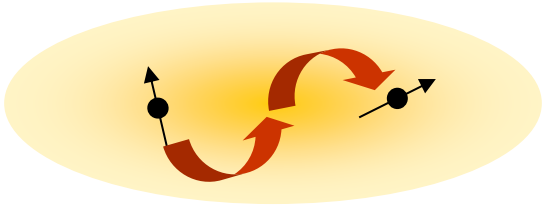
NMR spectroscopy

- J – interaction / J – coupling
- Splitting patterns
- Homonuclear and heteronuclear couplings
- Typical values, Karplus equation

J interaction

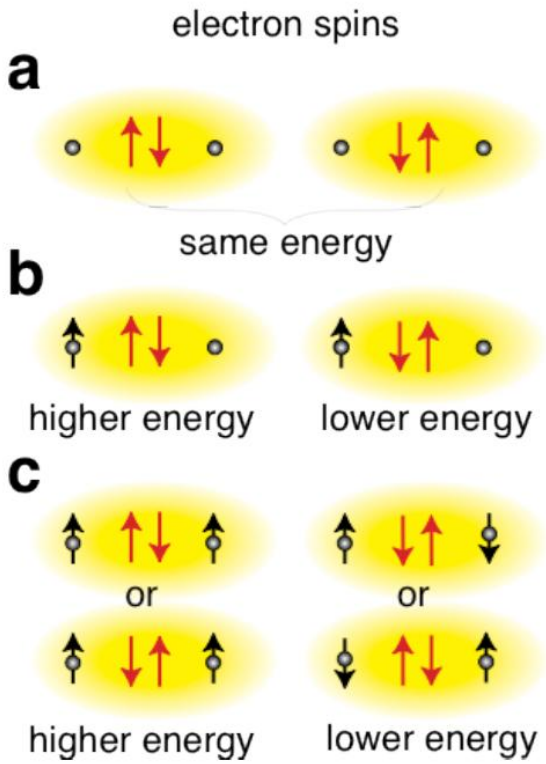
Indirect spin-spin interaction

scalar coupling

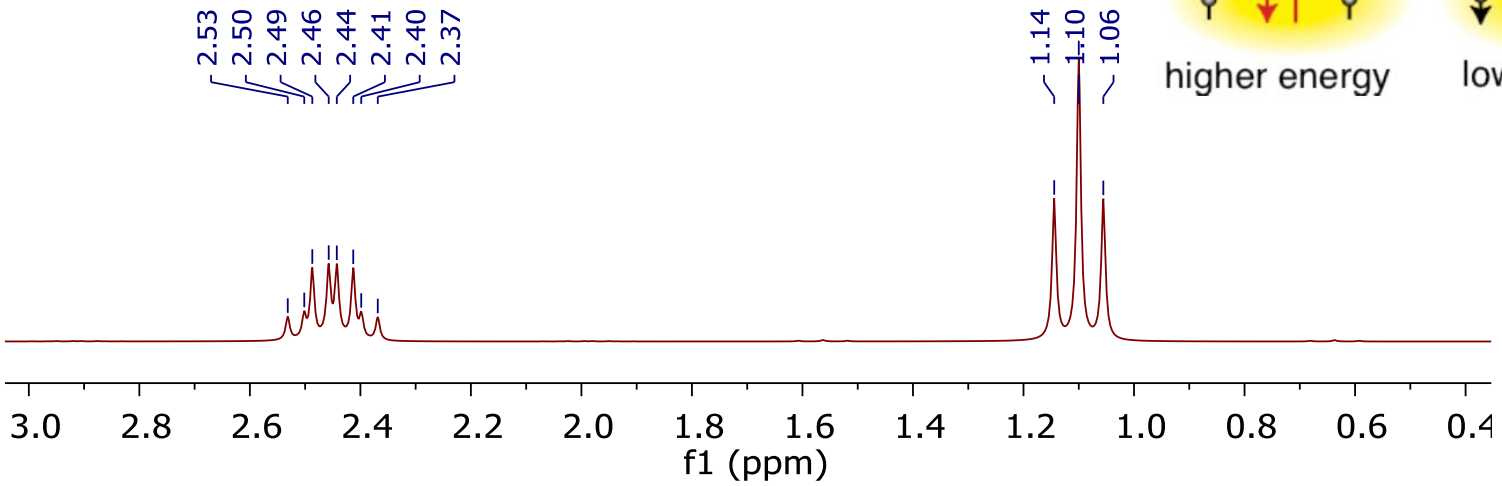


interaction mediated by common Electrons

nucleus „feels “ spin state of nearby nuclei



- Causes fine splitting of signals
- Carries information about nearby NMR-active nuclei
- Magnitude ***DOES NOT DEPEND*** on magnetic field



Quantum view

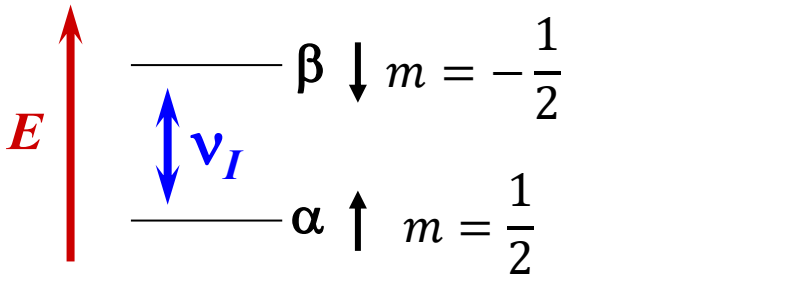
Energy of magnetic moment in magnetic field

$$E = -\vec{\mu}\cdot\vec{B} = -\mu_z B_0 = -\gamma I_z B_0 = -m\gamma\hbar B_0$$

