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:

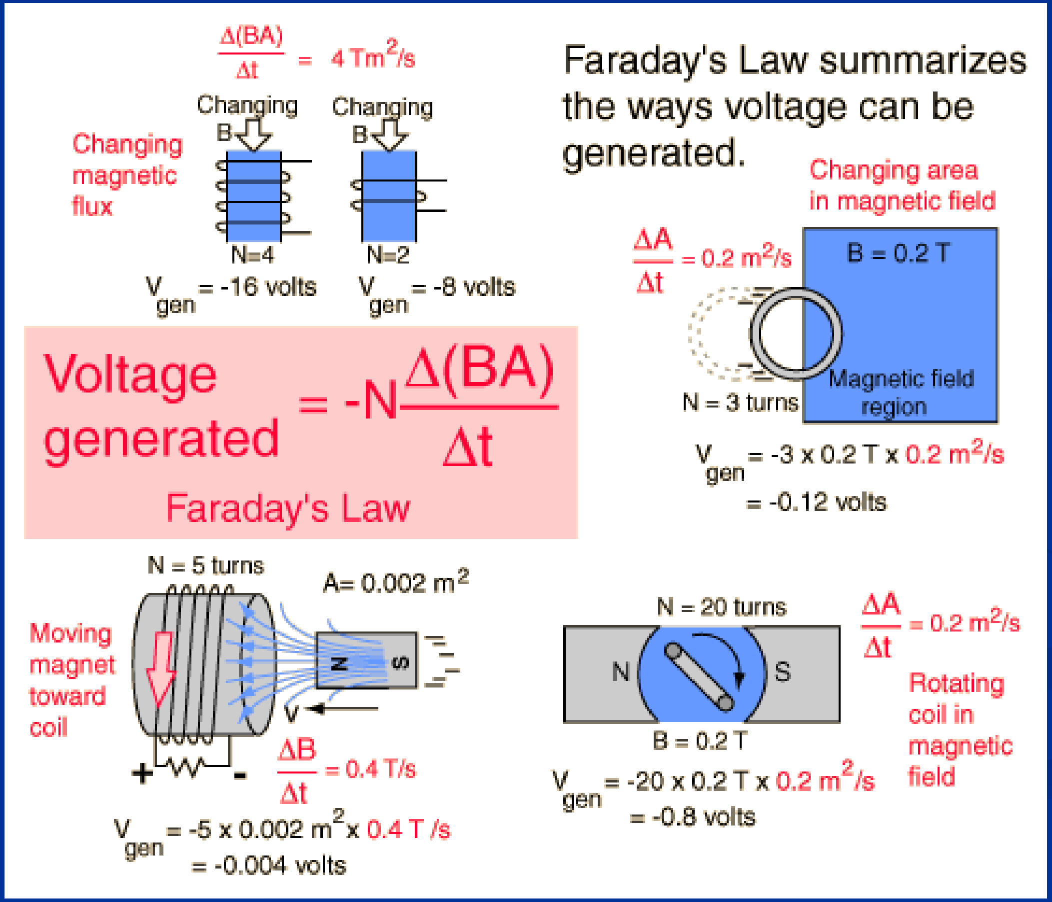
$\Delta E = \gamma \hbar B_0(1 - \sigma) = \varpi \hbar$ shielding constant σ

- In solution, the nuclear magnetic shielding constant σ is a <u>scalar</u> quantity

- In solids, σ is a <u>tensor</u> (3 x 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



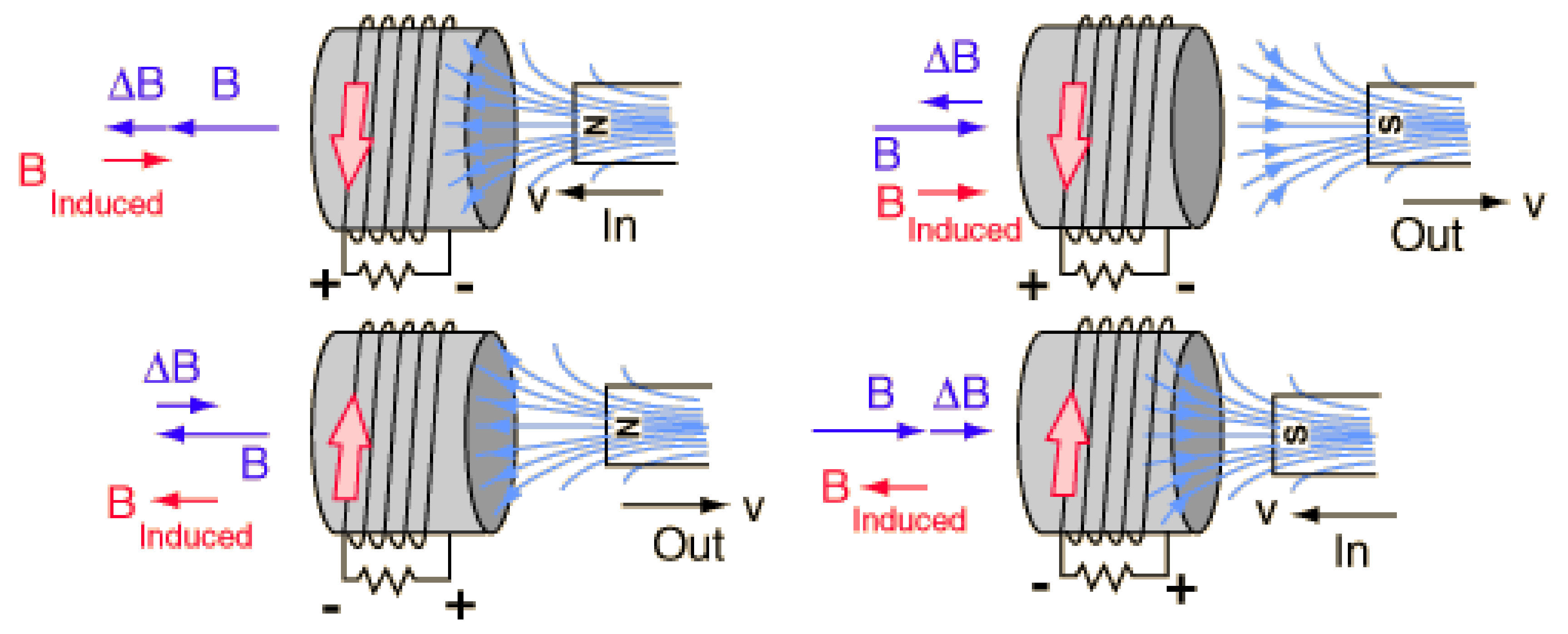
Faraday's Law summarizes the ways voltage can be generated.

