ANALITIČKA KEMIJA II

- uvodno predavanje
- općenito – uzorkovanje; norme i standardi; intelektualno vlasništvo
- STATISTIKA – osnove
- EKSTRAKCIJA, KROMATOGRAFIJA - osnove
- ELEKTROANALITIČKE METODE
- BOLTZMANNOVA RAZDIOBA
- SPEKTROSKOPIJA – osnove; zadaci
- INSTRUMENTACIJA – osnove; zadaci
- ATOMSKA SPEKTROSKOPIJA; zadaci
- MOLEKULSKA SPEKTROSKOPIJA – UV/VIS, fluorescencija
- IR i Ramanova spektroskopija
- **NMR - uvod**

nositelj: prof.dr.sc. P. Novak; šk.g. 2012/13.

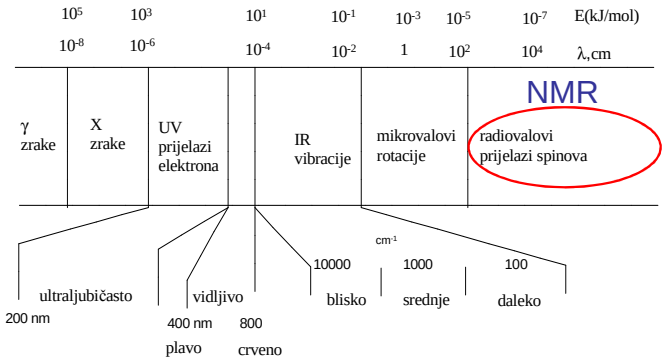
Nuklearna Magnetna Rezonancija
NMR

POVIJESNI RAZVOJ NMR-a

- 1924. W. Pauli - teorijski temelji NMR
- 1939. Rabi i sur. - dokaz o postojanju nuklearnog spina (molekulski snop LiCl)
- 1944. Nobelova nagrada iz fizike Rabiju
- 1946. Bloch (Stanford) i Purcell (Harvard)- prvi uspješni eksperimenti efekta NMR
- 1952. Nobelova nagrada iz fizike za NMR Blochu i Purccelu
- 1953. Prvi komercijalni NMR spektrometar (Varian 30 MHz)
- 1960. Spektrometri od 100 MHz
- 1970. Pulsni spektrometri s Fourierovom transformacijom
- 1980. Spektrometri od 400 MHz
- 1970.-1980. Dvodimenzijske metode i tehnike (2D NMR)

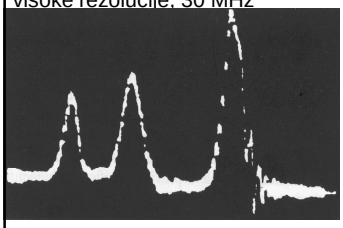
- 1970. Oslikavanje magnetnom rezonancijom (magnetic resonance imaging, MRI)
- 1991. Nobelova nagrada iz kemije za NMR, R. R. Ernst
- 1992. Magnet od 17.61 T (750) MHz
- 1995. Magnet od 21.14 T (900 MHz)
- 1999. Prvi komercijalni 900 MHz spektrometar
- 2002. Nobelova nagrada iz kemije za NMR, K. Wütrich
- 2003. Nobelova nagrada iz medicine za MRI, P. Lauterbur i P. Mansfield (fizičari)
- 2005. Magnet od 22.31 T (950 MHz)
- 2009. Magnet od 1000 MHz (1GHz)

Spektar elektromagnetnoga zračenja

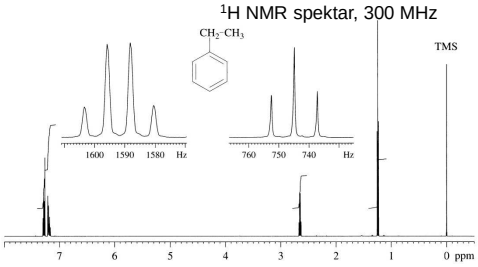


NMR visoke rezolucije

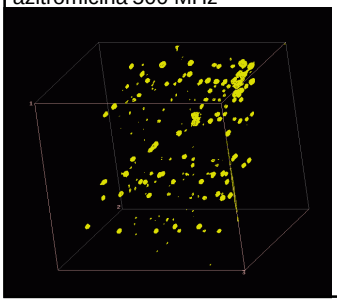
Prvi publicirani NMR spektar visoke rezolucije, 30 MHz



