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Diploma of academic Master

By :

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Entitled :

Structural determination by Nuclear Magnetic Resonance (NMR –^{1}H) of an organic compound

Presented on 03/07/2019 in front of the jury composed of:

CHARIFI Zoulikha,	University Mohamed Boudiaf - M'sila	President
LATELLI H'mida,	University Mohamed Boudiaf - M'sila	Supervisor
BAAZIZ Hakim.	University Mohamed Boudiaf - M'sila	Examiner

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I thank all the people of the laboratory with which I interact for a intellectual exchange or simply by the sympathy.

I thank deeply the members of my family, my mother my father, my brothers, my sisters, thanks to your support, motivation, confidence and your love, I have always been able to push my limits and to do my best in all areas. You are my reason to live and my source of inspiration.

Oumelkheir DJAFER

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Introduction

INTRODUCTION

At the present time, nuclear magnetic resonance (NMR) is without doubt one of the most valuable tools of analysis available. It has not only allowed the chemists to identify much more easily than before their molecules, or to characterize those extracted from the nature in order to develop new drugs, but also to obtain a non-invasive method and non-ionisante of study of the human body (magnetic resonance imaging, MRI, which in a first time has permitted to obtain images of soft parts, previously inaccessible by conventional methods, and now, of dynamic images, allowing to check for example the blood flow in the different regions of the human body).

The technological and methodological advances in succession in solid-state NMR over the years have led to a significant improvement in the sensitivity and the spectral resolution. In effect, the probes in rotation at the magic angle (MAS) capable of achieving a rotational frequency of 110 kHz, the increase of the static magnetic field (1 GHz) [1,2], the techniques of the hyperpolarization (DNP, gas hyper polarized [3–5], etc.) and developments of pulse sequences, the multiple acquisitions, acquisitions ultra-fast [6–8], the sampling not uniform [9], the chemistry of isotopic enrichment, the adaptation of the sequences of the NMR of the liquid to the solid, etc [10].

The nuclear magnetic resonance (NMR) became, therefore, a spectroscopic tool essential for the study of a wide variety of molecules. The NMR to determine the structural information by the interpretation of the behavior of the nuclear magnetization (magnetic moment of the kernel) in the presence of a static magnetic field intense B_0 (a few Teslas) and after irradiation by a magnetic field frequency signal B_{RF} very low before B_0.

In this context, our work has been to establish a kind of road map for the future students who wanted to work in this area.

The plan of the memory is the following :

In the first chapter, we recall the principle of the NMR, the magnetic properties of the nuclie, the magnetic magnetization of nuclei and some general information concerning the phenomena of relaxation and the equations of motion of the magnetization.

The second chapter is devoted to the chemical shift. In this part, very important, we make the point on the concept of the constant of screen, the concept of equivalent protons and some factors that may influence the chemical shift. We will finish this chapter by a method of analysis of the nmr spectrum.

Chapter Three, exposes the spin–spin coupling which is responsible for the multiplicity of NMR spectrum. We will deal with the different systems: AX, AX_2, A_2X_3, etc.

Finally, the results of analysis of a experimental spectrum are presented in the last chapter.

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Chapter 1 :

Principle of NMR

1. Introduction

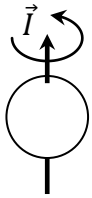
The Nuclear Magnetic Resonance (NMR), highlighted by Felix Bloch and Edward Purcell (Nobel prize 1952), is a spectroscopic technique used to determine the structure of organic molecules and biomolecules in solution.

The NMR relies on the magnetic properties of the nucleus of the atom, when it is placed in a strong magnetic field. We find that some of the nuclei resonate at a characteristic frequency in the range of radio frequencies in the electromagnetic spectrum.

Any variation in this range will give us detailed information on the molecular properties.

2. Nuclear magnetic properties

Some nuclei have a spin, the nuclear spin I, which is a vector quantity associated with the rotation of the nuclei on themselves.



The spin I gives the nuclei a magnetic moment μ defined by :

$$\vec{\mu} = \gamma.\vec{L} = \gamma.\hbar.\vec{I}$$

Where γ is the gyromagnetic constant of the nucleus considered. It is expressed in radian.$T^{-1}.s^{-1}$

The nuclei used the most by NMR are those for which $I = 1/2$ and are grouped in the table below.

Nucleus	γ(rad.s^{-1}.T^{-1})	Natural abundance (%)
$^{1}_{1}H$	26.75×10^{7}	99.98
$^{13}_{6}C$	6.73×10^{7}	1.10
$^{15}_{7}N$	-2.71×10^{7}	0.37
$^{19}_{9}F$	25.18×10^{7}	100
$^{31}_{15}P$	10.84×10^{7}	100

Only the nuclei of spin i ≠ 0 are active in the NMR. The nuclei for which $I > 1/2$, have a electric quadrupole nuclear moment which leads to disturbances in the spectra. They are studied by NQR.

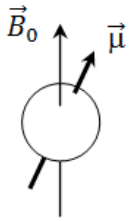
3. The classical model

In an experiment of nuclear magnetic resonance, the sample to be studied is immersed in a intense static magnetic induction B_0 (a few Teslas) and very uniform in order to polarize the nuclear moments of individual nuclei.

The vector product of the $\vec{\mu}$ With $\vec{B}_0$ generates a twist-in torque (torsion torque) :

$$\vec{\Gamma} = \vec{\mu} \wedge \vec{B}_0$$

This torque causes all spins in a rotation around $\vec{B}_0$: it is the **precession of Larmor.**



The speed of this precession is given by **the equation of Larmor** :

$$\vec{\omega}_0 = -\gamma \vec{B}_0$$

In this paragraph we have briefly described in purely classical terms, that is to say that we consider the magnetic moments of the nuclei are simple vectors. The Quantum approach, complete and rigorous, of the principle of the NMR is presented to the paragraphe next.

4. The quantum model

Let a spin $I = 1/2$, placed in a magnetic field B_0 parallel to the axis z. We define the Magnetic moment of the spin as :

$$\vec{\mu} = \gamma \vec{L} = \gamma \hbar \vec{I}$$

a) The Zeeman effect

The hamiltonian of the Zeeman writes :

$$H_Z = -\vec{\mu} \vec{B}_0 = -\gamma \hbar B_0 I_z$$

The eigenstates of H_z are then those of I_z so | +> and | ->.

In addition, the quantity 2I + 1 determines the number of orientations that can take the nuclei and each orientation is defined by the magnetic quantum number m : $-\mathrm{I} \leq \mathrm{m} \leq \mathrm{I}$. In the case of the proton ${}^{1}H$, $m = 1/2$ and $-1/2$.

The energies of these States expressed as a function of B_0 are given by :

$$\mathrm{E}_{|+>} = -\frac{1}{2}\,\gamma\,\hbar\,\mathrm{B}_0$$

$$\mathrm{E}_{|->} = +\frac{1}{2}\,\gamma\,\hbar\,\mathrm{B}_0$$

The sign of the energy depends on the sign of γ.

Then there is lifting of degeneration causing the separation of the lines in two components:

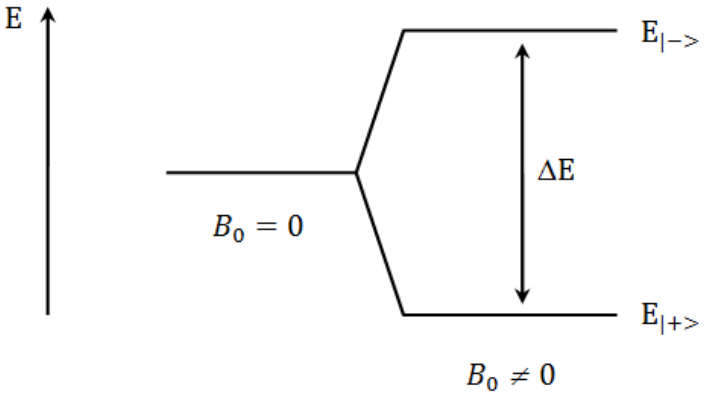


Figure I.1: Zeeman effect.

In the absence of an external magnetic field ($B_0 = 0$), all the nuclei of a macroscopic sample, whatever their nuclear magnetic moment μ, have the same energy : it is said that all the magnetic states of the nucleus are **degenerate**. When the nuclei are placed in a non-zero magnetic field ($B_0 \neq 0$), we then observe the separation of the quantum states of the magnetic moment, we speak of **degeneration lift** or Zeeman effect.

