

## **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

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

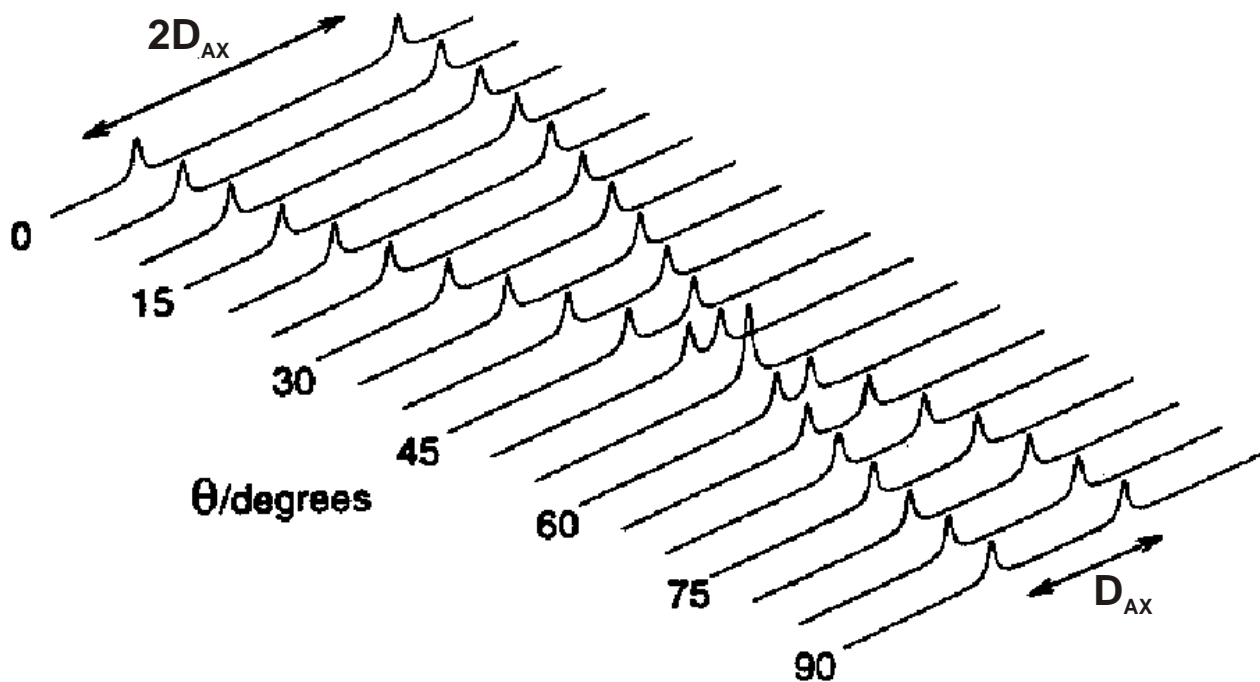
# Dipolar Coupling

Dipolar coupling constant

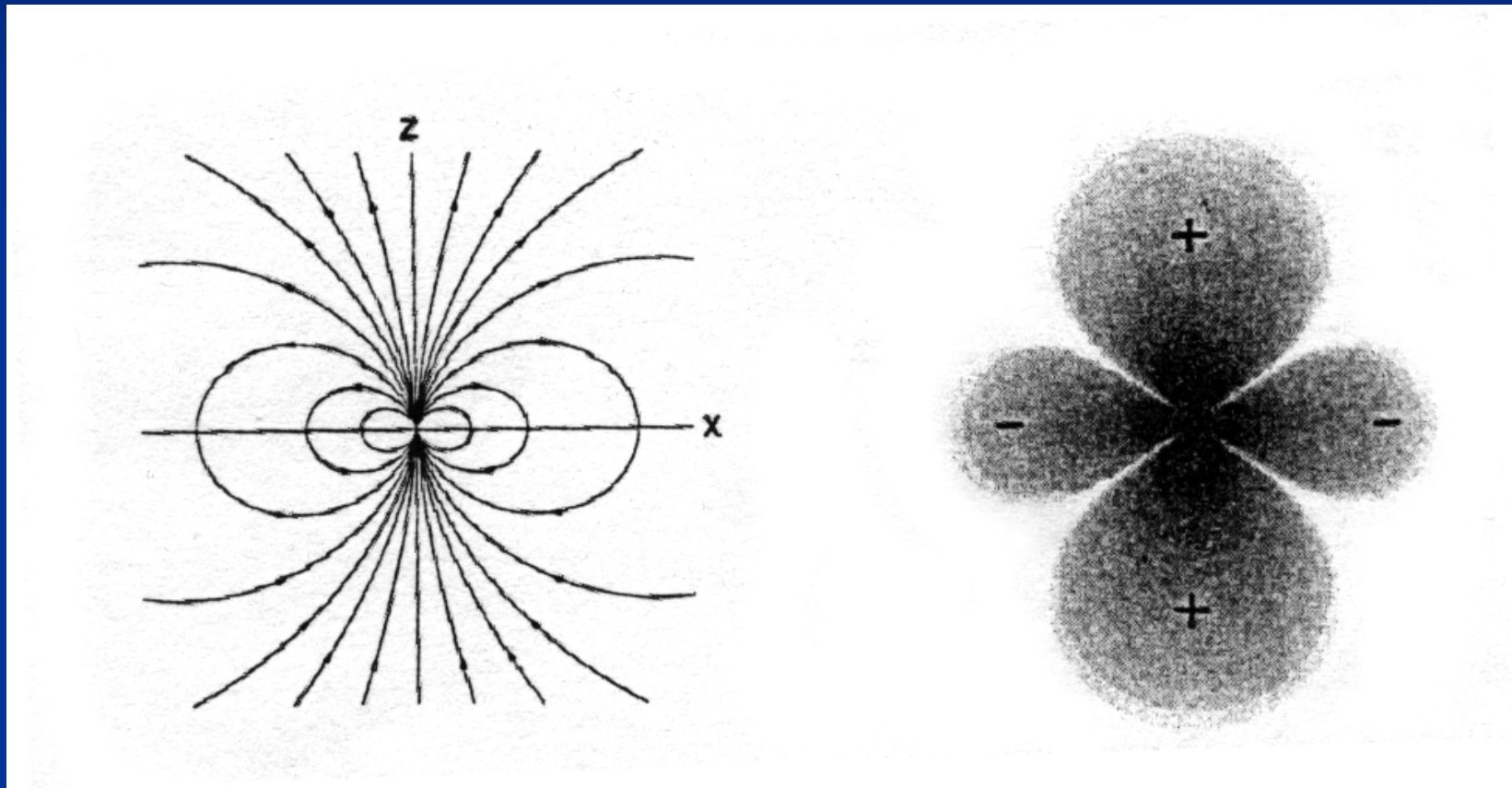
$$D_{AX} \sim h \gamma_A \gamma_X r_{AX}^{-3}$$

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

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



# 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

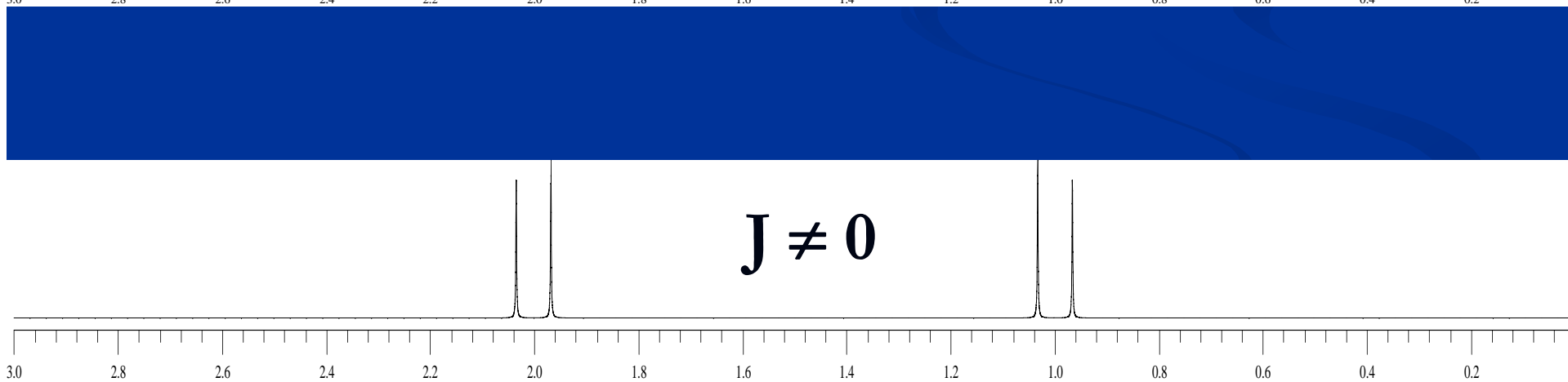
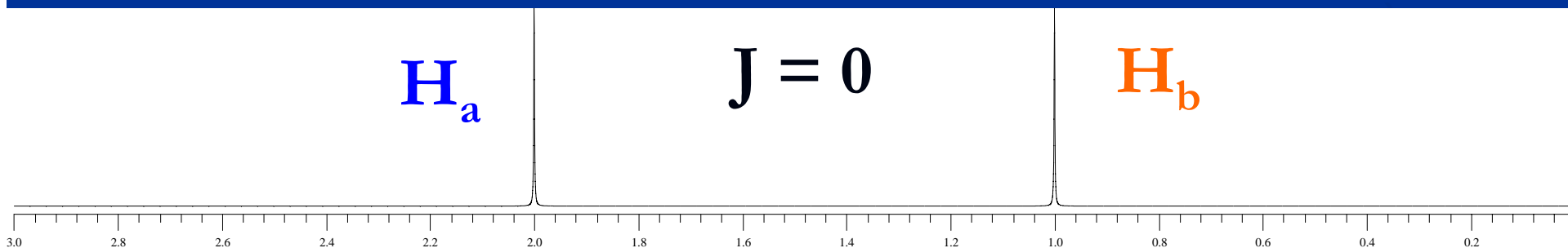
# Scalar (Spin-Spin) Coupling

The simplest case:

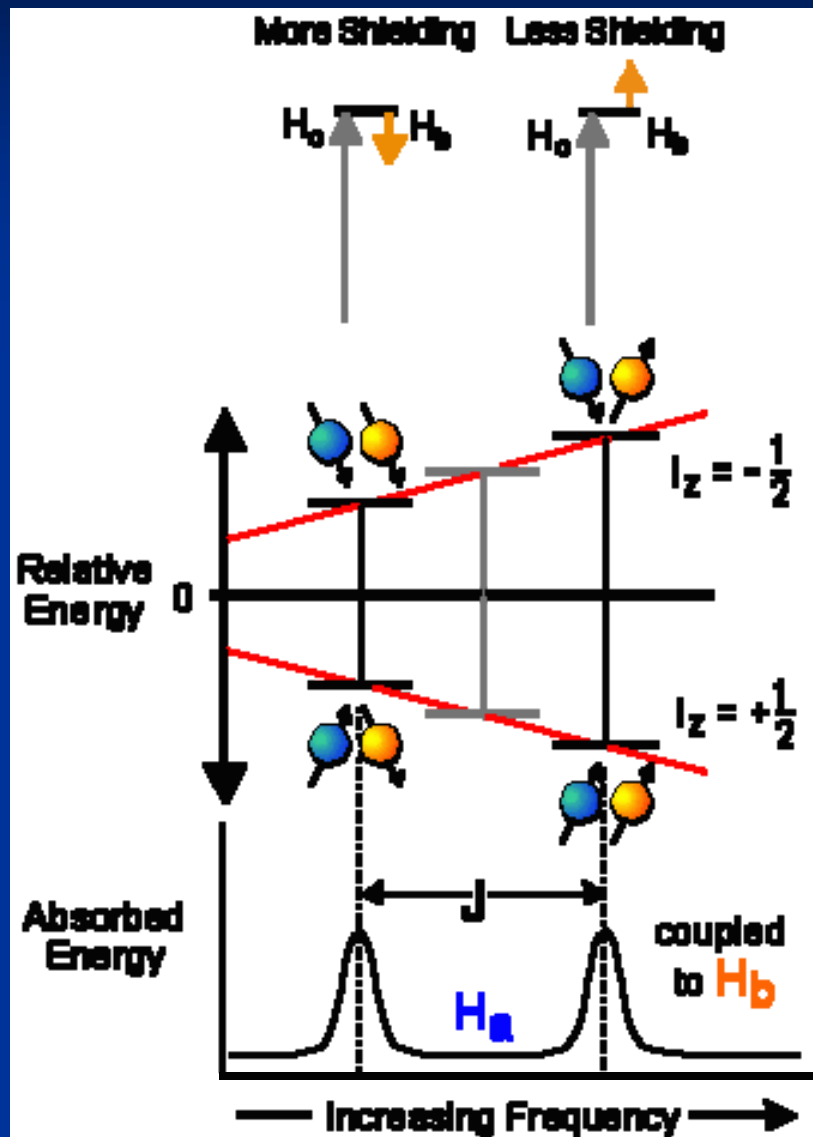
Two magnetically active nuclei

Interacting through bonds (see each other)

Both spins  $I = 1/2$



# Scalar Coupling



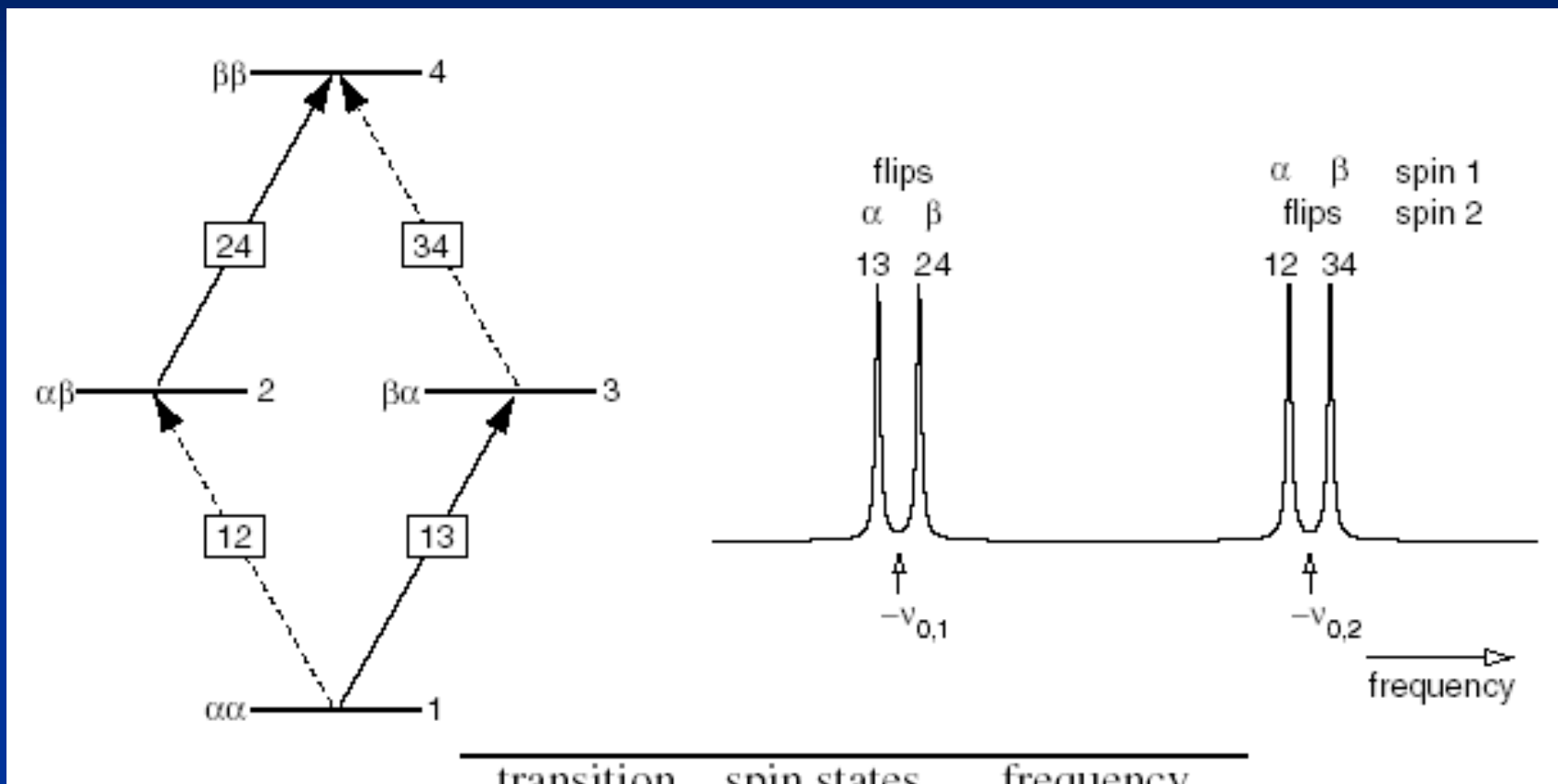
A splitting of a signal = more energy levels involved in the transitions

