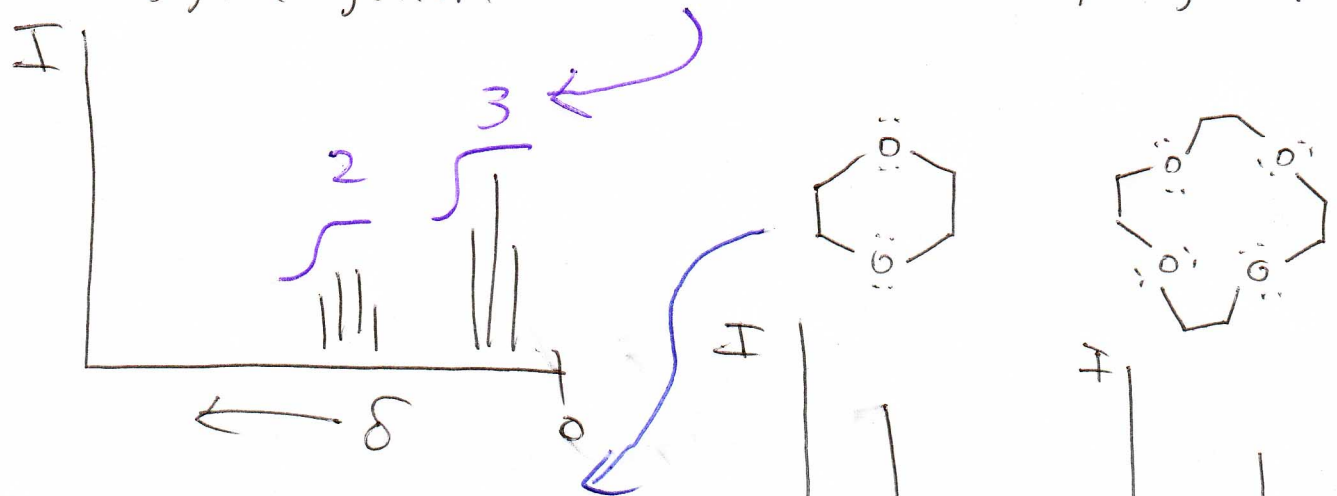Integration – For ^1H-NMR, there is a good linear relationship between the strength of an NMR signal generated and the # of hydrogens involved.

Both of these compounds would produce nearly equivalent spectra (only one absorption). Although # of hydrogens is linearly proportional to signal strength, that proportionality constant can only be determined by measurement. Without that constant, these two compounds could not be distinguished.
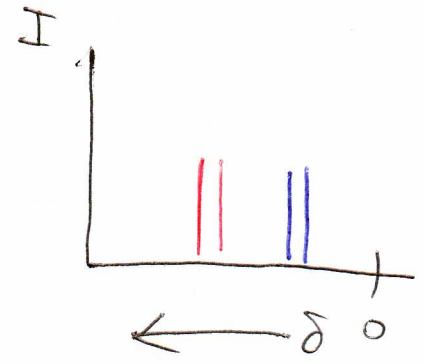

Splitting

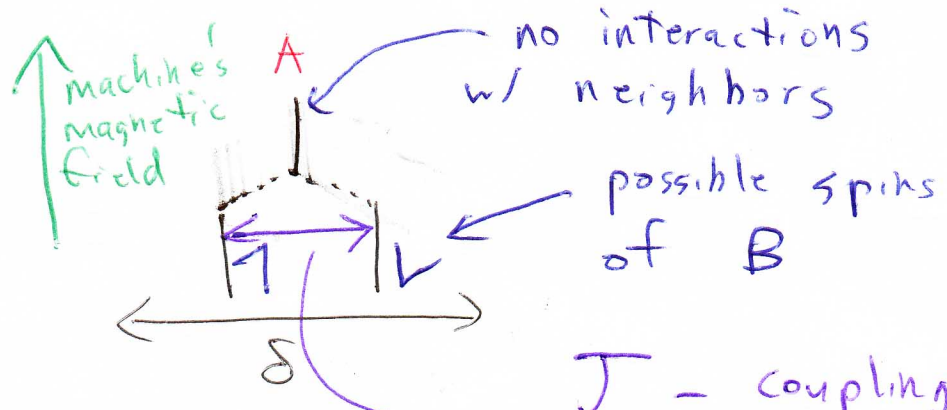— Caused by two non-equivalent hydrogens interacting with each other.
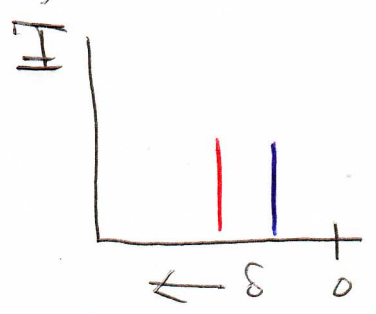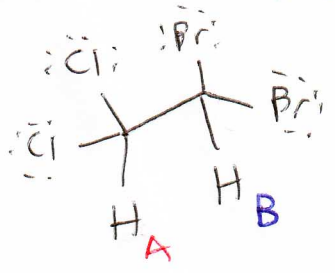
(guess)