Projection of nuclear angular momentum I_z is quantized: $2I + 1$ values

$$m = (-I), (-I+1), \ldots (I+1), I$$

Spin $I = 1/2$

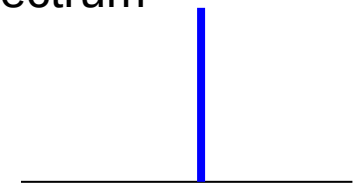


(various labels of energy levels)

$$\Delta E = \hbar\gamma B_0$$

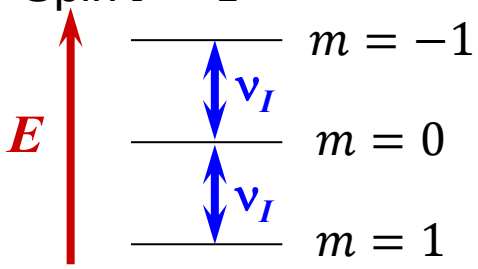
frequency ν_I

spectrum

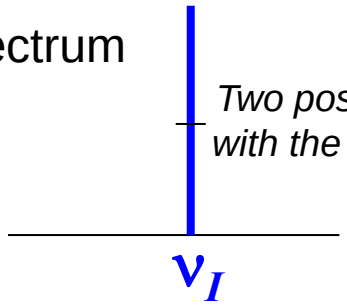


Position of the signal in the spectrum

Spin $I = 1$



spectrum



Two possible transitions with the same frequency

Spin $I = 3/2$ has levels

-3/2, -1/2, +1/2, +3/2

J interaction

Two nuclei with spin1/2

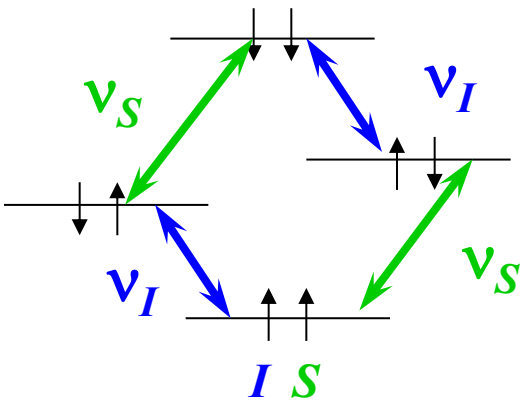
Magnitude of interaction: J [Hz]

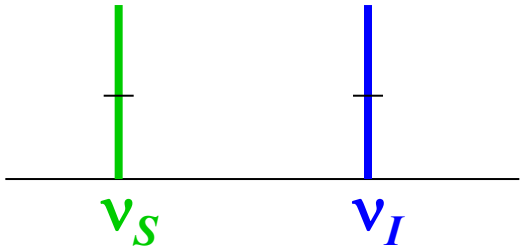
$$H = 2\pi J\, \vec{I} \cdot \vec{S}$$

Energy contribution

$$E_J = h\, J\, m_I\, m_S \qquad m_I, m_S = \pm\frac{1}{2}$$

No interaction

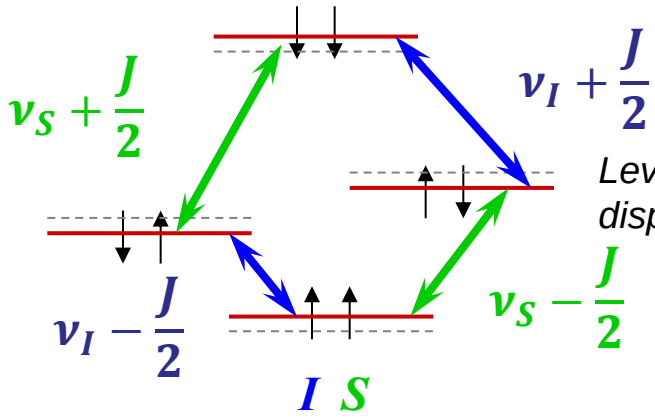




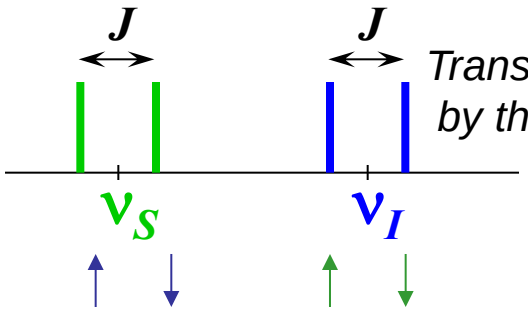
both transitions are equal

No matter of the spin state of the second nucleus

With J-couplings



Levels are displaced



Transitions differ by the value of J

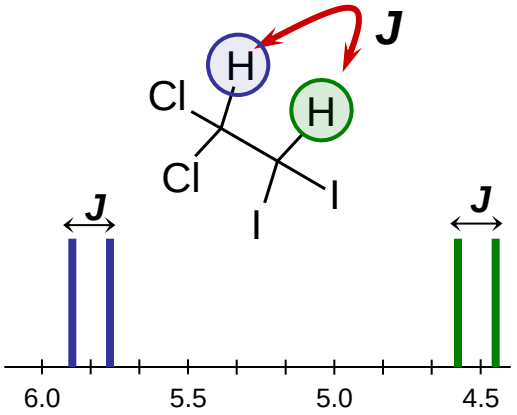
Possible states of nucleus I

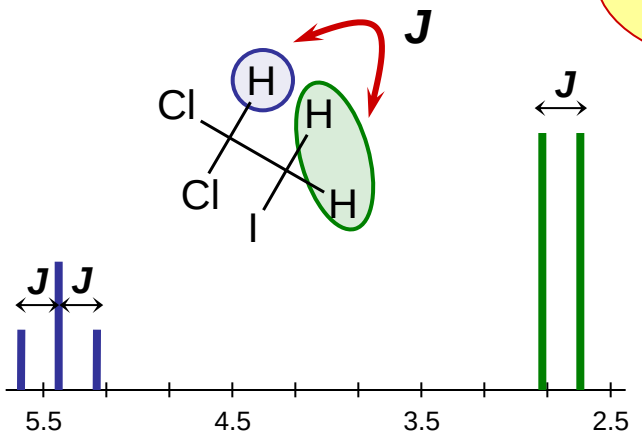
Possible states of nucleus S

J-coupling in ^{1}H spectra

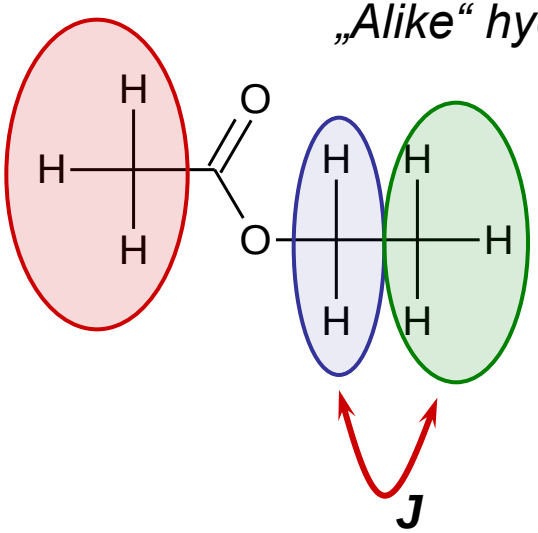
Signals are split by hydrogens that are „different“