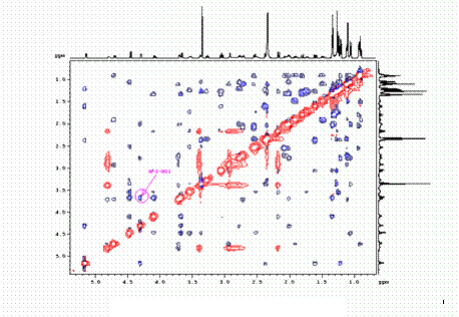
^{1}H NMR spektar, 300 MHz



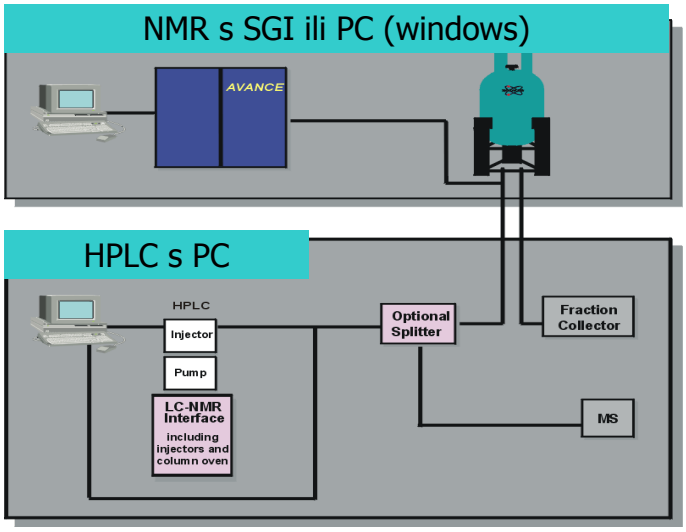
3D HMQC-TOCSY NMR spektar azitromicina 500 MHz



2D TPPI-NOESY spektar azitromicina, 500 MHz

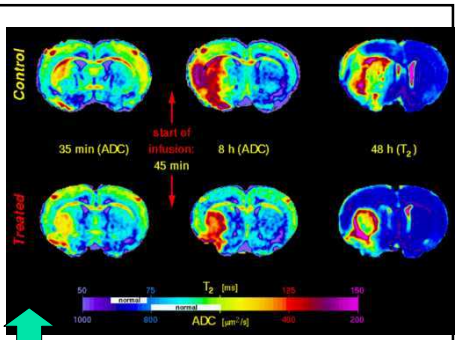


Sprega tekućinske kromatografije i NMR-a

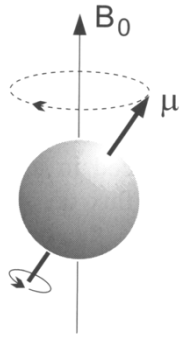


LC-SPE-NMR-MS sustav

MRI/MRS sustav



Spin jezgre i rezonancija

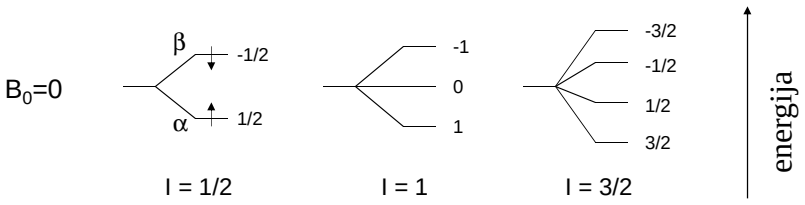


$\mu = \gamma P$

$P = I\, h/2\pi$

$I = (0, 1/2, 1, 3/2, ...7)$

Jezgra s kvantnim brojem I može imati $2I_n$ + 1orijentaciju

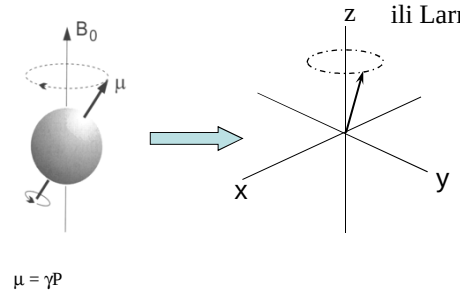


Svojstva nekih jezgri sa spinom ½

izotop	Prorodna zastupljenost (%)	NMR frekvencija (MHz) B_0=11.7 T	Relativna osjetljivost
^{1}H	99.98	400.0	1.0
^{3}H	0	426.7	1.2[a]
^{13}C	1.11	100.6	1.76×10^{-4}
^{15}N	0.37	40.5	3.85×10^{-6}
^{19}F	100	376.3	0.83
^{29}Si	4.7	79.5	3.69×10^{-4}
^{31}P	100	161.9	6.63×10^{-2}

[a]ako ima 100% ^{3}H

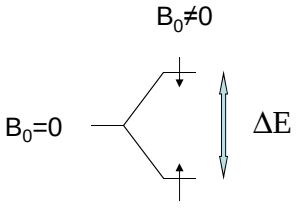
Dogovorom je prihvaćeno da je smjer primjenjenog magnetnog polja smjer osi z u Cartesijevom koordinatnom sustavu



