TÁMOP-4.1.1.F-14/1/KONV-2015-0006
SZTE TTIK, KTCS, 1a) Duális és moduláris képzésfejlesztés a mesterképzéshez

Spektroszkópiai módszerek 1.

Pálinkó István, egyetemi tanár

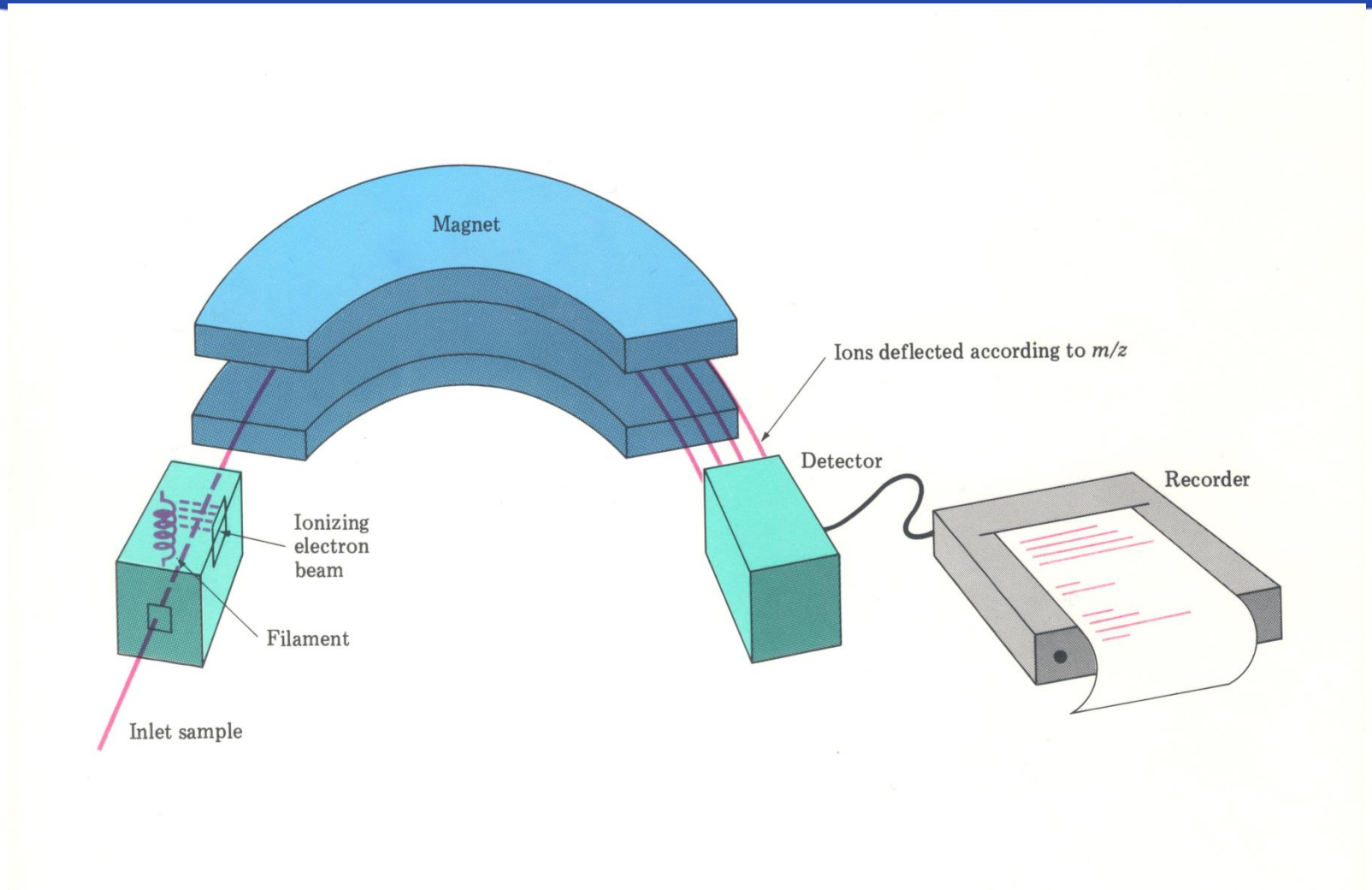
SZÉCHENYI 2020
MAGYARORSZÁG KORMÁNYA
Európai Unió
Európai Szociális Alap
BEFEKTETÉS A JÖVŐBE

Tömegspektro(metria)szkópia

Röntgenkrisztallográfia
Ultraibolya-látható (UV-VIS) spektroszkópia
F(ourier-)T(transzformációs) infravörös spektroszkópia
Magmágneses rezonancia (NMR) spektroszkópia

- **^{1}H NMR**
- **^{13}C NMR**

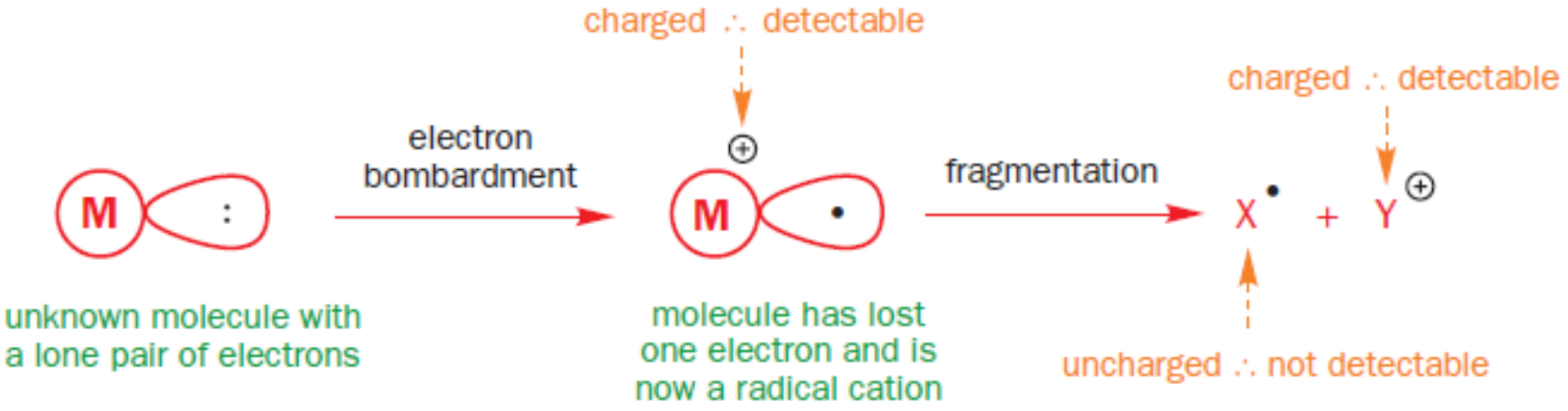
Tömegspektrometria



a time-of-flight tömegspektrométer vázlatos rajza

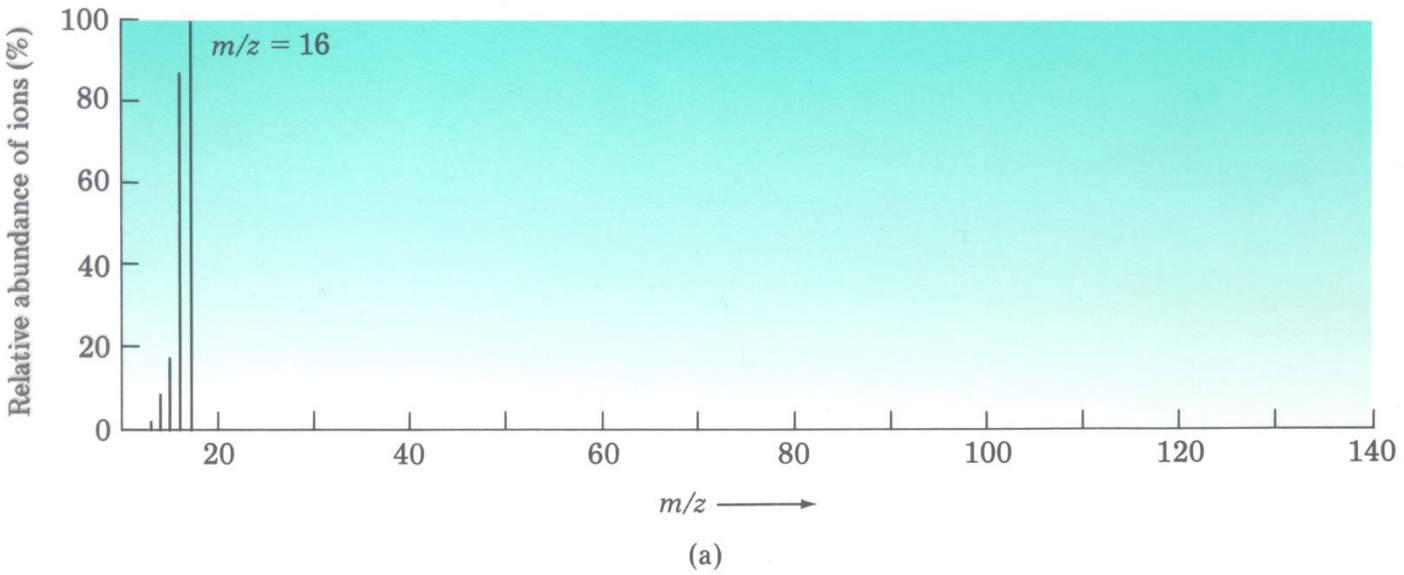
egy time-of-flight tömegspektrométer

E(lectron)I(mpact) ionizáció (általában 70 eV)

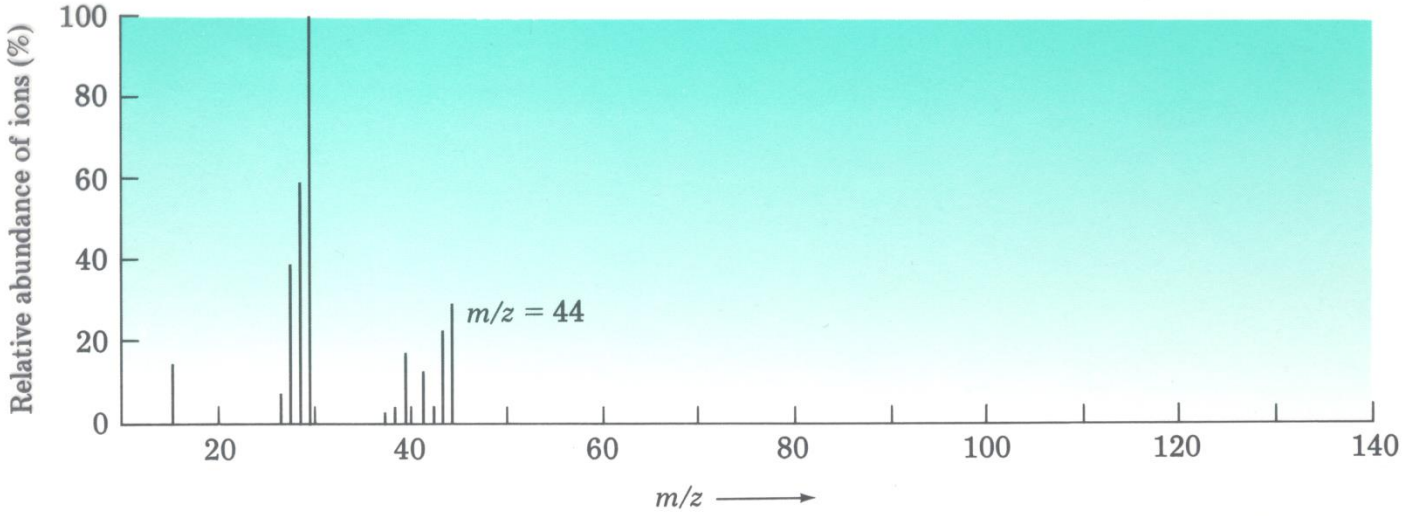


loss of one electron
leaves a radical cation

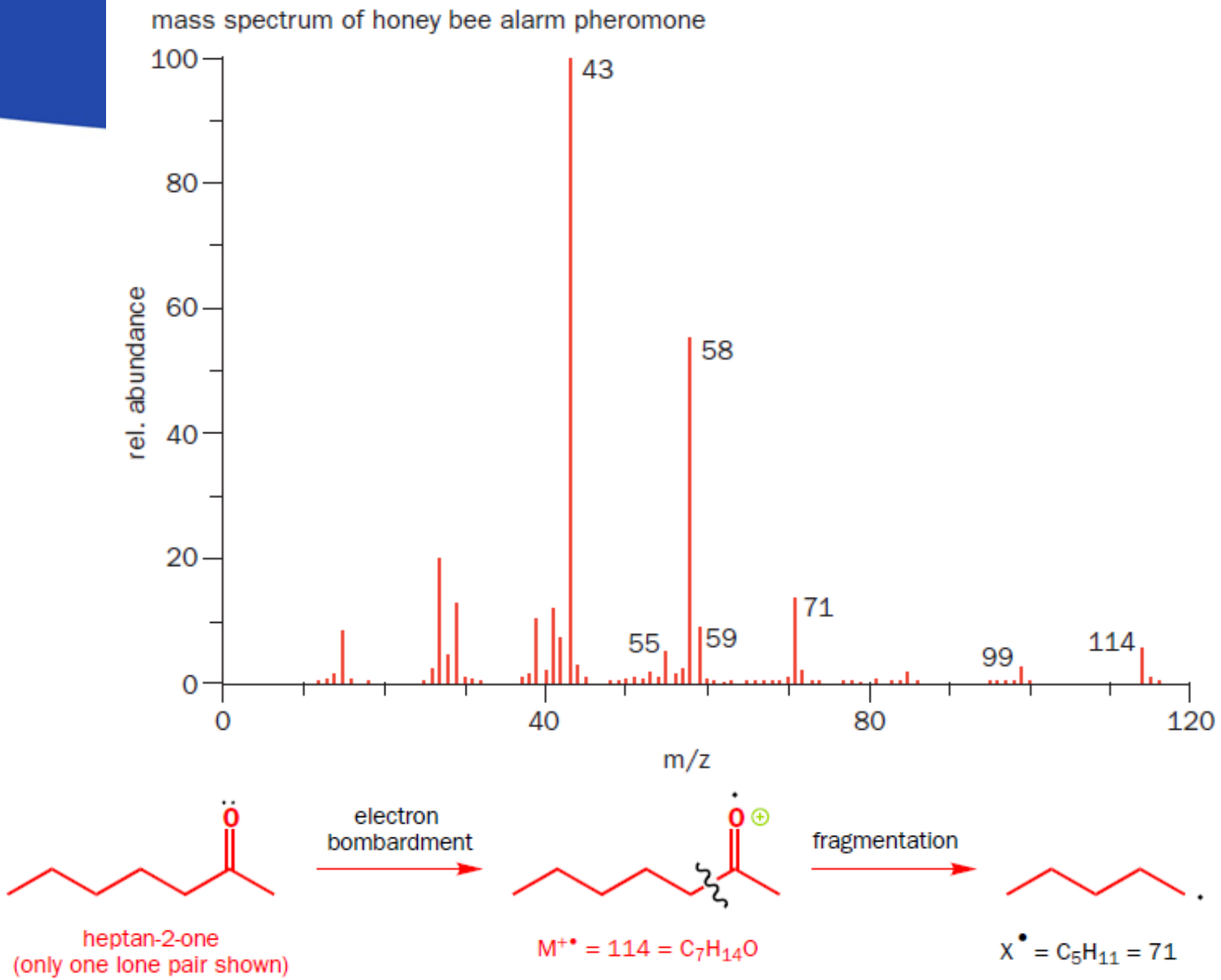
a metán és a propán EI tömegspektrumai



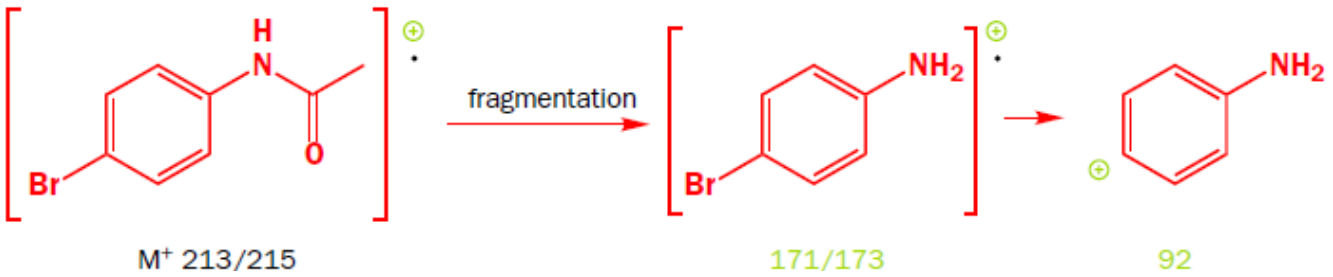
(a)