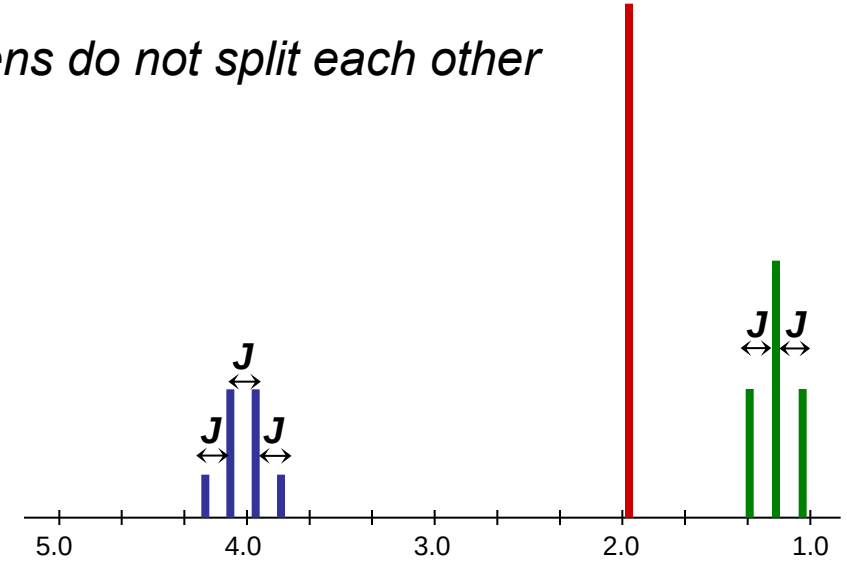
Restricting to $^{3}J_{HH}$



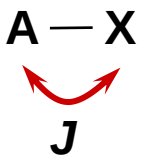


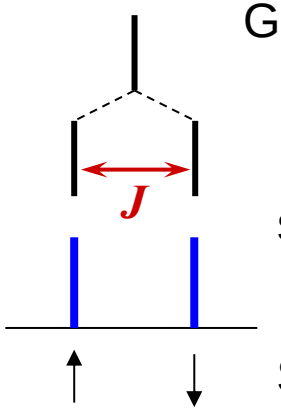
„Alike“ hydrogens do not split each other





J-coupling and system of splitting



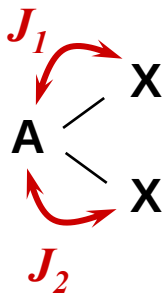


Graphical representation of splitting

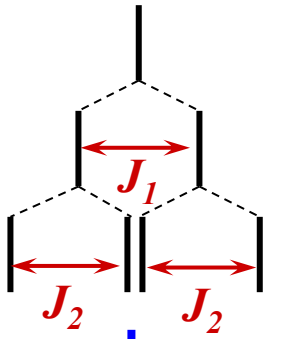
Assuming all nuclei have I=1/2

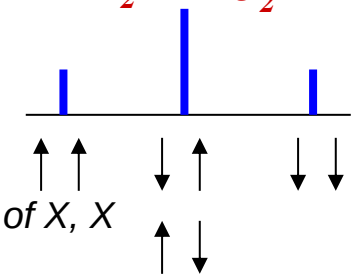
spectrum of nucleus A is a **doublet** d

Spin-states of X



$J_1 = J_2$

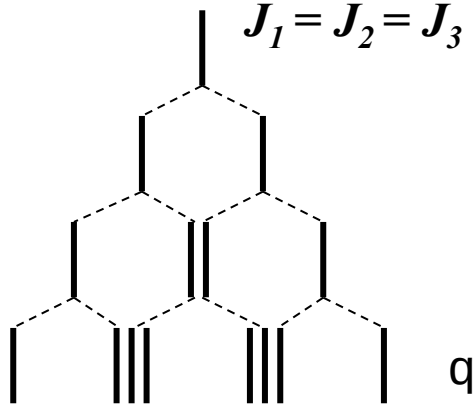




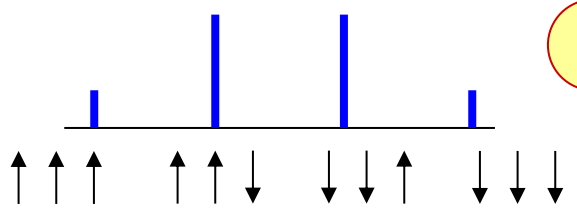
t triplet

Spin-states of X, X

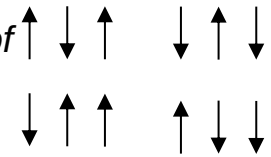
AX_3 $J_1 = J_2 = J_3$



quartet q



Spin-states of X, X, X

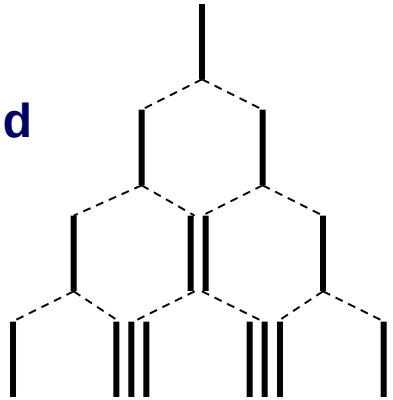


J-coupling and system of splitting

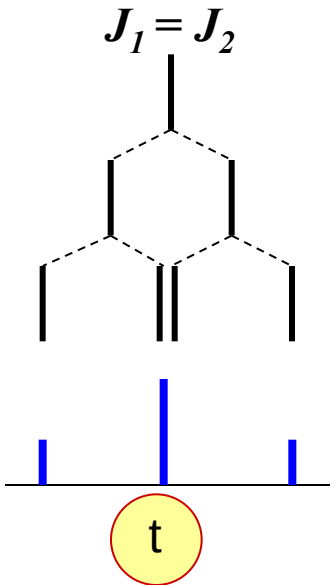
Splitting by ***n*** equivalent Hydrogens