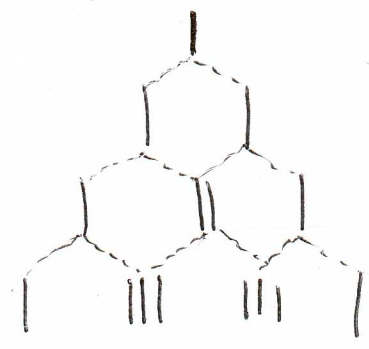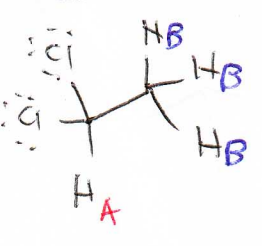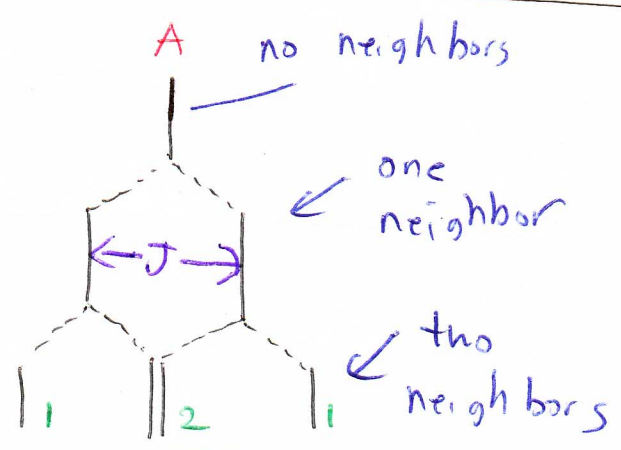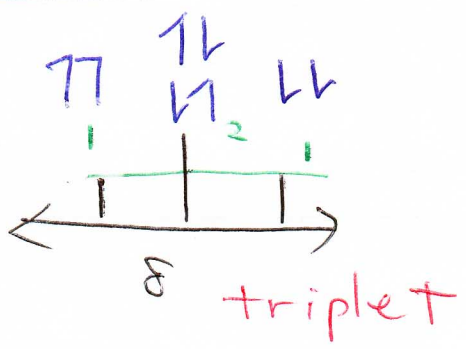A neighboring (B) non-equivalent hydrogen can effectively add to or subtract from the machine's primary magnetic field. This neighbor (B) therefore can cause an increase or decrease in the chemical shift of the proton being observed. (A)

Statistically, both possibilities occur with equal probability, so both peaks are generated ⟶ doublet → as experience by A,

* Assume achiral solvents for all examples

machine's magnetic field

A — no interactions w/ neighbors

↑ ↓ ← possible spins of B

δ

J – coupling constant –
extent of splitting between two neighbors

:Cl: :Br:

Cl—⟨⟩—H_B
       H_B
H_A

↑↑   ↑↓   ↓↓
      ↓↑

| 1 | 2 | 1 |

δ **triplet**

A   no neighbors

one neighbor

←J→

1   2   1

two neighbors

:Cl: H_B
:Cl—⟨⟩—H_B
       H_B
H_A

↑↑↓ ↑↓↓
↑↑↑ ↑↓↑ ↓↑↓ ↓↓↓
     ↓↑↑ ↓↓↑

| 1 | 3 | 3 | 1 |

quartet
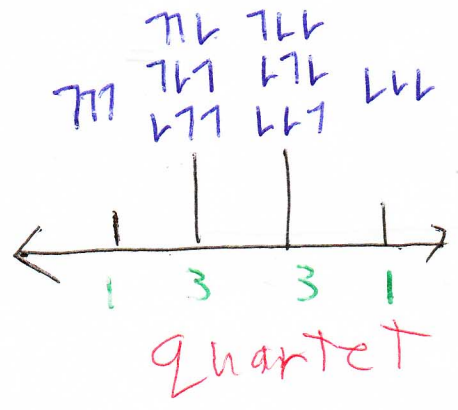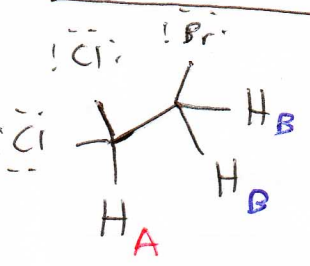
$$(x+y)^1 = 1x + 1y$$
$$(x+y)^2 = 1x^2 + 2xy + 1y^2$$
$$(x+y)^3 = 1x^3 + 3x^2y + 3xy^2 + 1y^3$$

let $x = 1$
let $y = 1$

n+1 rule — when observing a proton that has 'n' neighbors, a multiplet with n+1 peaks will be generated (if all neighbors are equivalent *or nearly equivalent*.)

NMR solvents ↗ ^1H

Since "normal" (protium-containing) solvents would effectively flood the signal of any compound dissolved in them, deuterated solvents are used in NMR spectroscopy.

$CODCl_3$ chloroform-d → $\delta = 7.26$
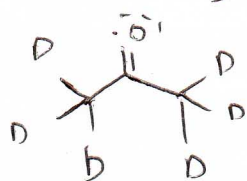
acetone-d_6

D_2O heavy water

Although 100% solvents can be used, often 99+% deuterated solvents are used instead, partly because they can be significantly less expensive, but also because the residual non-deuterated solvent signal can be used to calibrate the chemical shift of an NMR spectrum.
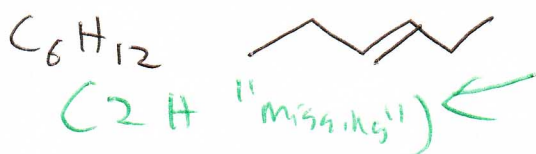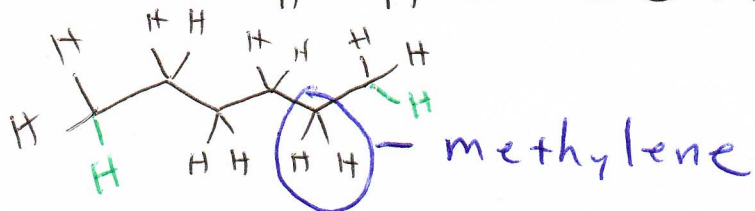
Sometimes TMS is added to an NMR solvent (regardless of the level of hydrogen depletion) as a primary calibration standard.
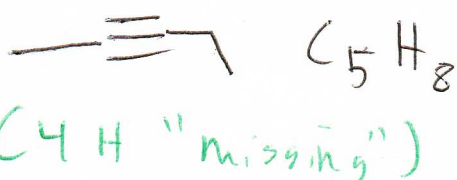
Degree of unsaturation

~~Dha~~ Saturated — a compound that contains the maximum number of hydrogens possible, given the number of carbons present.

$$\# H = 2C + 2$$

$3 \times 3 + 1 + 2 = 12$

— methylene

 C_6H_{12}

$(2H \text{ "missing"})$

 C_5H_8
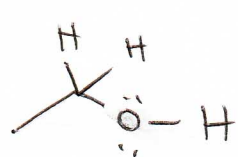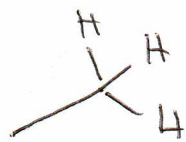
$(4H \text{ "missing"})$

A ring and a double bond each count as one degree of unsaturation.