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  $H_a$

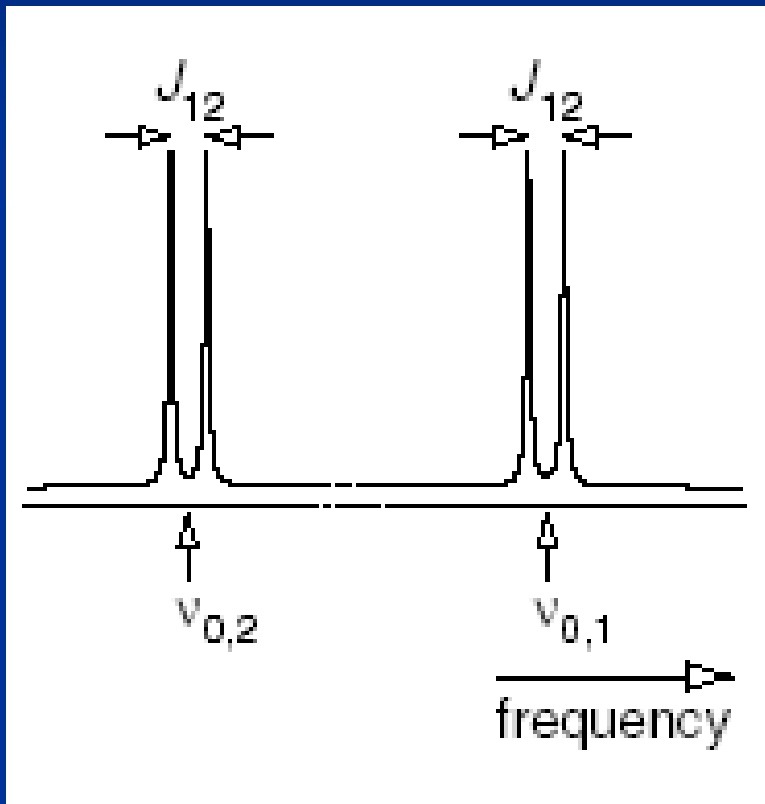
# Two Spins $I = \frac{1}{2}$



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

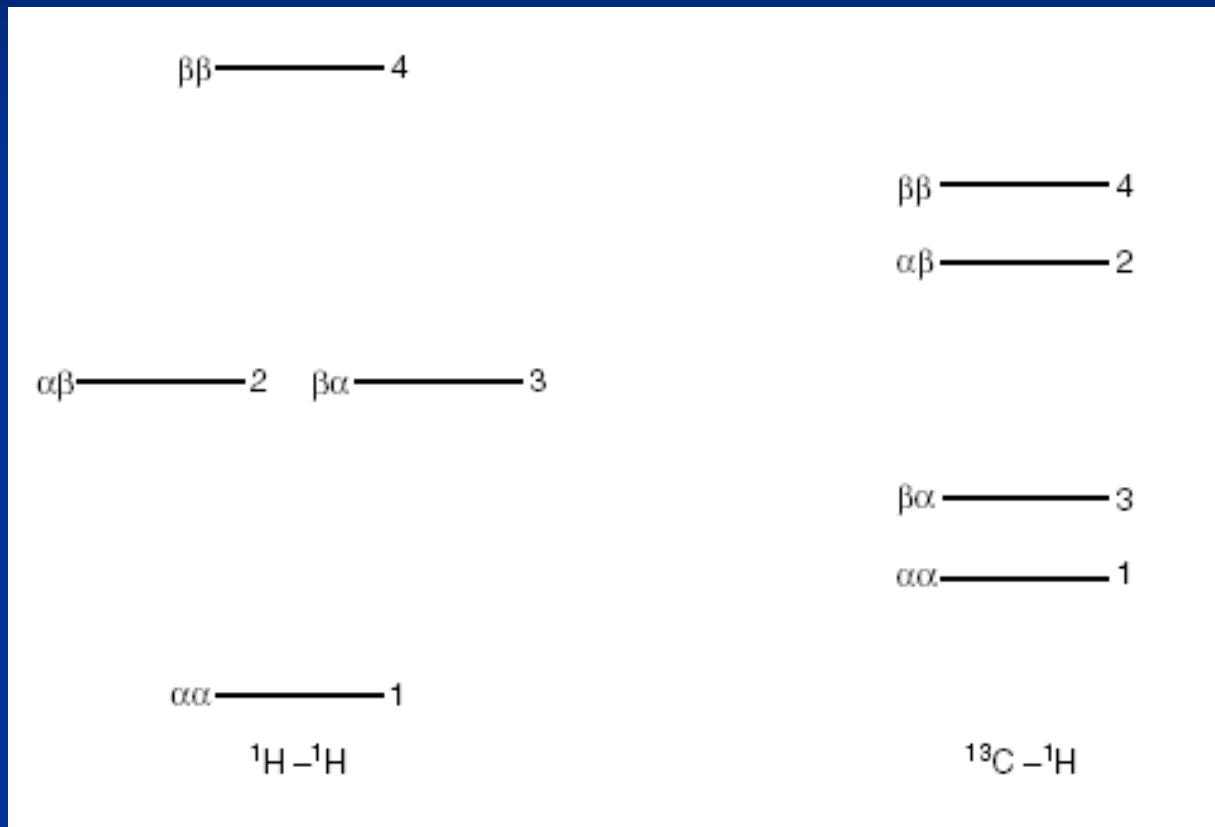


# Two Spins $I = \frac{1}{2}$

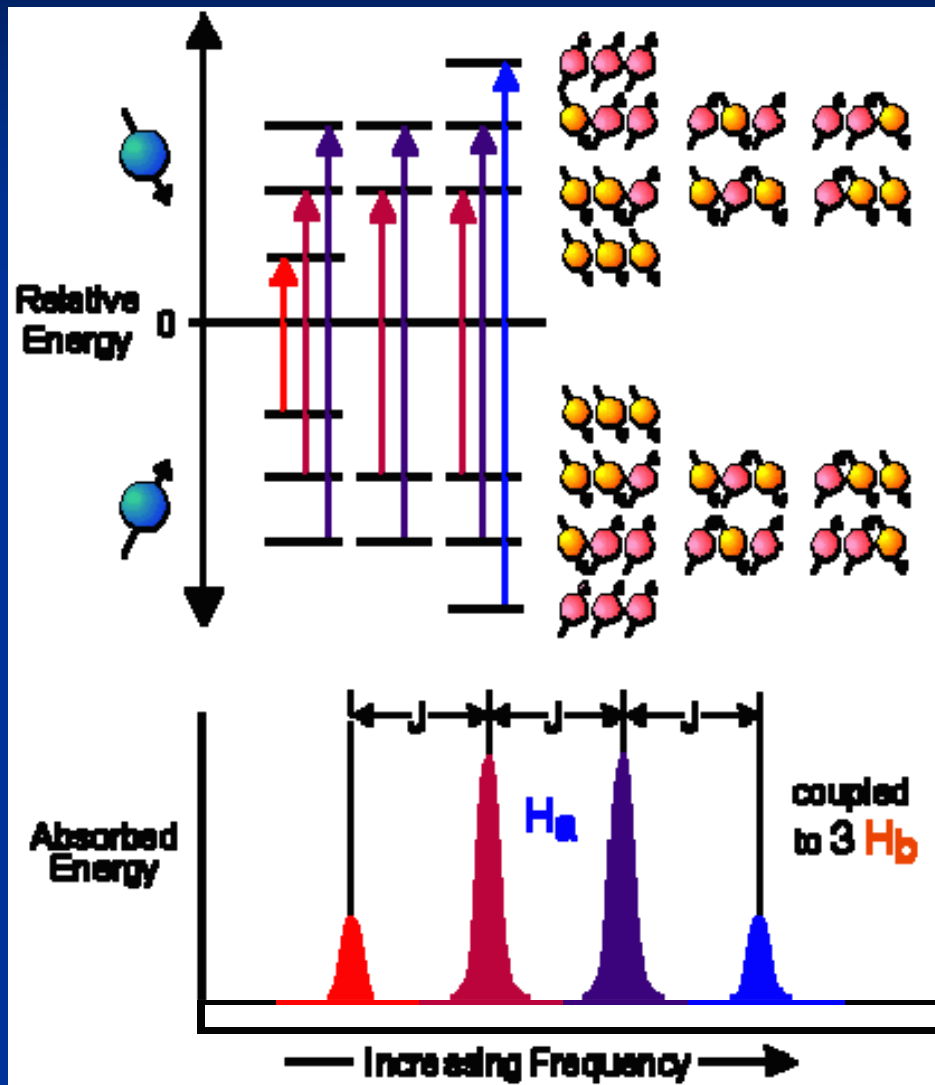


transition	spin states	frequency
$1 \rightarrow 2$	$\alpha\alpha \rightarrow \alpha\beta$	$-\nu_{0,2} - \frac{1}{2}J_{12}$
$3 \rightarrow 4$	$\beta\alpha \rightarrow \beta\beta$	$-\nu_{0,2} + \frac{1}{2}J_{12}$
$1 \rightarrow 3$	$\alpha\alpha \rightarrow \beta\alpha$	$-\nu_{0,1} - \frac{1}{2}J_{12}$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

# Homo vs. Hetero Coupling



# Scalar Coupling

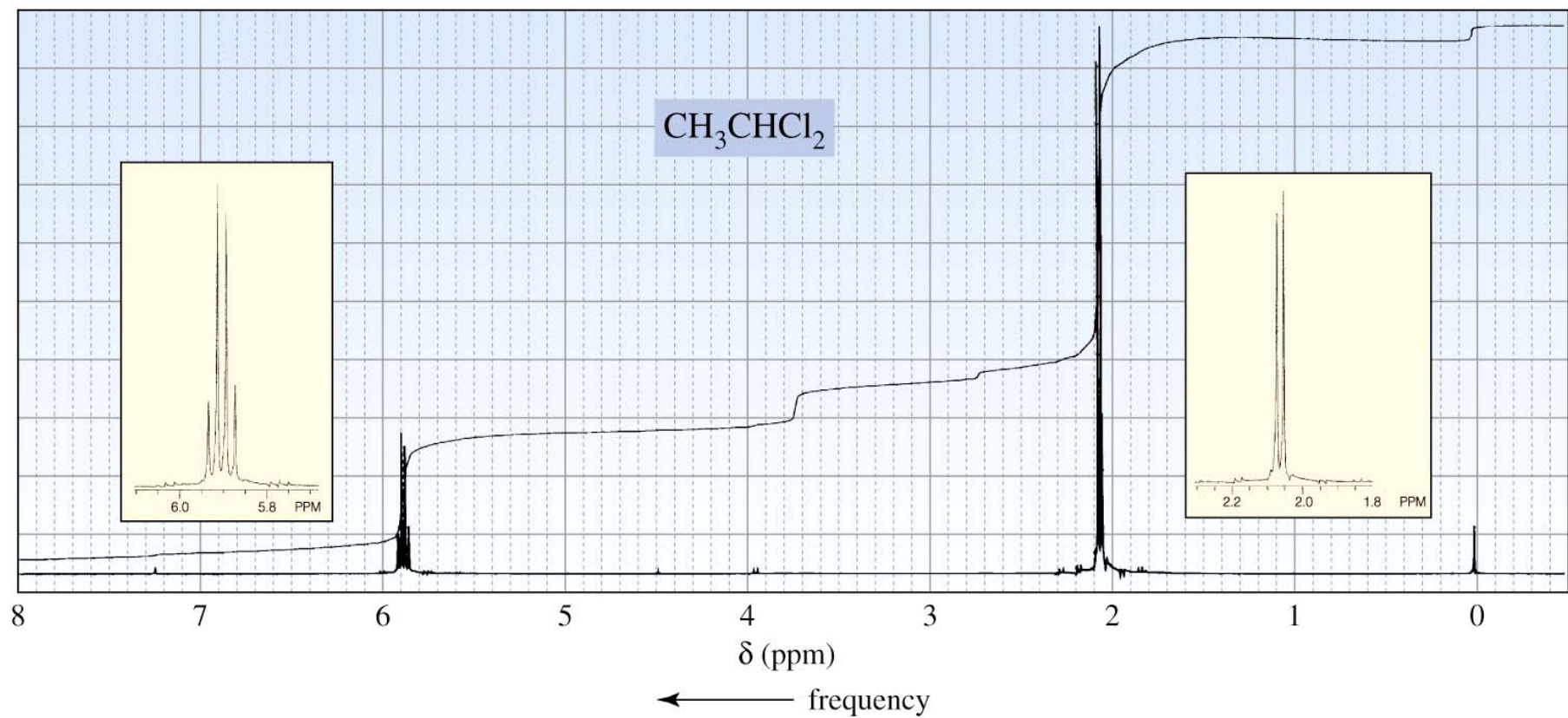


$3\text{H}_b$

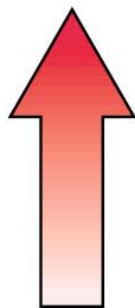
$\text{H}_a$

$$M = 2nI + 1$$

$$M = 2nI + 1$$

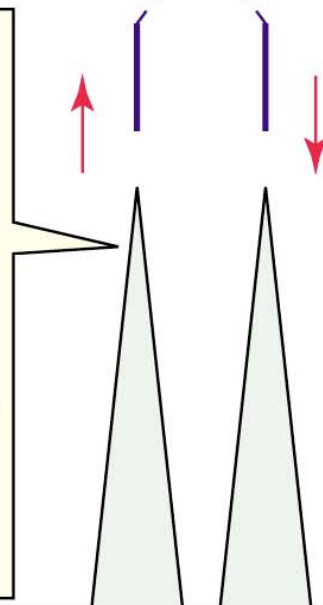


direction of  
the applied  
field



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

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

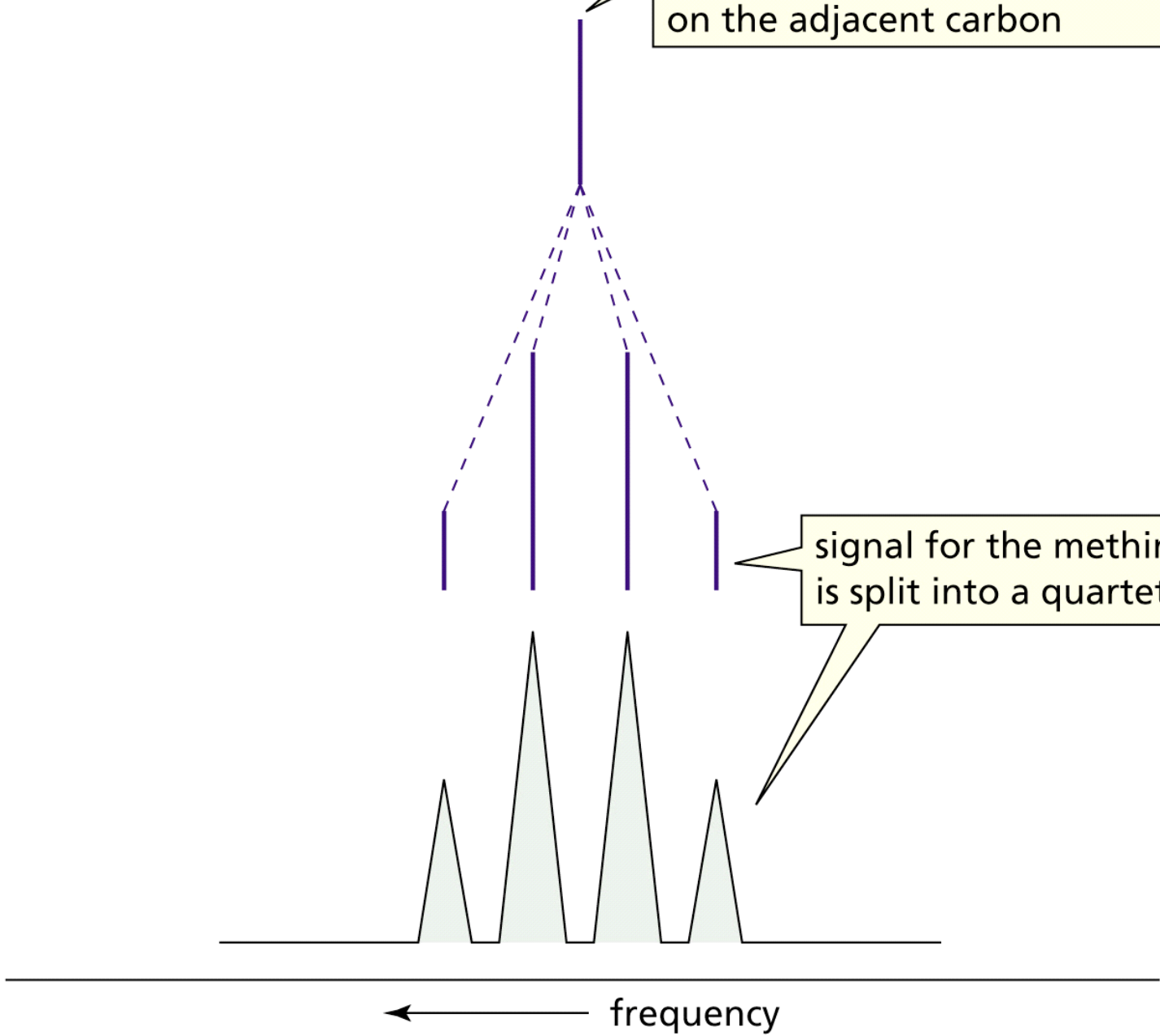


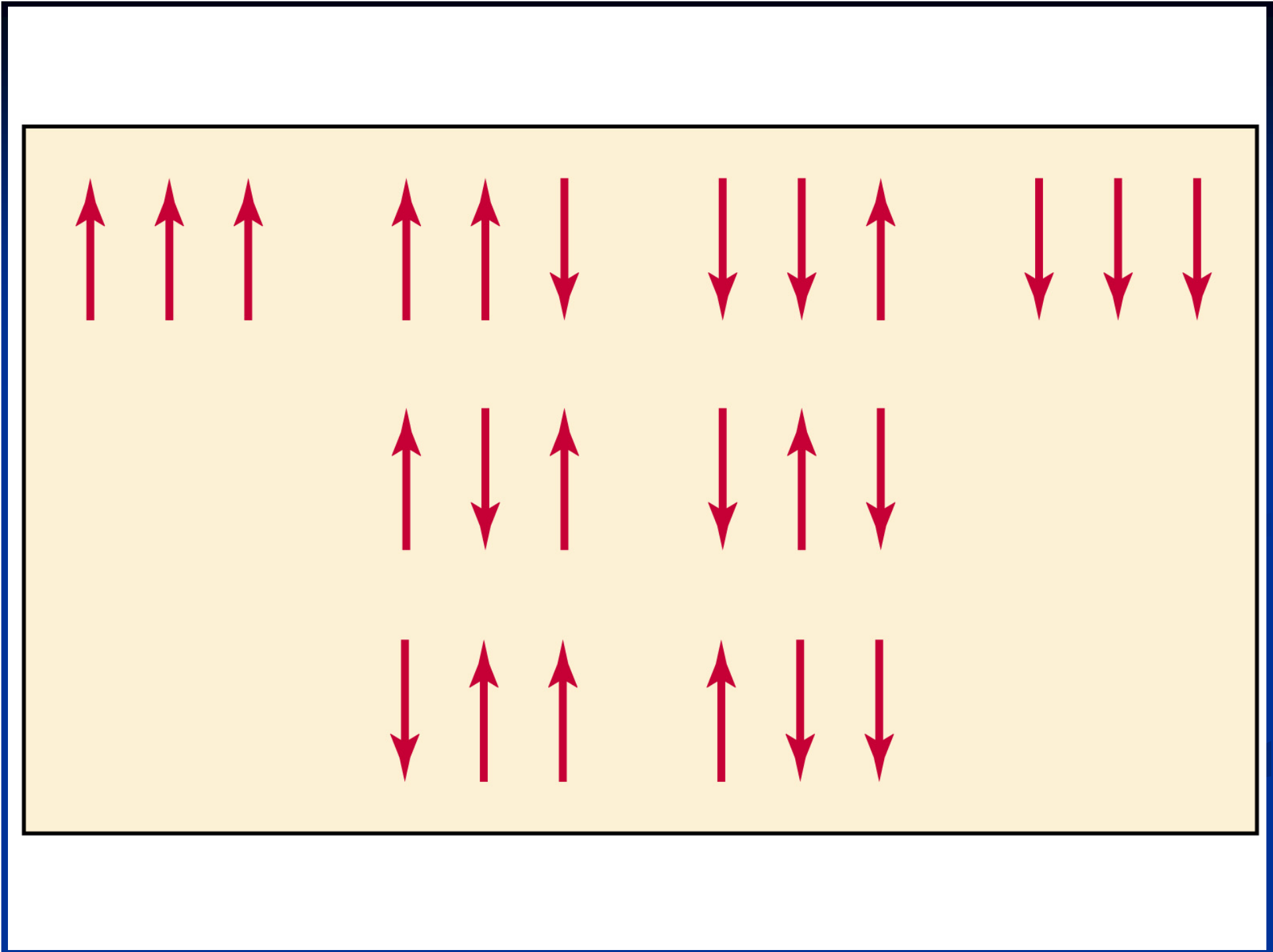
if the magnetic field  
of the methine proton is  
lined up against the applied  
magnetic field, it will subtract  
from the applied magnetic  
field, so the adjacent methyl  
protons will show a signal at  
a slightly lower frequency