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

Faraday's Law

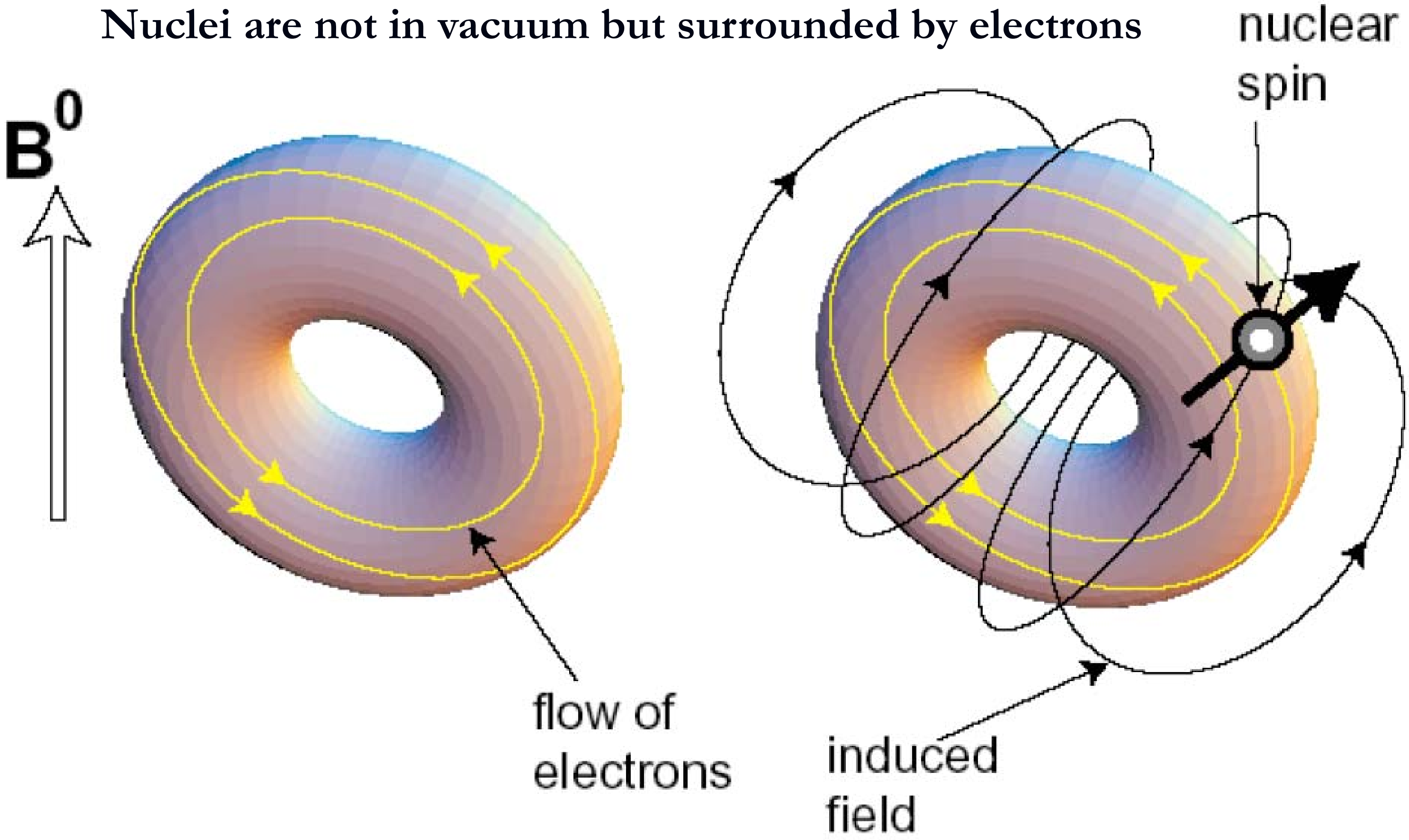
Lenz's Law

- 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

Nuclei are not in vacuum but surrounded by electrons



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

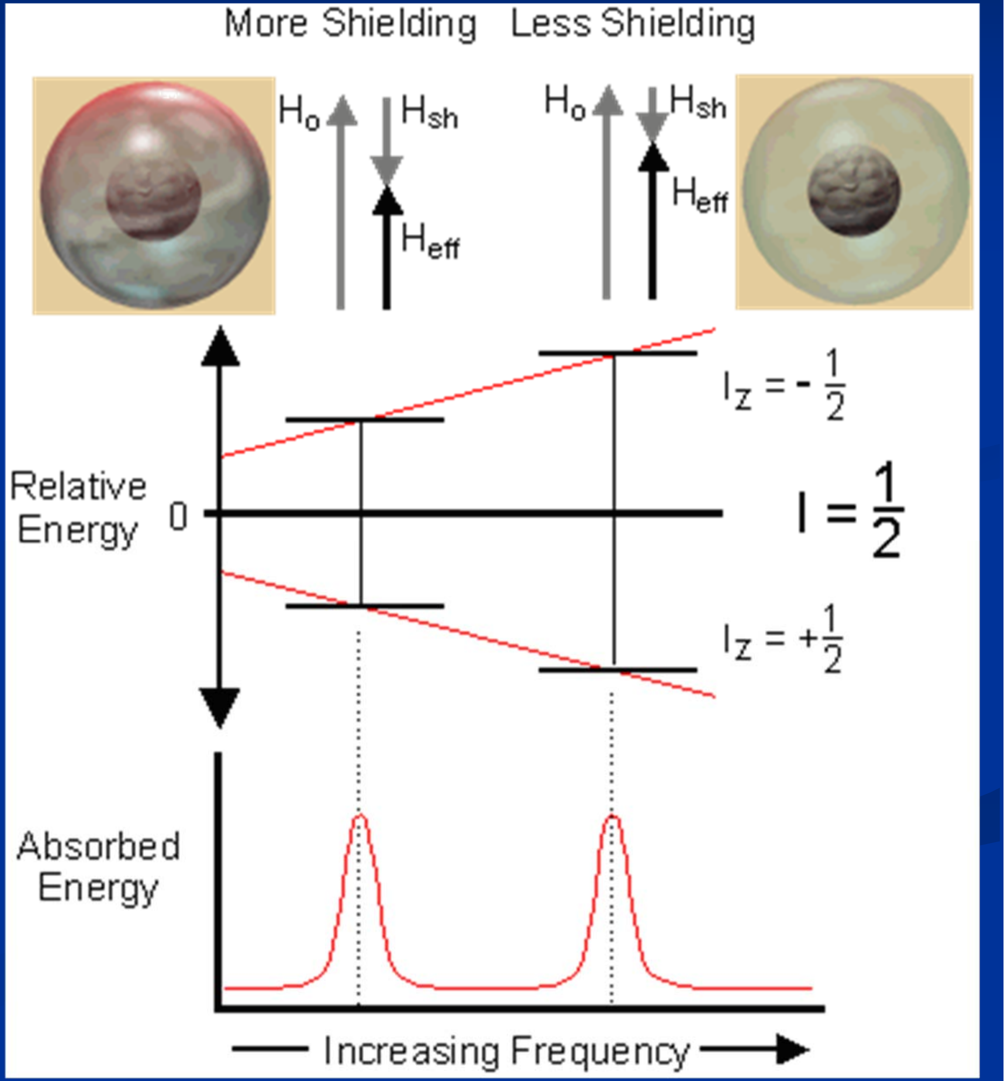
$B_{nucl} = B_0 - B_{shield}$

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

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

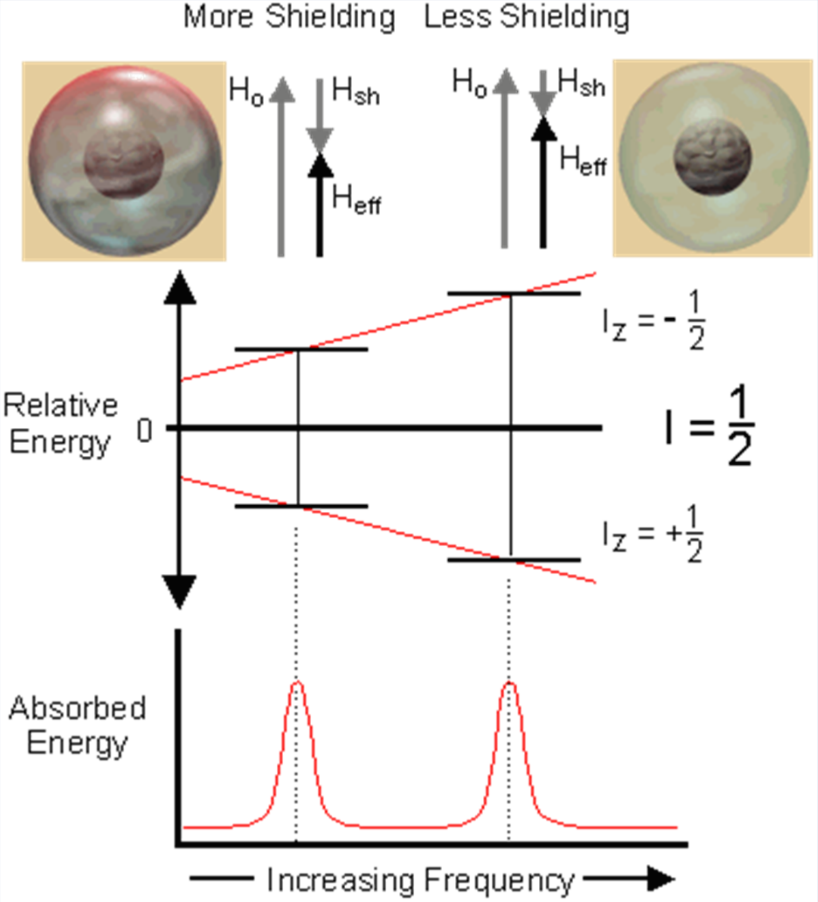
$\varpi = \gamma\, B_{nucl} = \gamma\, B_0(1-\sigma)$

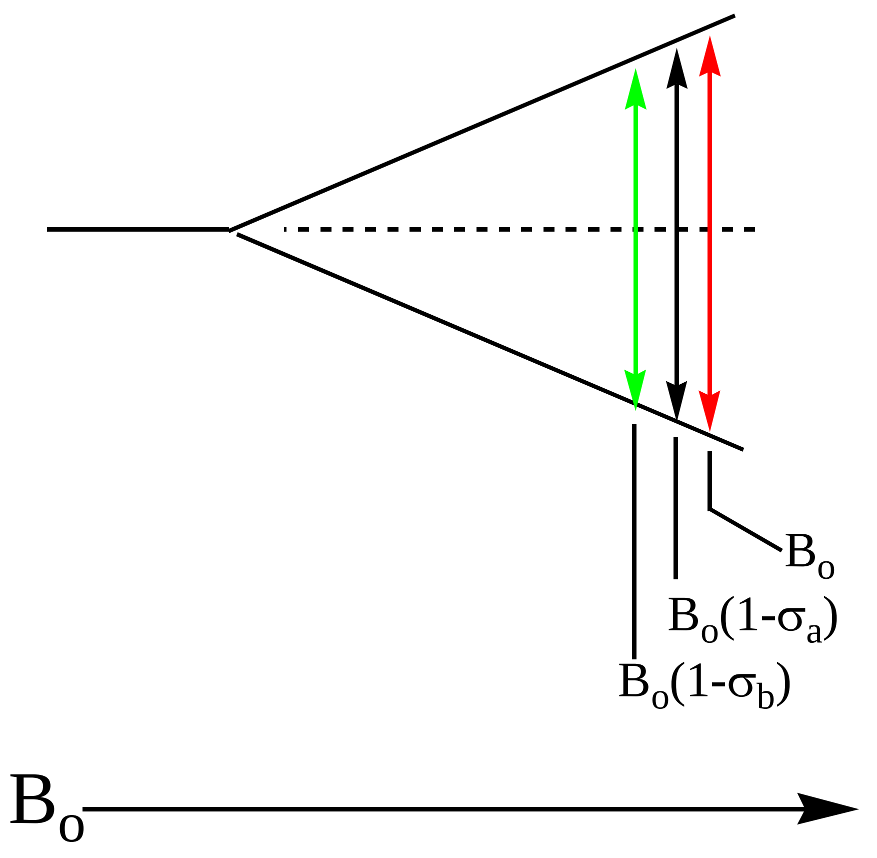
B = the magnetic flux density or magnetic induction (T)
H = the magnetic field (strength) (A/m)
$B = \mu \times H$



Nuclear Magnetic Shielding σ

$$\varpi = \gamma\, B_{nucl} = \gamma\, B_0(1 - \sigma)$$





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

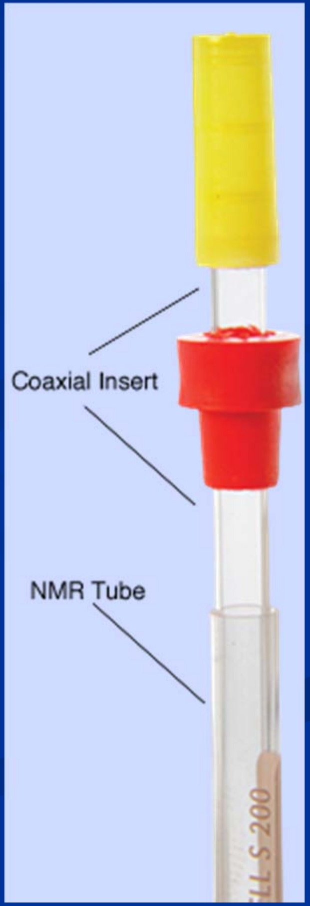
MHz vs. Hz 1:10^6

Relative Magnetic Shielding

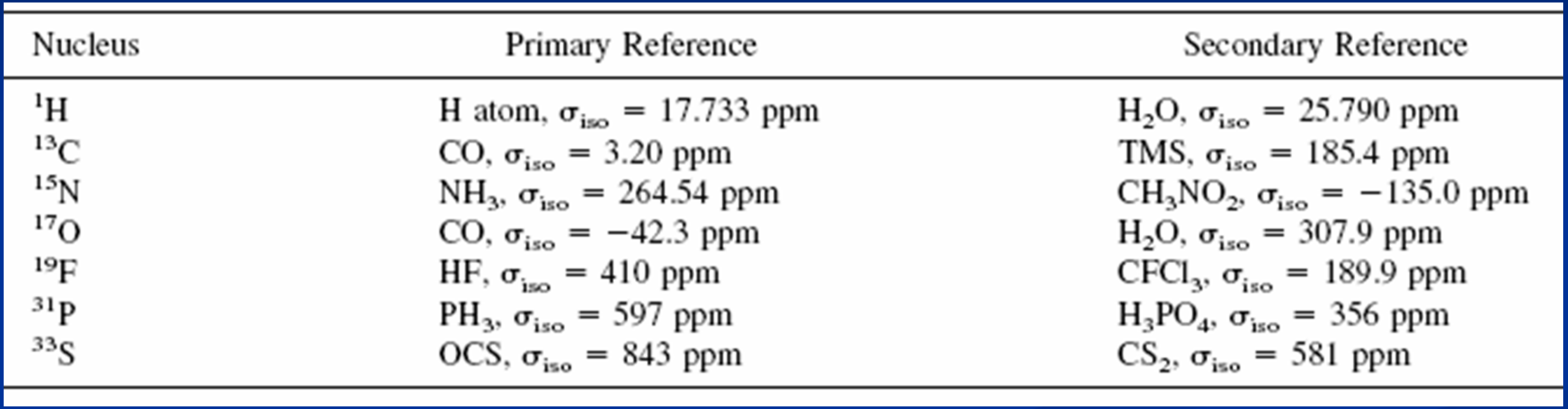
Requires measurement of differences of resonance frequencies between a sample and a standard

(much more easily done)

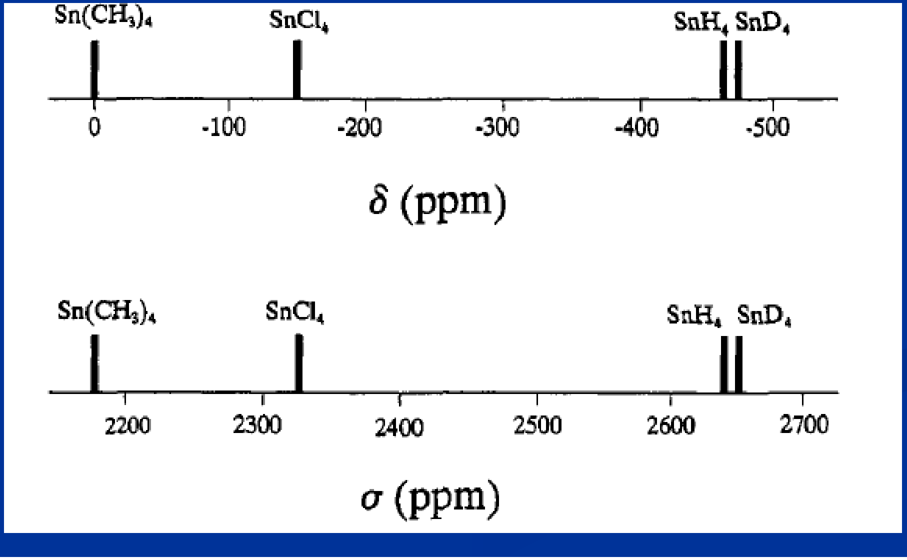
- **Internal** standard - a reference compound is in the same sample, preferred from spectroscopic point of view, may cause chemical problems – reaction
- **External** standard - in a different sample tube



Absolute Chemical Shieldings



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



^{119}Sn chemical shift scale

absolute chemical shielding

Chemical Shift

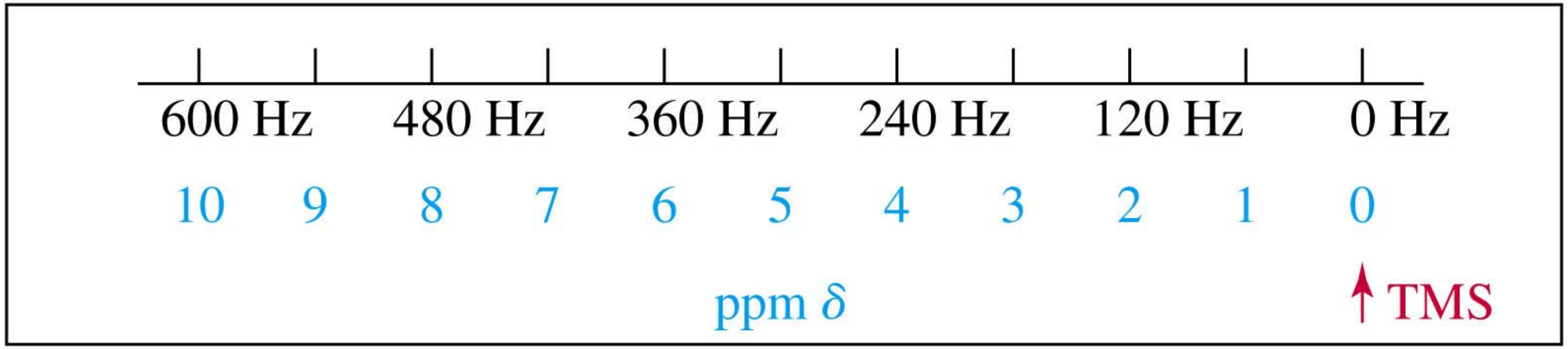
$$\delta = \frac{\upsilon_s - \upsilon_{ref}\left[Hz\right]}{\upsilon_0\left[MHz\right]}$$

Strength of Field:	**B_0 = 1.41 T**	**B_0 = 2.35 T**
Operating Frequency, ν_0:	**60 MHz**	**100 MHz**
Shift From TMS:	**162 Hz**	**270 Hz**
δ value:	**2.70 ppm**	**2.70 ppm**

