

Chemical Shift

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

Nuclear Magnetic Shielding σ

Basic physical phenomenon: Nuclear Magnetic Shielding σ

For diamagnetic samples, the nuclear magnetic shielding can be expressed as correction to the Zeeman splitting:

$$\Delta E = \gamma \hbar B_0(1 - \sigma) = \omega \hbar \quad \text{shielding constant } \sigma$$

- In solution, the nuclear magnetic shielding constant σ is a scalar quantity
- In solids, σ is a tensor ($3 \times 3 = 9$, only 6 measurable)

Faraday's Law

Changes in the magnetic flux through a coil of wire induce a voltage (emf) in the coil

$\frac{\Delta(BA)}{\Delta t} = 4 \text{ Tm}^2/\text{s}$

Changing magnetic flux

$N=4$ $V_{\text{gen}} = -16 \text{ volts}$

$N=2$ $V_{\text{gen}} = -8 \text{ volts}$

Faraday's Law summarizes the ways voltage can be generated.

Changing area in magnetic field

$\frac{\Delta A}{\Delta t} = 0.2 \text{ m}^2/\text{s}$

$N = 3 \text{ turns}$ $B = 0.2 \text{ T}$

Magnetic field region

$V_{\text{gen}} = -3 \times 0.2 \text{ T} \times 0.2 \text{ m}^2/\text{s}$
 $= -0.12 \text{ volts}$

Voltage generated = $-N \frac{\Delta(BA)}{\Delta t}$

Faraday's Law

Moving magnet toward coil

$N = 5 \text{ turns}$ $A = 0.002 \text{ m}^2$

$\frac{\Delta B}{\Delta t} = 0.4 \text{ T/s}$

$V_{\text{gen}} = -5 \times 0.002 \text{ m}^2 \times 0.4 \text{ T/s}$
 $= -0.004 \text{ volts}$

Rotating coil in magnetic field

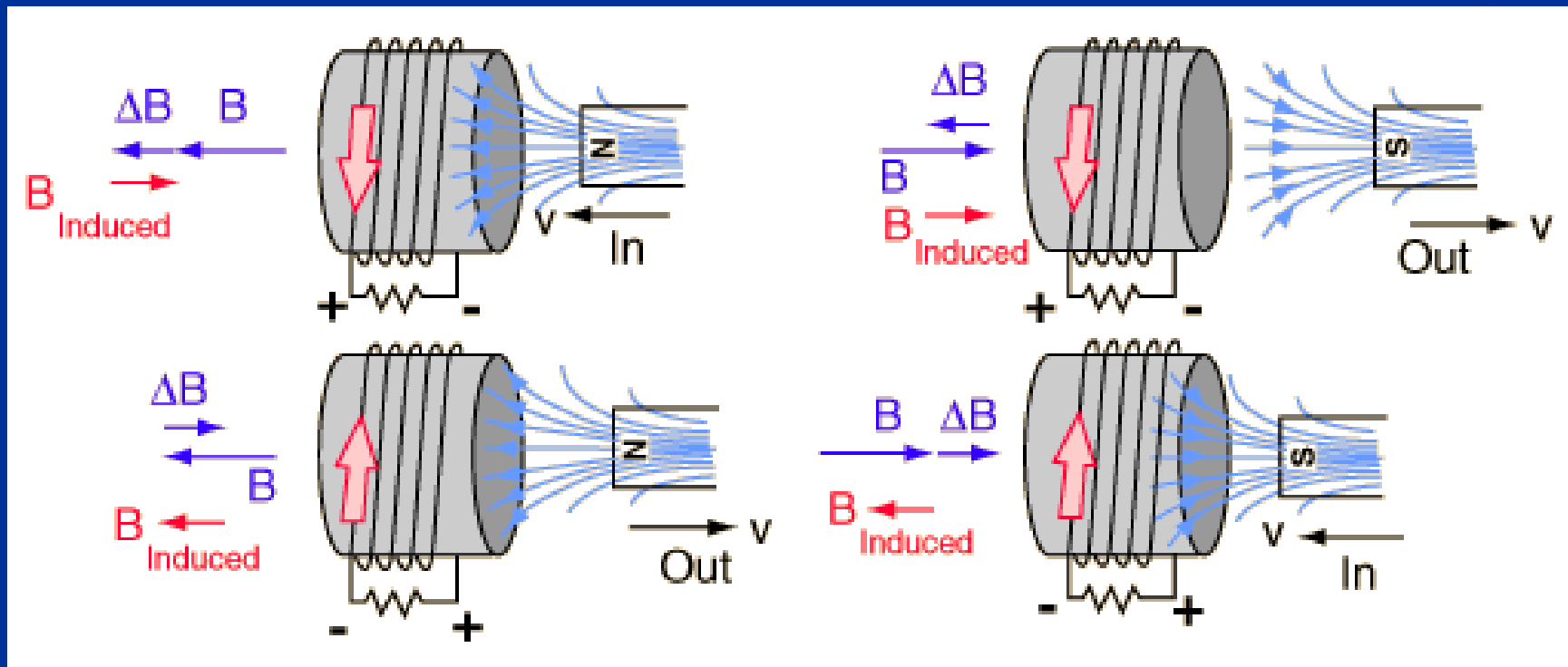
$N = 20 \text{ turns}$ $B = 0.2 \text{ T}$

$\frac{\Delta A}{\Delta t} = 0.2 \text{ m}^2/\text{s}$

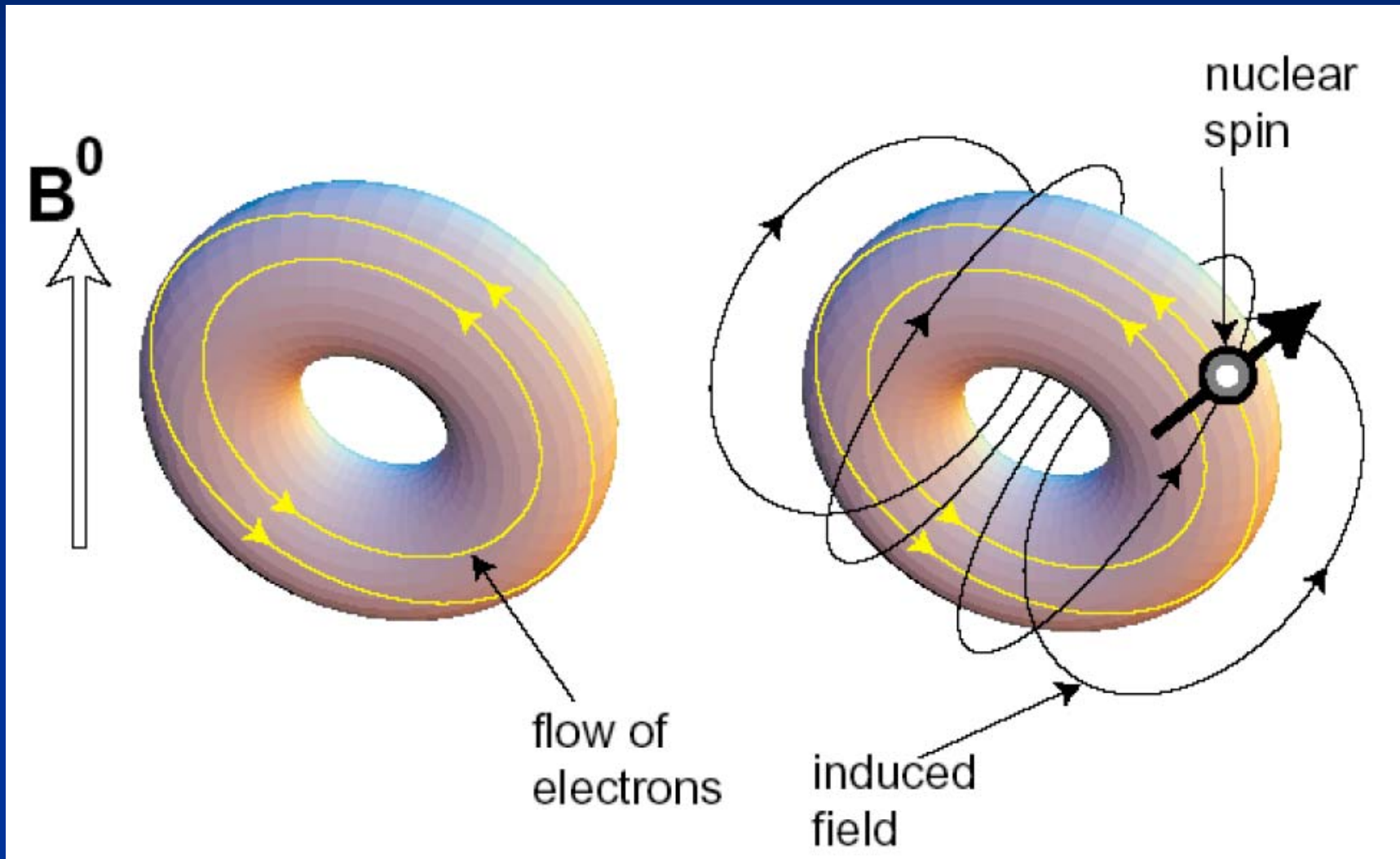
$V_{\text{gen}} = -20 \times 0.2 \text{ T} \times 0.2 \text{ m}^2/\text{s}$
 $= -0.8 \text{ volts}$

Lenz's Law

- A voltage is generated by a change in magnetic flux
- The polarity of the induced emf is such that it produces a current whose magnetic field **opposes** the change which produces it
- The induced magnetic field inside any loop of wire always acts to keep the magnetic flux in the loop constant.



Nuclear Magnetic Shielding



Nuclear Magnetic Shielding σ

s-electrons

spherically symmetric

precess in the applied magnetic field = circulating electron is an electric current, producing a magnetic field at the nucleus which opposes the external field

the resonant condition - the applied field must be increased

- **diamagnetic** shift (shielding)

all atoms have diamagnetic shifts

p,d,f-electrons

no spherical symmetry, and produce large magnetic fields

at the nucleus - **paramagnetic** shifts (deshielding)

Nuclear Magnetic Shielding σ

Two different nuclei

$$B_{\text{nucl}} = B_0 - B_{\text{shield}}$$

$$B_{\text{shield}} = B_0 \sigma \quad \text{Lenz's rule}$$

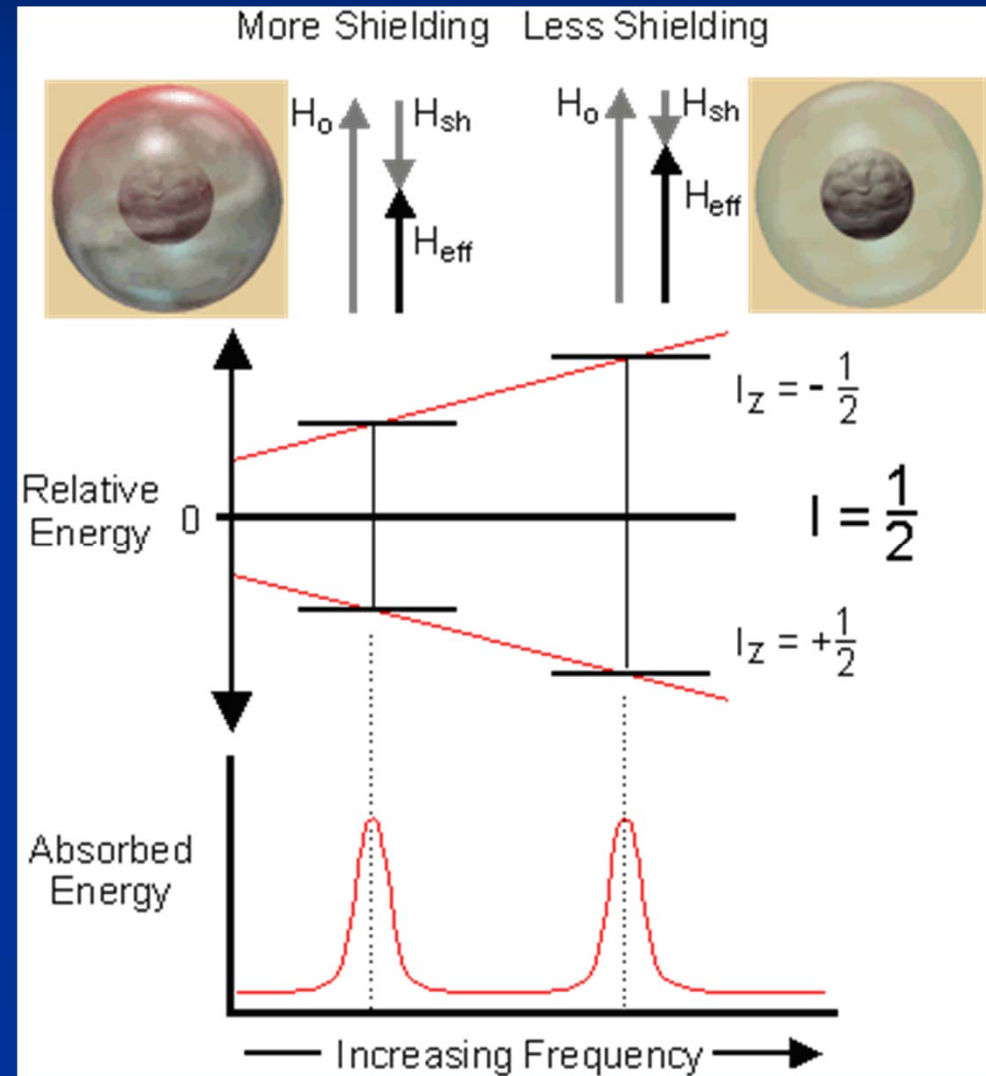
$$B_{\text{nucl}} = B_0 - B_0 \sigma = B_0(1 - \sigma)$$

$$\omega = \gamma B_{\text{nucl}} = \gamma B_0(1 - \sigma)$$

B = the magnetic flux density or magnetic induction (T)

