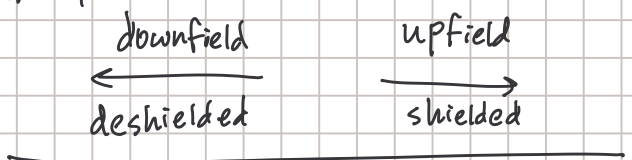
Ch 13 NMR

Note Title 10/24/2005

NMR spectrum



Chemical shift quantitative shifting upfield/downfield

- field strength is difficult to measure accurately
- radio frequency is more accurate/precise
  proportional to field strength (Hz)

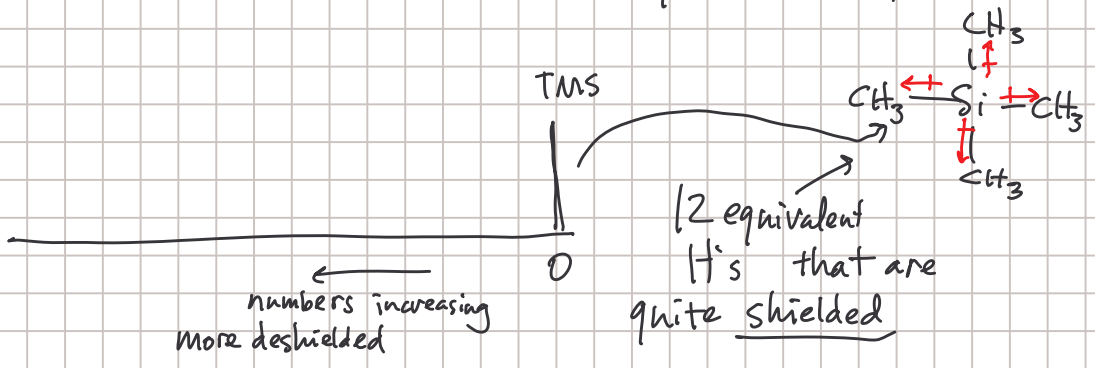
but this varies w/ spectrometer type

U of M NMR lab

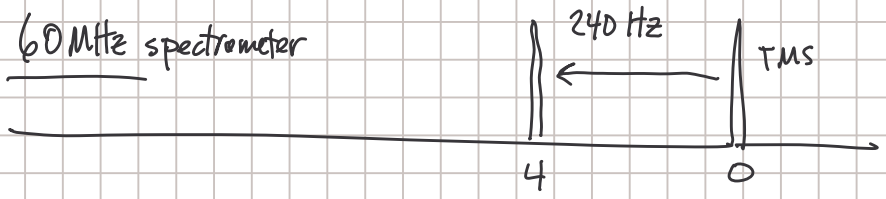
smallest				
60 MHz	200/300 MHz	500 MHz		800 MHz
small 4-yr universities	large univ. research labs	large univ major research		few in country

Chemical shift corrected radio frequency (for any size spectrometer) relative to a reference peak.

most common reference: tetramethylsilane (TMS)

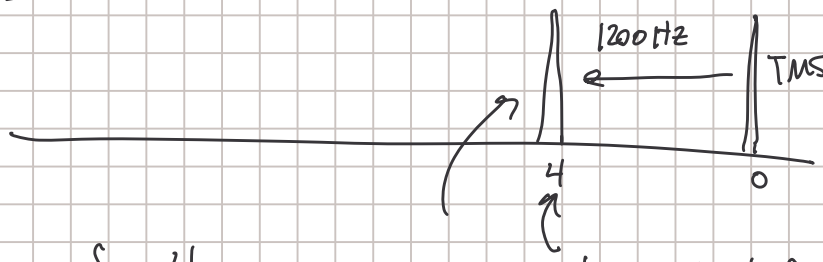


60 MHz spectrometer



$$\frac{240\ \text{Hz}}{60\ \text{MHz}} = 4$$

300 MHz spec.



$$\frac{1200\ \text{Hz}}{300\ \text{MHz}} = 4$$

$\delta = 4$ ppm

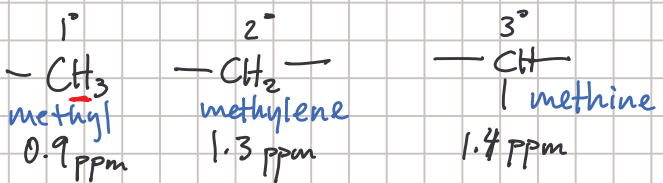
Chemical shift, δ (lowercase delta)

unit = ppm

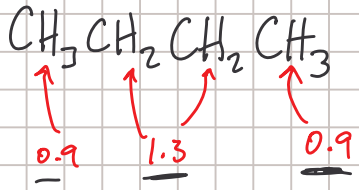
$$\delta = \frac{\text{shift df. from TMS (Hz)}}{\text{spec. freq. (MHz)}}$$

