Chemical shift for a given molecule:

- Number of signals = nonequivalent nuclei
molecular symmetry

- Relative intensity = number of nuclei

- Position in the spectrum = shielding/chemical shift
electronic structure

- **Multiplicity** = connectivity of atoms and groups

Magnetic Coupling

The interaction of nuclear spins is composed of two parts:

1. Dipolar coupling

direct interaction of magnetic moments thru space

solids
oriented phases
NOE
relaxation

$$B_{\mu z} \sim \mu\, r_{AX}^{-3}(3\cos^2\Theta - 1)$$

2. Scalar coupling

indirect interaction mediated by electrons
chemical information about the bonding

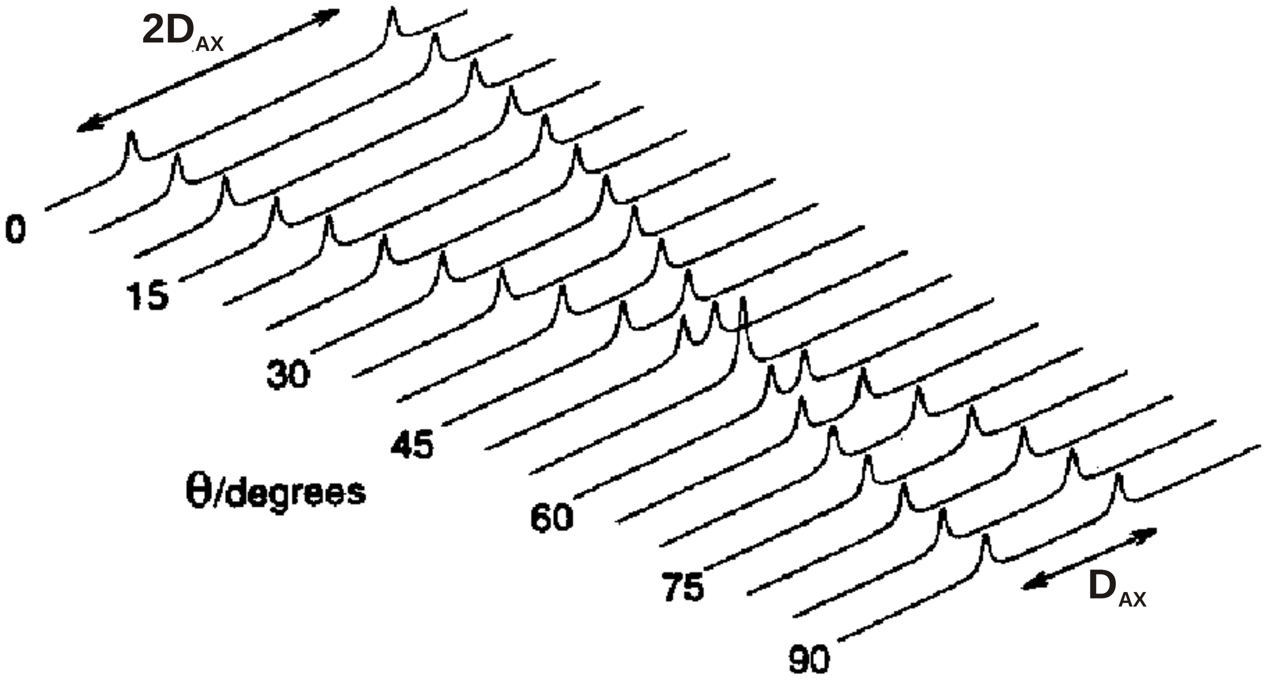
Dipolar Coupling

Dipolar coupling constant

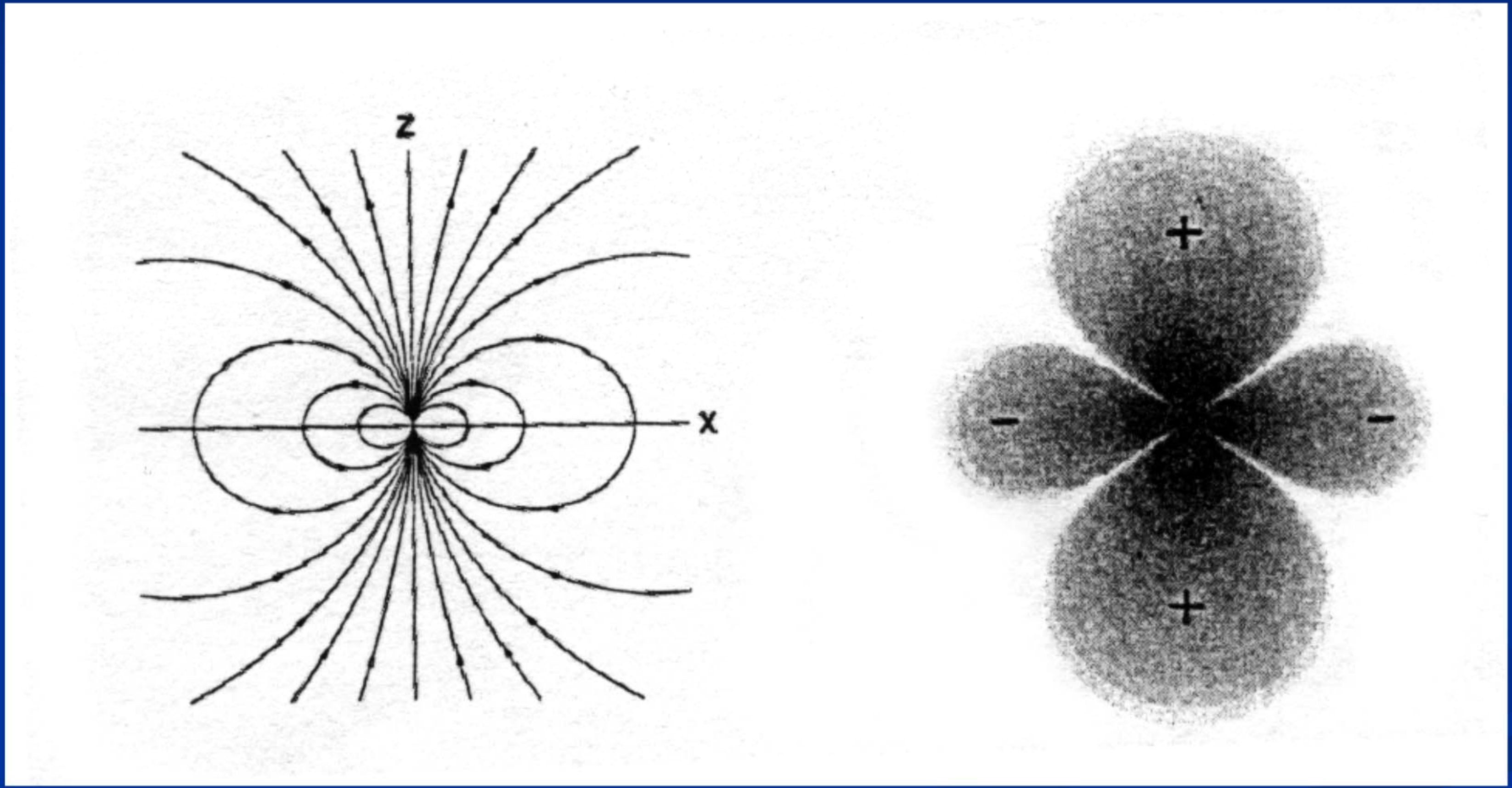
$D_{AX} \sim h\, \gamma_A\, \gamma_X\, r_{AX}^{-3}$

$$\Delta\nu_{hetero} = D_{AX}(3\cos^2\Theta - 1)$$

$$\Delta\nu_{homo} = 1.5\, D_{AX}(3\cos^2\Theta - 1)$$



Dipolar Coupling



$$B_{\mu z} \sim \mu\, r_{AX}^{-3}(3\cos^2\Theta - 1)$$

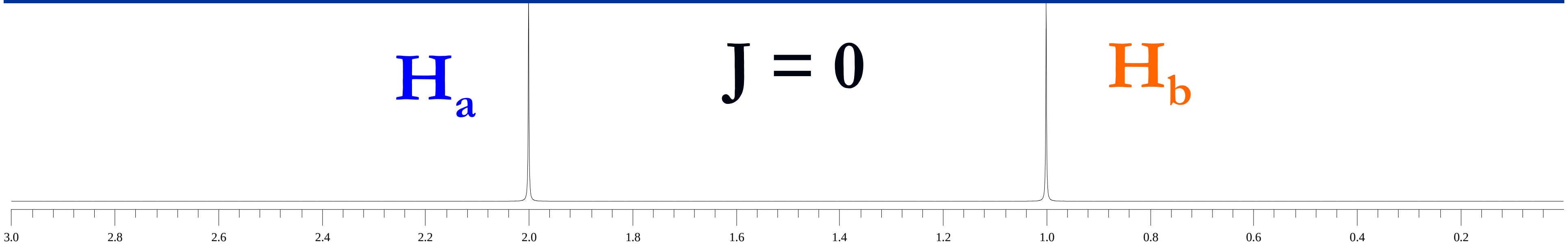
Scalar Coupling

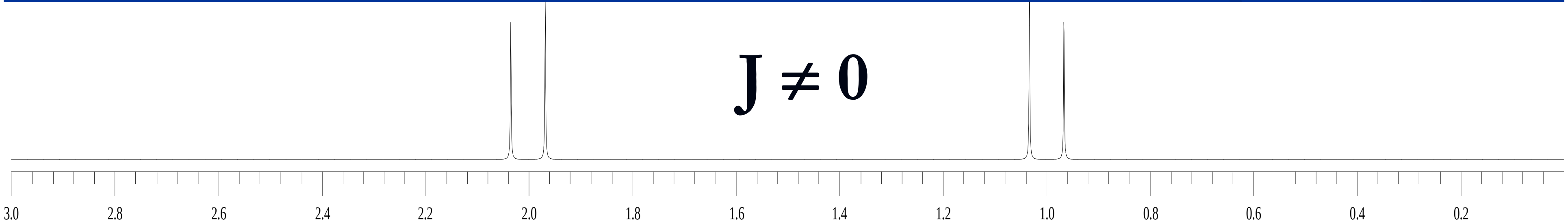
Analysis of the coupling patterns consists of three parts:

- number of lines in a multiplet
- relative intensities of lines in the multiplet
- magnitude (and possibly sign) of the coupling constants (Hz)

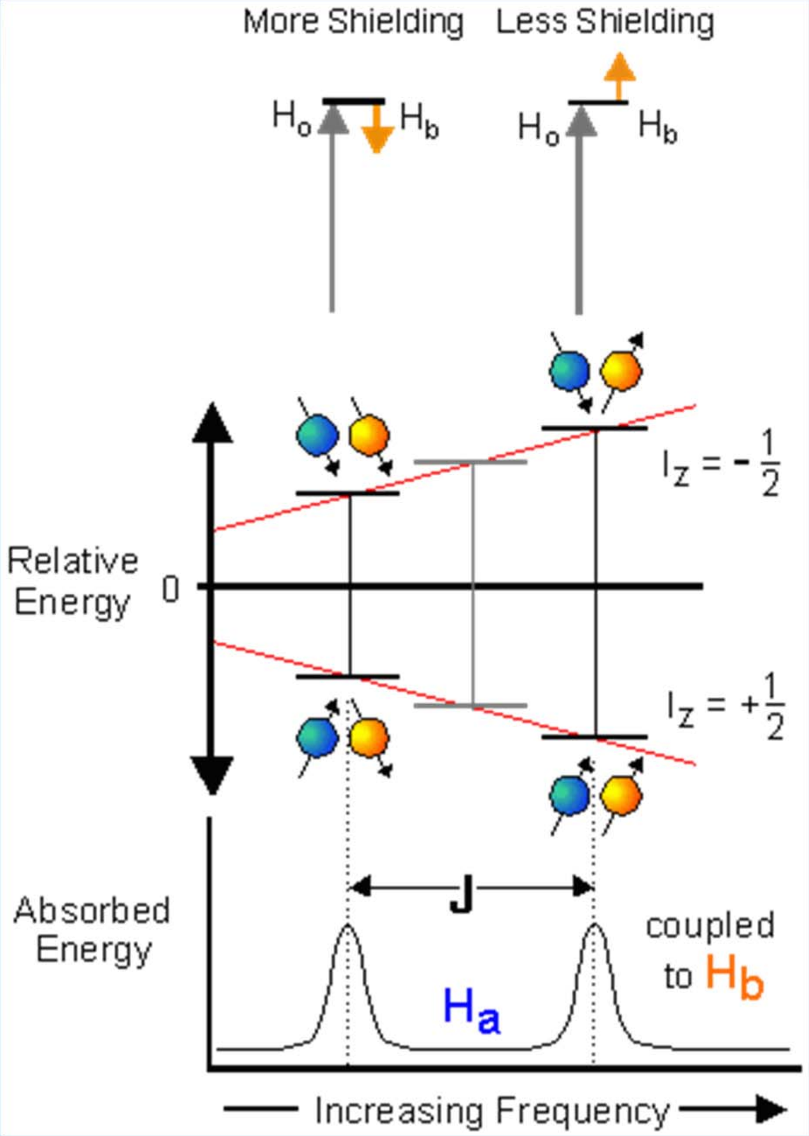
Scalar (Spin-Spin) Coupling

The simplest case:
Two magnetically active nuclei
Interacting through bonds (see each other)
Both spins I = ½



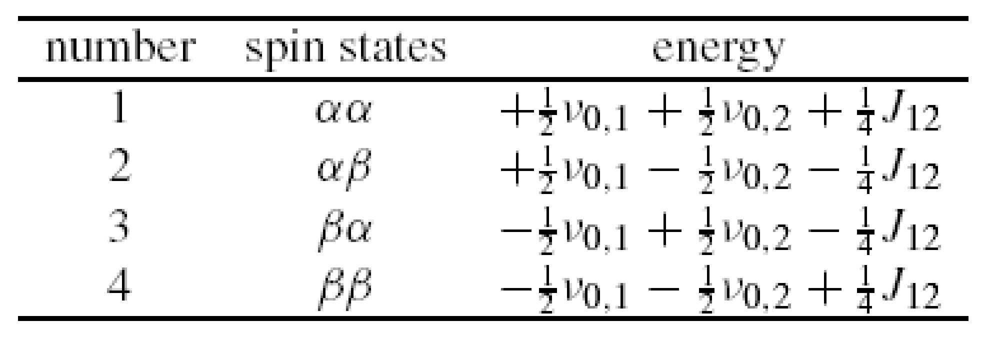


Scalar Coupling



A splitting of a signal = more energy levels involved in the transitions

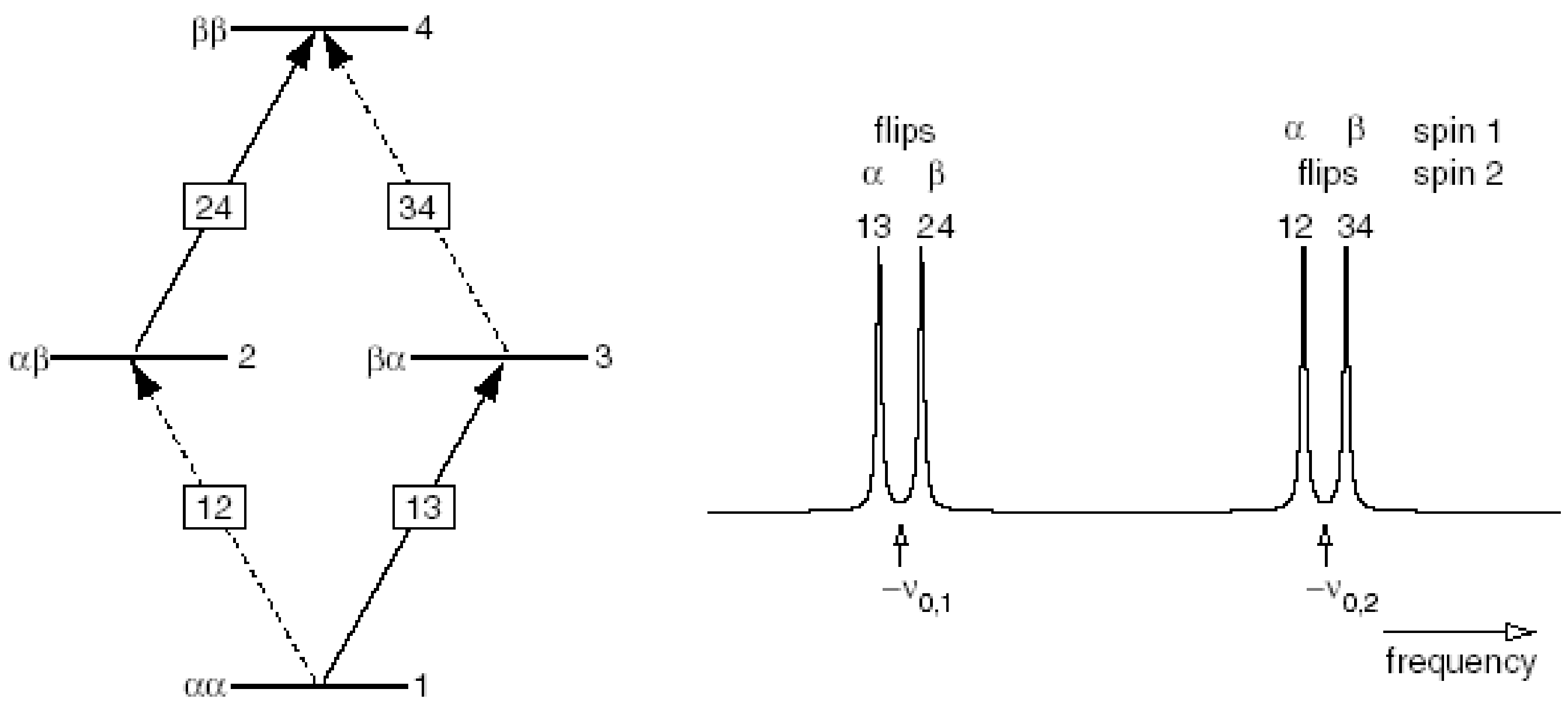
Origin = The magnetic moment of the nucleus H_a produces polarization at H_b (and vice versa)



number	spin states	energy
1	$\alpha\alpha$	$+\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} + \frac{1}{4}J_{12}$
2	$\alpha\beta$	$+\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} - \frac{1}{4}J_{12}$
3	$\beta\alpha$	$-\frac{1}{2}\nu_{0,1} + \frac{1}{2}\nu_{0,2} - \frac{1}{4}J_{12}$
4	$\beta\beta$	$-\frac{1}{2}\nu_{0,1} - \frac{1}{2}\nu_{0,2} + \frac{1}{4}J_{12}$