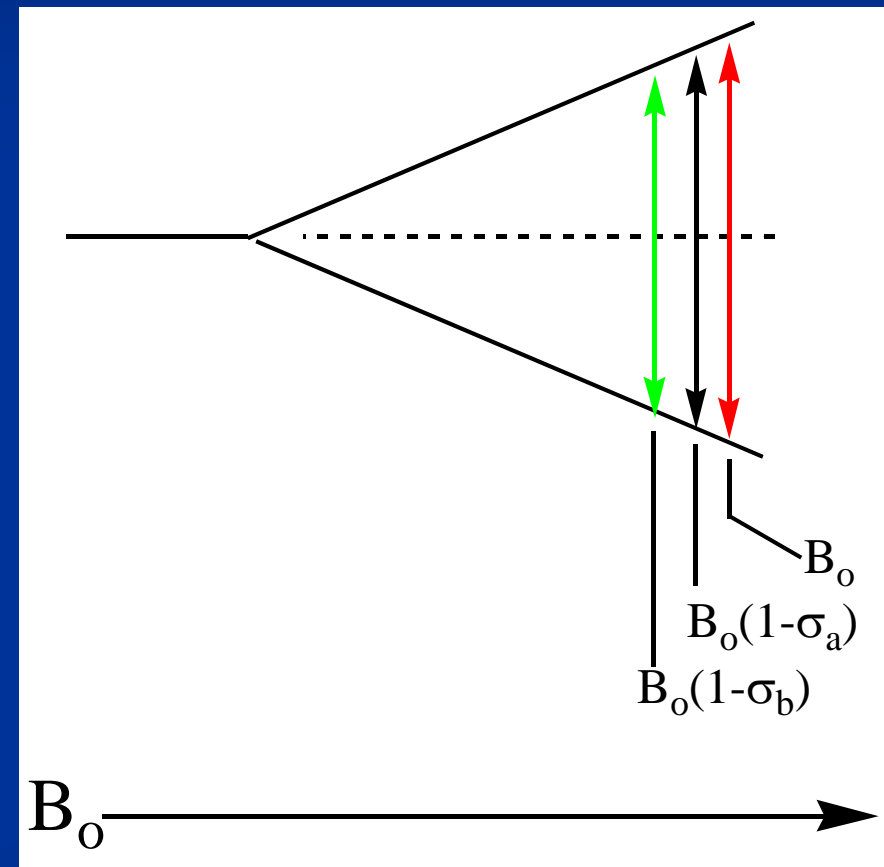
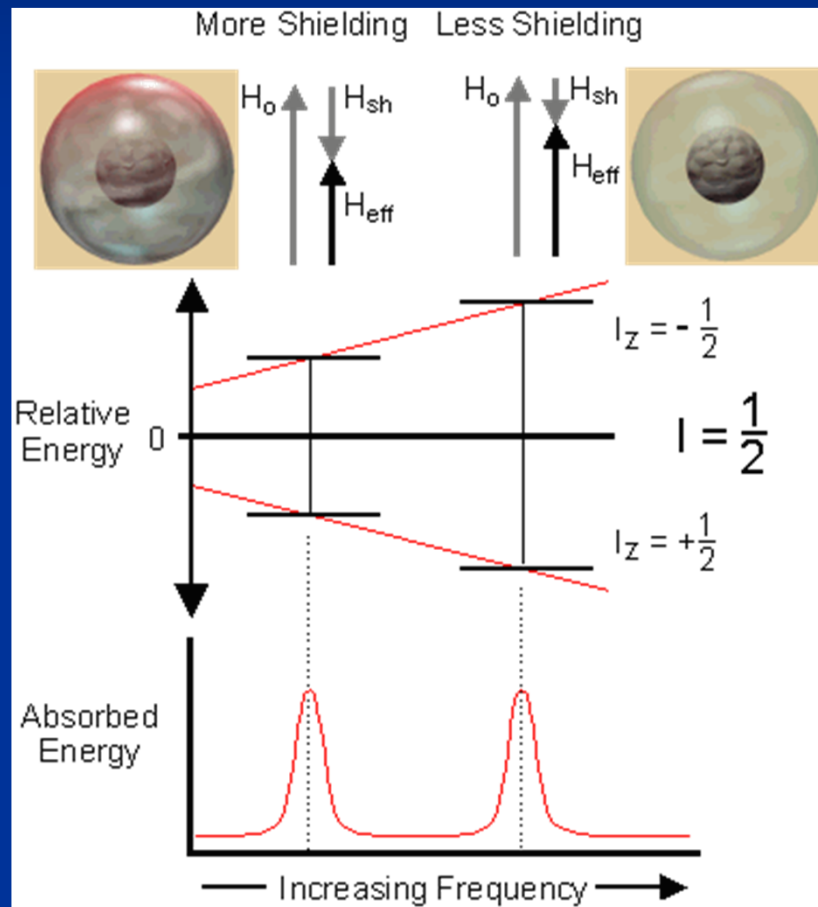
H = the magnetic field (strength) (A/m)

$$B = \mu H$$



Nuclear Magnetic Shielding σ

$$\omega = \gamma B_{\text{nucl}} = \gamma B_0(1 - \sigma)$$



Absolute Magnetic Shielding

the absolute value of the nuclear magnetic shielding constant **cannot be measured experimentally by NMR**, difficult to measure, but can be done for atoms or small molecules

MHz vs. Hz $1:10^6$

Relative Magnetic Shielding

Requires measurement of differences of resonance frequencies between a sample and a **standard** (much more easily done)

- **Internal standard** - a reference compound is in the same sample preferred from spectroscopic point of view, may cause chemical problems
- **External standard** - in a different sample tube

Absolute Chemical Shieldings

Nucleus	Primary Reference	Secondary Reference
^1H	H atom, $\sigma_{\text{iso}} = 17.733$ ppm	H_2O , $\sigma_{\text{iso}} = 25.790$ ppm
^{13}C	CO , $\sigma_{\text{iso}} = 3.20$ ppm	TMS, $\sigma_{\text{iso}} = 185.4$ ppm
^{15}N	NH_3 , $\sigma_{\text{iso}} = 264.54$ ppm	CH_3NO_2 , $\sigma_{\text{iso}} = -135.0$ ppm
^{17}O	CO , $\sigma_{\text{iso}} = -42.3$ ppm	H_2O , $\sigma_{\text{iso}} = 307.9$ ppm
^{19}F	HF , $\sigma_{\text{iso}} = 410$ ppm	CFCl_3 , $\sigma_{\text{iso}} = 189.9$ ppm
^{31}P	PH_3 , $\sigma_{\text{iso}} = 597$ ppm	H_3PO_4 , $\sigma_{\text{iso}} = 356$ ppm
^{33}S	OCS , $\sigma_{\text{iso}} = 843$ ppm	CS_2 , $\sigma_{\text{iso}} = 581$ ppm

Chemical Shift

$$\delta = \frac{\nu_s - \nu_{ref} [\text{Hz}]}{\nu_0 [\text{MHz}]}$$

Strength of Field:

$B_0 = 1.41 \text{ T}$

$B_0 = 2.35 \text{ T}$

Operating Frequency, ν_0 :

60 MHz

100 MHz

Shift From TMS:

162 Hz

270 Hz

δ value:

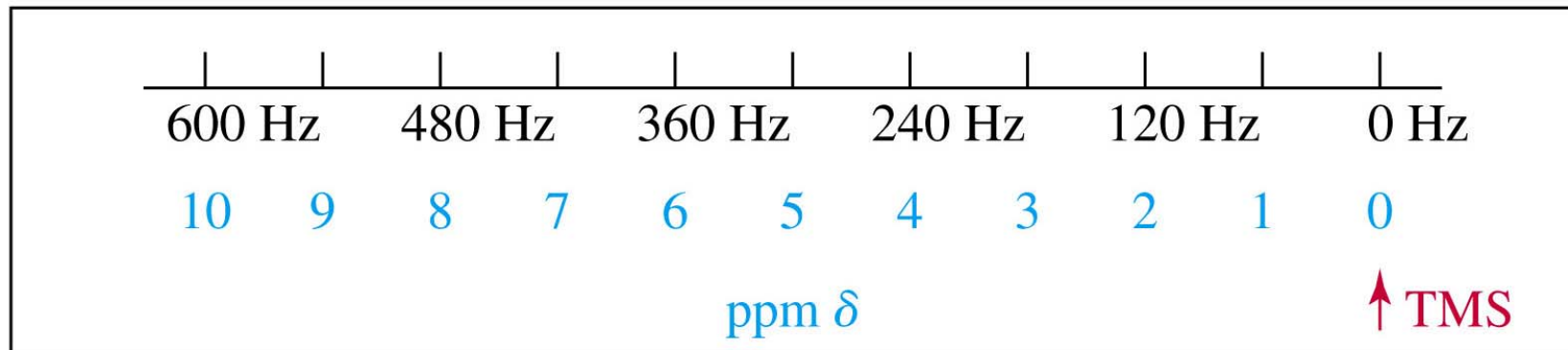
2.70 ppm

2.70 ppm

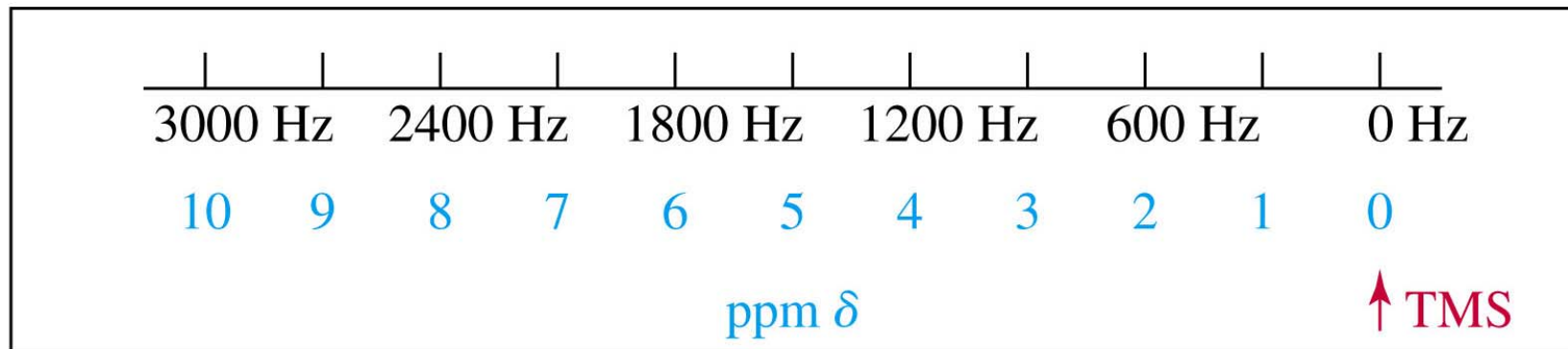
The δ scale (or ppm scale) is independent of the instrument used to obtain the spectrum

Chemical Shift

$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$



60 MHz



300 MHz

The relative shielding of the sample can be expressed as:

