Isotopomers

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

Some isotopomers:

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

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

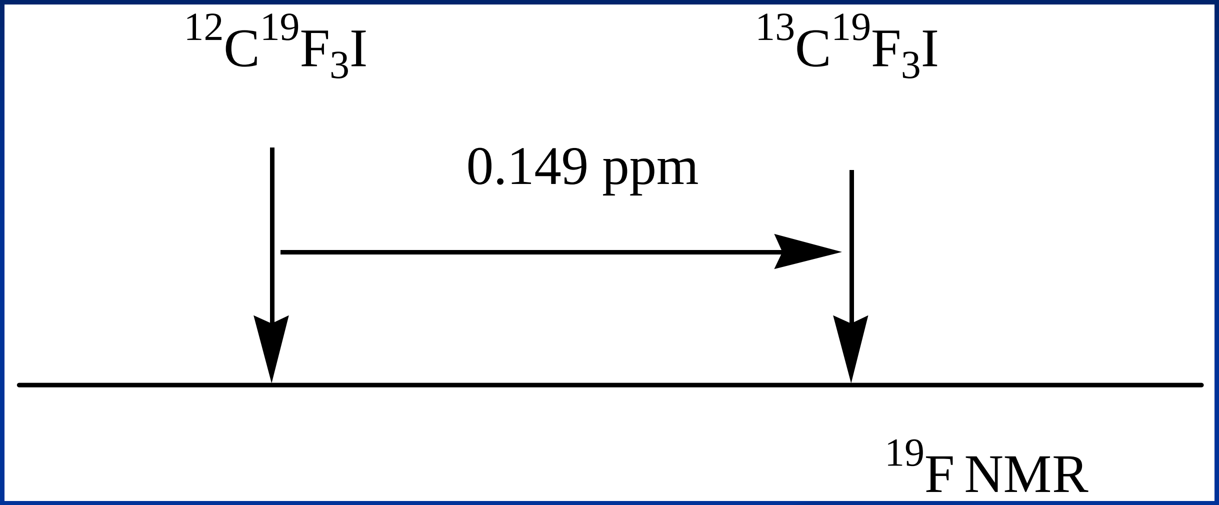
Magnitude expressed in ppb, decreases with distance, n