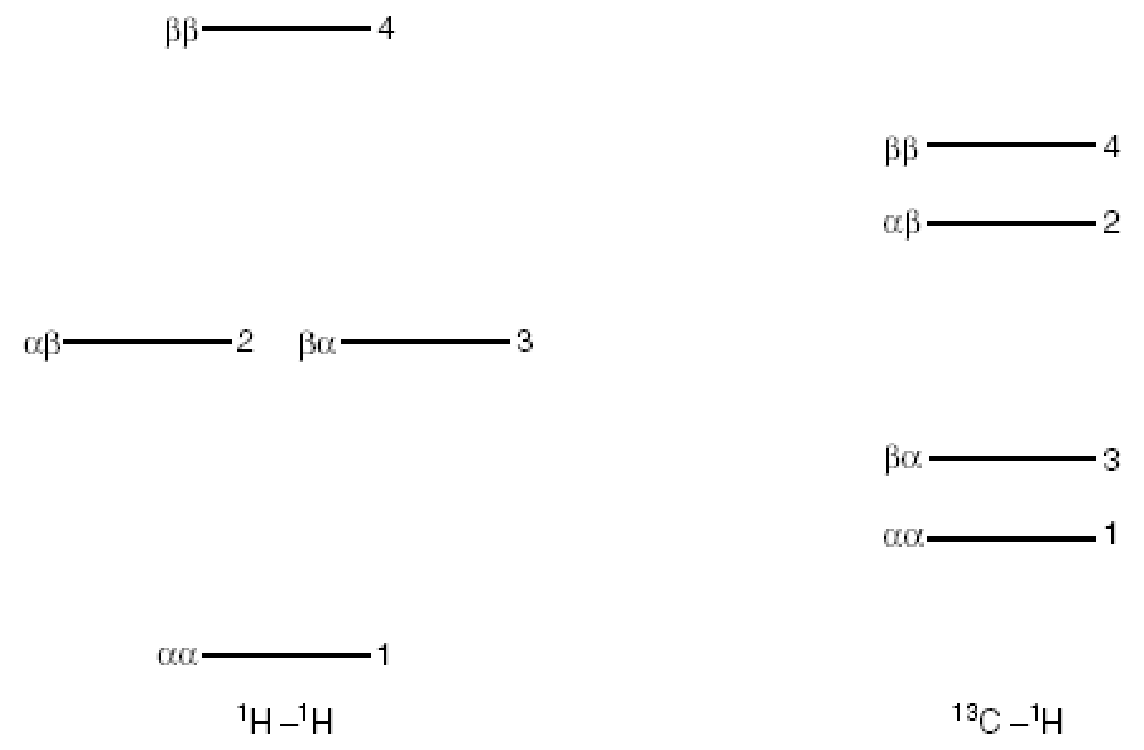
Spectrum of H_a

Two Spins I = ½

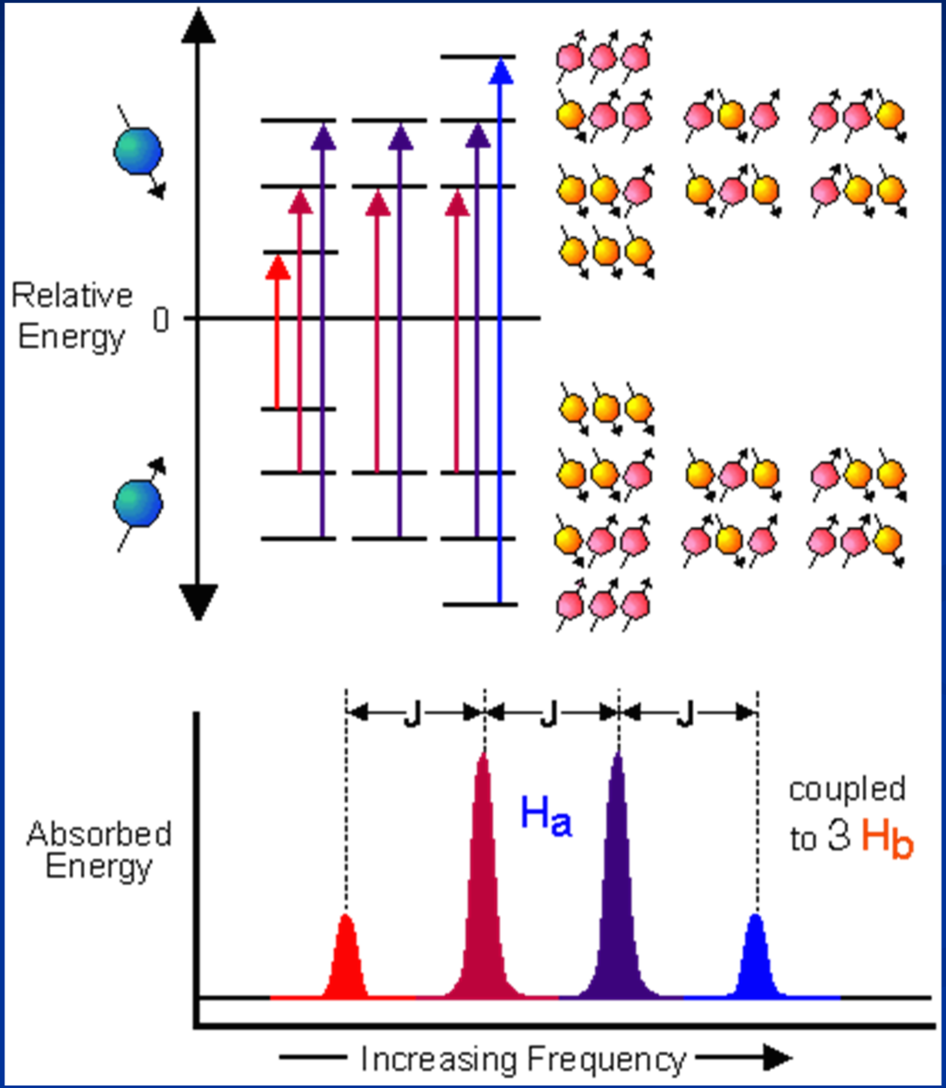


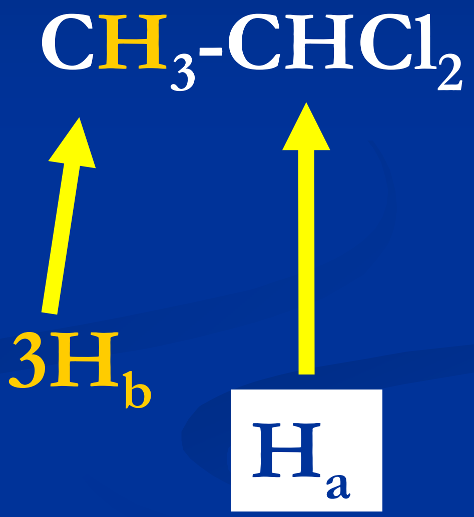
transition	spin states	frequency
$1 \rightarrow 2$	$\alpha\alpha \rightarrow \alpha\beta$	$-\nu_{0,2} - \frac{1}{2}J_{12}$
$3 \rightarrow 4$	$\beta\alpha \rightarrow \beta\beta$	$-\nu_{0,2} + \frac{1}{2}J_{12}$
$1 \rightarrow 3$	$\alpha\alpha \rightarrow \beta\alpha$	$-\nu_{0,1} - \frac{1}{2}J_{12}$
$2 \rightarrow 4$	$\alpha\beta \rightarrow \beta\beta$	$-\nu_{0,1} + \frac{1}{2}J_{12}$

Homo vs. Hetero Coupling



Number of Lines in a Multiplet

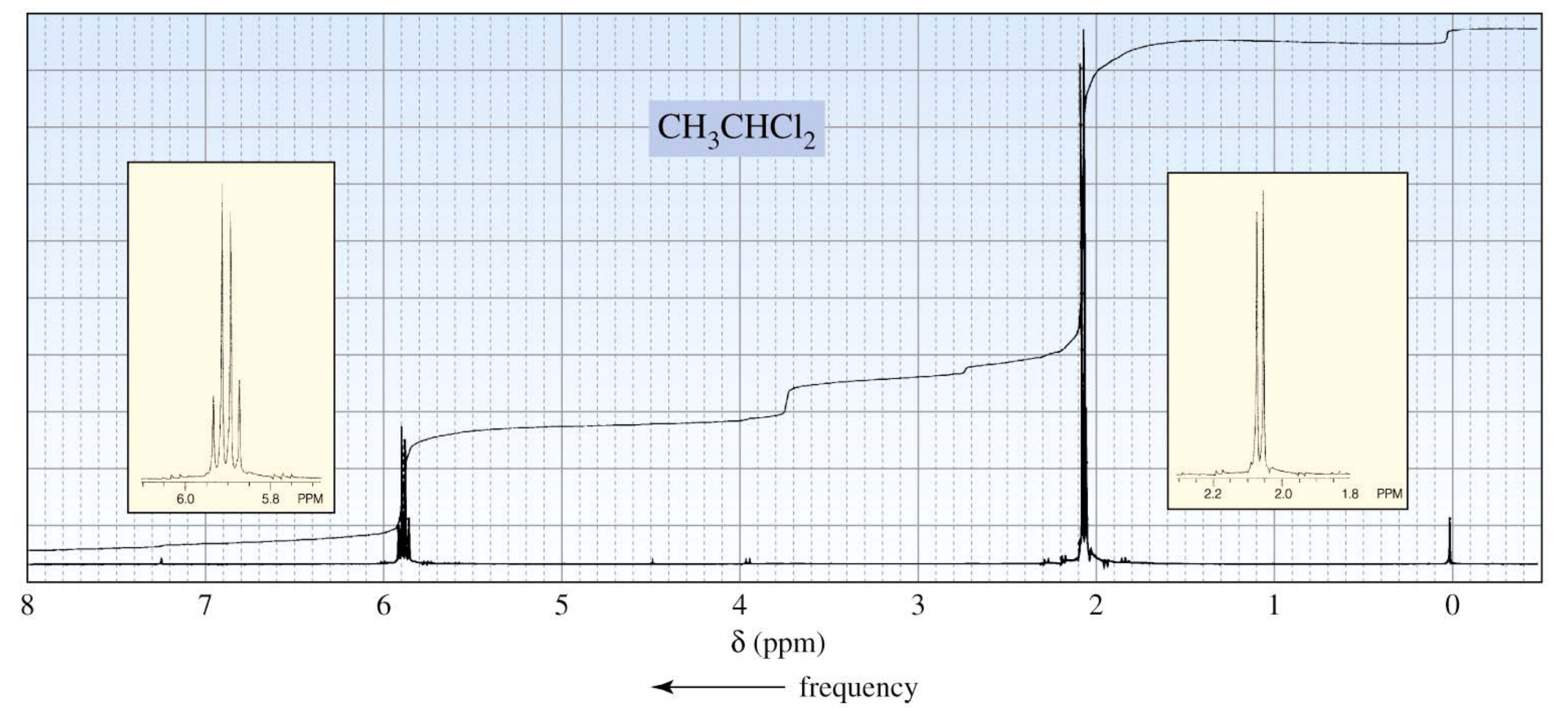


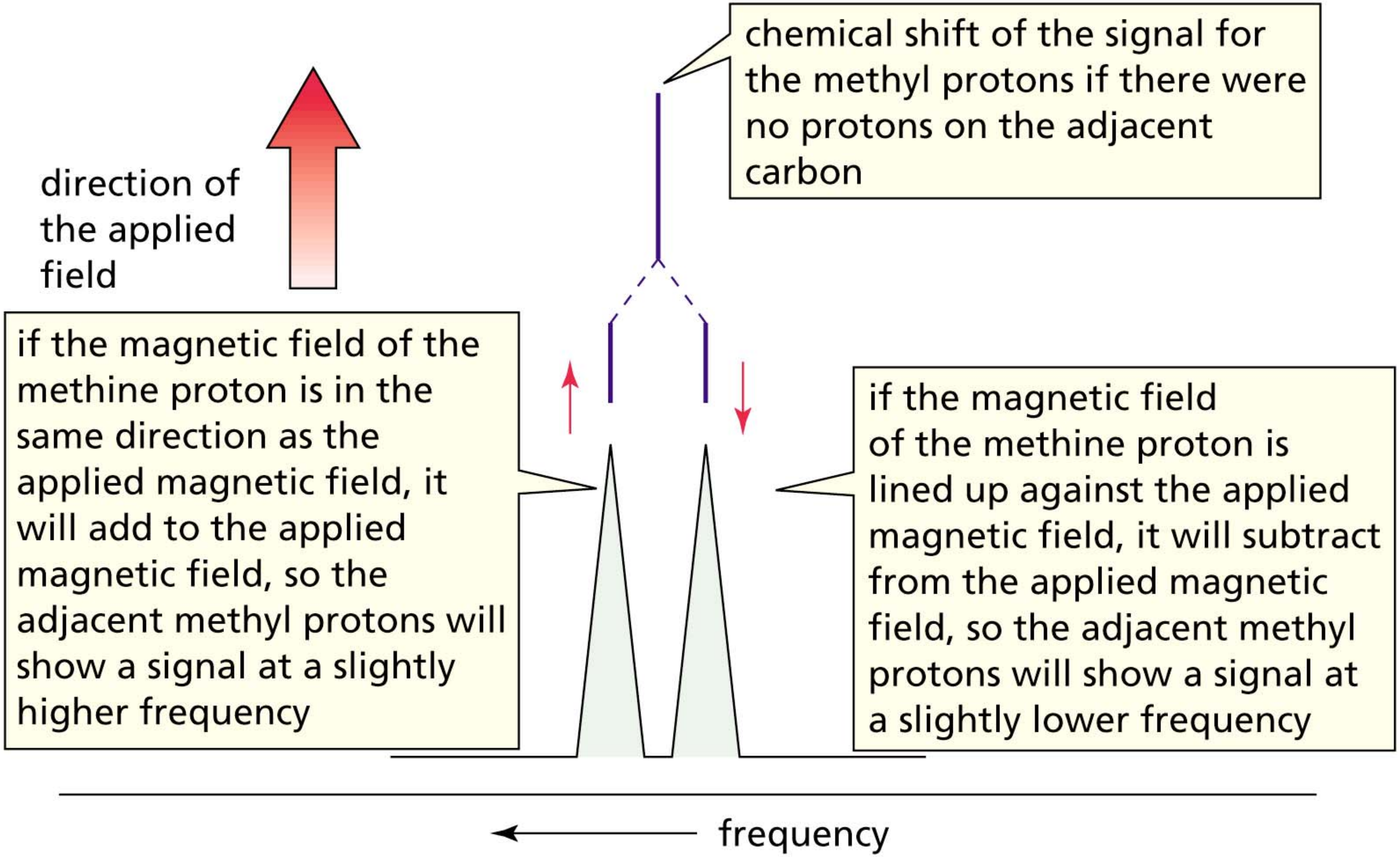


$CH_3\text{-}CHCl_2$

M = 2 n I + 1

$M = 2nI + 1$



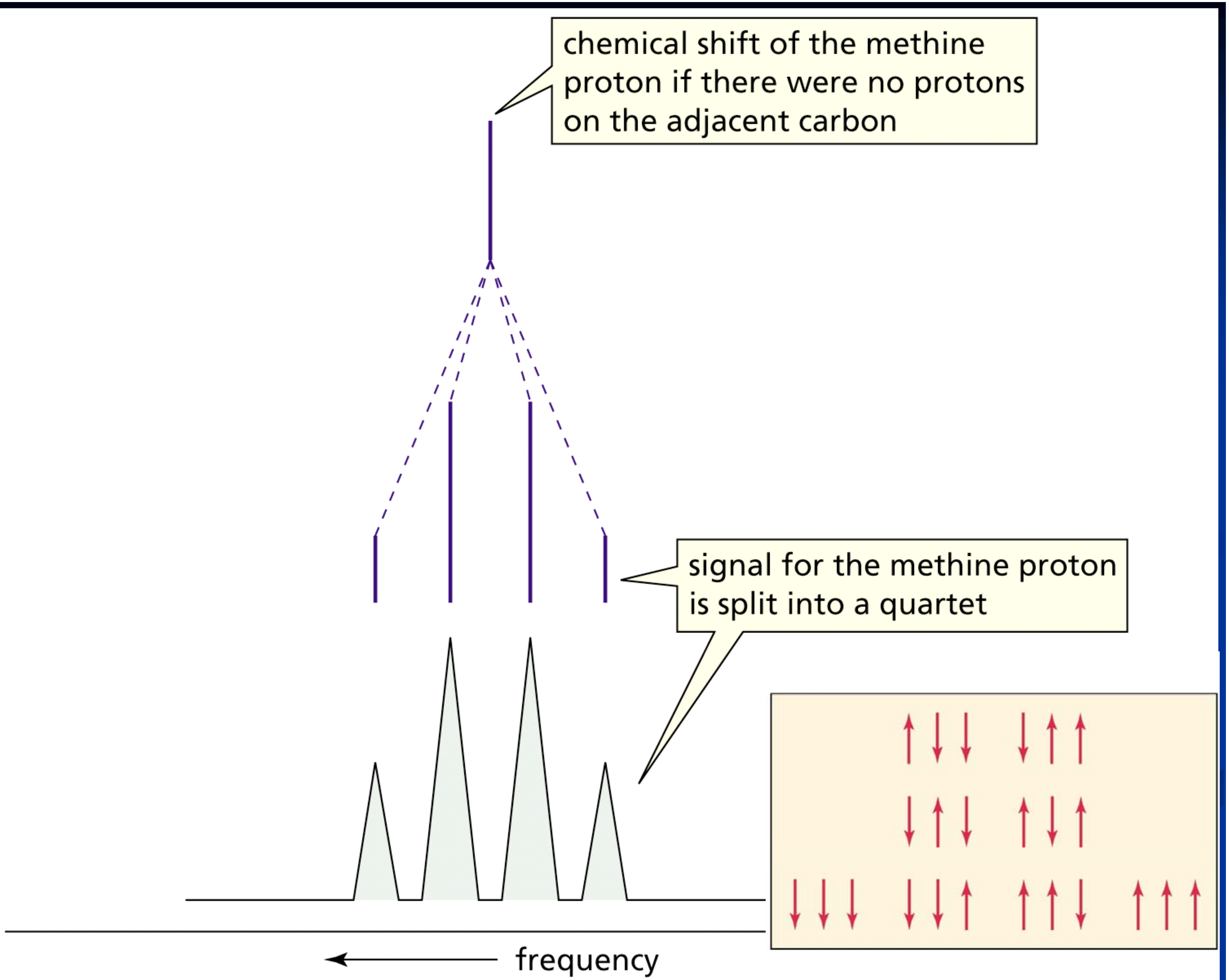


chemical shift of the signal for the methyl protons if there were no protons on the adjacent carbon

direction of the applied field

if the magnetic field of the methine proton is in the same direction as the applied magnetic field, it will add to the applied magnetic field, so the adjacent methyl protons will show a signal at a slightly higher frequency

if the magnetic field of the methine proton is lined up against the applied magnetic field, it will subtract from the applied magnetic field, so the adjacent methyl protons will show a signal at a slightly lower frequency

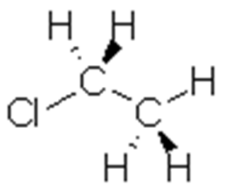


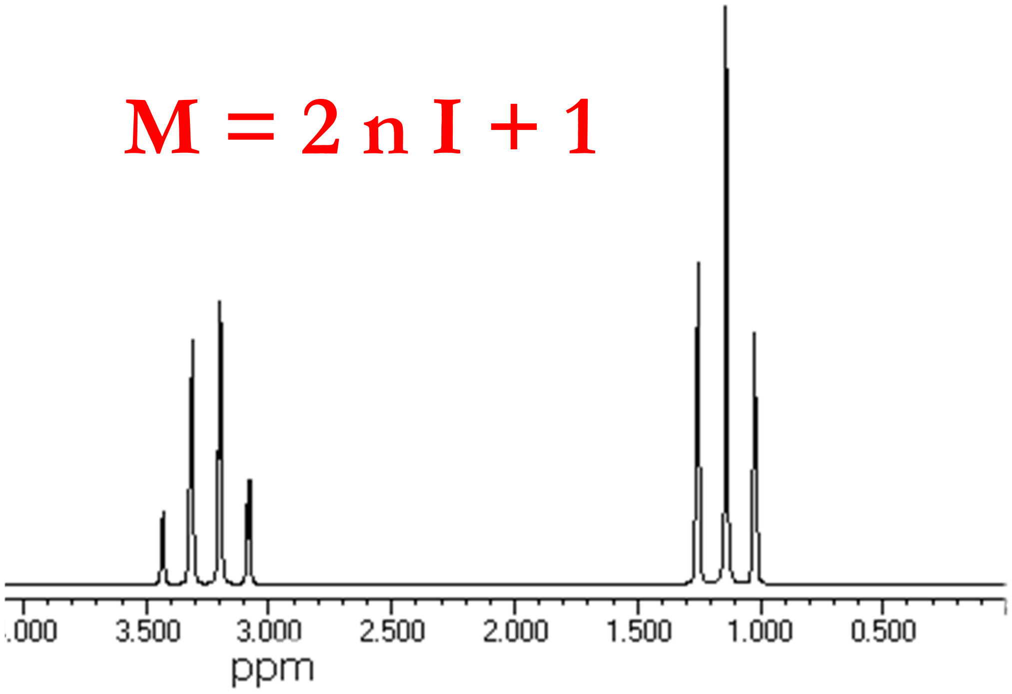
chemical shift of the methine proton if there were no protons on the adjacent carbon

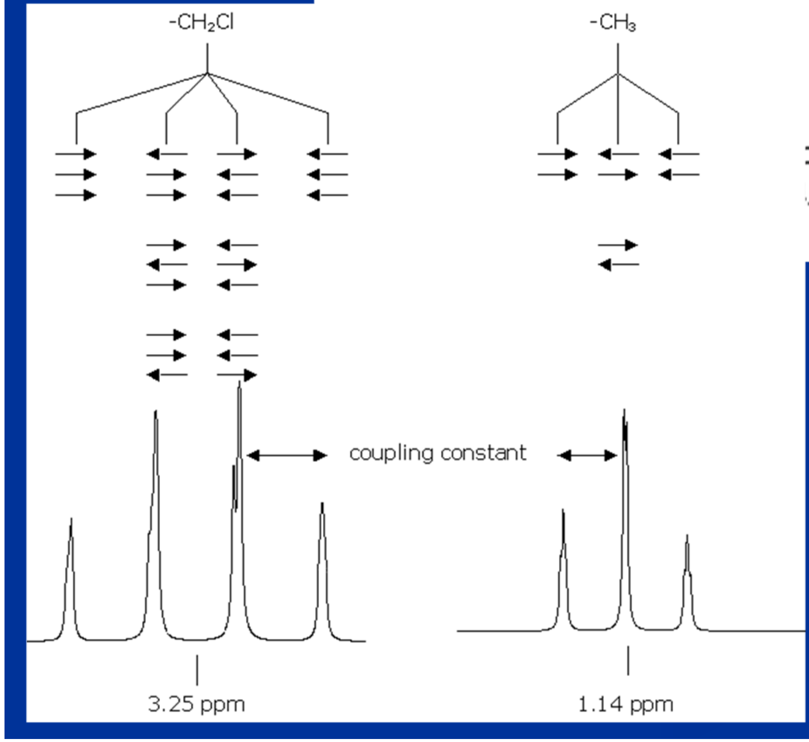
signal for the methine proton is split into a quartet

