

Spectroscopy Charts and Rules – NMR, MS, and IR

The ^1H NMR “Rules”

1. **n+1** rule applies to neighbors that are three bonds apart (for two bonds apart only if hydrogens are diastereotopic)
2. The chemical shift range is 0-10 ppm (some shifts can go as far as 14 ppm)
3. For chemical shift ranges see the handout, **Proton Chemical Shift Range**.
4. Multiplicity notation is:

Simple multiplets

Symbol	Name of pattern (#or peaks)	Number of neighbors (protons)
s	singlet (1)	0
d	doublet (2)	1
t	triplet (3)	2
q	quartet (4)	3
-	quintet (5)	4

More complicated multiplets are possible, some examples are:

dd – “doublet of doublets” – 2 different neighbors – one of each

dt – “doublet of triplet” – 2 different neighbors – one of one type and two of another (different J values)

dq – “doublet of quartets” – 2 different neighbors – one of one type and three of another

ddd – “doublet of doublet of doublets” – 3 different neighbors – one of each type

Undetermined multiplicity

m – “multiplet” (many peaks) – can’t tell how many neighbors, can’t tell all of the coupling, but at least might know the integration of the peak which tells the number of hydrogens represented.

5. “Exchangeable” means that the hydrogen is on an O or N (or rarely, a special type of C, like an α -carbon).
6. Integration of NMR peaks leads to the smallest whole number ratio of the types of hydrogens in a molecule, which is not necessarily the actual ratio (the molecular formula can confirm this).

The ^{13}C NMR "Rules"

1. The chemical shift range is 0-220 ppm
2. The following are the *approximate* ranges depending on where the carbon is in a molecule. See also the handout, **Carbon Chemical Shift Range**.

alkanes are 0-60 (this is always the order $\text{CH} > \text{CH}_2 > \text{CH}_3$)

carbons next to N are 30-50

carbons next to O are 40-80

carbons next to X are 25-80

alkynes are 65-90

alkene carbons are 100-150

aromatic carbons are 110-170

carbonyl carbons are 150-220

acids, esters, amides are 150-180

aldehydes and ketones are 190-220

Note the effects are additive, e.g., two oxygens attached to a carbon is almost (but always less than) twice the value of one oxygen attached. Also, note the overlap of the regions – *the chemical shift alone doesn't tell which electronegative atoms is attached to carbon*.

3. If the data provided has a letter next to the number, then it comes from a separate test (e.g, the DEPT experiment, the APT, or even the older "off-resonance" experiment) and indicates how many hydrogens are attached to that particular carbon through the "n+1" rule.

s-singlet (single peak) – 0 attached hydrogens

d-doublet (two peaks) – 1 attached hydrogen

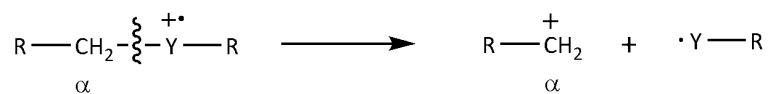
t-triplet (three peaks) – 2 attached hydrogens

q- quartet (four peaks) – 3 attached hydrogens

4. If a number appears in parentheses next to the letter, it indicates how many of that type of carbon are in the molecule – ones that are identical (chemically equivalent). (Integration for carbon NMR doesn't work, so other methods are used to determine the number of carbons that are equivalent.)
5. If the DEPT spectrum is given, the ^{13}C spectrum indicates positive peaks for each carbon that has an odd number of hydrogens (CH , CH_3) and negative peaks for even numbers of hydrogens (CH_2). If the ^{90}C spectrum is also provided, it will show positive peaks for only carbons with exactly one hydrogen (CH). Peaks that are present in the regular ^{13}C NMR spectrum that do not appear in the DEPT are for carbons that do not have any hydrogens on them.

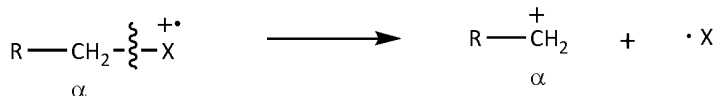
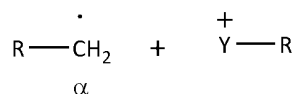
Mass Spectrometry – Common Fragmentation Patterns

α -cleavage



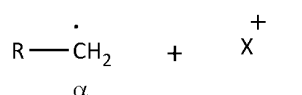
Y = alkyl, O, N

OR



X = halogen

OR



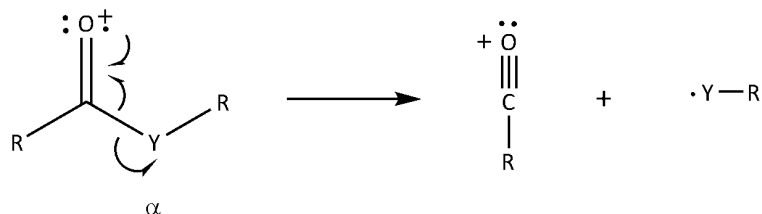
Isotopic ratios

$^{19}\text{F} = 100\%$

$^{35}\text{Cl}/^{37}\text{Cl} = 75:25 (3:1)$

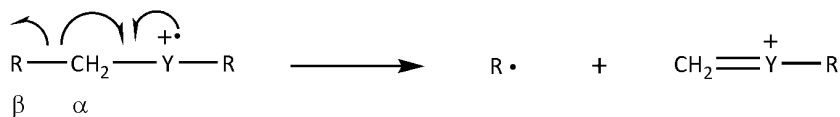
$^{79}\text{Br}/^{81}\text{Br} = 49:51 (1:1)$