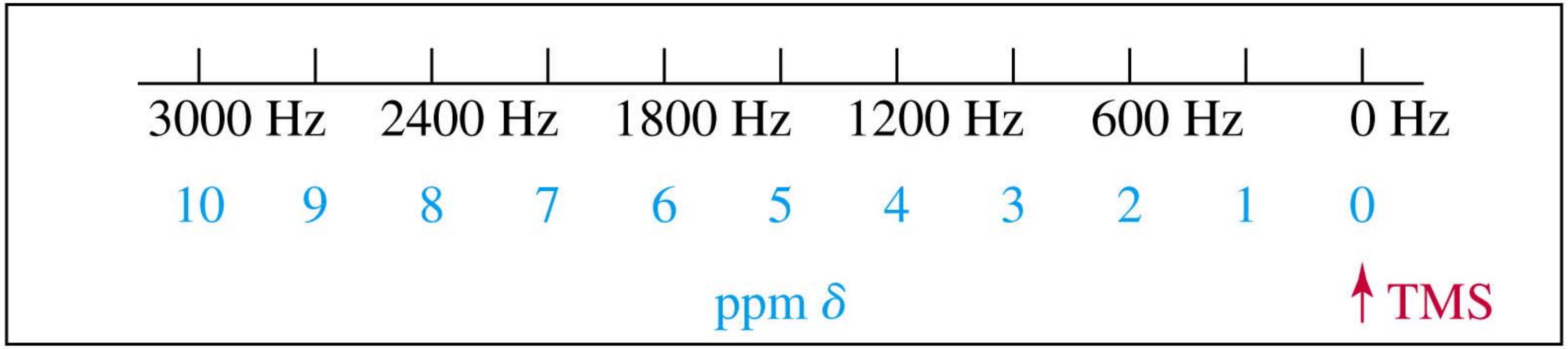
The δ scale (or ppm scale) is independent of the instrument used to obtain the spectrum

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):

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

ν_{nucl} = absolute resonance frequency of the atom

ν_s = absolute resonance frequency of the signal

Chemical Shift (δ-scale):

$\delta (H_3PO_4) = 0$

$\sigma (H_3PO_4) = 320$

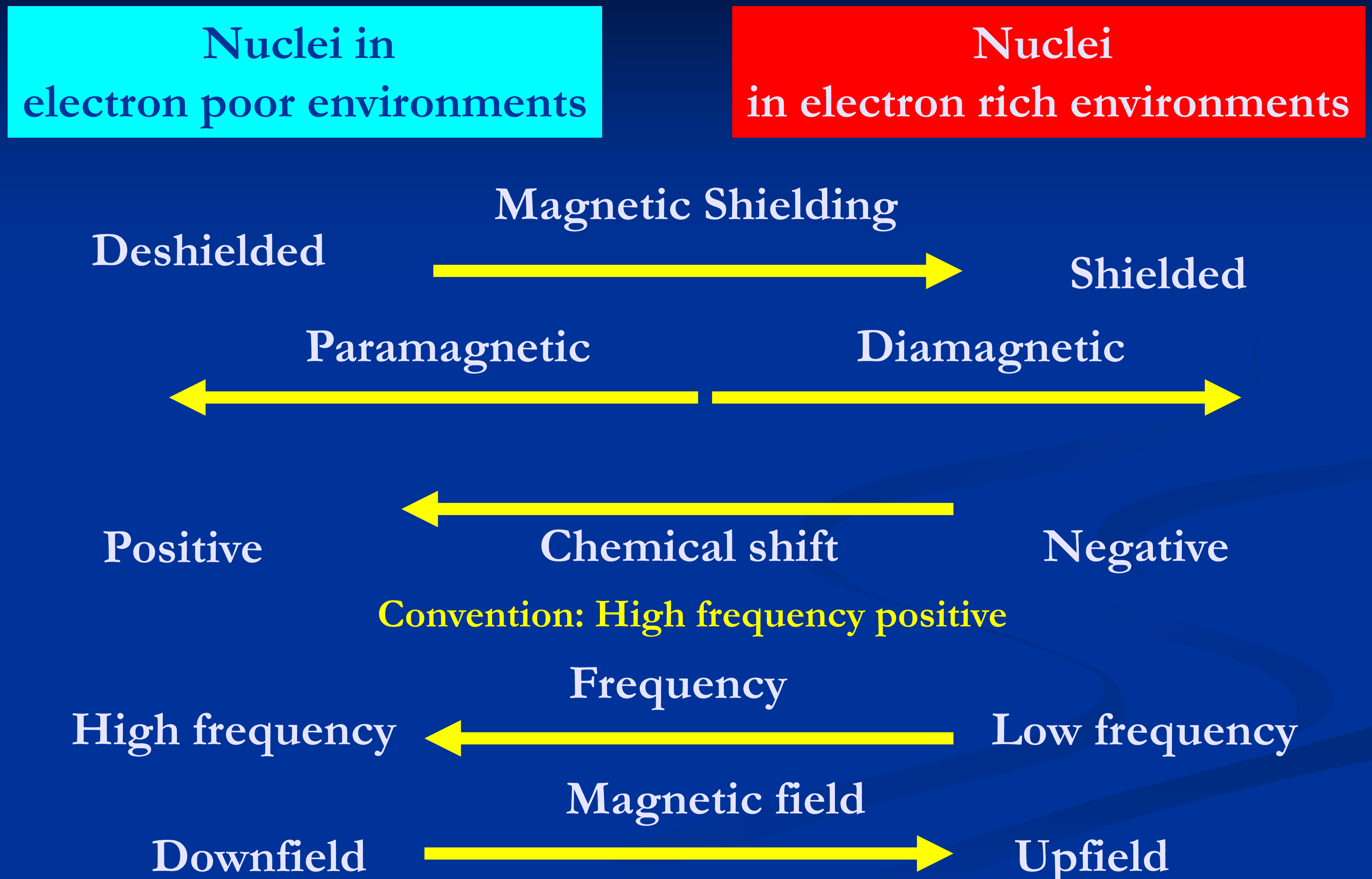
$\delta = 10^6 (\nu_s - \nu_{ref}) / \nu_{ref}$

ν_{ref} = resonance frequency of the standard

Conversion between both scales:

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

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



Nuclei in electron poor environments

Nuclei in electron rich environments

Magnetic Shielding

Deshielded → Shielded

Paramagnetic ←

Diamagnetic →

Positive ← Chemical shift Negative

Convention: High frequency positive

Frequency

High frequency ← Low frequency

Magnetic field

Downfield → Upfield

Chemical Shift References

^{1}H	ppm	
$SiMe_4$	0	
DSS	0	$Me_3Si\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}SO_3Na$
TSP	0	$Me_3Si\text{-}CD_2\text{-}CD_2\text{-}COONa$

^{19}F	ppm
$CFCl_3$	0
CF_3COOH	–78.5
C_6F_6	–162.9
HF	198.4
F_2	422.9

^{129}Xe (I = ½ , 26.4 %)

^{131}Xe (I = 3/2 , 21.1 %)

Xenon in freon

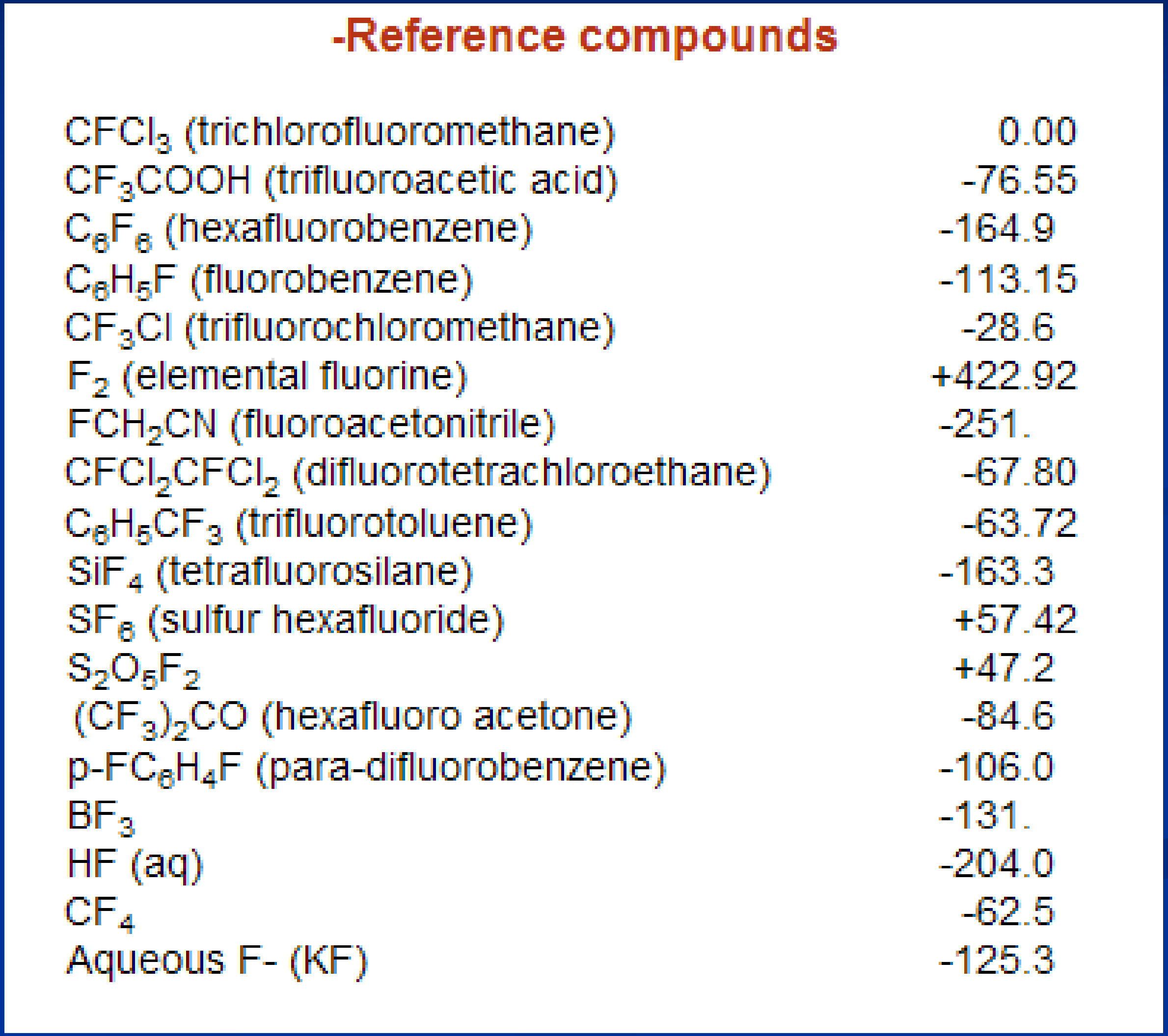
Liquid $XeOF_4$

Chemical Shift References

^{19}F, ppm

Be careful with literature data

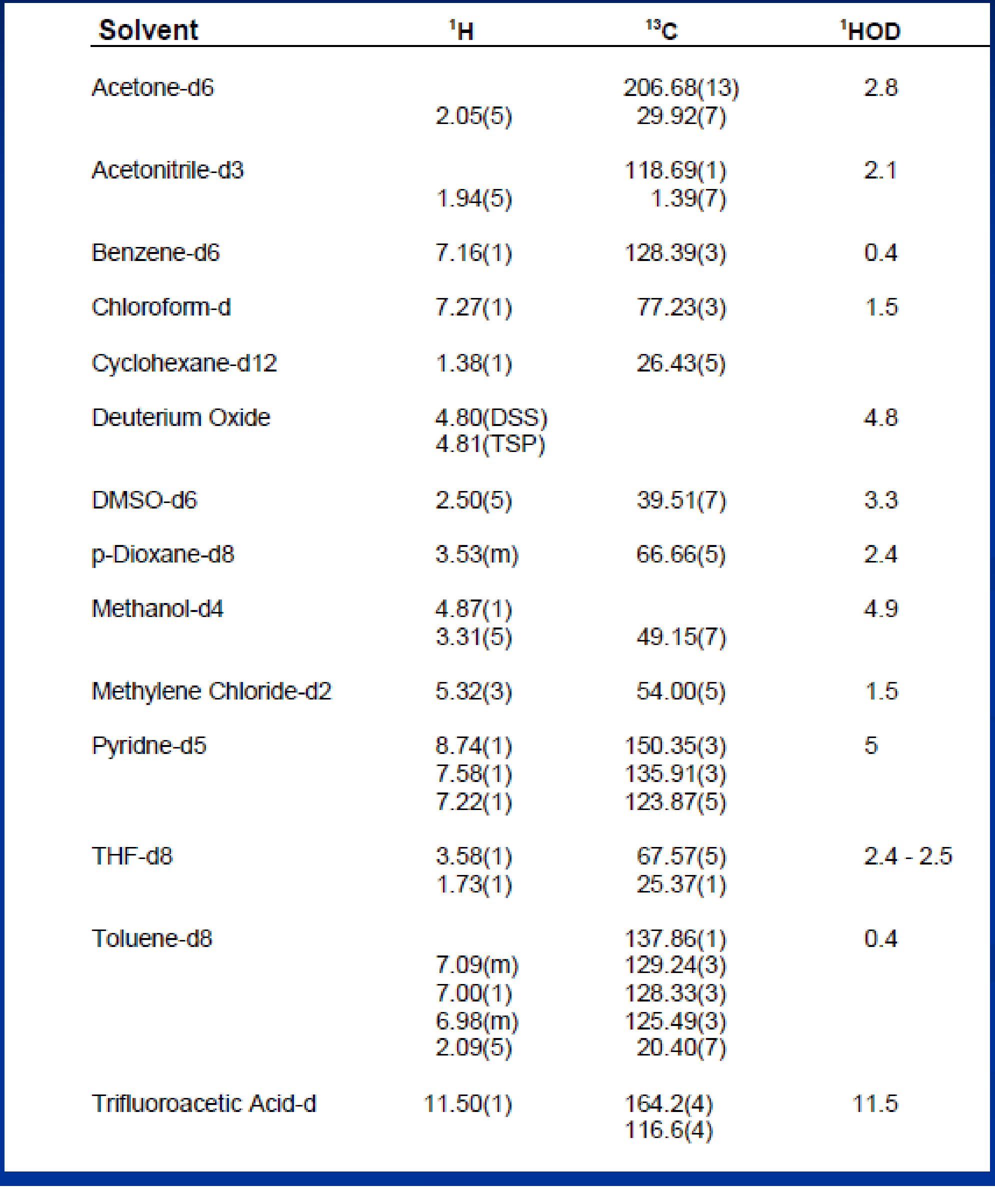
Sometimes C_6F_6 = 0



-Reference compounds

$CFCl_3$ (trichlorofluoromethane)	0.00
CF_3COOH (trifluoroacetic acid)	-76.55
C_6F_6 (hexafluorobenzene)	-164.9
C_6H_5F (fluorobenzene)	-113.15
CF_3Cl (trifluorochloromethane)	-28.6
F_2 (elemental fluorine)	+422.92
FCH_2CN (fluoroacetonitrile)	-251.
$CFCl_2CFCl_2$ (difluorotetrachloroethane)	-67.80
$C_6H_5CF_3$ (trifluorotoluene)	-63.72
SiF_4 (tetrafluorosilane)	-163.3
SF_6 (sulfur hexafluoride)	+57.42
$S_2O_5F_2$	+47.2
$(CF_3)_2CO$ (hexafluoro acetone)	-84.6
p-FC_6H_4F (para-difluorobenzene)	-106.0
BF_3	-131.
HF (aq)	-204.0
CF_4	-62.5
Aqueous F- (KF)	-125.3