← frequency

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

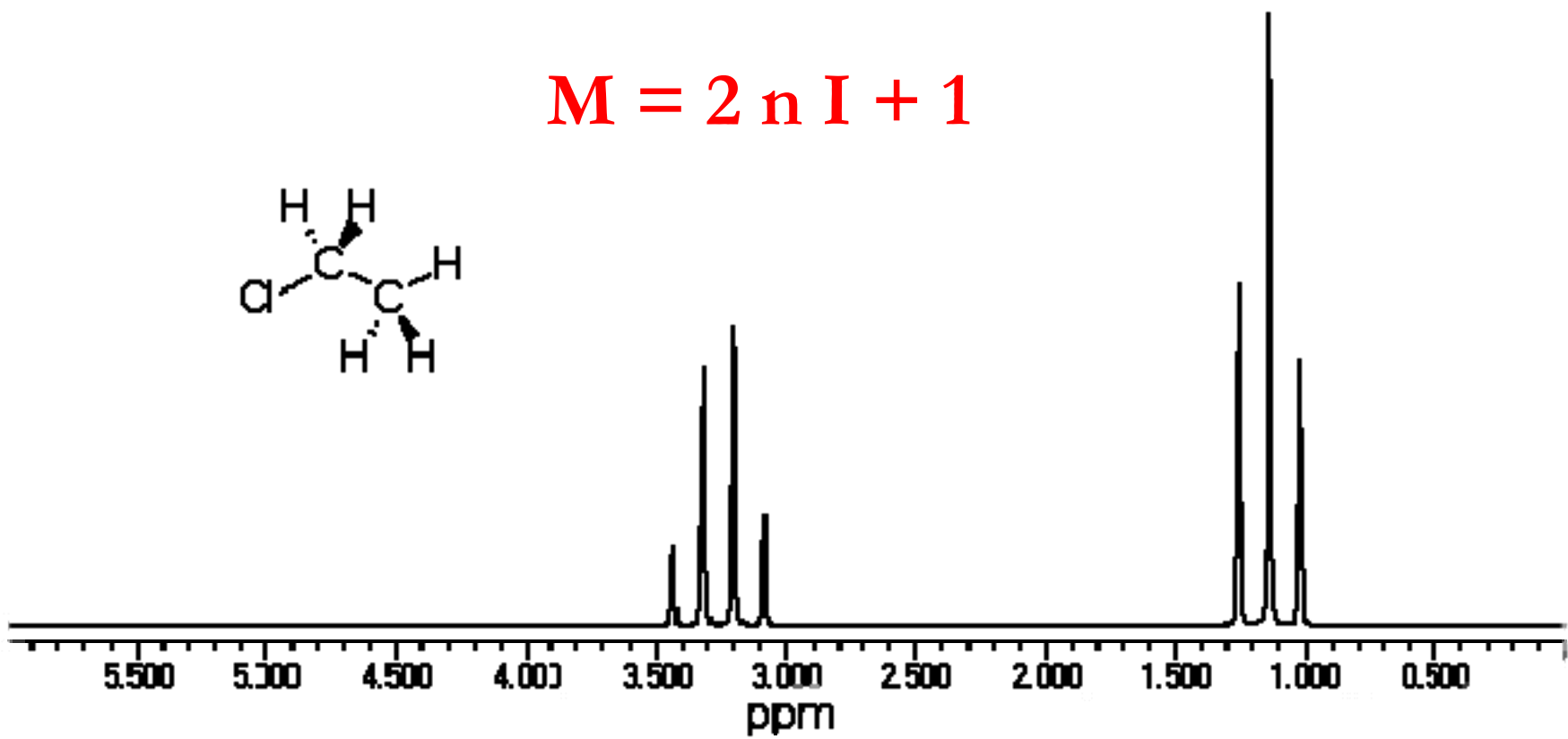
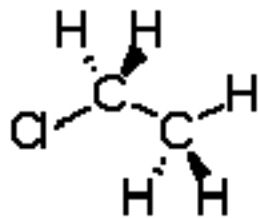
signal for the methine proton is split into a quartet





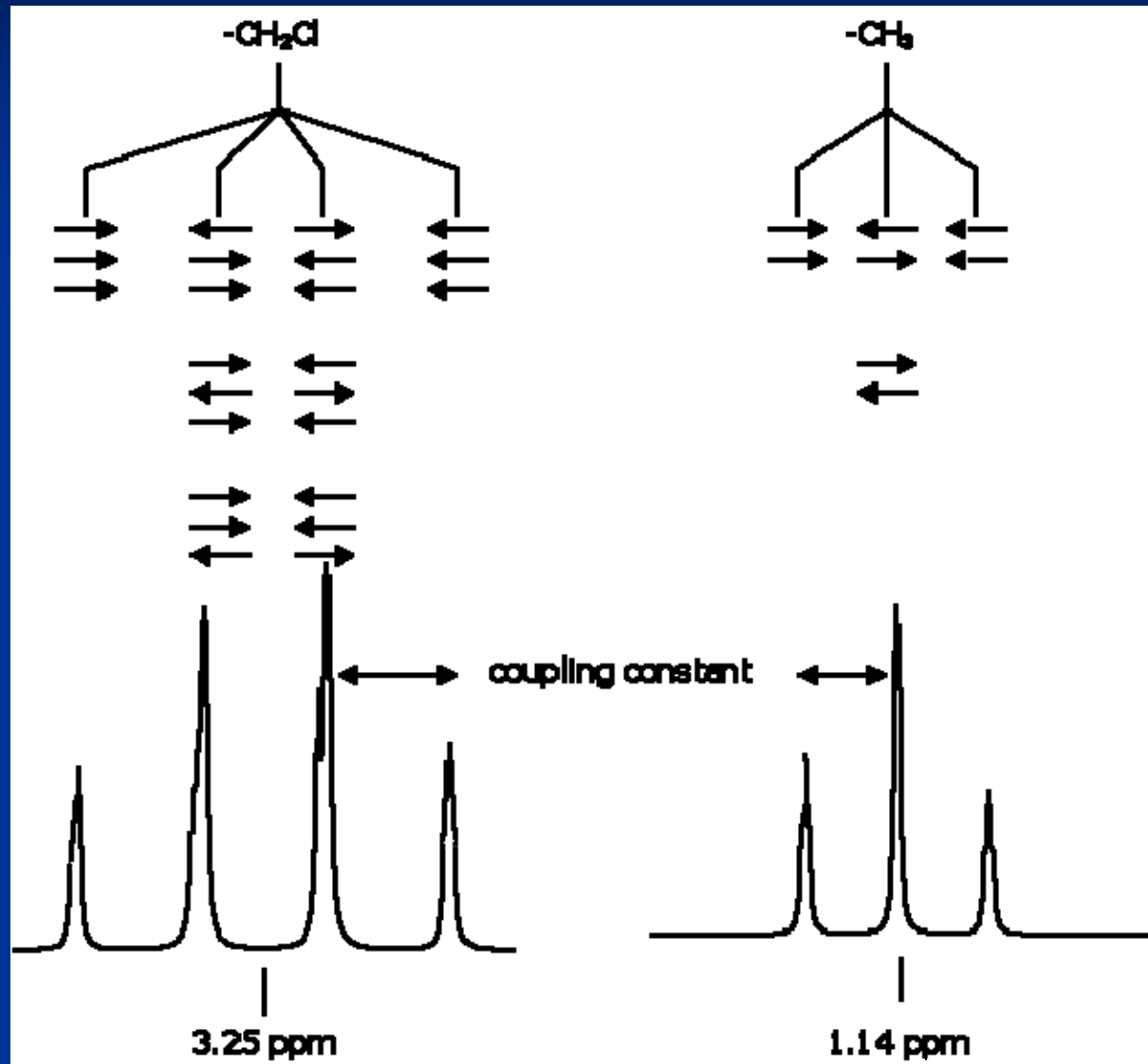
# Scalar Coupling

$$M = 2nI + 1$$



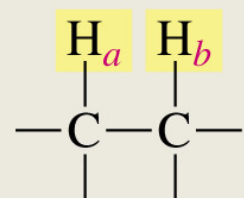


# Scalar Coupling

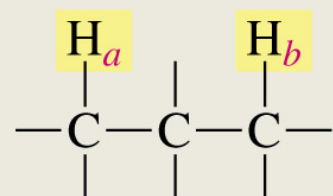


**Table 14.3 Approximate Values of Coupling Constants**

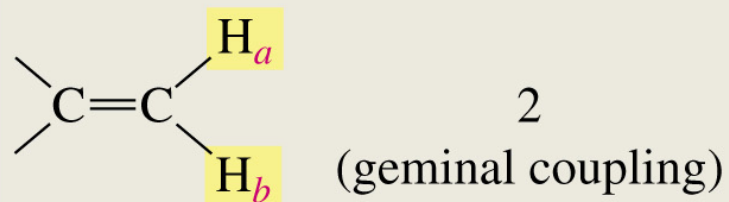
Approximate value of  $J_{ab}$  (Hz)



7

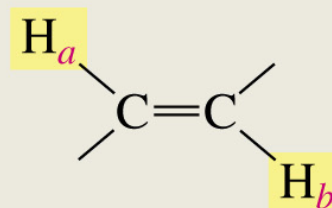


0

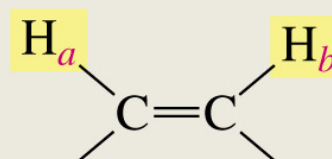


2

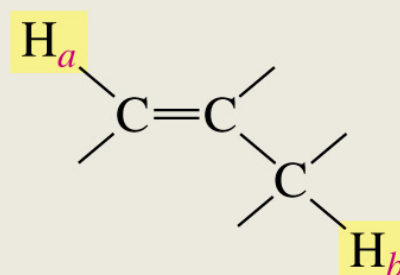
Approximate value of  $J_{ab}$  (Hz)



15 (trans)



10 (cis)



1  
(long-range  
coupling)

# First Order NMR Coupling Patterns

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

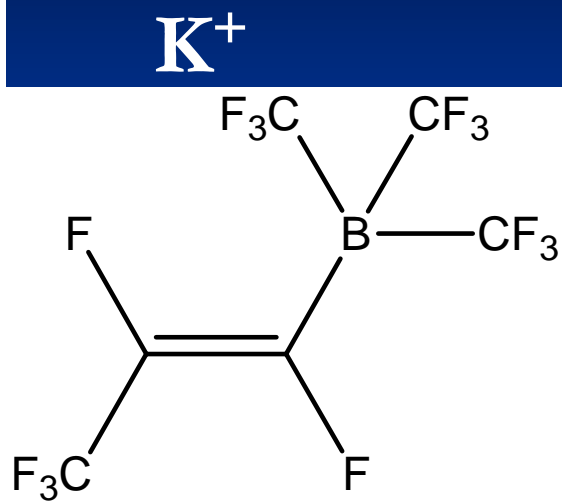
$$AX_n$$

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

# Spin $\frac{1}{2}$ 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 .....		

# Coupling with Several Spins

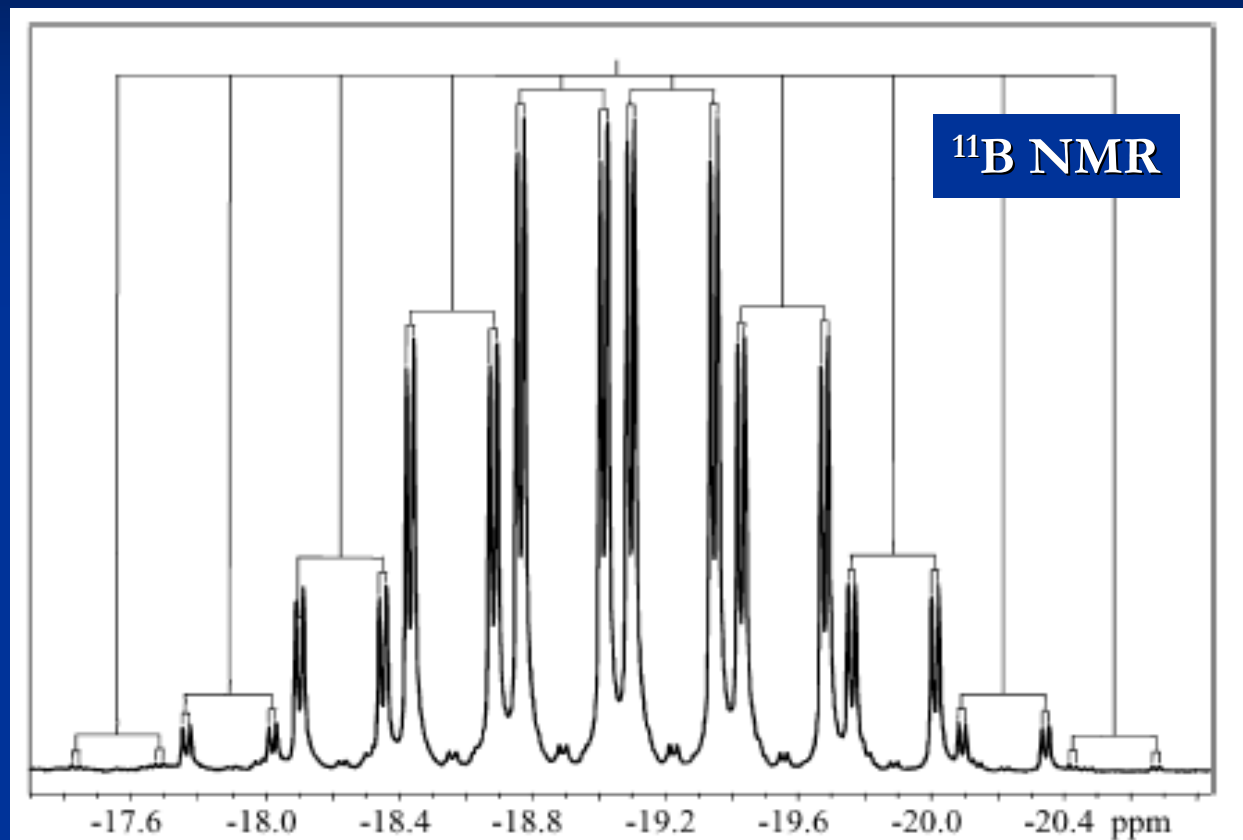


$CF_3$   $n = 9$

$F(2)$   $n = 1$

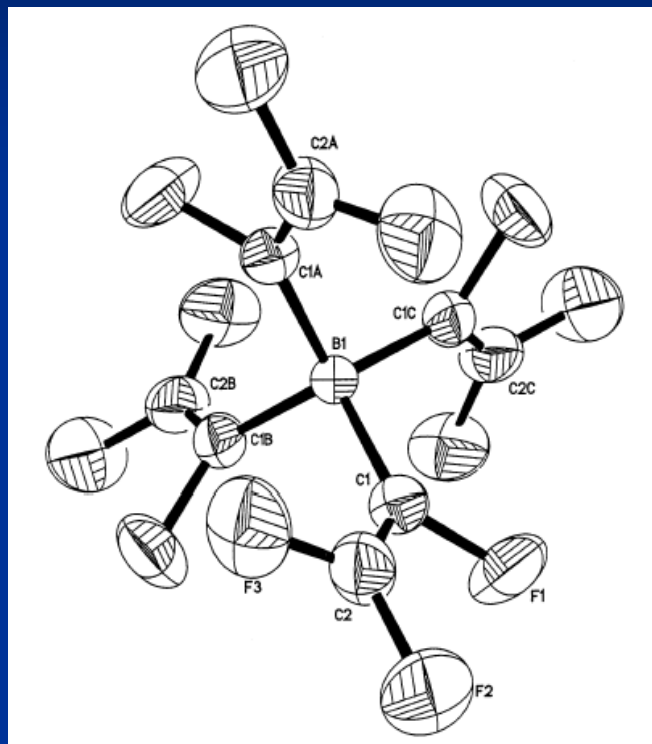
$F(3)$   $n = 1$

$CF_3$ (too far)

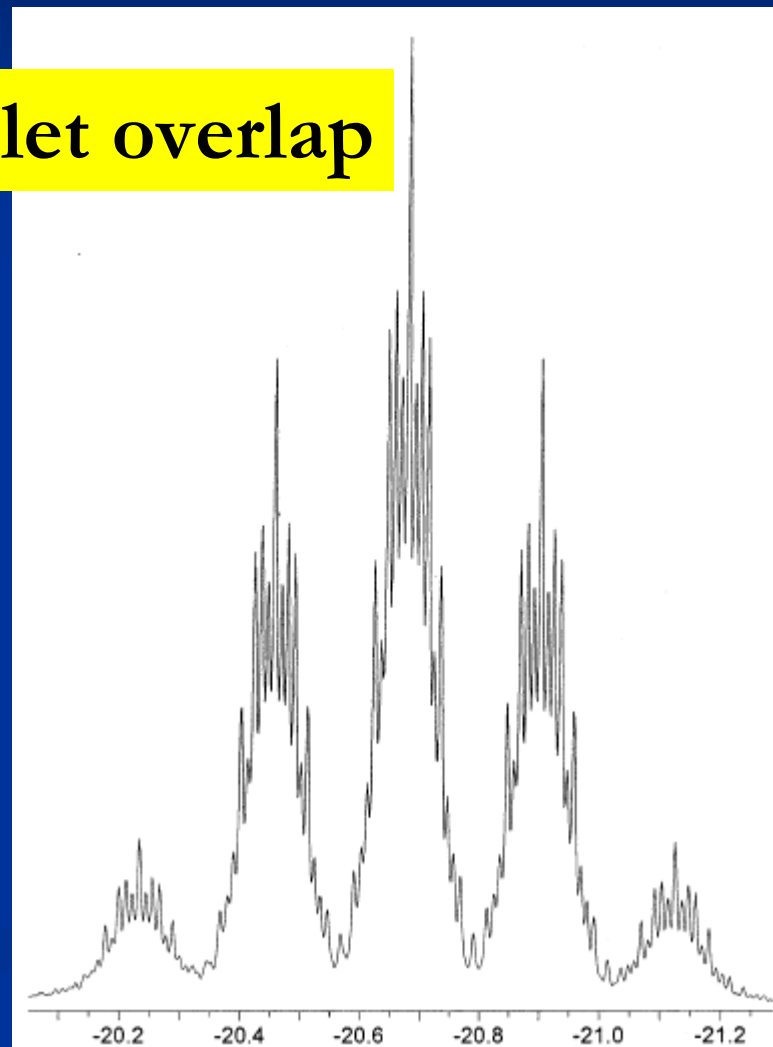


$$M = \prod (2 n_i I_i + 1)$$

# $^{11}\text{B}$ NMR Spectrum of $\text{K}[\text{B}(\text{CF}=\text{CF}_2)_4]$



Multiplet overlap

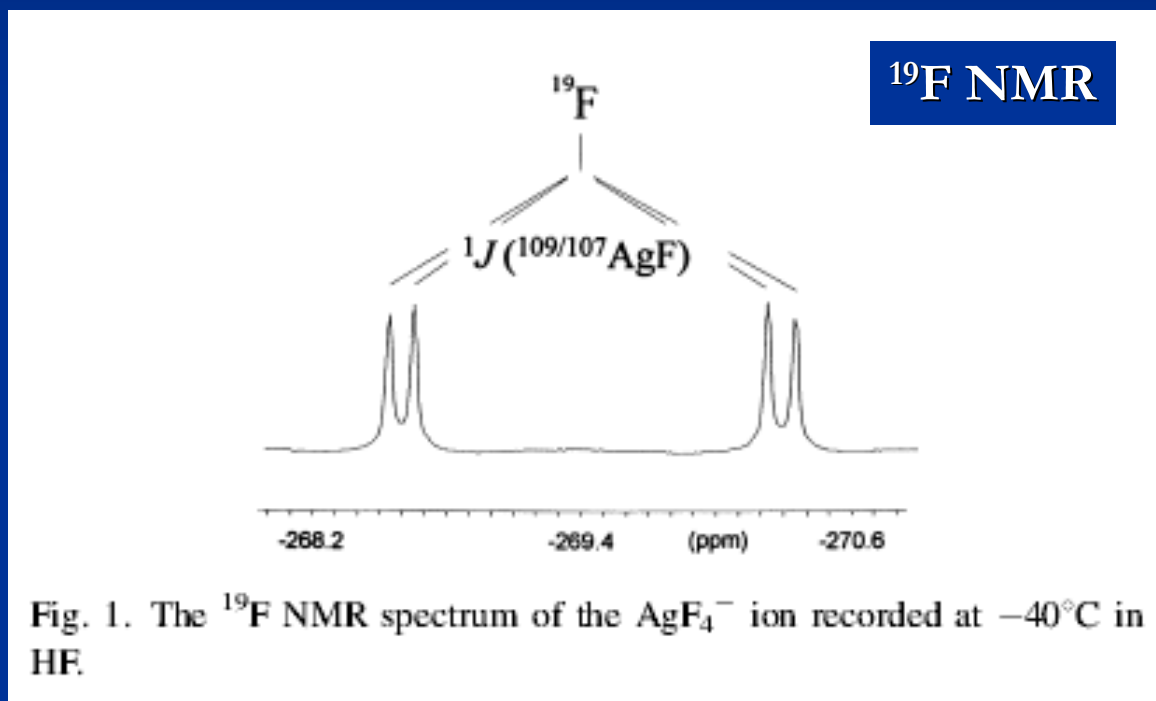


$^{11}\text{B}$  NMR spectrum of  $\text{K}[\text{B}(\text{CF}=\text{CF}_2)_4]$  in  $\text{CD}_3\text{CN}$ : an overlapping quintet of quintets

( $^2J_{\text{B,F}} = 21.5$ ,  $^3J_{\text{B,F}} = 3.2$ ,  $^3J_{\text{B,F}} = 2.2$  Hz).