Absolute Magnetic Shielding (σ -scale):

$$\sigma = 10^6 (\nu_{\text{nucl}} - \nu_s) / \nu_{\text{nucl}}$$

ν_{nucl} = absolute resonance frequency of the atom

ν_s = absolute resonance frequency of the signal

Chemical Shift (δ -scale):

$$\delta (\text{H}_3\text{PO}_4) = 0$$

$$\sigma (\text{H}_3\text{PO}_4) = 320$$

$$\delta = 10^6 (\nu_s - \nu_{\text{ref}}) / \nu_{\text{ref}}$$

ν_{ref} = resonance frequency of the standard

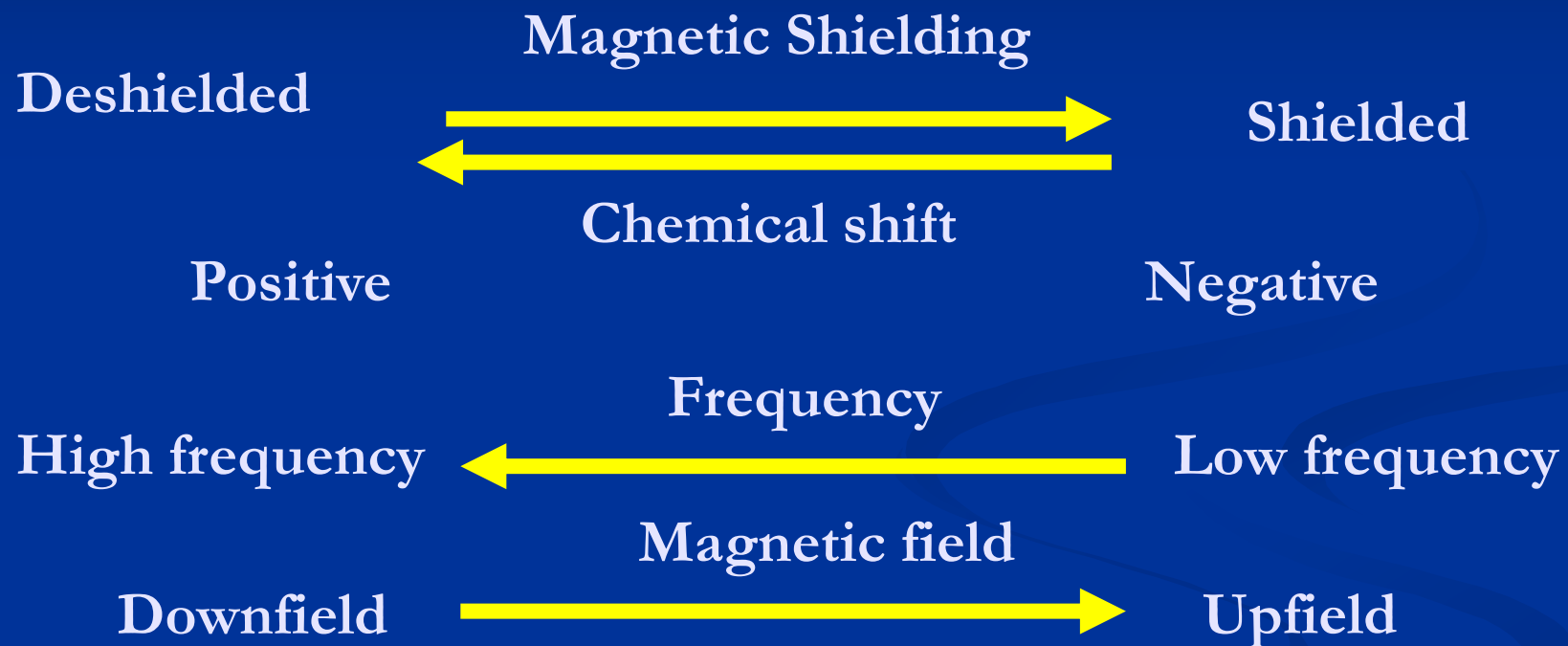
Conversion between both scales:

$$\delta = (\sigma_{\text{ref}} - \sigma_s) / (1 - \sigma_{\text{ref}}) \sim (\sigma_{\text{ref}} - \sigma_s)$$

σ_{ref} = absolute magnetic shielding value of the standard

**Nuclei in
electron poor environments**

**Nuclei
in electron rich environments**



Convention: High frequency positive

Chemical Shift References

^1H	ppm	
SiMe_4	0	
DSS	0	$\text{Me}_3\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-SO}_3\text{Na}$
TSP	0	$\text{Me}_3\text{Si-CD}_2\text{-CD}_2\text{-COONa}$

^{19}F	ppm	
CFCl_3	0	^{129}Xe (I = $\frac{1}{2}$, 26.4 %)
CF_3COOH	-78.5	^{131}Xe (I = $\frac{3}{2}$, 21.1 %)
C_6F_6	-162.9	
HF	198.4	Xenon in freon
F_2	422.9	Liquid XeOF_4

Chemical Shift References

^{19}F , ppm

Be careful with
literature data

Sometimes $\text{C}_6\text{F}_6 = 0$

-Reference compounds

CFCl_3 (trichlorofluoromethane)	0.00
CF_3COOH (trifluoroacetic acid)	-76.55
C_6F_6 (hexafluorobenzene)	-164.9
$\text{C}_6\text{H}_5\text{F}$ (fluorobenzene)	-113.15
CF_3Cl (trifluorochloromethane)	-28.6
F_2 (elemental fluorine)	+422.92
FCH_2CN (fluoroacetonitrile)	-251.
$\text{CFCl}_2\text{CFCl}_2$ (difluorotetrachloroethane)	-67.80
$\text{C}_6\text{H}_5\text{CF}_3$ (trifluorotoluene)	-63.72
SiF_4 (tetrafluorosilane)	-163.3
SF_6 (sulfur hexafluoride)	+57.42
$\text{S}_2\text{O}_5\text{F}_2$	+47.2
$(\text{CF}_3)_2\text{CO}$ (hexafluoro acetone)	-84.6
p- $\text{FC}_6\text{H}_4\text{F}$ (para-difluorobenzene)	-106.0
BF_3	-131.
HF (aq)	-204.0
CF_4	-62.5
Aqueous F^- (KF)	-125.3

Factors Influencing Chemical Shifts

- (1) The physical state of the sample (solid, liquid, solution or gas)
- (2) For solutions, the solvent and the concentration of solute
- (3) The nature of the reference procedure, e.g. internal, external (coaxial tubes or substitution), absolute frequency
- (4) The reference compound and, if used internal to a solution, its concentration
- (5) The temperature and pressure of the sample
- (6) Whether oxygen and other gases have been removed from the sample
- (7) Any chemical present in the sample, in addition to the compound under investigation and any reference compound

Factors Influencing Chemical Shifts

(1) Intramolecular factors

Diamagnetic contribution
Paramagnetic contribution
Magnetic anisotropy
Ring currents
van der Waals repulsion

(2) Intermolecular factors

Volume susceptibility
van der Waals forces
Induced electric field
Collision complexes

Fundamental Contributions to the Magnetic Shielding Constant

$$\sigma^A = \sigma_{\text{dia}}^A + \sigma_{\text{para}}^A + \sum \sigma_{\text{nonloc}}^{AB}$$

σ_{dia}^A - Interaction of electrons of nucleus A with the external magnetic field B_0 induces a diamagnetic current density. This produces an induced field at the nucleus A which is proportional to B_0 and **opposite in sign**
SHIELDING CONTRIBUTION



The subtraction of the internal field from the applied field causes nuclei A to resonate at a high applied field

Fundamental Contributions to the Magnetic Shielding Constant

$$\sigma^A = \sigma_{\text{dia}}^A + \sigma_{\text{para}}^A + \sum \sigma_{\text{nonloc}}^{AB}$$

σ_{para}^A - Interaction of B_0 with electrons with non-vanishing orbital moments induces a polarisation of the electron distribution. This produces an additional induced field at the nucleus A which is proportional to B_0 and **equal in sign**
DESHIELDING CONTRIBUTION



The addition of the internal field to the applied field causes nuclei to resonate at a low applied field

Fundamental Contributions to the Magnetic Shielding Constant

$$\sigma^A = \sigma_{\text{dia}}^A + \sigma_{\text{para}}^A + \sum \sigma_{\text{nonloc}}^{\text{AB}}$$

$\sum \sigma_{\text{nonloc}}^{\text{AB}}$ - Electrons localized at distant nuclei B may contribute to the shielding at nucleus A (ring currents in aromatic molecules, solvent influences, shielding anisotropy of carbonyl groups) **SHIELDING** or **DESHIELDING** CONTRIBUTION

Generally lower in magnitude than σ_{dia} or σ_{para} .



Magnetic Shielding

Which Electrons contribute to σ_{dia} and σ_{para} ?

		σ_{dia}	σ_{para}
Core Electrons	Total orbital magnetic moment for closed shells : $\ell = 0$	+	-
Valence s-Electrons	$\ell = 0$	+	-
Valence p,d,f-Electrons	$\ell = 1,2,3$	+	+

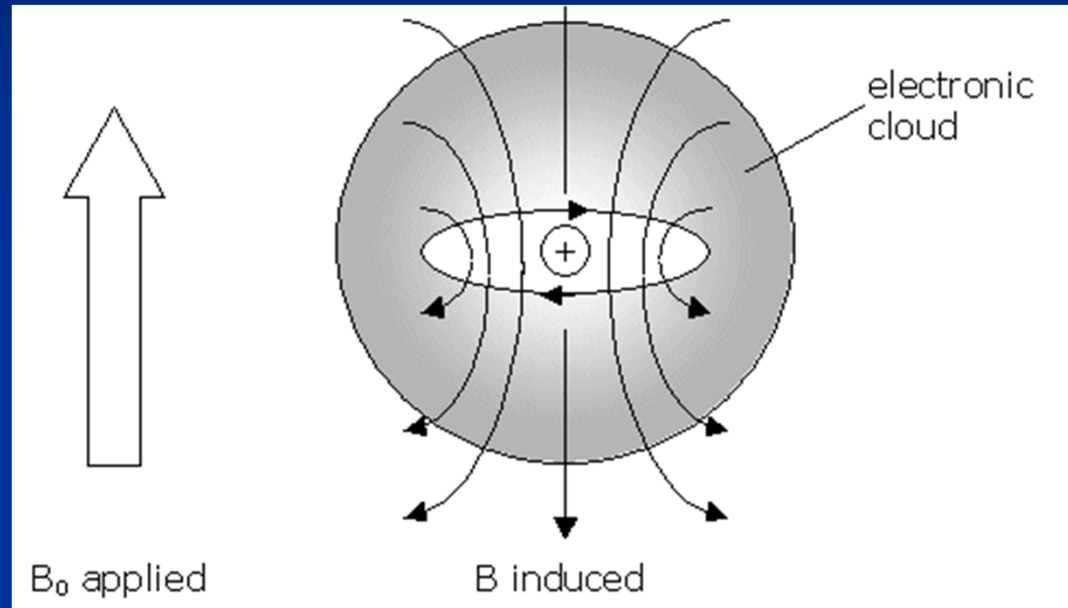
$\sigma_{\text{para}} = 0$ for spherical closed-shell atoms or ions (F^-)

Magnetic Shielding

Magnetic Shielding Contributions for Different Elements

s-Block Elements	<p>valence p-orbitals absent (H) or hardly occupied (group 1, 2 metals) ⇒ diamagnetic term dominates ⇒ large non-local contributions (up to 20% for ^1H)</p>
p,d-Block Elements	<p>valence p,d-orbitals involved in bonding ⇒ paramagnetic term dominates ⇒ non-local contributions mostly not important (but may become important for nuclei with lone pairs)</p>

The Diamagnetic Contribution to the Magnetic Shielding Constant



$$\mathbf{B}_{\text{nucl}} = \mathbf{B}_0 - \mathbf{B}_{\text{induced}} = \mathbf{B}_0 - \mathbf{B}_0 \sigma$$

$$\mathbf{B}_{\text{nucl}} = \mathbf{B}_0(1 - \sigma)$$

$$\omega = \gamma \mathbf{B}_{\text{nucl}} = \gamma \mathbf{B}_0(1 - \sigma)$$

The Diamagnetic Contribution to the Magnetic Shielding Constant

$$\sigma = \sigma^{d,is} + \sigma^d$$

$\sigma^{d,is}$ Shielding Constant for an isolated atom

(LAMB, easily computed from first principles, electron in a spherical orbit)

$$\sigma^{d,is} = \frac{\mu_0 e^2}{4\pi m_e} \left\langle \Psi^0 \left| r^{-1} \right| \Psi^0 \right\rangle$$