The resonance energy which is the energy needed to make a transition between the states $|+>$ and $|->$ is so :

$$\Delta E = \mathrm{E}_{|->} - \mathrm{E}_{|+>} = \gamma\,\hbar\,\mathrm{B}_0$$

b) Resonance frequency

Therefore the resonance frequency (Larmor frequency):

$$\nu_0 = \frac{\Delta E}{2\pi\hbar} = \frac{\gamma \mathrm{B}_0}{2\pi}$$

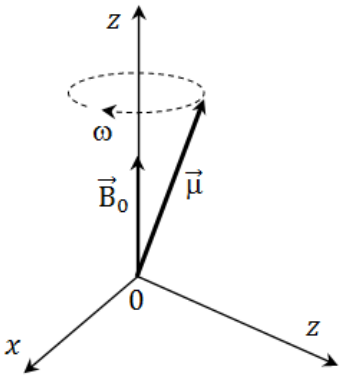
For a macroscopic sample, the statistics of Boltzmann predicts that there is slightly more of nuclei in the State $|+>$ than in the State $|->$.

The ratio between the two populations N_α and N_β in the State $|+>$ and in the state $|->$, respectively, for a magnetic field B_0 of 1.4 Tesla, for example, it is given by [1–4] :

$$\frac{N_\alpha}{N_\beta} = 1 + \frac{\gamma \hbar B_0}{k_B T} \approx 1.0000001$$

This ratio, although low, is manifested by the appearance of a macroscopic nuclear magnetization (M) directed in the direction of the B_0 field (Figure 15). In NMR, it is this slight difference in population between energy levels that is measured. Therefore, we understand the interest of using the strongest magnetic field possible.

The angular velocity of the precession motion is given by :



Precession in clockwise direction [7] of the magnetic moment $\vec{\mu}$ around the static field $\vec{B}_0$ at the frequency :

$$\omega_0 = 2\pi\nu = -B_0\gamma$$

The minus sign (-) is due to the rotation in the retrograde direction if γ is positive

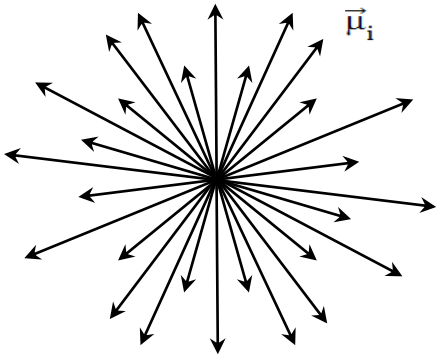
c) Magnetization

The macroscopic magnetization is defined by the vector sum of the magnetic moments of all the nuclei:

$$\vec{M} = \sum_i N_i \vec{\mu}_i$$

In the absence of magnetic field ($\vec{B}_0 = \vec{0}$) and at thermodynamic equilibrium, the magnetic moments of nuclei can take any orientation in space. The vector sum of the N individual magnetic moments is therefore zero on average (sea urchin state) and there is therefore no polarization or macroscopic magnetization resulting.

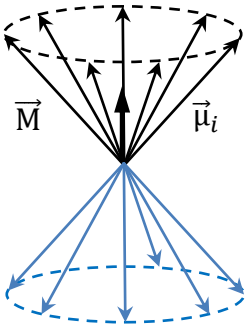
is :



$\vec{B}_0 = \vec{0},\ \vec{M} = \vec{0}$

In the presence of a magnetic field ($\vec{B}_0 \neq \vec{0}$), the magnetic moments start to turn around this field, but since there is no change of orientation related to their interaction with the field, it does not occur nothing new. The NMR spectrum should therefore not be able to be observed in these conditions [5].

However, the statistics of Boltzmann shows that these reorientations are not completely isotropic, that is to say that the probability that the magnetic moments are oriented in the direction of the applied magnetic field (Positive polarization) is slightly more important than the opposite (negative polarization). The proportion of magnetic moments in each of the polarizations is indeed given by Boltzmann's statistical distribution law which favors the lowest energies.



$\vec{B}_0 \neq \vec{0},\ \vec{M} \neq \vec{0}$

The Nuclear paramagnetism comes from the polarization M appearing gradually when the sample is placed in a magnetic field. The results in the appearance of a net polarization (macroscopic magnetization) non zero :

The module $\vec{M}$ can be calculated from the levels α and β :

$$M = N_\alpha \mu_\alpha + N_\beta \mu_\beta = \gamma \hbar\, I_\alpha N_\alpha + \gamma \hbar\, I_\beta N_\beta = \frac{1}{2} \gamma \hbar\, (N_\alpha - N_\beta)$$

Knowing that populations on different energy levels are governed by the Boltzmann equation :

$$\frac{N_\alpha}{N_\beta} = exp\left(\frac{\Delta E}{k_B T}\right)$$

Taking into account the energies involved in NMR, $\Delta E \ll k_B T$:

$$\frac{N_\alpha}{N_\beta} = 1 + \frac{\Delta E}{k_B T}$$

By asking:

$$N = N_\alpha + N_\beta$$

N being the total number of spins detected.
And knowing that:

$$\Delta E = \gamma \hbar B_0$$

We obtain:

$$M = \frac{\gamma^2 \hbar^2 B_0}{4 k_B T} N$$

The magnetization is therefore proportional to the total number of nuclei (*N*), and it is she who is measured by NMR.

5. Equation of motion of a spin $\vec{\mu}$ (approach semi-classical)

We will study, in this paragraph, the evolution over time of the magnetization vector that characterizes all the spins present in the sample.

The speed of variation of the cinematic moment of a system is equal to the torque acting on the system, either :

$$\frac{d\vec{L}}{dt} = \vec{\mu} \wedge \vec{B}_0$$

Knowing that:

$$\vec{\mu} = \gamma \vec{L}$$

we obtain:

$$\frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \wedge \vec{B}_0$$

This is Bloch's equation without taking relaxation into consideration.

In a fixed reference (x, y, z), we can prove that:

$$\frac{d}{dt}\left(\vec{\mu} \,.\, \vec{B}_0\right) = 0$$

The magnetic moment $\vec{\mu}$ thus evolves in keeping a constant module and making a constant angle with the field $\vec{B}_0$.

If we project the Bloch equation in the plane perpendicular to $\vec{B}_0 = B_0 \vec{k}$, we obtain :

$$\frac{d\mu_x}{dt} = -\gamma \mu_y B_0 = \mu_y \omega_0$$

$$\frac{d\mu_y}{dt} = -\gamma \mu_x B_0 = -\mu_x \omega_0$$

$$\frac{d\mu_z}{dt} = 0$$

The solutions of these equations are of the form:

$$\mu_x(t) = \mu_x(0) \sin(\omega_0 t)$$

$$\mu_y(t) = \mu_y(0) \cos(\omega_0 t)$$

$$\mu_z(t) = \mu_t(0)$$

The nuclear magnetization M is by definition the sum of all the nuclei contained in a unit of volume [6]. If there is only one isotope in this volume ($\gamma_i = \gamma$), then M must check the equation :

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \wedge \vec{B}_0$$

The nuclear magnetization $\vec{M}$ therefore rotates around the magnetic field $\vec{B}_0$ in the same way as $\vec{\mu}$.

As we have seen, the magnetization is proportional to the number of nuclei, and it is this which is measured in NMR. However, the magnetization M is not observable when it is parallel to $\vec{B}_0$, so it must therefore be switched by 90°.

6. Relaxation phenomenon

At thermal equilibrium, at temperature T, the nuclear magnetization M is parallel to the zaxis z, is :

$$M_x = 0, M_y = 0, \quad M_z = M_0$$

If we provoke a change in the orientation of the spins, by any perturbation, the magnetization will return to its value at the thermal equilibrium in a characteristic time, called the relaxation time.

A) longitudinal relaxation (spin relaxation - Network)

Spin-net relaxation transfers the energy absorbed by the spins to the network. It allows to restore the balance in the direction of Oz.