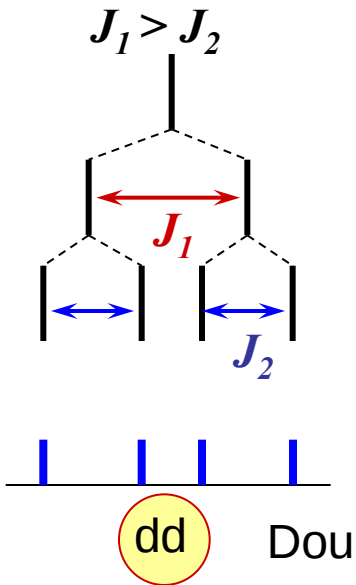
n		
	1	singlet s
1	1 1	Doublet d
2	1 2 1	triplet t
3	1 3 3 1	quartet q
4	1 4 6 4 1	pentet p

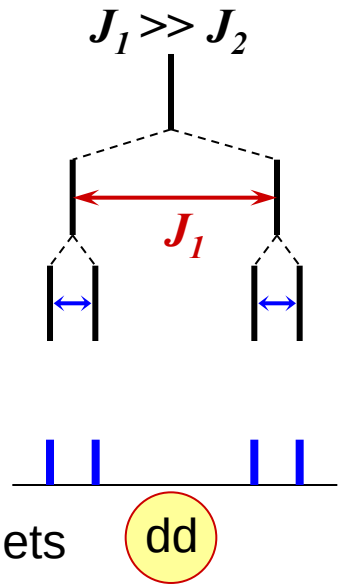
Pascal's triangle



Rule of n+1 lines



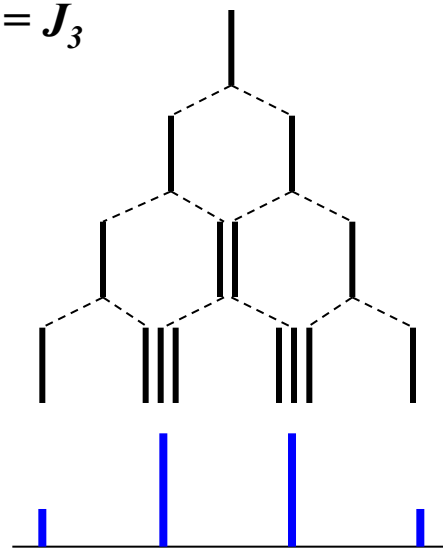




Doublet of doublets

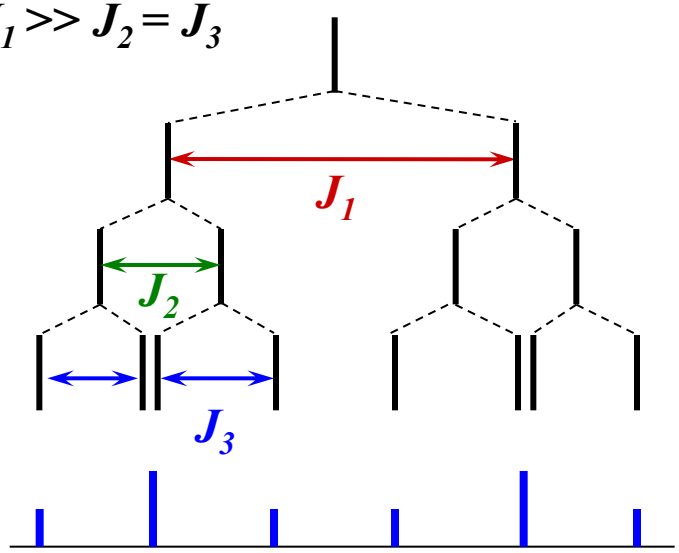
J-couplings – structure of multiplets

$J_1 = J_2 = J_3$



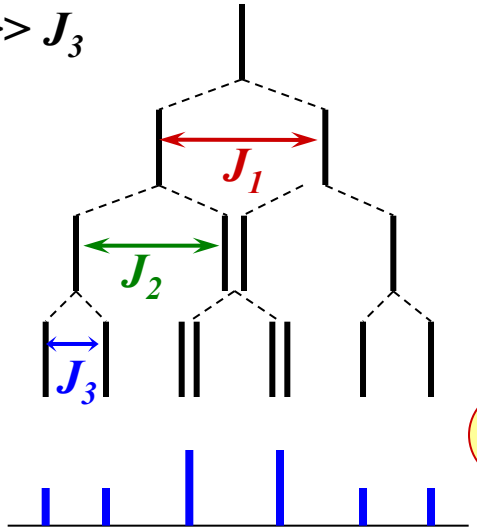
q

$J_1 >> J_2 = J_3$



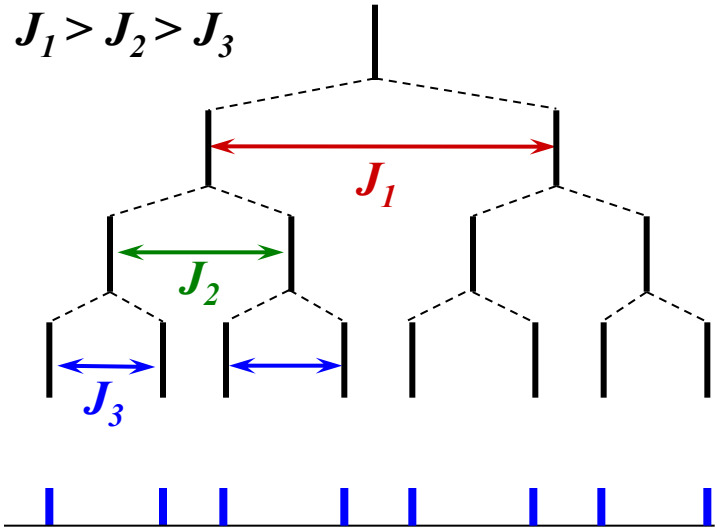
dt

$J_1 = J_2 >> J_3$



td

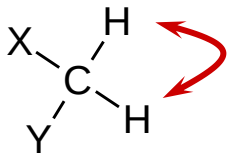
$J_1 > J_2 > J_3$



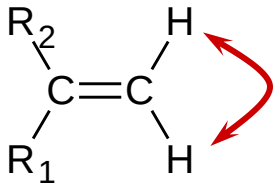
ddd

J-couplings in hydrogen spin systems

Geminal $^{2}J_{HH}$ *(Through two bonds)*

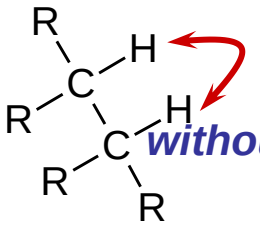


5 – 20 Hz



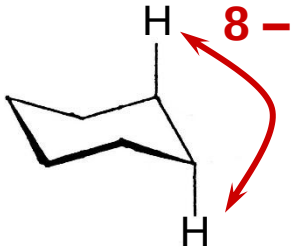
0 – 2 Hz

Vicinal $^{3}J_{HH}$ *(Through three bonds)*

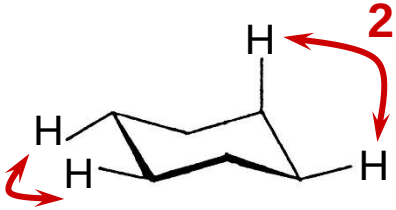