Ψ_0 = wavefunction of the ground state

$\mu_0 = 4\pi \cdot 10^{-7} \text{ N A}^{-2}$ permeability of free space

m_e = electron mass

r = electron radius

The Diamagnetic Contribution to the Magnetic Shielding Constant

$$\sigma = \sigma^{\text{d,is}} + \sigma^{\text{d}}$$

σ^{d} Correction for Atoms in Molecules
(Approximation by FLYGARE)

$$\sigma^{\text{d}} = \frac{\mu_0 e^2}{4\pi m_e} \sum_{\text{ligands}} \frac{Z_i}{r_i} = k \sum_{\text{ligands}} \frac{Z_i}{r_i}$$

Shielding increases when

- element number Z_i of the ligands increases
- coordination number of the observed atom increases
- bond distance r_i decreases

Diamagnetic Shifts for Isolated Atoms

σ_{dia}	ppm
^1H	18
^{13}C	261
$^{14/15}\text{N}$	325
^{17}O	395
^{19}F	471
^{21}Ne	552
^{31}P	961
^{33}S	1050
^{83}Kr	3246
^{127}I	5502
^{129}Xe	5642
^{195}Pt	9396
^{207}Pb	10061

Alkalides M^-

^{23}Na -62

^{39}K -105

^{87}Rb -185

^{133}Cs -280

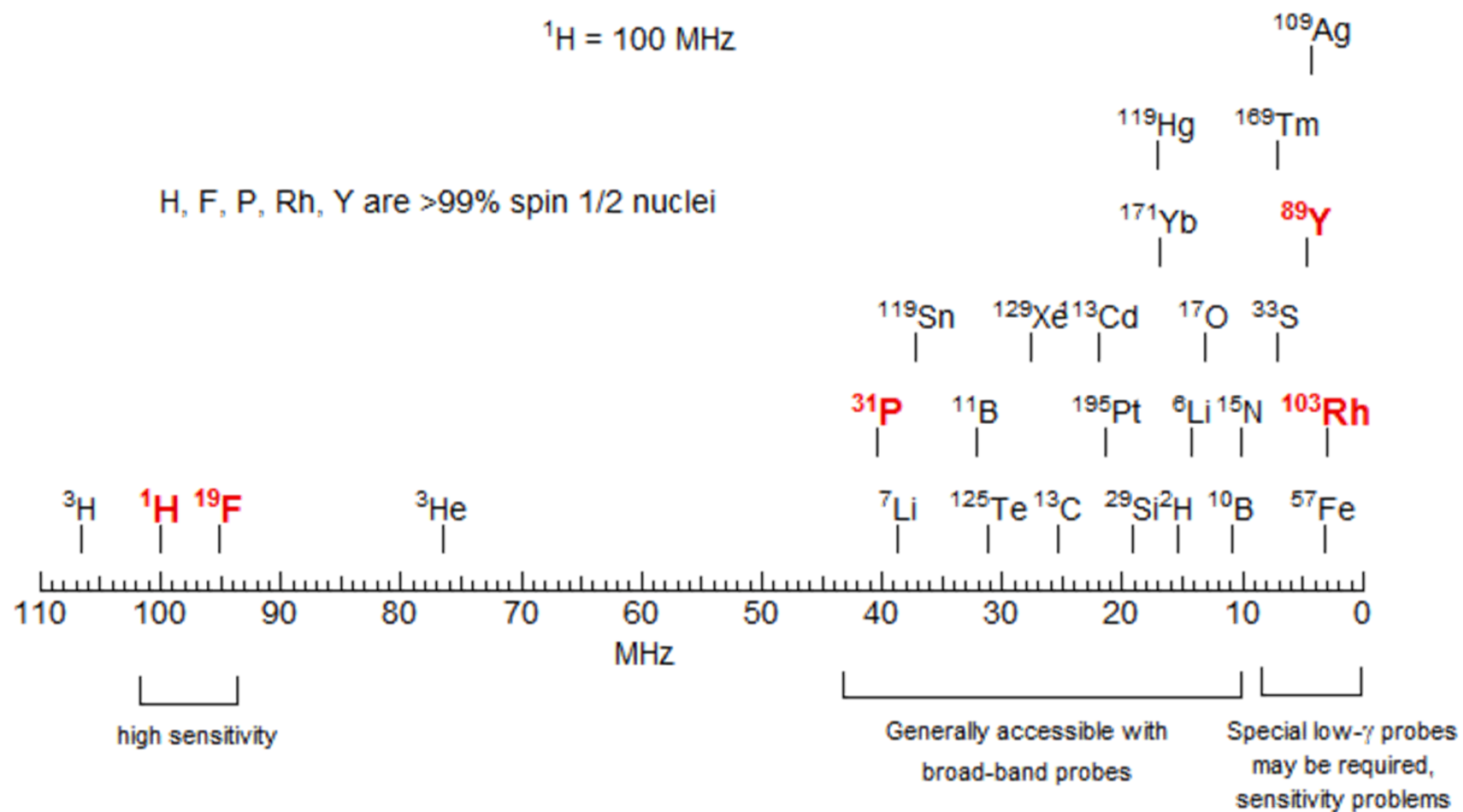
Shielding increases when element number Z of the observed atom increases

$$\sigma^{\text{d}} \sim 0.319 \cdot 10^{-4} Z^{4/3}$$

Large and heavy atoms have large diamagnetic shielding

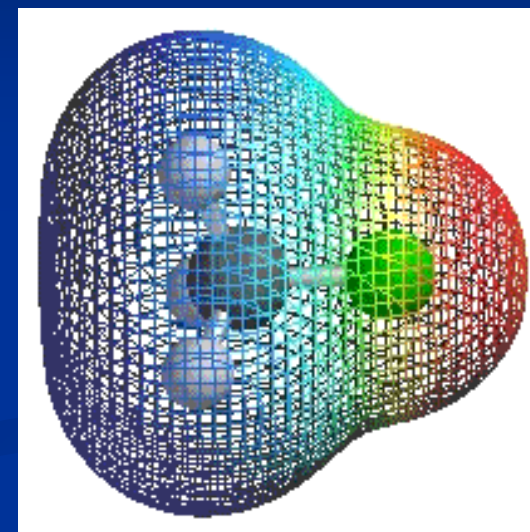
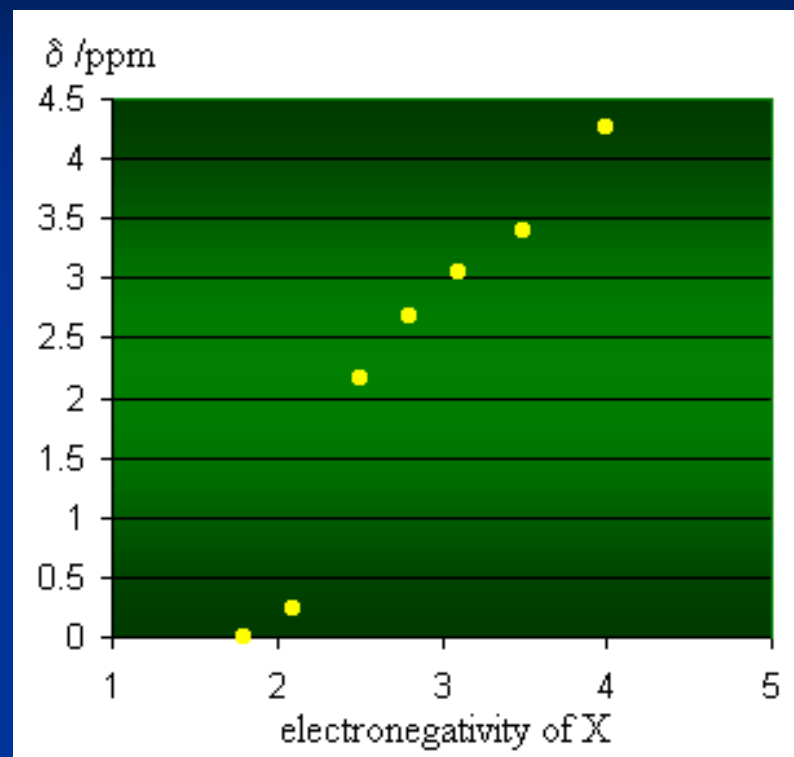
$^1\text{H} = 100 \text{ MHz}$

H, F, P, Rh, Y are >99% spin 1/2 nuclei



Influence of Electronegativity

$\delta (^1\text{H}) / \text{ppm}$



Compound, CH_3X
X

CH_3F
F

CH_3OH
O

CH_3Cl
Cl

CH_3Br
Br

CH_3I
I

CH_4
H

$(\text{CH}_3)_4\text{Si}$
Si

Elnegat of X

4.0

3.5

3.1

2.8

2.5

2.1

1.8

Chemical shift, δ / ppm

4.26

3.4

3.05

2.68

2.16

0.23

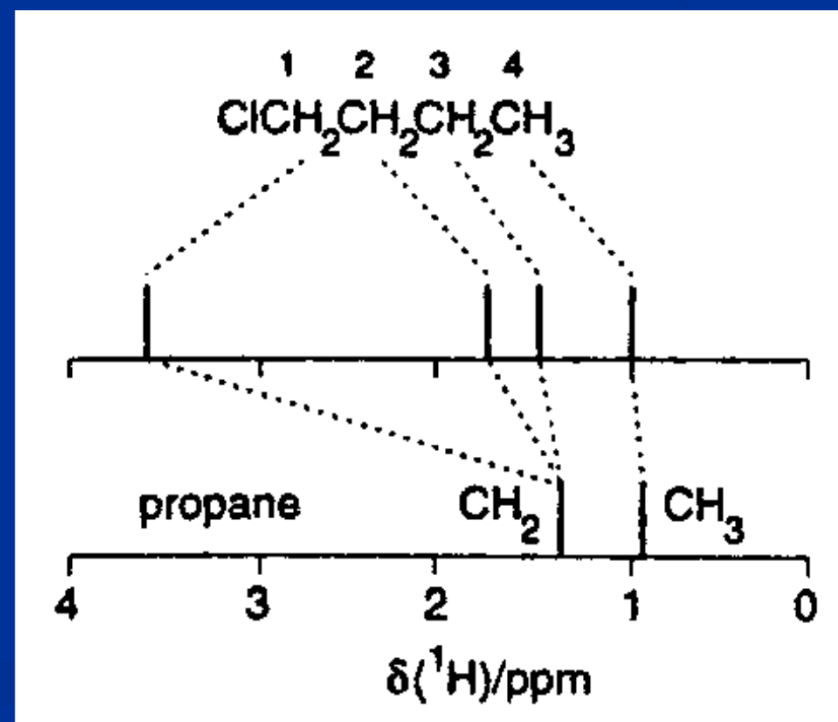
0

Influence of Electronegativity

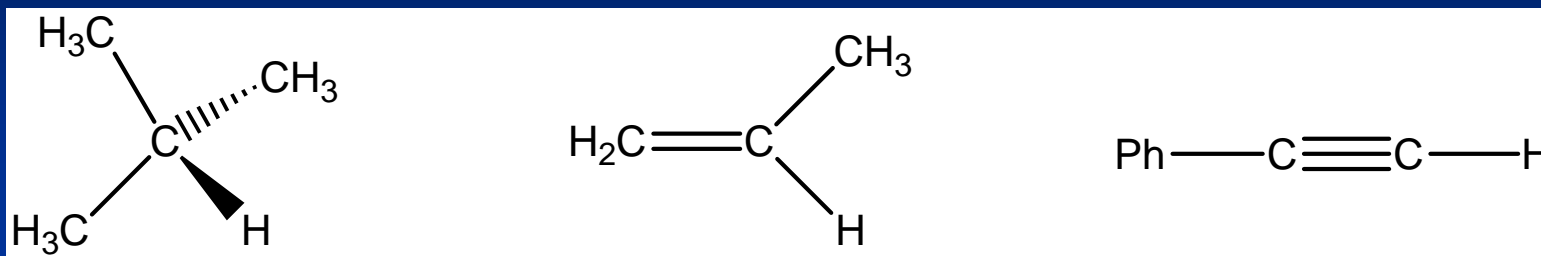
Compound	CHCl_3	CH_2Cl_2	CH_3Cl	CH_4
$\delta(^1\text{H}) / \text{ppm}$	7.27	5.30	3.05	0.23

Influence of electronegative substituents :