$^{127}\text{I} = 100\%$



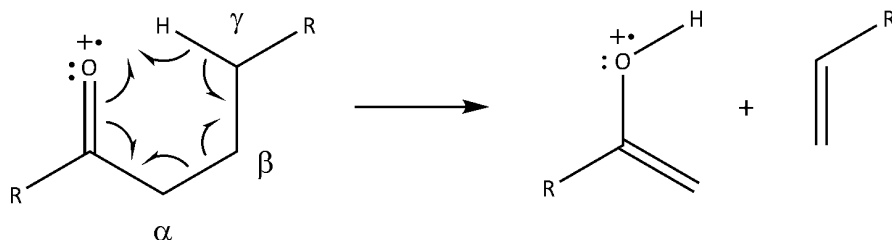
Y = alkyl (ketones)
O (esters)
N (amides)

β -cleavage

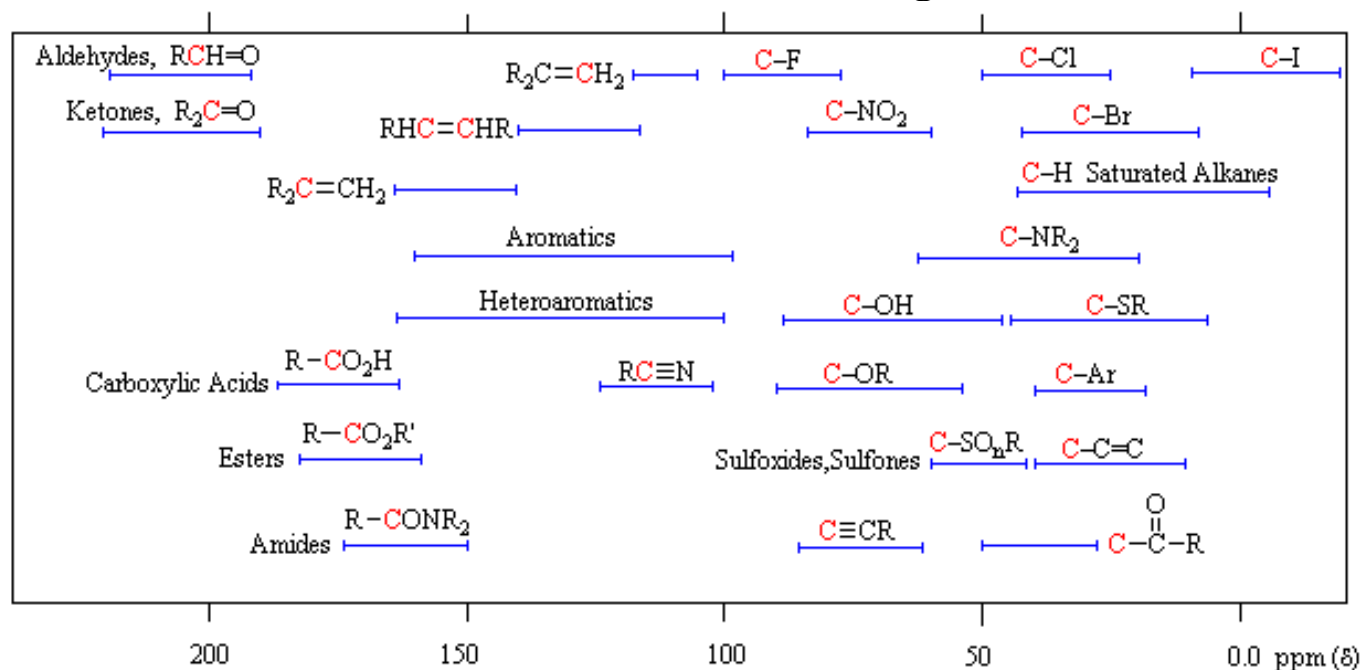


Y = O, N

McLafferty rearrangement

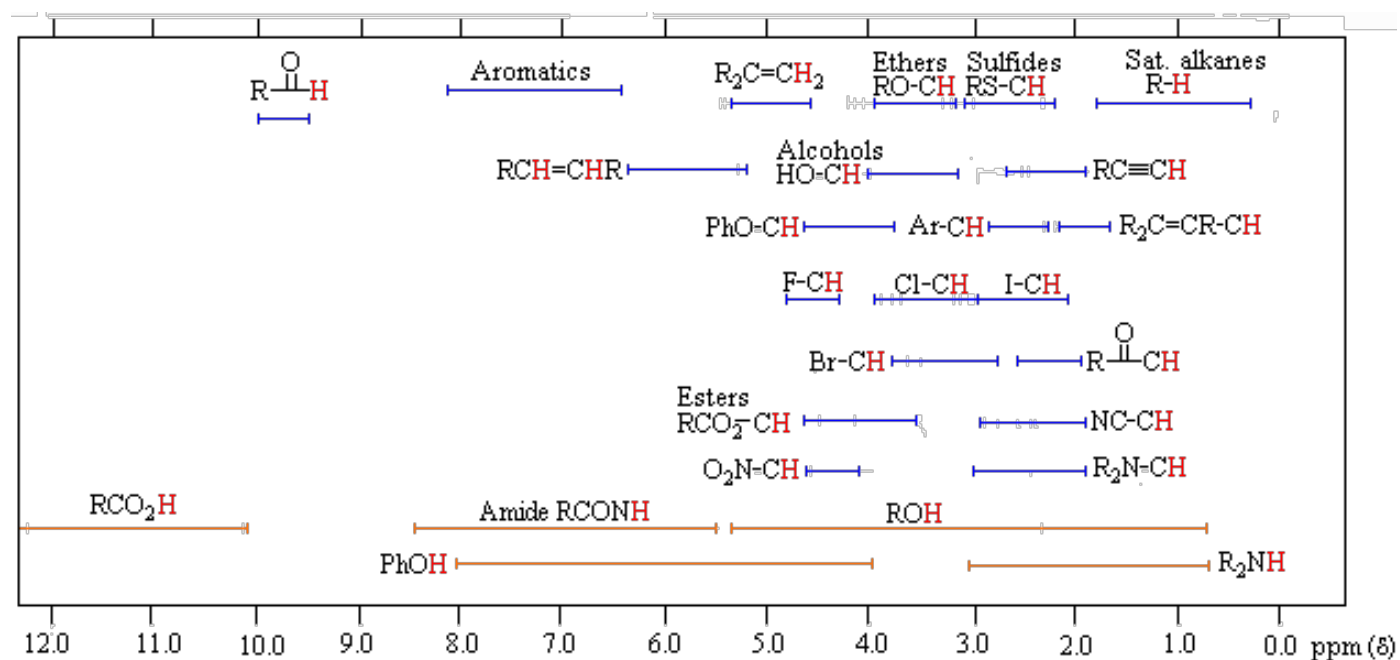


Carbon Chemical Shift Ranges



(Source: <https://www2.chemistry.msu.edu/faculty/reusch/orgpage/nmr.htm>, accessed 11/25/19)

Proton Chemical Shift Ranges



(Source: <https://www2.chemistry.msu.edu/faculty/reusch/orgpage/nmr.htm>, accessed 12/25/19)

Infrared Spectra: Tables of Reference

X-H Region

Phenols and Alcohols	ROH	3700-3500 sharp or 3200-3600 broad(H-bonded)
Acids	RCO ₂ H	2800-3600 very broad
Amides and Amines	RCONHR R ₂ NH	3300-3500
C-H bonds	C≡C-H	3100-3300
	C=C-H	3000-3200
	C-C-H	2850-3000
	RCHO	2700-2800

sp Region


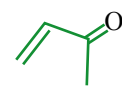
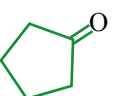
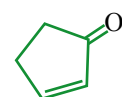

