

Espectroscopia no Infra-vermelho (IV)

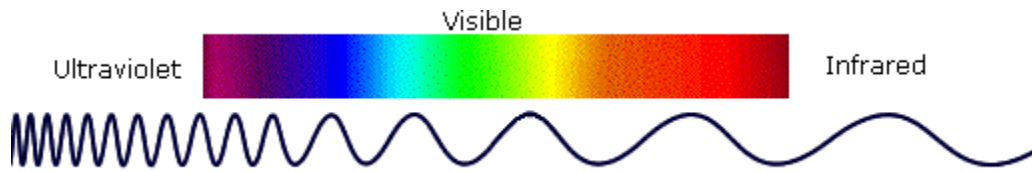
Espectrometria de Massas (MS)

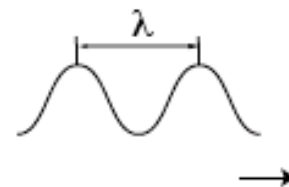
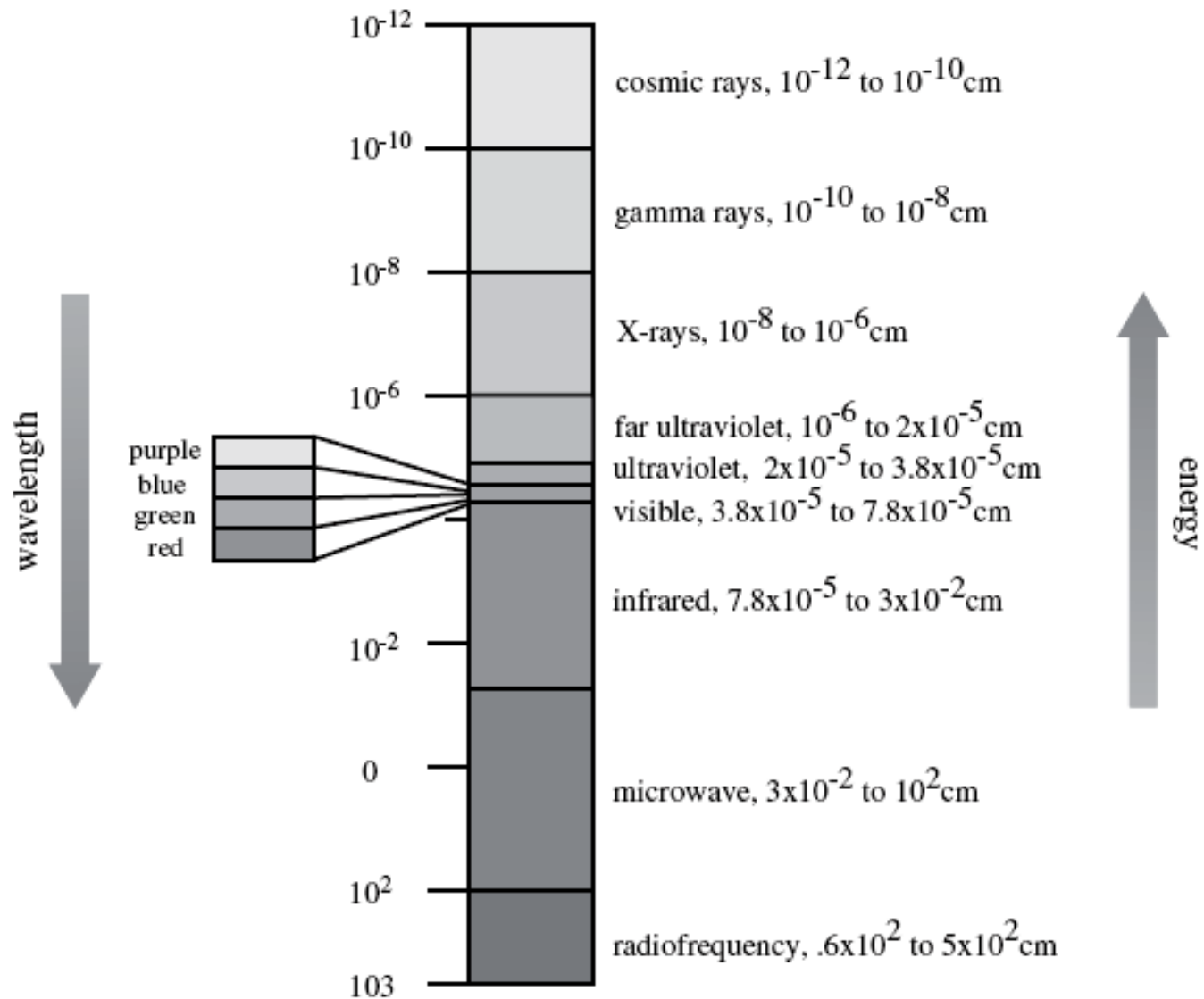
Ressonância Magnética Nuclear (RMN)

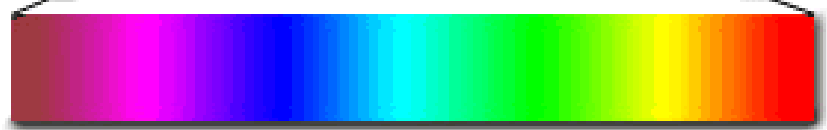
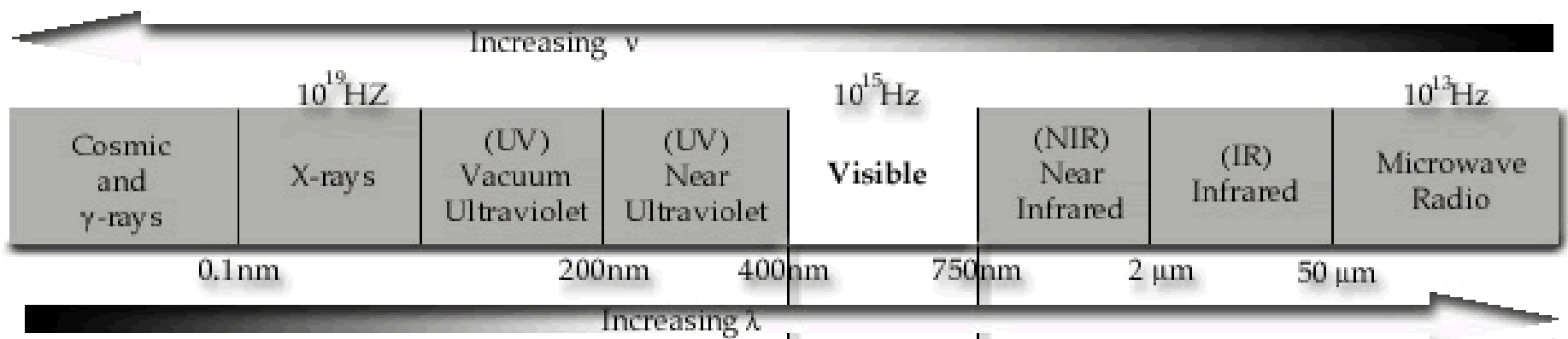
Marcos N Eberlin

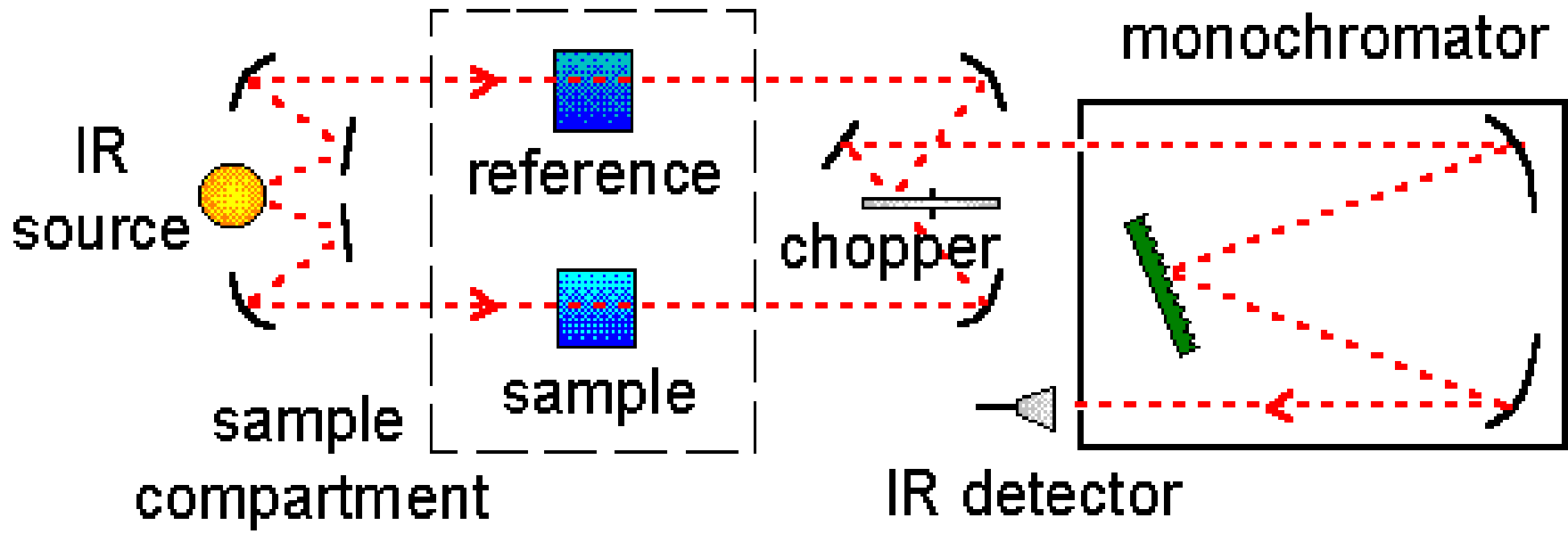
InfraVermelho

IR



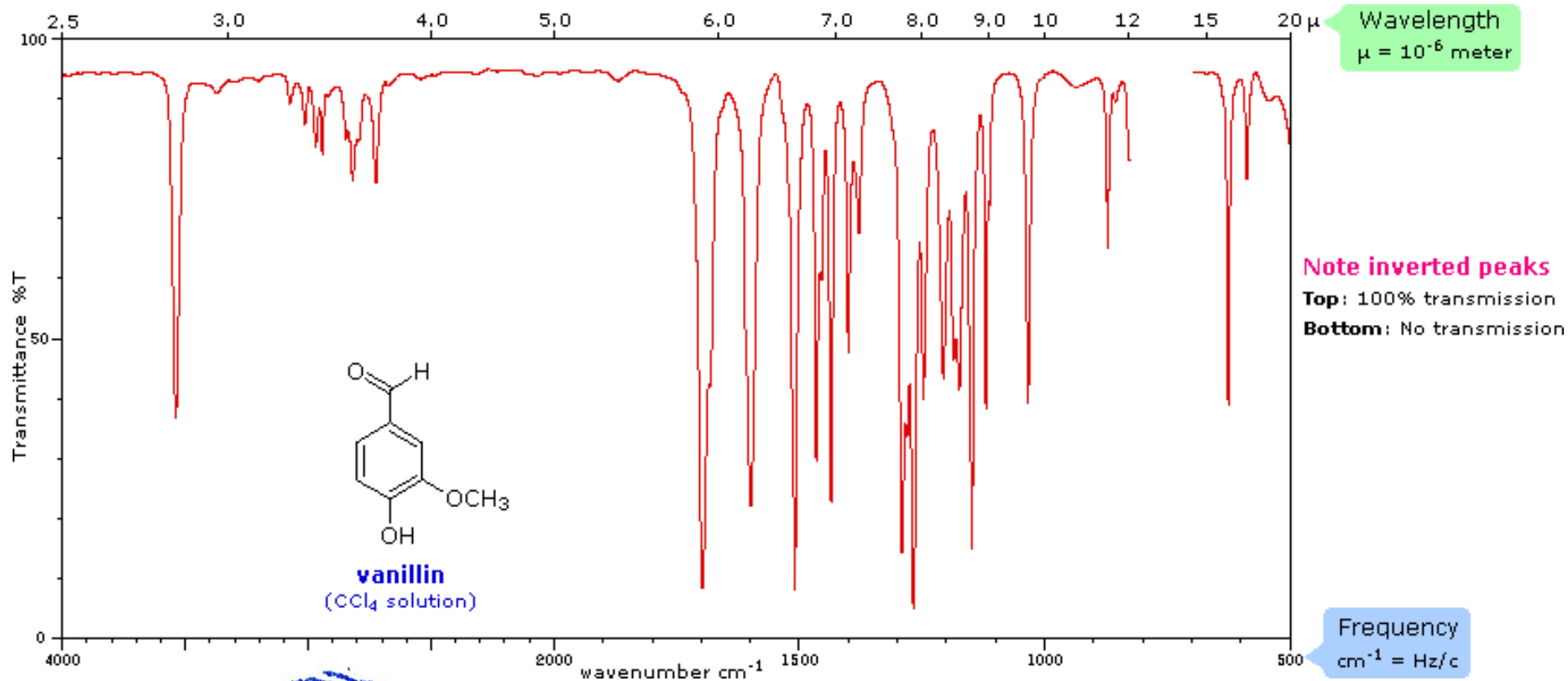


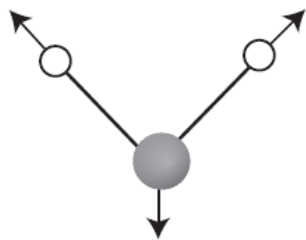
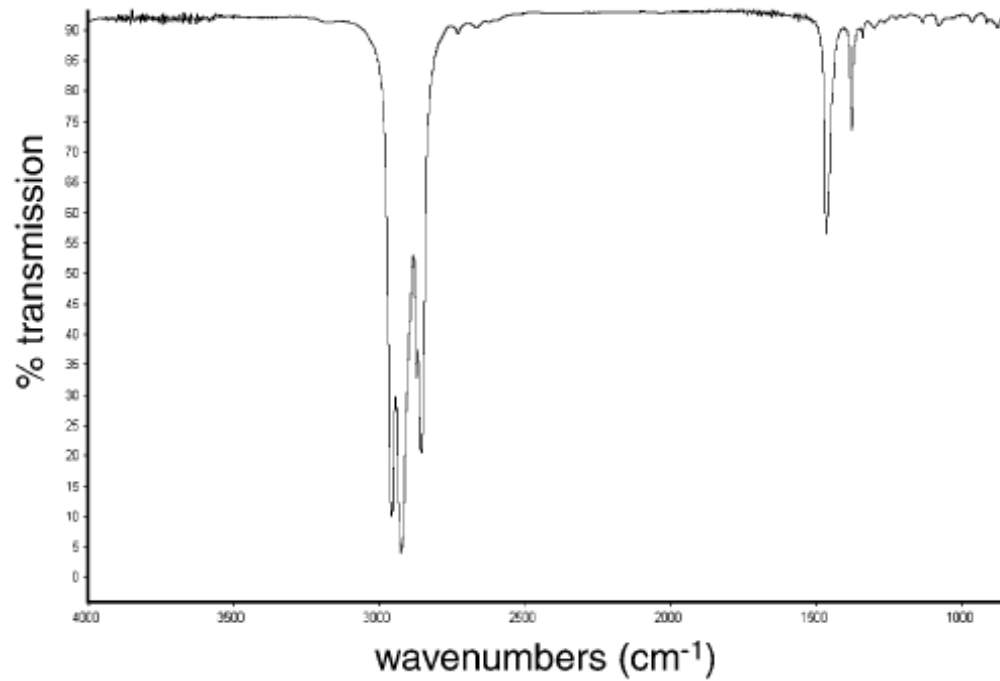




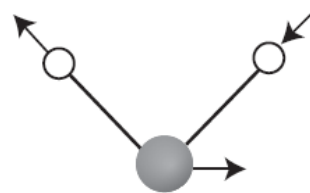
©1995 CHP



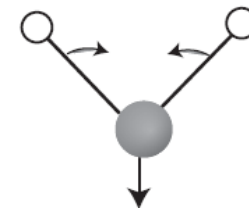




symmetrical stretching



asymmetrical stretching



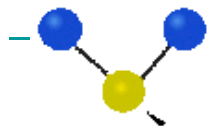
scissoring (bending)

Figure 15.4 : Stretching and bending vibrational modes for H₂O

Symmetrical stretching



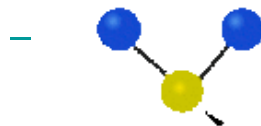
Antisymmetrical stretching



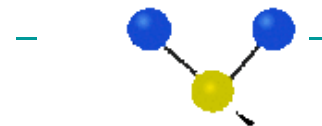
Scissoring



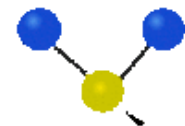
Rocking



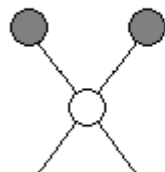
Wagging



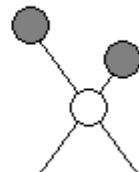
Twisting



Stretching vibrations

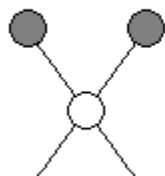


Symmetric

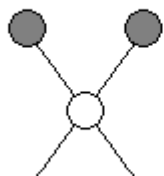


Asymmetric

Bending vibrations

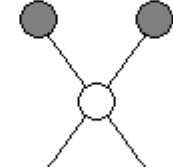


In-plane rocking



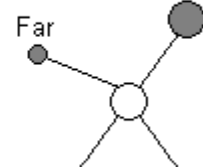
In-plane scissoring

Near Near

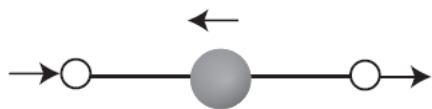


Out-of-plane wagging

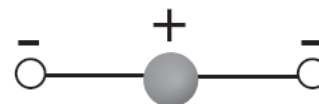
Far Near



Out-of-plane twisting



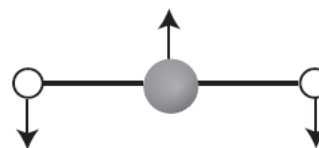
asymmetrical stretching



scissoring (bending in and out of the plane of the paper)

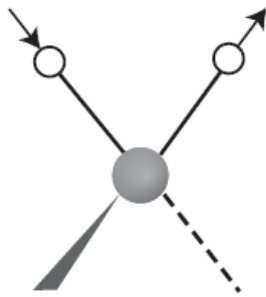


symmetrical stretching

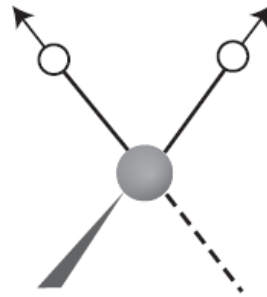


scissoring (bending in the plane of the paper)

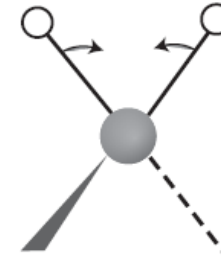
Figure 15.5 : Stretching and bending vibrational modes for CO_2



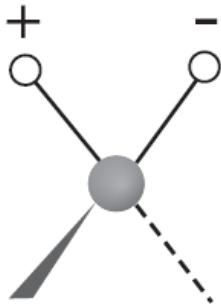
asymmetrical stretching
2925 cm^{-1}



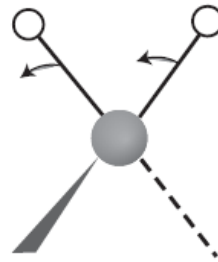
symmetrical stretching
2850 cm^{-1}



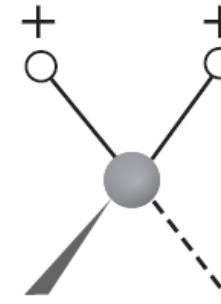
scissoring, or bending in-plane
1465 cm^{-1}



twisting, or bending out-of-plane
1350-1150 cm^{-1}



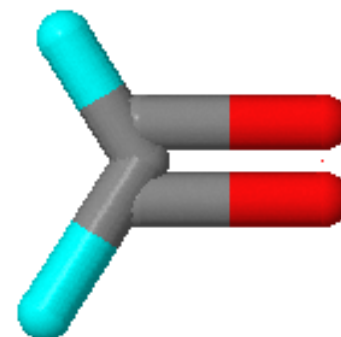
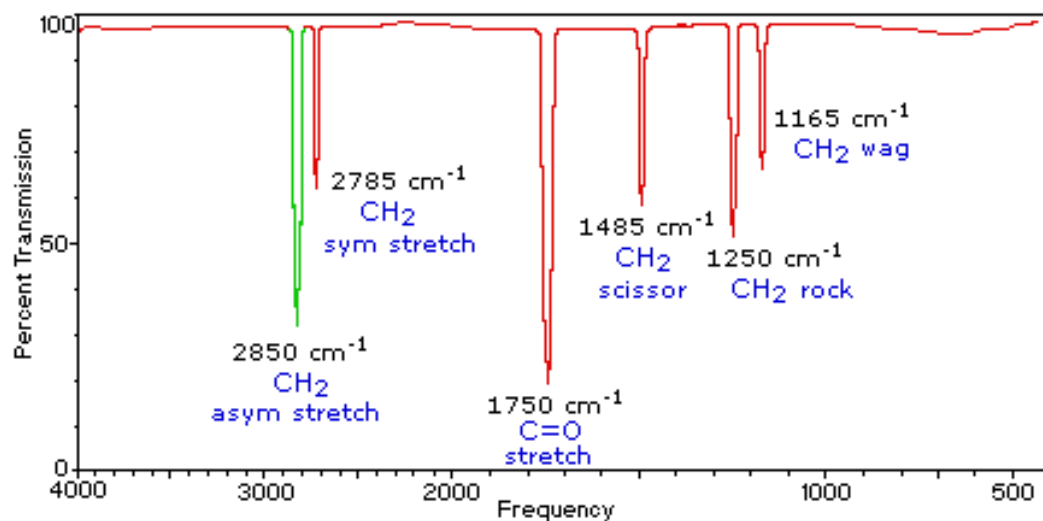
rocking, or bending in-plane
720 cm^{-1}



wagging, or bending out-of-plane
1350-1150 cm^{-1}

Figure 15.6 : Stretching and bending vibrational modes for a CH_2 group.

Gas Phase Infrared Spectrum of Formaldehyde, $\text{H}_2\text{C}=\text{O}$



View CH_2 Asymmetric Stretch

View CH_2 Symmetric Stretch

View $\text{C}=\text{O}$ Stretch

View CH_2 Scissoring

View CH_2 Rocking

View CH_2 Wagging

Ball&Stick Model

Spacefill Model

Stick Model

Motion Off

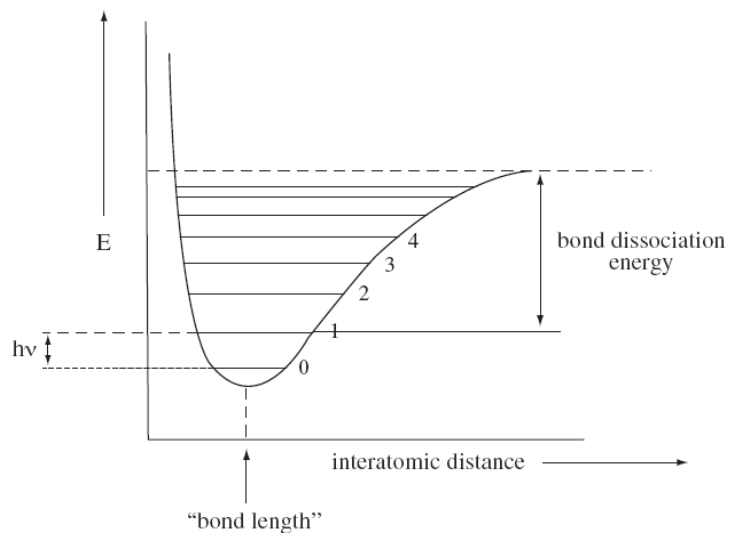


$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

where k is the force constant

m is the mass

ν is the frequency of the vibration



C=C, C=O, C=N, N=O

1500–1900

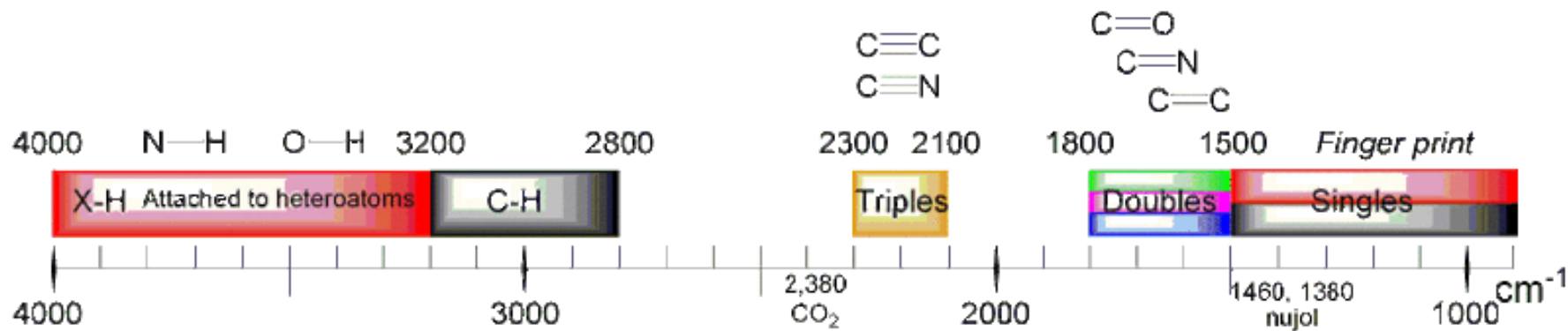
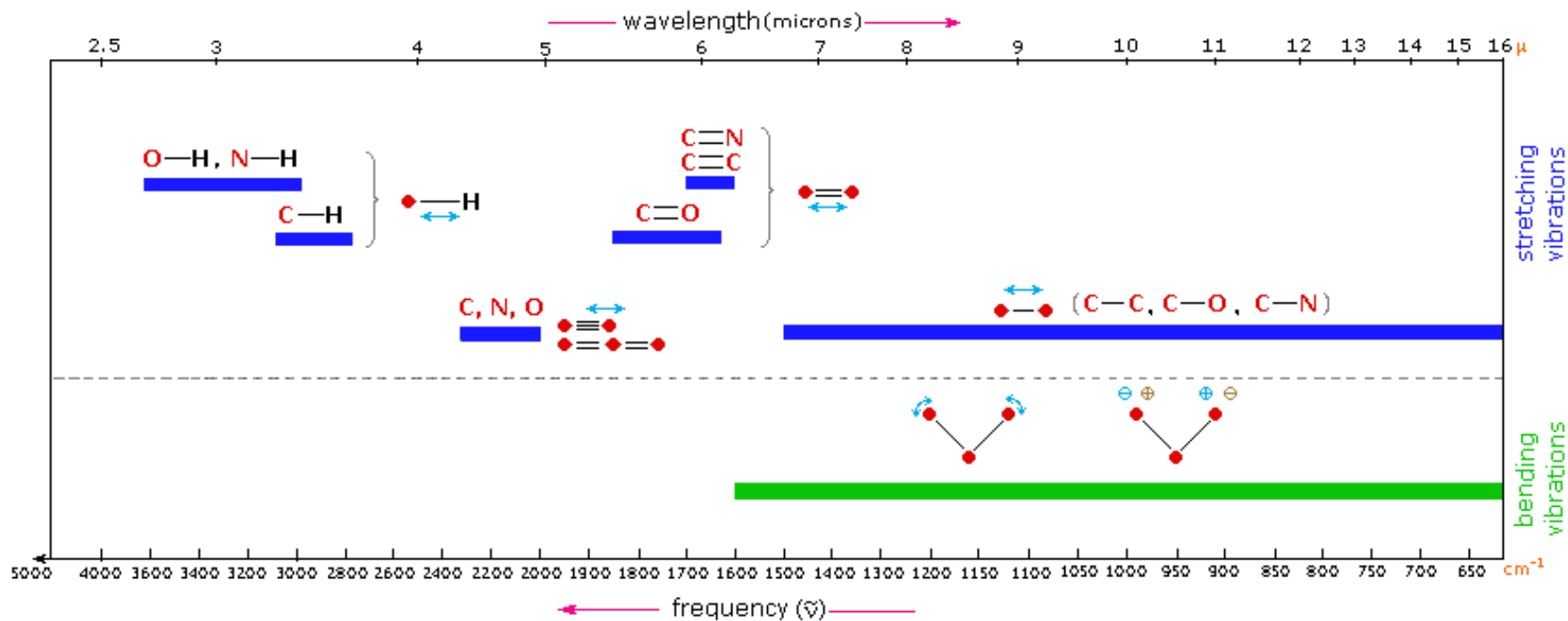
C≡C, C≡N