A triple bond counts as two degrees of unsaturation.

$$D.O.U = \left(\begin{array}{c} \# \text{ of H based on} \\ \# C \end{array} \right) - (\# \text{ of hydrogens present})$$

$$ \overline{} \\ 2$$

Oxygen (and sulfur) do not affect the hydrogen count because they are divalent.
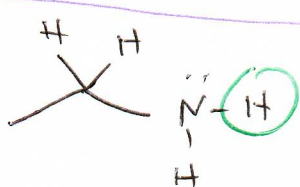
Nitrogen (and phosphorus) add to the hydrogen count because they are trivalent.
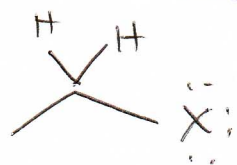
Halogens subtract from the hydrogen count because they are monovalent

$$D.O.U = \frac{[2C+2] + N - X - H}{2}$$

Gas chromatography

injection port

oven

Carrier gas

column:

Carrier gas → metal)

Sample → mobile phase

inside coating → separatory material (stationary phase)
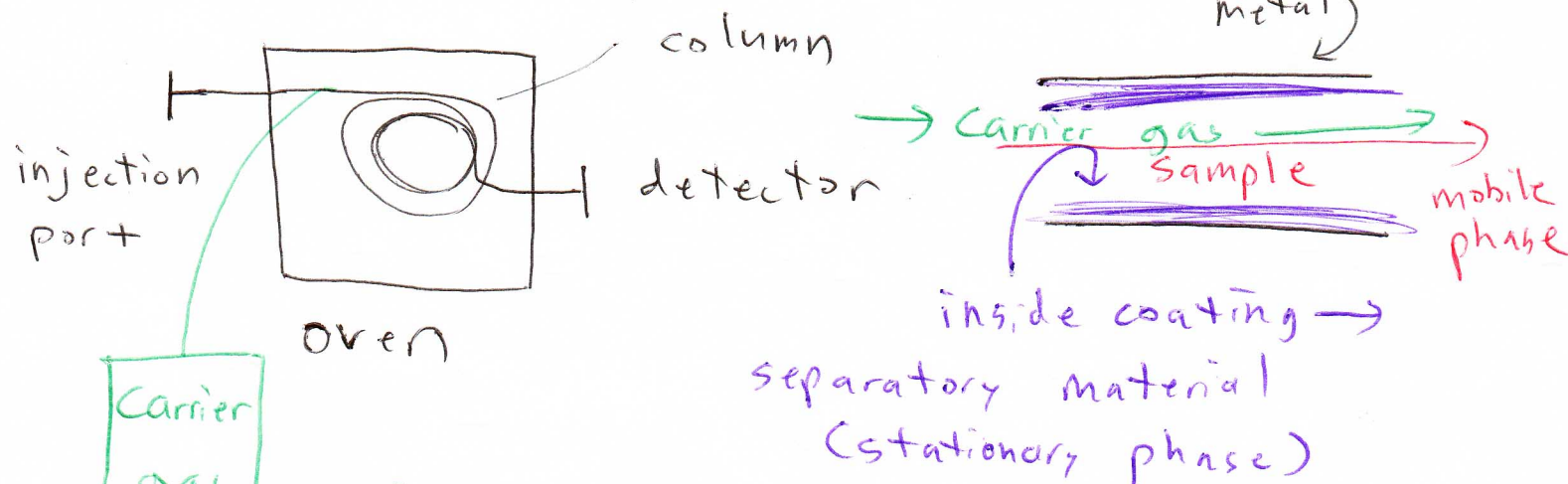
In GC, a liquid sample is injected into a port which is heat, causing the sample to be vaporized upon injection. The sample then passes through a column that is also heated to ensure the sample remains vaporized. A carrier gas (an inert gas, usually N_2, He, or Ar) is used to help push the sample through the column (mobile phase). As the sample mixture passes through the column, the components of the mixture will be separated on the basis of polarity and/or boiling point. As the compounds successfully pass through the column, they will then be detected.

I (quantity observed)

retention time →

The identity of a compound can be determined by its retention time. The quantity of the compound can be determined by the peak area.

time it takes for a compound to travel from the injection port to the detector.