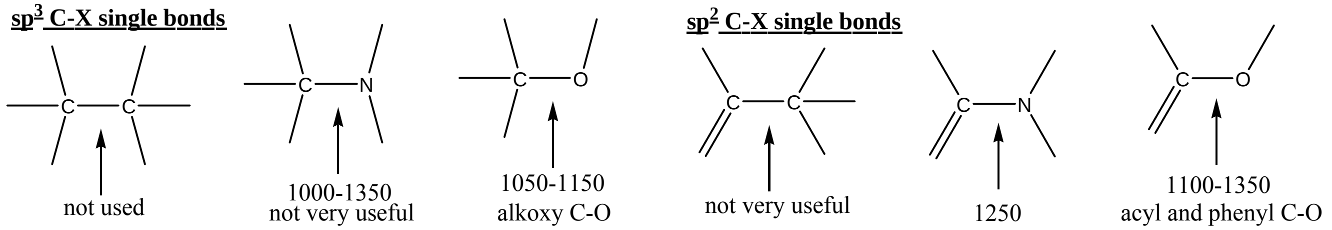
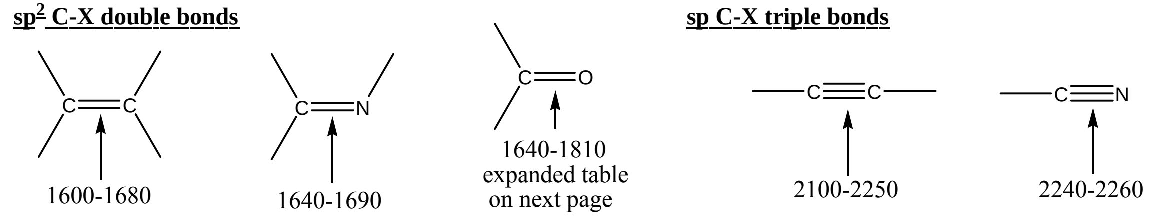
Infrared Tables (short summary of common absorption frequencies)

The values given in the tables that follow are typical values. Specific bands may fall over a range of wavenumbers, cm^{-1}. Specific substituents may cause variations in absorption frequencies. Absorption intensities may be stronger or weaker than expected, often depending on dipole moments. Additional bands may confuse the interpretation. In very symmetrical compounds there may be fewer than the expected number of absorption bands (it is even possible that all bands of a functional group may disappear, i.e. a symmetrically substituted alkyne!). Infrared spectra are generally informative about what functional groups are present, but not always. The ^{1}H and ^{13}C NMR's are often just as informative about functional groups, and sometimes even more so in this regard. Information obtained from one spectroscopic technique should be verified or expanded by consulting the other spectroscopic techniques.

IR Summary - All numerical values in the tables below are given in wavenumbers, cm^{-1}

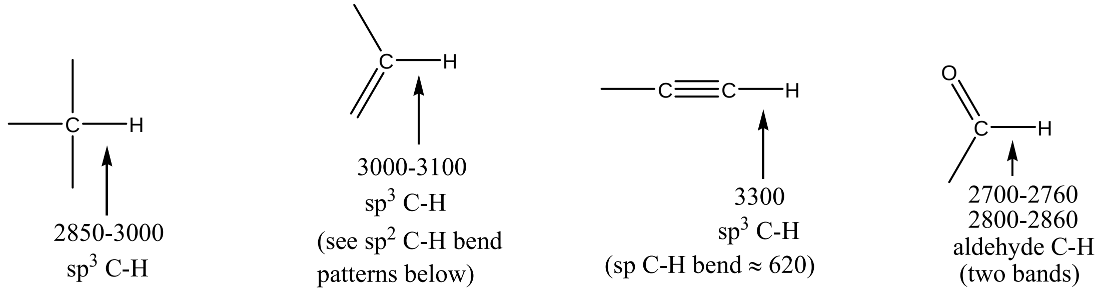
Bonds to Carbon (stretching wave numbers)

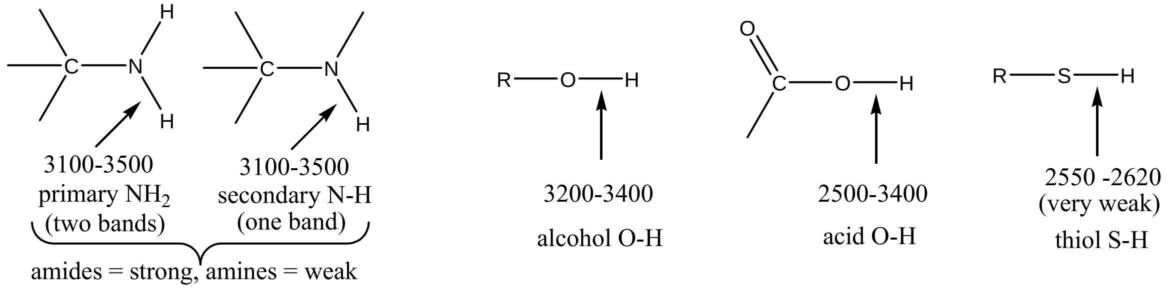




Stronger dipoles produce more intense IR bands and weaker dipoles produce less intense IR bands (sometimes none).

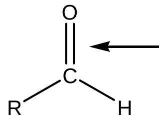
Bonds to Hydrogen (stretching wave numbers)





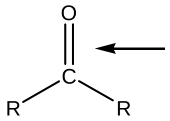
Carbonyl Highlights (stretching wave numbers)

Aldehydes



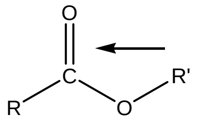
saturated = 1725
conjugated = 1690
aromatic = 1700

Ketones



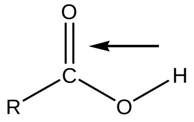
saturated = 1715
conjugated = 1680
aromatic = 1690
6 atom ring = 1715
5 atom ring = 1745
4 atom ring = 1780
3 atom ring = 1850

Esters



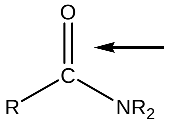
saturated = 1735
conjugated = 1720
aromatic = 1720
6 atom ring = 1735
5 atom ring = 1775
4 atom ring = 1840

Acids



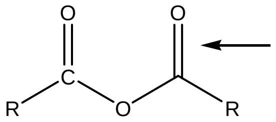
saturated = 1715
conjugated = 1690
aromatic = 1690

Amides



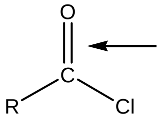
saturated = 1650
conjugated = 1660
aromatic = 1660
6 atom ring = 1670
5 atom ring = 1700
4 atom ring = 1745
3 atom ring = 1850

Anhydrides



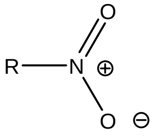
saturated = 1760, 1820
conjugated = 1725, 1785
aromatic = 1725, 1785
6 atom ring = 1750, 1800
5 atom ring = 1785, 1865

Acid Chlorides



saturated = 1800
conjugated = 1770
aromatic = 1770

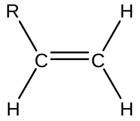
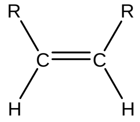
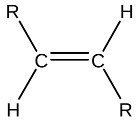
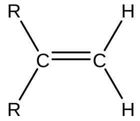
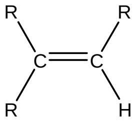
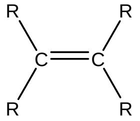
nitro



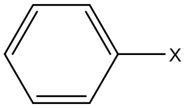
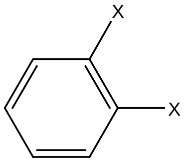
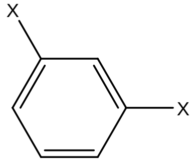
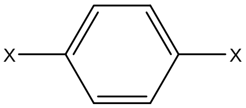
asymmetric = 1500-1600
symmetric = 1300-1390

Very often there is a very weak C=O overtone at approximately 2 x $\bar{\nu}$ (≈3400 cm^{-1}). Sometimes this is mistaken for an OH or NH peak.,

sp^2 C-H bend patterns for alkenes

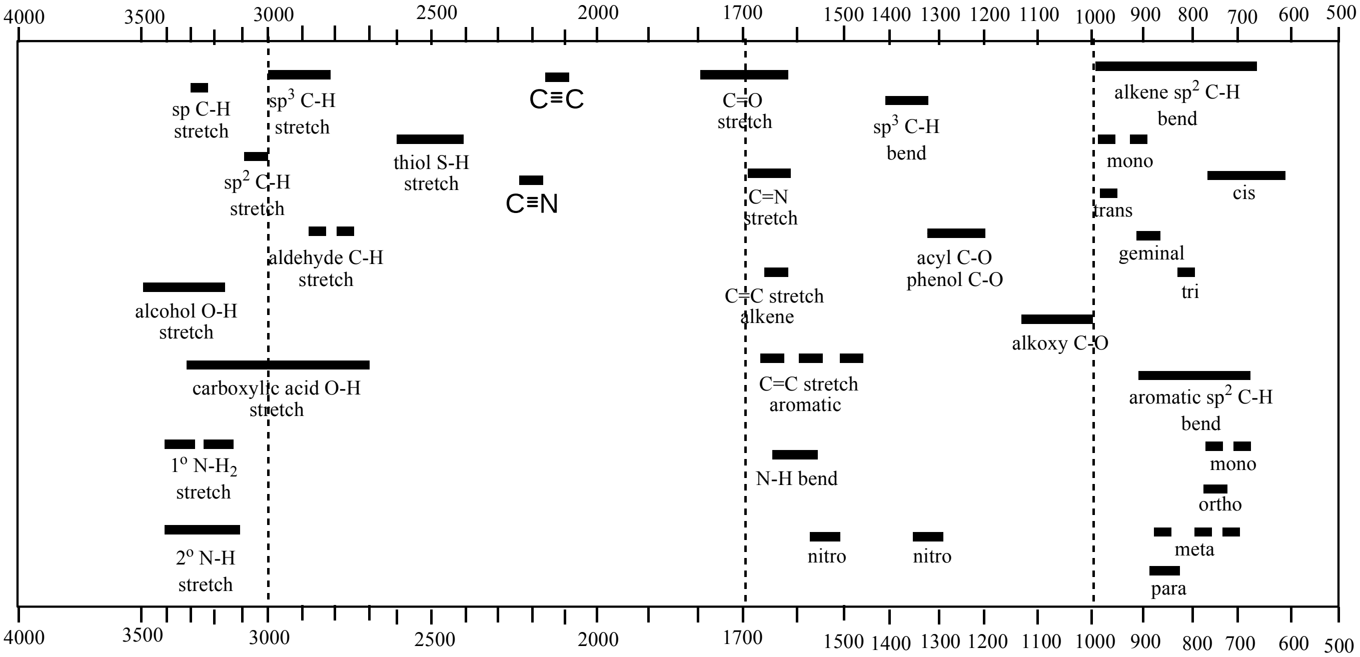
alkene substitution pattern	descriptive alkene term	absorption frequencies (cm^{-1}) due to sp^2 CH bend
	monosubstituted alkene	985-1000 900-920
	cis disubstituted alkene	675-730 (broad)
	trans disubstituted alkene	960-990
	geminal disubstituted alkene	880-900
	trisubstituted alkene	790-840
	tetrasubstituted alkene	none