(b)


mass spectrum of honey bee alarm pheromone
rel. abundance
100
80
60
40
20
0
0
40
80
120
m/z
43
58
71
55
59
99
114
electron bombardment
fragmentation
heptan-2-one
(only one lone pair shown)
M+• = 114 = C7H14O
X• = C5H11 = 71
Y⊕ = C2H5O= 43

izotópcsúcsok



M^+ 213/215 171/173 92

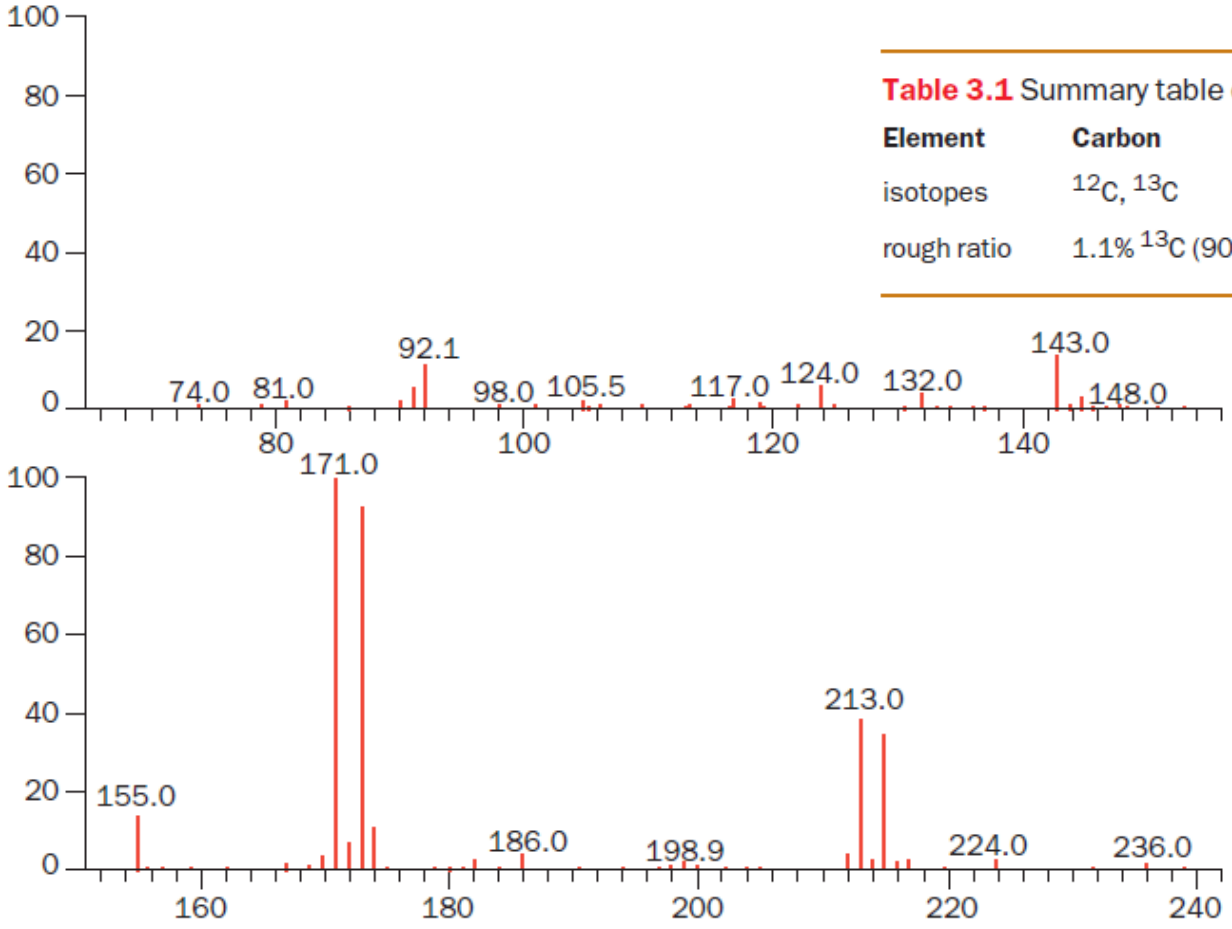


Table 3.1 Summary table of main isotopes for mass spectra

Element	Carbon	Chlorine	Bromine
isotopes	^{12}C, ^{13}C	^{35}Cl, ^{37}Cl	^{79}Br, ^{81}Br
rough ratio	1.1% ^{13}C (90:1)	3:1	1:1

pontos tömegmérés nagyfelbontású tömegspektrométerrel

Table 3.3 Exact masses of common elements

Element	Isotope	Atomic weight	Exact mass
hydrogen	^{1}H	1	1.00783
carbon	^{12}C	12	12.00000
carbon	^{13}C	13	13.00335
nitrogen	^{14}N	14	14.00307
oxygen	^{16}O	16	15.99492
fluorine	^{19}F	19	18.99840
phosphorus	^{31}P	31	30.97376
sulfur	^{32}S	32	31.97207
chlorine	^{35}Cl	35	34.96886
chlorine	^{37}Cl	37	36.96590
bromine	^{79}Br	79	78.91835
bromine	^{81}Br	81	80.91635

▶

The reason that exact masses are not integers lies in the slight mass difference between a proton (1.67262×10^{-27} kg) and a neutron (1.67493×10^{-27} kg) and in the fact that electrons have mass (9.10956×10^{-31} kg).

Table 3.4 Exact mass determination for the bee alarm pheromone

Composition	Calculated M^+	Observed M^+	Error in p.p.m.
$C_6H_{10}O_2$	114.068075	114.1039	358
$C_6H_{14}N_2$	114.115693	114.1039	118
$C_7H_{14}O$	**114.104457**	**114.1039**	5
C_8H_{18}	114.140844	114.1039	369

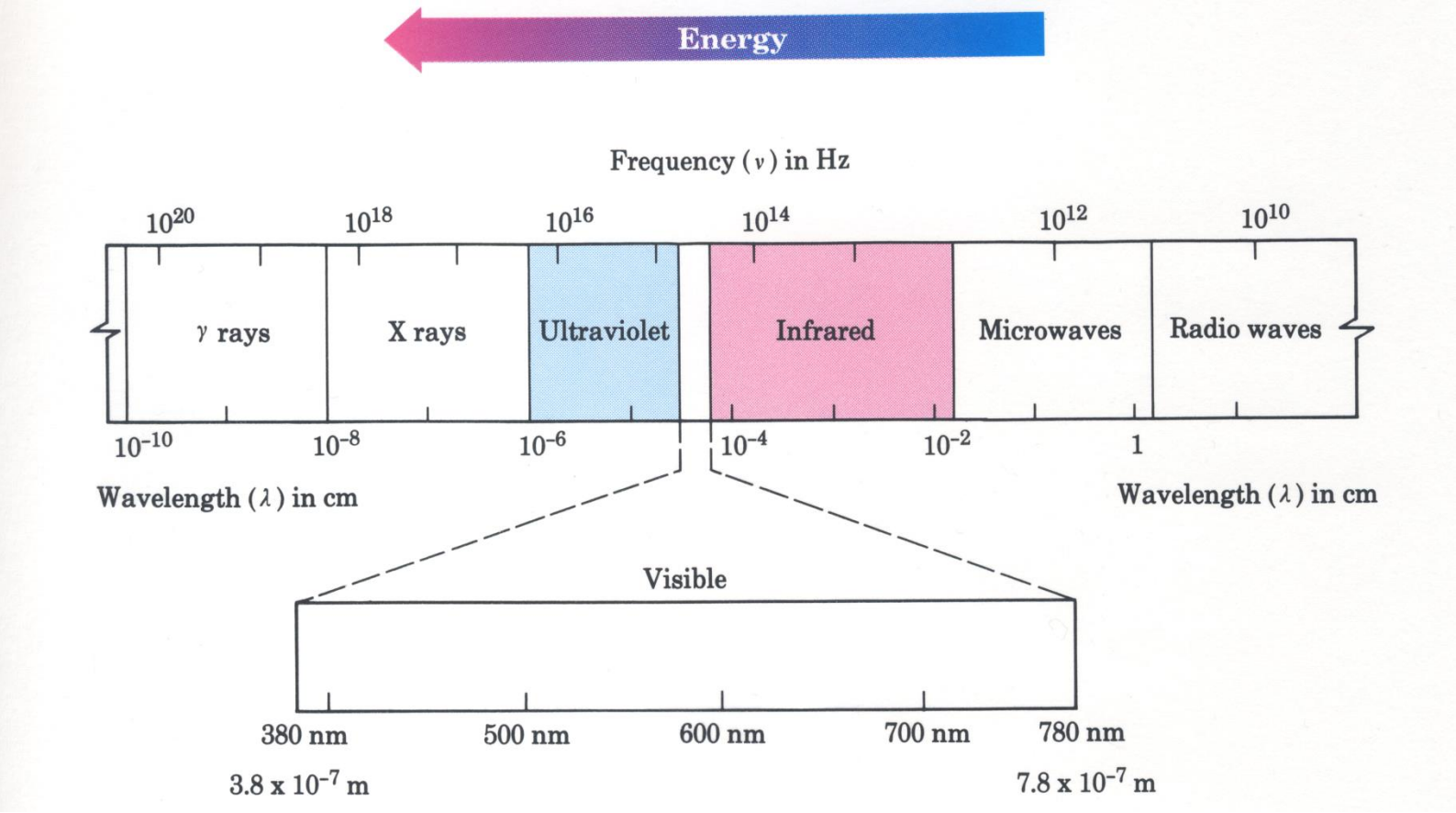
Egyéb tömegspektrometriás módszerek:

- tömegspektrometria kémiai ionizációval
- negatív ion tömegspektrometria
- E(lectron)S(pray)I(onisation) tömegspektromeria
- M(atrix)A(ssited)L(aser)I(onisation) tömegspektrometria

A megvalósítás módja:

- time-of-flight, egyszerű
- kvadrupól, egyszerű
- mindkét fajta, tandem

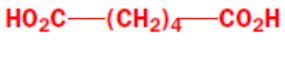
Az elektromágneses spektrum



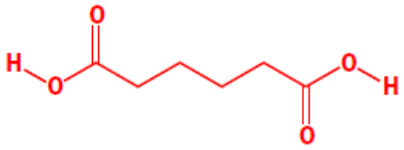
az anyag és az elektromágneses sugárzás kölcsönhatásai

Röntgenkrisztallográfia

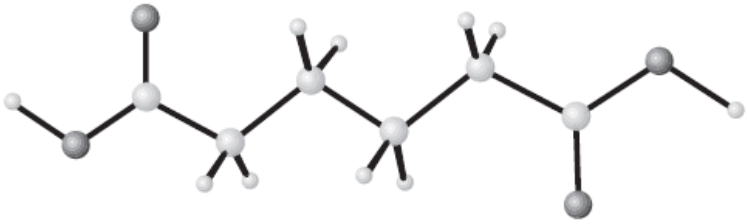
X-ray crystal structures are determined by allowing a sample of a crystalline compound to diffract X-rays. From the resulting diffraction pattern, it is possible to deduce the precise spatial arrangement of the atoms in the molecule—except, usually, the hydrogen atoms, which are too light to diffract the X-rays and whose position must be inferred from the rest of the structure.



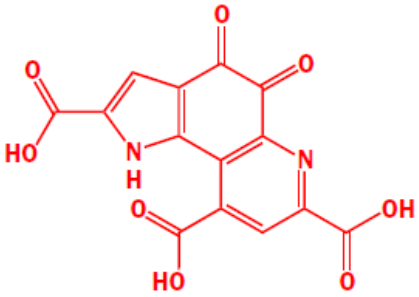
hexanedioic acid



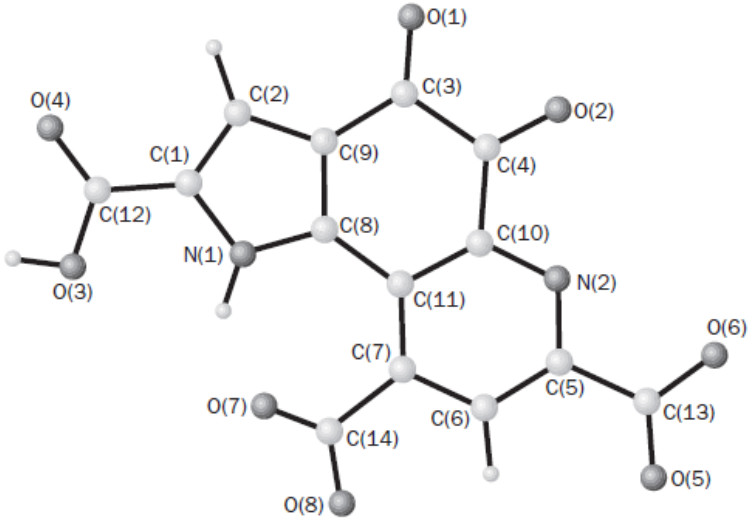
shape of hexanedioic acid



data for structure taken from Cambridge Crystallographic Data Centre



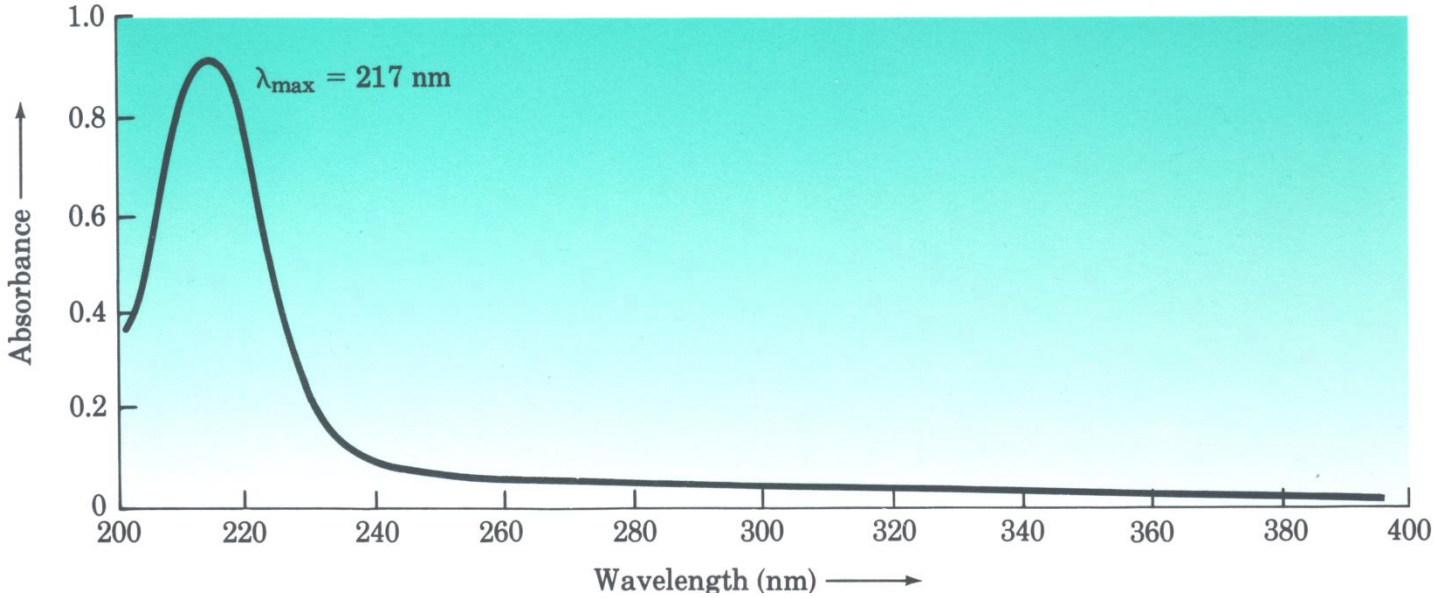
methoxatin



data for the X-ray structure taken from the Cambridge Crystallographic Data Centre

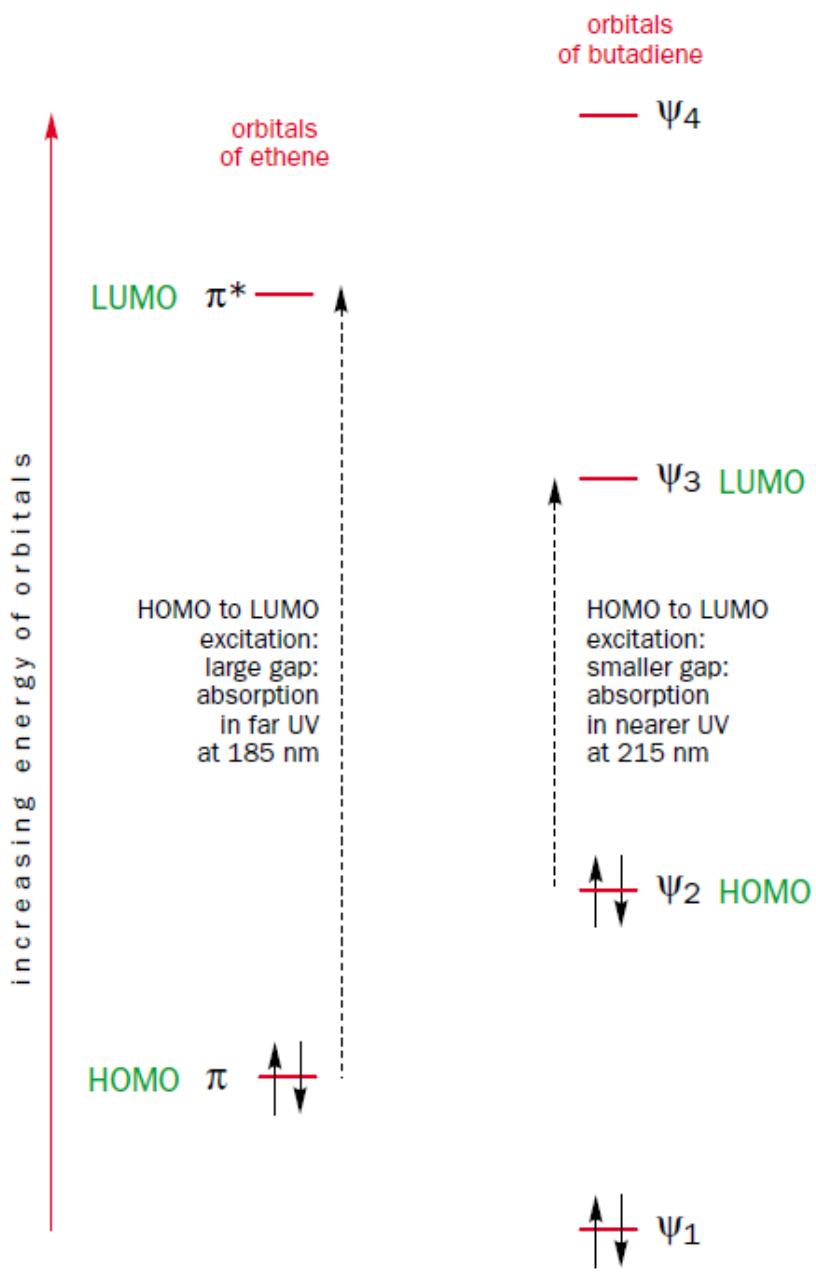
UV-VIS spektroszkópia

az elektronrendszer gerjesztése (+rezgési+forgási energiaszintek)

