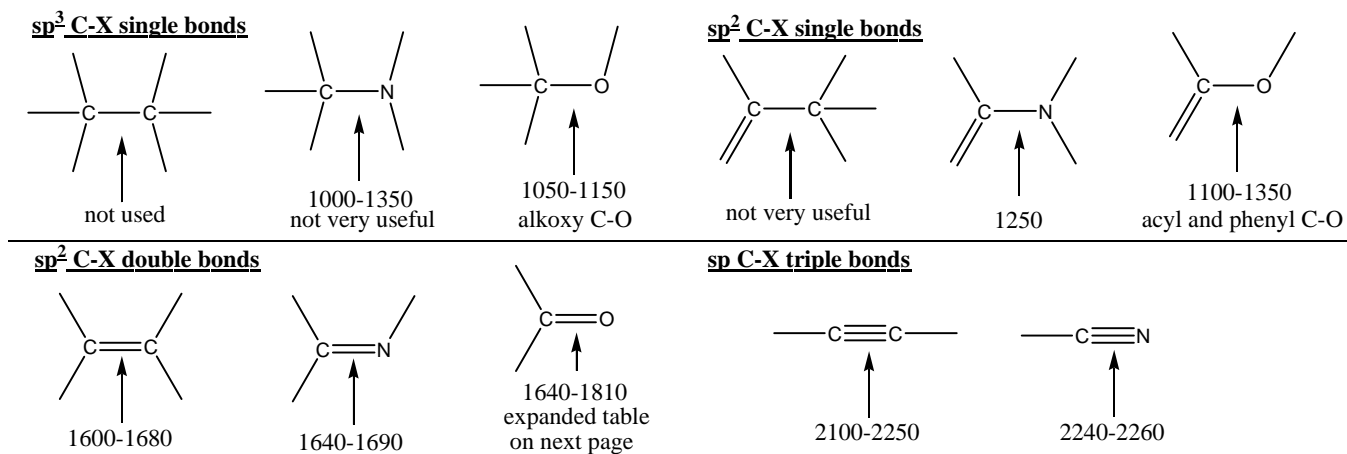


Infrared Tables (short summary of common absorption frequencies)

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 ^1H 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.

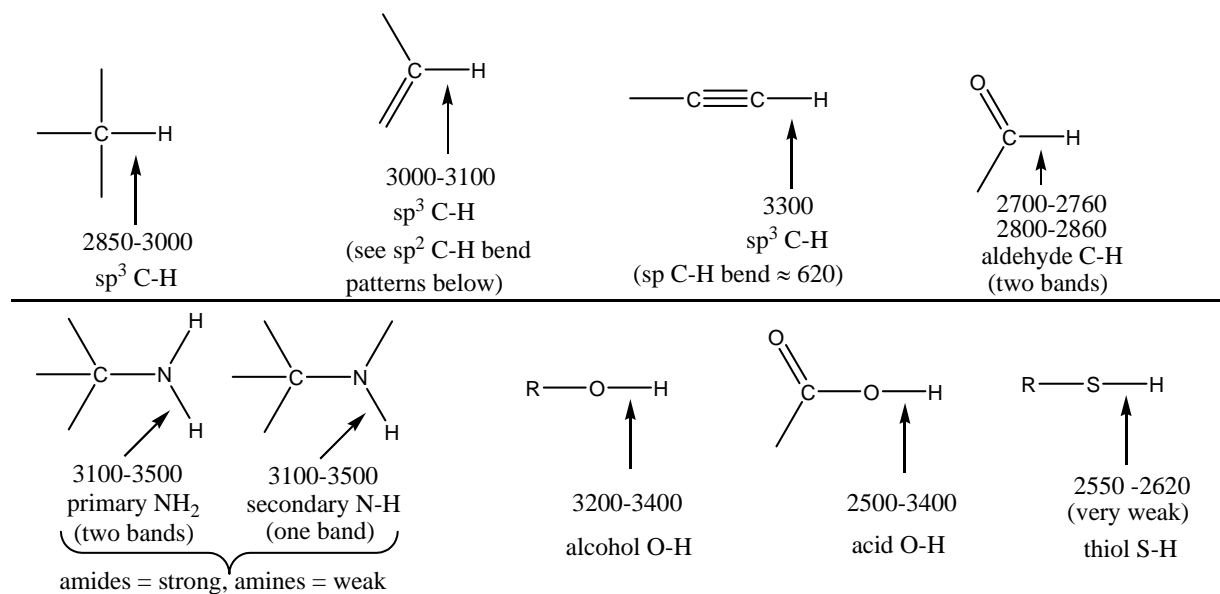
IR Summary - All numerical values in the tables below are given in wavenumbers, cm^{-1}

Bonds to Carbon (stretching wave numbers)

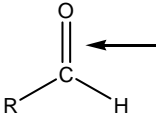
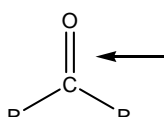
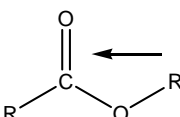
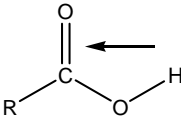
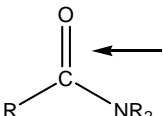
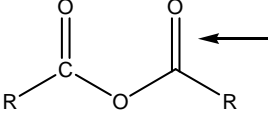
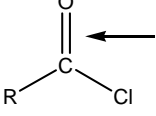
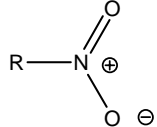


Stronger dipoles produce more intense IR bands and weaker dipoles produce less intense IR bands (sometimes none).

Bonds to Hydrogen (stretching wave numbers)

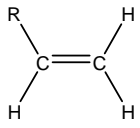
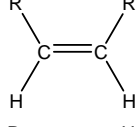
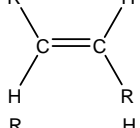
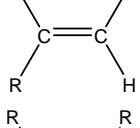
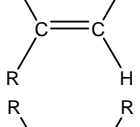
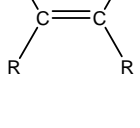


Carbonyl Highlights (stretching wave numbers)

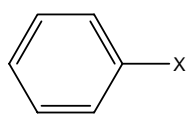
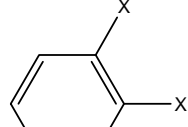
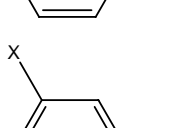
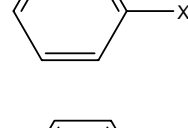
Aldehydes	Ketones	Esters	Acids
 <p>saturated = 1725 conjugated = 1690 aromatic = 1700</p>	 <p>saturated = 1715 conjugated = 1680 aromatic = 1690 6 atom ring = 1715 5 atom ring = 1745 4 atom ring = 1780 3 atom ring = 1850</p>	 <p>saturated = 1735 conjugated = 1720 aromatic = 1720 6 atom ring = 1735 5 atom ring = 1775 4 atom ring = 1840</p>	 <p>saturated = 1715 conjugated = 1690 aromatic = 1690</p>
Amides	Anhydrides	Acid Chlorides	nitro
 <p>saturated = 1650 conjugated = 1660 aromatic = 1660 6 atom ring = 1670 5 atom ring = 1700 4 atom ring = 1745 3 atom ring = 1850</p>	 <p>saturated = 1760, 1820 conjugated = 1725, 1785 aromatic = 1725, 1785 6 atom ring = 1750, 1800 5 atom ring = 1785, 1865</p>	 <p>saturated = 1800 conjugated = 1770 aromatic = 1770</p>	 <p>asymmetric = 1500-1600 symmetric = 1300-1390</p>