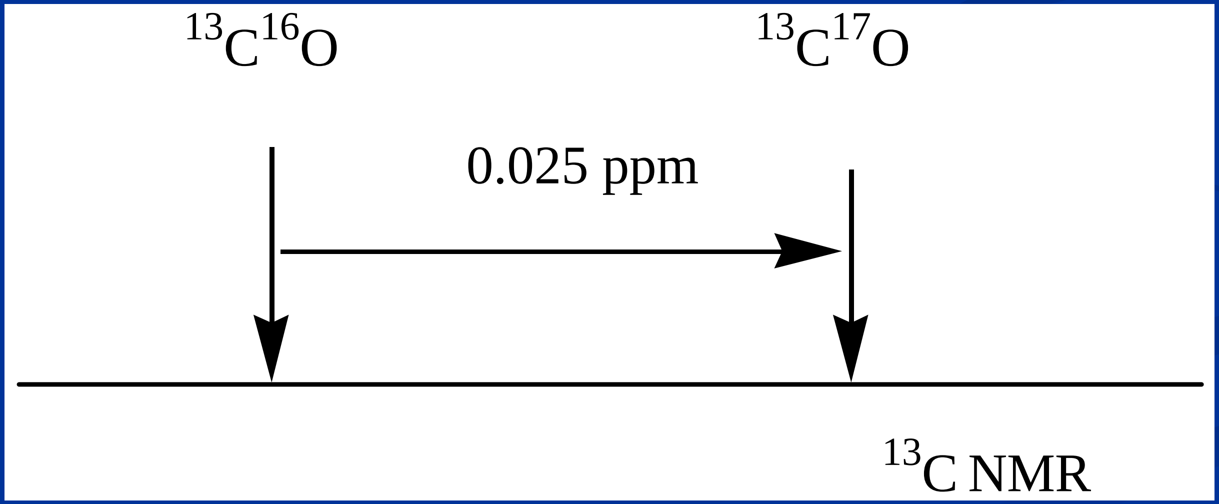
Generally

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

Heavy isotope shields more

Isotope Effect





CO bond length difference 5 fm

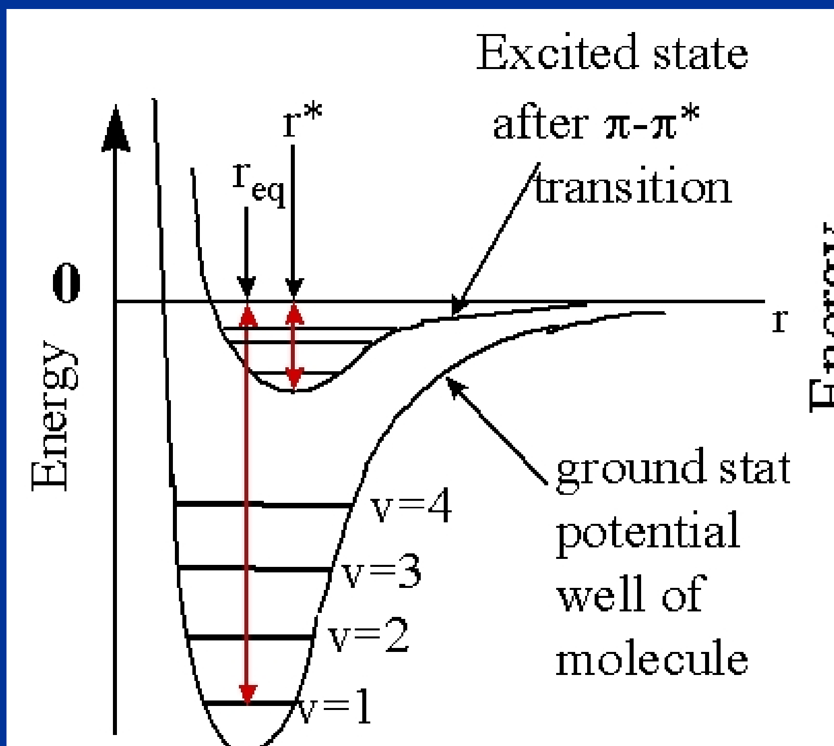
Isotope Effect

