Espectroscopia no Infra-vermelho (IV)
Espectrometria de Massas (MS)
Ressonância Magnética Nuclear (RMN)

Marcos N Eberlin
InfraVermelho

IR
- Cosmic rays: $10^{-12}$ to $10^{-10}$ cm
- Gamma rays: $10^{-10}$ to $10^{-8}$ cm
- X-rays: $10^{-8}$ to $10^{-6}$ cm
- Far ultraviolet: $10^{-6}$ to $2 \times 10^{-5}$ cm
- Ultraviolet: $2 \times 10^{-5}$ to $3.8 \times 10^{-5}$ cm
- Visible: $3.8 \times 10^{-5}$ to $7.8 \times 10^{-5}$ cm
- Infrared: $7.8 \times 10^{-5}$ to $3 \times 10^{-2}$ cm
- Microwave: $3 \times 10^{-2}$ to $10^2$ cm
- Radiofrequency: $0.6 \times 10^2$ to $5 \times 10^2$ cm
Note inverted peaks

Top: 100% transmission
Bottom: No transmission

Wavelength
$\mu = 10^{-6}$ meter

Frequency
$\text{cm}^{-1} = \text{Hz}/c$
Figure 15.4: Stretching and bending vibrational modes for H₂O
Symmetrical stretching

Antisymmetrical stretching

Scissoring

Rocking

Wagging

Twisting

Stretching vibrations

Symmetric

Asymmetric

Bending vibrations

In-plane rocking

In-plane scissoring

Out-of-plane wagging

Out-of-plane twisting
Figure 15.5: Stretching and bending vibrational modes for CO₂
Figure 15.6: Stretching and bending vibrational modes for a CH$_2$ group.
Gas Phase Infrared Spectrum of Formaldehyde, $\text{H}_2\text{C}=\text{O}$

- $2785 \text{ cm}^{-1}$ CH$_2$ sym stretch
- $2850 \text{ cm}^{-1}$ CH$_2$ asym stretch
- $1750 \text{ cm}^{-1}$ C=O stretch
- $1485 \text{ cm}^{-1}$ CH$_2$ scissor
- $1250 \text{ cm}^{-1}$ CH$_2$ rock
- $1165 \text{ cm}^{-1}$ CH$_2$ wag

http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/InfraRed/infrared.htm
\[ \nu = \frac{1}{2\pi\sqrt{\frac{k}{m}}} \]

where \( k \) is the force constant

\( m \) is the mass

\( \nu \) is the frequency of the vibration

C=C, C=O, C=N, N=O  
1500–1900

C≡C, C≡N  
2000–2300

C–H, N–H, O–H  
2700–3800

Figure 15.8: Energy curve for an anharmonic oscillator (showing the vibrational levels for a vibrating bond).
note that this band is greater than 3000

3083  =C–H stretch
alkene C–H

2966  2863

1644  C=C
1465  C–H scissoring

1378  methyl rock
1004  C–H bend

917   =C–H bend

C–H stretch
alkane C–H

1-octene
note that the aromatic C–H stretches are to the left of 3000, and the alkyl C–H stretches are to the right of 3000.
2-butanone

C–H stretch

C=O stretch

2991

1715

Wavenumbers (cm⁻¹)
<table>
<thead>
<tr>
<th>Range</th>
<th>Type of Compound</th>
<th>Such as:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1750-1735 cm(^{-1})</td>
<td>Saturated aliphatic esters</td>
<td>(\text{CH}_2\text{COOR})</td>
</tr>
<tr>
<td>1740-1720 cm(^{-1})</td>
<td>Saturated aliphatic aldehydes</td>
<td>(\text{CH}_2\text{CHO})</td>
</tr>
<tr>
<td>1730-1715 cm(^{-1})</td>
<td>(\alpha, \beta)-unsaturated esters</td>
<td>(\text{CH}_2\text{C(OR)}_2)</td>
</tr>
<tr>
<td>1715 cm(^{-1})</td>
<td>Saturated aliphatic ketones</td>
<td>(\text{CH}_2\text{C(OR)}_2)</td>
</tr>
<tr>
<td>1710-1665 cm(^{-1})</td>
<td>(\alpha, \beta)-unsaturated aldehydes and ketones</td>
<td>(\text{CH}(\text{OR})_2)</td>
</tr>
</tbody>
</table>

![Chemical structures](image)
hexanoic acid

O–H stretch (and C–H stretch)

C=O stretch

Wavenumbers (cm⁻¹)

% Transmittance

2971

1419

1296

948

O–H bend

C–O stretch
An infrared spectrum of aniline showing:

- N–H stretches (primary amines) at 3442 cm⁻¹ and 3360 cm⁻¹
- Shoulder band
- C–N stretch at 1281 cm⁻¹
- N–H bend (primary amines) at 1619 cm⁻¹
- N–H wag (primary, secondary amines) at 764 cm⁻¹
Diethylamine