Frekvencija precesije
ili Larmorova frekvencija

$\mu = \gamma P$

Rezonancija



$\mu = \gamma P$

$P = Ih/2\ \pi$

$E = -\mu_0 B_0 = -\gamma h I B_0/2\pi$

$\Delta E = \gamma h B_0/2\pi \qquad \Delta E = h\nu$

$\nu = \gamma B_0/2\pi$

Osnovni uvjet rezonancije

$\nu_1 = \nu_0$

Boltzmanova raspodijela

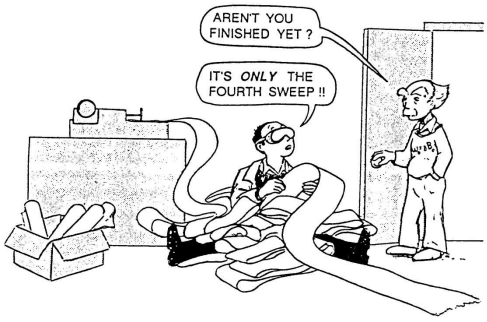
$N_\alpha / N_\beta = e^{\Delta E/kT}$

N- broj jezgri

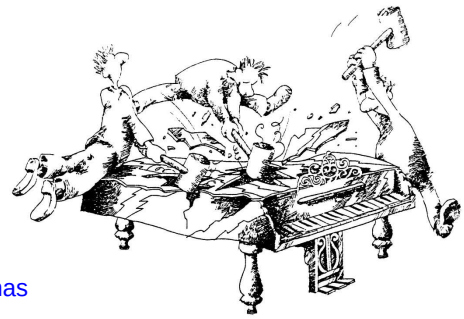
k- Boltzmanova konstanta ($1.38066 \times 10\text{-}23\ JK^{-1}$)

T- temperatura

Samo 1 jezgra na milijun više u
osnovnom energijskom stanju !!

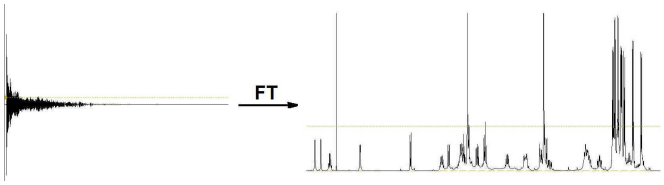


nekad



danas

vremenska domena frekvencijska domena



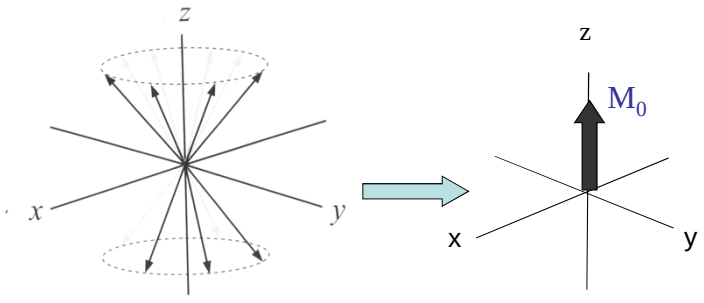
$$F(\omega) = \int_{-\infty}^{+\infty} f(t)\, e^{i\omega t}\, dt$$

$e^{i\omega t} = \cos \omega t + i \sin \omega t$

realno — imaginarno

Apsorpcijski sigal — Disperzijski sigal

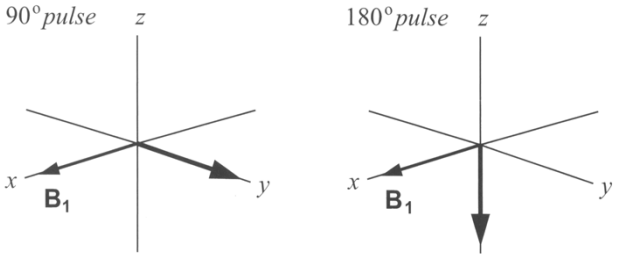
Vektorski model

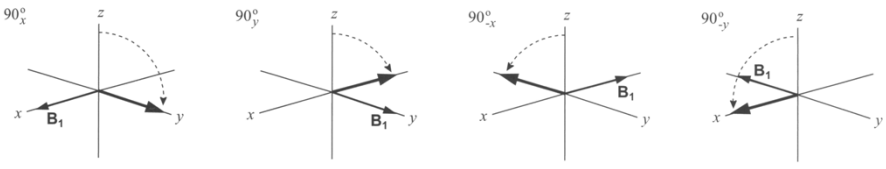


S obzirom da ima više istovrsnih spinova u stanju α vektor ukupne magnetizacije ima smjer + z

