Isotopologues

Molecules of ISOTOPOLOGUES have <u>different</u> isotopic composition

^{1}H NMR of CH_3CH_2OH : consider ^{1}H, ^{2}H, ^{12}C, ^{13}C, ^{16}O, ^{17}O, ^{18}O

Some isotopologues:

$^{12}C^{1}H_3{}^{12}C^{1}H_2{}^{16}O^{1}H$ System: A_3B_2C

$^{13}C^{1}H_3{}^{12}C^{1}H_2{}^{16}O^{1}H$ System: XA_3B_2C

$^{12}C^{1}H_3{}^{12}C^{1}H^{2}H^{16}O^{1}H$ System: A_3BXC

288 isotopic varieties, 192 of which magnetically distinct

These give rise to 184 ^{1}H spectra, 184 ^{2}H spectra, 144 ^{13}C spectra and 96 ^{17}O spectra, all nontrivial and distinct from each other

The least abundant of these isotopologues is so rare that one would need over 100 moles of ethanol to have any chance to meet one of its molecules, but that can change completely with isotopic enrichment

Isotopomers

Molecules of ISOTOPOMERS have the same isotopic composition, the isotope sits at different positions - isotopic isomers

Some isotopomers:

$^{13}C^{1}H_3{}^{12}C^{1}H_2{}^{16}O^{1}H$

$^{12}C^{1}H_3{}^{13}C^{1}H_2{}^{16}O^{1}H$

$^{13}C^{1}H_3{}^{13}C^{1}H_2{}^{16}O^{1}H$ - Isotopologue

$^{12}C^{1}H_3{}^{12}C^{1}H^{2}H^{16}O^{2}H$ Constitutional Isotopomers

$^{12}C^{1}H_3{}^{12}C^{1}H^{2}H^{16}O^{1}H$

$^{12}C^{1}H_3{}^{12}C^{2}H^{1}H^{16}O^{1}H$ Stereo Isotopomers (R/S)

Isotope Effects

$(D/H)\ {}^{n}\Delta({}^{13}C)$

Isotope shift of M signal caused by substitution of H by D, n bonds away

M – X n = 1 primary isotope shift

M – C – X n = 2 secondary isotope shift

Magnitude expressed in ppb, decreases with longer distance, n

Generally

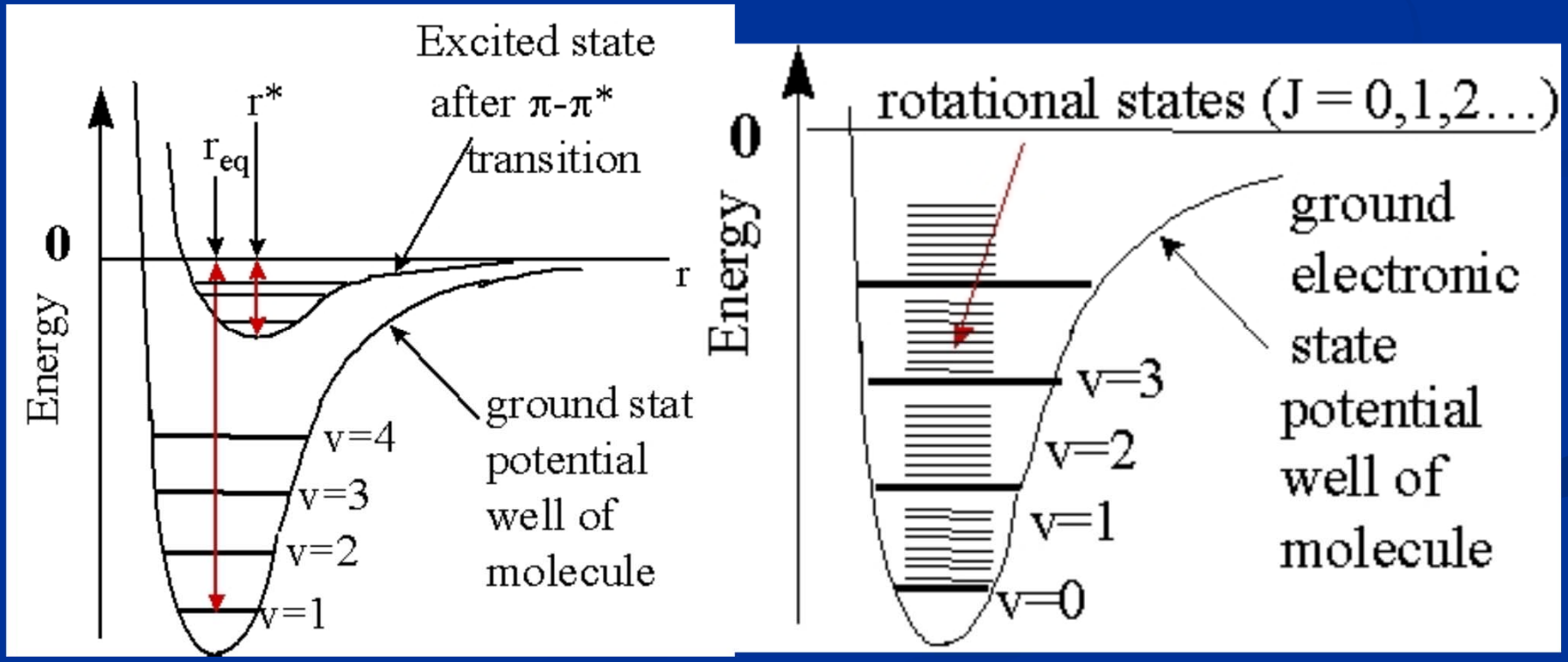
$${}^{n}\Delta({}^{A}M) = \delta_{HEAVY} - \delta_{LIGHT} < 0$$