# K[AgF<sub>4</sub>]

K[AgF<sub>4</sub>] d<sup>8</sup> square planar



<sup>109</sup>Ag I = 1/2    NA = 48.2%    γ = - 1.2448 10<sup>7</sup> rad T<sup>-1</sup> s<sup>-1</sup>

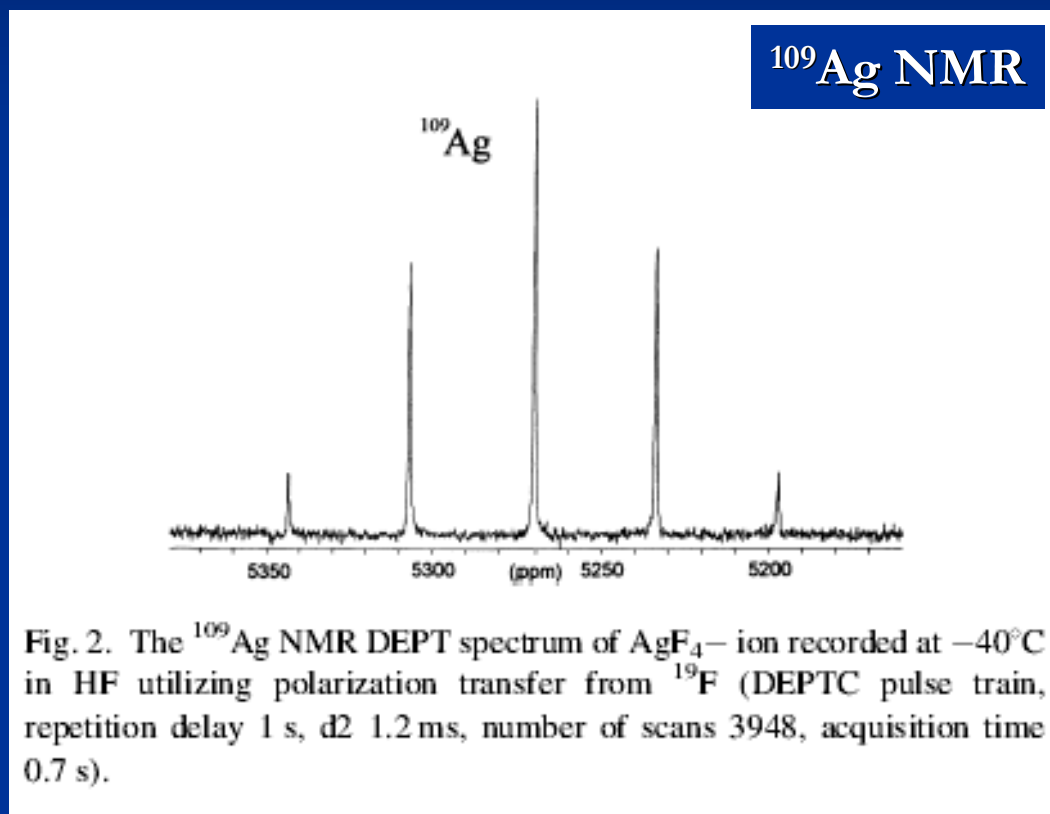
<sup>107</sup>Ag I = 1/2    NA = 51.8%    γ = - 1.0828 10<sup>7</sup> rad T<sup>-1</sup> s<sup>-1</sup>

# K[AgF<sub>4</sub>]

$$M = 2nI + 1$$

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

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

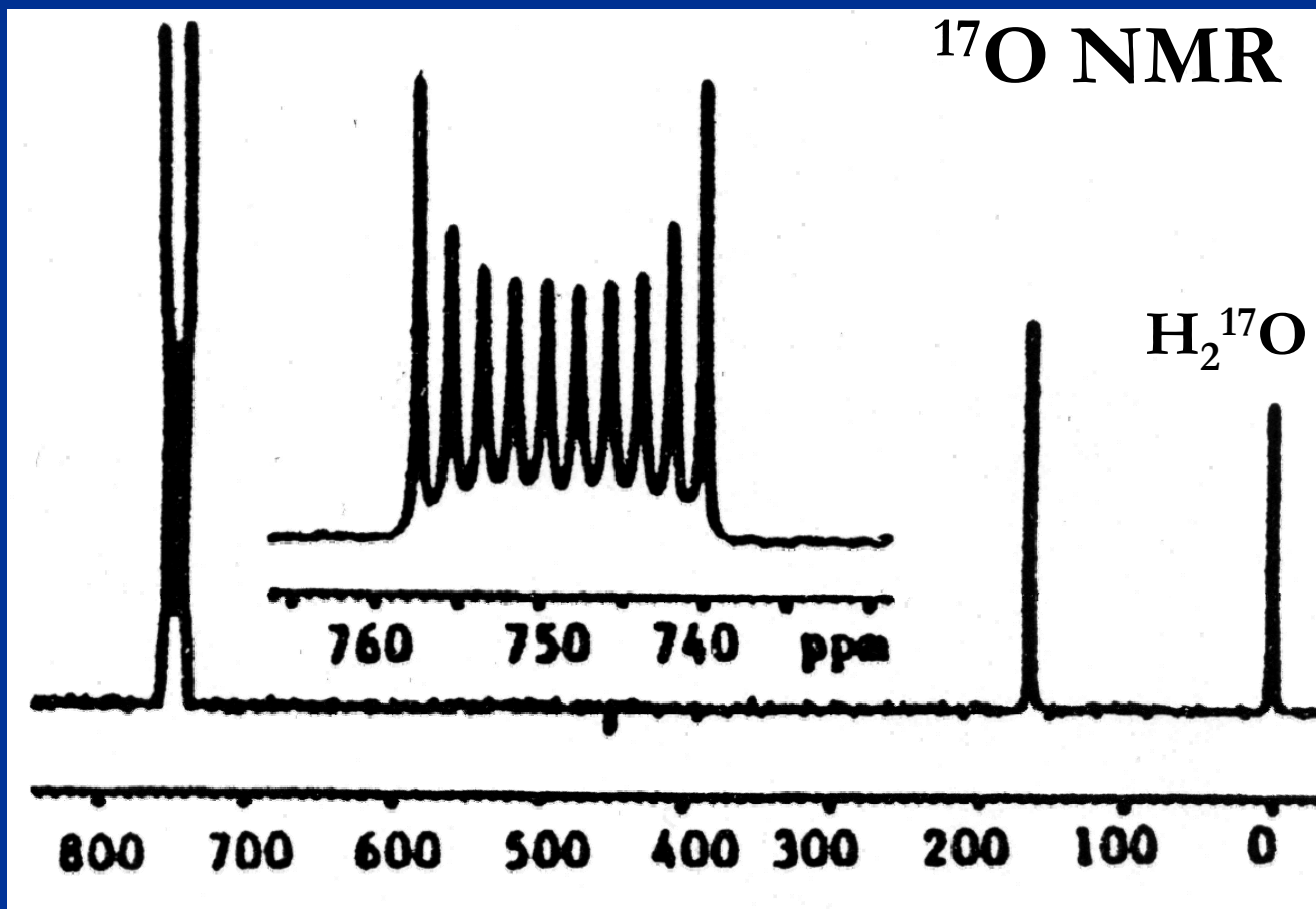


${}^1J({}^{109}\text{Ag} - \text{F})$  must have the same value in both  ${}^{109}\text{Ag}$  and  ${}^{19}\text{F}$  spectra

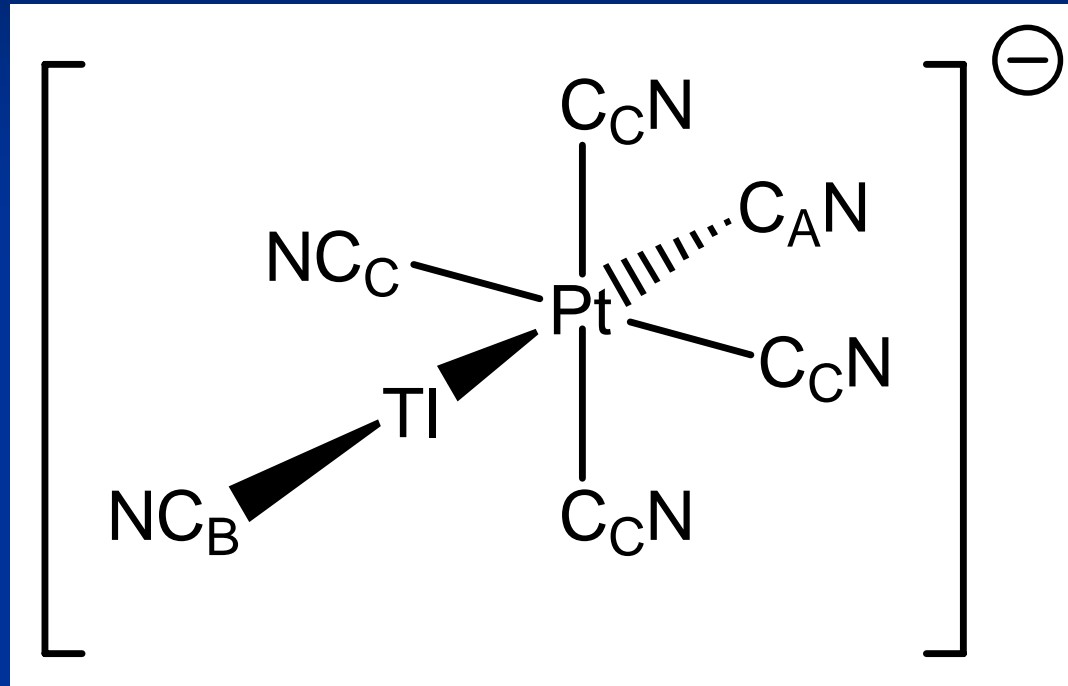


# Signal Multiplicity

$\text{TcO}_4^-$  in 20.1% enriched  $\text{H}_2^{17}\text{O}$ .



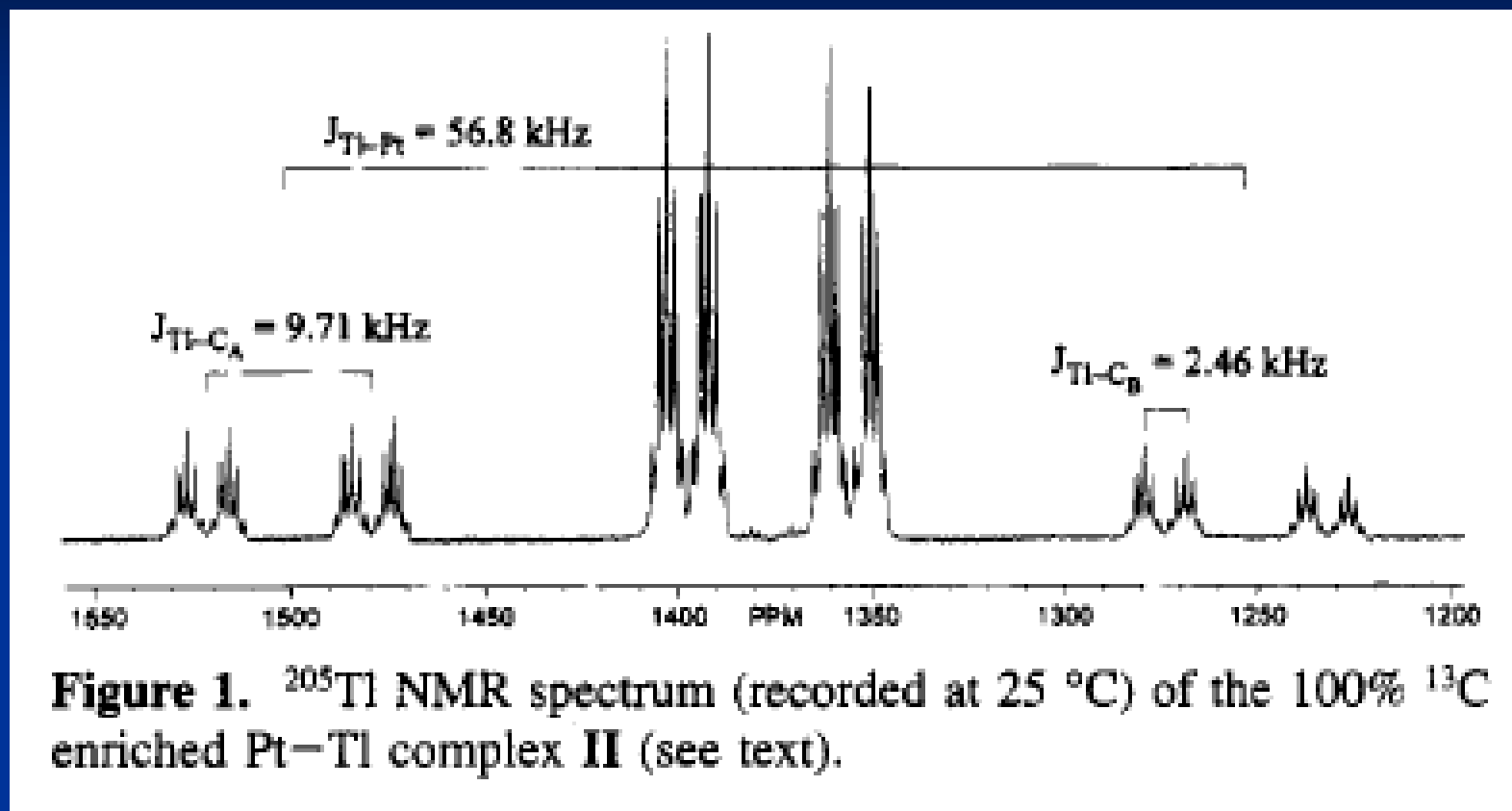
# Signal Multiplicity



<sup>13</sup>C enriched CN<sup>-</sup>

$$M = \prod (2 n_i I_i + 1)$$

# $^{205}\text{Tl}$ NMR



$${}^2J (\text{Tl}-\text{C}_C) < {}^1J (\text{Tl}-\text{C}_B) < {}^2J (\text{Tl}-\text{C}_A)$$

cis	$\text{C}_C$	0.45 kHz
trans	$\text{C}_A$	9.71 kHz

# Scalar Coupling

## Indirect nuclear spin–spin coupling constants

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

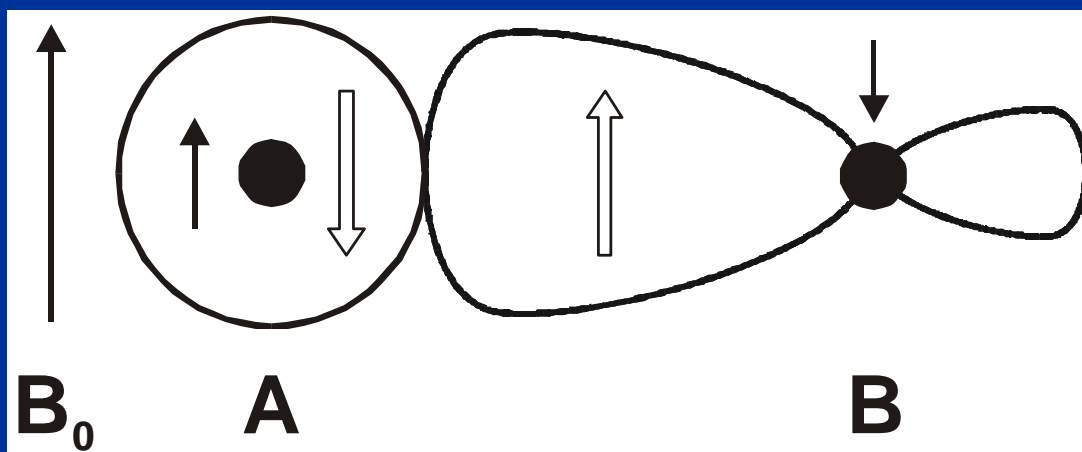
Spin-spin couplings between two nuclei will be dependent upon several factors:

- 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

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

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**  ${}^nJ$  where  $n$  denotes the number of bonds between coupled nuclei  
Dimension  $[J] = \text{s}^{-1}$  [Hz]

The magnitude of  $J$  depends on the gyromagnetic ratios  $\gamma_A, \gamma_B$  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  $[K] = 10^{19} \text{ N A}^2 \text{ m}^{-3}$

# Scalar Coupling Constants

To compare substituent influences on coupling for different nuclei, use

the EFFECTIVE REDUCED COUPLING CONSTANT  $K'$

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

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



# 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

$$\frac{K_{AB}}{J_{AB}} > 0 \quad \text{if } \gamma_A, \gamma_B \text{ have same sign}$$

$$J_{AB} < 0 \quad \text{if } \gamma_A, \gamma_B \text{ have different sign}$$

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  ${}^1K_{EH}$  is generally positive.