- increases with their increasing number
- decreases with increasing distance



Influence of Electronegativity



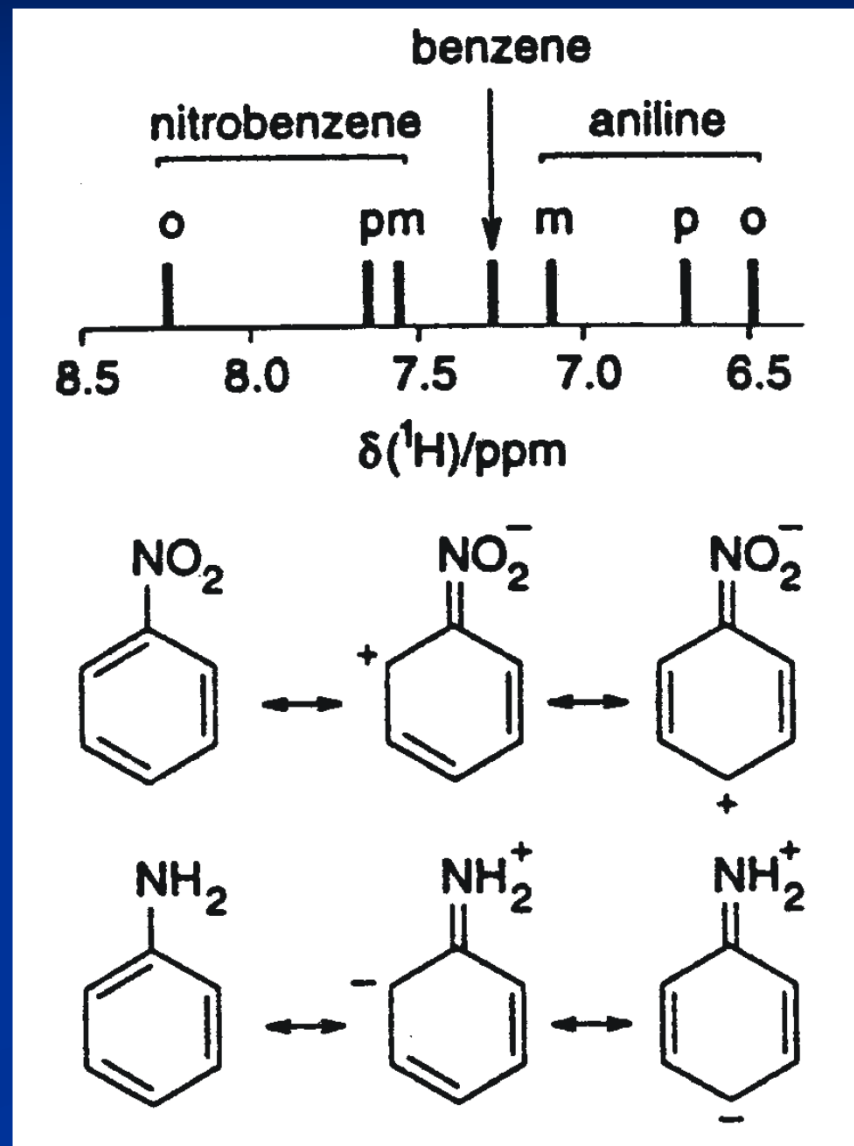
pK_a (in DMSO)	~55	44	28.8
acidity of C increases			
% C-H s-character	25	33	50
electronegativity of C increases			

Aromatic Proton Shifts

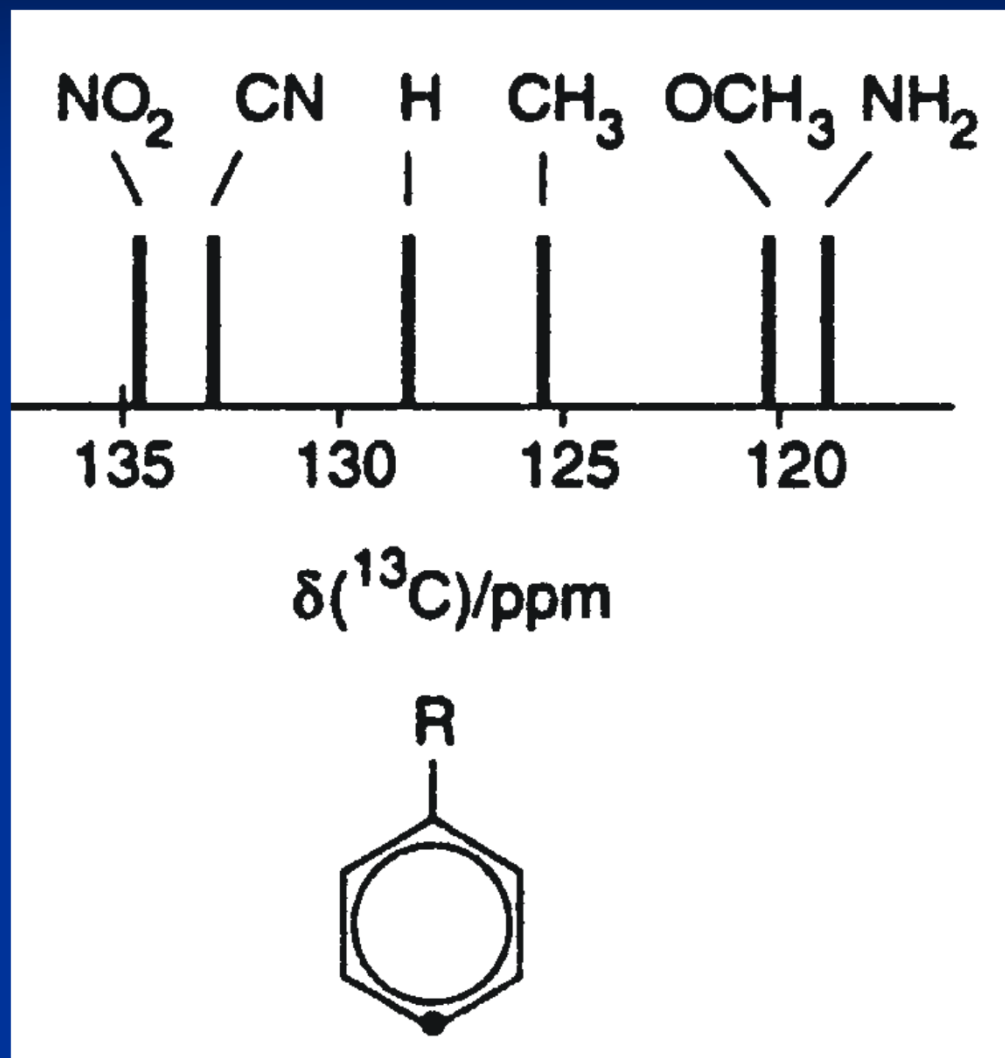
Electrophilic substitution

Meta directing
Strongly deactivating

Ortho, para directing
Strongly activating

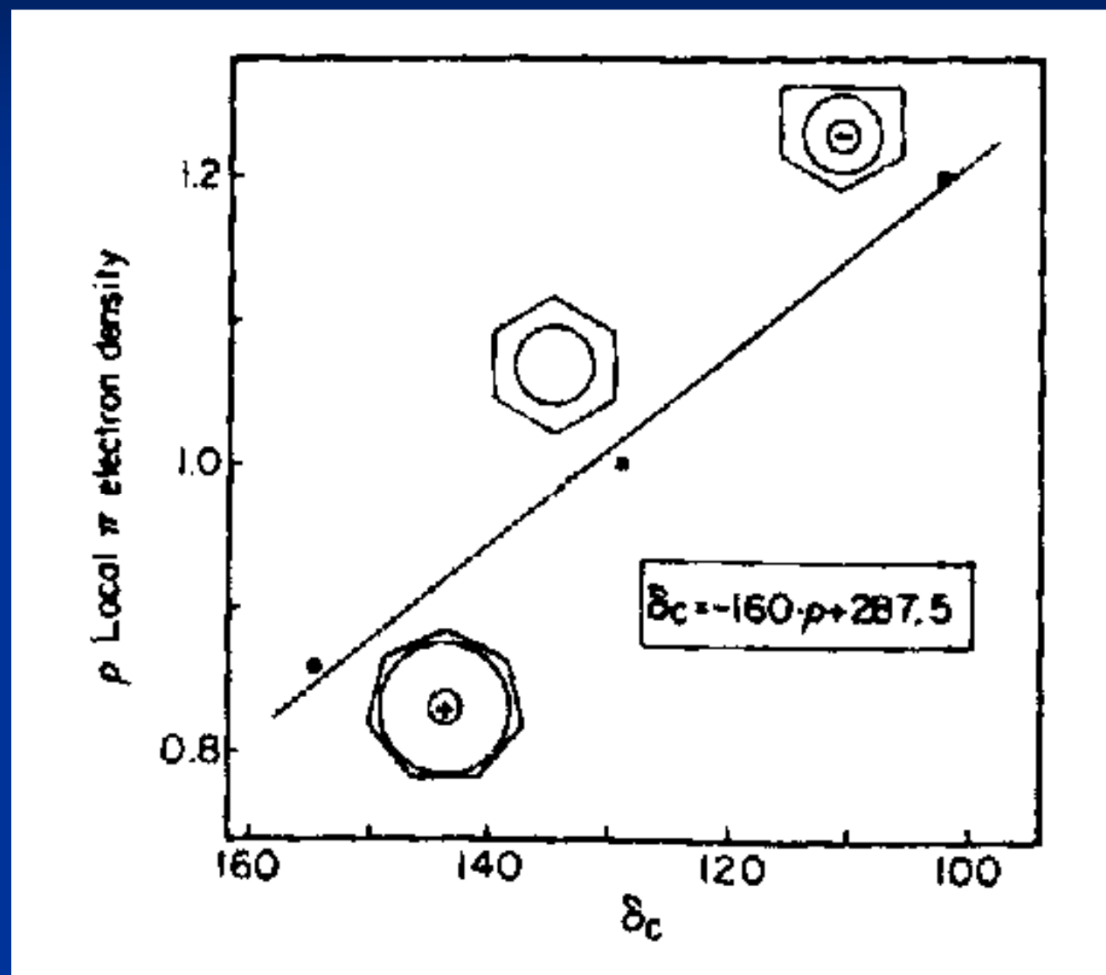


Aromatic Carbon Shifts



Aromatic Carbon Shifts

Number of
 π electrons
per C



$\delta (^{13}\text{C}) / \text{ppm}$

The Paramagnetic Contribution to the Magnetic Shielding Constant

Quantum chemical approach by RAMSEY: The electron polarization leading to σ_{para} is described in terms of mixing of the wave functions of the molecular ground state with excited states under the influence of the magnetic field.

Approximative expressions for σ_{para} were given for

main-group elements by KARPLUS and POPLE:

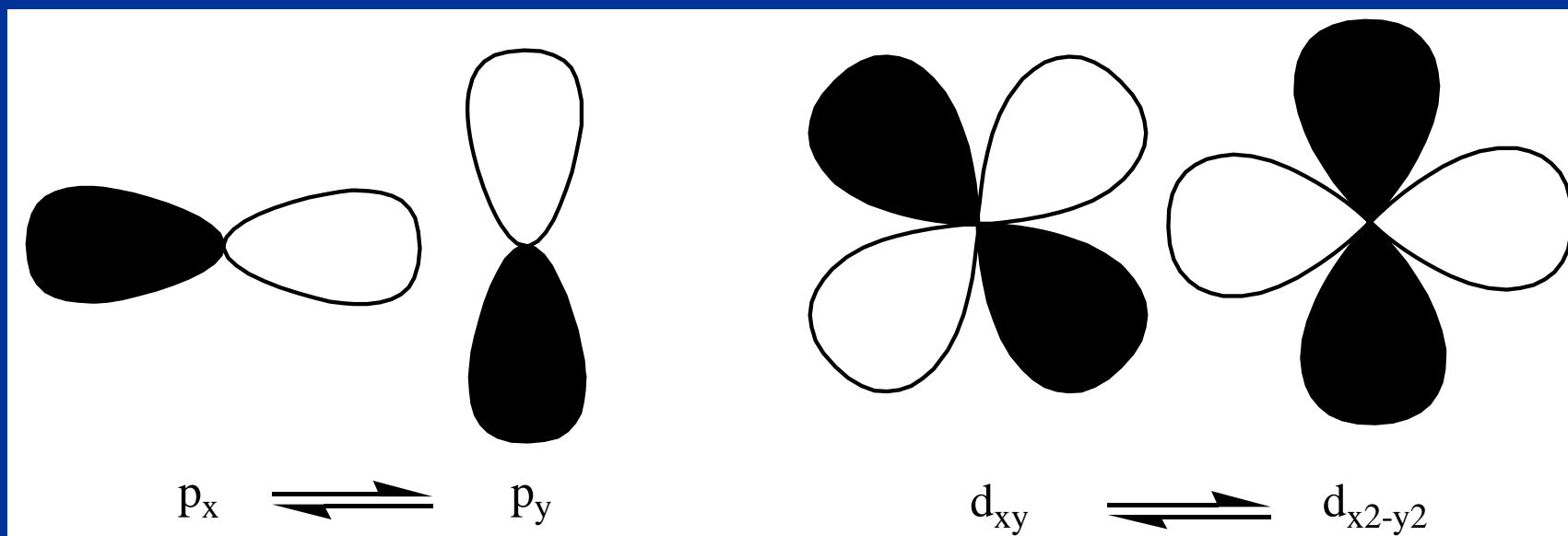
$$\sigma_{\text{para}} \approx -\frac{\mu_0 \mu_B^2}{2\pi} \Delta E^{-1} r_{\langle np \rangle}^{-3} \sum_{\text{bonds}} Q_i$$

and for transition metals by GRIFFIN and ORGEL:

$$\sigma_{\text{para}} \approx -\frac{\mu_0 \mu_B^2}{2\pi} \Delta E^{-1} r_{\langle (n-1)d \rangle}^{-3} \langle \mathbf{0} | \mathbf{L}^2 | \mathbf{0} \rangle$$