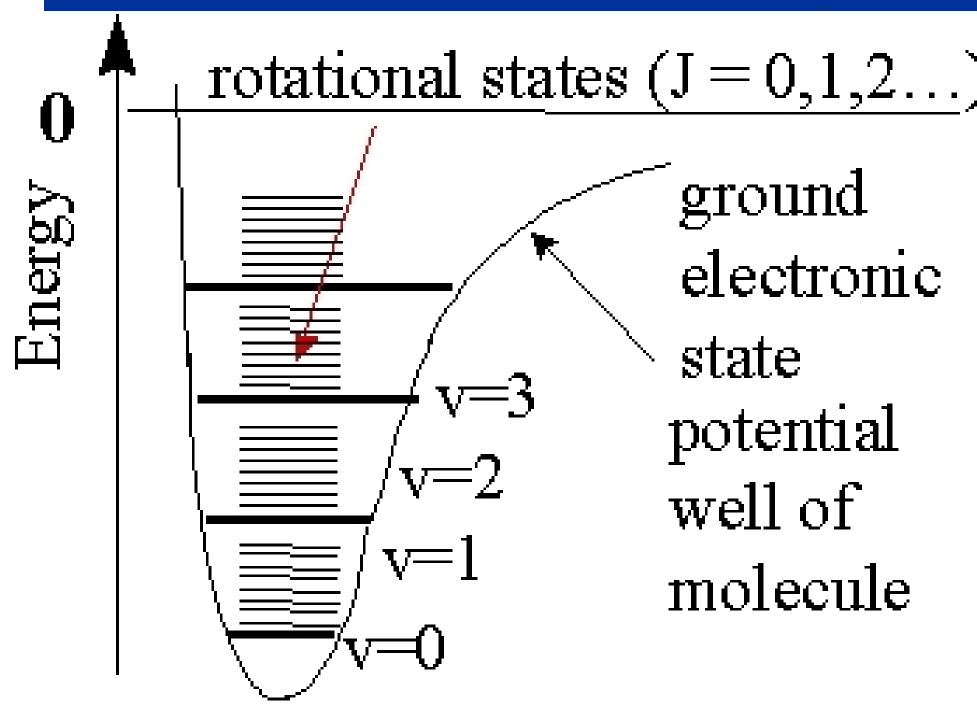
H	D	(D/H) $^{n}\Delta(^{31}P)$ ppm
PH_3	PDH_2	– 0.804
PH_3	PD_2H	– 0.845
PH_3	PD_3	– 0.888

Isotope Effects

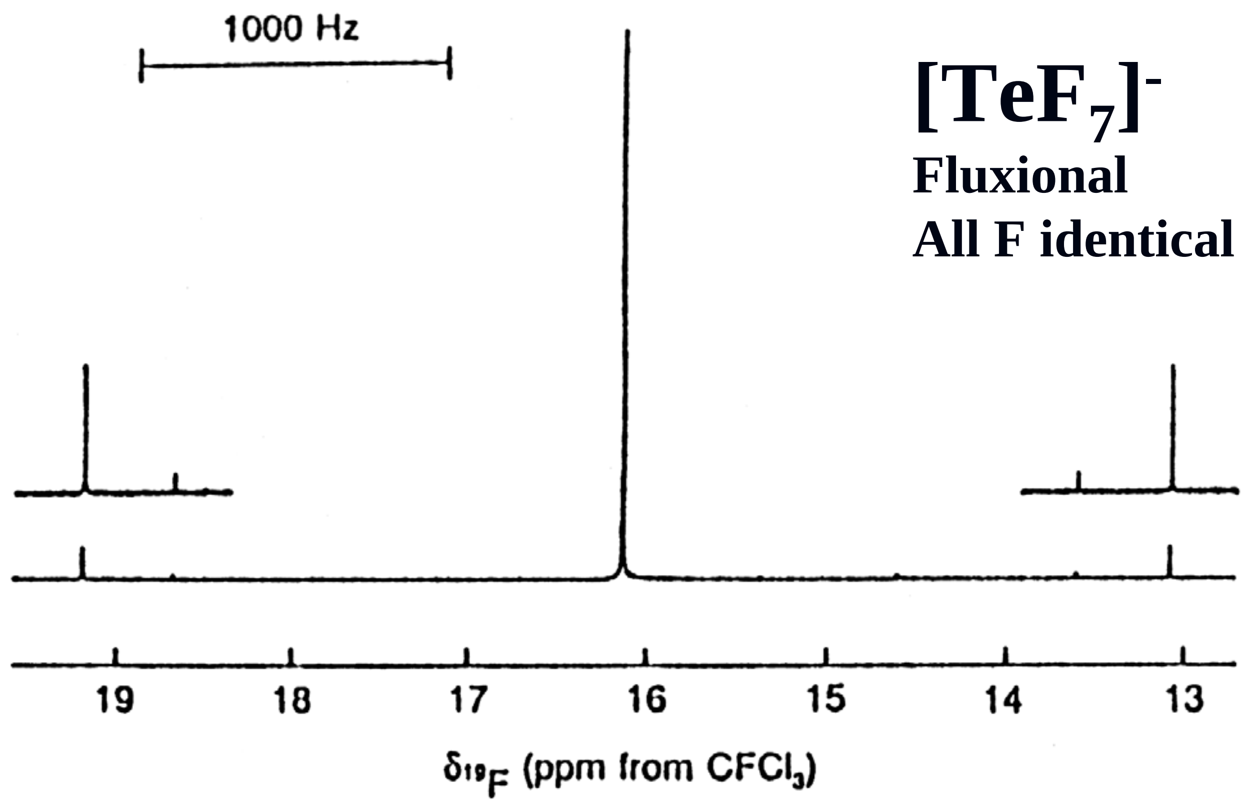
Occupation of vibrational levels changes with temperature

