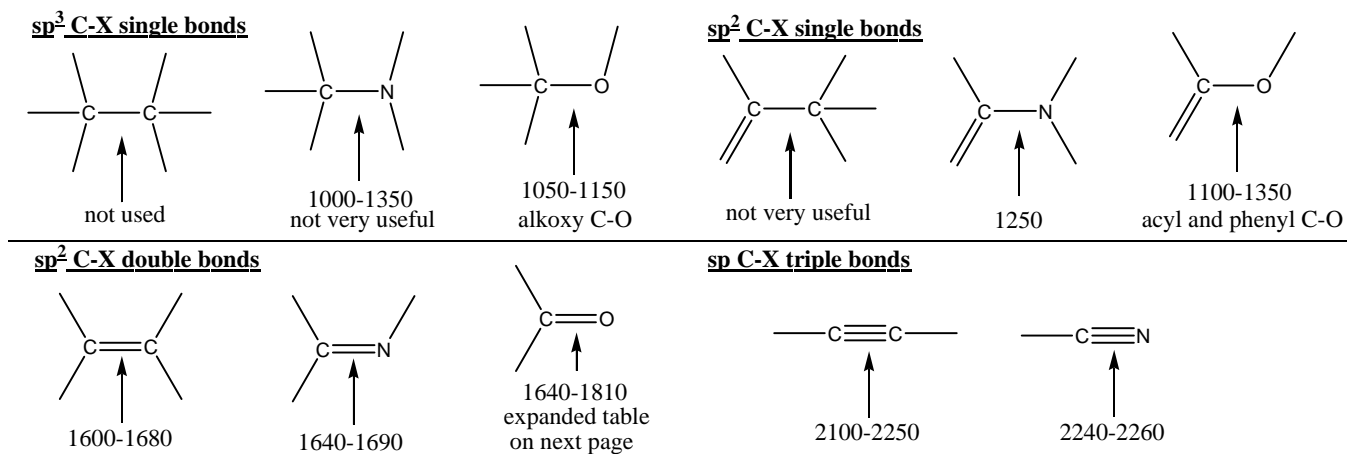## Infrared Tables (short summary of common absorption frequencies)

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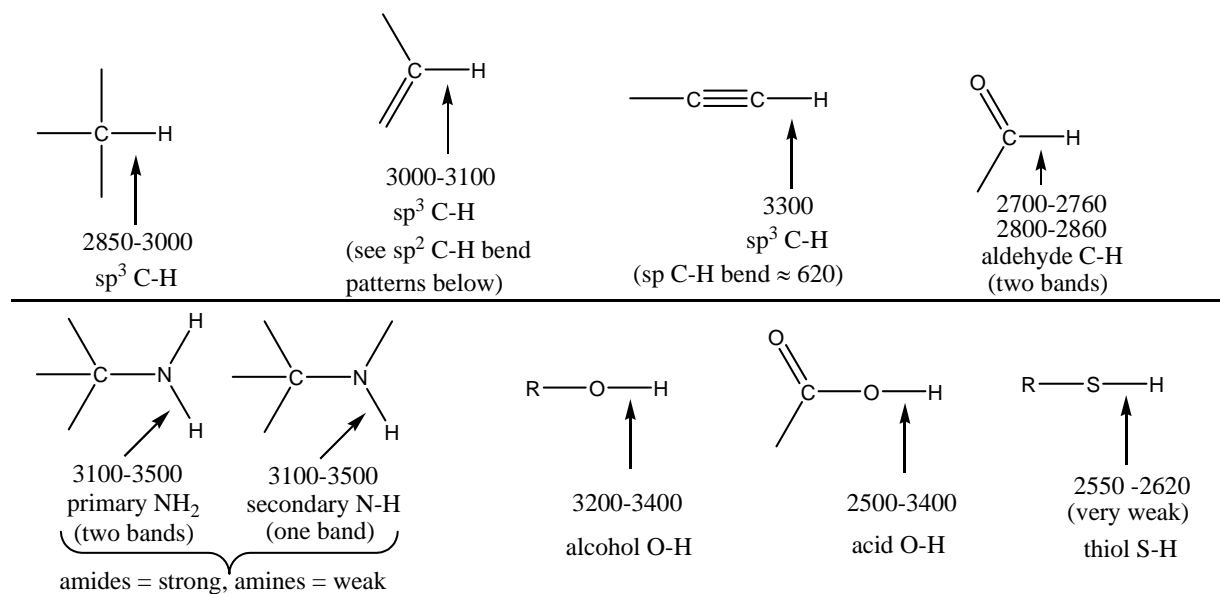
IR Summary - All numerical values in the tables below are given in wavenumbers, cm^{-1}

Bonds to Carbon (stretching wave numbers)