Scalar Coupling

$M = 2\,n\,I + 1$







Relative Intensities of Lines in the Multiplet

Line intensities of the multiplet A are given by the coefficients of polynomial expansion

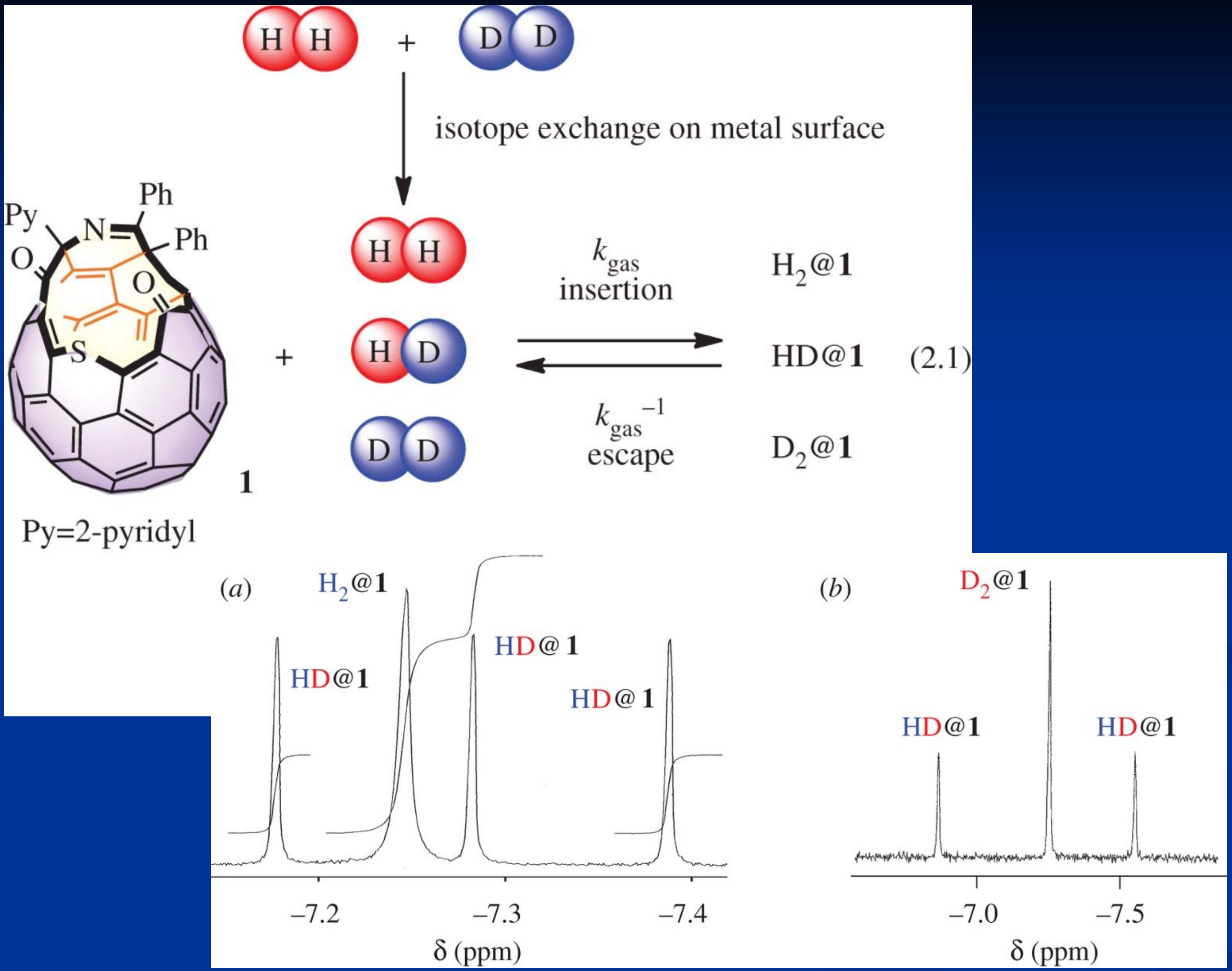
AX_n

Spin, I_X	Polynomial, n = number of nuclei X	Examples
1/2	$(x + y)^n$	^1H
1	$(x^2 + xy + y^2)^n$	^2H, ^6Li, ^{14}N
3/2	$(x^3 + x^2y + xy^2 + y^3)^n$	^{11}B, ^7Li
2	$(x^4 + x^3y + x^2y^2 + xy^3 + y^4)^n$	-
5/2	$(x^5 + x^4y + x^3y^2 + x^2y^3 + xy^4 + y^5)^n$	^{17}O, ^{27}Al
3	$(x^6 + x^5y + x^4y^2 + x^3y^3 + x^2y^4 + xy^5 + y^6)^n$	^{10}B
7/2	$(x^7 + x^6y + x^5y^2 + x^4y^3 + x^3y^4 + x^2y^5 + xy^6 + y^7)^n$	^{51}V, ^{59}Co

Spin ½ Pascal's Triangle

Pattern	n	Relative Peak Height $(x + y)^n$
Singlet	0	1
Doublet	1	1 : 1
Triplet	2	1 : 2 : 1
Quartet	3	1 : 3 : 3 : 1
Quintet	4	1 : 4 : 6 : 4 : 1
Sextet	5	1 : 5 : 10 : 10 : 5 : 1

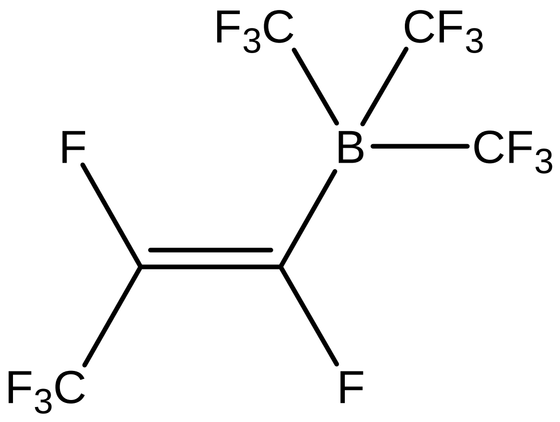
And so on ……

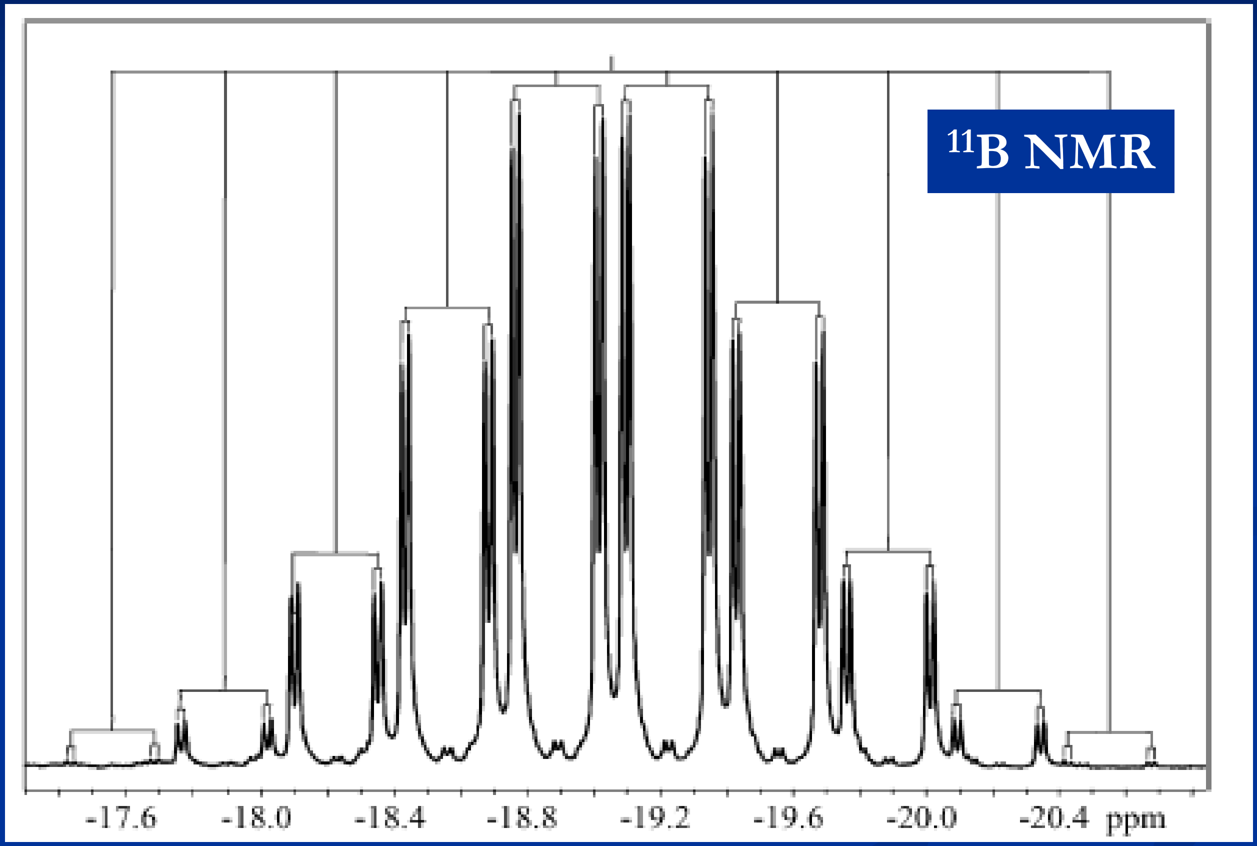


(a) ^{1}H (400 MHz) and (*b*) ^{2}H NMR (60.7 MHz) spectra (*o*-dichlorobenzene-d_4) of the region for encapsulated hydrogen molecule inside open-cage fullerene 1

Coupling with Several Spins

K^+





CF_3 n = 9

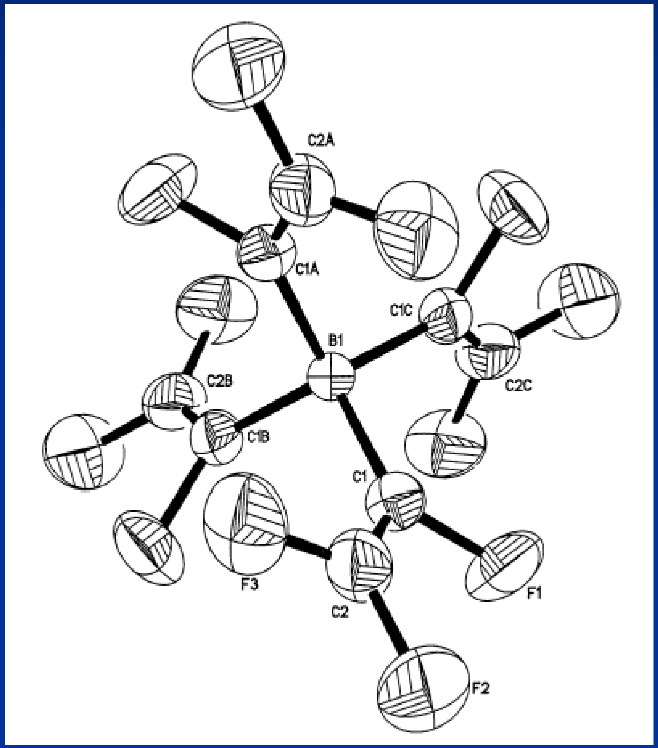
F(2) n = 1

F(3) n = 1

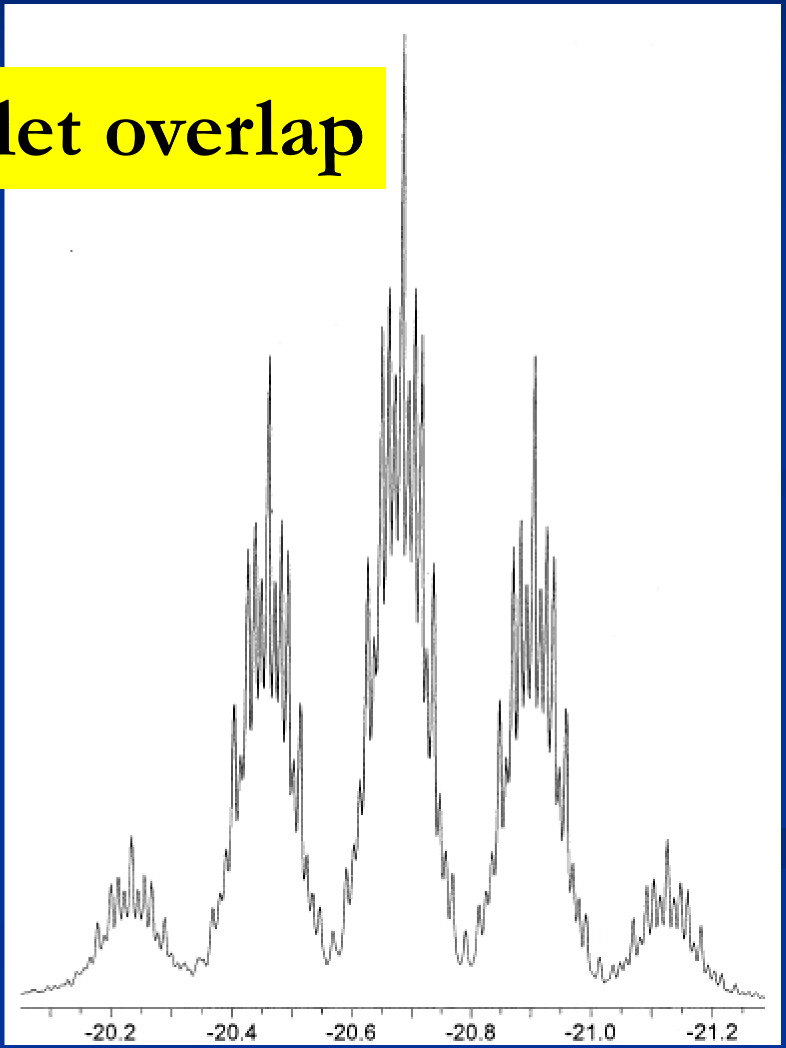
CF_3(too far)

$$M = \Pi(2\, n_i\, I_i + 1)$$

^{11}B NMR Spectrum of $K[B(CF{=}CF_2)_4]$



Multiplet overlap



^{11}B NMR spectrum of $K[B(CF{=}CF_2)_4]$ in CD_3CN: an overlapping quintet of quintets of quintets ($^2J_{B,F}$ = 21.5, $^3J_{B,F}$ = 3.2, $^3J_{B,F}$ = 2.2 Hz).

K[AgF_4]

K[AgF_4] d^8 square planar

^{19}F NMR

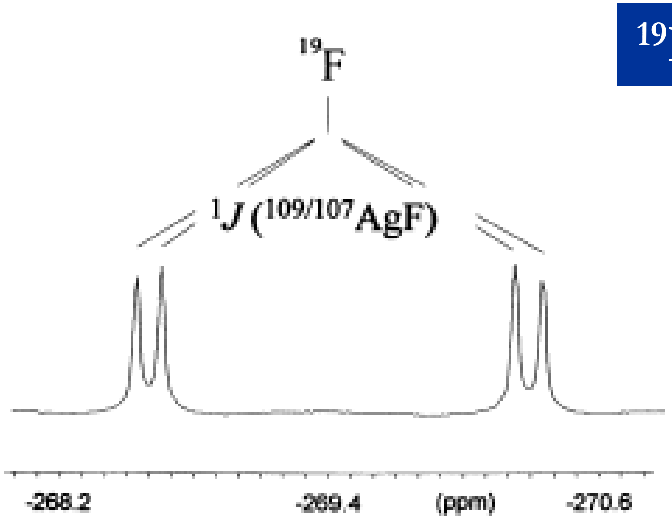


Fig. 1. The ^{19}F NMR spectrum of the AgF_4^- ion recorded at −40°C in HF.

^{109}Ag I = ½ NA = 48.2% γ = - 1.2448 10^7 rad T^{-1} s^{-1}

^{107}Ag I = ½ NA = 51.8% γ = - 1.0828 10^7 rad T^{-1} s^{-1}

$K[AgF_4]$

$M = 2nI + 1$

$^1J(^{109}Ag - F) = 425.8\ Hz$

$^1J(^{107}Ag - F) = 370.4\ Hz$

^{109}Ag NMR

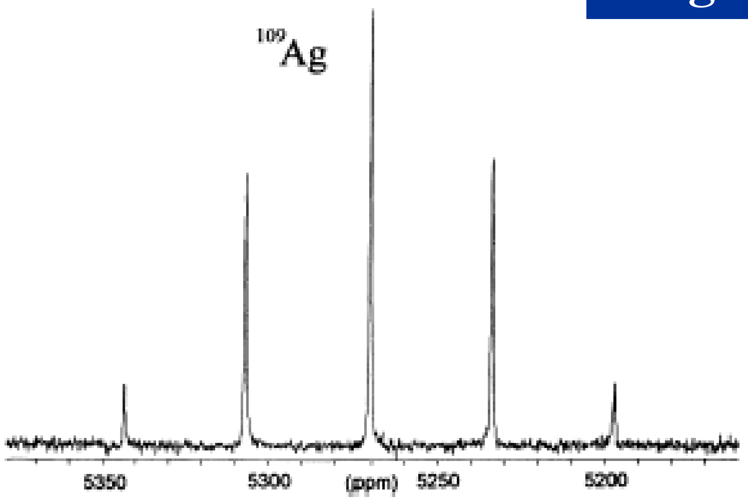
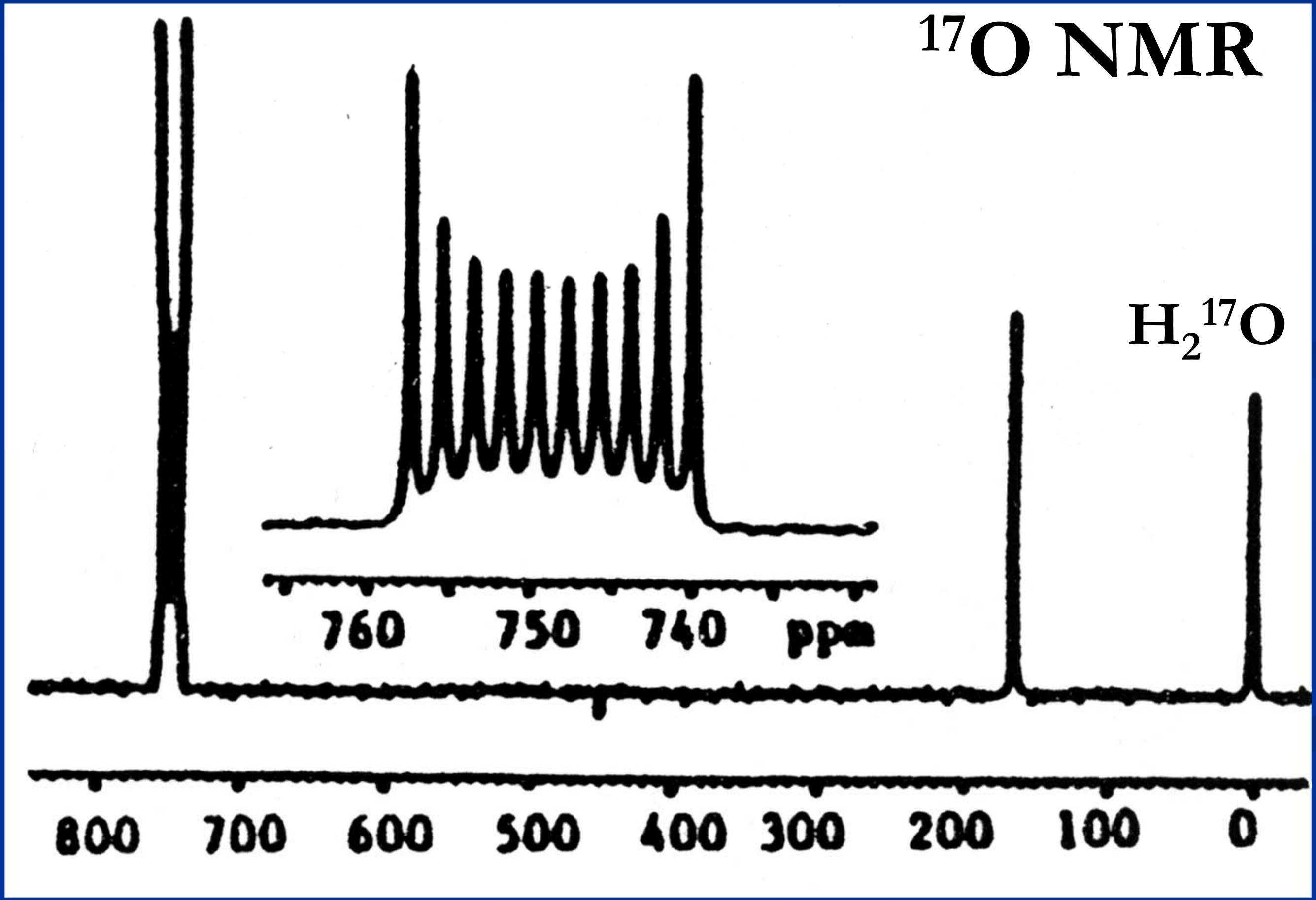


Fig. 2. The ^{109}Ag NMR DEPT spectrum of AgF_4- ion recorded at −40°C in HF utilizing polarization transfer from ^{19}F (DEPTC pulse train, repetition delay 1 s, d2 1.2 ms, number of scans 3948, acquisition time 0.7 s).