Radiofrekventni puls

Pulsni kut $\Phi = 360\gamma B_1 t_p / 2\pi$





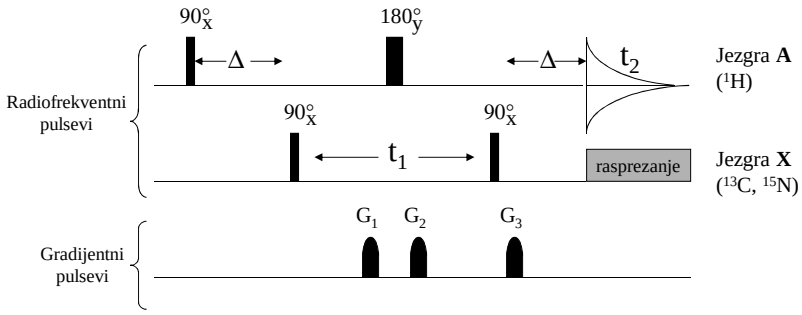
Pozitivna apsorpcija

Pozitivna disperzija

negativna apsorpcija

Negativna disperzija

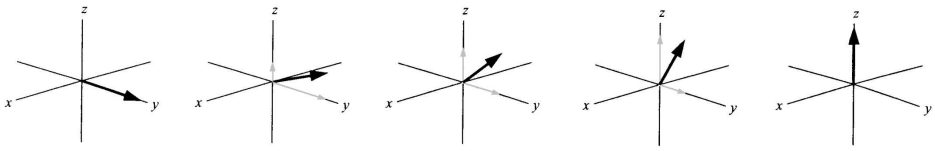
Pulsni slijed



NMR parametri

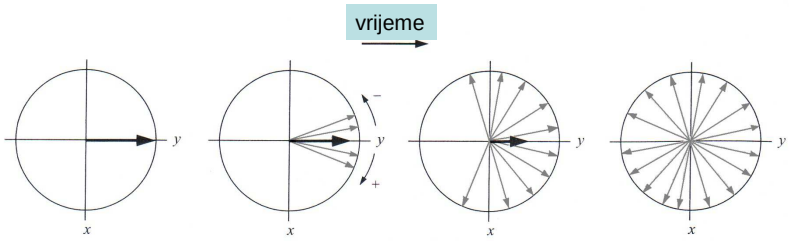
a) Vremena opuštanja ili relaksacije

- ➢) vrijeme opuštanja spin-rešetka (longitudinalno), T_1
  - ➢ $dM_z/dt = (M_0-M_z)/T_1$ Blochova jednadžba
  - ➢ Intenzitet NMR signala



➢) vrijeme opuštanja spin-spin (transverzalno), T_2

- ➢ $dM_x/dt = (M_x)/T_2$
- ➢ $dM_y/dt = (M_y)/T_2$
- ➢ Širina NMR linija $\Delta\nu_{1/2} = 1/T_2$



Mehanizmi opuštanja spin-rešetka

➢ $1/T_1^{uk} = 1/T_1^{DD} + 1/T_1^{CSA} + 1/T_1^{SR} + 1/T_1^{SC}$

DD- dipol-dipol (najučinkovitiji)

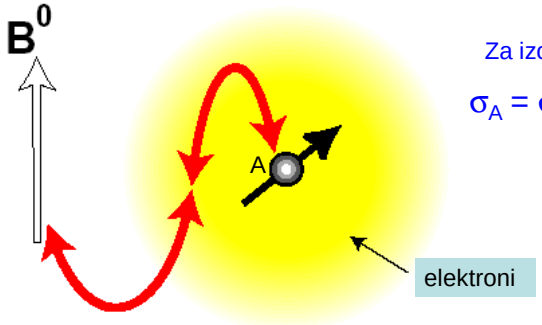
CSA- anizotropija kemijskog pomaka

SR- spinska rotacija (rotori npr. CH_3)

SC- skalarna sprega (bliska Larmorova frekvencija ^{13}C-^{37}Br)

b) Kemijski pomak, nuklearno zasjenjenje

Levitt



Za izotropni medij

$\sigma_A = \sigma^{dia} + \sigma^{para} + \sum_{A \neq x} \sigma_x$

Elektroni koji okružuju jezgru A stvaraju magnetno polje (zasjenjenje) koje utječe na ukupno magnetno polje koje osjećaju jezgre

- $B_{ef} = B_0 - B_{ind}$

  $B_{ind} = \sigma_{ef} B_0$
- $B_{ef} = B_0 - (1 - \sigma_{ef})$

$\nu = \gamma B_0 / 2\pi$

Uvjet rezonancije

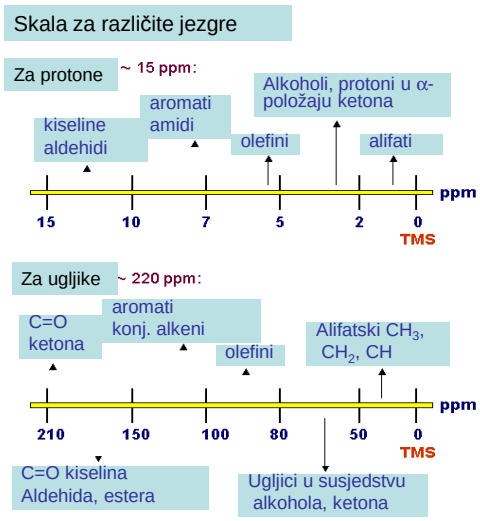
$\nu = \gamma (1 - \sigma_{ef}) B_0 / 2\pi$