Heavy isotope shields more

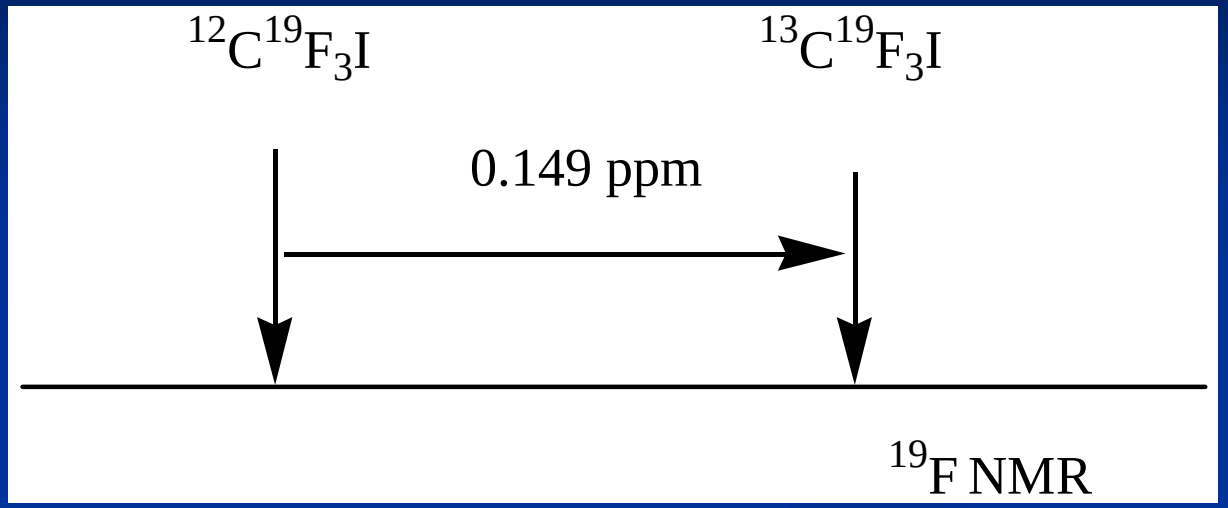
Isotope Effects

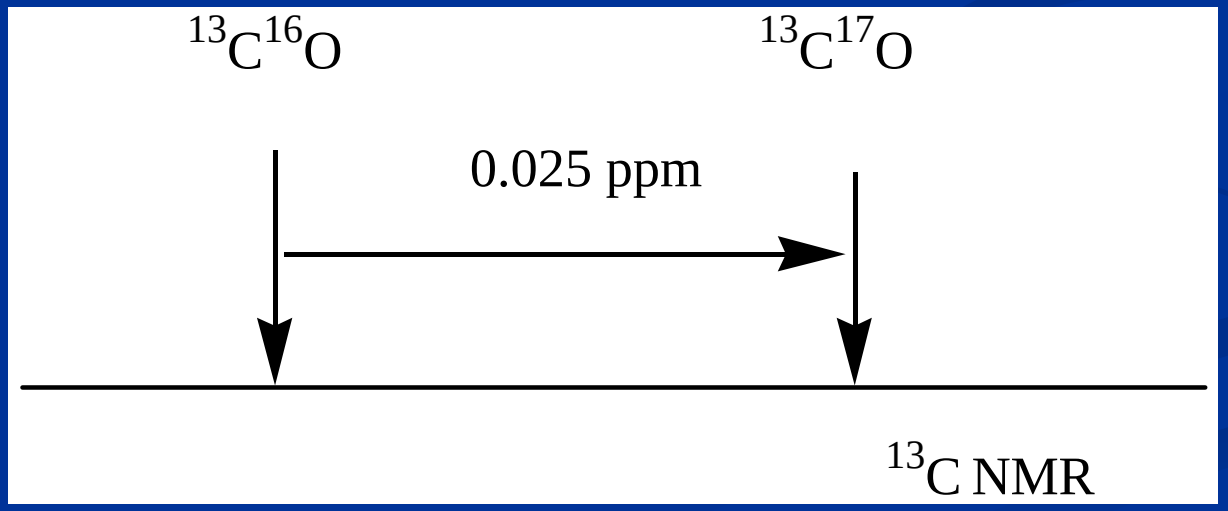
Occupation of vibrational levels changes with temperature

Level spacing changes with mass of bound atoms



Isotope Effect



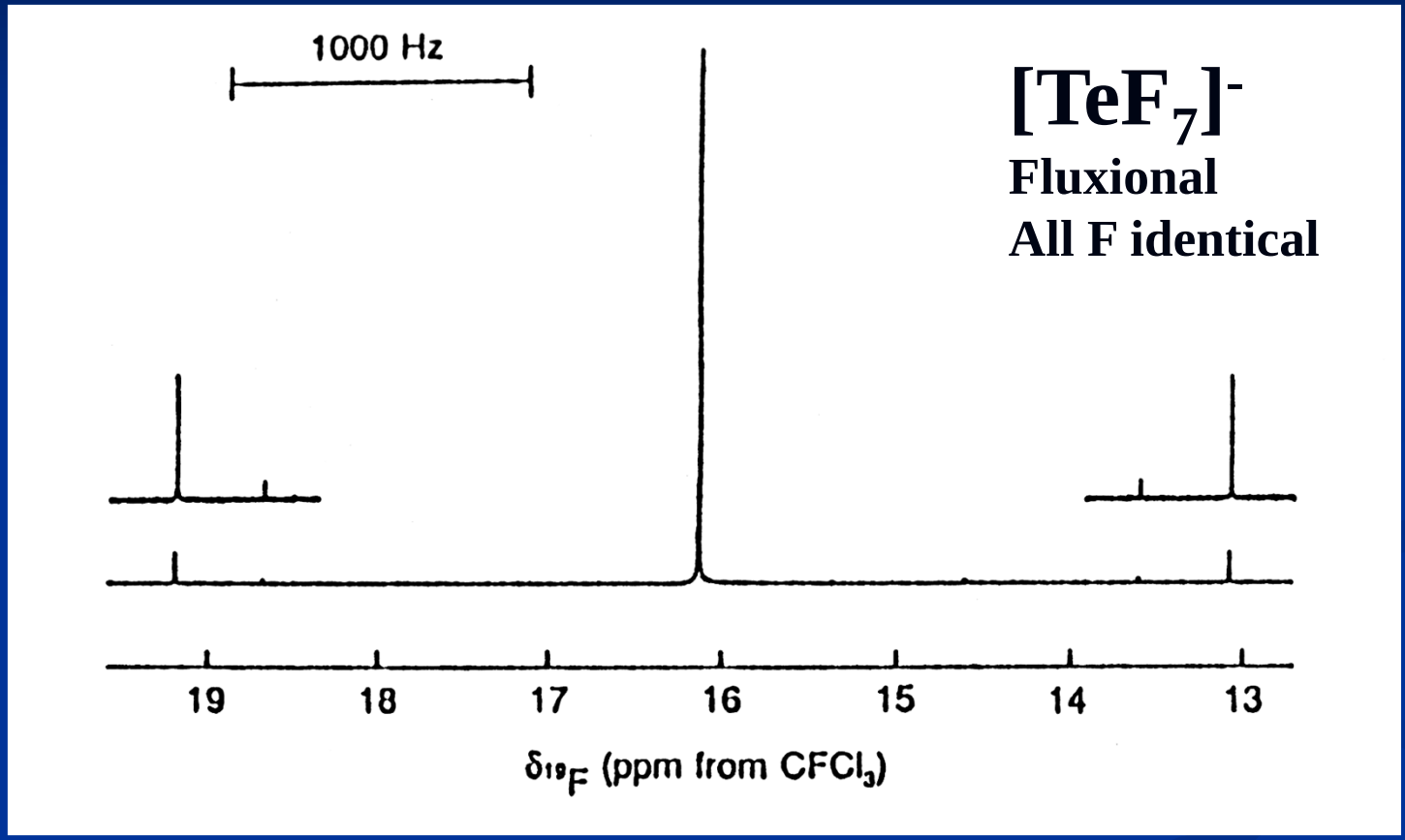


CO bond length difference 5 fm

Isotope Effect

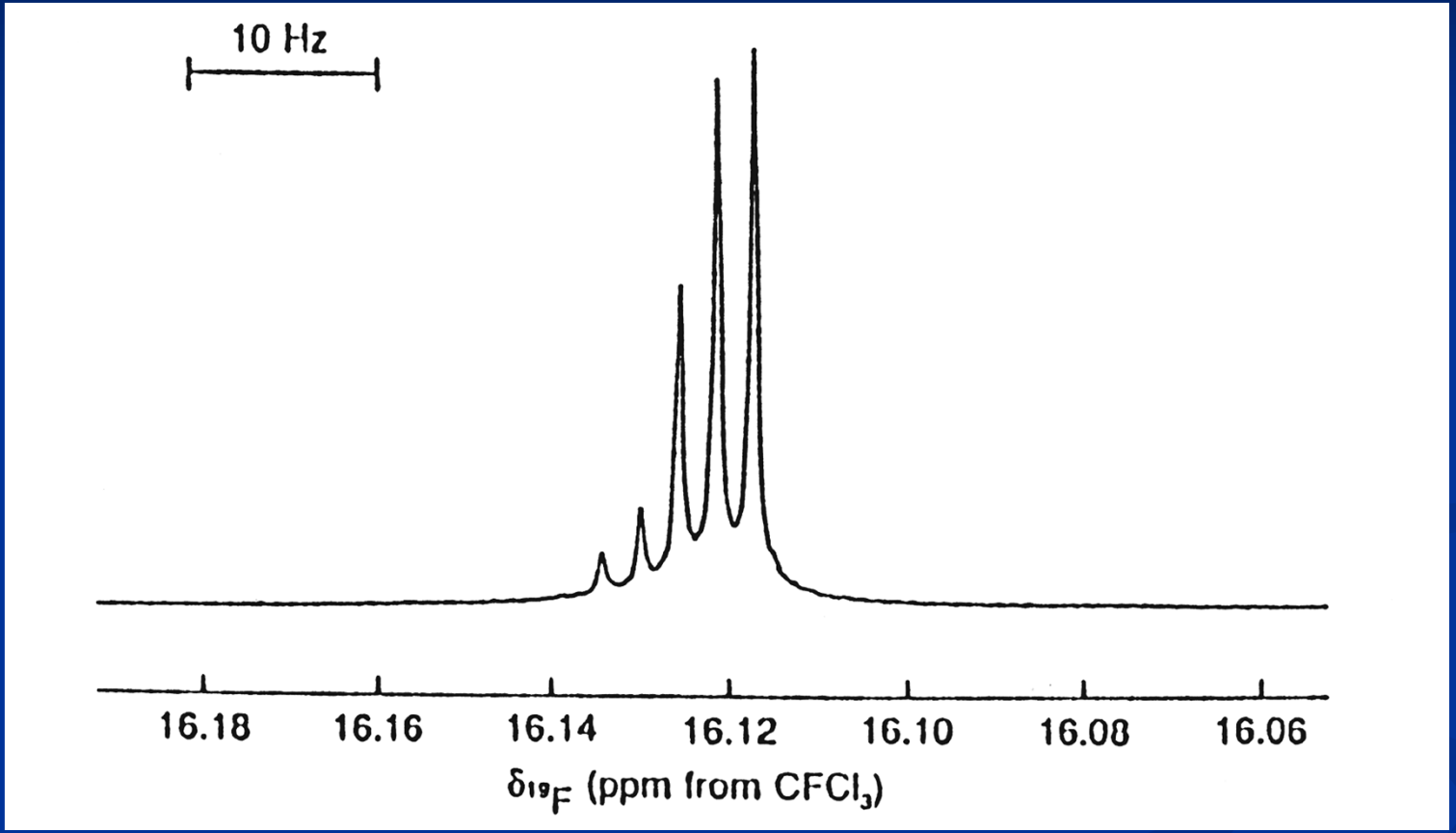
H	D	(D/H) $^{n}\Delta(^{31}P)$ ppm
PH_3	PDH_2	– 0.804
PH_3	PD_2H	– 0.845
PH_3	PD_3	– 0.888