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

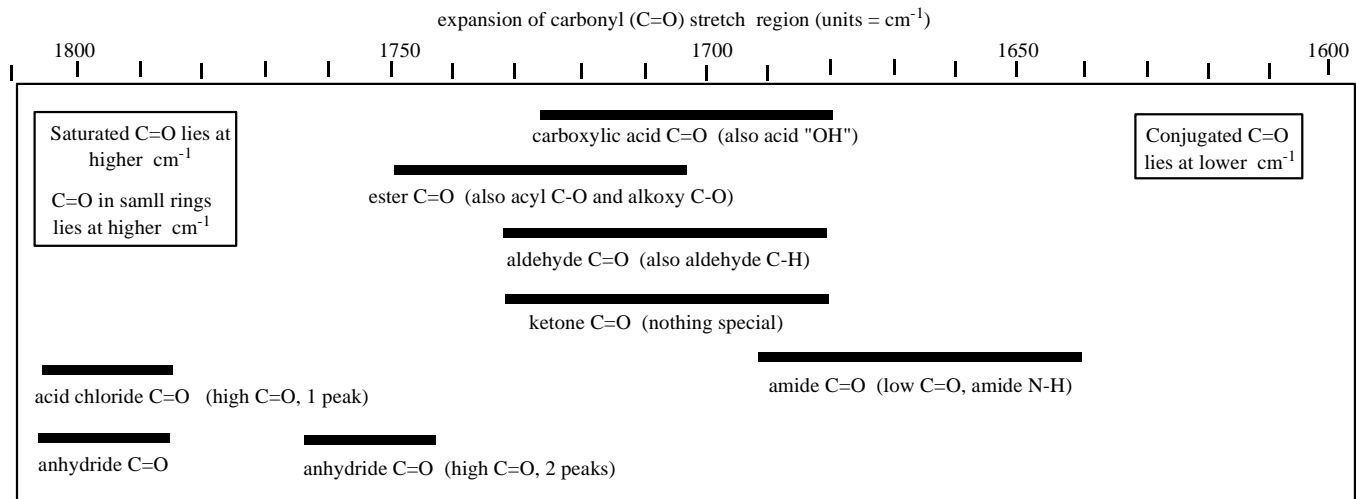
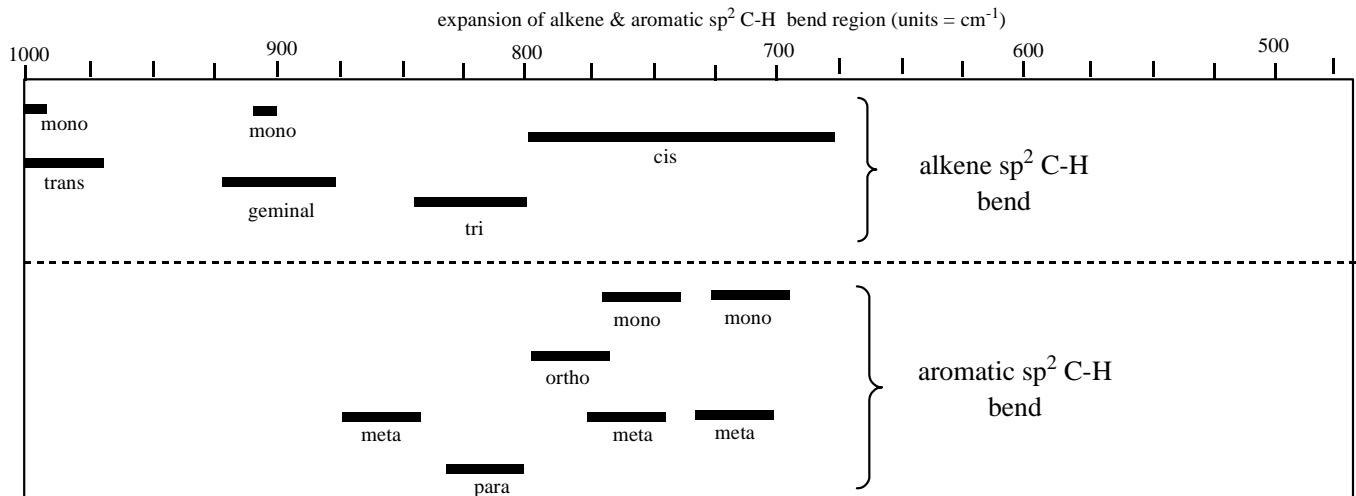
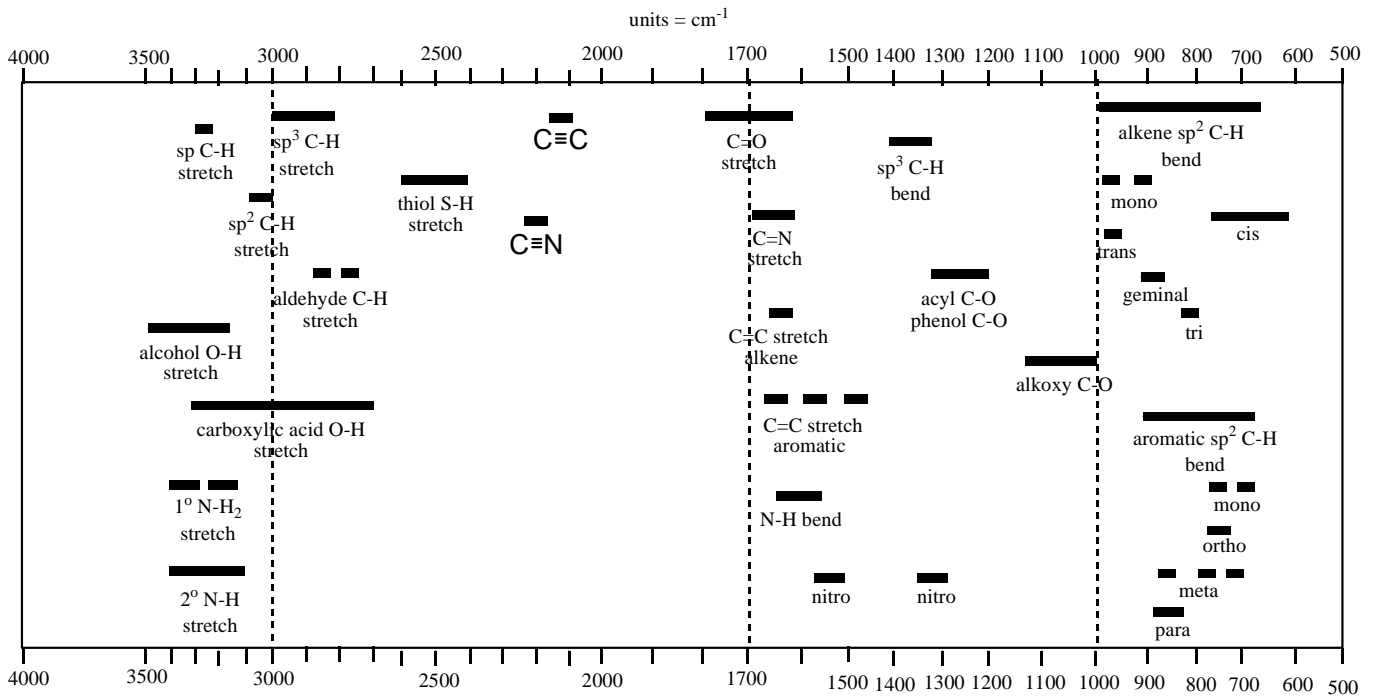
sp² C-H bend patterns for alkenes

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

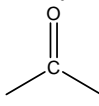
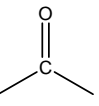
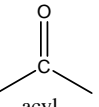
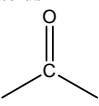
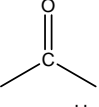
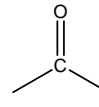
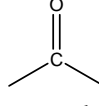
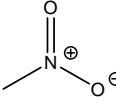

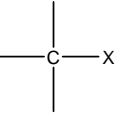
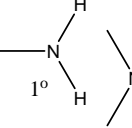
sp² C-H bend patterns for aromatics

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.