sp^3 C-X single bonds

not used

1000-1350
not very useful

1050-1150
alkoxy C-O

sp^2 C-X single bonds

not very useful

1250

1100-1350
acyl and phenyl C-O

sp^2 C-X double bonds

1600-1680

1640-1690

1640-1810
expanded table
on next page

sp C-X triple bonds

2100-2250

2240-2260

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

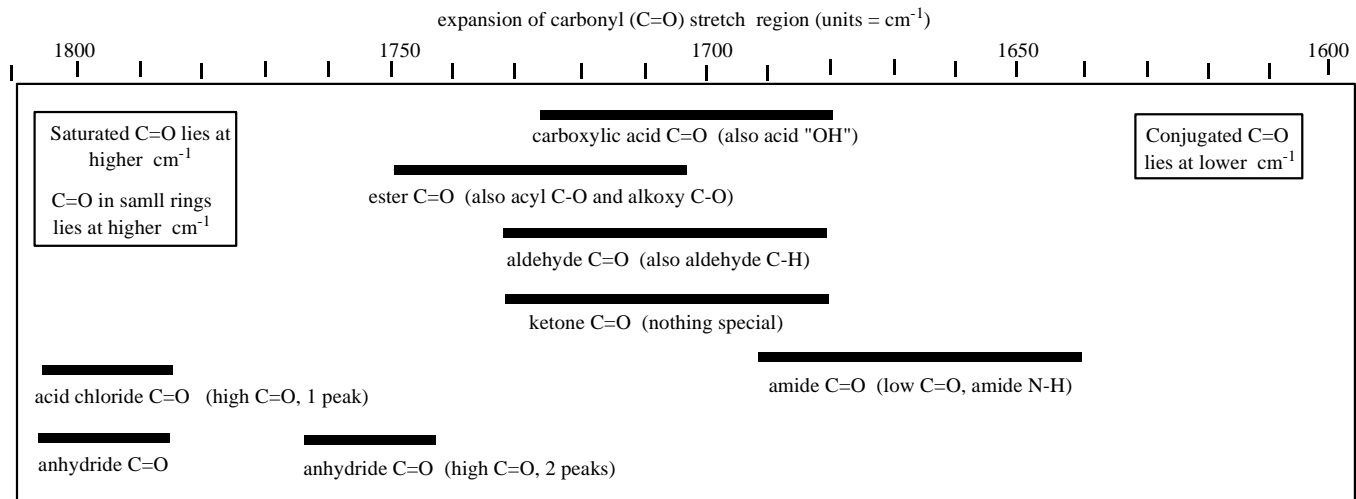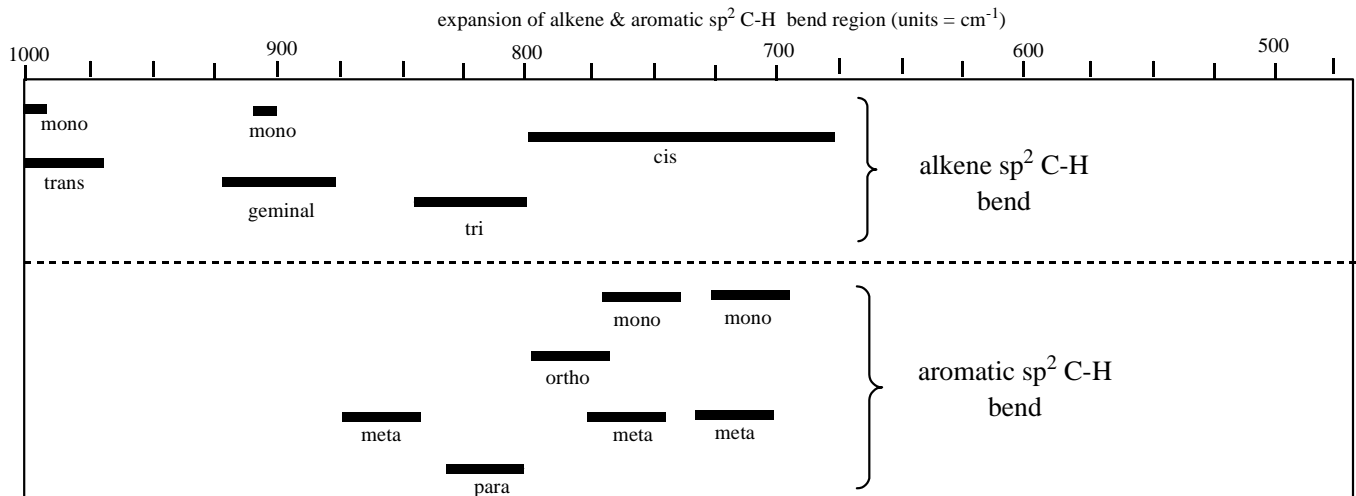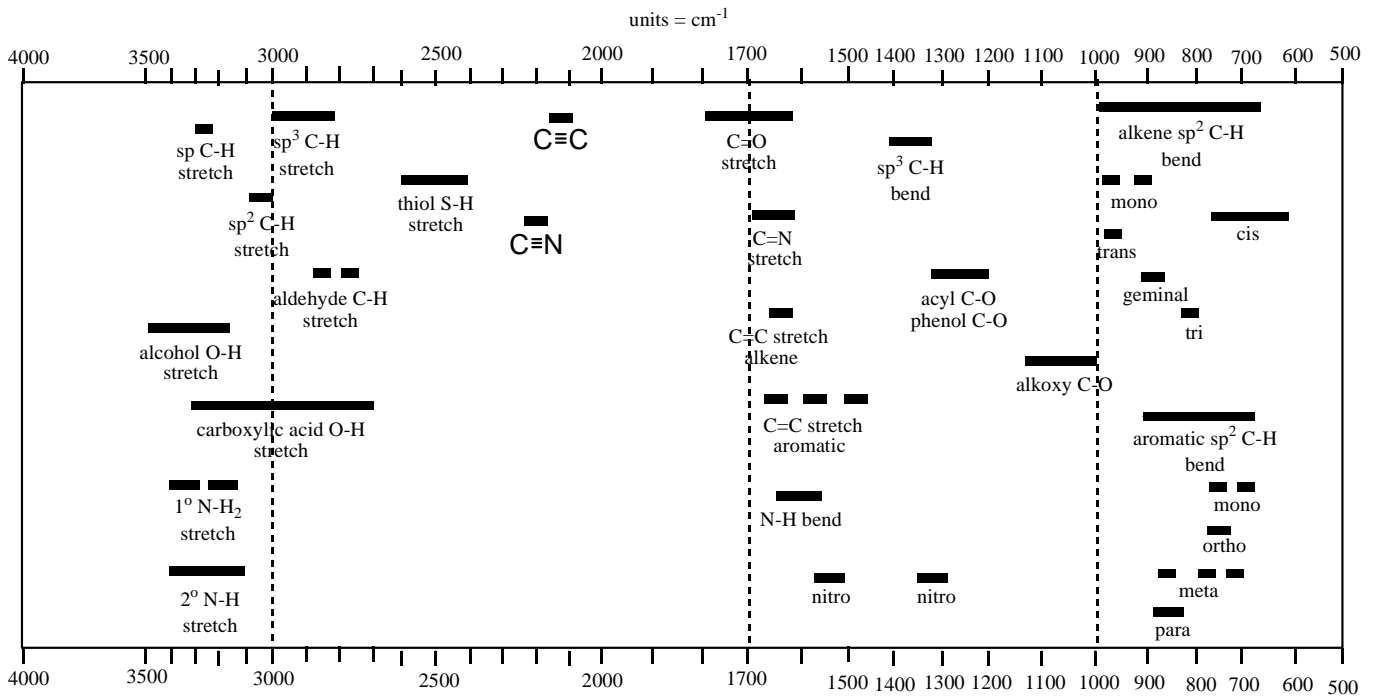## Bonds to Hydrogen (stretching wave numbers)

2850-3000
sp^3 C-H

3000-3100
sp^3 C-H
(see sp^2 C-H bend
patterns below)

3300
sp^3 C-H
(sp C-H bend ≈ 620)

2700-2760
2800-2860
aldehyde C-H
(two bands)

3100-3500
primary NH$_2$
(two bands)

3100-3500
secondary N-H
(one band)

amides = strong, amines = weak

3200-3400

alcohol O-H

2500-3400

acid O-H

2550 -2620
(very weak)

thiol S-H

Carbonyl Highlights (stretching wave numbers)

Aldehydes	Ketones	Esters	Acids

saturated = 1725
conjugated = 1690
aromatic = 1700

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

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

saturated = 1715
conjugated = 1690
aromatic = 1690

Amides	Anhydrides	Acid Chlorides	nitro

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

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

saturated = 1800
conjugated = 1770
aromatic = 1770

asymmetric = 1500-1600
symmetric = 1300-1390

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

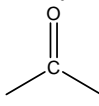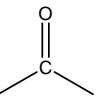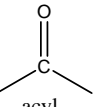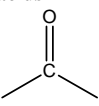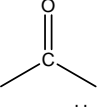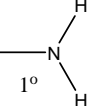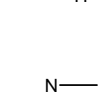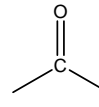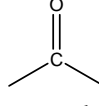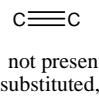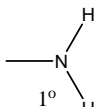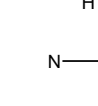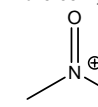### sp^2 C-H bend patterns for alkenes