Level spacing changes with mass of bound atoms





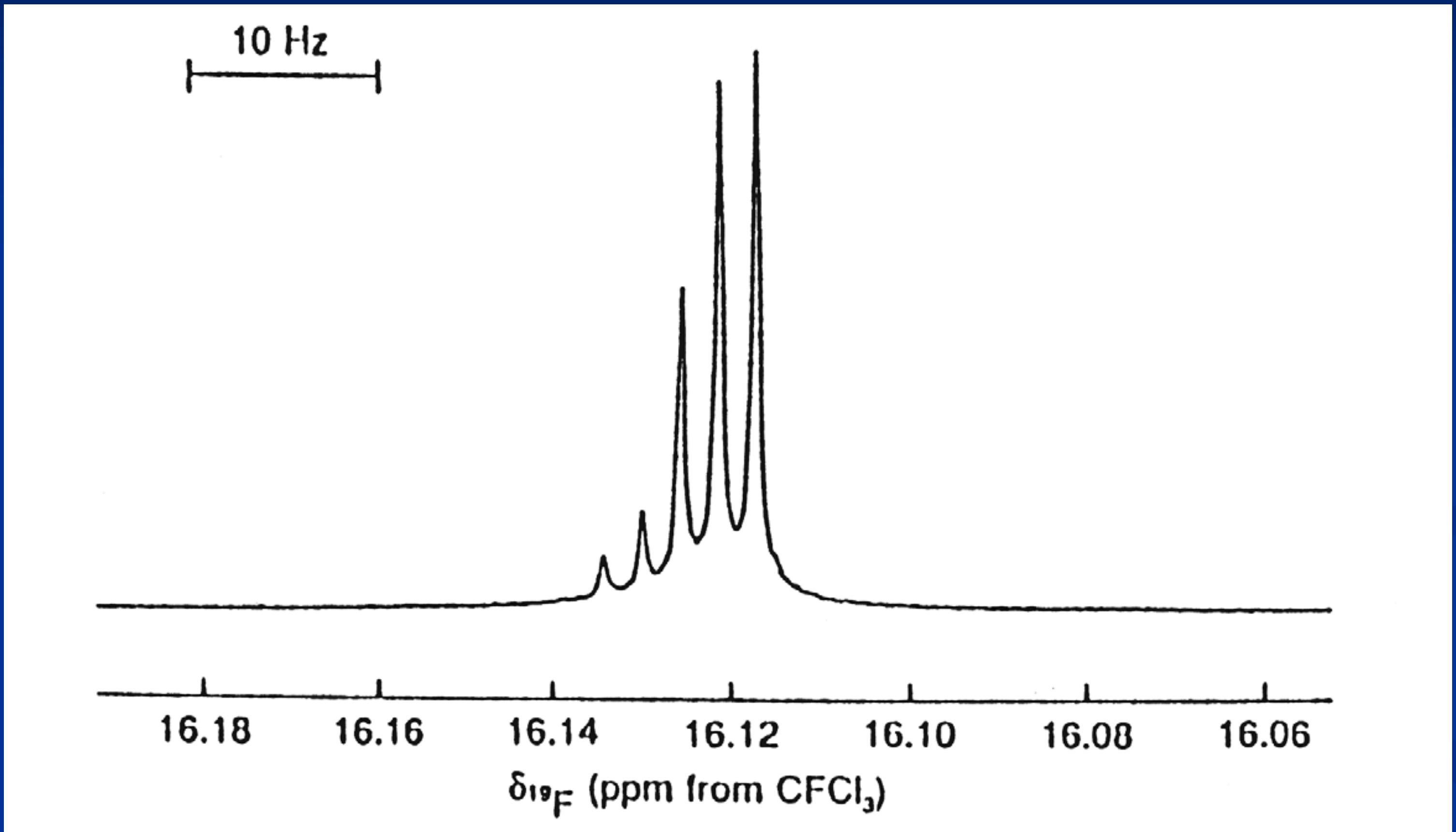
Isotope Effect



$[TeF_7]^-$
Fluxional
All F identical

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

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 $Si(CH_3)_4$

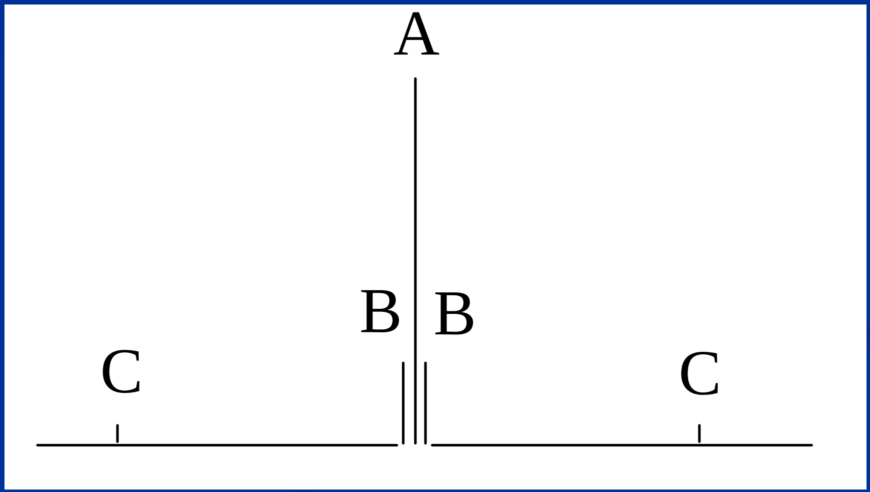
^1H

Isotopomers

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

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