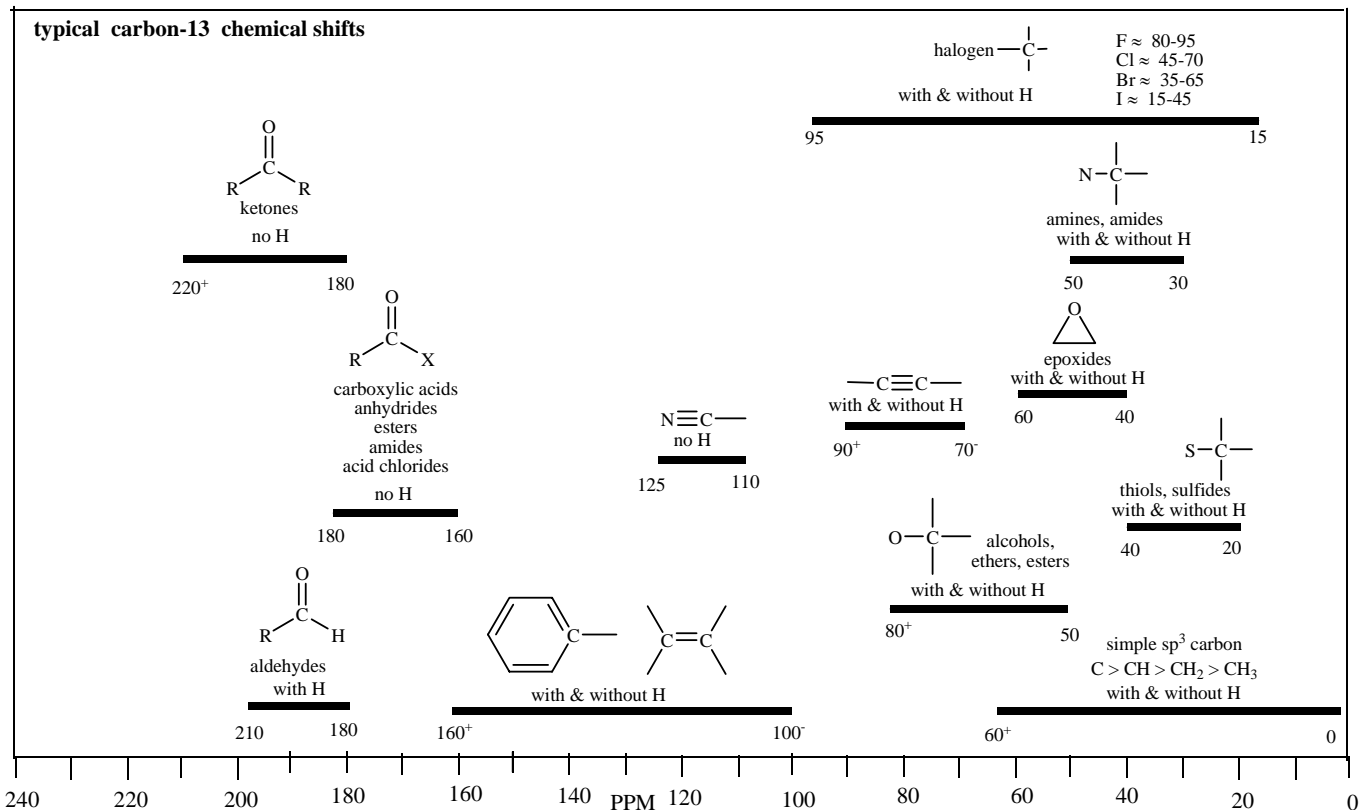
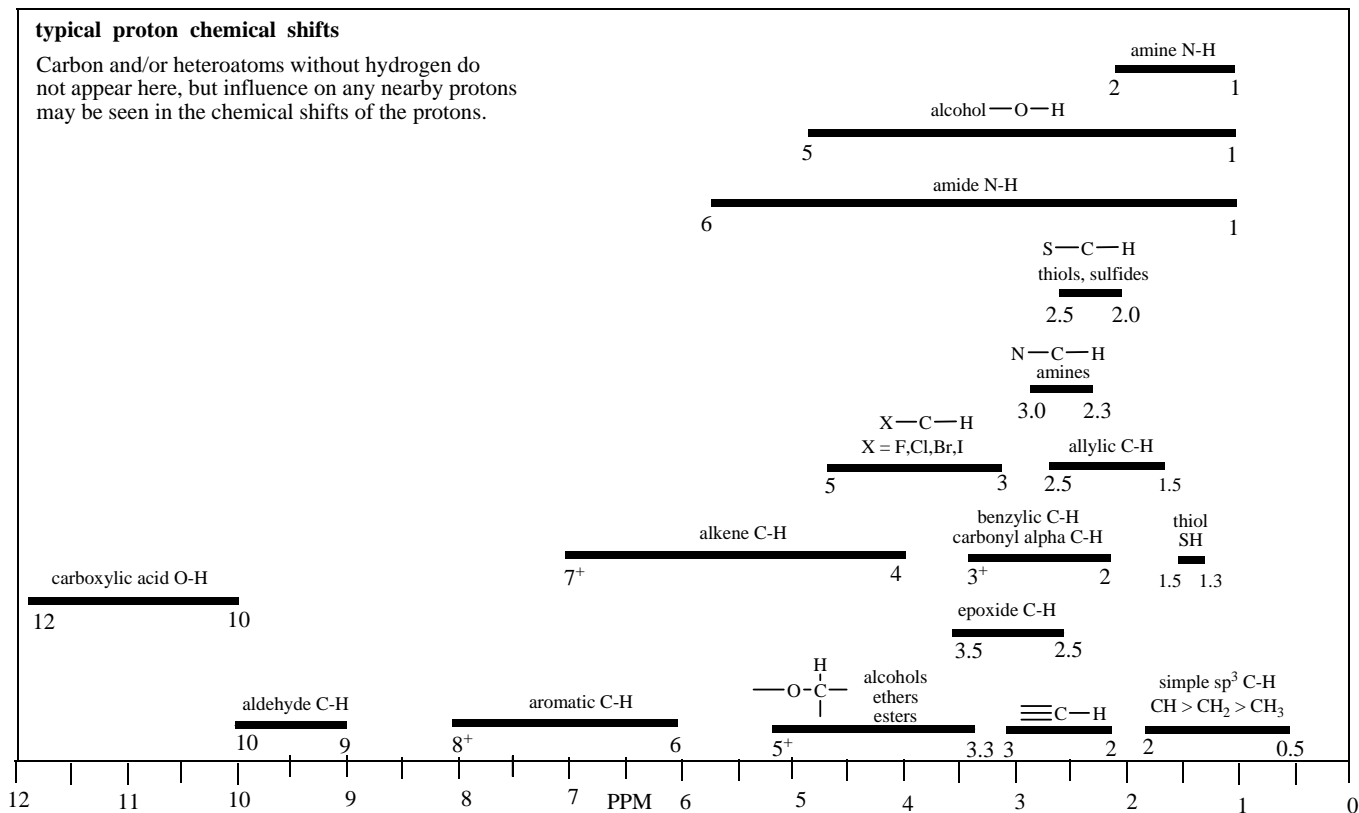
IR Flowchart to determine functional groups in a compound (all values in cm^{-1}).

