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Course on Spectroscopic Analysis and separation Methods

(Master 2 option Organic chemistry and didactic of concepts)

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Preface

This handout is intended for second year Master's students with an organic chemistry option and didactic concepts, it concerns analysis and separation methods

The taught program covers various basic concepts on spectral techniques such as infrared, raman, visible UVand NMR spectroscop

This work is the result of the courses I taught in the Methods of Analysis and Separation unit, where concepts were simplified and applications were used to clarify the idea for students.

This document contains four chapters

Chapter1 :**Infrared spectroscopy**

Chapter2 : **Raman spectroscopy**

Chapter 3 : **UV-Visible spectroscopy**

Chapter 4 : **NMR spectroscopy**

.

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Preface

Chapter 1

Infrared Spectroscopy

Master of organic chemistry and didactic of concepts (M2) Methods of analysis and separation

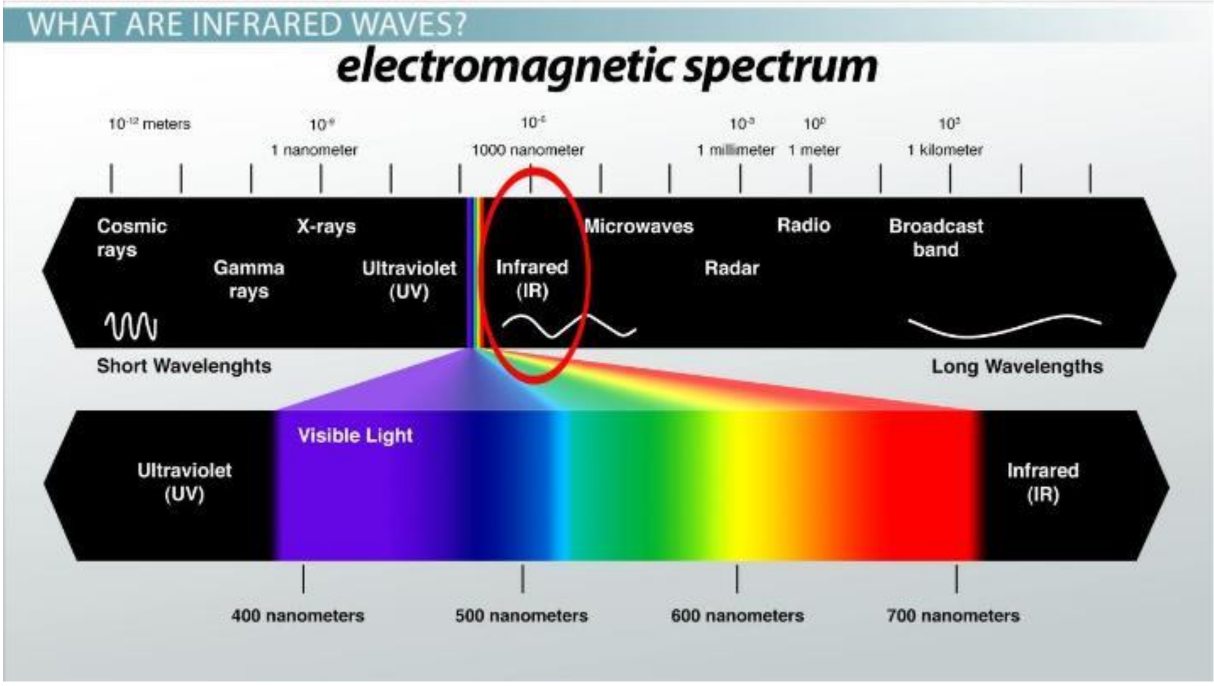
Chapter 1 Infrared spectroscopy

Introduction

Infrared radiation (IR), invisible to the naked eye, is located in the wavelength range greater than 800 nm.

If visible spectroscopy involves transitions between electronic energy levels, infrared spectroscopy concerns the absorption of radiation which causes transitions between the vibration and rotation energy levels of the molecule.

The energy levels used by infrared spectroscopy are those of the vibration energies of molecular bonds.

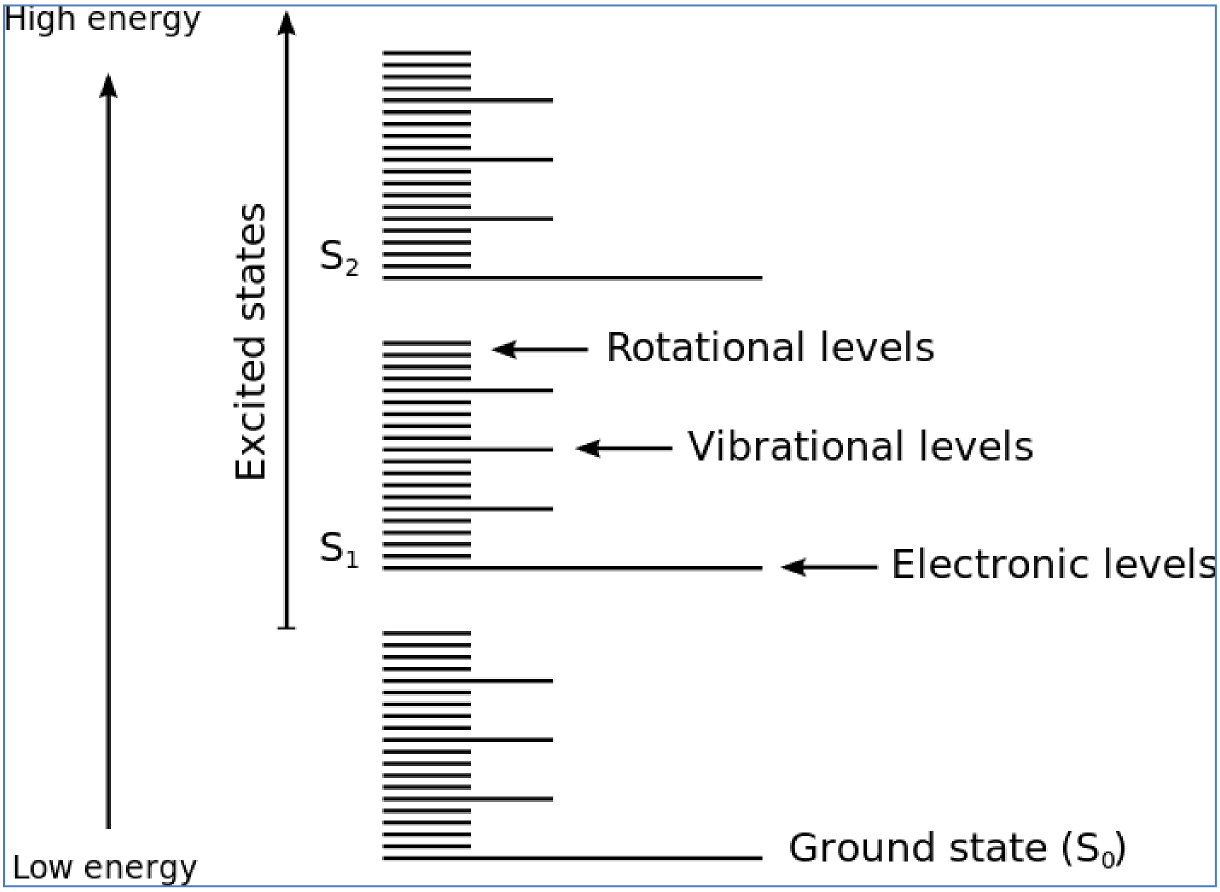


Infrared spectrum

The representation of the spectrum shows that it is possible to use several quantities to characterize an electromagnetic wave. We can use several scales (obviously linked to each other):

- **Frequency ν** in hertz (Hz), but ultimately little used.
- **The wavelength λ** in meters (m but especially nm) used mainly for the UV-visible range
- **The wave number σ**, used in infrared and sometimes for UV-visible (σ is expressed in m^{-1} but especially cm^{-1}).

$$E_{molecule}=E_{electro}+E_{Vib}+E_{rot}+E_{trans}$$



Note: UV-Visible spectroscopy requires higher energy than infrared.

The IR range extends from approximately 700 nm to approximately 50 µm; we distinguish three intervals: the near IR, the middle IR and the far IR represented in the previous spectrum. It should be noted that a vibration mode is active in infrared if the dipole moment of the molecule varies during the vibration.

Ex: CO_2 is a linear molecule: during the symmetrical elongation of CO_2, there is no variation in the dipole moment: this mode is therefore inactive in infrared. For these same reasons, a symmetrical C=C double bond will absorb very little around $1640 cm^{-1}$.

Vibration Modes

When an IR light beam passes through a sample, part of the light is absorbed. It is thanks to this absorption that we will be able to detect the presence of characteristic groups of atoms. The molecules, when passing IR radiation, undergo internal vibration movements (elongation and deformation).

Stretching

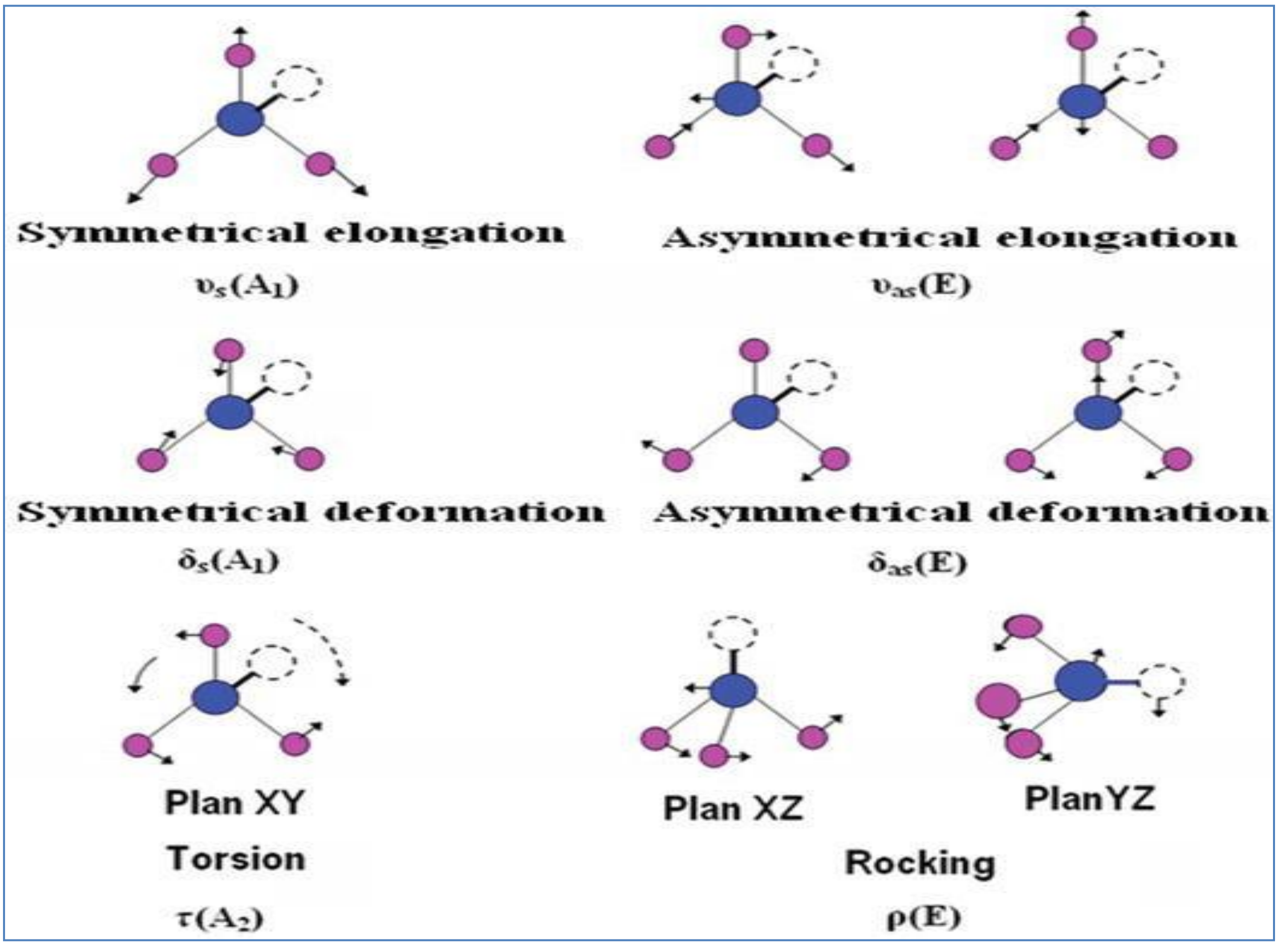
Also called valence vibration or "stretching", this mode concerns the vibration of the molecule along the bonds. The frequency of the electromagnetic wave which induces the elongation vibration is given by the relation:

$$\boxed{\nu\,(Hz) = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}}$$

Where K is the force constant of the bond (considered here as a spring), proportional to the bond energy, and m the reduced mass of the two atoms connected by this bond. Thus, multiple bonds, more energetic than single ones, will have a higher force constant, therefore a vibration frequency (replaced in practice by the wave number) higher than those of single bonds between identical atoms: C– C absorbs around 1100, C=C around 1600 and C≡ C around 2100. On the other hand, X–H bonds, where X is any atom (C, N, O, etc.), will have a higher elongation frequency than that of a C–X bond, because the reduced mass μ y is smaller: for C–H, $\mu = 0.92$ a.u.; for C–C, $\mu = 6$ a.u.

Deformations in and out of plane.