6 – 8 Hz

without conformational preference



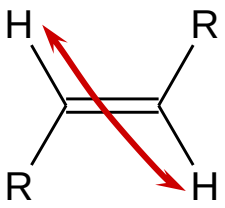
8 – 10 Hz



2 – 3 Hz

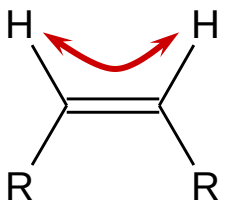
2 – 3 Hz

trans

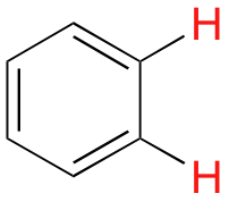


14 – 18 Hz

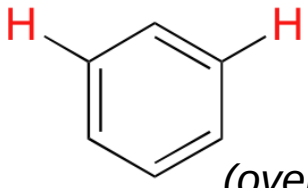
cis



7 – 12 Hz



ortho-benzylic:
^{3}J = 6-10 Hz

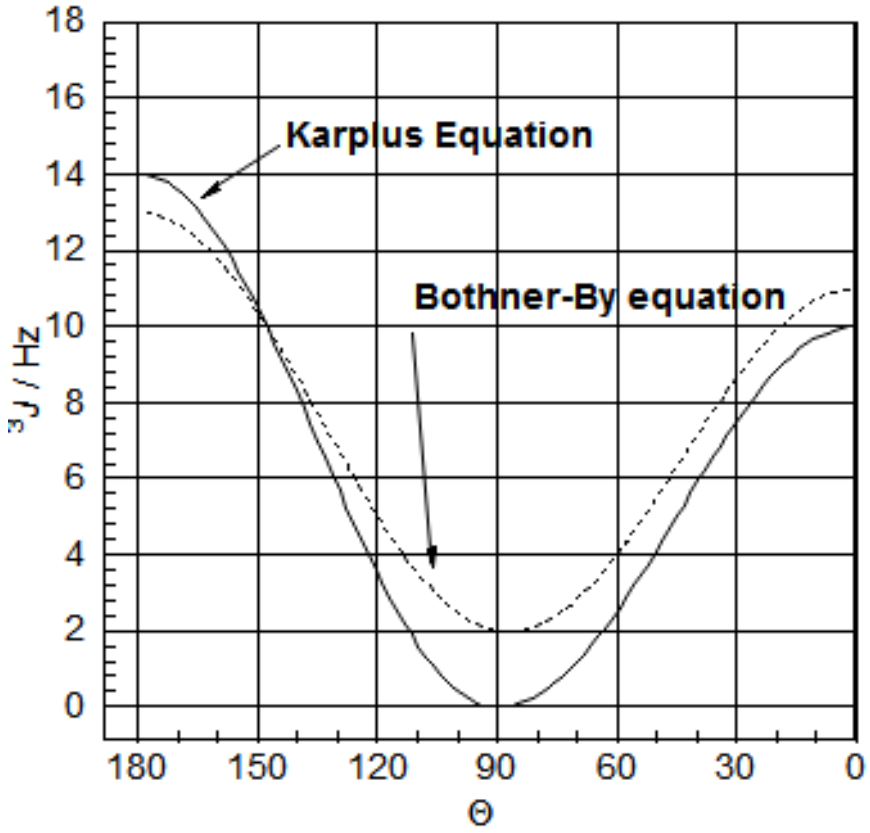


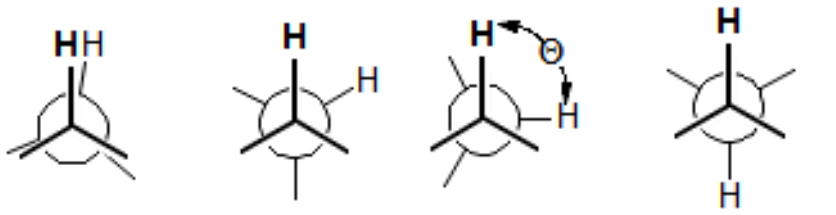
(over 4 bonds)

meta-benzylic:
^{4}J = 0-4 Hz

Karplus equation

Dependency of $^3J_{HH}$ on the dihedral angle





Θ = 0° ^3J = 7-11 Hz

Θ = 60° ^3J = 2-5 Hz

Θ = 90° ^3J = 0-2 Hz

Θ = 180° ^3J = 8-15 Hz

Karplus Equation

$^3J_{HH} = J_o \cdot \cos^2\Theta - K$

J_o = 14 (90-180°), J_o = 10 (0-90°), K = 0

Bothner-By equation

$^3J_{HH} = 7 - \cos\Theta + 5 \cdot \cos 2\Theta$

This empirical dependence of the size of the J-coupling can be used to determine the conformation of the molecule