Isotope Effect



^{19}F NMR spectrum of $[NMe_4][TeF_7]$ in CH_3CN at 30 °C

Isotope Effect



Central line of the ^{19}F NMR spectrum of $[NMe_4][TeF_7]$

Tellurium Isotopes

Z		A	NA%	I
52	Te	120	0.09 (1)	
		122	2.55 (12)	
		123	0.89 (3)	½
		124	4.74 (14)	
		125	7.07 (15)	½
		126	18.84 (25)	
		128	31.74 (8)	
		130	34.08 (62)	

Satellite Spectra of $Si(CH_3)_4$

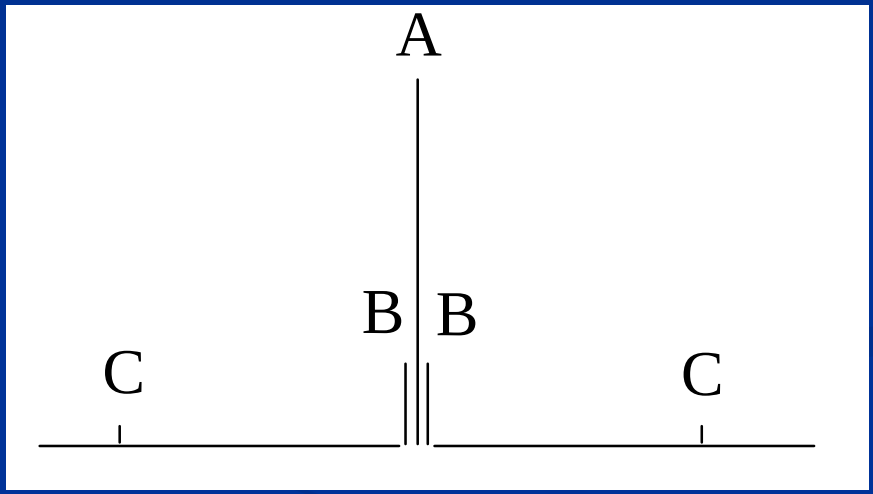
^{1}H

Isotopologues

$^{28}Si(^{12}CH_3)_4$

$^{29}Si(^{12}CH_3)_4$

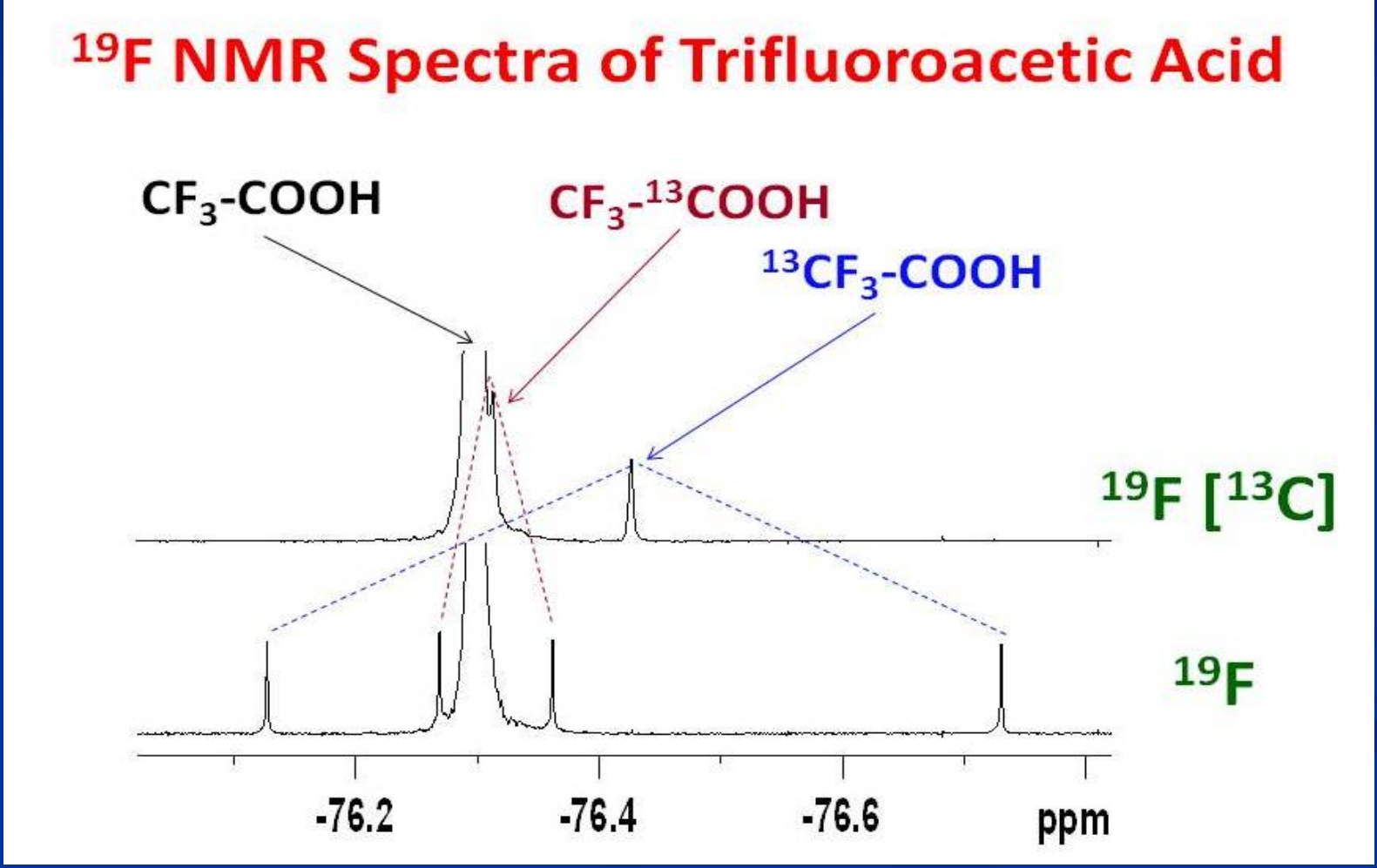
$^{28}Si(^{13}CH_3)(^{12}CH_3)_3$



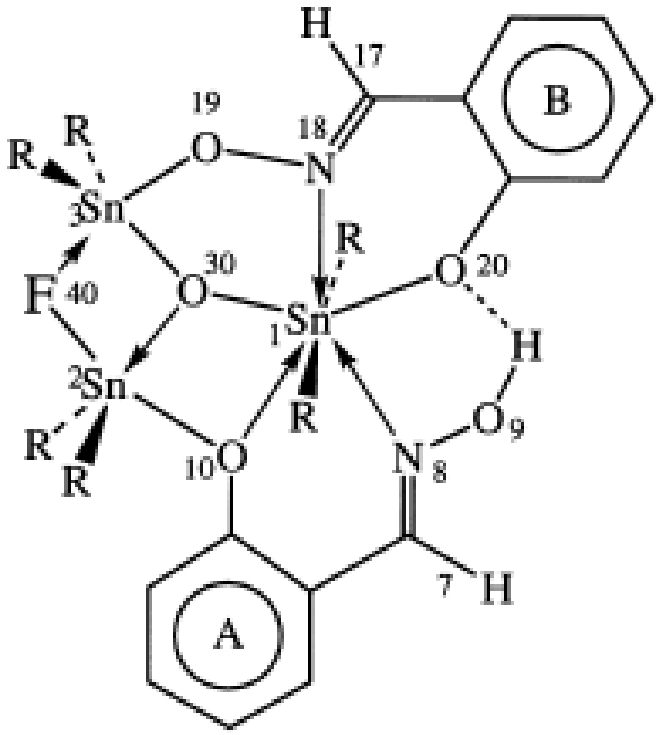
Other isotopologues have too low concentration