Typical chemical shifts

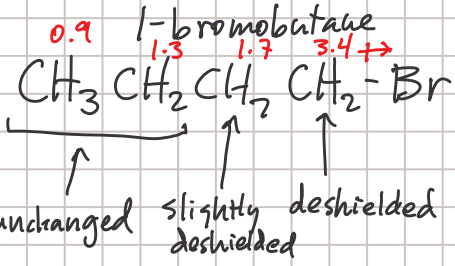
alkanes



butane

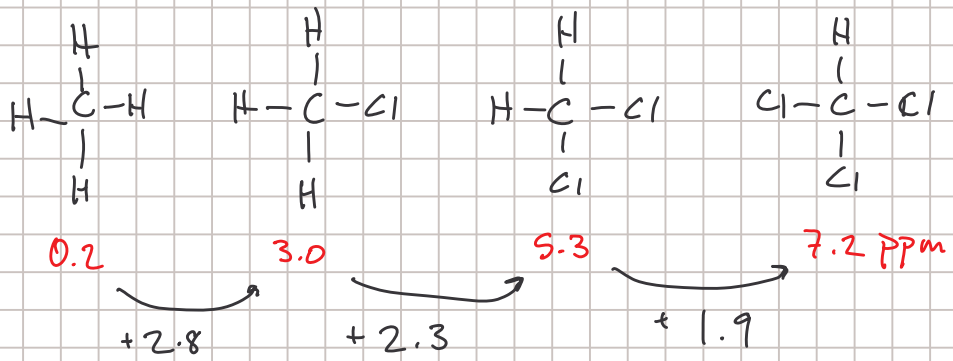


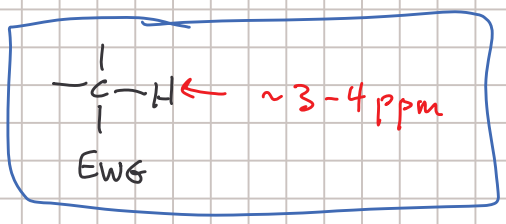
1-bromobutane



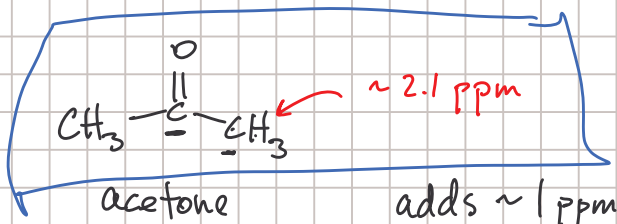
a single EWG (electron-withdrawing group) (halogen or O)

will add 2-3 ppm to adjacent H's





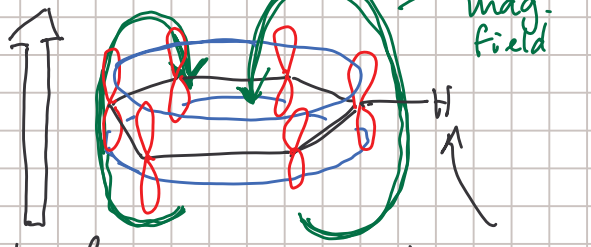
Carbonyl (C=O) groups also deshield nearby H's



adds ~1 ppm to H's on adjacent C

Aromatic H's are deshielded significantly

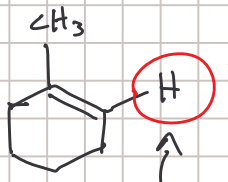
in general, Ar-H
~7-8 ppm



this proton feels extra magnetic field (downfield)
effectively deshielded

Vinyl protons

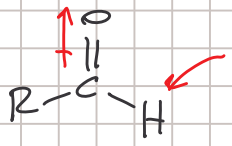
→ attached to C=C



deshielded similarly to aromatic protons (to a lesser extent)

δ 5-6 ppm in general

Aldehyde protons



δ 9-10 ppm

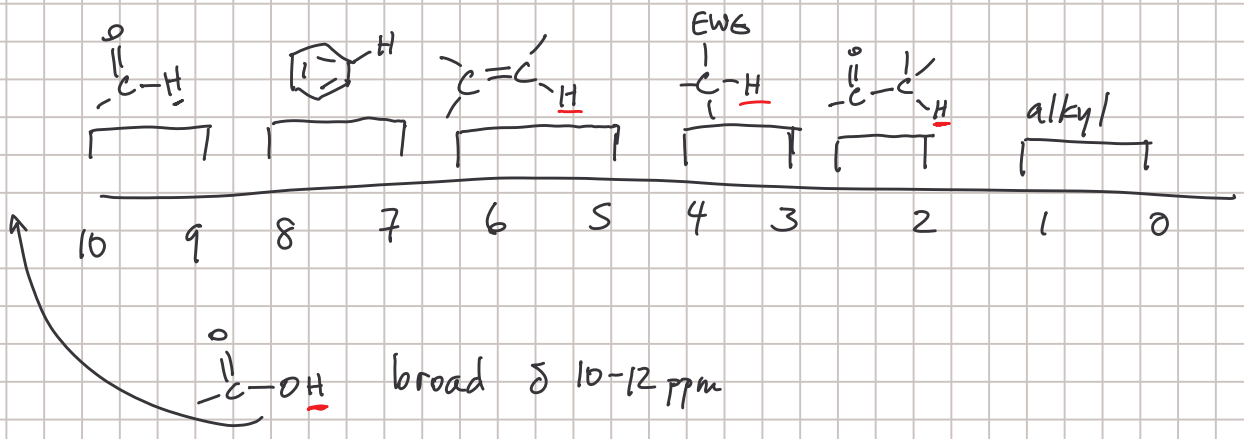
electron-withdrawing AND C=C-like effective deshielding

H-bonded protons

broad peak just like IR

R-OH R-NH-R' R-NH$_2$

chemical shifts are variable



C(=O)-OH broad δ 10-12 ppm