Chemical Shift References



Solvent	^{1}H	^{13}C	^{1}HOD
Acetone-d6	2.05(5)	206.68(13) 29.92(7)	2.8
Acetonitrile-d3	1.94(5)	118.69(1) 1.39(7)	2.1
Benzene-d6	7.16(1)	128.39(3)	0.4
Chloroform-d	7.27(1)	77.23(3)	1.5
Cyclohexane-d12	1.38(1)	26.43(5)	
Deuterium Oxide	4.80(DSS) 4.81(TSP)		4.8
DMSO-d6	2.50(5)	39.51(7)	3.3
p-Dioxane-d8	3.53(m)	66.66(5)	2.4
Methanol-d4	4.87(1) 3.31(5)	49.15(7)	4.9
Methylene Chloride-d2	5.32(3)	54.00(5)	1.5
Pyridne-d5	8.74(1) 7.58(1) 7.22(1)	150.35(3) 135.91(3) 123.87(5)	5
THF-d8	3.58(1) 1.73(1)	67.57(5) 25.37(1)	2.4 - 2.5
Toluene-d8	7.09(m) 7.00(1) 6.98(m) 2.09(5)	137.86(1) 129.24(3) 128.33(3) 125.49(3) 20.40(7)	0.4
Trifluoroacetic Acid-d	11.50(1)	164.2(4) 116.6(4)	11.5

^{1}H NMR

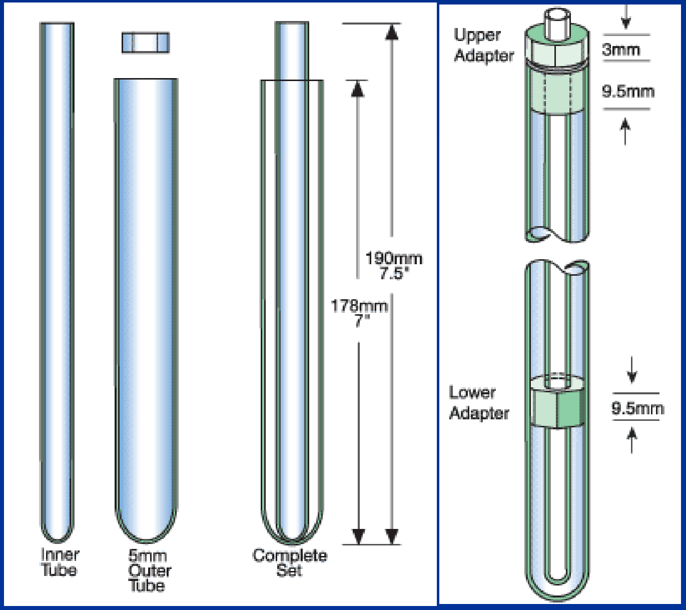
Residual protic impurities in deuterated solvents

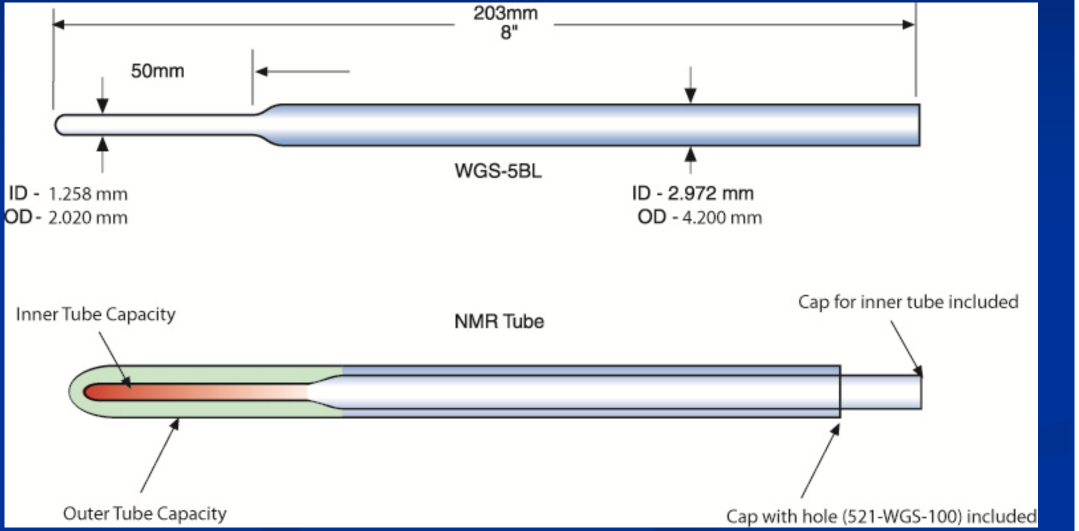
^{13}C NMR

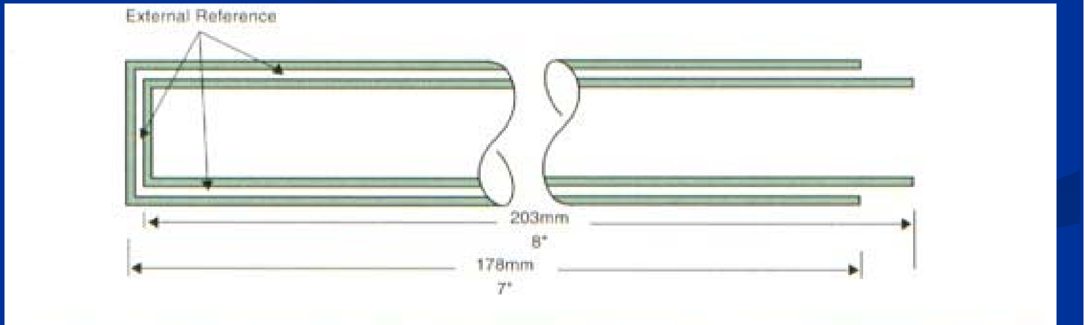
Resonances of deuterated solvents

Chemical Shift References

Coaxial NMR tubes







Each insert fits snugly into the outer tube, much like a syringe plunger fits its barrel. The flat bottom helps force reference liquid upward between the inner and outer tubes.

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

Shielding Constant Calculations

Ramsay $\sigma^{A} = \sigma^{A}{}_{dia} + \sigma^{A}{}_{para}$

GIAO (Gauge-Including Atomic Orbital)
An ab initio program that calculates NMR isotropic shielding values, a subroutine in Gaussian

IGLO (Individualized Gauge for Localized Orbitals)

CSGT (Continuous Set of Gauge Transformations)

DFT methods

Fundamental Contributions to the Magnetic Shielding Constant

$$\sigma^{A} = \sigma^{A}_{dia} + \sigma^{A}_{para} + \Sigma\, \sigma^{AB}_{nonloc}$$

σ^{A}_{dia} - 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 substraction 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

$$\sigma^{A} = \sigma^{A}_{dia} + \sigma^{A}_{para} + \Sigma\, \sigma^{AB}_{nonloc}$$

σ^{A}_{para} - 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

$$\sigma^{A} = \sigma^{A}_{\mathrm{dia}} + \sigma^{A}_{\mathrm{para}} + \Sigma\, \sigma^{AB}_{\mathrm{nonloc}}$$

$\Sigma\, \sigma^{AB}_{\mathrm{nonloc}}$ - 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	$\ell = 1,2,3$	+	+

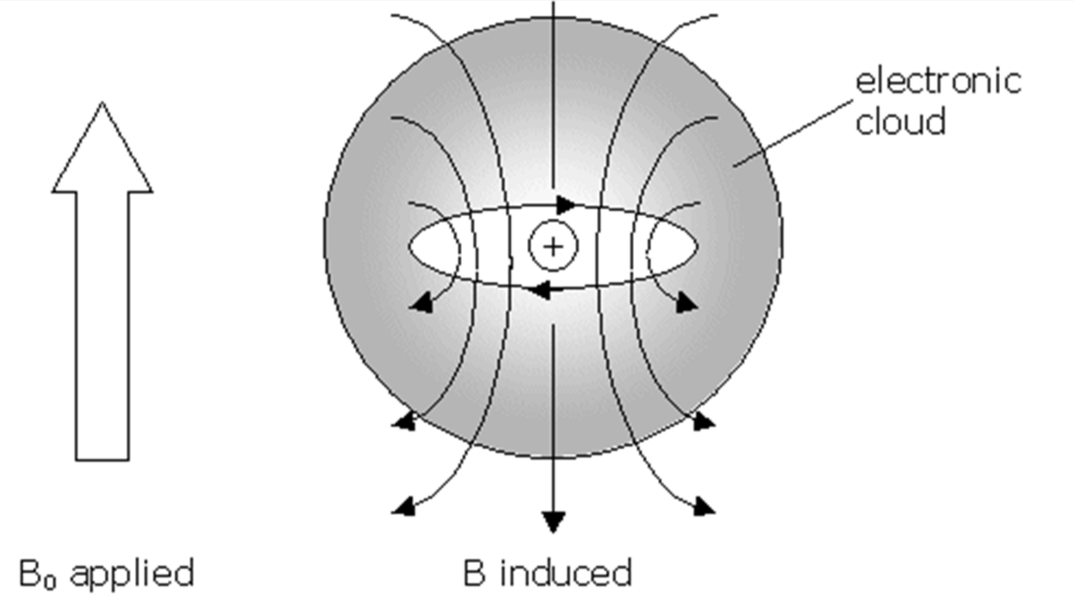
$\sigma_{para} = 0$ **for spherical closed-shell atoms or ions (F^-)**

Magnetic Shielding

Magnetic Shielding Contributions for Different Elements

s-Block Elements	valence p-orbitals absent (H) or hardly occupied (group 1, 2 metals) ⇒ diamagnetic term dominates ⇒ large non-local contributions (up to 20% for ^{1}H)
p,d-Block Elements	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)

The Diamagnetic Contribution to the Magnetic Shielding Constant



$$B_{nucl} = B_0 - B_{induced} = B_0 - B_0\,\sigma$$

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

$$\varpi = \gamma\, B_{nucl} = \gamma\, B_0(1 - \sigma)$$

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)

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

Ψ_0 = vawefunction of the ground state
$\mu_0 = 4\pi\ 10^{-7}\ \mathrm{N\ A^{-2}}$ permeability of free space
m_e = electron mass
r = electron radius

The Diamagnetic Contribution to the Magnetic Shielding Constant

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

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

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

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
^{1}H	18
^{13}C	261
$^{14/15}N$	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
^{113}Cs	–280

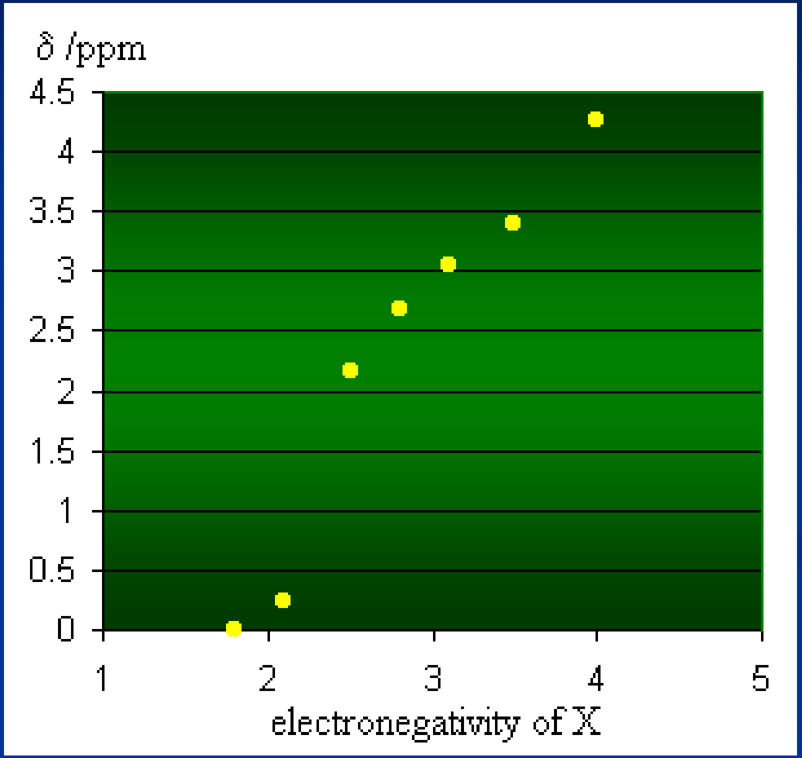
Shielding increases when element number Z of the observed atom increases