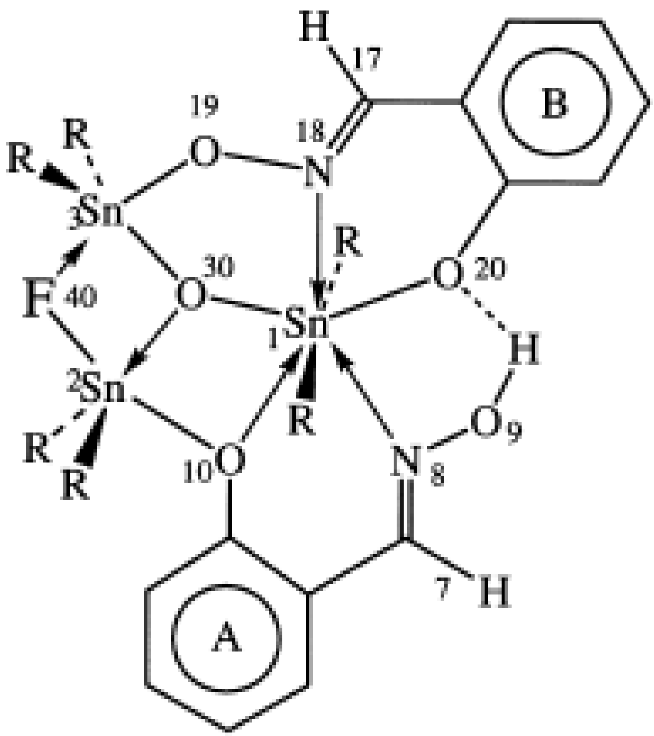
$^{28}Si(^{13}CH_3)(^{12}CH_3)_3$

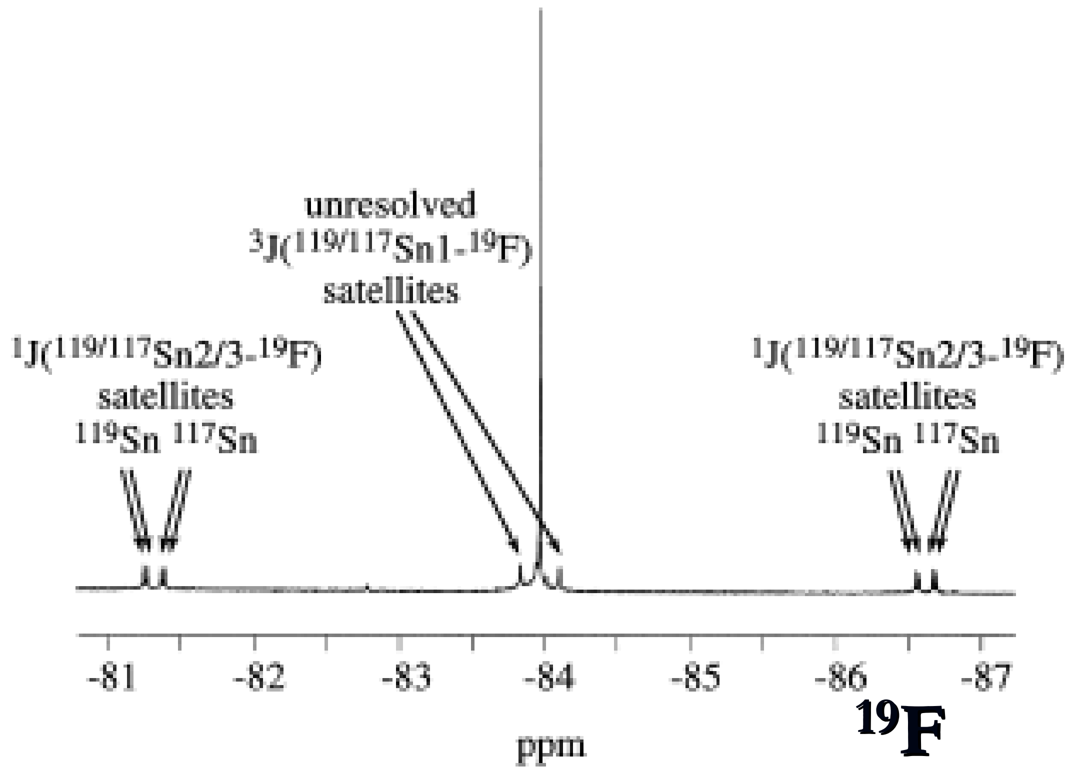


Other isotopomers have too low concentration

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

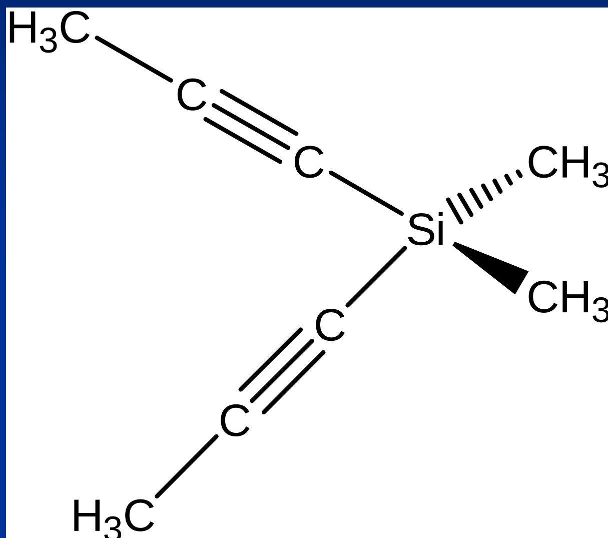
Satellite Spectra



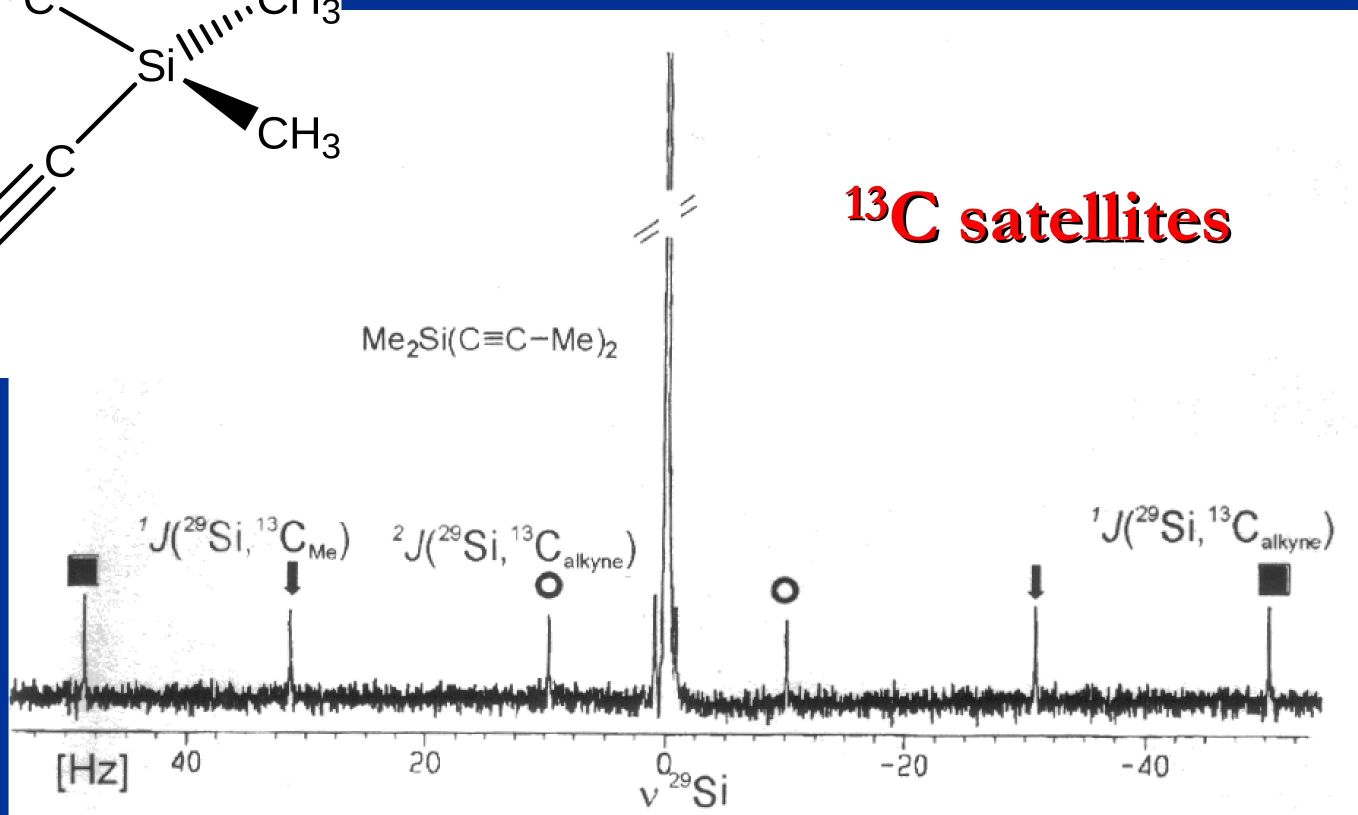


$[(R_2Sn)_2(R_2SnO)(F)(HONZO)(ONZO)]$, R = Me
HONZOH = salicylaldoxime,*ortho*-HO–N=CH–C_6H_4OH