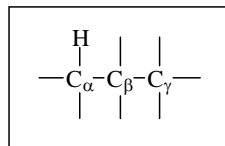
IR Spectrum		IR Spectrum	
has C=O band (1650-1800 cm^{-1}) very strong		does not have C=O band	
<p>aldehydes</p>  <p>1725-1740 (saturated) 1660-1700 (unsaturated)</p> <p>aldehyde C-H 2860-2800 (both weak) ← sometimes lost in sp^3 CH peaks</p>		<p>alkanes</p> <p>sp^3 C-H stretch 2850-3000</p> <p>sp^3 C-H bend 1460 & 1380</p> <p>C—C not useful</p>	
<p>ketones</p>  <p>1710-1720 (saturated) 1680-1700 (unsaturated) 1715-1810 (rings: higher in small rings)</p>		<p>alkenes</p> <p>sp^2 C-H stretch 3000-3100</p> <p>sp^2 C-H bend 650-1000 (see table for spectral patterns)</p> <p>C=C 1600-1660 weak or not present</p>	
<p>esters - rule of 3</p>  <p>1735-1750 (saturated) 1715-1740 (unsaturated) 1735-1820 (higher in small rings)</p> <p>acyl C—O 1150-1350 (acyl, strong)</p> <p>alkoxy C—O (1000-1150, alkoxy, medium)</p>		<p>alkynes</p> <p>C≡C 2150 (variable intensity)</p> <p>not present or weak when symmetrically substituted, a little lower when conjugated</p> <p>sp C-H stretch 3300 sharp, strong</p> <p>sp C-H bend 620</p>	
<p>acids</p>  <p>1700-1730 (saturated) 1715-1740 (unsaturated) 1680-1700 (higher in small rings)</p> <p>acyl C—O 1210-1320 (acyl, strong)</p> <p>acid O—H 2400-3400, very broad (overlaps C-H stretch)</p>		<p>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).</p>	
<p>amides</p>  <p>1630-1680 (saturated) 1745 (in 4 atom ring)</p> <p>1° 3350 & 3180, two bands for 1° amides, one band for 2° amides, stronger than in amines, extra overtone sometimes at 3100</p> <p>2°</p> <p>N—H N-H bend, 1550-1640, stronger in amides than amines</p>		<p>alkynes</p> <p>C≡N \approx 2250 sharp, stronger than alkynes, a little lower when conjugated</p>	
<p>acid chlorides</p>  <p>1800 (saturated) 1770 (unsaturated)</p> <p>Inductive pull of Cl increases the electron density between C and O.</p>		<p>aromatics</p> <p>sp^2 C-H stretch 3050-3150</p> <p>sp^2 C-H bend 690-900 (see table), overtone patterns between 1660-2000</p> <p>C=C 1600 & 1480 can be weak</p>	
<p>anhydrides</p>  <p>1760 & 1820 (saturated) 1725-1785 (unsaturated) two strong bands</p> <p>acyl C—O 1150-1350 (acyl, strong)</p>		<p>Alkene sp^2 C-H bending patterns</p> <p>monosubstituted (985-1000, 900-920)</p> <p>geminal disubstituted (960-990)</p> <p>cis disubstituted (675-730)</p> <p>trans disubstituted (880-900)</p> <p>trisubstituted (790-840)</p> <p>tetrasubstituted (none, no sp^2 C-H)</p>	
<p>nitro compounds</p>  <p>1500-1600, asymmetric (strong) 1300-1390, symmetric (medium)</p>		<p>Aromatic sp^2 C-H bending patterns</p> <p>monosubstituted (730-770, 690-710)</p> <p>ortho disubstituted (735-770)</p> <p>meta disubstituted (880-900, sometimes, 750-810, 680-725)</p> <p>para disubstituted (790-840)</p>	
<p>ethers</p>  <p>1120 (aliphatic) 1040 & 1250 (aromatic)</p>		<p>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.</p>	
<p>carbon-halogen bonds</p>  <p>usually not very useful</p> <p>X = F, Cl, Br, I</p>		<p>thiols</p> <p>thiol S—H \approx 2550 (weak) (easy to overlook)</p>	
<p>amines</p>  <p>1° 3300 - 3500, two bands for 1° amines, one band for 2° amines, weaker than in amides,</p> <p>2°</p> <p>N—H N-H bend, 1550-1640, stronger in amides than amines</p> <p>N—C 1000-1350 (uncertain)</p>		<p>nitro compounds</p> <p>1500-1600, asymmetric (strong) 1300-1390, symmetric (medium)</p>	

deshielding side = less electron rich
(inductive & resonance)

Typical ¹H and ¹³C NMR chemical shift values.

shielding side = more electron rich
(inductive & resonance)



Calculation of chemical shifts for protons at sp^3 carbons

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 ₂ N- (amine nitrogen)	1.5	0.2	0.1
RCONH- (amide nitrogen)	2.1	0.3	0.1
O ₂ N- (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 ₂ C- (carboxylic acid)	1.1	0.3	0.1
RO ₂ C- (ester, carbon side)	1.1	0.3	0.1
H ₂ NOC- (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

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

$$\delta CH_3 = 0.9 + \sum(\beta + \gamma) \quad H_3C-\begin{array}{c} | \\ C_\beta-C_\gamma \\ | \end{array}$$

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 (CH₂) using the following formula

$$\delta CH_2 = 1.2 + \sum(\alpha + \beta + \gamma) \quad \begin{array}{c} H \\ | \\ H-C_\alpha-C_\beta-C_\gamma \\ | \end{array}$$

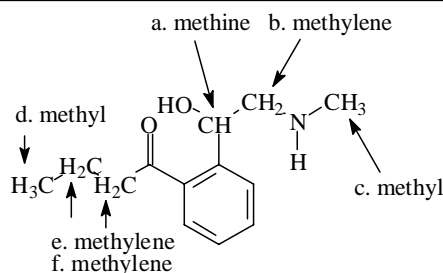
Σ is the summation symbol for all substituents considered

Starting value and equation for CH's

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

$$\delta CH = 1.5 + \sum(\alpha + \beta + \gamma) \quad \begin{array}{c} H \\ | \\ -C_\alpha-C_\beta-C_\gamma \\ | \end{array}$$

Σ is the summation symbol for all substituents considered



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

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

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

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

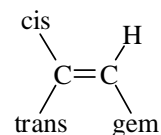
$$\text{c. methine} = 1.5 + (1.4)_\alpha + (2.3)_\alpha + (0.2)_\beta = 5.4 \text{ ppm} \\ \text{actual} = 5.2$$

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

Estimated chemical shifts for protons at alkene sp^2 carbons

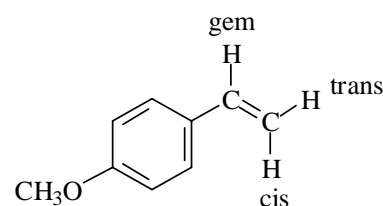
Substituent	α_{geminal}	α_{cis}	α_{trans}
H-Hydrogen	0.0	0.0	0.0
R-Alkyl	0.5	-0.2	-0.3
$C_6H_5CH_2$ -Benzyl	0.7	-0.2	-0.2
X- CH_2 -Halomethyl	0.7	0.1	0.0
(H)/ $ROCH_2$ -alkoxymethyl	0.6	0.0	0.0
(H) $_2$ /R $_2$ N CH_2 -aminomethyl	0.6	-0.1	-0.1
$RCOCH_2$ - α -keto	0.7	-0.1	-0.1
N $CCCH_2$ - α -cyano	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-alkoxy (ether)	1.2	-1.1	-1.2
RCO_2 -O-ester	2.1	-0.4	-0.6
(H) $_2$ /R $_2$ N-N-amino	0.8	-1.3	-1.2
RCONH-N-amide	2.1	-0.6	-0.7
O $_2$ N-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 $_2$ C-C-acid	0.8	1.0	0.3
RO $_2$ C-C-ester	0.8	1.0	0.5
H $_2$ NOC-C-amide	0.4	1.0	0.5
NC-Nitrile	0.3	0.8	0.6

Substitution relative to calculated "H"



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

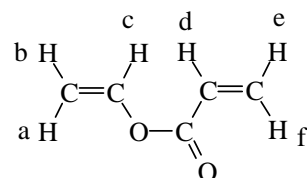
Example Calculation



$$\begin{aligned} \delta_{\text{gem}} &= 5.2 + 1.4 = 6.6 \\ \text{actual} &= 6.6 \end{aligned}$$

$$\begin{aligned} \delta_{\text{trans}} &= 5.2 - 0.1 = 5.1 \\ \text{actual} &= 5.1 \end{aligned}$$

$$\begin{aligned} \delta_{\text{cis}} &= 5.2 + 0.4 = 5.7 \\ \text{actual} &= 5.6 \end{aligned}$$



$$\begin{aligned} \delta_a &= 5.2 + (-0.4) = 4.8 \\ \text{actual} &= 4.9 \text{ (J = 14, 1.6 Hz)} \end{aligned}$$

$$\begin{aligned} \delta_b &= 5.2 + (-0.6) = 4.6 \\ \text{actual} &= 4.6 \text{ (J = 6, 1.6 Hz)} \end{aligned}$$

$$\begin{aligned} \delta_c &= 5.2 + 2.1 = 7.3 \\ \text{actual} &= 7.4 \text{ (J = 14, 6 Hz)} \end{aligned}$$

$$\begin{aligned} \delta_d &= 5.2 + 0.8 = 6.0 \\ \text{actual} &= 6.2 \text{ (J = 18, 11 Hz)} \end{aligned}$$