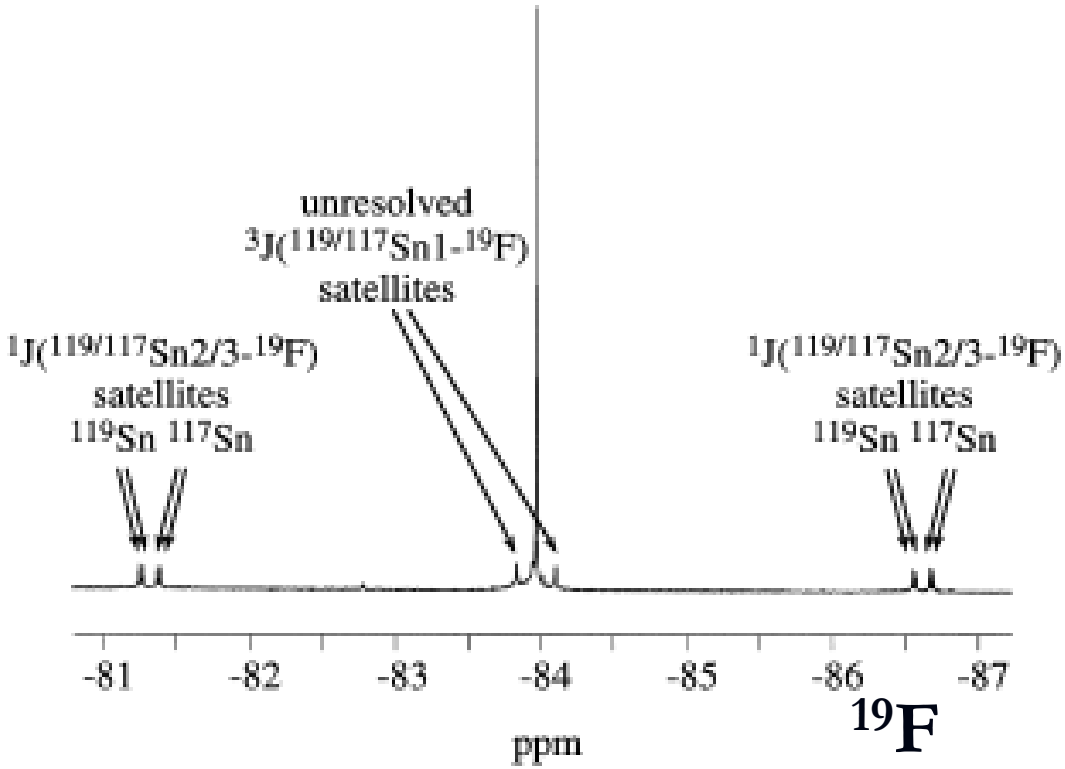
$^{28/29}Si(^{12}CH_3)_{4-n}(^{13}CH_3)_n$

Isotope Effect on Satellite Spectra



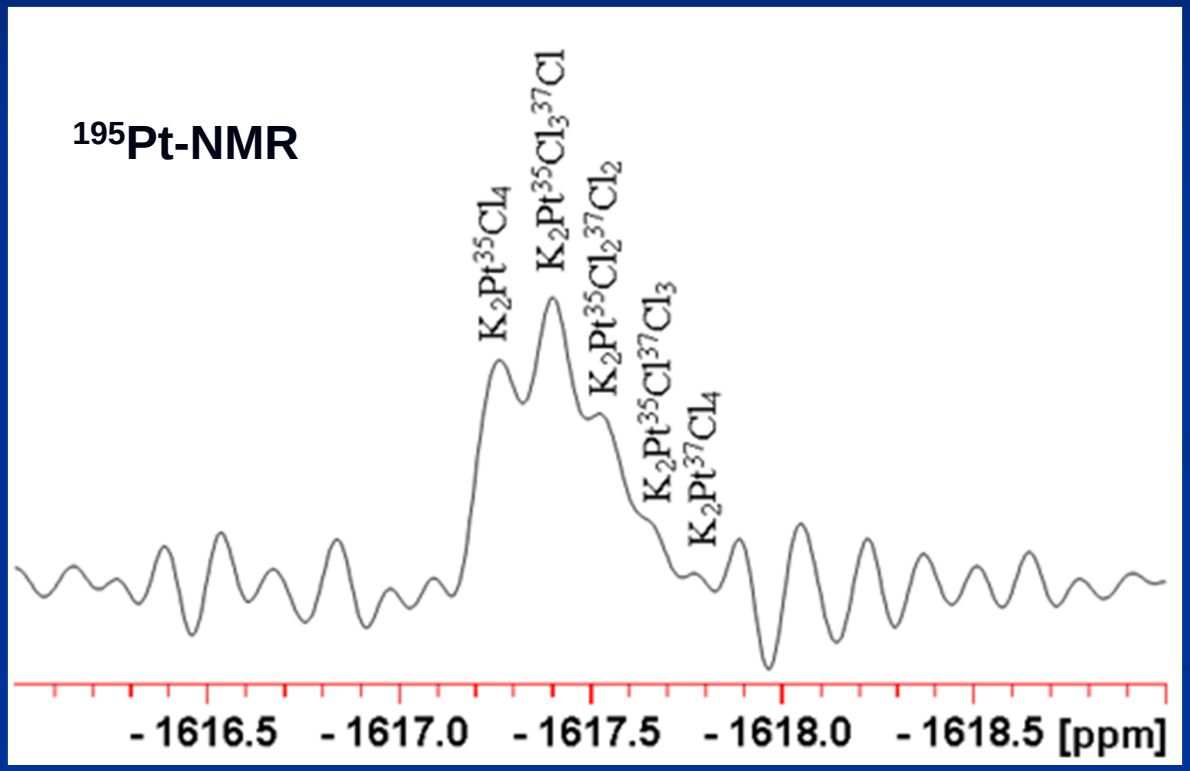
Satellite Spectra





$[(R_2Sn)_2(R_2SnO)(F)(HONZO)(ONZO)]$, R = Me
HONZOH = salicylaldoxime, *ortho*-HO–N=CH–C_6H_4OH