In addition to the valence vibration, the angle of the bonds can vary: there is bending or deformation. These deformations can take place in the plane of the two connections concerned (we denote them δ) or outside the plane (we denote them γ or δ). There is also the possibility of symmetrical and asymmetrical deformations. here are some examples :



Chapter 1 Infrared spectroscopy

Calculation of normal modes of vibration

*Linear molecules

3N-5

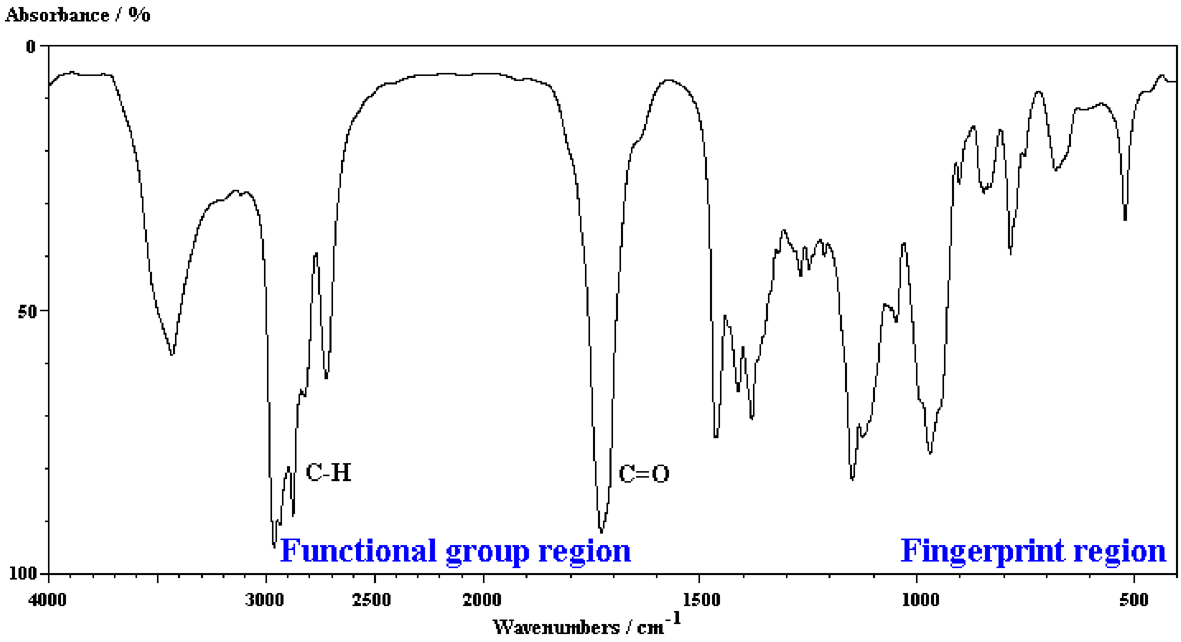
N:Number of atoms

*Nonlinear molecules

3N-6

Zones of the Infrared spectrum

There are two main zones in an IR spectrum: A first zone on the left corresponding to a wave number greater than 1400 cm^{-1} where the characteristic bands of the bonds of the molecule are found. A second zone on the right corresponding to a wave number lower than 1400 cm^{-1}, called a “fingerprint” which we will not be able to analyze because of its complexity.

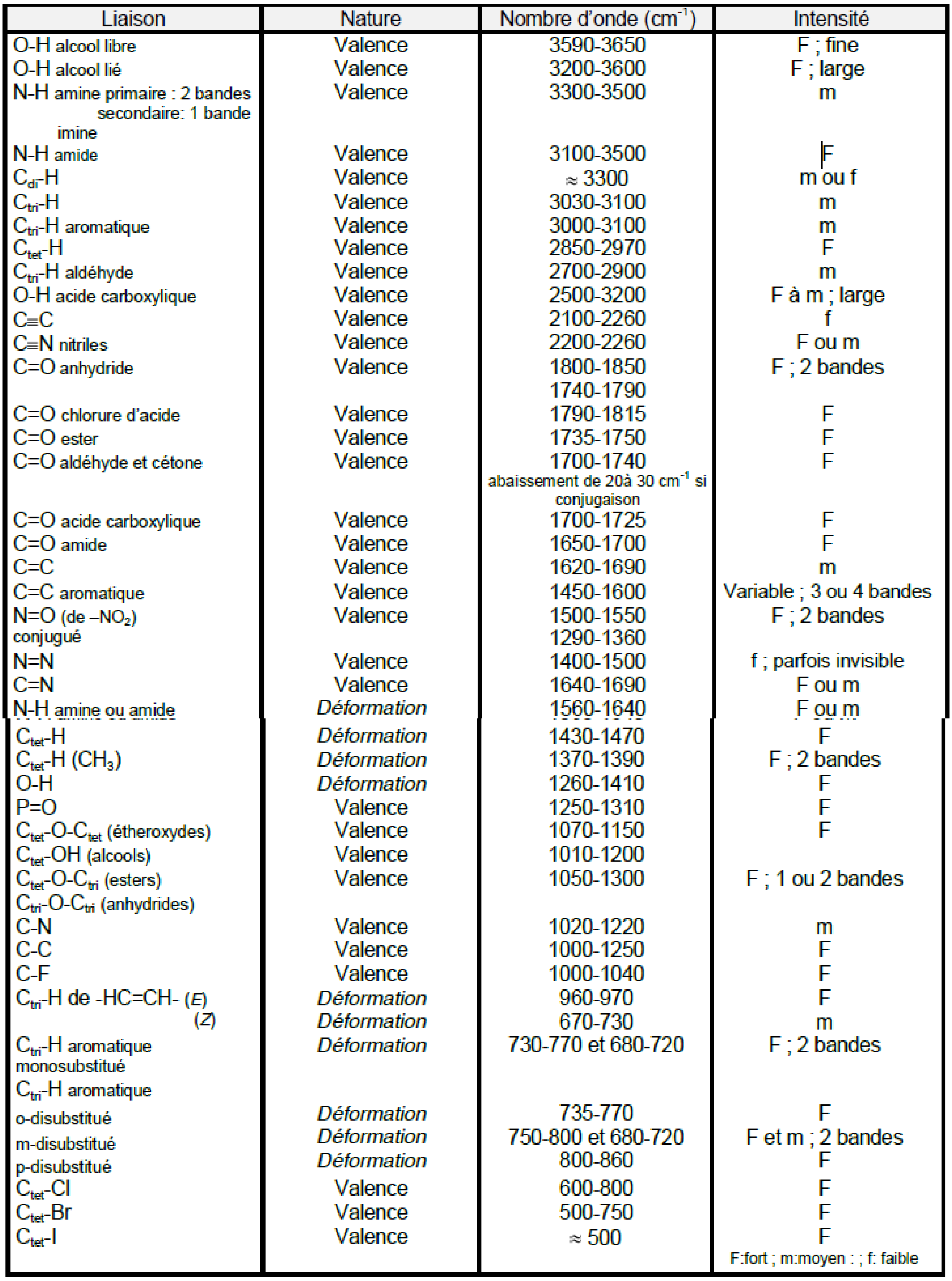


Functional groups

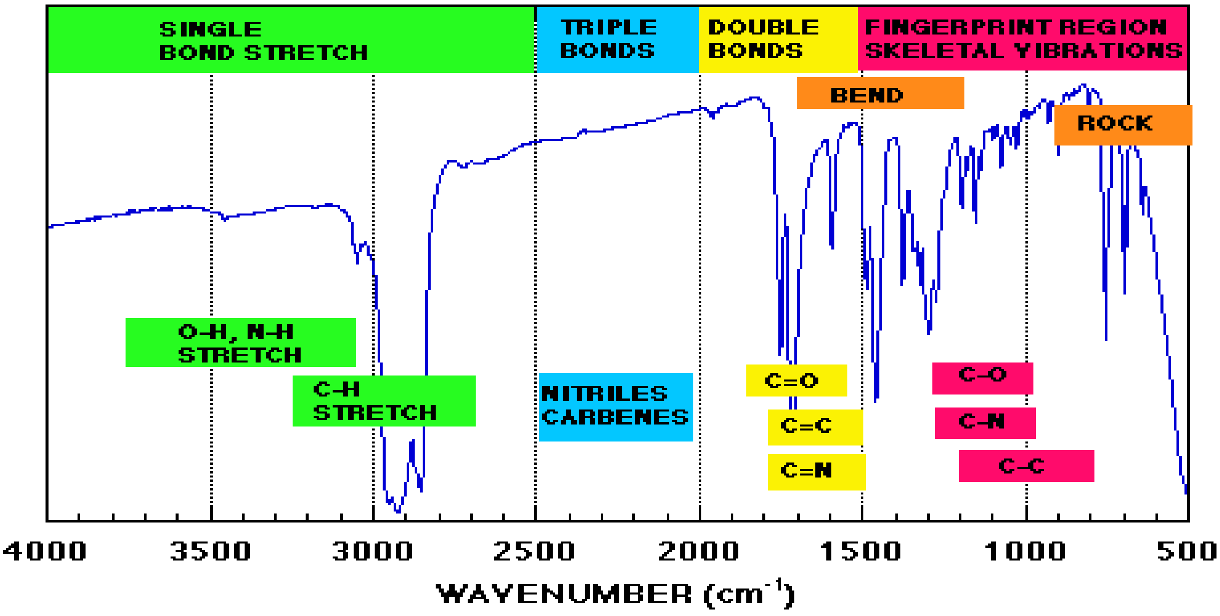
The most common groupings of atoms (also called functional groups) detectable by IR spectrum are:

- Alcohols
- Carboxylic acids
- Aldehydes
- Ketones
- Esters
- Amines
- Amides

Beyond detecting these groups, it is difficult to obtain sufficient information of an IR spectrum to be able to deduce the entire structure of the molecule, especially for alkanes and alkenes. In order to identify the functional groups present in a molecule, we arrange the table following which contains some bonds from some families of compounds:



Liaison	Nature	Nombre d'onde (cm^{-1})	Intensité
O-H alcool libre	Valence	3590-3650	F ; fine
O-H alcool lié	Valence	3200-3600	F ; large
N-H amine primaire : 2 bandes secondaire: 1 bande imine	Valence	3300-3500	m
N-H amide	Valence	3100-3500	F
C_{di}-H	Valence	≈ 3300	m ou f
C_{tri}-H	Valence	3030-3100	m
C_{tri}-H aromatique	Valence	3000-3100	m
C_{tet}-H	Valence	2850-2970	F
C_{tri}-H aldéhyde	Valence	2700-2900	m
O-H acide carboxylique	Valence	2500-3200	F à m ; large
C≡C	Valence	2100-2260	f
C≡N nitriles	Valence	2200-2260	F ou m
C=O anhydride	Valence	1800-1850 1740-1790	F ; 2 bandes
C=O chlorure d'acide	Valence	1790-1815	F
C=O ester	Valence	1735-1750	F
C=O aldéhyde et cétone	Valence	1700-1740 abaissement de 20à 30 cm^{-1} si conjugaison	F
C=O acide carboxylique	Valence	1700-1725	F
C=O amide	Valence	1650-1700	F
C=C	Valence	1620-1690	m
C=C aromatique	Valence	1450-1600	Variable ; 3 ou 4 bandes
N=O (de $-NO_2$) conjugué	Valence	1500-1550 1290-1360	F ; 2 bandes
N=N	Valence	1400-1500	f ; parfois invisible
C=N	Valence	1640-1690	F ou m
N-H amine ou amide	*Déformation*	1560-1640	F ou m
C_{tet}-H	*Déformation*	1430-1470	F
C_{tet}-H (CH_3)	*Déformation*	1370-1390	F ; 2 bandes
O-H	*Déformation*	1260-1410	F
P=O	Valence	1250-1310	F
C_{tet}-O-C_{tet} (étheroxydes)	Valence	1070-1150	F
C_{tet}-OH (alcools)	Valence	1010-1200	
C_{tet}-O-C_{tri} (esters) C_{tri}-O-C_{tri} (anhydrides)	Valence	1050-1300	F ; 1 ou 2 bandes
C-N	Valence	1020-1220	m
C-C	Valence	1000-1250	F
C-F	Valence	1000-1040	F
C_{tri}-H de -HC=CH- (*E*)	*Déformation*	960-970	F
(*Z*)	*Déformation*	670-730	m
C_{tri}-H aromatique monosubstitué	*Déformation*	730-770 et 680-720	F ; 2 bandes
C_{tri}-H aromatique			
o-disubstitué	*Déformation*	735-770	F
m-disubstitué	*Déformation*	750-800 et 680-720	F et m ; 2 bandes
p-disubstitué	*Déformation*	800-860	F
C_{tet}-Cl	Valence	600-800	F
C_{tet}-Br	Valence	500-750	F
C_{tet}-I	Valence	≈ 500	F
			F:fort ; m:moyen : ; f: faible



The hydrogen bond

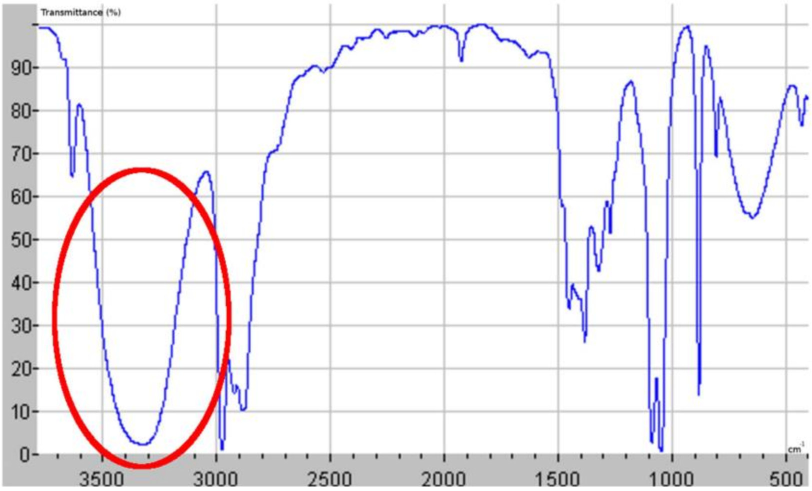
The hydrogen bond is an electrical interaction between molecules. Without hydrogen bonding, for example, there is no water in the solid or liquid state. Because of the different electronegativities of the atoms making up the water molecule (H20), there will be a surplus of electrons at the oxygen atom (the most electronegative) and a deficit of electrons at the two hydrogen atoms (the least electronegative). The percentage of transmittance of the IR spectrum and the shape of the absorption bands will be modified by the presence of this hydrogen bond.

OH free

In the gaseous state, a strong and thin absorption band around 3620cm-1 is characteristic of O-H bonding. there is no hydrogen bond between the ethanol molecules in this physical state; the O-H bond is called “free O-H”. The same behavior will be observed when the alcohol is very diluted.

OH bound

In the liquid state, a strong and broad absorption band from 3200cm-1 to 3400cm-1 is characteristic of the O-H bond. Hydrogen bonds established between alcohol molecules weaken O-H bonds. This then implies a widening of the band. The O-H bondis in this case called “O-H linked”.