sp^2 C-H bend patterns for aromatics

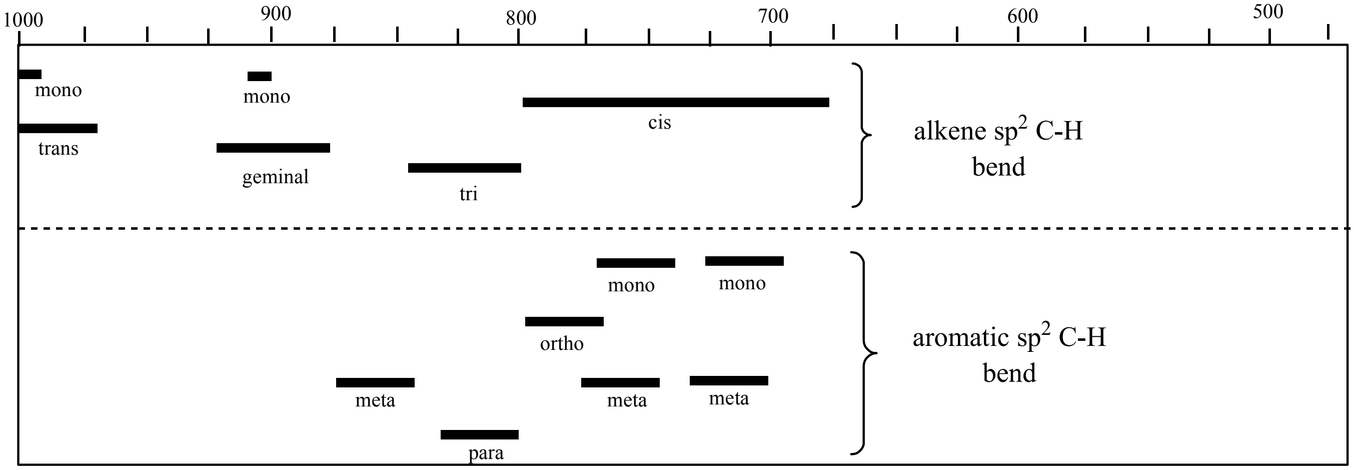
aromatic substitution pattern	descriptive aromatic term	absorption frequencies (cm^{-1}) due to sp^2 CH bend
	monosubstituted aromatic	690-710 730-770
	ortho disubstituted aromatic	735-770
	meta disubstituted aromatic	680-725 750-810 880-900 (sometimes)
	para disubstituted aromatic	790-840

Aromatic compounds have characteristic weak overtone bands that show up between 1650-2000 cm^{-1}). Some books provide pictures for comparison (not here). A strong C=O peak will cover up most of this region.

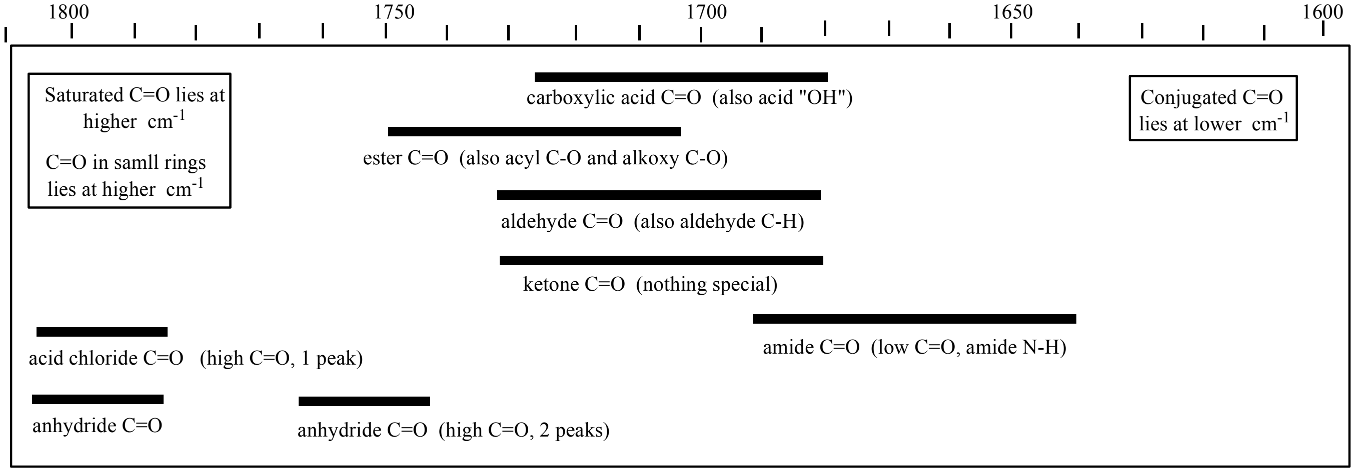
units = cm^{-1}



expansion of alkene & aromatic sp^2 C-H bend region (units = cm^{-1})



expansion of carbonyl (C=O) stretch region (units = cm^{-1})



IR Flowchart to determine functional groups in a compound (all values in cm^{-1}).

IR Spectrum

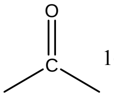
has C=O band ($1650-1800\ cm^{-1}$) very strong

$C\equiv C$

$C\equiv N$

does not have C=O band

aldehydes



1725-1740 (saturated)
1660-1700 (unsaturated)

aldehyde C-H	2860-2800 ← 2760-2700 (both weak)	sometimes lost in sp^3 CH peaks

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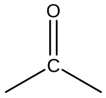
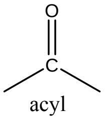
ketones



1710-1720 (saturated)
1680-1700 (unsaturated)
1715-1810 (rings: higher in small rings)

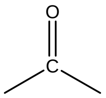
esters - rule of 3



1735-1750 (saturated)
1715-1740 (unsaturated)
1735-1820 (higher in small rings)

acyl C——O	1150-1350 (acyl, strong)
alkoxy C——O	(1000-1150, alkoxy, medium)

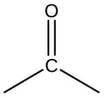
acids



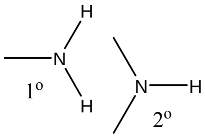
1700-1730 (saturated)
1715-1740 (unsaturated)
1680-1700 (higher in small rings)

acyl C——O	1210-1320 (acyl, strong)
acid O——H	2400-3400, very broad (overlaps C-H stretch)

amides



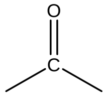
1630-1680 (saturated)
1745 (in 4 atom ring)



3350 & 3180, two bands for 1° amides, one band for 2° amides, stronger than in amines, extra overtone sometimes at 3100

N——H	N-H bend, 1550-1640, stronger in amides than amines

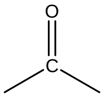
acid chlorides



1800 (saturated)
1770 (unsaturated)

Inductive pull of Cl increases the electron density between C and O.

anhydrides



1760 & 1820 (saturated)
1725-1785 (unsaturated)
two strong bands

acyl C——O	1150-1350 (acyl, strong)

nitriles

$C\equiv N$

≈ 2250
sharp, stronger than alkynes,

a little lower when conjugated

alkynes

$C\equiv C$	2150 (variable intensity)

not present or weak when symmetrically substituted, a little lower when conjugated

sp C-H stretch	3300 sharp, strong
sp C-H bend	620

All IR values are approximate and have a range of possibilities depending on the molecular environment in which the functional group resides. Resonance often modifies a peak's position because of electron delocalization (C=O lower, acyl C-O higher, etc.). IR peaks are not 100% reliable. Peaks tend to be stronger (more intense) when there is a large dipole associated with a vibration in the functional group and weaker in less polar bonds (to the point of disappearing in some completely symmetrical bonds).

Alkene sp^2 C-H bending patterns

monosubstituted alkene (985-1000, 900-920)
geminal disubstituted (960-990)
cis disubstituted (675-730)
trans disubstituted (880-900)
trisubstituted (790-840)
tetrasubstituted (none, no sp^2 C-H)

Aromatic sp^2 C-H bending patterns

monosubstituted (730-770, 690-710)
ortho disubstituted (735-770)
meta disubstituted (880-900,sometimes, 750-810, 680-725)
para disubstituted (790-840)

There are also weak overtone bands between 1660 and 2000, but are not shown here. You can consult pictures of typical patterns in other reference books. If there is a strong C=O band, they may be partially covered up.

alkanes

sp^3 C-H stretch	2850-3000
sp^3 C-H bend	1460 & 1380
C——C	not useful

alkenes

sp^2 C-H stretch	3000-3100
sp^2 C-H bend	650-1000 (see table for spectral patterns)
C═C	1600-1660 weak or not present

aromatics

sp^2 C-H stretch	3050-3150
sp^2 C-H bend	690-900 (see table), overtone patterns between 1660-2000
C═C	1600 & 1480 can be weak

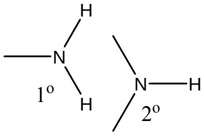
alcohols

alcohol O——H	3600-3500
alkoxy C——O	1000-1260 ($3^o > 2^o > 1^o$)

thiols

thiol S——H	≈ 2550 (weak) (easy to overlook)

amines



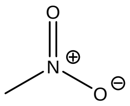
3300 - 3500, two bands for 1° amines, one band for 2° amines, weaker than in amides,

N——H	N-H bend, 1550-1640, stronger in amides than amines
N——C	1000-1350 (uncertain)

ethers

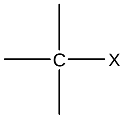
alkoxy C——O	1120 (alphatic) 1040 & 1250 (aromatic)

nitro compounds



1500-1600, asymmetric (strong)
1300-1390, symmetric (medium)