We have seen that the magnetization of a system of spin I = 1/2, at equilibrium, is :

$$M_z = M_0 \propto (N_\alpha - N_\beta)$$

In most systems, we observe that $M_z$increases exponentially with time towards $M_0$and follows a law of variation of the form :

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}$$

Where T_1 is the characteristic time of restoration of the value at the thermal equilibrium of the magnetization in the direction Oz. This is the longitudinal relaxation time.

b) Transverse relaxation (Spin-spin relaxation)

This type of relaxation is due to the interaction between the different neighboring nuclei. It represents energy exchanges within a spin system without any change in total energy.

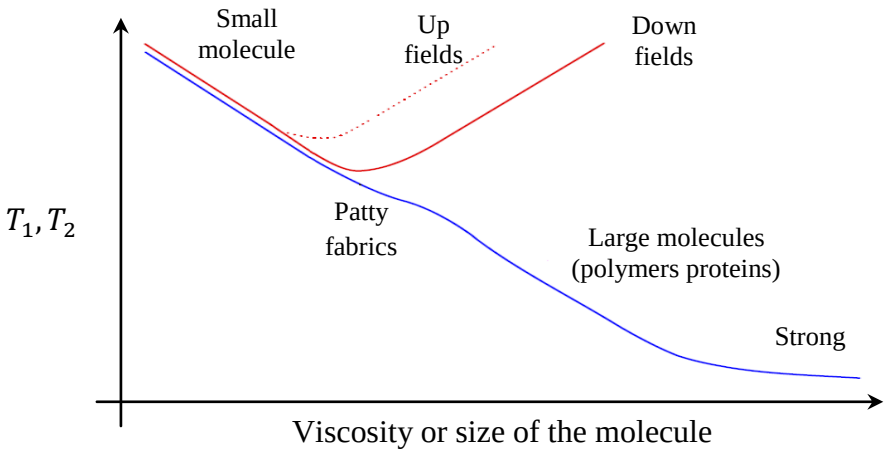
After the impulse, M_x and M_y phase out and decay exponentially according to:

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2}$$

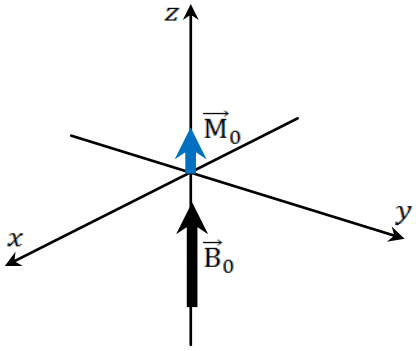
Where T_2 is the characteristic time of loss of magnetization in the xy plane **(transverse relaxation time**). This constant depends in particular on the spin-spin interactions that occur in the solid or liquid state due to the small internuclear distances and the high density of the nuclei.

The value of $T_1$and T_2 (tissue for example) depends, among other factors, on the viscosity of the medium (Figure I.12).

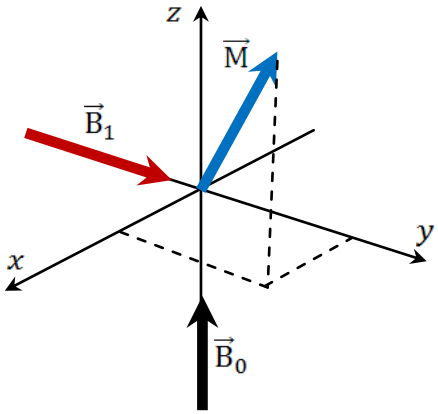


7. Excitation by a radio frequency field (RF)

The magnetization M_0 is not detectable, because it is on the same axis as B_0 :



And because it is very low compared to B_0, we apply a different magnetic field B_1 of frequency v_1 that fact switch M_0 in the transverse plane (xy).



This RF pulse must respect the resonance condition : $v_1 = v_0$.is :

$$\vec{B}_1 = B_1 \cos(\omega_1 t)\,\vec{\imath} + B_1 \sin(\omega_1 t)\,\vec{\jmath}$$

$\vec{B}_1$ is a rotating magnetic field (circularly polarized) at the frequency ω in the plane (xy).
We put : $\omega_1 = -B_1\gamma$

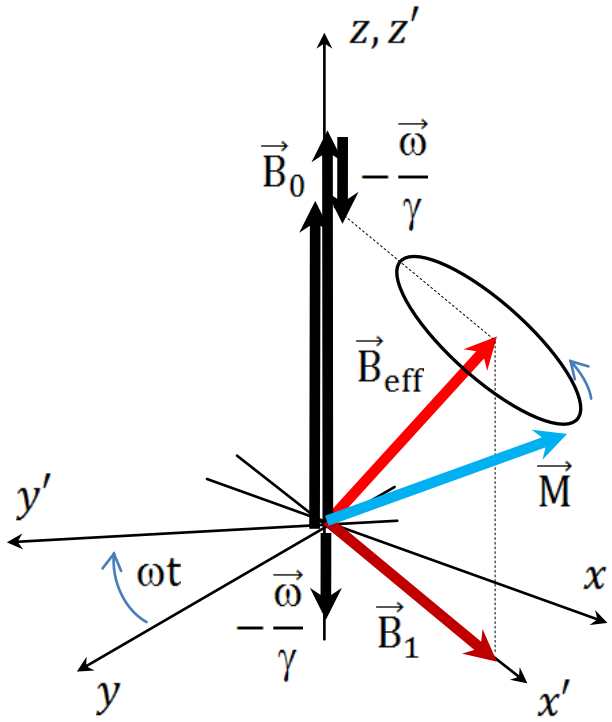
To analyze the behavior of magnetization in this magnetic field depends on time , we use the equation of motion :

$$\frac{d\vec{M}}{dt} = \gamma\,\vec{M} \wedge \vec{B}$$

With:

$$\vec{B} = \vec{B}_0 + \vec{B}_1$$

In fact, this analysis is easier to carry out in the rotating repository (x ', y', z ') at the frequency ω of the radio frequency field $\vec{B}_1$ (see figure below).



$$\vec{B}_{eff} = \vec{B}_0 - \frac{\vec{\omega}}{\gamma} + \vec{B}_1$$

In this reference, the radiofrequency field $\vec{B}_1$ appears stationary and aligned along the x axis. The z or z 'axis is the axis of the static magnetic field $\vec{B}_0$.

$$\begin{cases} \vec{\imath}' = \cos(\omega t)\,\vec{\imath} + \sin(\omega t)\,\vec{\jmath} \\ \vec{\jmath}' = -\sin(\omega t)\,\vec{\imath} + \cos(\omega t)\,\vec{\jmath} \\ \vec{k}' = \vec{k} \end{cases}$$

In the fixed reference :

$$\frac{d\vec{M}}{dt} = \gamma\,\vec{M} \wedge \vec{B}$$

Where :

$$\vec{M} = M_x(t)\vec{\imath} + M_y(t)\vec{\jmath} + M_z(t)\vec{k}$$

In the relative reference, $\vec{M}$is written :

$$\vec{M} = M_{x'}(t)\vec{\imath}' + M_{y'}(t)\vec{\jmath}' + M_{z'}(t)\vec{k}'$$

However, since :

$$\frac{d\vec{\imath}'}{dt} = \omega\vec{k} \wedge \vec{\imath}' \quad , \quad \frac{d\vec{\jmath}'}{dt} = \omega\vec{k} \wedge \vec{\jmath}' \quad , \quad \frac{d\vec{k}'}{dt} = \omega\vec{k} \wedge \vec{\imath}'$$

Then :

$$\frac{d\vec{M}}{dt} = \frac{\delta\vec{M}}{\delta t} + \omega\vec{k} \wedge \vec{M}$$

where :

$$\frac{\delta\vec{M}}{\delta t} = \frac{dM_{x'}}{dt}\vec{i}' + \frac{dM_{y'}}{dt}\vec{j}' + \frac{dM_{z'}}{dt}\vec{k}'$$

In the relative coordinate system, we have :

$$\frac{\delta\vec{M}}{\delta t} = \frac{d\vec{M}}{dt} - \omega\vec{k} \wedge \vec{M} = \gamma\,\vec{M} \wedge \vec{B} - \omega\vec{k} \wedge \vec{M}$$

Therefore in the repository running, the equation of motion for the magnetization is written :

$$\frac{d\vec{M}}{dt} = \gamma\,\vec{M} \wedge \vec{B}_{eff}$$

where:

$$\vec{B}_{eff} = \vec{B}_1\,\vec{i}' + \left(B_0 + \frac{\omega}{\gamma}\right)\vec{k}' = \frac{1}{\gamma}\left[-\omega_1\,\vec{i}' + (\omega - \omega_0)\vec{k}'\right]$$

The relative movement of the magnetization vector $\vec{M}$ is thus a rotation around the effective field, which is static by report to the rotating reference frame (see FIG. 7). To obtain the absolute motion of $\vec{M}$, it suffices to compose this precession around $\vec{B}_{eff}$ with a rotation around [0z] of angular velocity ω [6].