Referentna δ Skala

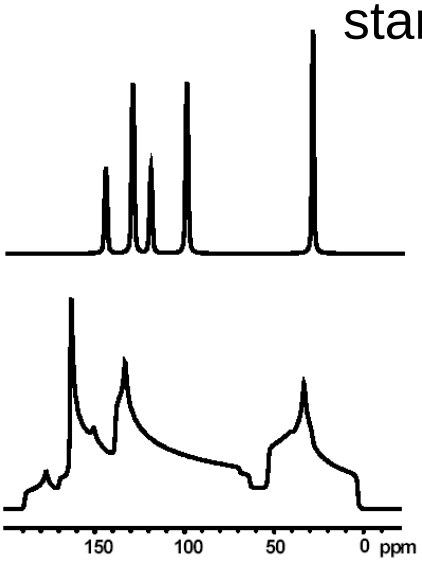
$\delta_{uzorak} = \nu_{uzorak} - \nu_{referentno} / \nu_{referentno}$

$= \Delta\nu$ (Hz) / $\nu_{referentno}$ (MHz)

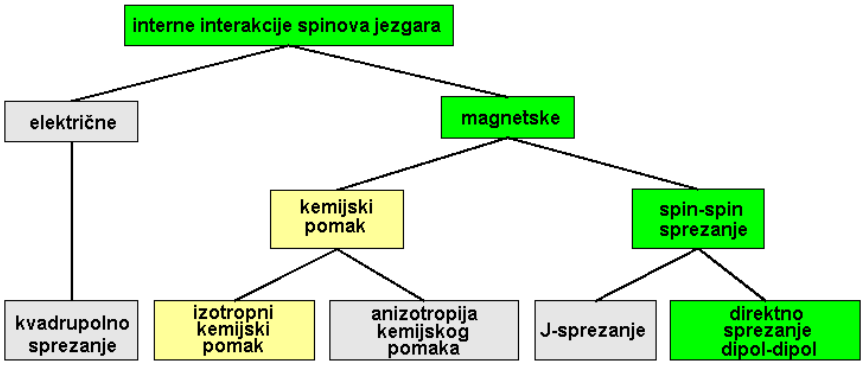
Skala u ppm!



NMR spektroskopija u čvrstom stanju

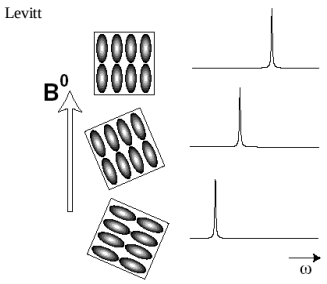


- ^{13}C NMR spektar u otopini
- ^{13}C NMR spektar u čvrstom stanju



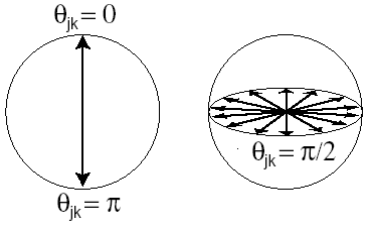
- Interakcije ovisne o položaju u prostoru

Anizotropija kemijskog pomaka (CSA)

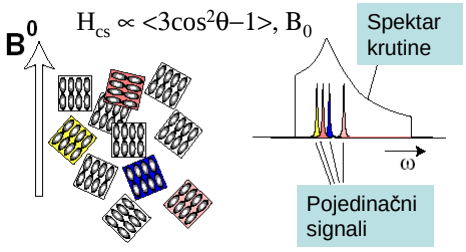


U NMR-u tekućina gibanje (tumbanje) molekula uzrok je simetričnosti vremenski uprosječenog elektronskog zasjenjenja. U NMR-u čvrstog stanja, molekule se ne gibaju izotropno pa kemijski pomak ne ovisi samo o kemijskom identitetu atoma nego i o prostornom odnosu između molekule i vanjskog magnetnog polja.