- N-H stretch (secondary amine)

- C-N stretch

- N-H wag (primary, secondary amines)

Triethylamine

- Note the absence of a N-H stretch in this compound, a tertiary amine

- C-N stretch
meta-nitrotoluene

\[ \text{H}_3\text{C} - \text{NO}_2 \]

Wavenumbers (cm\(^{-1}\))

Transmittance

1537 N−O stretch
1358 N−O stretch
Cyclobutanol, 2-butanone, ethyl vinyl ether, 2-methyl-2-propen-1-ol, 2-methylpropanal.

The IR spectrum shows peaks at 3136, 3121, 3050, 2984, 2934, 2907, and 2883 cm\(^{-1}\) for \(\text{sp}^3\) C-H and \(\text{sp}^3\) C-H. Two C=C absorptions reflect two distinct and significant conformers of this molecule. Additional peaks include 1641, 1614, 1072, 966, 814, and 1218 cm\(^{-1}\).
When the Duke of Devonshire offered to pay for building the laboratory in 1870, the idea of a laboratory devoted to experimental physics was considered an innovation.
The father of MS and the first mass spectrometrist to win the Nobel Prize.

Pure species and mixtures

JJ Thomson's *Plum Pudding Model* of the atom, a sphere of positive charge containing electrons
The Nobel Prize in Physics 1906

"in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases"
Mass spectra and isotopes

The Nobel Prize in Chemistry 1922

"for his discovery, by means of his mass spectrograph, of isotopes, in a large number of non-radioactive elements, and for his enunciation of the whole-number rule"

Francis William Aston

At the end of 1909 he accepted the invitation of Sir J.J. Thomson to work as his assistant at the Cavendish Laboratory, Cambridge, on studies of positive rays. It was during this period that he obtained definite evidence for the existence of two isotopes of the inert gas neon.
$^{12}\text{C}/^{13}\text{C}$ varies in nature

$^{238}\text{U}$, $^{235}\text{U}$, $^{234}\text{U}$ = few mg of pure $^{235}\text{U}$
Calutron “Racetracks” at Oak Ridge produced enriched $^{235}\text{U}$ for the world’s first atomic weapons.
Vaporizar

Fase Gasosa

Ionizar

+50V

Vácuo

Medir relação
m/z

Detectar

Moléculas na Fase Condensada
EI : Electron Ionization 70 eV
(Dempster & Nier)
A Dupla Dinâmica!
Espécies Moleculares e Fragmentos

\[
\begin{align*}
\text{M}^{+} & \quad m/z = 121 \\
\text{M - 16} & \quad m/z = 105 \\
\text{M - 77} & \quad m/z = 44
\end{align*}
\]
1. inject sample
2. heater to vapourise sample
3. electron beam ionises sample
4. particles accelerated into magnetic field
5. magnetic field separates particles based on mass/charge ratio

- charged particle beam
- electrons
- lightest
- heaviest
- x^+
- y^+
- z^+
- detector
Quadrupolos Lineares: $Q/q$
Paul & Steinwedel 1953

- A varredura é feita variando simultaneamente $U$ (DC) e $V_0$ (AC) mas mantendo constante a relação $U/V_0$. 

Wolfgang Paul
Prêmio Nobel 1989
ATRÁS DE UM TUBO DE COMPRIMENTO L (~1m) SOB ALTO VÁCUO, ÍONS FORMADOS POR IONIZAÇÃO PULSADA (~0,25 A 1 ms) SÃO ACCELERADOS PELA APlicaÇÃO DE UMA VOLTAGEM V (~1-10 KV), E ADQUIREM VELOCIDADES PROPORCIONAIS AS SUAS m/z's. OCORRE DISPERSAO EM TEMPO, E ÍONS DE DIFERENTES m/z's CHEGAM AO DETECTOR EM TEMPOS DIFERENTES:

\[ t = \left( \frac{m}{2zeV} \right)^{1/2} L \]

PRINCÍPIO BÁSICO: DISPERSAO NO TEMPO DE ÍONS POR ACELERAÇÃO SEGUIDA DA MEDIDAS DE SEUS TEMPOS DE VÔO "LIVRE".
Massa Exata = Composição Elementar