The Paramagnetic Contribution to the Magnetic Shielding Constant

Nonspherical circulation of electrons under influence of B_0



Paramagnetic Contribution to the Magnetic Shielding

Average energy approximation

$$\sigma_{para} = -const \frac{\Delta P_{imbalance}}{\Delta E \times \langle r_p \rangle^3}$$

The Paramagnetic Contribution to the Magnetic Shielding Constant

Characteristics of σ_{para} :

Magnitude of σ_{para} (= deshielding) increases when



• the mean electronic excitation energy decreases ($\sigma_{para} \sim \Delta E^{-1}$)

HOMO-LUMO gap, Δ_0

shielding is most susceptible to changes in ΔE^{-1} (1 eV = 30 ppm)

least precisely known

• the effective radius of the valence shell decreases ($\sigma_{para} \sim r^{-3}$)

more electrons = more e-e repulsion = larger r

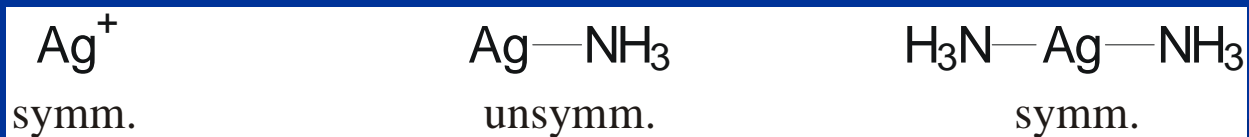
• the imbalance of valence electrons increases
increasing symmetry = decreasing imbalance
higher bond order = shielding

$$\sigma_{para} = -const \frac{\Delta P_{imbalance}}{\Delta E \times \langle r_p \rangle^3}$$

$$(\sigma_{para} = f(Q_i / L^2))$$

The Paramagnetic Contribution to the Magnetic Shielding Constant

Contributions to σ_{para} by individual valence electron pairs are anisotropic and may cancel out because of symmetry reasons !



$\sigma_{\text{para}} = 0$ for spherical symmetry, closed shell atoms (e.g. F^-)

Patterns of Chemical Shifts

For p- and d-block elements, chemical shifts are dominated by the paramagnetic contribution to the magnetic shielding, σ_{para} .
The Karplus-Pople approach proves useful to rationalize some important general patterns of chemical shifts in terms of variations of

$\langle r^{-3} \rangle$
“radial term”

Different total chemical shift ranges of different elements

ΔE^{-1}
“energy term”

Correlation between chemical shifts and electronic transitions

$Q_i(L^2)$
“orbital term”

Comparable chemical shift patterns for electronically similar compounds of different elements


Patterns of Chemical Shifts

$$\langle r^{-3} \rangle$$

“radial term”


$$\sigma_{para} = -const \frac{\Delta P_{imbalance}}{\Delta E \times \langle r_p \rangle^3}$$

	NH_4^+	NH_3
$\delta (^{15}\text{N})$	-325.9	-380.2



Positive charge = p orbital contraction, less e-e repulsion,
radius decreases = deshielding

	CMe_3^+	H CMe_3
$\delta (^{13}\text{C})$	335.7	50



Patterns of Chemical Shifts

$\langle r^{-3} \rangle$
“radial term”

^{129}Xe Chemical Shift dependence on the oxidation state

Xe(VIII)	Xe(VI)	Xe(IV)	Xe(II)	Xe(0)
XeO_6^{2-}	XeO_3	XeF_4	XeF_2	Xe
2077	217	253	-1592	-5331
	XeOF_4	$\text{Xe}(\text{OTeF}_5)_4$	$\text{Xe}(\text{OTeF}_5)_2$	
	0	-637	-2379	

Higher oxidation state = more positive charge = smaller $\langle r \rangle$ = deshielding



Patterns of Chemical Shifts

^{109}Ag NMR Chemical Shift dependence on the oxidation state

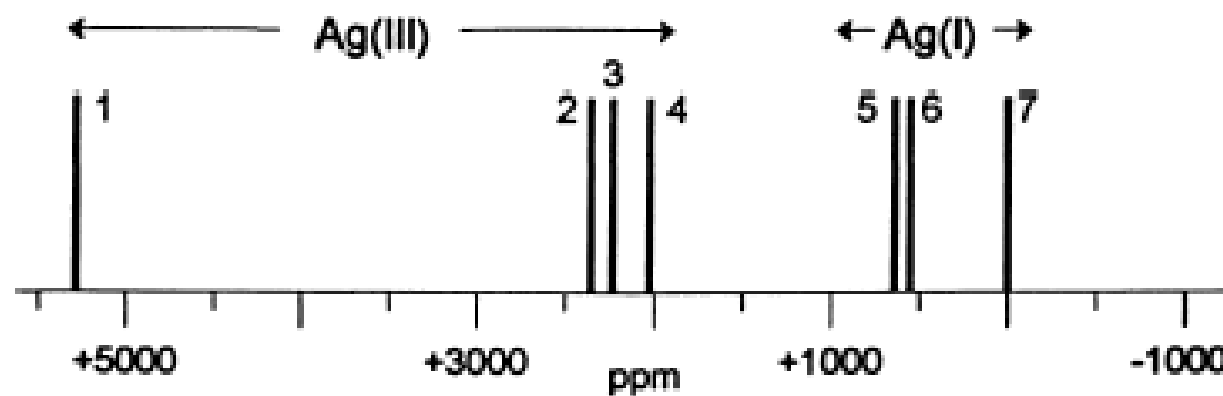


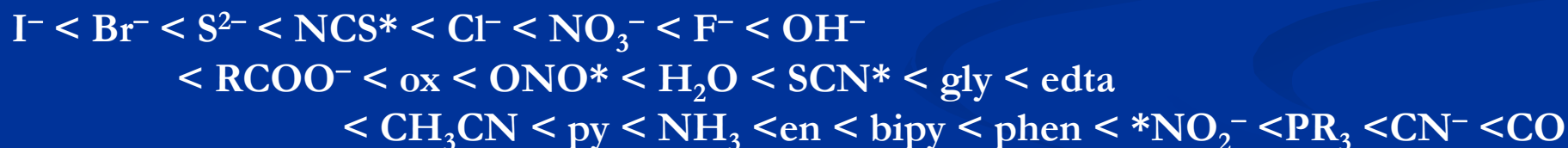
Fig. 3. The range of ^{109}Ag NMR chemical shifts. 1: $\text{Ag}^{\text{III}}\text{F}_4^-$; 2: $\text{Ag}^{\text{III}}(\text{CF}_3)(\text{CN})_3^-$ [6]; 3: $\text{Ag}^{\text{III}}(\text{CF}_3)_4^-$ [6]; 4: $\text{Ag}^{\text{III}}(\text{CF}_2\text{H})_4^-$ [5]; 5: $\text{Ag}^{\text{I}}(\text{CF}_2\text{H})_2^-$ [5]; 6: $\text{Ag}^{\text{I}}(\text{CF}_3)_2^-$ [6]; 7: $\text{Ag}_{\text{aq}}^{\text{I}}$ +.

Patterns of Chemical Shifts

Chemists are interested in correlations between NMR chemical shifts and other molecular properties related to changes in molecular structures or reactivities. Some useful relations are found in particular for transition metal compounds:

Chemical Shifts and the Spectrochemical Series of Ligands (Δ_o)

Spectrochemical Series = increase in $\Delta E(d-d)$ = energy term decreases



Weak ligands = deshielding
weak bonds
 σ_{para} large

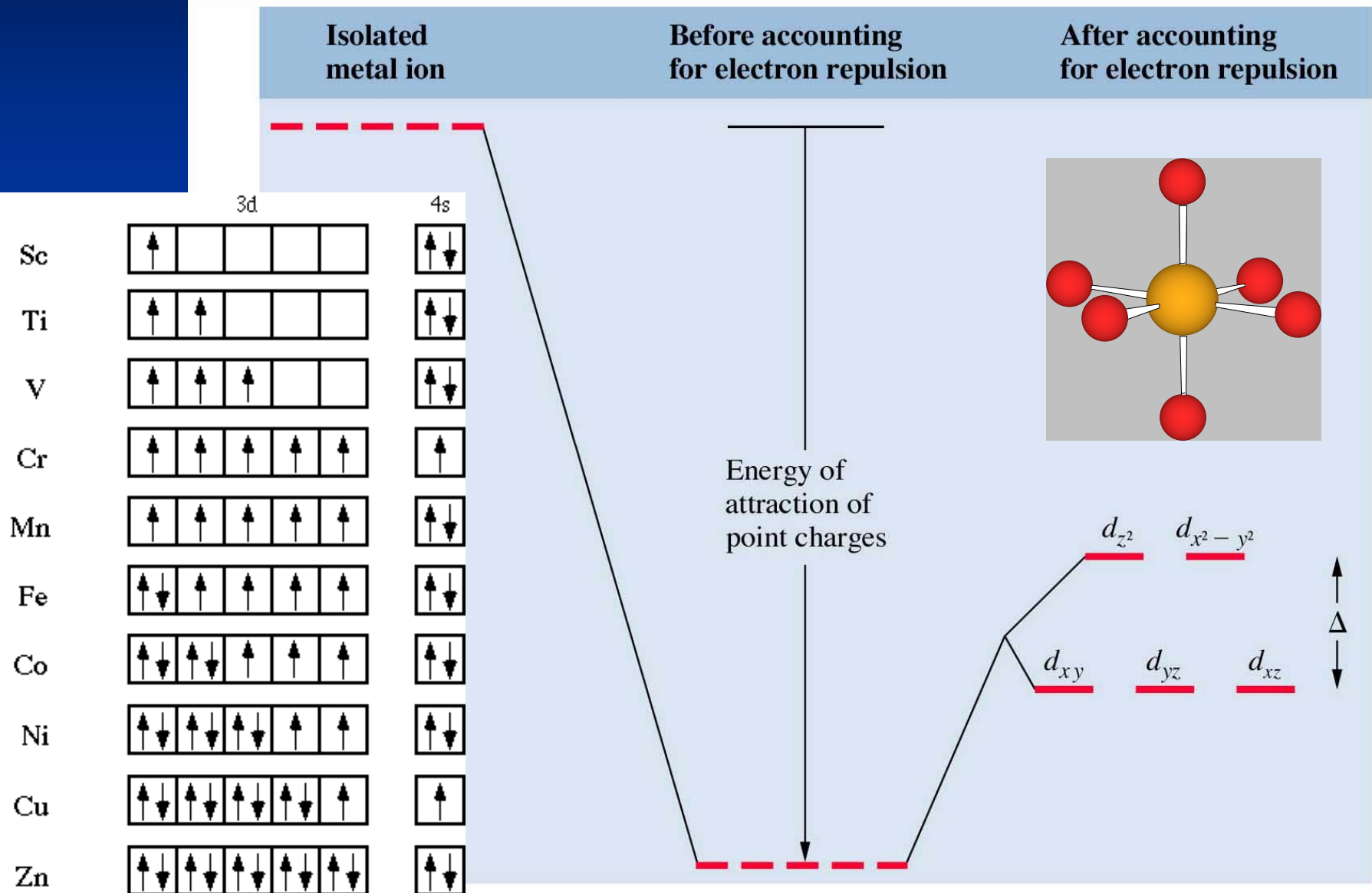


ΔE^{-1}
“energy term”