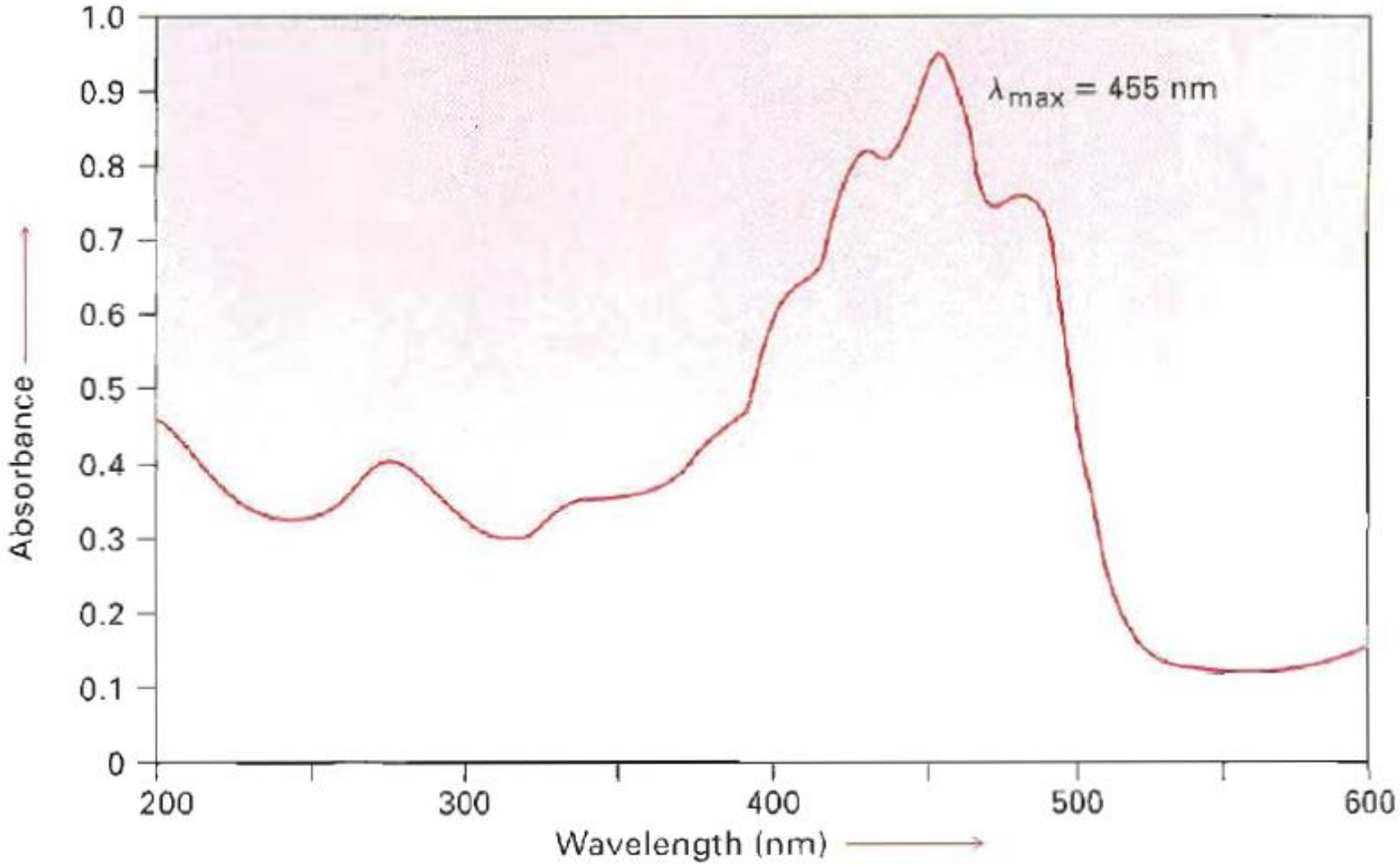


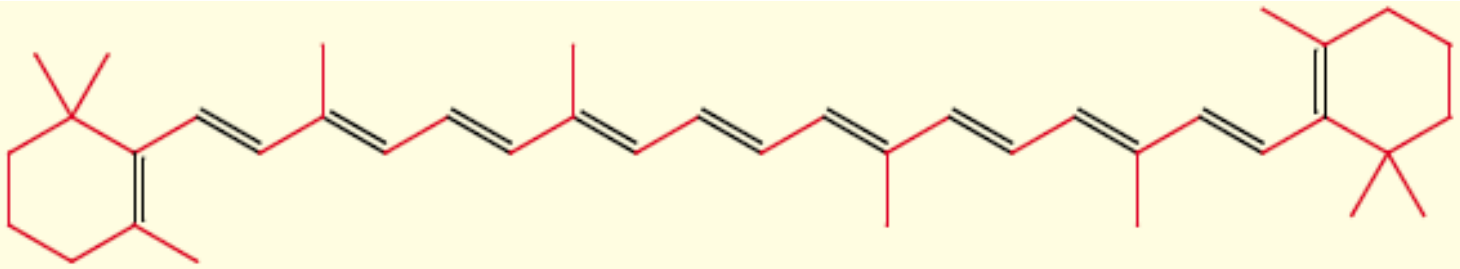
a butadién spektruma

kvantitatív analízisre alkalmas: Lambert-Beer törvény (A=εcl – de inkább előzetes kalibráció)



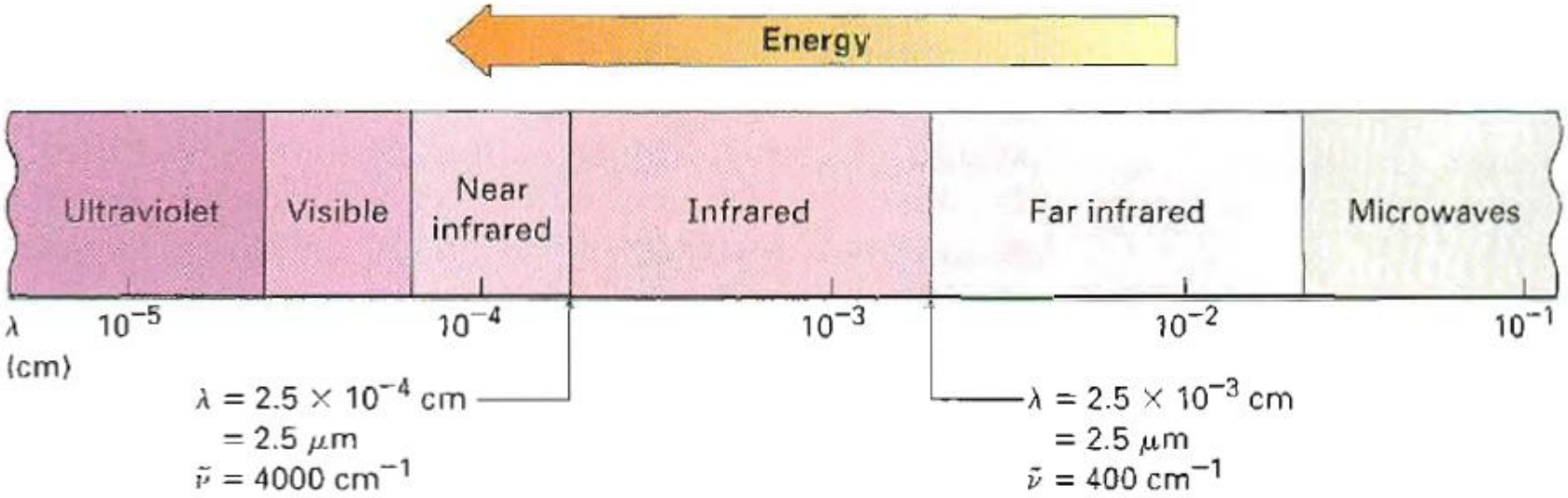
- The more conjugated a compound is, the smaller the energy transition between its HOMO and LUMO and hence the longer the wavelength of light it can absorb. Hence UV–visible spectroscopy can tell us about the conjugation present in a molecule.





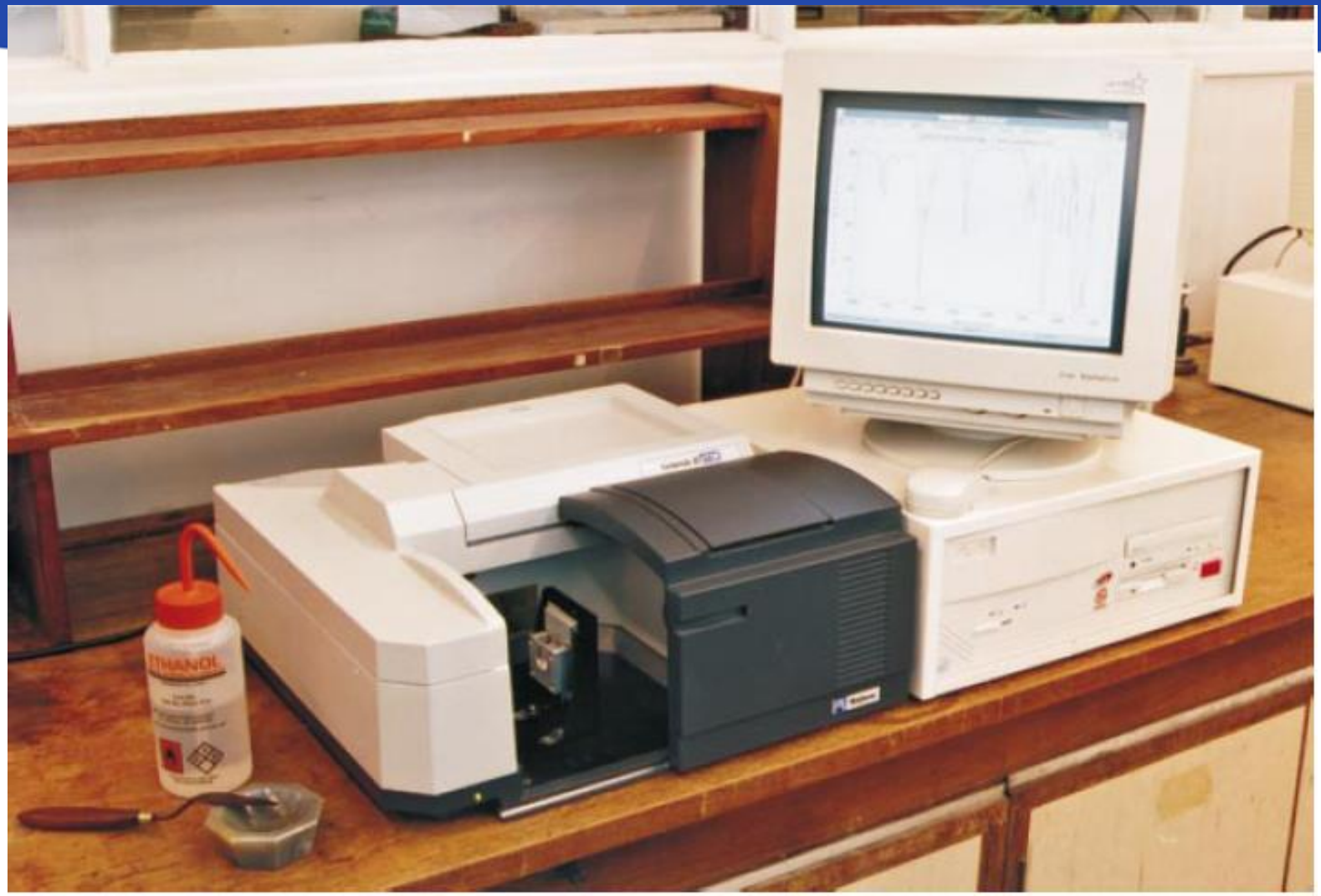
β-carotene, the red pigment in carrots and other vegetables

Infravörös spektroszkópia

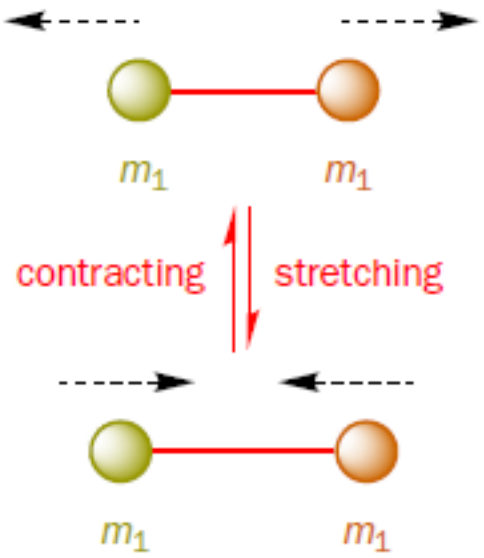


egy molekula csak akkor mutat elnyelést az infravörös tartományban, ha legalább egy olyan rezgése van, ami megváltoztatja a molekula dipólmomentumát

egy FT-IR spektrofotométer

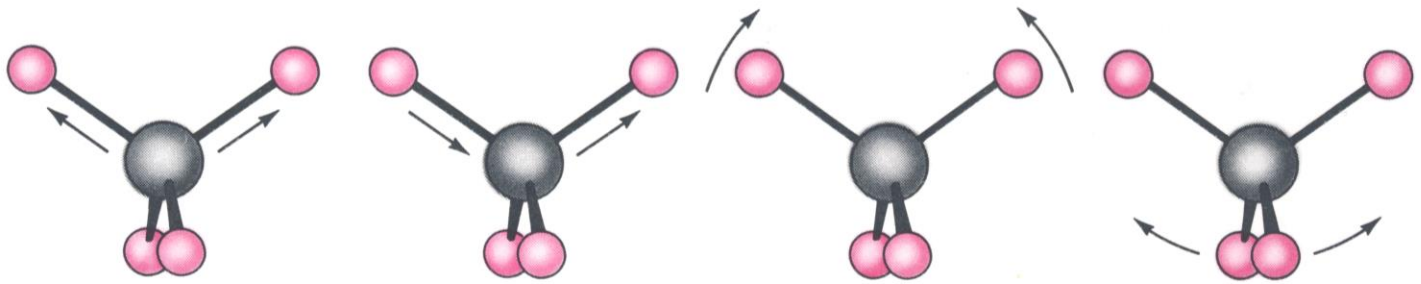


bond vibration in the infrared

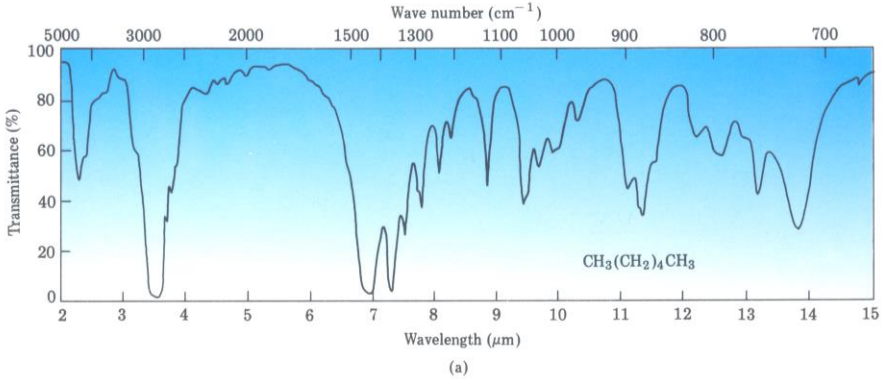


$$E = h\nu = h\frac{c}{\lambda} \qquad \lambda = \frac{c}{\nu} \qquad \nu^* = 1/\lambda = \nu/c$$

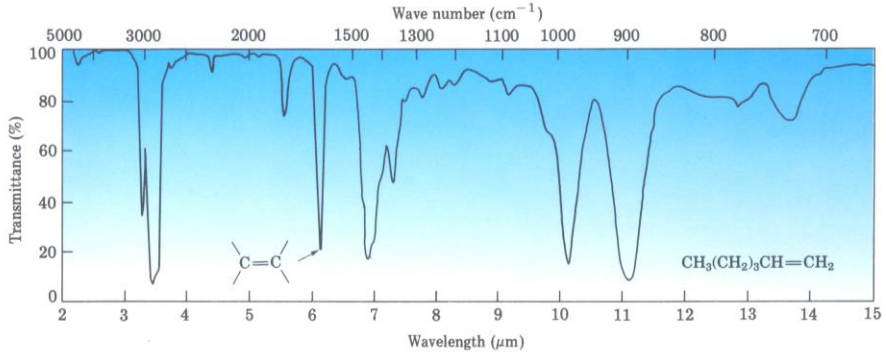
$$\nu = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$



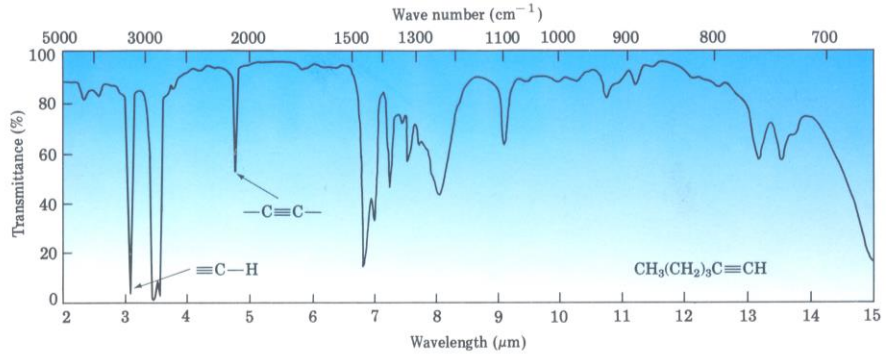
IR spectra of (a) hexane, (b) 1-hexene, and (c) 1-hexyne



(a)



(b)



(c)

IR spectrum of benzaldehyde

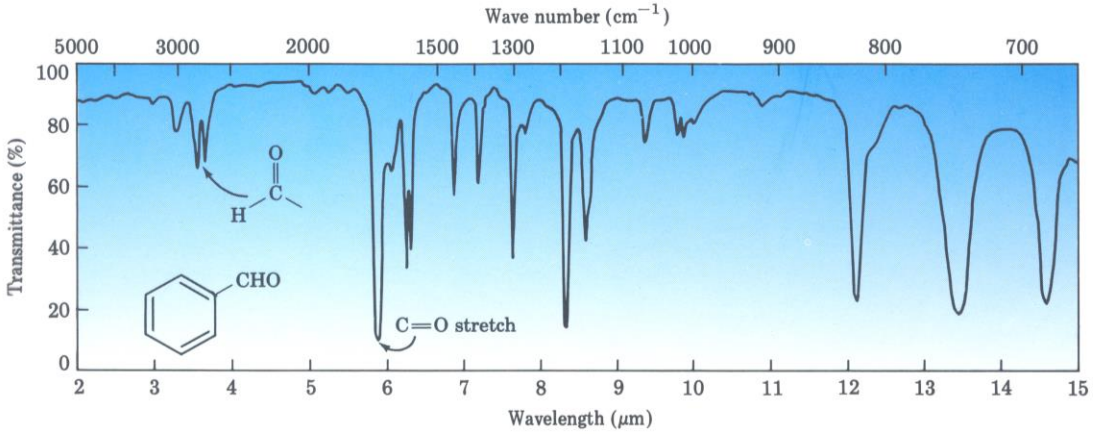
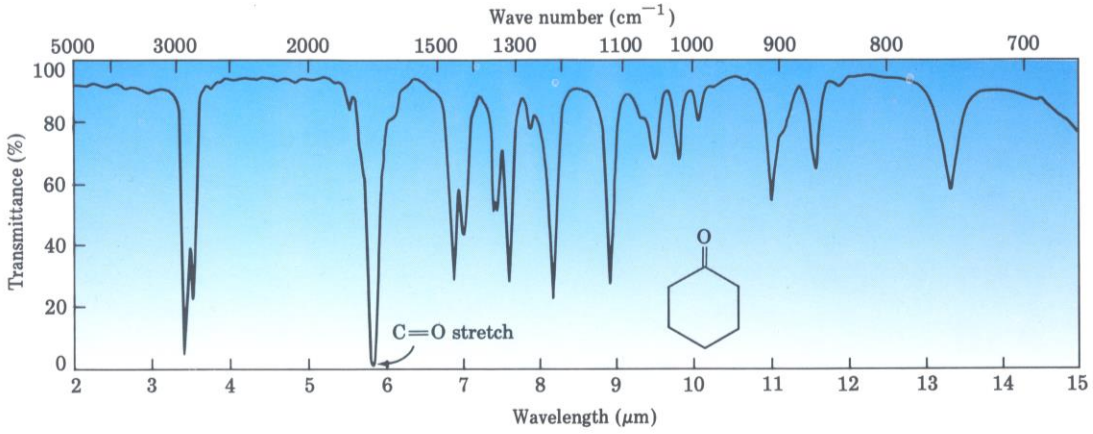


Figure 19.17 *Page* 747

IR spectrum of cyclohexanone



Stronger bonds vibrate faster and so do lighter atoms.