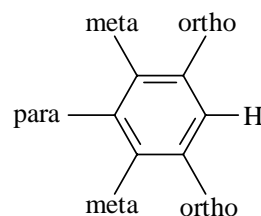
$$\begin{aligned} \delta_e &= 5.2 + 0.5 = 5.7 \\ \text{actual} &= 5.8 \text{ (J = 11, 1.4 Hz)} \end{aligned}$$

$$\begin{aligned} \delta_f &= 5.2 + 1.0 = 6.2 \\ \text{actual} &= 6.4 \text{ (J = 18, 1.4 Hz)} \end{aligned}$$

Estimated chemical shifts for protons at aromatic sp^2 carbons

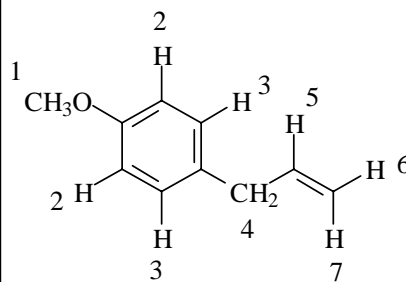
Substituent	α ortho	α meta	α para
H- Hydrogen	0.0	0.0	0.0
CH ₃ - Methyl	-0.2	-0.1	-0.2
ClCH ₂ - Chloromethyl	0.0	0.0	0.0
Cl ₃ C- Halomethyl	0.6	0.1	0.1
HOCH ₂ - Hydroxymethyl	-0.1	-0.1	-0.1
R ₂ C=CR- Alkenyl	0.1	0.0	-0.1
C ₆ H ₅ - Phenyl	1.4	0.4	-0.1
F- Fluoro	-0.3	0.0	-0.2
Cl- Chloro	0.0	0.0	-0.1
Br- 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"



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

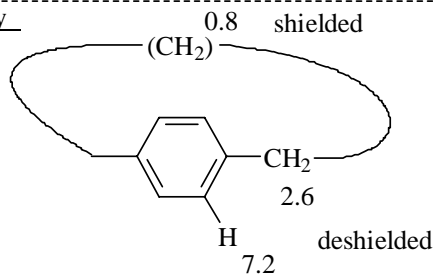
Example Calculation



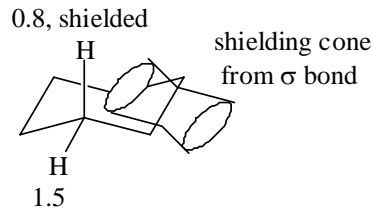
- $\delta(\text{CH}_3) = 0.9 + 2.8 = 3.7$
actual = 3.8
- $\delta(2) = 7.3 + (-0.5)_{\text{ortho}} + (-0.1)_{\text{para}} = 6.7$
actual = 6.8
- $\delta(3) = 7.3 + (-0.2)_{\text{ortho}} + (-0.4)_{\text{para}} = 6.7$
actual = 7.1
- $\delta(\text{CH}_2) = 1.2 + (0.8)\alpha + (1.4)\alpha = 3.4$
actual = 3.3
- $\delta(5) = 5.2 + (0.7)_{\text{gem}} = 5.9$
actual = 5.9
- $\delta(6) = 5.2 + (-0.2)_{\text{trans}} = 5.0$
actual = 5.1
- $\delta(7) = 5.2 + (-0.2)_{\text{cis}} = 5.0$
actual = 5.1

Real Examples of Combination Effects on Chemical Shifts

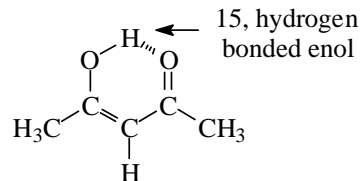
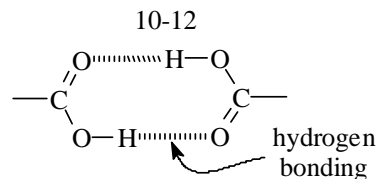
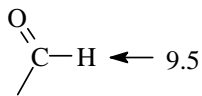
π bond anisotropy



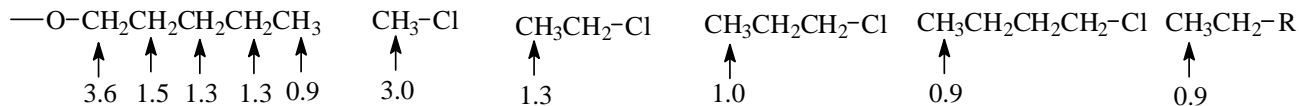
σ bond example too



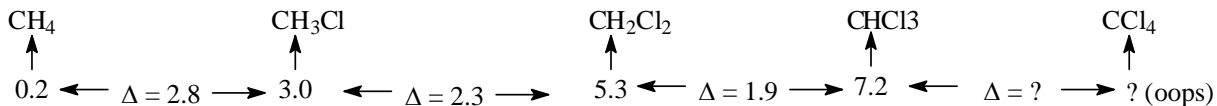
electronegativity and π bond



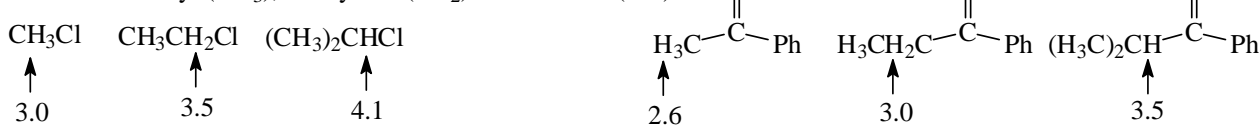
electronegative substituent and distance from protons



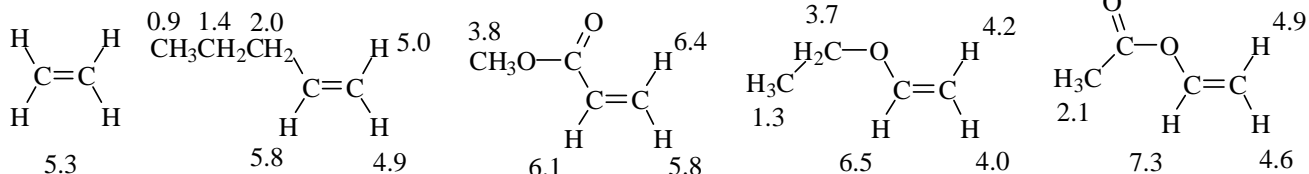
multiple substituents



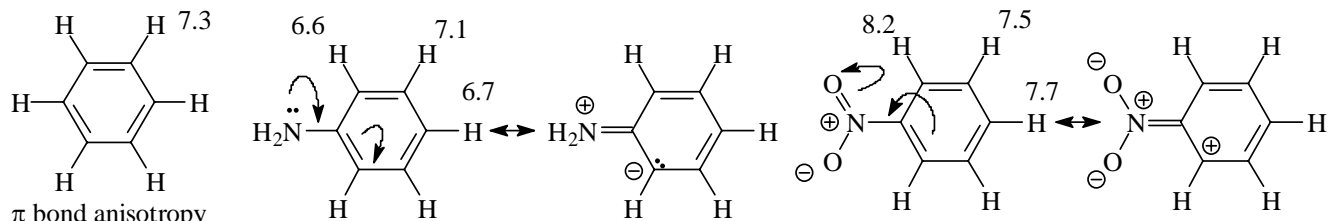
substituents at methyl (CH₃), methylene (CH₂) and methine (CH)



alkene substituent resonance and inductive effects



aromatic resonance and inductive effects



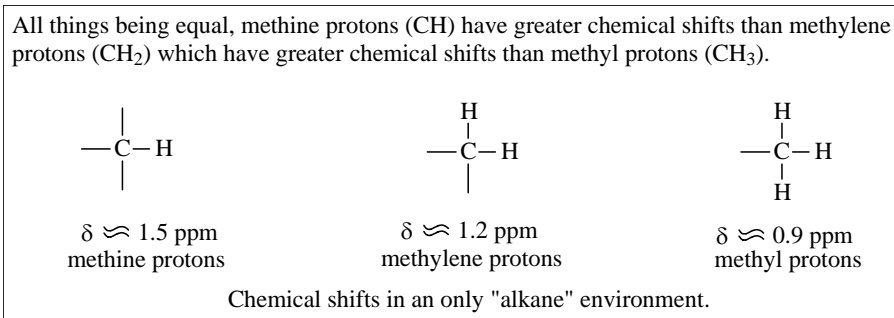
π bond anisotropy produces deshielding effect on aromatic protons.