(E = any first to fourth row atom)

If the relative sign of a coupling constant  ${}^nK_{XY}$  can be determined from  ${}^nK_{XY} / {}^1K_{EH}$ , 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

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

the energy splitting between states with parallel and antiparallel nuclear spins

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

$\varepsilon_{AB}(\mathbf{r})$  = the coupling energy density (CED)

integral of CED over all space =  $K_{AB}$

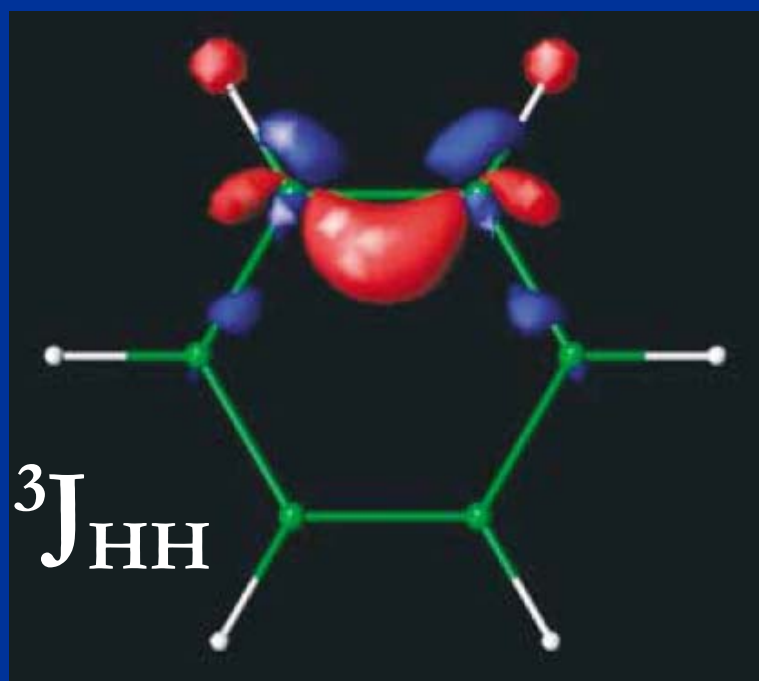
CED is a realspace function, can be visualized in 3D

contains all the information about the propagation of the nuclear spin–spin interaction throughout a molecule

# Visualization of Spin-Spin Coupling

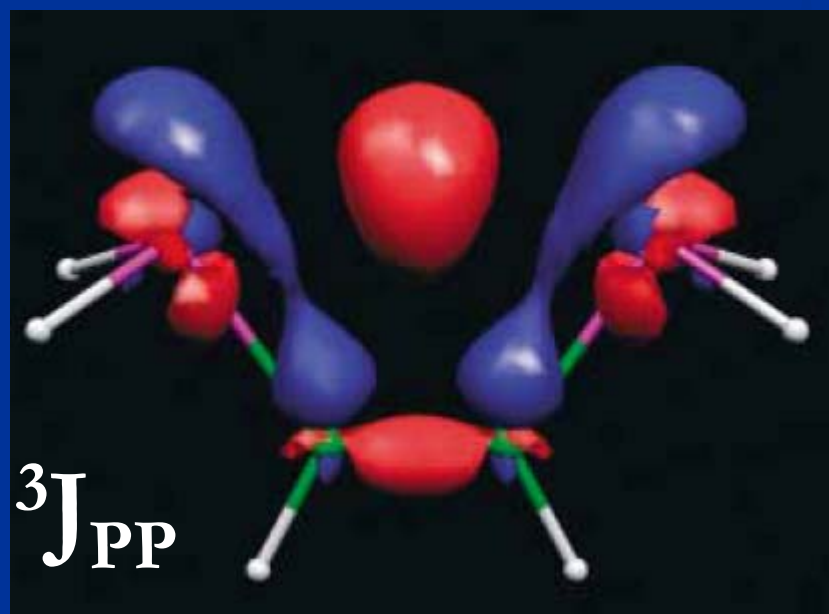
$$J_{AB} = \frac{\hbar}{2\pi} \gamma_A \gamma_B K_{AB} = \frac{1}{2} \int [\varepsilon^{\uparrow\uparrow}(r) - \varepsilon^{\uparrow\downarrow}(r)] dV = \frac{\hbar}{2\pi} \gamma_A \gamma_B \int \varepsilon_{AB}(r) dV$$

Benzene



through-bond

$H_2P-CH_2-CH_2-PH_2$

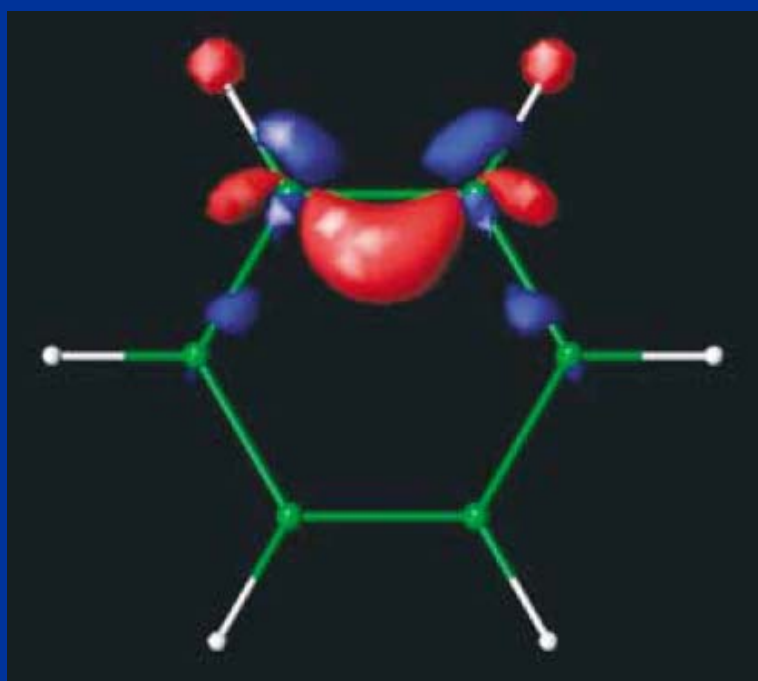


through-space

# Visualization of Spin-Spin Coupling

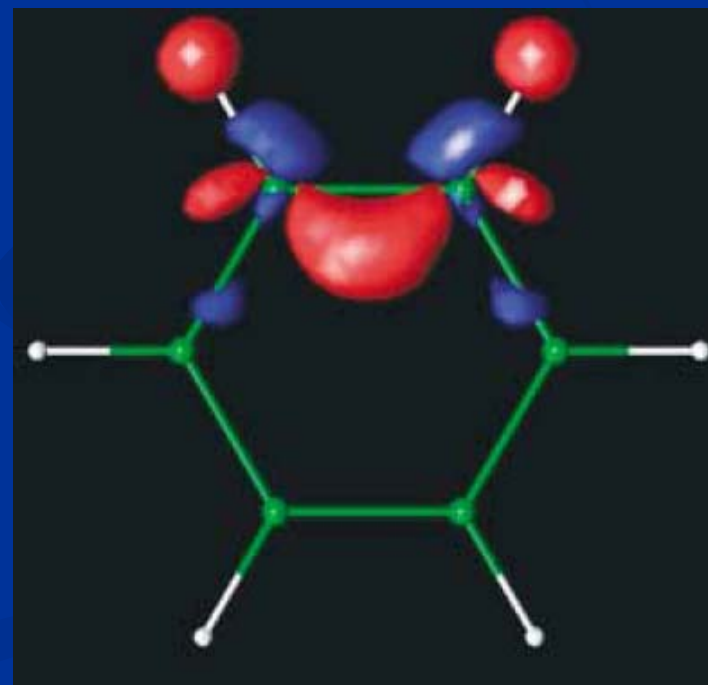
$$\rho_{AB}(r) = \frac{\rho^{\uparrow\uparrow}(r) - \rho^{\uparrow\downarrow}(r)}{\lambda_1 \lambda_2}$$

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



CED

${}^3J_{HH}$



CDD

# Types of Coupling

Coupling between two nuclei can be categorized as follows:

## *Homonuclear Coupling*

- coupling between nuclei of the same type



## *Heteronuclear Coupling*

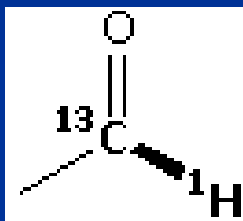
- coupling between nuclei of different types



# Distance Dependence

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

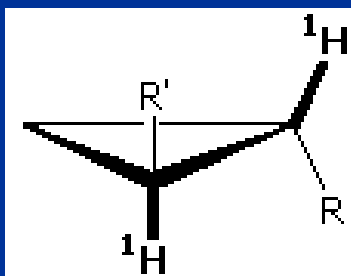
The order of the strength of coupling is as follows:  ${}^1J > {}^2J > {}^3J > {}^4J > {}^nJ$



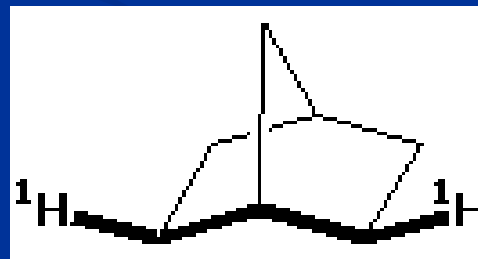
${}^1J$  one-bond or direct



${}^2J$  two-bond or geminal



${}^3J$  three-bond or vicinal

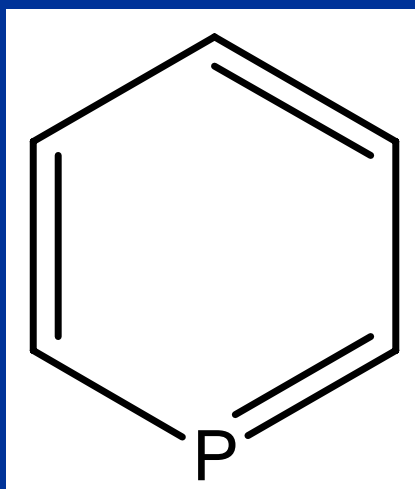


${}^nJ$  long-range



# Distance Dependence

$${}^1J > {}^3J > {}^2J$$



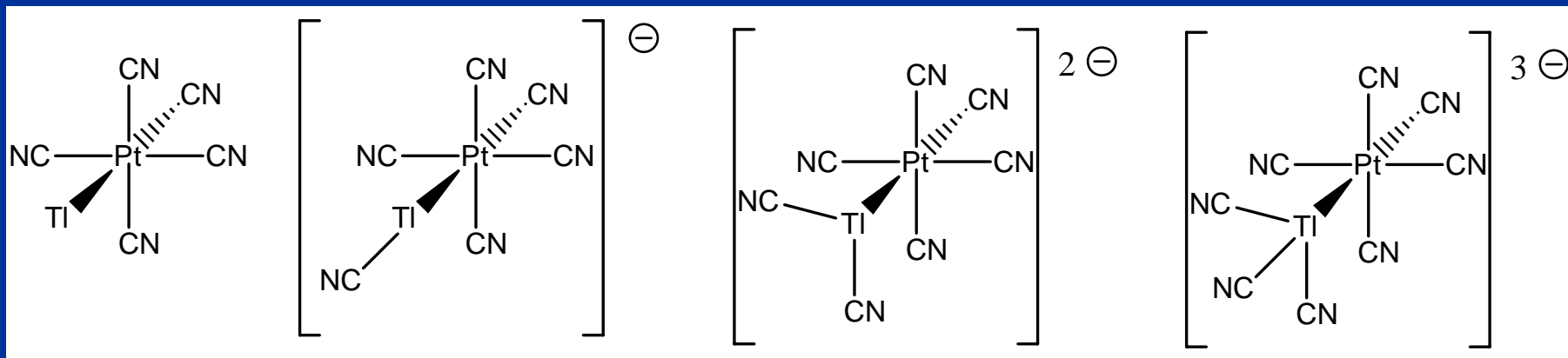
$${}^3J_{\text{PCCC}} = 14 \text{ Hz}$$

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

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

# Largest Heteronuclear J

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



71

57

47

38



# Dependence on Magnetogyric Ratio

For the same elements, different nuclides

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



$${}^1J({}^{11}\text{B} - \text{H}) = 80 \text{ Hz}$$

$$\gamma({}^{11}\text{B}) = 8.57 \cdot 10^7 \text{ rad T}^{-1}\text{s}^{-1}$$

$${}^1J({}^{10}\text{B} - \text{H}) = 28 \text{ Hz}$$

$$\gamma({}^{10}\text{B}) = 2.87 \cdot 10^7 \text{ rad T}^{-1}\text{s}^{-1}$$

# Dependence on Magnetogyric Ratio

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

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

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

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

The nuclide with larger  $\gamma$  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	$\gamma$ (X) $10^7 \text{ rad T}^{-1}\text{s}^{-1}$	$^1J(^{117}\text{Sn} - \text{X})$ Hz	$^1J(^{119}\text{Sn} - \text{X})$ Hz
$^n\text{Bu}_3\text{Sn} - \text{H}$	26.7510	1505	1575
$^n\text{Bu}_3\text{Sn} - \text{D}$	4.1064	231	242
$^n\text{Bu}_3\text{Sn} - \text{T}$	28.5335	1610	1685

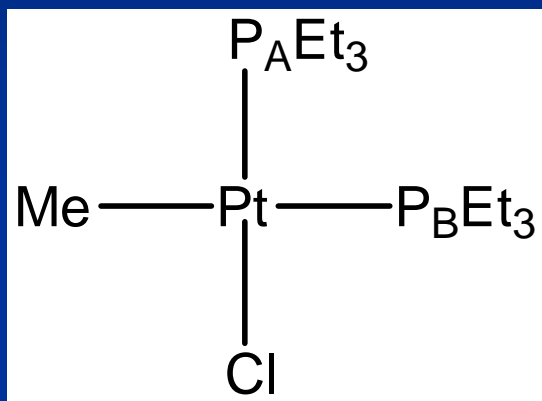
# Effects of Electronegative Substituents

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

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**

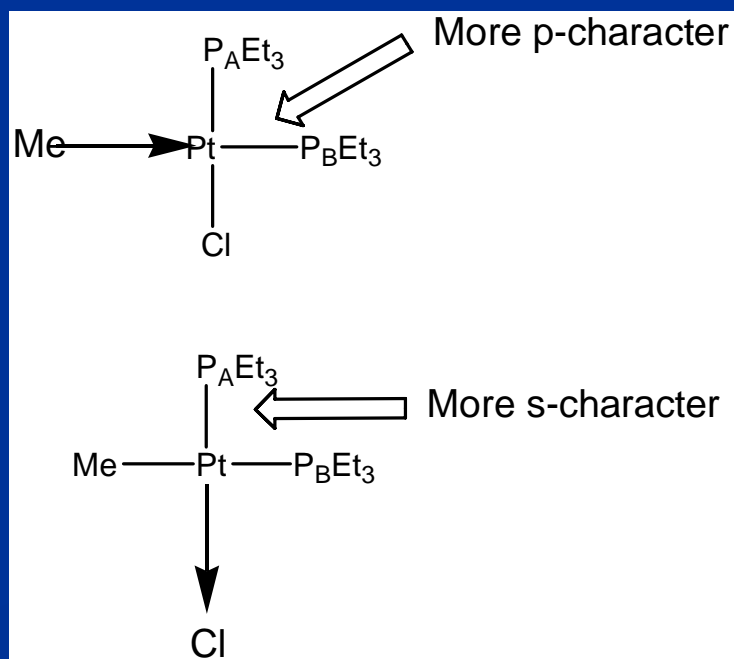
# Effects of Electronegativity

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



$$^1J(^{195}\text{Pt} - \text{P}_A) = 4179 \text{ Hz}$$

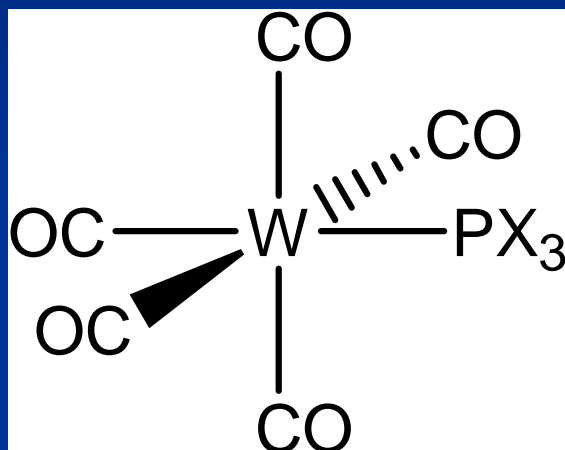
$$^1J(^{195}\text{Pt} - \text{P}_B) = 1719 \text{ Hz}$$





# Effects of Electronegativity

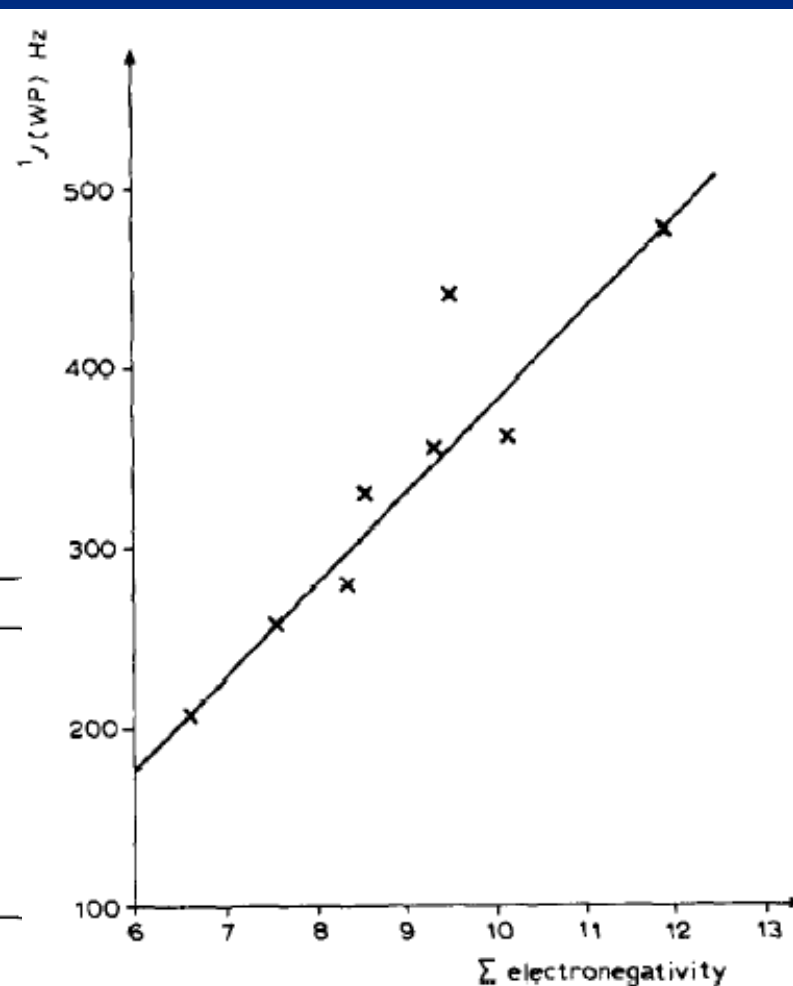
$J$  increases with increasing sum of substituent electronegativity



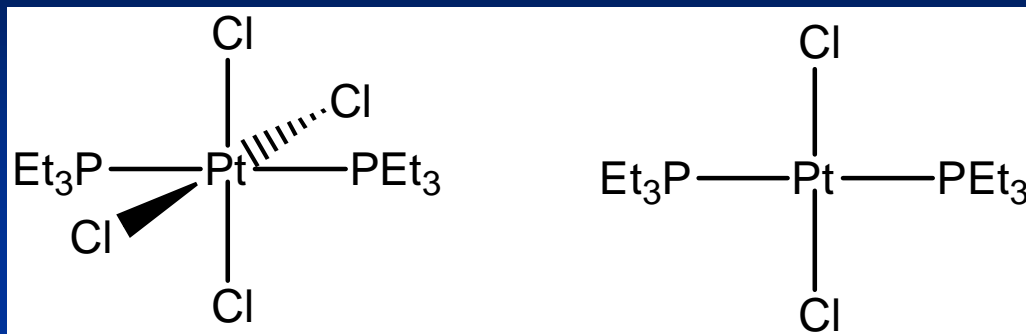
$^1J(\text{WP})$  (in Hz) data for some complexes of the type  $[\text{W}(\text{CO})_5(\text{P}X_n\text{H}_{3-n})]$

Compound	$^1J(\text{WP})$	$\Sigma x^a$
$[\text{W}(\text{CO})_5(\text{PH}_3)]$	215.8	6.6
$[\text{W}(\text{CO})_5(\text{PH}_2\text{Cl})]$	267.0	7.6
$[\text{W}(\text{CO})_5(\text{PH}_2\text{F})]$	284.4	8.4
$[\text{W}(\text{CO})_5(\text{PHCl}_2)]$	336.9	8.6
$[\text{W}(\text{CO})_5(\text{PHFCl})]$	361.0	9.4
$[\text{W}(\text{CO})_5(\text{PCl}_3)]$	213.0	9.6
$[\text{W}(\text{CO})_5(\text{PFH}_2)]$	376.0	10.2
$[\text{W}(\text{CO})_5(\text{PF}_3)]$	485.0	12.0

<sup>a</sup> The sum of electronegativities of the substituents on phosphorus.



