^{13}C NMR (Sections 13.13,14)

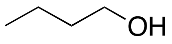
- ^{13}C is NMR active, ^{12}C is not
- Signals are much weaker, C-13 spectra are harder to get
  - C-13 gives about 1/10,000th as strong a signal as H-NMR
  - Because the natural abundance is only 1%, and the inherent sensitivity is only 1%
- A result is that for C-13 NMR, one or more of the following is usually true:
  1. Take longer
  2. Not as clean a baseline
  3. Higher sample/solvent concentration used
  4. Data processing tricks used in order to shorten the process. These often result in:
     - Loss of splitting information (our C-13 NMR's in lab…)
     - Loss of integration information (our C-13 NMR's in lab…)

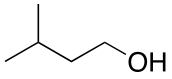
Summary of C-13 NMR Interpretation:

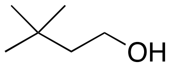
1. **Count how many lines** you have. **This will tell you how many types of carbons** you have. (Symmetry equivalent carbons can at times cause the number of lines to be less than the number of carbons in your structure.)
2. **Check diagnostic frequency windows** ("chemical shift windows") of the lines **to provide yes-or-no answers regarding the presence or absence of key functional groups** in your molecule.
3. If **splitting** information is provided, decide which carbons are CH_3, CH_2, CH, and no-H C's.

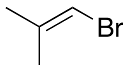
1. **Count how many lines** you have. **This will tell you how many types of carbons** you have.
   1. Each "unique" carbon gives a separate line.
   2. Symmetry duplicates give the same line.
   3. If there are more carbons in your formula than there are lines in your spectrum, it means you have some symmetry.

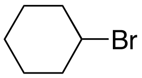
Q: How many lines would show in the C-13's for the following?

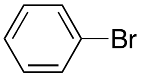












2. **Chemical Shifts: Where do the Lines Come?**

220-160 C=O carbonyl carbons, sp^2 hybridized

160-180 → typically ester

- for formulas that have two oxygens, being able to recognize ester group helps a ton

180-220 → other carbonyls (ketone, aldehyde, carboxylic acid, amide)

160-100 C alkene or aromatic carbons, sp^2 hybridized

- If a molecule has alkene or aromatic, it's usually easy to tell which it is based on chemical formula or on the number of lines in the 100-160 zone (2 for alkene, usually more for aromatics

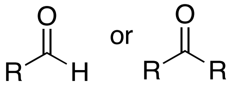
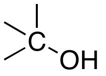
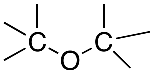
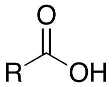
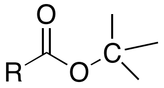
100-50 C-O oxygen-bearing carbons, single bonds only, sp^3 hybridized
80-30 C-N nitrogen bearing carbons, single bonds only, sp^3 hybridized
80-30 C-X halogen bearing carbons, single bonds only, sp^3 hybridized

50-0 C alkyl carbons, no oxygens attached, sp^3 hybridized

- This is the default zone for sp^3 carbons with no attached heteroatoms
- Allylic carbons still fall into the 50-0 zone, unlike in H-NMR where allylic hydrogens are distinct

- Halogens or nitrogens complicate things a bit, because they can appear on either side of the 50-divider.
- But for formulas involving only C, H, and O, the 50-divider is very, very useful.

Using the "Oxygen Zones" for Oxygenated Systems

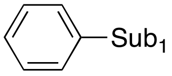
			220-160 Zone	100-50 Zone
One-Oxygen Formulas	Ketone, Aldehyde		180-220	
	Alcohol			One
	Ether			Two
Two-Oxygen Formulas	Acid		180-220	
	Ester		160-180	One
	Aldehyde/Ketone And Alcohol		180-220	One
	Aldehyde/Ketone And Ether		180-220	Two

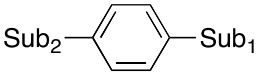
3. **Splitting**.
   - C13 NMR's are often acquired as "decoupled" spectra, in which each carbon signal appears as a singlet. This is the way our laboratory C13 NMR's come out.
   - However, at the cost of extra time it is also possible to get "coupled" C13 NMR's with splitting. The C-13 atoms are split by directly attached hydrogens.
   - These splitting values are very useful, and follow the N+1/N-1 rules (the number of lines is one greater than the number of attached H's).

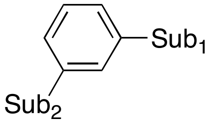
Quartert (q)	CH_3
Triplet (t)	CH_2
Doublet (d)	CH
Singlet (s)	C (no attached hydrogens)

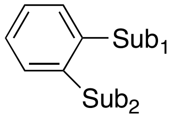
Aromatics, Symmetry, Splitting. Most aromatics have symmetry, and both the number of aromatic lines and the splitting of the aromatic lines can be indicative of the substitution pattern on a benzene. Mono- and para-disubstituted benzenes have symmetry.

4 lines	s, d, d, d	Monosubstituted benzene. (Has symmetry)
4 lines	s, s, d, d	Para-disubstituted benzene. (Has symmetry)
6 lines	s, s, d, d, d, d	Ortho- or meta-disubstituted benzene. (Has no symmetry)









4. **Signal Height/Size** Unlike 1H-NMR, where integration is really important, signal size is not very important in C-13 NMR.
   a. Signal amplification tricks (to save time) compromise accurate integration
   b. Even when lines have equal area, a narrower one looks much taller than a fatter one
   c. Two patterns that can be somewhat helpful.
      1. Carbons without any attached H's are short. Common in:
         a. carbonyls (aldehydes are the only carbonyl carbons that have hydrogens attached)
         b. substituted carbons in aromatic rings.
         c. T-butyl carbons
      2. Symmetry duplication multiplies signal height (if you have two copies of a carbon, the line will probably be taller than normal!)