Heteronuclear J-interaction

$^{13}C-H$

Spin-satets of H

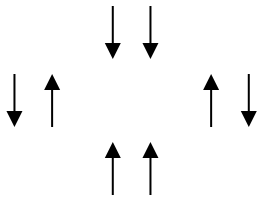
m = -1/2 ↓

m = +1/2 ↑

Doublet

1 : 1

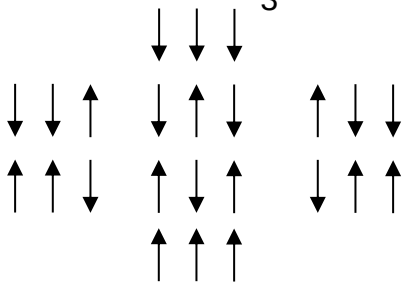
$^{13}C-H_2$



triplet

1 : 2 : 1

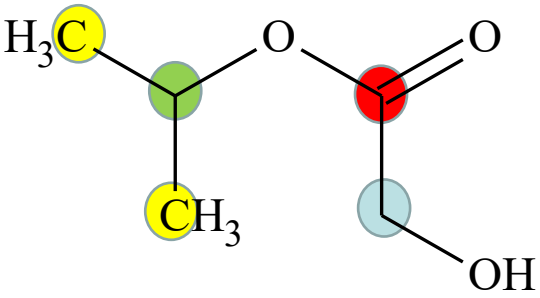
$^{13}C-H_3$



quartet

1 : 3 : 3 : 1

13C spectrum



No hydrogen

singlet

One hydrogen bound

Doublet

Two hydrogens bound

triplet

Three hydrogens bound

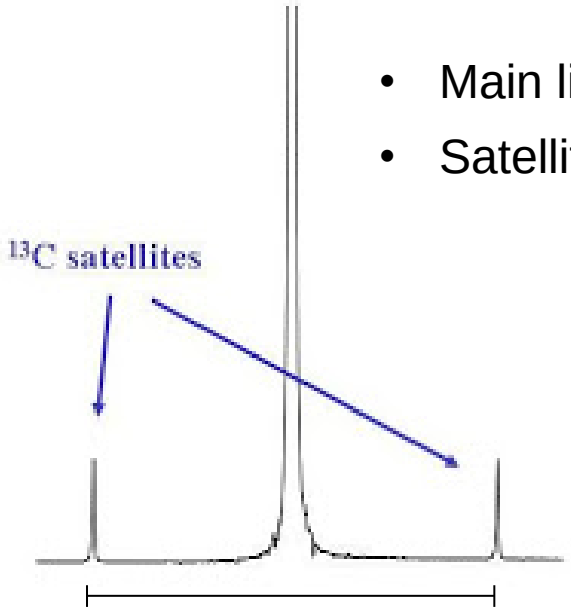
quartet

Heteronuclear J-interaction

	H_3C-CH_3	H_2C=CH_2	C_6H_6	HC≡CH
$^1J_{CH}$	124,9	156,4	158,4	249,0

$^2J_{CH}$ *and* $^3J_{CH}$ is about 8 Hz

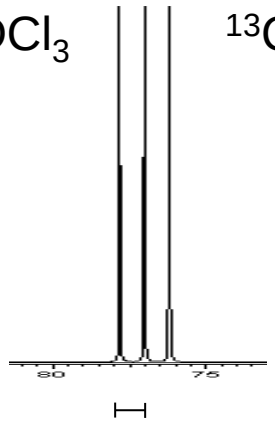
<u>^{1}H spectrum</u> $CHCl_3$



208 Hz

- Main line – 1H bound to 12C (99%)
- Satellites – 1H bound to 13C (1%)