Exercise 1

Calculation of the number of unsaturation

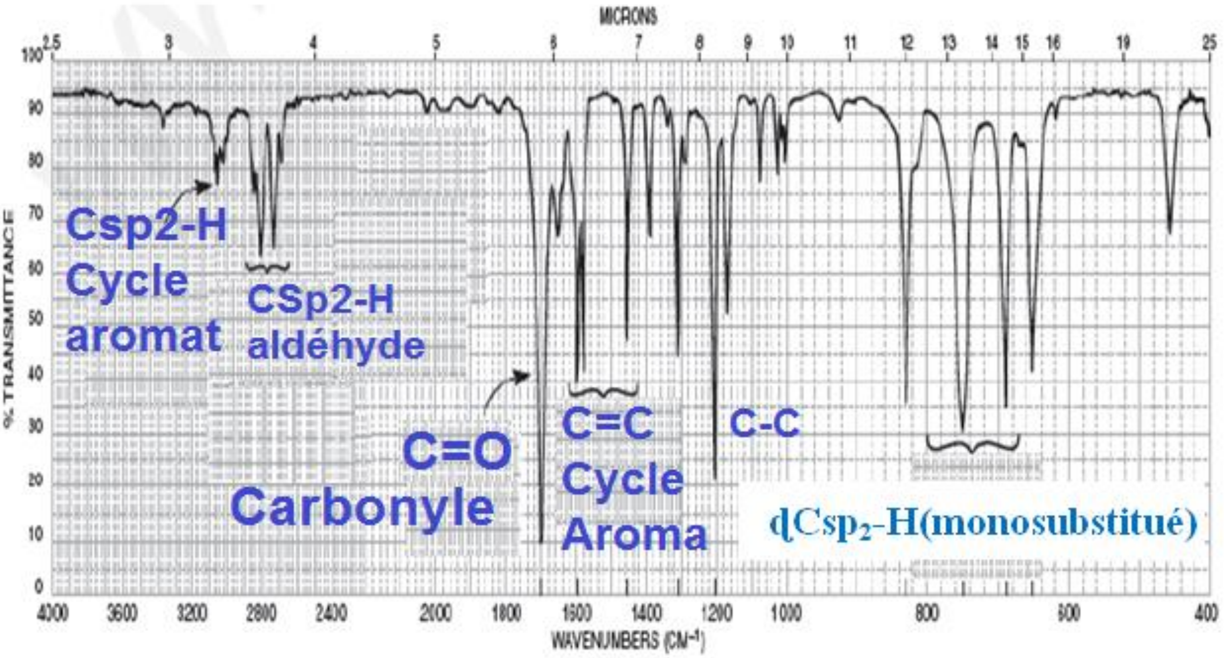
CxHyOzNwXx

DBE=(2x-y+w-x+2)/2

DBE=14-6+2/2

DBE==5

C_7H_6O



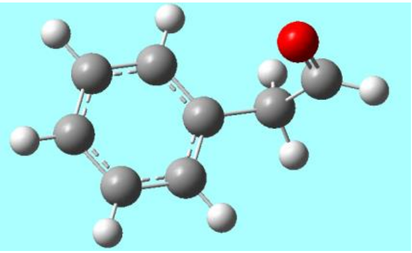
We notice after using the reference table for IR:

-The presence of an aromatic ring (bands between 1450cm^{-1} and 1600cm^{-1})

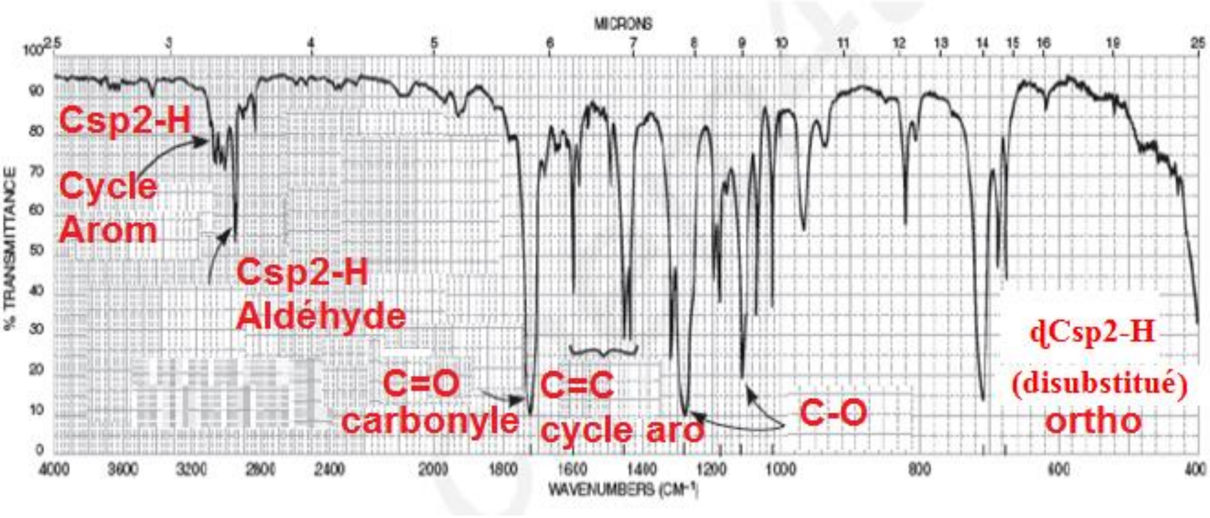
-The presence of an intense band corresponding to a C=O function (aldehyde)

-The presence of two intense bands of C-H deformation of the aromatic ring between 600 and 800 cm^{-1} which corresponds to the monosubstituted cycle.

The final structure of the compound



$C_8H_8O_2$



DBE=16-8+2/2

DBE=5

We notice after using the reference table for IR:

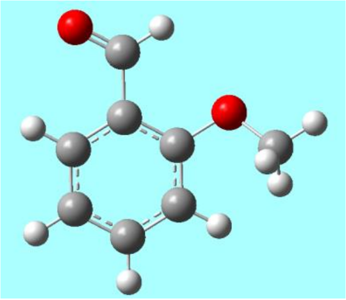
-The presence of an aromatic ring (bands between 1450cm-1 and 1600cm-1)

-The presence of an intense band corresponding to a C=O function (aldehyde)

-The presence of two bands between 1000 and 1200 cm-1 corresponding to the C-O bond

-The presence of an intense C-H deformation band of the aromatic ring between 600 and 700 cm-1 which corresponds to the disubstituted (ortho) ring.

The final structure of the compound



Chapter2 Raman spectroscopy

Introduction

Since its discovery at the beginning of the 20th century, Raman spectroscopy has revolutionized scientific research in several fields. Researchers and experimenters around the world have dedicated themselves to exploiting this physical phenomenon with the aim of pushing the limits of technology as we know it today. this technique opens up applications in the biological or medical field,because the Raman scattering of water is very weak, which allows its use as a solvent.

History of Raman spectroscopy

Raman spectroscopy or the Raman effect, was discovered in 1928 by the physicist Sir Chandrashekhara Ventaka Raman and his student Sir Kariamanickam Srinivasa Krishnan. His research on this physical phenomenon earned him the 1930 Nobel Prize in Physics. This phenomenon , based on the interaction of light with matter, is commonly used to study both organic and inorganic substances down to the molecular level.

Principle of Raman spectroscopy

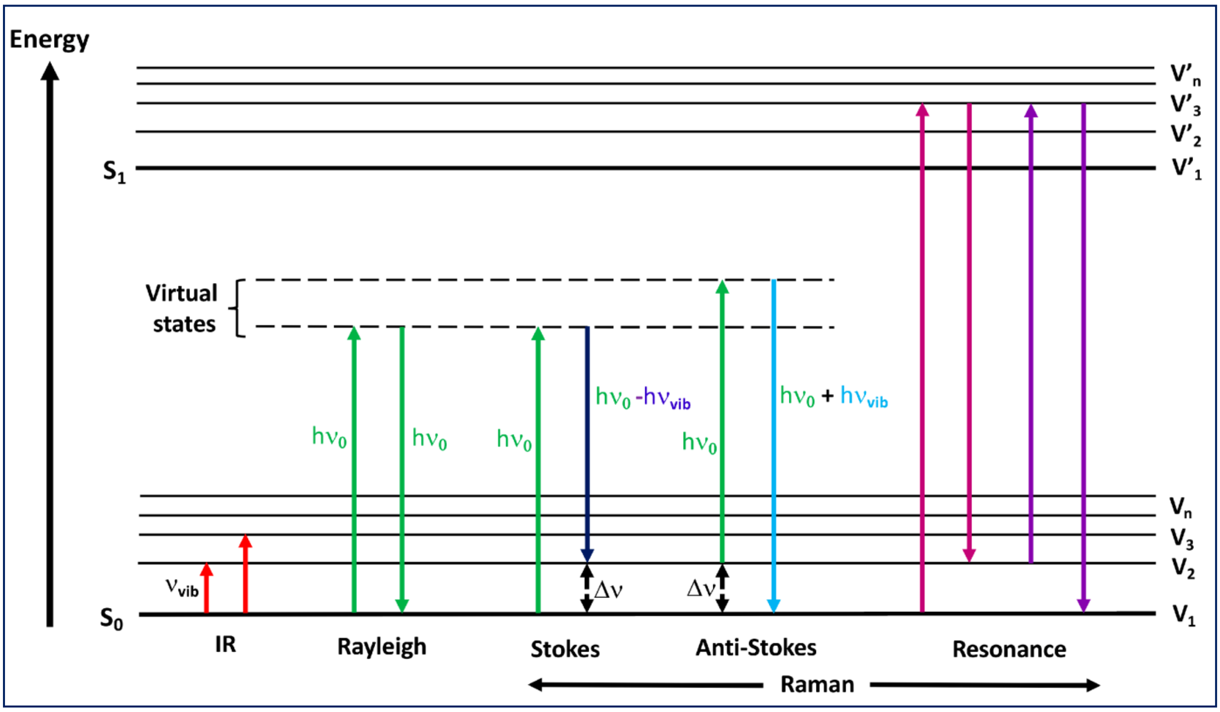
As like infrared (IR) spectroscopy, Raman spectroscopy provides access to vibrational and rotational levels of molecules. The process involved is linked to a variation in the polarizability of the molecule during a vibrational transition. Unlike IR spectroscopy, of which it is nevertheless complementary by its rules of selection, Raman spectroscopy has long remained a little-used method despite the many attractive advantages it presents. First of all, sample preparation can be reduced to a minimum since it is possible to work in the liquid, gaseous or solid state. an electromagnetic wave interacts with the vibrations of atoms. A photon interacts with a phonon. If the incident photon has the same energy as a vibration level, there is absorption of the photon, principle of infrared spectroscopy. If the incident photon has an energy much higher than the vibration energy levels, we observe a phenomenon diffusion (Raman Spectroscopy).

Diffusion phenomenon

When a transparent sample is subjected to a monochromatic electromagnetic wave, most of the incident beam is transmitted, but a small part of the light is scattered (change in direction of propagation not obeying the laws of geometric optics). The frequency analysis of this scattered light then high lights:

-A component of the same wavelength as the incident beam, Elastic diffusion $1/10^4$.

-A component of wavelength different from the incident beam, Inelastic diffusion, here RAMAN diffusion $1/10^8$



A fraction of the incident radiation is:

-Is diffused at the same frequency as that of the incident radiation ν0, this is elastic light diffusion called: Rayleigh diffusion.

-If it is diffused at a frequency ν different from that of the incident radiation, it will be inelastic light diffusion, called: Raman diffusion.

In the case of Raman scattering:

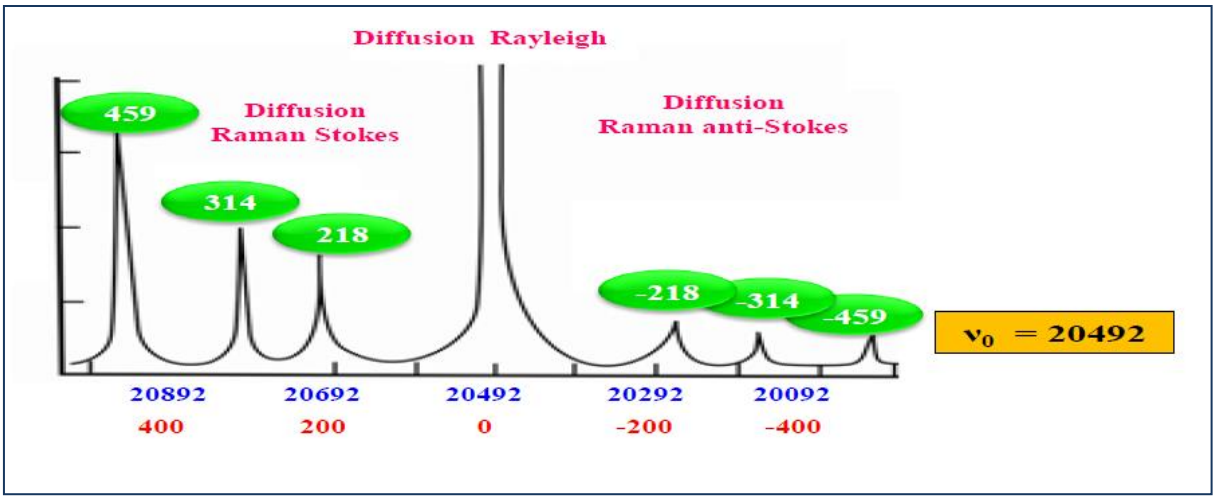
- If $\nu > \nu_0$: Anti-Stokes photon process scattered at higher energy. The molecule in an excited state has given up to the incident photon a quantity of energy corresponding to the vibration energy during the transition from the excited state E1 (v=1) to the ground state E0 (v=0).
- If $\nu < \nu_0$: Stokes process the photon scattered at lower energy. The incident photon transferred to the molecule at rest a quantity of energy corresponding to the vibration energy necessary for the transition from the ground state E0 (v=0) to the excited state E1 (v=1).

Remarks

1. The anti-Stokes process only concerns electrons in the excited state, which is a smaller population than that of electrons in the ground state. This is at the origin of the amplification of the Raman Stokes intensities compared to the anti-Stokes Raman intensities.

2. Regardless of the frequency of the incident radiation, we always obtain the same Raman spectrum. It is therefore important to use a monochromatic light source to avoid the superposition of several Raman spectra.