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.

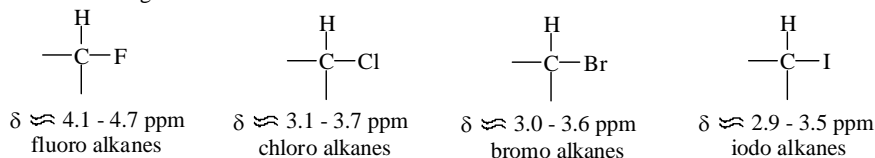
sp C-H	RO-H alcohol H = 1-5	R ₂ N-H amine H = 1-5	enol H = 10-17
H-C≡C-H 2.4	ArO-H phenol H = 4-10	R-C(=O)-NH ₂ amide H = 5-8	H-O-C=C
R-C≡C-H 1.9	RS-H thiol H = 1-2.5		
Ar-C≡C-H 3.0	ArO-H aromatic thiol H = 3-4		R-C(=O)-O-H acid H = 10-13

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.

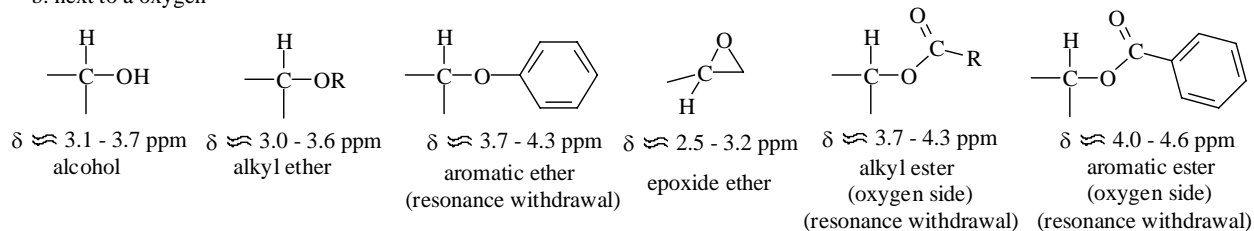


1. **sp^3 C-H** Electronegative atoms in the vicinity of hydrogen deshield protons and produce a larger chemical shift. If the electronegative atom is in resonance with an adjacent pi system that further withdraws electron density, the chemical shift is increased.

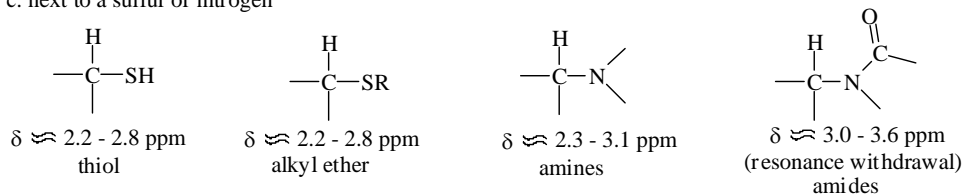
a. next to a halogen



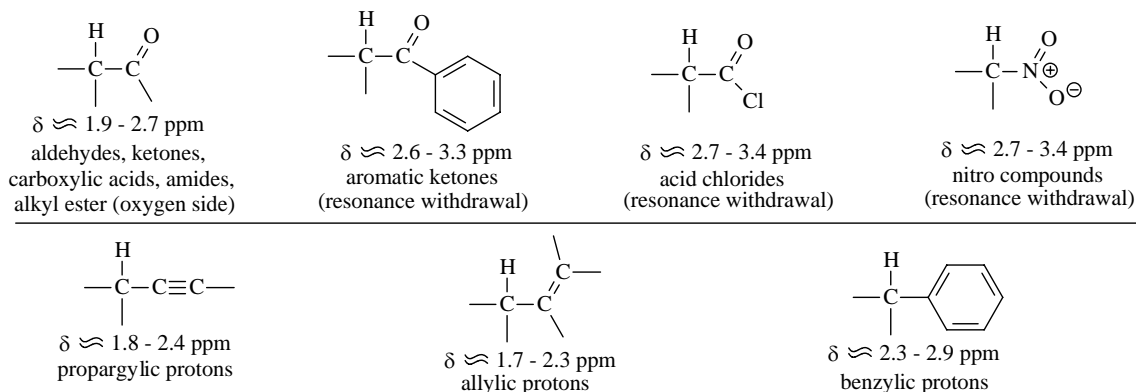
b. next to a oxygen



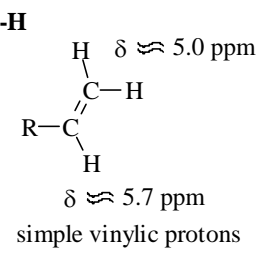
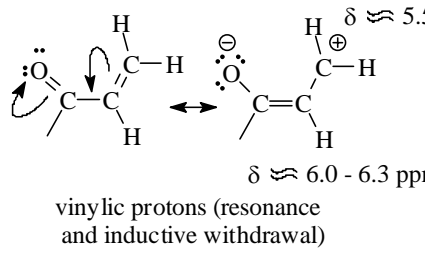
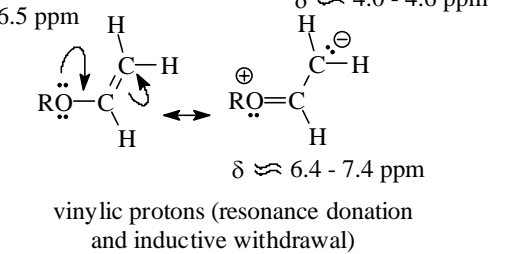
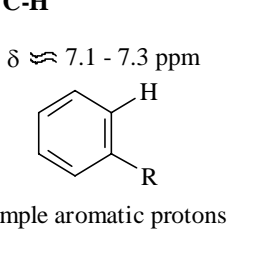
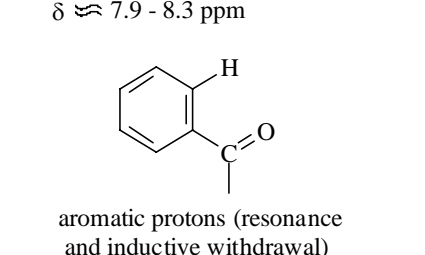
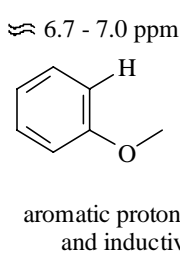
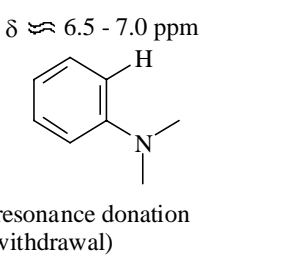
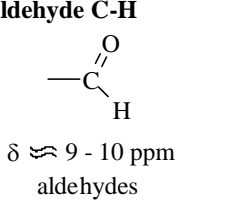

c. next to a sulfur or nitrogen



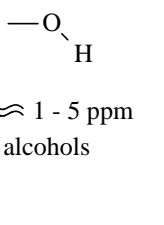
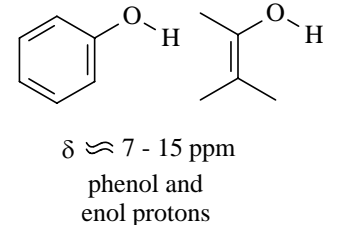
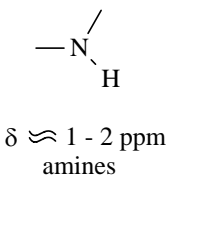
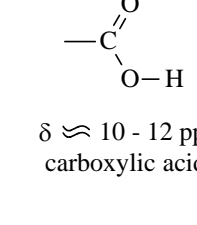
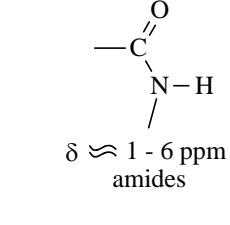
2. **sp^3 C-H** Pi bonds in the vicinity of hydrogen also deshield protons via pi bond anisotropy and produce a larger chemical shift. The closer the sp^3 C-H is to the pi bond the greater chemical shift observed. When an electronegative atom is part of the pi bond, the chemical shift also increases.