carbon-halogen bonds



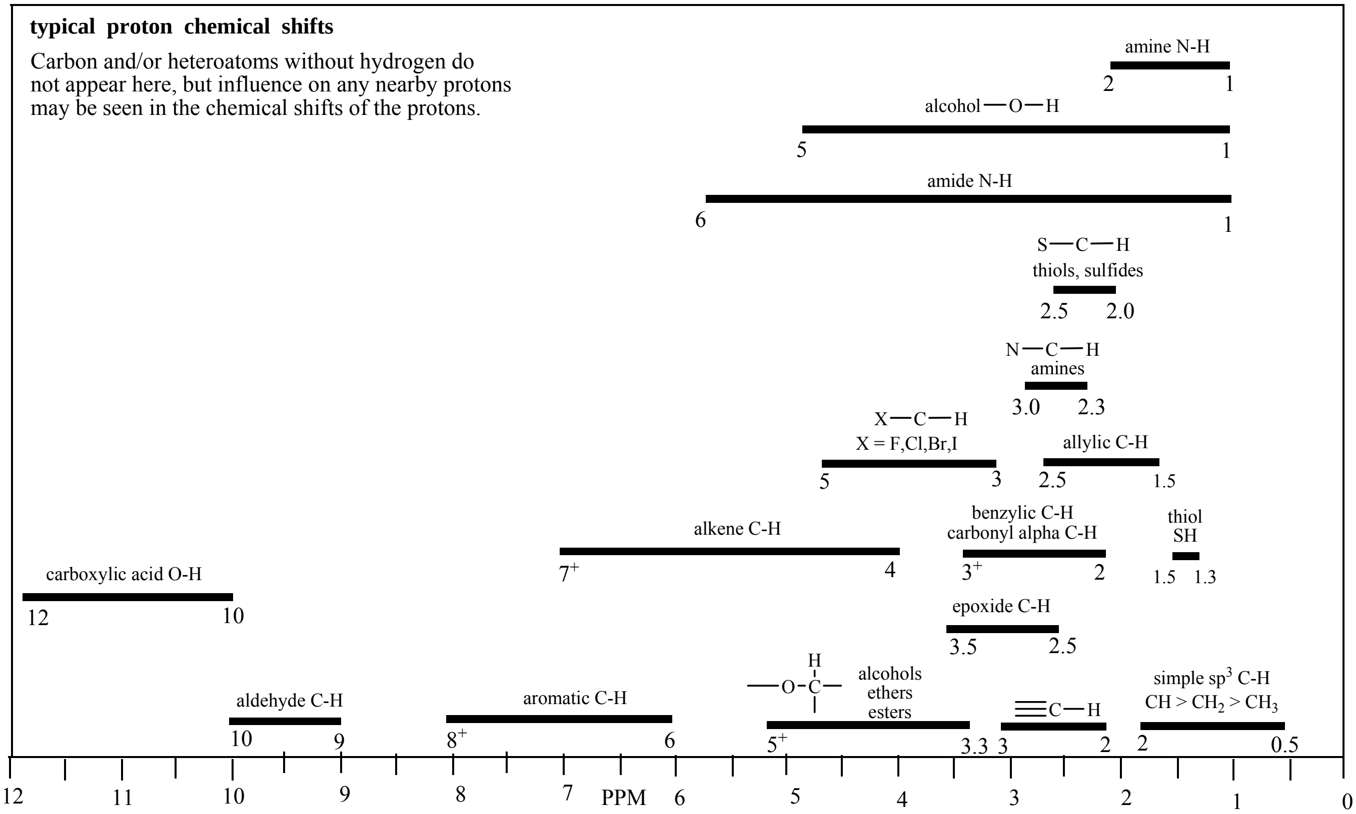
usually not very useful

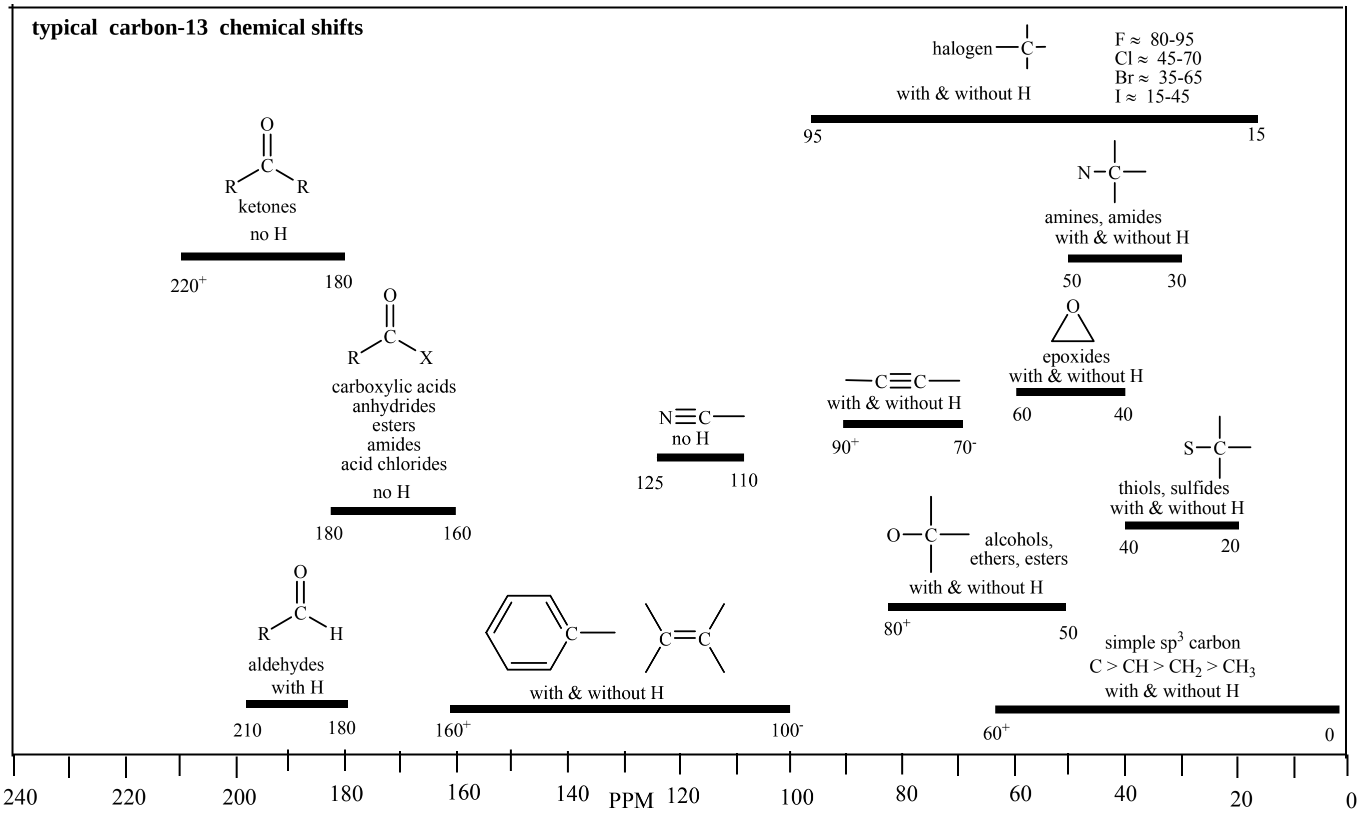
X = F, Cl, Br, I

Typical ^{1}H and ^{13}C NMR chemical shift values.

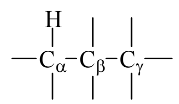
deshielding side = less electron rich
(inductive & resonance)

shielding side = more electron rich
(inductive & resonance)





Calculation of chemical shifts for protons at sp^3 carbons



$$-\overset{H}{\underset{|}{C_\alpha}}-\underset{|}{C_\beta}-\underset{|}{C_\gamma}-$$

Estimation of sp^3 C-H chemical shifts with multiple substituent parameters for protons within 3 C's of consideration.

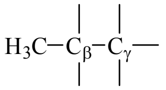
α = directly attached substituent, use these values when the hydrogen and substituent are attached to the same carbon
β = once removed substituent, use these values when the hydrogen and substituent are on adjacent (vicinal) carbons
γ = twice removed substituent, use these values when the hydrogen and substituent have a 1,3 substitution pattern

X = substituent	α	β	γ
R- (alkyl)	0.0	0.0	0.0
R_2C=CR- (alkenyl)	0.8	0.2	0.1
RCC- (alkynyl)	0.9	0.3	0.1
Ar- (aromatic)	1.4	0.4	0.1
F- (fluoro)	3.2	0.5	0.2
Cl- (chloro)	2.2	0.5	0.2
Br- (bromo)	2.1	0.7	0.2
I- (iodo)	2.0	0.9	0.1
HO- (alcohol)	2.3	0.3	0.1
RO- (ether)	2.1	0.3	0.1
epoxide	1.5	0.4	0.1
R_2C=CRO- (alkenyl ether)	2.5	0.4	0.2
ArO- (aromatic ether)	2.8	0.5	0.3
RCO_2- (ester, oxygen side)	2.8	0.5	0.1
$ArCO_2$- (aromatic ester, oxygen side)	3.1	0.5	0.2
$ArSO_3$- (aromatic sulfonate, oxygen)	2.8	0.4	0.0
H_2N- (amine nitrogen)	1.5	0.2	0.1
RCONH- (amide nitrogen)	2.1	0.3	0.1
O_2N- (nitro)	3.2	0.8	0.1
HS- (thiol, sulfur)	1.3	0.4	0.1
RS- (sulfide, sulfur)	1.3	0.4	0.1
OHC- (aldehyde)	1.1	0.4	0.1
RCO- (ketone)	1.2	0.3	0.0
ArCO- (aromatic ketone)	1.7	0.3	0.1
HO_2C- (carboxylic acid)	1.1	0.3	0.1
RO_2C- (ester, carbon side)	1.1	0.3	0.1
H_2NOC- (amide, carbon side)	1.0	0.3	0.1
ClOC- (acid chloride)	1.8	0.4	0.1
NC- (nitrile)	1.1	0.4	0.2
RSO- (sulfoxide)	1.6	0.5	0.3
RSO_2- (sulfone)	1.8	0.5	0.3

Starting value and equations for CH_3's

$\delta CH_3 = 0.9 + \alpha$ $H_3C—\alpha$

$\delta CH_3 = 0.9 + \Sigma(\beta + \gamma)$



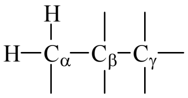
$$H_3C-\underset{|}{\overset{|}{C_\beta}}-\underset{|}{\overset{|}{C_\gamma}}-$$

Σ is the summation symbol for all substituents considered

Starting value and equation for CH_2's

In a similar manner we can calculate chemical shifts for methylenes (CH_2) using the following formula

$\delta CH_2 = 1.2 + \Sigma(\alpha + \beta + \gamma)$



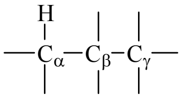
$$H-\overset{H}{\underset{|}{C_\alpha}}-\underset{|}{\overset{|}{C_\beta}}-\underset{|}{\overset{|}{C_\gamma}}-$$

Σ is the summation symbol for all substituents considered

Starting value and equation for CH's

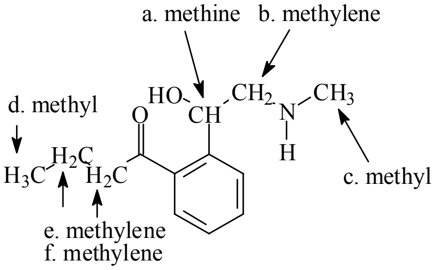
In a similar manner we can calculate chemical shifts for methines (CH) using the following formula

$\delta CH = 1.5 + \Sigma(\alpha + \beta + \gamma)$



$$-\overset{H}{\underset{|}{C_\alpha}}-\underset{|}{\overset{|}{C_\beta}}-\underset{|}{\overset{|}{C_\gamma}}-$$

Σ is the summation symbol for all substituents considered



Calculations are generally close to actual chemical shifts for a single substituent, but are less reliable as the number of substituent factors goes up. Multiple substituent factors tend to overestimate an actual chemical shift.