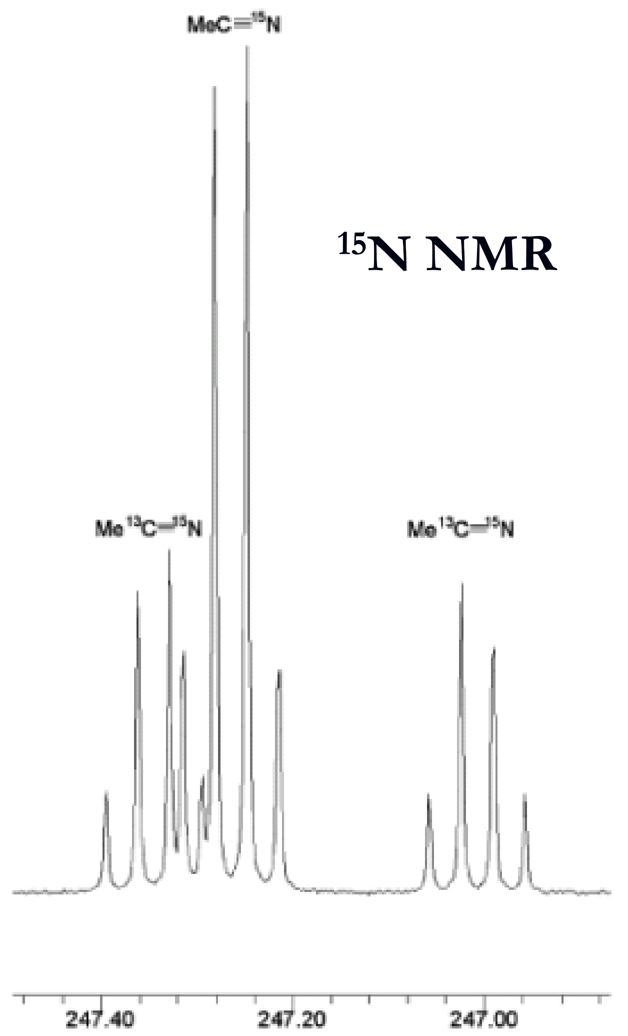
Satellite Spectra



^{29}Si NMR



Isotope Effect on Satellite Spectra



^{15}N NMR

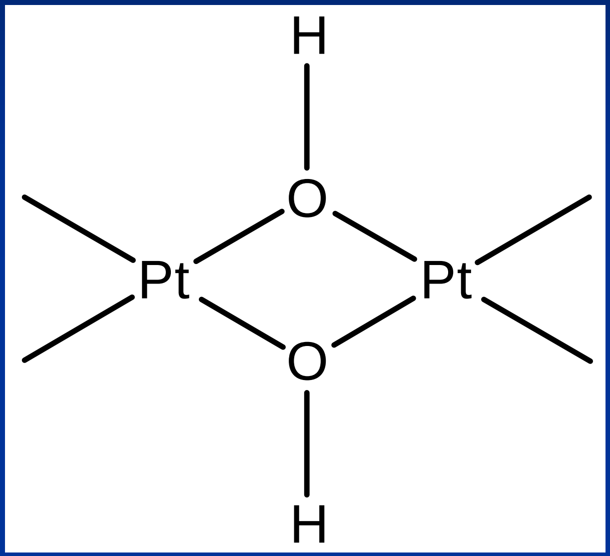
Me-C≡N

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

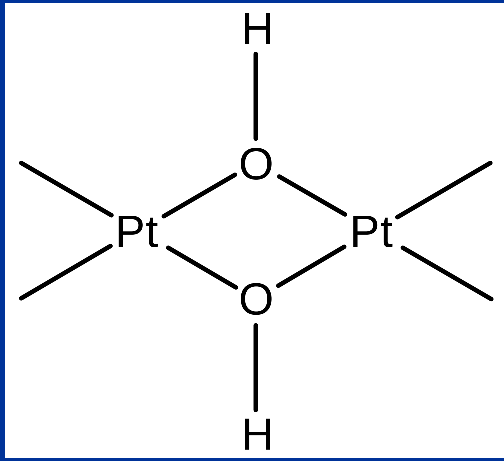
Calculation of Abundance of Isotopomers

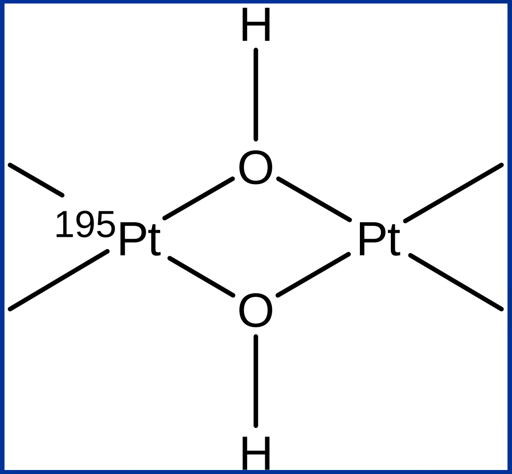


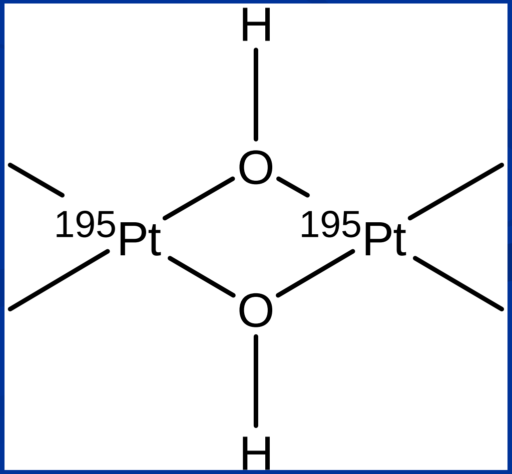
^{1}H NMR spectrum

^{195}Pt I = ½, NA = 33.8 %

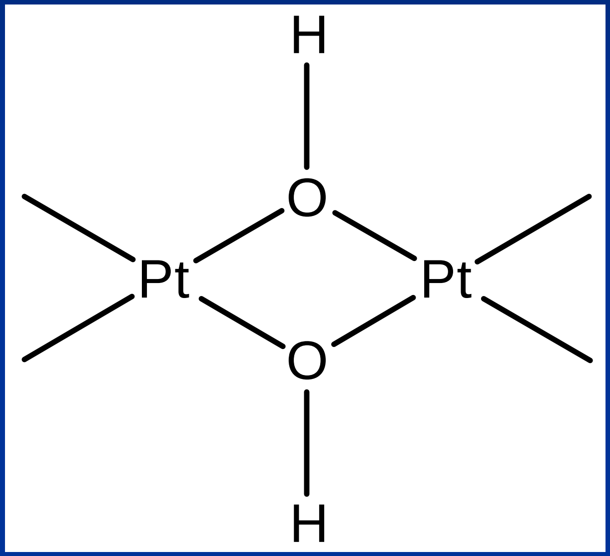
NMR inactive Pt nuclides 66.2 %







Calculation of Abundance of Isotopomers



^{1}H NMR spectrum

^{195}Pt I = ½, NA = 33.8 %

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

Calculation of Abundance of Isotopomers

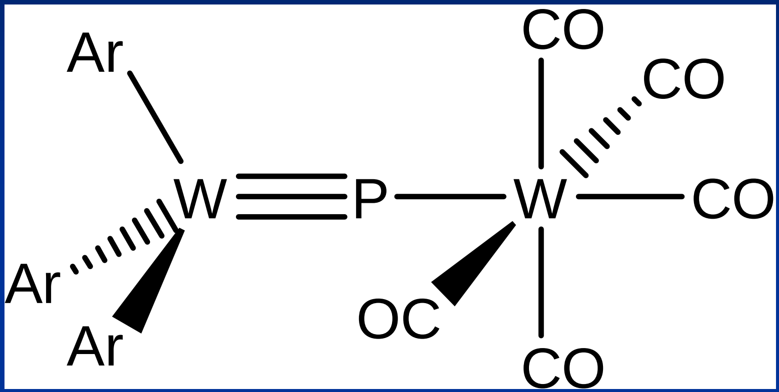