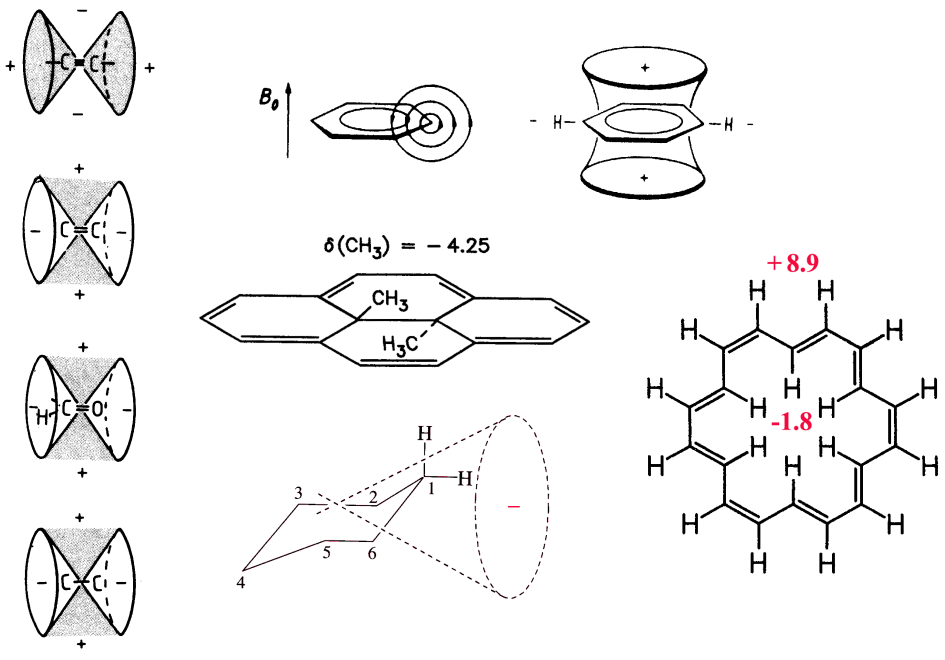
Vjerojatnost orijentacije



$H_{cs} \propto \langle 3\cos^2\theta - 1 \rangle, B_0$

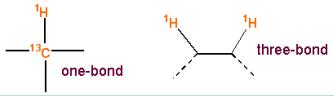


Anizotropija kemijskog pomaka i prstenaste struje

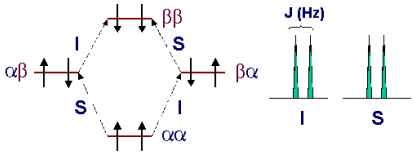


c) Konstanta sprege spin-spin

Spinsko stanje susjedne jezgre može utjecati na energetske razine promatrane jezgre. Za takve jezgre kažemo da su međusobno spregnute preko jedne ili više kemijskih veza



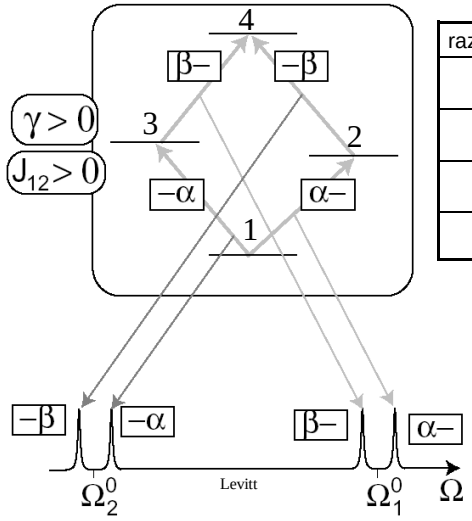
Energetski dijagram. Svaki spin sada ima dvije podrazine ovisno o stanju spina s kojim je u sprezi



Razlika između dvije linije dubleta se zove konstanta sprege J i ima jedinicu Hz

Način sprezanja bitan je za identifikaciju spinskog sustava u molekuli i za određivanje njene strukture

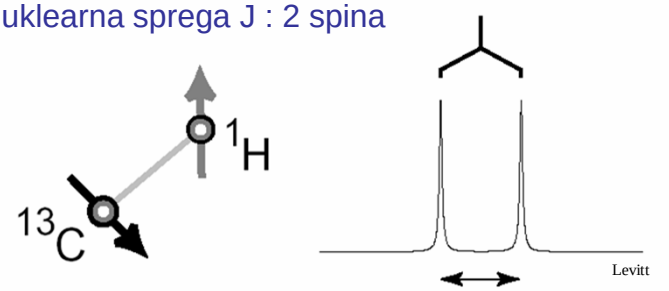
Homonuklearna sprega J : 2 spina



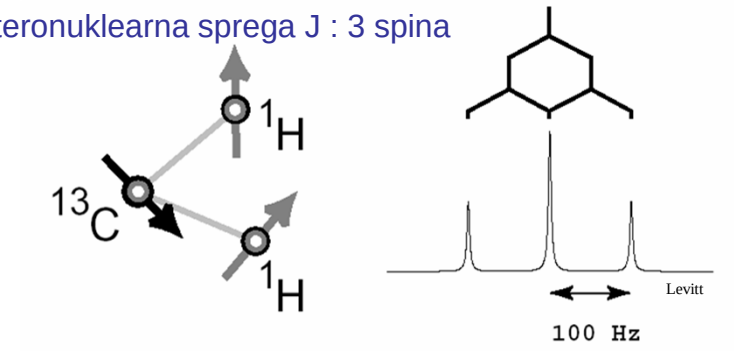
razina	Spinsko stanje	energija
1	αα	$-\frac{1}{2}\nu_0^1-\frac{1}{2}\nu_0^2+\frac{1}{4}J_{12}$
2	αβ	$+\frac{1}{2}\nu_0^1-\frac{1}{2}\nu_0^2-\frac{1}{4}J_{12}$
3	βα	$-\frac{1}{2}\nu_0^1+\frac{1}{2}\nu_0^2-\frac{1}{4}J_{12}$
4	ββ	$+\frac{1}{2}\nu_0^1+\frac{1}{2}\nu_0^2+\frac{1}{4}J_{12}$

prijelaz	energija
1→2	$\nu_0^1-\frac{1}{2}J_{12}$
3→4	$\nu_0^1+\frac{1}{2}J_{12}$
1→3	$\nu_0^2-\frac{1}{2}J_{12}$
2→4	$\nu_0^2+\frac{1}{2}J_{12}$