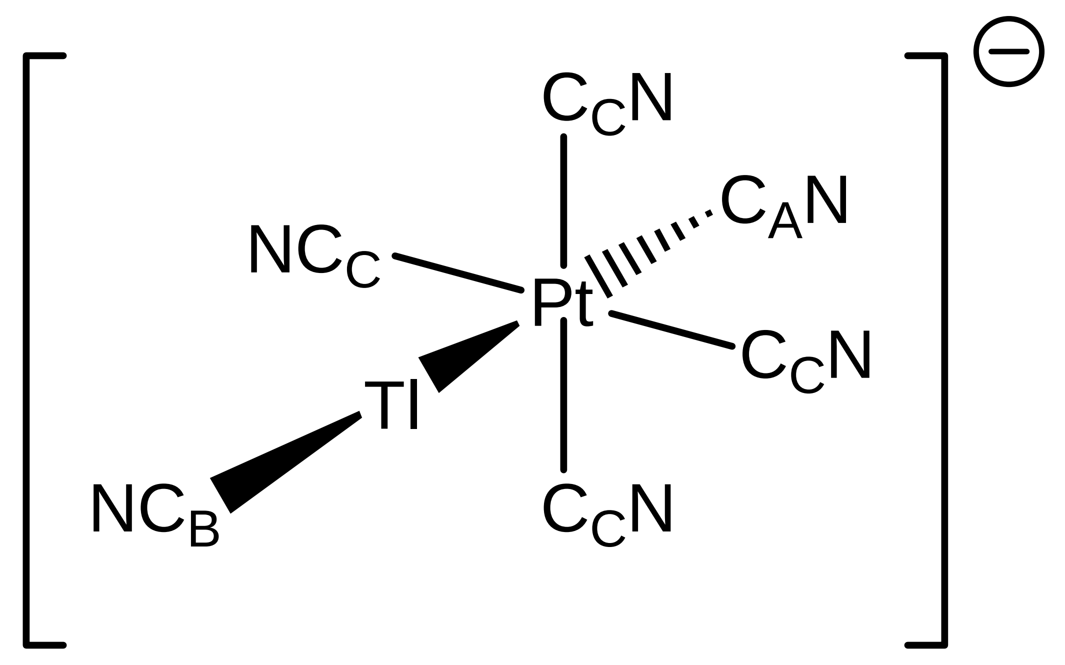
$^1J(^{109}Ag - F)$ must have the same value in both ^{109}Ag and ^{19}F spectra

Signal Multiplicity

TcO_4^- in 20.1% enriched $H_2{}^{17}O$.



Signal Multiplicity



^{13}C enriched CN^-

$M = \Pi(2\, n_i\, I_i + 1)$

^{205}Tl NMR

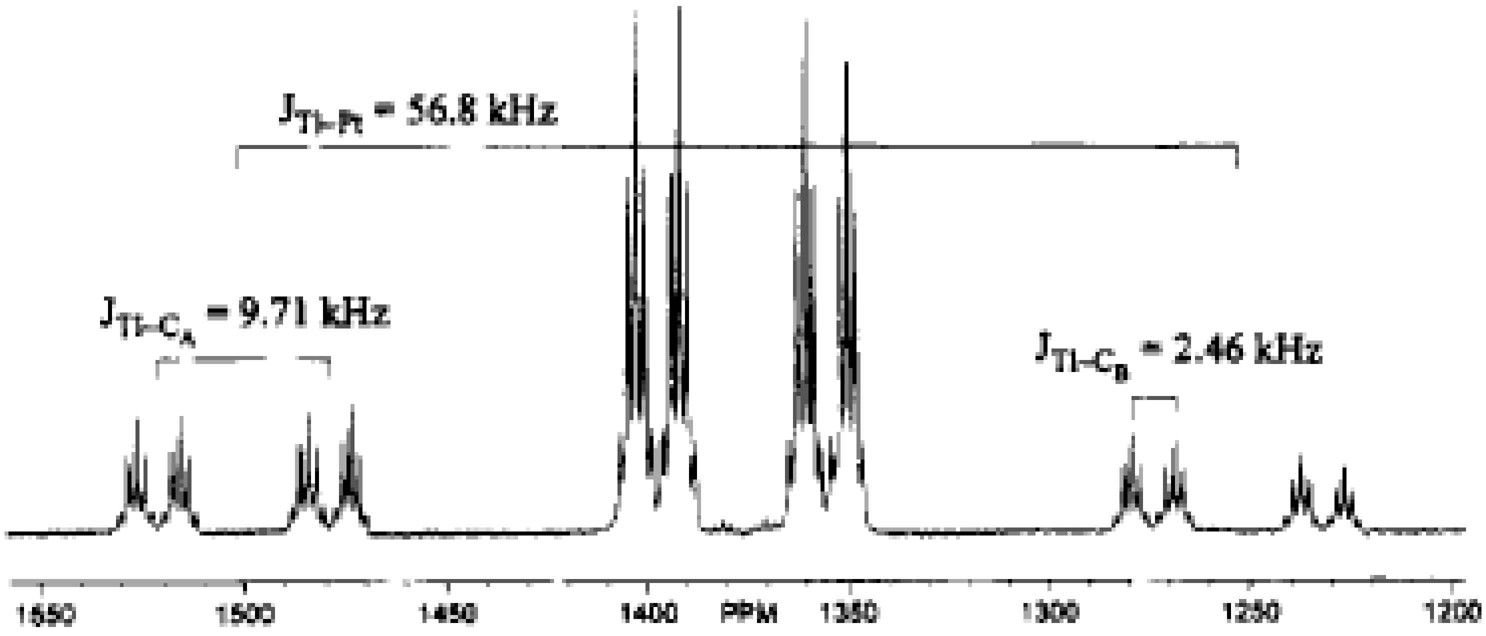


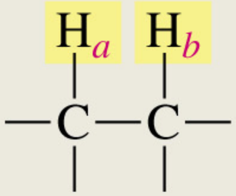
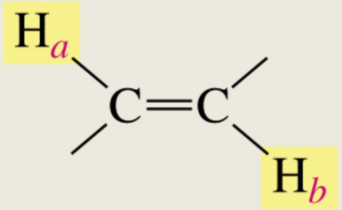
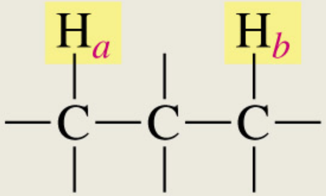
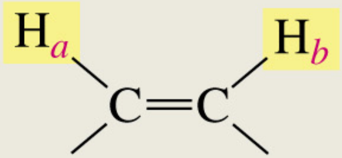
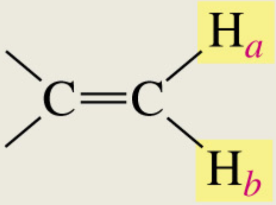
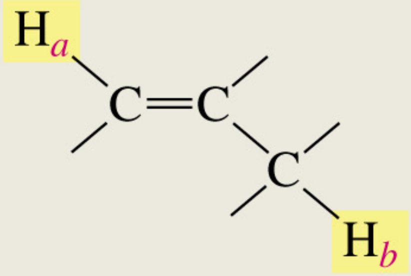
Figure 1. ^{205}Tl NMR spectrum (recorded at 25 °C) of the 100% ^{13}C enriched Pt−Tl complex **II** (see text).

$^{2}J\ (\mathrm{Tl}-C_C) < {}^{1}J\ (\mathrm{Tl}-C_B) < {}^{2}J\ (\mathrm{Tl}-C_A)$

cis	C_C	0.45 kHz
trans	C_A	9.71 kHz

^{1}H Scalar Coupling

Table 14.3 Approximate Values of Coupling Constants

Approximate value of J_{ab} (Hz)		Approximate value of J_{ab} (Hz)	
	7		15 (trans)
	0		10 (cis)
	2 (geminal coupling)		1 (long-range coupling)

Magnitude and Sign of the Coupling Constants

Indirect nuclear spin–spin coupling constants

- through-bond
- through-space
- through hydrogen bonds

Spin-spin couplings between two nuclei will be dependent upon several factors:

- the nuclei involved – magnetogyric ratio
- the distance between the two nuclei
- the angle of interaction between the two nuclei
- the nuclear spin of the nuclei

Scalar Coupling
Isotropic part of *J*

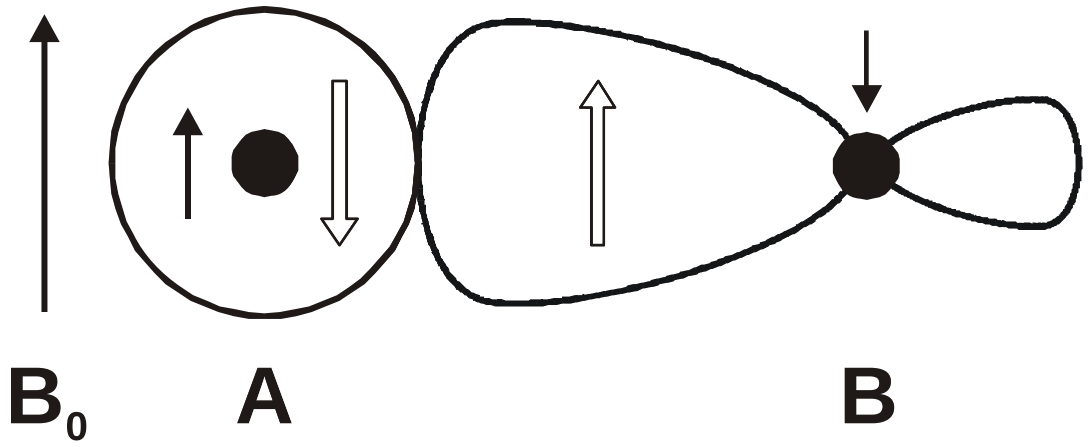
Four (Ramsey) contributions:

- Fermi-contact (FC)
- Spin-dipolar (SD)
- Paramagnetic orbital (PARA)
- Diamagnetic orbital (DIA)

Scalar Coupling

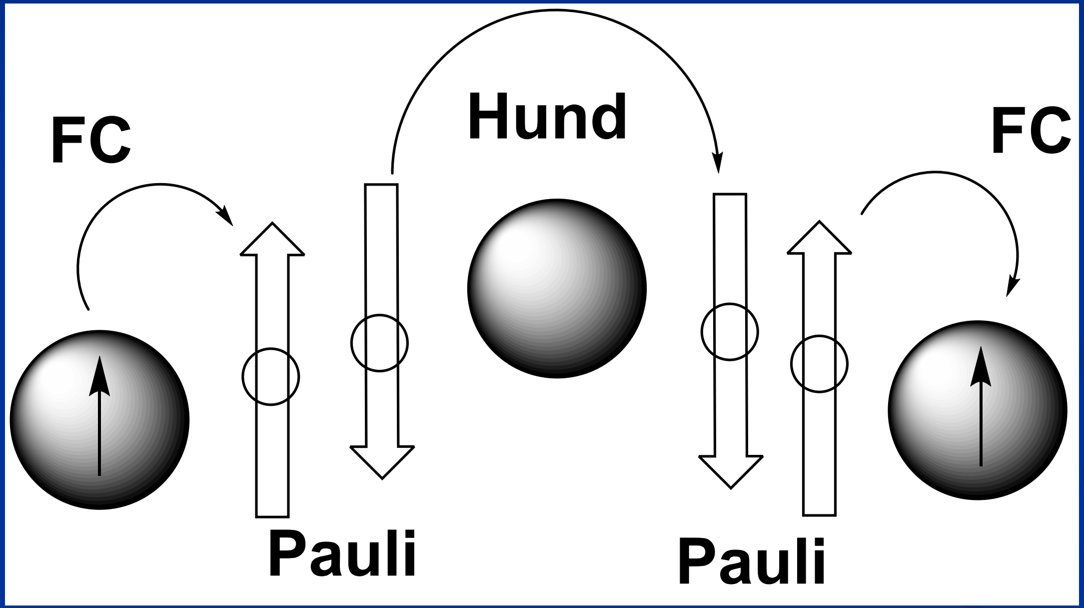
The most important contribution to scalar coupling arises from the FERMI-CONTACT INTERACTION

which can be described in the Dirac-vector model:



The nuclear spin polarization of nucleus A in a magnetic field polarizes the spins of a bonding electron pair, which in turn transfer this polarization to nuclear spin B.

Scalar Coupling



Scalar Coupling

FERMI-CONTACT INTERACTION is mediated only by s-electrons (p, d, f electrons have no contact with the nucleus)

s-electron has definite probability at nucleus
e-spin and nuclear spin can interact only when they occupy same space

An approximate expression for the scalar coupling constant J was given by Mc CONNELL:

$$J_{AB} \sim \gamma_A \ \gamma_B \ s_A{}^2(0) \ s_B{}^2(0) \ (\Delta E)^{-1} \alpha_{AB}{}^2$$

$s^2(0)$ = s-electron density at the nucleus
$\alpha_{AB}{}^2$ = s-character in the A-B bond

Conventions on the Notation of Scalar Coupling Constants

Spin-spin couplings are generally expressed in terms of the COUPLING CONSTANT ^{n}J
where n denotes the number of bonds between coupled nuclei
Dimension $[J] = \mathrm{s}^{-1}$ [Hz]

The magnitude of J depends on the gyromagnetic ratios γ_A, γ_B of the coupled nuclei. For comparison of coupling constants involving different isotopes use
the REDUCED COUPLING CONSTANT K

$$K_{AB} = (4\pi^2/h)\,(\gamma_A\ \gamma_B)^{-1}\, J_{AB}$$

Dimension $[\,\mathrm{K}\,] = 10^{19}\ \mathrm{N\ A^2\ m^{-3}}$

Scalar Coupling Constants

To compare substituent influences on coupling for different nuclei, use

the EFECTIVE REDUCED COUPLING CONSTANT K’

$$K'_{AB} \;=\; K_{AB}\;[\mathrm{s_A}^2(0)\;\mathrm{s_B}^2(0)]^{-1}$$

Dimension $[K']$ = 10^{42} N A^{-2} m^3

Signs of Scalar Coupling Constants

Signs of scalar coupling may be both POSITIVE or NEGATIVE. The sign of a coupling constant is defined as follows:

$K_{AB} < 0$ if PARALLEL alignment of the spins I(A) and I(B) is energetically favored

$K_{AB} > 0$ if ANTIPARALLEL alignment of the spins I(A) and I(B) is energetically favored

Signs of Scalar Coupling Constants

$$\frac{K_{AB}}{J_{AB}} \qquad \begin{array}{ll} > 0 & \text{if } \gamma_A, \gamma_B \text{ have same sign} \\ < 0 & \text{if } \gamma_A, \gamma_B \text{ have different sign} \end{array}$$

NMR spectroscopic measurements in liquids yield generally only information on RELATIVE SIGNS of two couplings,
i.e. $K_{AB} / K_{AC} > 0$ or $K_{AB} / K_{AC} < 0$.
Determination of absolute signs for K_{AB} or K_{AC} requires other experiments (e.g. molecular beam experiments, observation of dipolar interactions in the solid state)

Signs of Scalar Coupling Constants

The sign of $^{1}K_{EH}$ is generally positive.

(E = any first to fourth row atom)

If the relative sign of a coupling constant $^{n}K_{XY}$ can be determined from $^{n}K_{XY}$ / $^{1}K_{EH}$, it can be translated into an absolute sign.

Methods for sign determination:

- analysis of higher order spectra
- homo- or heteronuclear 2D-Experiments
- selective irradiation experiment

Coupling signs may provide useful structural information on:

- the number of bonds connecting two nuclei
- the oxidation state of elements
- the stereochemical details (conformation and configuration analysis)

Visualization of Spin–Spin Coupling

$$J_{AB} = \frac{\hbar}{2\pi}\gamma_A\gamma_B K_{AB} = \frac{1}{2}\left[E(\uparrow\uparrow) - E(\uparrow\downarrow)\right]$$

the energy splitting between states with parallel
and antiparallel nuclear spins

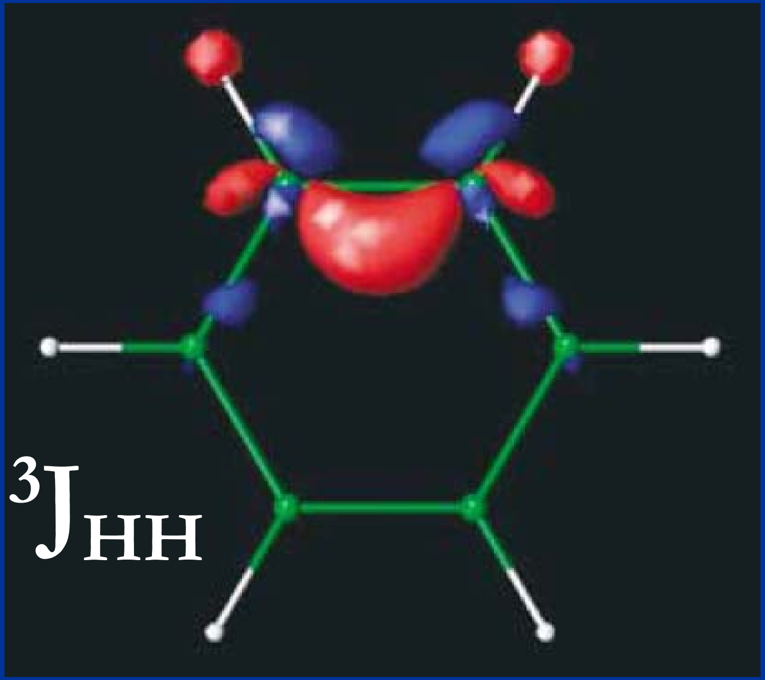
$$J_{AB} = \frac{\hbar}{2\pi}\gamma_A\gamma_B K_{AB} = \frac{1}{2}\int\left[\varepsilon^{\uparrow\uparrow}(r) - \varepsilon^{\uparrow\downarrow}(r)\right]dV = \frac{\hbar}{2\pi}\gamma_A\gamma_B\int\varepsilon_{AB}(r)dV$$

$\varepsilon_{AB}(r)$ = the coupling energy density (CED)
integral of CED over all space = K_{AB}
CED is a real-space function, can be visualized in 3D
contains all the information about the propagation of the nuclear spin–spin interaction throughout a molecule

Visualization of Spin–Spin Coupling

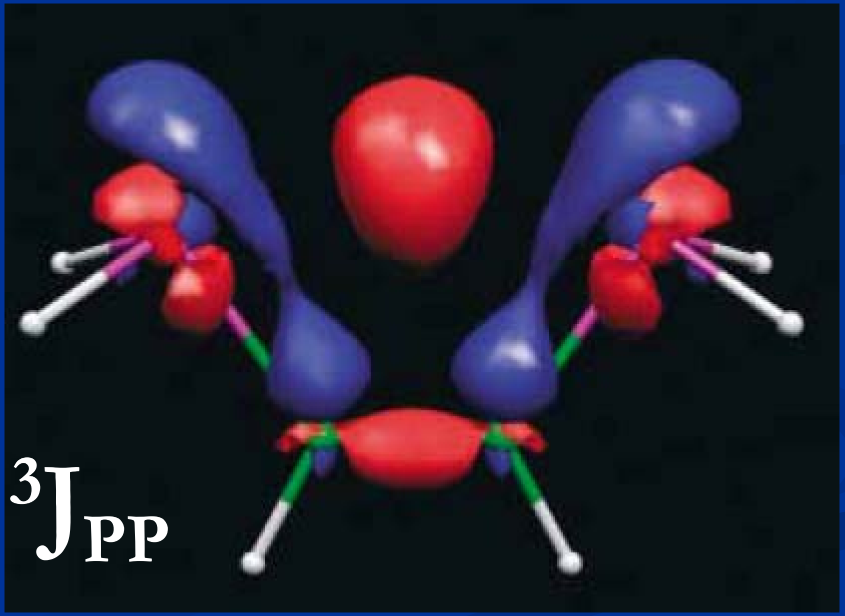
$$J_{AB} = \frac{\hbar}{2\pi}\gamma_A\gamma_B K_{AB} = \frac{1}{2}\int\left[\varepsilon^{\uparrow\uparrow}(r) - \varepsilon^{\uparrow\downarrow}(r)\right]dV = \frac{\hbar}{2\pi}\gamma_A\gamma_B\int\varepsilon_{AB}(r)dV$$