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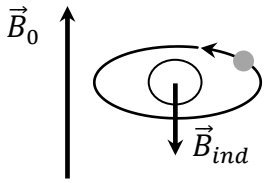
Chapter 2 :

Chemical shift

1. Introduction

Placed in a magnetic field$\vec{B}_0$, the electrons close to the nucleus i induce at its level an additional magnetic field $\vec{B}_{ind}$of direction opposite to $\vec{B}_0$:



$$\vec{B}_{ind} = \sigma_i \vec{B}_0$$

σ_i is called the screen constant, its value is determined by the electron density of the 1s hydrogen orbital.

The screen constant σ_i can be obtained from the methods of quantum chemistry but here we will confine ourselves to a qualitative description. σ_i Can be decomposed as follows:

$$\sigma_i = \sigma_d + \sigma_p$$

In this expression, σ_d is the diamagnetic contribution [1,2] : under the effect of the field $\vec{B}_0$, the electronic charges precede and induce an additional local field (Lentz's law) which moves the resonance frequencies.σ_p is the paramagnetic contribution; it comes from the interaction of the field $\vec{B}_0$ with the unpaired electrons in the electronic states close to the fundamental state [1].

The field felt locally by the nucleus i is not $\vec{B}_0$ but rather :

$$\vec{B}_i = \vec{B}_0 - \vec{B}_{ind} = (1 - \sigma_i)\vec{B}_0$$

The resonance frequency of the nucleus i being proportional to the value of the local magnetic field (Chapter 1) :

$$v_i = \frac{\gamma_i B_i}{2\pi} = \frac{\gamma_i}{2\pi}(1 - \sigma_i)B_0$$

The resonance frequency of the nucleus i is therefore dependent on its electronic environment.Wespeak of chemical shift notedδ and defined by :

$$\delta_i = \frac{v_i - v_{ref}}{v_0} \times 10^6$$

v_i : resonance frequency of the nucleus i,

v_{ref} : resonance frequency of the TMS reference, this is the frequency of the protons of tetramethylsilane, Si $(CH3)_4$ (TMS).This relatively inert compound in many media has 12 protons that are identical and a chemical shift that is superimposed very rarely with those of the compounds studied [3]. Other benefits of TMS as a reference substance are :

- A constant screen, σ_{TMS} , very high,
- The presence of 12 equivalent protons and therefore an intense NMR signal,
- A low boiling point (120C), facilitating its elimination.

v_0 : frequency of the staticfieldB_0 or frequency of the spectrometer.

The coefficient $10^6$is due to the difference $\mathrm{v_i} - \mathrm{v_{ref}}$ which is of the order of a few Hz while $\mathrm{v_0}$ is of the order of hundreds of MHz.

The chemical shift is thus independent of the field B_0 and thenwe have values of δ in ppm (parts per million).

The chemical shift $\delta(^1\mathrm{H})$ depends on many factors:

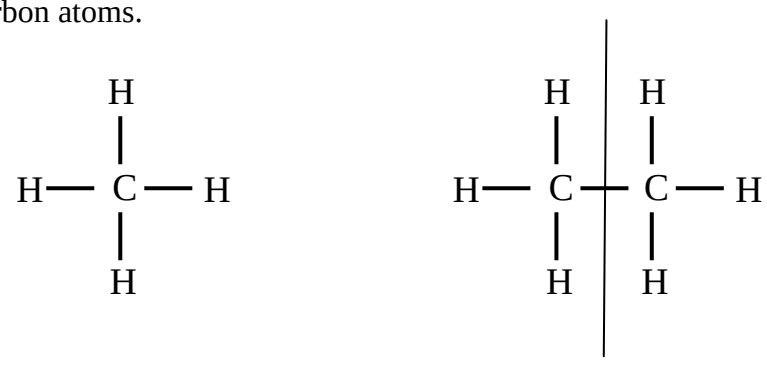
- Electronic density (importance of inductive effects),
- existence of H-bonds (intra or intermolecular),
- solvent,
- concentration,
- delocalisation (π electrons),
- chemical exchange (case of labile protons OH, NH ...).

2. Factors influencing the chemical shift

a) Notion of equivalent protons

Protons are considered equivalent if they are carried by the same carbon atom, or if they are carried by two carbon atoms involved in a symmetry relation in the molecule.

in the example below, here are two groups of protons equivalent for the first, the protons are carried by the same atom, and for the second, the protons are carried by two symmetrical carbon atoms.



Equivalent protons are represented by the same signal on the spectrum. Indeed, several protons can contribute to the same signal. Protons are equivalent if they have the same chemical environment. Such atoms are then symmetrical to one another by one of the symmetry elements of the molecule (plane, axis or center of symmetry).

b) Influence of electronegativity on chemical shift

The screen constant and the chemical shift are now determined by the electron density around the nucleus under consideration.In a molecule, this density is very dependent on the nature of the neighboring chemical groups, and in particular on their electronegativity (donor, acceptor).The following table illustrates this situation.

	CH_3F	CH_3Cl	CH_3Br	CH_3I	CH_3H
δ(ppm)	4.13	2.84	2.45	1.98	0.13

Chemical shifts for methylhalides [3].

It should also be mentioned that for molecules containing a metal atom, the chemical shift decreasesas a function of the ionic nature of the metal present.

It happens however, sometimes it is not possible to explain the chemical shift only from the electronegativity of neighboring groups. The movements of the electrons in the rest of the molecule can also disturb the local field felt by the nuclei in question.

These effects diminish when the proton being considered is further awayfrom the multiple bonds. Thus, protons that are on branches related to an aromatic ring will be little influenced by the cycle current, as the carbon chain lengthens.

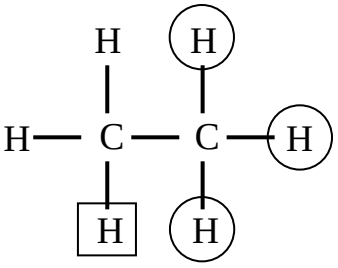
The values of the chemical shifts also depend on the group to which the hydrogen belongs (methyl group CH3, methylene CH2, methyne CH).Usually, a CH3 group gives a signal whose chemical shift is less than that of a CH2 group, it self lower than that of a CH group, when they have the same environment.

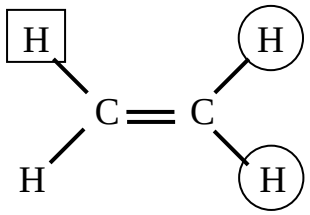
3. Multiplicity of signals

The resonance signal may have several peaks and is then called multiplet (or massive).This signal multiplication is due to interactions between neighboring non-equivalent protons.

a) Neighborhood concept

Two protons are called neighbors if they are separated by three links, single or multiple.





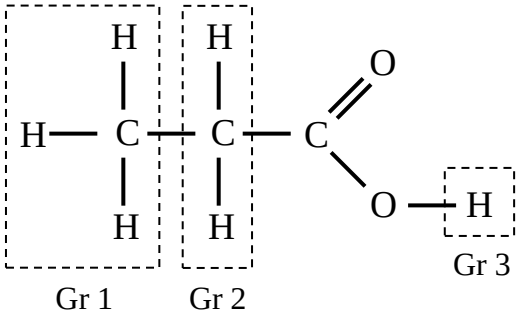
Thus the hydrogen atom surrounded by a square has three neighbors surrounded by circles in the first group and two neighbors in the second group.

If hydrogen atoms are separated by more than 3 single bonds, they are not neighbors.

