Shielding Tutorial

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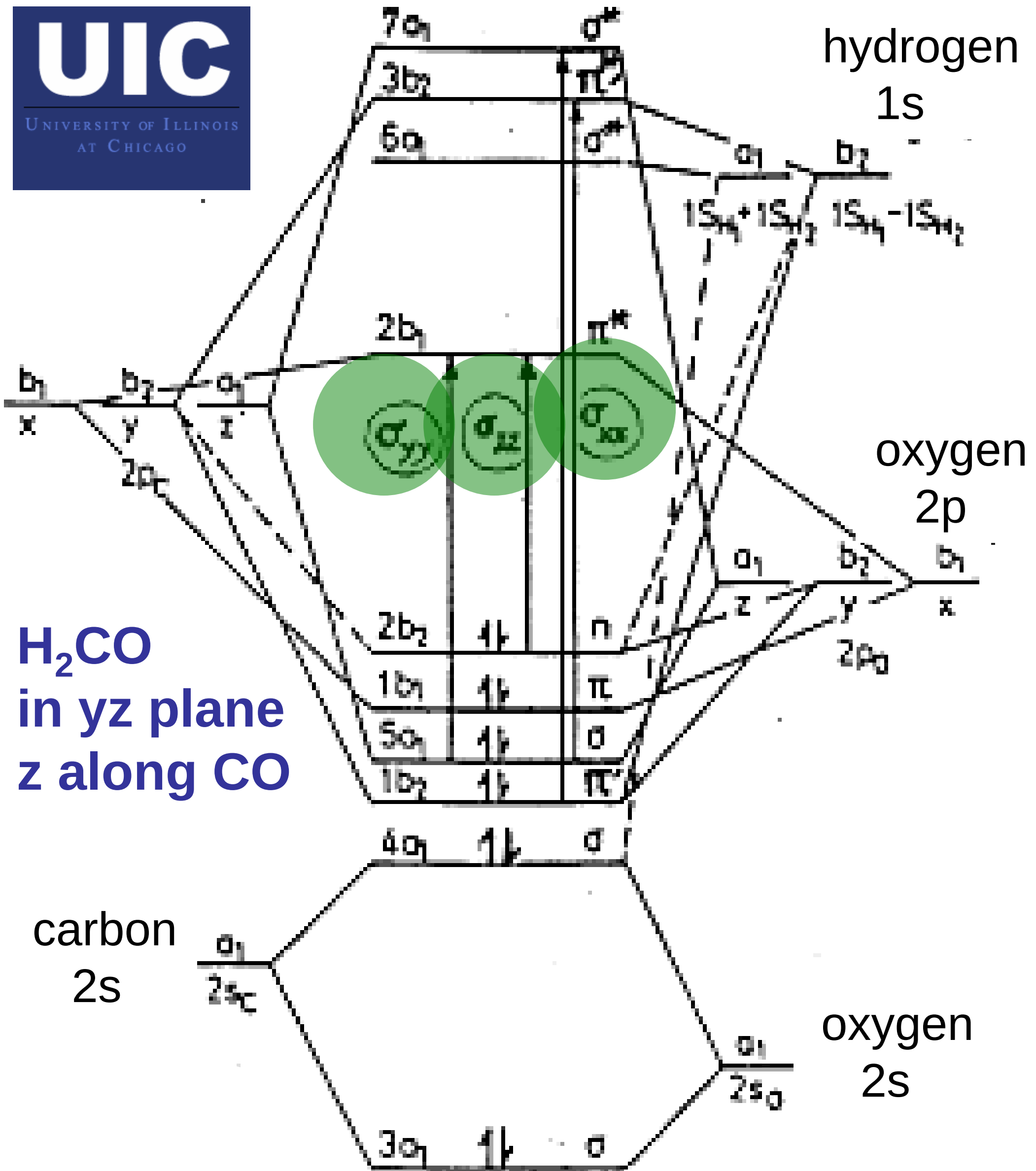
magnetic dipole allowed transitions contribute to	orbital transitions OMO → UMO	molecular transitions Ψground → Ψexcited
σ_{zz}	**$2b_2 \rightarrow 2b_1$** **n π^*_{CO}**	$^1A_1 \rightarrow {}^1A_2$
σ_{yy}	**$5a_1 \rightarrow 2b_1$** **σ_{CO} π^*_{CO}**	$^1A_1 \rightarrow {}^1B_1$
σ_{xx}	**$1b_2 \rightarrow 7a_1$** **π' σ^***	$^1A_1 \rightarrow {}^1B_2$
σ_{xx}	**5a1→3b2** **σ_{CO} π'^***	$^1A_1 \rightarrow {}^1B_2$



hydrogen 1s

carbon 2p

oxygen 2p

H_2CO
in yz plane
z along CO

carbon 2s

oxygen 2s

Shielding Tutorial

Understanding Chemical Shifts

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Relation between observed NMR chemical shifts δ and the fundamental electronic property nuclear magnetic shielding σ

Energy term in the molecular Hamiltonian

$$W = -\mu\bullet(\mathbf{u}_\mathbf{B} - \boldsymbol{\sigma}\bullet\mathbf{u}_\mathbf{B})B_0$$

resonance frequency

$$\omega=|\gamma|B_0\,(1 - \sigma)$$

more correctly

$$\omega=|\gamma|B_0\,[\mathbf{u}_\mathbf{B}{}^{\dagger}\bullet(\mathbf{1}-\sigma^{\dagger})(\mathbf{1}-\sigma)\bullet\mathbf{u}_\mathbf{B}]^{1/2}$$

Experimental definition of chemical shift:

$$\delta \equiv (\omega_{sample}-\omega_{ref})/\omega_{ref}$$

$$\delta = (\boldsymbol{\sigma}_{ref} - \boldsymbol{\sigma}_{sample})/(1 - \boldsymbol{\sigma}_{ref})$$

with a Xe atom as reference,

$$\delta_{calc} \approx (\boldsymbol{\sigma}_{Xe\ atom} - \boldsymbol{\sigma}_{calc})$$

The SHIELDING TENSOR

Norman F. Ramsey 1950s

Non-relativistic treatment

second order

$$\sigma = \sigma^{(1)}_{\text{diamagnetic}} + \sigma^{(2)}_{\text{paramagnetic}}$$

ground
electronic state

$$\sigma^{(1)}_{\text{diamagnetic, }xx} = (e^2/2mc^2)\,\langle\Psi_0|\textstyle\sum_i(y_{Ni}^2 + z_{Ni}^2)/r_{Ni}^3|\Psi_0\rangle$$

excited
electronic state

$$\sigma^{(2)}_{\text{paramagnetic, }xx} = -\,(e^2/2m^2c^2)\textstyle\sum_q(E_q - E_0)^{-1}$$

$$\times\langle\Psi_0|\textstyle\sum_i\mathcal{L}_{xNi}|\Psi_q\rangle$$

$$\times\langle\Psi_q|\textstyle\sum_i(\mathcal{L}_{xNi}/r_{Ni}^3)|\Psi_0\rangle$$

electronic angular momentum
X component for the ith electron

Identity relation **for nucleus N**

between paramagnetic shielding & spin rotation tensors:

molecular rotation constant *atomic number*

$\sigma^{(2)}_{\textit{paramagnetic, xx}}$

$$= 1836.1\,(C_{xx}/B_{xx})/2g_N - (e^2/2mc^2)\sum_{N'} \mathcal{Z}_{N'}(Y_{NN'}{}^2+Z_{NN'}{}^2)/R_{NN'}{}^3$$

m_p/m_e *spin-rotation tensor component*

Use of Flygare approximation:

$\sigma^{(1)}_{\textit{diamagnetic, xx}}$ 14.09 ppm Å

$$\approx \sigma(\text{free atom}) + (e^2/2mc^2) \sum_{N'} \mathcal{Z}_{N'} (Y_{NN'}{}^2+Z_{NN'}{}^2)/R_{NN'}{}^3$$

leads to

$$\sigma_{xx} \approx 1836.1(C_{xx}/B_{xx})/2g_N + \sigma(\text{free atom})$$

shielding ***spin-rotation tensor***

IDENTITY RELATION APPLIES ONLY IN NON-RELATIVISTIC THEORY

SYMMETRY
and the shielding tensor

How many different non-zero components?

depends on the **nuclear site symmetry**

(which could be lower than the
symmetry of the molecule as a whole).

Nuclear site symmetry	# non-vanishing	# indep	Non-vanishing components
	total	indep	
C_1, C_i	9	9	All nine
C_2, C_s, C_{2h}	5	5	xx yy zz xy yx H in H_2O, xy molecular plane
C_3, C_{3h}, C_4, C_{4h} C_6, C_{6h}, S_4, S_6	5	3	xx=yy xy=yx zz
	diagonal		
C_{2v}, D_2, D_{2h}	3	3	xx yy zz C,O in H_2CO C,H in benzene
	|| ⊥ only		
C_{3v}, C4v, C6v, C∞v D_{2d}, D_3, D_{3d}, D_{3h} D_4, D_{4h}, D_6, D_{6h},$D_{\infty h}$	3	2	xx=yy, zz N in NH_3 middle C in allene
	isotropic		
T, T_h, T_d, O, O_h, K_h	3	1	xx=yy=zz C in CH_4 Se in SeF_6

A. D. Buckingham
and S. Malm, 1971
Mol. Phys. 22, 1127.
W. T. Raynes and
C. I. Ratcliffe,
Mol. Phys. 1979
37, 571.

THE PARAMAGNETIC PART

$$\sigma^{(2)}_{\text{paramagnetic, } xx}$$

$$= -\,(e^2/2m^2c^2)\sum_q (E_q - E_0)^{-1}$$

$$\times\langle\Psi_0|\sum_i \mathcal{L}_{xNi}|\Psi_q\rangle\langle\Psi_q|\sum_i (\mathcal{L}_{xNi}/r_{Ni}{}^3)|\Psi_0\rangle$$

Let us take a look at these, when are they not zero?

symmetry species of the angular momentum operators

nuclear site symmetry	$\mathcal{L}_z$	$\mathcal{L}_x$	$\mathcal{L}_y$	examples
C_{3v}	A_2	E		^{15}N in NH_3
O_h		T_{1g}		^{59}Co in CoL_6
T_d		T_1		^{13}C in CF_4
D_{2h}	B_{1g}	B_{3g}	B_{2g}	
C_{2v}	A_2	B_2	B_1	^{17}O in $H_2C{=}O$
C_s	A'	A''	A''	^{15}N in NOCl
C_{4v}	A_2	E		^{55}Mn in $Mn(CO)_5$
$D_{\infty h}$	Σ_g^-	π_g		^{19}F in F_2
$C_{\infty v}$	Σ^-	π		^{1}H or ^{19}F in HF

(z is the highest symmetry axis)

Consider linear molecules

$C_{\infty v}$	Σ^-	π	^{1}H or ^{19}F in HF
	$\mathcal{L}_z$	$\mathcal{L}_x , \mathcal{L}_y$	

$$\langle\Psi_{\text{ground}}|\ \mathcal{L}_z\ |\Psi_{\text{excited}}\rangle$$

Linear molecules that are stable (closed shells) have zero orbital angular momentum about the line of centers, i.e.,
$\langle\Psi_{\text{ground}}|$ belongs to symmetry species Σ^+

$$\langle \Psi_{\text{ground}} | \mathcal{L}_z | \Psi_{\text{excited}} \rangle = \langle \Sigma^{+} | \Sigma^{-} | \Psi_{\text{excited}} \rangle$$

By symmetry, the only *non-vanishing* matrix elements of $\mathcal{L}_z$ are those for which

$|\Psi_{\text{excited}}\rangle$ also belongs to symmetry species Σ^{-}

$$\langle \Psi_{\text{ground}} | \mathcal{L}_z | \Psi_{\text{excited}} \rangle = \langle \Sigma^{+} | \mathcal{L}_z | \Sigma^{-} \rangle.$$

But Σ^{-} means zero orbital angular momentum, so the only matrix element non-zero by symmetry is itself zero.

Therefore, in the non-relativistic case

$\sigma^{(2)}_{\text{paramagnetic}, \|} = 0$ ***for all linear molecules***

Paramagnetic contribution appears only in the perpendicular component in linear molecules.

IN GENERAL,

$\langle \Psi_0 | \mathcal{L}_x | \Psi_q \rangle$ eventually translates to terms like

$$\langle \mathrm{OMO} | \mathcal{L}_x | \mathrm{UMO} \rangle$$

occupied *unoccupied*

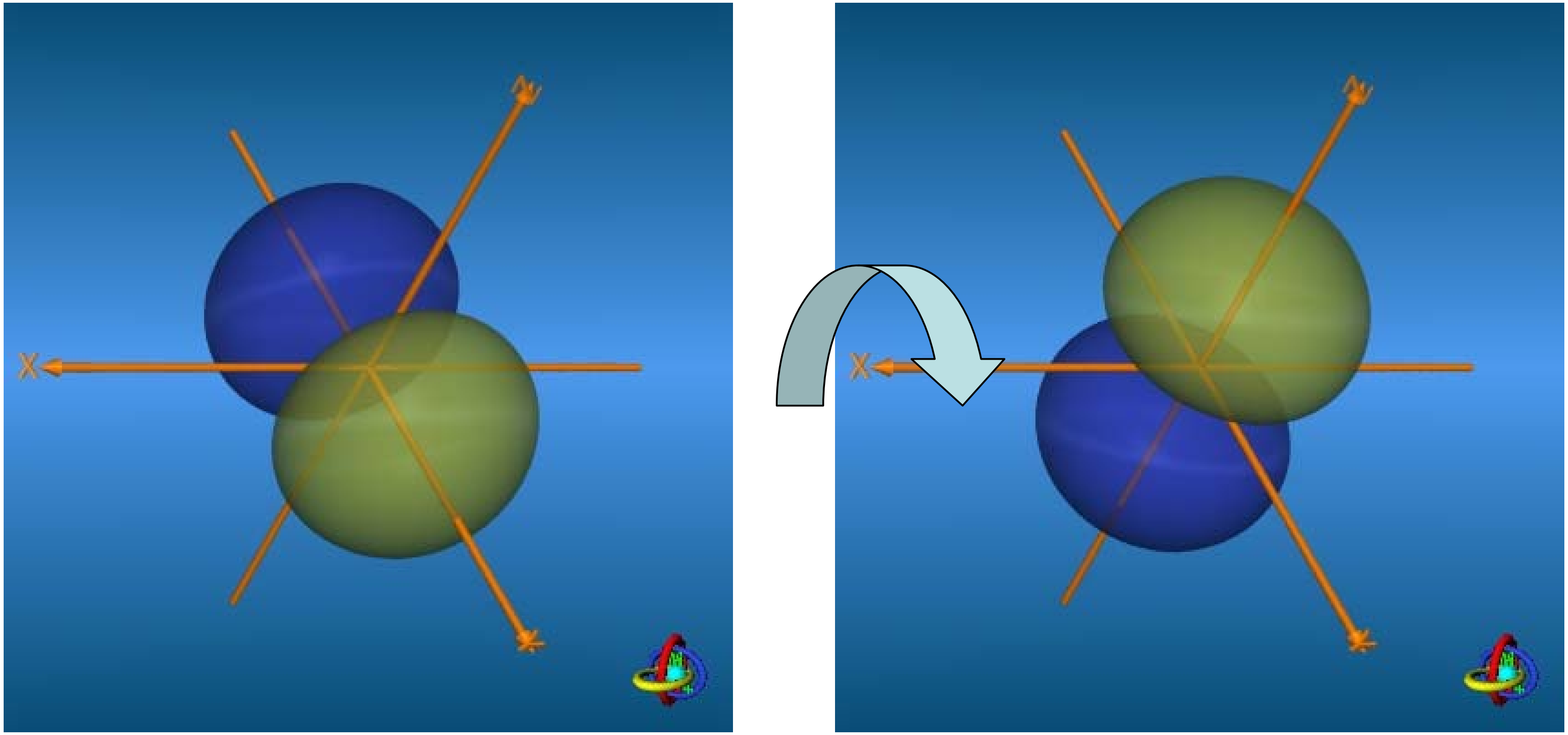
We have already seen that

$\mathcal{L}_x$ $\mathcal{L}_y$ and $\mathcal{L}_z$ belong to the same symmetry species as ROTATIONS about these axes.