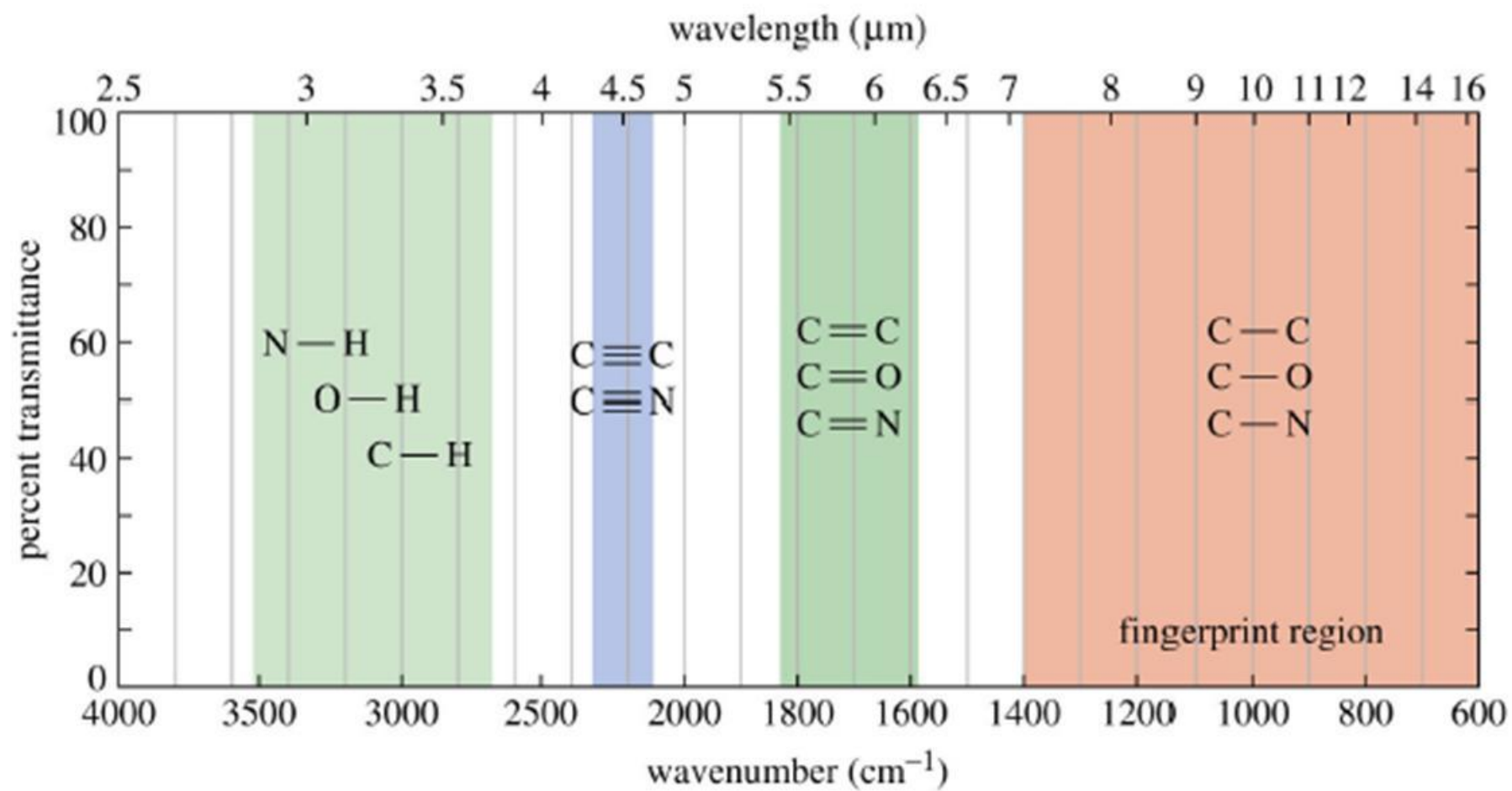
2000–2300

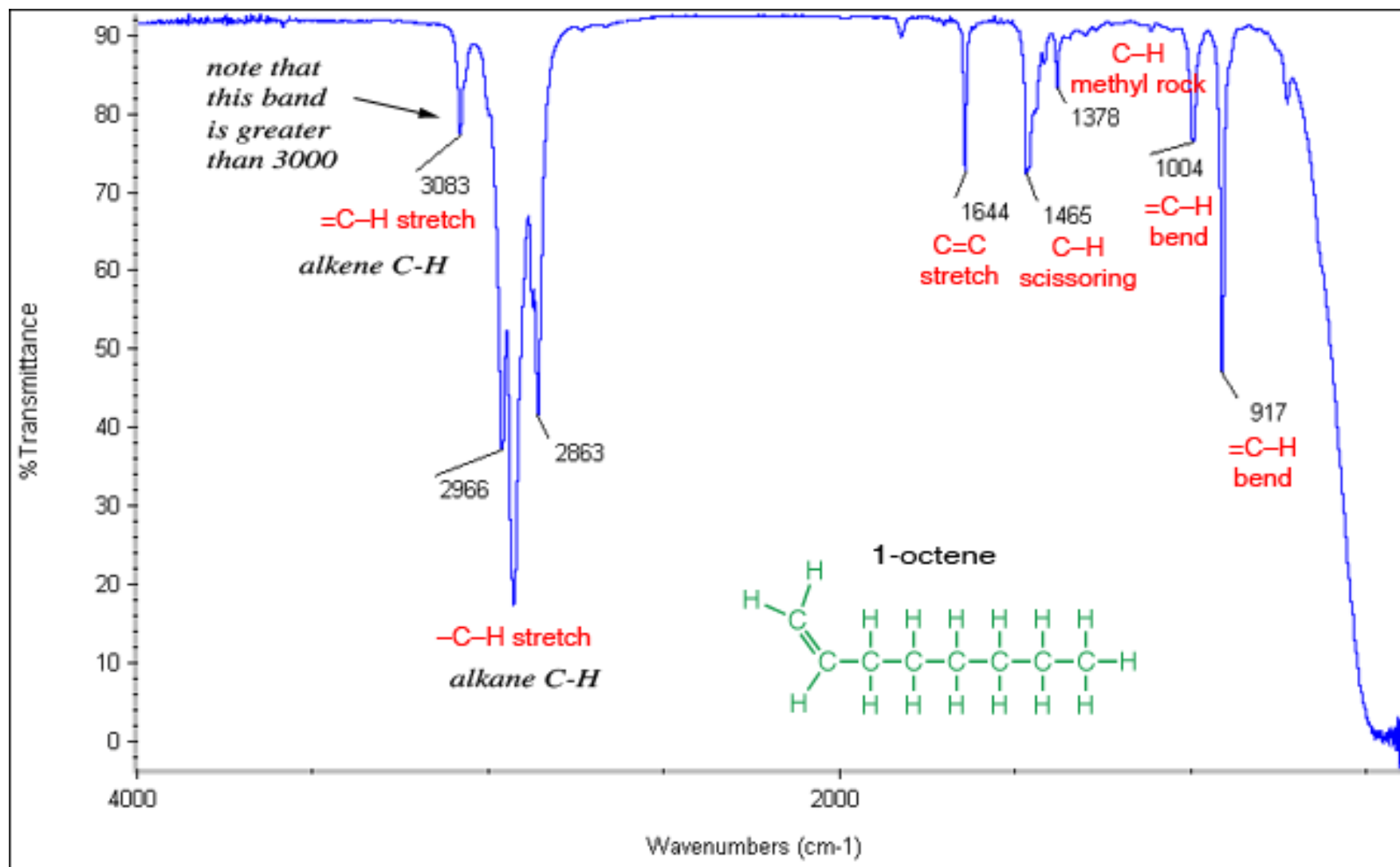
C-H, N-H, O-H

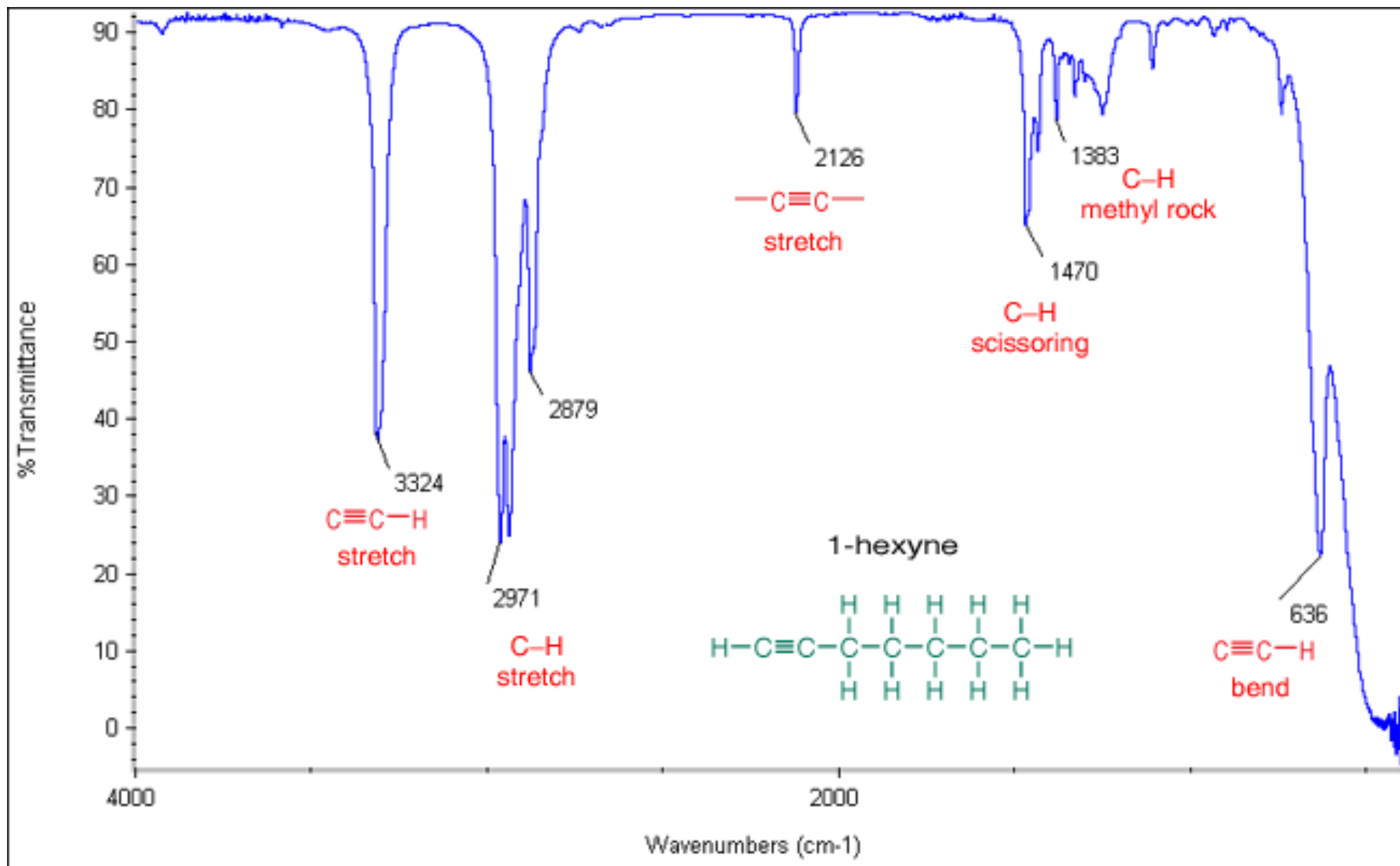
2700–3800

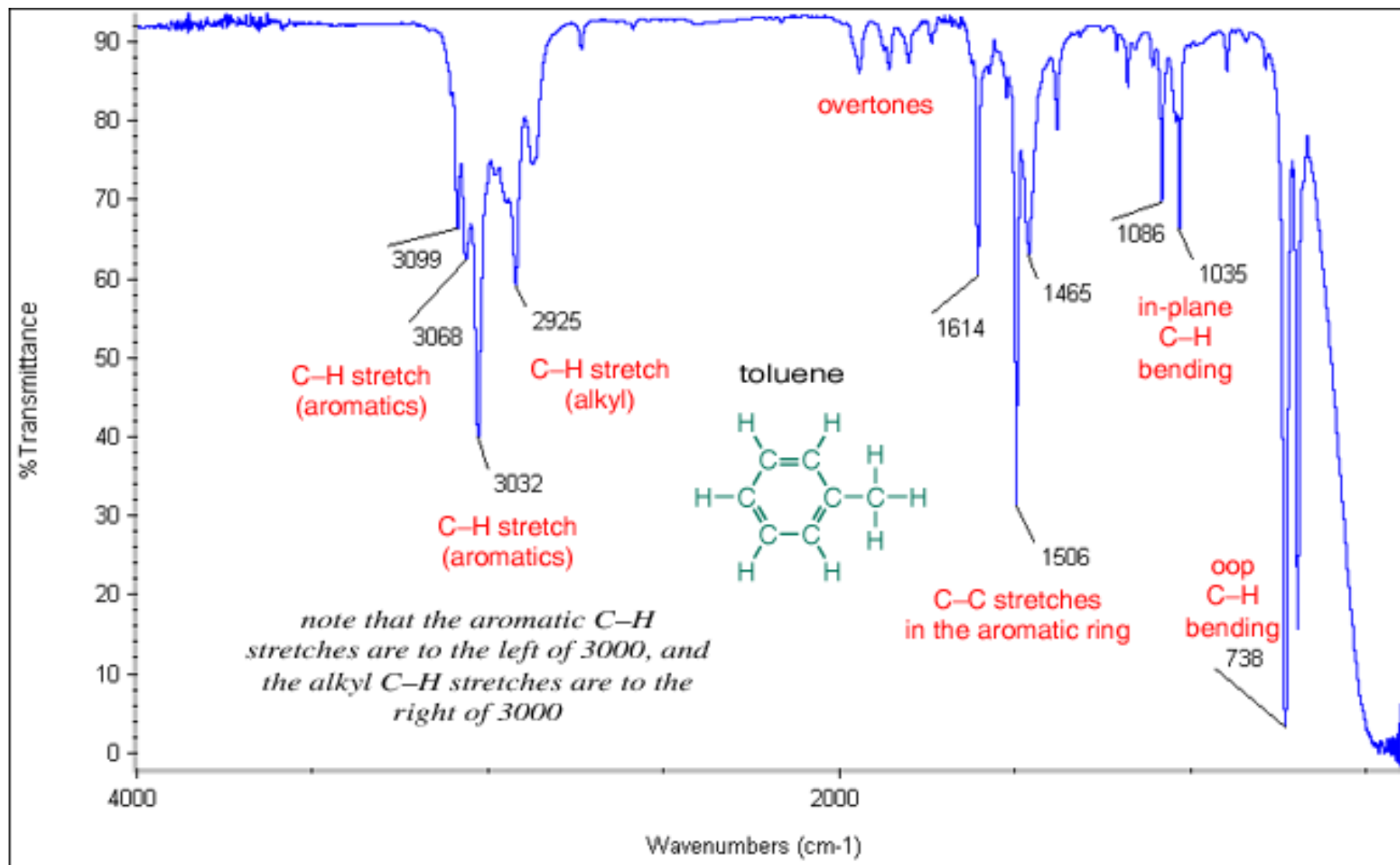
Figure 15.8 : Energy curve for an anharmonic oscillator (showing the vibrational levels for a vibrating bond).

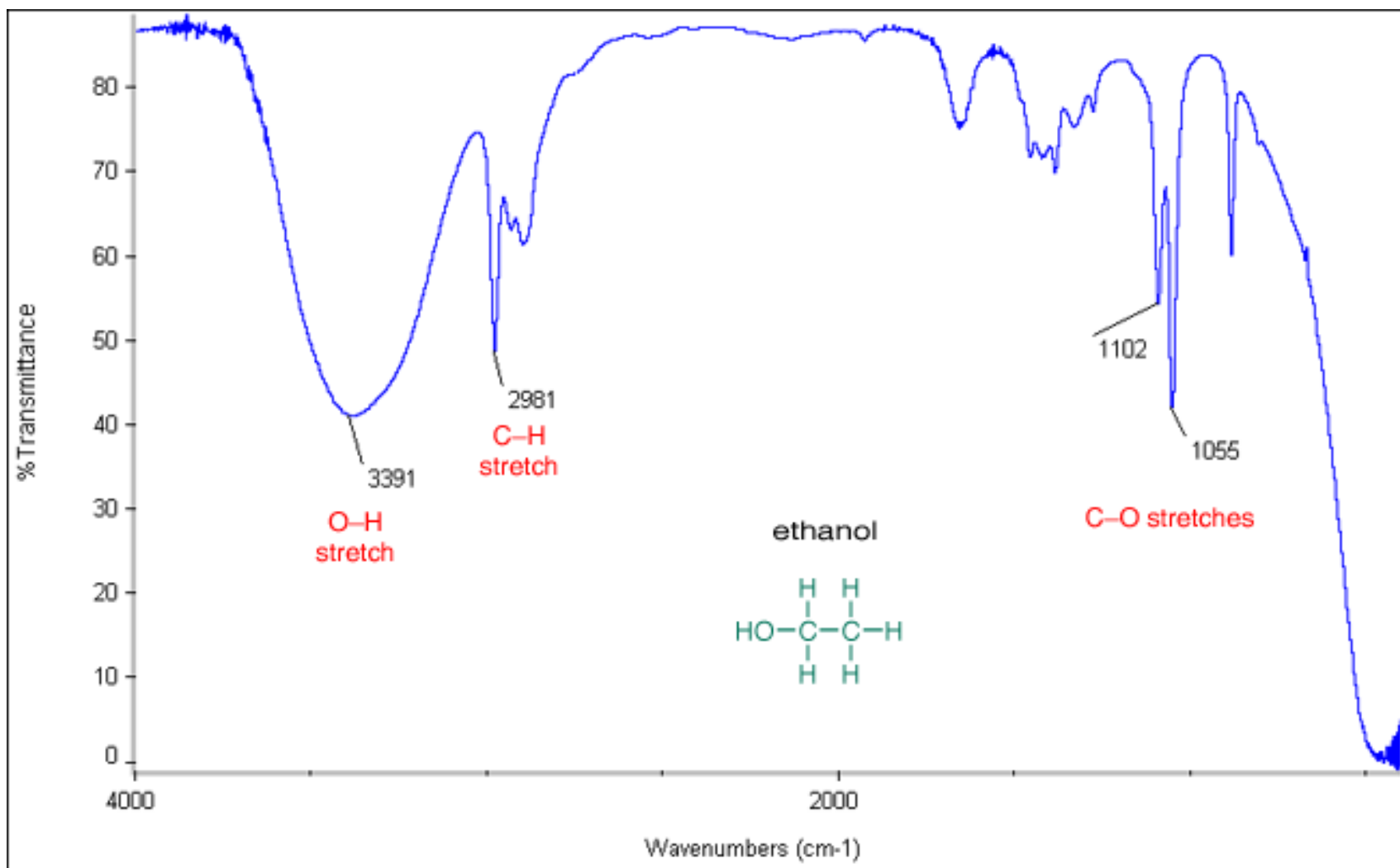


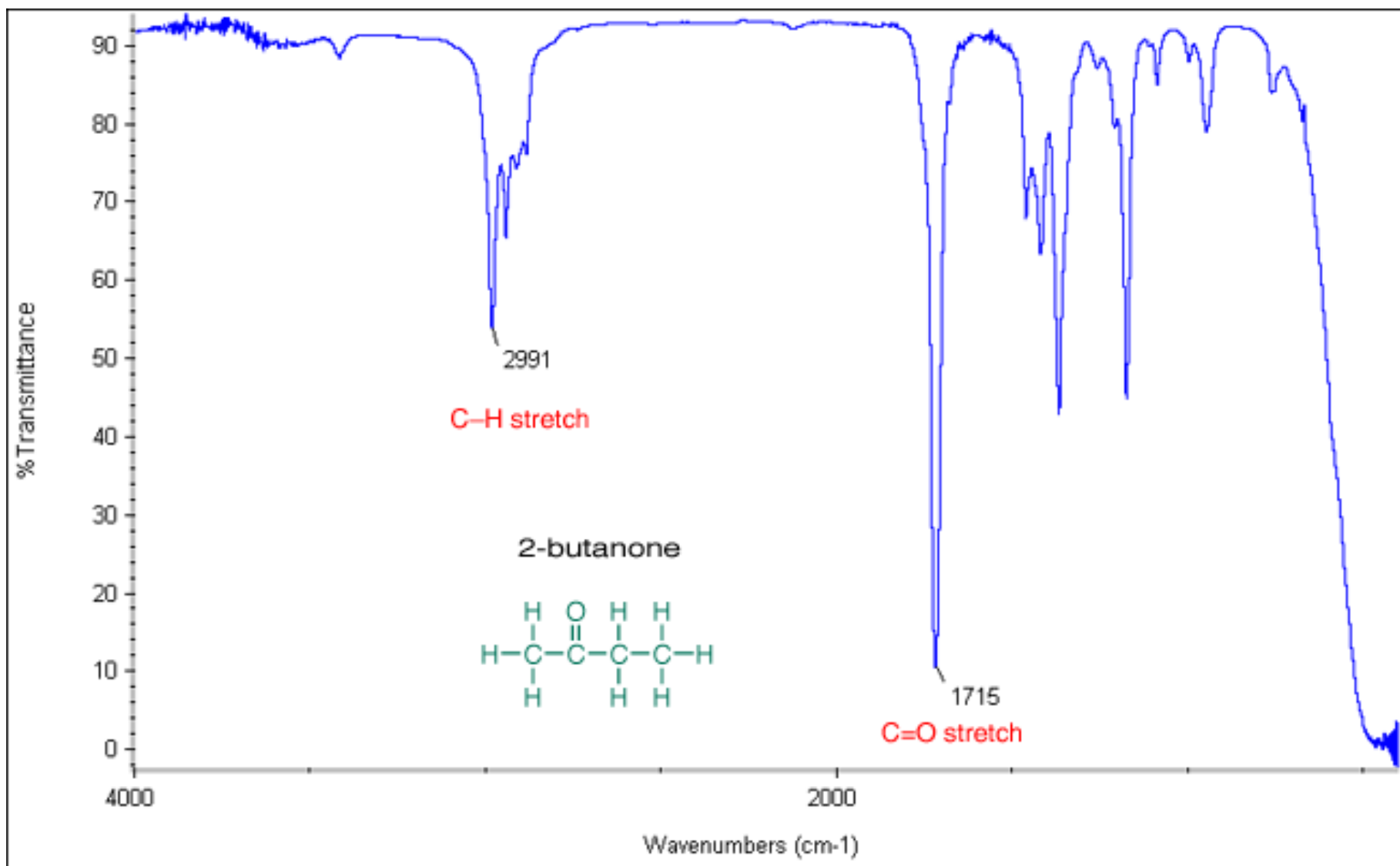




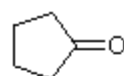




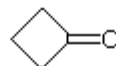




<i>range</i>	<i>type of compound</i>	<i>such as:</i>
1750-1735 cm^{-1}	saturated aliphatic esters	
1740-1720 cm^{-1}	saturated aliphatic aldehydes	
1730-1715 cm^{-1}	α , β -unsaturated esters	
1715 cm^{-1}	saturated aliphatic ketones	
1710-1665 cm^{-1}	α , β -unsaturated aldehydes and ketones	



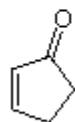
1748 cm^{-1}



1783 cm^{-1}

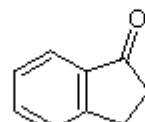


1850 cm^{-1}

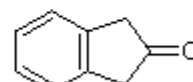


1710 cm^{-1}

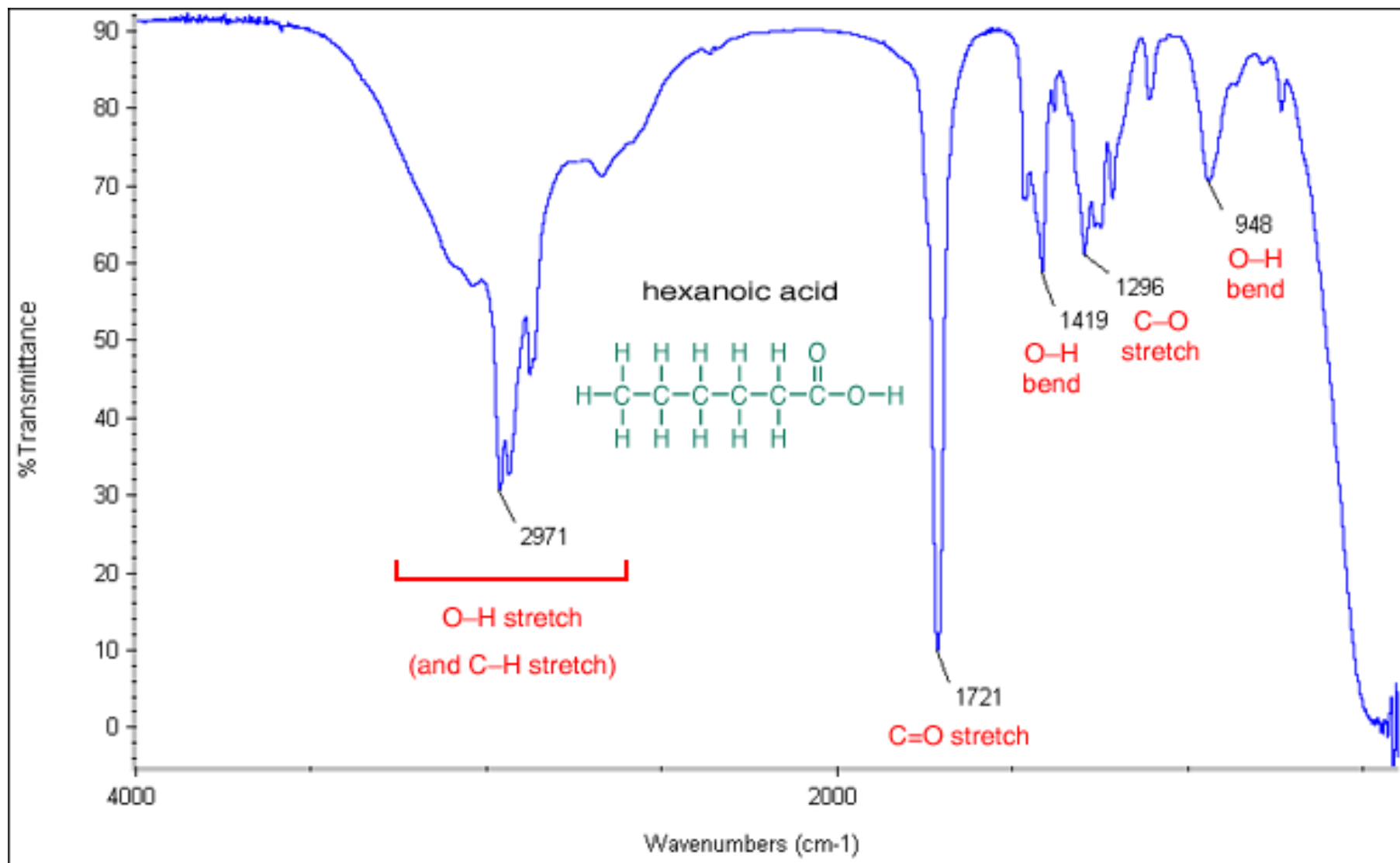
1650 (C=C)

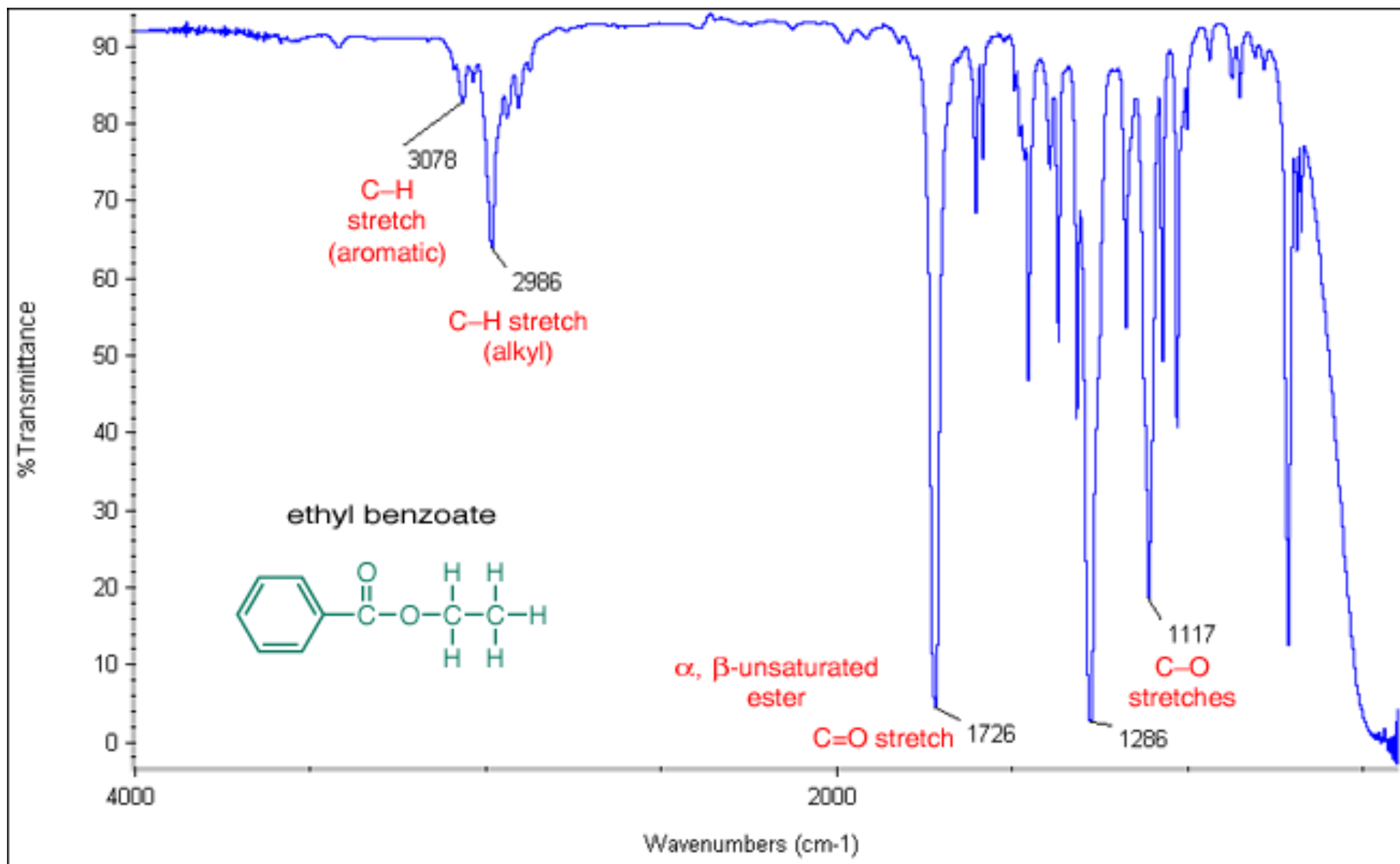


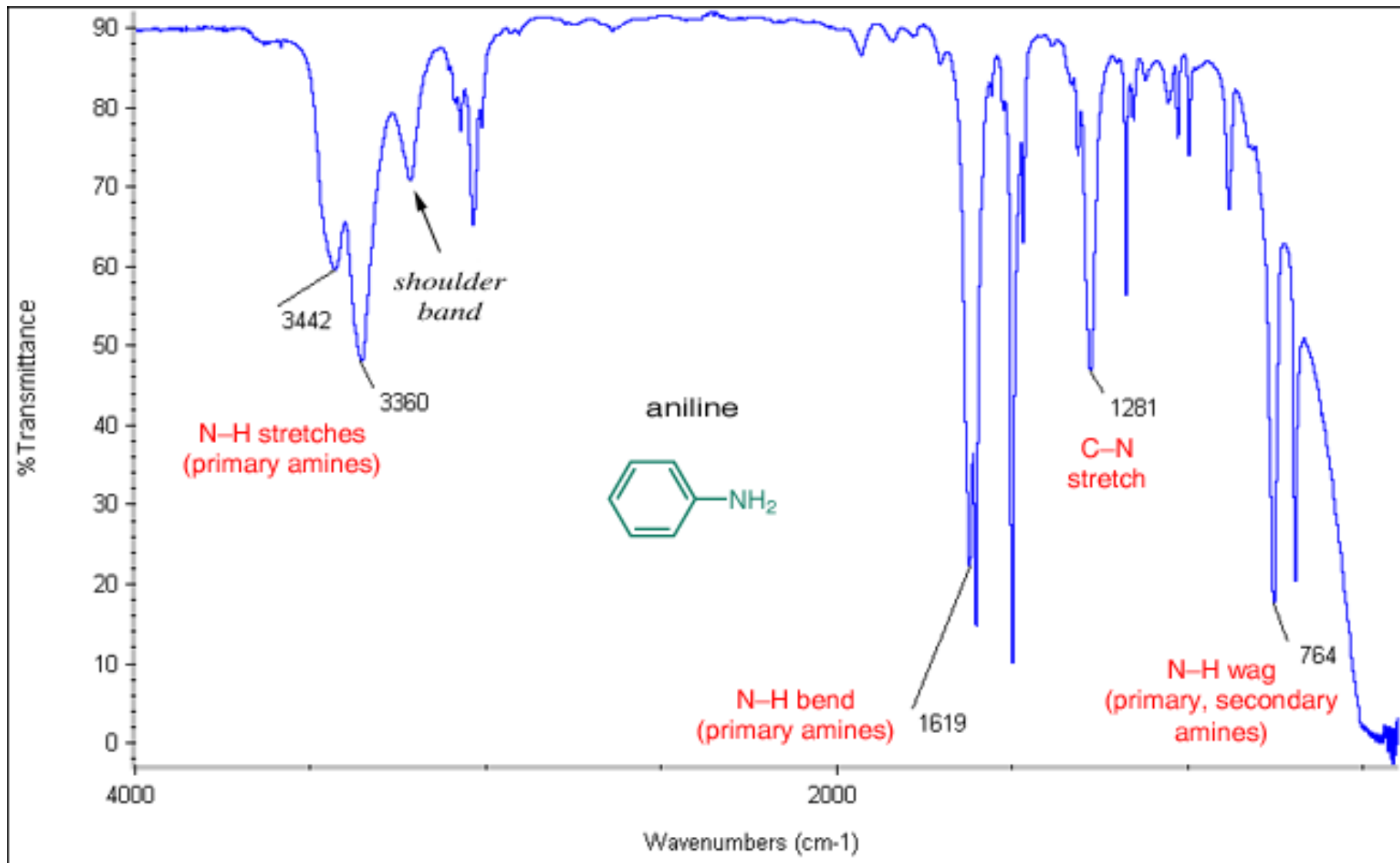
1712 cm^{-1}

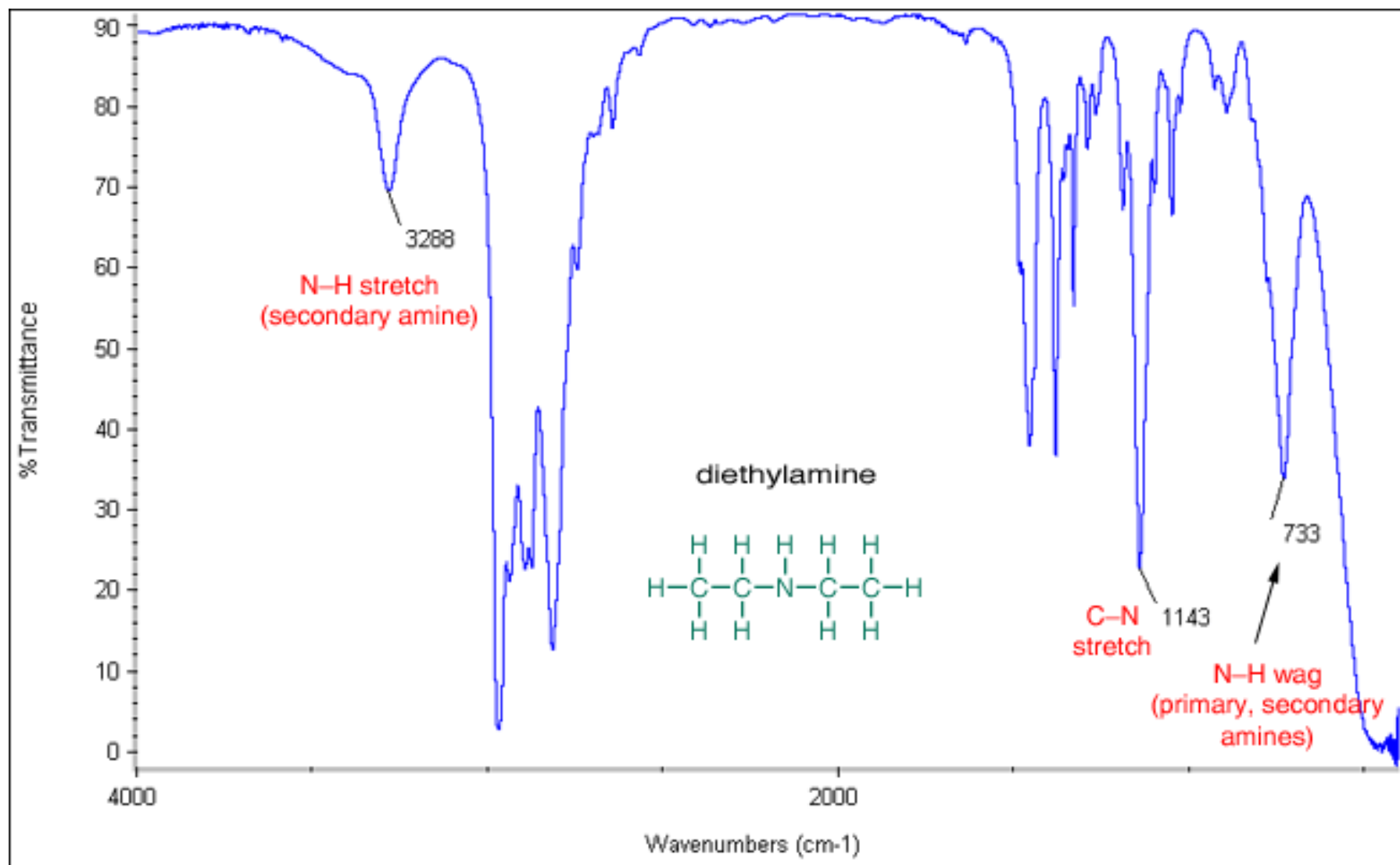


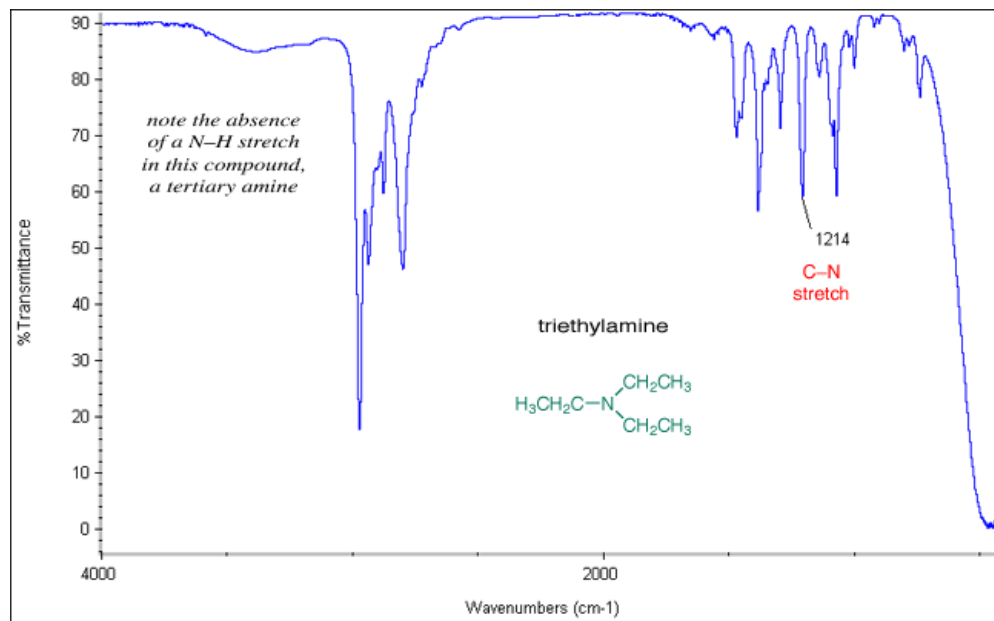
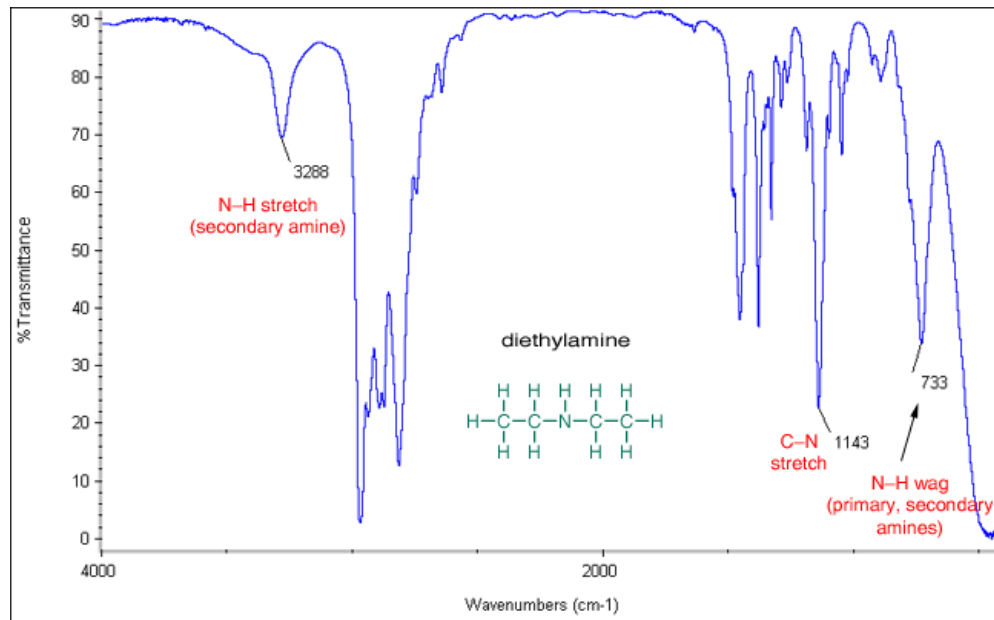
1750 cm^{-1}