Benzene



through-bond

$H_2P\text{-}CH_2\text{-}CH_2\text{-}PH_2$

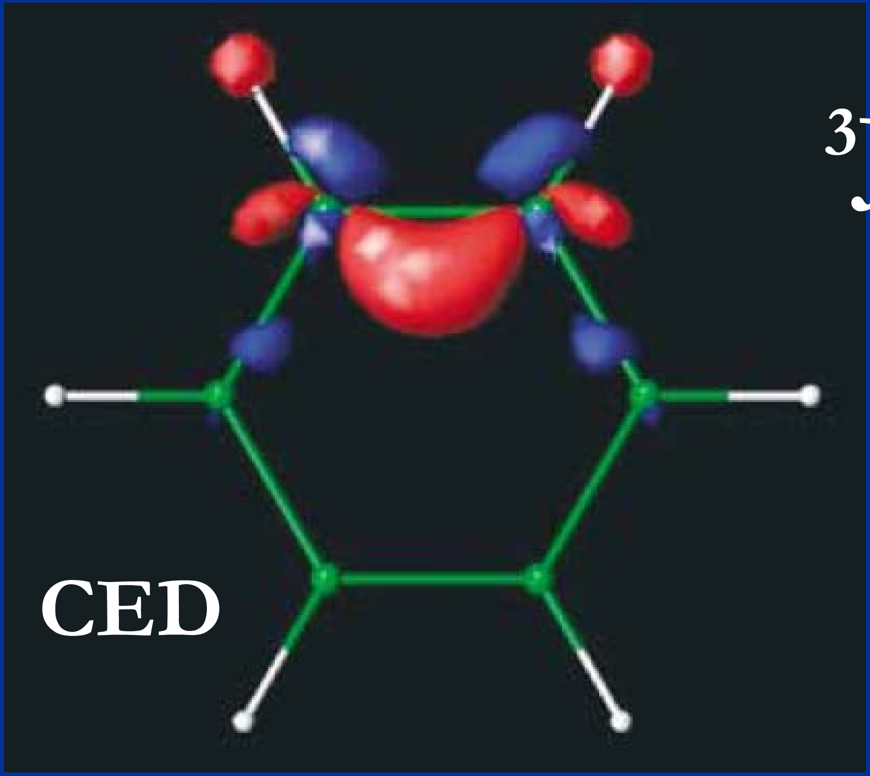


through-space

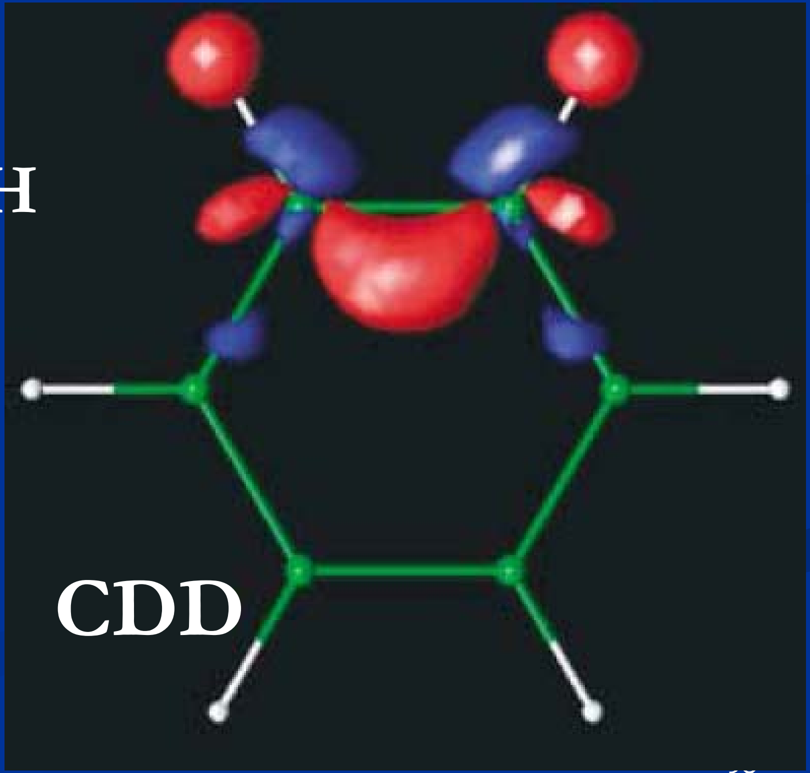
Visualization of Spin–Spin Coupling

$$\rho_{AB}(r) = \frac{\rho^{\uparrow\uparrow}(r) - \rho^{\uparrow\downarrow}(r)}{\lambda_1 \lambda_2}$$

The coupling electron deformation density (CDD), the integration of CDD over space = 0



$^3J_{HH}$



Types of Coupling

Coupling between two nuclei can be categorized as follows:

Homonuclear Coupling

- coupling between nuclei of the same type

$^{1}H\text{-}C\text{-}C\text{-}^{1}H$, $^{195}Pt\text{-}^{195}Pt$, $^{31}P\text{-}C\text{-}^{31}P$, $^{199}Hg\text{-}C\text{-}C\text{-}^{199}Hg$

Heteronuclear Coupling

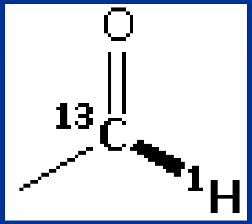
- coupling between nuclei of different types

$^{1}H\text{-}^{13}C$, $^{1}H\text{-}^{31}P$, $^{205}Tl\text{-}^{195}Pt$, $^{14}N\text{-}^{51}V$

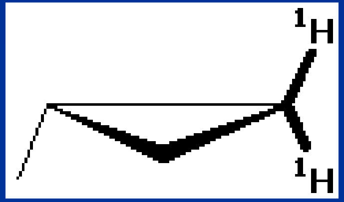
Distance Dependence

The absolute value of the coupling constant decreases as the number of interceding bonds between coupled nuclei increases.

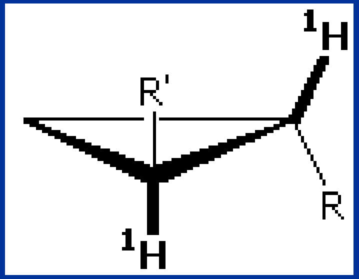
The order of the strength of coupling is as follows: $^1J > ^2J > ^3J > ^4J > ^nJ$



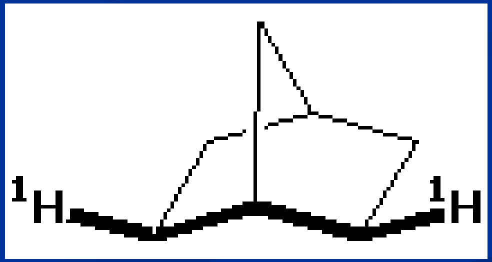
^1J one-bond or direct



^2J two-bond or geminal



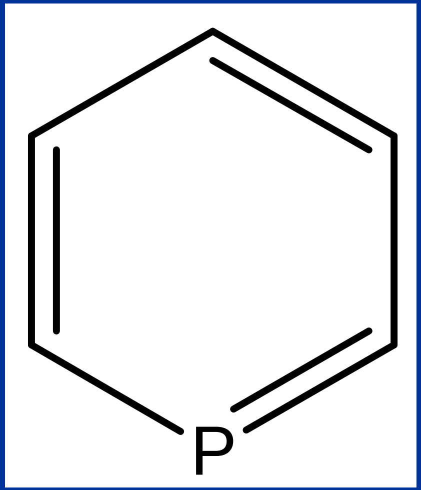
^3J three-bond or vicinal



^nJ long-range

Distance Dependence

$^1J > ^3J > ^2J$



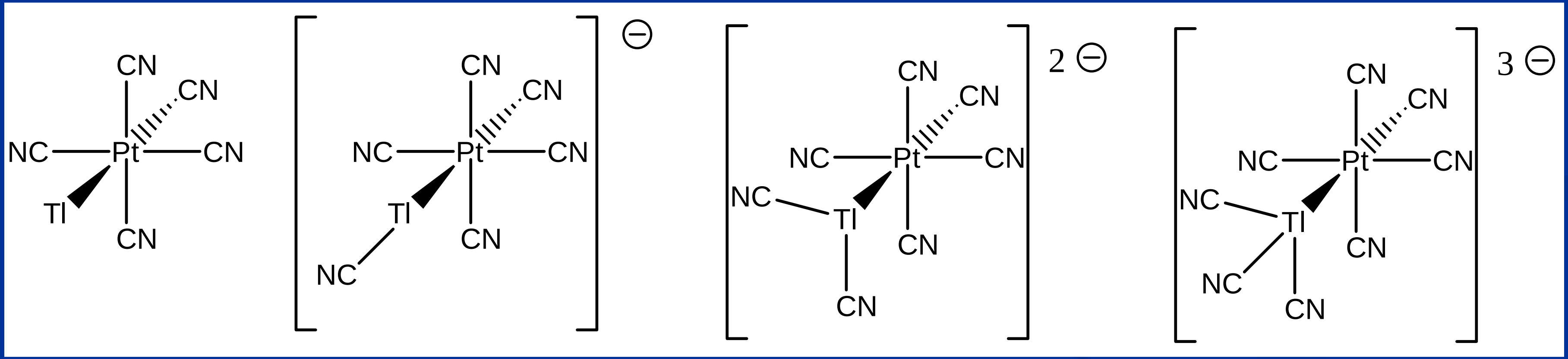
$^3J_{\mathrm{PCCC}} = 14$ Hz

$^2J_{\mathrm{PCC}} = 12$ Hz

$^1J_{\mathrm{PC}} = 55$ Hz

Largest Heteronuclear J

$^{1}J(^{205}\mathrm{Tl}\text{-}^{195}\mathrm{Pt})$, kHz !!!!



71 57 47 38

Largest Homonuclear J

$^{1}J(^{199}Hg\text{-}^{199}Hg)$ =

220 300 Hz

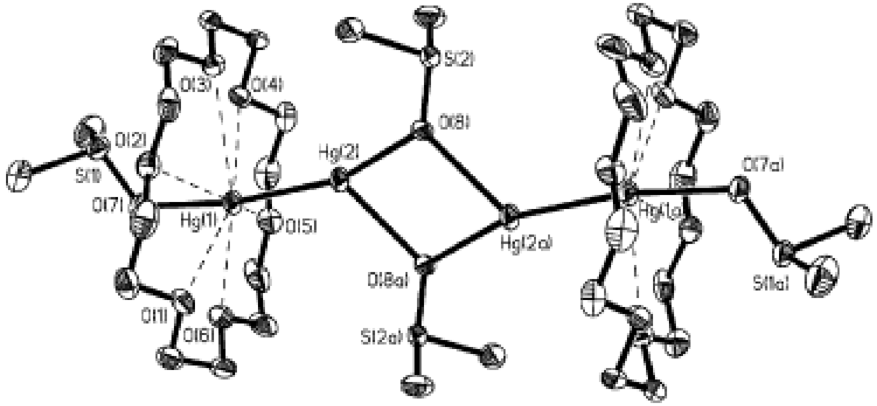


Fig. 1 Structure of $\{[Hg_2(18\text{-crown-}6)_2(Me_2SO)(\mu\text{-}Me_2SO)]\}_2^{4+}$ (cation of **2**). Thermal ellipsoids are shown at the 20% probability level.

$^{1}J(^{199}Hg\text{-}^{199}Hg)$ =

263 200 Hz in CD_2Cl_2
284 100 Hz in MeOH

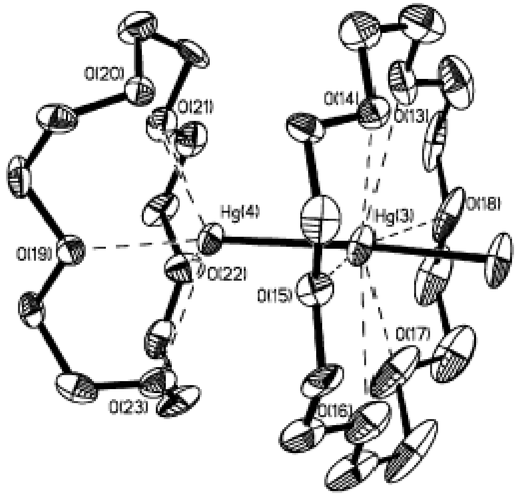
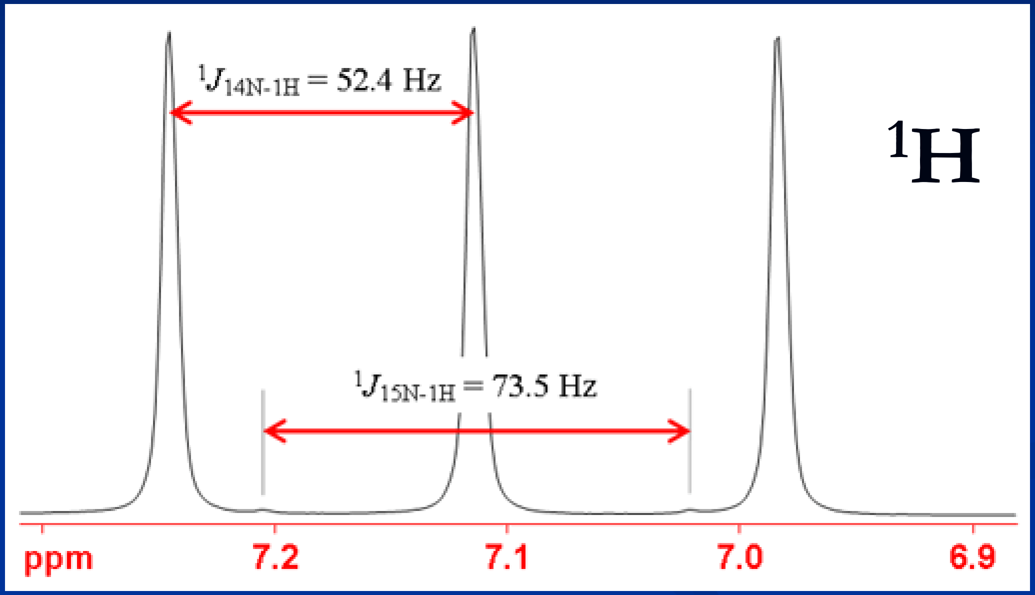


Fig. 2 Structure of $\{[Hg_2(18\text{-crown-}6)(15\text{-crown-}5)(H_2O)]^{2+}$ (part of **3c**). Thermal ellipsoids are shown at the 20% probability level.

Dependence of J on Magnetogyric Ratio



^{1}H spectrum of natural abundance NH_4Cl (1.5 M) in 1M HCl/H_2O

- coupling to ^{14}N (I = 1) – a triplet (1:1:1)
- coupling to ^{15}N – a weak doublet

The ^{14}N coupling constant is smaller than that of ^{15}N WHY??

Dependence on Magnetogyric Ratio

For the same elements, different nuclides

$J_{AB} \sim \gamma_A\ \gamma_B\ s_A{}^2(0)\ s_B{}^2(0)\ (\Delta E)^{-1}\ \alpha_{AB}{}^2$

BH_4^-

$^1J(^{11}B - H) = 80$ Hz $\qquad \gamma(^{11}B) = 8.57\ 10^7$ rad $T^{-1}s^{-1}$

$^1J(^{10}B - H) = 28$ Hz $\qquad \gamma(^{10}B) = 2.87\ 10^7$ rad $T^{-1}s^{-1}$

Dependence on Magnetogyric Ratio

$$J(\text{A-B}) \sim \gamma_A\ \gamma_B\ s_A^{\,2}(0)\ s_B^{\,2}(0)\ (\Delta E)^{-1}\,\alpha_{AB}^{\ 2}$$

$$J(A-B) = \gamma_A \gamma_B F$$

$$J(A-B^*) = \gamma_A \gamma_{B^*} F$$

$$\frac{J(A-B)}{J(A-B^*)} = \frac{\gamma_B}{\gamma_{B^*}}$$

The nuclide with larger γ has larger coupling constant

Dependence on Magnetogyric Ratio

$$J_{AB} \sim \gamma_A \ \gamma_B \ s_A{}^2(0) \ s_B{}^2(0) \ (\Delta E)^{-1} \alpha_{AB}{}^2$$

compound	γ (X) 10^7 rad $T^{-1}s^{-1}$	$^1J(^{117}Sn - X)$ Hz	$^1J(^{119}Sn - X)$ Hz
$^nBu_3Sn - H$	26.7510	1505	1575
$^nBu_3Sn - D$	4.1064	231	242
$^nBu_3Sn - T$	28.5335	1610	1685

Effects of Electronegative Substituents

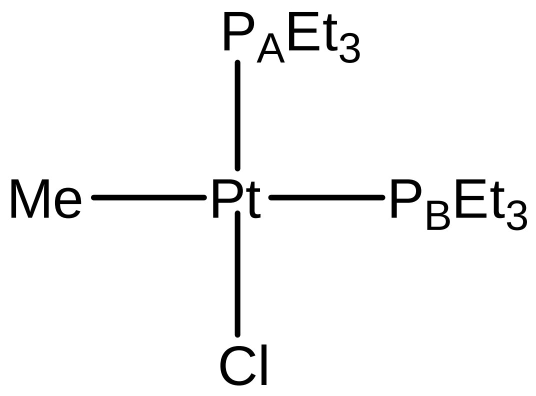
$$J_{AB} \sim \gamma_A \ \gamma_B \ s_A{}^2(0) \ s_B{}^2(0) \ (\Delta E)^{-1} \alpha_{AB}{}^2$$

1. Changes in hybridization: Bent's rule, more electronegative substituents prefer orbitals with more p-character. Remaining orbitals have more s-character - $\alpha_{AB}{}^2$, hence the J increases

2. Removal of electron density increases effective nuclear charge, contraction of e-cloud, s-density increases - $s_A{}^2(0)$, hence the J increases

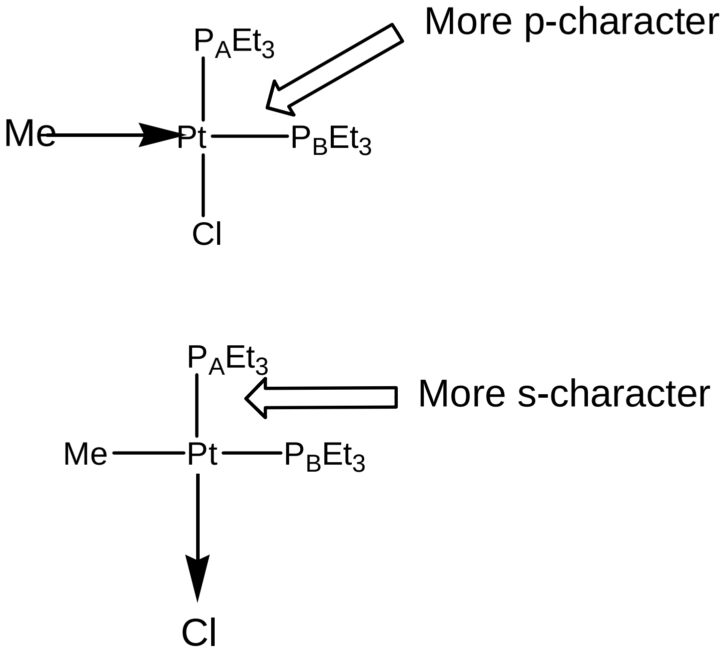
Effects of Electronegativity

$$J_{AB} \sim \gamma_A \ \gamma_B \ s_A{}^2(0)\ s_B{}^2(0)\ (\Delta E)^{-1}\ \alpha_{AB}{}^2$$