Values chiefly affected by mass of atoms: (lighter atom, higher frequency)

C–H	C–D	C–O	C–Cl
3000 cm^{-1}	2200 cm^{-1}	1100 cm^{-1}	700 cm^{-1}

Values chiefly affected by bond strength (stronger bond, higher frequency)

C≡O	C=O	C–O
2143 cm^{-1}	1715 cm^{-1}	1100 cm^{-1}

The regions of the infrared spectrum

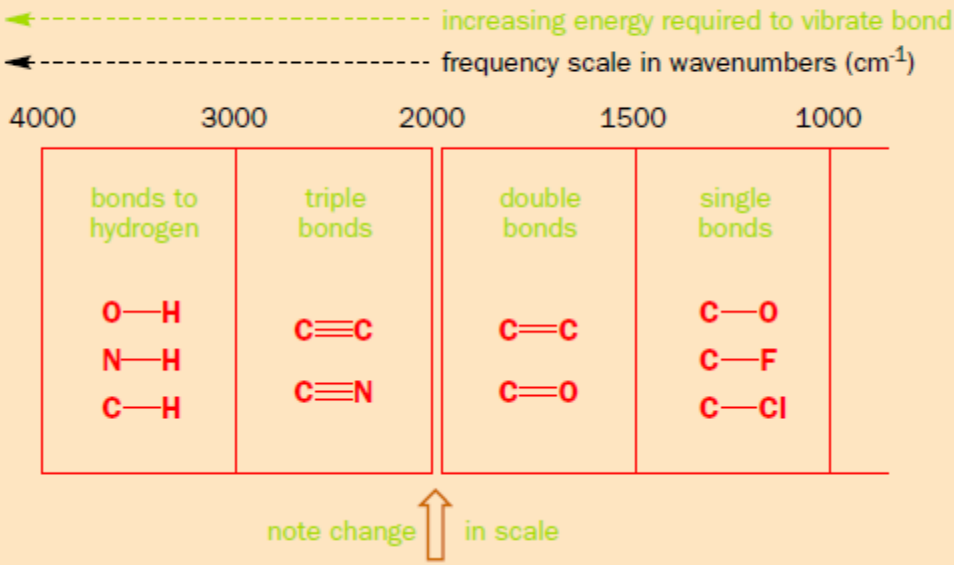
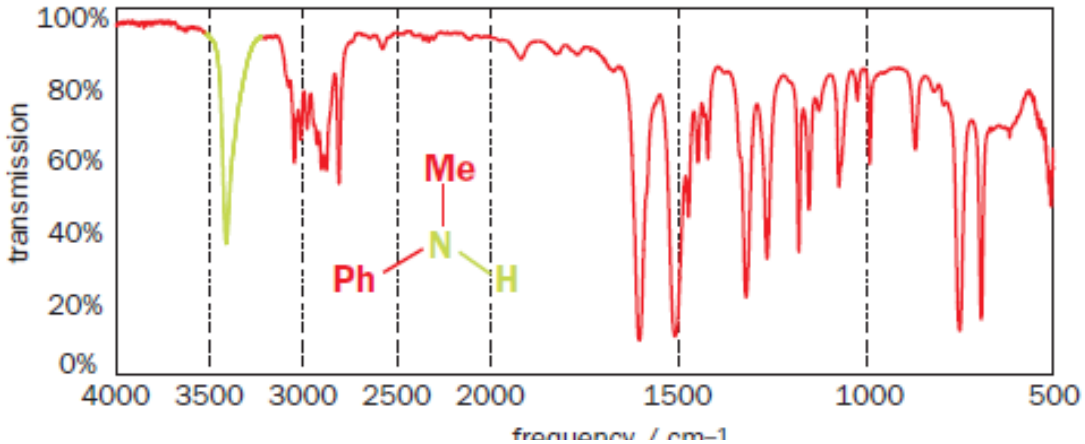
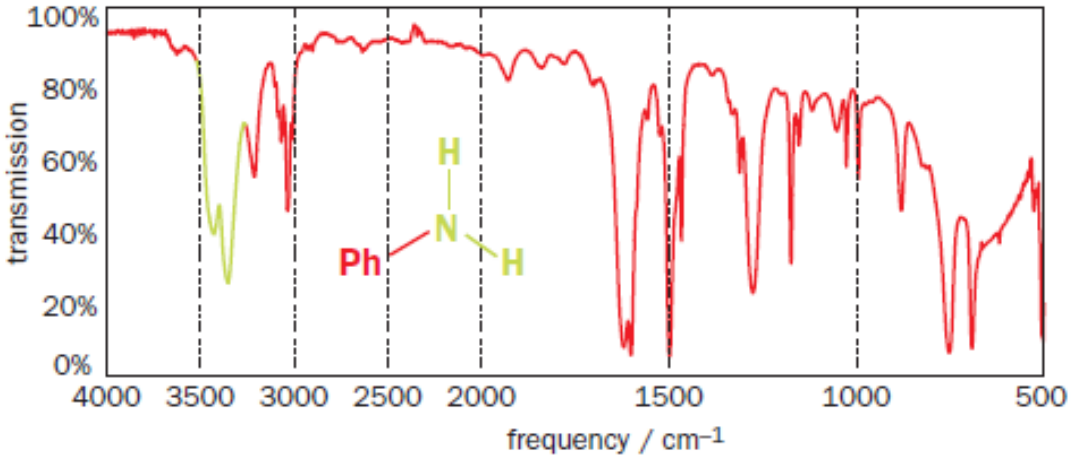


Table 3.6 IR bands for bonds to hydrogen

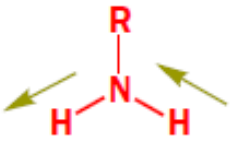
Bond	Reduced mass, μ	IR frequency, cm^{-1}	Bond strength, $kJ\ mol^{-1}$
C–H	12/13 = 0.92	2900–3200	CH_4: 440
N–H	14/15 = 0.93	3300–3400	NH_3: 450
O–H	16/17 = 0.94	3500–3600[a]	H_2O: 500

[a]When not hydrogen-bonded: see below.



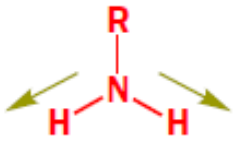


antisymmetric NH_2 stretch

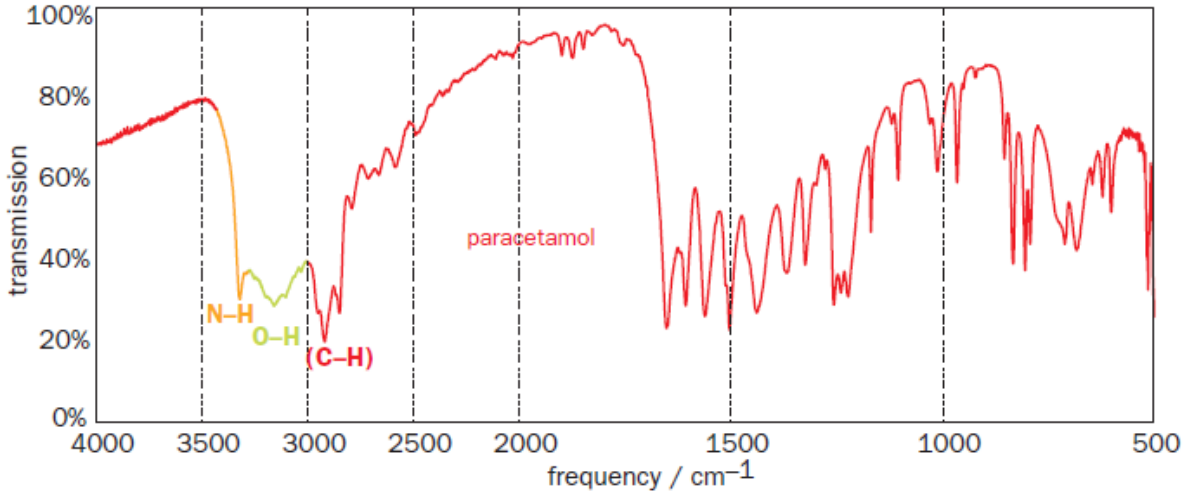


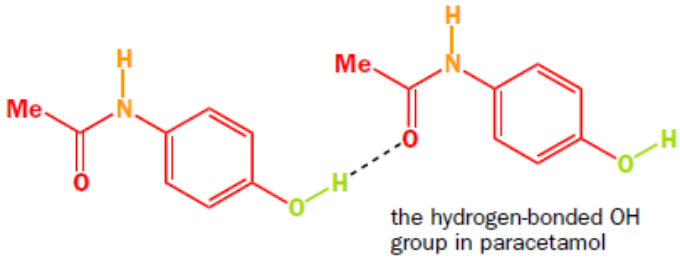
about 3400 cm^{-1}

symmetric NH_2 stretch

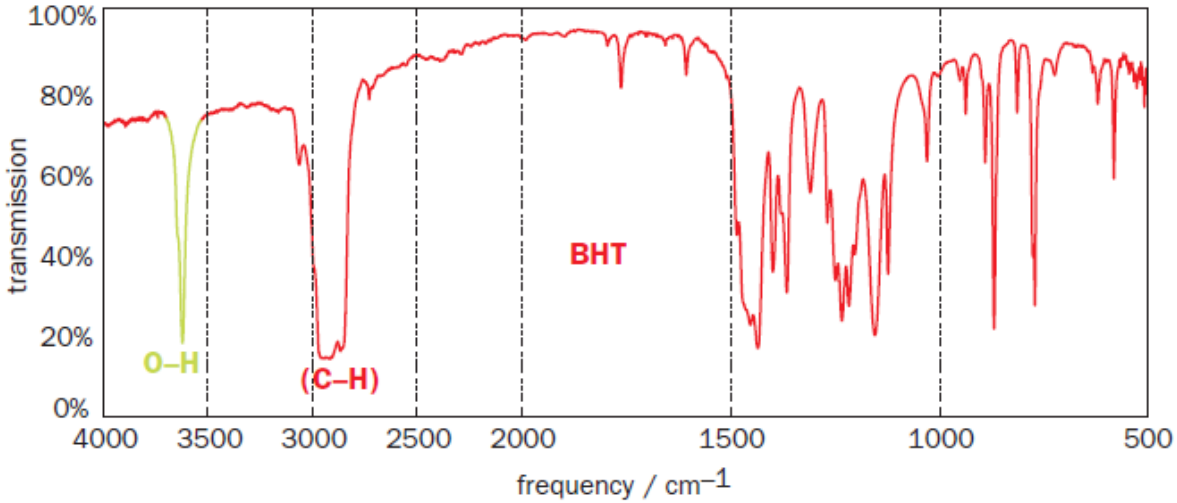


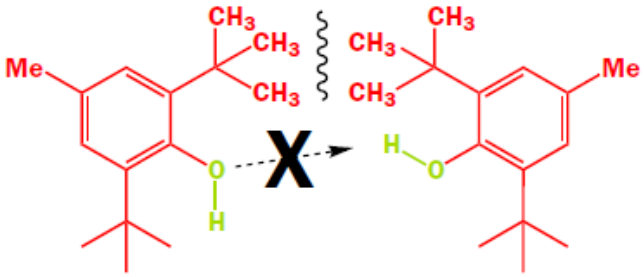
about 3300 cm^{-1}





the hydrogen-bonded OH group in paracetamol





in BHT H-bonding is prevented by large *t*-butyl groups

- The summary chart shows some typical peak shapes and frequencies for X–H bonds in the region 4000–3000 cm^{-1}.

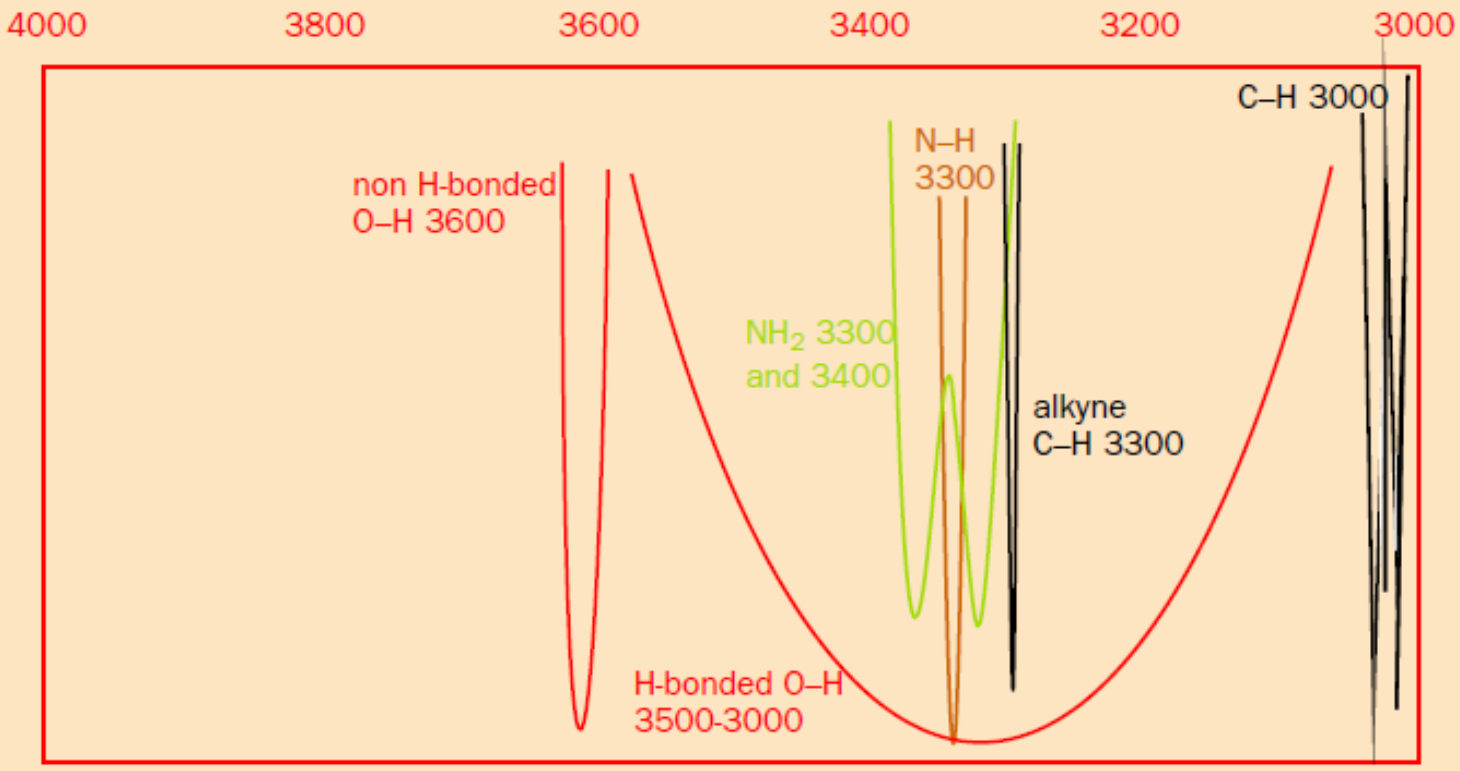
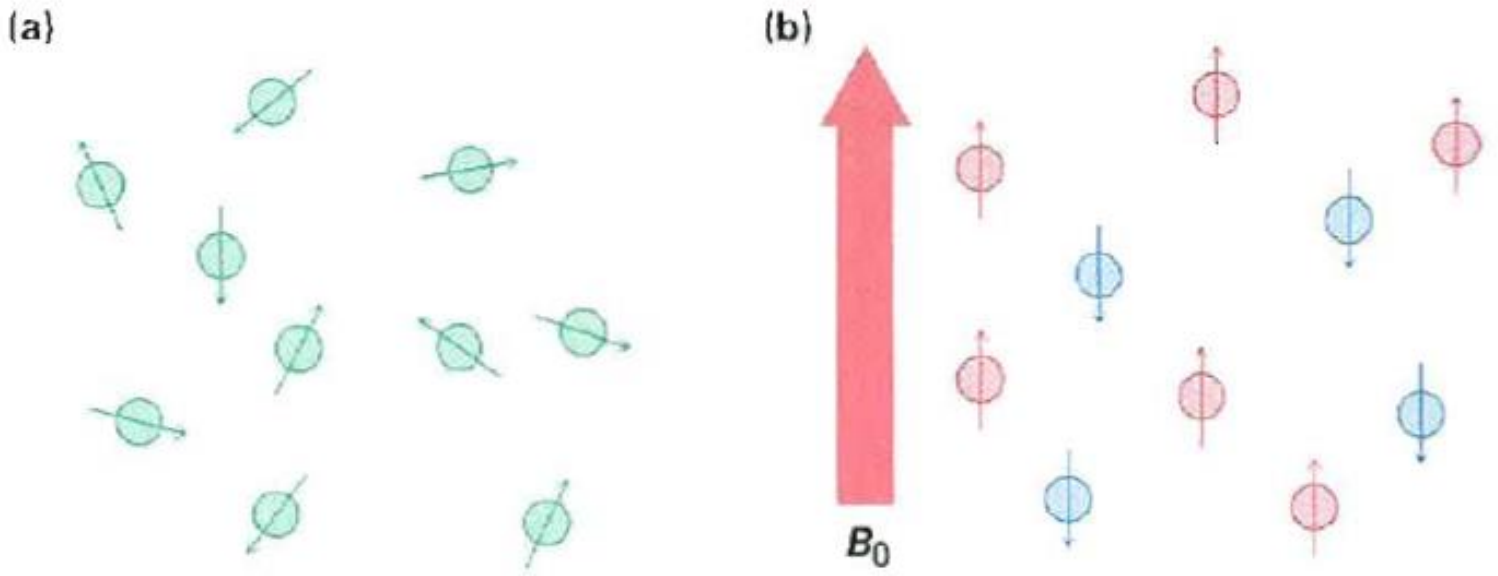