Satellite Spectra

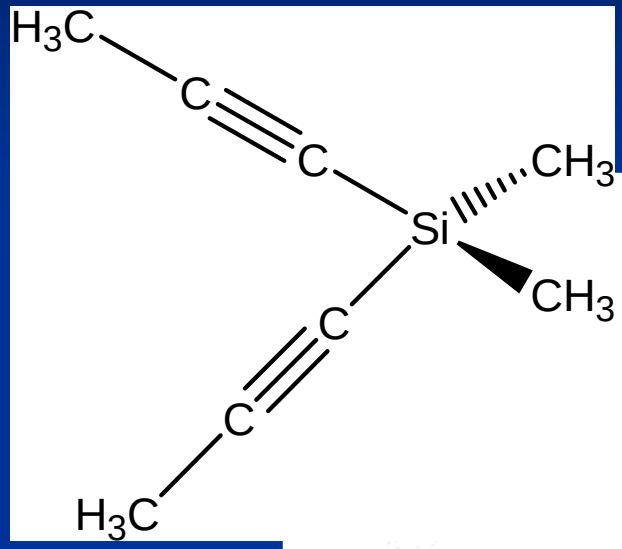


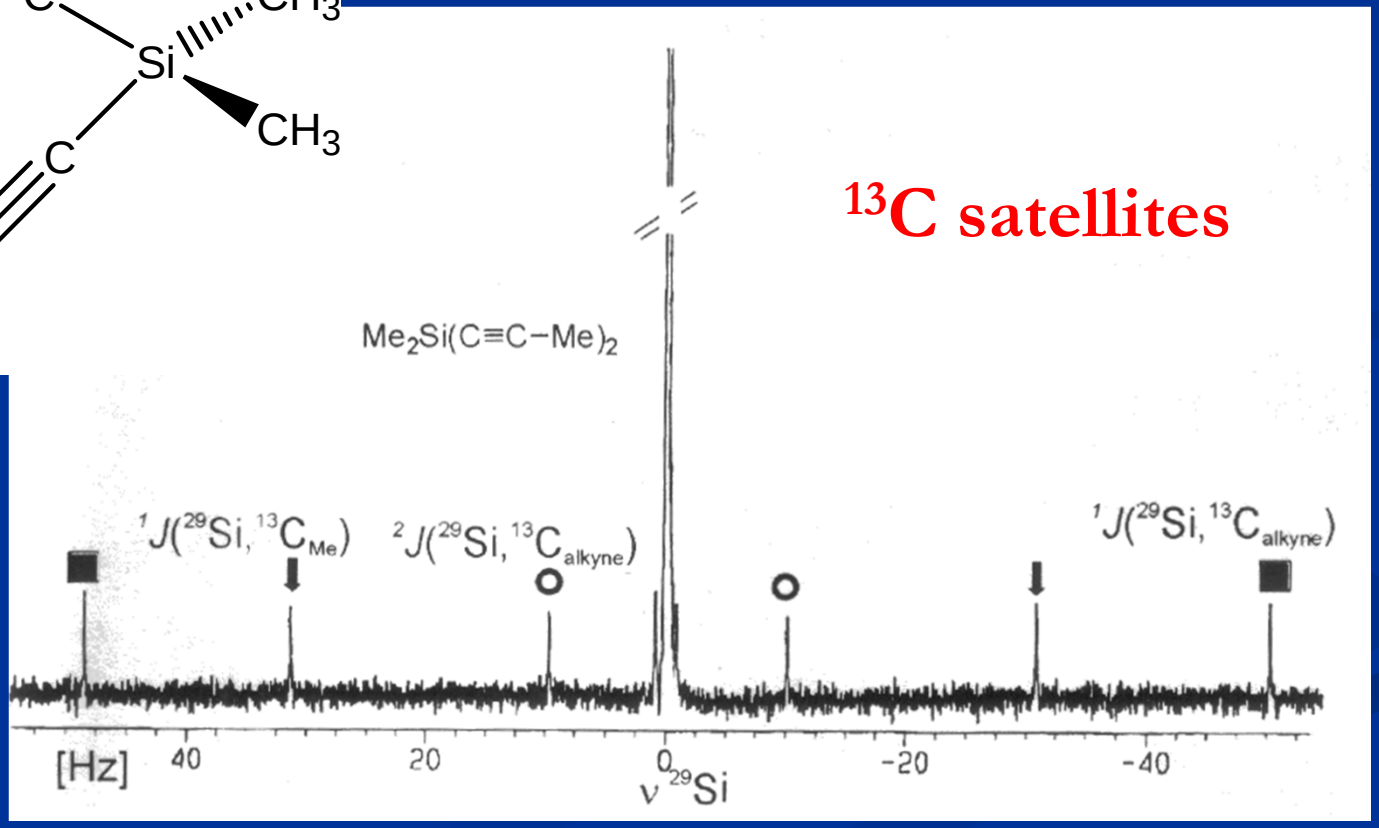
^{35}Cl 75.5 %
^{37}Cl 24.5 %

Resolution-enhanced ^{195}Pt-NMR spectrum of K_2PtCl_4 in D_2O showing all five possible isotopologues (^{35}Cl / ^{37}Cl).