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}

| 4000 | 3500 | 3000 | 2500 | 2000 | 1700 | 1500 1400 1300 1200 1100 | 1000 900 800 700 | 600 500 |

sp C-H
stretch

sp^3 C-H
stretch

C≡C

C=O
stretch

sp^3 C-H
bend

alkene sp^2 C-H
bend

mono

thiol S-H
stretch

C≡N

sp^2 C-H
stretch

aldehyde C-H
stretch

C=N
stretch

cis

trans

alcohol O-H
stretch

C=C stretch
alkene

acyl C-O
phenol C-O

geminal

tri

carboxylic acid O-H
stretch

C=C stretch
aromatic

alkoxy C-O

aromatic sp^2 C-H
bend

1° N-H$_2$
stretch

N-H bend

mono

2° N-H
stretch

nitro

nitro

ortho

meta

para

| 4000 | 3500 | 3000 | 2500 | 2000 | 1700 | 1500 1400 1300 1200 1100 | 1000 900 800 700 600 | 500 |

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

| 1000 | 900 | 800 | 700 | 600 | 500 |

mono

mono

cis

trans

geminal

alkene sp^2 C-H
bend

tri

mono

mono

ortho

aromatic sp^2 C-H
bend

meta

meta

meta

para

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

| 1800 | 1750 | 1700 | 1650 | 1600 |

Saturated C=O lies at
higher cm^{-1}

C=O in samll rings
lies at higher cm^{-1}

carboxylic acid C=O (also acid "OH")

Conjugated C=O
lies at lower cm^{-1}

ester C=O (also acyl C-O and alkoxy C-O)

aldehyde C=O (also aldehyde C-H)

ketone C=O (nothing special)

amide C=O (low C=O, amide N-H)

acid chloride C=O (high C=O, 1 peak)

anhydride C=O

anhydride C=O (high C=O, 2 peaks)

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≡C
C≡N

does not have
C=O band

aldehydes

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

sometimes lost
in sp^3 CH peaks

2860-2800 ←
2760-2700
(both weak)

aldehyde C-H

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 1º amides,
one band for 2º amides,
stronger than in amines, extra
overtone sometimes at 3100

1º   2º

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≡N

≈ 2250
sharp, stronger
than alkynes,

a little lower
when conjugated

alkynes

C≡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 (3º > 2º > 1º)

thiols

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

amines

H
|
—N
1º \H

N—H
2º

3300 - 3500, two bands
for 1º amines, one band
for 2º 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

—C—X   usually not
very useful

X = F, Cl, Br, I

deshielding side = less electron rich
(inductive & resonance)

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

shielding side = more electron rich
(inductive & resonance)

typical proton chemical shifts

Carbon and/or heteroatoms without hydrogen do
not appear here, but influence on any nearby protons
may be seen in the chemical shifts of the protons.

amine N-H
2   1

alcohol—O—H
5   1

amide N-H
6   1

S—C—H
thiols, sulfides
2.5   2.0

N—C—H
amines
3.0   2.3

X—C—H
X = F,Cl,Br,I
5   3

allylic C-H
2.5   1.5

alkene C-H
7$^+$ 4

benzylic C-H
carbonyl alpha C-H
3$^+$ 2

thiol
SH
1.5   1.3

carboxylic acid O-H
12   10

epoxide C-H
3.5   2.5

aldehyde C-H
10   9

aromatic C-H
8$^+$ 6

—O—C—H
alcohols
ethers
esters
5$^+$

≡C—H
3.3 3   2

simple sp^3 C-H
CH > CH$_2$ > CH$_3$
2   0.5

12   11   10   9   8   7   PPM 6   5   4   3   2   1   0

typical carbon-13 chemical shifts

halogen—C—
with & without H

F ≈ 80-95
Cl ≈ 45-70
Br ≈ 35-65
I ≈ 15-45

95   15

ketones
no H
220$^+$ 180

N—C—
amines, amides
with & without H
50   30

epoxides
with & without H
60   40

carboxylic acids
anhydrides
esters
amides
acid chlorides
no H
180   160

—C≡C—
with & without H
90$^+$ 70$^-$

N≡C—
no H
125   110

O—C—
alcohols,
ethers, esters
with & without H
80$^+$ 50

S—C—
thiols, sulfides
with & without H
40   20

aldehydes
with H
210   180

with & without H
160$^+$ 100$^-$

simple sp^3 carbon
C > CH > CH$_2$ > CH$_3$
with & without H
60$^+$ 0

240   220   200   180   160   140   PPM 120   100   80   60   40   20   0

Calculation of chemical shifts for protons at sp³ carbons
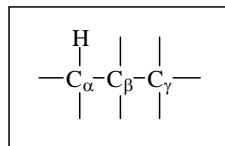
Estimation of sp³ C-H chemical shifts with multiple substituent parameters for protons within 3 C's of consideration.

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 CH₃'s

$$\delta\ CH_3 = 0.9 + \alpha \qquad\qquad H_3C-\alpha$$

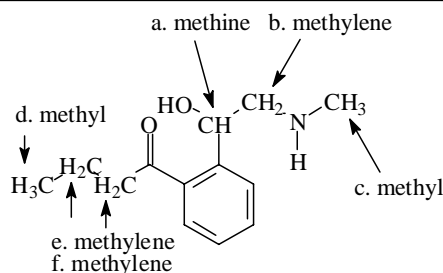$$\delta\ CH_3 = 0.9 + \Sigma(\beta + \gamma) \qquad H_3C-C_\beta-C_\gamma-$$

Σ is the summation symbol for all substituents considered

Starting value and equation for CH₂'s

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

$$\delta\ CH_2 = 1.2 + \Sigma(\alpha + \beta + \gamma) \qquad H-C_\alpha-C_\beta-C_\gamma-$$

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

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

Σ is the summation symbol for all substituents considered

a. methine   b. methylene
d. methyl
c. methyl
e. methylene
f. methylene

a. methyl = $0.9 + (1.5)_\alpha + (0.1)_\gamma = 2.5$ ppm
actual = 2.6

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

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

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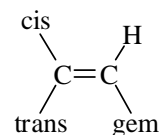
$\delta(ppm) = 5.2 + \alpha_{gem} + \alpha_{cis} + \alpha_{trans}$

Example Calculation
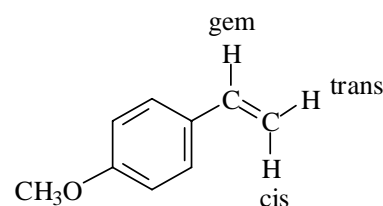
$\delta\ gem = 5.2 + 1.4 = 6.6$
  actual $= 6.6$

$\delta\ trans = 5.2 - 0.1 = 5.1$
  actual $= 5.1$

$\delta\ cis = 5.2 + 0.4 = 5.7$
  actual $= 5.6$
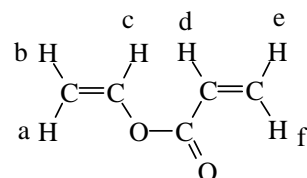
$\delta_a = 5.2 + (-0.4) = 4.8$
  actual $= 4.9$ (J = 14, 1.6 Hz)
- -
$\delta_b = 5.2 + (-0.6) = 4.6$
  actual $= 4.6$ (J = 6, 1.6 Hz)
- -
$\delta_c = 5.2 + 2.1 = 7.3$
  actual $= 7.4$ (J = 14, 6 Hz)
- -
$\delta_d = 5.2 + 0.8 = 6.0$
  actual $= 6.2$ (J = 18, 11 Hz)
- -
$\delta_e = 5.2 + 0.5 = 5.7$
  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