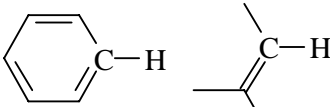
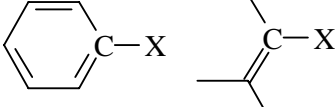
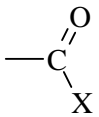
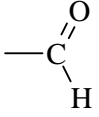
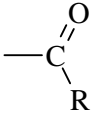
3. **sp^2 C-H** Hydrogens at the side of a pi bond are deshielded even more than above via pi bond anisotropy. An aldehyde produces the largest effect due to the electronegative oxygen, followed by an aromatic ring, followed by alkenes and finally terminal alkynes. (One sp C-H)

<p>alkene C-H</p>  <p>$\delta \approx 5.0$ ppm simple vinylic protons</p>	 <p>$\delta \approx 5.5 - 6.5$ ppm vinylic protons (resonance and inductive withdrawal)</p>	 <p>$\delta \approx 4.0 - 4.6$ ppm vinylic protons (resonance donation and inductive withdrawal)</p>	
<p>aromatic C-H</p>  <p>$\delta \approx 7.1 - 7.3$ ppm simple aromatic protons</p>	<p>$\delta \approx 7.9 - 8.3$ ppm</p>  <p>aromatic protons (resonance and inductive withdrawal)</p>	<p>$\delta \approx 6.7 - 7.0$ ppm</p>  <p>aromatic protons (resonance donation and inductive withdrawal)</p>	<p>$\delta \approx 6.5 - 7.0$ ppm</p>  <p>aromatic protons (resonance donation and inductive withdrawal)</p>
<p>aldehyde C-H</p>  <p>$\delta \approx 9 - 10$ ppm aldehydes</p>	<p>alkyne C-H</p>  <p>$\delta \approx 1.9 - 3.2$ ppm terminal alkyne protons</p>		

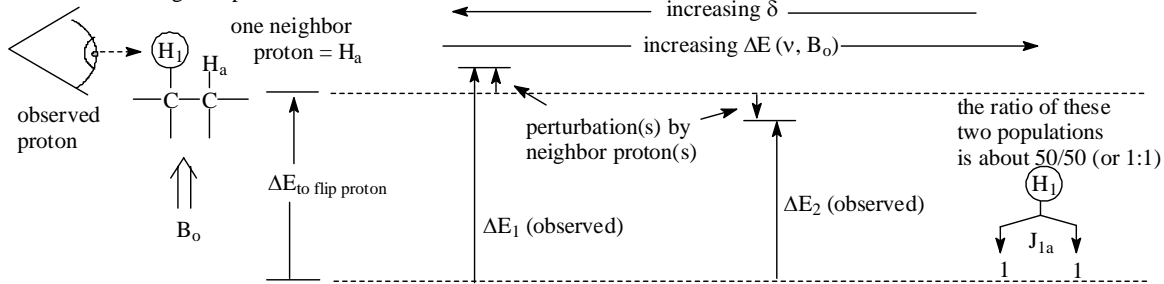
4. There are several kinds of hydrogen attached to heteroatoms. Some of these are listed below. Often these hydrogens do not follow the N+1 rule because they exchange via acid/base proton exchanges and are not next to neighbor protons long enough to allow coupling to be observed. They are often observed 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.

 <p>$\delta \approx 1 - 5$ ppm alcohols</p>	 <p>$\delta \approx 7 - 15$ ppm phenol and enol protons</p>	 <p>$\delta \approx 1 - 2$ ppm amines</p>	 <p>$\delta \approx 10 - 12$ ppm carboxylic acids</p>	 <p>$\delta \approx 1 - 6$ ppm amides</p>
---	---	---	---	---

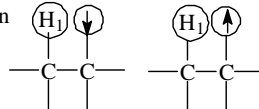
When carbons are decoupled from their attached hydrogens they all appear as singlets (as if there were no hydrogen neighbors). When carbons are coupled to their hydrogens, carbons follow the N+1 rule. Methyls appear as quartets = q, methylenes appear as triplets = t, methines appear as doublets = d, 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- $\delta \approx 0 - 30 \text{ ppm}$ (q)	$-\text{CH}_2$ $\delta \approx 20 - 40 \text{ ppm}$ (t)	$-\text{CH}$ $\delta \approx 30 - 50 \text{ ppm}$ (d)	$-\text{C}-$ $\delta \approx 30 - 60 \text{ ppm}$ (s)
sp^3 carbon next to oxygen	CH_3- $\delta \approx 50 - 60 \text{ ppm}$ (q)	$-\text{CH}_2$ $\delta \approx 55 - 80 \text{ ppm}$ (t)	$-\text{CH}$ $\delta \approx 60 - 80 \text{ ppm}$ (d)	$-\text{C}-$ $\delta \approx 70 - 90 \text{ ppm}$ (s)
sp^3 carbon next to nitrogen	CH_3- $\delta \approx 10 - 50 \text{ ppm}$ (q)	$-\text{CH}_2$ $\delta \approx 35 - 55 \text{ ppm}$ (t)	$-\text{CH}$ $\delta \approx 50 - 70 \text{ ppm}$ (d)	$-\text{C}-$ $\delta \approx 50 - 70 \text{ ppm}$ (s)
sp^3 carbon next to bromine or chlorine		$-\text{CH}_2$ $\delta \approx 25 - 50 \text{ ppm}$ (t)	$-\text{CH}$ $\delta \approx 60 - 80 \text{ ppm}$ (d)	$-\text{C}-$ $\delta \approx 60 - 80 \text{ ppm}$ (s)
sp carbon (alkynes)	$-\text{C}\equiv\text{C}-$ $\delta \approx 70 - 90 \text{ ppm}$		sp carbon (nitriles)	$-\text{C}\equiv\text{N}$ $\delta \approx 110 - 125 \text{ ppm}$
sp^2 carbon (alkenes and aromatics)	 $\delta \approx 100 - 140 \text{ ppm}$ simple sp^2 carbon resonance donation moves δ lower, resonance withdrawal moves δ higher		 $\delta \approx 140 - 160^+ \text{ ppm}$ sp^2 carbon attached to an electronegative atom (X = oxygen, nitrogen, halogen) or C_β carbon conjugated with a carbonyl group	
	 $\delta \approx 160 - 180 \text{ ppm}$ carboxyl carbons (acids, esters, amides) (s)	 $\delta \approx 190 - 210 \text{ ppm}$ aldehyde carbons, lower values when conjugated (d)	 $\delta \approx 190 - 220 \text{ ppm}$ ketone carbons, lower values when conjugated (s)	

1. One nearest neighbor proton

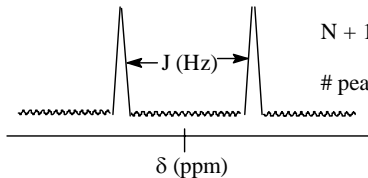


Protons in this environment have a small cancellation of the external magnetic field, B_0 , and produce a smaller energy transition by that tiny amount.



Protons in this environment have a small additional increment added to the external magnetic field, B_0 , and produce a higher energy transition by that tiny amount.