Table 3.9 Useful absorptions in the fingerprint region

Frequency, cm^{-1}	Strength	Group	Comments
1440–1470	medium	CH_2	deformation (present in nujol)
~1380	medium	CH_3	deformation (present in nujol)
~1350	strong	NO_2	symmetrical N=O stretch
1250–1300	strong	P=O	double bond stretch
1310–1350	strong	SO_2	antisymmetrical S=O stretch
1120–1160	strong	SO_2	symmetrical S=O stretch
~1100	strong	C–O	single bond stretch
950–1000	strong	C=CH	*trans* alkene (out-of-plane deformation)
~690 *and* ~750	strong	Ar–H	five adjacent Ar–H (out-of-plane)
~750	strong	Ar–H	four adjacent Ar–H (out-of-plane)
~700	strong	C–Cl	single bond stretch

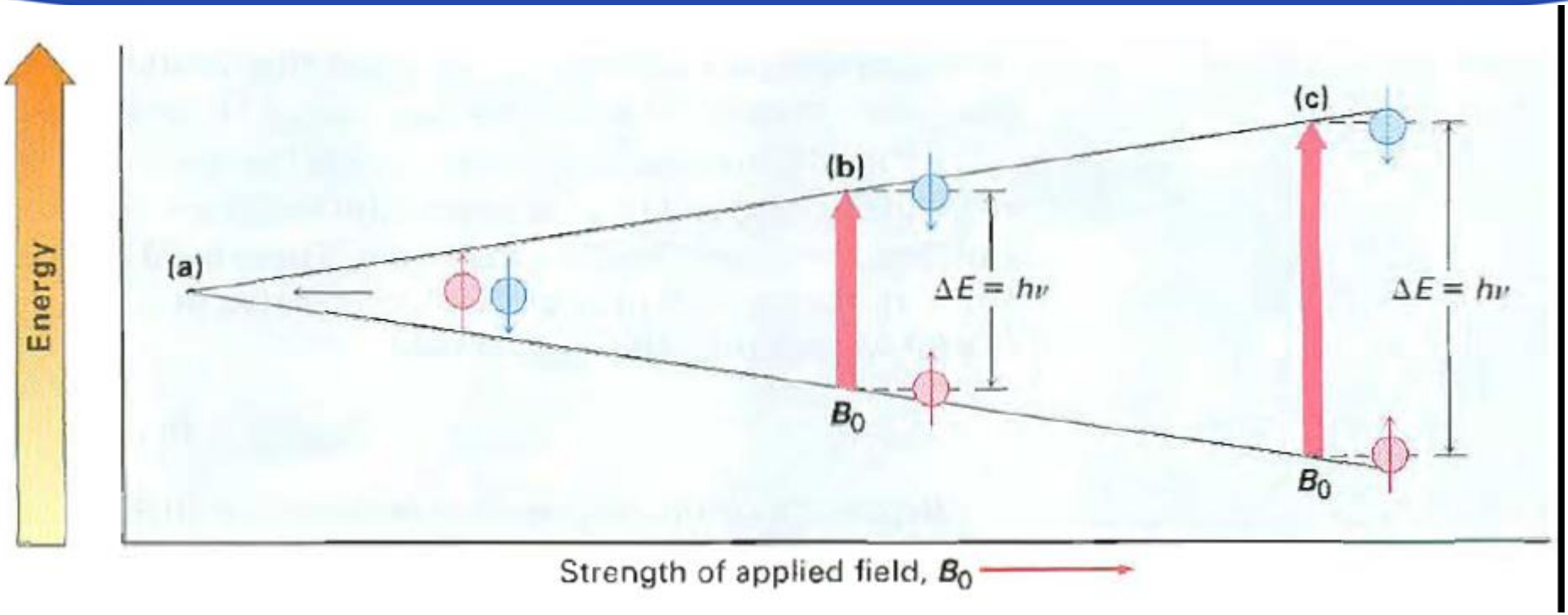
Az IR spektroszkópia fő haszna a funkciós csoportok azonosítása. Elvben kvantitatív analízisre is használható (kisebb-nagyobb közelítéssel teljesül a Lambert-Beer törvény), de erre a célra csak újabban, az IR spektrofotométerek ugrásszerű fejlődése után használják.

NMR spektroszkópia



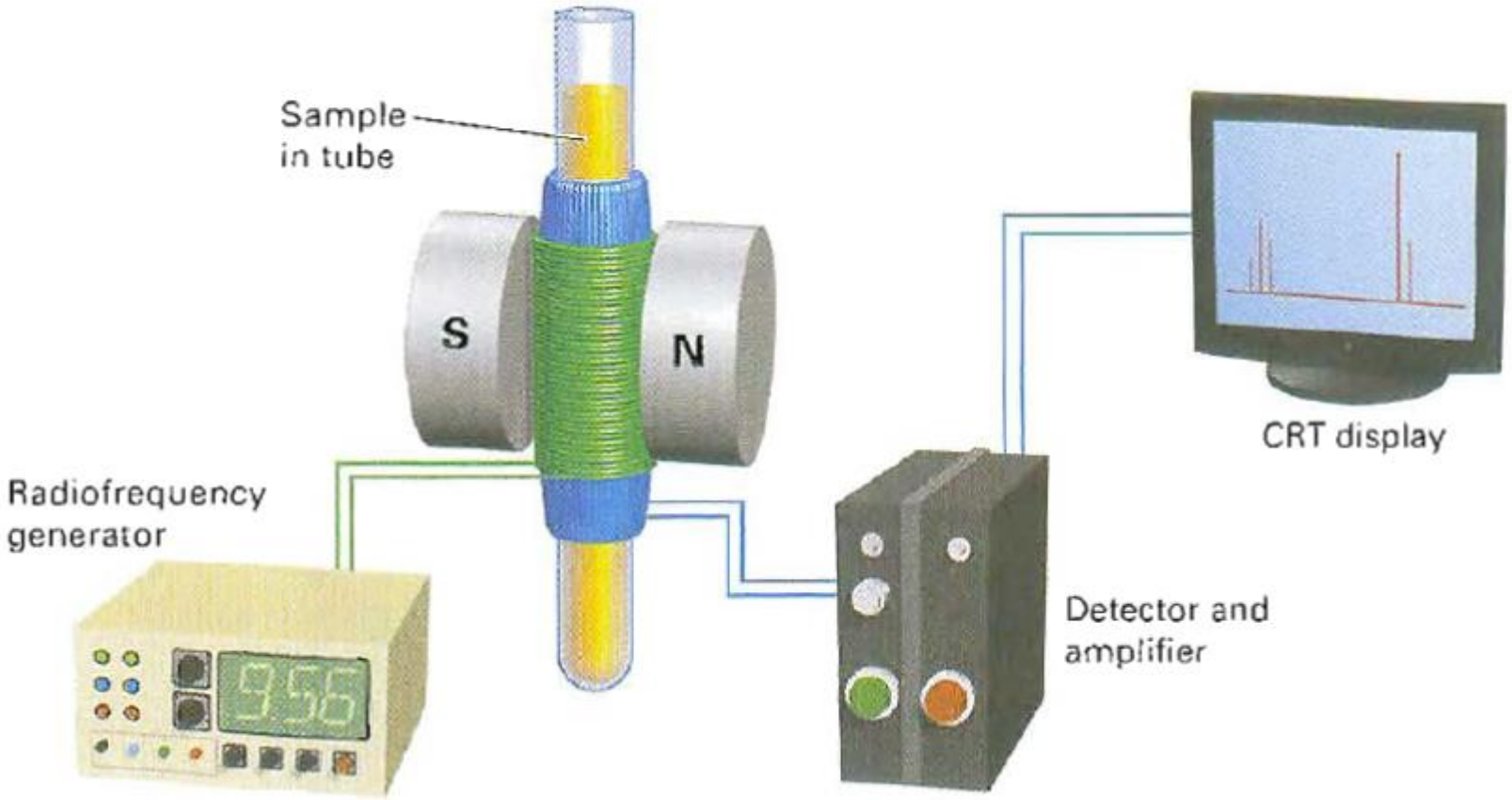
magspinek rendeződése külső mágneses tér hatására

az eredő magspin nem nulla, ha a magot alkotó nukleonok közül legalább az egyik páratlan – a szerves kémiában leggyakrabban használt magok ^{1}H és ^{13}C



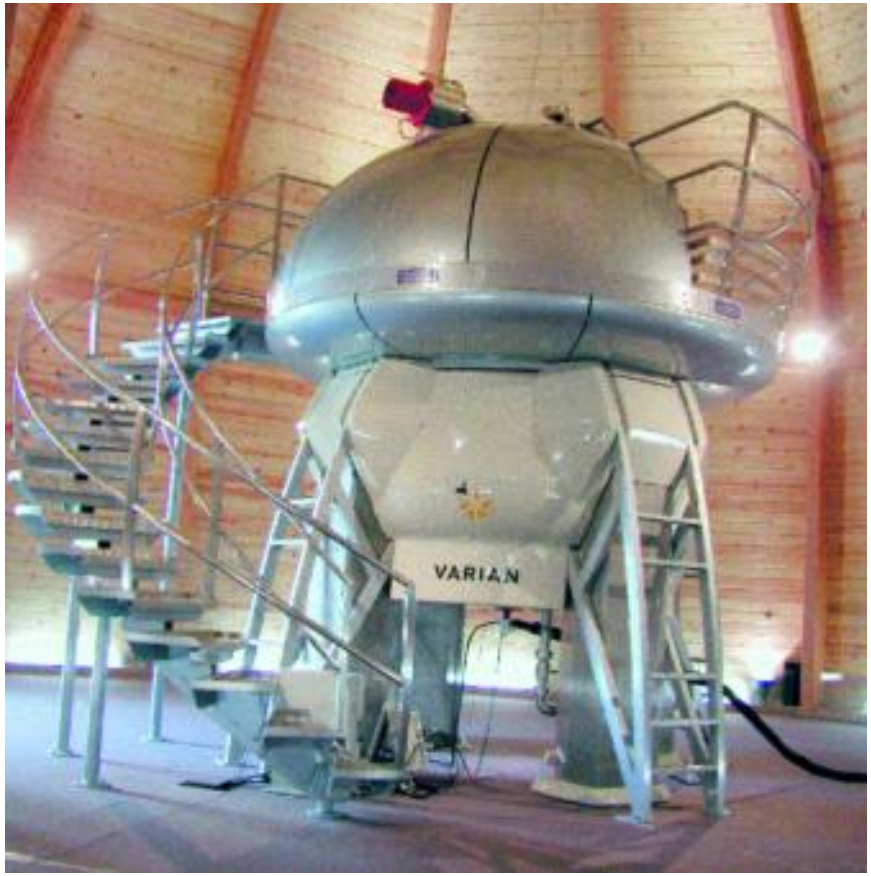
az energiaszintek közti távolság függése a külső mágneses tértől

egy NMR készülék sematikus rajza

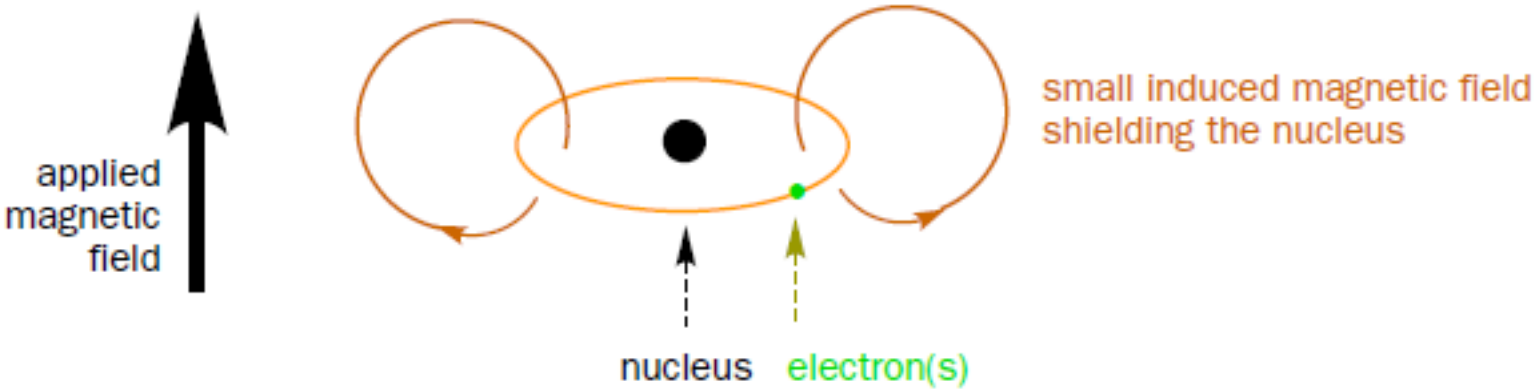


egy modern NMR készülék (400 MHz)

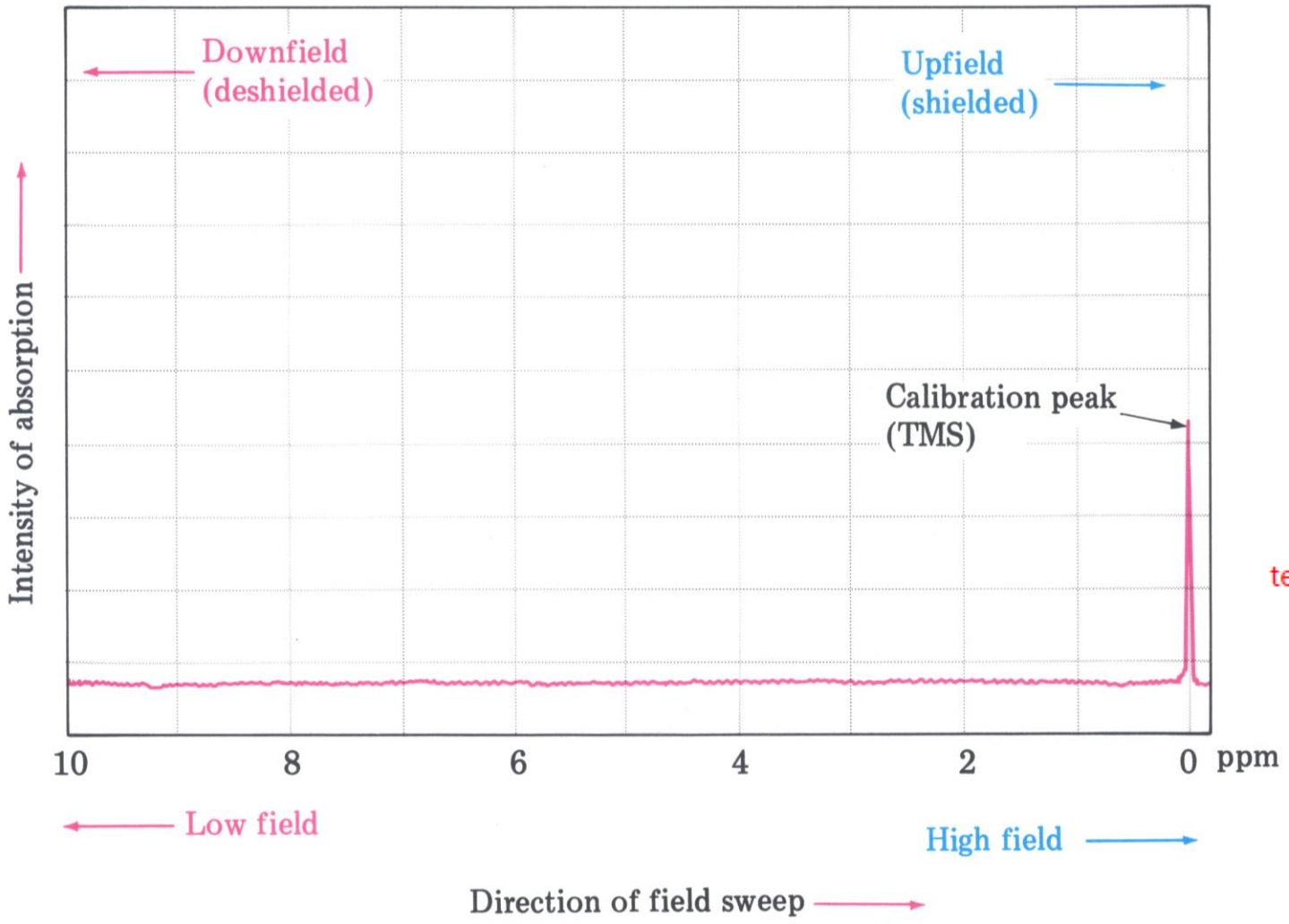
egy még modernebb NMR készülék (900 MHz)