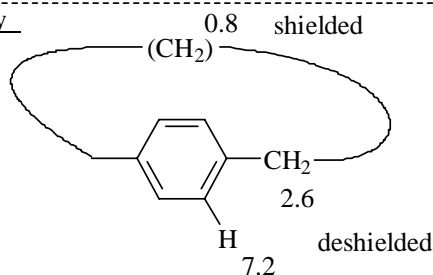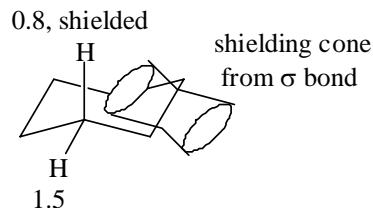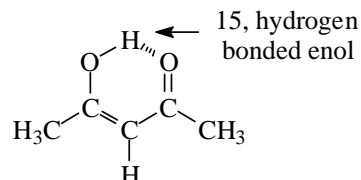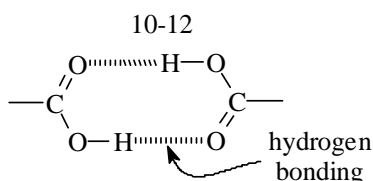| Substituent	α ortho	α meta	α para
H- Hydrogen	0.0	0.0	0.0
CH$_3$- Methyl	-0.2	-0.1	-0.2
ClCH$_2$- Cholromethyl	0.0	0.0	0.0
Cl$_3$C- Halomethyl	0.6	0.1	0.1
HOCH$_2$- Hydroxymethyl	-0.1	-0.1	-0.1
R$_2$C=CR- Alkenyl	0.1	0.0	-0.1
C$_6$H$_5$- Phenyl	1.4	0.4	-0.1
F- Fluoro	-0.3	0.0	-0.2
Cl- Chloro	0.0	0.0	-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$_2$N- N-amino	-0.8	-0.2	-0.7
RCONH- N-amide	0.1	-0.1	-0.3
O$_2$N- 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$_2$C- C-acid	0.9	0.2	0.3
RO$_2$C- C-ester	0.7	0.1	0.2
H$_2$NOC- C-amide	0.6	0.1	0.2
NC- Nitrile	0.4	0.2	0.3

Substitution relative to calculated "H"
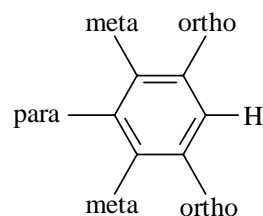
$$\delta(ppm) = 7.3 + \alpha_{ortho} + \alpha_{meta} + \alpha_{para}$$

Example Calculation
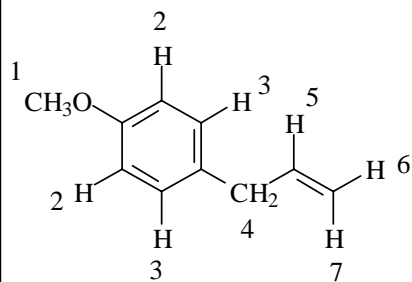
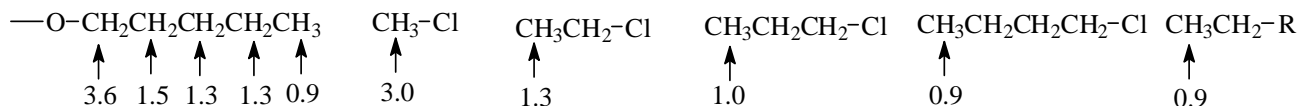1. $\delta\,(CH_3) = 0.9 + 2.8 = 3.7$
      actual = 3.8

2. $\delta\,(2) = 7.3 + (-0.5)_{ortho} + (-0.1)_{para} = 6.7$
      actual = 6.8

3. $\delta\,(3) = 7.3 + (-0.2)_{ortho} + (-0.4)_{para} = 6.7$
      actual = 7.1

4. $\delta\,(CH_2) = 1.2 + (0.8)\alpha + (1.4)\alpha = 3.4$
      actual = 3.3

5. $\delta\,(5) = 5.2 + (0.7)_{gem} = 5.9$
      actual = 5.9

6. $\delta\,(6) = 5.2 + (-0.2)_{trans} = 5.0$
      actual = 5.1

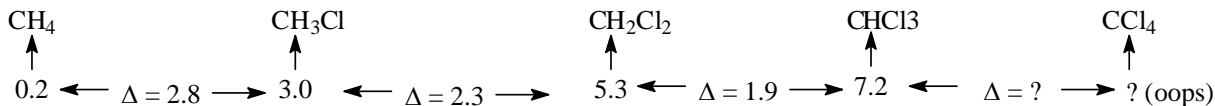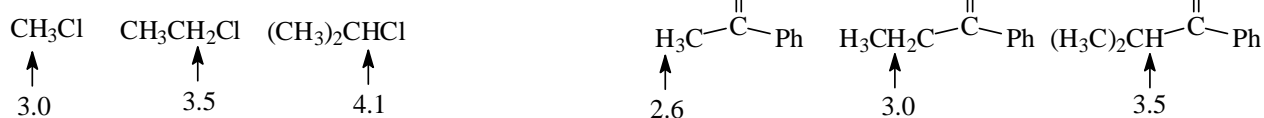7. $\delta\,(7) = 5.2 + (-0.2)_{cis} = 5.0$
      actual = 5.1

Real Examples of Combination Effects on Chemical Shifts

<u>π bond anisotropy</u>　　　　　　　0.8　shielded　　　　　<u>σ bond example too</u>

(CH_2)

CH_2
2.6

H
7.2　deshielded

0.8, shielded
H

shielding cone
from σ bond

H
1.5

----

electronegativity and π bond　　　　　　10-12　　　　　　　　　15, hydrogen
bonded enol

O
‖
C—H　←　9.5

O⋯⋯⋯H—O
| |
—C　　　　　C—
| |
O—H⋯⋯⋯⋯O　　hydrogen
bonding

H—O⋯O
| ‖
H_3C—C=C—C—CH_3
|
H

----
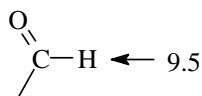
electronegative substituent and distance from protons

—O–$CH_2CH_2CH_2CH_2CH_3$　　CH_3–Cl　　CH_3CH_2–Cl　　$CH_3CH_2CH_2$–Cl　　$CH_3CH_2CH_2CH_2$–Cl　CH_3CH_2–R

　3.6　1.5　1.3　1.3　0.9　　3.0　　　　1.3　　　　　1.0　　　　　　0.9　　　　　　0.9

----

multiple substituents

CH_4　　　　　　CH_3Cl　　　　　　CH_2Cl_2　　　　　　CHCl3　　　　　　CCl_4

0.2　←　Δ = 2.8　→　3.0　←　Δ = 2.3　→　5.3　←　Δ = 1.9　→　7.2　←　Δ = ?　→　? (oops)