*Defeitos de Massas*

<table>
<thead>
<tr>
<th>Element</th>
<th>Nuclide</th>
<th>Nominal Mass</th>
<th>Exact Mass</th>
<th>Mass Defect</th>
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<tbody>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1</td>
<td>1.0078</td>
<td>0.0078</td>
</tr>
<tr>
<td>Carbon</td>
<td>$^{12}\text{C}$</td>
<td>12</td>
<td>12.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$^{14}\text{N}$</td>
<td>14</td>
<td>14.0031</td>
<td>0.0031</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{16}\text{O}$</td>
<td>16</td>
<td>15.9949</td>
<td>-0.0051</td>
</tr>
<tr>
<td>Fluorine</td>
<td>$^{19}\text{F}$</td>
<td>19</td>
<td>18.9984</td>
<td>-0.0016</td>
</tr>
<tr>
<td>Sulfur</td>
<td>$^{32}\text{S}$</td>
<td>32</td>
<td>31.9721</td>
<td>-0.0279</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$^{35}\text{Cl}$</td>
<td>35</td>
<td>34.9689</td>
<td>-0.0311</td>
</tr>
</tbody>
</table>

*Exact Mass and Mass Defect of Common Elements*
Reading the mass spectrum: Propyl bromide!
As “Pequenas” Moléculas

Produtos Naturais, Síntese, VOCs, ....
As “Pequenas” Moléculas

O casal perfeito!
ESI-MS “Ion Fishing”

Flying Molecular Elephants
ESI-MS

HPLC/MS

“The Perfect Couple”

HPLC SYSTEM
Figure 2. Positive-ion, ionspray mass spectra of sildenafil (m/z 200 to 700). Conditions: syringe infusion (50 µL/min) of a 10-µg/mL solution of sildenafil in a mixture of (acetonitrile + 10 µg/mL trimethylamine)/2mM NH₄COOH, pH 3.0 buffer (50:50, v/v), sprayer set at 4.5 kV. A, low-voltage spectrum (OR = +0 V) and B, high-voltage spectrum (OR = +100 V).
MS
30JULYCAP_04 13 (0.440) Sm (Mn, 2x1.00); Cm (12:15)
Scan ES-
1.46e5

MS/MS CE = 12
30JULYCAP_03 2 (0.068) Sm (Mn, 2x1.00); Cm (2:32)
Daughters of 321ES-
6.50e5

ESI-MS

ESI-MS/MS
Characterization of Vegetable Oils by Electrospray Ionization Mass Spectrometry Fingerprinting: Classification, Quality, Adulteration, and Aging

Rodrigo Ramos Catharino,† Renato Haddad,† Liliane Girotto Cabrini,† Ildenieze B. S. Cunha,‡ Alexandra C. H. F. Sawaya,*,† and Marcos N. Eberlin*,†
Wine characterization by direct infusion electrospray ionization mass spectrometry

Rodrigo R. Catharino a, Ildenize B. S. Cunha a, Aline O. Fogaça c, Elizete M. P. Facco b, Helena T. Godoy b, Carlos E. Daudt c Marcos N. Eberlin a and Alexandra C. H. F. Sawaya a*

“Grape juice : must”
Isótopos

- Cloro (Cl): Isótopos 35Cl y 37Cl
- Bromo (Br): Isótopos
- Iodo (I): Isótopos
Ressonância Magnética Nuclear (RMN)
Sample and detector coil
RF coil
Magnet
Transmitter
Receiver
Magnet Power Supply
Magnetic Field Sweep
Recorder
y-axis
x-axis
After Becker
Increasing magnetic field

No field

With field

Ground state

Excited state

High energy

Low energy

$\Delta E = 0$

$E_1$

$E_2$

$E_1'$

$E_2'$

$H_0$

$H_0'$

$\Delta E$

$\Delta E'$
Deshield  
Downfield

Shield  
Upfield

$H_{o}$  
$H_{e}$

$H_{eff} = H_{o} - H_{e}$

spectrometer field
Schematic diagram of shielding cones for common pi systems. The + denotes shielding areas and - denotes deshielding areas. Remember shielding lowers the chemical shift, $\delta$, and deshielding increases $\delta$. Typical H $\delta$ values are also shown.
1,1-dichloroethane contains two types of hydrogen atoms, so we see two sets of peaks, a doublet at 2.1 ppm and a quartet at 5.9 ppm.

Fields are aligned which effectively deshields the neighbouring protons, and resonance occurs at higher frequency.

Fields are opposed which effectively shields the neighbouring protons, and resonance occurs lower frequency.

$\text{CH}_3\text{CHCl}_2$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

3 types of H
middle methylene appears as 6 lines due
to 5 neighbours, 3 + 2

triplet, so $n=2$
deshielded

triplet, so $n=2$
shielded

6 lines,
so $n=5$
high resolution nmr spectrum for methyl propanoate, CH₃CH₂COOCH₃
No Coupled Hydrogens

One Coupled Hydrogen

Two Coupled Hydrogens

Three Coupled Hydrogens

A Singlet

A Doublet

A Doublet of Doublets

A Doublet of Doublet of Doublets

J_A

J_B

J_C

J_D
R = CH₃CH₂CO₂H
CH₃CH₂COCH₃