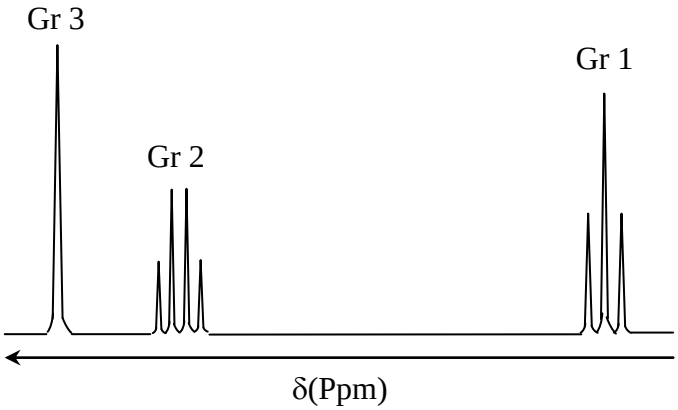
a) Rule of $(n+1)$– Tuples

A group of equivalent protons (a) having as neighbors n protons (b) not equivalent to (a) has a resonance signal in the form of a multiplet of (n 1) peaks.

Example: Either the following developed formula :



The massif corresponding to each group is represented on the following Spectrum:



4. Special cases

a) The chemical exchange

In the case of the alcohol -O-H function : the proton carried by the oxygen atom can be exchanged with the protons of the solvent (the water molecules) which are located in the neighborhood. Thus, the protons of the other groups can not perceive the presence of this proton -O-H.

To summarize: the proton of the alcohol function (but also carboxylic acid, amine and amide) will give a single peak regardless of the number of hydrogen atoms carried by the neighboring carbon.

b) The case of aldehydes and Low resolution spectra

The proton of the aldehyde gives a singlet in a low resolution spectrum. However, at high resolution, we can observe multiplets, because the coupling with the protons of neighboring atoms is very weak.

c) Shielding / deshielding

The resonant frequency of the hydrogen proton depends on its neighborhood. The
Closer this proton is to a very electronegative substitute (oxygen, halogens, ...), the more it will be deshielded.
If a proton is deshielded, its displacement will be much higher compared to a proton placed next to an alkyl group type of $-CH_2$ or $-CH_3$.

For example, in the CH_3-CH_2-Br molecule, the CH_2 protons are said to be deshielded because they are close to the more electronegative Bromine atom. They have the highest chemical shift.

The protons in CH_3 are said to beshielded because no particularly electronegative atom is nearby.

5. Relative intensities of peaks in a multiplet

The intensity of a peak in a multiplet is given by Pascal's triangle.

1 → Singulet

1 1 → Doublet

1 2 1 → Triplet

1 3 3 1 → Quadruplet

1 4 6 4 1 → Quintuplet

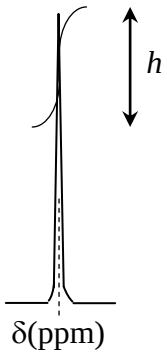
1 5 10 10 5 1 → Sextuplet

1 6 15 20 15 6 1 → Septuplet

Pascal triangl.

6. Integration curve

The next step in the analysis of the proton NMR spectrum is to proceed with its integration, in the mathematical sense of the term. The integration curve of the NMR spectrum corresponds to the number of equivalent hydrogen atoms responsible for the signal.



The relative height (h) of a bearing is proportional to the number of equivalent protons forming the multiplet of the signal. To know the number of hydrogen atoms responsible for a peak or set of peaks, we measure to the rule :

- the overall height of the curve,
- the height of each landing.

Then, by knowing the total number of hydrogen atoms of the molecule through the empirical formula, we can deduce the corresponding number of equivalent hydrogen atoms.

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[1] Ramsey N. F. and Purcell E. Mr. interactions between nuclear spins in molecules. Phys. Rev., (85):143_144, 1952.
[2] Ramsey N. F. Electron coupled interactions between nuclear spins in molecules. Phys. Rev., (91):303_307, 1953.
[3] S. Akoka, 'An introduction to the NMR', Univ. of Nantes
Http://www.sciences.univ-nantes.fr/CEISAM/pedago.php.

Chapter 3 :

Spin-spin coupling

1. Introduction

Consider a molecule of the type:

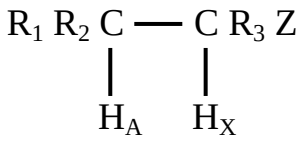


Figure 3.1 : coupling between H_A and H_X (system AX).

The electrons of the molecule enter in to magnetic interaction with both the proton H_A spin and the proton H_X spin. The electron cloud thus establishes a 'coupling' between the spins of the two nuclei: this is the spin –spin coupling.

Through this coupling, each of the two protons creates, reciprocally, a small local field at the level of the other, this field being reversed when its spin state is reversed.

As well, the proton H_X creates a local magnetic field $\vec{B}_{loc}$, very weak, at the level of the proton H_A. This local field is added to the field $(1-\sigma)\vec{B}_0$ (chapter 2) when the spin of H_X is parallel to$\vec{B}_0$, on the other hand it retracts from$(1-\sigma)\vec{B}_0$ when the spin of H_X is anti-parallel to $\vec{B}_0$. The Proton H_A is therefore submitted, according to the orientation of the spin of H_X, the fields $(1-\sigma)B_0 + B_{loc}$ or $(1-\sigma)B_0 - B_{loc}$ and it will resonate at two different frequencies :

$$v_{A1} = \frac{\gamma}{2\pi}[(1-\sigma)B_0 + B_{loc}]$$

And:

$$v_{A2} = \frac{\gamma}{2\pi}[(1-\sigma)B_0 - B_{loc}]$$

Separated by the constant J_{AX}(Figure 3.2):

$$J_{AX} = v_{A1} - v_{A2} = \frac{\gamma B_{loc}}{\pi}$$

The difference between these two lines is noted J_{AX}.One of theselinesis the NMR signal of the protons A which have a neighbor X in the state α and the other is the signal of the protons A which have a neighbor X in the stateβ.Since the B_{loc} field is independent of B_0, the J_{AX} constant isalsoindependent of B_0 and is measured in Hz.

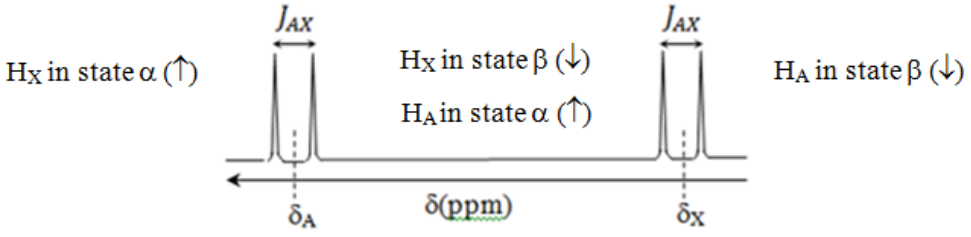


Figure 3.2: Constant of the coupling between two proton neighbors.

2. Generalization

If there is a group of n protons H_X equivalents, coupled to a proton H_A, each one of them creates a local field of the same size which, according to its state of spin, is subdivided or adds to the level of the proton H_A.

The addition of these local fields gives rise, for the signal relative to the proton H_A to a multiplet with n + 1 peaks, separated from each other by the same interval, equal to the coupling constant. The intensities of the peaks are distributed according to Pascal's triangle (chapter 2).

3. Multiple coupling

Now consider a molecule of the type:

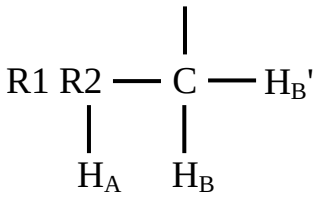


Figure 3.3: coupling between H_A and H_B on the one hand and on the other hand, between HA and $H_{B'}$.

In this figure, the proton H_A can be coupled to the proton H_B with the constant J_{AB} and the proton $H_{B'}$ with the constant $J_{AB'}$.

We must begin, for example, by looking at the appearance of the massif A. If A was coupled only with B ; it would be a doublet, with two identical lines (AX system).

Let us now consider the protons corresponding to one of these two lines (say the protons A which have a neighbor in the state α).Part of these protons has a neighbor B' in state α and another has a neighbor B' in state β.This leads therefore to split again but the coupling constant is now$J_{AB'}$,since this second resolution results from the interaction of the proton A with the proton B' (Figure 3.4).The proton A massif is therefore a doublet of doublets.