Satellite Spectra

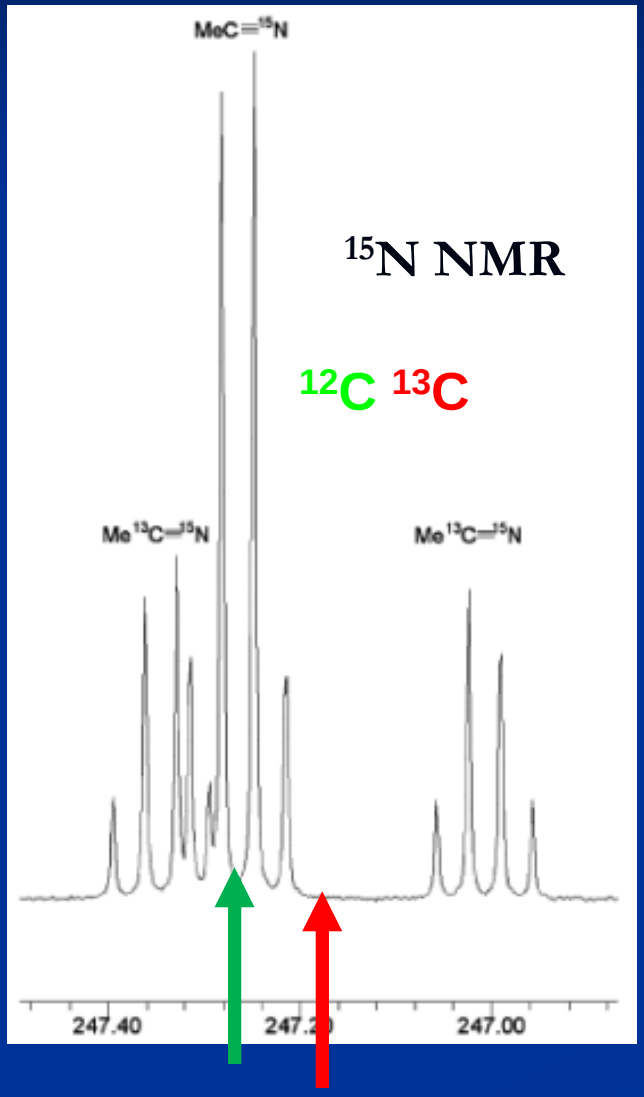
^{29}Si NMR





^{13}C satellites

Isotope Effect on Satellite Spectra



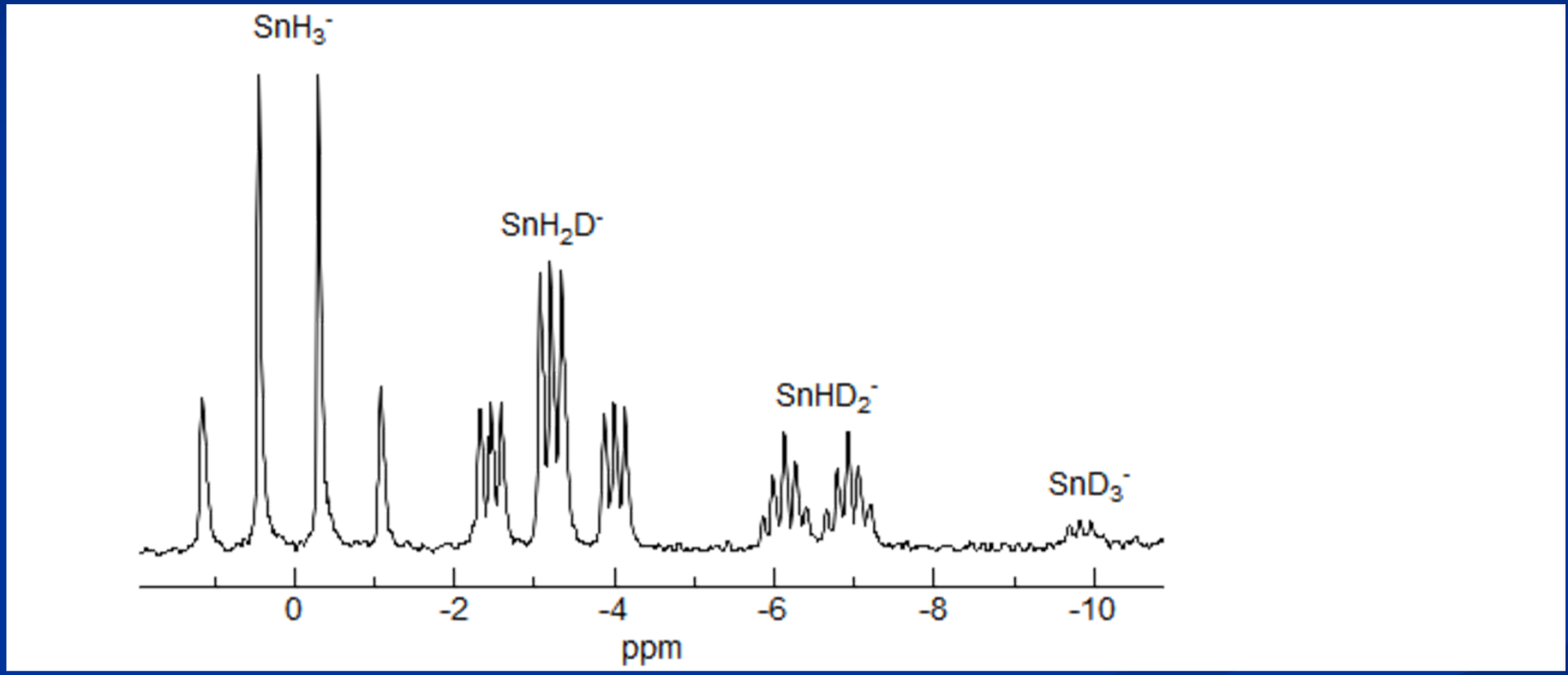
CH_3-C≡N

^{15}N signal shows coupling to:
^{1}H $^{3}J(^{1}H\text{-}^{15}N)$ = 1.7 Hz
^{13}C $^{1}J(^{13}C\text{-}^{15}N)$ = 17 Hz

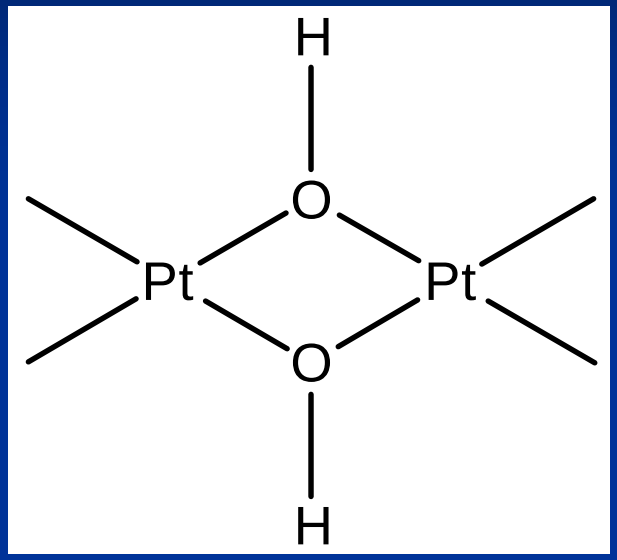
The signal appears as a central 1:3:3:1 quartet flanked by ^{13}C satellites

The unsymmetrical nature of the ^{13}C satellites arises from $^{12}C/^{13}C$ isotopic chemical shift perturbation.

Isotope Effect on Satellite Spectra



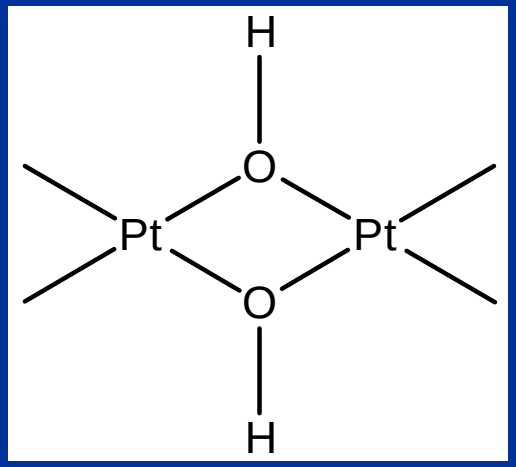
Calculation of Abundance of Isotopologues

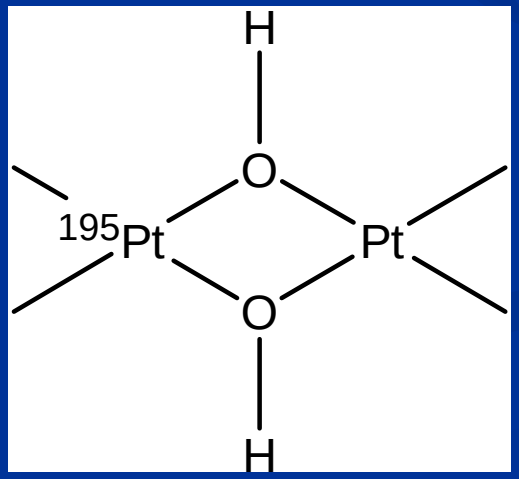


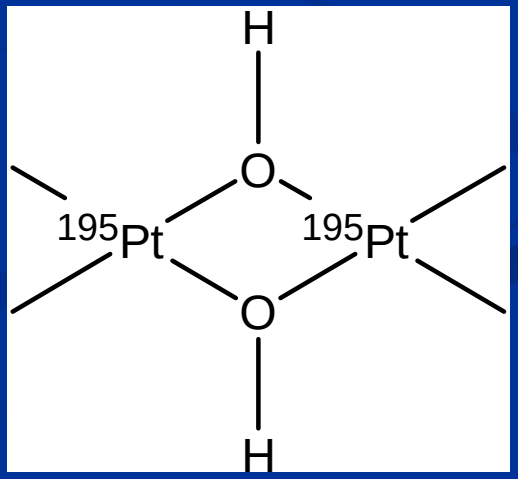
^{1}H NMR spectrum

^{195}Pt I = ½, NA = 33.8 %

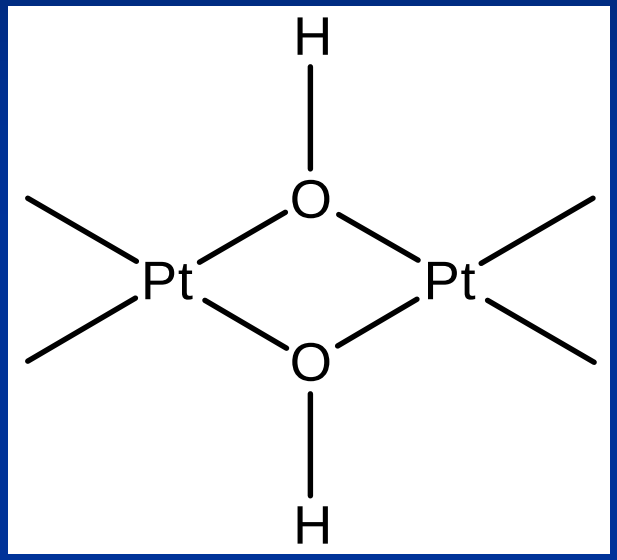
NMR inactive Pt nuclides 66.2 %







Calculation of Abundance of Isotopologues



^{1}H NMR spectrum

^{195}Pt I = ½, NA = 33.8 %

$$f_i = \frac{\sigma}{\sigma_i} a^x b^y c^z ....$$

Calculation of Abundance of Isotopologues

Isotopologues and isotopomers

$$f_i = \frac{\sigma}{\sigma_i} a^x b^y c^z ....$$

f_i = the fractional abundance of an isotopologue *i*

σ = the symmetry number of the parent molecule isotopically pure = the order of rotation group C_n

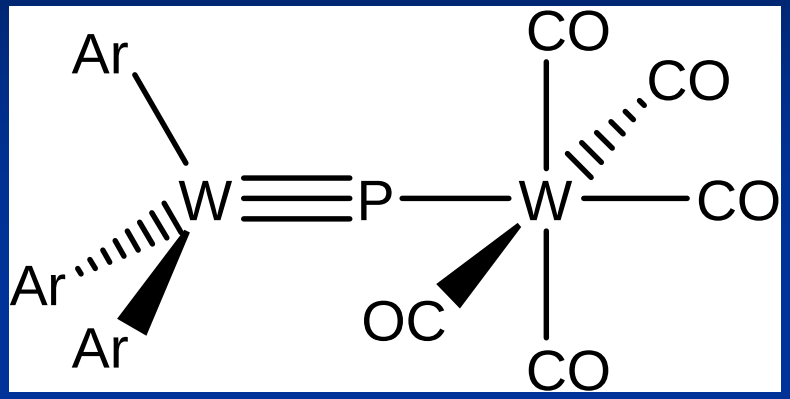
σ_i = the symmetry number of the isotopologue

a = abundance of an isotope occuring x-times (in atomic %)

b = abundance of an isotope occuring y-times (in atomic %)