Isotopic isomers = isotopomers

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

f_i = the fractional abundance of isotopomer 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 isotopomer
a = abundance of an isotope occuring x-times in atomic %
b = abundance of an isotope occuring y-times in atomic %
.
.

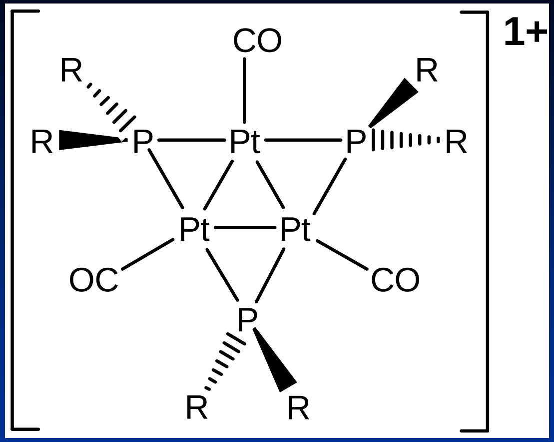
Abundance of Isotopomers

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



Isotopomer	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

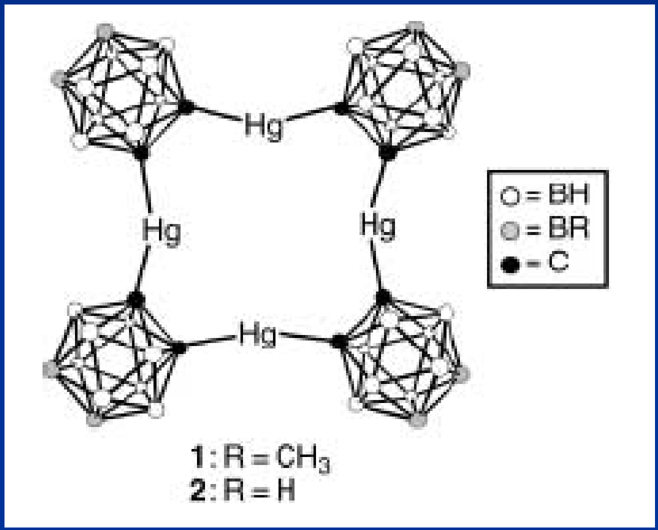
Isotopomers



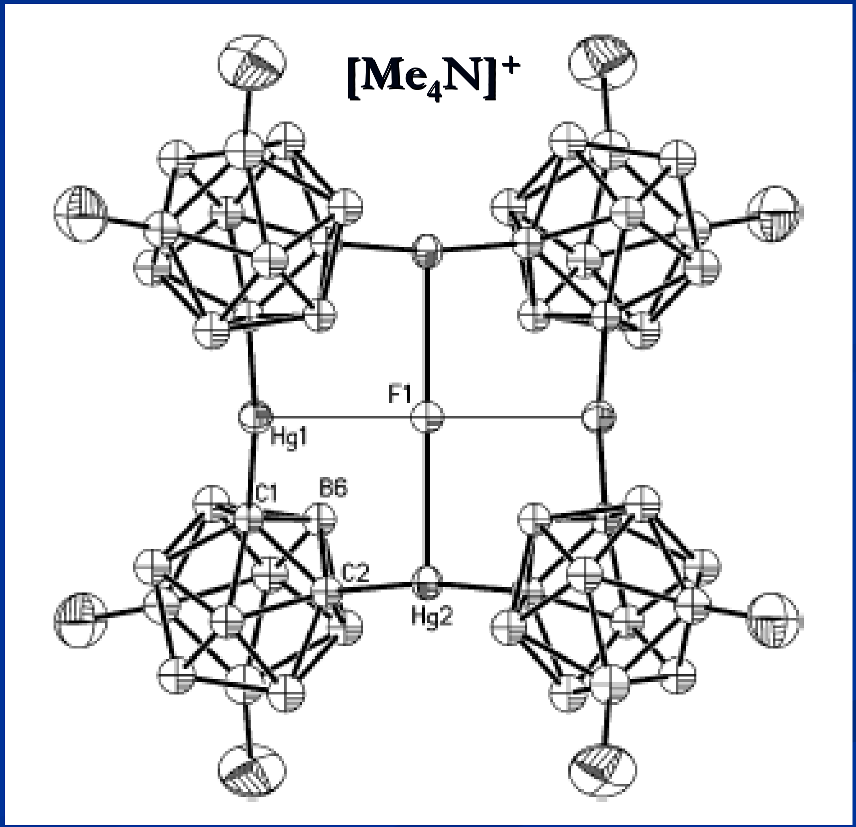
Isotopomer	Pt1	Pt2	Pt3	f_i
A	*	*	*	0.290
B	195	*	*	0.148
C	*	195	*	0.148
D	*	*	195	0.148
E	195	195	*	0.076
F	195	*	195	0.076
G	*	195	195	0.076
H	195	195	195	0.038