$CDCl_3$ ^{13}C spectrum



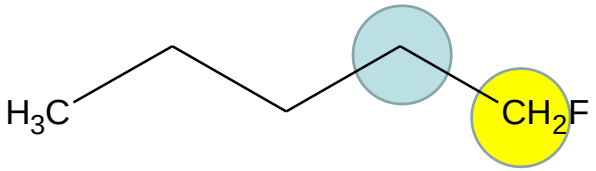
32 Hz

$$\frac{J_{CH}}{J_{CD}} = \frac{\gamma_H}{\gamma_D}$$

= 6.51

J interaction with other nuclei: -^{19}F

$I = 1/2$



$^{1}J_{CF}$ = 167 Hz $^{2}J_{CF}$ = 26 Hz $^{3}J_{CF}$ = 7 Hz

13C spectrum

1H spectrum

$^{2}J_{HF}$ = 47 Hz

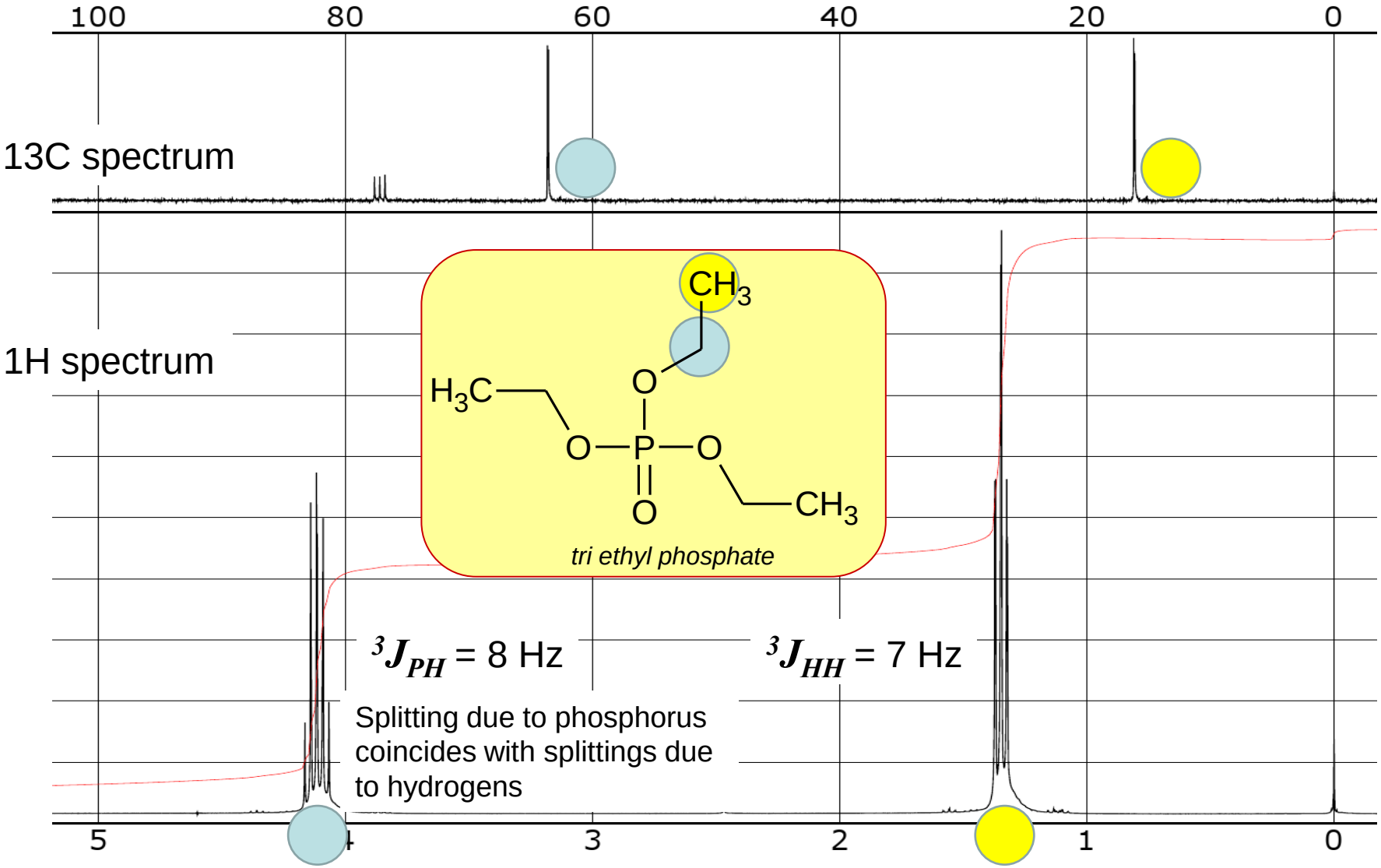
$^{3}J_{HF}$ = 24 Hz

$^{3}J_{HH}$ = 7 Hz

J-interaction with 19F is pronounced through many chemical bonds

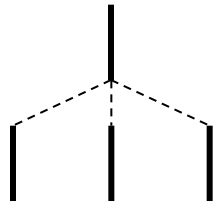
J interaction with other nuclei : ^{1}H-^{31}P

$I = 1/2$



J interaction with other spins

AX



1 : 1 : 1

$CDCl_3$

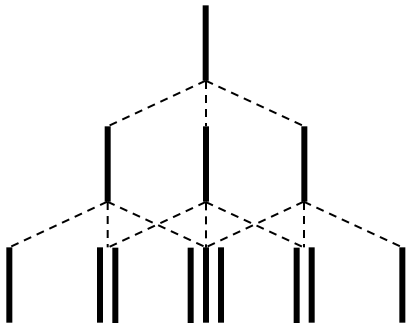
… applies to hydrogens in NH_4+ too

When X has spin $I = 1$

possible states

-1, 0, +1

AX_2



1 : 2 : 3 : 2 : 1

CD_2Cl_2

11B (80%) : spin-3/2

Possible states

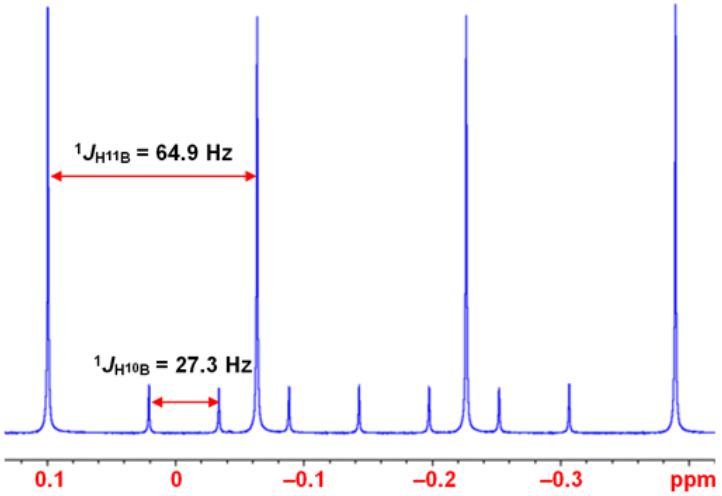
-3/2, -1/2, +1/2, +3/2

Boron has two naturally occurring NMR active isotopes

10B (20%) : spin-3

Possible states

Proton spectrum of $^{+}BH_4$



Magnetic equivalence

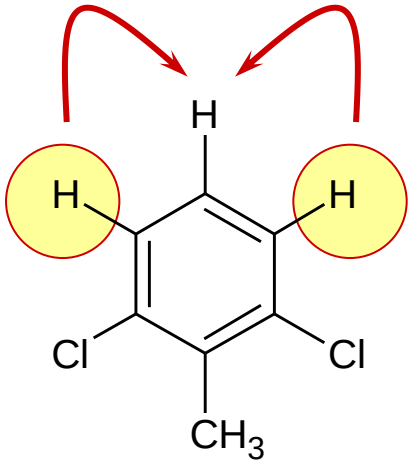
Nuclei are magnetically equivalent if:

- are chemically equivalent

and at the same time

- have the same geometric configuration in relation to all other NMR active nuclei in the molecule (that is, have the same J-interaction)