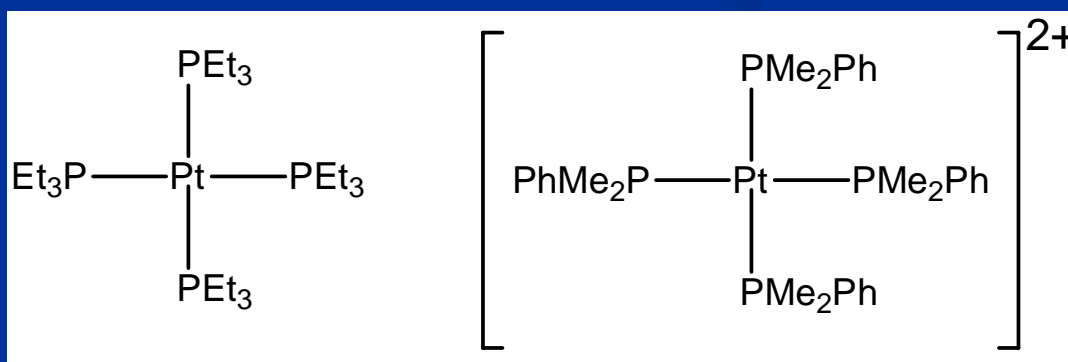
# Effects of Coordination Number



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

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

Increasing coordination number results in decreasing J



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

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

# Effects of Coordination Number



Increasing coordination number results in decreasing J

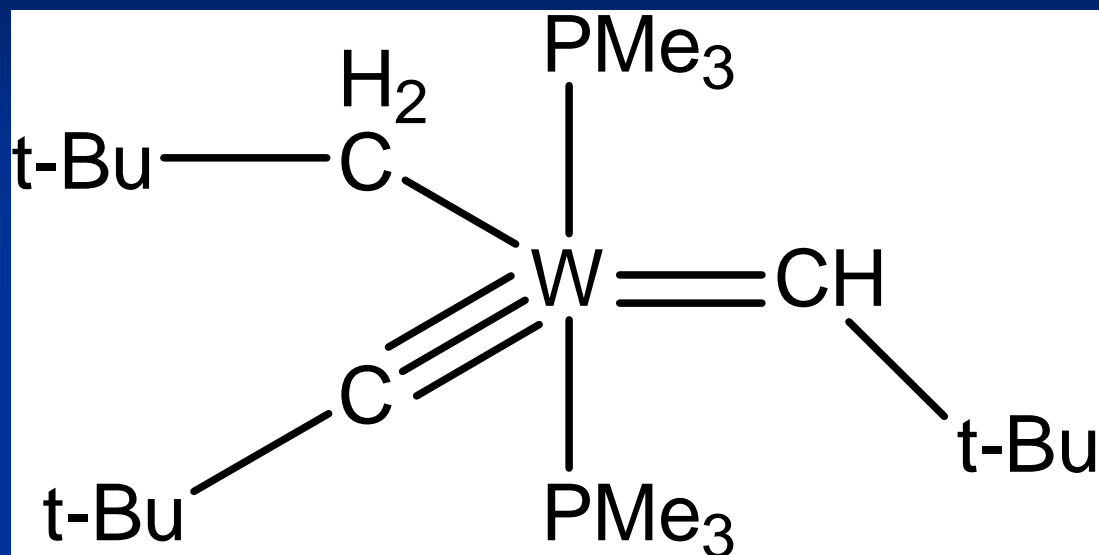
# Effects of s-Character

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

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

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

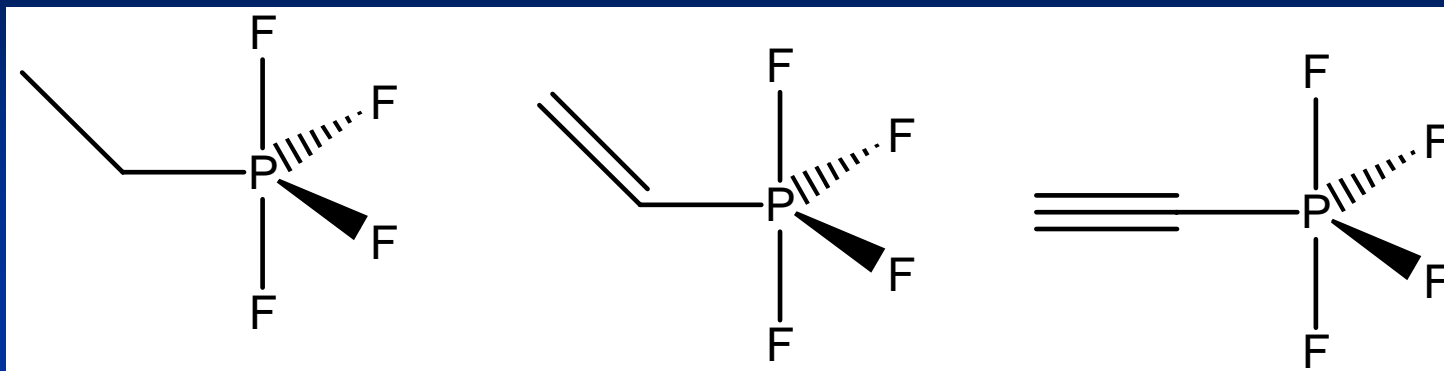
# Effects of s-Character



W oxidation state

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

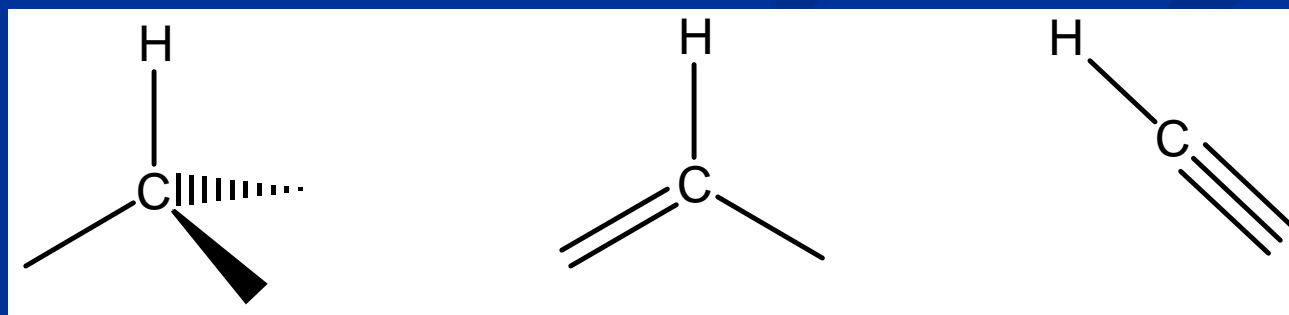
# Effects of s-Character



$$^1J(^{31}\text{P} - \text{C}) = 189.2 \text{ Hz}$$

$$261.1 \text{ Hz}$$

$$476.0 \text{ Hz}$$

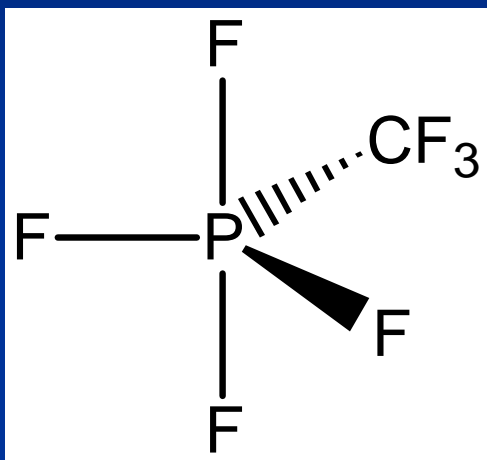


$$^1J(^{13}\text{C} - \text{H}) = 120 \text{ Hz}$$

$$160 \text{ Hz}$$

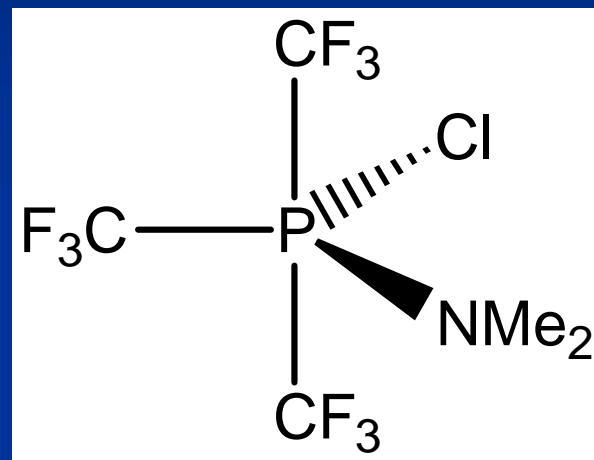
$$250 \text{ Hz}$$

# Effects of s-Character



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

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

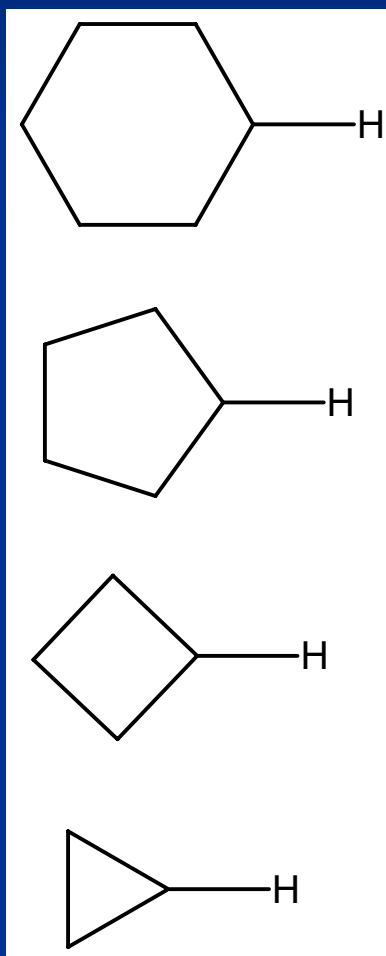


$${}^2J(\text{P-F}_{\text{axial}}) = 53 \text{ Hz}$$

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

# Effects of s-Character

$^1J$  (C-H), Hz



123

130

134

161

Increasing J

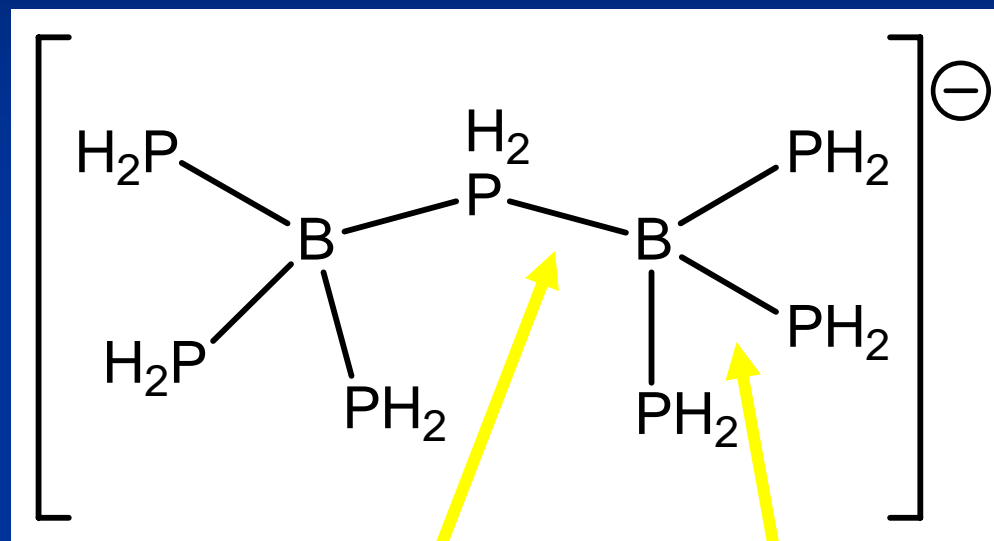
Intraring angle decreases

More p-character in C-C

More s-character in C-H



# Effects of s-Character

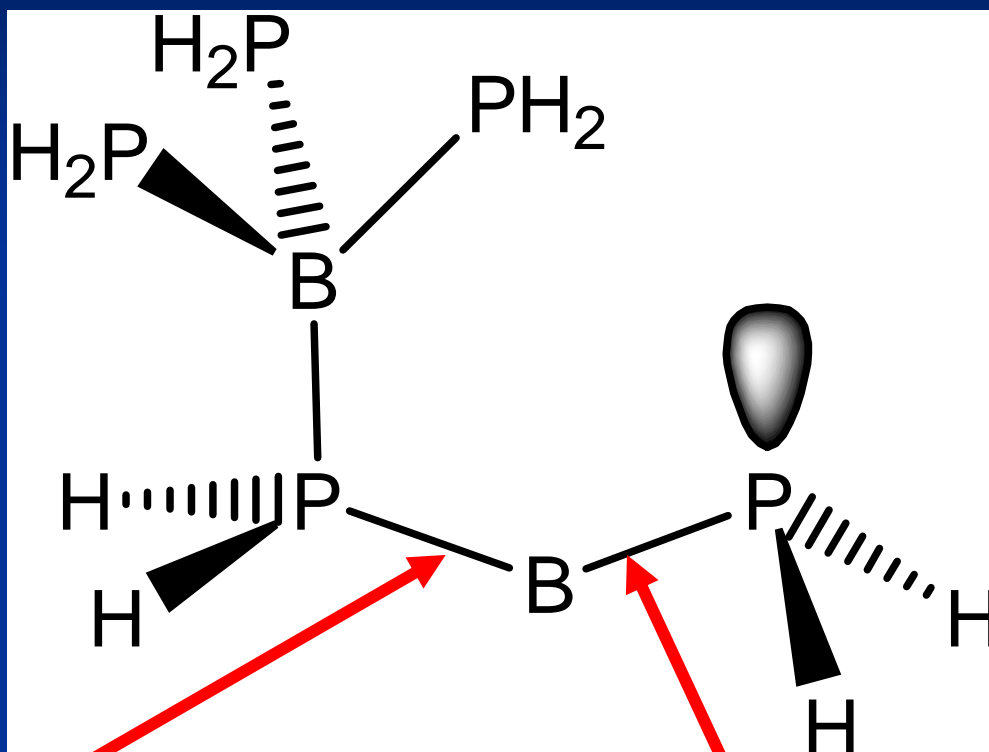


$${}^1J(\text{P-}^{11}\text{B}) = 56.9 \text{ Hz}$$

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

**Explain the difference**

# Effects of s-Character



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

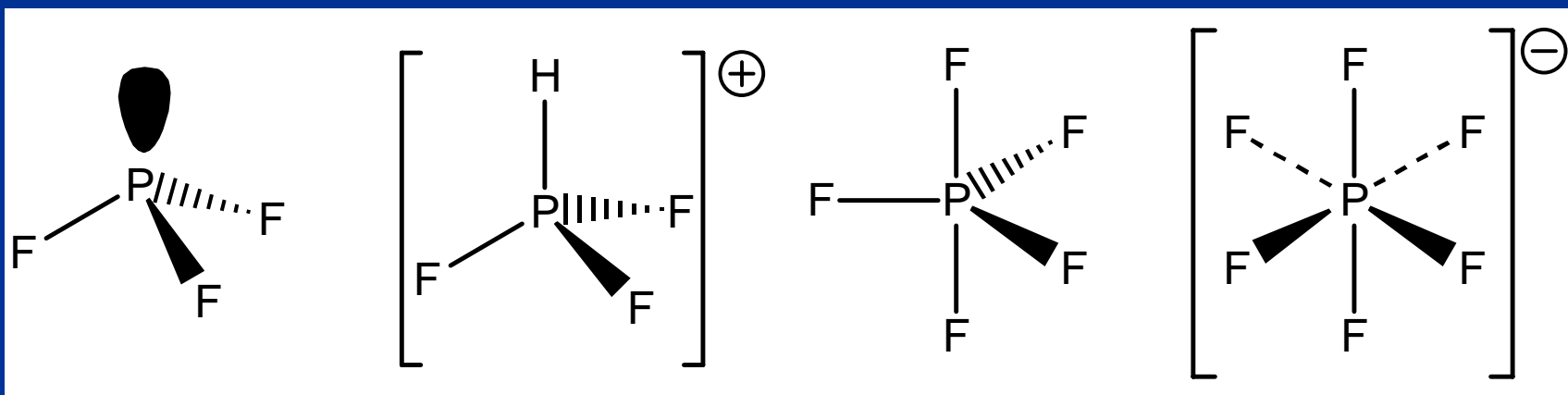
$${}^1J(\text{P}-{}^{11}\text{B}) = 26.3 \text{ Hz}$$

Lone pair = substituent  
with zero electronegativity

Resides in orbital with large s-character

# Effects of Coordination Number

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



-1400 Hz

-1109 Hz

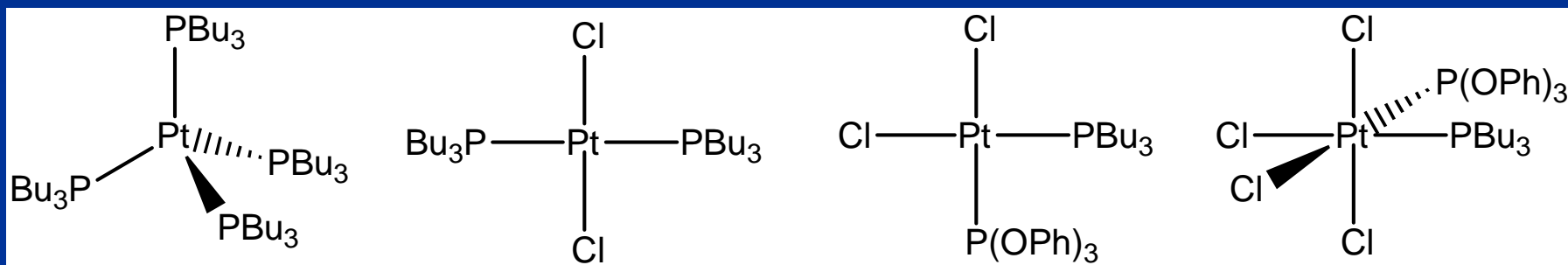
-1080 Hz

-706 Hz

Increasing coordination number results in decreasing  $J$   
Dilution of s-character into more bonds