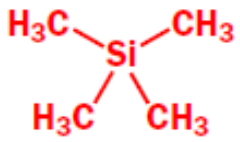


shielding of nuclei from an applied magnetic field by electrons:



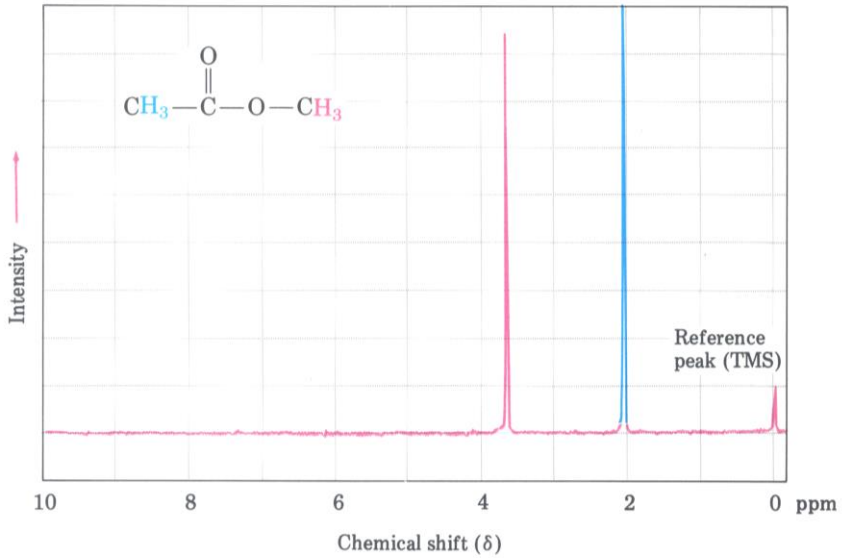
$$B_{\text{effective}} = B_{\text{applied}} - B_{\text{local}}$$





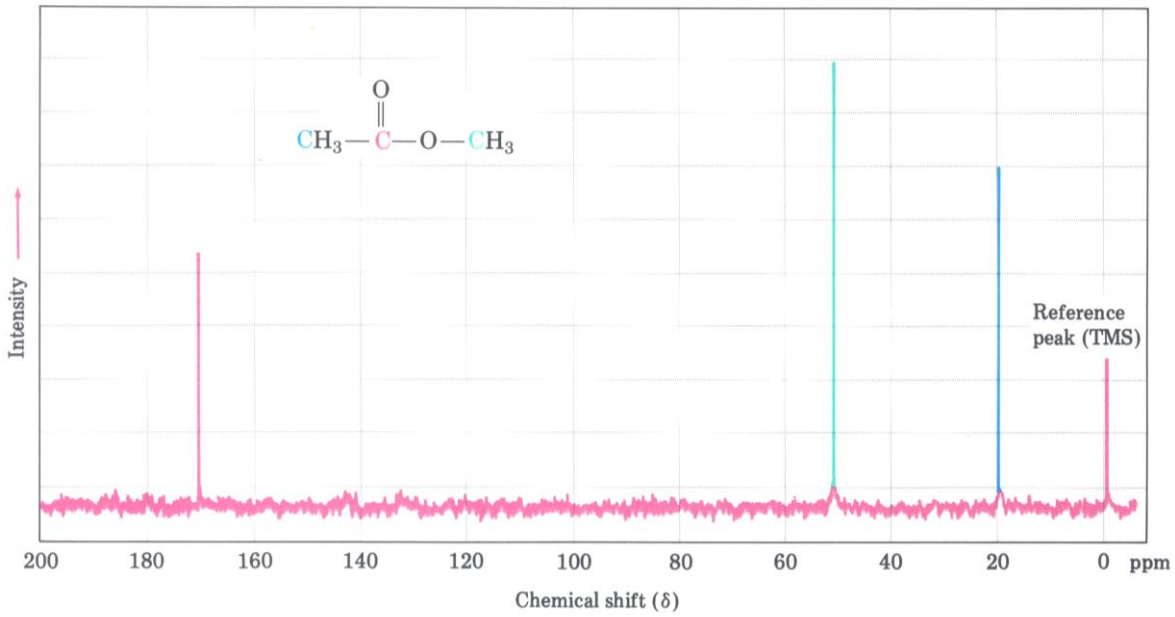
tetramethylsilane, TMS

^{1}H NMR

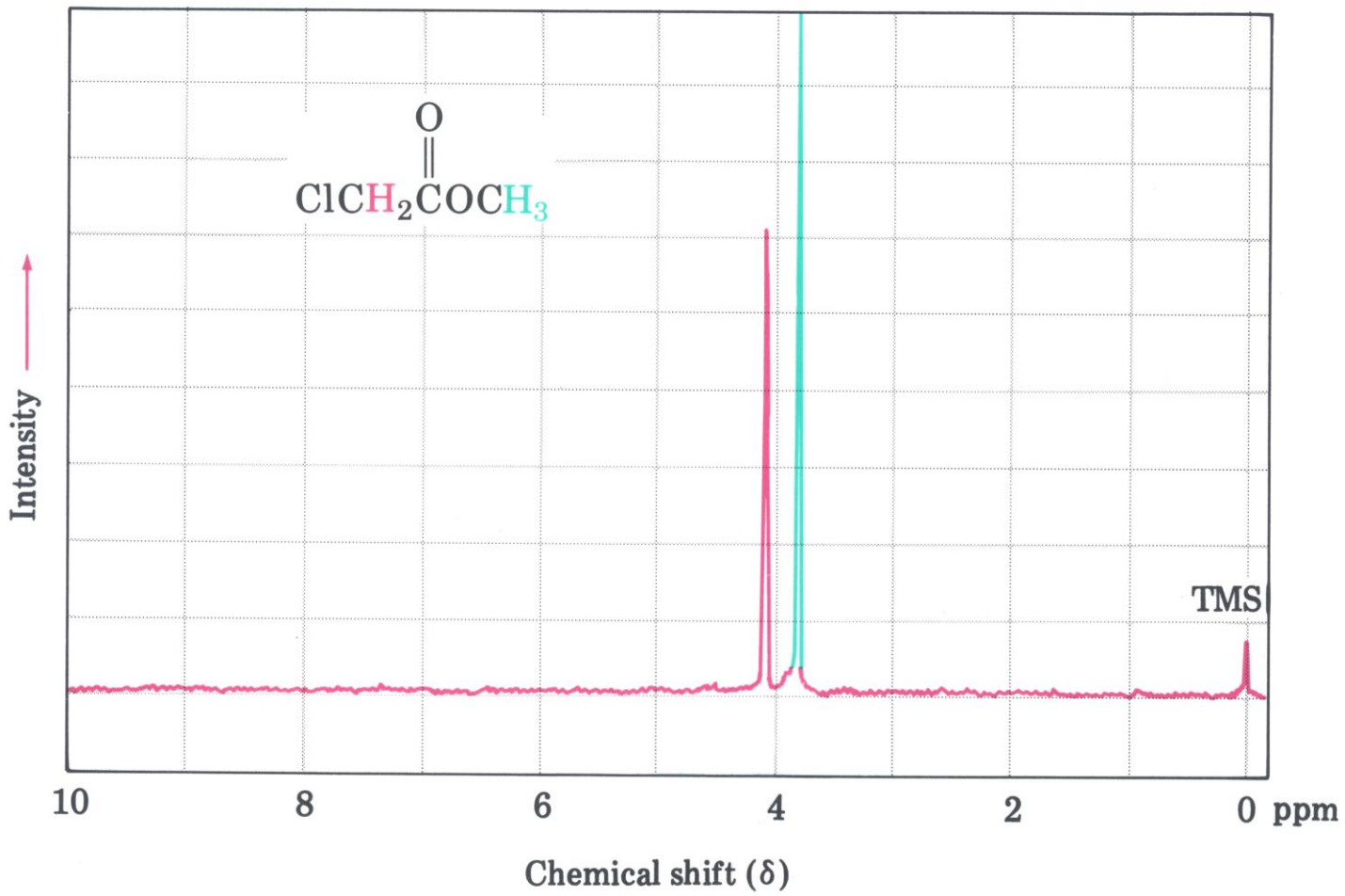


(a)

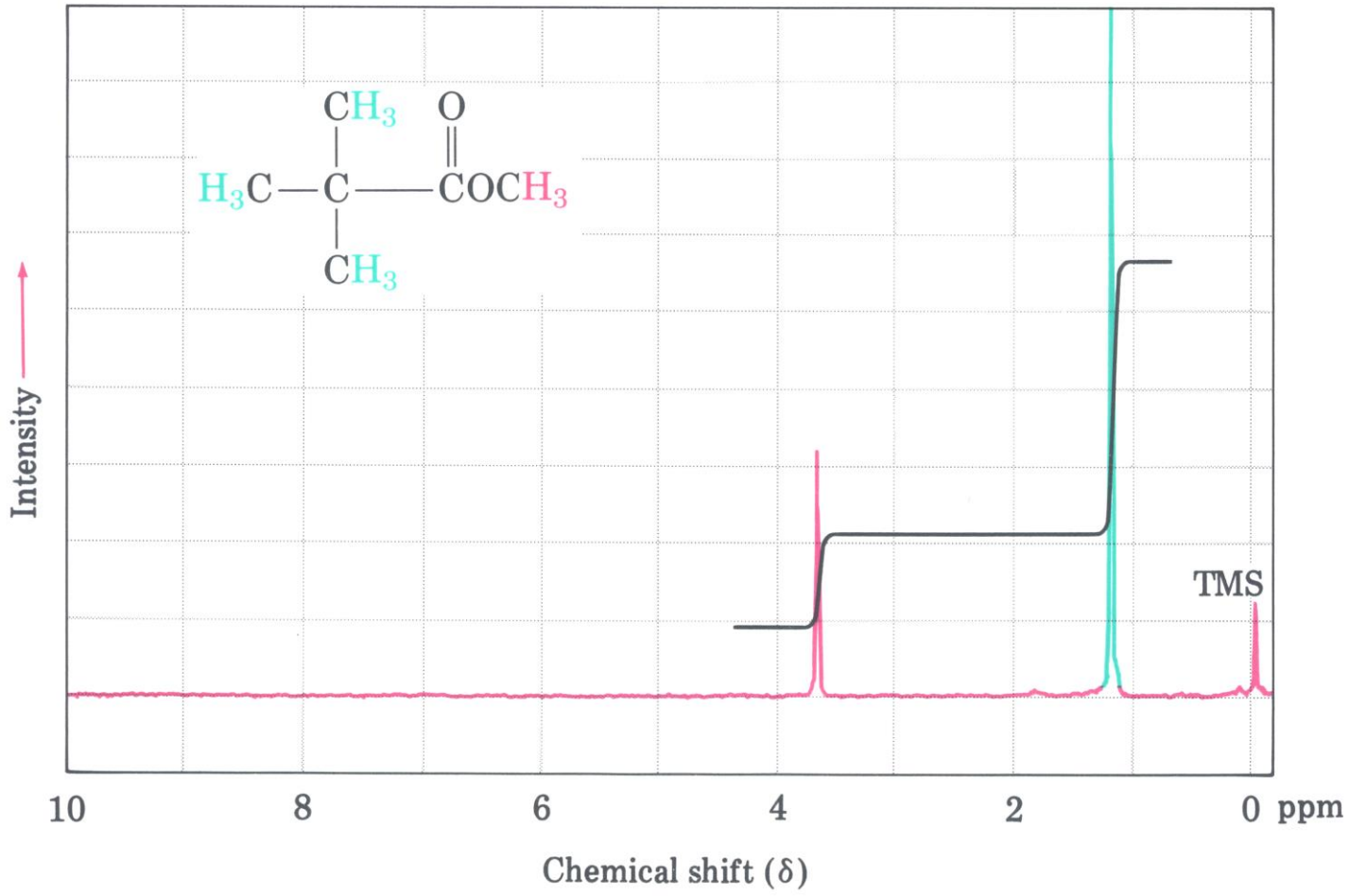
^{13}C NMR

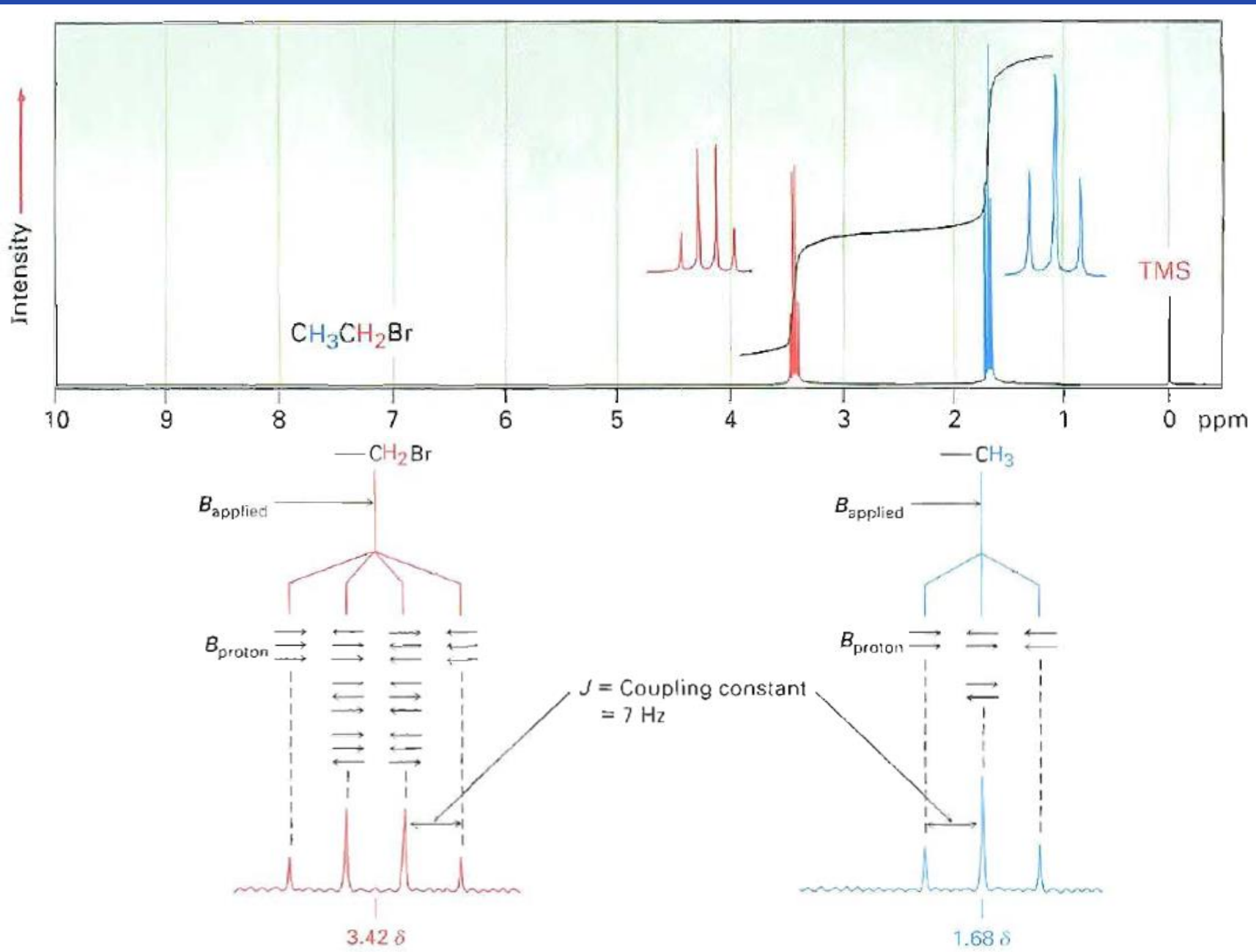


(b)

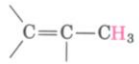
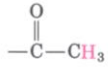
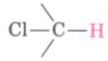
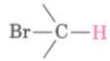
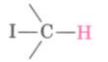
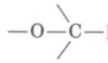
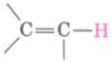
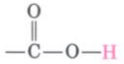
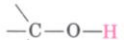

O
ClCH2COCH3
Intensity
TMS
10
8
6
4
2
0 ppm
Chemical shift (δ)

^{1}H NMR - integrált




Intensity
CH3CH2Br
TMS
10
9
8
7
6
5
4
3
2
1
0
ppm
—CH2Br
Bapplied
Bproton
J = Coupling constant
= 7 Hz
3.42 δ
—CH3
Bapplied
Bproton
1.68 δ