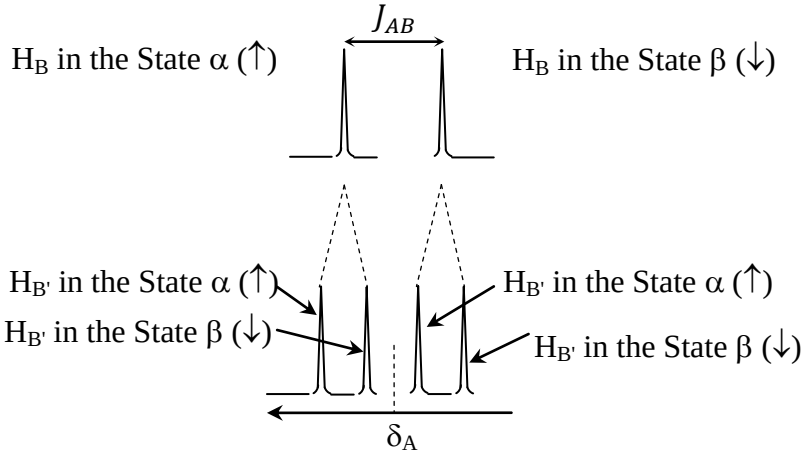


Figure 3.4: The massif has is a doublet of doublets.

When the two protons B and B 'coupled to A have the same coupling constant : $J_{AB'} = J_{AB}$, the two central lines are superimposed which leads to a triplet whose relative intensities are, according to Pascal's triangle, of the form1-2-1 (Figure 3.5).

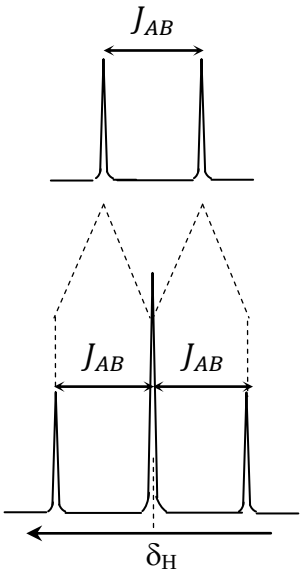


Figure 3.4: The massif A is a triplet.

When three protons are coupled to the nucleus A the massif is a doublet of doublets of doublets, or eight lines in total. But if the three coupling constants are identical, then many superpositions occur and the observed mass is a quadruplet: four lines whose relative intensities are 1-3-3-1.

In general, we can say that in the case of coupling with n protons with the same coupling constant: the observed mass is a multiplet of n + 1 lines whose relative intensities are given by Pascal's triangle.

4. Quantum treatment

In the case of a system with two hydrogen nuclei A and B that can interact together, the spin Hamiltonian contains three terms:

- The Zeeman term describing the interaction between the magnetic moments and the field $\vec{B}_0$,
- The term electronic screen at the origin of the chemical shift,
- The term of the spin-spin coupling, also called scalar coupling.

The other magnetic interactions, the dipole coupling and the quadrupole burst for spin nuclei higher than 1/2, are not taken into account for the calculation of the spectra since these averages are zero in isotropic medium. Note neverless that these terms will have to be taken into account if we work in a non-isotropic medium (solid, liquid crystals, etc.).

a) The Zeeman Hamiltonian

The interaction of a magnetic moment $\vec{\mu}$ with a magnetic field $\vec{B}_0$isgiven, in Chapter 1, by:

$$H_Z = -\vec{\mu}\vec{B}_0 = -\gamma\hbar\vec{B}_0 \,.\, \vec{I}$$

Where $\vec{I}$ is the spin operator vector.We simplify this equation by admitting that we know how to make an infinitely homogeneous field in the *z* direction of the laboratory, that is to say that we suppose that the components of the field are:

$$B_x = B_y = 0 \text{ And } B_Z = B_0$$

The Zeeman Hamiltonian then becomes:

$$H_Z = -\vec{\mu}\vec{B}_0 = -\gamma\hbar B_0 I_z$$

As in our system we have two nuclei, it is necessary to add the terms Zeeman of the two spins :

$$H_Z = -\gamma_A\hbar B_0 I_{zA} - \gamma_B\hbar B_0 I_{zB}$$

b) The Hamiltonian of the chemical shift

It is a magnetic field, due to the effect of $\vec{B}_0$ on the electrons of the immediate environment of the nuclei, the corresponding Hamiltonian is given by:

$$H_\sigma = \hbar\gamma_i\sigma_i B_0 I_{zi}$$

For our system AB, this interaction is written:

$$H_\sigma = \hbar\gamma_A\sigma_A B_0 I_{zA} + \hbar\gamma_B\sigma_B B_0 I_{zB}$$

The terms Zeeman and chemical shift can be grouped since they involve the same spin operators:

$$H_\delta = H_Z + H_\sigma = -\hbar\gamma_A B_0(1-\sigma_A)\, I_{zA} - \hbar\gamma_B B_0(1-\sigma_B)\, I_{zB}$$

Recalling in addition that the NMR resonance frequency of one nucleus is equal to:

$$v_i = \frac{\gamma_i}{2\pi}(1-\sigma_i)B_0$$

c) The hamiltonian of spin-spin coupling

This term is much more complex and we do not have a classical representation. It involves two spin operators since this coupling corresponds to the interaction, via the connecting electrons, between the two magnetic moments that are our nuclei:

$$H_J = hJ_{AB}\vec{I}_A\vec{I}_B$$

In developing, we obtain:

$$H_J = hJ_{AB}\ (I_{zA}I_{zB} + I_{xA}I_{xB} + I_{yA}I_{yB})$$

In this expression, J_{AB} is the coupling constant between the nuclei A and B.

This interaction is very small compared to Zeeman energy, so it will be treated as a simple disturbance.

5. The total Hamiltonian

The total Hamiltonian corresponds to the sum of the different Hamiltonians:

$$H_T = H_Z + H_\delta + H_J$$

It is this energy operator whose we are looking for eigenvalues according to the equation:

$$H_T|\Psi> = E|\Psi>$$

In this highly condensed equation, $|\Psi>$ represents the set of eigenvectors of H_T and $E$the set of associatedeigenvalues of the energyoperator.

Chapter 4 :

Analysis of an NMR spectrum

1. Introduction

A NMR–^{1}H spectrum has a lot of redundant information. For example, the number of equivalent nuclei of a massif is given by the integral but also by the nature of the multiplets of the massifs that are coupled to it. The NMR–^{1}H spectrum thus contains much more information than the minimum necessary for determining the developped formula of a molecule.

Moreover, the observation of a ^{1}H chemical shift table makes it possible to realize that the ranges are generally narrower for the groups having weak chemical shifts. As a result, the interpretation of a chemical shift value is even less ambiguous because it is small.

From these observations, we can state two principles that will be useful for the analysis of a NMR–^{1}H spectrum :

- keep the most complex massif for the end (if the analysis of the other massifs is correctly carried out, this massif is generally not essential to determine the developed formula of the molecule),
- start from the right of the spectrum (small chemical shifts are generally easier to assign unambiguously).

From these two principles, the next step in the spectrum analysis will be to choose a simple massive and the rightmost of the spectrum.

The purpose of this chapter is to present a rational approach to determine the developped formula of a crude molecule, based on the information contained in a NMR–^{1}H spectrum. For this, the spectrum shown in Figure 4.1 will serve as an example.

We know the raw formula $C_{11}H_{12}O_2$, we are going to start looking for the developped formula, but the way in which we will have trouble identifying the number of bonds that hydrogen establishes with carbon and oxygen has therefore appealed to us. another law known as 'number of unsaturation (DI)'.

2. Number of unsaturation

The unsaturation of a molecule shows the existence of multiple bonds (double or triple), or determines the presence of a cycle, or we can see both at the same time. When a molecule has one to several unsaturations, it is said to be unsaturated.

The number of unsaturation of a molecule is the number of cycles and multiple bonds it has.

Its determination makes it possible to know the number of unsaturations (that is to say the number of π bonds) or of the ring present in a molecule. It suffices to know the crude formula ($C_{11}H_{12}O_2$) of the compound.

$$DI = \frac{2N_c - N_H + N_N - N_{Cl} + 2}{2}$$

N_c : number of carbon atoms,

N_H : number of hydogen atoms,

N_N : number of nitrogen atoms (or of another trivalent atom such as phosphorus),

N_{Cl} : number of chlorine atoms (or another divalent atom such as F, Br or I).