Thus, contributions to paramagnetic shielding occur when the UMO, <u>after rotation</u>, “looks like” (has sizable overlap with) the OMO .

Examples of non- vanishing matrix elements are

$\langle p_y | \mathcal{L}_x | p_z \rangle$ $\langle d_{xy} | \mathcal{L}_z | dx^2\text{-}y^2 \rangle$ $\langle d_{yz} | \mathcal{L}_x | dz^2 \rangle$

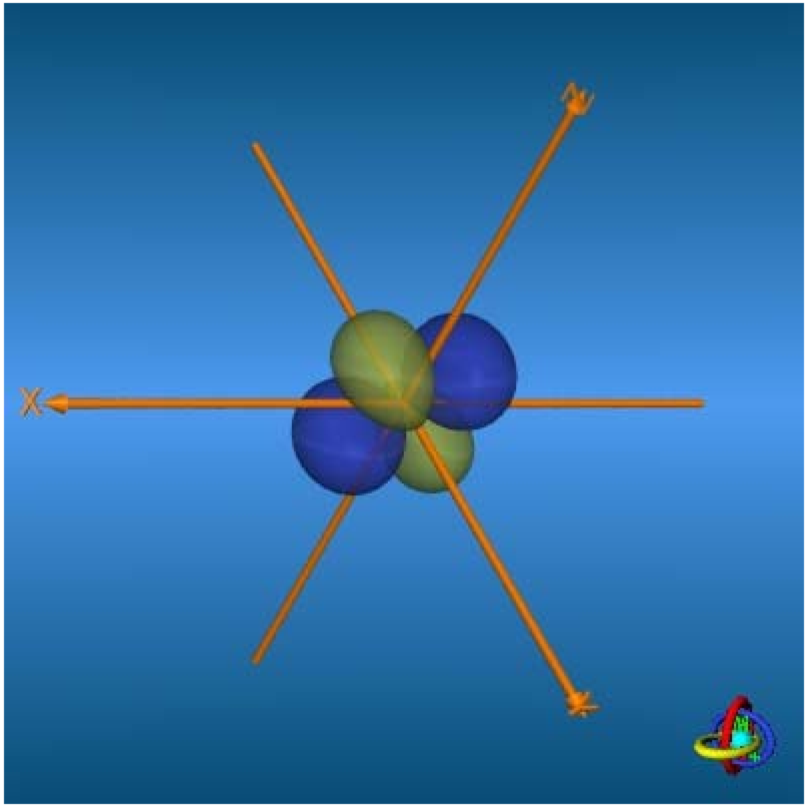


$2p_y$ $2p_z$

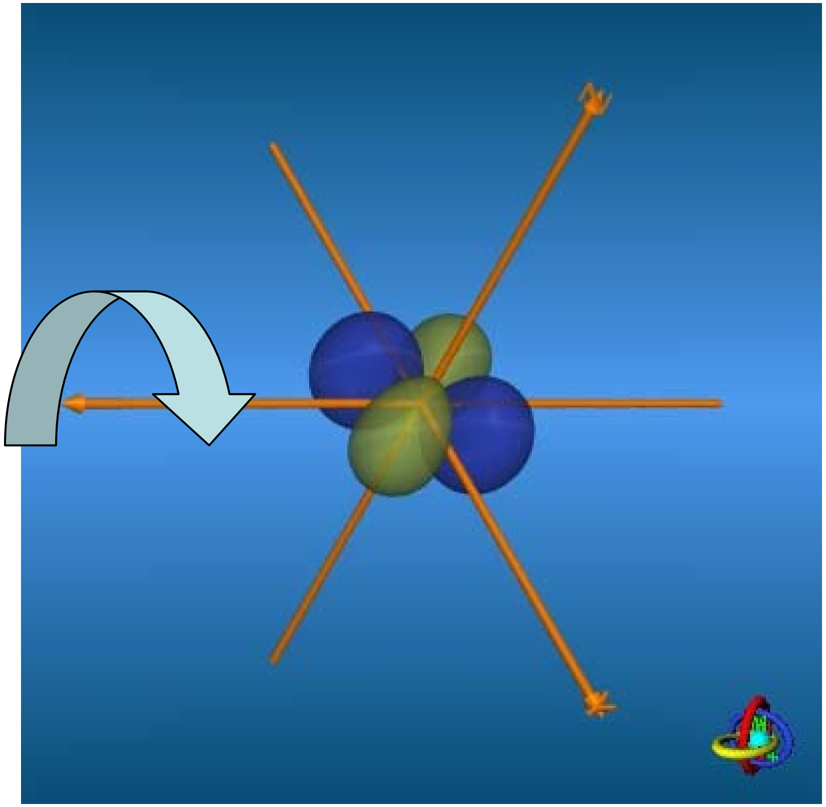
$\langle p_y|\mathcal{L}_x|p_z\rangle \neq 0$

imagine a rotation R_x operation on $2p_z$ function

$\mathcal{L}_x|p_z\rangle = |p_y\rangle$ $\mathcal{L}_x|p_y\rangle = -|p_z\rangle$



3d$_{xz}$

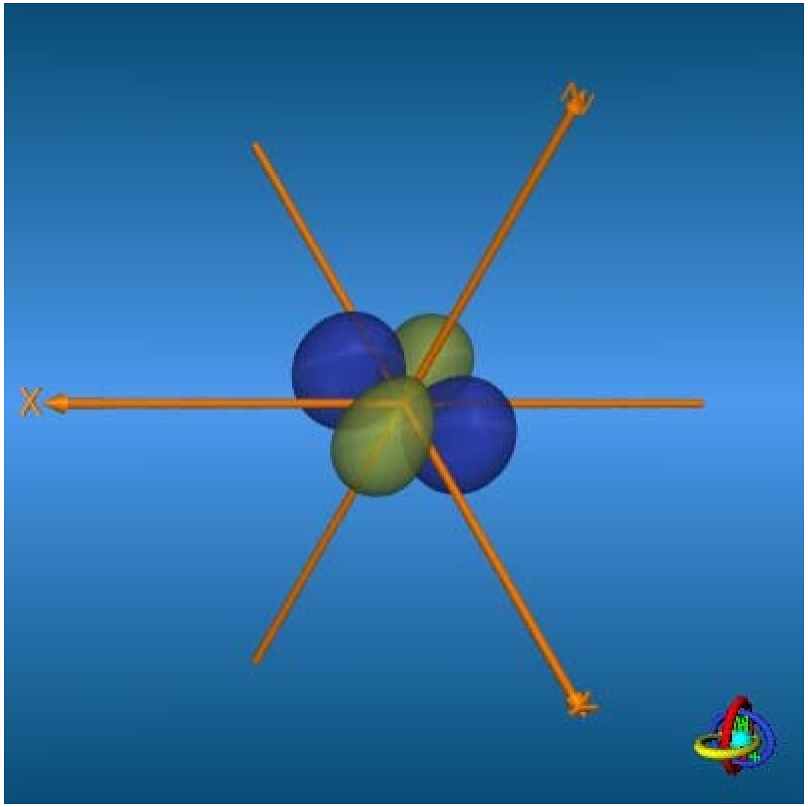


3d$_{xy}$

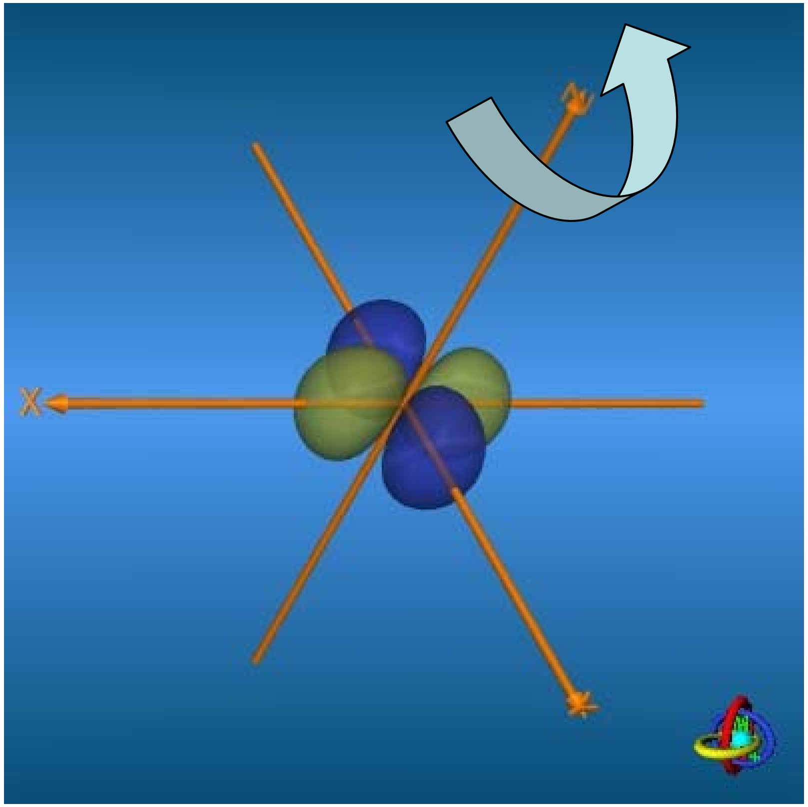
$$\langle d_{xz}|\mathcal{L}_{\mathbf{x}}|d_{xy}\rangle \neq 0$$

imagine a rotation R_x operation on 3d$_{xy}$ **function**

$\mathcal{L}_{\mathbf{x}}\, |d_{xy}\rangle = -|d_{xz}\rangle$ $\quad$ $\mathcal{L}_{\mathbf{x}}\, |d_{xz}\rangle = |d_{xy}\rangle$