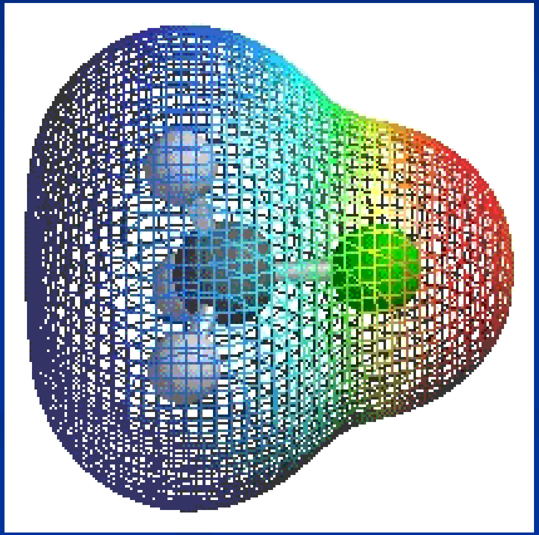
$$\sigma^{d} \sim 0.319\ 10^{-4}\ Z^{4/3}$$

Large and heavy atoms have large diamagnetic shielding

Influence of Electronegativity

δ (^{1}H) / ppm





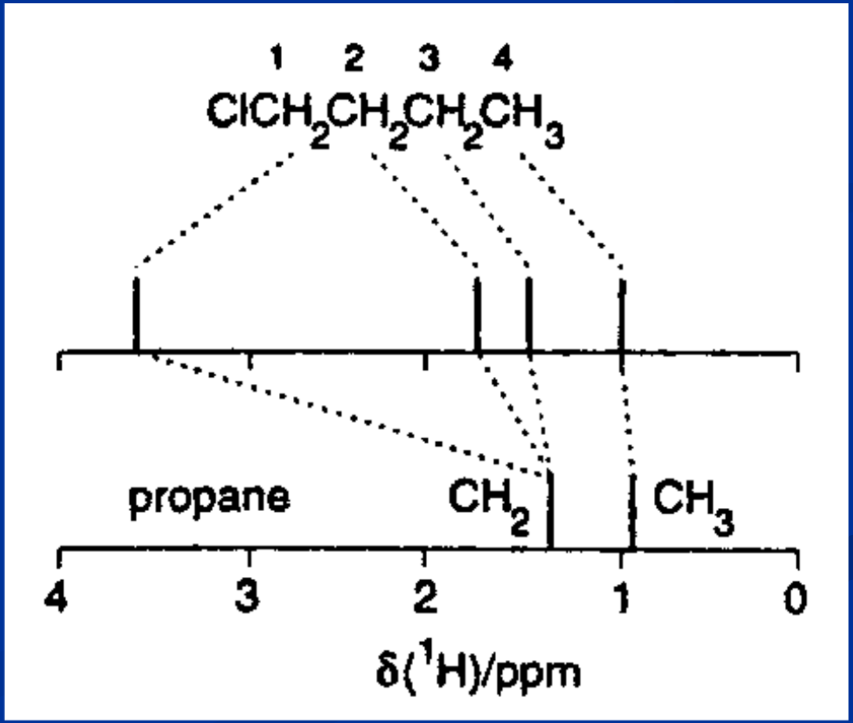
Compound, CH_3X X	CH_3F F	CH_3OH O	CH_3Cl Cl	CH_3Br Br	CH_3I I	CH_4 H	$(CH_3)_4Si$ Si
Elnegat of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift, δ / ppm	4.26	3.4	3.05	2.68	2.16	0.23	0

Influence of Electronegativity

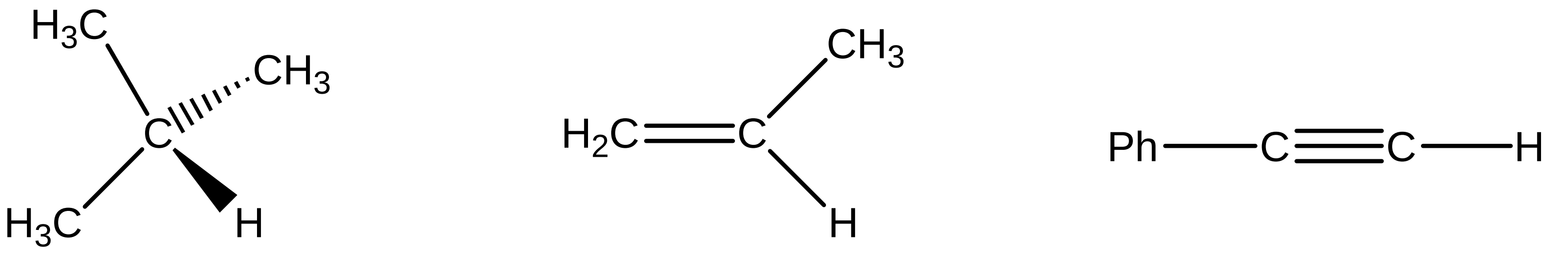
Compound	$CHCl_3$	CH_2Cl_2	CH_3Cl	CH_4
δ (^{1}H) / ppm	7.27	5.30	3.05	0.23

Influence of electronegative substituents :

- increases with their increasing number
- decreases with increasing distance



Influence of Electronegativity



pK_a ~55 44 28.8
(in DMSO)