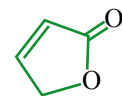
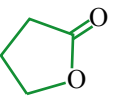
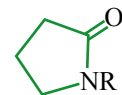
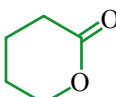
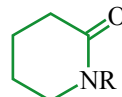
Acetylenes	C≡C	2100
Nitriles	C≡N	2200
Ketenes	C=C=O	2150
Allenes	C=C=C	1950

Double Bond Region

Alkenes	C=C	1600-1670 weak unless conjugated
Imines	C=N	1600-1700
Nitro	-NO ₂	1350-1550(two bands)

Carbonyl Groups

Note: subtract ca. 30 cm⁻¹ for conjugation (e.g. Ketones R₂C=O 1710 (subtract ca. 30 cm⁻¹ for conjugation) with a double bond or aromatic ring)

Anhydrides RC(O)OCOR	1740-1780, 1800-1840 (two bands)		6-membered and larger cyclic ketones 1710		1680
Acid Chlorides RCOCl	1790-1815		1740		1715
Esters RCO ₂ R	1725-1755		1780		1740
Acids RCO ₂ H	1700-1725		1770		1690-1740
Amides RCONR ₂	1630-1700		1730		1650
Urethanes R ₂ NCO ₂ R	1700				
Aldehydes RCHO	1720-1740				