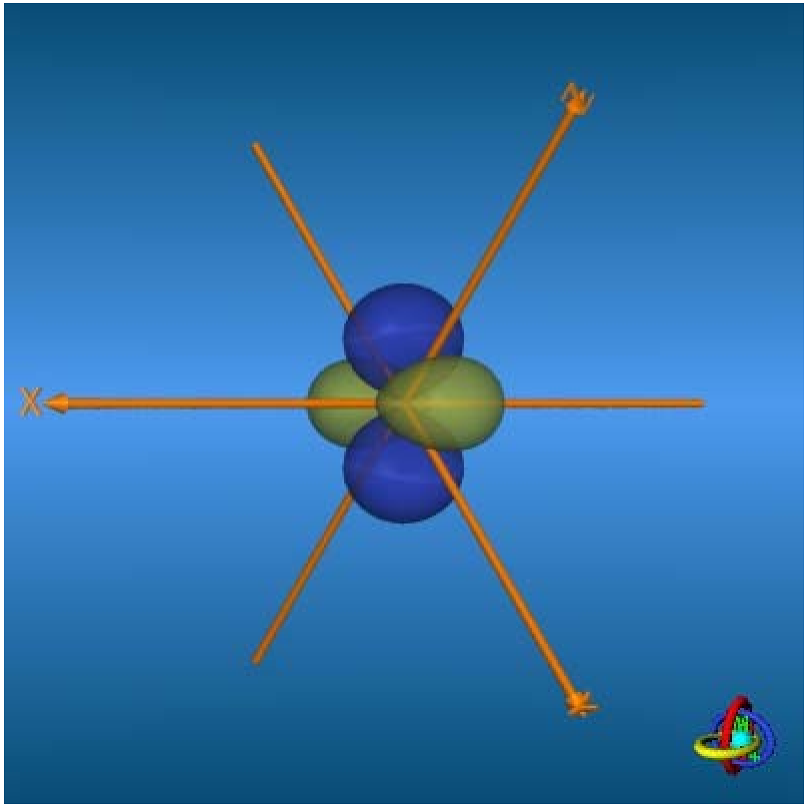
$3d_{xy}$



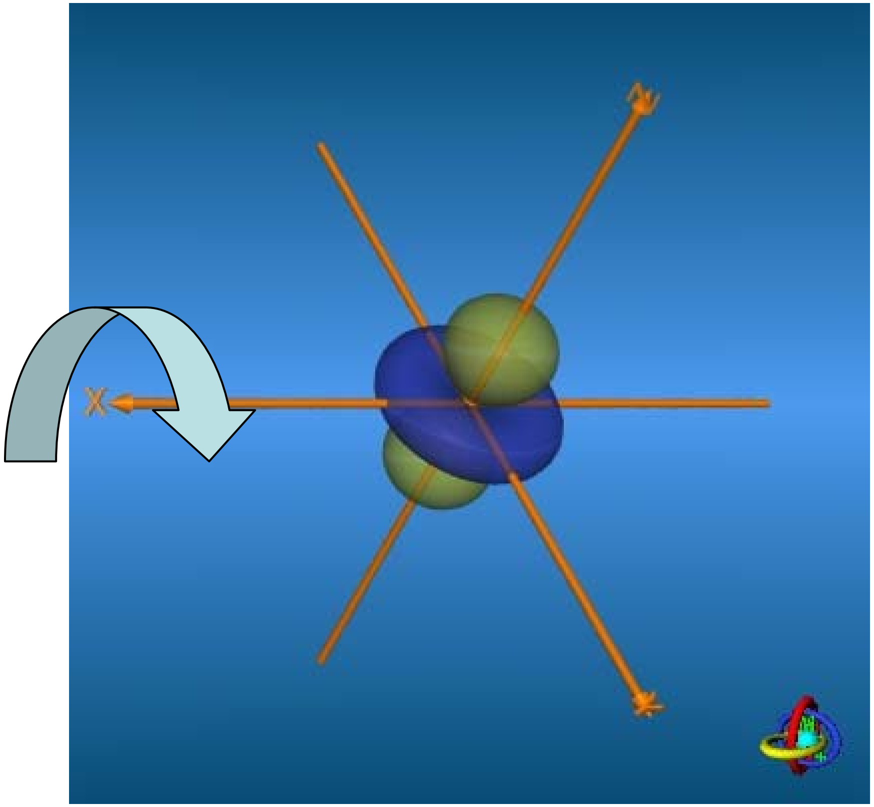
$3d_{x2-y2}$

$$\langle d_{xy}|\mathcal{L}_{\mathbf{z}}|d_{x2\text{-}y2}\rangle \neq 0$$

imagine a rotation R_z operation on $3d_{x2\text{-}y2}$ **function**



$3d_{yz}$

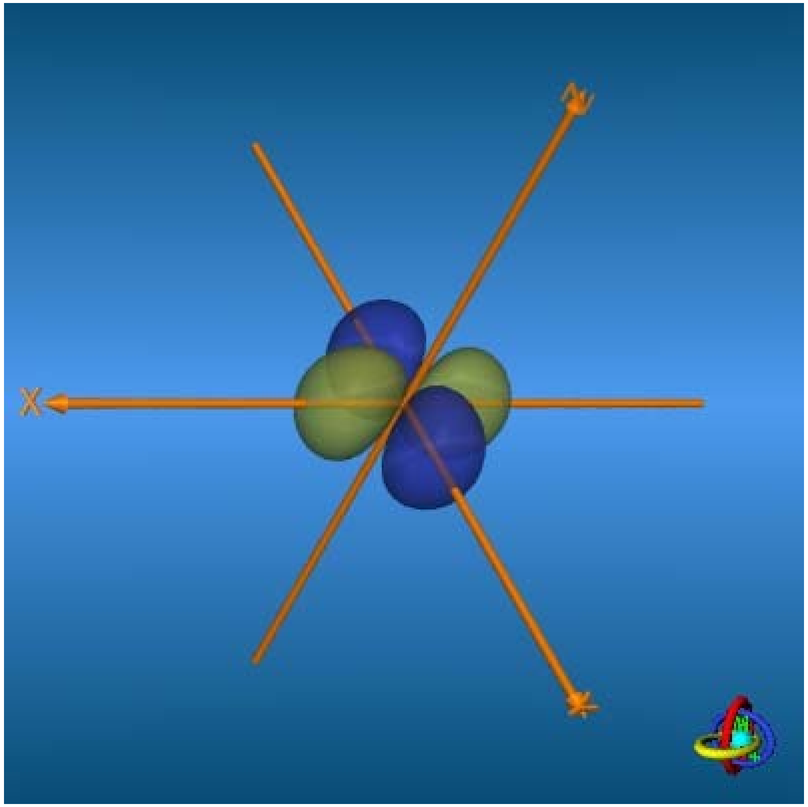


$3d_{z2}$

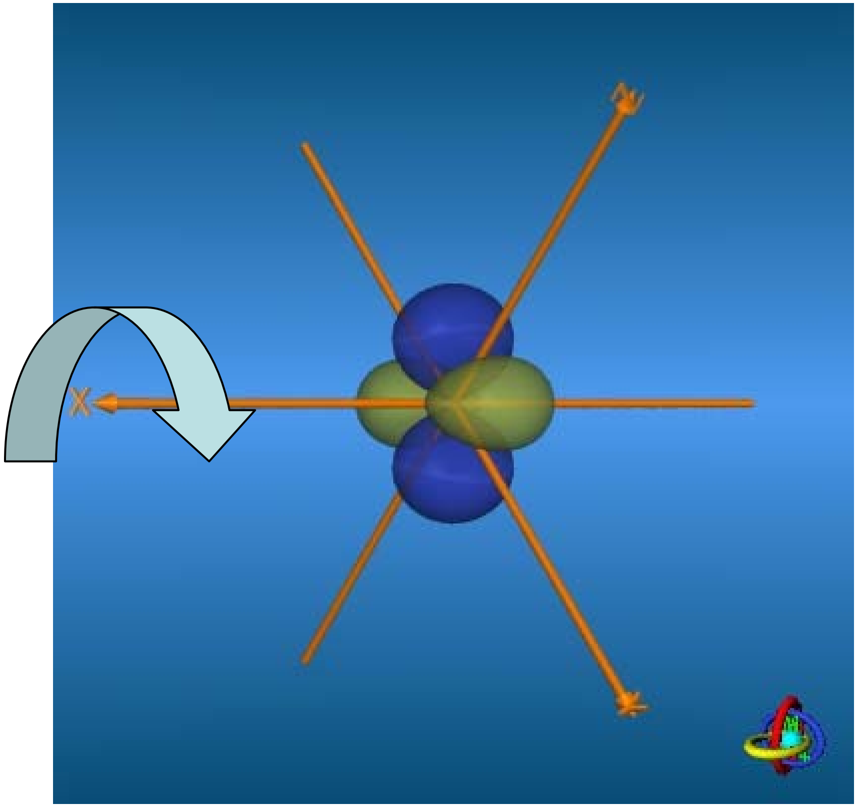
$$\langle d_{yz}|\mathcal{L}_{\mathbf{x}}|d_{z2}\rangle \neq \mathbf{0}$$

imagine a rotation R_x operation on $3d_{z2}$ function

$$\mathcal{L}_{\mathbf{x}}|d_{yz}\rangle = -\sqrt{3}|d_{z2}\rangle - |d_{x2-y2}\rangle$$



$3d_{x2\text{-}y2}$



$3d_{yz}$

$$\langle d_{x2\text{-}y2}|\mathcal{L}_{\mathbf{x}}|d_{yz}\rangle \neq 0$$

imagine a rotation *R_x* operation on $3d_{yz}$ **function**

$$\mathcal{L}_{\mathbf{x}}|d_{yz}\rangle = -\sqrt{3}|d_{z2}\rangle - |d_{x2\text{-}y2}\rangle$$

Consider the H_2CO molecule

The molecule has C_{2V} symmetry.

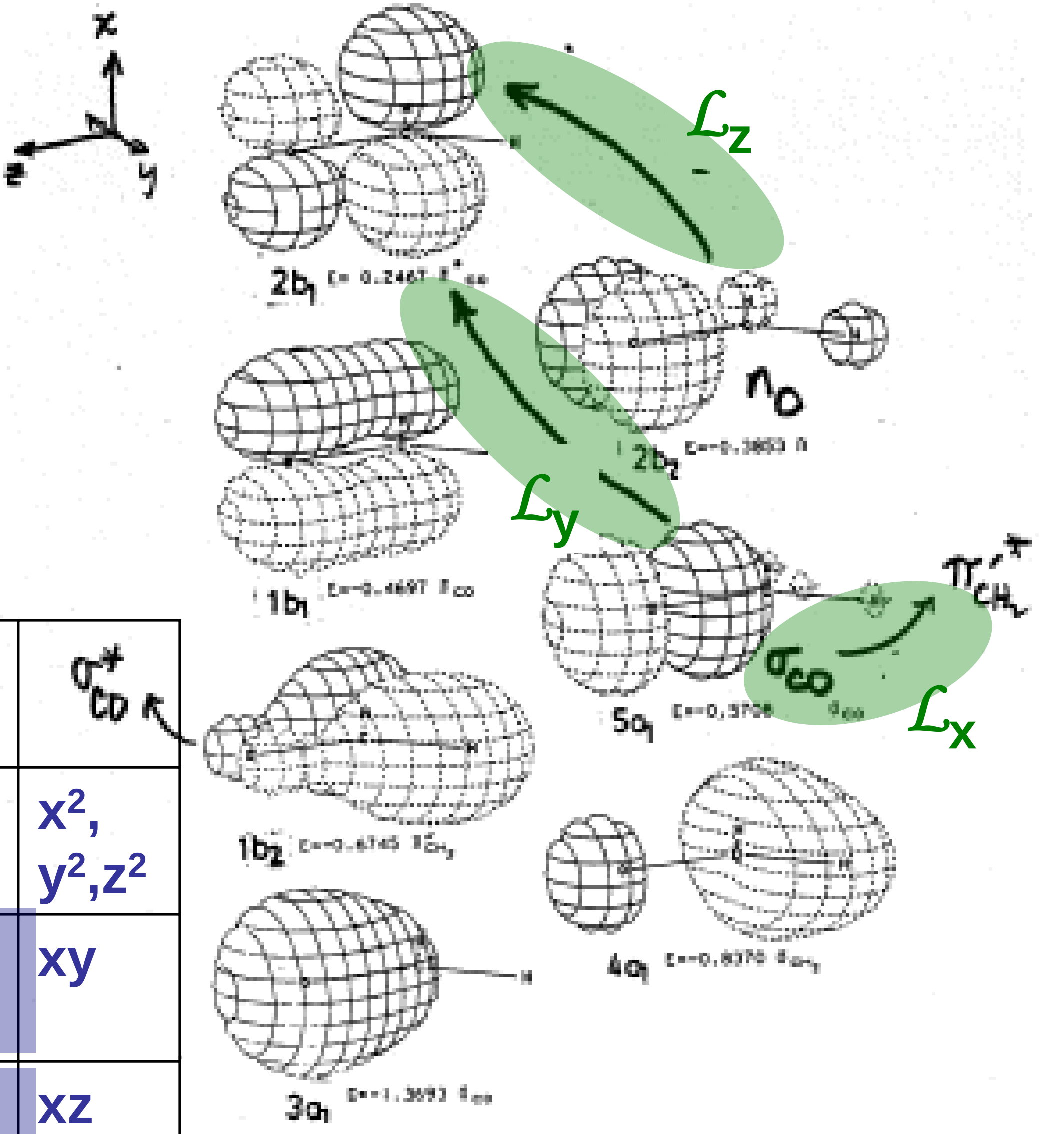
The molecular states Ψ,
and the individual molecular orbitals
of the H_2CO molecule belong to the
irreducible representations (symmetry species)
of C_{2v} point group.

The nuclear site symmetry at the ^{17}O nucleus
is C_{2v} and at the ^{13}C nucleus is also C_{2V}

$\mathcal{L}_z$ belongs to symmetry species A_2

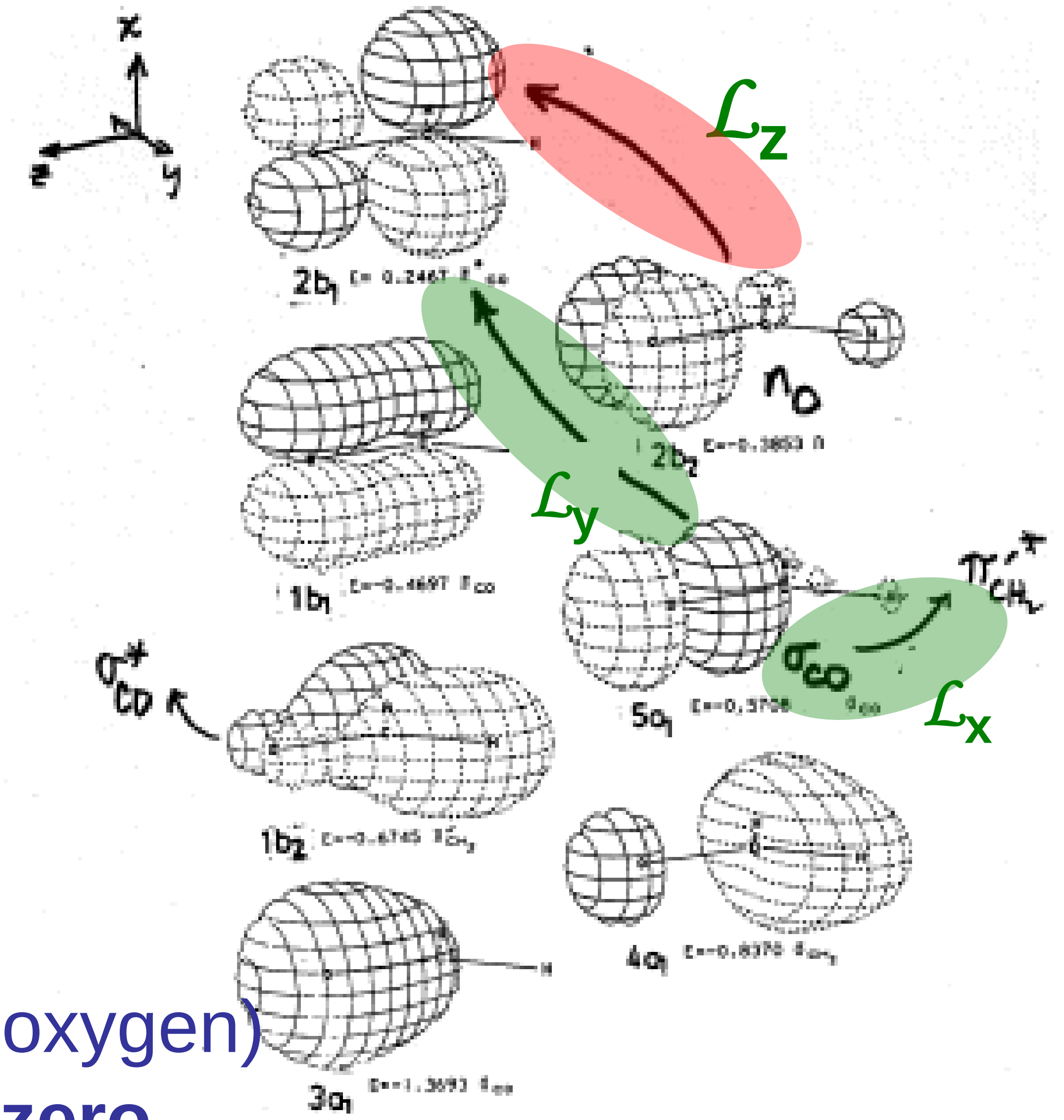
$\mathcal{L}_y$ to B_1

$\mathcal{L}_x$ to B_2



C_{2v}	E	C_2 (z)	σ_v (xz)	σ_v (yz)		
A_1	1	1	1	1	z	x^2, y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Let us look at $\mathcal{L}_z$