a. methine = $1.5 + (1.4)_\alpha + (2.3)_\alpha + (0.2)_\beta = 5.4$ ppm
actual = 5.2

b. methylene = $1.2 + (1.5)_\alpha + (0.4)_\beta + (0.3)_\beta = 3.4$ ppm
actual = 3.0 and 3.2

c. methyl = $0.9 + (1.5)_\alpha = 2.4$ ppm
actual = 2.6

d. methyl = $0.9 + (0.1)_\alpha = 1.0$ ppm
actual = 1.0

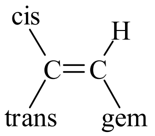
e. methylene = $1.2 + (0.3)_\alpha = 1.5$ ppm
actual = 1.7

f. methylene = $1.2. + (1.7)_\alpha = 2.9$ ppm
actual = 2.9

Estimated chemical shifts for protons at alkene sp^2 carbons

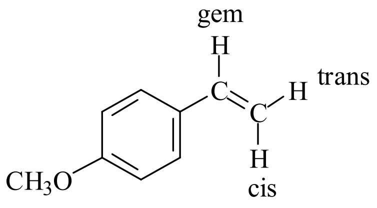
Substituent	α_{geminal}	α_{cis}	α_{trans}
H- Hydrogen	0.0	0.0	0.0
R- Alkyl	0.5	-0.2	-0.3
$C_6H_5CH_2$- Benzyl	0.7	-0.2	-0.2
X-CH_2- Halomethyl	0.7	0.1	0.0
(H)/ROCH$_2$- alkoxymethyl	0.6	0.0	0.0
$(H)_2/R_2NCH_2$- aminomethyl	0.6	-0.1	-0.1
$RCOCH_2$- α-keto	0.7	-0.1	-0.1
$NCCH_2$- α-cyano	0.7	-0.1	-0.1
$R_2C{=}CR$- Alkenyl	1.2	0.0	0.0
C_6H_5- Phenyl	1.4	0.4	-0.1
F- Fluoro	1.5	-0.4	-1.0
Cl- Chloro	1.1	0.2	0.1
Br- Bromo	1.1	0.4	0.6
I- Iodo	1.1	0.8	0.9
RO- akoxy (ether)	1.2	-1.1	-1.2
RCO_2- O-ester	2.1	-0.4	-0.6
$(H)_2/R_2N$- N-amino	0.8	-1.3	-1.2
RCONH- N-amide	2.1	-0.6	-0.7
O_2N- Nitro	1.9	1.3	0.6
RS- Thiol	1.1	-0.3	-0.1
OHC- Aldehyde	1.0	1.0	1.2
ROC- Ketone	1.1	0.9	0.7
HO_2C- C-acid	0.8	1.0.	03
RO_2C- C-ester	0.8	1.0	0.5
H_2NOC- C-amide	0.4	1.0	0.5
NC- Nitrile	0.3	0.8	0.6

Substitution relative to calculated "H"



$$\delta(\text{ppm}) = 5.2 + \alpha_{\text{gem}} + \alpha_{\text{cis}} + \alpha_{\text{trans}}$$

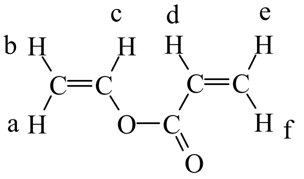
Example Calculation



δ gem = 5.2 + 1.4 = 6.6
actual = 6.6

δ trans = 5.2 - 0.1 = 5.1
actual = 5.1

δ cis = 5.2 + 0.4 = 5.7
actual = 5.6



$\delta_a = 5.2 + (-0.4) = 4.8$
actual = 4.9 (J = 14, 1.6 Hz)

$\delta_b = 5.2 + (-0.6) = 4.6$
actual = 4.6 (J = 6, 1.6 Hz)

$\delta_c = 5.2 + 2.1 = 7.3$
actual = 7.4 (J = 14, 6 Hz)

$\delta_d = 5.2 + 0.8 = 6.0$
actual = 6.2 (J = 18, 11 Hz)

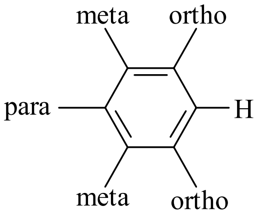
$\delta_e = 5.2 + 0.5 = 5.7$
actual = 5.8 (J = 11, 1.4 Hz)

$\delta_f = 5.2 + 1.0 = 6.2$
actual = 6.4 (J = 18, 1.4 Hz)

Estimated chemical shifts for protons at aromatic sp^2 carbons

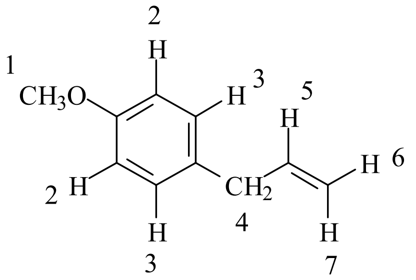
Substituent	α ortho	α meta	α para
H- Hydrogen	0.0	0.0	0.0
CH_3- Methyl	-0.2	-0.1	-0.2
$ClCH_2$- Cholromethyl	0.0	0.0	0.0
Cl_3C- Halomethyl	0.6	0.1	0.1
$HOCH_2$- Hydroxymethyl	-0.1	-0.1	-0.1
$R_2C=CR$- Alkenyl	0.1	0.0	-0.1
C_6H_5- Phenyl	1.4	0.4	-0.1
F- Fluoro	-0.3	0.0	-0.2
Cl- Chloro	0.0	0.0	-0.1
Br- Bromo	0.2	-0.1	0.0
I- Iodo	0.4	-0.2	0.9
HO- Hydroxy	-0.6	-0.1	-0.5
RO- Alkoxy	-0.5	-0.1	-0.4
RCO_2- O-ester	-0.3	0.0	-0.1
$(H)_2/R_2N$- N-amino	-0.8	-0.2	-0.7
RCONH- N-amide	0.1	-0.1	-0.3
O_2N- Nitro	1.0	0.3	0.4
RS- thiol/sulfide	-0.1	-0.1	-0.2
OHC- Aldehyde	0.6	0.2	0.3
ROC- Ketone	0.6	0.1	0.2
HO_2C- C-acid	0.9	0.2	0.3
RO_2C- C-ester	0.7	0.1	0.2
H_2NOC- C-amide	0.6	0.1	0.2
NC- Nitrile	0.4	0.2	0.3

Substitution relative to calculated "H"



$$\delta(\text{ppm}) = 7.3 + \alpha_{\text{ortho}} + \alpha_{\text{meta}} + \alpha_{\text{para}}$$

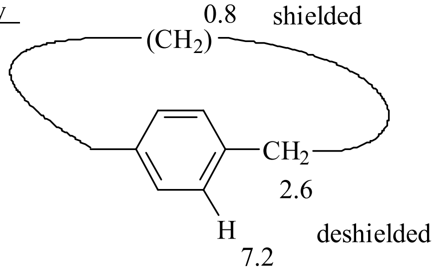
Example Calculation



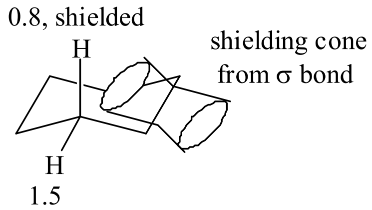
1. $\delta\ (CH_3) = 0.9 + 2.8 = 3.7$
   actual = 3.8
2. $\delta\ (2) = 7.3 + (-0.5)_{\text{ortho}} + (-0.1)_{\text{para}} = 6.7$
   actual = 6.8
3. $\delta\ (3) = 7.3 + (-0.2)_{\text{ortho}} + (-0.4)_{\text{para}} = 6.7$
   actual = 7.1
4. $\delta\ (CH_2) = 1.2 + (0.8)\alpha + (1.4)\alpha = 3.4$
   actual = 3.3
5. $\delta\ (5) = 5.2 + (0.7)_{\text{gem}} = 5.9$
   actual = 5.9
6. $\delta\ (6) = 5.2 + (-0.2)_{\text{trans}} = 5.0$
   actual = 5.1
7. $\delta\ (7) = 5.2 + (-0.2)_{\text{cis}} = 5.0$
   actual = 5.1

Real Examples of Combination Effects on Chemical Shifts

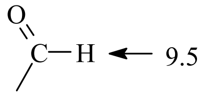
π bond anisotropy

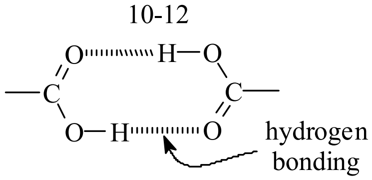


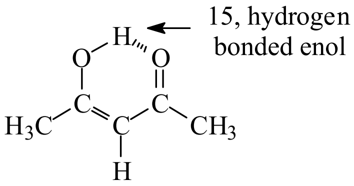
σ bond example too



electronegativity and π bond







electronegative substituent and distance from protons

$—O–CH_2CH_2CH_2CH_2CH_3$ ↑ 3.6 1.5 1.3 1.3 0.9

$CH_3–Cl$ ↑ 3.0

$CH_3CH_2–Cl$ ↑ 1.3

$CH_3CH_2CH_2–Cl$ ↑ 1.0

$CH_3CH_2CH_2CH_2–Cl$ ↑ 0.9

$CH_3CH_2–R$ ↑ 0.9

multiple substituents

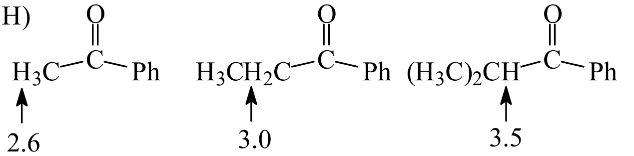
CH_4 ↑ 0.2 ← $\Delta = 2.8$ → CH_3Cl ↑ 3.0 ← $\Delta = 2.3$ → CH_2Cl_2 ↑ 5.3 ← $\Delta = 1.9$ → CHCl3 ↑ 7.2 ← Δ = ? → CCl_4 ↑ ? (oops)

substituents at methyl (CH_3), methylene (CH_2) and methine (CH)

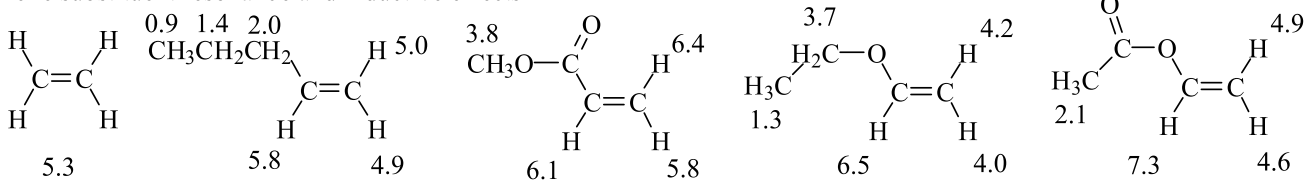
CH_3Cl ↑ 3.0

CH_3CH_2Cl ↑ 3.5

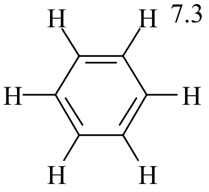
$(CH_3)_2CHCl$ ↑ 4.1



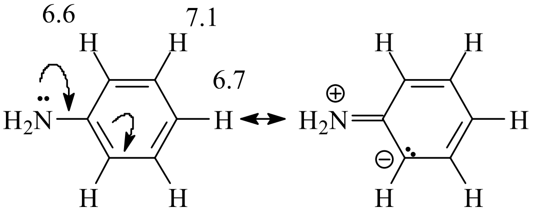
alkene substituent resonance and inductive effects



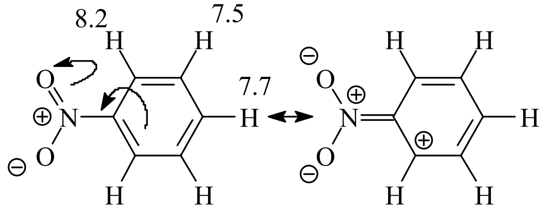
aromatic resonance and inductive effects



π bond anisotropy produces deshielding effect on aromatic protons.