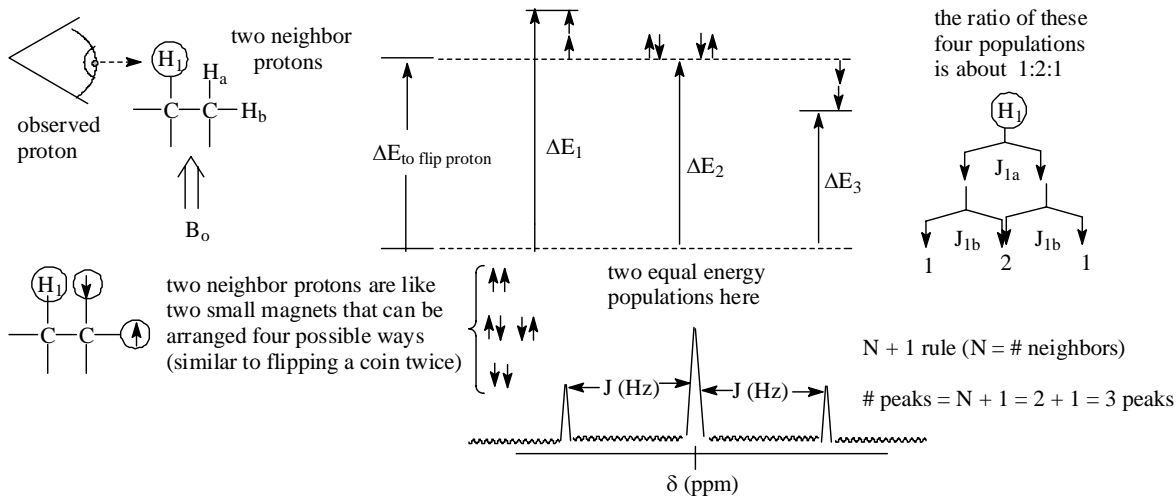
J = coupling constant
small difference in energy due to differing neighbor's spin (in Hz)



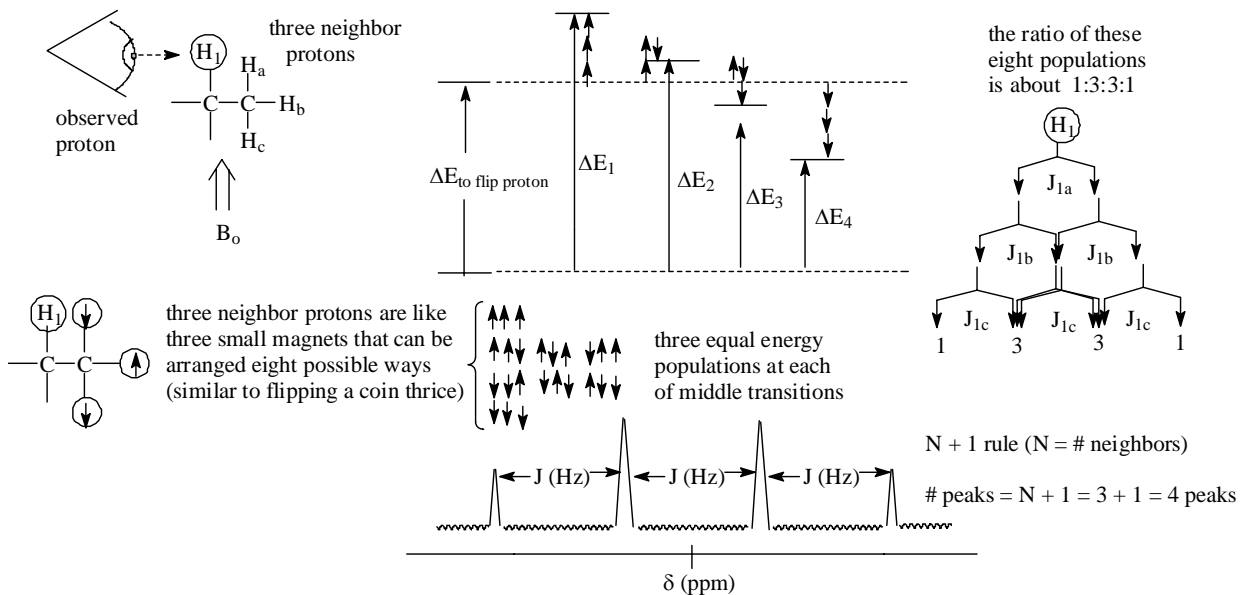
$N + 1$ rule ($N = \#$ neighbors)

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

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



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



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

s = singlet									1 peak = 100%
d = doublet									
t = triplet									
q = quartet									
qnt = quintet									
sex = sextet									
sep = septet									
o = octet									

1
 1 1
 1 2 1
 1 3 3 1
 1 4 6 4 1
 1 5 10 10 5 1
 1 6 15 20 15 6 1
 1 7 21 35 35 21 7 1

} relative sizes of peaks in multiplets

Combinations of these are possible.

dd = doublet of doublets

ddd = doublet of doublet of doublets


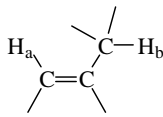
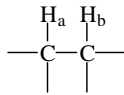
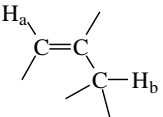
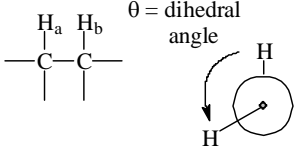
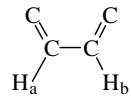
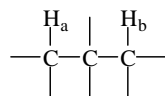
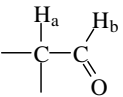
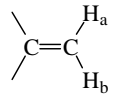
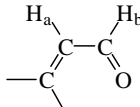
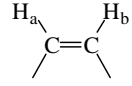
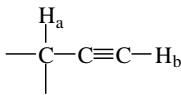
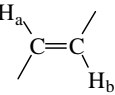
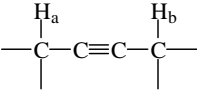
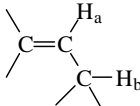
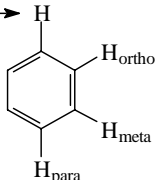
dddd = doublet of doublet of doublet of doublets

dt = doublet of triplets

td = triplet of doublets

etc.

Typical Coupling Constants

	<u>Range</u>	<u>Typical</u>		<u>Range</u>	<u>Typical</u>
 <p>geminal protons - can have different chemical shifts and split one another if they are diastereotopic</p>	0-30 Hz	14 Hz	 <p>cis / allylic coupling, notice through 4 bonds</p>	0-3 Hz	1 Hz
 <p>vicinal protons are on adjacent atoms, when freely rotating coupling averages out to about 7 Hz</p>	6-8 Hz	7 Hz	 <p>trans / allylic coupling, notice through 4 bonds</p>	0-3 Hz	1 Hz
 <p>θ = dihedral angle</p> <p>depends on dihedral angle, see plot of Karplus equation</p>	0-12 Hz	7 Hz	 <p>sp^2 vicinal coupling (different π bonds)</p>	9-13 Hz	10 Hz
 <p>protons rarely couple through 4 chemical bonds unless in a special, rigid shapes (i.e. W coupling)</p>	0-1 Hz	0 Hz	 <p>sp^3 vicinal aldehyde coupling</p>	1-3 Hz	2 Hz
 <p>sp^2 geminal coupling</p>	0-3 Hz	2 Hz	 <p>sp^2 vicinal aldehyde coupling</p>	5-8 Hz	6 Hz
 <p>sp^2 cis (acylic) coupling (always smaller than the trans isomer)</p>	5-11 Hz	10 Hz	 <p>sp / propargylic coupling notice through 4 bonds</p>	2-3 Hz	2 Hz
 <p>sp^2 trans coupling (always larger than the cis isomer)</p>	11-19 Hz	17 Hz	 <p>bis-propargylic coupling notice through 5 bonds</p>	2-3 Hz	3 Hz
 <p>sp^2 / sp^3 vicinal coupling</p>	4-10 Hz	7 Hz	<p>ortho, meta and para coupling to this proton</p>  <p>ortho H_{ortho} meta H_{meta} para H_{para}</p>	ortho 6-10 Hz meta 2-3 Hz para 0-1 Hz	9 Hz 2 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.