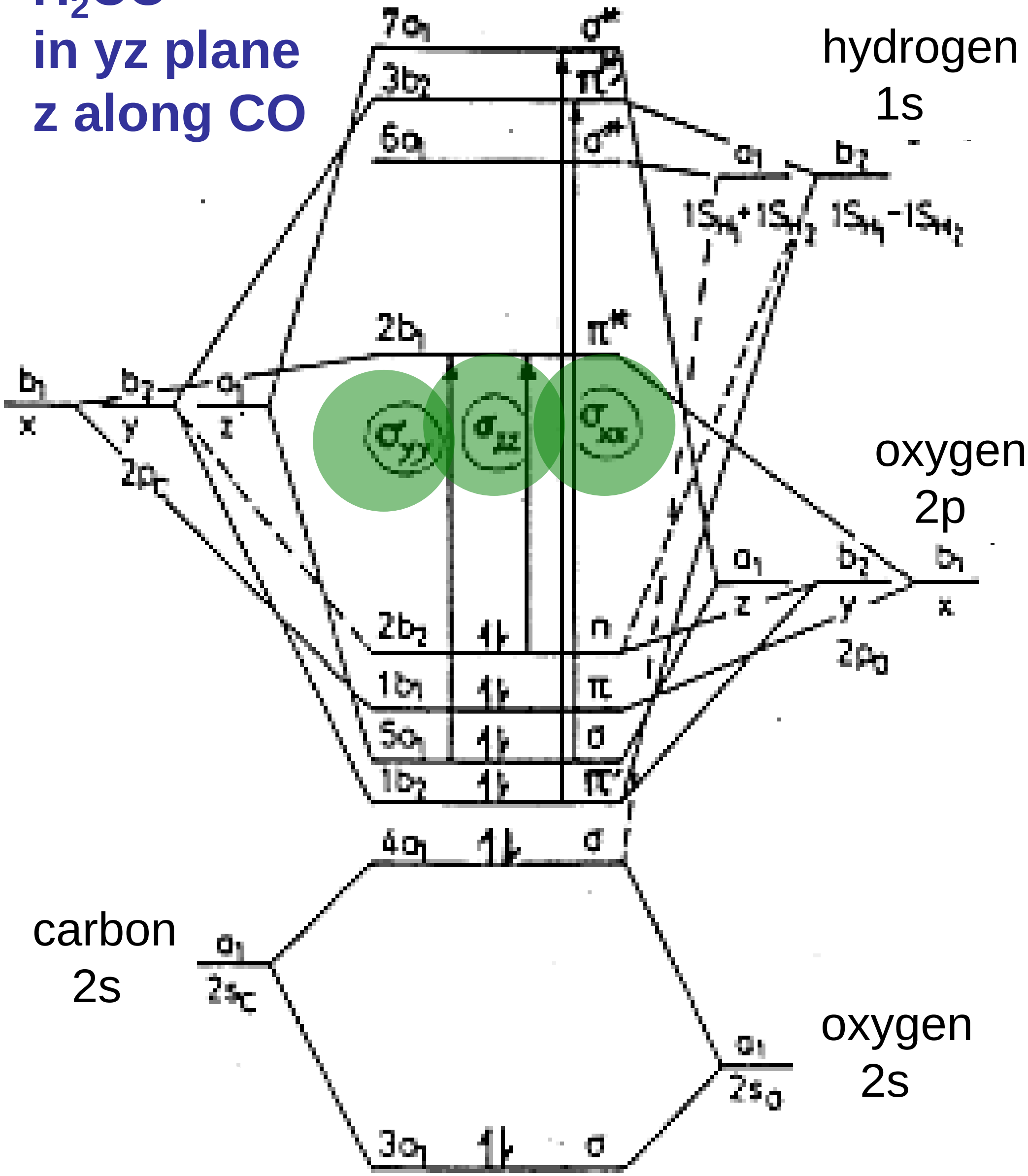
$\langle \mathrm{OMO}|\mathcal{L}_z|\mathrm{UMO}\rangle$

$\mathcal{L}_z$ belongs to symmetry species A_2

For $\langle \mathrm{OMO}|$ **belonging to symmetry species B_2**
(mostly lone pair on the oxygen)
$\langle \mathrm{OMO}|\mathcal{L}_z|\mathrm{UMO}\rangle$ **is non-zero**
if $|\mathrm{UMO}\rangle$ **belongs to B_1**
(the π^* molecular orbital)

magnetic dipole allowed transitions contribute to	orbital transitions OMO →UMO	molecular transitions Ψground → Ψexcited
σ_{zz}	**$2b_2 \rightarrow 2b_1$** **n π^*_{CO}**	$^1A_1 \rightarrow {}^1A_2$
σ_{yy}	**$5a_1 \rightarrow 2b_1$** **σ_{CO} π^*_{CO}**	$^1A_1 \rightarrow {}^1B_1$
σ_{xx}	**$1b_2 \rightarrow 7a_1$** **π' σ^***	$^1A_1 \rightarrow {}^1B_2$
σ_{xx}	**5a1→3b2** **σ_{CO} π'^***	$^1A_1 \rightarrow {}^1B_2$

H_2CO
in yz plane
z along CO



Consider the $(E_q-E_0)^{-1}$ factor:

unoccupied
occupied

Since (E_q-E_0) is related to $(\varepsilon_{UMO} - \varepsilon_{OMO})$,

where the UMO and OMO symmetries are appropriate, the largest contributions come from mixing in which the UMO-OMO gap is small,

i.e., the same kind of state mixing that give rise to magnetic-dipole transitions in electronic spectroscopy.
($n \rightarrow \pi^*$, $d \rightarrow d$, ..)

as in the H_2CO example

Co^{3+} d^6 ion

All d atomic orbitals have the same energy (degenerate).

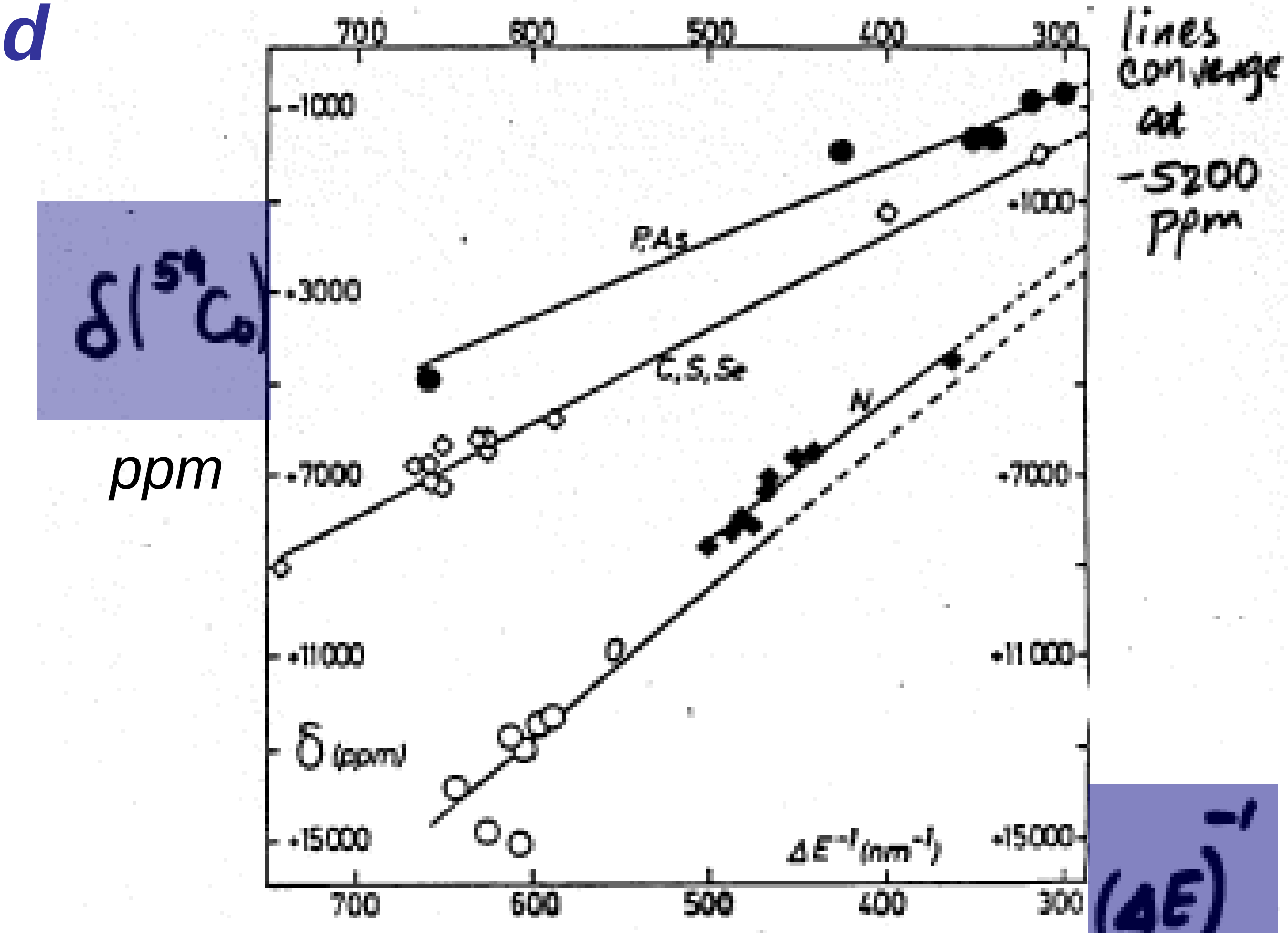
Perturbation by the approach of 6 ligands to form an octahedral CoL_6 complex, in the first approximation (crystal field approximation), leads to a splitting into two symmetry species t_{2g} and e_g ,
the higher energy corresponding to e_g (d_{z2} , d_{x2-y2})
and the lower energy to t_{2g} (d_{xz} , d_{yz} , d_{xy}) .

✪**The energy splitting is in the visible region of the electromagnetic spectrum. Optical transitions for CoL_6 in this region are largely $d \rightarrow d$.** ***(the accurate description is more complex than this)***

✪non-vanishing matrix elements in paramagnetic term:

$\langle dxy|\mathcal{L}_z|dx^2\text{-}y^2\rangle$ $\langle dyz|\mathcal{L}_x|dz^2\rangle$ $\langle dxz|\mathcal{L}_y|dz^2\rangle$

d→d



ppm

lines converge at -5200 ppm

FIGURE 9. δ(^{59}Co) (relative to [Co(CN)$_6$]$^{3-}$) vs. ΔE^{-1} for CoL$_6$ complexes (L = [illegible] C, S, Se; P, As). Data were taken from Ref. 131; see also Table 24 I, and II. The common intersection for the correlation lines at ΔE → ∞ is at −5200 ppm.

nm^{-1}

CoL$_6$ complexes

HISTORICAL DIGRESSION

The Journal of Chemical Physics
Vol. 40, No. 6, 1714-1724, 15 March 1964
Calculation of Chemical Shifts.
I. General Formulation and the Z Dependence
Cynthia Juan Jameson and H. S. Gutowsky
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61803
(Received 21 October 1963)

The Journal of Chemical Physics
Vol. 40, No. 6, 2285-2293, 15 April 1964
Calculation of Chemical Shifts.
II. The Xenon Fluorides

Table VI. Range of chemical shifts (ppm) as of 1963

n	ns	ns^2	np	np^2	np^3	np^4	np^5	np^6
1	H							
	20							
2	Li		B	C	N	O	F	
	5		140	316	626	690	625	
3			Al	Si	P		Cl	
			220	140	670		820	
4								
5	Rb			Sn		Se		Xe
	149			1852		1500		5785
6	Cs	Hg	Tl	Pb				
	252	2460	4800	7300				

$$\sigma^{(2)}_{\text{paramagnetic}, xx} = -(e^2/2m^2c^2)\sum_q (E_q - E_0)^{-1} \langle \Psi_0 | \sum_i \mathcal{L}_{xNi} | \Psi_q \rangle \langle \Psi_q | \sum_i (\mathcal{L}_{xNi} / r_{Ni}{}^3) | \Psi_0 \rangle$$

$\sigma^{(2)}_{\text{paramagnetic}, xx}$ depends on

$$\langle r_{Ni}{}^{-3} \rangle$$

and $(E_q - E_0)^{-1}$

and $\langle 0 | \mathcal{L}_x | q \rangle \langle q | \mathcal{L}_x | 0 \rangle$

The dependence on $\langle r_{Ni}{}^{-3} \rangle$ is most pronounced when comparing the sensitivity of the shielding of different nuclei.

What about $\langle r_{Ni}^{-3} \rangle$?

Largest for i<u>th</u> electron in the p, d, f, .. atomic orbitals <u>centered at</u> nucleus N

How to find a measure of $\langle r_{Ni}^{-3} \rangle$ for atoms?

spin-orbit coupling!!

from JCP 1964

"An experimental quantity which gives a quite direct measure of $\langle 1/r^3 \rangle$ is the spin orbit interaction, which is available from tables of atomic energy levels."