Extra electron density via resonance produces shielding effect on aromatic protons, especially at ortho/para positions.



Withdrawal of electron density via resonance produces deshielding effect on aromatic protons, especially at ortho/para positions.

sp C-H

$H—C≡C—H$ 2.4

$R—C≡C—H$ 1.9

$Ar—C≡C—H$ 3.0

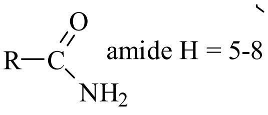
$RO—H$ alcohol H = 1-5

$ArO—H$ phenol H = 4-10

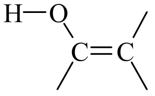
$RS—H$ thiol H = 1-2.5

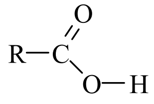
$ArO—H$ aromatic thiol H = 3-4

$R_2N—H$ amine H = 1-5



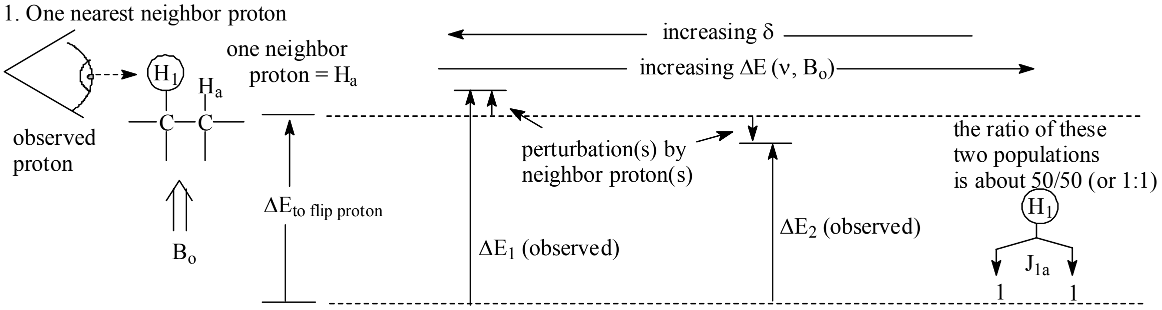
enol H = 10-17





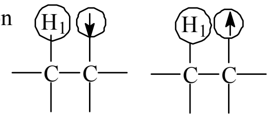
acid H = 10-13

1. One nearest neighbor proton



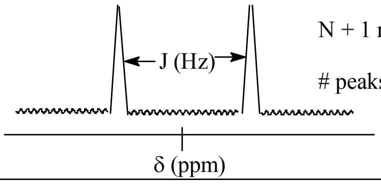
the ratio of these two populations is about 50/50 (or 1:1)

Protons in this environment have a small cancellation of the external magnetic field, B$_o$, and produce a smaller energy transition by that tiny amount.



Protons in this environment have a small additional increment added to the external magnetic field, B$_o$, and produce a higher energy transition by that tiny amount.

J = coupling constant small difference in energy due to differing neighbor's spin (in Hz)

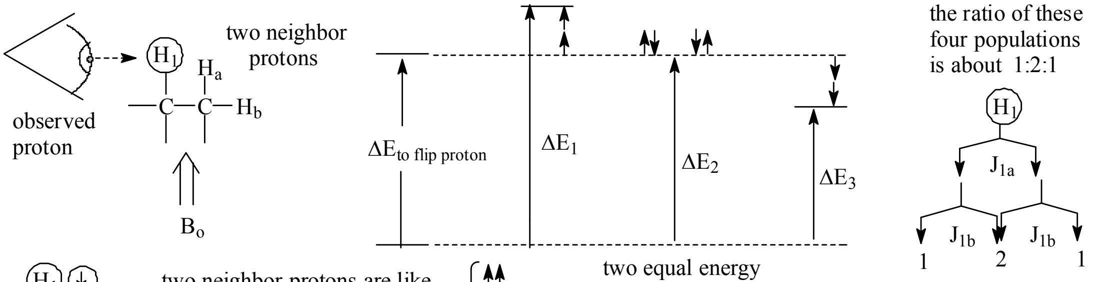


N + 1 rule (N = # neighbors)

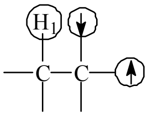
peaks = N + 1 = 1 + 1 = 2 peaks

---

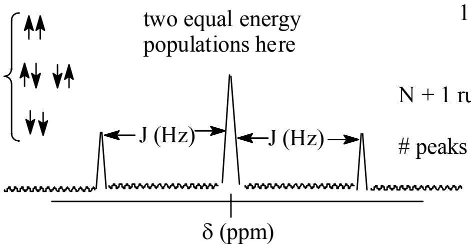
2. Two nearest neighbor protons (both on same carbon or one each on separate carbons)



the ratio of these four populations is about 1:2:1



two neighbor protons are like two small magnets that can be arranged four possible ways (similar to flipping a coin twice)



N + 1 rule (N = # neighbors)

peaks = N + 1 = 2 + 1 = 3 peaks

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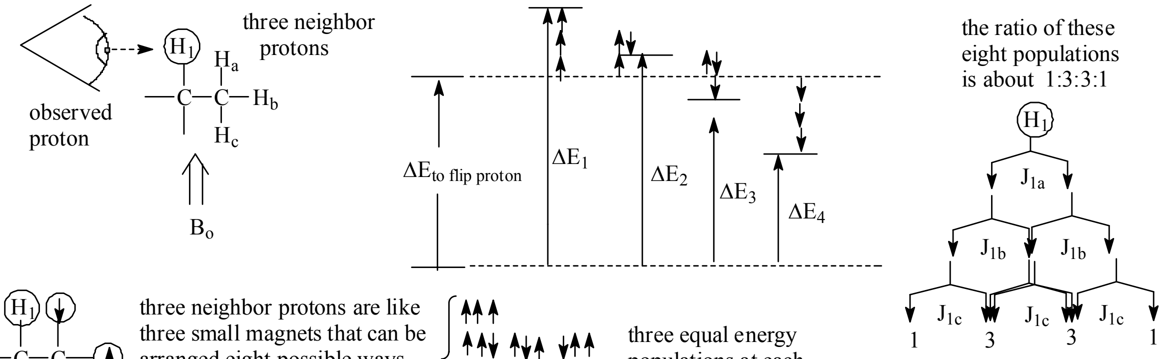
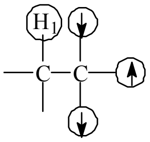
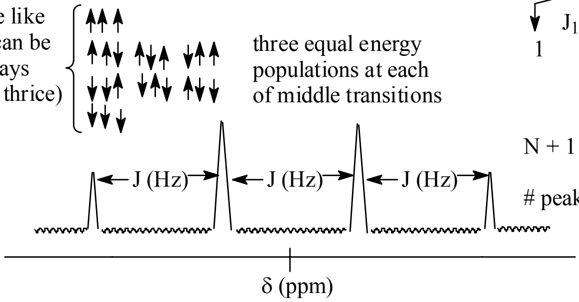
3. Three nearest neighbor protons (on same carbon, or two on one and one on another, or one each on separate carbons)



the ratio of these eight populations is about 1:3:3:1



three neighbor protons are like three small magnets that can be arranged eight possible ways (similar to flipping a coin thrice)



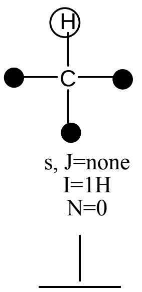
N + 1 rule (N = # neighbors)

peaks = N + 1 = 3 + 1 = 4 peaks

Splitting patterns when the N+1 rule works (common, but not always true)

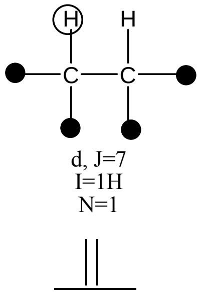
● = group without any coupled proton(s)