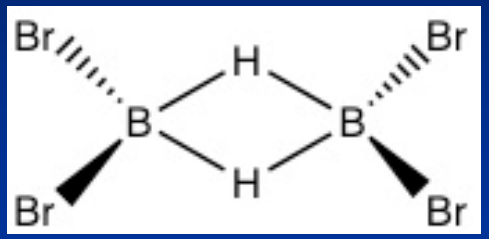
Abundance of Isotopologues

$$f_i = \frac{\sigma}{\sigma_i} a^x b^y c^z ....$$



Isotopologue	σ_i	a (0.144)	b (0.856)	f_i
W≡P–W	1	a^0	b^2	0.733
W≡P–^{183}W	1	a^1	b^1	0.123
^{183}W≡P–W	1	a^1	b^1	0.123
^{183}W≡P–^{183}W	1	a^2	b^0	0.021

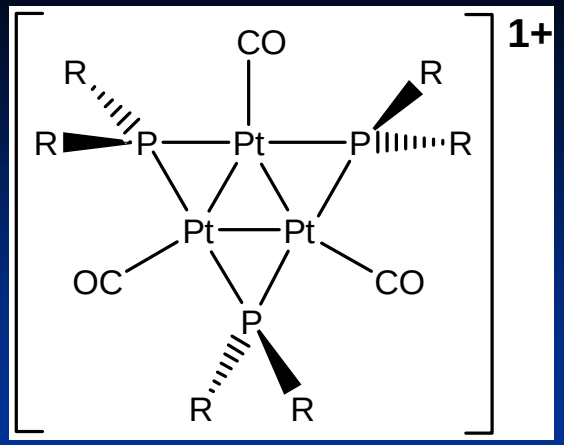
Abundance of Isotopologues



$$f_i = \frac{\sigma}{\sigma_i} a^x b^y c^z ....$$

Isotopoloque	σ_i	a (0.1958)	b (0.8042)	f_i
$^{10}B–^{10}B$	2	a^2	b^0	0.0383
$^{10}B–^{11}B$	1	a^1	b^1	0.3149
$^{11}B–^{11}B$	2	a^0	b^2	0.6467

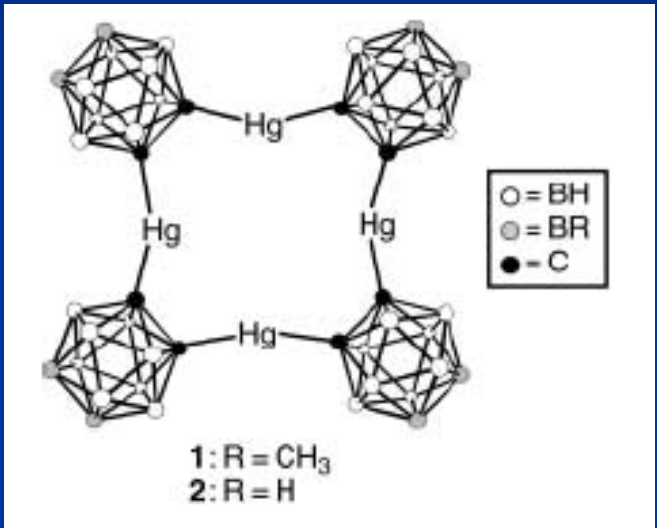
Isotopologues



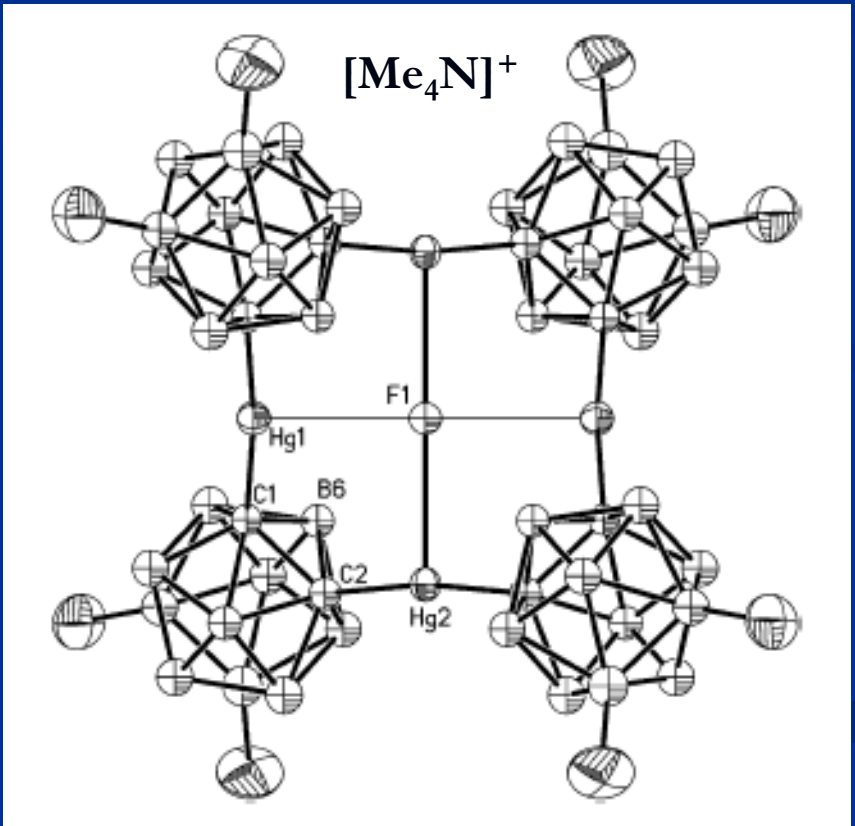
Isotopomer	Pt1	Pt2	Pt3	f_i
A	*	*	*	0.290
B	195	*	*	0.148
C	*	195	*	0.148
D	*	*	195	0.148
E	195	195	*	0.076
F	195	*	195	0.076
G	*	195	195	0.076
H	195	195	195	0.038