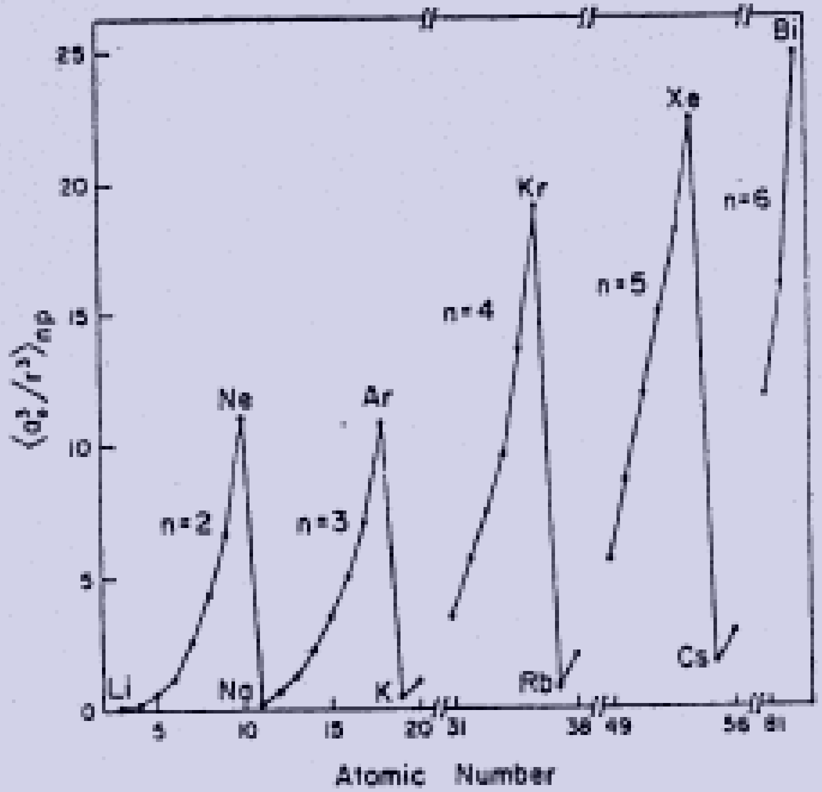
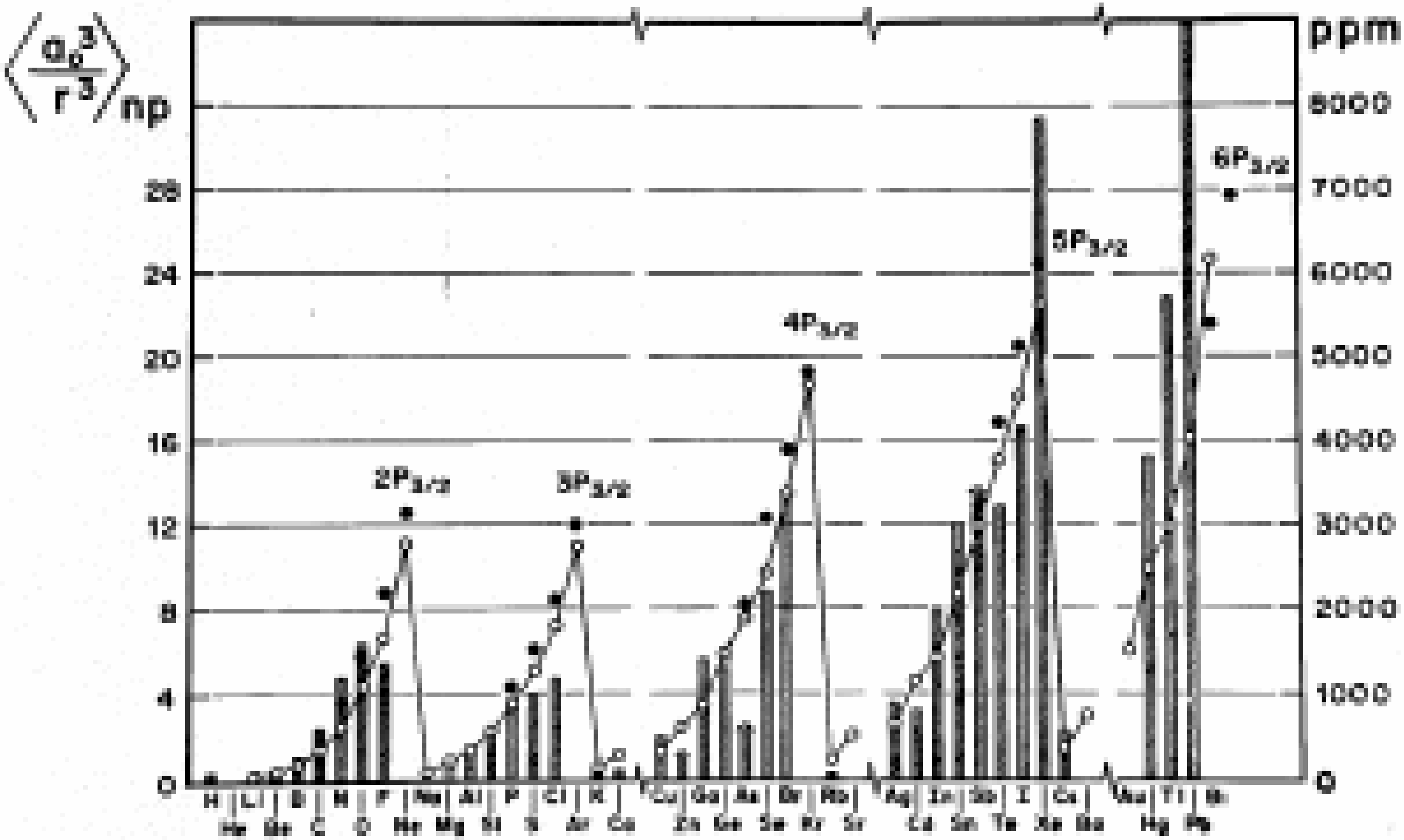


FIG. 1. The variation of $\langle a_0^3/r^3 \rangle_{np}$ with atomic number, as calculated, mainly in Ref. 15, from the observed atomic spin-orbit splittings without relativistic correction.

as $\langle a_0^3/r^3 \rangle$ varies with atomic number, $\mathcal{Z}$, expect range of δ varies with $\mathcal{Z}$

in same way

Ref. 15
R. G. Barnes and W. V. Smith
Phys. Rev. 93, 95 (1954)



from C. J. Jameson and J. Mason,
in *Multinuclear NMR*, Plenum, 1987

24 years later

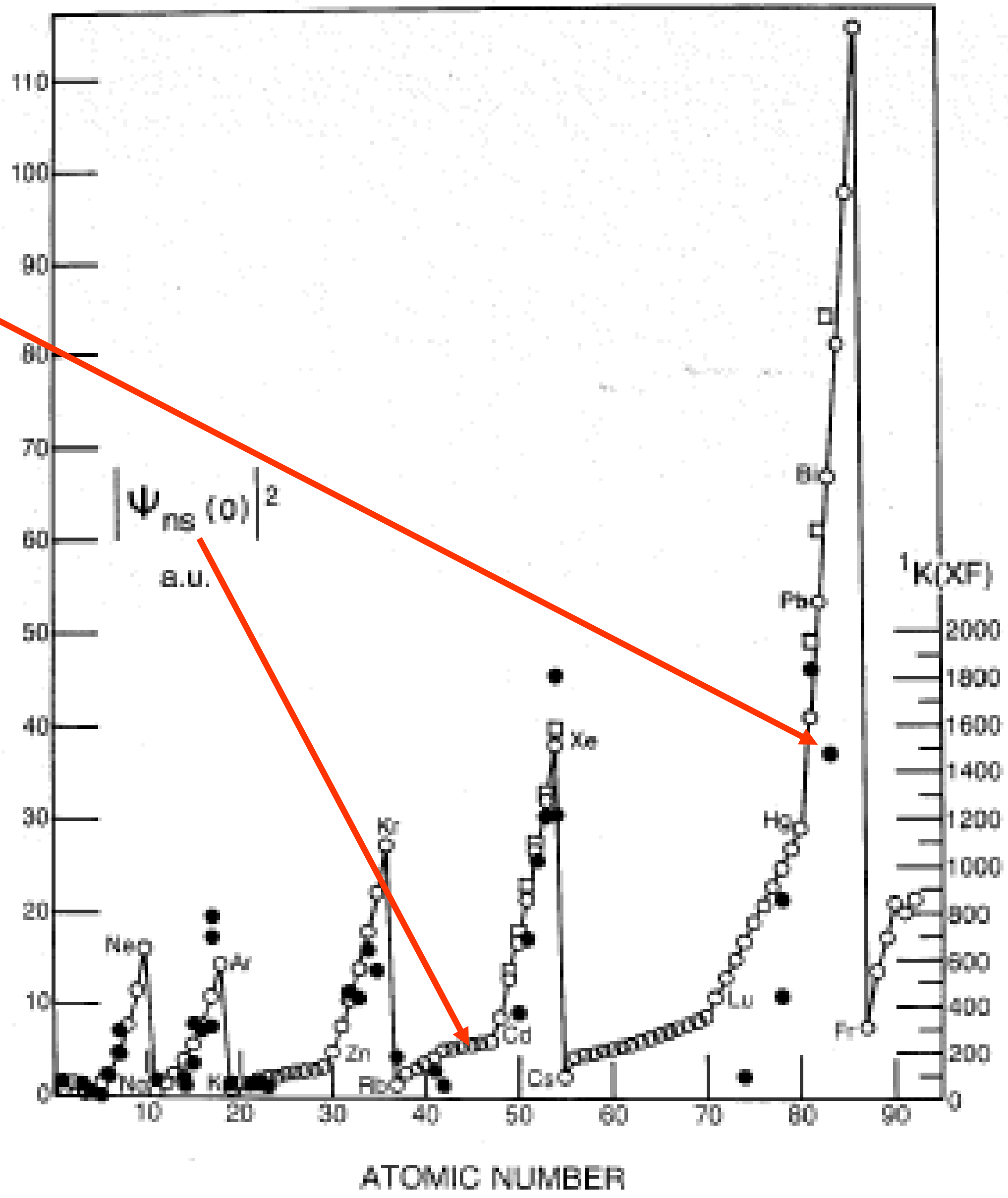
**“Another related general phenomenon, for which there are more complex but similar periodicities to those for the chemical shifts,
is the electron coupling of nuclear spins.”**

$$J_{MH}/\gamma_M\gamma_H \approx (C/\Delta)\,|\psi_{sM}(0)|^2\,|\psi_{sH}(0)|^2$$

**“Therefore, one would expect $J_{MH}/\gamma_M\gamma_H$ to reflect
the periodicity in $|\psi_{sM}(0)|^2$ for the atoms.
However, the experimental data available for J_{AB}
do not not permit as detailed a survey of periodicities
in its magnitude as was possible for the chemical shifts.”**

from Jameson and Gutowsky JCP **1964**

$X^{19}F$
spin-spin coupling
is likewise periodic



from C. J. Jameson,
in *Multinuclear NMR*, Plenum, 1987

END OF DIGRESSION

Back to H_2CO example

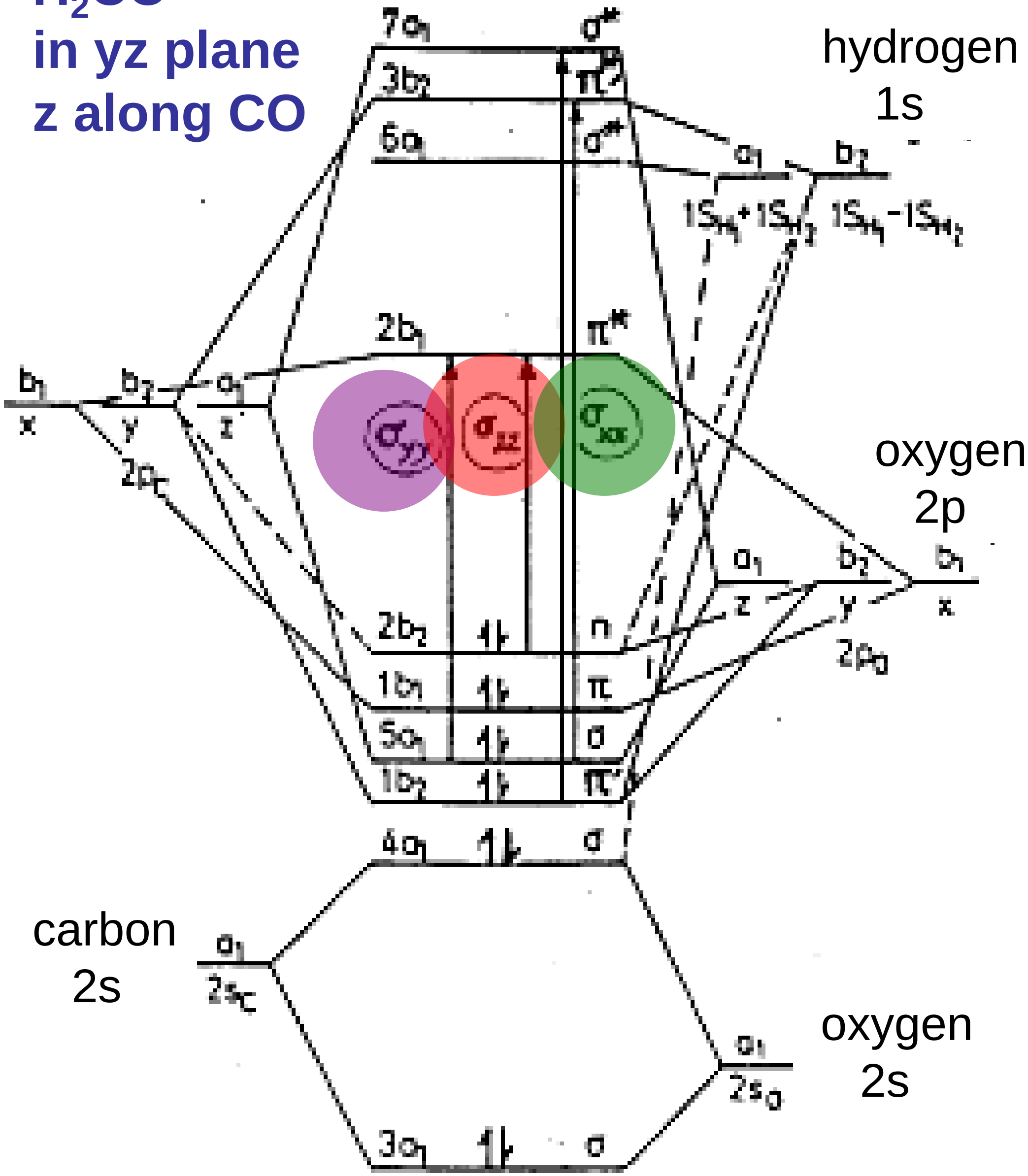
Let us consider first ^{17}O and then ^{13}C after.

The nuclear site symmetry is the same for both, so all previous discussion applies to both.

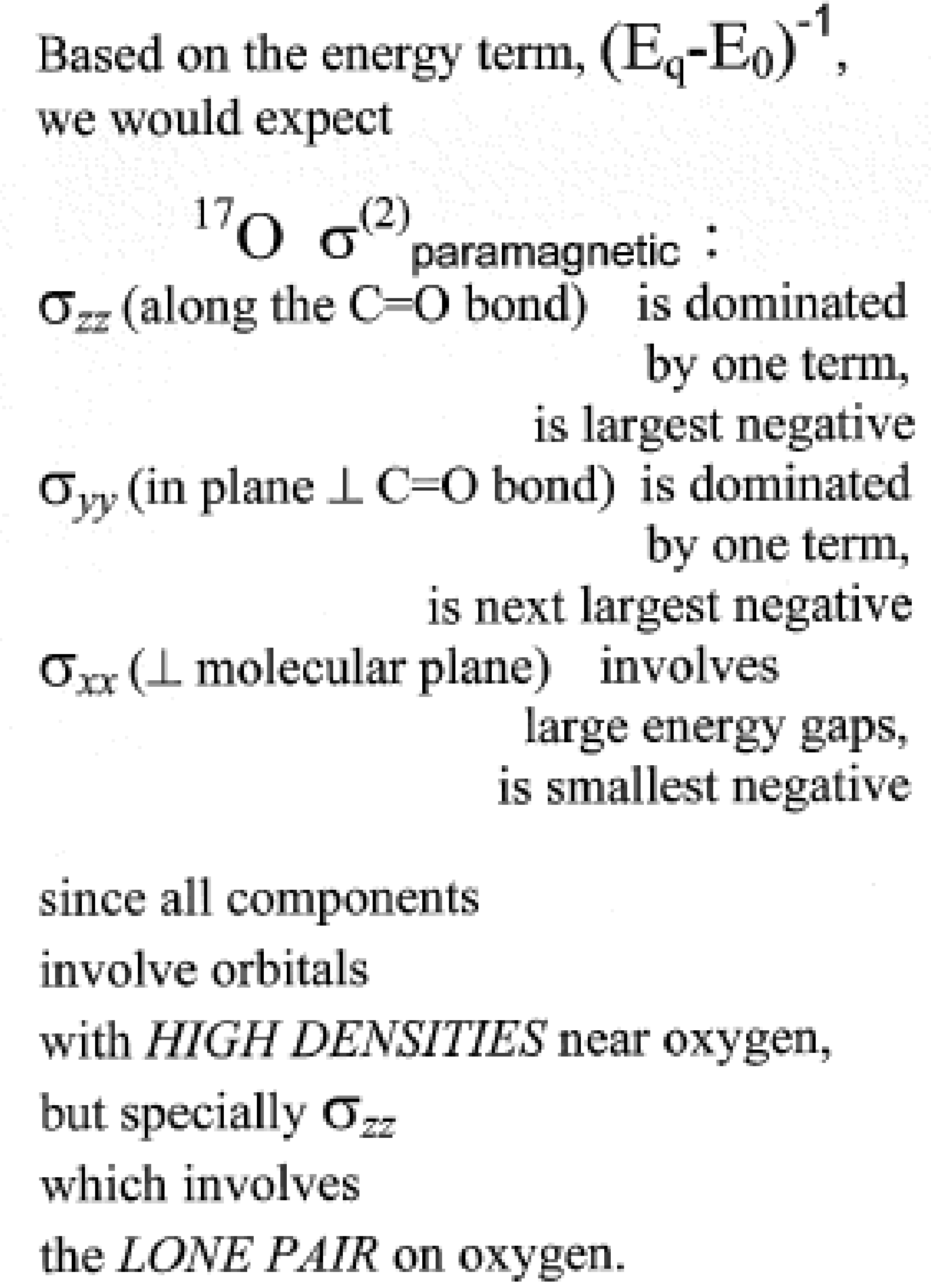
However, the same MOs have different densities in the vicinity of the two nuclei

magnetic dipole allowed transitions contribute to	orbital transitions OMO →UMO	molecular transitions Ψground → Ψexcited
σ_{zz}	**$2b_2 \rightarrow 2b_1$** **n** π^*_{CO}	$^1A_1 \rightarrow {}^1A_2$
σ_{yy}	**$5a_1 \rightarrow 2b_1$** σ_{CO} π^*_{CO}	$^1A_1 \rightarrow {}^1B_1$
σ_{xx}	**$1b_2 \rightarrow 7a_1$** π' σ^*	$^1A_1 \rightarrow {}^1B_2$
σ_{xx}	**5a1→3b2** σ_{CO} π'^*	$^1A_1 \rightarrow {}^1B_2$