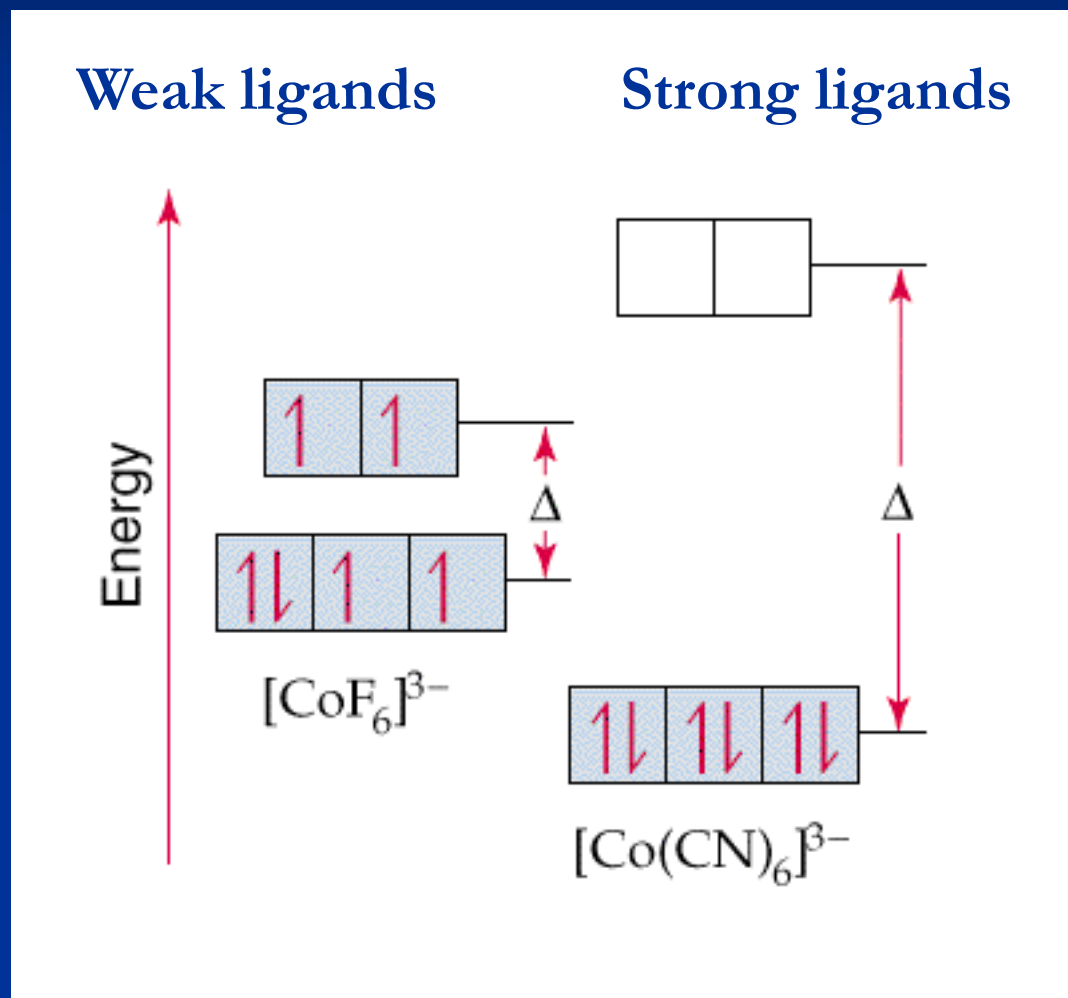
Strong ligands = shielding
strong bonds
 σ_{para} small



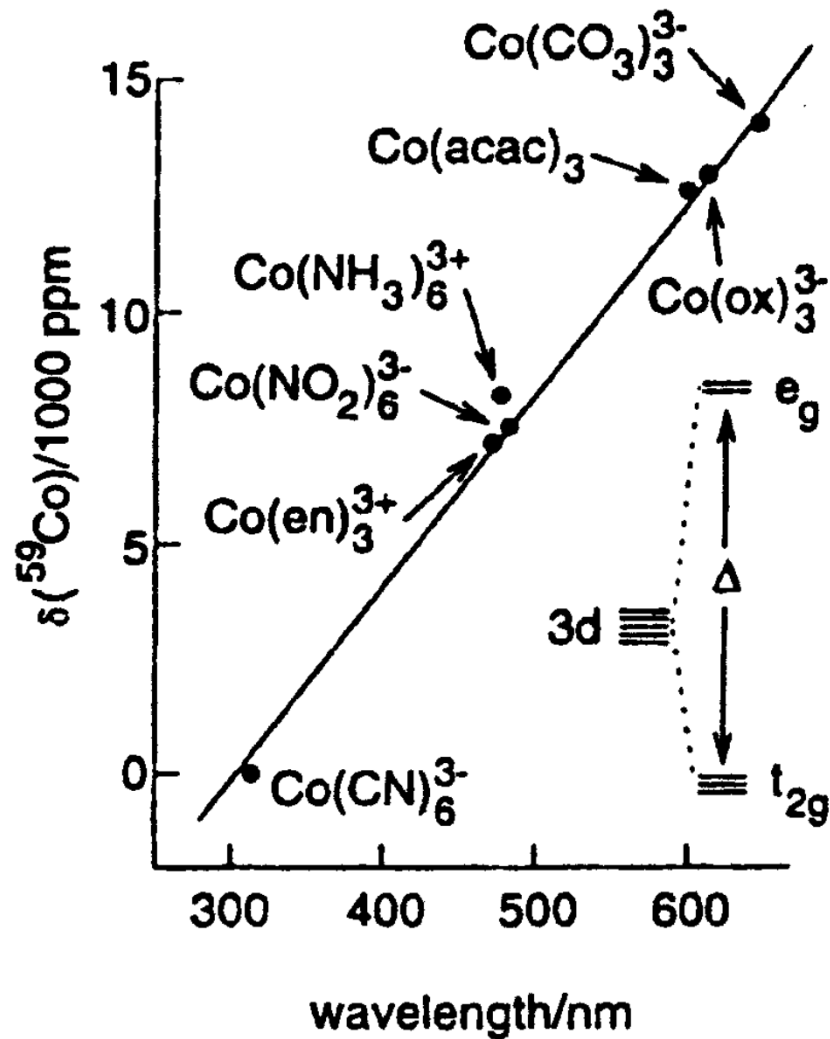
Octahedral Complexes



Ligand Field Splitting



Spectrochemical Series



$$\sigma_{para} = -const \frac{\Delta P_{imbalance}}{\Delta E \times \langle r_p \rangle^3}$$

ΔE^{-1}
“energy term”

^{17}O Chemical Shifts in Oxoanions

ΔE^{-1}
“energy term”

$$\sigma_{para} = -const \frac{\Delta P_{imbalance}}{\Delta E \times \langle r_p \rangle^3}$$

$[\text{VO}_4]^{3-}$	$[\text{CrO}_4]^{2-}$	$[\text{MnO}_4]^-$	$[\text{SO}_4]^{2-}$	$[\text{ClO}_4]^-$
568	835	1230	167	290
	$[\text{MoO}_4]^{2-}$	$[\text{TcO}_4]^-$	$[\text{SeO}_4]^{2-}$	
	530	749	204	
	$[\text{WO}_4]^{2-}$	$[\text{ReO}_4]^-$		
	420	569		

Nephelauxetic Series

$\langle r^{-3} \rangle$
"radial term"

Nephelauxetic effect = expansion of d-orbitals
 $\langle r \rangle$ increases = radial term decreases



Nephelauxetic effect increases = $\langle r \rangle$ increases



Electronegativity increases



Ionic bonding
 $\langle r \rangle$ decreases
Deshielding

$$\sigma_{para} = -const \frac{\Delta P_{imbalance}}{\Delta E \times \langle r_p \rangle^3}$$

Covalent bonding
 $\langle r \rangle$ increases
Shielding



Patterns of Chemical Shifts

Change of ligands induces usually changes of both the energy and radial terms

$$\langle r^{-3} \rangle$$

“radial term”

Nephelauxetic effect

Normal halogen dependence

F Cl Br I



Deshielding with increasing electronegativity
(similar to diamagnetic term)

$$\Delta E^{-1}$$

“energy term”

Spectrochemical Series

Inverse halogen dependence

I Br Cl F



Shielding with increasing electronegativity

Depending on which effect dominates, the variation of $\sigma(M)$ with the electronegativity of X may follow completely different patterns.

Patterns of Chemical Shifts

$$\sigma_{para} = -const \frac{\Delta P_{imbalance}}{\Delta E \times \langle r_p \rangle^3}$$

I. Normal Halogen (Ligand) Dependence

$\delta(M)$ follows the nephelauxetic series of ligands, increases in the series I < Br < Cl < F

$$\langle r^{-3} \rangle$$

“radial term”

Observed for

many compounds of p-block elements

many transition metal complexes with partly filled or filled d-shells

II. Inverse Halogen (Ligand) Dependence

$\delta(M)$ follows the spectrochemical series of ligands, increases in the series F < Cl < Br < I

$$\Delta E^{-1}$$

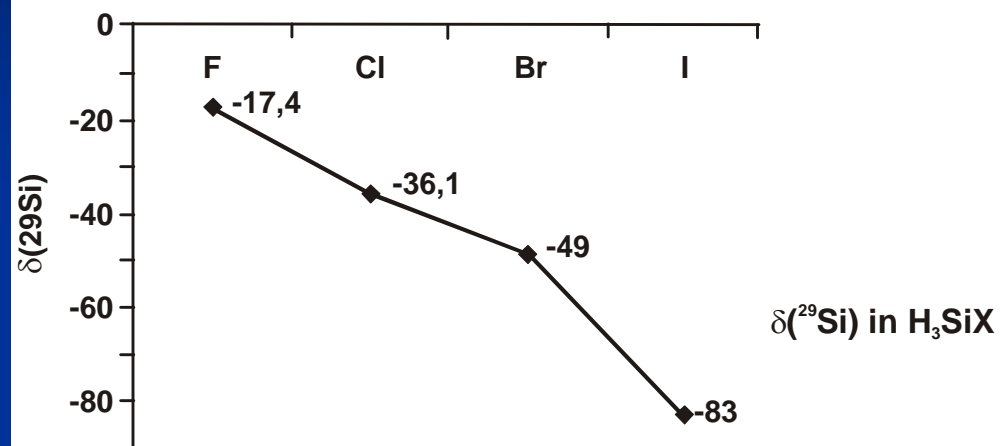
“energy term”

Observed for

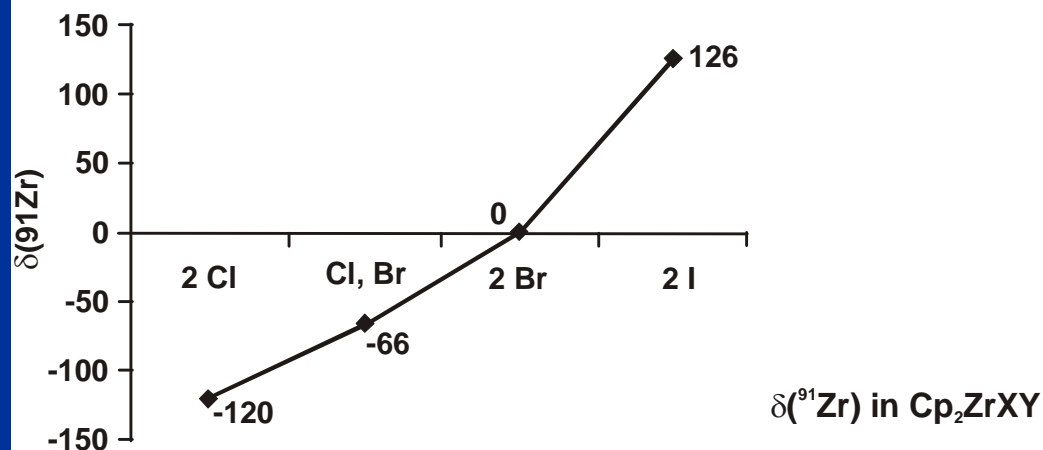
many transition metal complexes with d⁰, d¹⁰- configurations, alkali metals

Patterns of Chemical Shifts

I. Normal Halogen(Ligand) Dependence



II. Inverse Halogen(Ligand) Dependence



^{51}V NMR of Vanadyl derivatives

$$\sigma_{para} = -const \frac{\Delta P_{imbalance}}{\Delta E \times \langle r_p \rangle^3}$$



432 (neat)