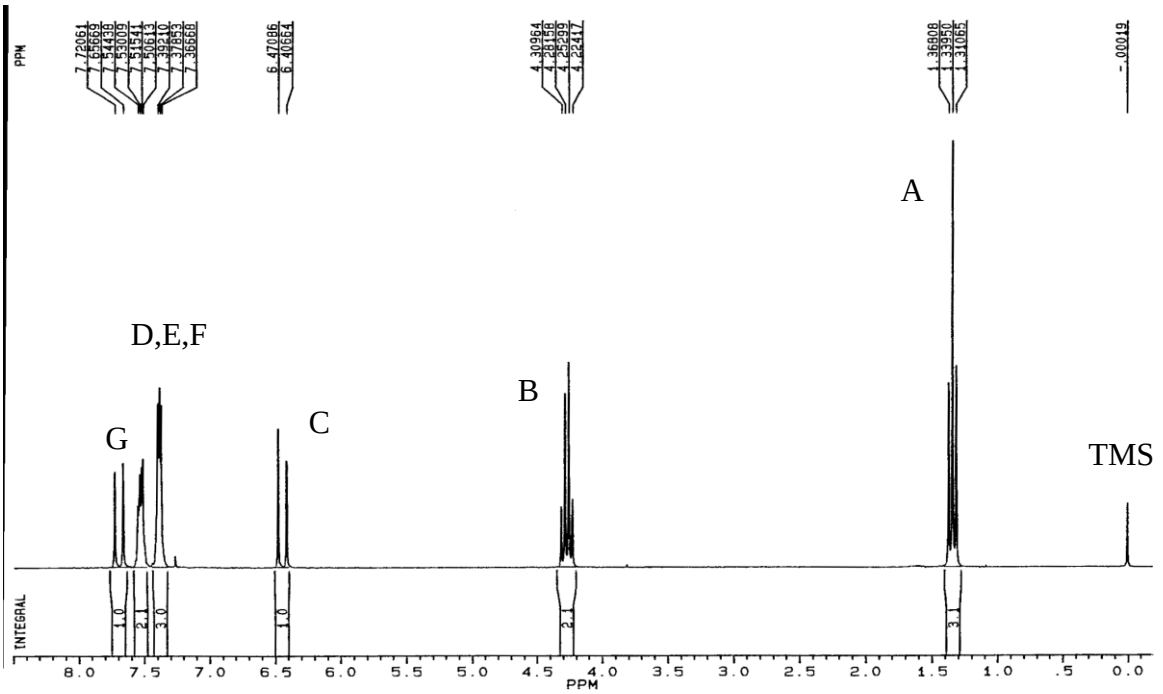


Figure 8.13. The 250-MHz ^{1}H spectrum of $C_{11}H_{12}O_2$.

Figure 4.1 : Experimental spectrum NMR–^{1}H of an organic compound of empirical formula $C_{11}H_{12}O_2$ obtained by a spectrometer 250 MHz [SH]. Each massif is labeled with a letter in order of increasing chemical shift.

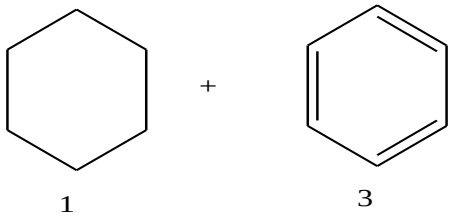
It will be noted that the number of oxygen atoms, or even of sulfur, does not intervene in this calculation.

In the case of the spectrum of Figure 4.1, this equation applied to the empirical formula $C_{11}H_{12}O_2$ leads to :

$$DI\ (C_{11}H_{12}O_2) = \frac{2 \times 11 - 0 + 0 - 12 + 2}{2} = 6$$

We therefore have 6 bonds in our formula, 4 bonds for the benzene ring and the other 2 double bonds between $(C = C)$ and $(C = O)$.

Aromatic cycle or benzene cycle



and the other two bonds : $C = C$ and $C = O$

3. Exploitation of the integration curve

The integration curve gives the relative number of hydrogen atoms present in each massif.

A. → 3H
B. → 2H
C. → 1H
D.
E. — Multiplet , 5H (benzene cycle).
F.
G. → 1H

4. Spectral analysis (spectrum interpretation)

Take the spectrum of Figure 4.1. The most right spectrum of the spectrum is the massif A. It is now necessary to extract from this massif all the information it contains: number of equivalent protons (given by the integration curve), chemical shift, nature of the multiplet, value of coupling constants.

On the basis of this information, one or more assumptions will be formulated on the nature of the grouping and its neighborhood.

The chemical shift of massif A is 1.3 ppm and its integral corresponds to 3 equivalent hydrogens. These two pieces of information tell us that this is a CH_3. On the other hand, this massif is a triplet with a coupling constant of 1.33 Hz. We can therefore hypothesize that the group responsible for the massif A is a CH_3 close to a CH_2.

This hypothesis also tells us how to continue the analysis. If it is exact, there exists in the spectrum a solid mass with very precise characteristics: three equivalent protons, a chemical shift of CH_3, a solid which is a triplet, and the coupling constant in the triplet is 1.3 Hz.

Rather than analyzing all the massifs of the spectrum in the order of the chemical shifts before starting to think, we will therefore look in the spectrum for the mass having the characteristics deduced from the first mass.

Once we have identified it, we will be able to extract all the information, complete our hypothesis of structure and obtain indications on the next mass to be analyzed. In this way, the progression logic is dictated by the structure of the molecule and not by the spectrum.

The hypothesis made on massif A then leads us to massif B. Its chemical shift is 4.3 ppm and the integral corresponds to 2 equivalent hydrogens, which is perfectly coherent with a CH_2. It is a quadruple with a coupling constant of 4.2 Hz. This is perfectly compatible with the hypothesis made from the massif A. Moreover, to explain this, we must now assume that the group responsible for the massif B is not close to any CH group, and therefore imagine the presence of a fragment: $CO–CH_2–CH_3$ in the molecule.

If this is true, there is a massif in the spectrum with the following characteristics: an equivalent proton, a chemical shift of CH, a massif which is a doublet, and the coupling constant in the doublet is 6.4 Hz. leads to mass C. Its chemical shift is equal to 6.4 ppm and the integral corresponds to an equivalent hydrogen, which is perfectly coherent with a CH (probably close to a double bond or a highly electro-attracting group, which could be an oxygen, given the raw formula).

Among the remaining masses to be elucidated, the simplest and most left of the spectrum is the G massif. Its chemical shift is equal to 7.64 ppm and the integral indicates an equivalent hydrogen. We will therefore assume that it is a CH. This massive very deshielded, is a doublet with a coupling constant equal to 7.5 Hz.

At this level, we have explained all the masses except the group D, E, F and we have six carbon atoms, five hydrogen atoms and two oxygen atoms for that. The last multiplet thus corresponds to an aromatic cycle (compatible with the observed shift, 7.3 ppm, and the absence of coupling).

From all these observations and hypotheses, the developped formula of our compound is presented in figure 4.2.

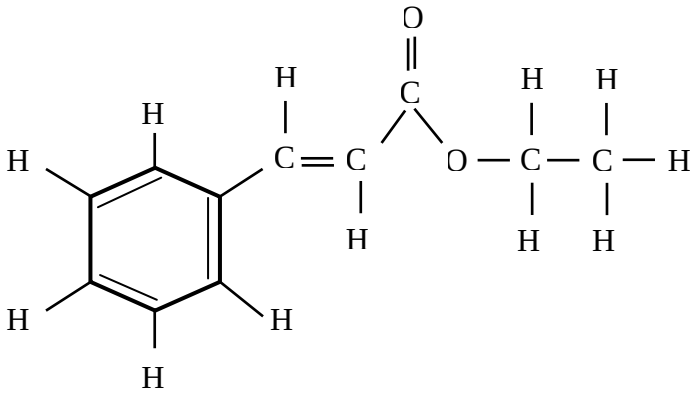


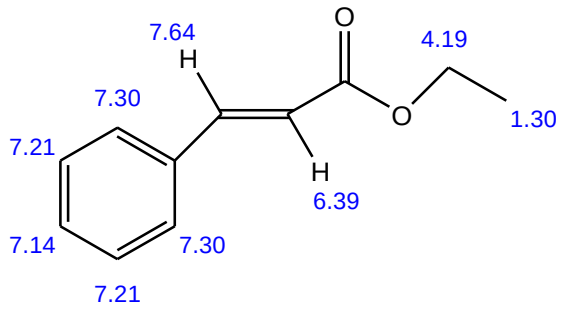
Figure 4.2 : Expanded Formula of $C_{11}H_{12}O_2$.