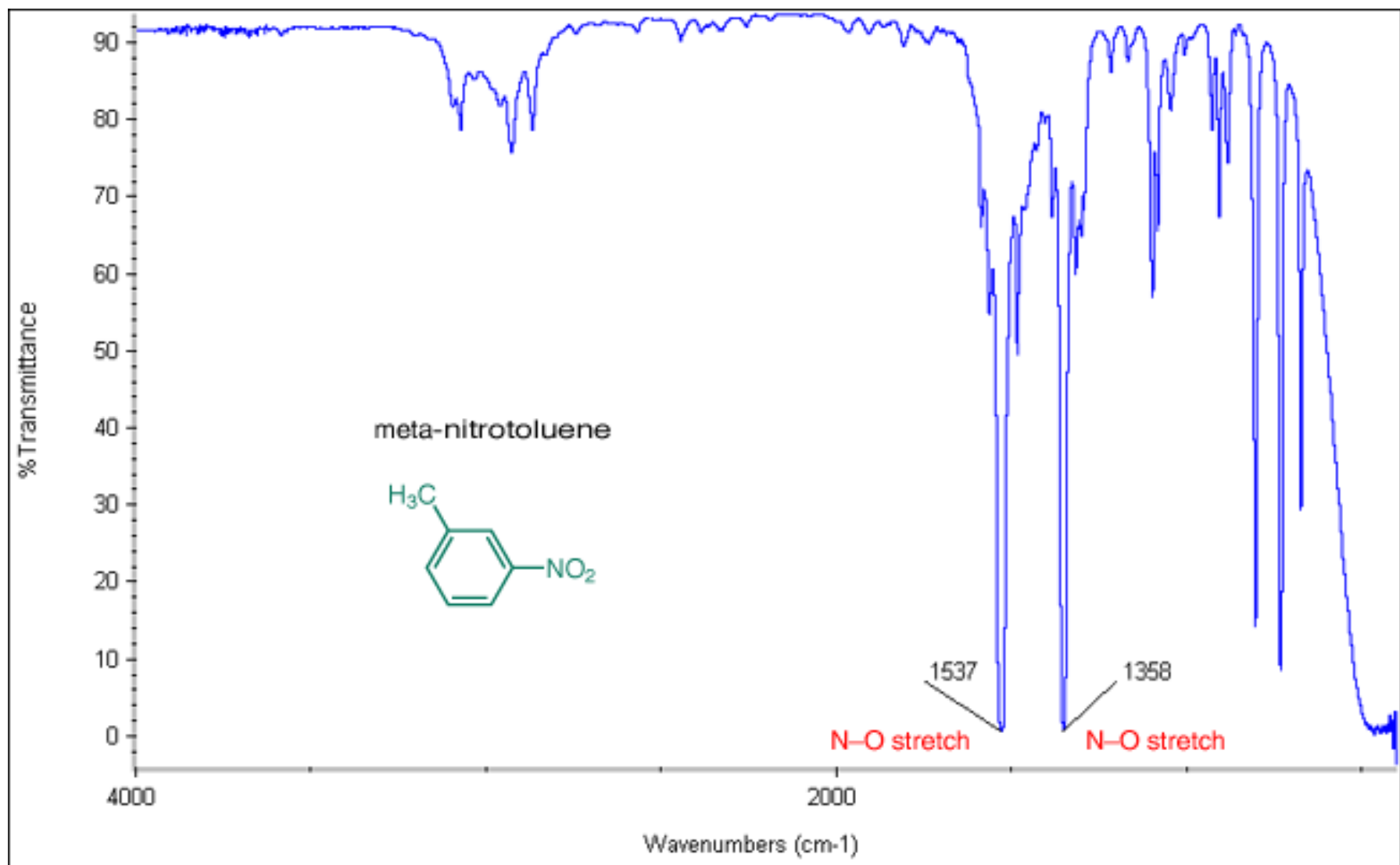


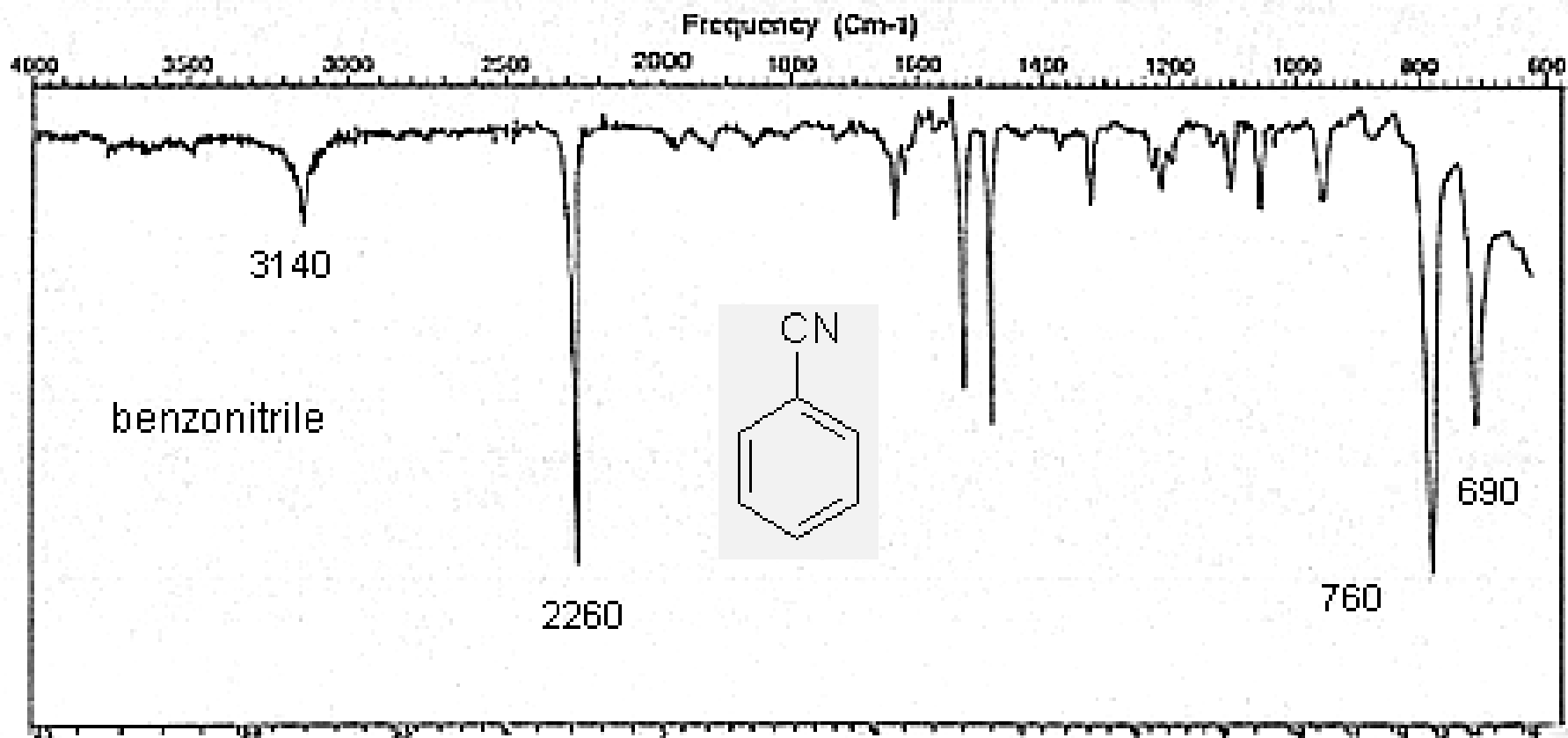


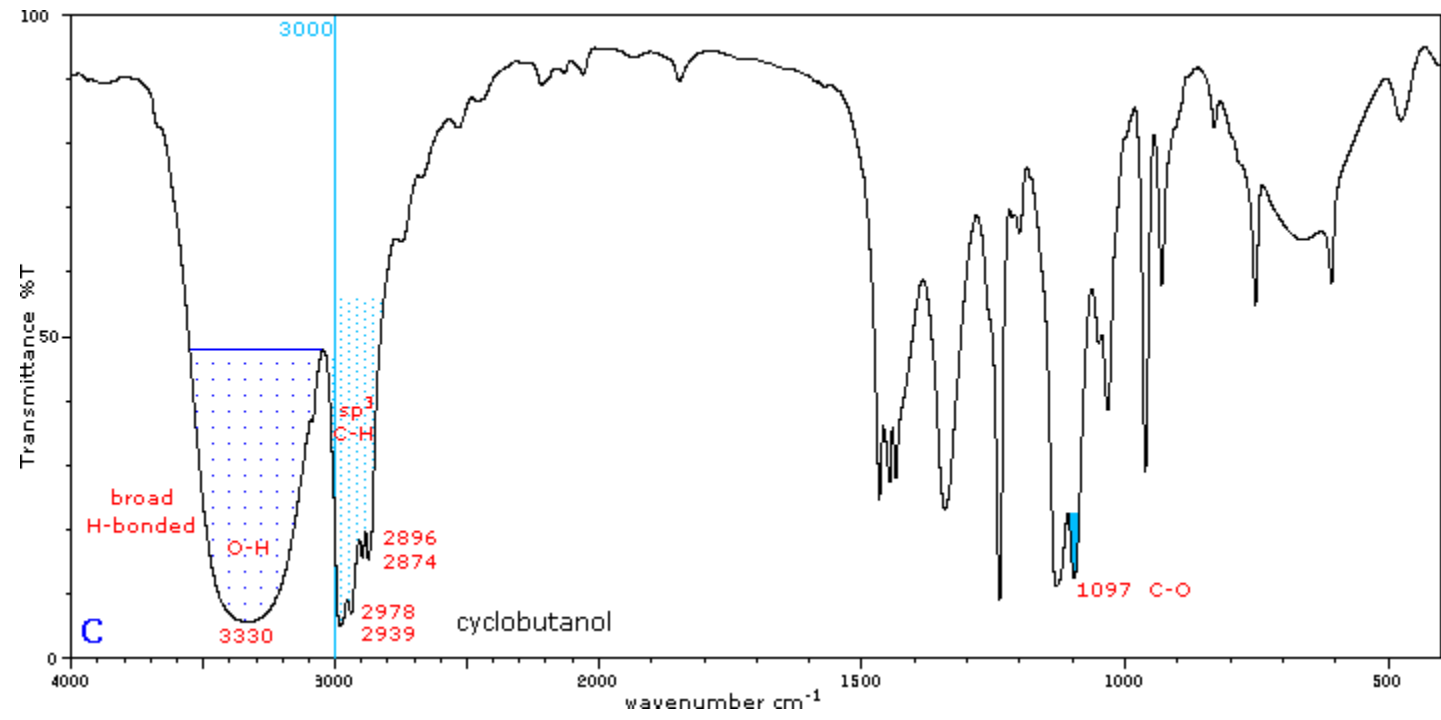
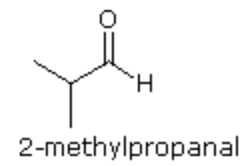
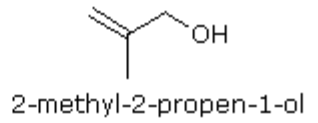
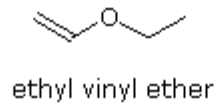
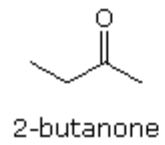
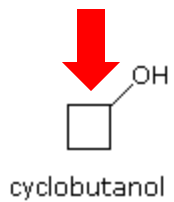


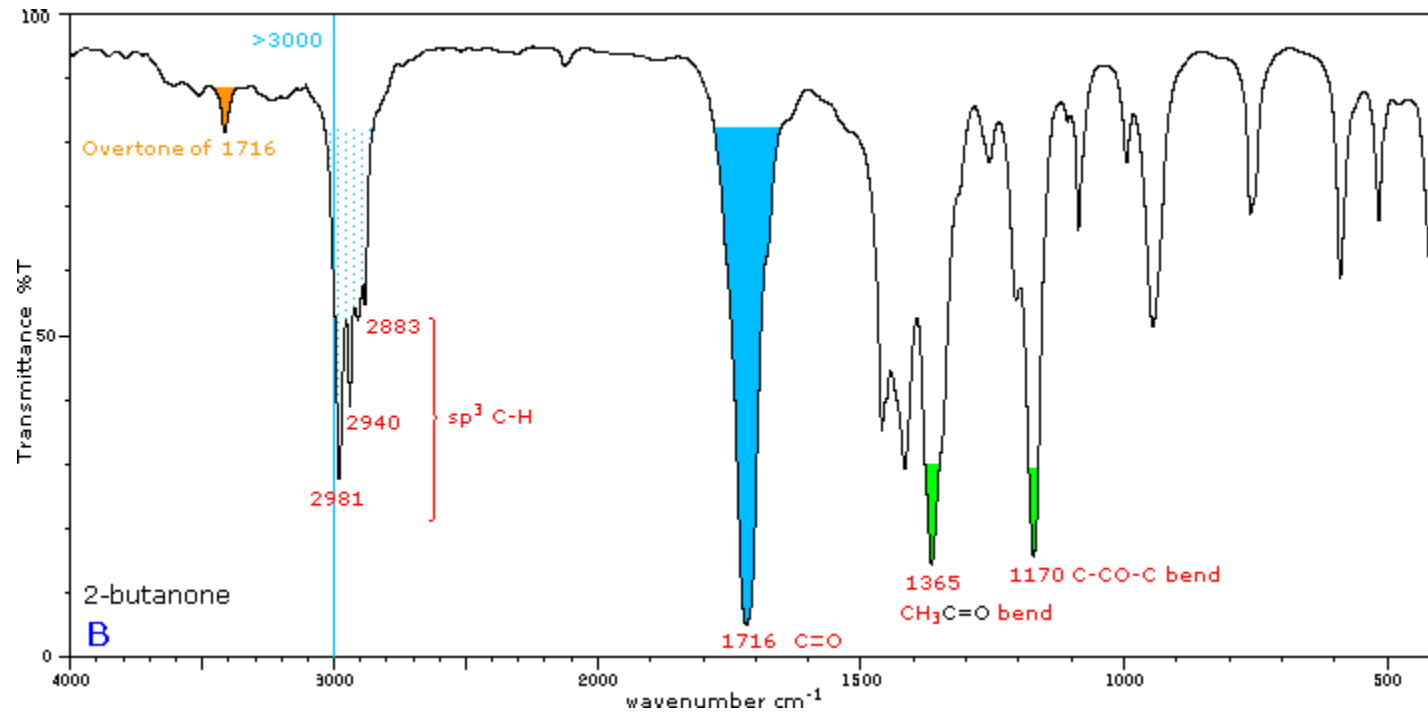
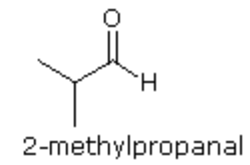
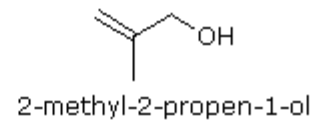
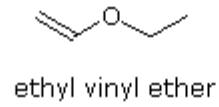
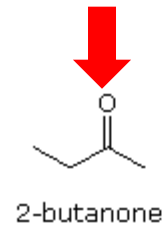
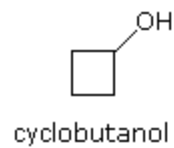


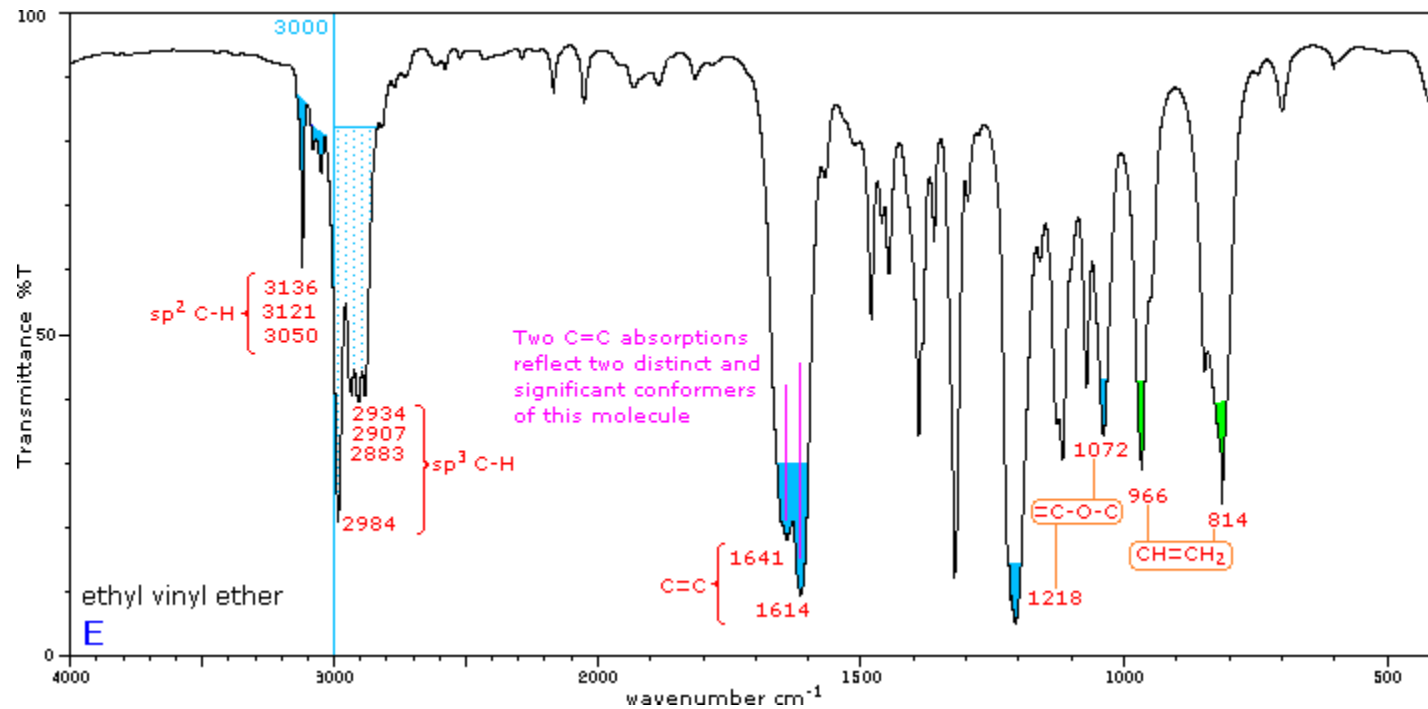
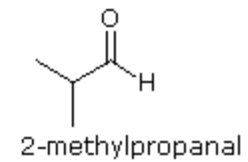
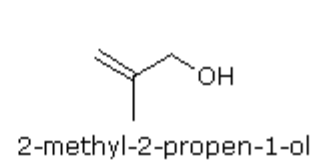
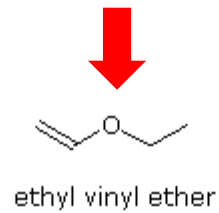
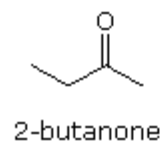
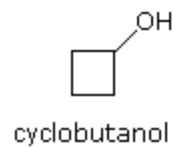


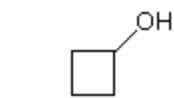




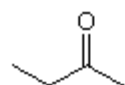




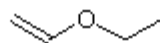




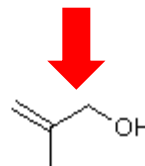
cyclobutanol



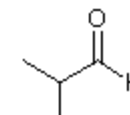
2-butanone



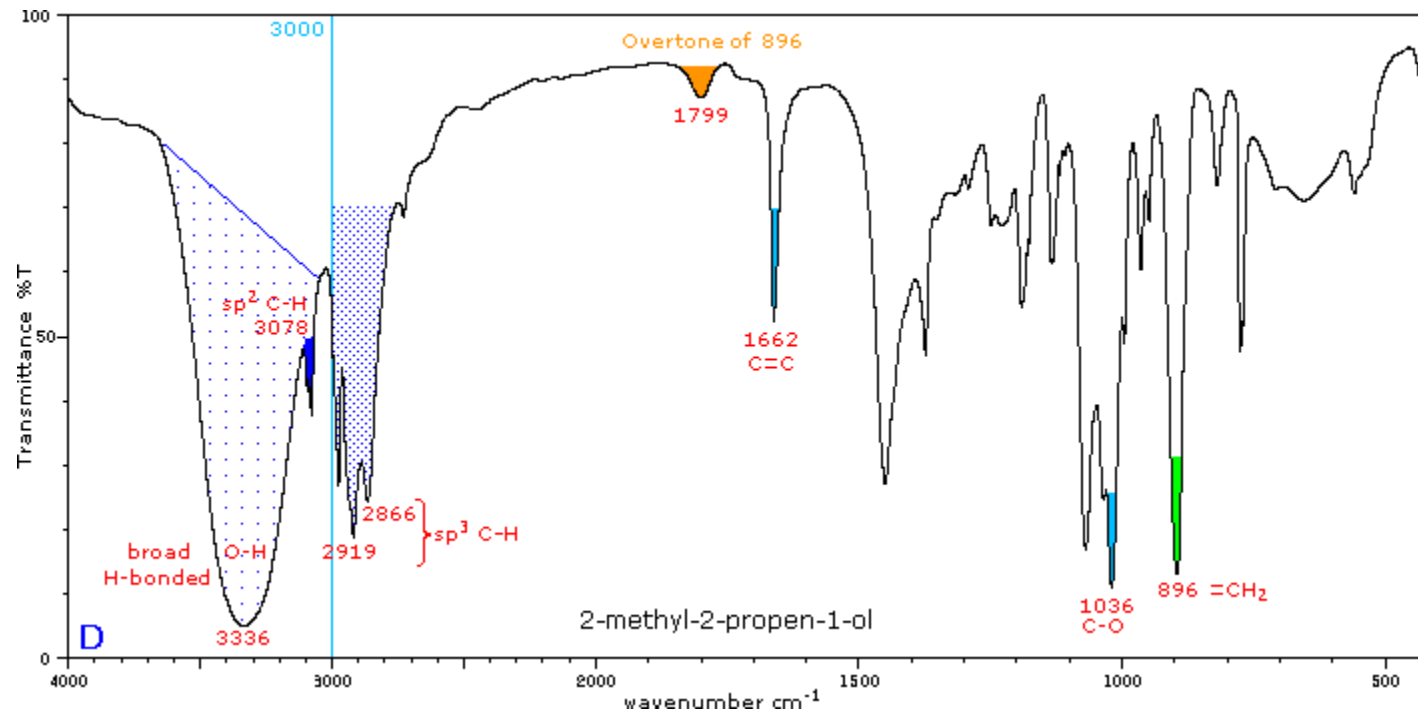
ethyl vinyl ether

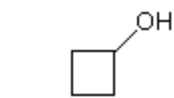


2-methyl-2-propen-1-ol

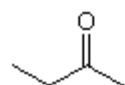


2-methylpropanal

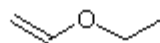




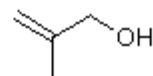
cyclobutanol



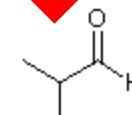
2-butanone



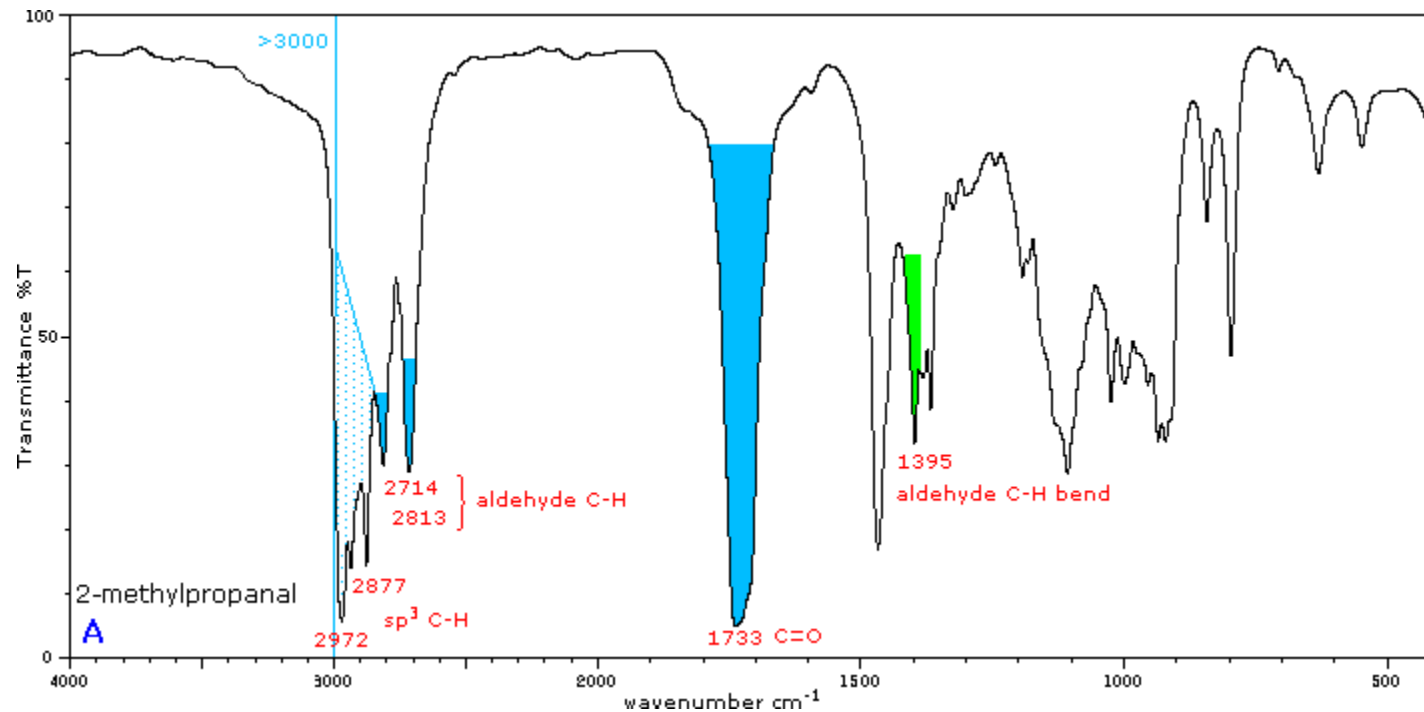
ethyl vinyl ether

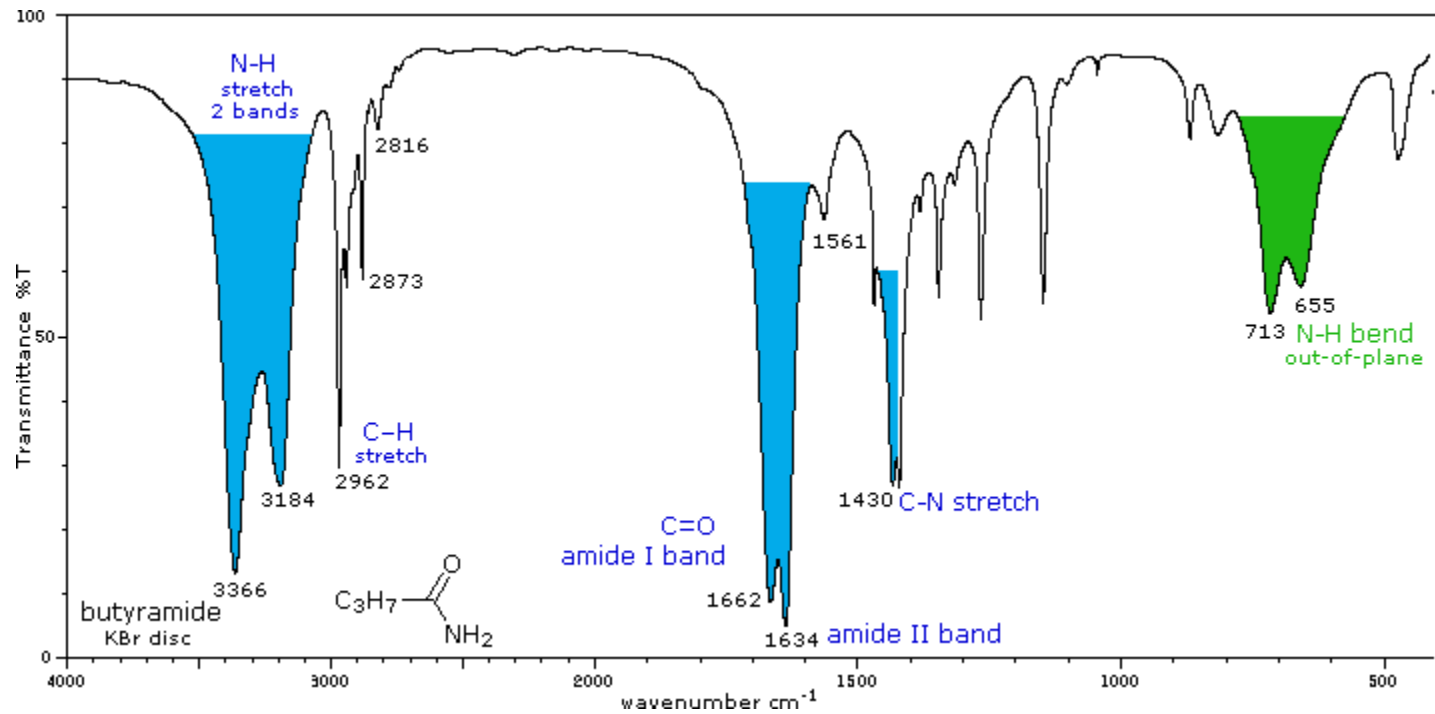


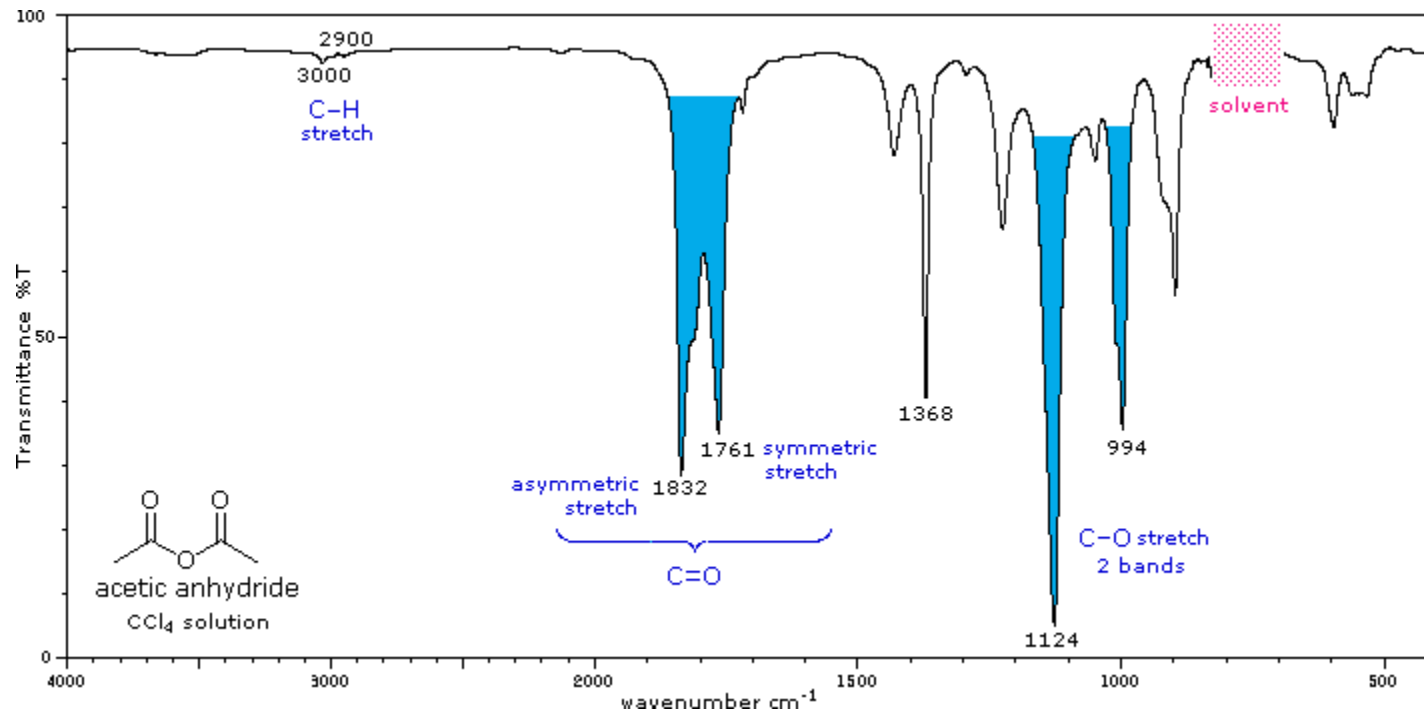
2-methyl-2-propen-1-ol



2-methylpropanal







Espectrometria de Massas (MS)

The Cavendish Laboratory, Cambridge, England.

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.



~1870

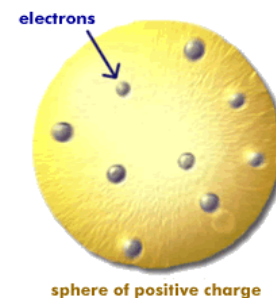
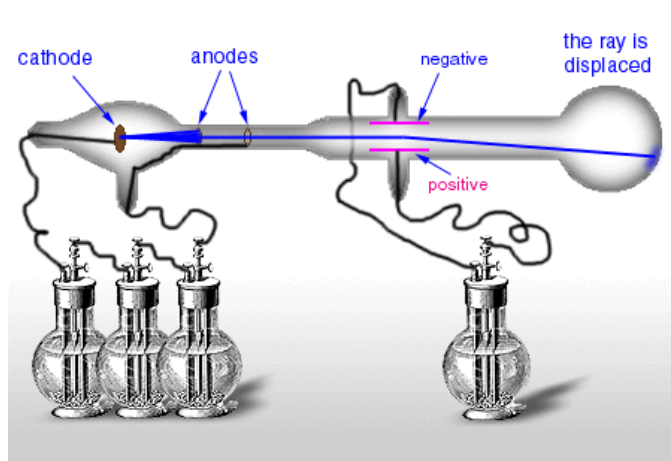




The father of MS and the first mass spectrometrists to win the Nobel Prize.

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"

N**BEL**
Prize in Physics 1906



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.