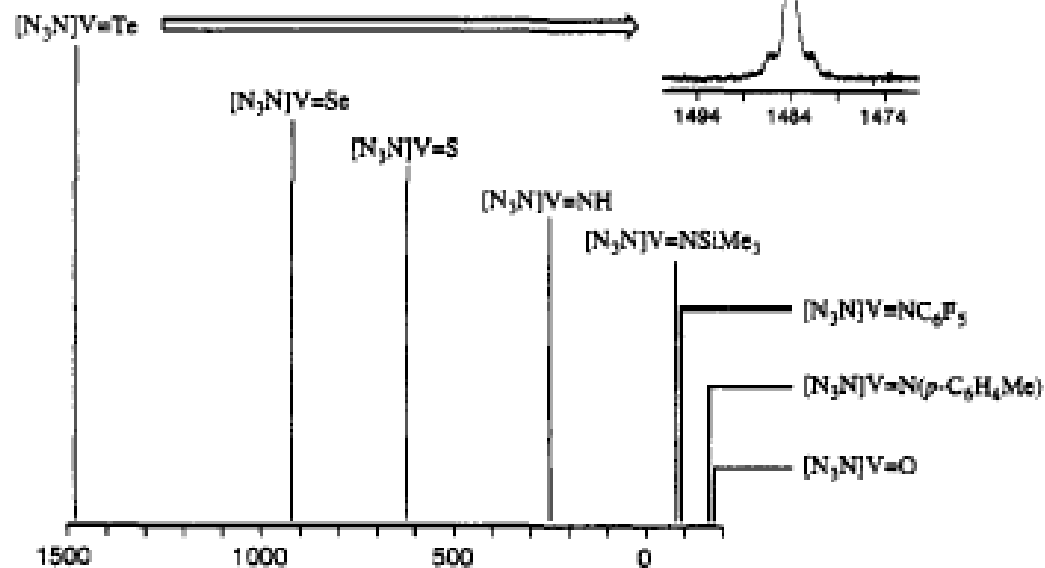
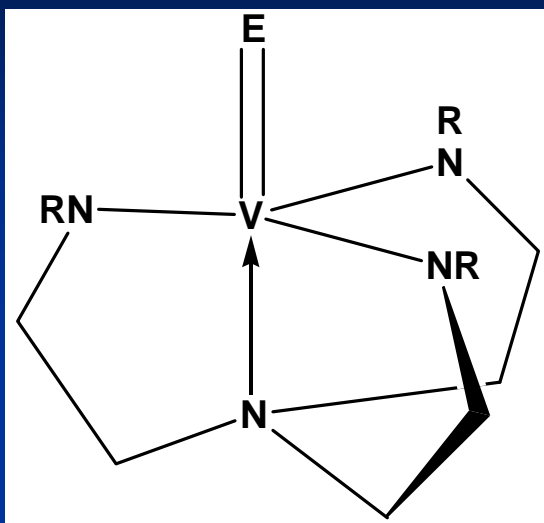
0 (neat)

-786 (CH_3CN)

Inverse Halogen (Ligand) Dependence

$$\sigma_{para} \approx -\frac{\mu_0 \mu_B^2}{2\pi} \Delta E^{-1} r_{\langle(n-1)d\rangle}^{-3} \langle \mathbf{0} | \mathbf{L}^2 | \mathbf{0} \rangle$$

^{51}V NMR of Vanadatranes



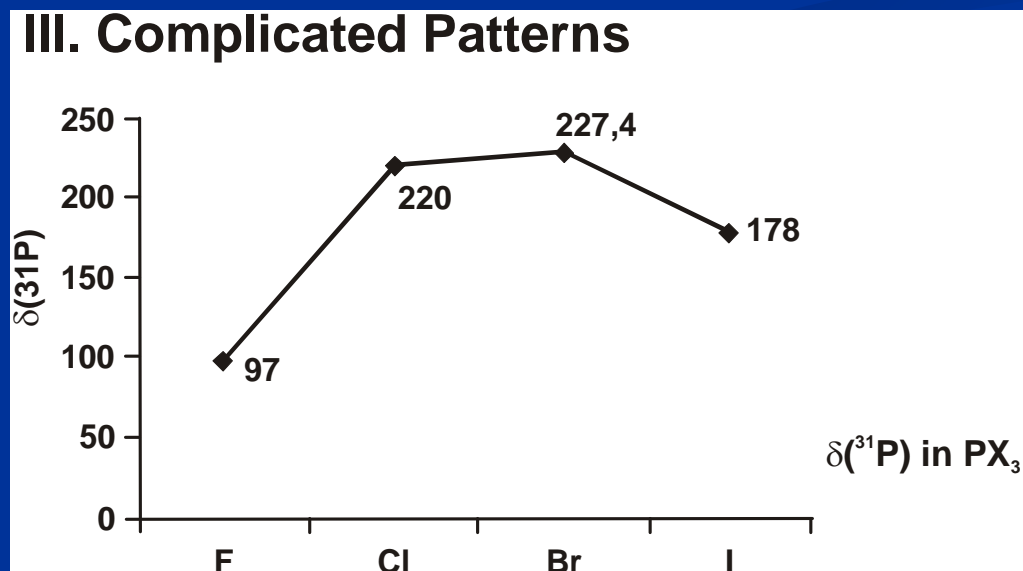
Patterns of Chemical Shifts

III. Complicated Patterns

Influence on $\langle r^{-3} \rangle$ and ΔE^{-1} of similar magnitude

Non-monotonous trend for $\delta(M)$

Observed for
some compounds of p-group elements



Symmetry and Chemical Shifts

	PCl_3	PCl_4^+	PCl_5	PCl_6^-
$\delta (^{31}\text{P})$ ppm	220	96	-81	-281

$Q_i(\text{L}^2)$
“orbital term”



Increasing symmetry = lower imbalance = shielding

Coordination Number and Chemical Shifts

Main group elements

Higher CN = shielding



Transition metals

Higher CN = deshielding



More π bonding = shielding

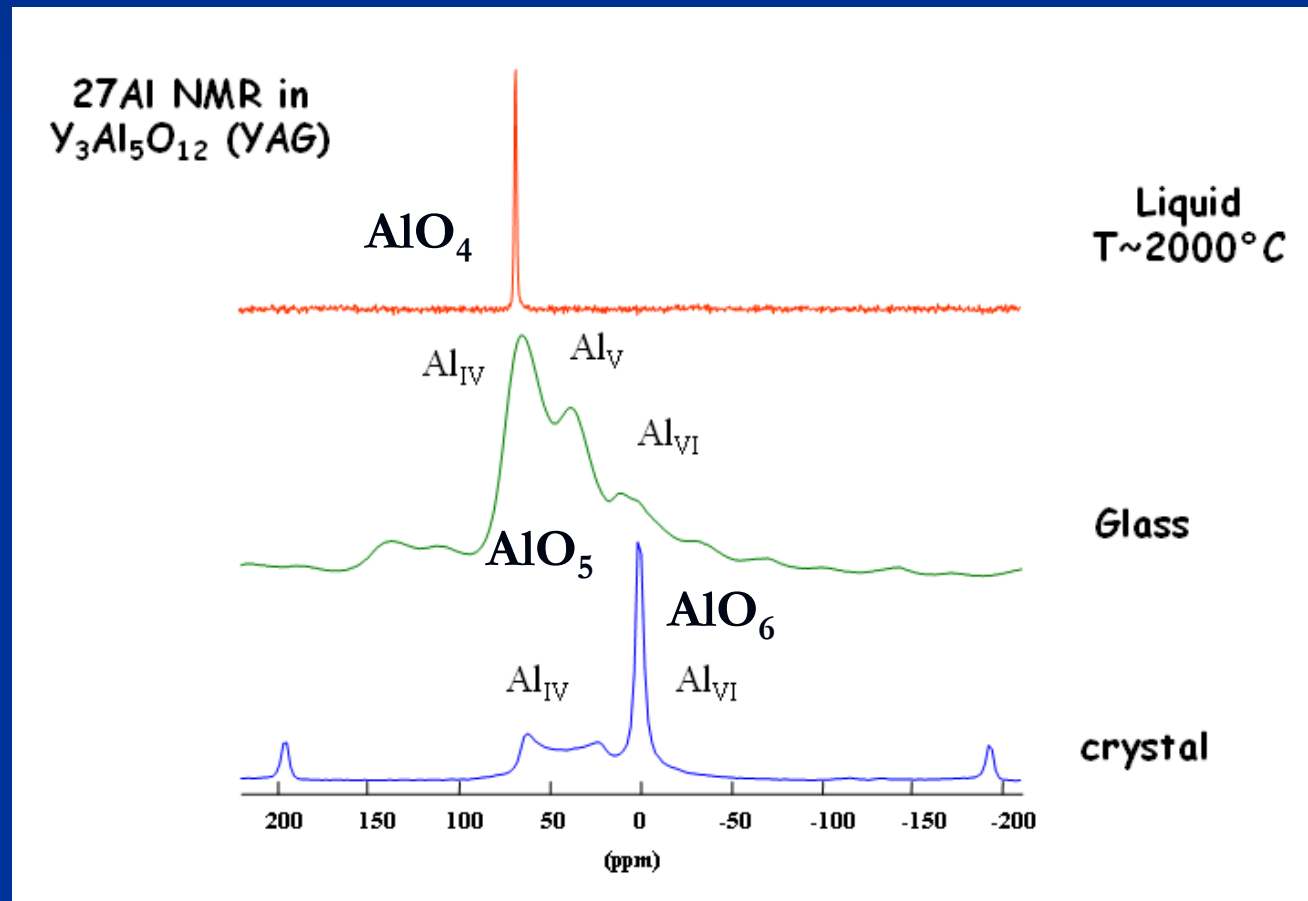
More σ bonding = deshielding

Coordination Number and Chemical Shifts

Higher CN = shielding



$\delta (^{27}\text{Al})$



Coordination Number and Chemical Shifts

Higher CN = shielding



$\delta (^{27}\text{Al})$

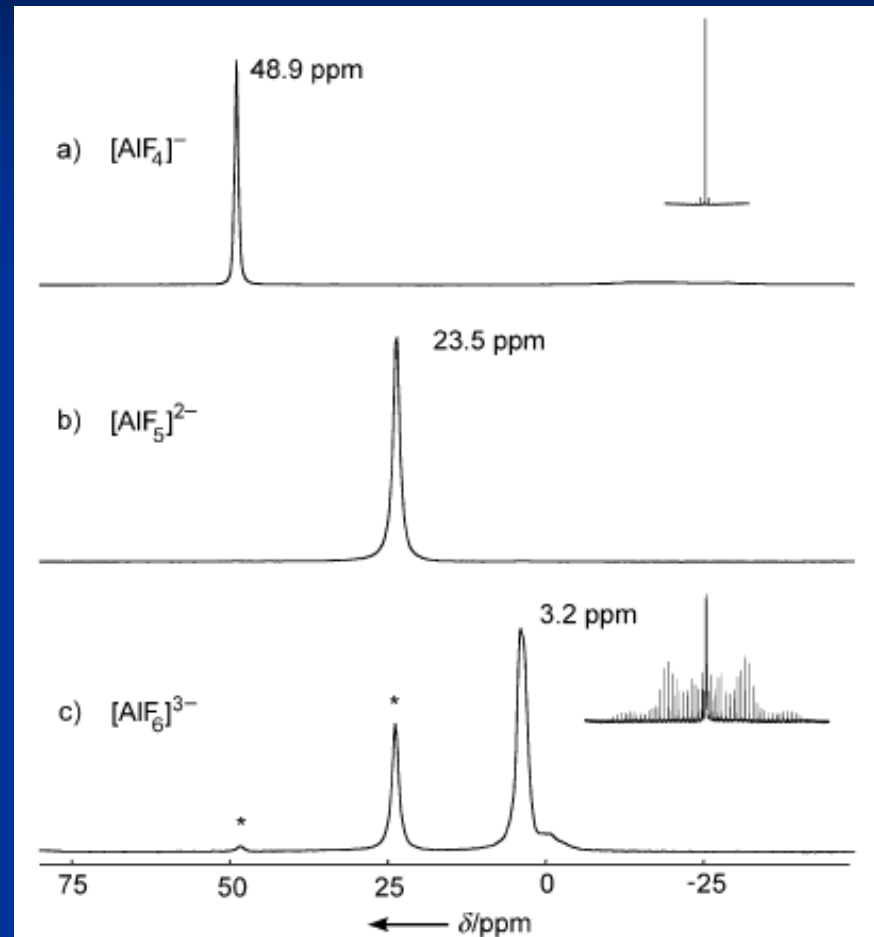


Abbildung 1. ^{27}Al -MAS-NMR-Spektren von a) $(\text{CH}_3)_4\text{N}^+[\text{AlF}_4]^-$, b) $[(\text{CH}_3)_4\text{N}^+]_2[\text{AlF}_5]^{2-}$ und c) $[(\text{CH}_3)_4\text{N}^+]_3[\text{AlF}_6]^{3-}$. Im Spektrum (c) sind Signale von (b) und (a) sichtbar (*); der Einschub zeigt das Satellitenspektrum infolge Quadrupolwechselwirkung in störungstheoretisch 1. Ordnung.