# Effects of Oxidation State

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



3740 Hz

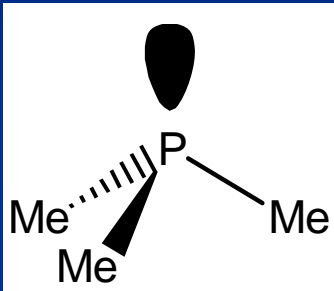
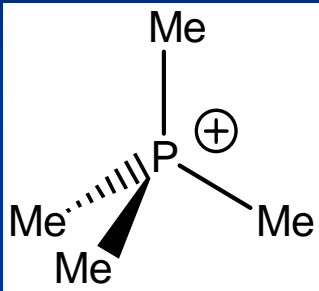
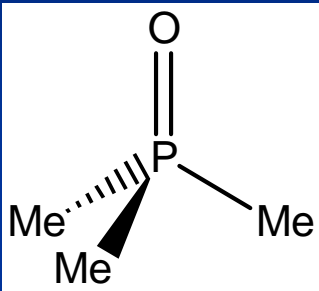
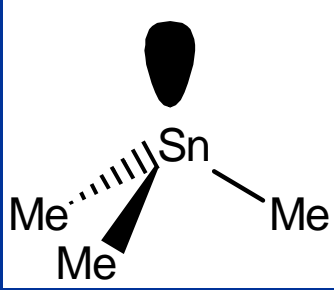
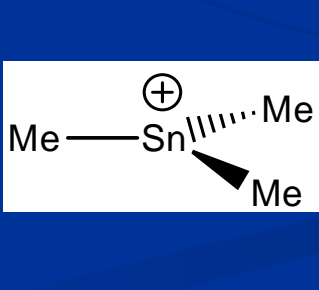
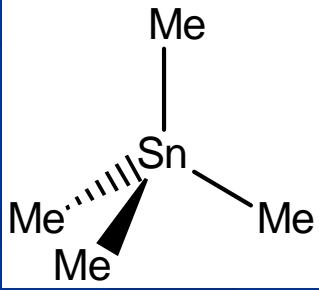
2411 Hz

Bu 3159  
OPh 6304

1921  
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			
$^1J(P - C)$	-14	56	68
	$Sn^{II}$	$Sn^{IV}$	$Sn^{IV}$
			
$^1J(Sn - C)$	155	-380	-339

# Angle Dependence

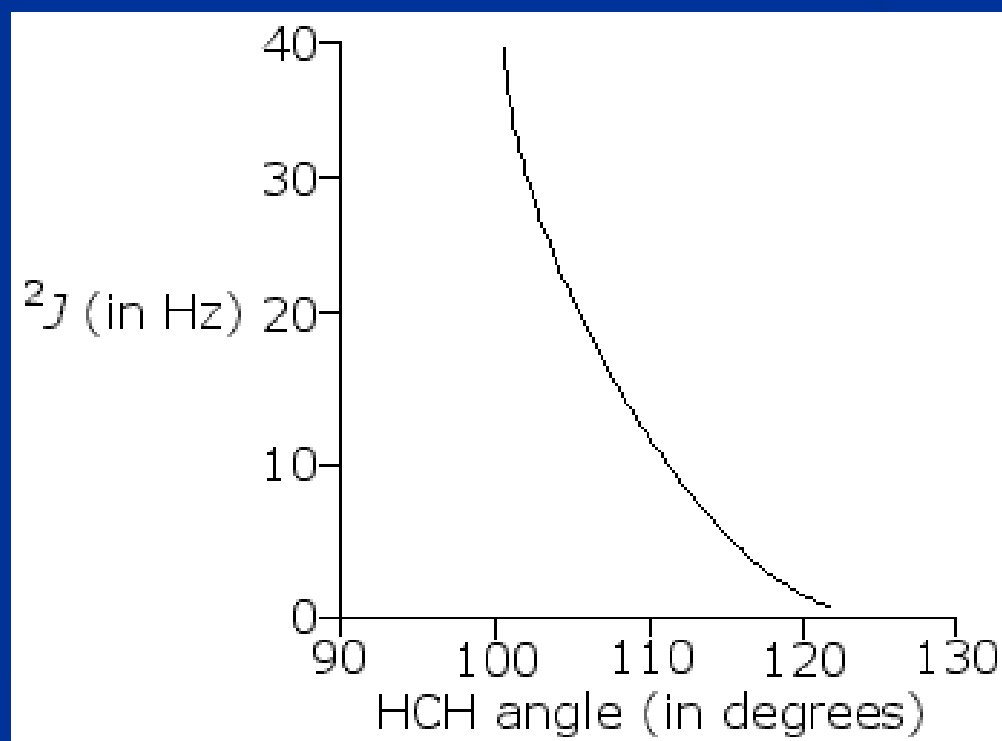
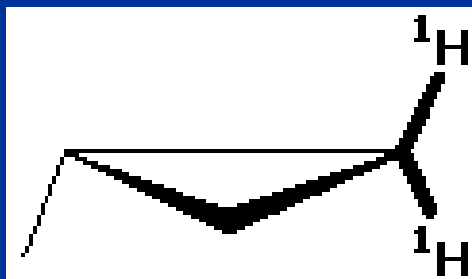
Two types of coupling are most affected by bond angles:

- geminal coupling (two-bond coupling or  $^2J$ )
- vicinal coupling (three-bond coupling or  $^3J$ )

# Geminal Coupling

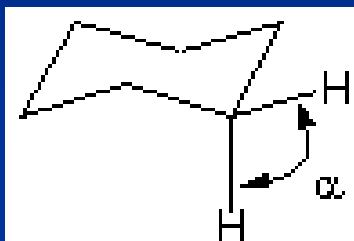
Geminal coupling or  $^2J$  coupling is dependent upon the bond angle between the nuclei.

The smaller the angle the bigger the coupling constant.

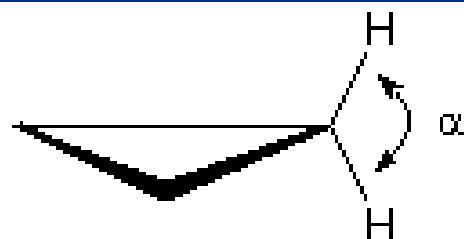


# Geminal Coupling

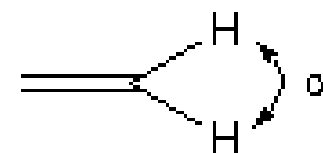
$${}^2J({}^1\text{H} - {}^1\text{H})$$



$$\alpha = 109^\circ$$
$${}^2J = 12 - 18 \text{ Hz}$$



$$\alpha = 118^\circ$$
$${}^2J = 3 - 7 \text{ Hz}$$



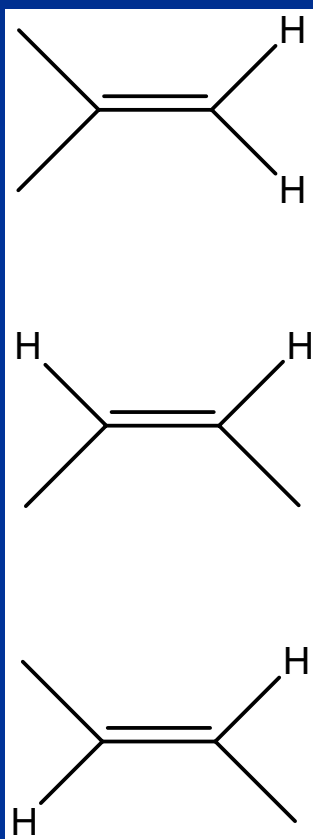
$$\alpha = 120^\circ$$
$${}^2J = 0 - 3 \text{ Hz}$$

The smaller the angle the bigger the coupling constant.



# Trans/Cis Coupling

${}^nJ({}^1\text{H} - {}^1\text{H}), \text{ Hz}$

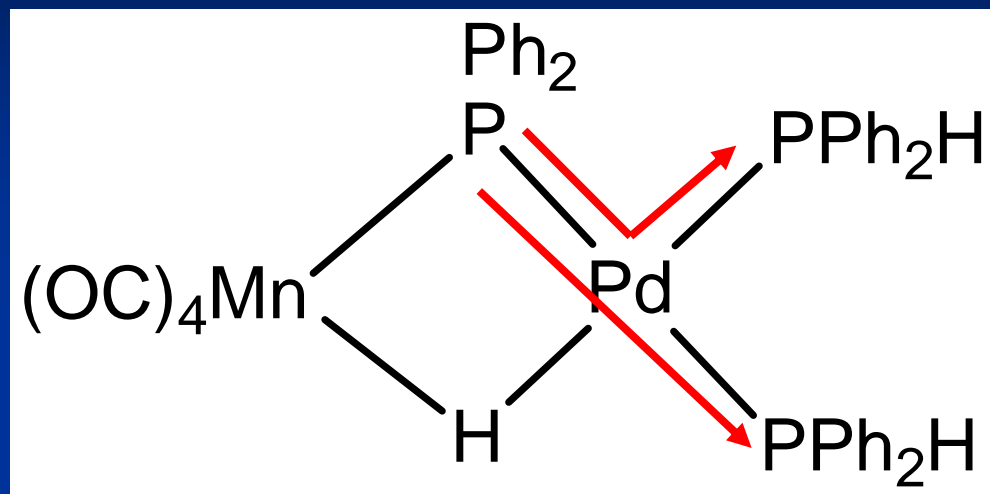


gem      0 – 3

vic cis      6 – 12

vic trans      12 – 18

# Trans/Cis Coupling



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

cis                    0 Hz

trans                213 Hz

# Trans/Cis Coupling

${}^2J$  ( ${}^{31}\text{P} - \text{M} - {}^{31}\text{P}$ )

**cis < trans**

Complex	Coord.	${}^2J_{\text{PP}}$ cis, Hz	${}^2J_{\text{PP}}$ trans, Hz
$\text{PdCl}_2(\text{PMe}_3)_2$	SP1	-8	610
$\text{PtBr}_2(\text{PMe}_3)_2$	SP1	-16	514
$\text{Cr}(\text{CO})_4(\text{PF}_3)_2$	Oh	-36	-28
$\text{Mo}(\text{CO})_4(\text{PF}_3)_2$	Oh	55	312
$\text{Mo}(\text{CO})_4[\text{P}(\text{NMe}_2)_3]_2$	Oh	12	101
$\text{W}(\text{CO})_4(\text{PF}_3)_2$	Oh	38	315
$\text{mer-RhCl}_3(\text{PMe}_3)_3$	Oh	-29	567

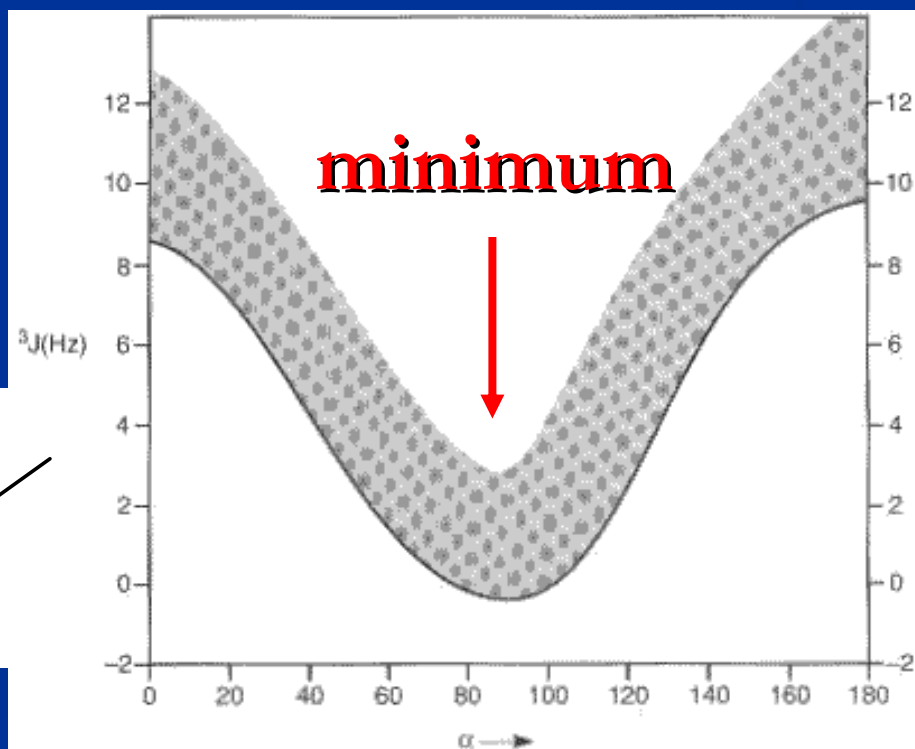
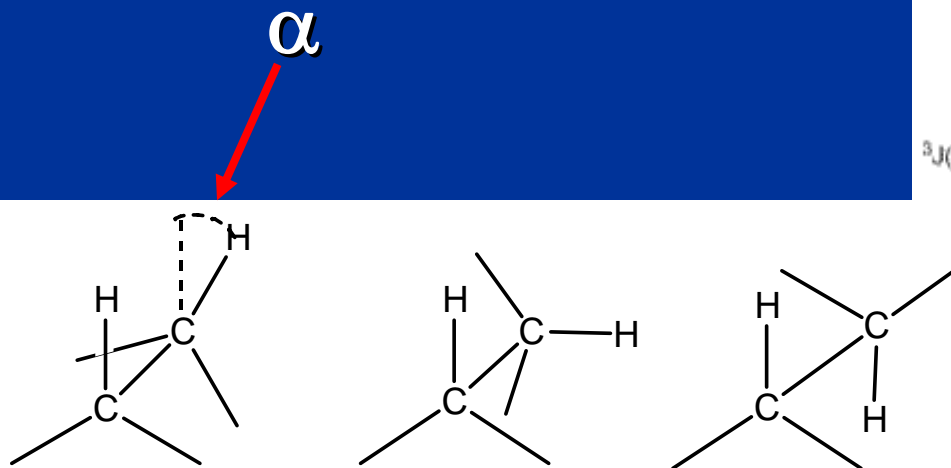
# Vicinal Coupling

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

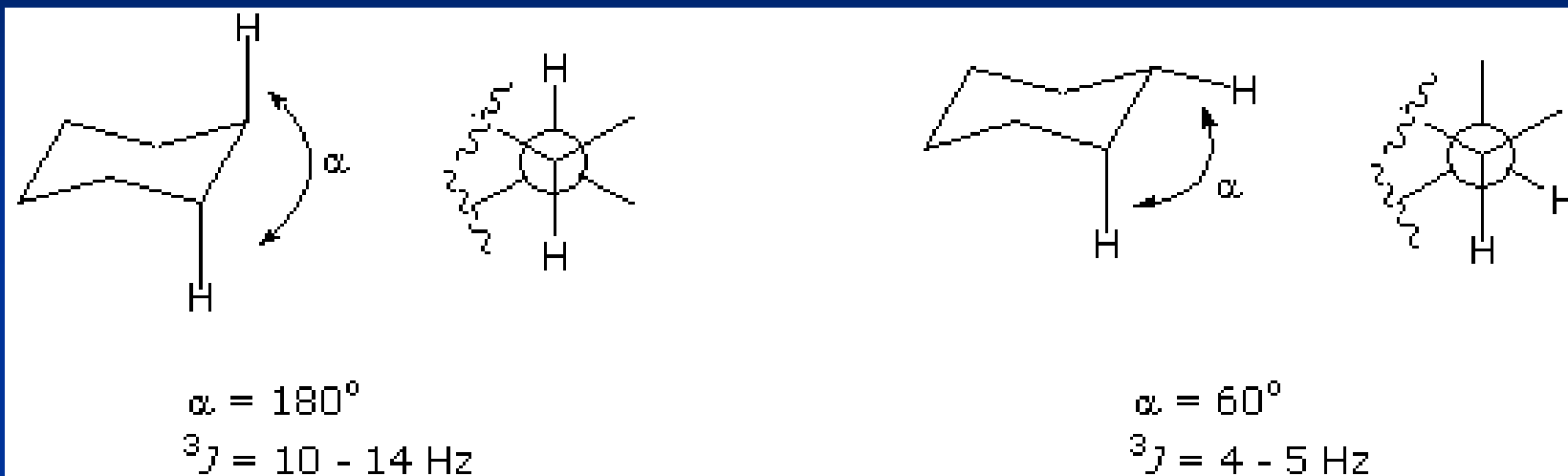
The more eclipsed or antiperiplanar the nuclei the greater the coupling constant.