An example of the Raman spectrum



Selection rules and vibration symmetry

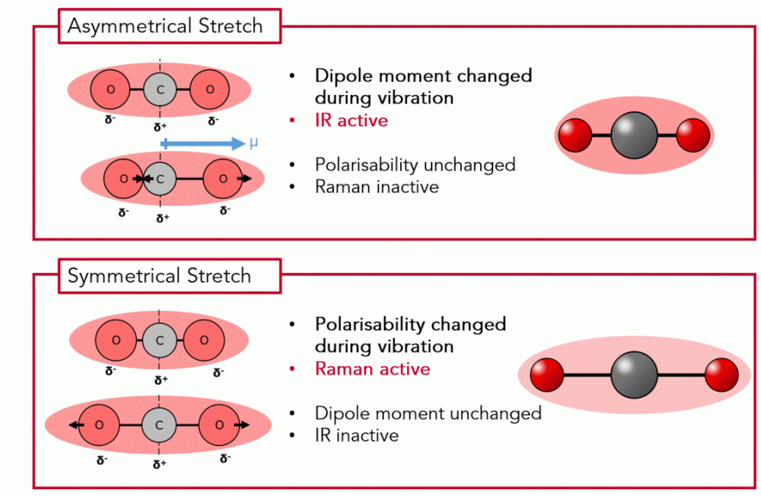
In Infrared spectroscopy: An active vibration is accompanied by a change in the dipole moment.

In Raman spectrometry: An active vibration is accompanied by a change in polarizability.

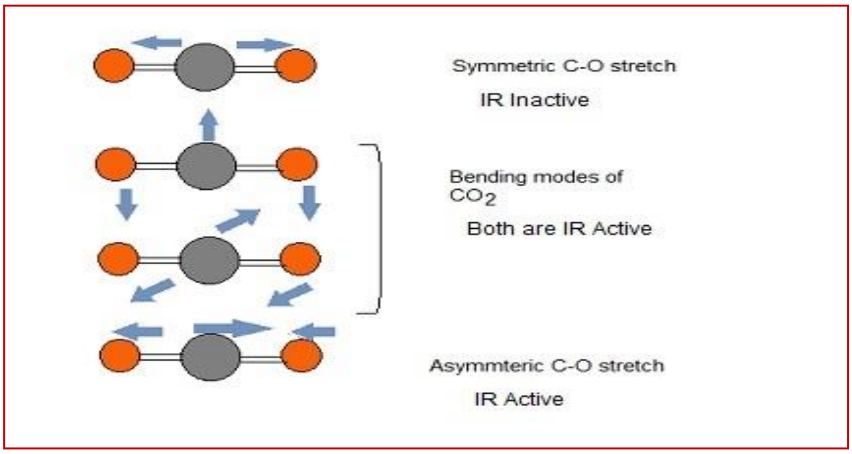
Polarizability is due to a momentary deformation of the electronic cloud distributed around a bond.

Example 1: Homonuclear molecules (N_2, Cl_2, H_2…)

Elongation causes a change in polarizability without changing the dipole moment



Example: Molecule CO_2



Exercise 1

1-What is the difference between Raman spectroscopy and infrared spectroscopy.

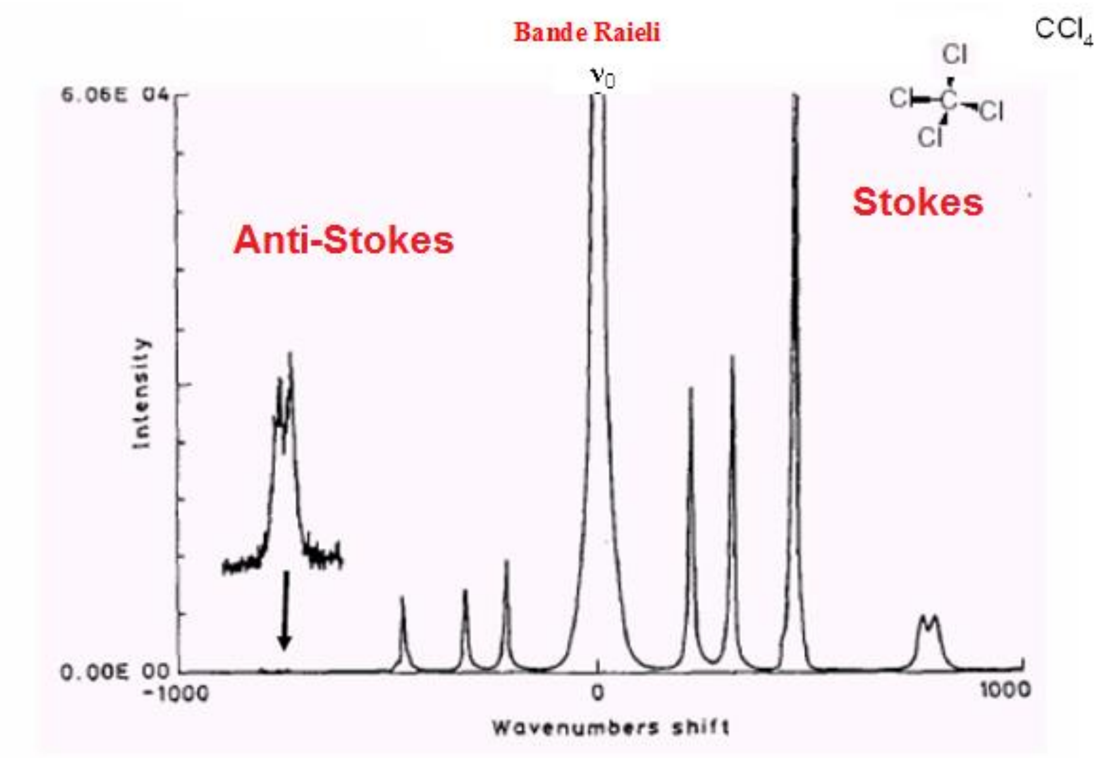
Infrared	Raman
Existence of dipole moments inside the molecule	**the polarizability of the bonds and the variability thereof during vibration.**
selection rule $\Delta J = \pm 1$	**selection rule** $\Delta J = \pm 2$
Absorption and transmission phenomenon	**Dispersion phenomenon**

2-What are the shortcomings of Raman spectroscopy?

1-limitation of databases which concern spectra.
2-The difficulty of doing Raman scattering for certain samples, particularly polyatomic molecules.
3- Very expensive technique.
4- Difficulty of sample preparation and choice of lasers.
5- Raman scattering can be completely hidden by fluorescence.

Exercise 2

- Here is the Raman spectrum of CCl4 explaining the bands of the latter



- The Raieli Band is the ν_0 exciting band
- If $\nu > \nu_0$: Anti-Stokes photon process scattered at higher energy. The molecule in an excited state has given up to the incident photon a quantity of energy corresponding to the vibration energy during the transition from the excited state E1 (v=1) to the ground state E0 (v=0).
-If $\nu < \nu 0$: Stokes process the photon scattered at lower energy. The incident photon transferred to the molecule at rest a quantity of energy corresponding to the vibration energy necessary for the transition from the ground state E_0 (v=0) to the excited state E1 (v=1).

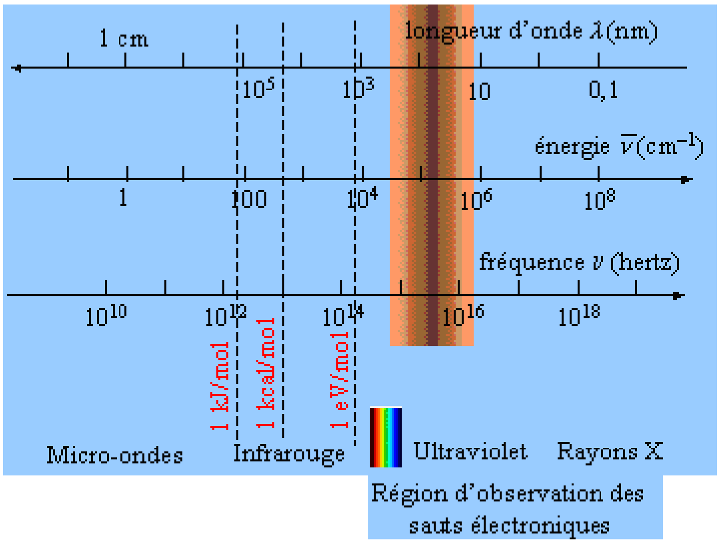
Master of organic chemistry and didactic of concepts (M2)

Methods of analysis and separation

Chapter 3 UV-Visible spectroscopy

Introduction

In a molecule, electronic transitions take place in the ultraviolet region (approximately 400-10 nm) and visible (800-400 nm).
-visible: 800 nm (red) - 400 nm (indigo)
-near-UV: 400 nm - 200 nm
-Far-UV: 200 nm - 10 nm.
The range of the ultraviolet spectrum usable in analysis extends from approximately 190 to 400 nm.
The visible spectrum ranges from approximately 400 to 800 nm. The UV or visible spectrum does not allow the identification of a product but that of the chromophore group it contains.
Electromagnetic radiation is characterized by the wavelength λ, or the frequency ν.**$\nu = c / \lambda$**

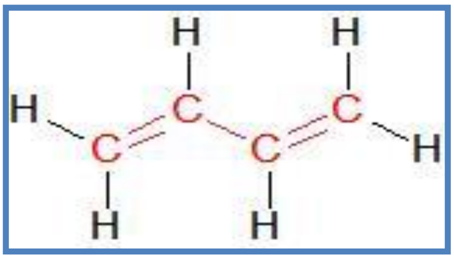


Spectre électromagnétique

Initial definitions

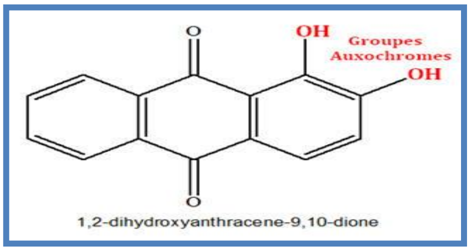
Chromophore group:

unsaturated functional groups carrying such electrons are called "chromophore". A chromophore is a function or group of atoms that modify the frequency of the wave as well as the absorption intensity (ε). covalent unsaturated group responsible for absorption (C=C, C=O, C=N, C≡C, C≡N, C=S, N=N …).



Auxochrome group:

saturated group linked to a chromophore and which modifies the wavelength and intensity of maximum absorption. Ex.: OH, NH_2, Cl…



Bathochrome effect:

The chromophore decreases the absorption frequency (increases the λ max). Shift of absorption towards longer wavelengths due to substitution or solvent effect.

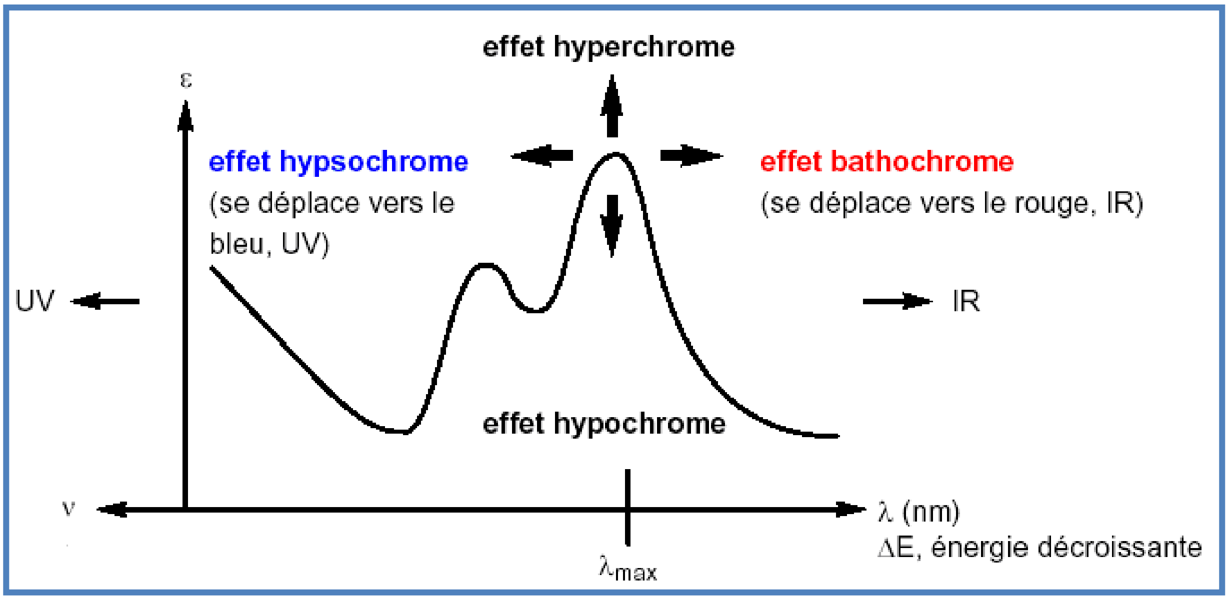
Hypsochrome effect:

The chromophore increases the absorption frequency (decreases the λ max). Shift of absorption towards shorter wavelengths due to substitution or solvent effect.

Hypochromic effect: the chromophore reduces the absorption intensity (decreases ε).

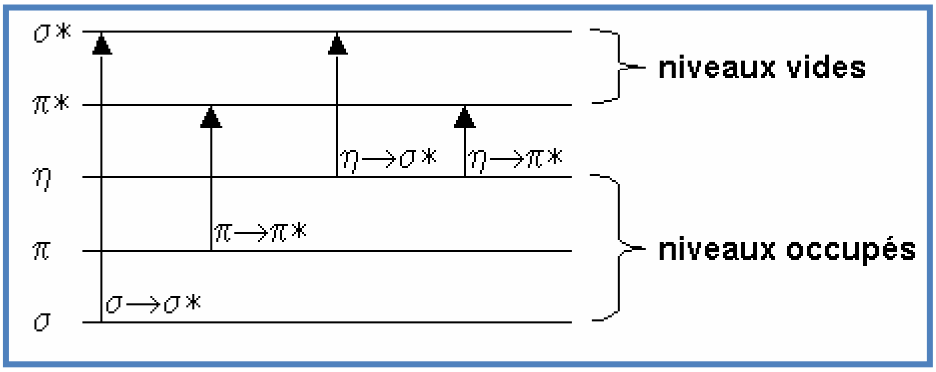
Hyperchrome effect: the chromophore increases the absorption intensity (increases ε).

These effects are illustrated in the following figure:



Transitions and selection rules

An electronic transition is analyzed as a population change between a fundamental molecular orbital HOMO (Highest Occupied Molecular Orbital) and a excited molecular orbital LUMO (Lowest Unoccupied Molecular Orbital). When she instead, the matter absorbs a photon whose energy corresponds to the energy difference between the fundamental term and an excited term. But all energetically possible transitions are not permitted.
The permitted transitions are those which cause a variation of the dipole moment electric. Furthermore, a permitted transition takes place if the orbitals involved during this processes are such that **$\Delta l = \pm 1$** et **$\Delta S = 0$**. In other words, the photon changes the symmetry of the orbital occupied by the electron before and after the transition but does not change the spin of this electron.