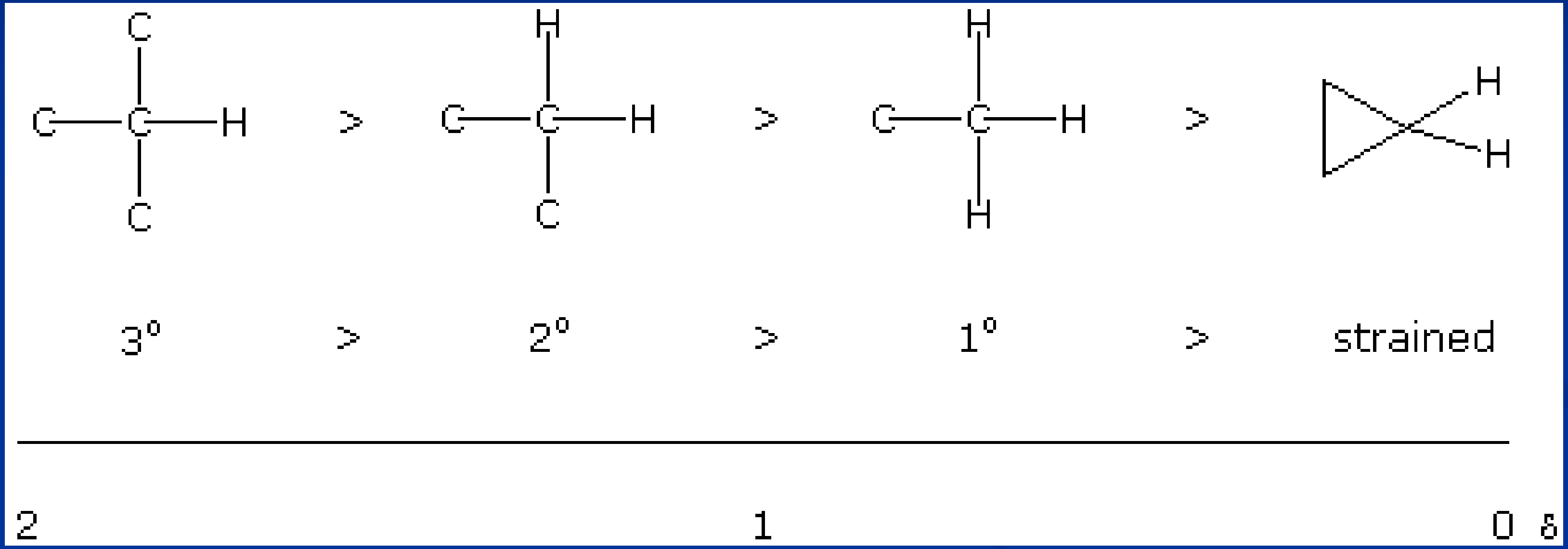
acidity of C increases →

% C-H s-character

25 33 50

electronegativity of C increases →

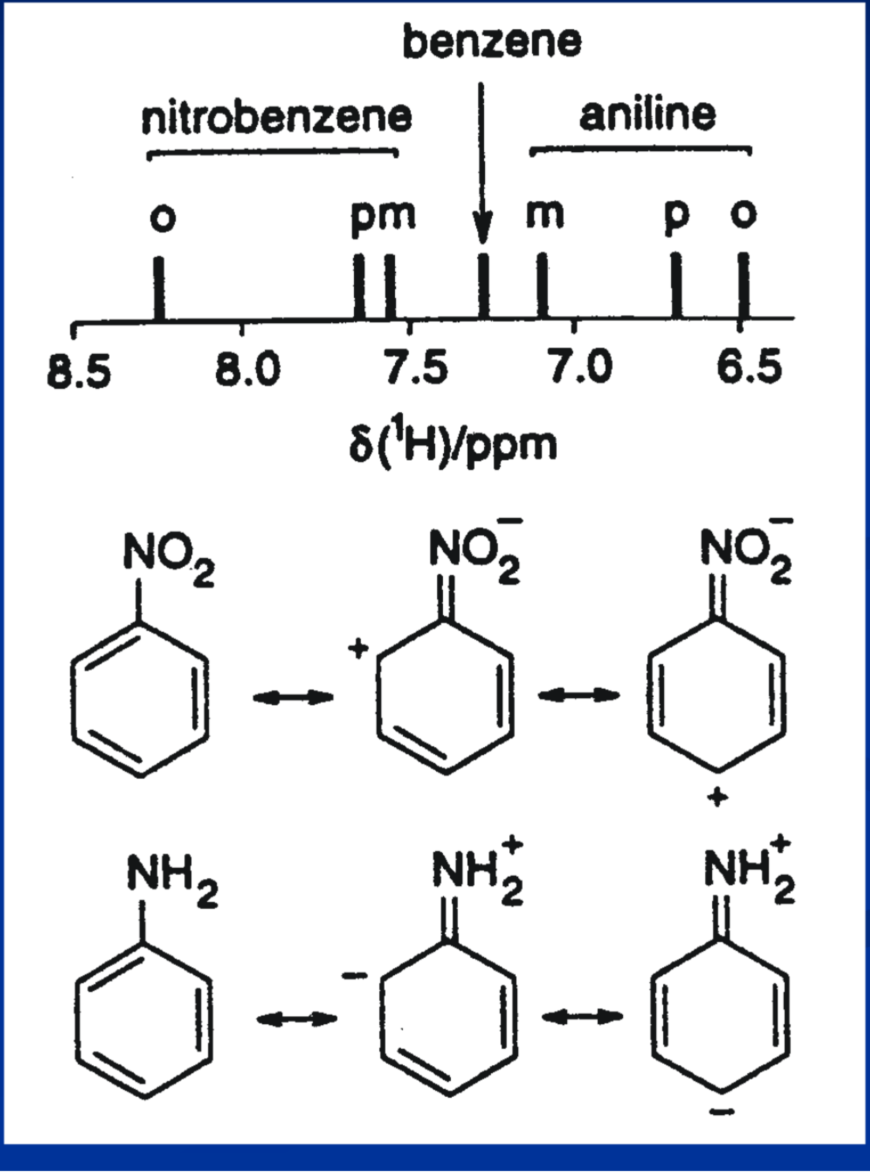
Influence of Electronegativity



Electronegativity

C	2.5
H	2.1

Aromatic Proton Shifts

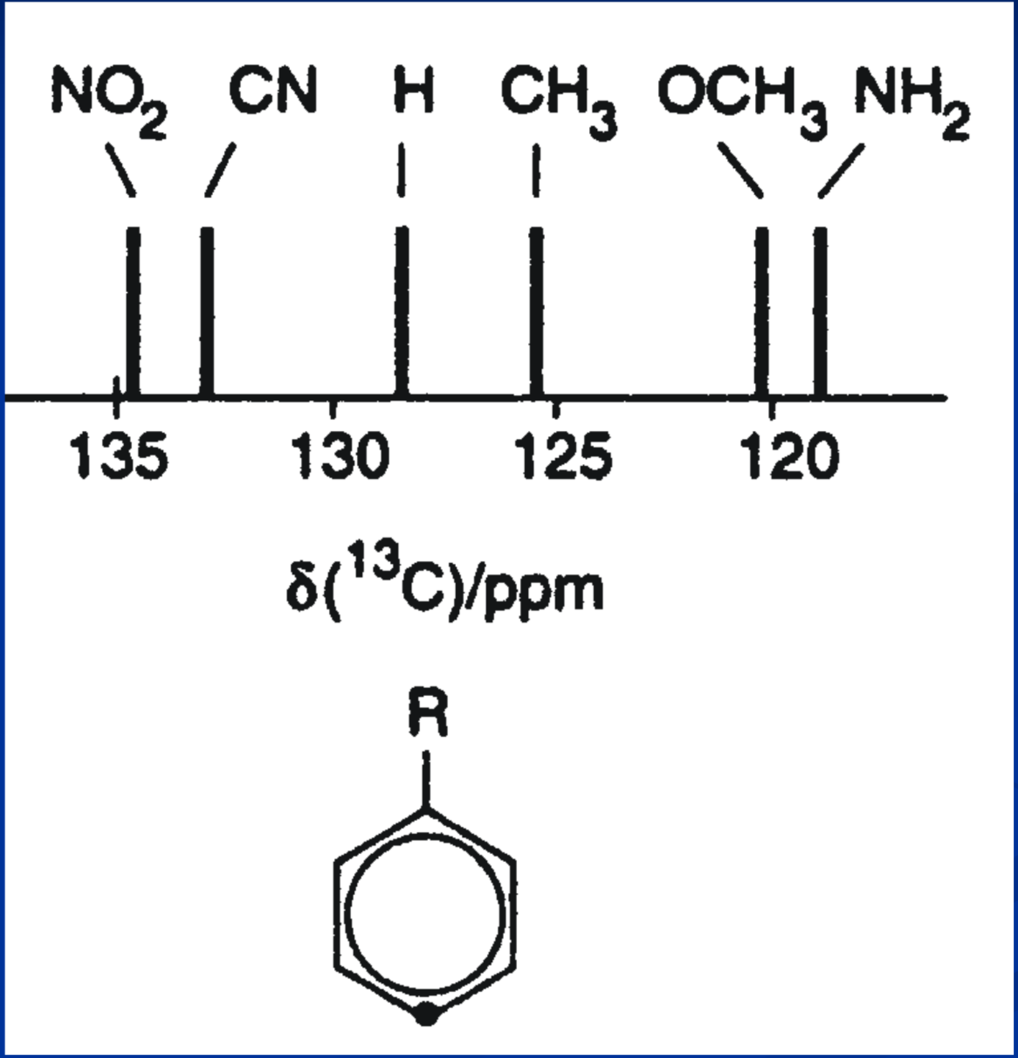


Electrophilic substitution

Meta directing
Strongly deactivating

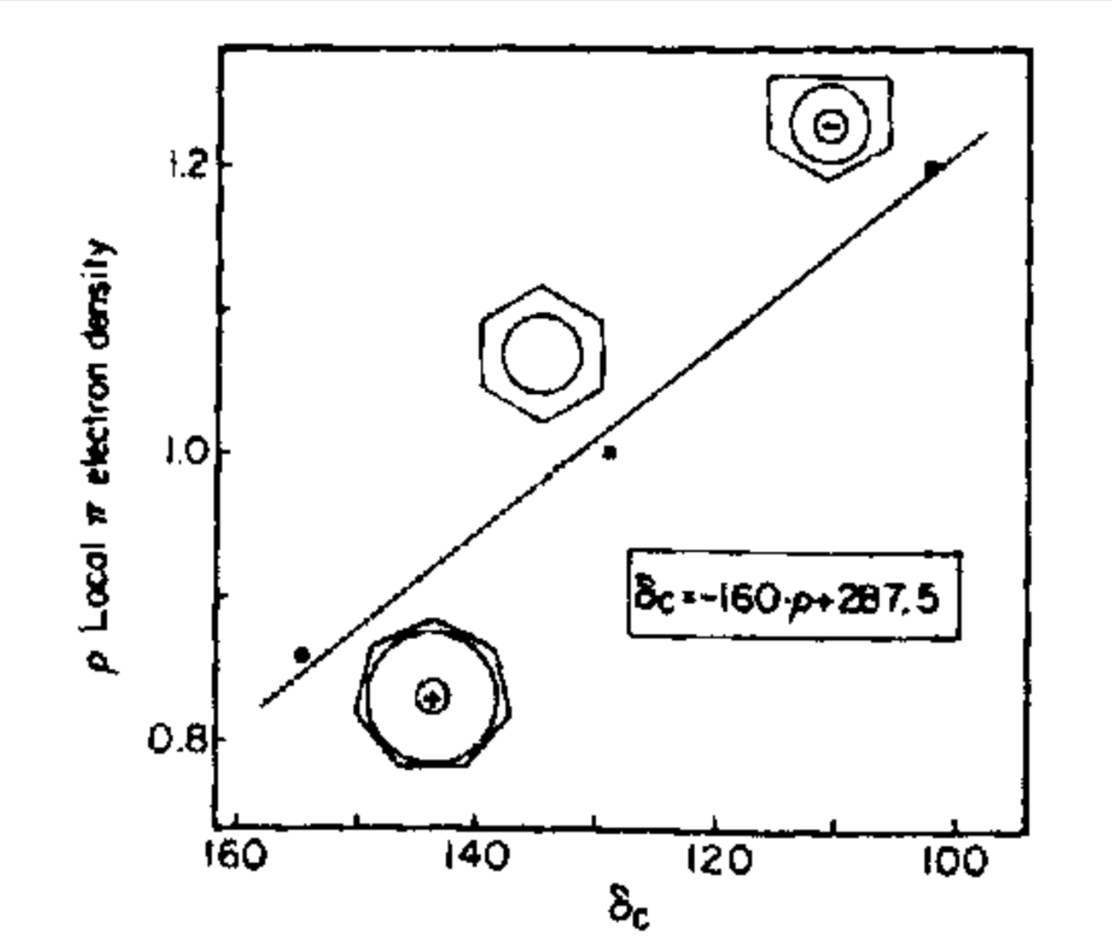
Ortho, para directing
Strongly activating

Aromatic Carbon Shifts



Aromatic Carbon Shifts

Number of
π electrons
per C



δ (^{13}C) / 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:

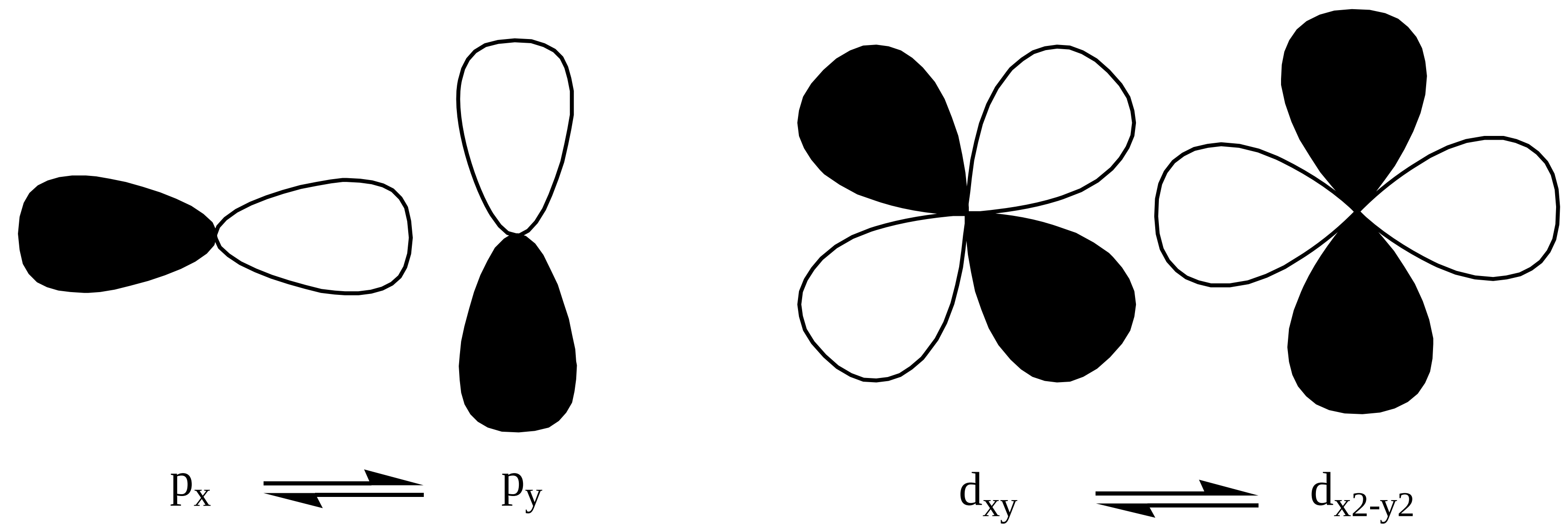
$$\sigma_{\mathrm{para}} \approx -\frac{\mu_0 \mu_B^2}{2\pi} \Delta E^{-1} r^{-3}_{<np>} \sum_{bonds} Q_i$$

and for transition metals by GRIFFIN and ORGEL:

$$\sigma_{\mathrm{para}} \approx -\frac{\mu_0 \mu_B^2}{2\pi} \Delta E^{-1} r^{-3}_{<(n-1)d>} < 0|\mathrm{L}^2|0 >$$

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

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

The Paramagnetic Contribution to the Magnetic Shielding Constant

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

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_O
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 ($\sigma_{para} = f(Q_i / L^2)$)
increasing symmetry = decreasing imbalance
higher bond order = shielding

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 !

Ag^+	$Ag—NH_3$	$H_3N—Ag—NH_3$
symm.	unsymm.	symm.

σ_{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

$<r^{-3}>$
"radial term"

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

	NH_4^+	NH_3
δ (^{15}N)	–325.9	–380.2

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

	CMe_3^+	$HCMe_3$
δ (^{13}C)	335.7	50

Patterns of Chemical Shifts

$<r^{-3}>$
"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
	$XeOF_4$	$Xe(OTeF_5)_4$	$Xe(OTeF_5)_2$	
	0	–637	–2379	

Higher oxidation state = more positive charge = smaller <r> = deshielding

←

Patterns of Chemical Shifts

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

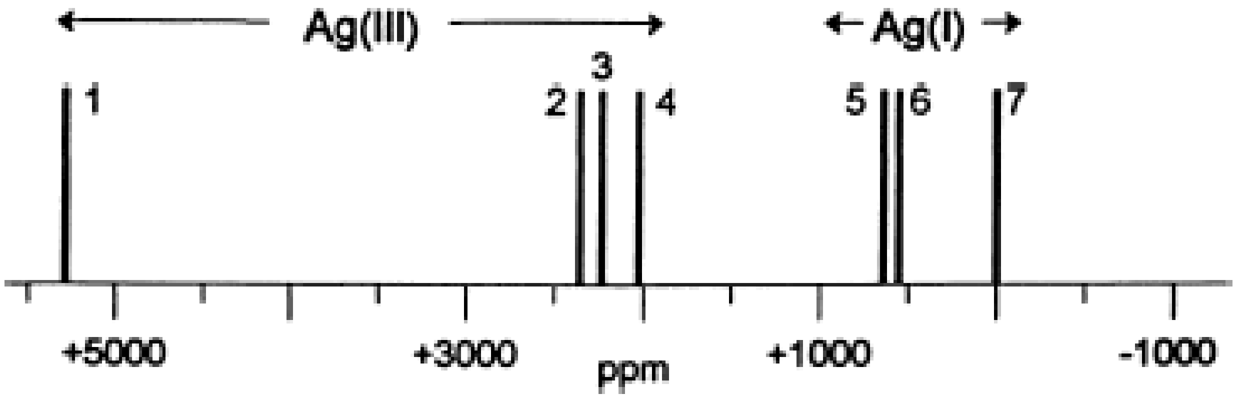


Fig. 3. The range of ^{109}Ag NMR chemical shifts. 1: $Ag^{III}F_4^-$; 2: $Ag^{III}(CF_3)(CN)_3^-$ [6]; 3: $Ag^{III}(CF_3)_4^-$ [6]; 4 $Ag^{III}(CF_2H)_4^-$ [5]; 5 $Ag^{I}(CF_2H)_2^-$ [5]; 6 $Ag^{I}(CF_3)_2^-$ [6]; 7: Ag_{aq}^{I} +.