----

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

CH_3Cl　　CH_3CH_2Cl　　$(CH_3)_2CHCl$

3.0　　　3.5　　　　4.1

O
‖
H_3C—C—Ph

O
‖
H_3CH_2C—C—Ph

O
‖
$(H_3C)_2CH$—C—Ph

2.6　　　　　　　3.0　　　　　　　3.5

----

alkene substituent resonance and inductive effects

H　　　H
　C=C
H　　　H
5.3

0.9　1.4　2.0
$CH_3CH_2CH_2$　　　H 5.0
　　　　　　C=C
　　　　　　H　　H
5.8　　　4.9

3.8
CH_3O—C
‖
O
C=C
H　　　H 6.4
H
6.1　　5.8

3.7
H_2C—O
H_3C　　　　H 4.2
　　　　C=C
1.3　　H　　H
6.5　　　4.0

O
‖
H_3C—C—O
H　　　4.9
　C=C
2.1　　H　　H
7.3　　　4.6

----
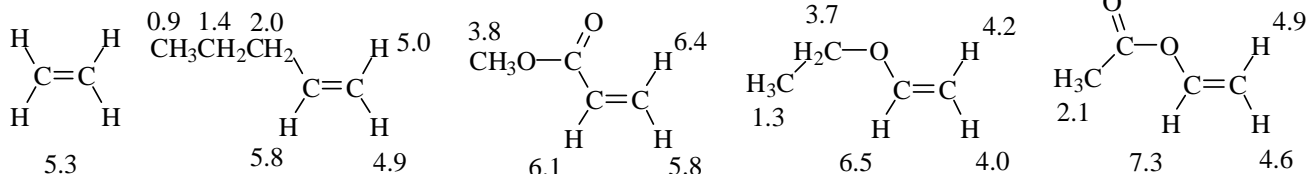
aromatic resonance and inductive effects

H　　H 7.3
H　　　　H
H　　　　H
H　　H

π bond anisotropy
produces deshielding
effect on aromatic
protons.

6.6　　　7.1
H　　　H
　　　　　6.7
H_2N　　　　　H ↔ $H_2N^{\oplus}$
H　　　H

H　　　H
H
H　　　H

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

8.2　　7.5
O　H　　H
‖　　　　　7.7
$^{\oplus}N$　　　　H ↔
|
O⊖　　H　　H

⊖
O　$N^{\oplus}$
H　　H
H　　H

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

O
‖
R—C　amide H = 5-8
|
NH_2

| enol H = 10-17　H—O
　　　　　　　　　　　C=C

O
‖
R—C
|
O—H　acid H = 10-13

Proton chemical shifts of hydrogen on sp^3 carbons depend on two main factors (electronegativity and pi bond anisotropy). All values listed below are only approximate and have a small plus or minus range about the listed value.
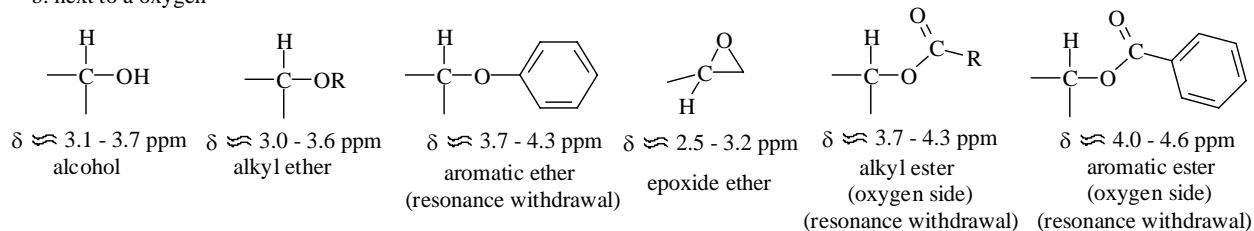
All things being equal, methine protons (CH) have greater chemical shifts than methylene protons (CH$_2$) which have greater chemical shifts than methyl protons (CH$_3$).

$\delta \approx 1.5$ ppm
methine protons

$\delta \approx 1.2$ ppm
methylene protons

$\delta \approx 0.9$ ppm
methyl protons

Chemical shifts in an only "alkane" environment.
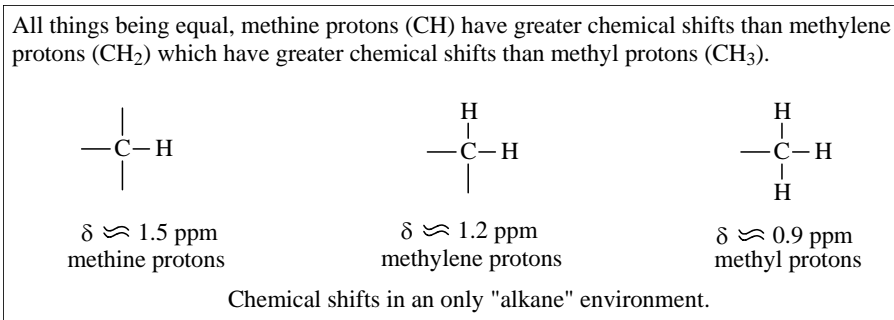
1. **sp^3 C-H** Electronegative atoms in the vicinity of hydrogen deshield protons and produce a larger chemical shift. If the electronegative atom is in resonance with an adjacent pi system that further withdraws electron density, the chemical shift is increased.

a. next to a halogen

$\delta \approx 4.1 - 4.7$ ppm
fluoro alkanes

$\delta \approx 3.1 - 3.7$ ppm
chloro alkanes

$\delta \approx 3.0 - 3.6$ ppm
bromo alkanes

$\delta \approx 2.9 - 3.5$ ppm
iodo alkanes

b. next to a oxygen

$\delta \approx 3.1 - 3.7$ ppm
alcohol

$\delta \approx 3.0 - 3.6$ ppm
alkyl ether

$\delta \approx 3.7 - 4.3$ ppm
aromatic ether
(resonance withdrawal)

$\delta \approx 2.5 - 3.2$ ppm
epoxide ether

$\delta \approx 3.7 - 4.3$ ppm
alkyl ester
(oxygen side)
(resonance withdrawal)

$\delta \approx 4.0 - 4.6$ ppm
aromatic ester
(oxygen side)
(resonance withdrawal)
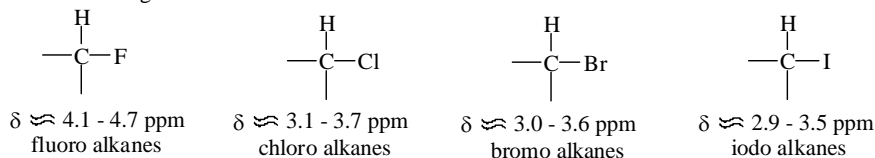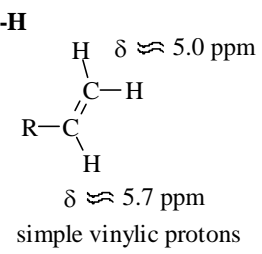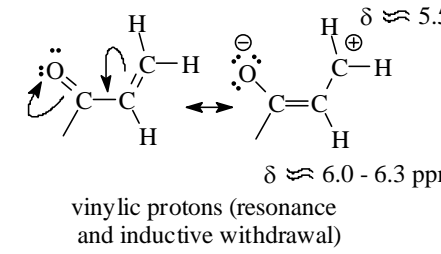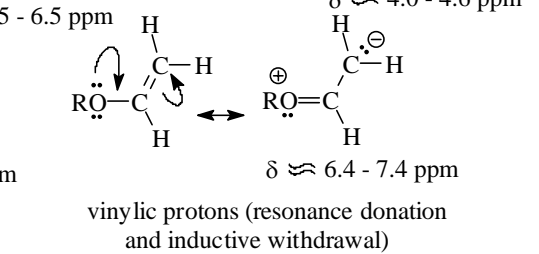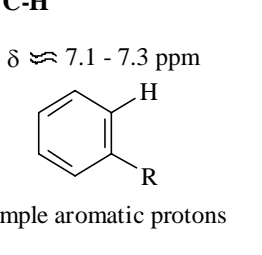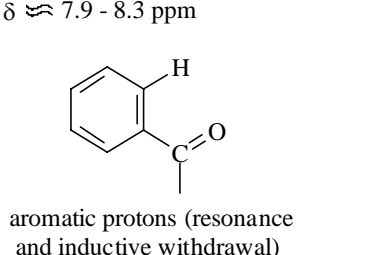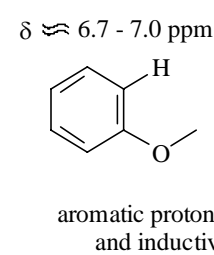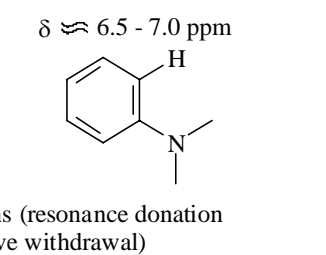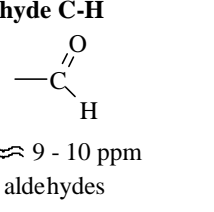
c. next to a sulfur or nitrogen