σ -σ*transition

The great stability of σ bonds in organic compounds means that the transition of an electron from a σ-bonding OM to an σ* anti-bonding OM requires a lot of energy. The corresponding absorption band is intense and located in the far-UV, around 130 nm.
The compounds concerned are alkanes for example

n -π*transition

This transition results from the passage of an electron from a non-bonding OM n to an anti-bonding OM π*. This type of transition takes place in the case of molecules comprising a heteroatom carrying free electronic doublets belonging to an unsaturated system. The best known band is that which corresponds to the carbonyl band located between 270 and 280 nm. The molar absorption coefficient is low.

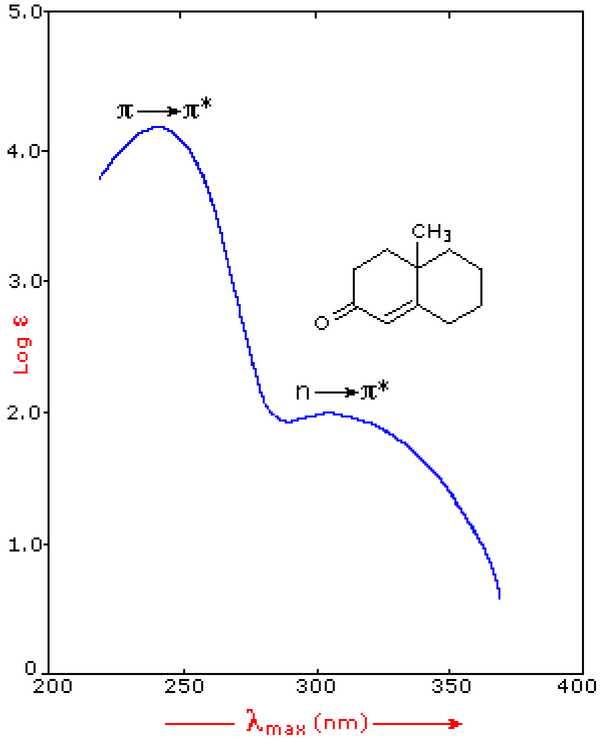
n - σ*transition

The transfer of an electron from the n doublet of a heteroatom (O, N, S, Cl..) to a level σ* is observed for alcohols, ethers, amines as well as for halogenated derivatives. This transition gives a band of average intensity which is located at the extreme limit of the near-UV.

π -π*transition

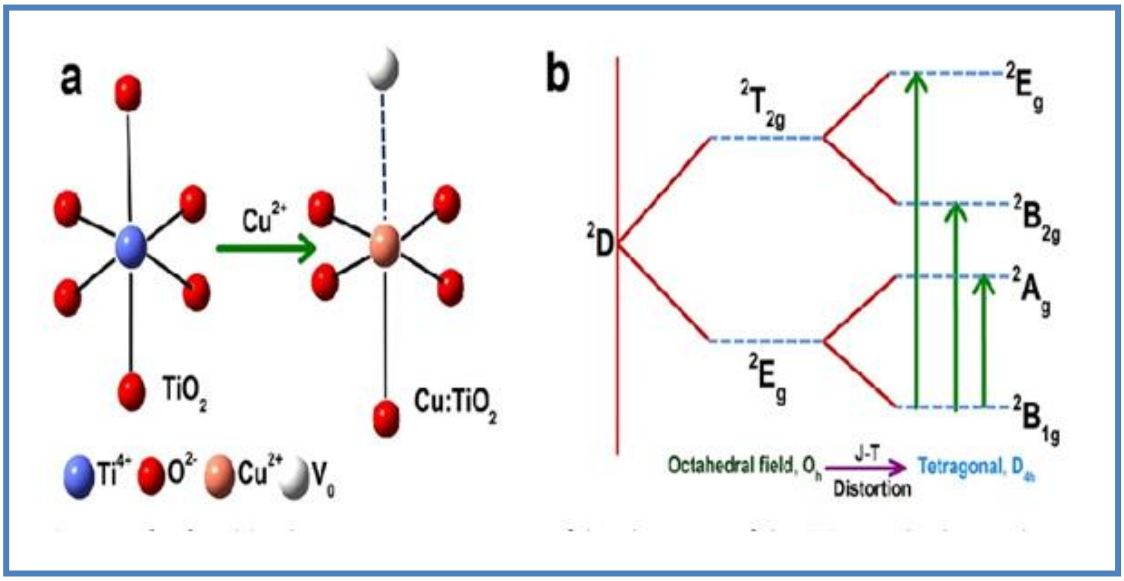
The electronic transition in compounds with an isolated double bond leadsat a strong absorption band around 165-200 nm. Example: ethylene λmax = 165 nm.

The transitions **n → π***and **n → σ*** have a relatively low intensity because they are in prohibited parts.



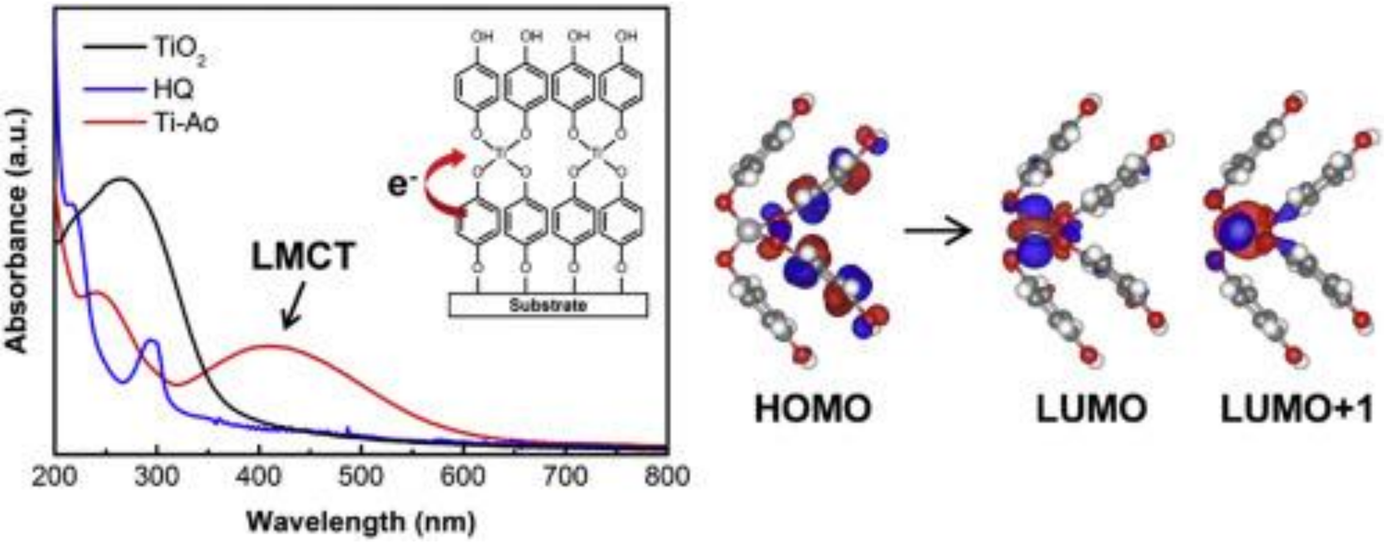
d-d transitions

In transition metal complexes, we witness, under the effect of the crystal field, a lifting of degeneracy of the orbitals d. In general, these complexes are colorful. Absorptions in the visible are most often due to a transition of an electron from a populated d orbital to an empty d orbital.The energy differences between the d orbitals which occur in these d-d transitions depend on the metal, its degree of oxidation, the coordination geometry and the nature of the ligand.



Charge transfer transitions

A compound that is transparent in a spectral range can become absorbent if it is placed in presence of a species with which it interacts by a donor-acceptor type mechanism (D-A). This phenomenon is linked to the passage of an electron belonging to a binding orbital of thedonor (the nucleophilic partner) towards a vacant orbital of the acceptor (the electrophile), of a close energy level. The transition is called charge transfer transition.

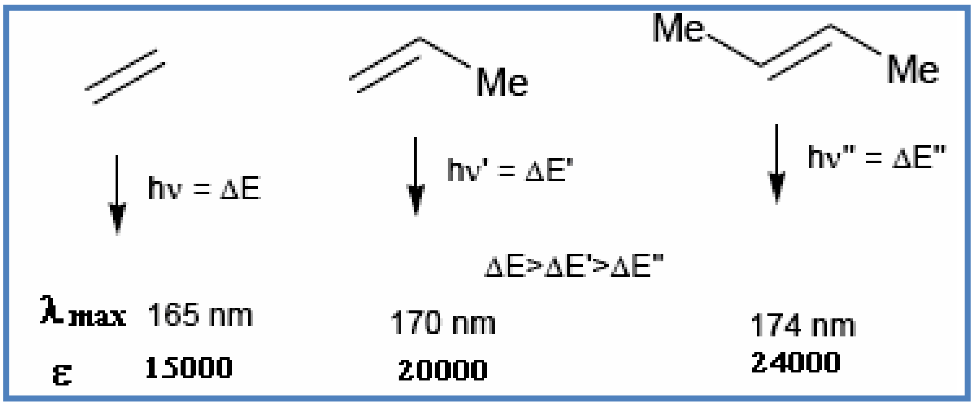


Donor-acceptor transfer mechanism HOMO: high occupied orbital LUMO: Low empty orbital Passage of an electron belonging to a binding orbital of the donor (the nucleophilic partner) to a vacant orbital of the acceptor (the electrophile), of a close energy level. Position of the absorption band depending on the ionization potential of the donor and the electronic affinity of the acceptor

Factors Affecting Wavelength

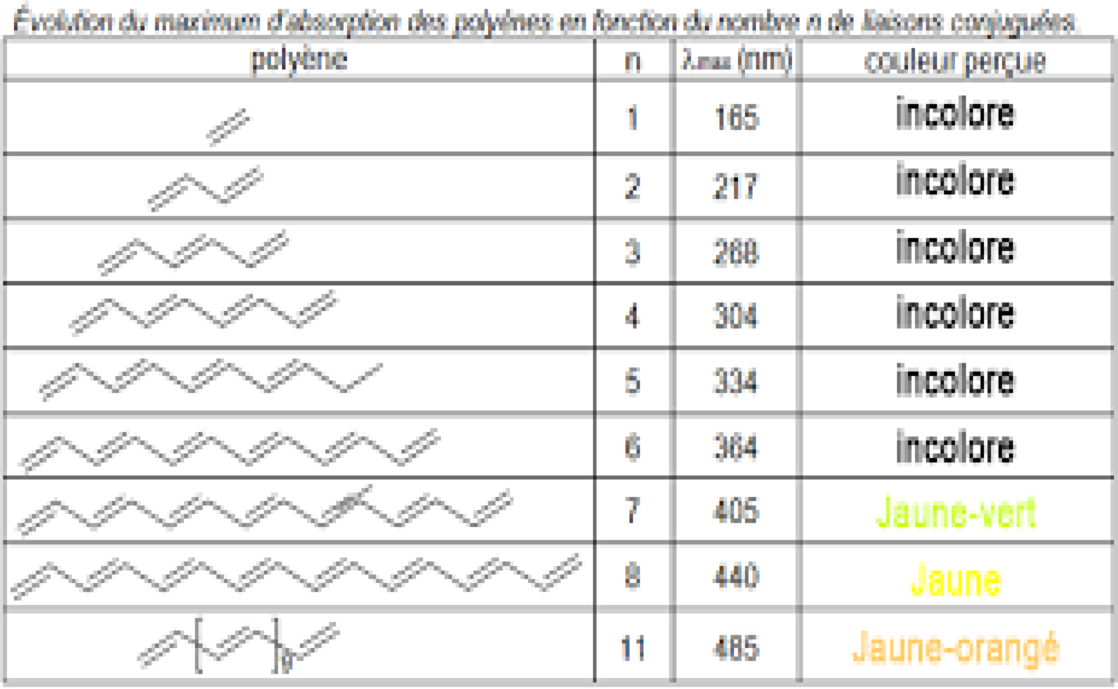
Effect of substitution

The donor inductive effect causes a bathochrome effect, this is the case of the presence of alkyl groups on double bonds.



Effet de la conjugaison

The increase in conjugation causes a bathochrome effect. In fact, the relocation of π electrons translates the ease of these electrons to move along the molecule, and it is accompanied by a rapprochement of energy levels..



Évolution du maximum d'absorption des polyènes en fonction du nombre n de liaisons conjuguées

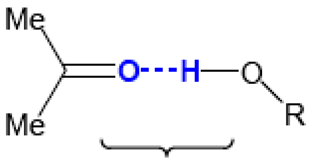
polyène	n	λ_{max} (nm)	couleur perçue
	1	165	incolore
	2	217	incolore
	3	268	incolore
	4	304	incolore
	5	334	incolore
	6	364	incolore
	7	405	Jaune-vert
	8	440	Jaune
	11	485	Jaune-orangé

Solvent effect

Position, intensity and shape of absorption bands of compounds in solution function of the solvent. These physical solute-solvent interactions change energy difference between ground state and excited state.

Excited state more polar than ground state: excited form more stabilized by a polar solvent.

- **λ decreases by increasing the polarity of the solvent**
- **Case of the transition n □□□* : Ex. ment carbonyle groupe of Ketones functions**

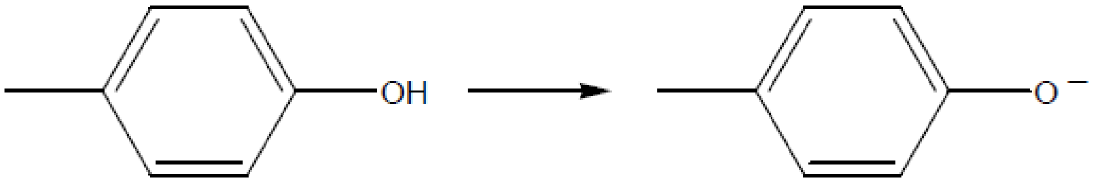


stabilisation de n(CO) par pont-H
(en stabilisant l'état fondamental on rend la transition électronique plus difficile, d'énergie plus élevée)

Bond $^{\delta+}$**C=O**$^{\delta-}$ stabilized by polaire solvant. More energy to cause the transition.