N = 0



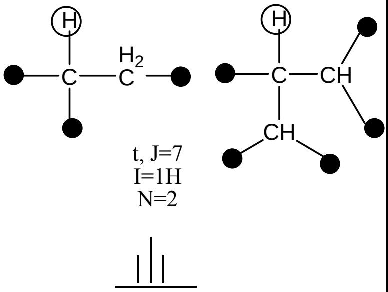
δ = calc or exp

N = 1



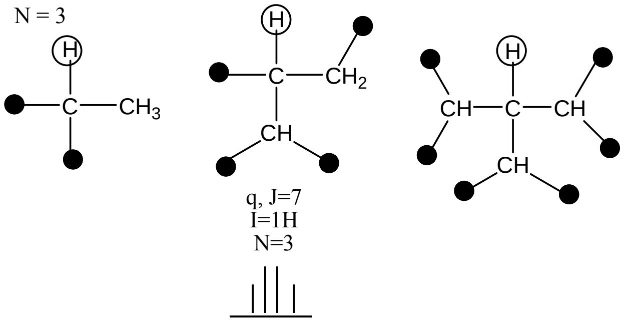
δ = calc or exp

N = 2



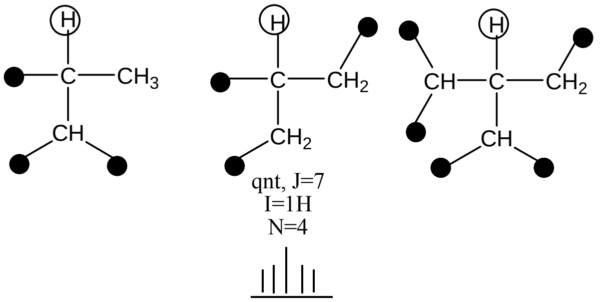
δ = calc or exp

N = 3



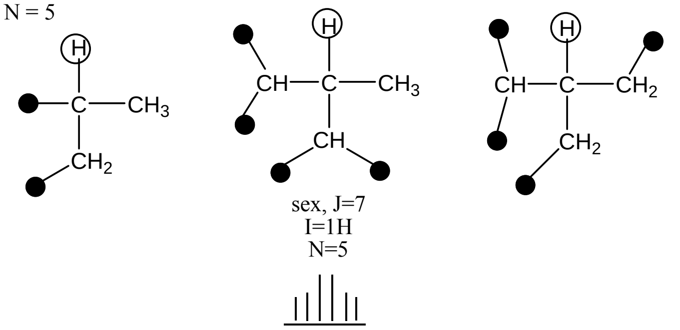
δ = calc or exp

N = 4



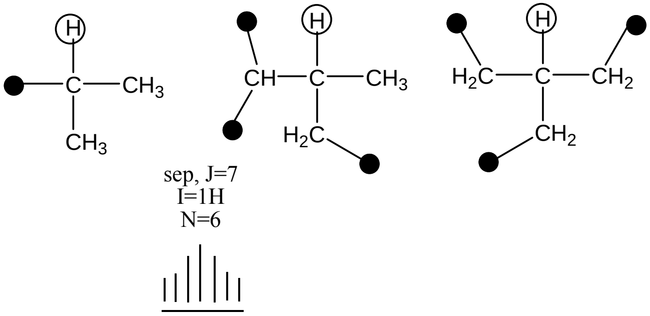
δ = calc or exp

N = 5



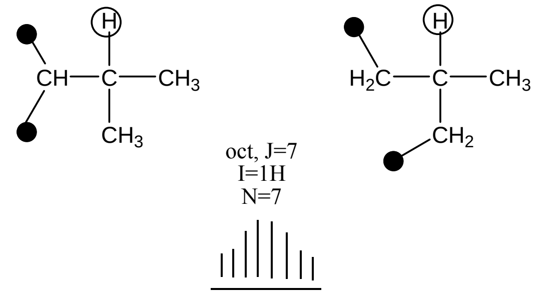
δ = calc or exp

N = 6



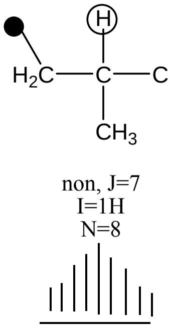
δ = calc or exp

N = 7



δ = calc or exp

N = 8



δ = calc or exp

Pascal's triangle = coefficients of variable terms in binomial expansion $(x + y)^n$, n = integer

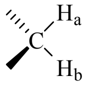
Multiplets when the N + 1 rule works (all J values are equal).

s = singlet	1	1 peak = 100%
d = doublet	1 1	1 peak = 50%
t = triplet	1 2 1	1 peak = 25%
q = quartet	1 3 3 1	1 peak = 12%
qnt = quintet	1 4 6 4 1	1 peak = 6%
sex = sextet	1 5 10 10 5 1	1 peak = 3%
sep = septet	1 6 15 20 15 6 1	1 peak = 1.5%
o = octet	1 7 21 35 35 21 7 1	1 peak = 0.8%

relative sizes of peaks in multiplets (% edge peak shown)

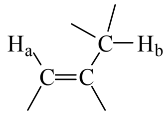
Combinations or these are possible.
dd = doublet of doublets; ddd = doublet of doublet of doublets; dddd = doublet of doublet of doublet of doublets; dt = doublet of triplets
td = triplet of doublets; etc.

Typical Coupling Constants



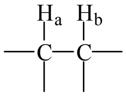
Range	Typical
0-30 Hz	14 Hz

geminal protons - can have different chemical shifts and split one another if they are diastereotopic



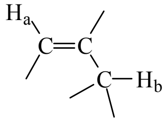
Range	Typical
0-3 Hz	1 Hz

cis / allylic coupling, notice through 4 bonds



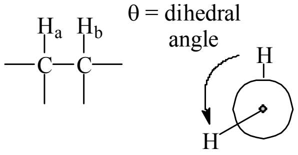
Range	Typical
6-8 Hz	7 Hz

vicinal protons are on adjacent atoms, when freely rotating coupling averages out to about 7 Hz



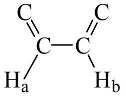
Range	Typical
0-3 Hz	1 Hz

trans / allylic coupling, notice through 4 bonds



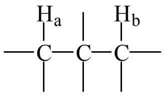
Range	Typical
0-12 Hz	7 Hz

depends on dihedral angle, see plot of Karplus equation



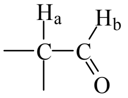
Range	Typical
9-13 Hz	10 Hz

sp^2 vicinal coupling (different π bonds)



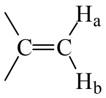
Range	Typical
0-1 Hz	0 Hz

protons rarely couple through 4 chemical bonds unless in a special, rigid shapes (i.e. W coupling)



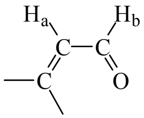
Range	Typical
1-3 Hz	2 Hz

sp^3 vicinal aldehyde coupling



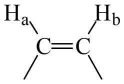
Range	Typical
0-3 Hz	2 Hz

sp^2 geminal coupling



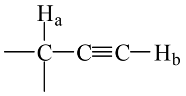
Range	Typical
5-8 Hz	6 Hz

sp^2 vicinal aldehyde coupling



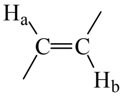
Range	Typical
5-11 Hz	10 Hz

sp^2 cis (acylic) coupling (always smaller than the trans isomer)



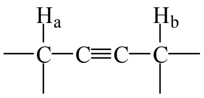
Range	Typical
2-3 Hz	2 Hz

sp / propargylic coupling notice through 4 bonds



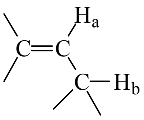
Range	Typical
11-19 Hz	17 Hz

sp^2 trans coupling (always larger than the cis isomer)



Range	Typical
2-3 Hz	3 Hz

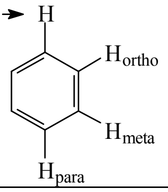
bis-propargylic coupling notice through 5 bonds



Range	Typical
4-10 Hz	7 Hz

sp^2 / sp^3 vicinal coupling

ortho, meta and para coupling to this proton --→ H



	Range	Typical
ortho	6-10 Hz	9 Hz
meta	2-3 Hz	2 Hz
para	0-1 Hz	0 Hz

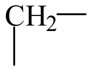
When J values are less than 1 Hz, it is often difficult to resolve them and a peak may merely appear wider and shorter.

Similar chemical shift information presented in a different format. Remember, proton decoupled carbons appear as singlets. When carbons are coupled to their hydrogens, carbons follow the N+1 rule. Methyls = q, methylenes = t, methines = d, and carbons without hydrogen appear as singlets = s. DEPT provides the same information. Carbon chemical shifts are spread out over a larger range than proton chemical shifts (they are more dispersed), so it is less likely that two different carbon shifts will fall on top of one another. The relative positions of various types of proton and carbon shifts have many parallel trends (shielded protons tend to be on shielded carbons, etc.)

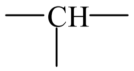
Simple alkane carbons

$CH_3—$

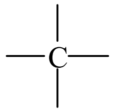
d ≈ 0 - 30 ppm
(q)


$CH_2—$

d ≈ 20 - 40 ppm
(t)


$—CH—$

d ≈ 30 - 50 ppm
(d)


$—C—$

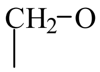
d ≈ 30 - 60 ppm
(s)

---

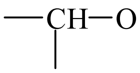
sp^3 carbon next to oxygen

$CH_3{-}O$

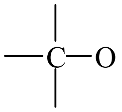
d ≈ 50 - 60 ppm
(q)


$CH_2{-}O$

d ≈ 55 - 80 ppm
(t)


$—CH—O$

d ≈ 60 - 80 ppm
(d)


$—C—O$

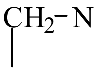
d ≈ 70 - 90 ppm
(s)

---

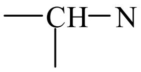
sp^3 carbon next to nitrogen

$CH_3{-}N$

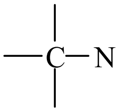
d ≈ 10 - 50 ppm
(q)


$CH_2{-}N$

d ≈ 35 - 55 ppm
(t)


$—CH—N$

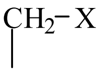
d ≈ 50 - 70 ppm
(d)


$—C—N$

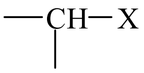
d ≈ 50 - 70 ppm
(s)

---

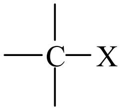
sp^3 carbon next to bromine or chlorine
(X = Cl, Br)


$CH_2{-}X$

d ≈ 25 - 50 ppm
(t)


$—CH—X$

d ≈ 60 - 80 ppm
(d)


$—C—X$

d ≈ 60 - 80 ppm
(s)

---

sp carbon (alkynes) $—C{\equiv}C—$

δ ≈ 70 - 90 ppm

sp carbon (nitriles) $—C{\equiv}N$

δ ≈ 110 - 125 ppm

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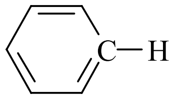
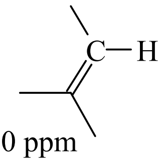
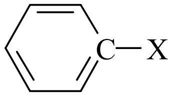
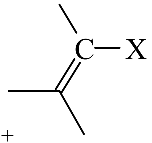
sp^2 carbon (alkenes and aromatics)

δ ≈ 100 - 140 ppm
simple sp^2 carbon
resonance donation moves δ lower,
resonance withdrawal moves δ higher

δ ≈ 140 - 160^+ ppm
sp^2 carbon attached to an electronegative atom (X = oxygen, nitrogen, halogen) or C_β carbon conjugated with a carbonyl group

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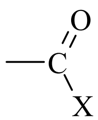
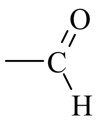
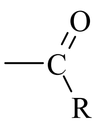


δ ≈ 160 - 180 ppm
carboxyl carbons
(acids, esters, amides)
(s)



δ ≈ 180 - 210 ppm
aldehyde carbons, lower values when conjugated
(d)



δ ≈ 180 - 220 ppm
ketone carbons, lower values when conjugated
(s)

Calculations of alkane ^{13}C chemical shifts not listed above.

sp^3 Carbon Chemical Shift Calculations

Calculations for sp^3 carbon ^{13}C chemical shifts of functionalized carbon skeletons can be performed starting from the actual shifts found in the corresponding alkane skeleton, and introducing corrections factors based on the functionality present in the molecule. This assumes that the alkane ^{13}C shifts are available, which is why several examples are provided below.

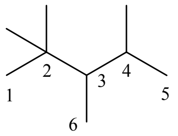
Examples of C_n alkanes as possible starting points for calculation ^{13}C shifts in ppm.

Steric Corrections for sp^3 carbon chemical shift calculations

The calculated carbon atom is: ↓	The attached C_α carbons are:			
	primary	secondary	tertiary	quaternary
primary	0	0	-1.1	-3.4
secondary	0	0	-2.5	-7.5
tertiary	0	-3.7	-9.5	-15.0
quaternary	-1.5	-8.4	-15.0	-25.0

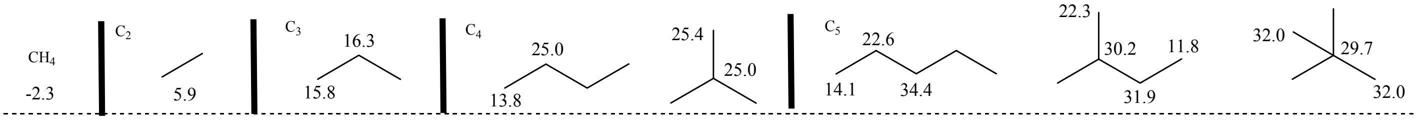
Approximate ^{13}C shift calculation from scratch.