$\delta \approx 2.2 - 2.8$ ppm
thiol

$\delta \approx 2.2 - 2.8$ ppm
alkyl ether

$\delta \approx 2.3 - 3.1$ ppm
amines

$\delta \approx 3.0 - 3.6$ ppm
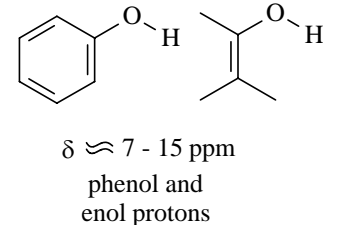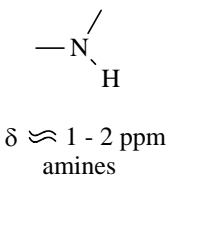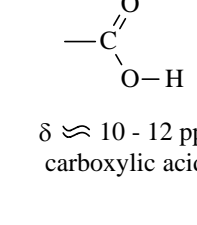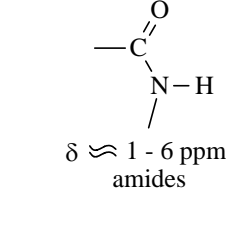(resonance withdrawal)
amides
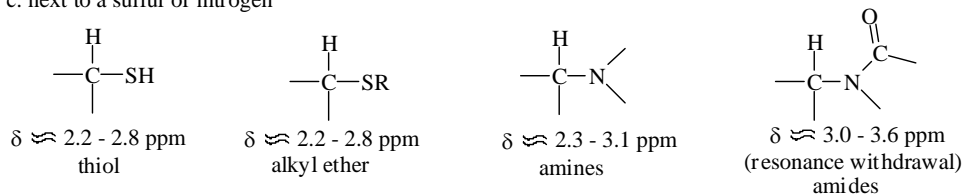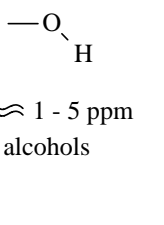
2. **sp^3 C-H** Pi bonds in the vicinity of hydrogen also deshield protons via pi bond anisotropy and produce a larger chemical shift. The closer the sp^3 C-H is to the pi bond the greater chemical shift observed. When an electronegative atom is part of the pi bond, the chemical shift also increases.
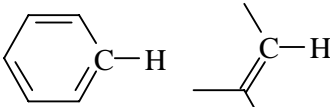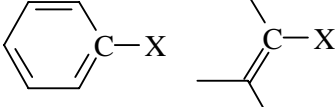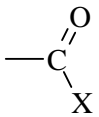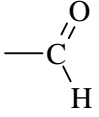
$\delta \approx 1.9 - 2.7$ ppm
aldehydes, ketones,
carboxylic acids, amides,
alkyl ester (oxygen side)

$\delta \approx 2.6 - 3.3$ ppm
aromatic ketones
(resonance withdrawal)

$\delta \approx 2.7 - 3.4$ ppm
acid chlorides
(resonance withdrawal)

$\delta \approx 2.7 - 3.4$ ppm
nitro compounds
(resonance withdrawal)

$\delta \approx 1.8 - 2.4$ ppm
propargylic protons

$\delta \approx 1.7 - 2.3$ ppm
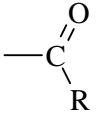allylic protons

$\delta \approx 2.3 - 2.9$ ppm
benzylic protons
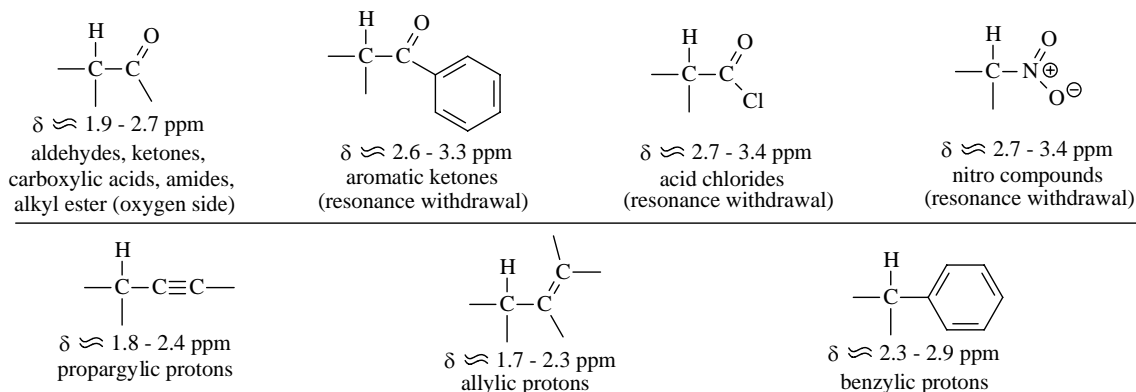
3. **sp² C-H** Hydrogens at the side of a pi bond are deshielded even more than above via pi bond anisotropy. An aldehyde produces the largest effect due to the electronegative oxygen, followed by an aromatic ring, followed by alkenes and finally terminal alkynes. (One sp C-H)

alkene C-H

$\delta \approx 5.0$ ppm

$\delta \approx 5.7$ ppm
simple vinylic protons

$\delta \approx 5.5 - 6.5$ ppm

$\delta \approx 6.0 - 6.3$ ppm
vinylic protons (resonance and inductive withdrawal)

$\delta \approx 4.0 - 4.6$ ppm

$\delta \approx 6.4 - 7.4$ ppm
vinylic protons (resonance donation and inductive withdrawal)

aromatic C-H

$\delta \approx 7.1 - 7.3$ ppm

simple aromatic protons

$\delta \approx 7.9 - 8.3$ ppm

aromatic protons (resonance and inductive withdrawal)