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 ΔE(d-d) = energy term decreases

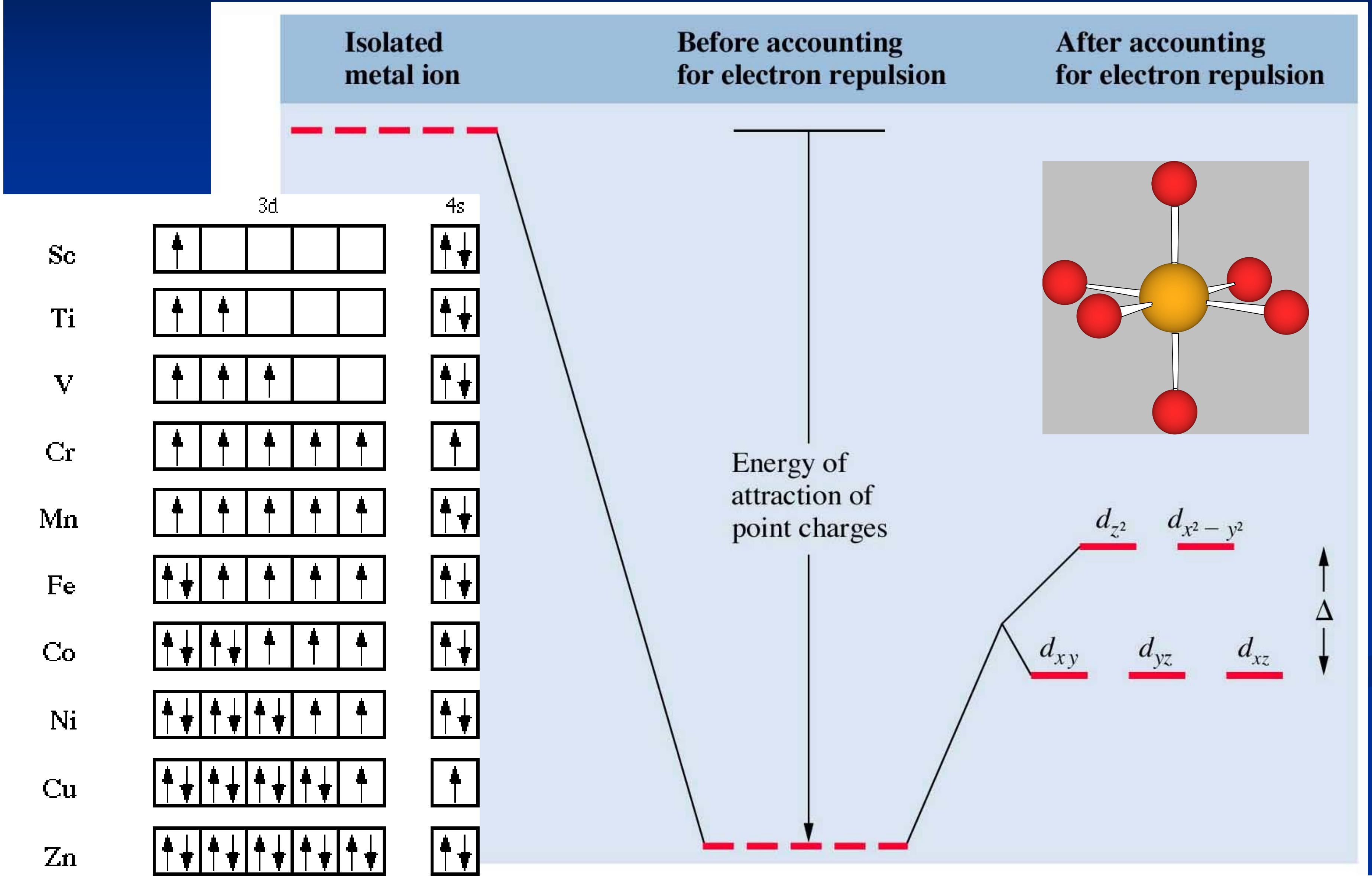
$I^- < Br^- < S^{2-} < NCS^* < Cl^- < NO_3^- < F^- < OH^-$
$< RCOO^- <$ ox $< ONO^* < H_2O < SCN^* <$ gly $<$ edta
$< CH_3CN <$ py $< NH_3 <$en $<$ bipy $<$ phen $< {}^*NO_2^- < PR_3 < CN^- < CO$

Weak ligands = deshielding
weak bonds
σ_{para} large
←

ΔE^{-1}
"energy term"

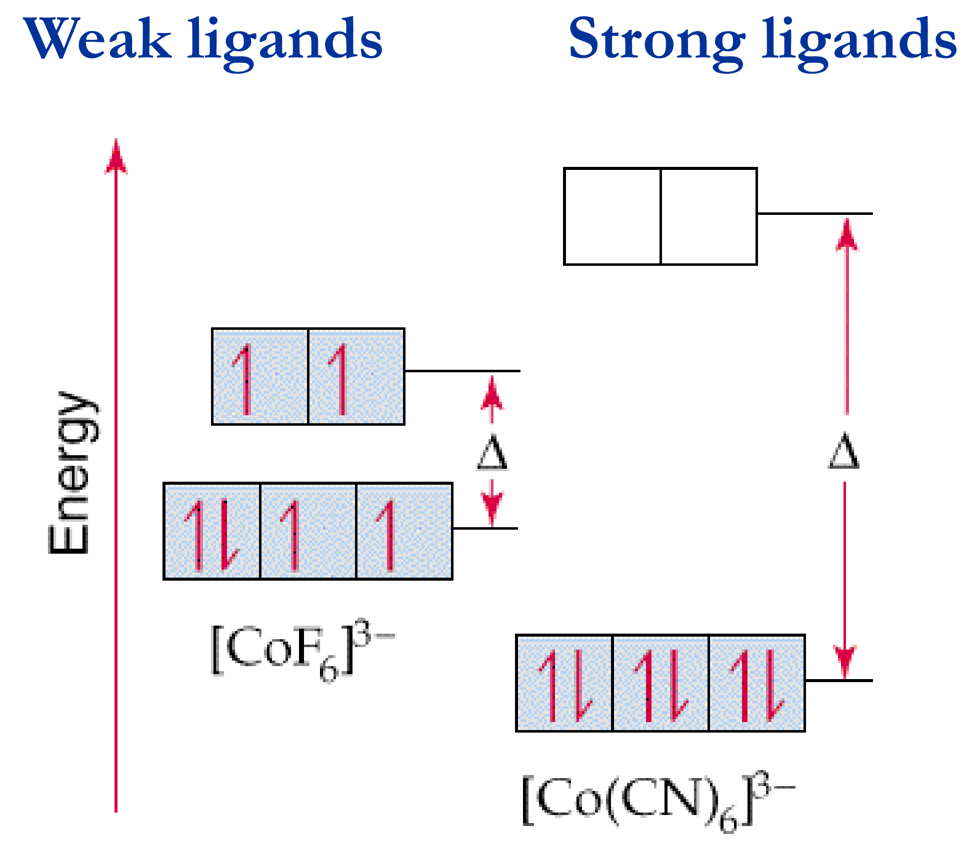
Strong ligands = shielding
strong bonds
σ_{para} small
→

Octahedral Complexes

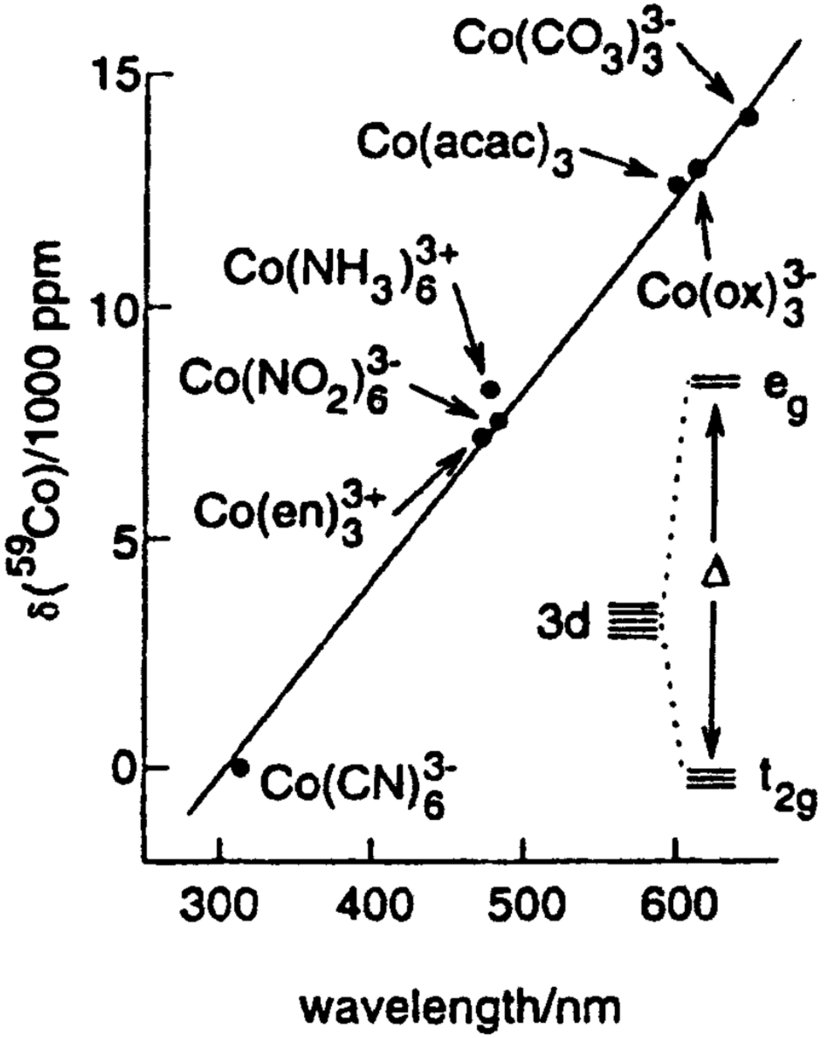


	3d					4s
Sc	↑					↑↓
Ti	↑	↑				↑↓
V	↑	↑	↑			↑↓
Cr	↑	↑	↑	↑	↑	↑
Mn	↑	↑	↑	↑	↑	↑↓
Fe	↑↓	↑	↑	↑	↑	↑↓
Co	↑↓	↑↓	↑	↑	↑	↑↓
Ni	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	↑↓	↑↓	↑↓	↑↓	↑	↑
Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Ligand Field Splitting



Spectrochemical Series



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

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

“energy term”

^{17}O Chemical Shifts in Oxoanions

ΔE^{-1}
"energy term"

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

$[VO_4]^{3-}$	$[CrO_4]^{2-}$	$[MnO_4]^{-}$	$[SO_4]^{2-}$	$[ClO_4]^{-}$
568	835	1230	167	290
	$[MoO_4]^{2-}$	$[TcO_4]^{-}$	$[SeO_4]^{2-}$	
	530	749	204	
	$[WO_4]^{2-}$	$[ReO_4]^{-}$		
	420	569		

Nephelauxetic Series

$<r^{-3}>$
"radial term"

Nephelauxetic effect = expansion of d-orbitals
$<r>$ increases = radial term decreases

$F^- < H_2O < NH_3 <$ en $<$ ox $<$ SCN* $< Cl^- < CN^- < Br^- < I^-$

Nephelauxetic effect increases = $<r>$ increases

→

Electronegativity increases

←

Ionic bonding
$<r>$ decreases
Deshielding

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

Covalent bonding
$<r>$ 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

Deshielding with increasing electronegativity (trend is similar to diamagnetic term)

ΔE^{-1}
"energy term"

Spectrochemical Series

Shielding with increasing electronegativity

Inverse halogen dependence

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

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

$<r^{-3}>$
"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

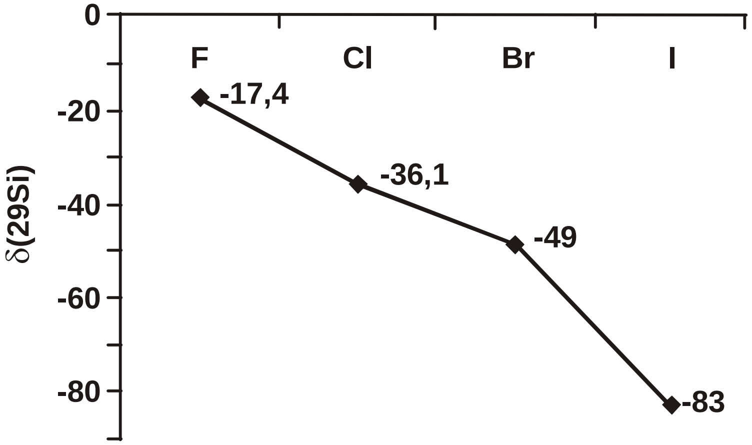
δ(M) follows the spectrochemical series of ligands,
increases in the series F < Cl < Br < I

ΔE^{-1}
"energy term"

Observed for
many transition metal complexes with d^0, d^{10}- configurations,
alkali metals