$^{1}J(^{195}Pt - P_A) = 4179$ Hz

$^{1}J(^{195}Pt - P_B) = 1719$ Hz

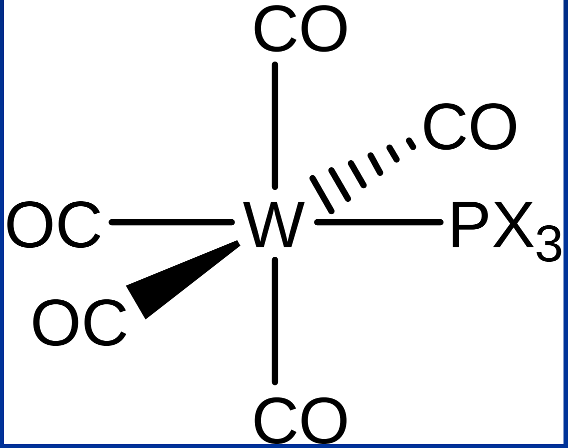


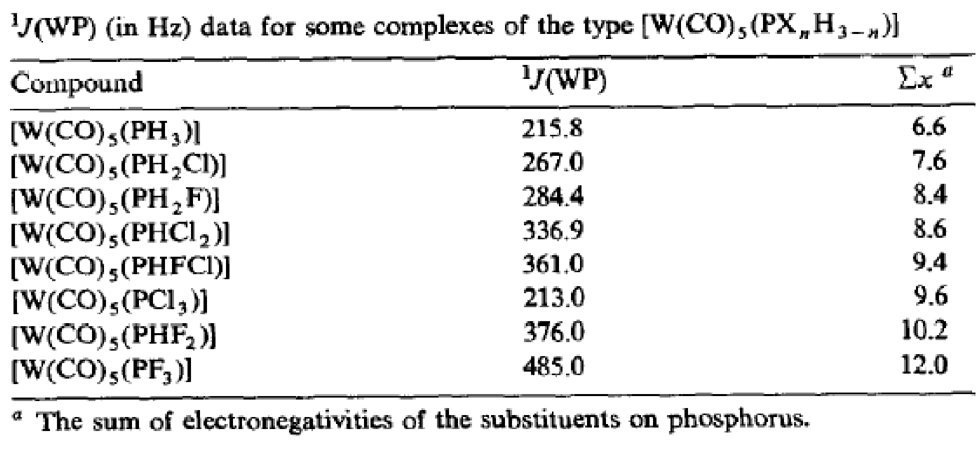
More p-character

More s-character

Effects of Electronegativity

J increases with increasing sum of substituent electronegativity

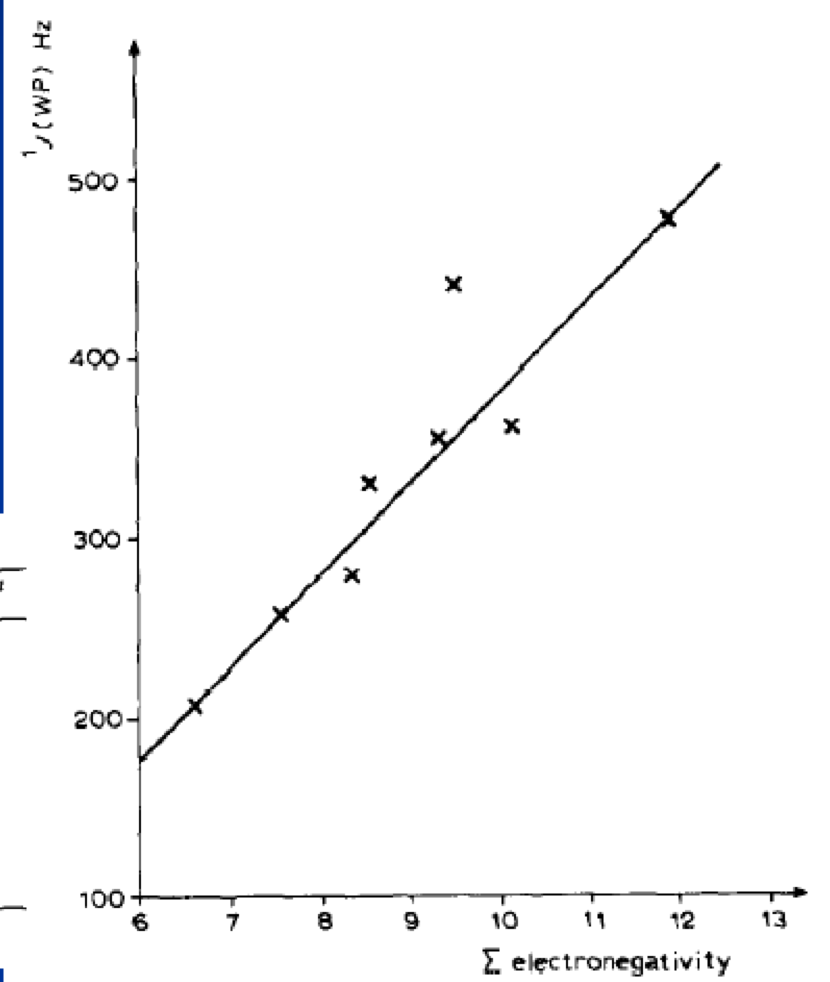




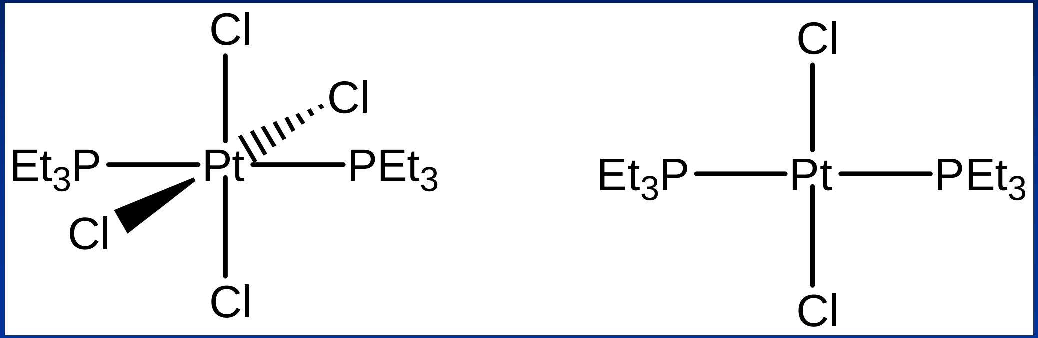
^1J(WP) (in Hz) data for some complexes of the type [$W(CO)_5(PX_nH_{3-n})$]

Compound	^1J(WP)	Σx [a]
[$W(CO)_5(PH_3)$]	215.8	6.6
[$W(CO)_5(PH_2Cl)$]	267.0	7.6
[$W(CO)_5(PH_2F)$]	284.4	8.4
[$W(CO)_5(PHCl_2)$]	336.9	8.6
[$W(CO)_5(PHFCl)$]	361.0	9.4
[$W(CO)_5(PCl_3)$]	213.0	9.6
[$W(CO)_5(PHF_2)$]	376.0	10.2
[$W(CO)_5(PF_3)$]	485.0	12.0

[a] The sum of electronegativities of the substituents on phosphorus.



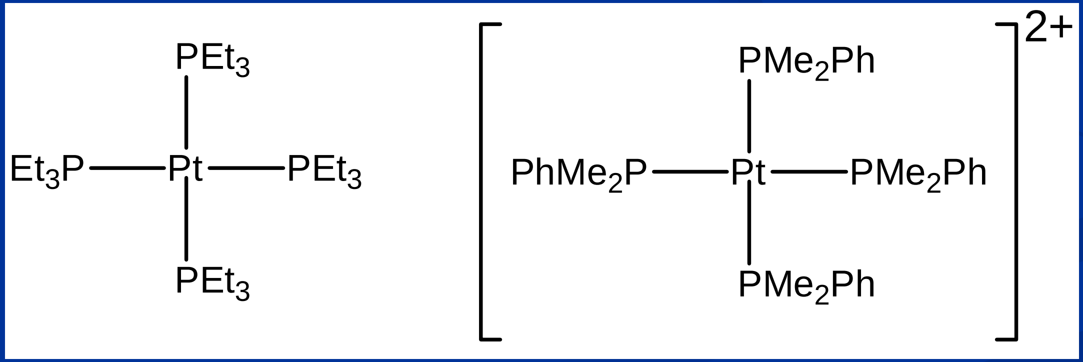
Effects of Coordination Number



$^{1}J(^{195}Pt - P) = 1455$ Hz

$^{1}J(^{195}Pt - P) = 2397$ Hz

Increasing coordination number results in decreasing J



$^{1}J(^{195}Pt - P) = 3740$ Hz

$^{1}J(^{195}Pt - P) = 2342$ Hz

Effects of Coordination Number

	$[Cp_2WH_2]$	$[Cp_2WH_3]^+$
$^1J(^{183}W - H) =$	73.2 Hz	47.8 Hz

Increasing coordination number results in decreasing J

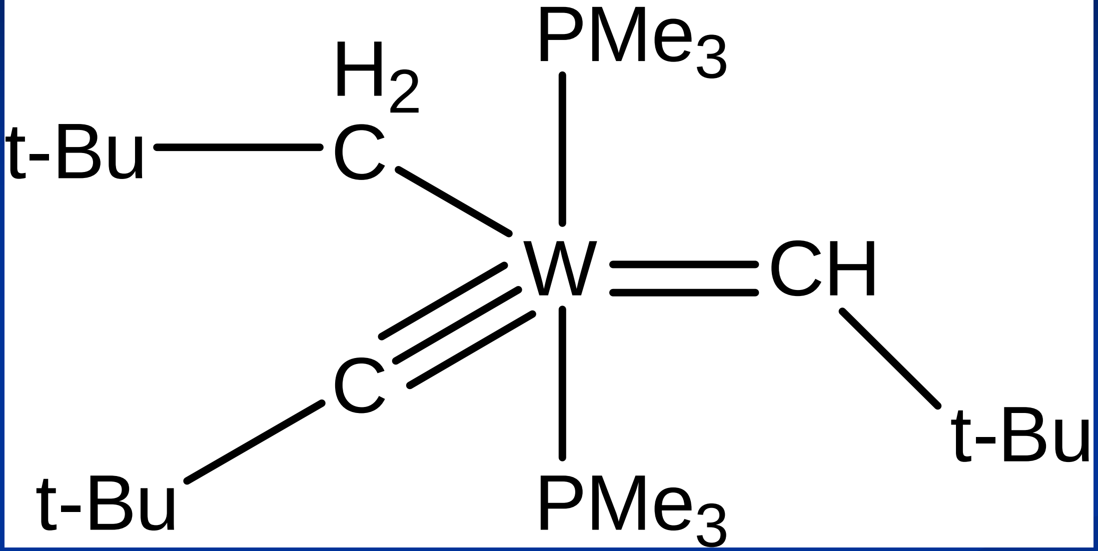
Effects of s-Character

$$^{1}J(P-X)=A\frac{\%s(P)\%s(X)}{1-s^{2}(P-X)}+B$$

s^2 (P-X) = overlap integral in the P-X bond

^{1}J(P - X) decreases with increasing coordination number and oxidation state

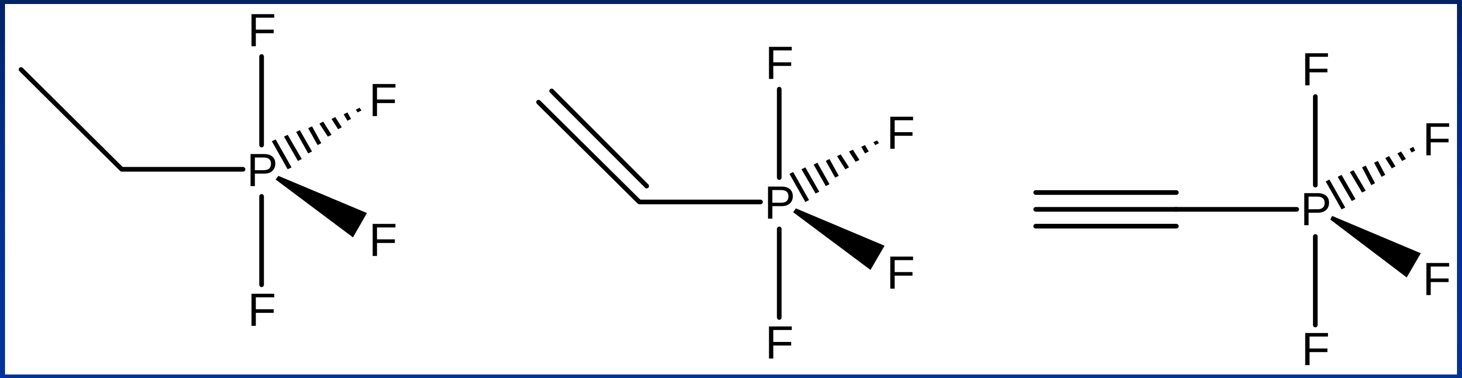
Effects of s-Character



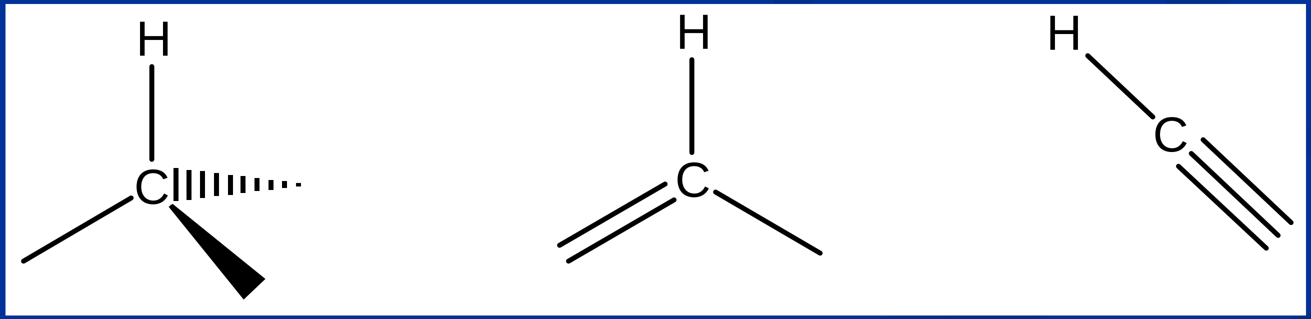
W oxidation state
Point group
Coupling C-H, P-C

Group	hybridization	$^1J(^{183}W - ^{13}C)$, Hz
alkyl	sp^3	80
alkylidene	sp^2	120
alkylidyne	sp	210

Effects of s-Character

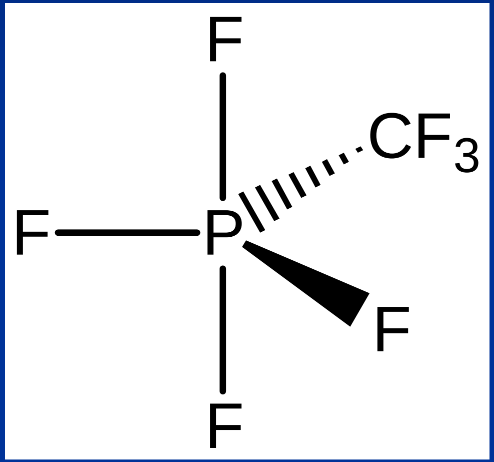


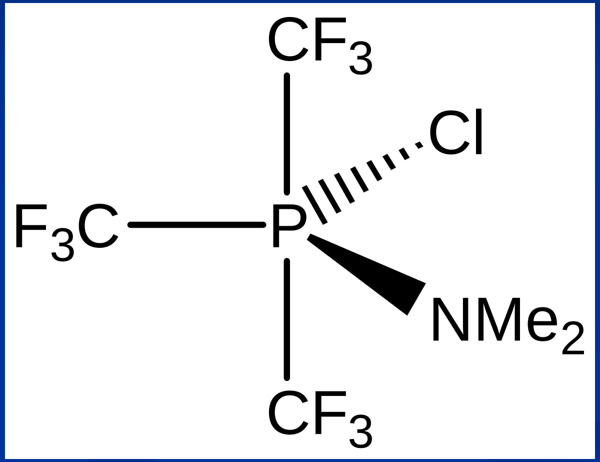
$^{1}J(^{31}P - C)$ = 189.2 Hz 261.1 Hz 476.0 Hz



$^{1}J(^{13}C - H)$ = 120 Hz 160 Hz 250 Hz

Effects of s-Character





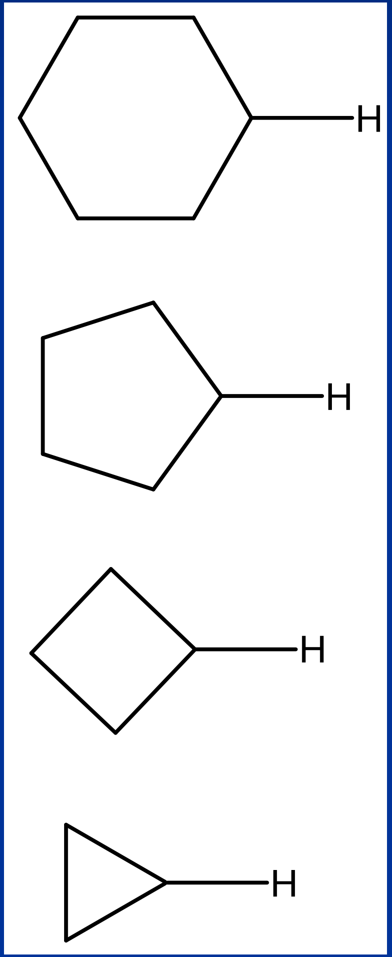
$^{1}J(\text{P-F}_{\text{axial}}) = 777$ Hz