H_2CO
in yz plane
z along CO



^{17}O



Based on the energy term, $(E_q-E_0)^{-1}$, we would expect

$$^{17}O\ \ \sigma^{(2)}{}_{\text{paramagnetic}}\ :$$

σ_{zz} (along the C=O bond) is dominated by one term, is largest negative

σ_{yy} (in plane ⊥ C=O bond) is dominated by one term, is next largest negative

σ_{xx} (⊥ molecular plane) involves large energy gaps, is smallest negative

since all components involve orbitals with *HIGH DENSITIES* near oxygen, but specially σ_{zz} which involves the *LONE PAIR* on oxygen.

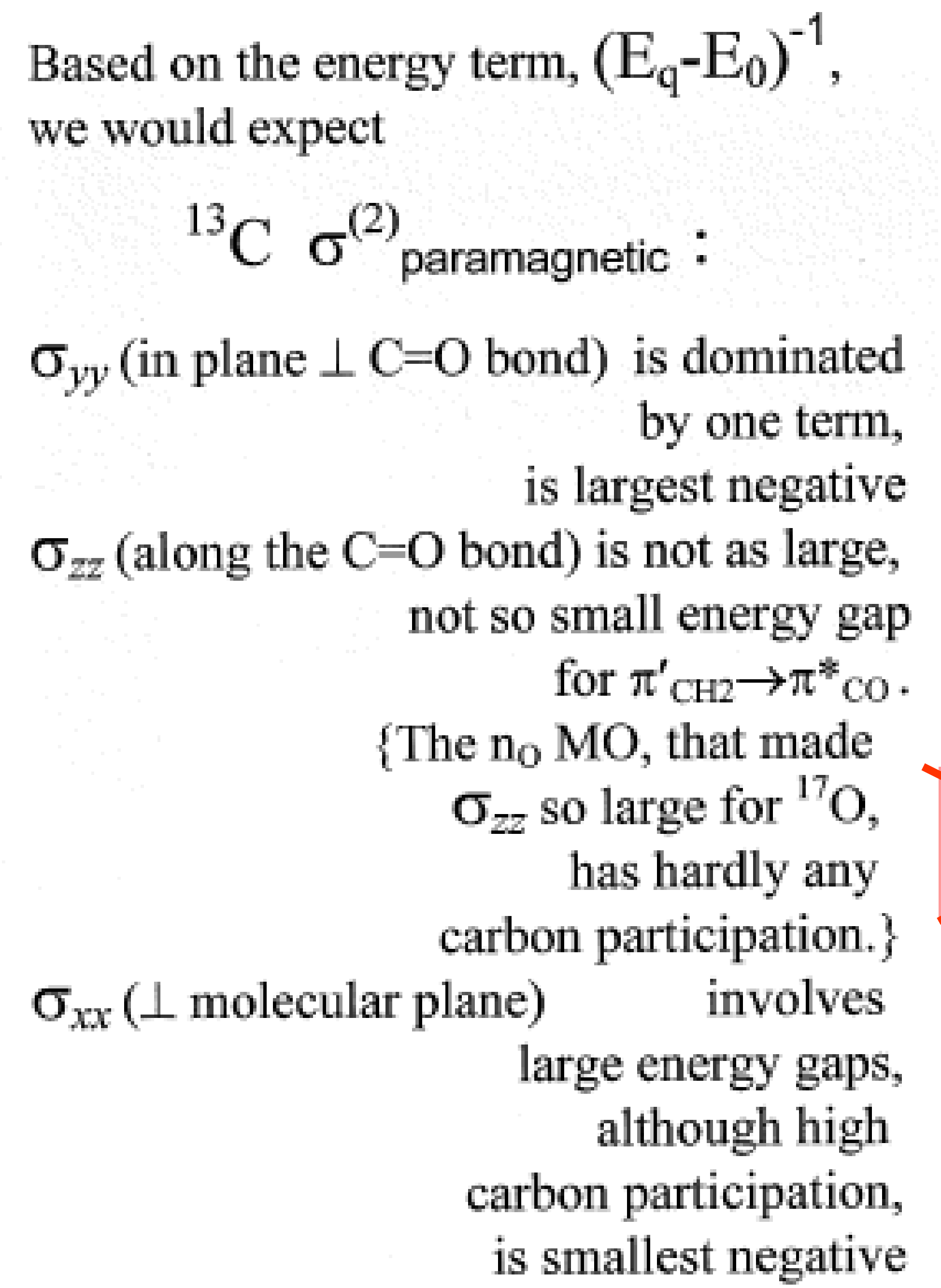
$n_O \rightarrow \pi_{CO}{}^*$

$\sigma_{CO} \rightarrow \pi_{CO}{}^*$

$\pi' \rightarrow \sigma^*$

$\sigma_{CO} \rightarrow \pi'^*$

^{13}C



Based on the energy term, $(E_q-E_0)^{-1}$, we would expect

^{13}C $\sigma^{(2)}{}_{\text{paramagnetic}}$:

σ_{yy} (in plane ⊥ C=O bond) is dominated by one term, is largest negative

σ_{zz} (along the C=O bond) is not as large, not so small energy gap for $\pi'_{CH2} \to \pi^*_{CO}$.
{The n_O MO, that made σ_{zz} so large for ^{17}O, has hardly any carbon participation.}

σ_{xx} (⊥ molecular plane) involves large energy gaps, although high carbon participation, is smallest negative

$\sigma_{CO} \to \pi_{CO}^*$

$\pi'_{CH2} \to \pi_{CO}^*$

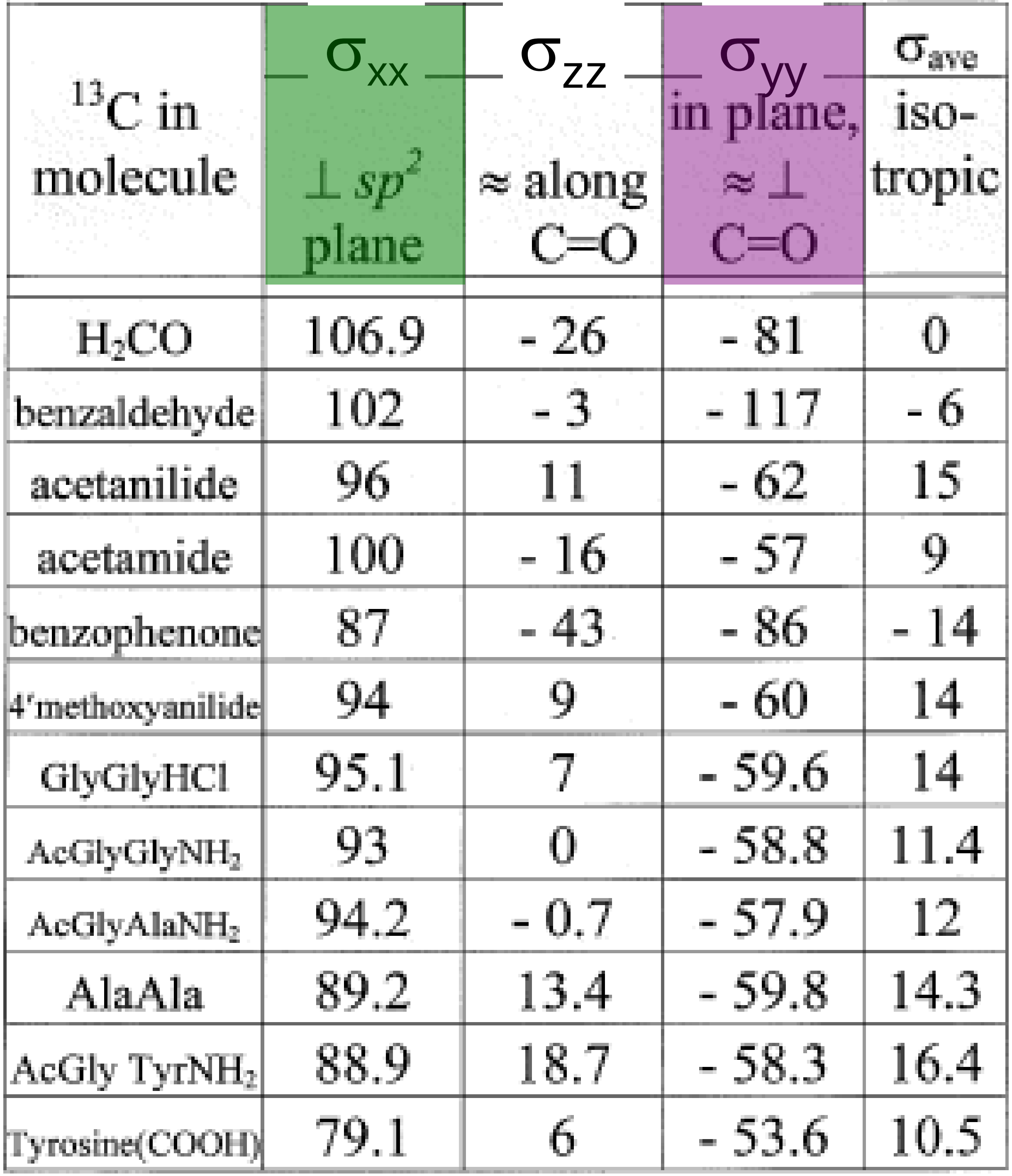
$1b_2$ $2b_1$

~~$n_O \to \pi_{CO}^*$~~

$\pi' \to \sigma^*$

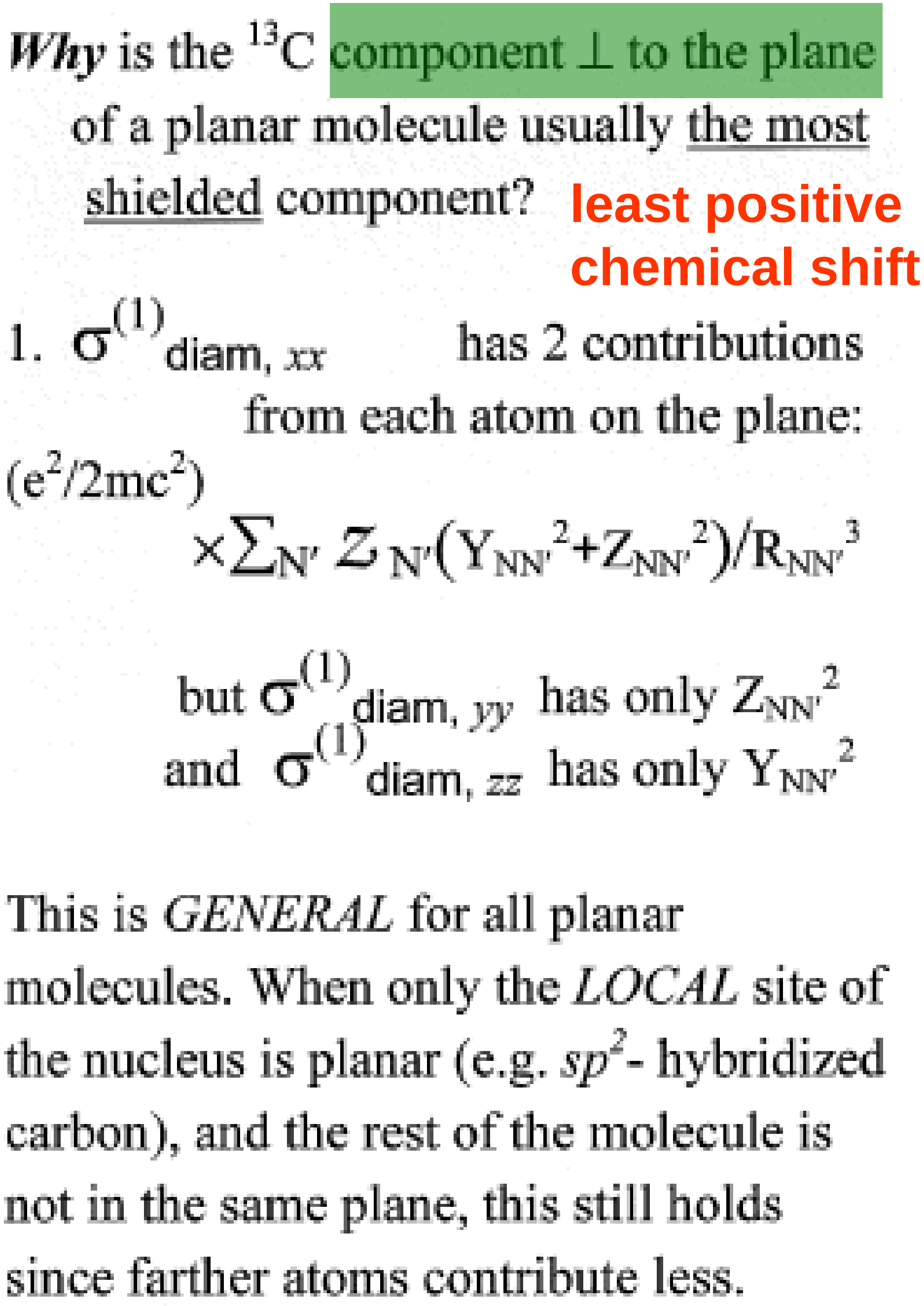
$\sigma_{CO} \to \pi'^*$

^{13}C shielding in >C=O



^{13}C in molecule	σ_{xx} ⊥ sp^2 plane	σ_{zz} ≈ along C=O	σ_{yy} in plane, ≈ ⊥ C=O	σ_{ave} iso-tropic
H_2CO	106.9	- 26	- 81	0
benzaldehyde	102	- 3	- 117	- 6
acetanilide	96	11	- 62	15
acetamide	100	- 16	- 57	9
benzophenone	87	- 43	- 86	- 14
4'methoxyanilide	94	9	- 60	14
GlyGlyHCl	95.1	7	- 59.6	14
$AcGlyGlyNH_2$	93	0	- 58.8	11.4
$AcGlyAlaNH_2$	94.2	- 0.7	- 57.9	12
AlaAla	89.2	13.4	- 59.8	14.3
$AcGly\ TyrNH_2$	88.9	18.7	- 58.3	16.4
Tyrosine(COOH)	79.1	6	- 53.6	10.5

perpendicular to the sp^2 plane



Why is the ^{13}C component ⊥ to the plane of a planar molecule usually the most shielded component?