$\delta \approx 6.7 - 7.0$ ppm $\delta \approx 6.5 - 7.0$ ppm

aromatic protons (resonance donation and inductive withdrawal)

aldehyde C-H

$\delta \approx 9 - 10$ ppm
aldehydes

alkyne C-H

C≡C—H

$\delta \approx 1.9 - 3.2$ ppm
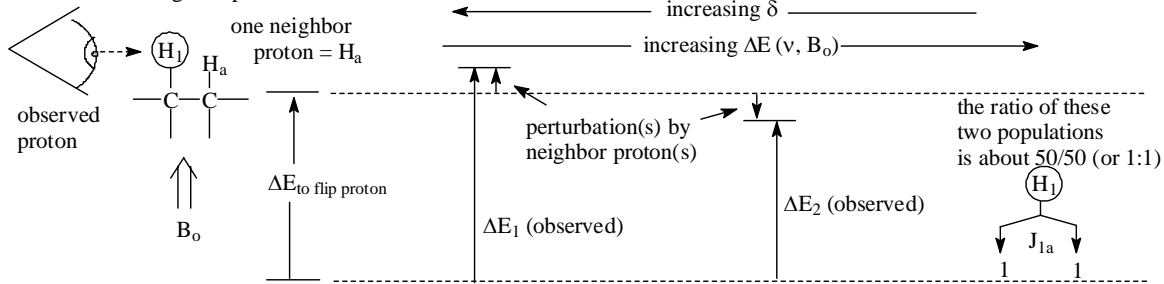terminal alkyne protons

4. There are several kinds of hydrogen attached to heteroatoms. Some of these are listed below. Often these hydrogens do not follow the N+1 rule because they exchange via acid/base proton exchanges and are not next to neighbor protons long enough to allow coupling to be observed. They are often observed as broad singlets (sometimes so broad they are not easily seen in the spectra). If the exchange rate is very fast among the exchangeable protons on the NMR time scale, all of the exchangeable protons may appear together at a single, averaged chemical shift.

$\delta \approx 1 - 5$ ppm
alcohols

$\delta \approx 7 - 15$ ppm
phenol and
enol protons

$\delta \approx 1 - 2$ ppm
amines

$\delta \approx 10 - 12$ ppm
carboxylic acids

$\delta \approx 1 - 6$ ppm
amides

When carbons are decoupled from their attached hydrogens they all appear as singlets (as if there were no hydrogen neighbors). When carbons are coupled to their hydrogens, carbons follow the N+1 rule. Methyls appear as quartets = q, methylenes appear as triplets = t, methines appear as doublets = d, and carbons without hydrogen appear as singlets = s. Carbon chemical shifts are spread out over a larger range than proton chemical shifts (they are more dispersed). It is less likely that two different carbon shifts will fall on top of one another. However, 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— $\delta \approx$ 0 - 30 ppm (q)	—CH_2 $\delta \approx$ 20 - 40 ppm (t)	—CH $\delta \approx$ 30 - 50 ppm (d)	—C— $\delta \approx$ 30 - 60 ppm (s)
sp^3 carbon next to oxygen	CH_3— $\delta \approx$ 50 - 60 ppm (q)	—CH_2 $\delta \approx$ 55 - 80 ppm (t)	—CH $\delta \approx$ 60 - 80 ppm (d)	—C— $\delta \approx$ 70 - 90 ppm (s)
sp^3 carbon next to nitrogen	CH_3— $\delta \approx$ 10 - 50 ppm (q)	—CH_2 $\delta \approx$ 35 - 55 ppm (t)	—CH $\delta \approx$ 50 - 70 ppm (d)	—C— $\delta \approx$ 50 - 70 ppm (s)
sp^3 carbon next to bromine or chlorine		—CH_2 $\delta \approx$ 25 - 50 ppm (t)	—CH $\delta \approx$ 60 - 80 ppm (d)	—C— $\delta \approx$ 60 - 80 ppm (s)

sp carbon (alkynes)   —C≡C— $\delta \approx$ 70 - 90 ppm   sp carbon (nitriles)   —C≡N $\delta \approx$ 110 - 125 ppm

sp^2 carbon (alkenes and aromatics)

C—H   C—H
$\delta \approx$ 100 - 140 ppm
simple sp^2 carbon
resonance donation moves δ lower,
resonance withdrawal moves δ higher

C—X   C—X
$\delta \approx$ 140 - 160$^+$ ppm
sp^2 carbon attached to an electronegative atom
(X = oxygen, nitrogen, halogen) or C_β carbon
conjugated with a carbonyl group

—C(=O)—X
$\delta \approx$ 160 - 180 ppm
carboxyl carbons
(acids, esters, amides)
(s)

—C(=O)—H
$\delta \approx$ 190 - 210 ppm
aldehyde carbons, lower
values when conjugated
(d)

—C(=O)—R
$\delta \approx$ 190 - 220 ppm
ketone carbons, lower
values when conjugated
(s)

1. One nearest neighbor proton

one neighbor proton = H_a

increasing δ

increasing ΔE (ν, B_o)

observed proton

$\Delta E_{to\ flip\ proton}$

perturbation(s) by neighbor proton(s)

B_o

ΔE_1 (observed)

ΔE_2 (observed)

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

H_1

J_{1a}

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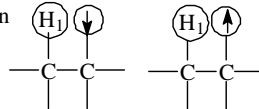
Protons in this environment have a small additional increment added to the external magnetic field, B_o, and produce a higher energy transition by that tiny amount.

J = coupling constant small difference in energy due to differing neighbor's spin (in Hz)
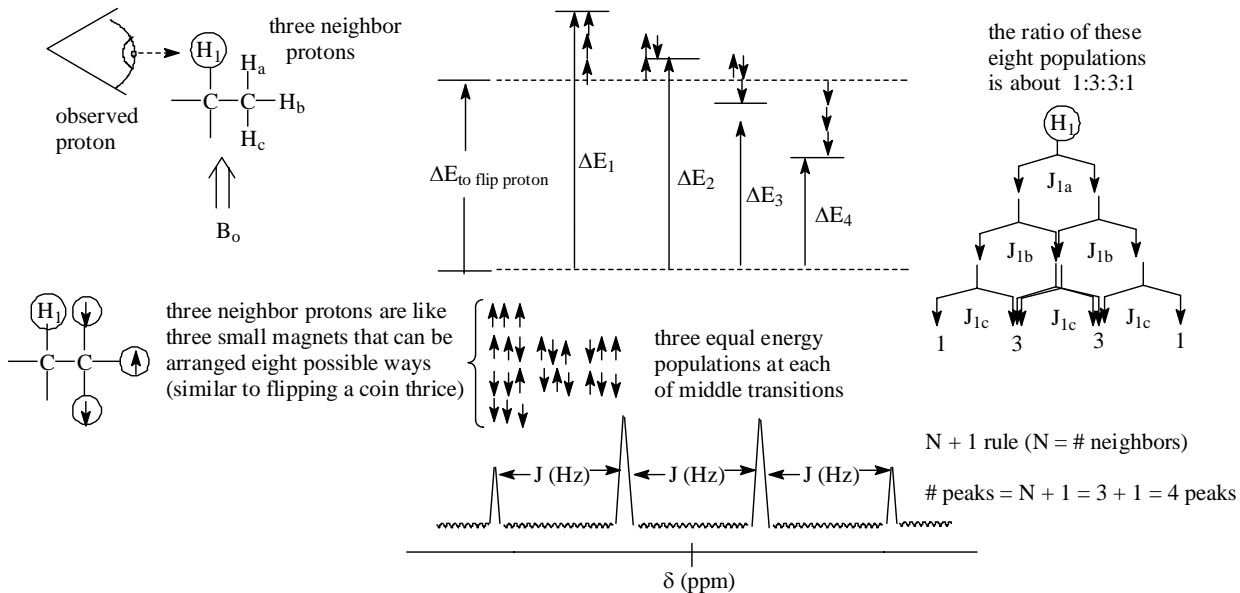
J (Hz)
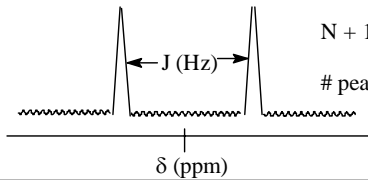
N + 1 rule (N = # neighbors)