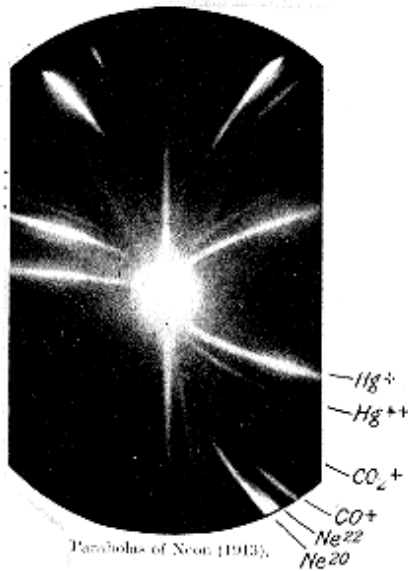
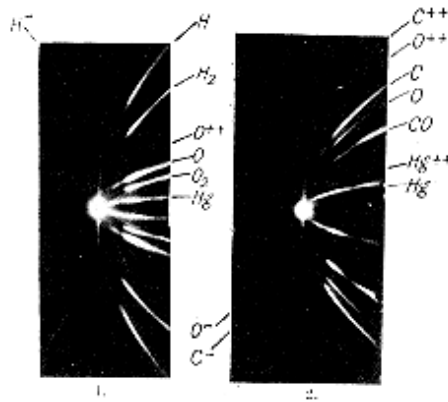
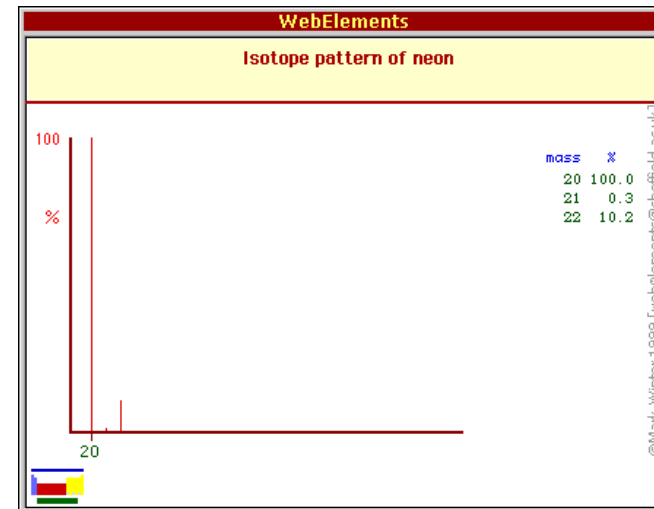
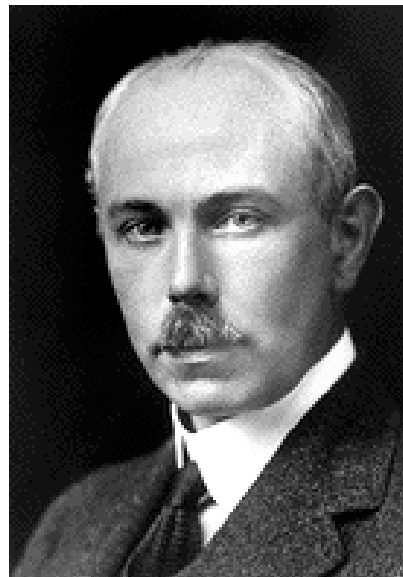
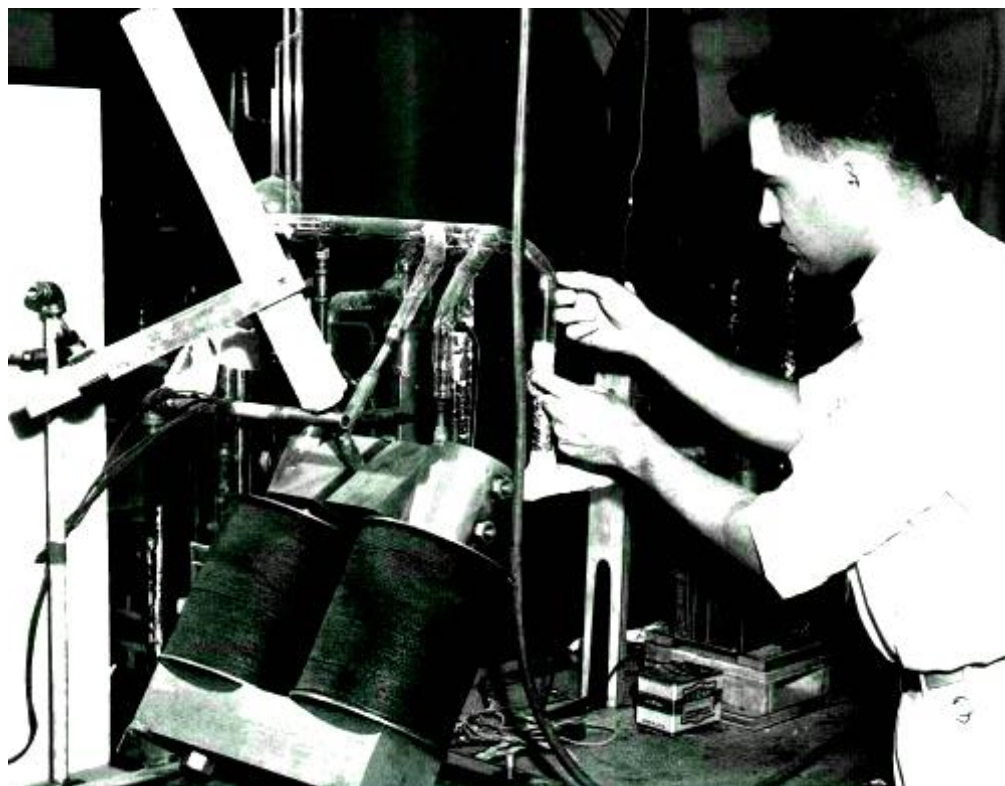


Figure 2



Alfred Nier

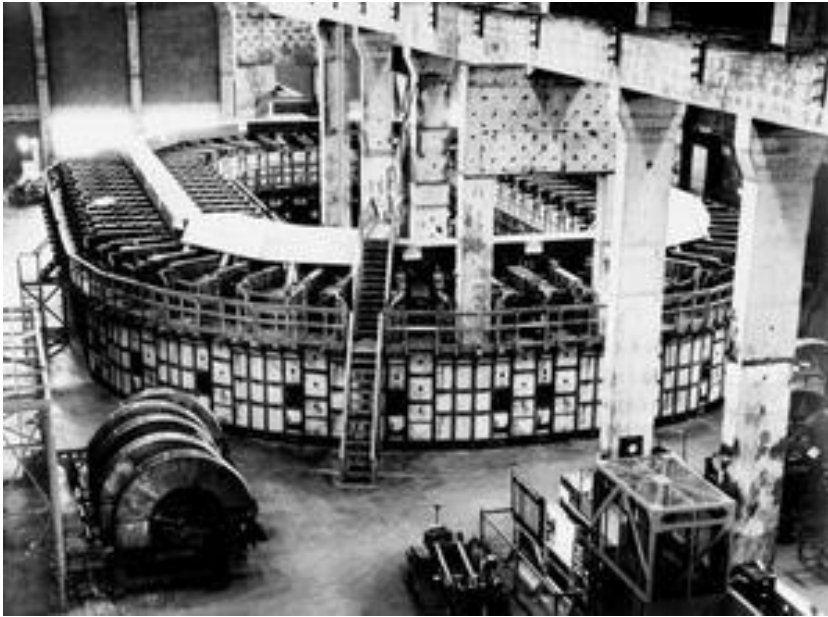
~1940 University of Minnesota



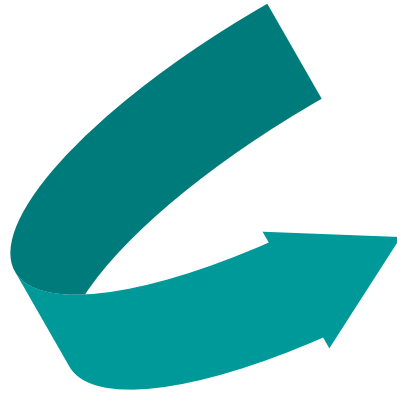
$^{12}\text{C}/^{13}\text{C}$ varies in nature

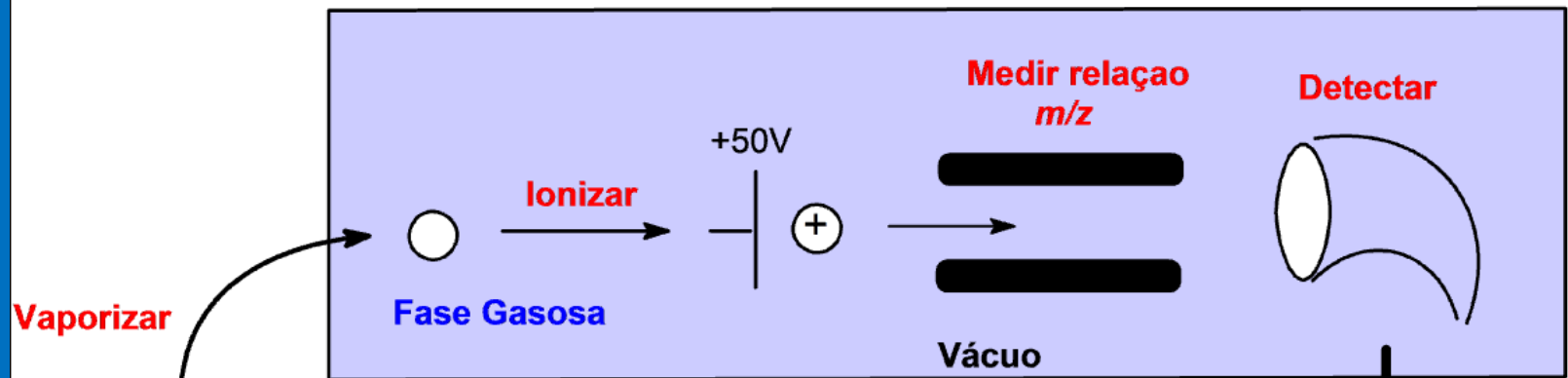
^{238}U , ^{235}U , ^{234}U = few mg of pure ^{235}U

Bomba Atômica

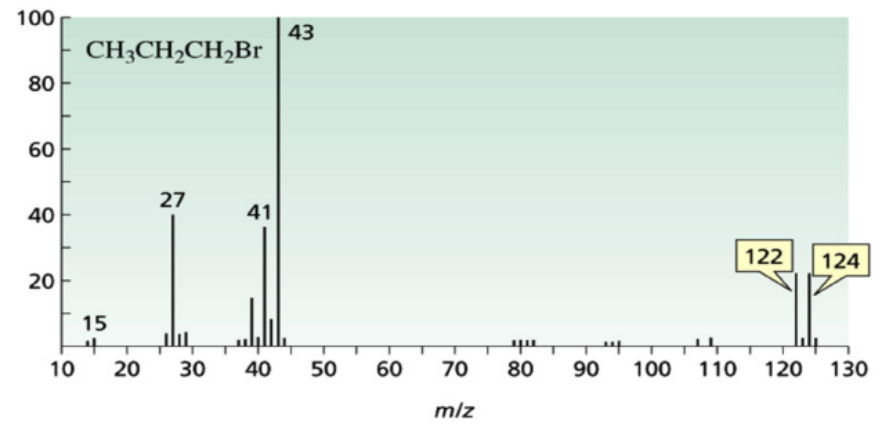


Calutron “Racetracks” at Oak Ridge produced enriched ^{235}U for the world’s first atomic weapons



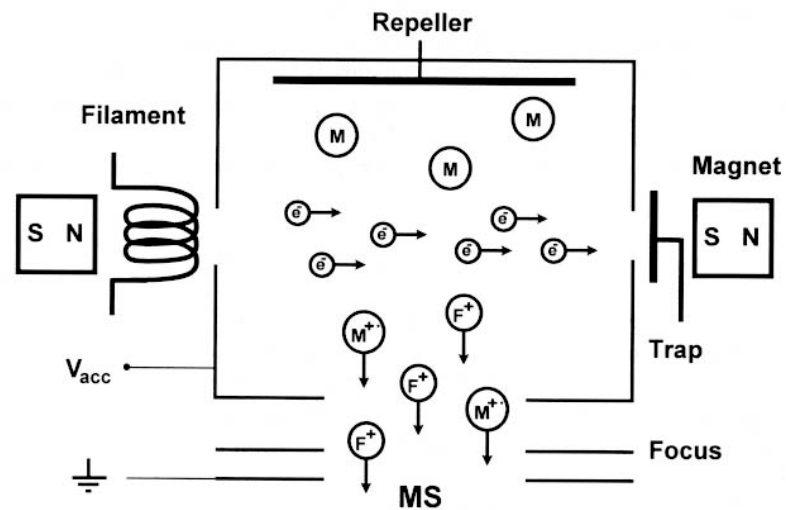
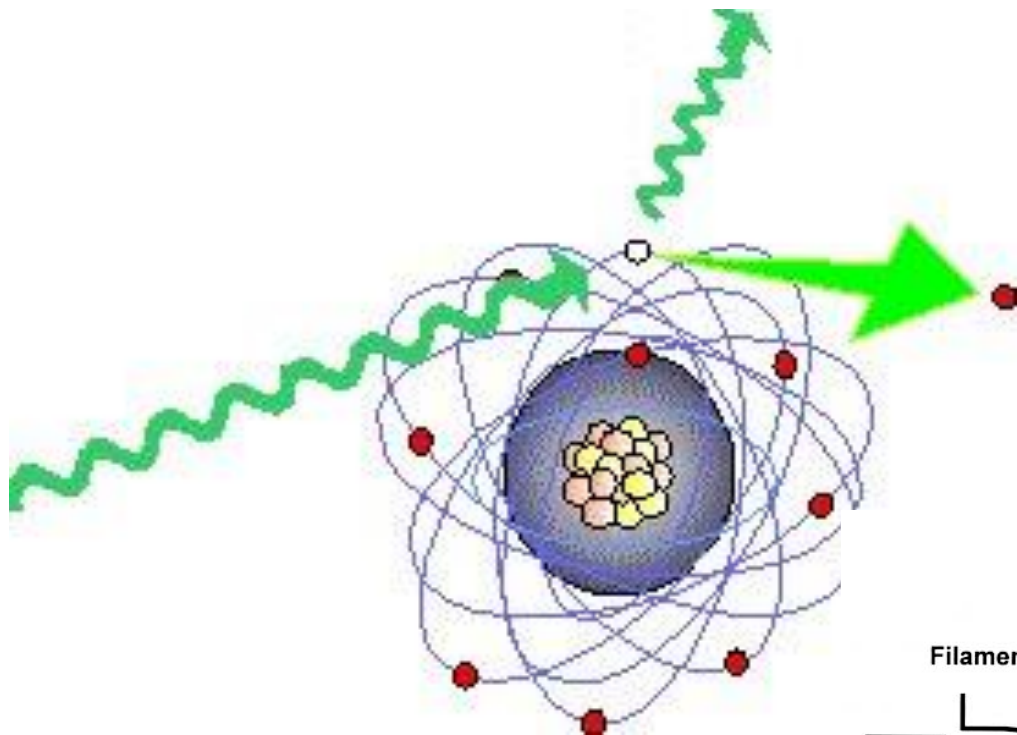


Moléculas na Fase Condensada



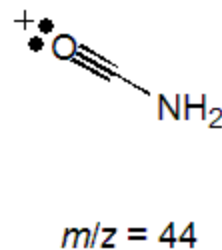
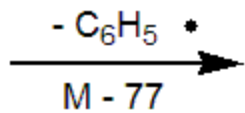
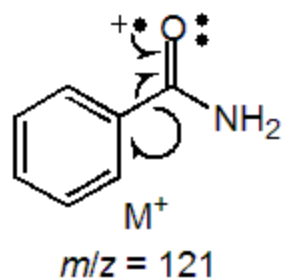
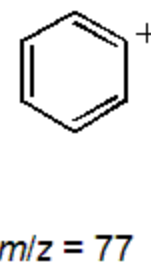
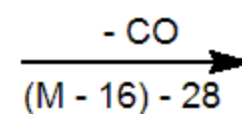
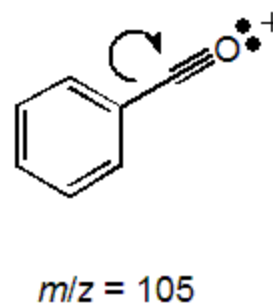
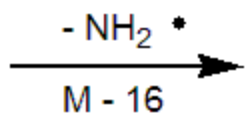
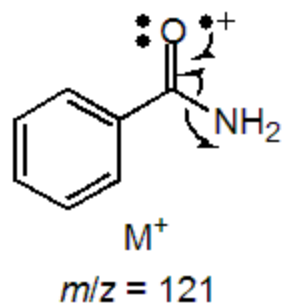
EI : Electron Ionization 70 eV

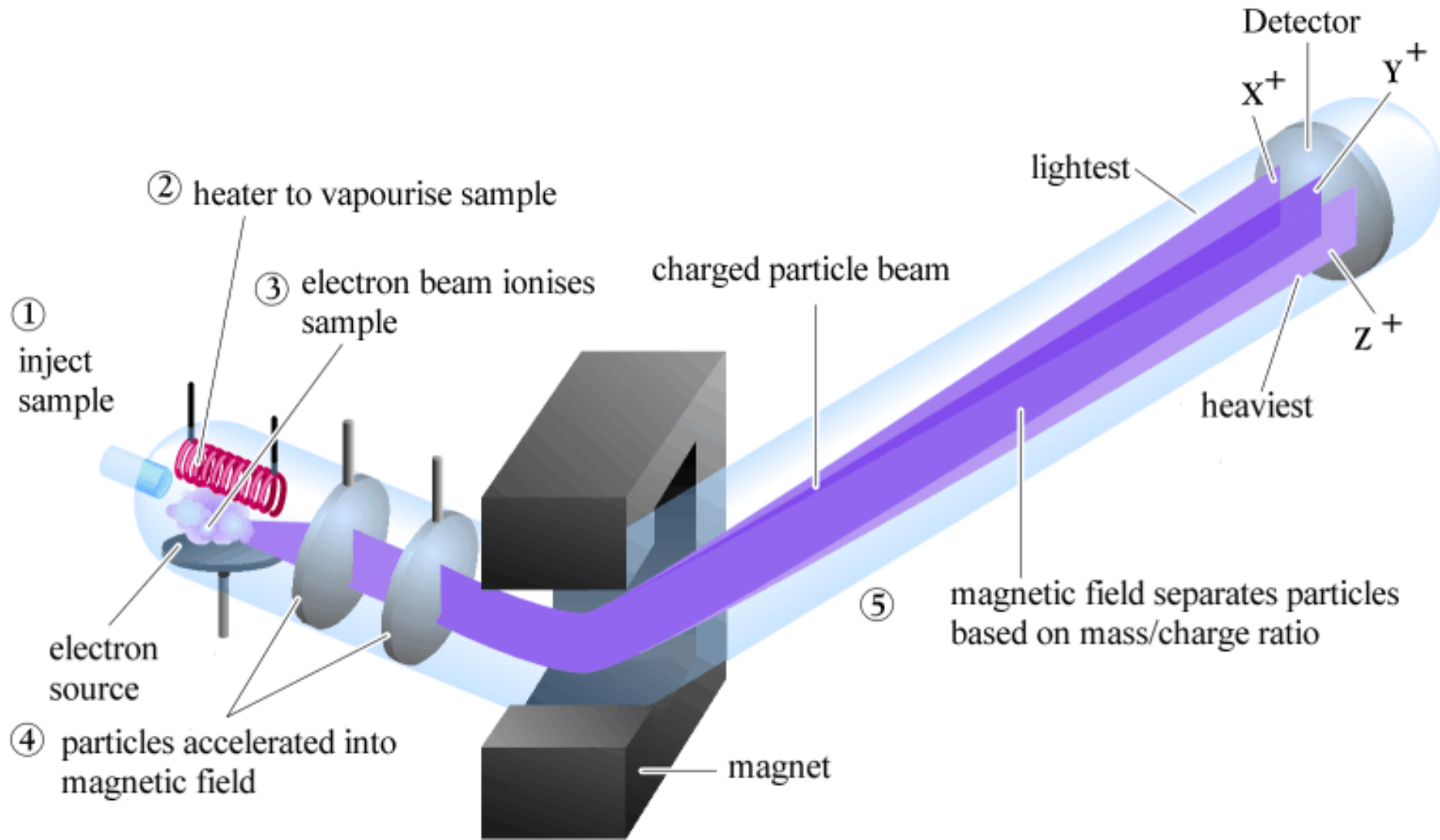
(Dempster & Nier)



A Dupla Dinâmica!

Espécies Moleculares e Fragmentos





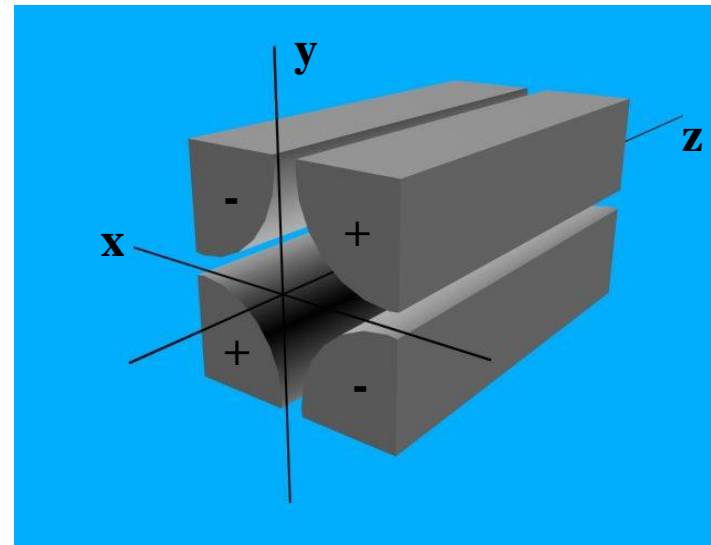
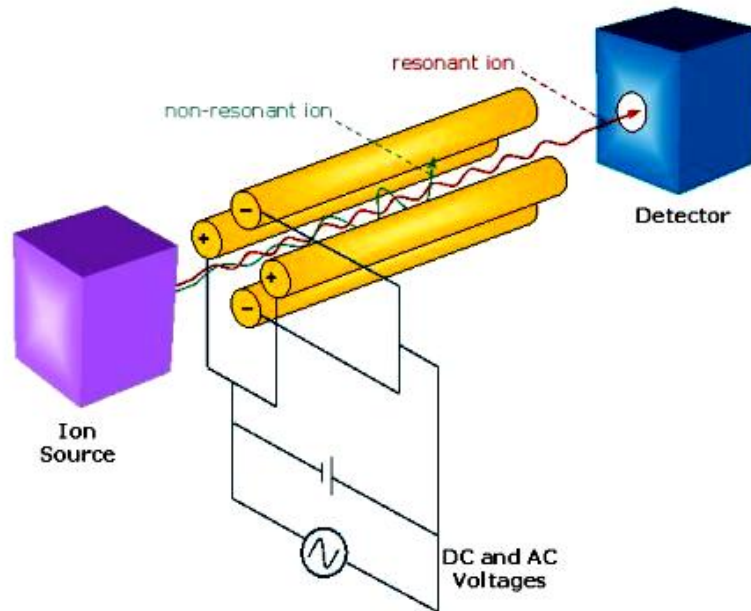
Quadrupolos Lineares : Q / q

Paul & Steinwedel 1953

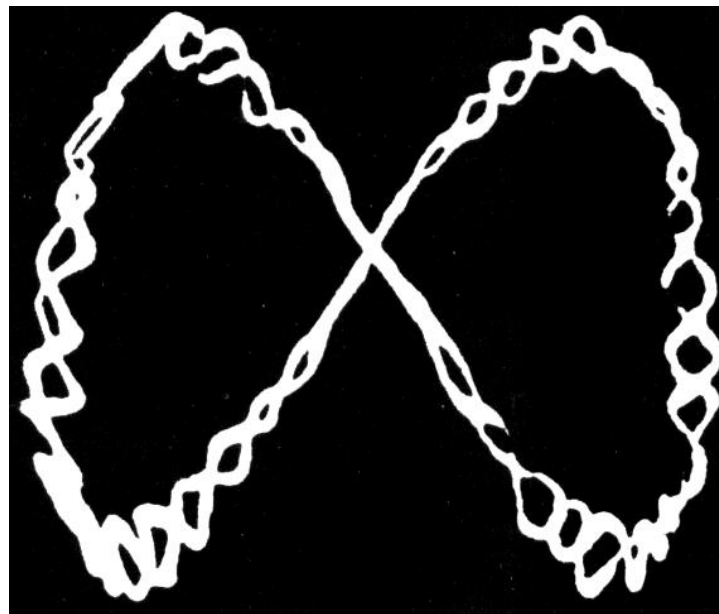
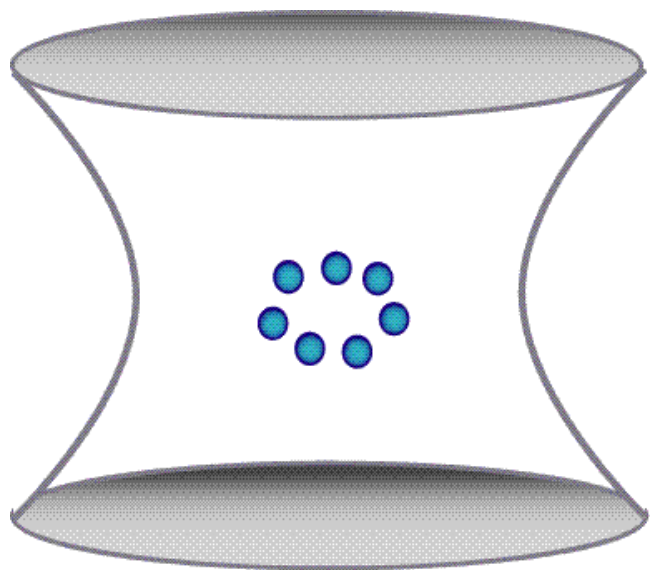


Wolfgang Paul
Prêmio Nobel 1989

Quadrupole Ion Filter

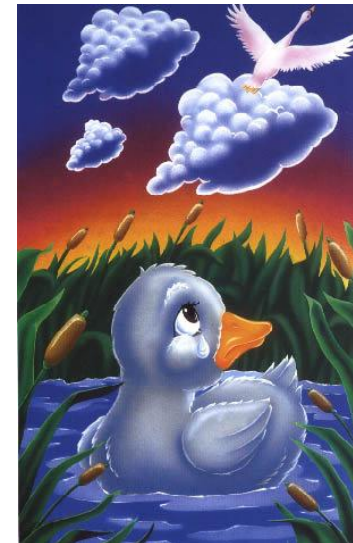
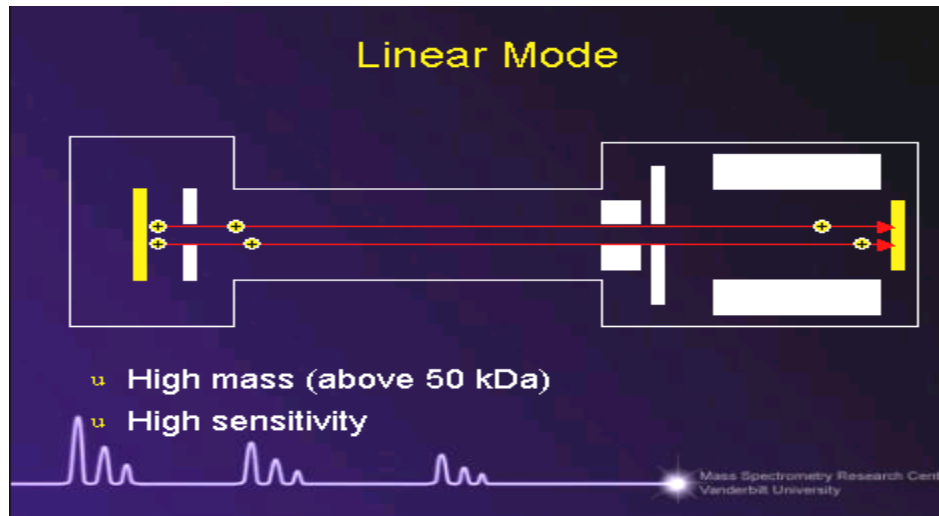


- A varredura é feita variando simultaneamente U (DC) e V_0 (AC) mas mantendo constante a relação U/V_0 .



Tempos de Vôo “TOF”

Cameron 1948



O patinho feio

• *Através de um tubo de comprimento L ($\sim 1m$) sob alto vácuo, íons formados por ionização pulsada (~ 0.25 a 1 ms) são acelerados pela aplicação de uma voltagem V ($\sim 1-10$ KV), e adquirem velocidades proporcionais as suas m/z 's. Ocorre dispersão em tempo, e íons de diferentes m/z 's chegam ao detector em tempos diferentes :*

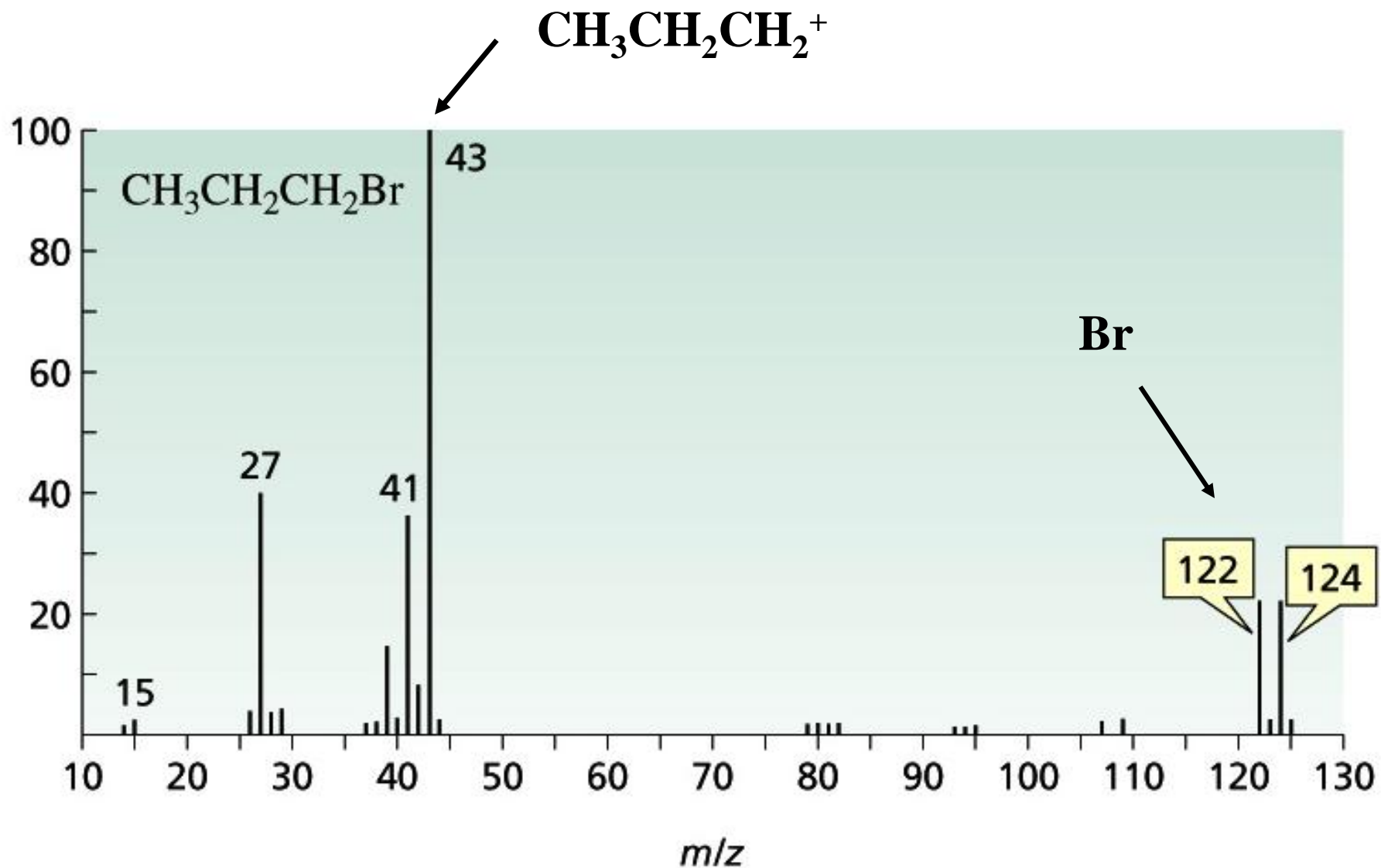
$$t = (m / 2zeV)^{1/2} L$$

• *Princípio básico: Dispersão no tempo de íons por aceleração seguida da medidas de seus tempos de vôo "livre".*

Massa Exata = Composição Elementar
Defeitos de Massas

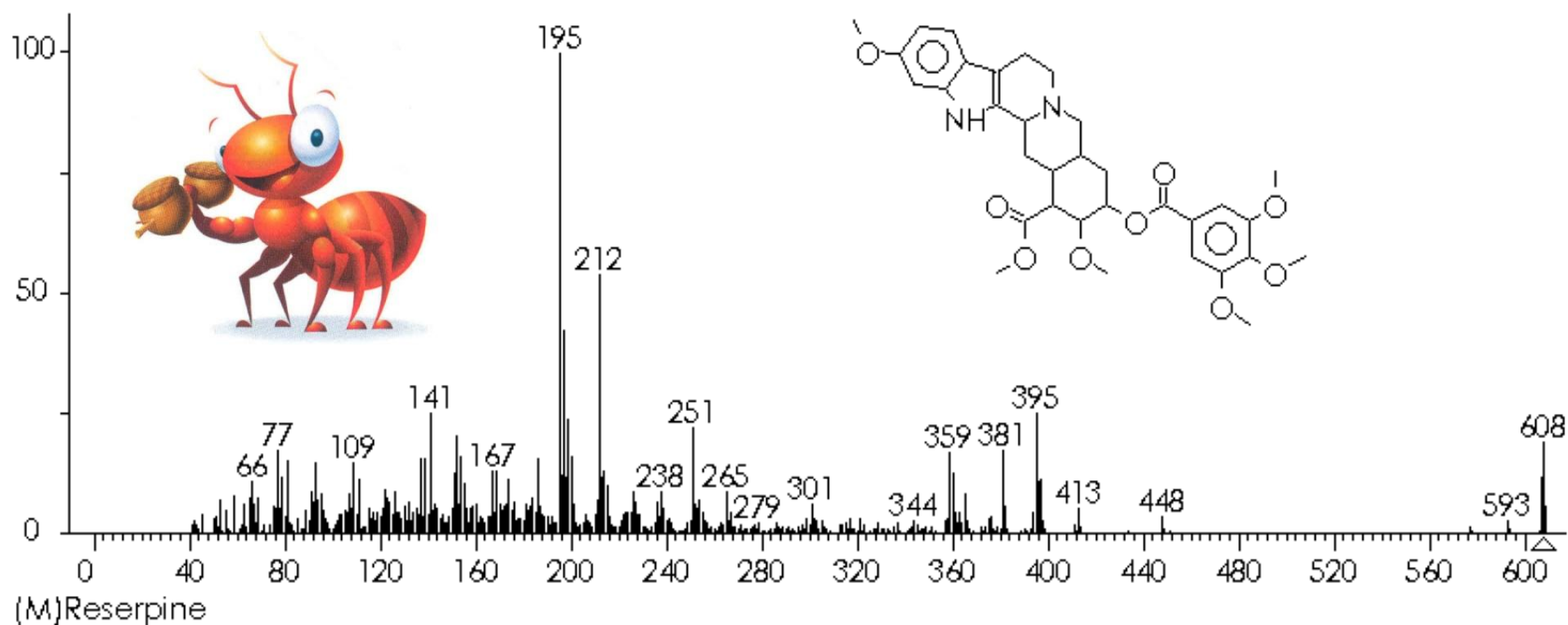
Element	Nuclide	Nominal Mass	Exact Mass	Mass Defect
Hydrogen	H	1	1.0078	0.0078
Carbon	^{12}C	12	12.0000	0.0000
Nitrogen	^{14}N	14	14.0031	0.0031
Oxygen	^{16}O	16	15.9949	-0.0051
Fluorine	^{19}F	19	18.9984	-0.0016
Sulfur	^{32}S	32	31.9721	-0.0279
Chlorine	^{35}Cl	35	34.9689	-0.0311

Exact Mass and Mass Defect of Common Elements



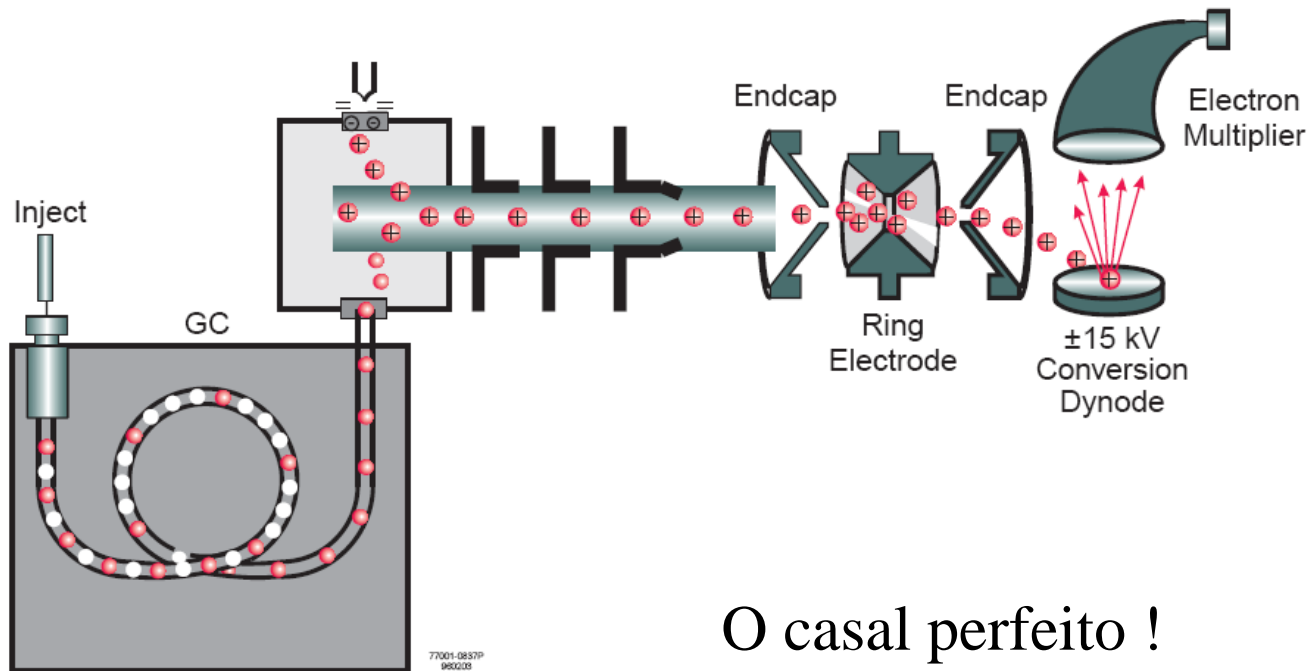
Reading the mass spectrum: Propyl bromide !