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

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

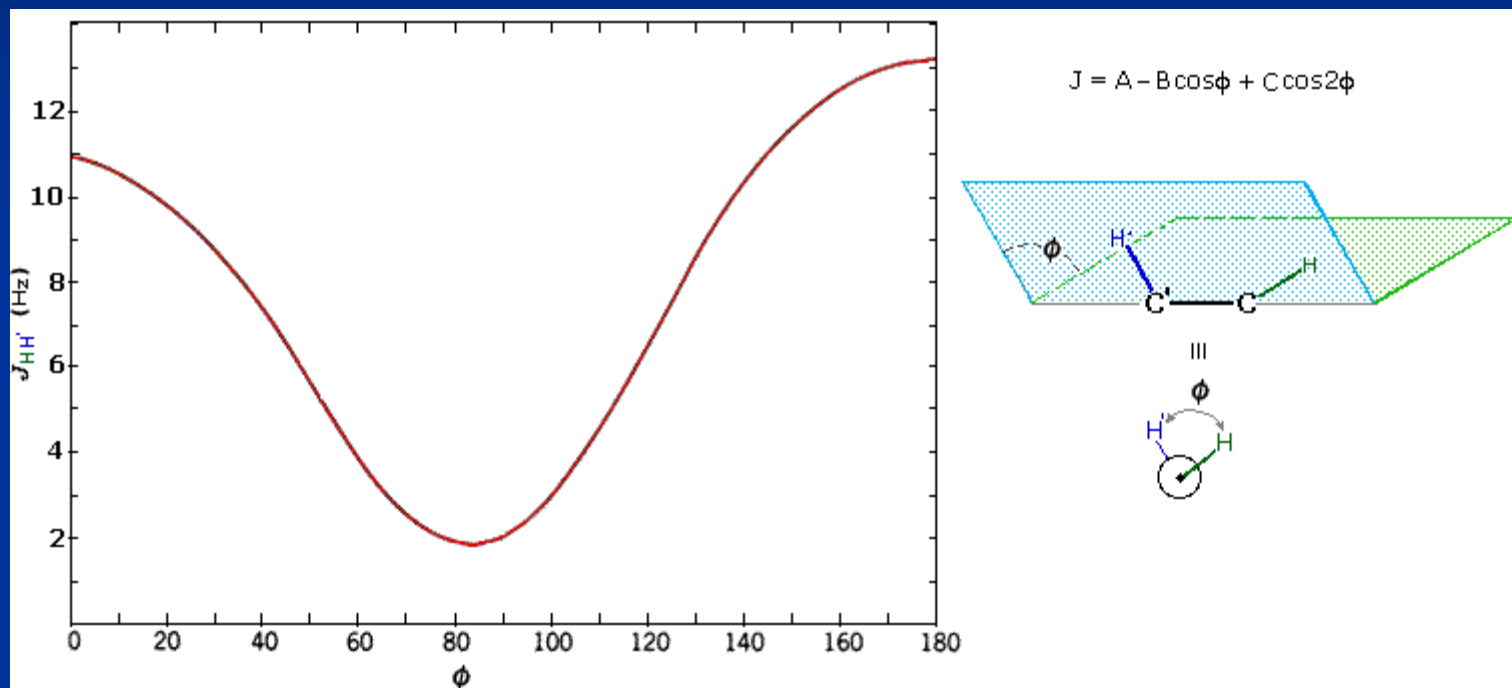


# Vicinal Coupling

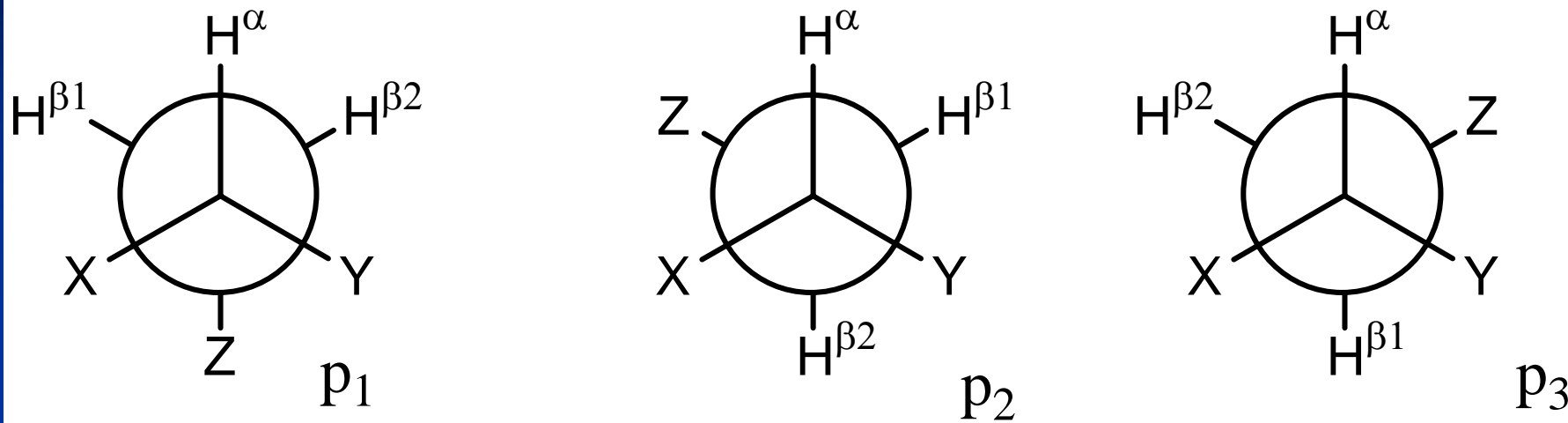


the Karplus equation

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



# Population Analysis



experiment

$$\langle J_{\alpha\beta 1} \rangle = J_g p_1 + J_g p_2 + J_t p_3$$

$$\langle J_{\alpha\beta 2} \rangle = J_g p_1 + J_t p_2 + J_g p_3$$

$$p_1 + p_2 + p_3 = 1$$

$$J_g (60^\circ)$$

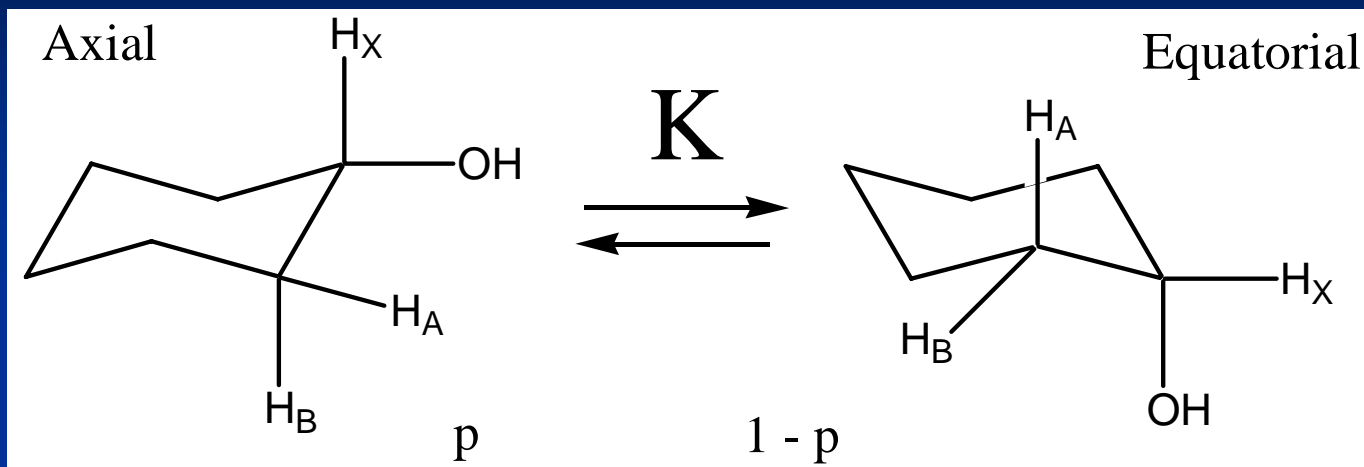
$$J_t (180^\circ)$$

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



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

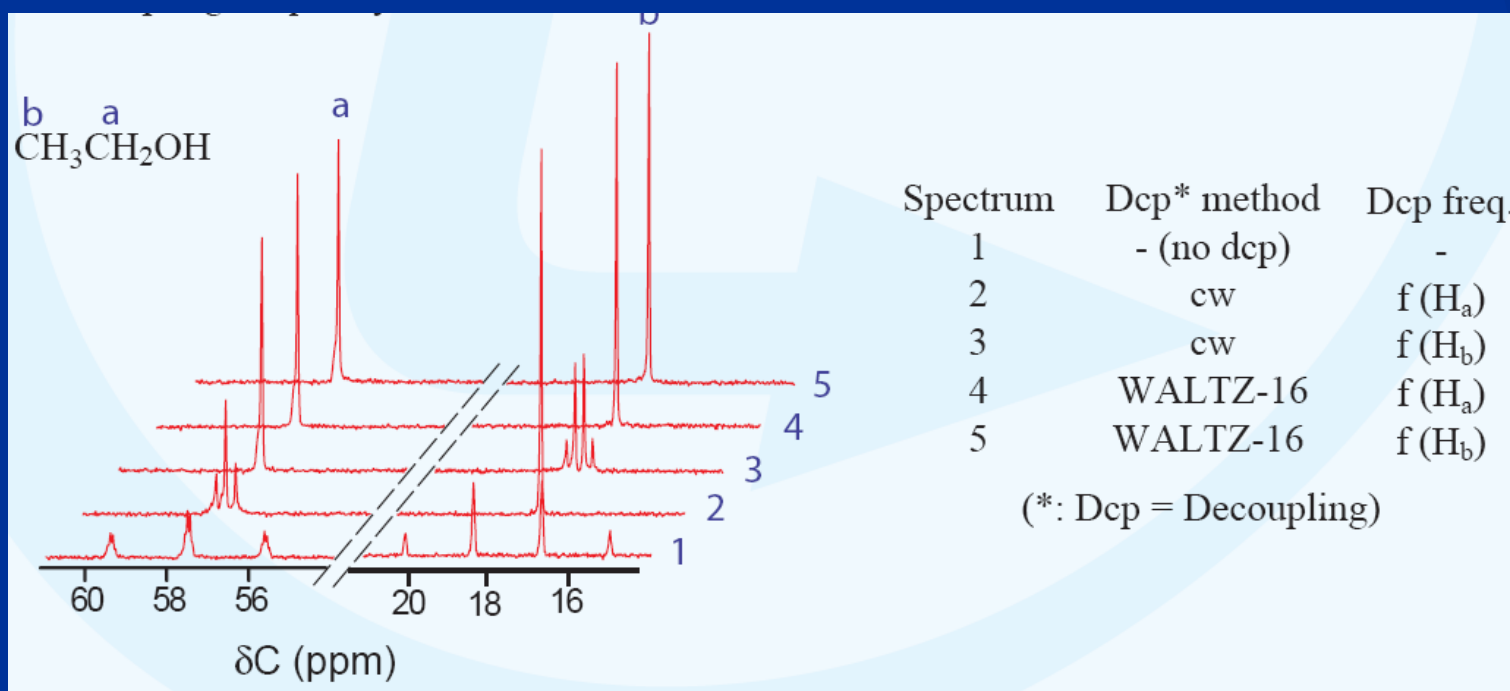
$$\langle J_{BX} \rangle = pJ_{BX}^{Axial} + (1 - p)J_{BX}^{Equ}$$

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

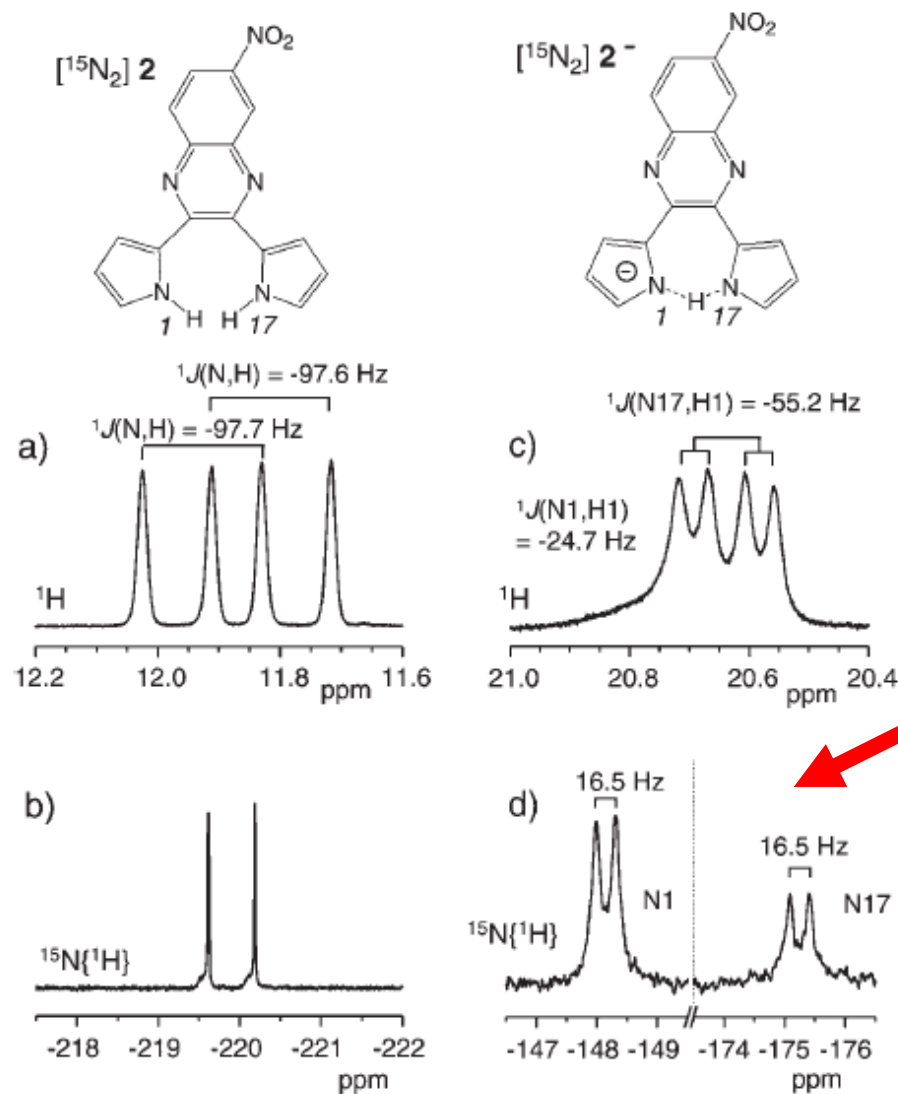


# Decoupling

## Heteronuclear broadband decoupling Selective homonuclear decoupling



# $^{15}\text{N}$ - $^{15}\text{N}$ Coupling Across an NHN Hydrogen Bond



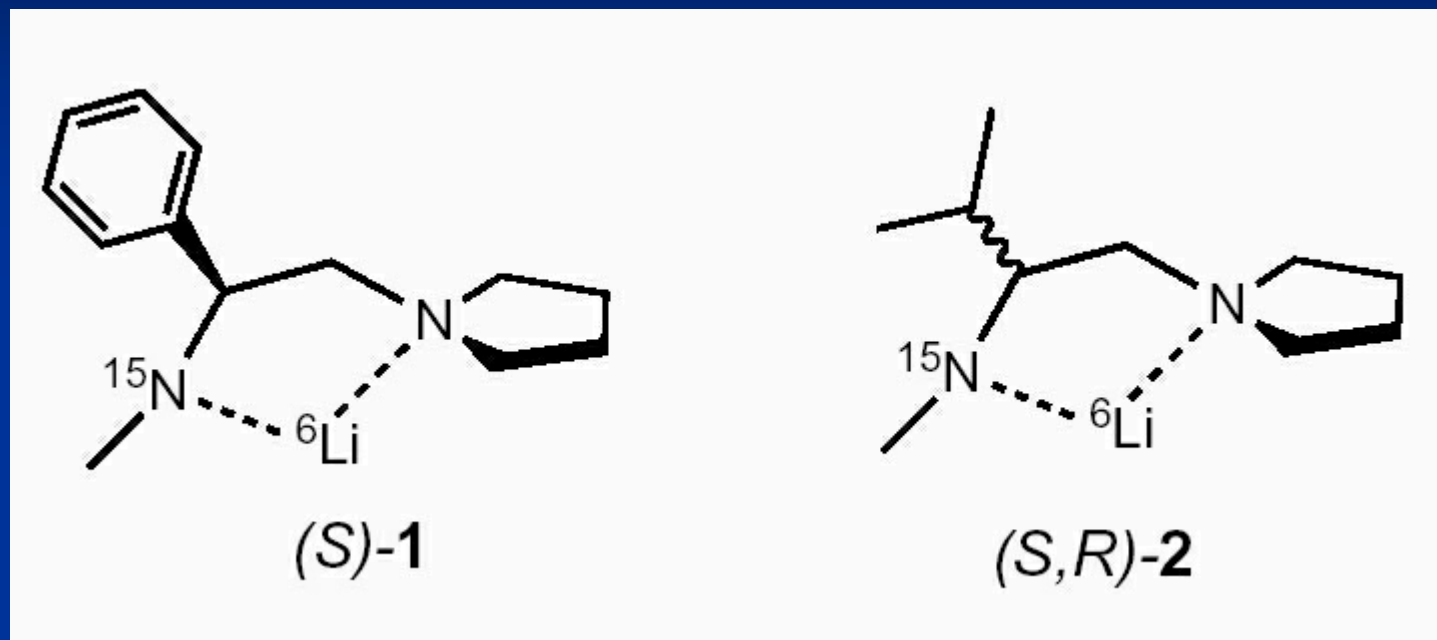
$\text{CD}_2\text{Cl}_2/[\text{d}_6]\text{DMSO}$  (5:1)

a) 233 K    b) 233 K

c) 193 K    d) 193 K

$$^2J(^{15}\text{N}-^{15}\text{N}) = 16.5 \text{ Hz}$$

# ${}^6\text{Li}-{}^{15}\text{N}$ Coupling



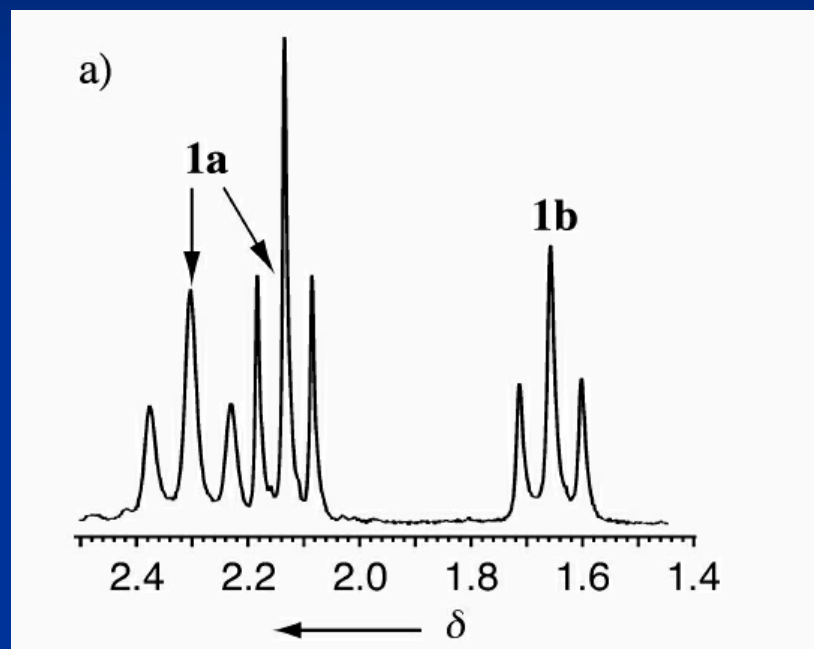
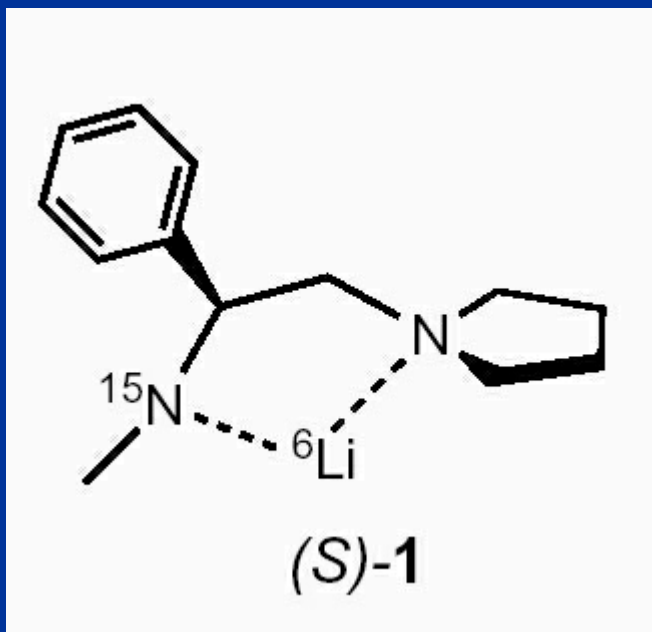
${}^6\text{Li}$  I = 1      NA = 7.42 %

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

# ${}^6\text{Li}-{}^{15}\text{N}$ Coupling

${}^6\text{Li}$  NMR:

- two triplets 1:1  $\delta = 2.15$  ppm ( $J_{\text{LiN}} = 3.7$  Hz) a  $\delta = 2.32$  ppm ( $J_{\text{LiN}} = 6.1$  Hz)
- triplet  $\delta = 1.63$  ppm ( $J_{\text{LiN}} = 4.5$  Hz)



# ${}^6\text{Li}-{}^{15}\text{N}$ Coupling

${}^6\text{Li}$  NMR:

- two triplets 1:1  $\delta = 2.15$  ppm ( $J_{\text{LiN}} = 3.7$  Hz) a  $\delta = 2.32$  ppm ( $J_{\text{LiN}} = 6.1$  Hz)
- triplet  $\delta = 1.63$  ppm ( $J_{\text{LiN}} = 4.5$  Hz)