Abundance of Isotopologues

Mercuracarborands



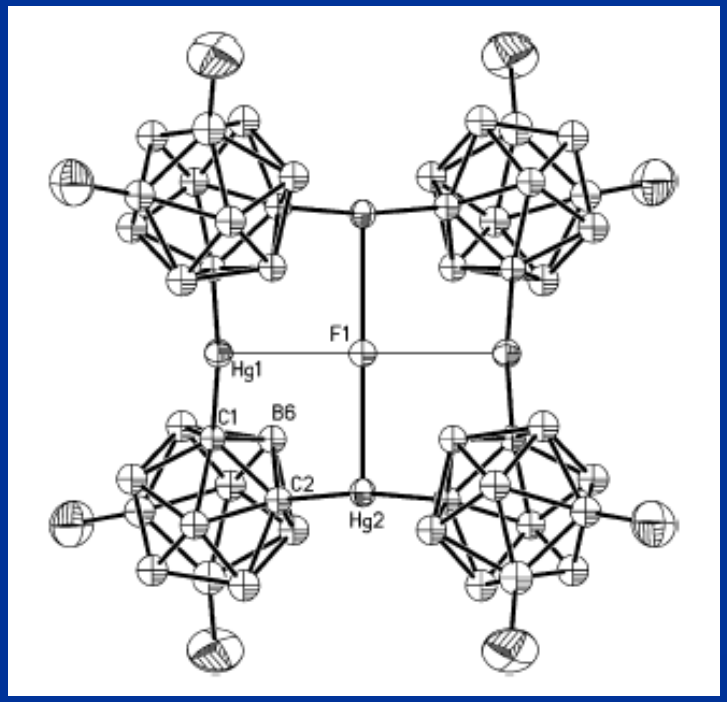
$[Me_4N]F$



Calculation of Abundance of Isotopologues

^{199}Hg I = ½ NA = 16.8%
^{201}Hg I = 3/2 NA = 13.2%
other Hg inactive in NMR

$$f_i = \frac{\sigma}{\sigma_i} a^x b^y$$

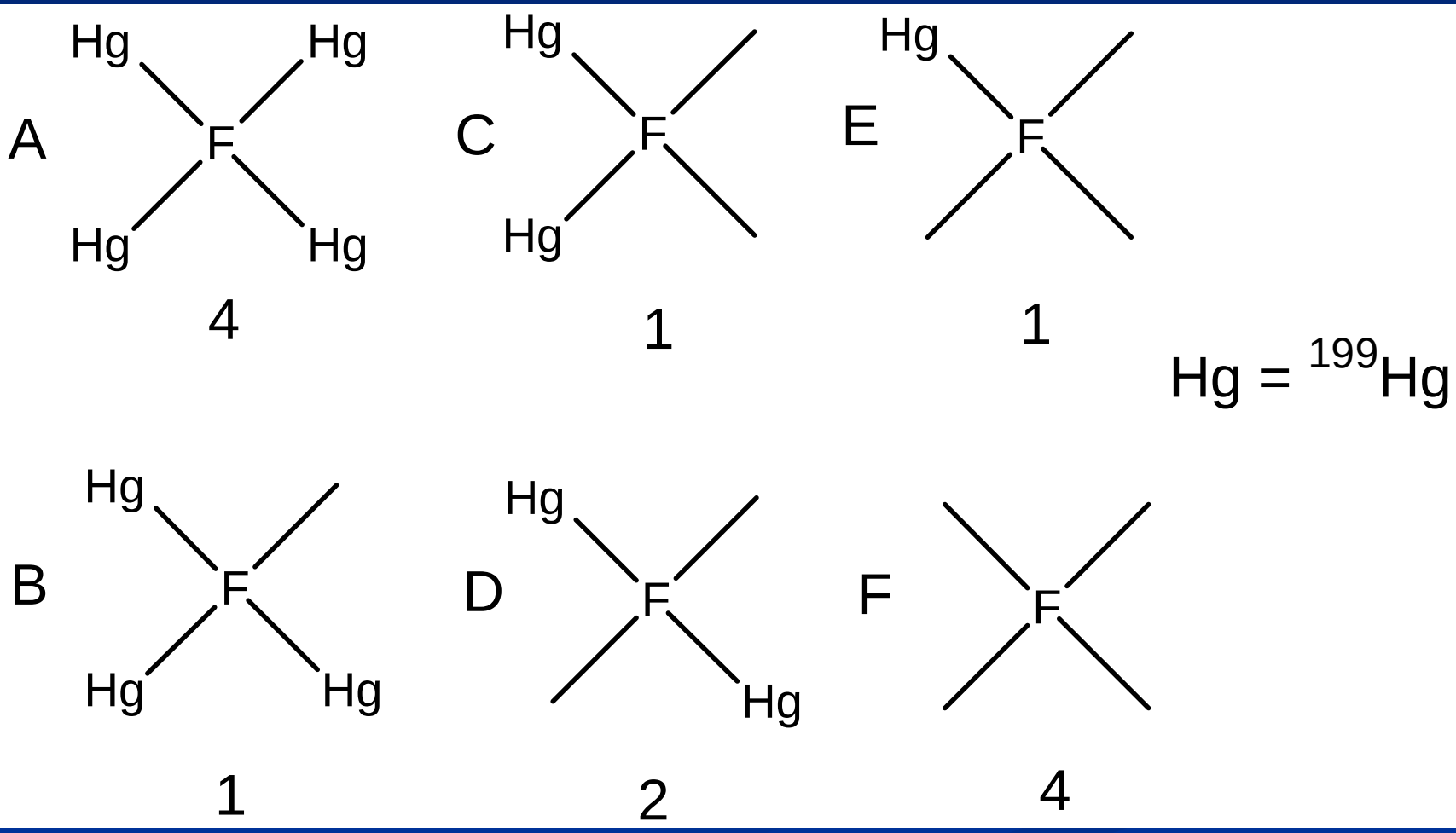


^{19}F NMR
Only coupling to ^{199}Hg observed
No coupling to ^{201}Hg visible

σ = 4

a = 16.8 % ^{199}Hg (active)
b = 83.2 % all other nuclides (inactive)

Isotopologues/Isotopomers

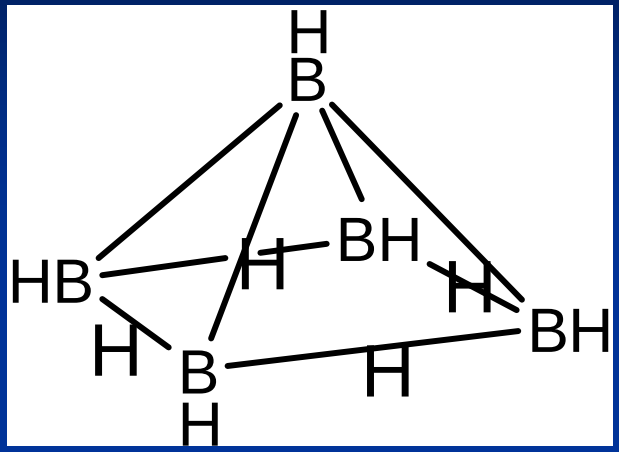


Isotopologue Abundances

$$f_i = \frac{4}{\sigma_i}(0.168)^x(0.832)^y$$

Isotopologue	σ_i	x	y	f_i	2nI + 1
A	4	4	0	0.00080	qn
B	1	3	1	0.01578	dt
C	1	2	2	0.03907	t
D	2	2	2	0.07815	t
E	1	1	3	0.38703	d
F	4	0	4	0.47917	s

B_5H_9


H
B
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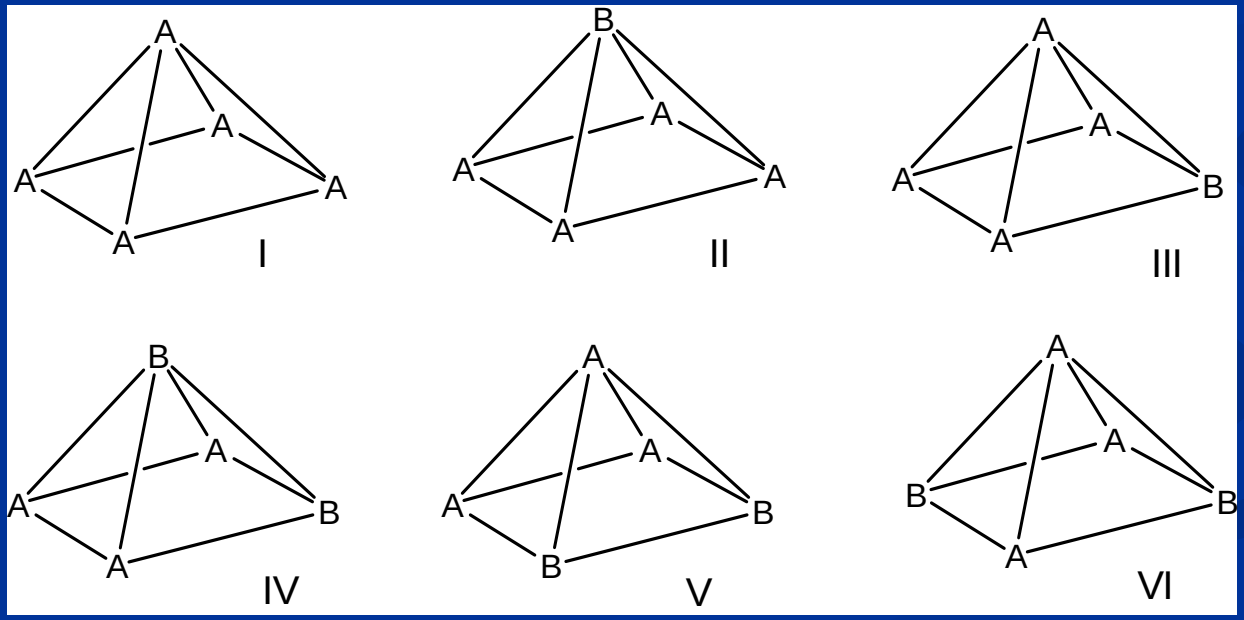
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VI