5. Using the ChemNMR program

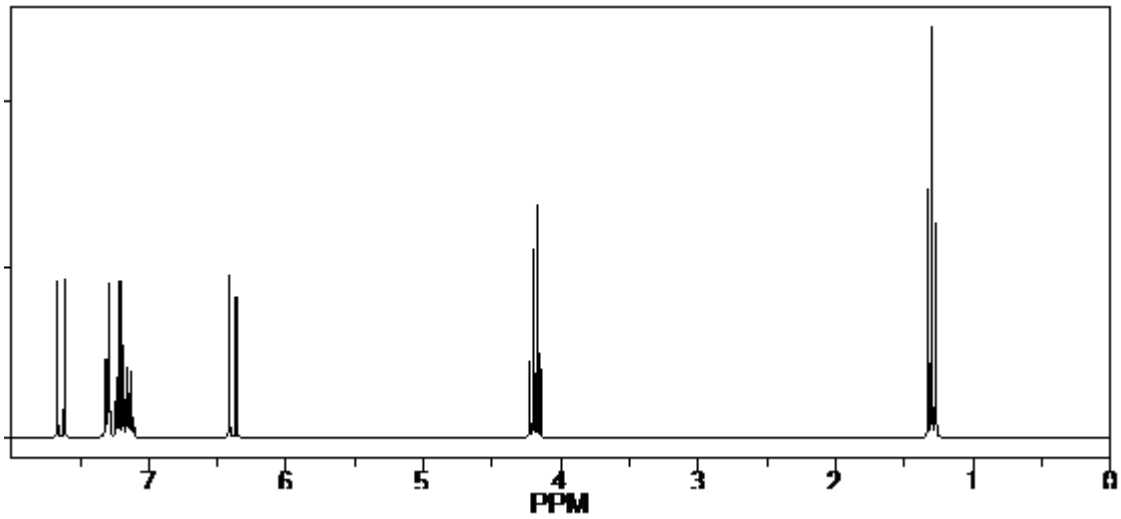
To determine this formula, the detailed analysis of the mass D, E, F was not necessary, which is traditional. Indeed, if all the information is actually extracted from each massif and no error of reasoning is made, the developed formula will, most of the time, be determined without the need to analyze the most complex massif. On the other hand, this massif must then serve to confirm the structure by a posteriori analysis.

To confirm our hypotheses, we used the program ChemNMR which is a software package ChemDraw Ultra 8.0, handy to accurately assess the chemical shifts of ^{1}H and ^{13}C spectra. The molecule and spectrum appear in a new window (Figure 4.3). The chemical shifts are displayed on the molecule.

The result of the calculations is shown in Figure 4.3 below :



Estimation Quality: blue = good, magenta = medium, red = rough



Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	7.21	7.26	1-benzene
		-0.05	1 -C=C
CH	7.14	7.26	1-benzene
		-0.12	1 -C=C
CH	7.21	7.26	1-benzene
		-0.05	1 -C=C
CH	7.30	7.26	1-benzene
		0.04	1 -C=C
CH	7.30	7.26	1-benzene
		0.04	1 -C=C
CH2	4.19	1.37	methylene
		0.00	1 alpha -C
		2.82	1 alpha -OC(=O)C=C
CH3	1.30	0.86	methyl
		0.44	1 beta -OC(=O)-C=C
H	7.64	5.25	1-ethylene
		1.38	1 -1:C*C*C*C*C*C*1 gem
		1.01	1 -C(=O)O-R cis
H	6.39	5.25	1-ethylene
		0.36	1 -1:C*C*C*C*C*C*1 cis
		0.78	1 -C(=O)O-R gem

As you can see, the results obtained by the calculation are in good agreement with the experimental results.

General conclusion

CONCLUSION GENERALE

The realization of this work allowed us to learn and master the proton nuclear magnetic resonance technique (RMN-1H) that our team 'Modeling and Simulation of Materials' then intends to use for future projects concerning the storage of hydrogen, a source of energy likely to occupy a fundamental place in the future (production and transport of energy).

In this study we presented a rational approach to determine the developed formula of a crude molecule, based on the information contained in a 1H-NMR spectrum.

We have found that instead of analyzing all the massifs of the spectrum in the order of chemical shifts, we must first look in the spectrum for the massif having the characteristics deduced from the first mass. The degree of unsaturation allowed us to know the different kinds of bonds and the existence of cycles in the developed formula.

Finally, we found that the experimental results correspond to the theoretical results. Our analyzes were confirmed by the use of a software (in freeware) called 'Chem NMR'.

We believe that a more detailed study of the part D, E, F of the recorded spectrum would be needed at more than 250 MHz, could give us more information on the aromatic cycle.

In the end, we hope to have laid the foundation stone in this area which will give impetus to local research in this area.

ملخص

الهدف الرئيسي من هذا العمل هو معرفة مبادئ الرنين المغناطيسي النووي وتعريف هذه التقنية من التحليل الطيفي و كيفية استخدامها لتحديد هياكل الجزيئات. للقيام بذلك، ناقشنا نظرية الرنين المغناطيسي النووي و تاريخها في النموذج الكلاسيكي والكمي، بالإضافة إلي شرح ظاهرة الاسترخاء ومعادلات الحركة.

في الفصل الثاني، نتحدث عن التحول الكيميائي، مع ذكر العوامل المختلفة التي يمكن أن تؤثر على هذه القيمة. في الفصل الثالث، ندرس اقتران الدوران، و هو المسؤول عن تعدد خطوط طيف الرنين المغناطيسي النووي وأنظمته المختلفة.

يخصص الفصل الأخير لطيف الرنين المغناطيسي النووي ^{1}H- RMN بصيغته التجريبية، بدءًا من أقصى الكتلة.

أخيرًا، ولتأكيد افتراضاتنا، استخدمنا برنامجًا مجانيًا لبرنامج لتقييم وتحديد التحول الكيميائي للكتل المختلفة بدقة.

الكلمات المفتاحية : NMR-^{1}H، تحول كيميائي، درجة عدم التشبع، البروتونات المجاورة، مكافئ البروتون، اقتران الدوران.

Abstract

The main objective of this work is to know the principles of NMR and the definition of this technique of spectroscopy and how to use it to identify the structures of molecules.

To do this, we have discussed in the first chapter the theory of NMR and its history as well as that mentioned in the classical and quantum model, in addition to explaining the phenomenon of relaxation and the equations of motion.

In chapter two, we talked about the chemical shift, mentioning the different factors that can influence this value. In the third chapter, we studied the spin-spin coupling, which is responsible for the multiplicity of the lines of the NMR spectrum and its different systems.

The last chapter is devoted to analyzing an NMR-^{1}H spectrum by knowing its empirical formula, starting with the rightmost mass.

Finally, and to confirm our assumptions, we used a ChemNMR freeware program to accurately evaluate and precise the chemical shift of the different massifs.

Key words : NMR-^{1}H, chemical shift, degree of unsaturation, neighboring protons, equivalent protons, spin-spin coupling.

Résumé

L'objectif principal de ce travail est de connaître les principes de la RMN et la définition de cette technique de spectroscopie et comment l'utiliser pour identifier les structures de molécules. Pour ce faire, nous avons abordé dans le premier chapitre la théorie de la RMN et sa petite histoire ainsi que celle mentionnée dans le modèle classique et quantique, en plus d'expliquer le phénomène de relaxation et les équations du mouvement.

Dans le chapitre deux, nous avons parlé du déplacement chimique, en mentionnant les différents facteurs qui peuvent influencer cette valeur. Au troisième chapitre, nous avons étudié le couplage spin-spin, qui est responsable de la multiplicité des raies du spectre RMN et de ses différents systèmes.

Le dernier chapitre est consacré à l'analyse d'un spectre RMN-^{1}H en connaissant sa formule brute, en commençant par le massif le plus à droite.

Enfin, et pour confirmer nos hypothèses, nous avons utilisé un programme ChemNMR en freeware pour évaluer avec précision les déplacements chimique des différents massifs.

Mots-clés : RMN-^{1}H, déplacement chimique, degré d'insaturation, protons voisins, protons équivalents, couplage spin-spin.