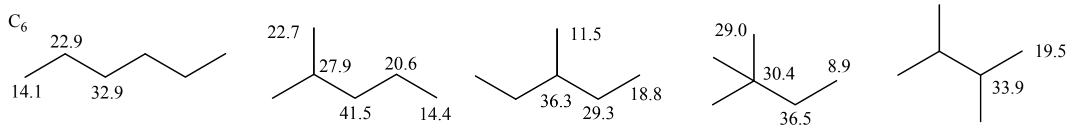
$$\boxed{\delta_C = -(2) + 9x(\#\alpha + \#\beta) - 2x(\#\gamma) + \text{steric corrections}}$$

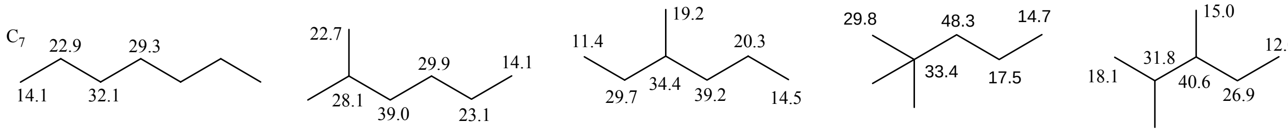


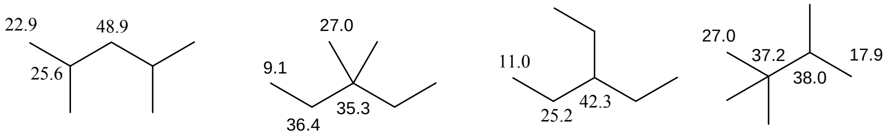
C1 = -2 + 9(1+3) - 2(2) + (-3) = 29 (actual = 28.3)
C2 = -2 + 9(4+2) - 2(2) + [3x(-1.5)+(-15.0)] = 28 (actual = 34.0)
C3 = -2 + 9(3+5) - 0(2) + [(-9.5)+(-15.0)] = 45 (actual = 47.9)
C4 = -2 + 9(3+2) - 3(2) + (-9.5) = 27 (actual = 27.2)
C5 = -2 + 9(1+2) - 2(2) + (-1) = 20 (actual = 19.5)
C6 = -2 + 9(1+2) - 5(2) + (-1) = 14 (actual = 8.5)

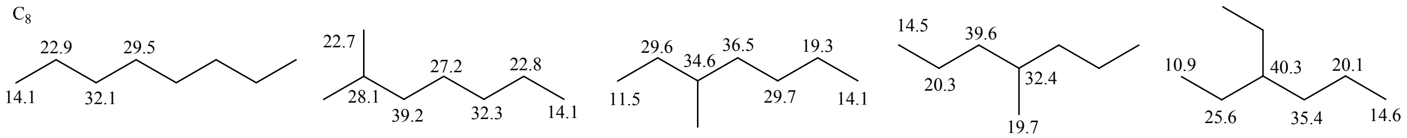
^{13}C shifts for various carbon alkane skeletons - useful starting points for calculating sp3 carbon chemical shifts

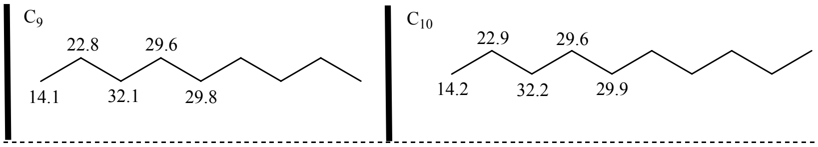


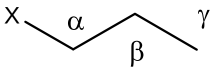


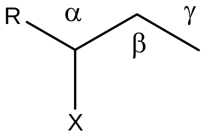


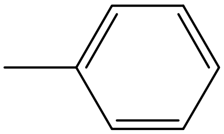


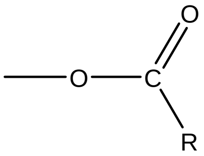
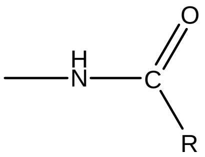


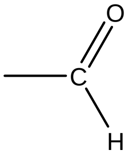
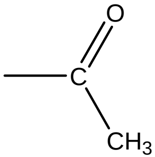
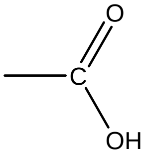


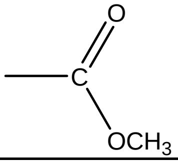
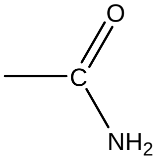
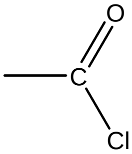




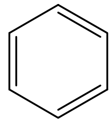
Substituent = X	X is attached to a terminal carbon atom (ppm)			X is attached to an internal carbon atom (ppm)		
	C_α correction	C_β correction	C_γ correction	C_α correction	C_β correction	C_γ correction
$-CH_3$	9	9	-2	6	8	-2
$-CH_2CH_3$	18	7	-2	9	6	-2
$-CH(CH_3)_2$	26	4	-2	14	3	-2
$-C(CH_3)_3$	32	2	-2	20	1	-2
$-\underset{H}{C}=CH_2$	20	6	-1	15	5	-1
$-C\equiv CH$	5	5	-4	2	6	-4
	23	9	-2	17	7	-2

Substituent = X	X is attached to a terminal carbon atom (ppm)			X is attached to an internal carbon atom (ppm)		
	C_α correction	C_β correction	C_γ correction	C_α correction	C_β correction	C_γ correction
$-OH$	48	10	-6	44	7	-4
$-OR$	60	7	-6	57	5	-6
 $-O-C(=O)R$	51	6	-6	49	5	-6
$-NH_2$	28	10	-5	24	8	-5
$-NH(CH_3)$	38	8	-5	32	5	-4
$-N(CH_3)_2$	45	5	-5	37	3	-4
 $-NH-C(=O)R$	26	7	-5	21	5	-5
$-NO_2$	62	5	-5	58	2	-5

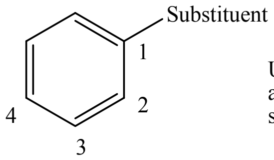
Substituent = X	X is attached to a terminal carbon atom (ppm)			X is attached to an internal carbon atom (ppm)		
	C_α correction	C_β correction	C_γ correction	C_α correction	C_β correction	C_γ correction
—F	70	8	-7	67	5	-7
—Cl	31	10	-5	36	8	-5
—Br	20	10	-4	28	10	-4
—I	-7	11	-2	7	11	-2
	30	0	-3	24	-1	-3
	31	1	-3	26	0	-3
	22	2	-3	18	1	-3

Substituent = X	X is attached to a terminal carbon atom (ppm)			X is attached to an internal carbon atom (ppm)		
	C_α correction	C_β correction	C_γ correction	C_α correction	C_β correction	C_γ correction
	20	2	-3	16	2	-3
	25	3	-3	19	2	-3
—C≡N	3	3	-3	3	3	-3
	33	2	-3	30	2	-3
—SH	11	10	-3	12	8	-3
—SR	22	8	-3	20	6	-3

Additional starting point for calculating ^{13}C chemical shifts (ppm) of substituted benzene rings (just a few possibilities)



128 ppm starting point for benzene carbon

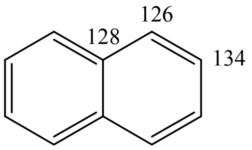


Use correction term for carbon atom in relative position to the substituent. Start with 128 ppm.

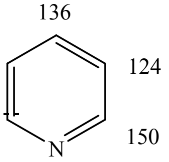
Substituent	Z_1	Z_2	Z_3	Z_4
-H	0	0	0	0
$-CH_3$	9	1	0	-3
$-CH_2CH_3$	12	-1	0	-3
$-CH_2CH_2CH_3$	10	0	0	-3
$-CH_2CH_2CH_2CH_3$	11	0	0	-3
$-CH(CH_3)_2$	20	-2	0	-3
$-C(CH_3)_3$	19	-3	0	-3
$-CH_2F$	8	-1	0	0
$-CH_2Cl$	9	0	0	0
$-CH_2Br$	9	1	0	0
$-CH_2I$	11	-1	0	-1
$-CH_2OH$	12	-1	0	-1
$-CH_2NH_2$	15	-1	0	-2
$-CH_2NO_2$	2	2	1	1
$-CH_2CN$	2	0	-1	-1
$-CH_2SH$	12	-1	0	-2
$-CH_2CHO$	7	1	0	-1
$-CH_2COCH_3$	6	1	0	-2
$-CH_2CO_2H$	6	1	0	-1
$-CH_2{=}CH_2$	13	-3	0	-1
-CCH	-6	4	0	0
$-C_6H_5$	8	-1	0	-1
-F	34	-13	2	-4
-Cl	5	0	1	2
-Br	-5	3	2	-1
-I	-31	9	2	-1

Substituent	Z_1	Z_2	Z_3	Z_4
-OH	29	-13	1	-7
$-OCH_3$	34	-14	1	-8
$-OC_6H_5$	28	-11	0	-7
$-NH_2$	18	-13	1	-10
$-NHCOCH_3$	10	-8	0	-4
-NHOH	22	-13	-2	-5
$-NHNH_2$	23	-16	1	-10
-N=N-R	22	-6	0	-3
-NO	37	-8	1	7
$-NO_2$	20	-5	1	6
-SH	4	1	0	-3
$-SCH_3$	10	-2	0	-4
$-S(O)CH_3$	18	-5	1	2
$-SO_2CH_3$	12	-1	1	5
$-SO_2Cl$	16	-2	1	7
-CN	-16	3	1	4
-CHO	8	1	0	6
$-COCH_3$	9	0	0	4
$-CO_2H$	2	2	0	5
$-CO_2CH_3$	2	1	0	4
$-CONH_2$	5	-1	0	3
-COCl	11	0	0	-3
-Li	-43	-13	2	3
-MgBr	-36	-11	3	4

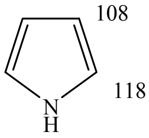
Starting points for other common ring systems. (ppm). No correction terms included for substituents.