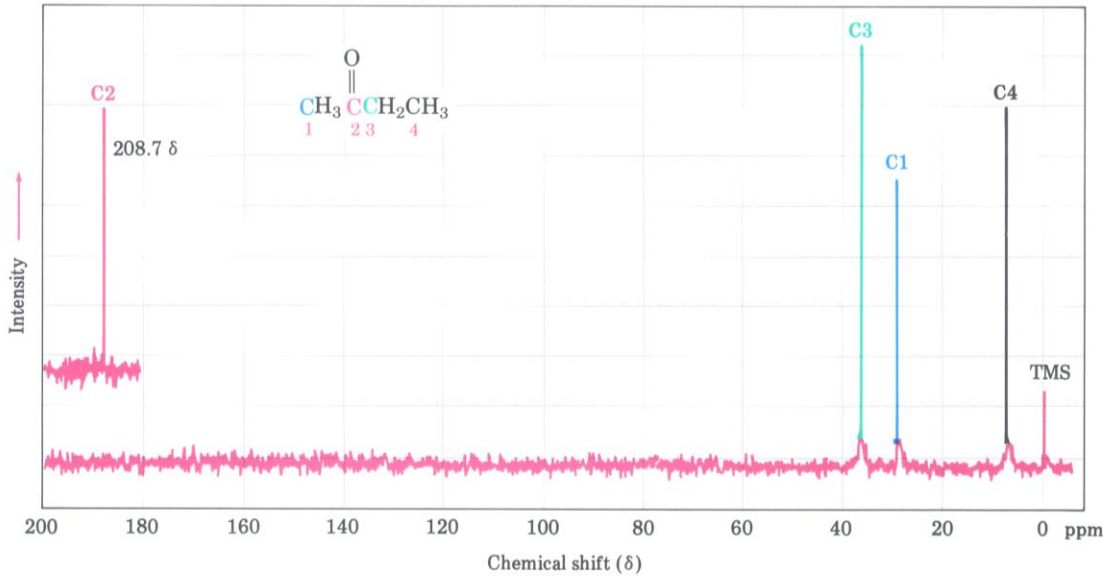
^{1}H NMR korrelációs táblázat

Type of proton	*Formula*	*Chemical shift (δ)*
Reference peak	$(CH_3)_4Si$	0
Saturated primary	$-CH_3$	0.7–1.3
Saturated secondary	$-CH_2-$	1.2–1.4
Saturated tertiary		1.4–1.7
Allylic primary		1.6–1.9
Methyl ketones		2.1–2.4
Aromatic methyl	$Ar-CH_3$	2.5–2.7
Alkyl chloride		3.0–4.0
Alkyl bromide		2.5–4.0
Alkyl iodide		2.0–4.0
Alcohol, ether		3.3–4.0
Alkynyl	$-C\equiv C-H$	2.5–2.7
Vinylic		5.0–6.5
Aromatic	$Ar-H$	6.5–8.0
Aldehyde		9.7–10.0
Carboxylic acid		11.0–12.0
Alcohol		Extremely variable

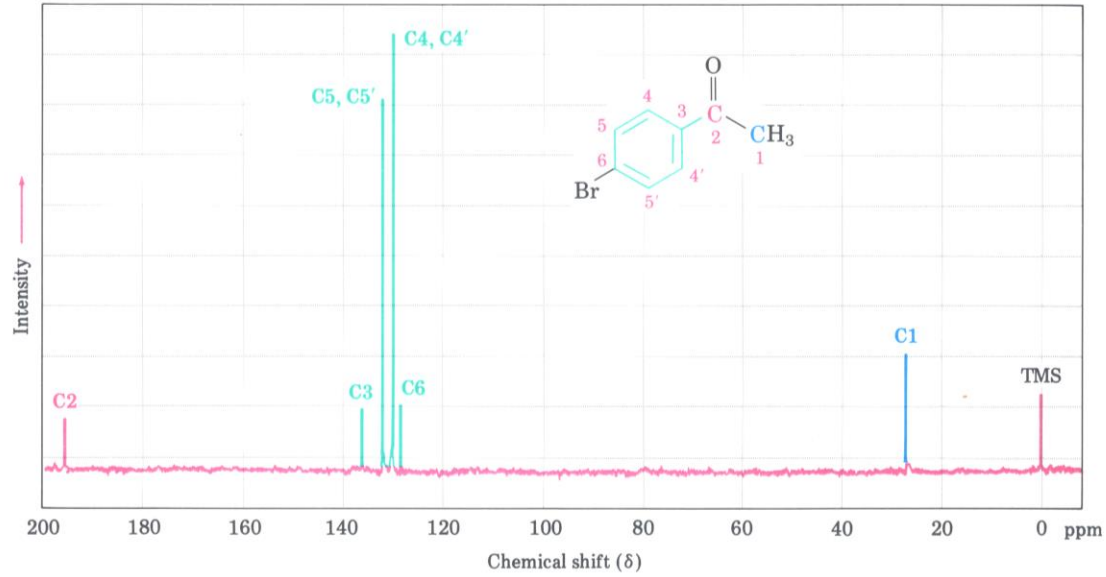
Az ^{1}H NMR spektrumokból nyerhető információk:

- a protonok kémiai környezete
- az egymástól kémiailag különböző környezetben lévő protonok relatív száma
- az egymástól kémiailag különböző környezetben lévő protonok "szomszédsági viszonyai"

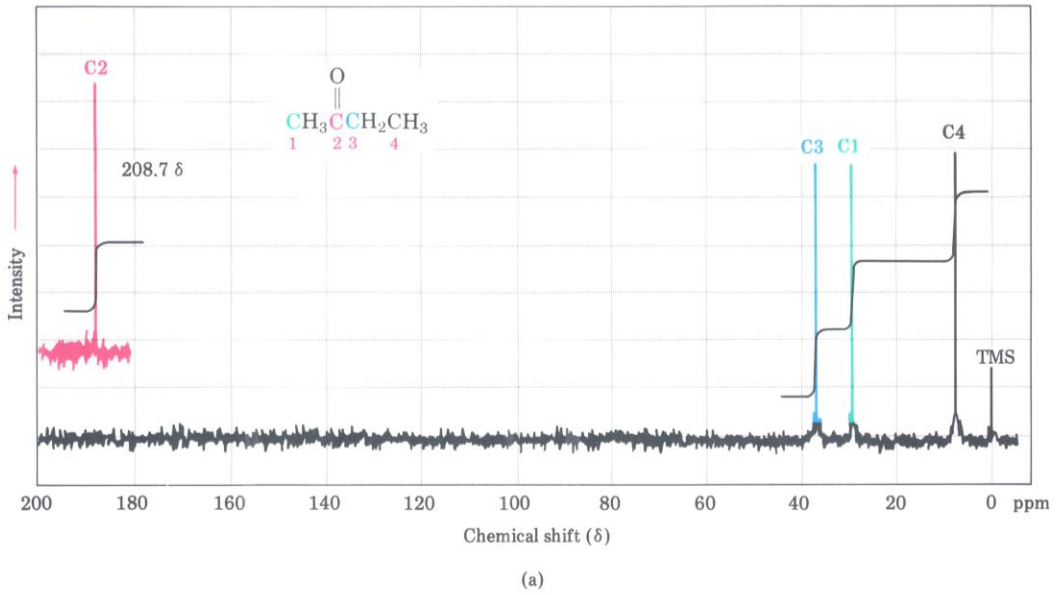
^{13}C NMR - spin lecsatolt



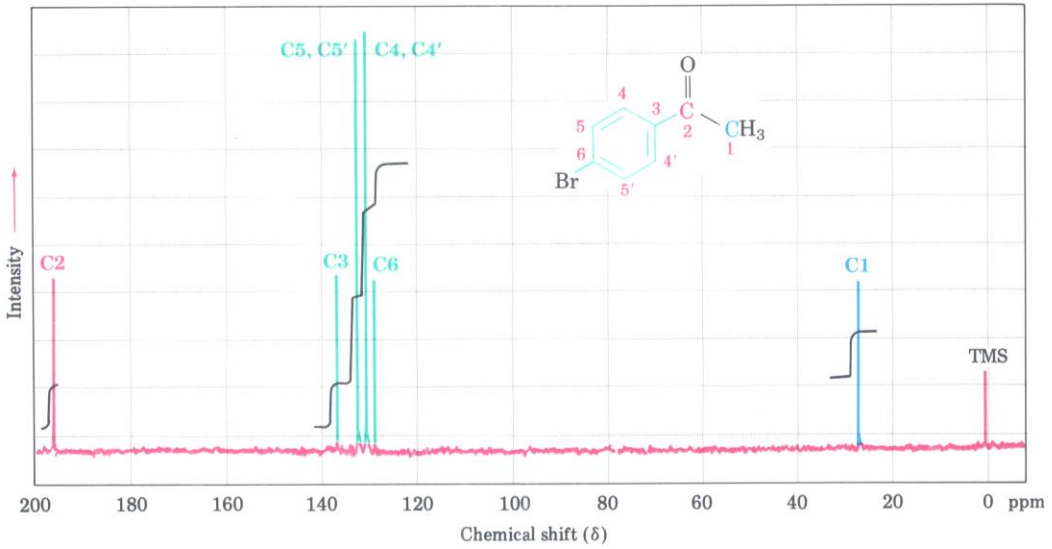
(a)



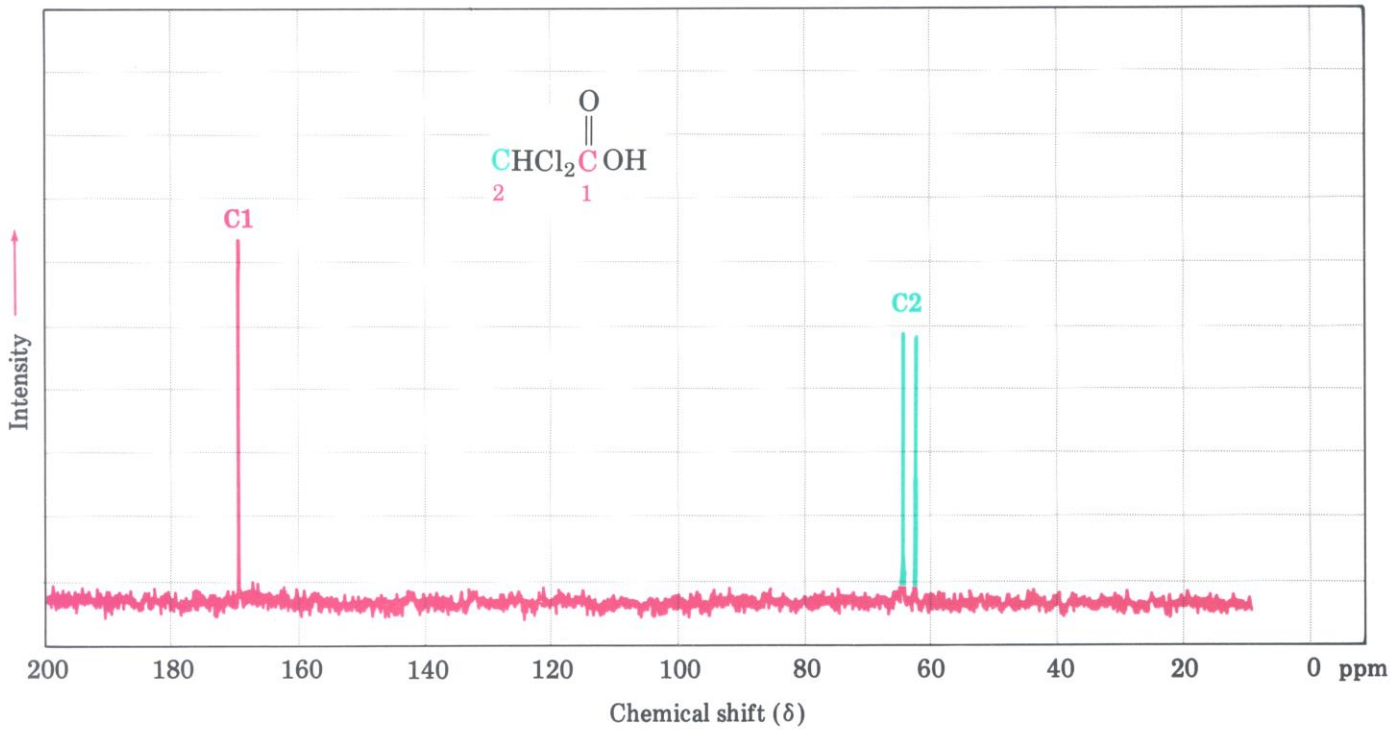
^{13}C NMR - integrált



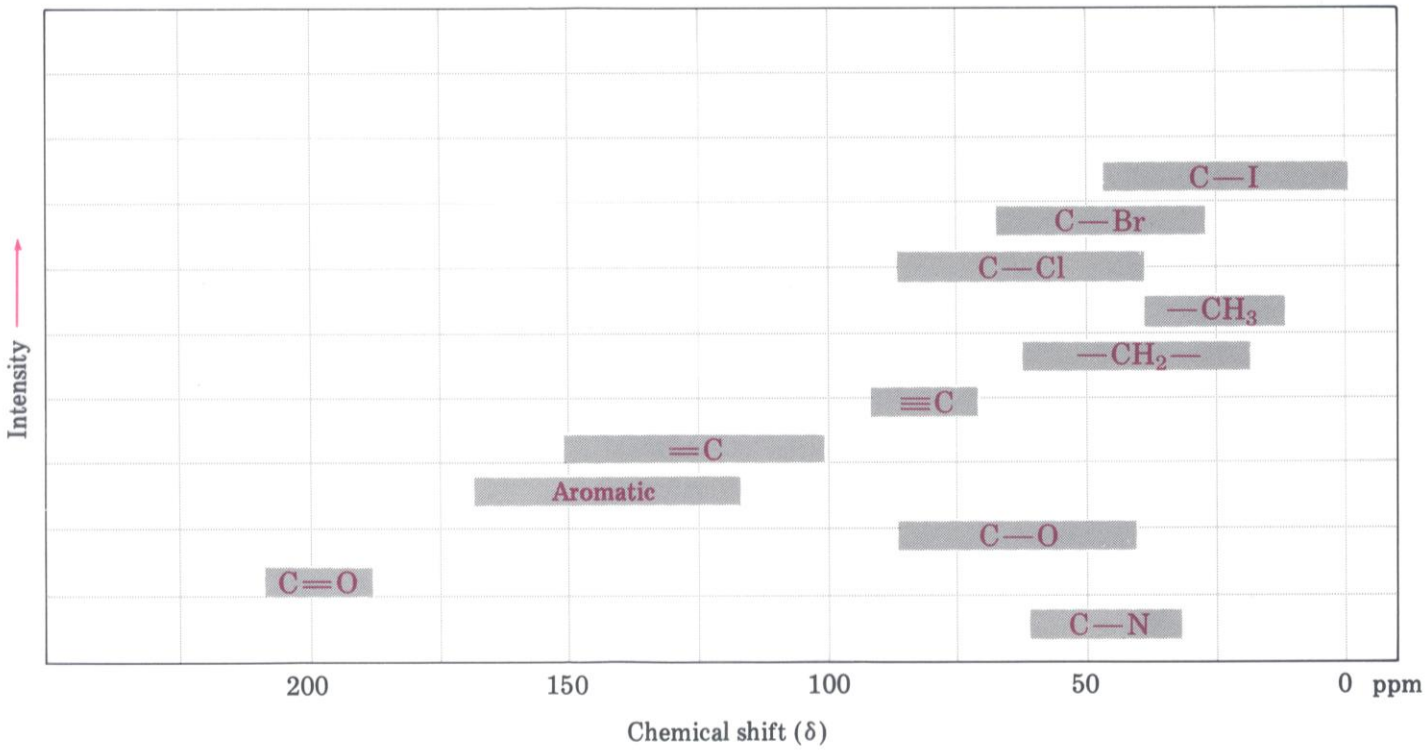
(a)



^{13}C NMR – spin csatolt



^{13}C NMR korrelációs diagram



^{13}C DEPT-NMR spectra

DEPT – distortionless enhancement by polarisation transfer

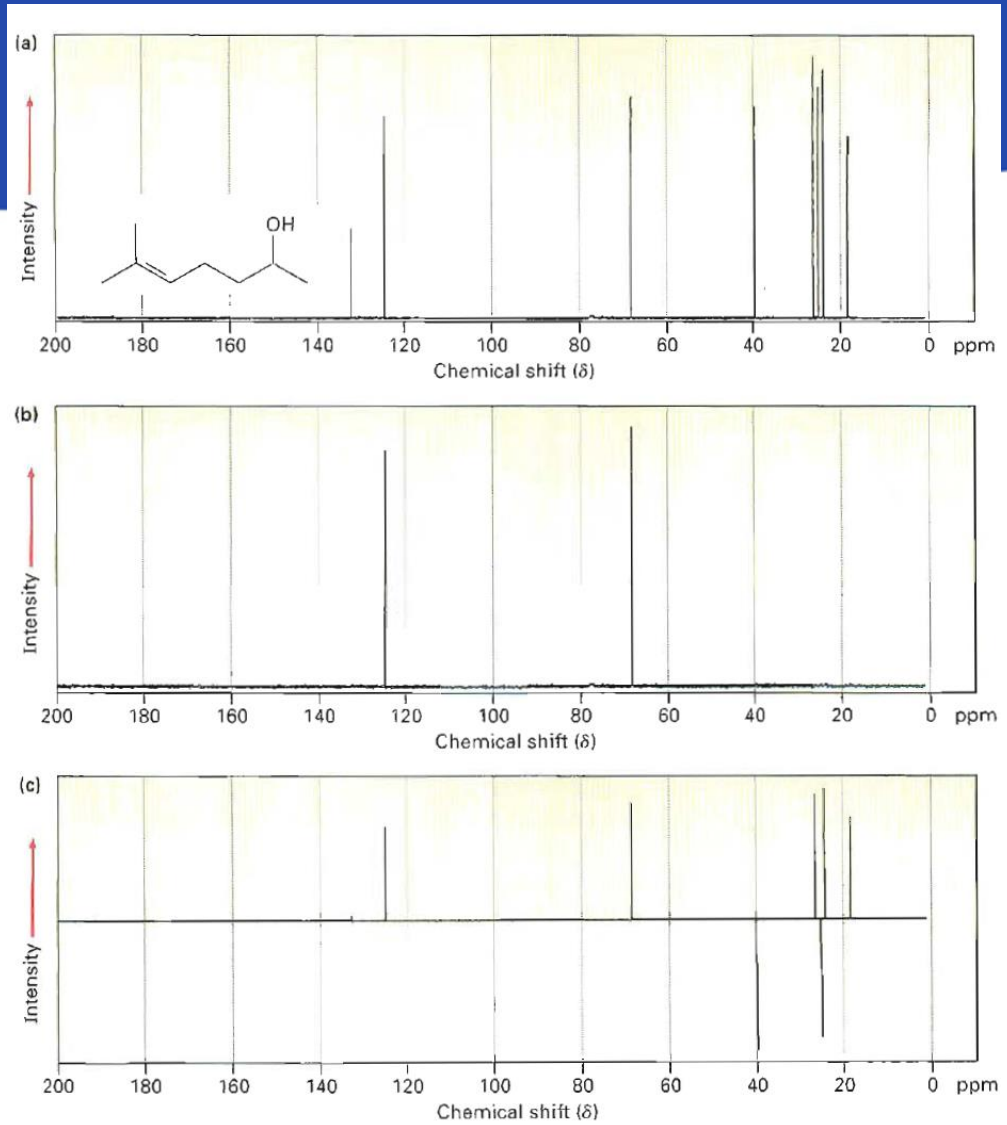


Figure 13.10 DEPT–NMR spectra for 6-methyl-5-hepten-2-ol. Part (a) is an ordinary broadband-decoupled spectrum, which shows signals for all eight carbons. Part (b) is a DEPT-90 spectrum, which shows only signals for the two CH carbons. Part (c) is a DEPT-135 spectrum, which shows positive signals for the two CH and three CH_3 carbons and negative signals for the two CH_2 carbons.