The excited state more polar than the ground state: excited form more stabilized by a polar solvent. λ increases by increasing the polarity of the solvent.

In water, spectrum sensitive to pH which modifies the ionization of certain chemical functions.



$\lambda_{max} = 274$ nm $\lambda_{max} = 295$ nm

Application of UV-Visible spectroscopy :

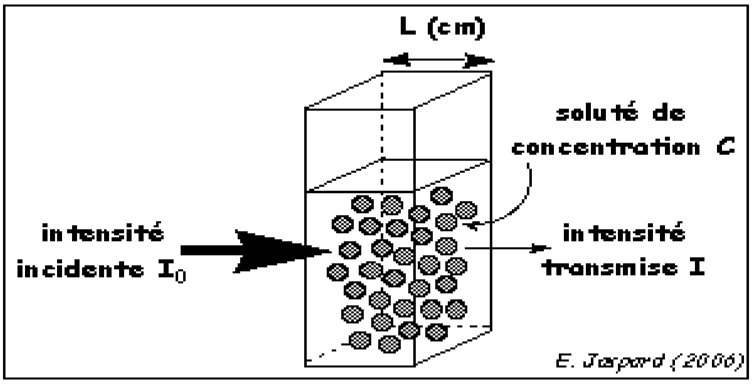
Qualitative analysis

UV-Visible spectrometry is not useful for characterizing organic compounds; the spectra present few bands which are not characteristic. Indeed, different chromophore groups can absorb at the same wavelength due to displacements due to their environment.

Quantitative analysis

When the spectrum of a molecule or an ion is known, UV-Visible spectrometry is very useful for quantitative analysis. We apply the law of **Beer Lambert :** $A = \varepsilon.C.l$

We consider a tank of length l, crossed by radiation of wavelength **λ** and the intensity **I0**. A compound in concentrated solution (C) is introduced into this tank. If there is absorption, the ray will come out with an intensity **I (I < I0).**



Beer Lambert's law establishes a link of proportionality between the absorbance A and the concentration C.

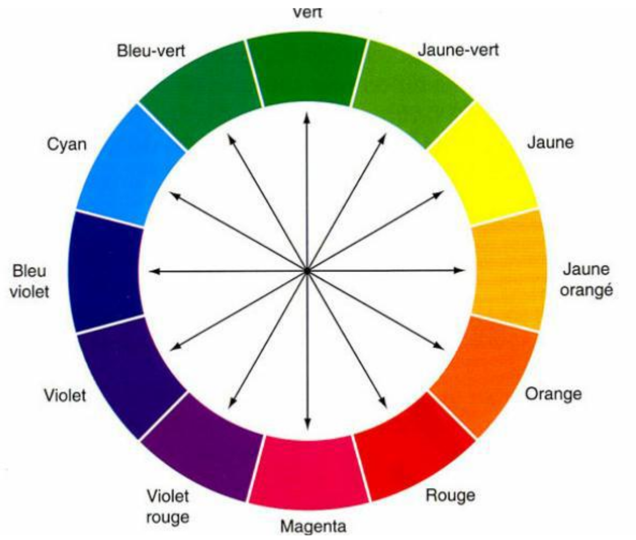
ε : extinction coefficient or molar absorption coefficient ($\text{mol}^{-1}.\text{L}.\text{cm}^{-1}$) . absorbance A is also called optical density (d.o).

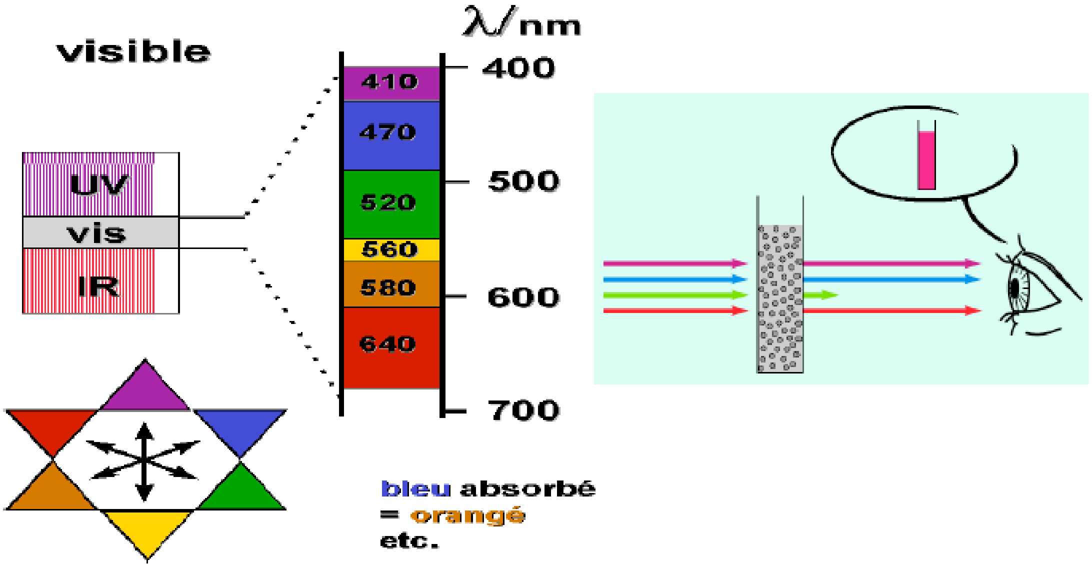
The Beer-Lambert law is additive. This means that the absorbance A, measured in a tank of thickness l of a mixture of two compounds 1 and 2 in solution in the same solvent, will be identical to the absorbance measured after passing through two tanks of the same thickness l, placed one after the other, one containing compound 1 and the other compound 2 (taken at the same concentrations as in the initial mixture). By giving the indices 1 to compound 1 and 2 to compound 2, we will therefore have:

$$A = A_1 + A_2 = l(\varepsilon_1 C_1 + \varepsilon_2 C_2)$$

Color of chemical species:

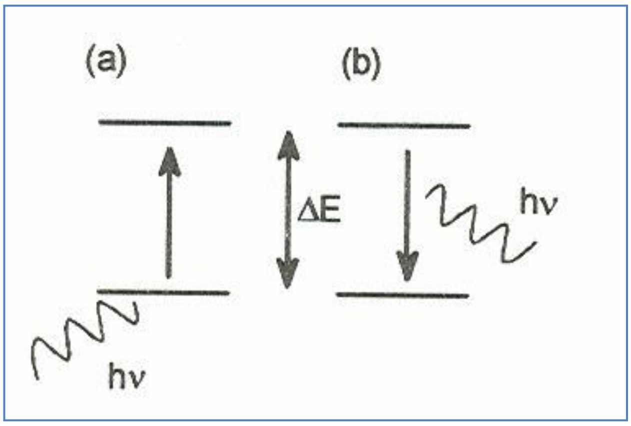
If the absorbance maximum corresponds to a wavelength belonging to the ultraviolet range (200 - 400 nm), then it is colorless. If λ_{max} belongs to the visible range (400 - 800 nm) then the chemical species has the color complementary to that corresponding to λ_{max}. The color wheel below represents some colors. We can know the complementary (absorbed) color: it is the one located opposite (indicated by an arrow).





Absorption and emission phenomena

Absorption: It is an electronic transition from a lower energy orbital to a higher energy orbital. It involves the photon of energy.
Emission: It is an electronic transition from a high energy orbital to a lower energy orbital. It also involves the photon of energy.

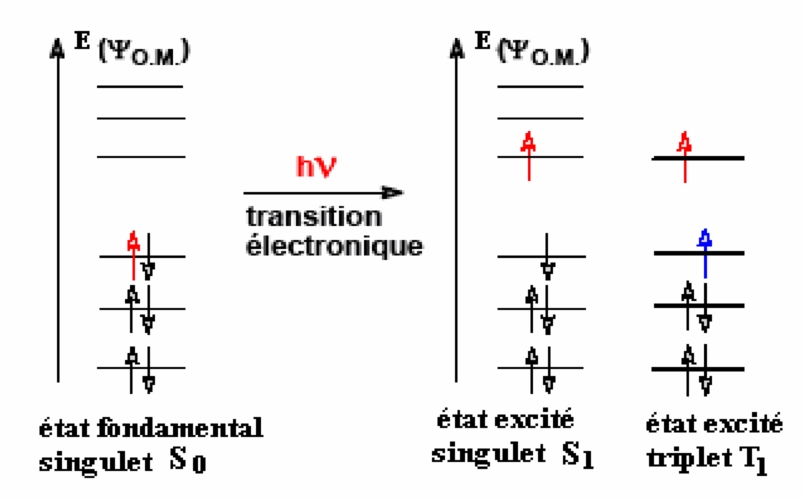


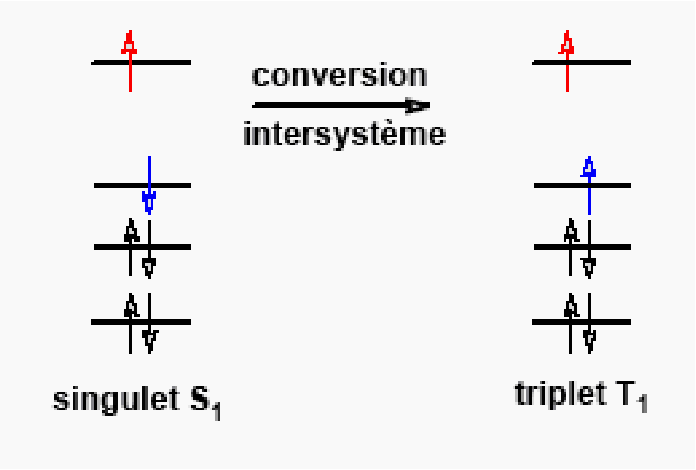
Deexcitation of molecules – fluorescence and Phosphorescence

En absorbant un photon, the molecule goes from the ground state to an excited state (phenomenon which lasts 10-16 s). Once in the excited state, the molecule will not be able to maintain itsenergy for a very long time. After the absorption stage, the captured energy can be restored either by a non-radiative process or by a radiative process (emission ofphotons).

Fluorescence

Fluorescence is the emission of light corresponding to the energy jump of the excited state singlet S1 to the ground state singlet S_0 ($S_1 \rightarrow S_0$).The molecule, initially at rest in the fundamental electronic state S_0, is found carried instantly after absorption of a photon in one of the states vi of the state S_1. Very quickly (10^{-12} s), by processes called internal conversion, the molecule joins without emit photon state v_0 of level S_1.





Chapter 3 UV-Visible spectroscopy

Exercise 1

Calculation of concentration of cobalt and nickel

Beer-Lambert law

$$A=\varepsilon.C.l$$

l=1cm

Wave length (nm)	Absorbance	ε
365	$A_1=0.814$	$\varepsilon_{Co}=3529$, $\varepsilon_{Ni}=3228$
700	$A_2=0.056$	$\varepsilon_{Co}=428.9$, $\varepsilon_{Ni}=0$

We have the absorbance of the solution at each wavelength equal to the sum of the absorbances of the metals.

$$A_1= \varepsilon_{Co}\ C_{Co}+ \varepsilon_{Ni}\ C_{Ni}$$
$$A_2= \varepsilon_{Co}\ C_{Co}+ \varepsilon_{Ni}\ C_{Ni}$$

By replacing the quantities in the equations with the values given in the table

$$0.814= 3529\ C_{Co}+ 3228\ C_{Ni}$$
$$0.056= 428.9\ C_{Co}+ 0$$

$C_{Co}= 0.056/428.9$

$C_{Co}=1.305.10^{-4}$ mol/l

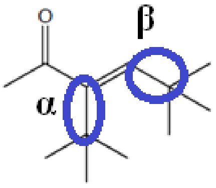
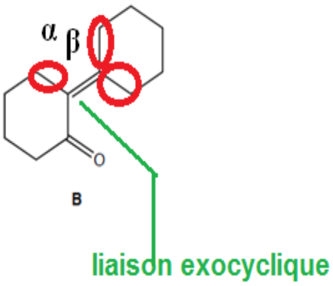
By replacing in equation 1

$0.814= 3529\ .1.305.10^{-4}+ 3228\ C_{Ni}$

$C_{Ni}=0.814-3529.1.\ 305.10^{-4}/3228$

$C_{Ni}=1.095.10^{-4}$ mol/l

Exercise 2

Compound	Calculated Wave length	Wave length(exp)
 A	λ_{max}(standard)=215 nm R(α)+R(β)=10+12=22nm λ_{max}(Calculated)=237 nm	λ_{max}(exp)=236 nm
 B	λ_{max}(standard)=215 nm R(α)+2R(β)=10+2*12=34nm (=)=5nm λ_{max}(Calculated)=254 nm	λ_{max}(exp)=256 nm

Chapter4 NMR spectroscopy

Introduction

Nuclear magnetic resonance (NMR) is a spectroscopic technique used to identify the structure of compounds (liquid or solid), to characterize their atomic sequence, and to obtain information on the environment (nature of close neighbors) of atomic nuclei. . This analysis method is powerful and very efficient, used both in structural analysis and in quantitative analysis. The NMR phenomenon corresponds to a selective absorption of energy by nuclei possessing a magnetic moment, placed in a magnetic field and irradiated by an electromagnetic wave. The combination of a powerful device and a computer can lead to exceptional results.

Properties of nuclei

Nuclei have: Mass, electric charge, magnetism, spin.

- If the first 2 properties are obvious, it is not the same for the last two, because they do not have a macroscopic equivalent, on our scale.
- It turns out that nuclei interact with magnetic fields, and can therefore be considered microscopic magnets.
- The concept of spin is less obvious. Roughly, we can admit that the nuclei rotate on themselves, like a planet or a top. We then represent the atom with an arrow (a vector), to represent the spin angular momentum (roughly the direction).
- Magnetism and spin are intrinsic properties of nuclei.

Objective

NMR is mainly used for the structural determination of chemical molecular compounds. It specifies the structural formula and the stereochemistry of the molecules. It is of particular importance in organic chemistry, biochemistry and macromolecular chemistry (polymers, gels, materials). It has also proven itself in the characterization of biological and mineral molecules (glass, ceramics, etc.) and has found applications in the agri-food (quality control) and pharmaceutical fields. Finally, NMR medical imaging (known as MRI), known to the general public, as well as in vivo NMR are developing strongly today.

Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance is part of so-called spectroscopy techniques, that is to say techniques which study the electromagnetic radiation absorbed by matter.