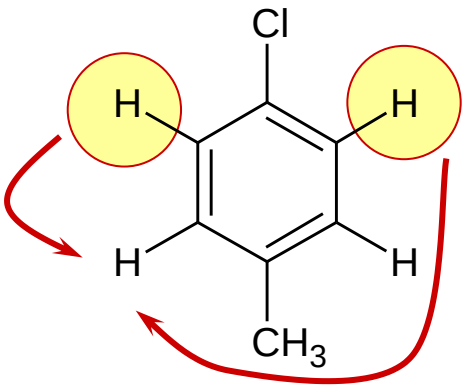
Equal configuration



Magnetically equivalent

J-interaction between these protons is not manifested in the spectrum

Different configurations

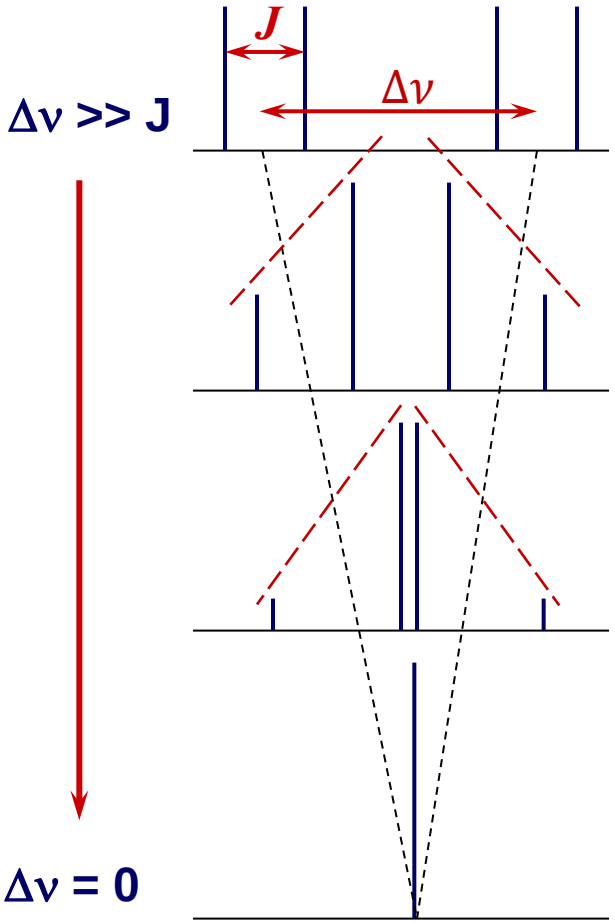


Chemically equivalent, but magnetically non-equivalent

Their J-interaction causes complicated splitting pattern

Order of the spectrum

Depends on magnitude of J-coupling and difference of chemical shifts $\Delta\nu$ (both in units of Hz)



AX

1st order spectrum

(1st order perturbation theory)

AB

"Pseudo-First Order"

AA'

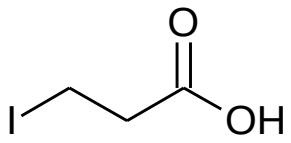
higher-order spectrum

Roof effect

A_2

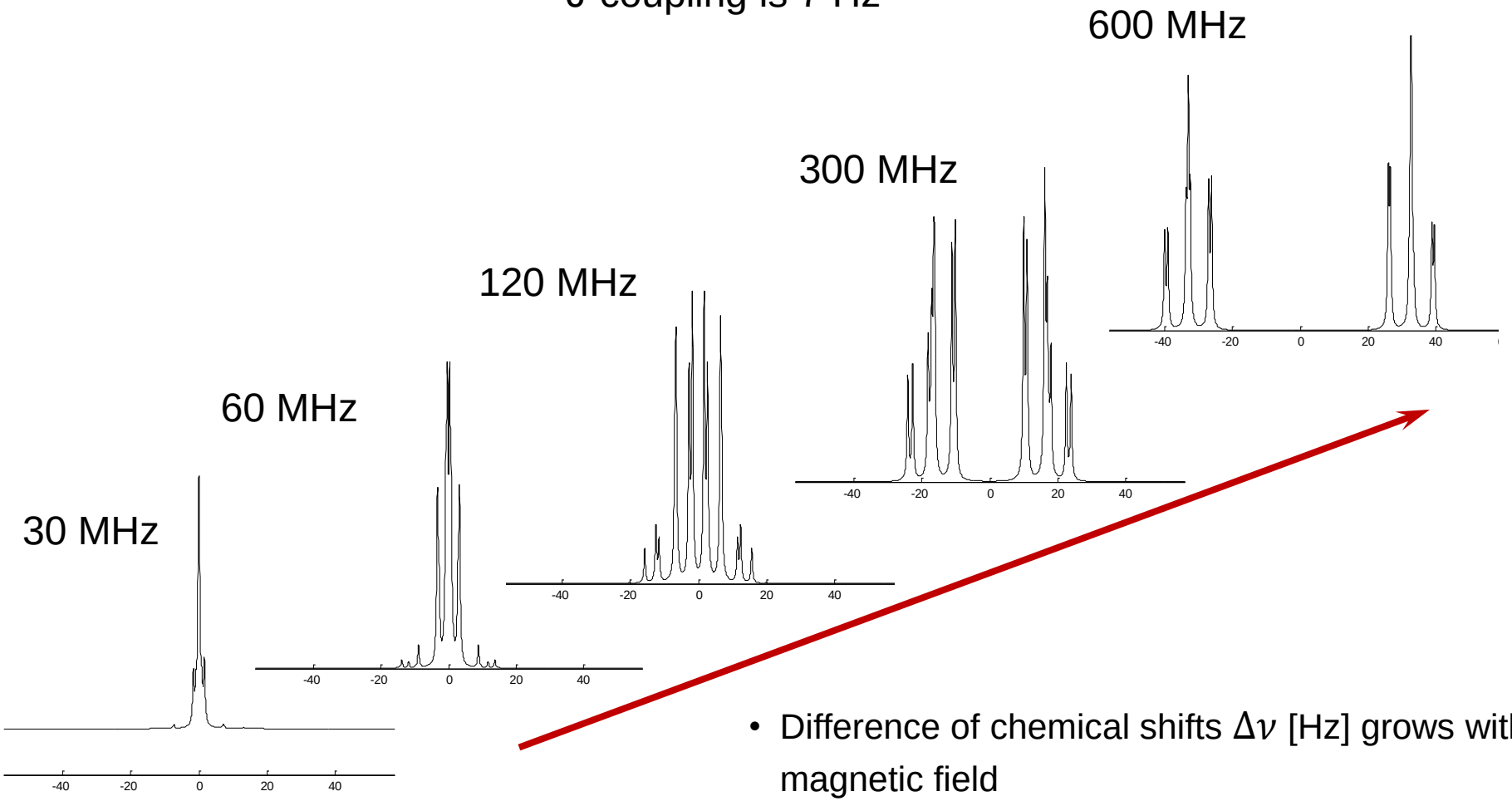
- The intensities of the lines in the doublet do not correspond to the ratio 1:1
- Inner lines (towards the coupling partner) have a higher intensity
- This can be used in the interpretation of spectra

Order of the spectrum



Chemical shift difference of 0.11 ppm

J-coupling is 7 Hz



- Difference of chemical shifts $\Delta\nu$ [Hz] grows with magnetic field
- J-coupling is independent of the magnetic field