$^{1}J(\text{P-F}_{\text{equat}}) = 966$ Hz

$^{2}J(\text{P-F}_{\text{axial}}) = 53$ Hz

$^{2}J(\text{P-F}_{\text{equat}}) = 130$ Hz

Effects of s-Character



^1J (C-H), Hz

123

130

134

161

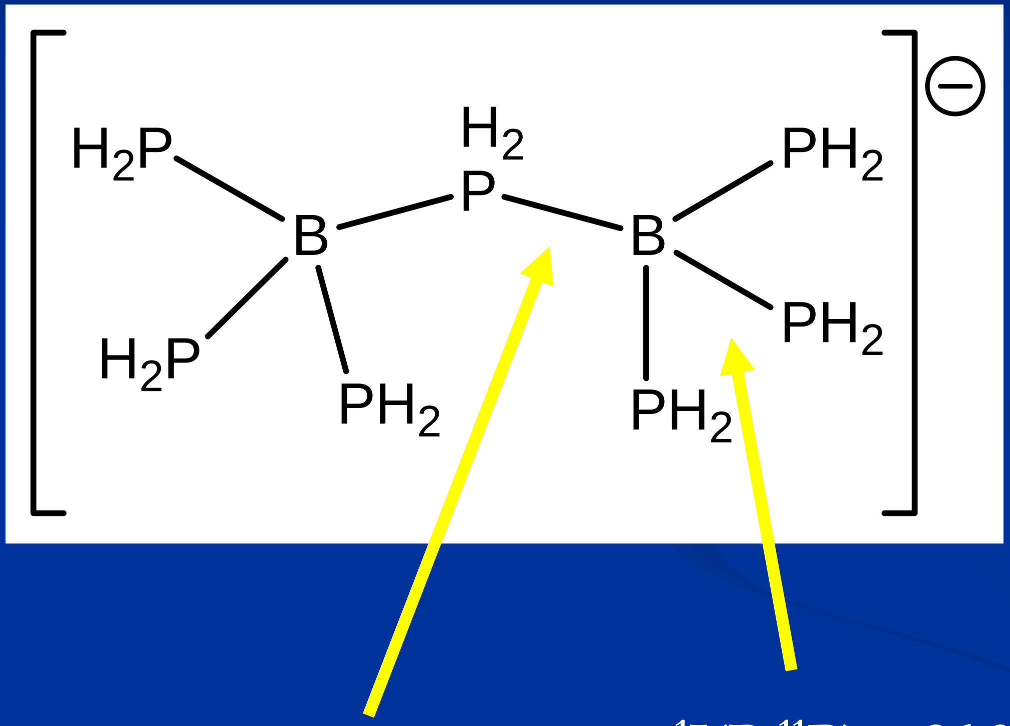
Increasing J

Intraring angle decreases

More p-character in C-C

More s-character in C-H

Effects of s-Character

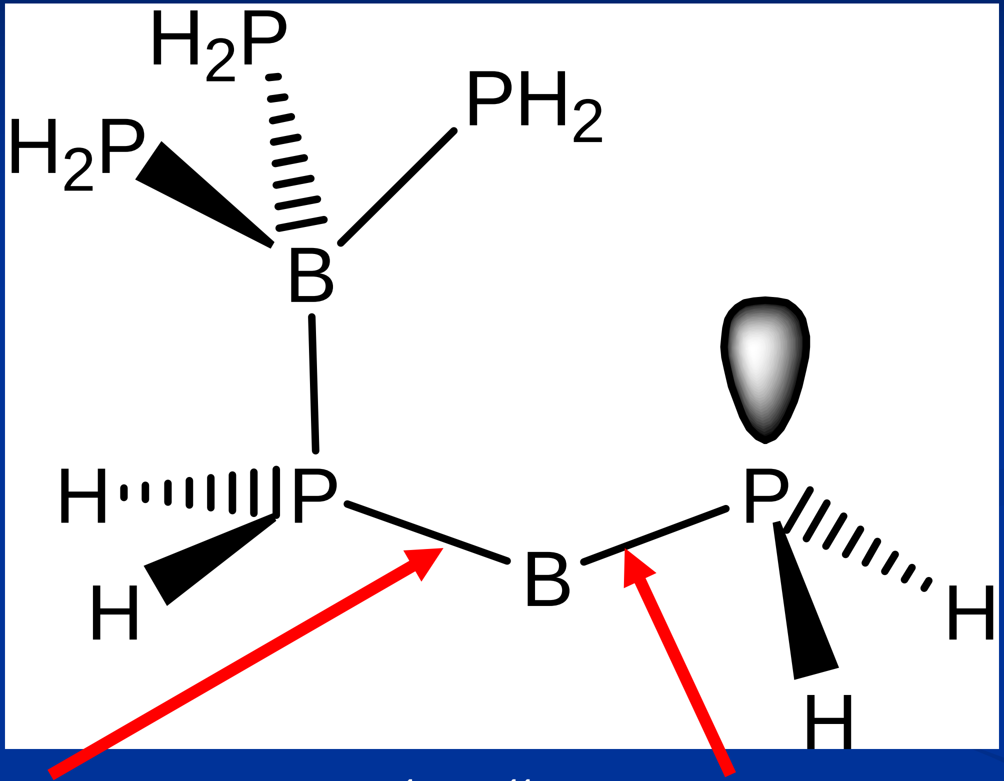


$^1J(P\text{-}^{11}B) = 56.9$ Hz

$^1J(P\text{-}^{11}B) = 26.3$ Hz

Explain the difference

Effects of s-Character



$^1J(P\text{-}^{11}B) = 56.9$ Hz

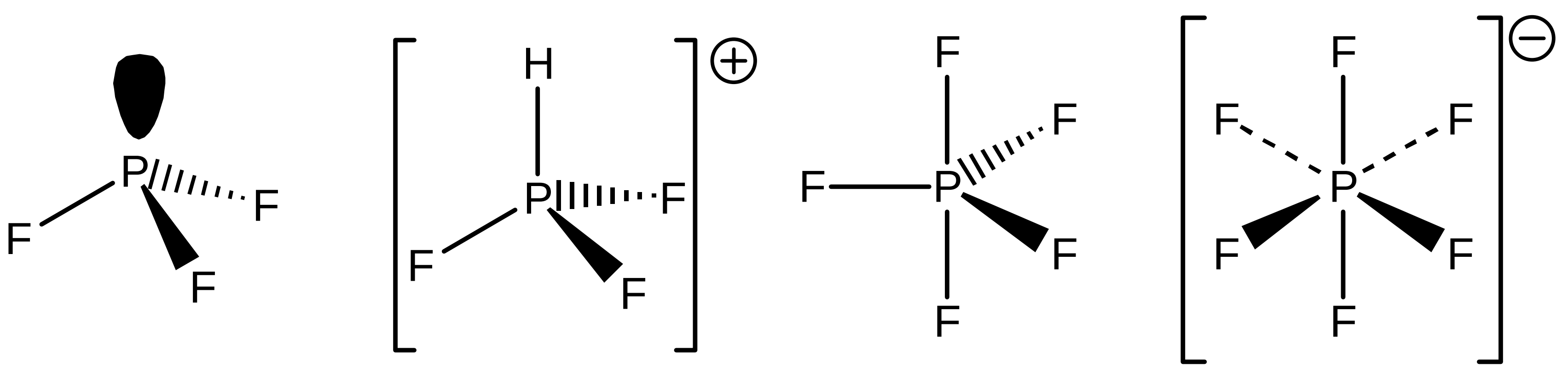
$^1J(P\text{-}^{11}B) = 26.3$ Hz

Lone pair = substituent with zero electronegativity

Resides in orbital with large s-character

Effects of Coordination Number

$^1J(^{31}P - F)$ negative



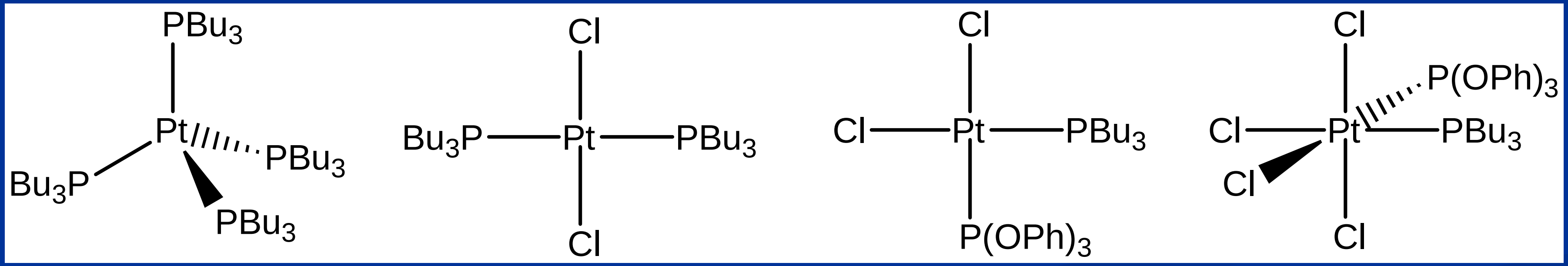
–1400 Hz –1109 Hz –1080 Hz –706 Hz

Increasing coordination number results in decreasing J

Dilution of s-character into more bonds

Effects of Oxidation State

$^{1}J\,(^{195}\mathrm{Pt} - {}^{31}\mathrm{P})$

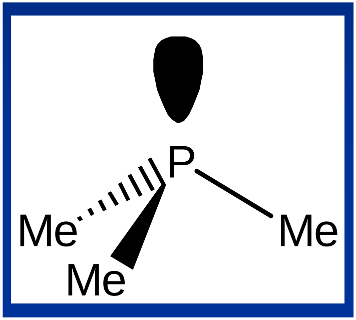
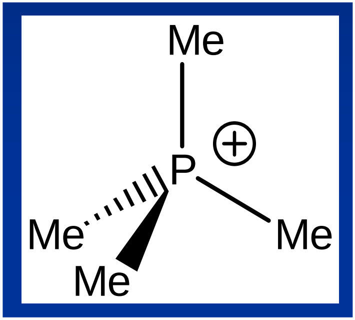
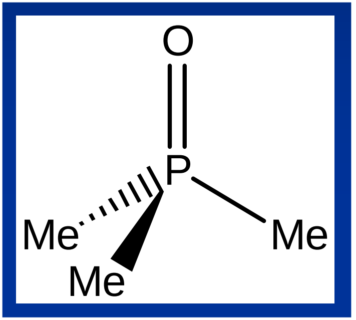
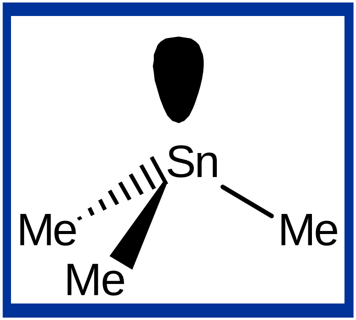
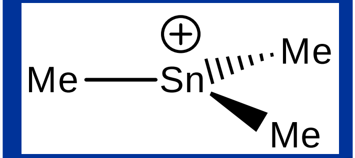
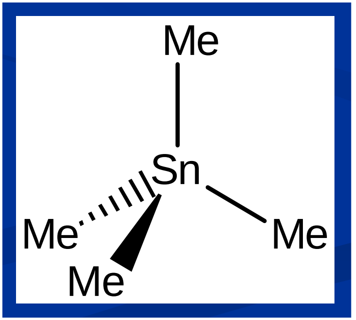


3740 Hz	2411 Hz	Bu	3159	1921
		OPh	6304	4060

Increasing oxidation state results in decreasing J

Decreasing electron density

Information from signs of K_{AB}

	P^{III}	P^{V}	P^{V}
lp changes sign			
$^{1}J(P - C)$	–14	56	68
	Sn^{II}	Sn^{IV}	Sn^{IV}
			
$^{1}J(Sn - C)$	155	–380	–339

Angle Dependence

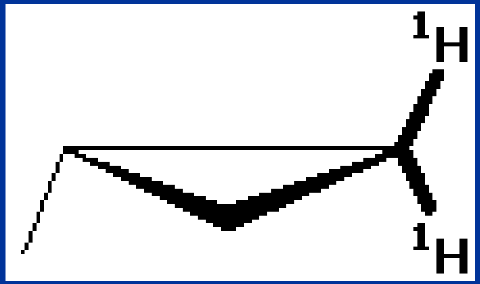
Two types of coupling are most affected by bond angles:

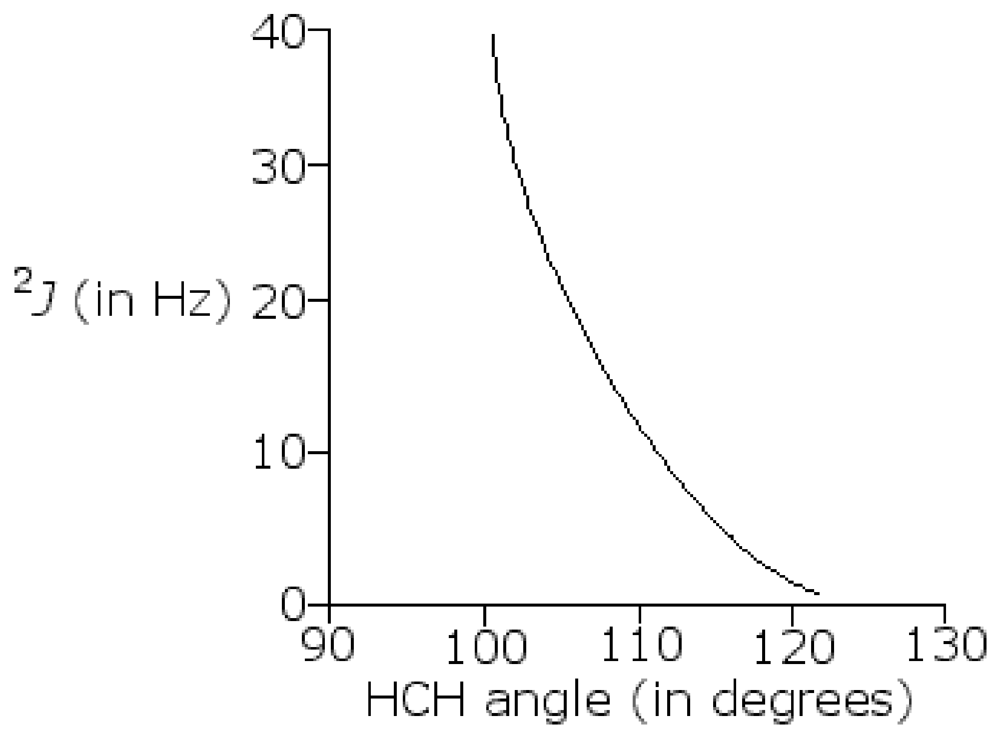
- **geminal coupling (two-bond coupling or ^{2}J)**
- **vicinal coupling (three-bond coupling or ^{3}J)**

Geminal Coupling

Geminal coupling or ^2J coupling is dependent upon the bond angle between the nuclei.

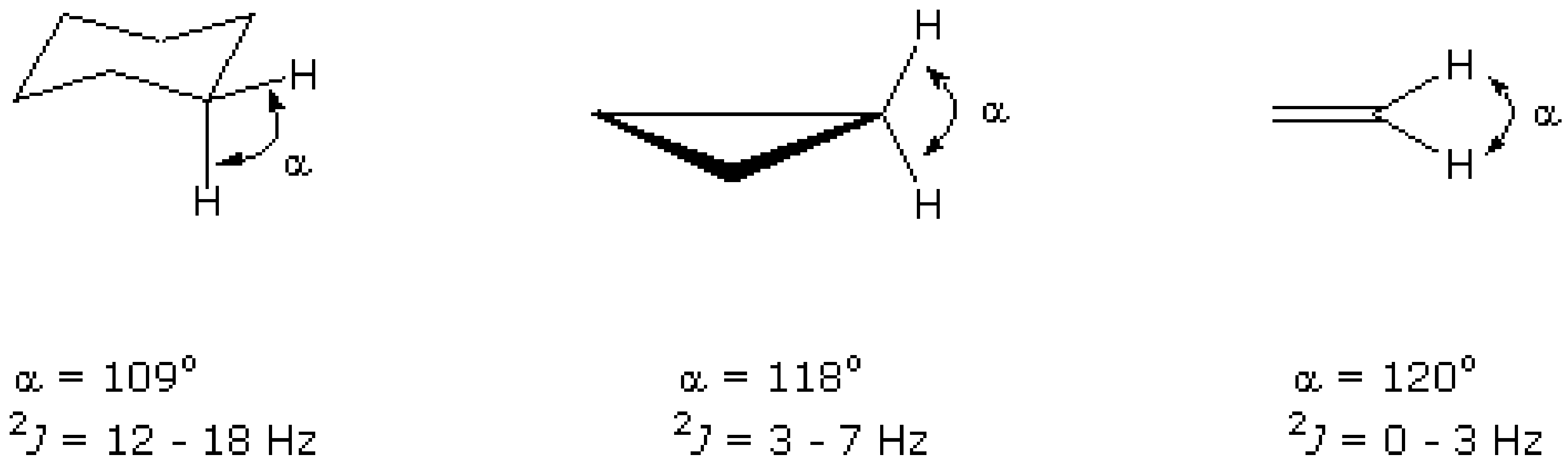
The smaller the angle the bigger the coupling constant.





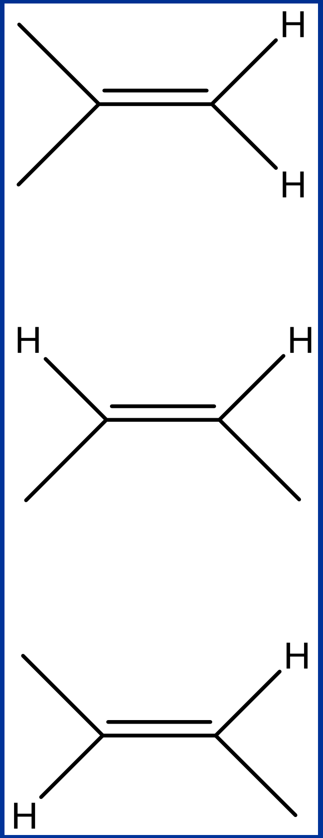
Geminal Coupling

$^{2}J\,(^{1}H - {}^{1}H)$



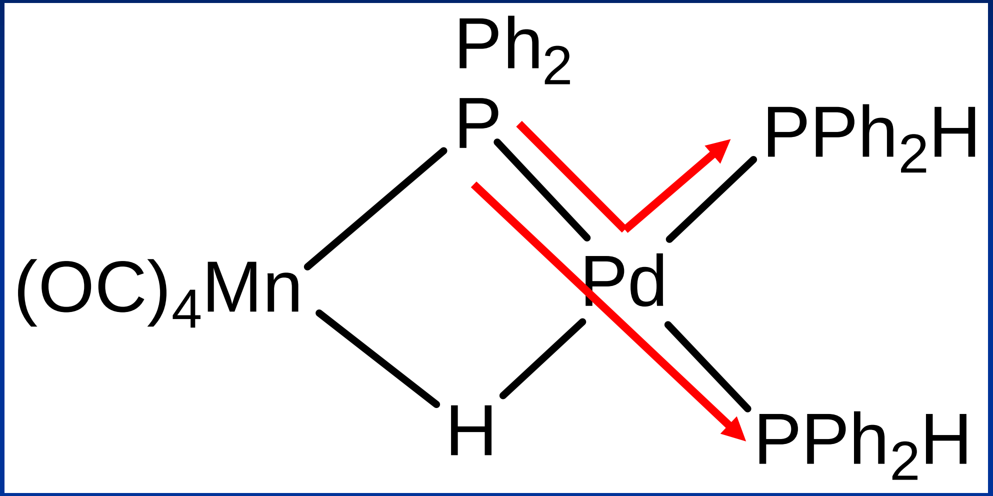
The smaller the angle the bigger the coupling constant.

Trans/Cis Coupling



	$^{n}J(^{1}H - ^{1}H)$, Hz
gem	0 – 3
vic cis	6 – 12
vic trans	12 – 18

Trans/Cis Coupling



$^{2}J\ (^{31}P\mu - Pd - {}^{31}P)$

cis	0 Hz
trans	213 Hz

Trans/Cis Coupling

$^{2}J\ (^{31}P - M - ^{31}P)$ cis < trans

Complex	Coord.	$^{2}J_{PP}$ cis, Hz	$^{2}J_{PP}$ trans, Hz
$PdCl_2(PMe_3)_2$	SP1	–8	610
$PtBr_2(PMe_3)_2$	SP1	–16	514
$Cr(CO)_4(PF_3)_2$	Oh	–36	–28
$Mo(CO)_4(PF_3)_2$	Oh	55	312
$Mo(CO)_4[P(NMe_2)_3]_2$	Oh	12	101
$W(CO)_4(PF_3)_2$	Oh	38	315
mer-$RhCl_3(PMe_3)_3$	Oh	–29	567

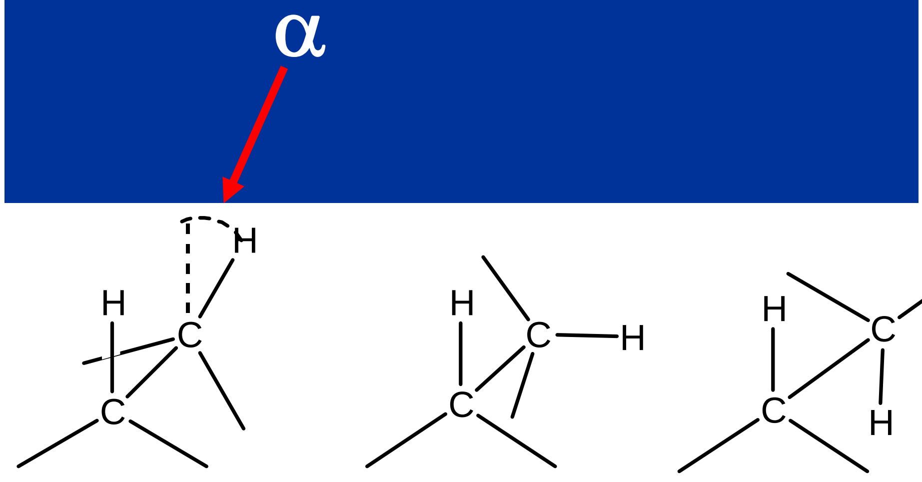
Vicinal Coupling

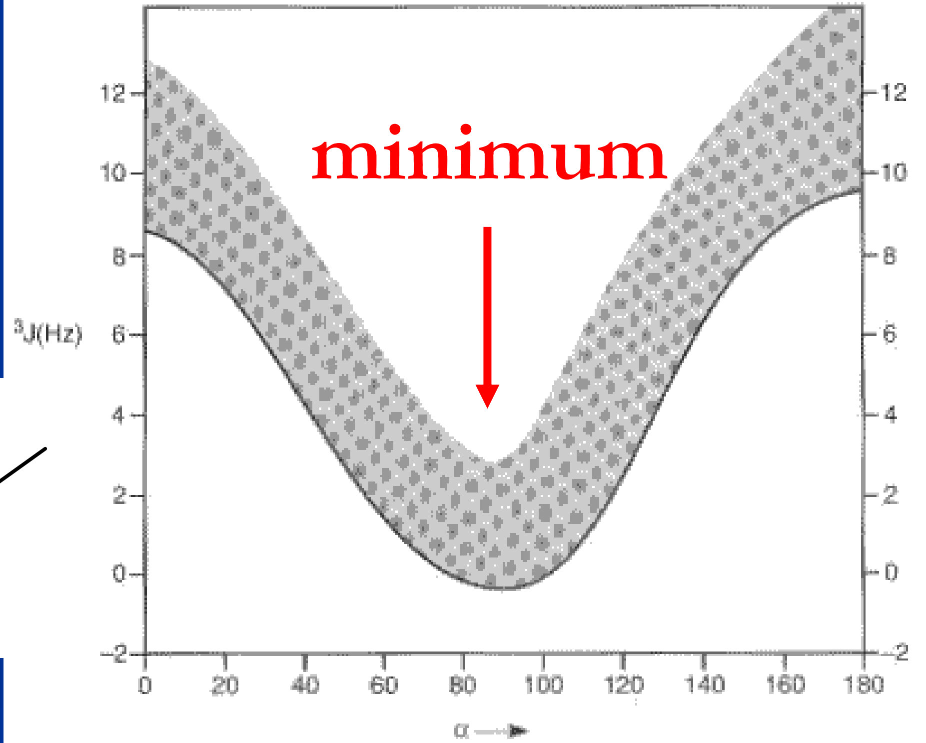
Vicinal coupling or ${}^3J$ coupling is dependent upon the dihedral angle between the nuclei.

The more eclipsed or antiperiplanar the nuclei the greater the coupling constant.