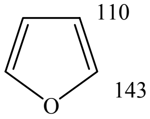
naphathalene



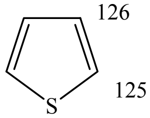
pyridine



pyrrole



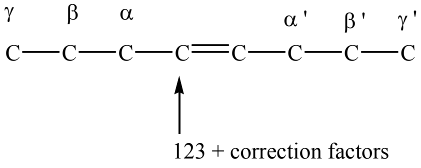
furan



thiophene

Additional starting point for calculating ^{13}C chemical shifts (ppm) of substituted alkenes (just a few possibilities)

123 ppm starting point for alkene carbon

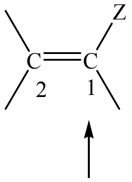


increments for directly attached carbon atoms

$\alpha = 11$ $\alpha' = -8$
$\beta = 5$ $\beta' = -2$
$\gamma = -2$ $\gamma' = 2$

steric corrections

for each pair of cis-α,α ' substituents	-1
for each pair of geminal-α,α substituents	-5
for each pair of geminal-α,α 'substituents	3
if one or more β sutstituents are present	2



δ_C = 123 ppm + Z_i

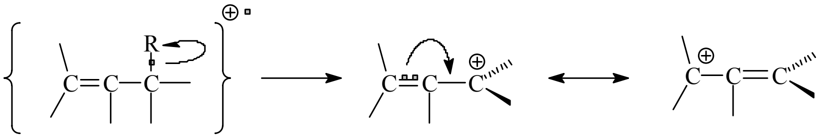
Effect of substituents on alkene ^{13}C shifts (ppm)

Substituent	Z_1	Z_2
-H	0	0
$-CH_3$	13	-7
$-CH_2CH_3$	17	-10
$-CH_2CH_2CH_3$	16	-9
$-CH(CH_3)_2$	23	-12
$-C(CH_3)_3$	26	-15
$-CH_2Cl$	10	-6
$-CH_2Br$	11	-5
$-CH_2I$	14	-4
$-CH_2OH$	14	-8
$-CH{=}CH_2$	14	-7
-CCH	-6	6
$-C_6H_5$	12	-11

Substituent	Z_1	Z_2
-F	24	-34
-Cl	3	-6
-Br	-9	-1
-I	-38	7
$-OCH_3$	29	-39
$-O_2CCH_3$	18	-27
$-N(CH_3\ )_2$	28	-32
$-NO_2$	22	-1
-CN	-15	14
$-SCH_2CH_3$	9	-13
-CHO	15	14
$-COCH_3$	14	5
$-CO_2H$	5	10
-COCl	8	14

Common fragmentation patterns in mass spectroscopy

1. Branch next to a π bond



radical cation

π bond of an alkene or an aromatic

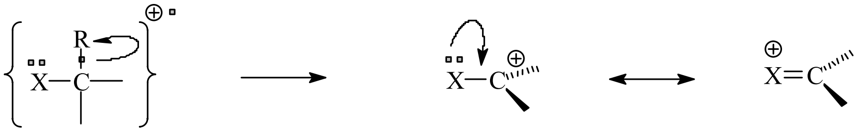
Pi electrons partially fill in loss of electrons at carbocation site via resonance. This is common fragmentation for alkenes and aromatics

Characteristic carboncation stability also applies.

$3^o R^{\oplus} > 2^o R^{\oplus} > 1^o R^{\oplus} > CH_3^{\oplus}$

---

2. Branch next to an atom with a lone pair of electrons



radical cation

X lone pair electrons partially fill in loss of electrons at carbocation site via resonance. This is a common fragmentation for any atom that has a lone pair of electrons (oxygen = alcohol, ether, ester; nitrogen = amine, amide, sulfur = thiol or sulfide, etc.). Alcohols often lose water (M-18) and primary amines can lose ammonia (M-17).

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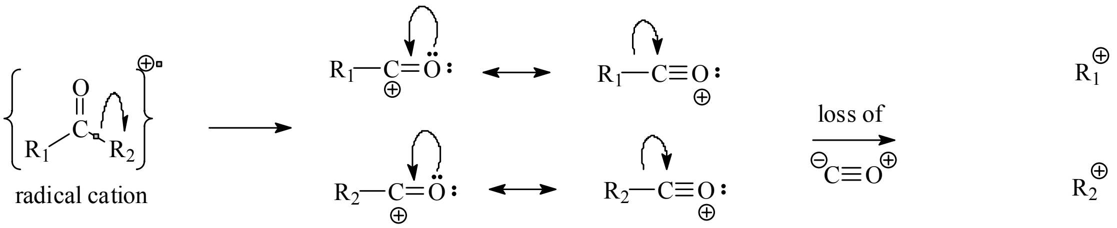
3. Branch next to a carbonyl (C=O) bond…and possible subsequent loss of carbon monoxide, CO



radical cation

R_1 or R_2 can be lost from aldehydes, ketones, acids, esters, amides...etc.

An oxygen lone pair partially fill in the loss of electrons at the carbocation site via resonance. This is a common fragmentation pattern for any carbonyl compound and can occur from either side, though some are more common than others.

subsequent loss of CO is possible after α fragmentation so not only can you see loss of an α branch you can see the mass of an α branch.

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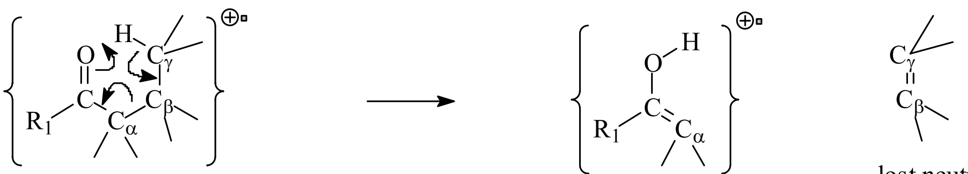
4. McLafferty Rearrangement



radical cation

still a radical cation

lost neutral fragment

Positive charge can be on either fragment, which typically have an even mass.

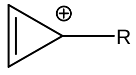
α = alpha position
β = beta position
γ = gama position

This is another common fragmentation pattern for carbonyl compounds (and other pi systems as well: alkenes, aromatics, alkynes, nitriles, etc.). If the pi bond has at least 3 additional nonhydrogen atoms attached and a hydrogen on the "gama" atom, the branch can curve around to a comfortable 6 atom arrangement and the pi bond can pick up a hydrogen atom and cut off a fragment between the C_α and C_β positions. The positive charge can be seen on either fragment and usually the fragments have an even mass (unless there is an odd number of nitrogen atoms).

Knowing these few fragmentation patterns will allow you to make many useful predictions and interpretations. Loss of small molecules, via elimination is common: H_2O = 18, H_2S = 34, CH_3OH = 32, C_2H_5OH = 46, NH_3 = 17, CH_3CO_2H = 62, HF = 20, HCl = 36/38, HBr = 80/82, etc.

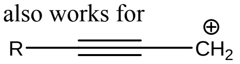
A sampling of unusual and/or miscellaneous peaks that are commonly seen, (even when they don't make sense).

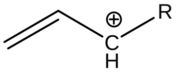
$CH_3^{\oplus}$ = 15
$CH_3CH_2^{\oplus}$ = 29
$C_3H_7^{\oplus}$ = 43
$C_4H_9^{\oplus}$ = 57
$C_5H_{11}^{\oplus}$ = 71
$C_6H_{13}^{\oplus}$ = 85



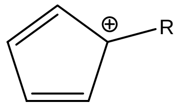
mass = 39 (R = H)
53 (R = CH_3)
67 (R= CH_2CH_3)

also works for

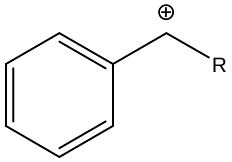




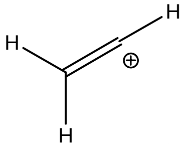
mass = 41 (R = H)
55 (R = CH_3)
69 (R= CH_2CH_3)



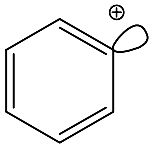
mass = 65 (R = H)
79 (R = CH_3)
93 (R= CH_2CH_3)



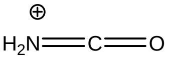
mass = 91 (R = H)
105 (R = CH_3)
119 (R= CH_2CH_3)



mass = 27

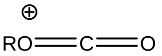


mass = 77



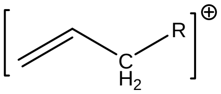
$H_2N{=}C{=}O^{\oplus}$

mass = 44

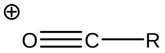


$RO{=}C{=}O^{\oplus}$

mass = 45 (R = H)
59 (R = CH_3)
73 (R= CH_2CH_3)



mass = 42 (R = H)
56 (R = CH_3)
70 (R= CH_2CH_3)



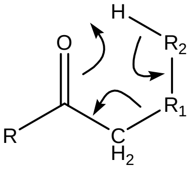
$O{\equiv}C{-}R^{\oplus}$

mass = 29 (R = H)
43 (R = CH_3)
57 (R= CH_2CH_3)
71 (R = C_3H_7)
105 (R = C_6H_5)

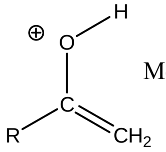
Loss of small molecules via elimination reactions.

	H_2O	H_2S	CH_3OH	C_2H_5OH	NH_3	CH_3CO_2H	HF	HCl	HBr
mass =	18	34	32	46	17	62	20	36 38	80 82

McLafferty Possibilities

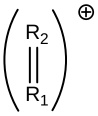


Notice!
even masses
→



McLafferty

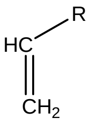
mass = 44 (R = H)
58 (R = CH_3)
72 (R= CH_2CH_3)
86 (R = C_3H_7)



variable mass,

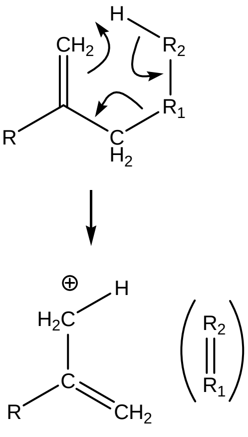
(can sometimes see
cation on this side too)

=

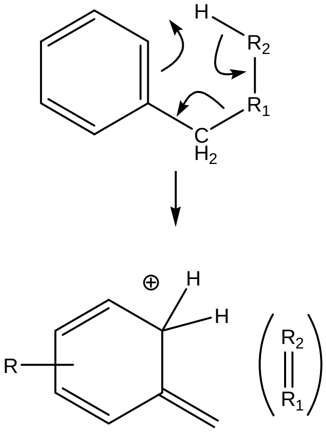


mass = 28 (R = H)
42 (R = CH_3)
56 (R= CH_2CH_3)
70 (R = C_3H_7)

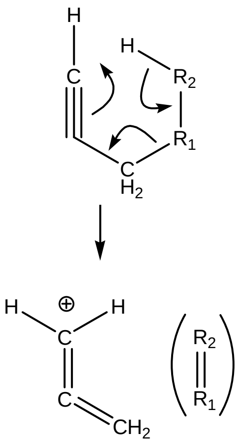
Similar Patterns



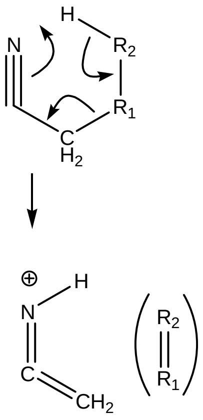
mass = 42 (R = H)
56 (R = CH_3)
70 (R= CH_2CH_3)
84 (R = C_3H_7)



mass = 92 (R = H)
106 (R = CH_3)
120 (R= CH_2CH_3)
134 (R = C_3H_7)



mass = 40 (R = H)
54 (R = CH_3)
68 (R= CH_2CH_3)
82 (R = C_3H_7)



mass = 41 (R = H)
55 (R = CH_3)
69 (R= CH_2CH_3)
83 (R = C_3H_7)