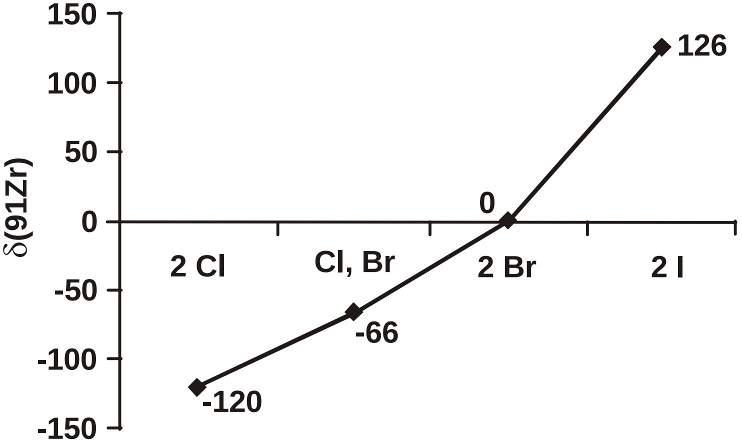
Patterns of Chemical Shifts

I. Normal Halogen(Ligand) Dependence



δ(^{29}Si) in H_3SiX

II. Inverse Halogen(Ligand) Dependence



δ(^{91}Zr) in Cp_2ZrXY

^{51}V NMR of Vanadyl derivatives

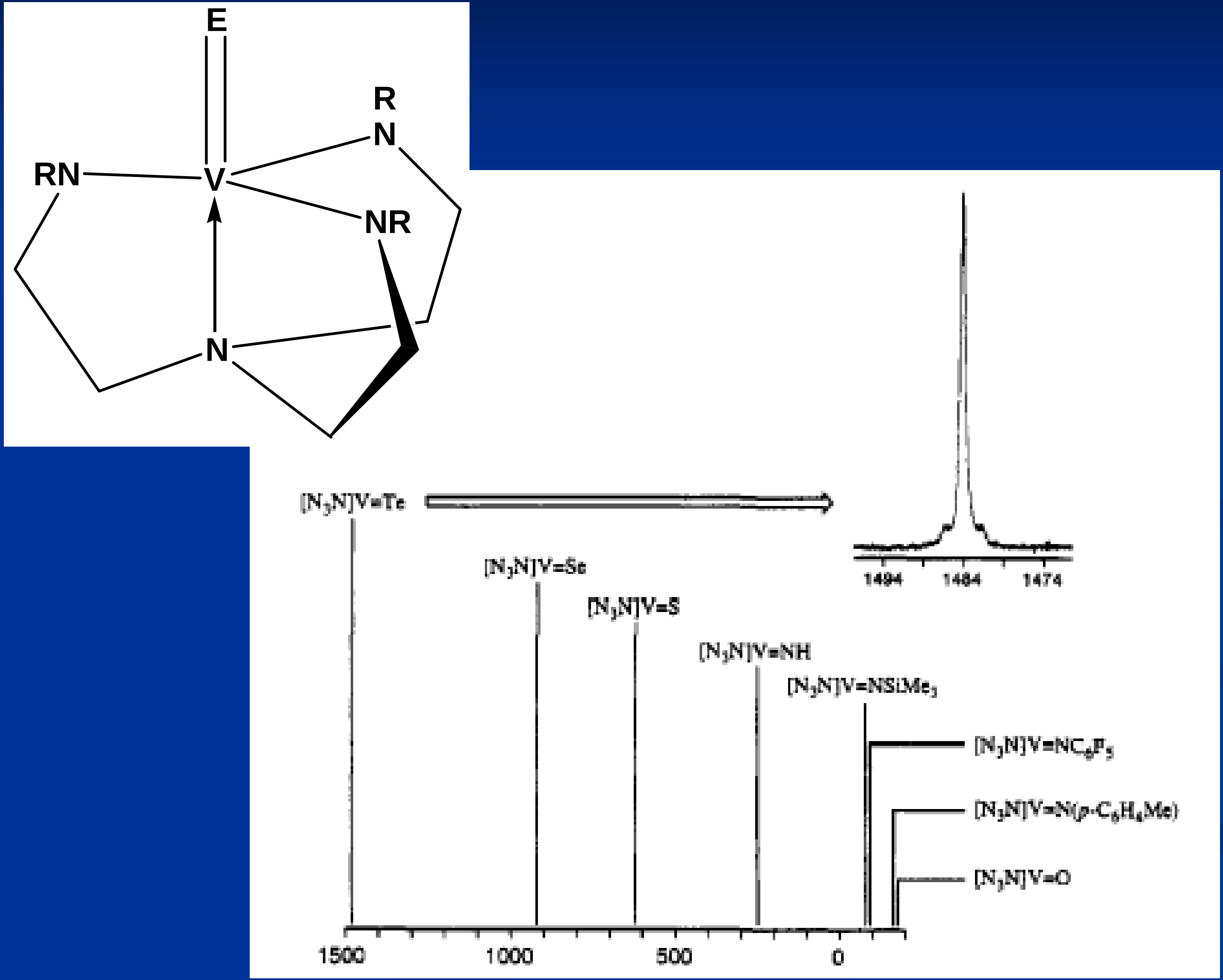
$$\sigma_{para} = -const \frac{\Delta P_{imbalance}}{\Delta E \times \langle r_p \rangle^3}$$

$VOBr_3$	$VOCl_3$	VOF_3
432 (neat)	0 (neat)	–786 (CH_3CN)

Inverse Halogen (Ligand) Dependence

$$\sigma_{para} \approx -\frac{\mu_0 \mu_B^2}{2\pi} \Delta E^{-1} r^{-3}_{<(n\text{-}1)d>} < 0|L^2|0 >$$

^{51}V NMR of Vanadatranes

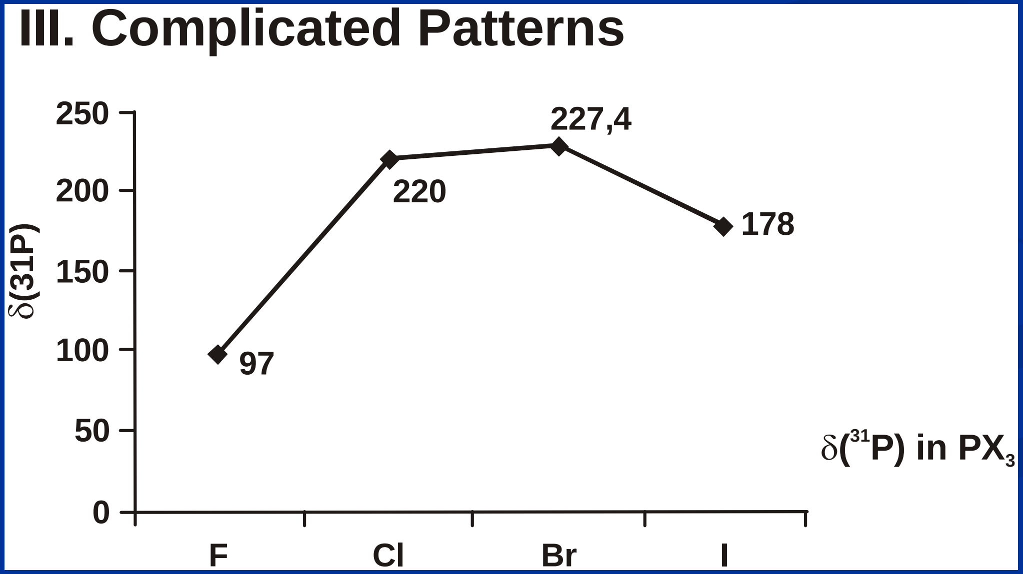


Patterns of Chemical Shifts

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^-
δ (^{31}P) ppm	220	96	–81	–281

$Q_i (L^2)$
"orbital term"

Increasing symmetry = lower imbalance = shielding

Coordination Number and Chemical Shifts

Main group elements

Higher CN = shielding

Transition metals

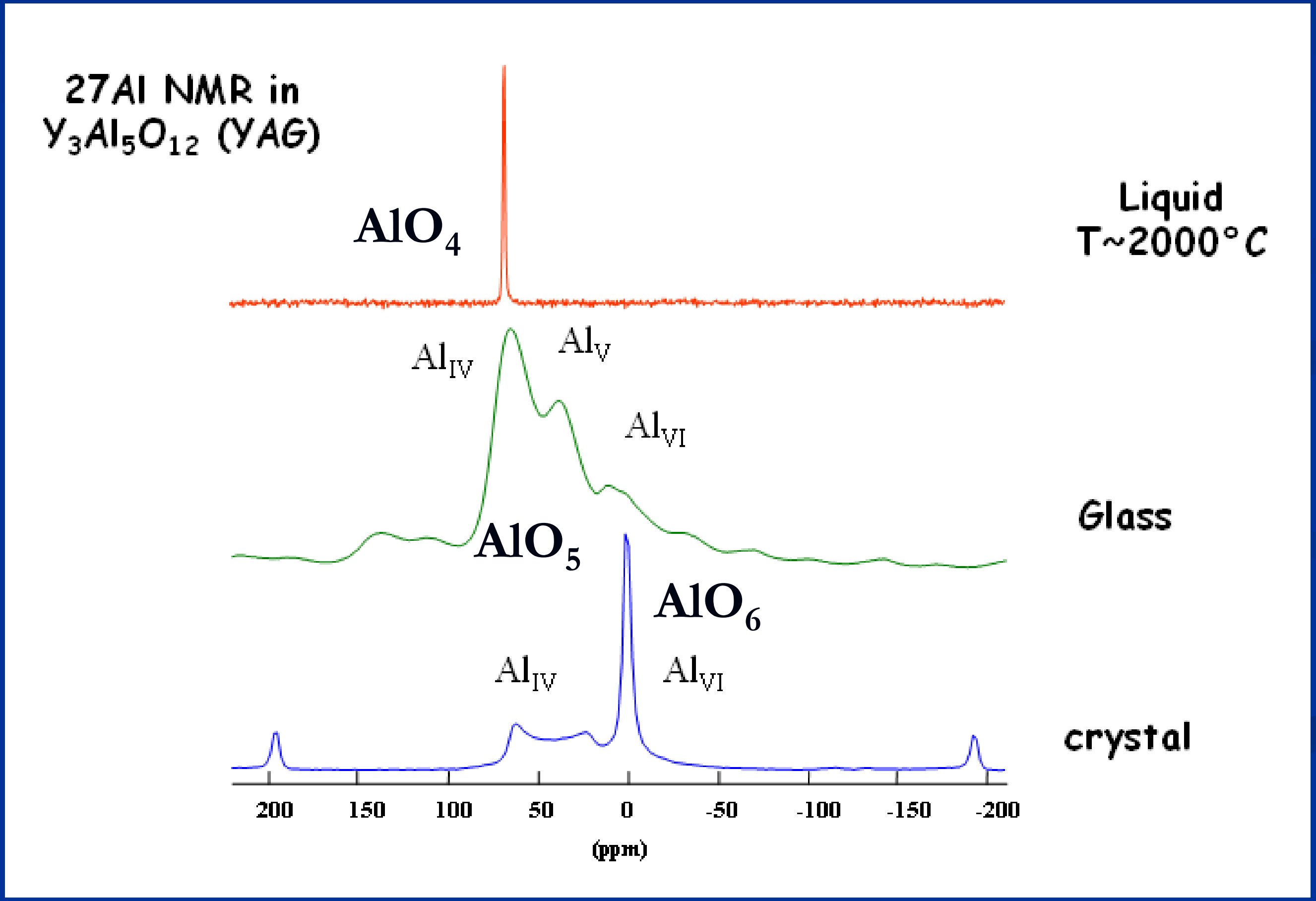
Higher CN = deshielding

More π bonding = shielding
More σ bonding = deshielding

Coordination Number and Chemical Shifts

Higher CN = shielding

δ (^{27}Al)



Coordination Number and Chemical Shifts

Higher CN = shielding

δ (^{27}Al)

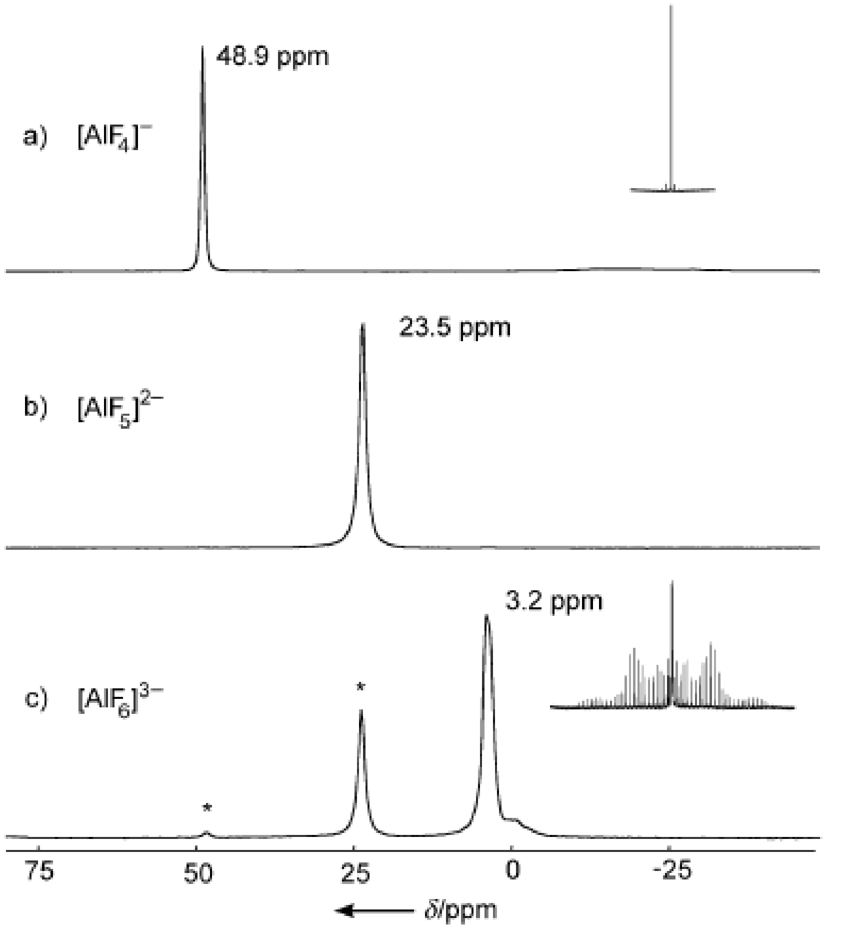


Abbildung 1. ^{27}Al-MAS-NMR-Spektren von a) $(CH_3)_4N^+[AlF_4]^-$, b) $[(CH_3)_4N^+]_2[AlF_5]^{2-}$ und c) $[(CH_3)_4N^+]_3[AlF_6]^{3-}$. Im Spektrum (c) sind Signale von (b) und (a) sichtbar (*); der Einschub zeigt das Satellitenspektrum infolge Quadrupolwechselwirkung in störungstheoretisch 1. Ordnung.