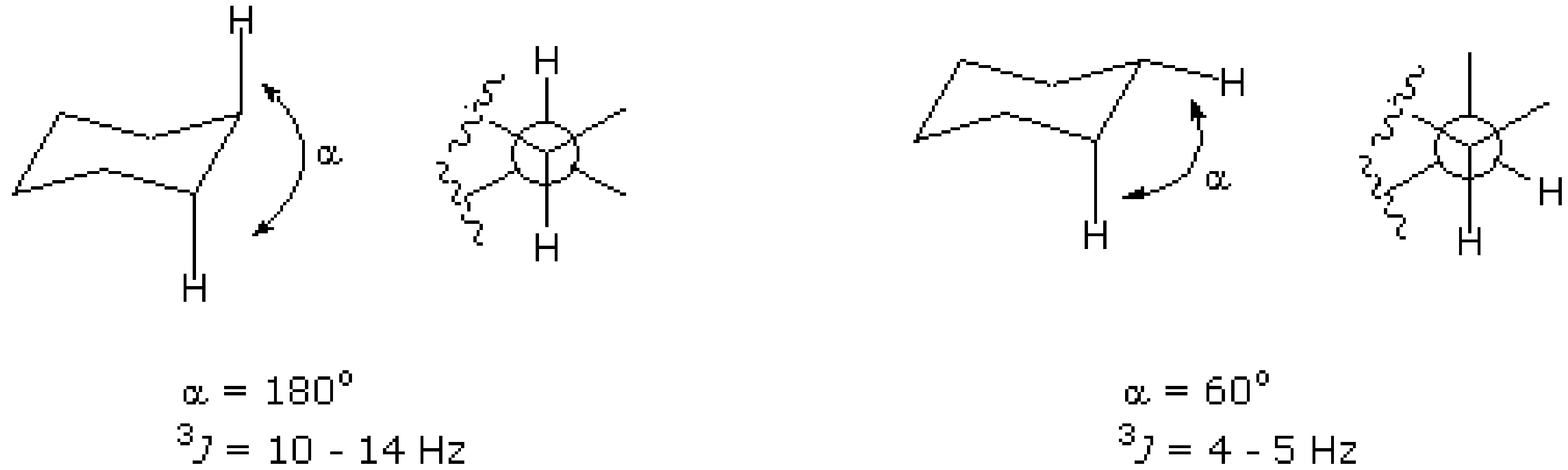
The relationship between dihedral angle and coupling constant is known as the **Karplus curve.**

$${}^3J = A + B\cos\alpha + C\cos^2\alpha$$





Vicinal Coupling



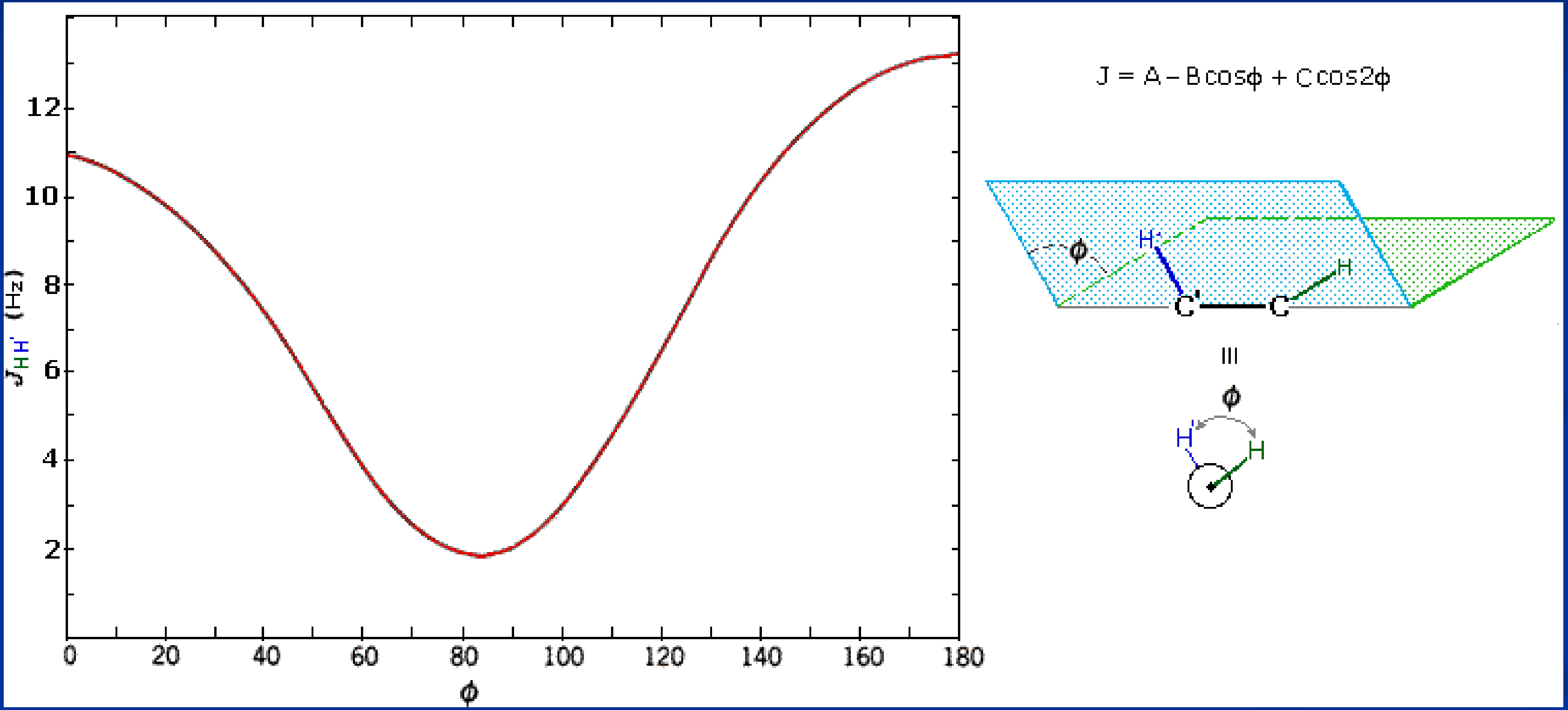
$\alpha = 180°$
$^3J = 10 - 14$ Hz

$\alpha = 60°$
$^3J = 4 - 5$ Hz

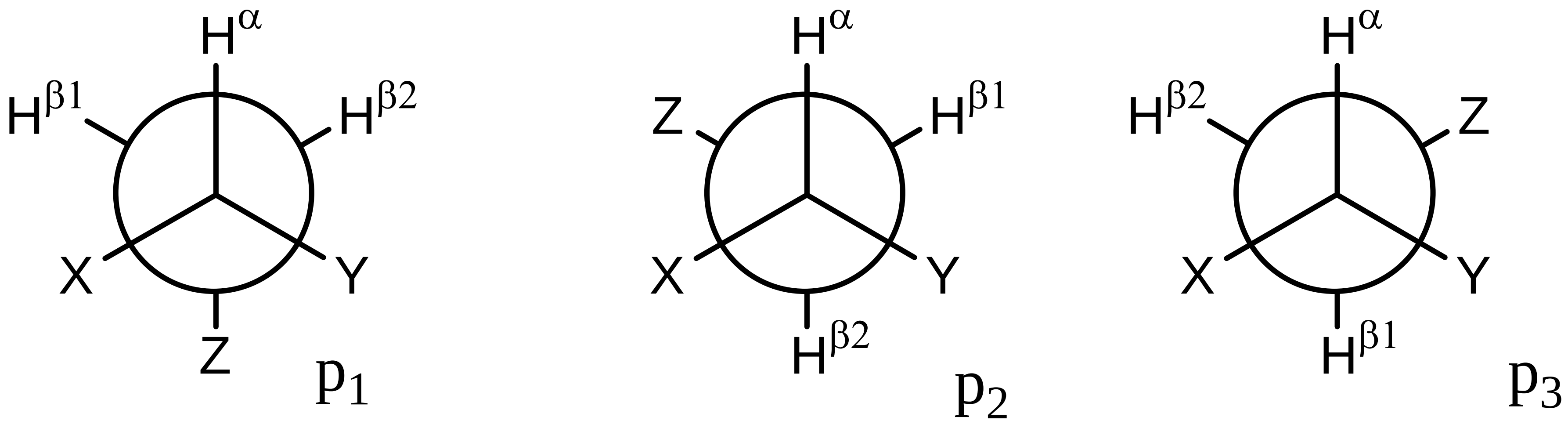
the Karplus equation

$$^3J = A + B\cos\alpha + C\cos^2\alpha$$

The Karplus Equation



Population Analysis



experiment

$$\langle J_{\alpha\beta1} \rangle = J_g p_1 + J_g p_2 + J_t p_3$$

$$\langle J_{\alpha\beta2} \rangle = J_g p_1 + J_t p_2 + J_g p_3$$

$$p_1 + p_2 + p_3 = 1$$

$$J_g(60^\circ) \longleftarrow$$

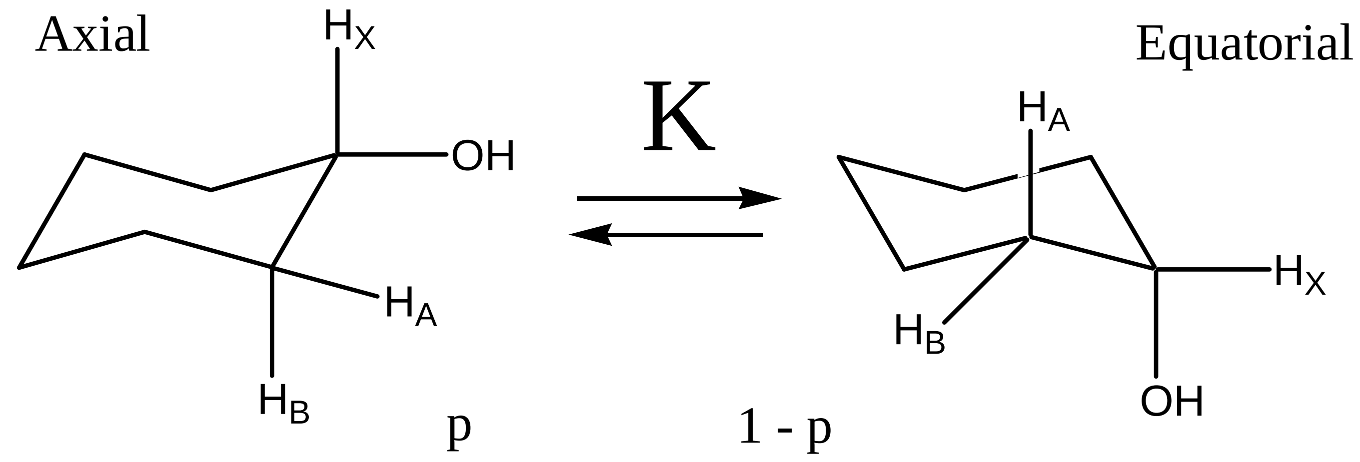
$$J_t(180^\circ) \longleftarrow$$

3 inequivalent protons
2 time-averaged vicinal J
(1 geminal J)

p_i = population of rotamers

g = gauche, t = trans
from independent
measurements

Population Analysis



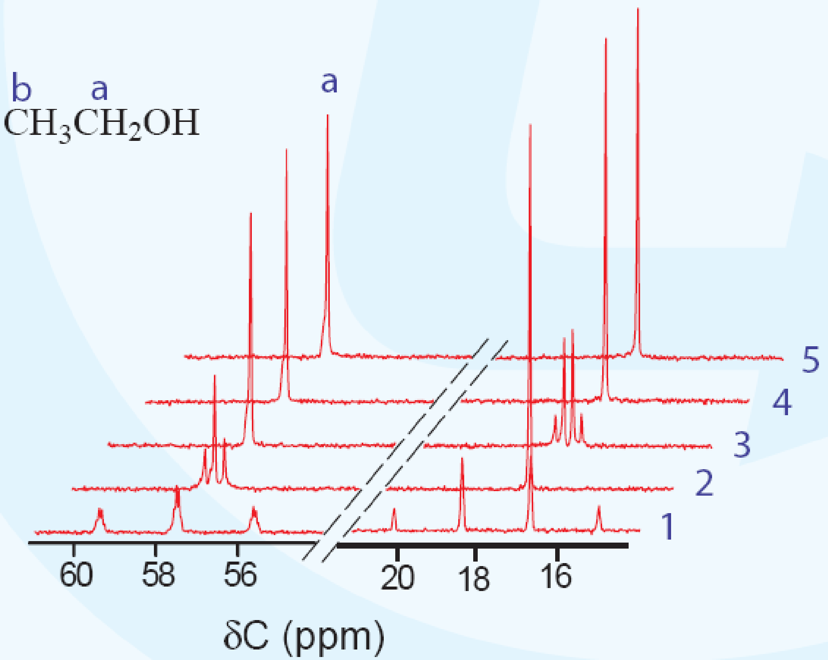
$$\langle J_{AX} \rangle = pJ_{AX}^{Axial} + (1-p)J_{AX}^{Equ}$$

$$\langle J_{BX} \rangle = pJ_{BX}^{Axial} + (1-p)J_{BX}^{Equ}$$

$$K = \frac{p}{1-p} = \exp\left(\frac{-\Delta G^0}{RT}\right)$$

Decoupling

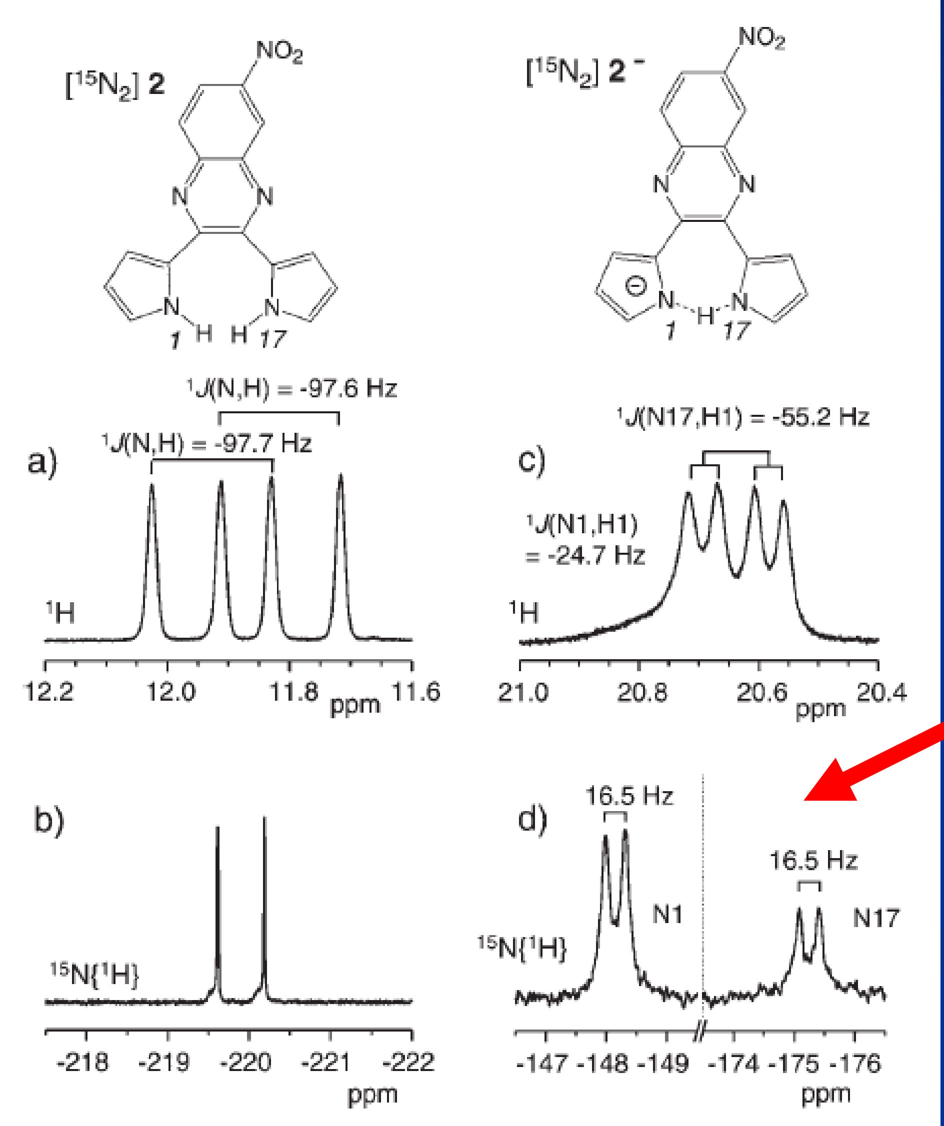
Heteronuclear broadband decoupling
Selective homonuclear decoupling



Spectrum	Dcp* method	Dcp freq.
1	- (no dcp)	-
2	cw	f (H_a)
3	cw	f (H_b)
4	WALTZ-16	f (H_a)
5	WALTZ-16	f (H_b)

(*: Dcp = Decoupling)

^{15}N–^{15}N Coupling Across an NHN Hydrogen Bond



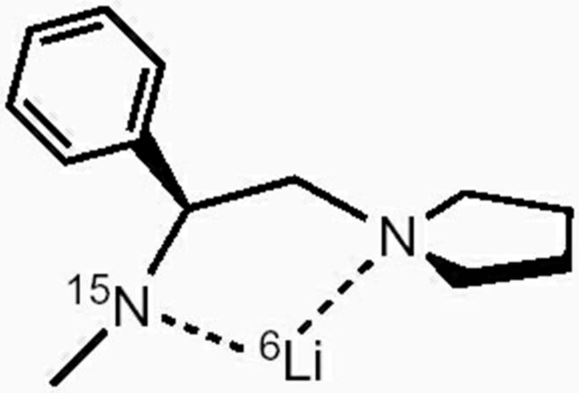
$CD_2Cl_2/[d_6]DMSO$ (5:1)

a) 233 K b) 233 K

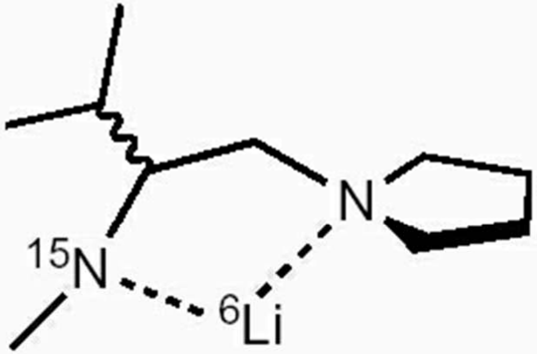
c) 193 K d) 193 K

$^2J(^{15}N–^{15}N) = 16.5$ Hz

^{6}Li–^{15}N Coupling



(*S*)-**1**



(*S*,*R*)-**2**

^{6}Li   I = 1   NA = 7.42 %

^{15}N   I = 1/2   NA = 0.37 %

^{6}Li–^{15}N Coupling

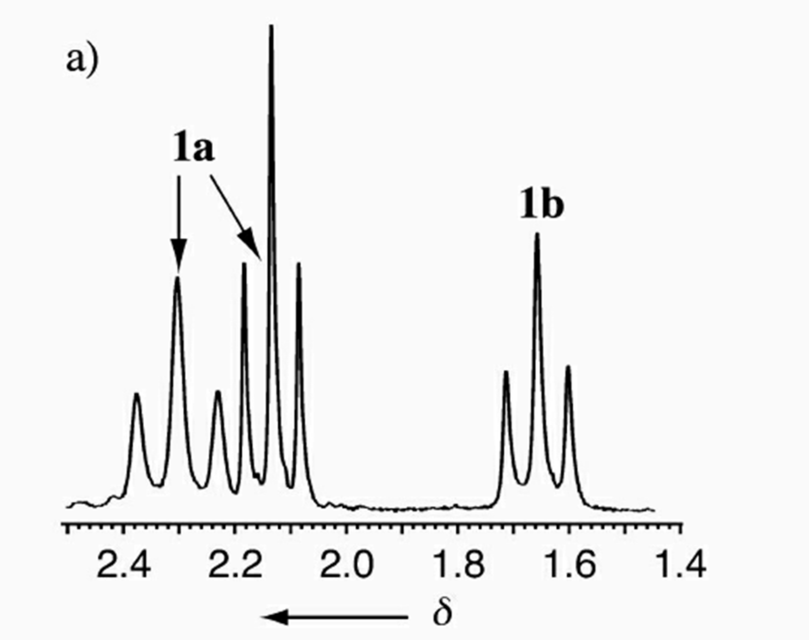
^{6}Li NMR:

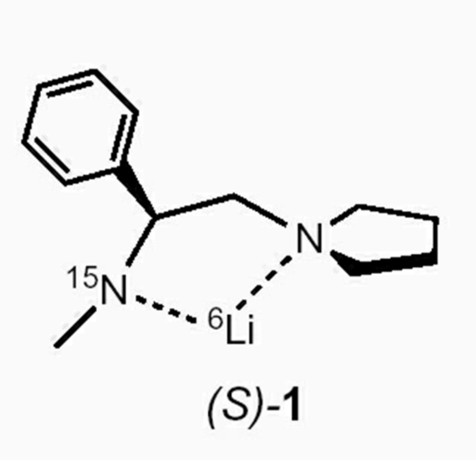
- **two triplets 1:1**

$\delta = 2.15$ ppm ($J_{LiN} = 3.7$ Hz)

$\delta = 2.32$ ppm ($J_{LiN} = 6.1$ Hz)

- **triplet $\delta = 1.63$ ppm ($J_{LiN} = 4.5$ Hz)**





(*S*)-**1**

^{6}Li–^{15}N Coupling

^{6}Li NMR:

- •two triplets 1:1 δ = 2.15 ppm (J_{LiN}= 3.7 Hz) a δ = 2.32 ppm (J_{LiN}= 6.1 Hz)
- •triplet δ = 1.63 ppm (J_{LiN}= 4.5 Hz)