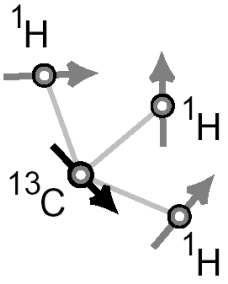
Heteronuklearna sprega J : 2 spina

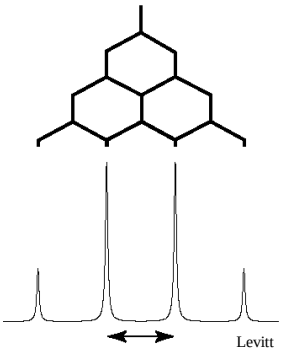


Heteronuklearna sprega J : 3 spina

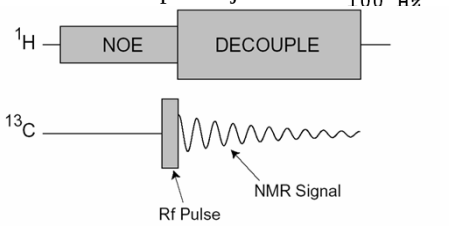


Heteronuklearna sprega J : 4 spina





Spektri se mogu pojednostavniti rasprezanjem

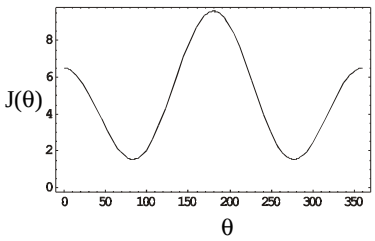


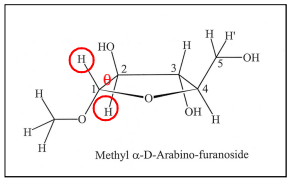
Spin-spin sprege kroz tri veze

Martin Karplus je pokazao da vicinalna sprega između ^1H atoma ovisi o diedarskom kutu između njih. Ova relacija se može iskazati pomoću **Karplusove jednadžbe**:

$$J(\theta) = A\cos^2(\theta) + B\cos(\theta) + C$$

A, *B*, i *C* su empirijski određeni parametri.





Sprega J omogućuje procjenu molekulske konformacije!

Spinski sustavi

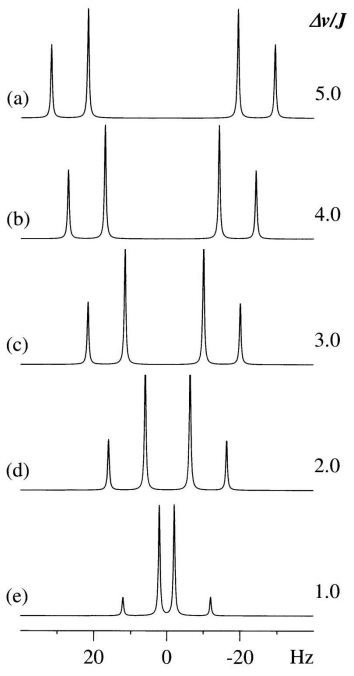
Pople-ova notacija: slova u abecedi označavaju kemijske pomake