A ^{13}C NMR spektrumokból nyerhető információ:

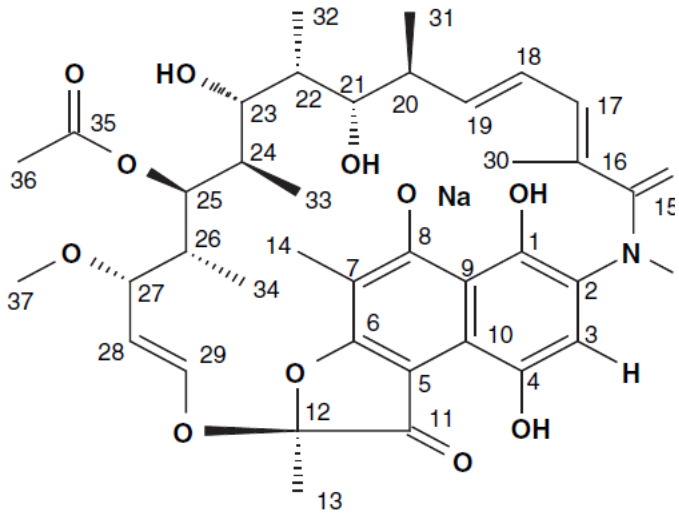
- a szénváz felépítése

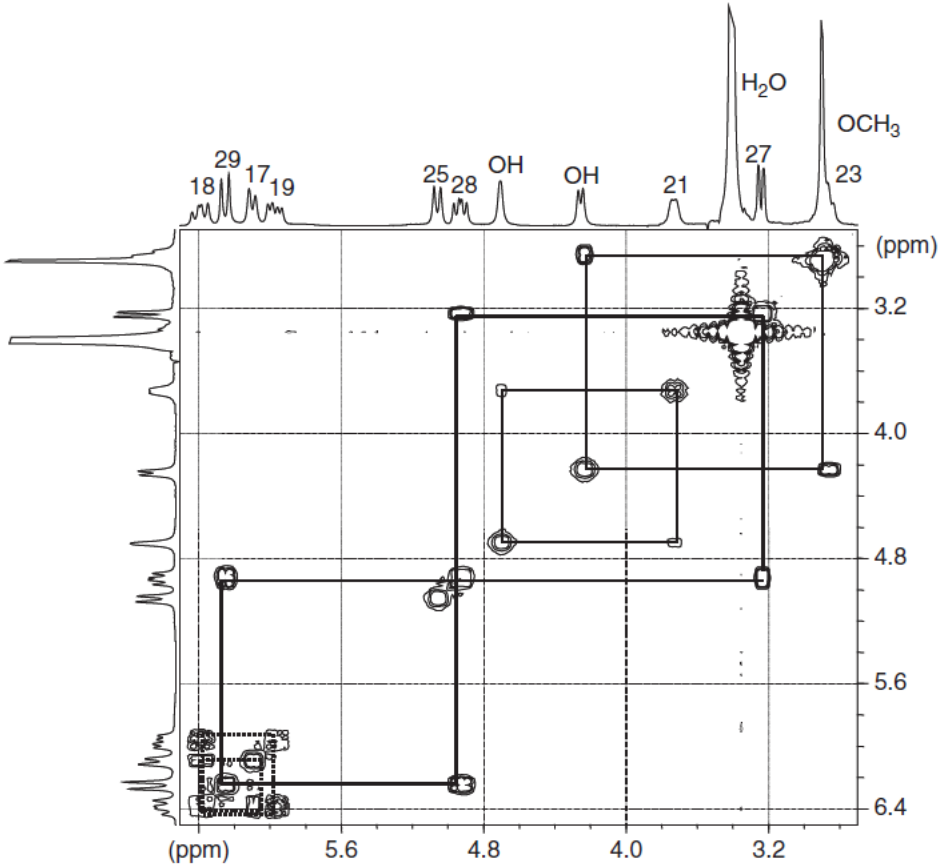
A legkönnyebben és legpontosabban akkor tudjuk egy molekula szerkezetét meghatározni, ha rendelkezésünkre állnak a tömeg-, az UV-VIS,az FT-IR, az ^{1}H NMR, a ^{13}C NMR spektrumok mindegyike.

fontos NMR-aktív magok és néhány tulajdonságuk

Isotope	Spin quantum no. I	Natural abundance (%)	NMR frequency (MHz) at 7.05 T
^{1}H	1/2	99.98	300
^{11}B	3 × 1/2	80.42	96.25
^{13}C	1/2	1.11	75.43
^{14}N	1	99.63	21.67
^{15}N	1/2	0.37	30.40
^{17}O	5 × 1/2	0.037	40.67
^{19}F	1/2	100	282.23
^{29}Si	1/2	4.7	59.6
^{31}P	1/2	100	121.44

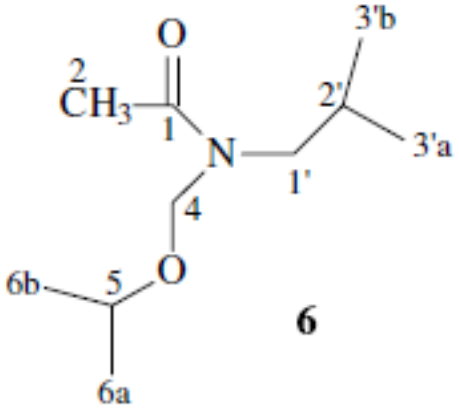
rimfamicin



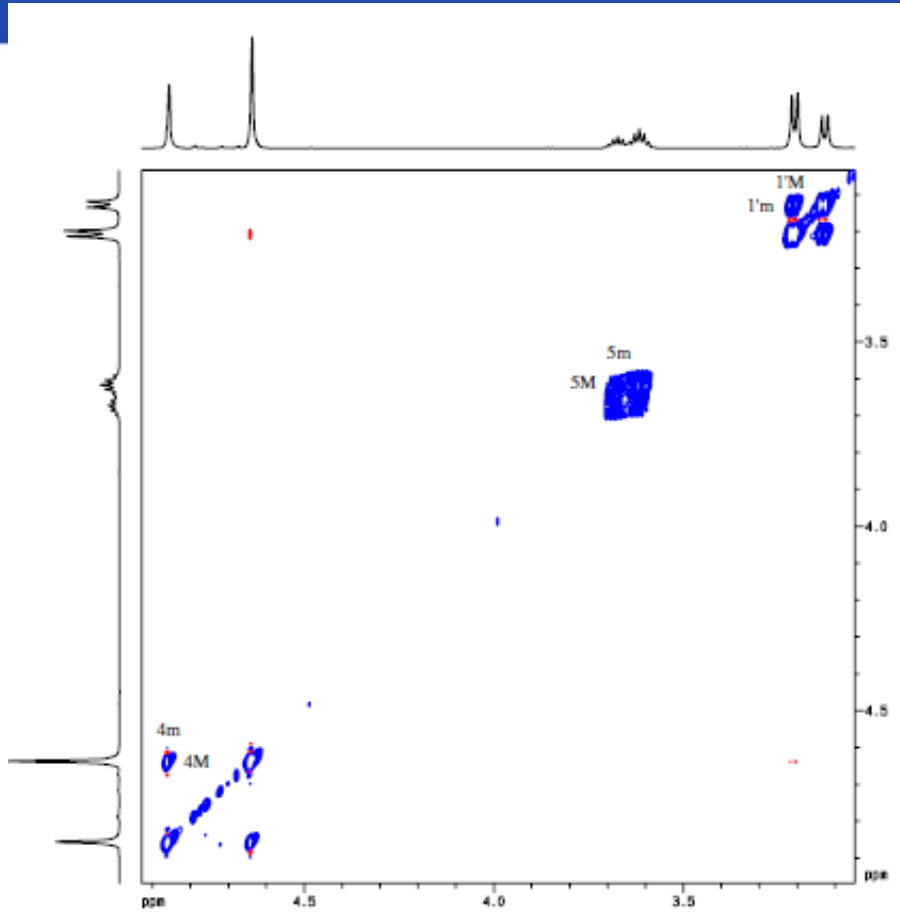


a rimfamicin COSY spektruma

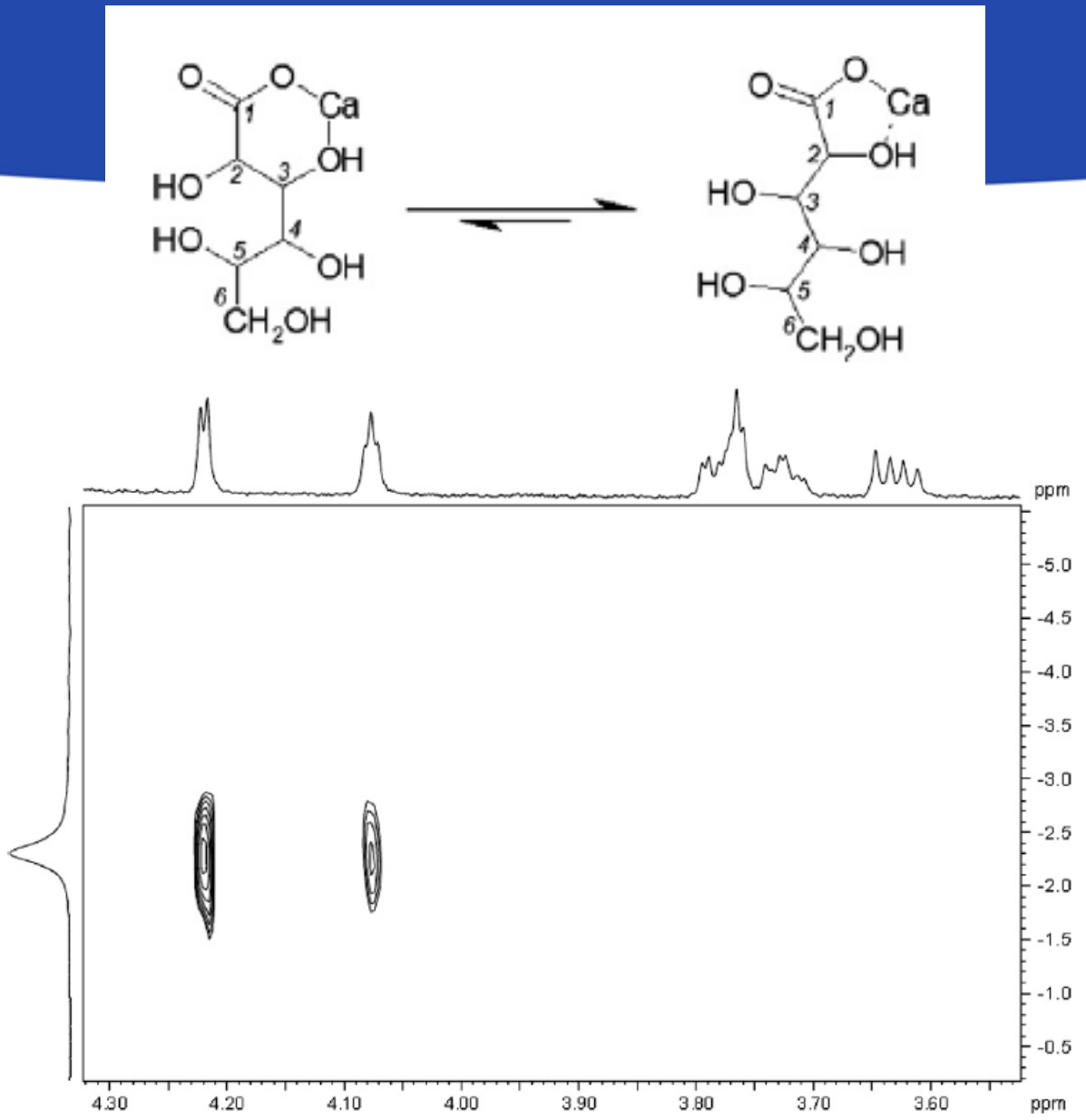
a vegyület



6



a vegyület ROESY spektruma



Ca-glükonát oldat $^{43}Ca–^{1}H$ 2D NMR spektruma

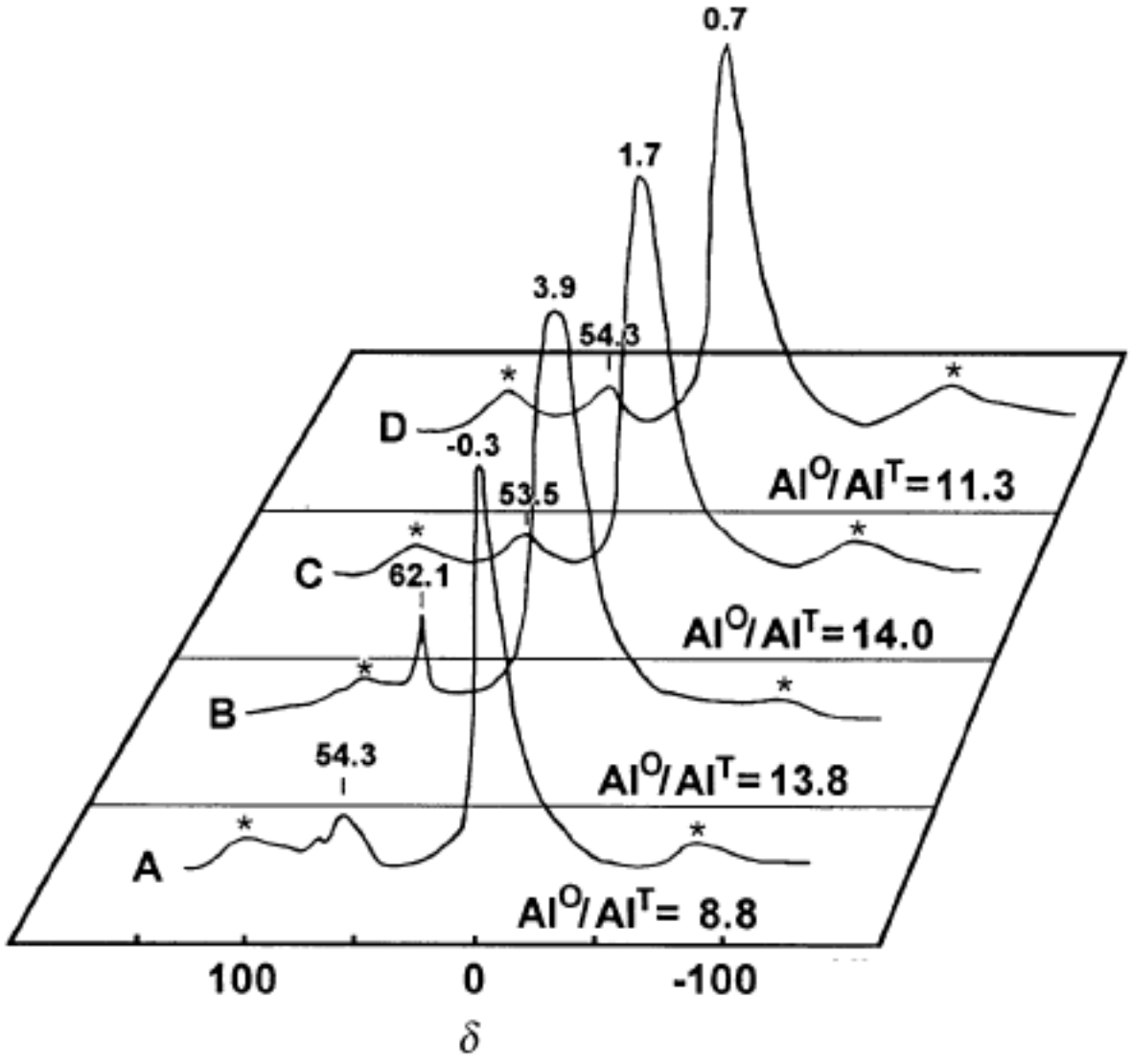


Fig. 4 ^{27}Al MAS NMR spectra of A, Na-montmorillonite and the pillared layer clay samples with synthetic metal/Al ratios; B, Fe(or Cr) : Al = 0 : 13; C, Fe : Al = 1 : 12 and D, Cr : Al = 1 : 12

Kvantitatív NMR spektroszkópia (qNMR)

alapösszefüggés: $I_x = K_S N_x$

I_x – integrált jelterület
N_x – a magok száma
K_s – a spektrométetrre jellemző állandó

Mérési módszerek:

relatív (aránymeghatározás) – $I_1/I_2=N_1/N_2$
abszolút – belső standard alkalmazása

gyakran használt belső standardok

^{1}H	^{19}F	^{31}P
1,3,5-benzenetricarboxylic acid	*Para*-fluorobenzoic acid sodium salt (FBEN)	Dimethyl-methylphosphonate
1,3,5-trimethoxybenzene	Sodium fluoroacetate	Methylphosphonic acid (MPA)
1,3,5-trioxane	Trifluoroacetic acid	Phenylphosphinic acid (PPA)
1,4-bis(TMS)-benzene	*Para*-fluoro-D-phenylalanine	Triphenylmethylphosphonium bromide
1,4-dinitrobenzene		glyphosate
1,4-dioxane		3-Aminopropylphosphonic acid
Anthracene		
Benzyl benzoate		
Biphenyl		
Dimethyl isophthalate		
Dimethylformamide		
Dimethylsulfone		
Formic acid		
Hexamethylcyclotrisiloxane		
Maleic acid		
Methenamine		
Phloroglucinol		
Sodium acetate		
Tert-butanol		
Tetramethylpyrazine		
TSP-d_4		
Etacrynic acid		
2,5-dimethylfuran		

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