As “Pequenas” Moléculas



Produtos Naturais, Síntese, VOCs, ...

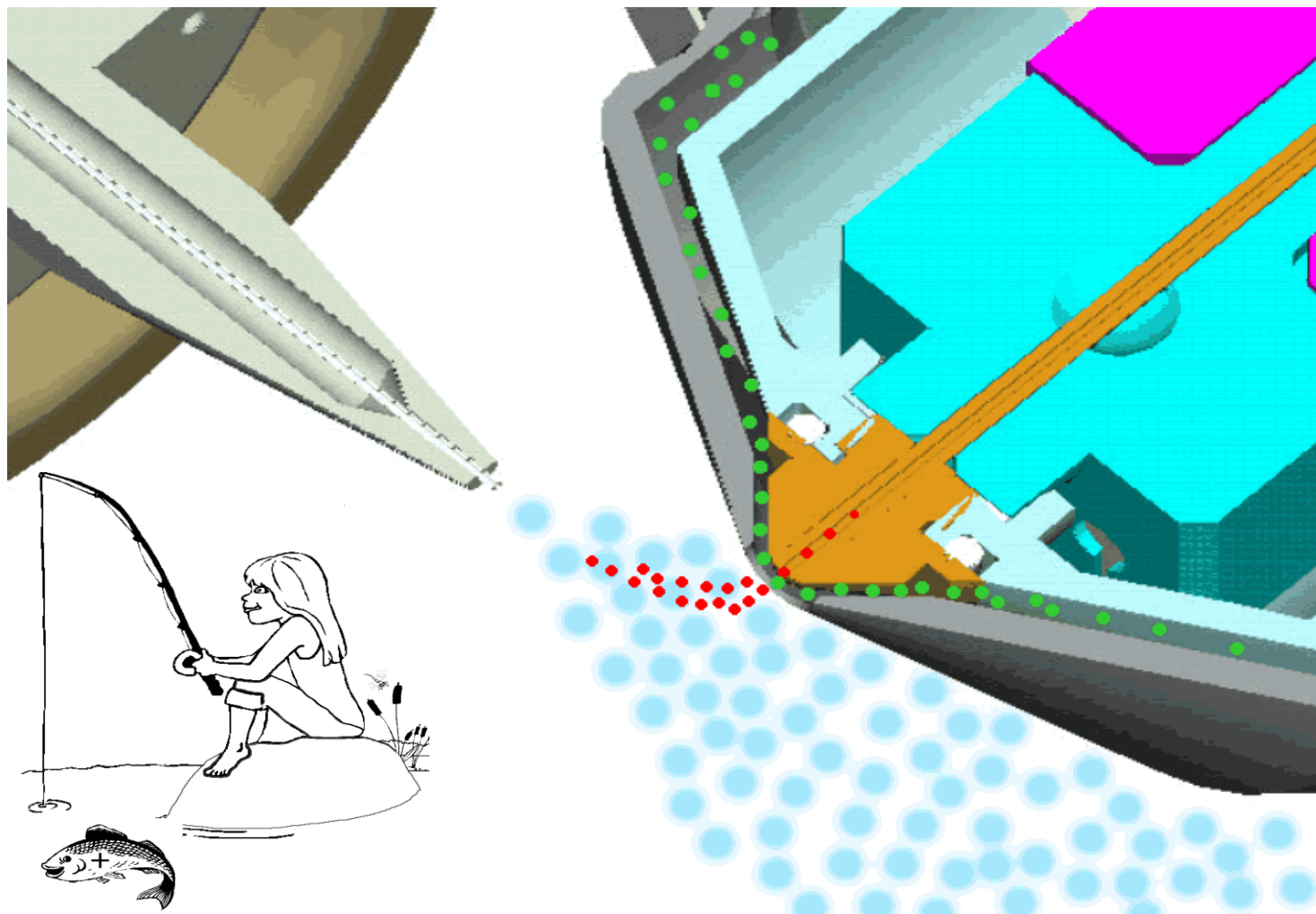
As “Pequenas” Moléculas



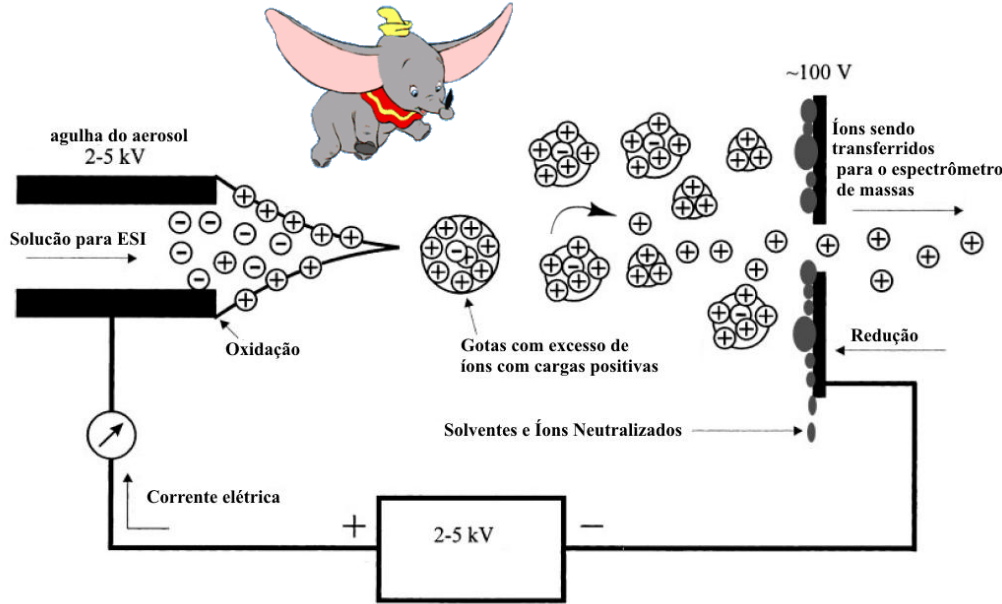
O casal perfeito !

ESI-MS “Ion Fishing”

Flying Molecular Elephants

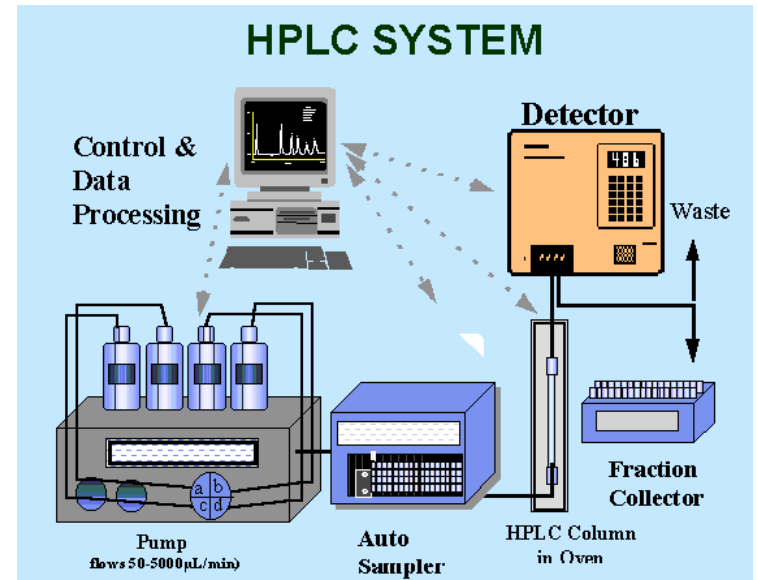


ESI-MS



“The Perfect Couple”

HPLC/MS



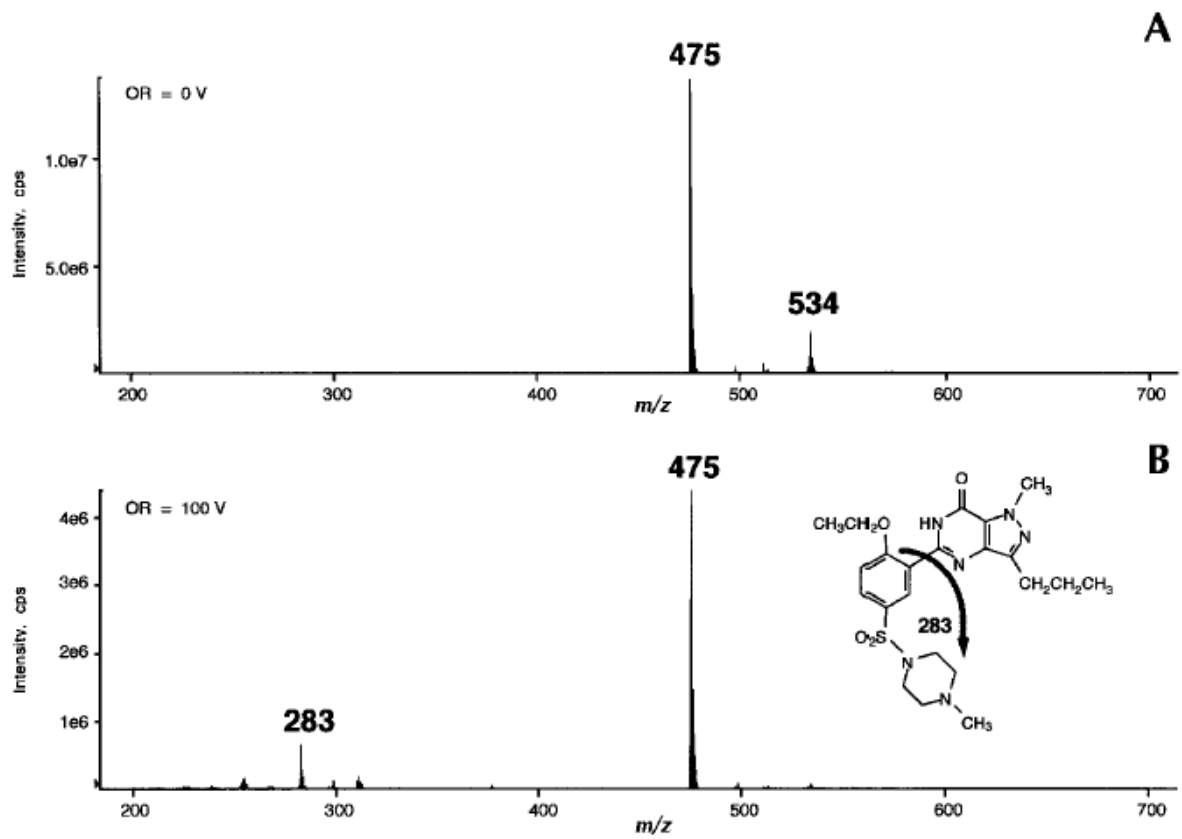
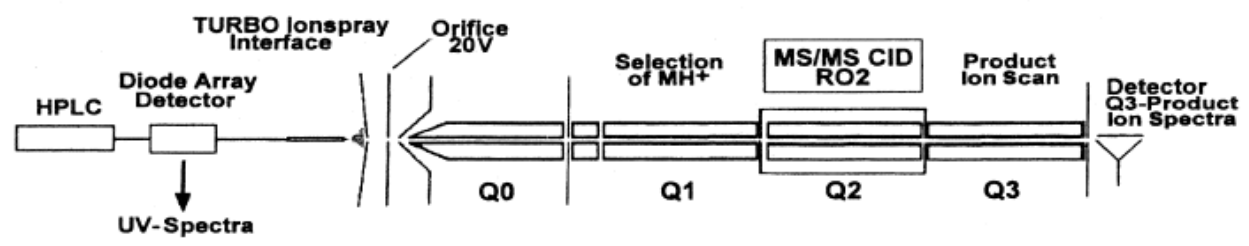


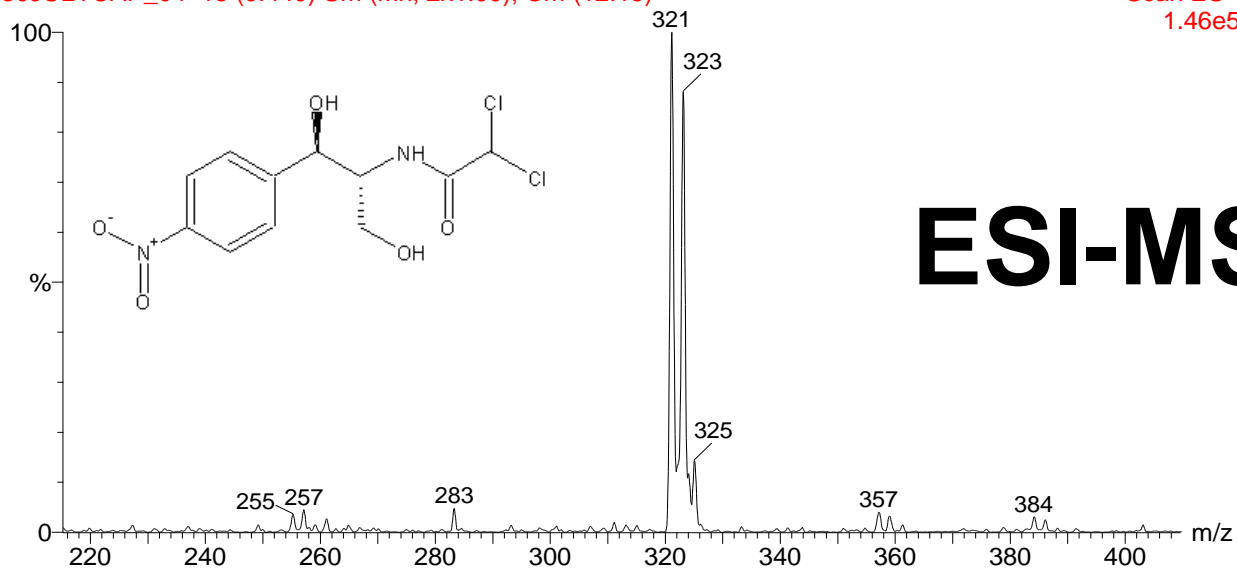
Figure 2. Positive-ion, ionspray mass spectra of sildenafil (m/z 200 to 700). Conditions: syringe infusion (50 $\mu\text{L}/\text{min}$) of a 10- $\mu\text{g}/\text{mL}$ solution of sildenafil in a mixture of (acetonitrile + 10 $\mu\text{g}/\text{mL}$ trimethylamine)/2mM NH_4COOH , pH 3.0 buffer (50:50, 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



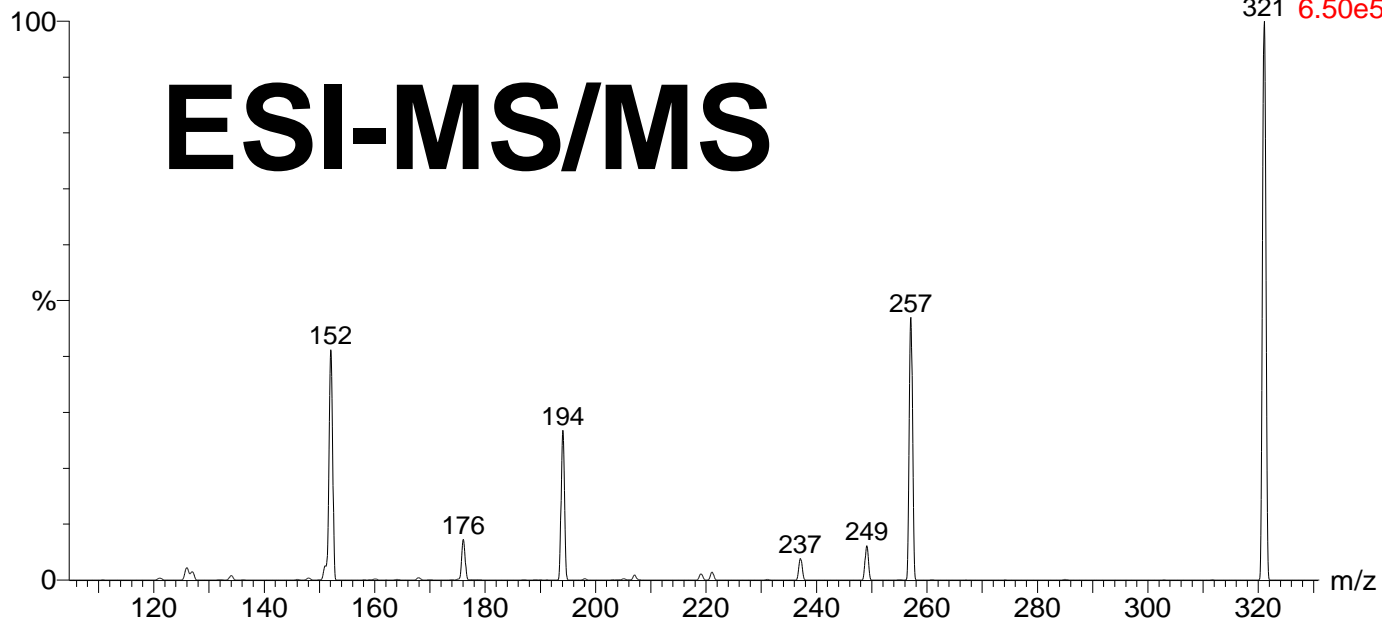
ESI-MS



MS/MS CE = 12

30JULYCAP_03 2 (0.068) Sm (Mn, 2x1.00); Cm (2:32)

Daughters of 321ES-
6.50e5



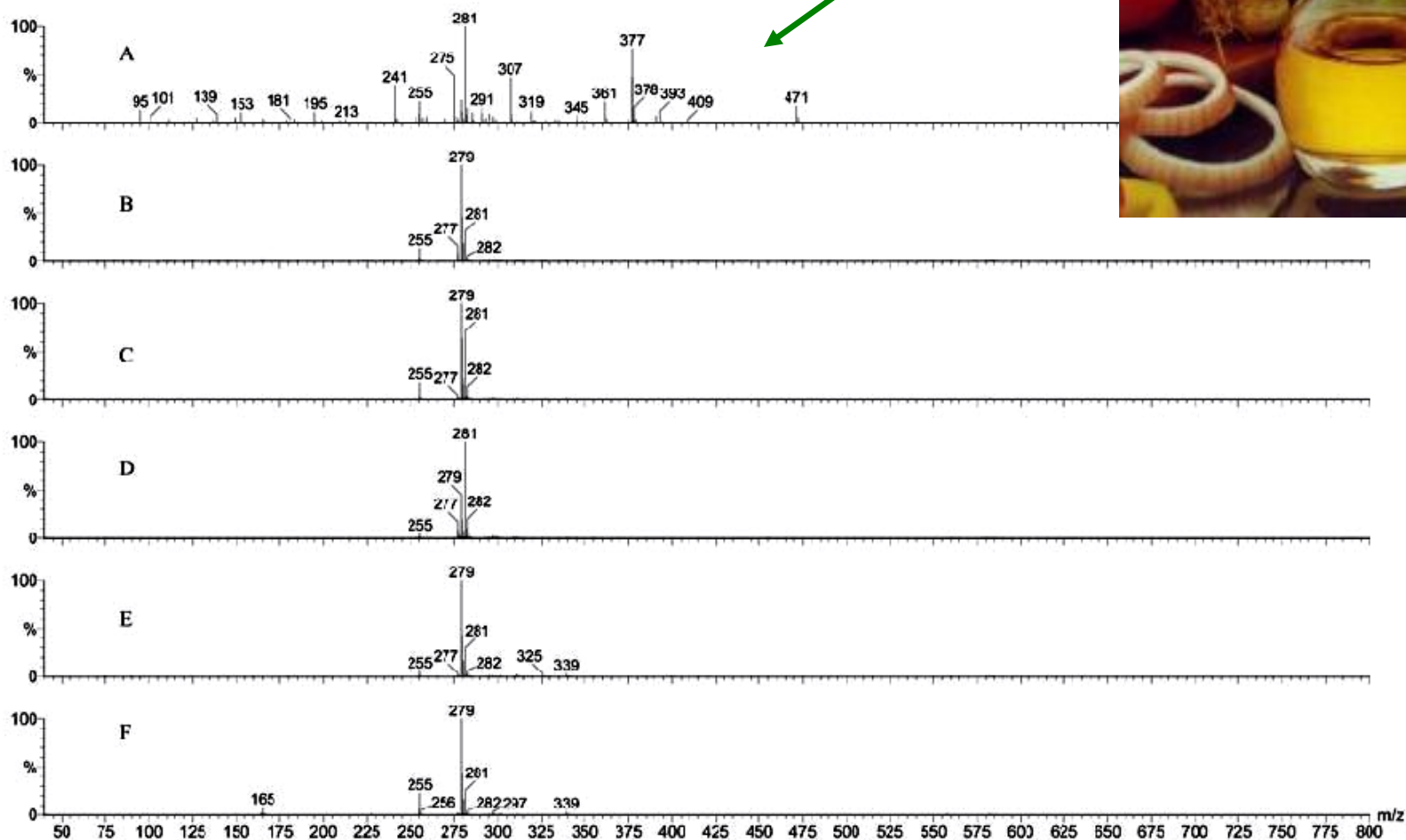
ESI-MS/MS

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

Rodrigo Ramos Catharino,[†] Renato Haddad,[†] Liliâne Giroto Cabrini,[†] Ildenize B. S. Cunha,[‡] Alexandra C. H. F. Sawaya,^{*,†} and Marcos N. Eberlin^{*,†}



Olive Oil

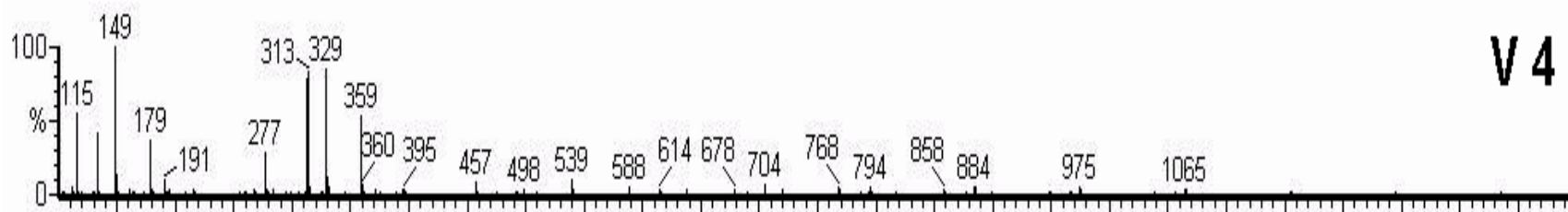


Wine characterization by direct infusion electrospray ionization mass spectrometry

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”

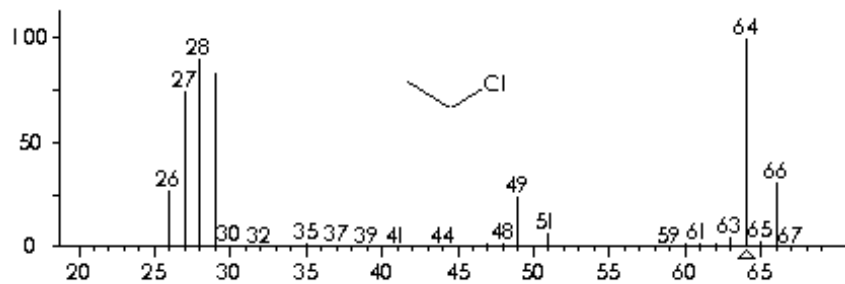


V 4

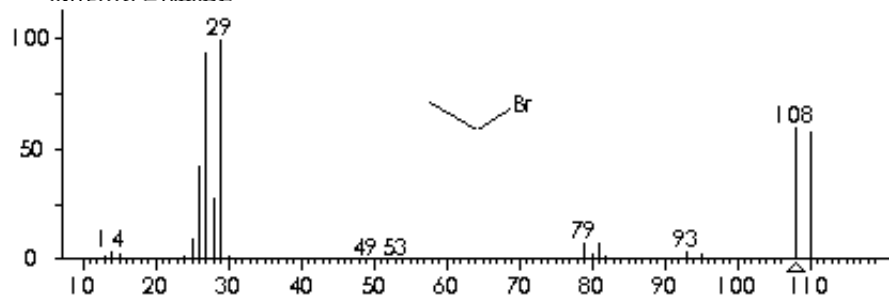
Wine



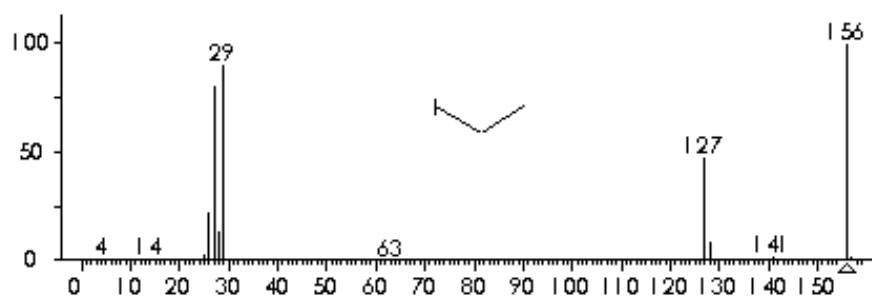
V 8



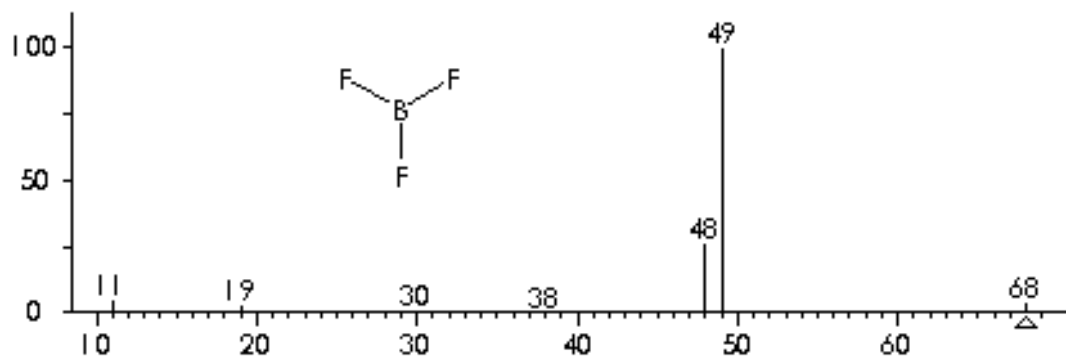
(M) Ethyl chloride



(M) Ethane, bromo-

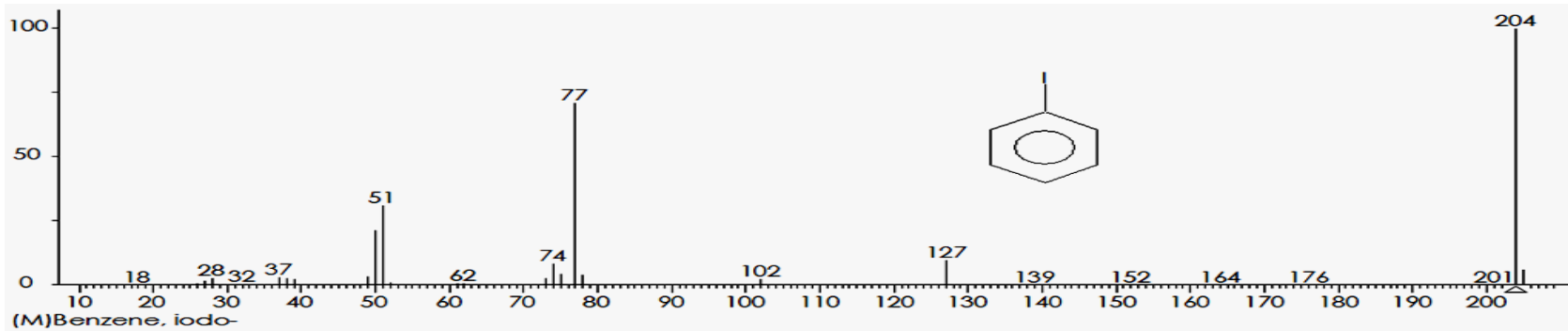
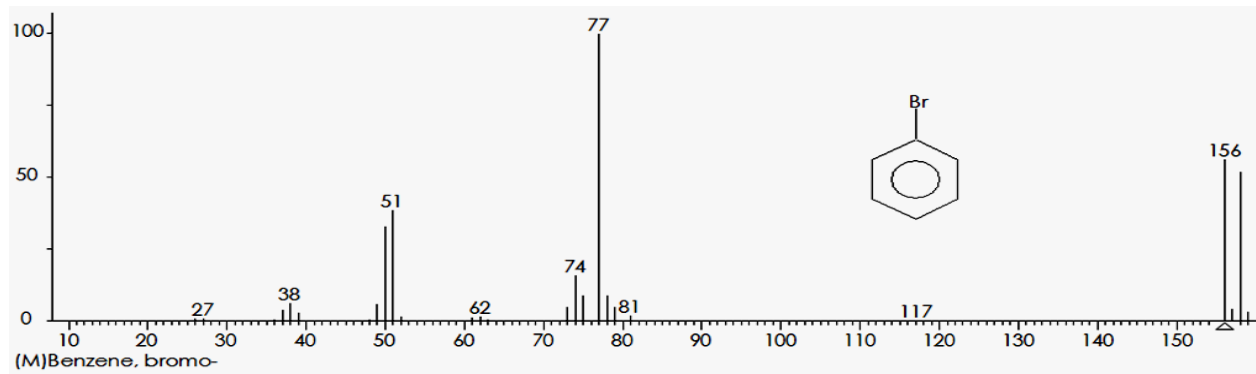
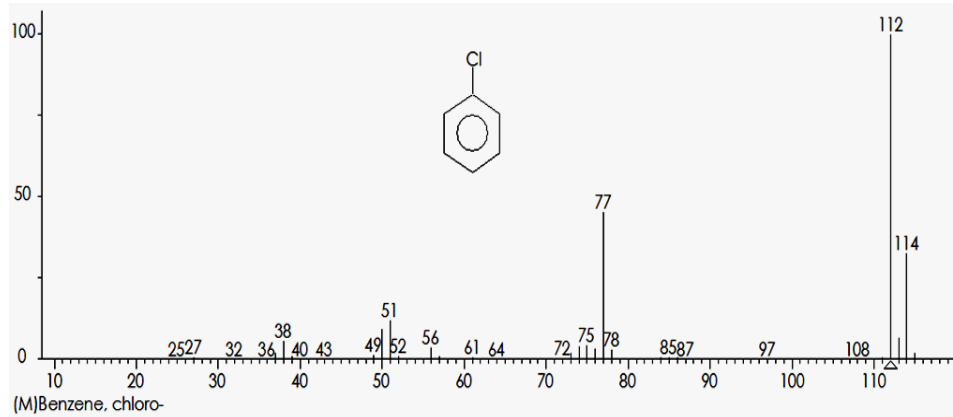
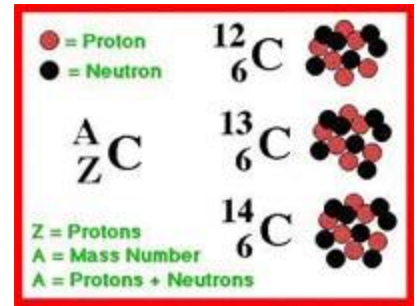


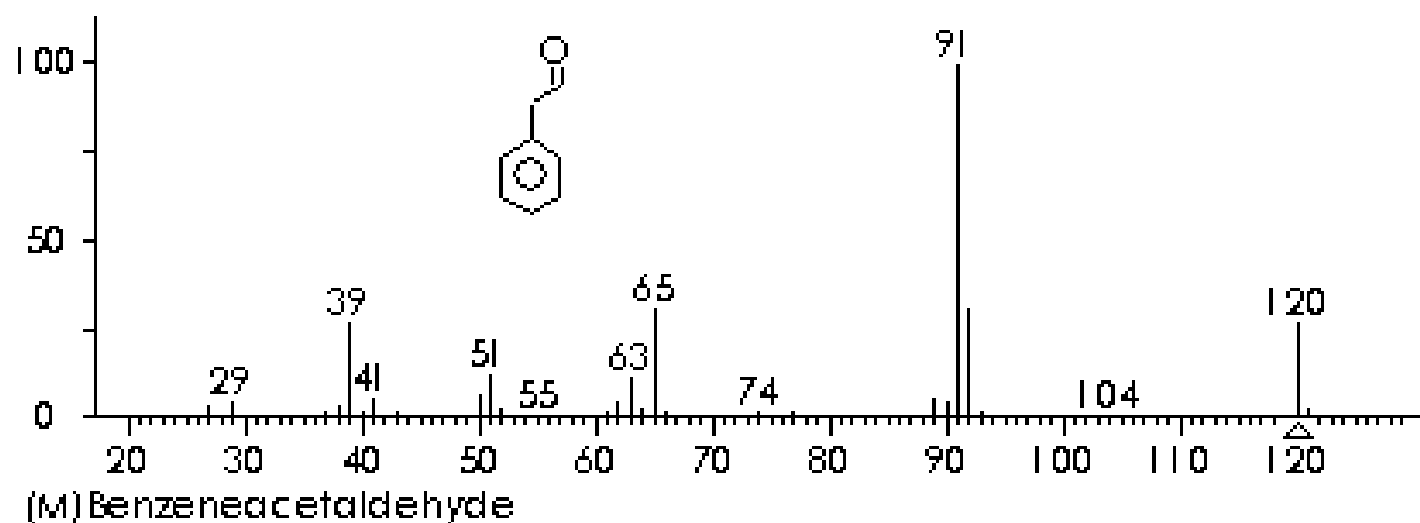
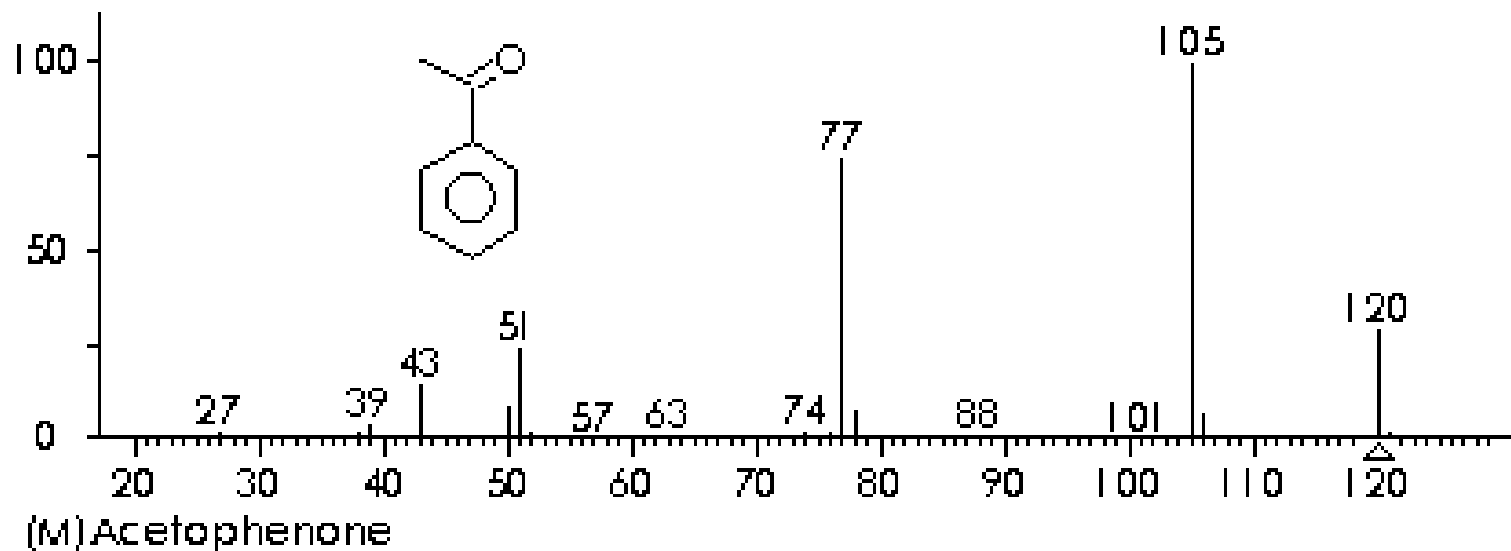
(M) Ethane, iodo-