A) A source emits electromagnetic radiation (light, for example).

B) This radiation passes through a monochromator, to select only part of the radiation.

C) The material will generally absorb part of the incident radiation. The emitted radiation is detected after passing through matter.

D) The difference between the incident ray and the detected radiation gives us a characteristic spectrum of the material studied.

Chapter4 NMR spectroscopy

Principle

All atomic nuclei have a rotating charge, identified as nuclear spin (they are comparable to small magnets and therefore can present a nuclear magnetic moment).

- Note: Some nuclei are not observable in NMR. because they do not have magnetic properties.

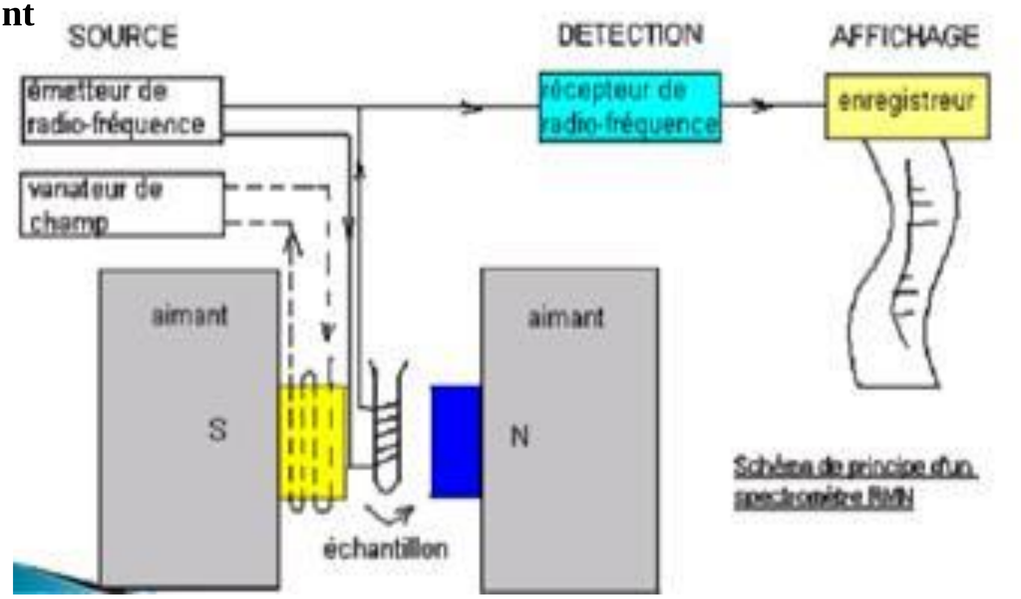
Under the action of a uniform external magnetic field, the atomic nucleus (its nuclear magnetic moment) can take different orientations.

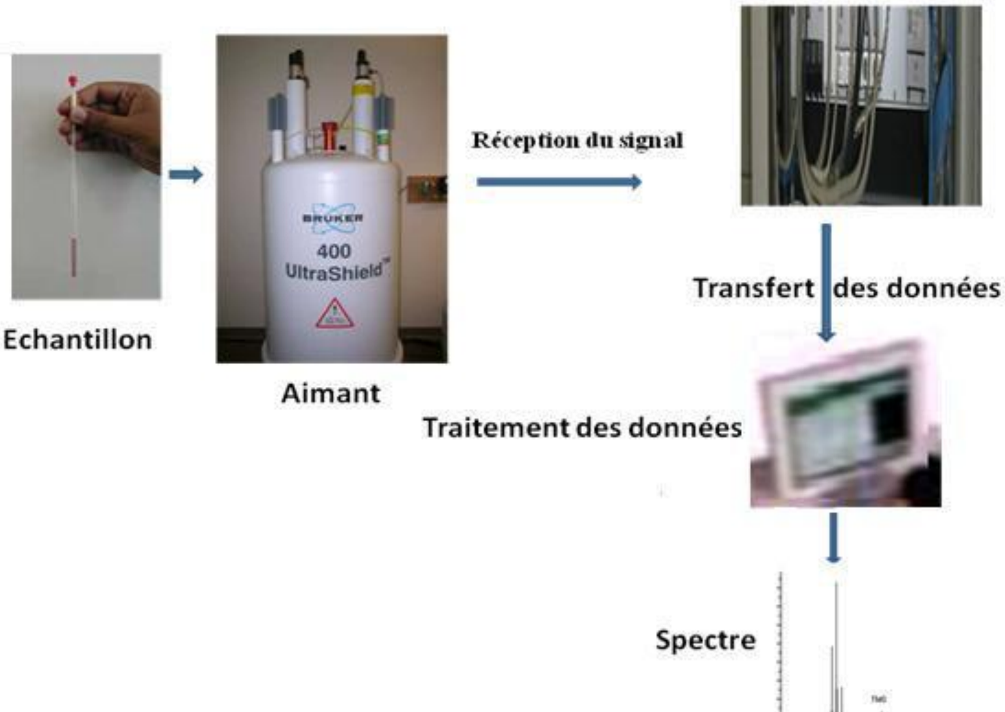
- These different orientations correspond to different energy levels:

- One of low energy, if the magnetic moment is parallel and in the same direction as the external field,

- The other of higher energy, if the direction is opposite.

Equipment





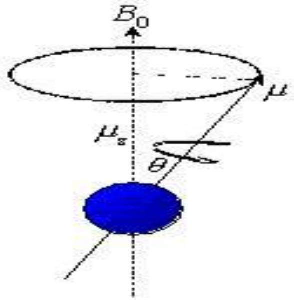
To have an answer in NMR, the spin number of a nuclide must be non-zero, therefore the numbers of mass A (or nucleons) and atomic number Z (number of protons) must not be simultaneously even. For example:

Cores 13C (A=13 and Z=6) and 19F (A=19 and Z=9) will give a resonance signal, while cores 12C (A=12 and Z=6) and 16O (A=16 and Z=8) cannot be studied by NMR.

We can remember that only nuclei with an odd number of nucleons (protons and neutrons) have a non-zero spin and are suitable for NMR. Sensitivity also varies enormously between nuclei.

NMR spectrometry (Nuclear Magnetic Resonance) is based on the magnetic properties of certain atomic nuclei. We will only study NMR. of the proton therefore of the nucleus of the hydrogen atom 1H.

The rise of NMR in chemistry is due to the particular specificity of the 1H isotope of the hydrogen atom. The hydrogen nucleus is made up of a single particle, the proton. It has a very high natural abundance (99.98%), and has a strong magnetic moment μ, which gives great sensitivity, and therefore ease of observation of resonance signals. It behaves like a compass, which aligns with the Earth's magnetic field. μ aligns with any static magnetic field.



Core shielding

When a molecule is subjected to an external magnetic field, this field not only acts on the nuclear spins, but at the same time it induces; in a plane perpendicular to its direction, acirculation of electrons around the proton. Hence the existence of an internal magnetic field.

- This field can be added to the external field: this is the phenomenon of deshielding
- This field can oppose the external field: this is the shielding phenomenon. The more intense the shielding, the stronger the proton must be subjected to an external field for resonance to occur. This results in a shift of the absorption peaks towards the right of the spectrum. The opposite in the case of deshielding.

Example

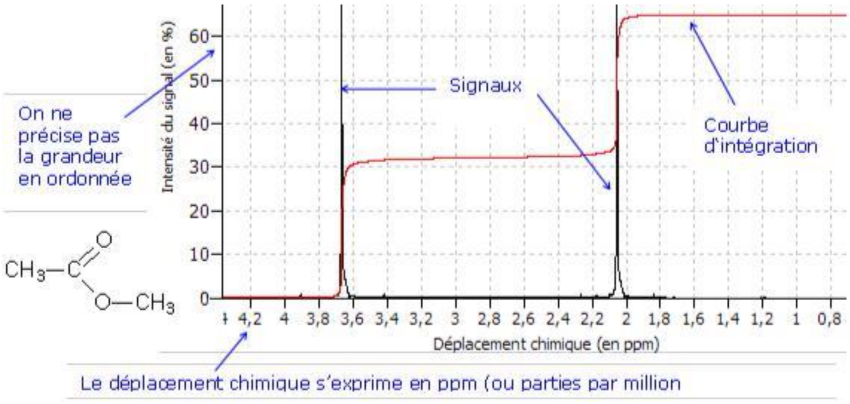
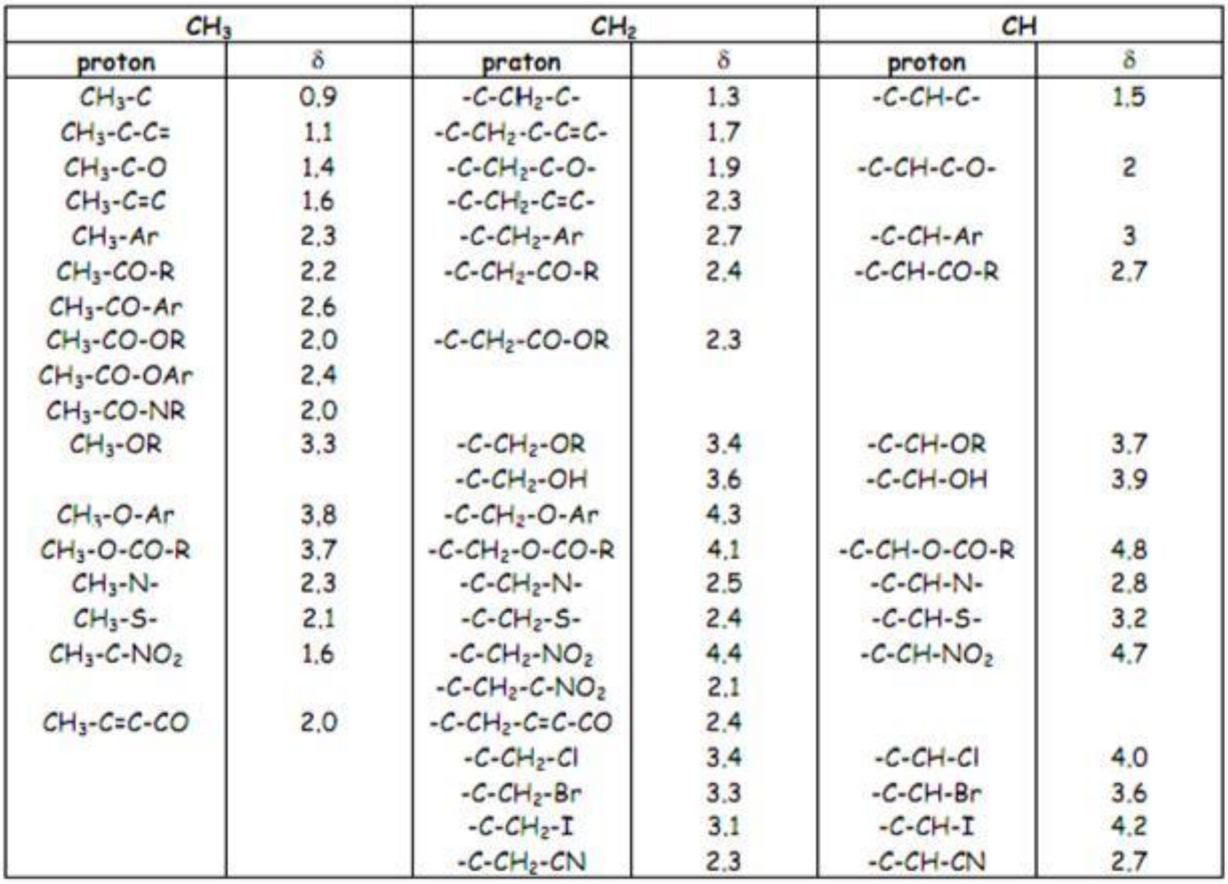
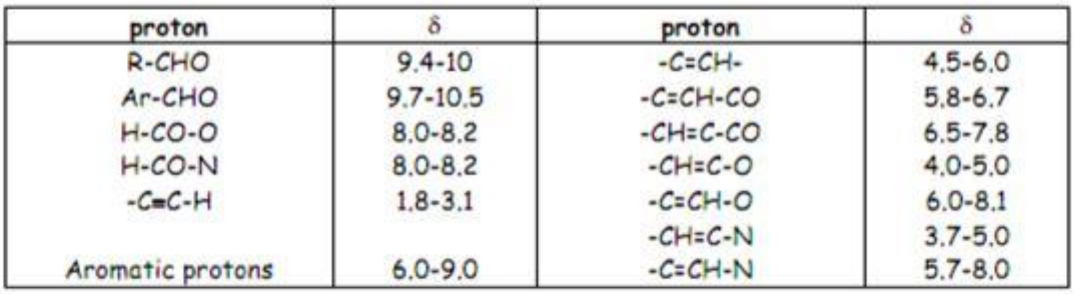


Table ^1H



CH_3		CH_2		CH	
proton	δ	praton	δ	proton	δ
CH_3-C	0,9	$-C-CH_2-C-$	1,3	$-C-CH-C-$	1,5
$CH_3-C-C=$	1,1	$-C-CH_2-C-C=C-$	1,7		
CH_3-C-O	1,4	$-C-CH_2-C-O-$	1,9	$-C-CH-C-O-$	2
$CH_3-C=C$	1,6	$-C-CH_2-C=C-$	2,3		
CH_3-Ar	2,3	$-C-CH_2-Ar$	2,7	$-C-CH-Ar$	3
CH_3-CO-R	2,2	$-C-CH_2-CO-R$	2,4	$-C-CH-CO-R$	2,7
$CH_3-CO-Ar$	2,6				
$CH_3-CO-OR$	2,0	$-C-CH_2-CO-OR$	2,3		
$CH_3-CO-OAr$	2,4				
$CH_3-CO-NR$	2,0				
CH_3-OR	3,3	$-C-CH_2-OR$	3,4	$-C-CH-OR$	3,7
		$-C-CH_2-OH$	3,6	$-C-CH-OH$	3,9
CH_3-O-Ar	3,8	$-C-CH_2-O-Ar$	4,3		
$CH_3-O-CO-R$	3,7	$-C-CH_2-O-CO-R$	4,1	$-C-CH-O-CO-R$	4,8
CH_3-N-	2,3	$-C-CH_2-N-$	2,5	$-C-CH-N-$	2,8
CH_3-S-	2,1	$-C-CH_2-S-$	2,4	$-C-CH-S-$	3,2
CH_3-C-NO_2	1,6	$-C-CH_2-NO_2$	4,4	$-C-CH-NO_2$	4,7
		$-C-CH_2-C-NO_2$	2,1		
$CH_3-C=C-CO$	2,0	$-C-CH_2-C=C-CO$	2,4		
		$-C-CH_2-Cl$	3,4	$-C-CH-Cl$	4,0
		$-C-CH_2-Br$	3,3	$-C-CH-Br$	3,6
		$-C-CH_2-I$	3,1	$-C-CH-I$	4,2
		$-C-CH_2-CN$	2,3	$-C-CH-CN$	2,7



proton	δ	proton	δ
$R-CHO$	9,4-10	$-C=CH-$	4,5-6,0
$Ar-CHO$	9,7-10,5	$-C=CH-CO$	5,8-6,7
$H-CO-O$	8,0-8,2	$-CH=C-CO$	6,5-7,8
$H-CO-N$	8,0-8,2	$-CH=C-O$	4,0-5,0
$-C\equiv C-H$	1,8-3,1	$-C=CH-O$	6,0-8,1
		$-CH=C-N$	3,7-5,0
Aromatic protons	6,0-9,0	$-C=CH-N$	5,7-8,0

Carbon 13C NMR spectrometry

Theory

The ^{12}C core is magnetically inactive (I = 0), but the 13C core with I=1/2 is active. However, as the natural abundance of 13C is only 1.1% its sensitivity in NMR is very low. Spectra recording requires significant quantities of material and fairly long acquisition times long.