Abundance of Isotopomers

Mercuracarborands



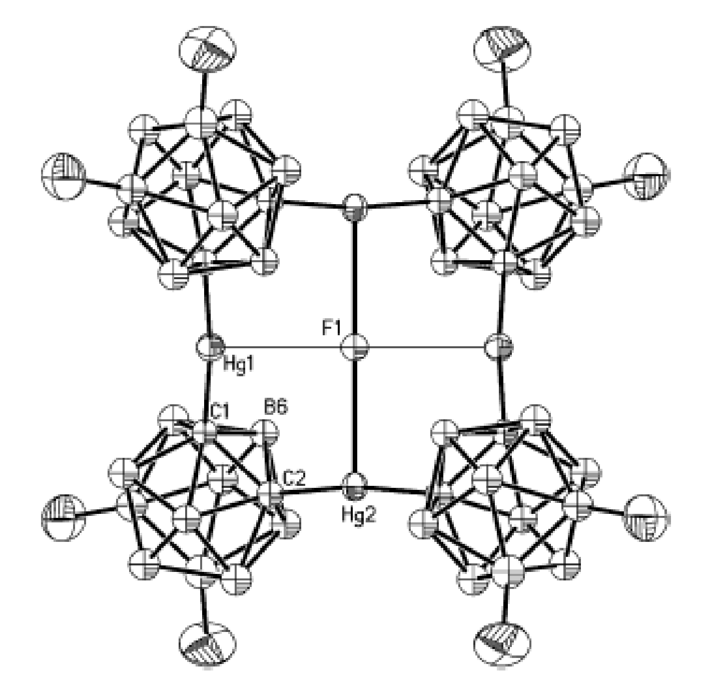
[Me$_4$N]F



Calculation of Abundance of Isotopomers

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

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

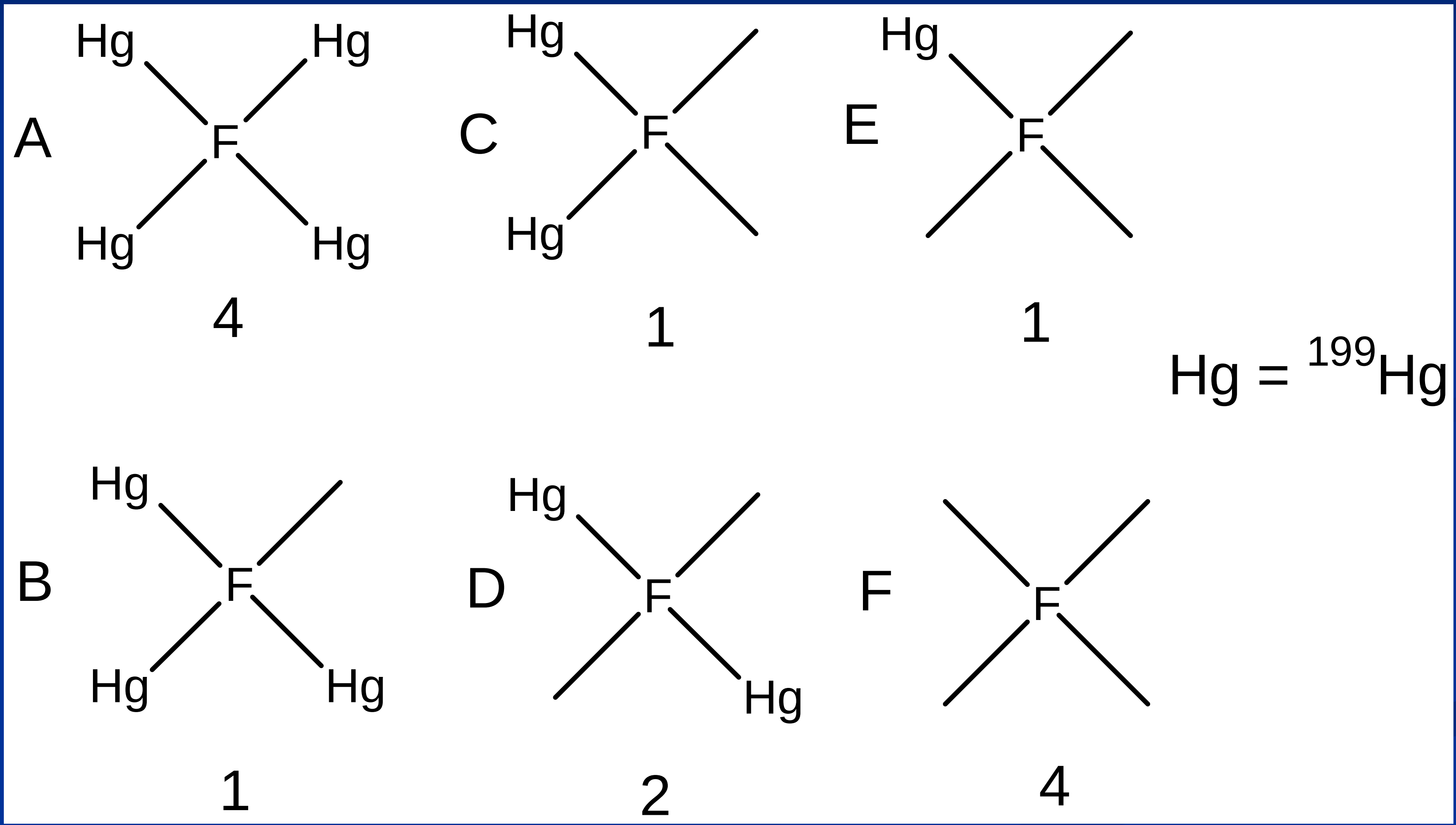


^{19}F NMR
Only coupling to ^{199}Hg observed
No coupling to ^{201}Hg visible

$\sigma = 4$

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

Isotopomers



Isotopomer Abundances

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

isotopomer	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