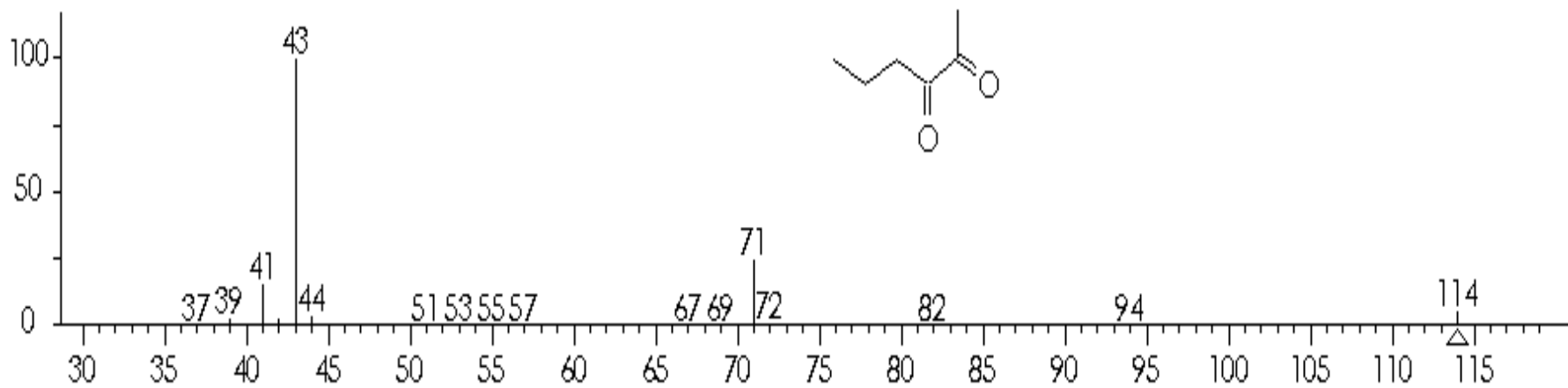
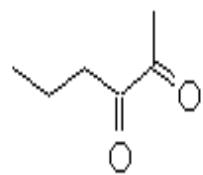


(M) Borane, trifluoro-

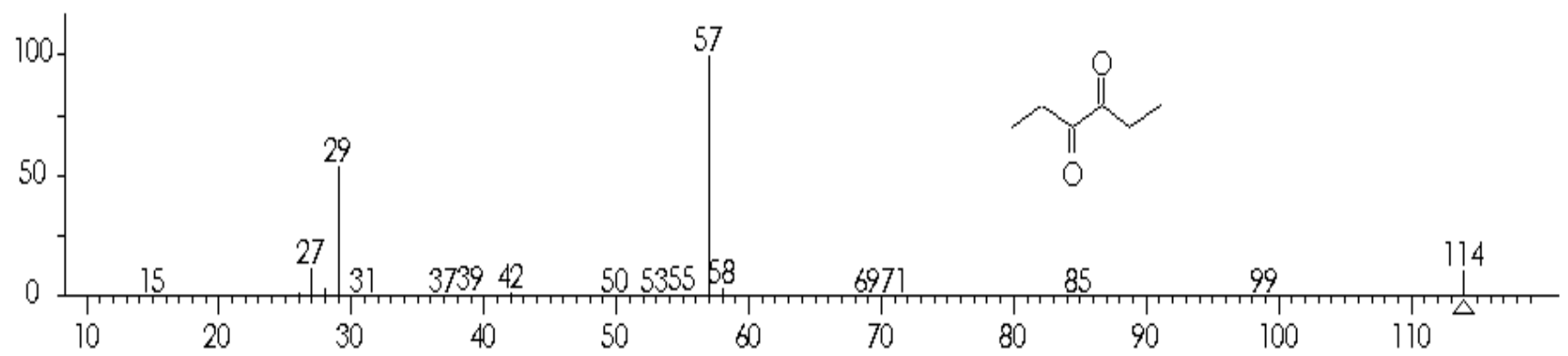
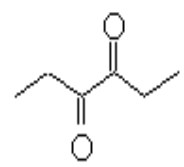
Isótopos





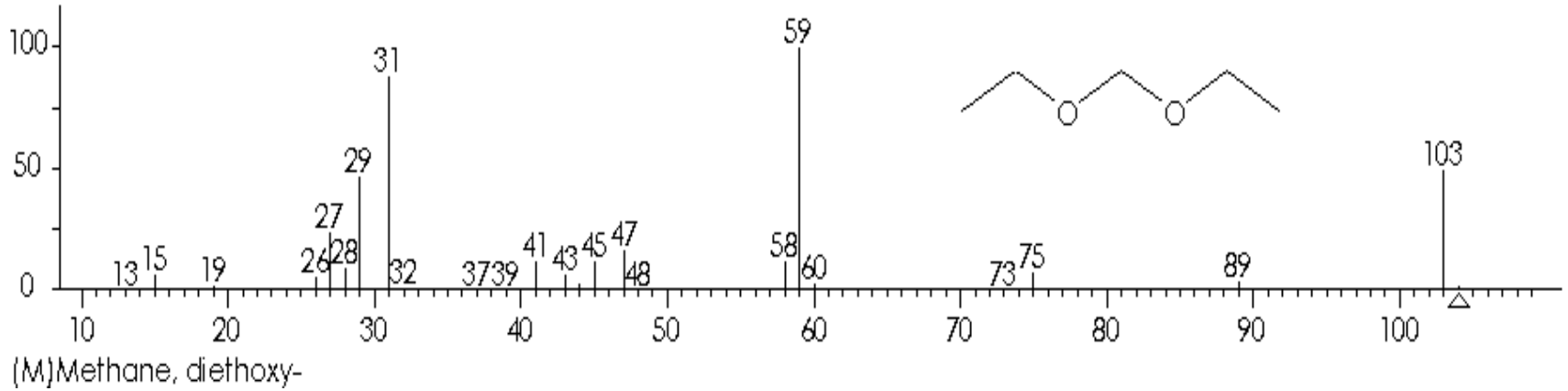
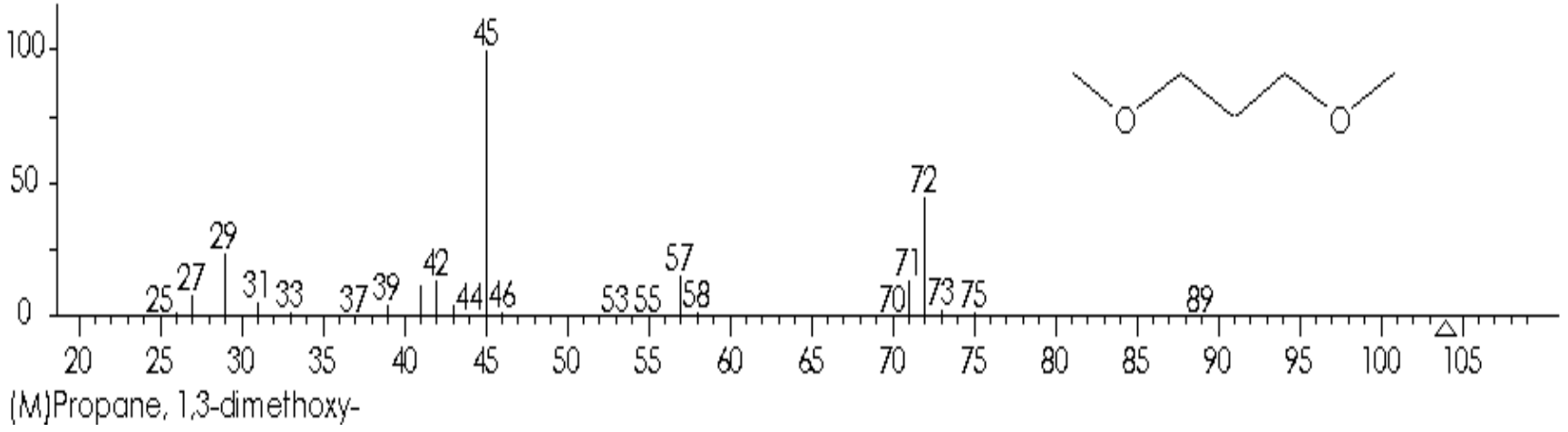


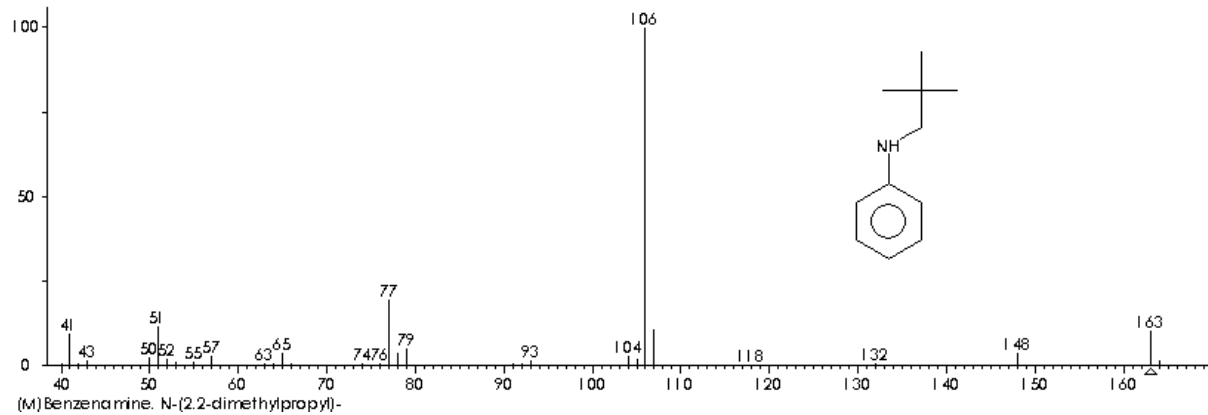
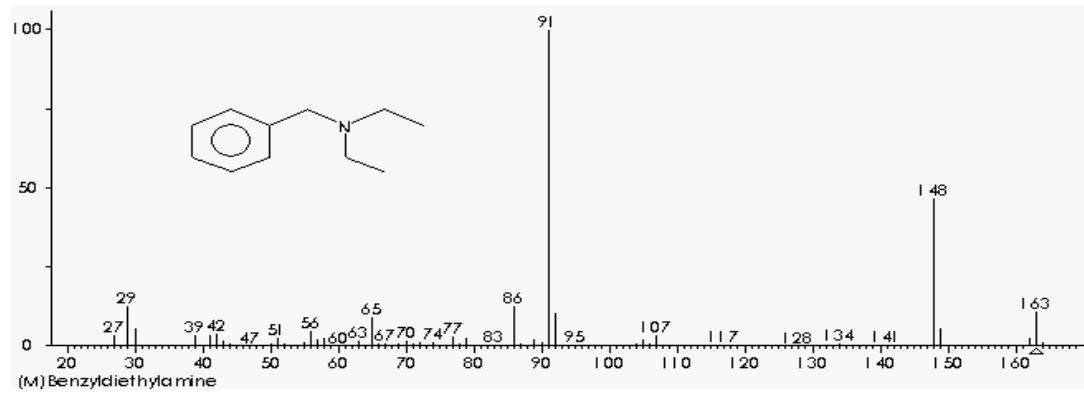
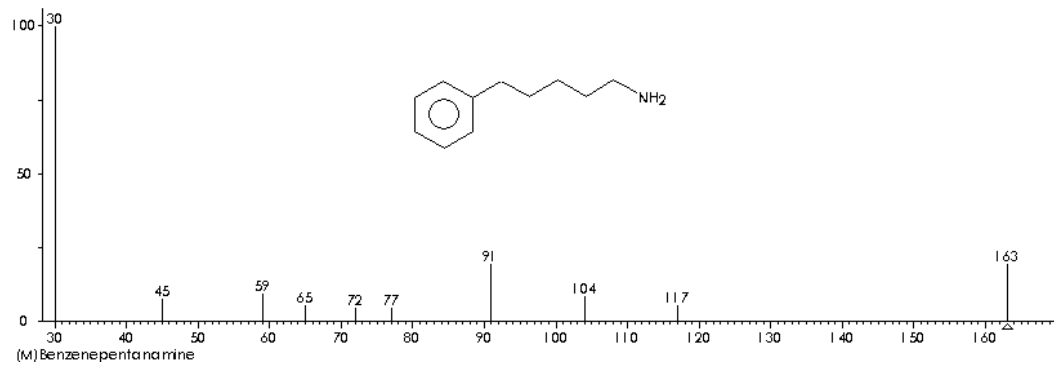
(M)2,3-Hexanedione

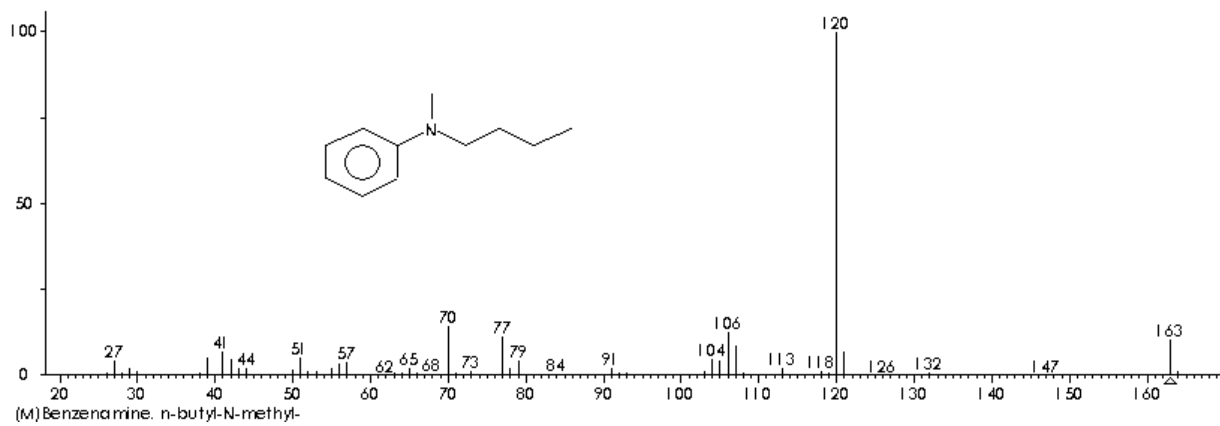
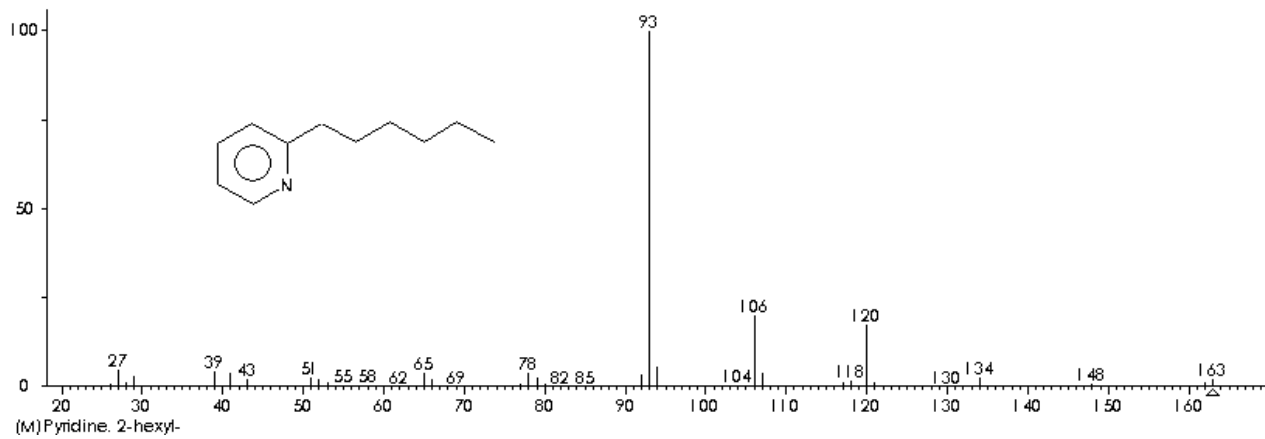


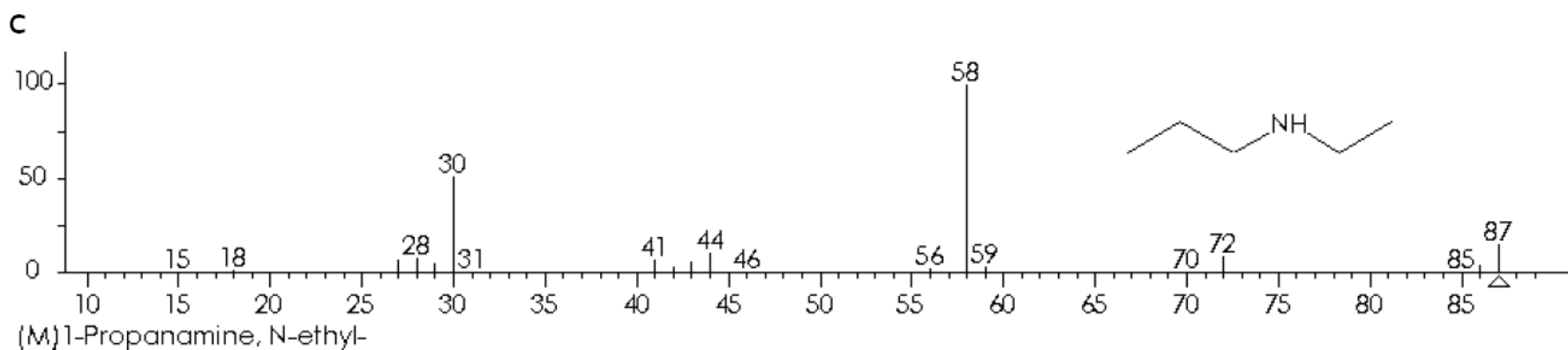
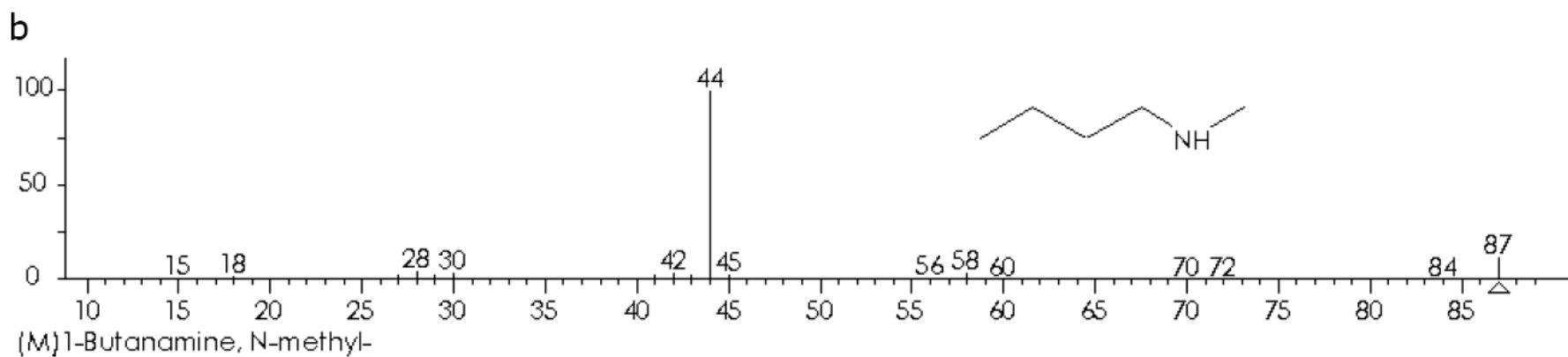
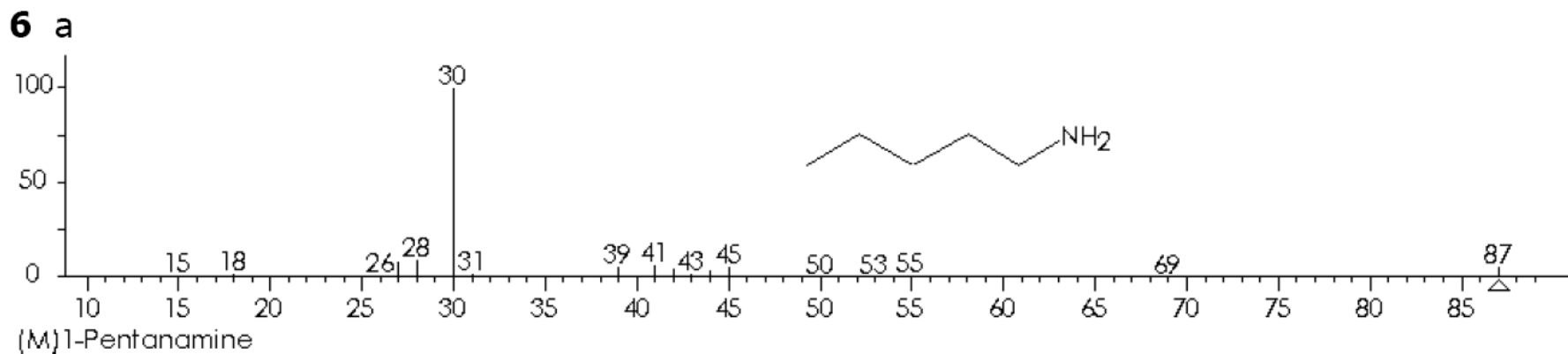
(M)3,4-Hexanedione

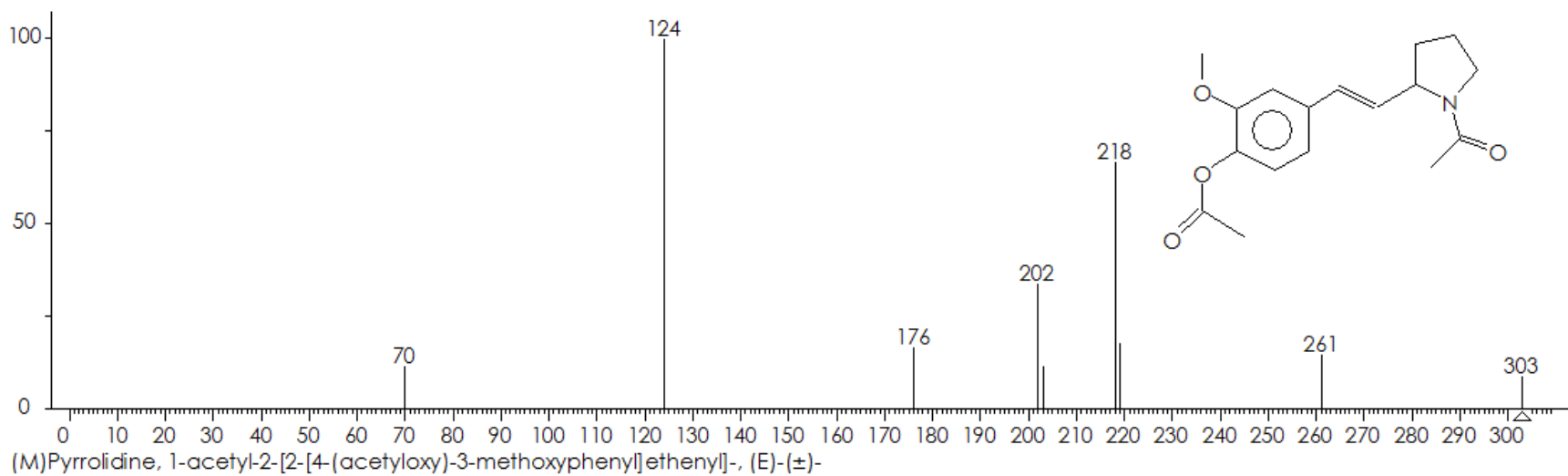
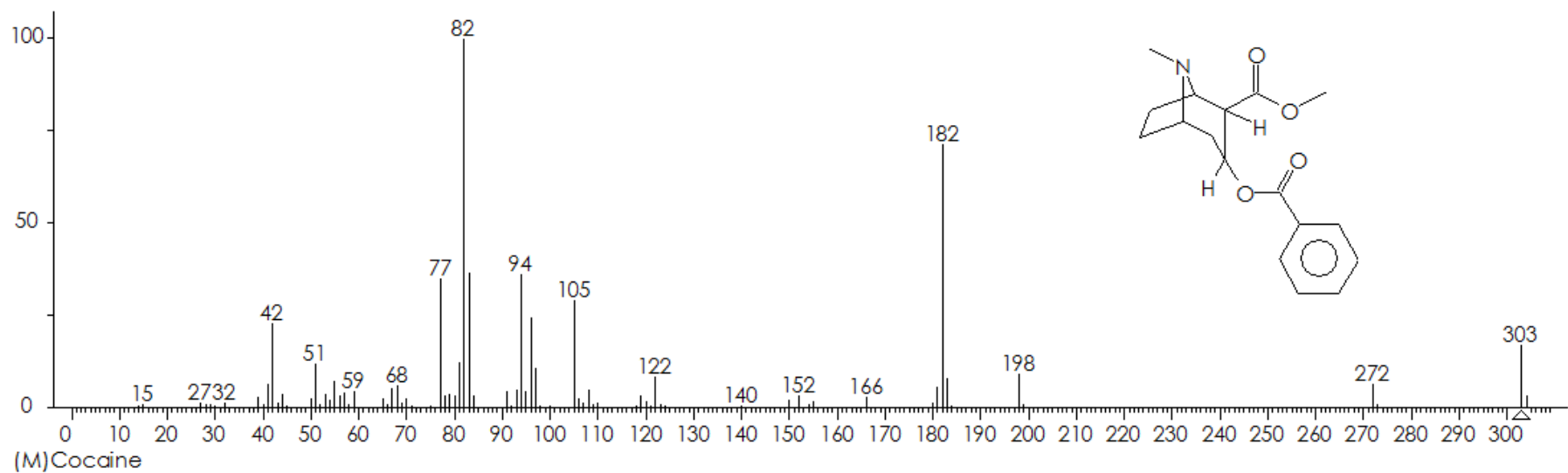
b



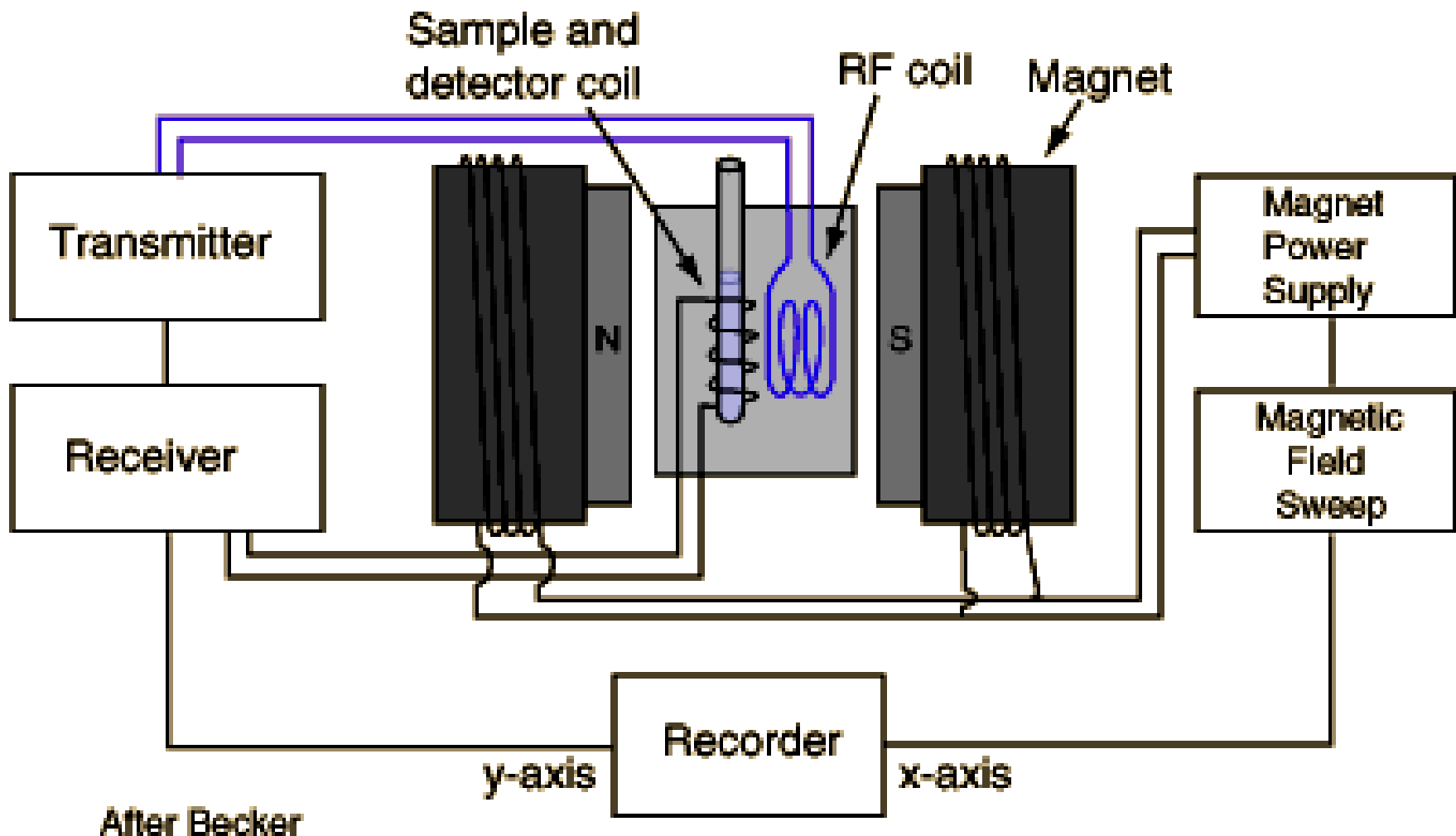


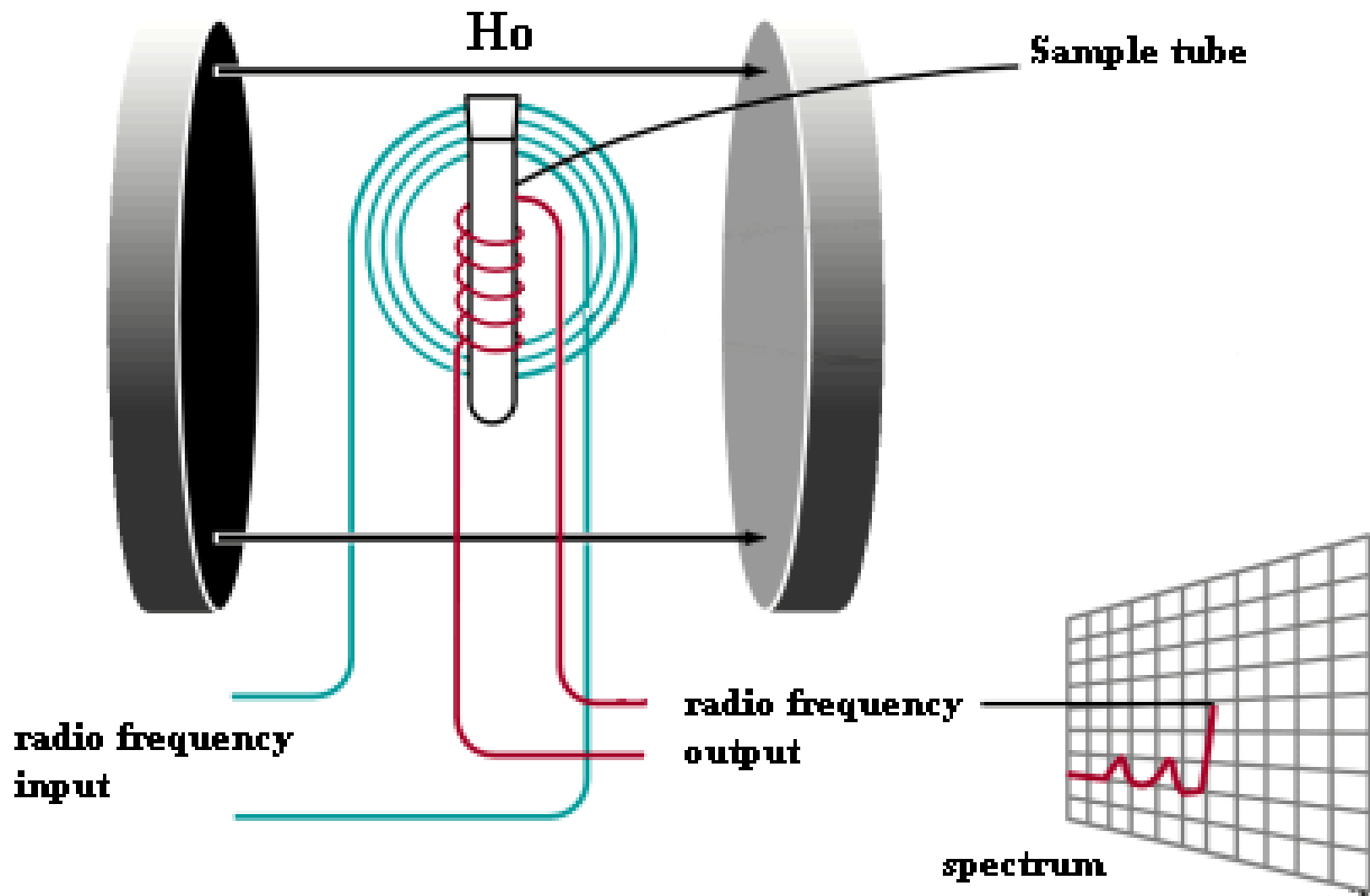


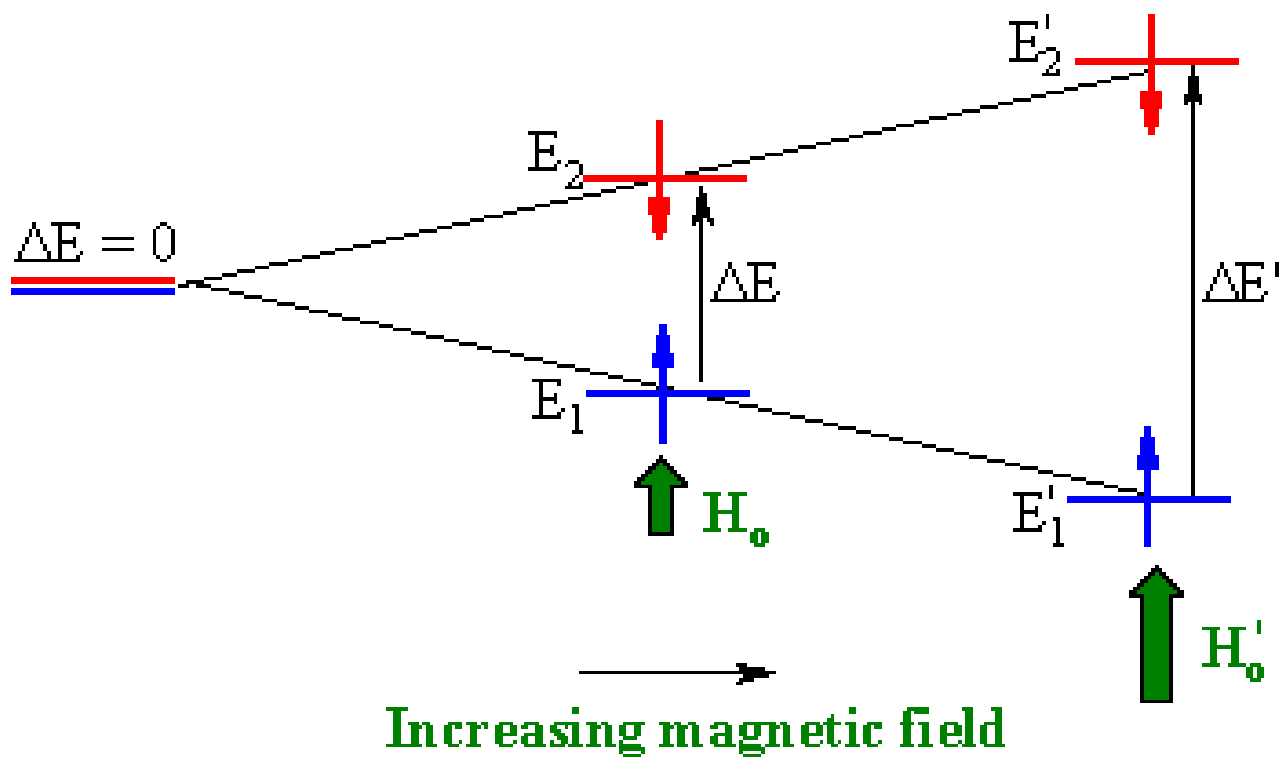
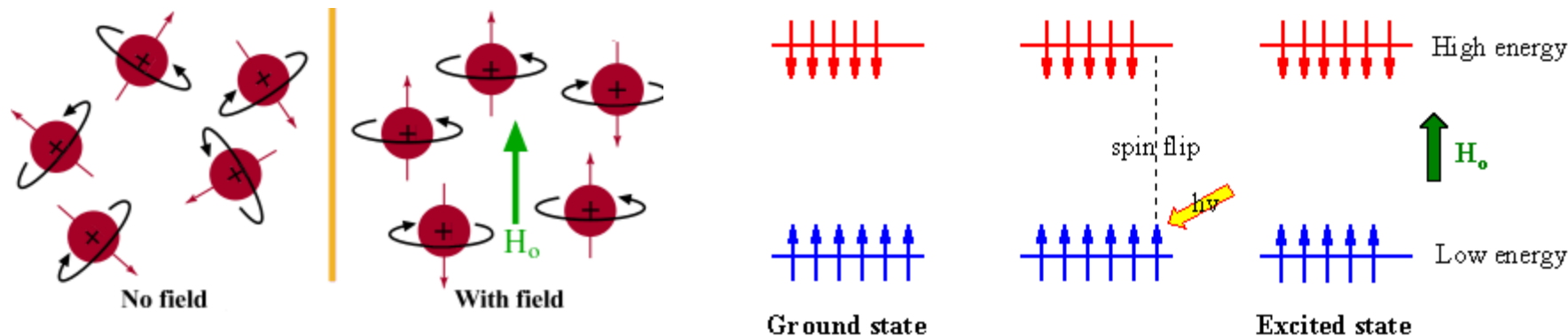