The advantage of the low abundance of 13C is the absence of C-C coupling. In Indeed, the probability that two 13C isotopes are located near each other is very weak.

On the other hand, the abundance of 1H (99.98%) means that there is coupling of 1H with the

13C, the 13C spectra thus exhibit very overlapping multiplets difficult to interpret protons over a wide frequency range eliminates these couplings, which makes it possible to obtain a 13C spectrum composed only of singlets.

The scale of chemical shifts is much larger than that of proton 1H, it extends over around 200 ppm. The intensities of the peaks on a 13C spectrum are not correlated with the number of carbon atoms.

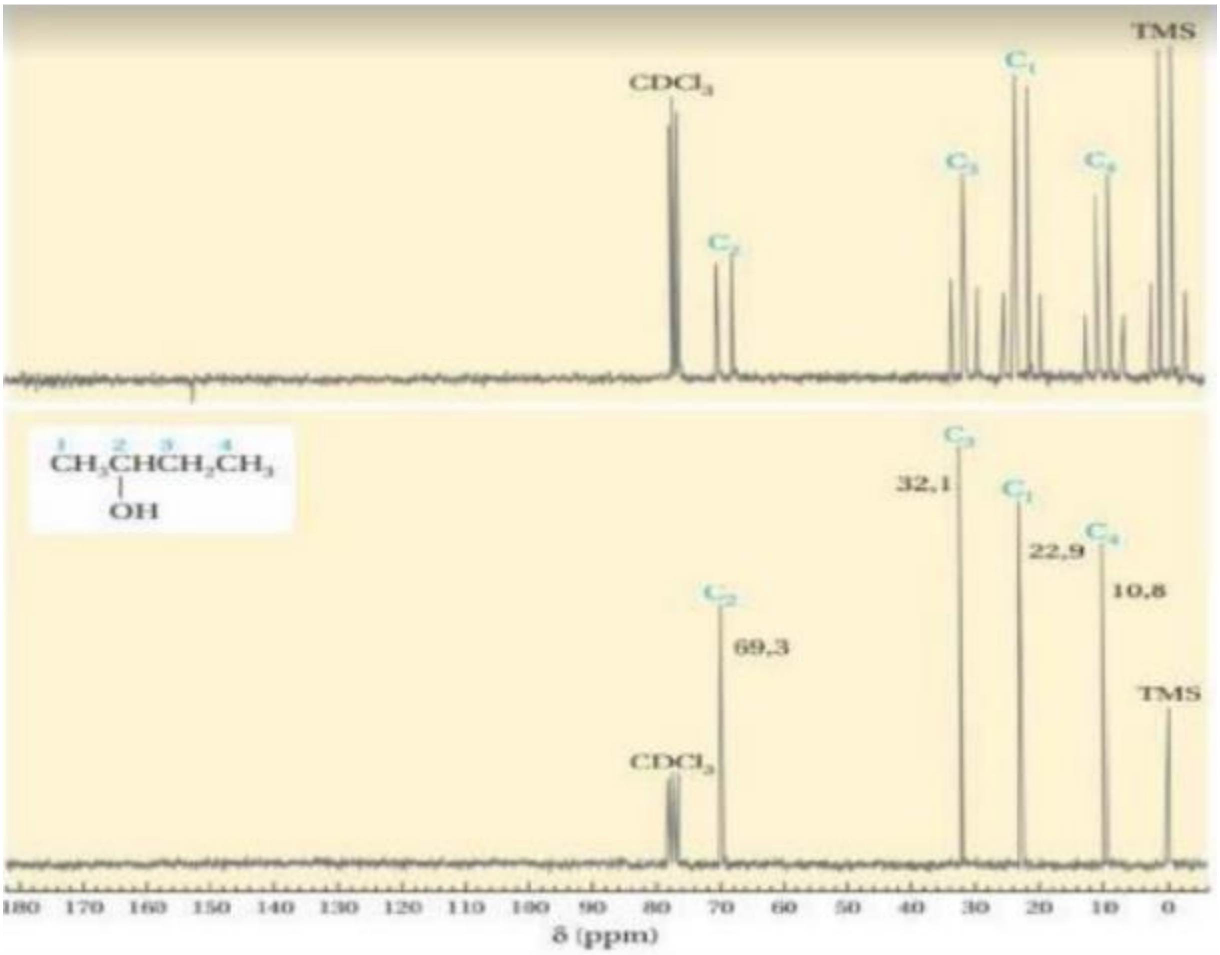
Carbon 13 spectrum

Carbon 13 (13C) is interesting for the study of organic molecules, but its isotopic abundance is very low. This requires very sensitive and several successive recordings to amplify the signal. However, measuring 13C with modern devices is purely routine. and we can obtain a very correct spectrum with a few milligrams in 30 min. The behavior with respect to a B0 field is comparable to that of hydrogen:

We obtain a resonance and a signal for each carbon atom. Chemical shifts also depend on the environment of the atom. C in the molecule. Chemical shifts of carbon 13C atoms range from 0 to 200 ppm.displacements are measured from the same reference compound, the TMS, of which all methyl carbon atoms are equivalent and produce a signal well defined

Example of the 13C NMR spectrum of butan-2-ol

The following figure shows the 13C NMR spectrum of butan-2-ol measured with and without 13C–1H coupling. The spectrum without 1H coupling (called proton decoupling spectrum) presents four singlets well defined, one for each type of carbon atom. The signal of The signal of the carbon atom carrying the hydroxyl group appears at higher fields low ($\delta = 69.3$ ppm), and the signals from the two methyl carbon atoms are well separated ($\delta = 10.8$ ppm and 22.9 ppm). In the spectrum with coupling 13C–1H, the n + 1 rule applies. The signal of each type of nucleus 13C is split because of the 1H nuclei directly linked to them. The signal from the two CH3 groups is a quadruplet (three hydrogen atoms, therefore, n + 1 = 4), the carbon atom of CH2 gives a triplet and that of CH a doublet.



Exercise 01

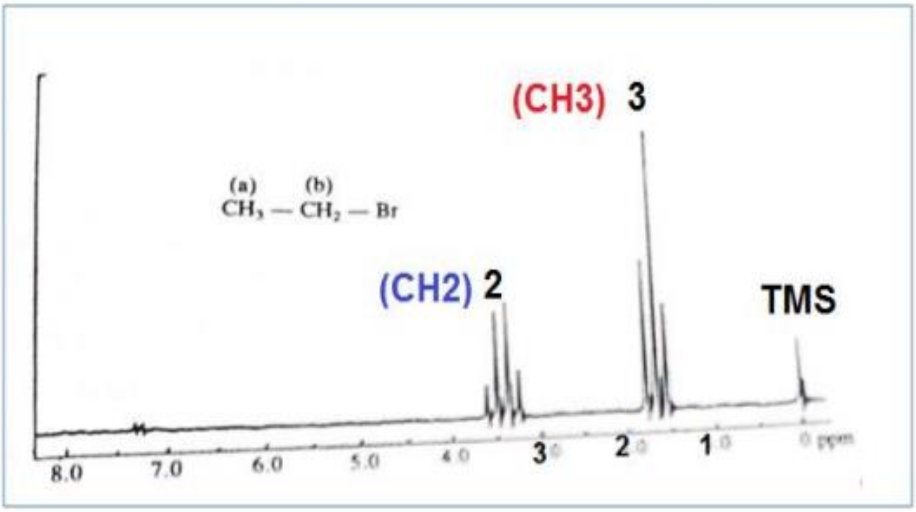
We give in the figure below the proton NMR spectrum of the compound

C_2H_5Br.

Solution :

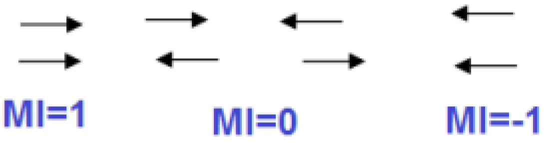
Degree of establishment

$DI=2x-y+w-r+2/2=4-5-1+2/2=0$



The compound below has two types of protons: the 3 protons equivalents of the methyl group denoted a and the 2 equivalent protons methylene group noted b. After coupling we obtain two signals, one triplet and the other quadruple.

There is a coupling between the various nuclear spin moments, the field applied magnetic implies that the two protons b are oriented in different ways, the possible combinations are:



Justify the choice of TMS as a reference.

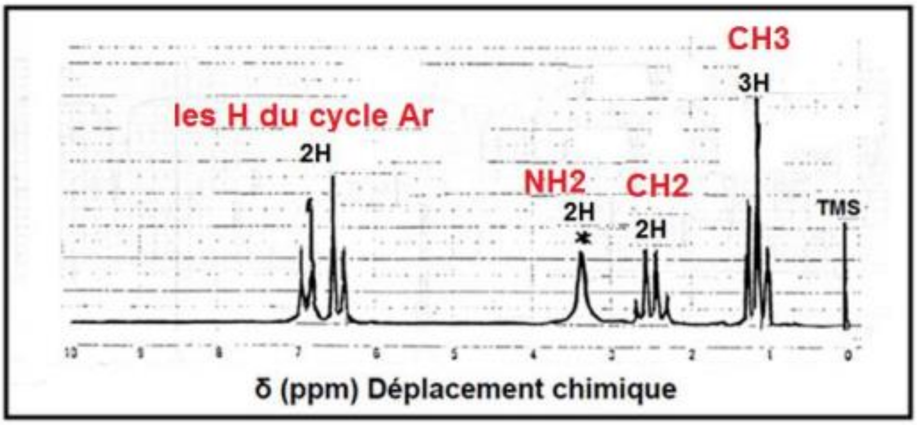
The advantage of TMS is that we obtain an intense peak even at low doses (12 protons having the same chemical environment). The protons of the TMS are strongly shielded therefore most of the protons of organic molecules have a resonance frequency higher than that of TMS.

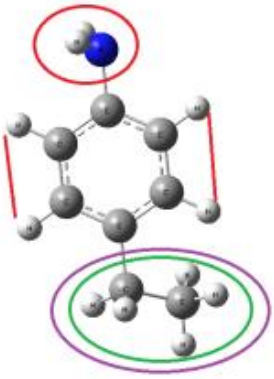
Exercise 2

Calculation of the degree of establishment:

$$DI=2x-y+w+2/2=16-11+1+2/2=4$$

Possibility of the presence of an aromatic ring (this is confirmed by the spectrum and the reference table.)





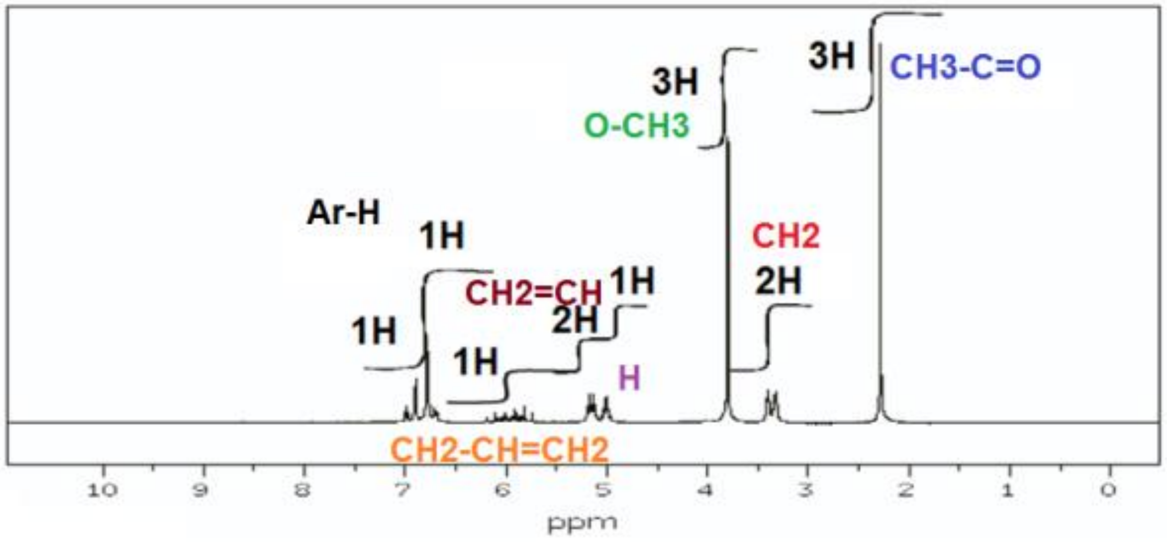
Exercise 3

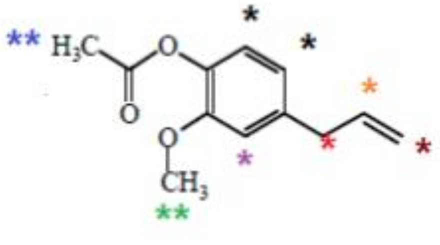
From the following proton NMR spectrum, give the developed structure of the compound of crude formula $\mathbf{C_{12}H_{14}O_3}$.

Justify your answer by indicating on the spectra the attribution of the NMR signals. What is the order of the spectra obtained.

(The order and 1 for the alkyl groups and 2 for the ring aromatic)

DI=6





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