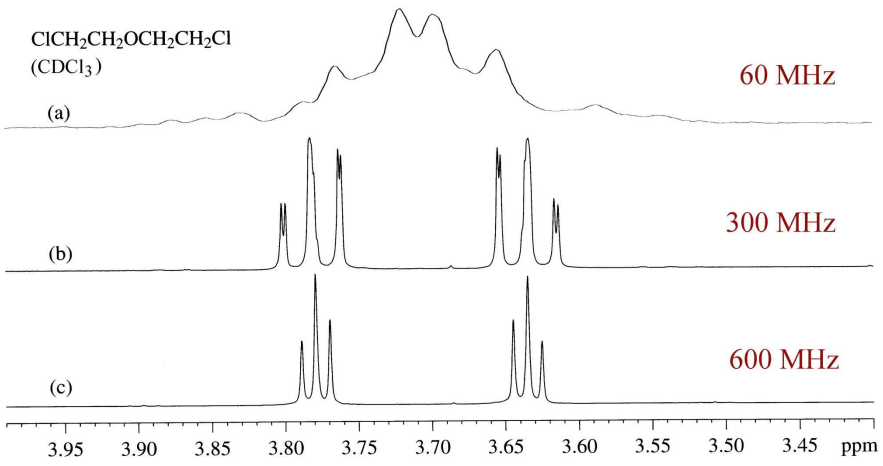
Prvi red: $\Delta\nu/J \geq 10$

oznake A i X

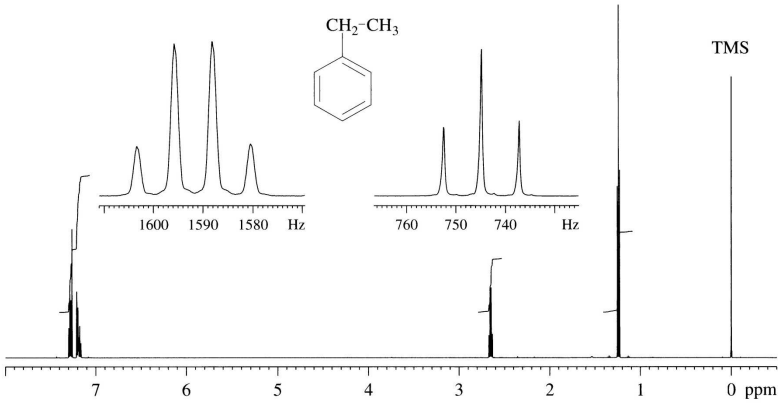
Viši red: $\Delta\nu/J \leq 10$

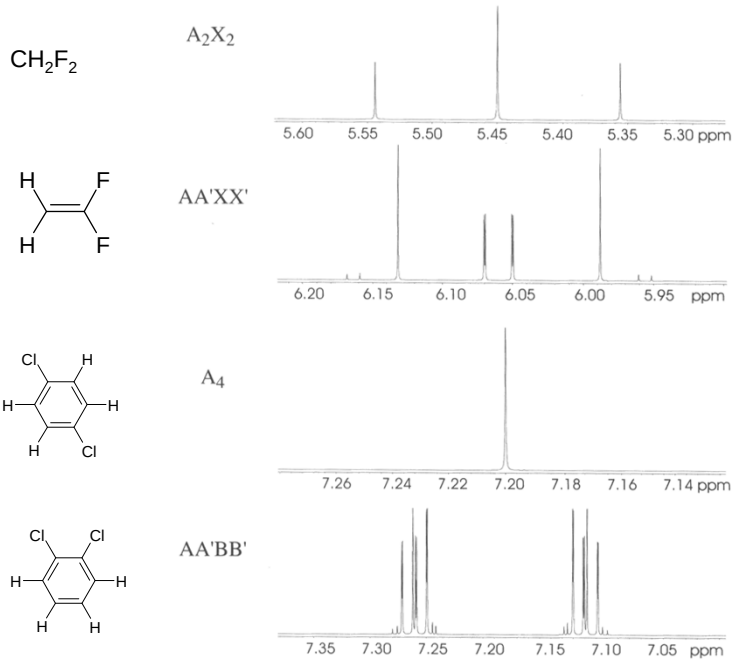
oznake A, B, C



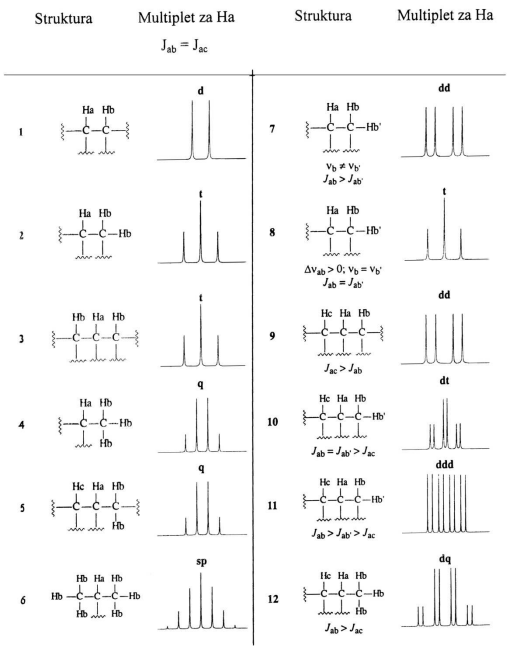


Više spinskih sustava unutar jedne molekule

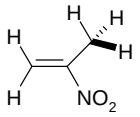




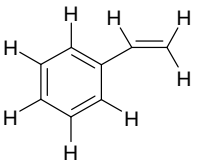
Cijepanja prvoga reda za neke spinske sustave



Odredite spinski sustav za slijedeće molekule



A_3MX



AMX

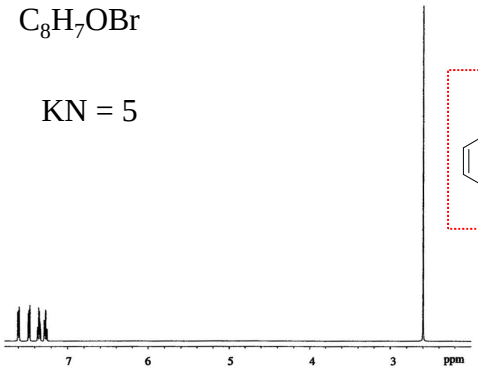
+

A_2B_2C

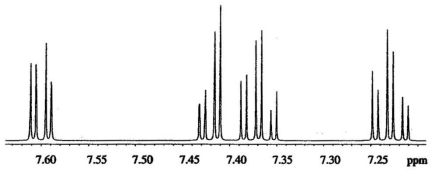
(AA'BB'C)

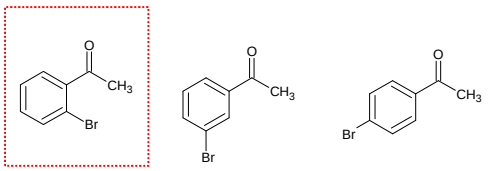
C_8H_7OBr

KN = 5



Expansion
2.1 Hz/mm





Odredite položaj supstitucije metilnih skupina u dimetilpiridinu