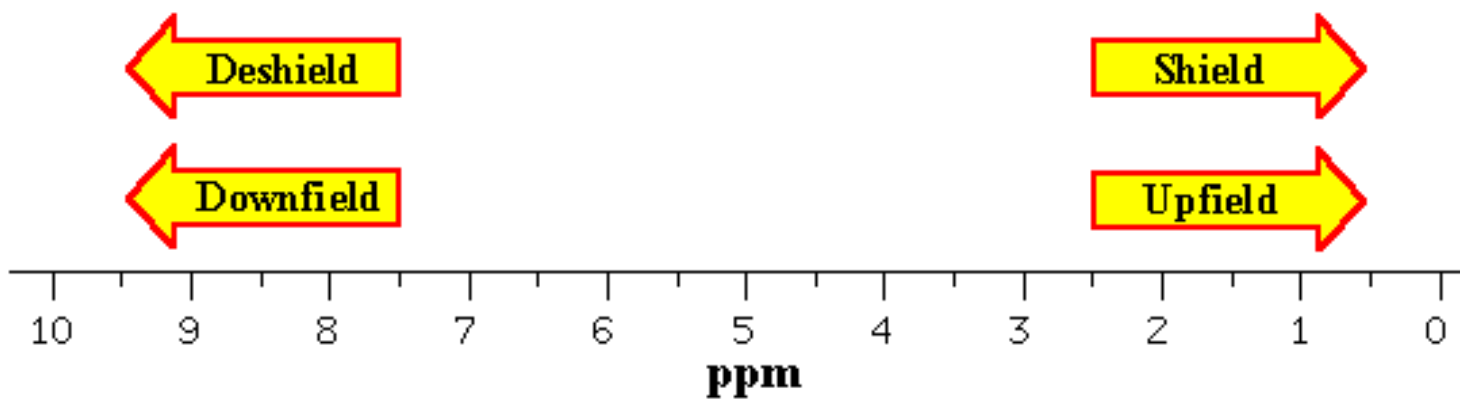


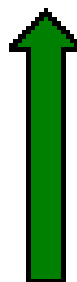
Ressonância Magnética Nuclear (RMN)

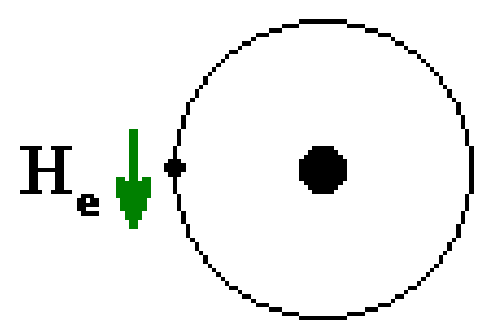




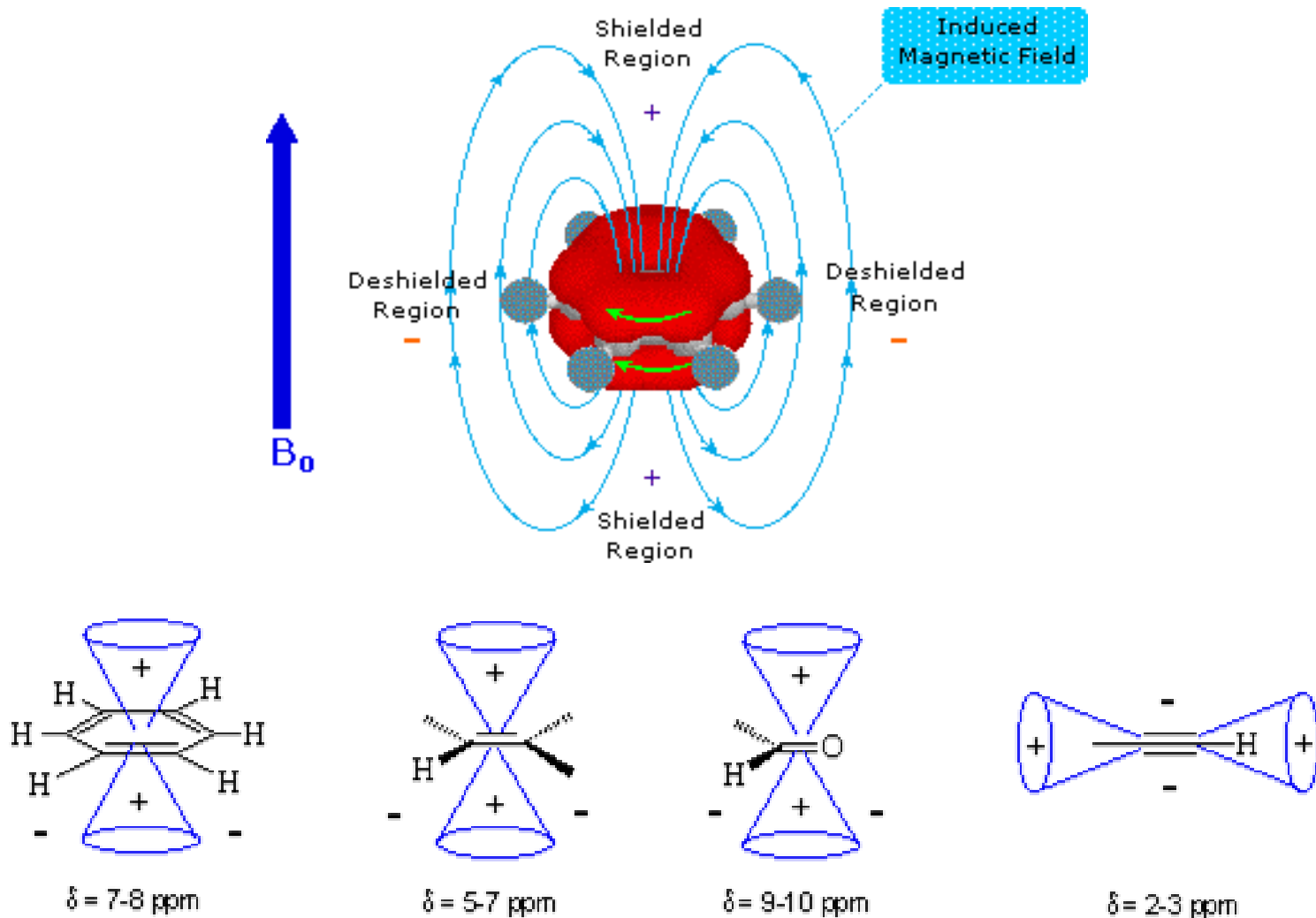




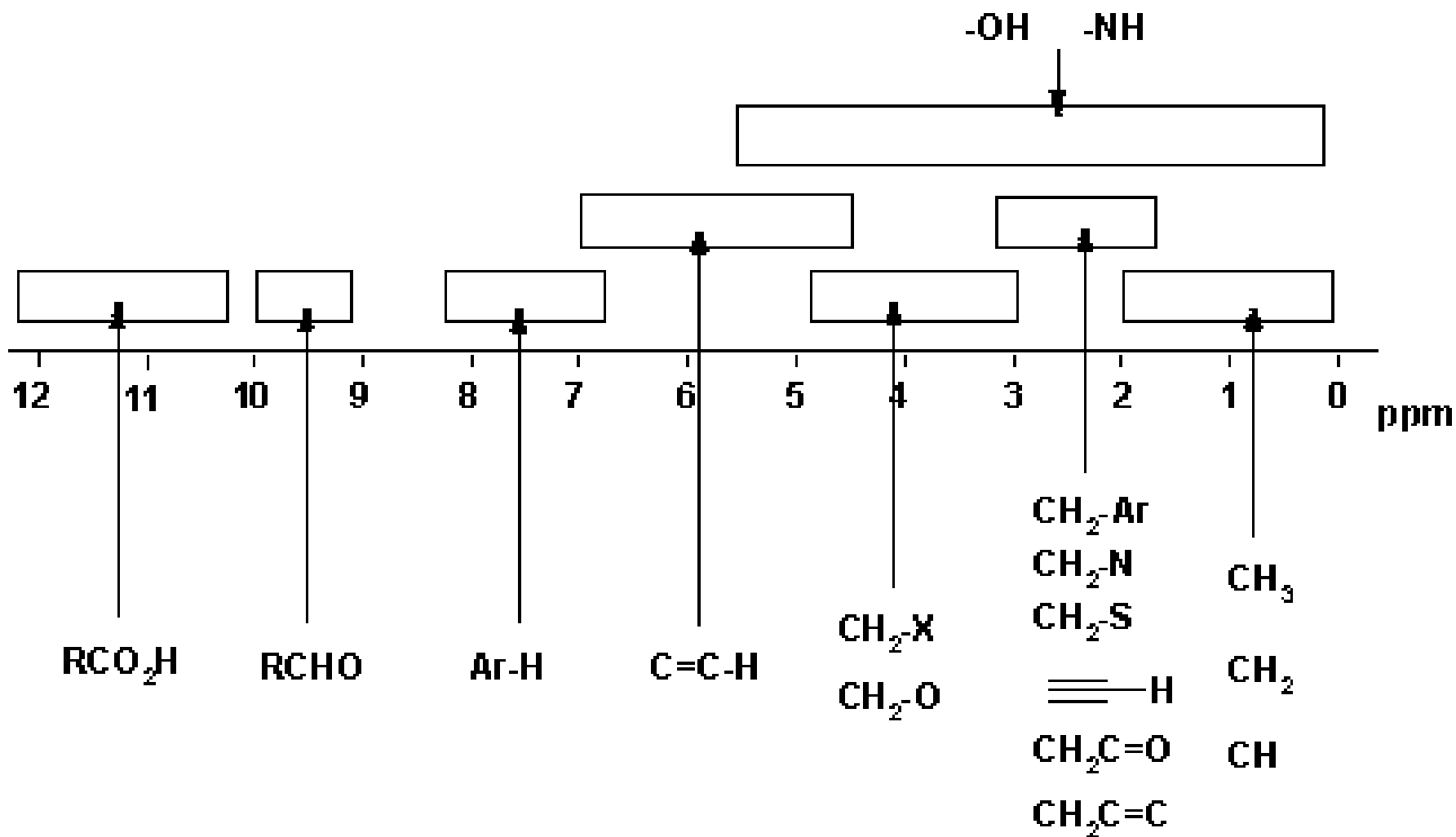
 H_o
spectrometer
field

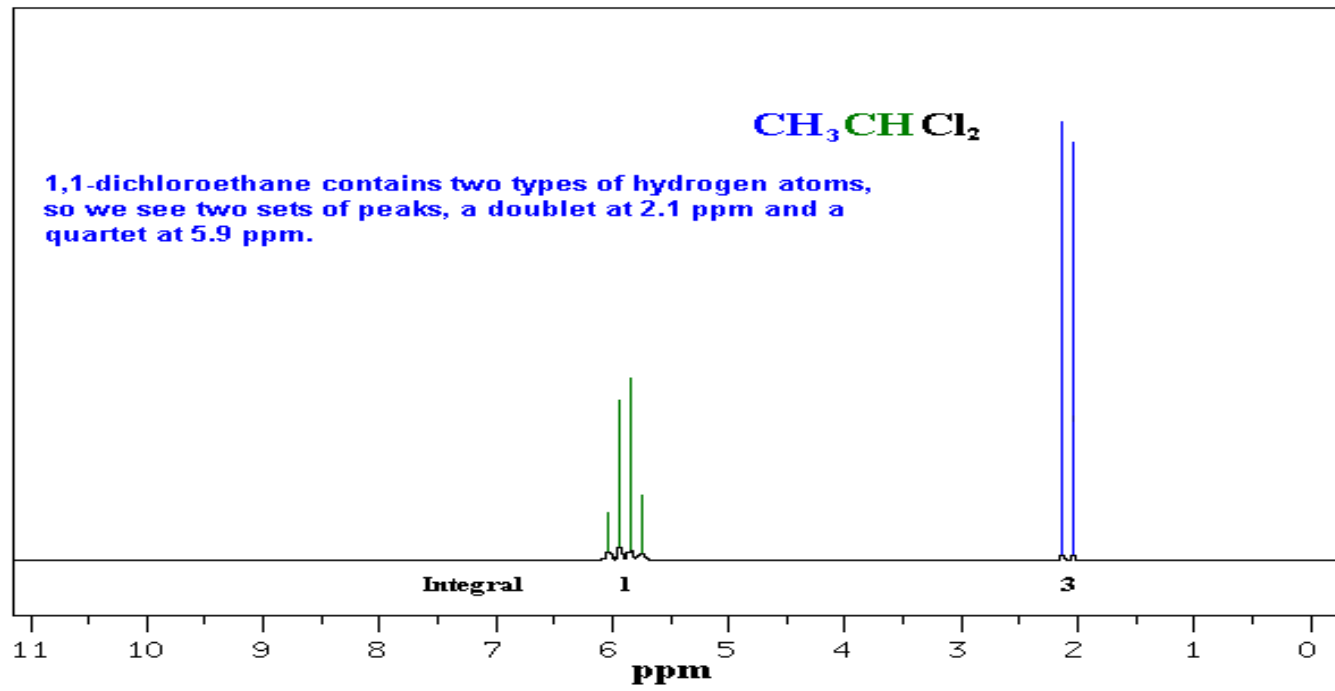


$$H_{\text{eff}} = H_o - H_e$$



Schematic diagram of shielding cones for common pi systems. The + denotes shielding areas and - denotes deshielding areas. Remember shielding lowers the chemical shift, δ and deshielding increases δ . Typical H δ values are also shown.





↑
spectrometer field
 H_o

↑

ClC(Cl)C

H-C-Cl
|
H-C-H
|
H

↓

ClC(Cl)C

H-C-Cl
|
H-C-H
|
H

$n=0$ 1 **singlet**

$n=1$ 1 1 **doublet**

$n=2$ 1 2 1 **triplet**

$n=3$ 1 3 3 1 **quartet**

$n=4$ 1 4 6 4 1 **quintet**

$n=5$ 1 5 10 10 5 1 **sextet**

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

↑
spectrometer field
 H_o

↑↑↑↑

↑↑↑↓

↑↑↓↓

↓↓↓↓

deshielding

↑↑↑↑

↑↓↑↓

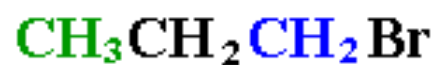
↑↓↑↓

↓↓↓↓

shielding

ClC(Cl)C

H-C-Cl
|
H-C-H
|
H



triplet, so $n=2$
deshielded

triplet, so $n=2$
shielded

6 lines,
so $n=5$

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

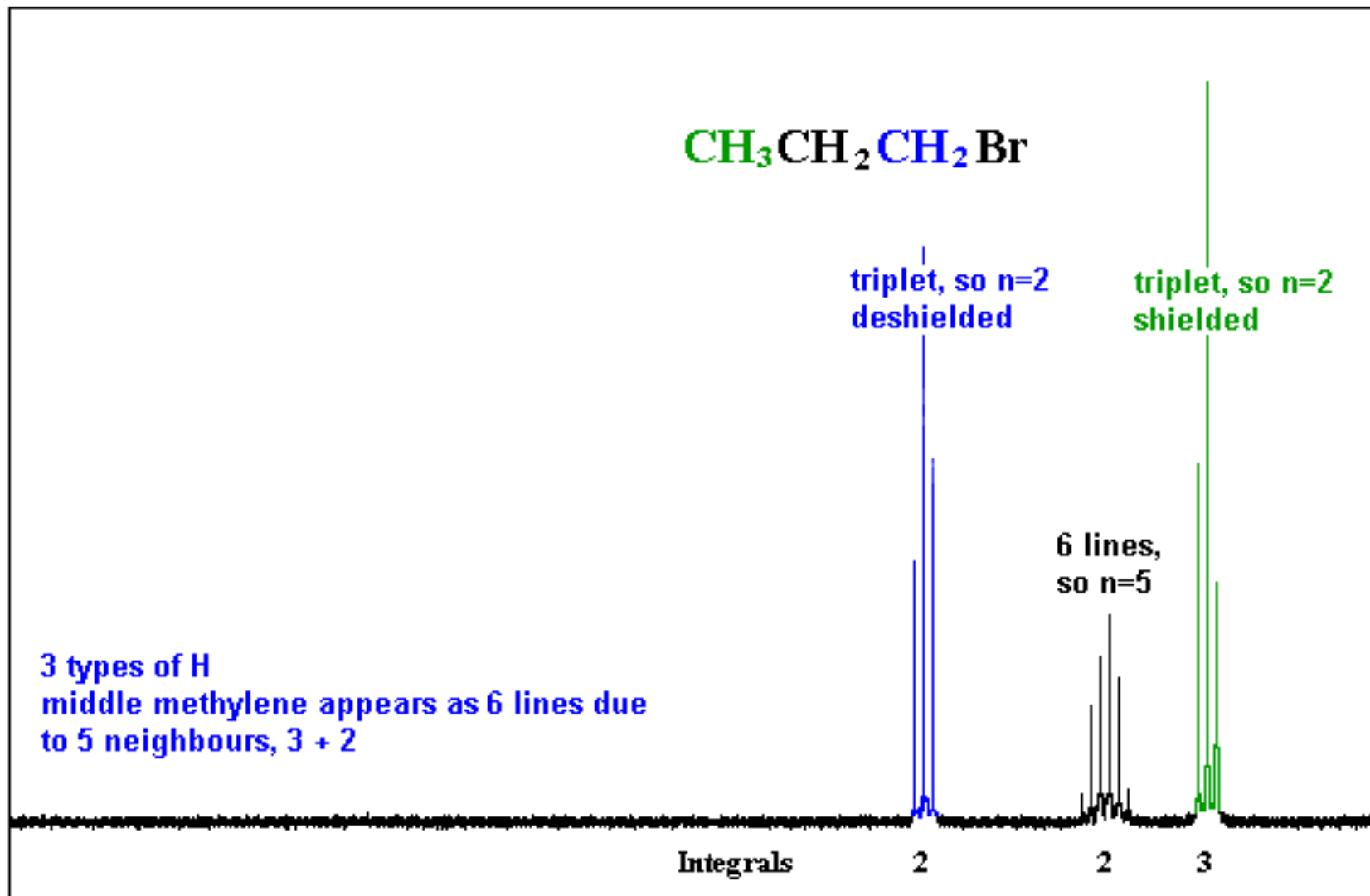
Integrals

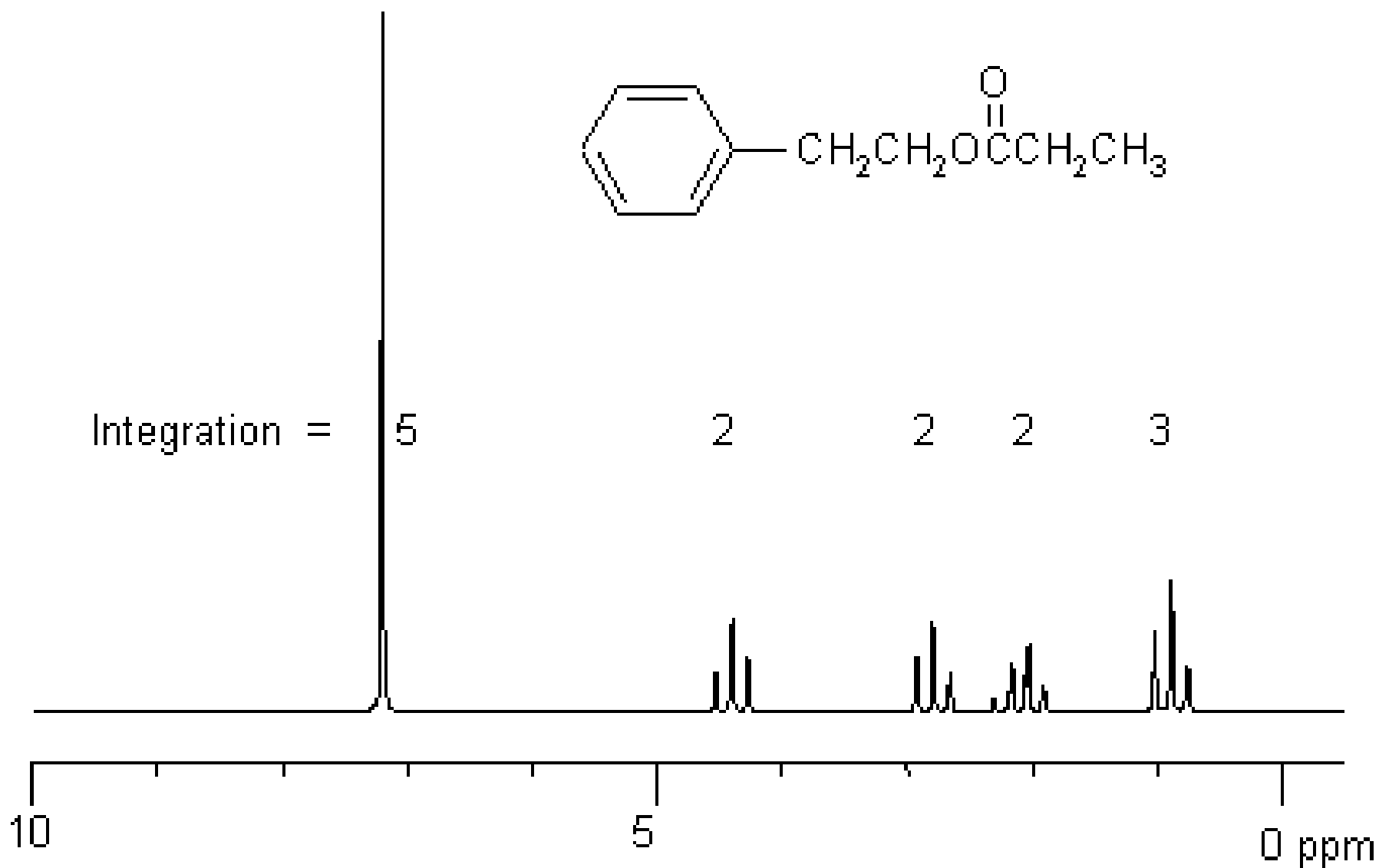
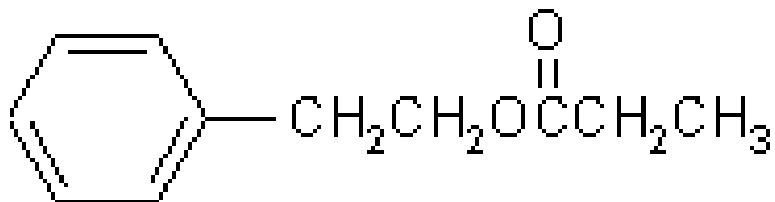
2

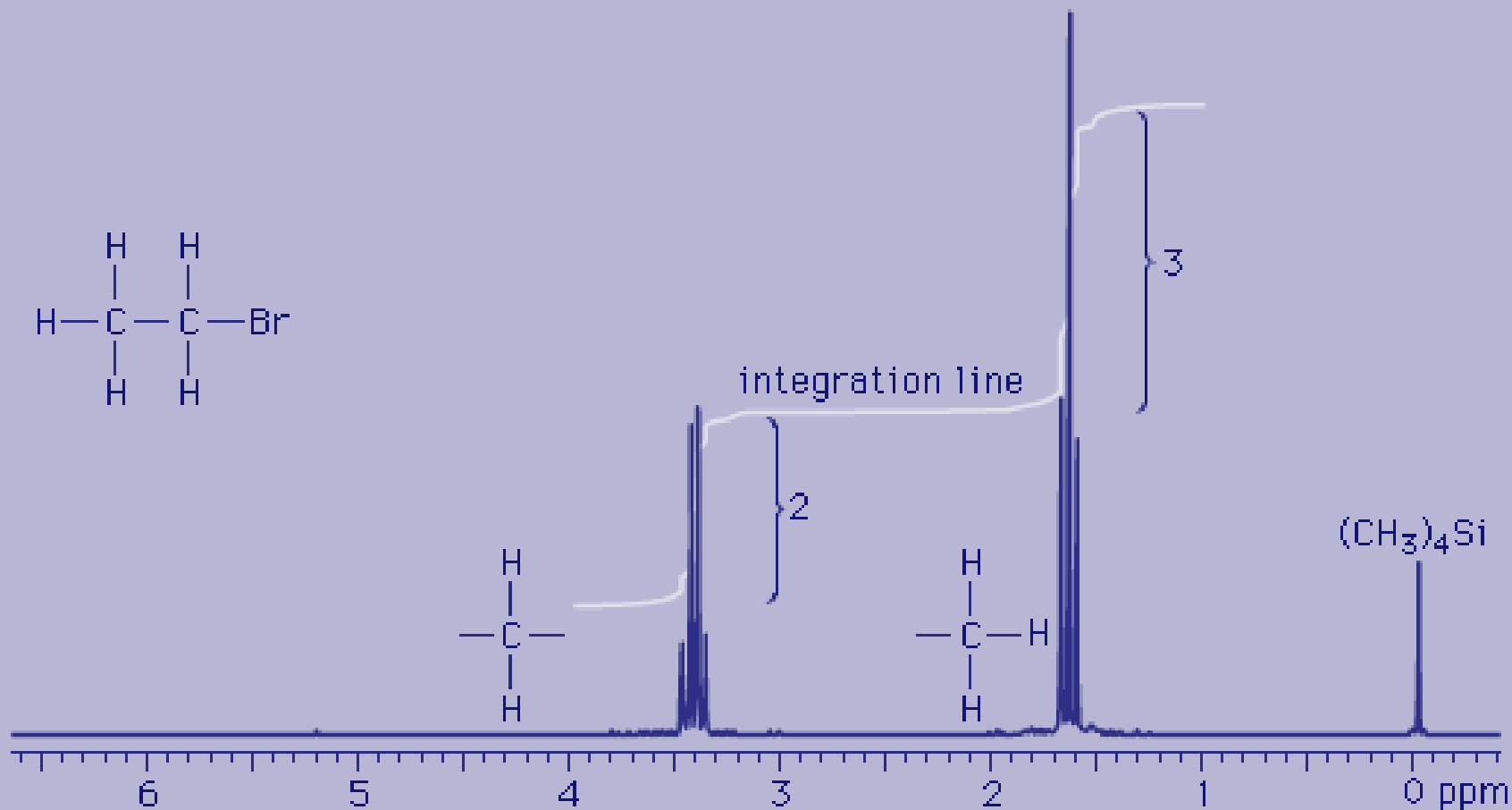
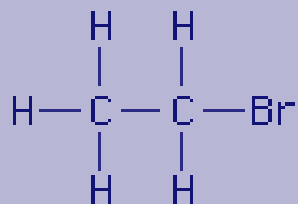
2

3

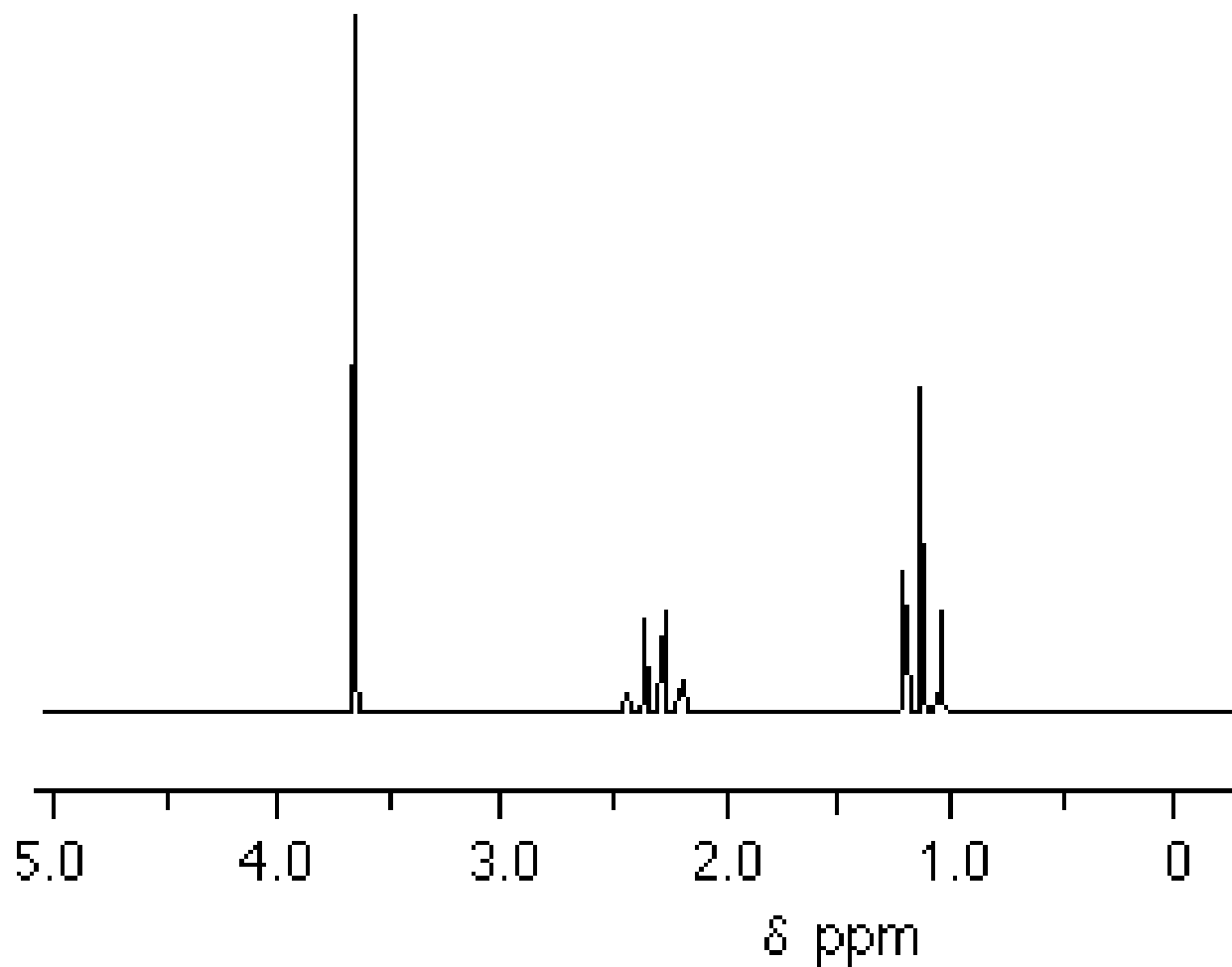
11 10 9 8 7 6 5 4 3 2 1 0
ppm

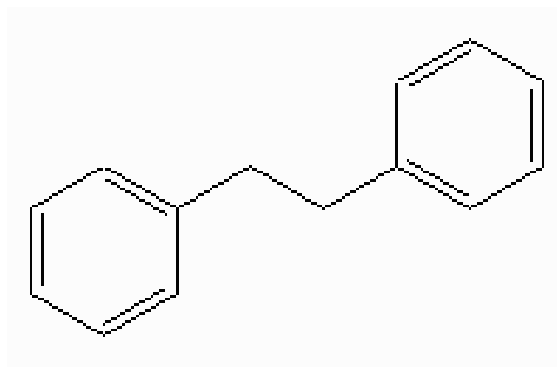
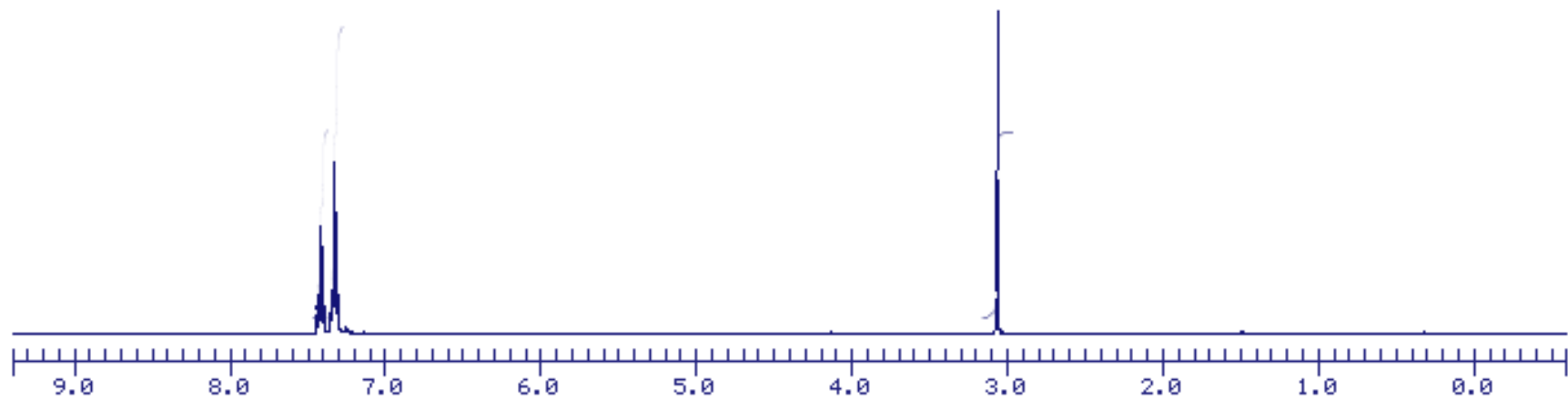