Problem Solving and C-13

Alone	In Support with H-NMR
1. Calculate EU 2. Symmetry? Check lines versus formula 3. Look for Obvious Things • Oxygen zones, aryl zone… 4. Use Splitting 5. Look for ends groups • Methyl, phenyl, OH, halogen	Look for obvious things 1. Carbonyls? (any, and if so ester or aldehyde?) 2. Oxygen zones? 3. Aromatic or alkene, and if so with what kind of substitution pattern? 4. Symmetry? 5. CH_3, CH_2, CH count

Infrared Spectroscopy (Chapter 12, Nice Summary in Section 12-11)

- Examples, Contrast to NMR
- Much more complex than NMR
    - In NMR, we expect to explain everything, and we can solve full structures
- In IR, two typical uses:
    a. Functional Group Identification: focus on a few key zones (our use)
    b. "Fingerprint" matchups of unknowns to knowns (we won't do)

Major overall zones:

1600-3600 useful (stretching, useful for functional group ID)
1600-600 vibrations "fingerprint", always busy, not very useful for function group ID

Major Bands that are of some Functional Group Interest

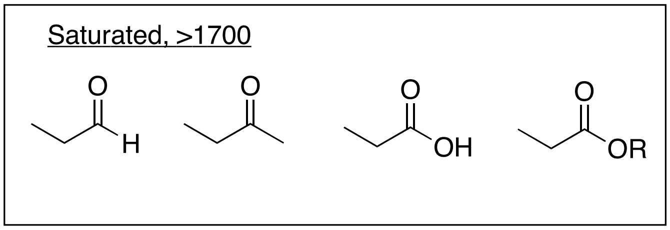
3500-2700	N-H, O-H, C-H single bonds
2300-2100	CN, CC triple bonds
1800-1580	C=O, C=N, C=C double bonds

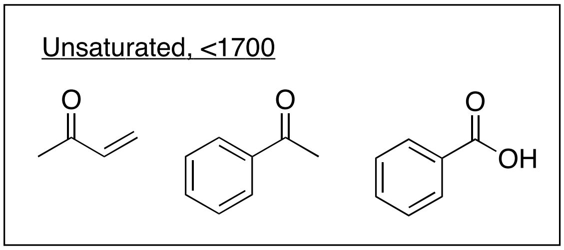
Practical Feature Groups

1. O-H/N-H Zone (except when O-H is a carboxylic acid O-H): 3500-3200
    - **Alcohol Recognition**
    - Amines or amides
    - Signals are sometimes rather broad due to hydrogen-bonding
    - Note: when looking at an actual spectrum, focus in specifically on the 3500-3200 range, don't just look generally around 3000
        - Because every organic molecule will have a big C-H signal around 2900-3000
        - That is ***not*** interesting or informative, and should ***not*** be mistaken for proof of alcohol
    - In contrast to alcohol O-H, carboxylic acid O-H signals are extremely broad, ranging somewhere within 3500-2200

2. Carbonyl Zone: Around 1710 ± 80
    - Very strong signal
    - First thing to check

    1700 rule
    - carbonyls >1700 are "saturated": no attached double-bonded carbons
    - carbonyls <1700 are "unsaturated": an sp^2 attached carbon (i.e. alkene or aromatic)


Saturated, >1700

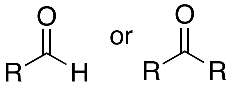
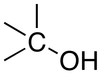
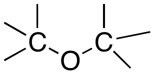
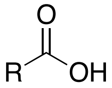
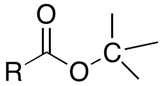

Unsaturated, <1700

Esters versus Ketones/Aldehydes/Acids
- Saturated esters 1735-1750
- Saturated ketones/aldehydes/acids: 1700-1720
- Very useful for recognizing when a two-oxygen formula contains an ester

Carboxyl Acids (versus hydroxy ketones)

- Acid has both a carbonyl in the ~1700 zone and a broad hydroxyl spread somewhere in the 3500-2200 zone
- A formula with two oxygens that has one as ketone and one as alcohol would give a carbonyl in the ~1700 zone but a tighter alcohol O-H in the 3500-3200 zone
- Very useful for quick recognition of carboxylic acids

Using the "Oxygen Zones" for Oxygenated Systems

			Carbonyl Zone	Hydroxyl Zone
One-Oxygen Formulas	Ketone, Aldehyde		1700-1720 (if saturated, <1700 if not)	
	Alcohol			3500-3200
	Ether			
Two-Oxygen Formulas	Acid		1700-1720 (if saturated, <1700 if not)	3500-3200 (**broad**)
	Ester		1735-1750 (if saturated)	
	Aldehyde/Ketone And Alcohol		1700-1720 (if saturated, <1700 if not)	3500-3200 (**broad**)
	Aldehyde/Ketone And Ether		1700-1720 (if saturated, <1700 if not)	

Practical Use for IR: Fast recognition of key functional group information
-helpful support for an NMR solution, if you know what functionality is present.

Summary of IR (Infrared) Interpretation

Check for Diagnostic Signals

3500-3200	OH or NH
1800-1641	C=O
3500-2500 + 1800-1640	CO_2H

Further Information in the "Carbonyl Zone"

<1700	Unsaturated C=O
>1700	Saturated C=O
1720-1701	Saturated ketones, aldehydes, acids
1750-1735	Saturated ester