least positive chemical shift

first reason

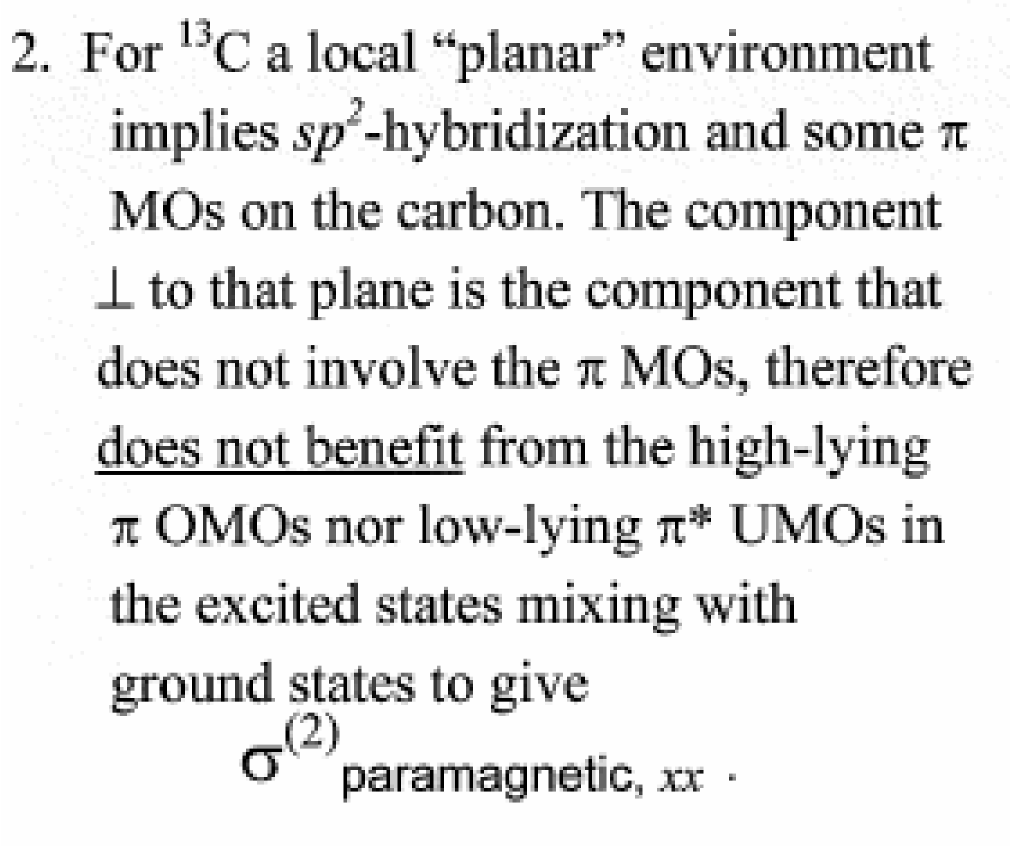
1. $\sigma^{(1)}{}_{\text{diam},\,xx}$ has 2 contributions from each atom on the plane:

$$(e^2/2mc^2) \times \sum_{N'} Z_{N'}(Y_{NN'}{}^2 + Z_{NN'}{}^2)/R_{NN'}{}^3$$

but $\sigma^{(1)}{}_{\text{diam},\,yy}$ has only $Z_{NN'}{}^2$
and $\sigma^{(1)}{}_{\text{diam},\,zz}$ has only $Y_{NN'}{}^2$

This is *GENERAL* for all planar molecules. When only the *LOCAL* site of the nucleus is planar (e.g. *sp*^{2}- hybridized carbon), and the rest of the molecule is not in the same plane, this still holds since farther atoms contribute less.

second reason



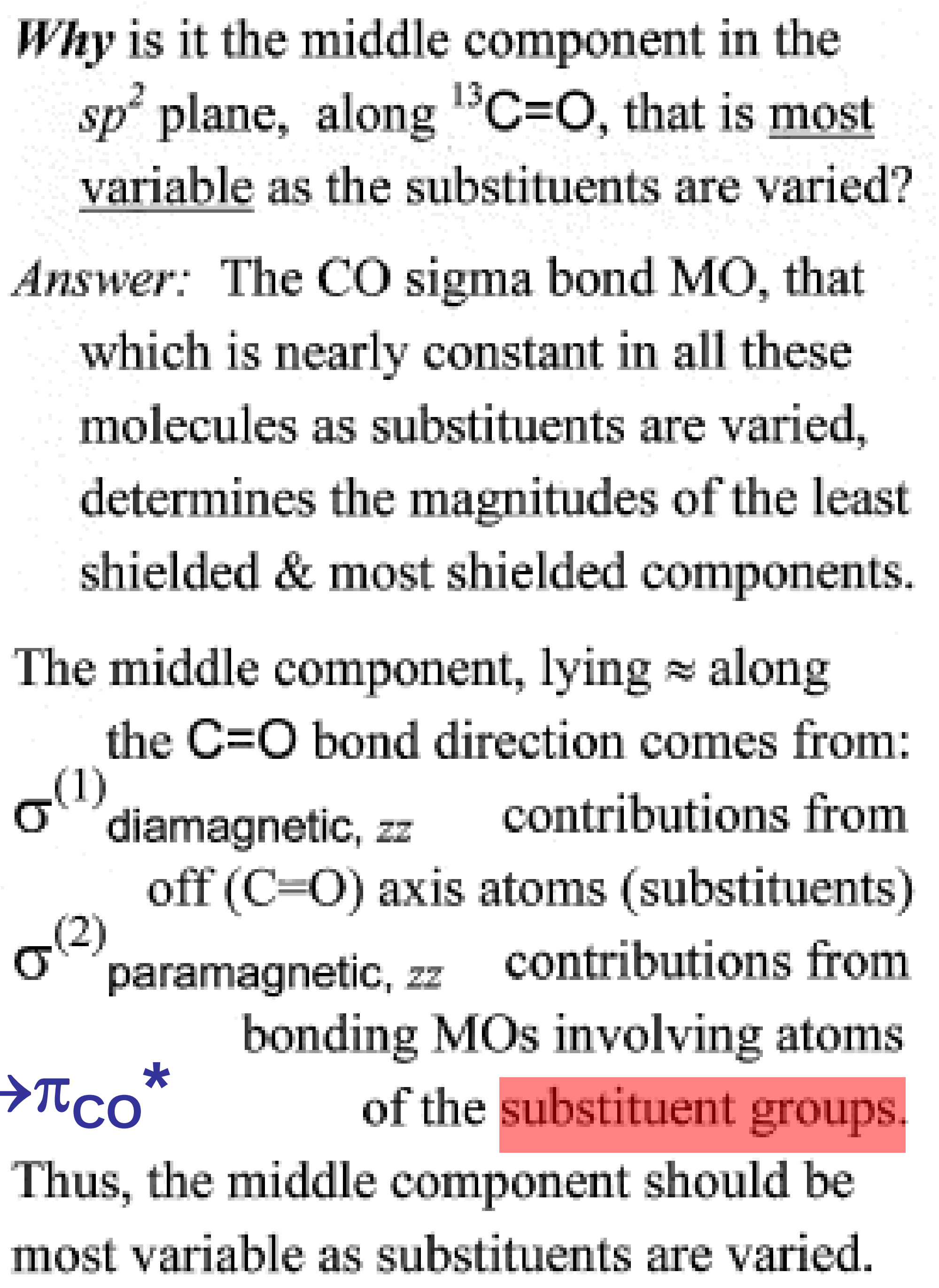
2. For ^{13}C a local “planar” environment implies sp^2-hybridization and some π MOs on the carbon. The component ⊥ to that plane is the component that does not involve the π MOs, therefore does not benefit from the high-lying π OMOs nor low-lying π* UMOs in the excited states mixing with ground states to give $\sigma^{(2)}_{\text{paramagnetic}, xx}$.

Why is that component in the sp^2 plane, ⊥ to $^{13}C{=}O$, usually the least shielded ^{13}C component?

most positive chemical shift

Answer: It is this component that involves the $\sigma_{CO} \rightarrow \pi^*_{CO}$ which leads to a large $\sigma^{(2)}_{\mathrm{paramagnetic},\, yy}$ since the π^* is a low-lying UMO, and there is a large involvement of the carbon *p* (as opposed to *s*) orbitals.

along the $^{13}C{=}O$



Why is it the middle component in the *sp*^{2} plane, along $^{13}C{=}O$, that is <u>most variable</u> as the substituents are varied?

Answer: The CO sigma bond MO, that which is nearly constant in all these molecules as substituents are varied, determines the magnitudes of the least shielded & most shielded components.

The middle component, lying ≈ along the C=O bond direction comes from:

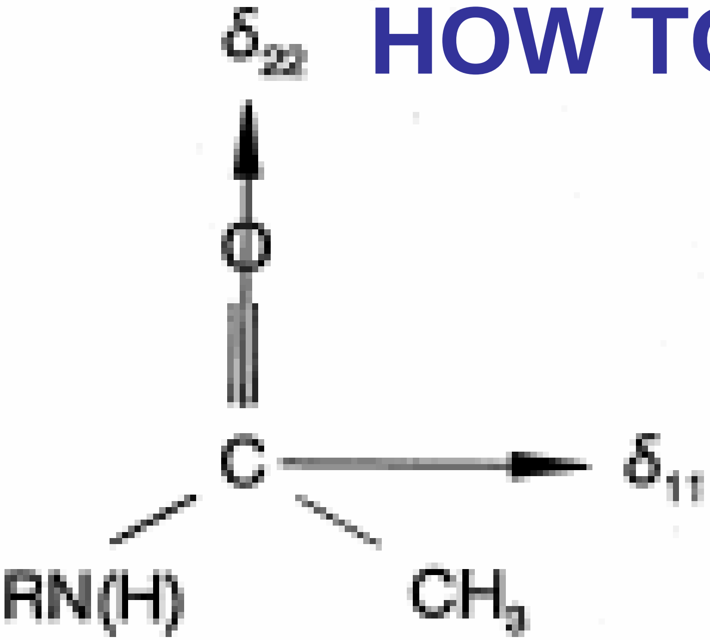
$\sigma^{(1)}_{\text{diamagnetic, } zz}$ contributions from off (C=O) axis atoms (substituents)

$\sigma^{(2)}_{\text{paramagnetic, } zz}$ contributions from bonding MOs involving atoms of the substituent groups.

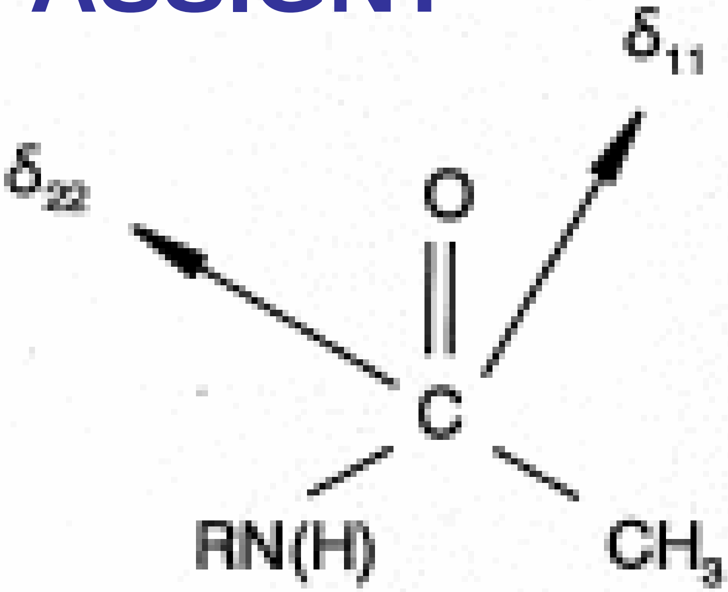
Thus, the middle component should be most variable as substituents are varied.

in H_2CO, $\pi'_{CH2} \rightarrow \pi_{CO}{}^*$

HOW TO ASSIGN?



a) THIS?