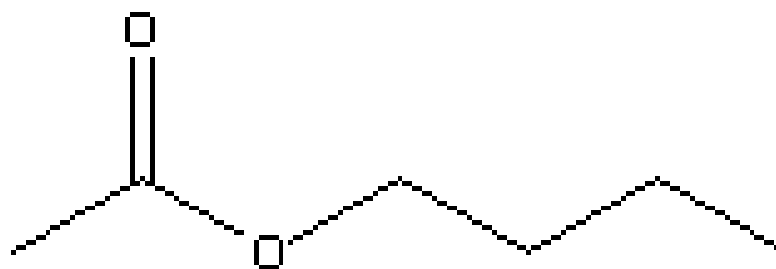
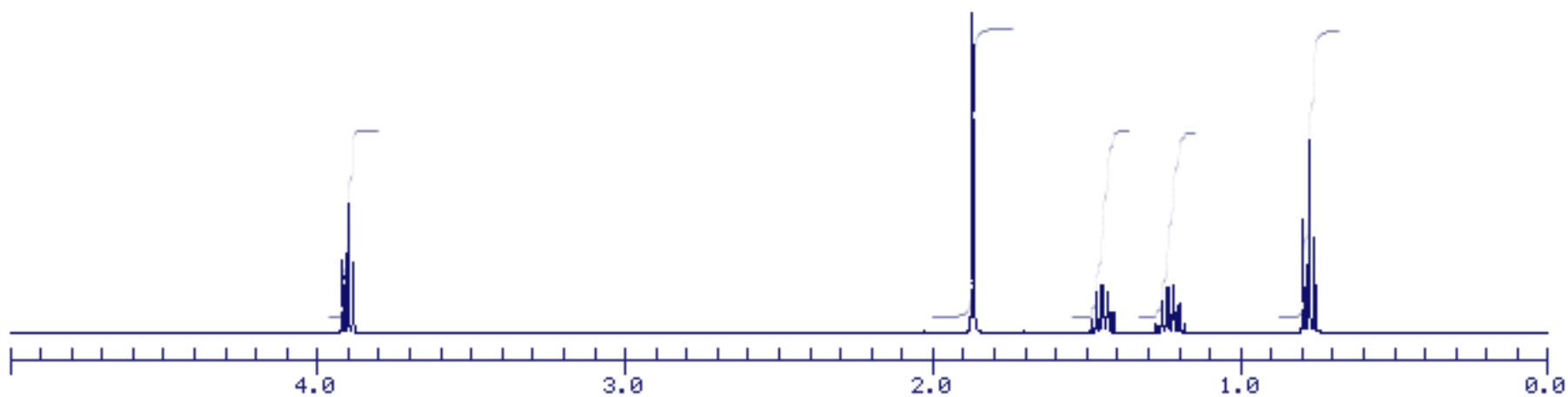


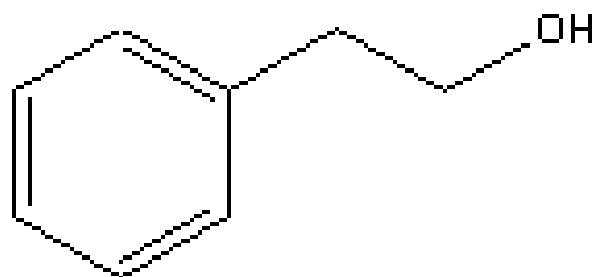
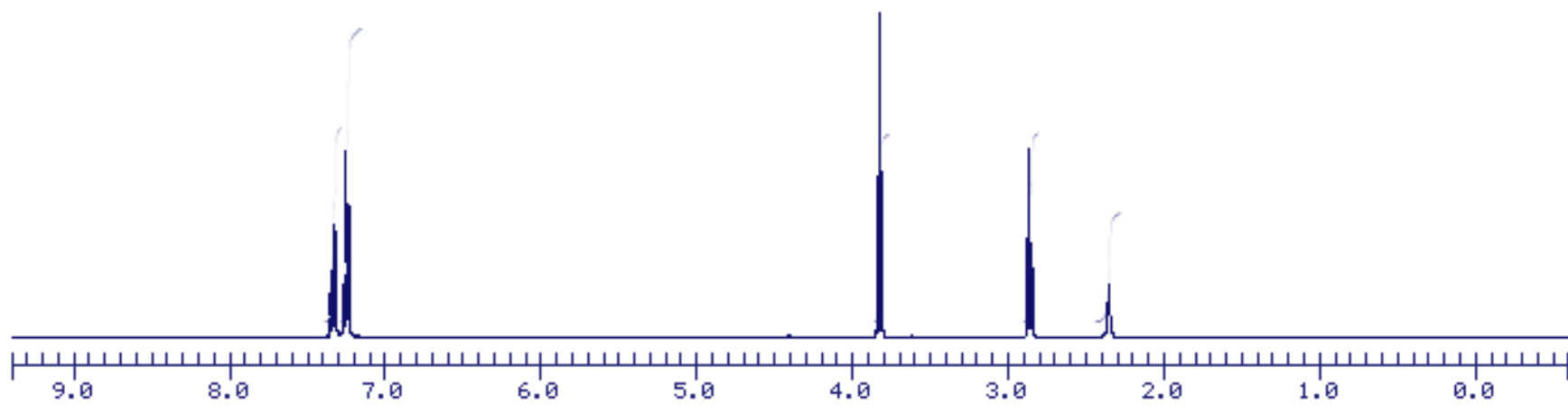


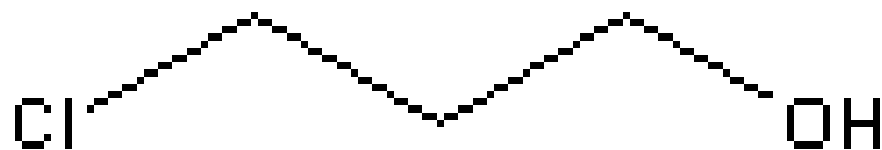
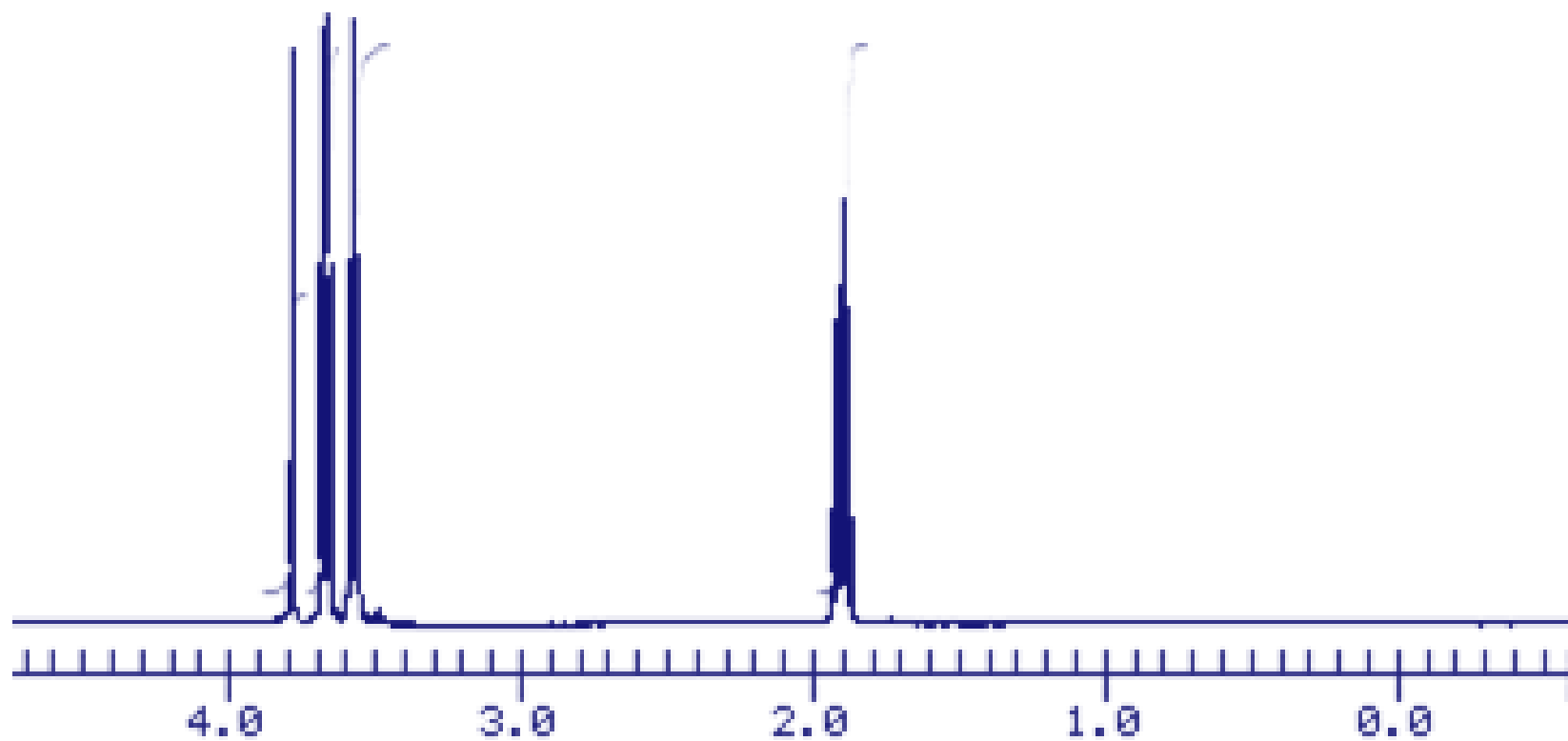
high resolution nmr spectrum for methyl propanoate, $\text{CH}_3\text{CH}_2\text{COOCH}_3$



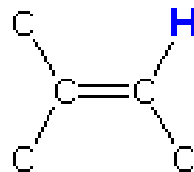




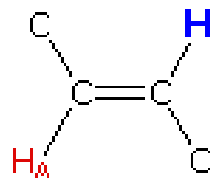




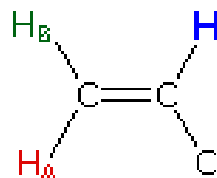
No Coupled
Hydrogens



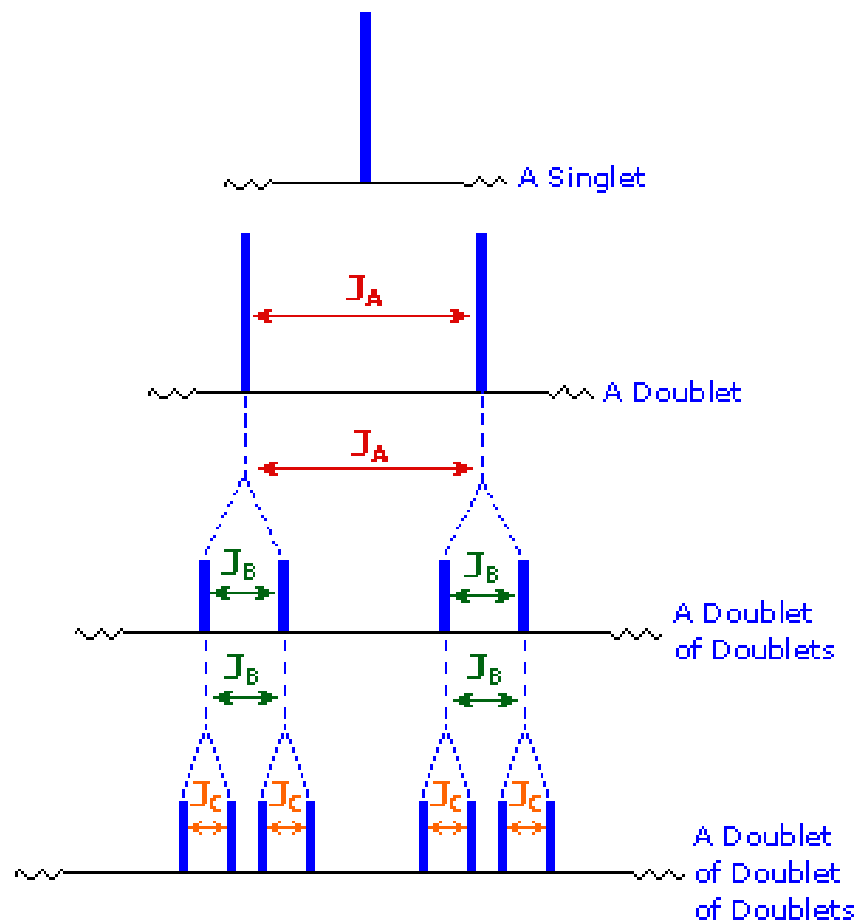
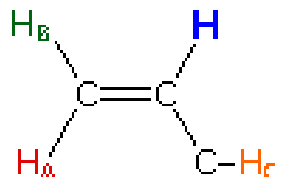
One Coupled
Hydrogen

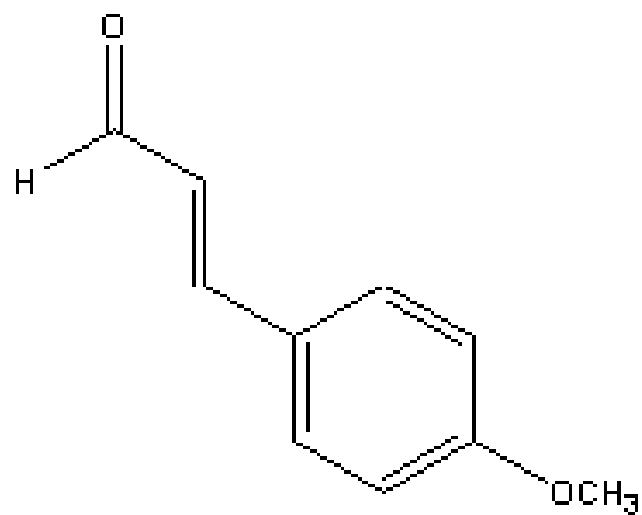
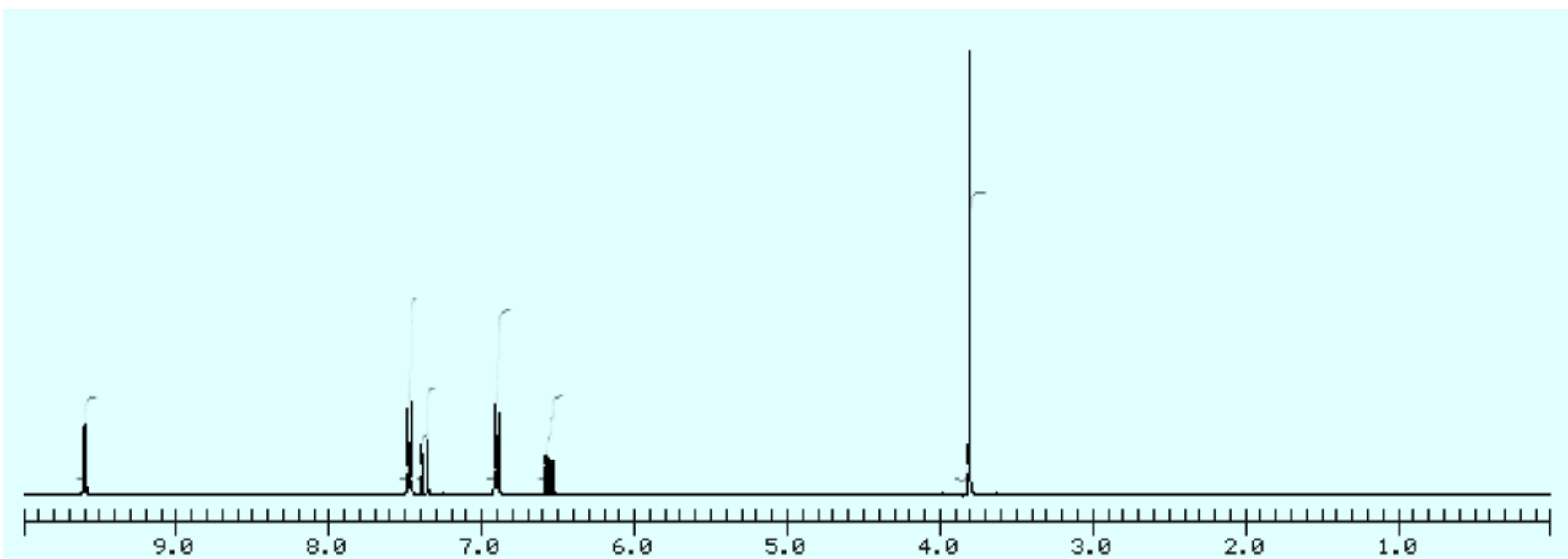


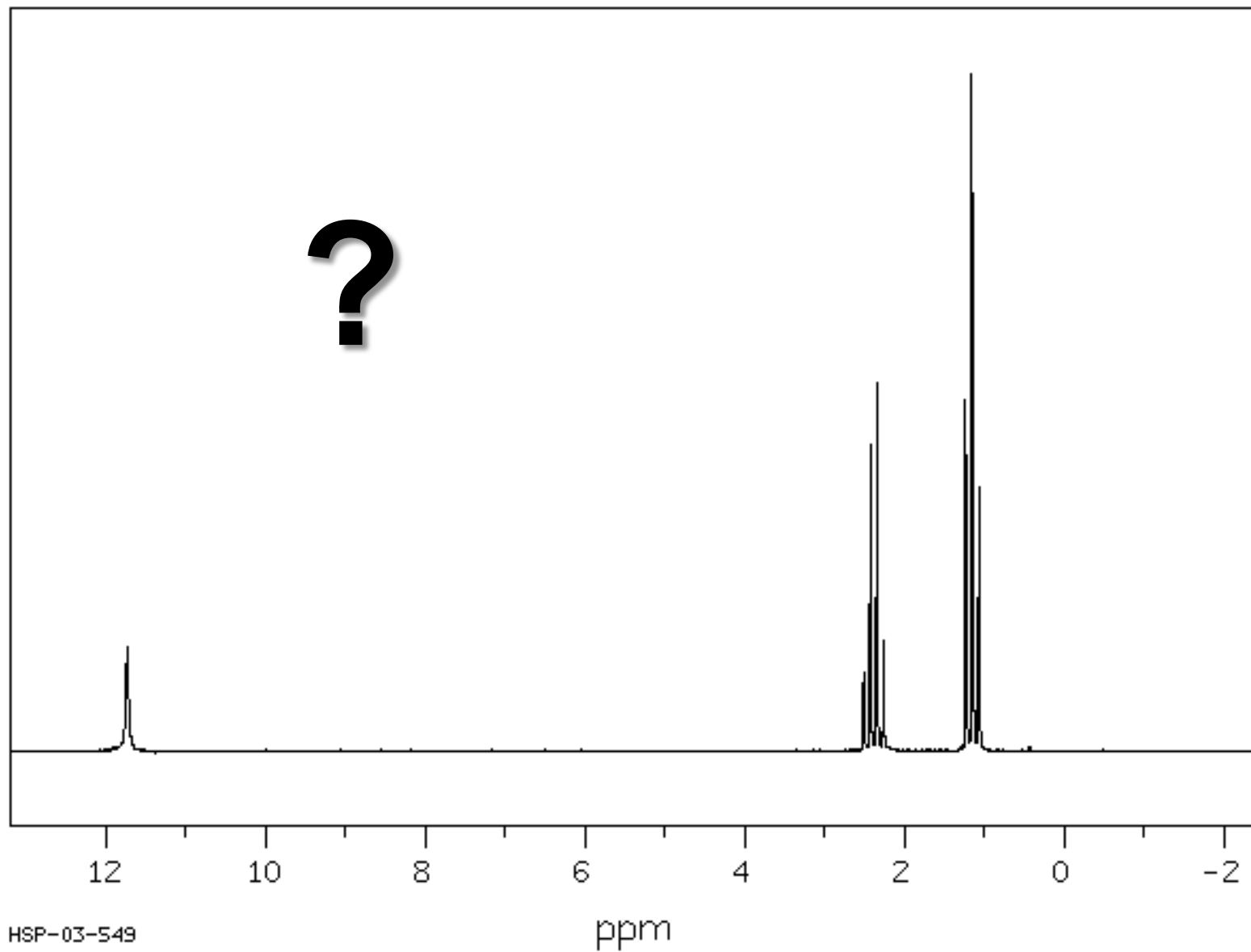
Two Coupled
Hydrogens

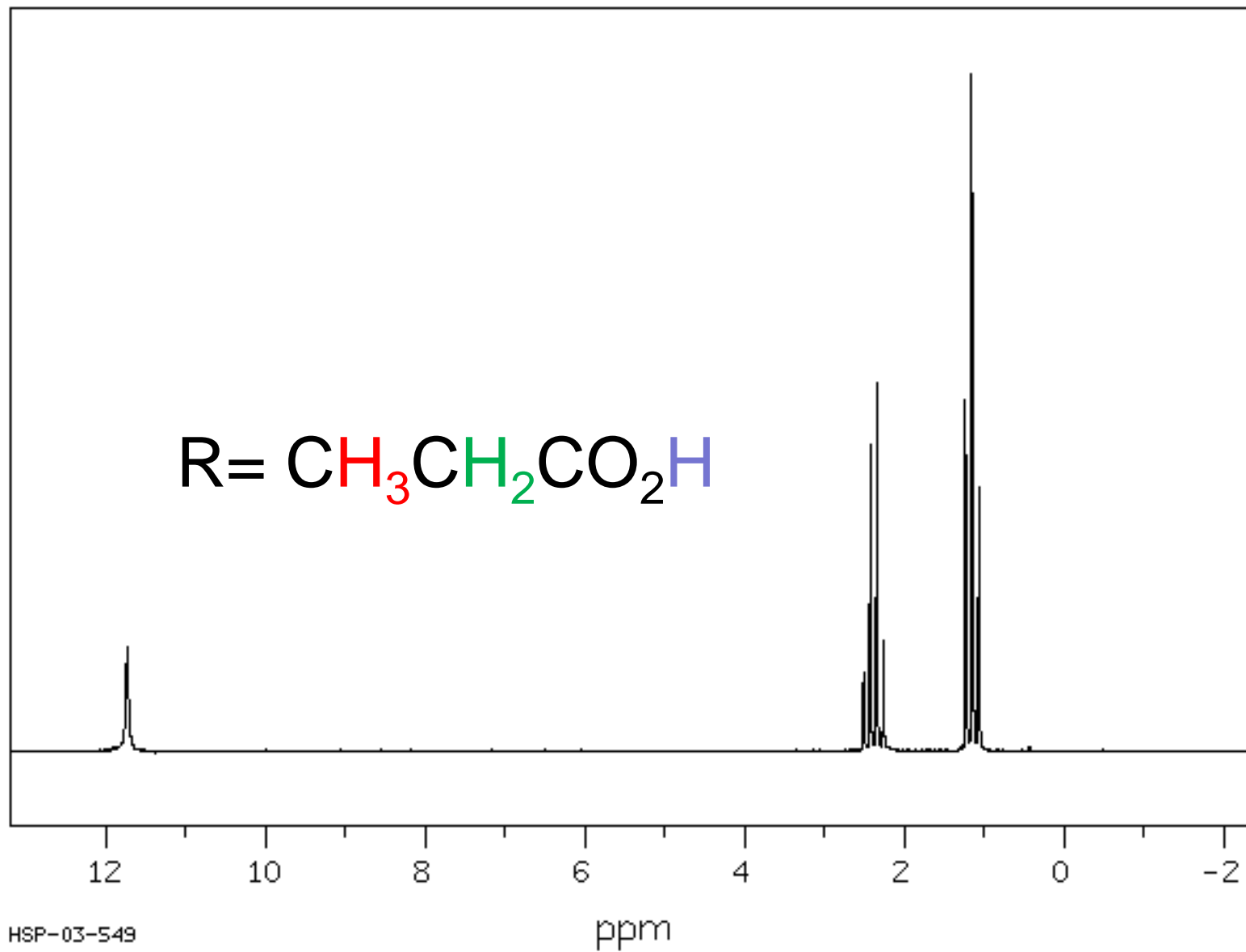


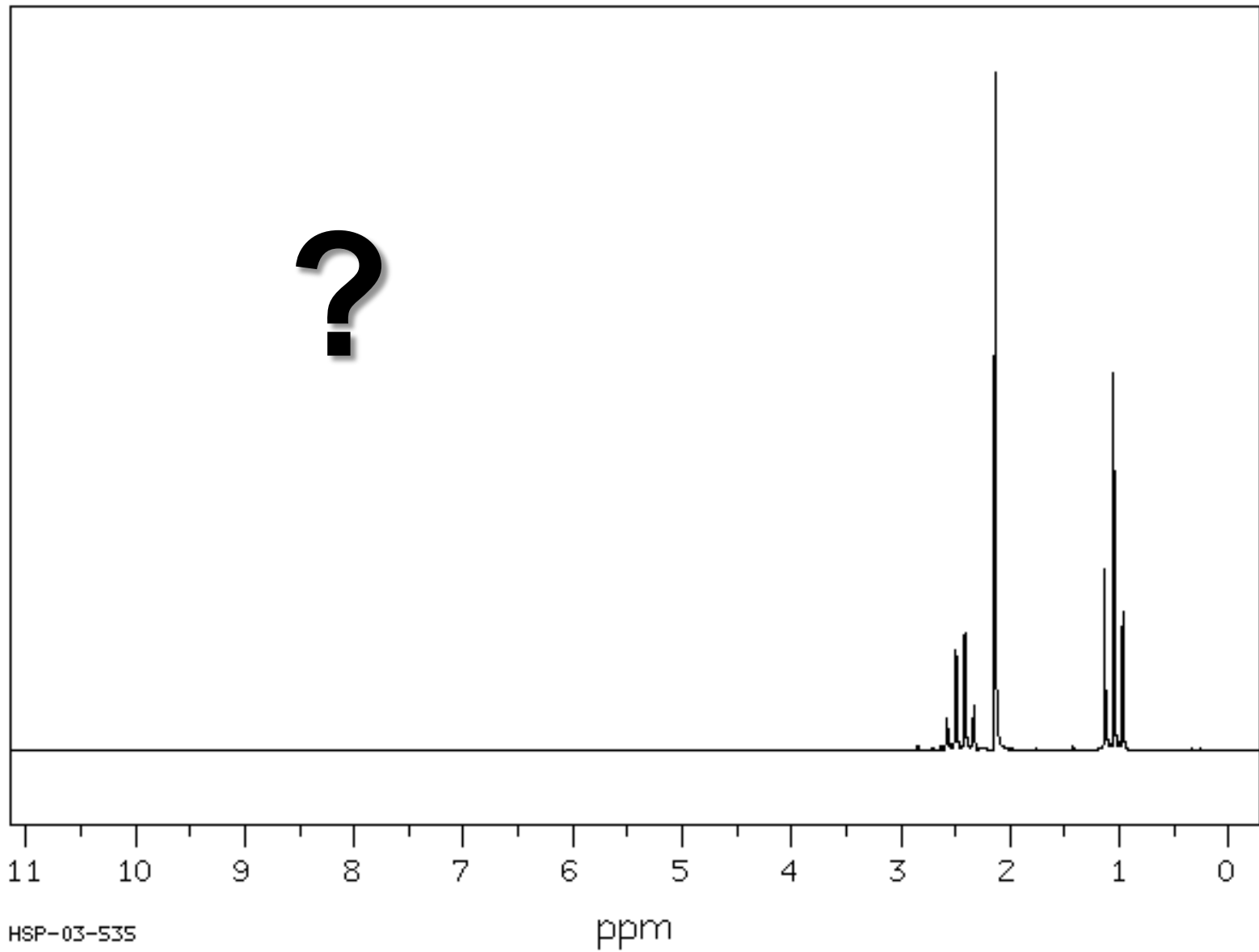
Three Coupled
Hydrogens



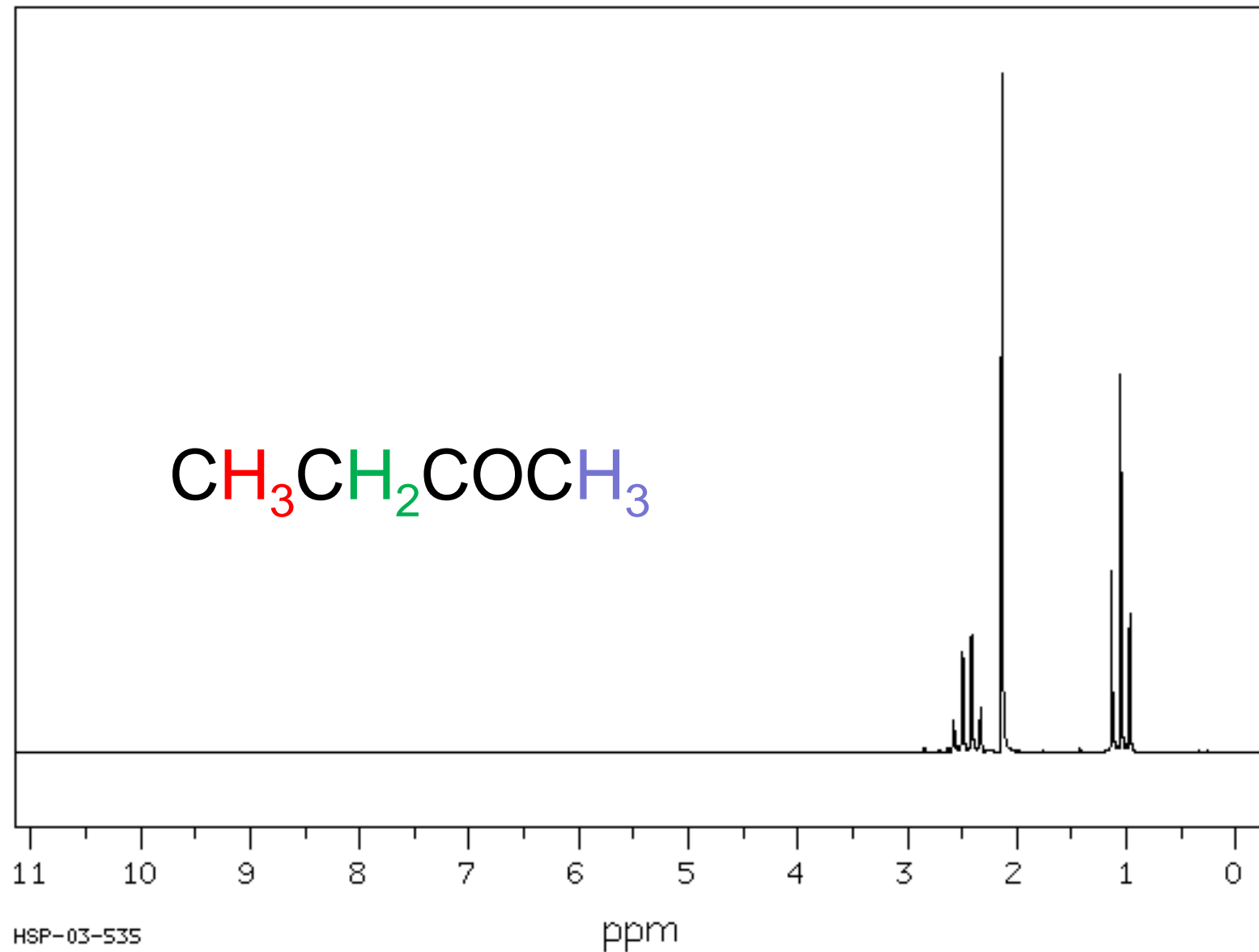
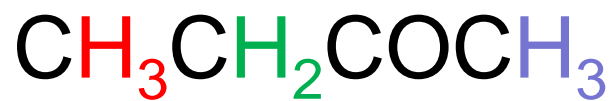




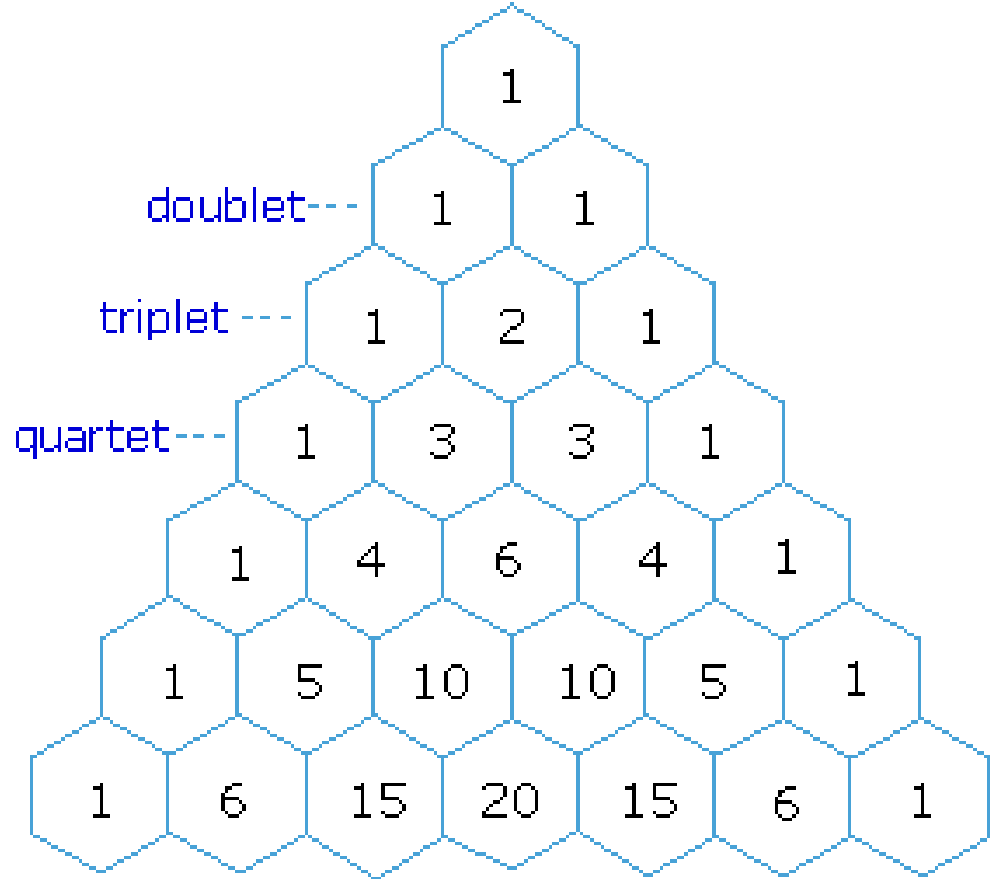




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Pascal's Triangle

