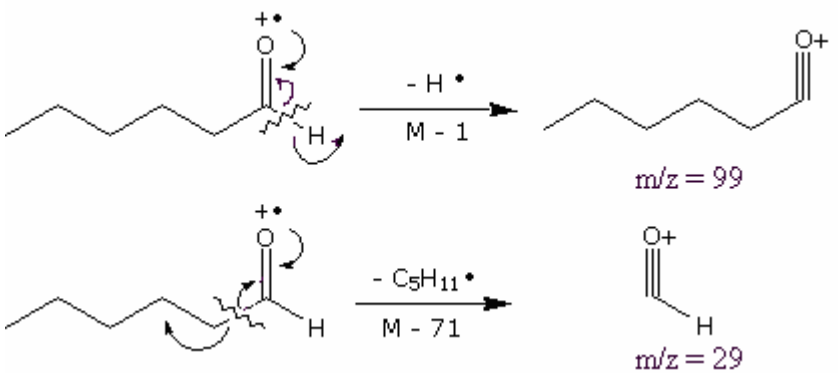
They lose a hydrogen or an alkyl group so as to form the aromatic tropylium cation at m/z = 91.



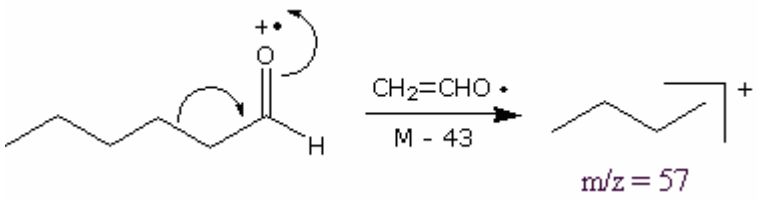
This ion is highly stabilized and often constitutes the basic peak of the mass spectrum.

3. The aldehydes

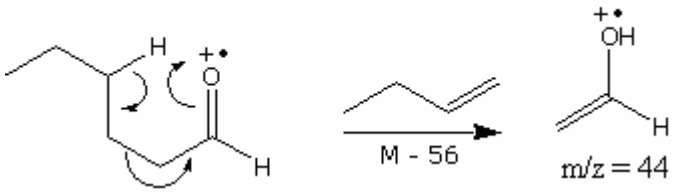
α Cleavage



β Cleavage



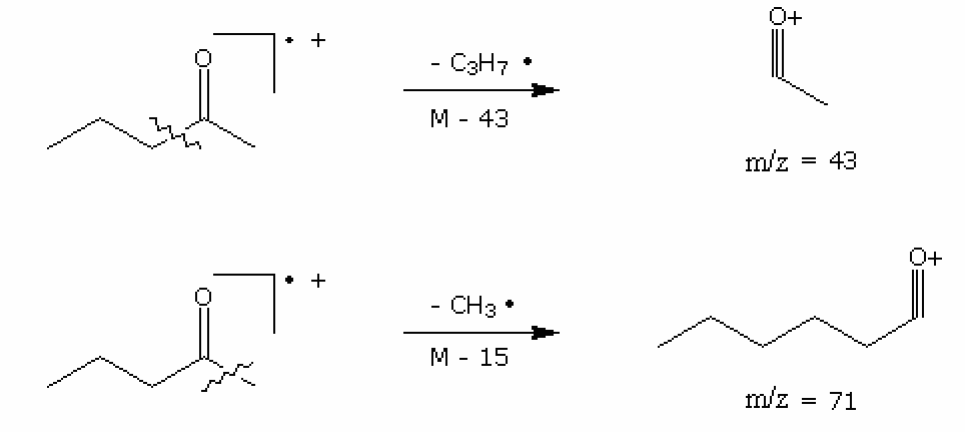
McLafferty rearrangement: In this example, we have an H in γ of the unsaturation (aldehyde function).



4. Ketones and esters

The most frequent mode of fragmentation of ketones and (**R'COR''** and **R'COOR'')** is the break in length which can give **R'CO$^+$** ou **R''CO$^+$**.

α Cleavage



Bibliographic References

A.EL HAJJI « **Cours Techniques Spectroscopiques d'Analyse** » Faculté Des Sciences, Université Mohammed V Rabat 2016.

Donald L. Pavia, Gary M. Lampman & George S. Kriz « **Introduction To Spectroscopy** » Third Edition Brooks/Cole, THOMSON LEARNING 2009.

E. Pretsch, P. Buhlmann & C. Affolter « **Structure Determination Of Organic Compounds** » Third Completely Revised And Enlarged English Edition, Springer 2014.

Edmond de hoffmann , Jean Charrette & Vincent Stroobant **« Spectrométrie de masse Cours et exercices corrigés** » 2° Edition 2011.

G. Ple, L. Grosu, S. Mager & M. Darabantu « **Résonance Magnétique Nucléaire Appliquée à l'analyse** » 1999.

Gwenola Burgot & Jean-Louis Burgot « **Méthodes Instrumentales D'analyse Chimique Et Applications** » Editions TEC & DOC Et Editions Médicales Internationales, Londres-Paris-New York 2010.

Manfred Hesse, Herbert Meier & Bernd Zeeh « **Méthodes Spectroscopiques Pour La Chimie Organique** » MASSON 2012.

Robert M. Silverstein, Francis X. Webster & David J. Kiemle « **Spectrometric Identification Of Organic C ompounds** » Seventh Edition 2012.

Shriner, Hermann, Morrill & Fuson « **The Systematic Identification Of Organic Compounds** » Eighth Edition 2016.

Smain HOCINE « **Méthodes d'Analyse Spectroscopiques en Chimie Organique** » Office des publications universitaires 3. Edition 1.03.5740. 2017.

Terence N. Mitchell & Burkhard Costisella « **NMR-From Spectra to structures An Experimental A pproach** » 2nd Edition 2004.