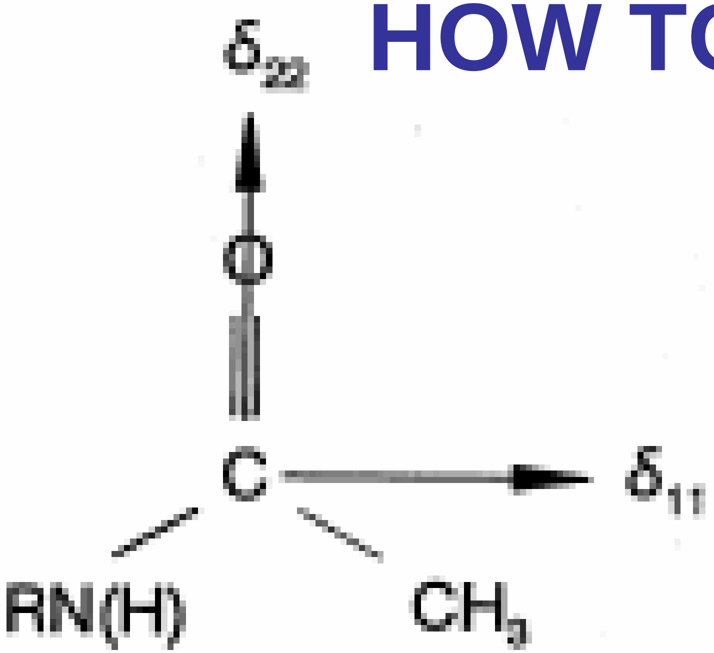
b) OR THIS?

most positive chemical shift is called δ_{11}

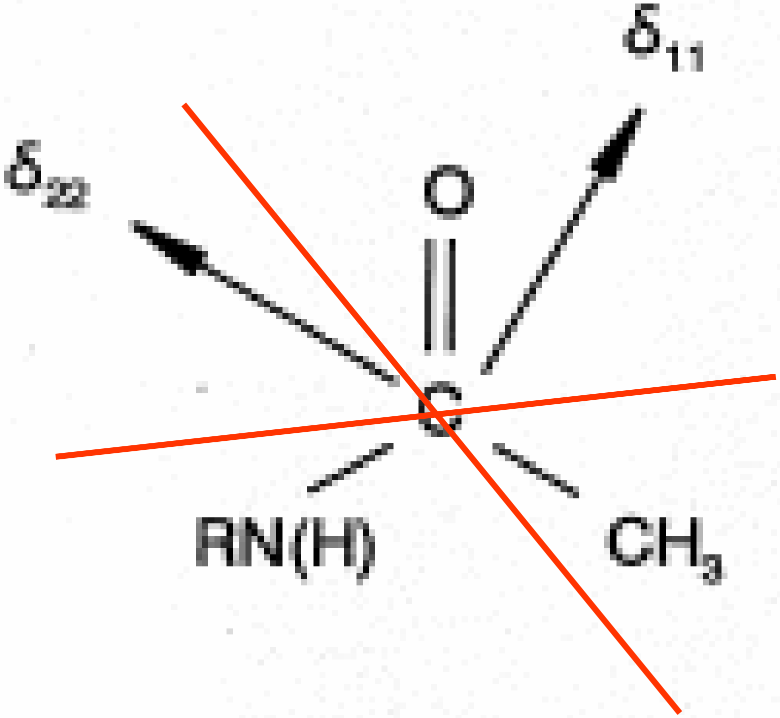
least positive chemical shift is called δ_{33}

3: Kirby, Lumsden, and Wasylishen

HOW TO ASSIGN



a) **THIS ONE**



b) **not this**

most positive chemical shift is called δ_{11}

is perpendicular to C=O

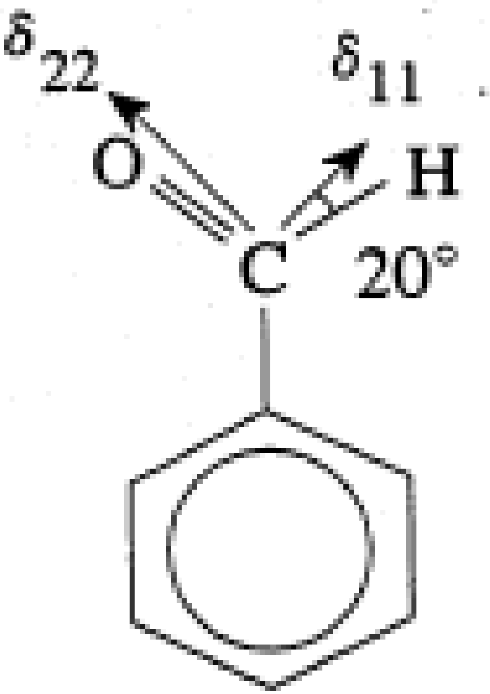
3: Kirby, Lumsden, and Wasylishen

least positive chemical shift is called δ_{33}

is perpendicular to the plane

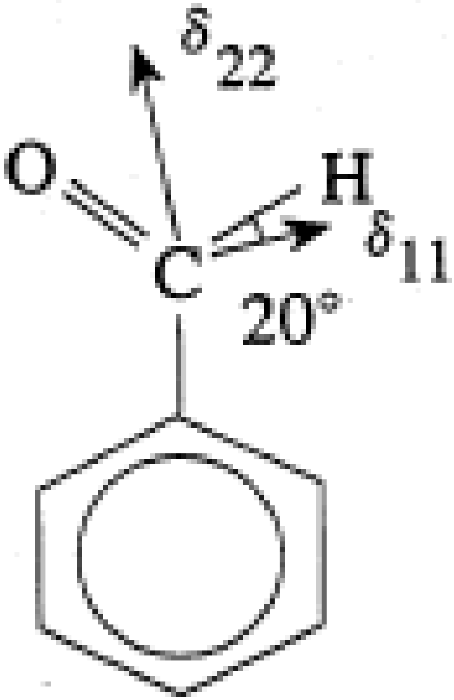
THIS ONE

(a)



NOT THIS

(b)



δ_{11} is perpendicular to C=O
δ_{33} is perpendicular to the plane

Wu et al. J. Chem. Phys. 99, 15306 (1995)

Same applies to $\rangle C=C \langle$ as for $\rangle C=O$

GENERAL for ^{13}C

in all molecules at such nuclear sites:

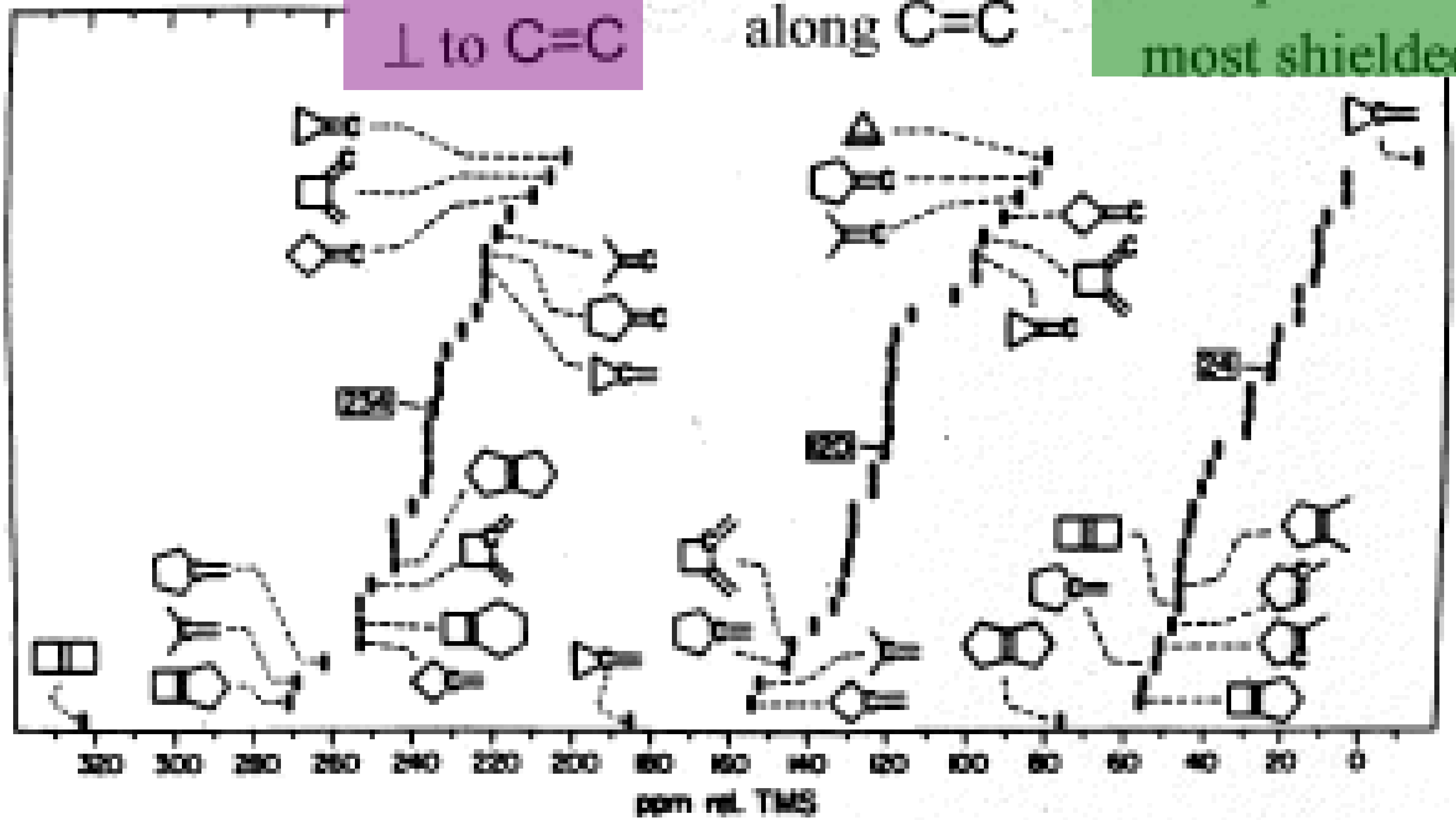
least positive chemical shift δ_{33}	middle δ_{22}	**most positive chemical shift δ_{11}**
⊥ to *sp*^{2} plane	along C=C	in-plane ⊥ to C=C
⊥ to *sp*^{2} plane	along C=O	in-plane ⊥ to C=O

EXPERIMENTAL values

δ_{11}
in plane,
⊥ to C=C

δ_{22}
along C=C

δ_{33}
⊥ to molecular
plane
most shielded



Chemical shift tensors of olefinic carbons
from D. M. Grant et al.

^{17}O shielding tensor in $\rangle$C=O,

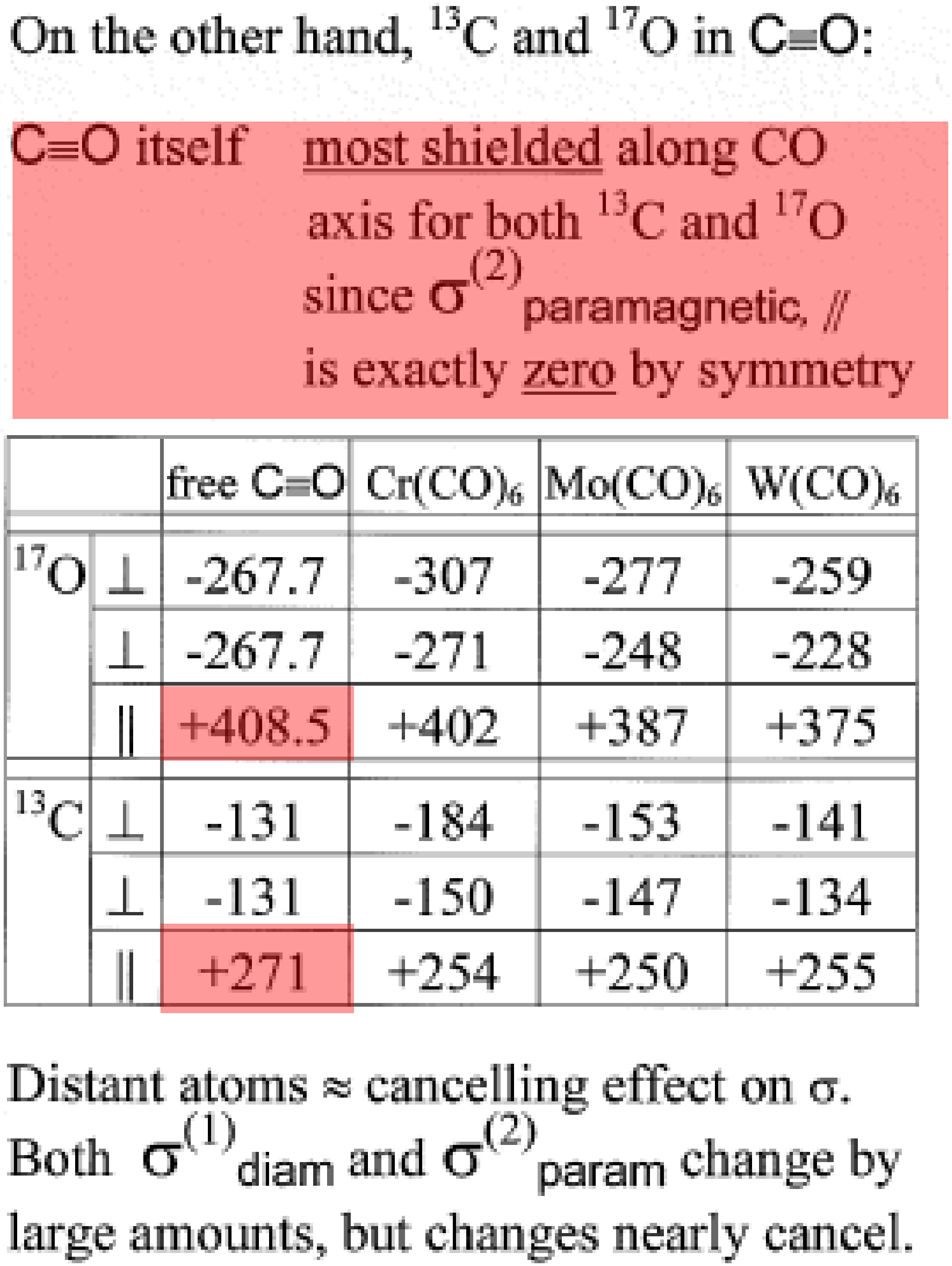
GENERAL for all molecules (provided C is *sp*^{2})

most shielded	middle	least shielded
σ_{33}	σ_{22}	σ_{11}
$\perp$ to *sp*^{2} plane	in-plane $\perp$ to C=O	along C=O

most positive chemical shift

This is different from ^{13}C case because of overwhelmingly large negative contribution to $\sigma^{(2)}{}_{\text{paramagnetic}, zz}$ due to the low-lying $n_O \rightarrow \pi^*_{CO}$, which also have very large contributions from orbitals at the O atom.

σ in C≡O



On the other hand, ^{13}C and ^{17}O in C≡O:

C≡O itself most shielded along CO axis for both ^{13}C and ^{17}O since $\sigma^{(2)}$ paramagnetic, // is exactly zero by symmetry

		free C≡O	Cr(CO)$_6$	Mo(CO)$_6$	W(CO)$_6$
^{17}O	⊥	-267.7	-307	-277	-259
	⊥	-267.7	-271	-248	-228
	∥	+408.5	+402	+387	+375
^{13}C	⊥	-131	-184	-153	-141
	⊥	-131	-150	-147	-134
	∥	+271	+254	+250	+255

Distant atoms ≈ cancelling effect on σ.
Both $\sigma^{(1)}_{\text{diam}}$ and $\sigma^{(2)}_{\text{param}}$ change by large amounts, but changes nearly cancel.

^{15}N

$n \rightarrow \pi^*$

- ***n*** high-lying OMO, a lone pair with favorable density near nucleus N
- ***π**** low-lying UMO involving p orbitals of the right symmetry relative to the lone pair

just knowing this leads to

The loss of the low-lying $n \rightarrow \pi^*$ is responsible for large changes in shielding upon protonation, hydrogen-bonding, association, formation of coordination complexes, all processes which compromise the lone pair.

gas to liquid shifts of ^{15}N in RNH_2 are deshielding, as is usual for nearly all nuclei, but is the opposite direction for ^{15}N in pyridine or CH_3CN.

coordination shifts of ^{15}N in $[N_3]^-$, $[NCS]^-$, pyridine

By these examples, we see that it is usually (not always) possible to understand observed chemical shifts by looking at the original Ramsey equations, although one no longer calculates chemical shifts using these equations directly.

THANK YOU FOR YOUR ATTENTION!

ANY QUESTIONS?