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

δ (ppm)

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

two neighbor protons

observed proton

B_o

$\Delta E_{to\ flip\ proton}$

ΔE_1

ΔE_2

ΔE_3

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

H_1

J_{1a}

J_{1b} J_{1b}

1   2   1

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

two equal energy populations here

J (Hz)   J (Hz)

N + 1 rule (N = # neighbors)

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

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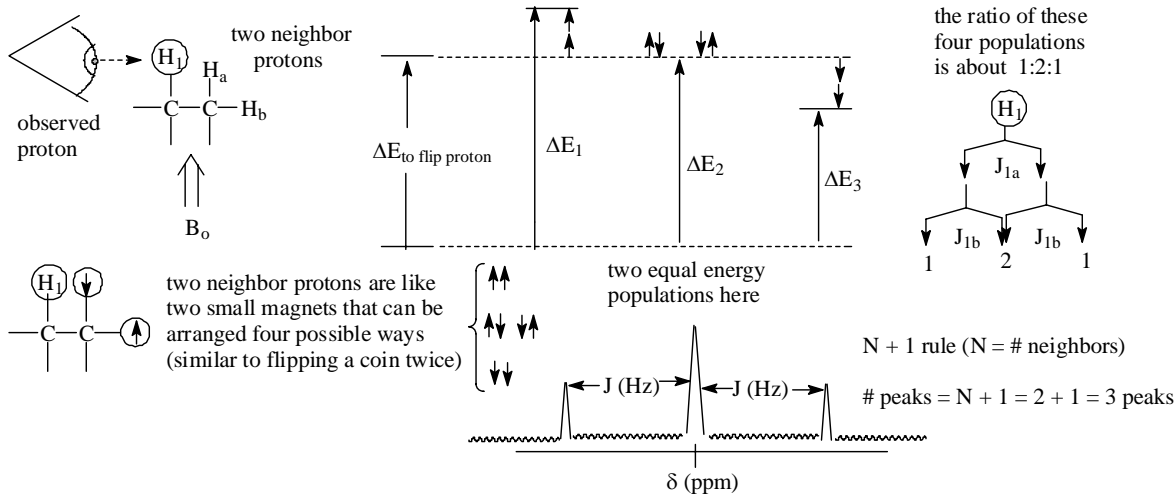
3. Three nearest neighbor protons (on same carbon, or two on one and one on another, or one each on separate carbons)

three neighbor protons

observed proton

B_o

$\Delta E_{to\ flip\ proton}$

ΔE_1

ΔE_2

ΔE_3

ΔE_4

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

H_1

J_{1a}

J_{1b} J_{1b}

J_{1c} J_{1c} J_{1c}

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)

three equal energy populations at each of middle transitions

J (Hz)   J (Hz)   J (Hz)

N + 1 rule (N = # neighbors)

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

δ (ppm)

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

s = singlet

d = doublet

t = triplet

q = quartet

qnt = quintet

sex = sextet

sep = septet

o = octet

```
                              1           1 peak = 100%
                                          1 peak = 50%
                          1       1       1 peak = 25%
                      1       2       1   1 peak = 12%
                  1       3       3       1   1 peak = 6%
              1       4       6       4       1   1 peak = 3%
          1       5      10      10      5       1   1 peak = 1.5%
      1       6      15      20      15      6       1   1 peak = 0.8%
  1       7      21      35      35      21      7       1
```

relative sizes of peaks in multiplets

Combinations or these are possible.

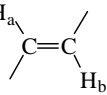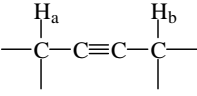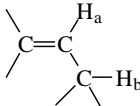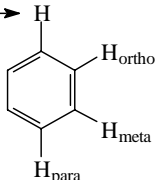dd = doublet of doublets
ddd = doublet of doublet of doublets
dddd = doublet of doublet of doublet of doublets
dt = doublet of triplets
td = triplet of doublets
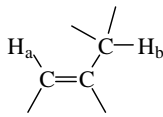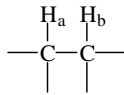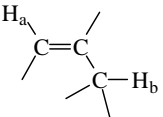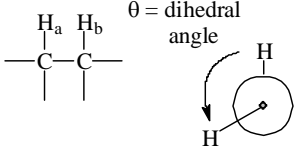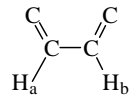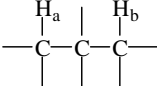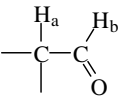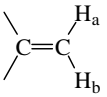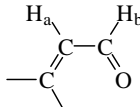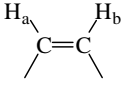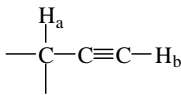
etc.

Typical Coupling Constants

	Range	Typical
geminal protons - can have different chemical shifts and split one another if they are diastereotopic	0-30 Hz	14 Hz

	Range	Typical
cis / allylic coupling, notice through 4 bonds	0-3 Hz	1 Hz

	Range	Typical
vicinal protons are on adjacent atoms, when freely rotating coupling averages out to about 7 Hz	6-8 Hz	7 Hz

	Range	Typical
trans / allylic coupling, notice through 4 bonds	0-3 Hz	1 Hz

	Range	Typical
θ = dihedral angle	0-12 Hz	7 Hz
depends on dihedral angle, see plot of Karplus equation		

	Range	Typical
sp^2 vicinal coupling (different π bonds)	9-13 Hz	10 Hz

	Range	Typical
protons rarely couple through 4 chemical bonds unless in a special, rigid shapes (i.e. W coupling)	0-1 Hz	0 Hz

	Range	Typical
sp^3 vicinal aldehyde coupling	1-3 Hz	2 Hz

	Range	Typical
sp^2 geminal coupling	0-3 Hz	2 Hz

	Range	Typical
sp^2 vicinal aldehyde coupling	5-8 Hz	6 Hz

	Range	Typical
sp^2 cis (acyclic) coupling (always smaller than the trans isomer)	5-11 Hz	10 Hz

	Range	Typical
sp / propargylic coupling notice through 4 bonds	2-3 Hz	2 Hz

	Range	Typical
sp^2 trans coupling (always larger than the cis isomer)	11-19 Hz	17 Hz

	Range	Typical
bis-propargylic coupling notice through 5 bonds	2-3 Hz	3 Hz

	Range	Typical
sp^2 / sp^3 vicinal coupling	4-10 Hz	7 Hz

ortho, meta and para coupling to this proton

	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.