

## INTEGRATION:

Difficult to get accurate values

- must be noise-free
- baseline must be flat
- all nuclei must have identical responses
- all nuclei must fully relax between pulses
- obtain the **RATIO OF HYDROGENS NOT THE NUMBER**

## CHEMICALLY EQUIVALENT

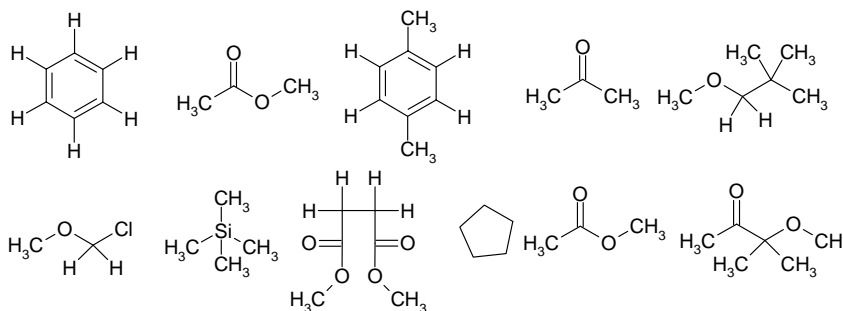
All of the protons in a chemically identical environment are said to be chemically equivalent.

Same environment = Same chemical shift!

When all of the protons in a molecule are equivalent, only one NMR absorption peak will be observed.

How many peaks do you expect to see for each of the molecules below?

## LOCAL DIAMAGNETIC SHIELDING



This typically refers to electron withdrawing groups that remove the intensity of the electron shield around neighboring protons.

**Spin-spin Splitting = n + 1 Rule** = The influence of neighboring spins on the multiplicity of peaks.

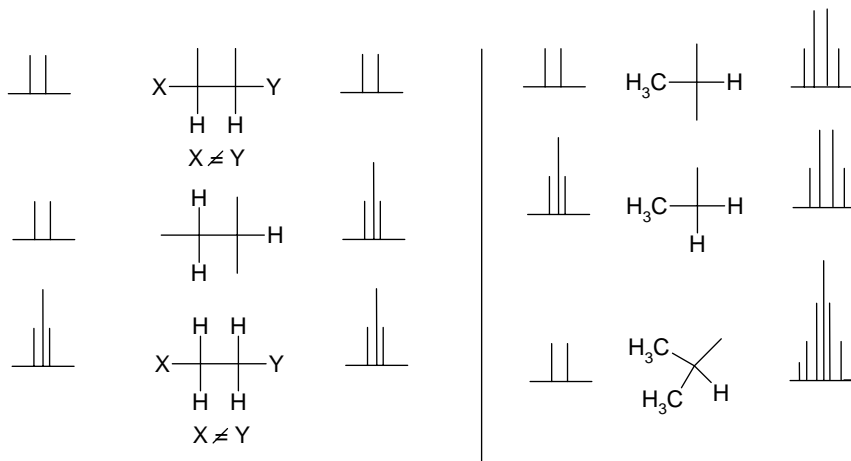
**Coupling Constant:**  $^3J_{HH}$

A measure of how strongly the nuclear spins influence each other for one nucleus split by a neighboring nucleus three bonds away.

The strength of the coupling is measured by the distance between the two peaks for the resonance of one nucleus split by another.

### Commonly observed splitting patterns!

\*Protons that are three bond neighbors can be spin up (+ 1/2) or down (- 1/2).



If neighboring protons are both the same spin and spin up, there is a deshielding effect.

If neighboring protons are of opposite spin, there is a shielding effect.

Based on your knowledge of organic chemistry, what would you expect the spectrum of 1,1-dichloropropane to look like? Explain the splitting pattern observed!

Use Pascal's Triangle to make sense out of the splitting pattern!

Back to coupling constants:

A measure of how strongly a nucleus is affected by the spin states of its neighbor.

### THE COUPLING CONSTANTS OF THE GROUPS OF PROTONS WHICH SPLIT ONE ANOTHER MUST BE IDENTICAL!

\*Tables of chemical shifts are useful, but intuition is worth a lot more!

Molecule	ppm	Molecule	ppm
TMS	0	Methane	0.2
Hydrocarbon	1-2	Methyl iodide	2.2
H-C-X where X= $\delta^-$ element	3-5	Methyl bromide	2.7
Alkenes	5-7	Methyl chloride	3.0
Aromatics	7-8	Methyl alcohol	3.4
Aldehydes	9-10	Methyl fluoride	4.3
Carboxylic Acids	10-12	chloroform	7.3

#### Explanation of Chemical Shifts:

- 1.) Hydrocarbon = 1-2 ppm; shielded environment, upfield shift, degree of shielding decreases with hybridization.
- 2.) Alkynes = 2-3 ppm; protons are shielded based on alignment with the magnetic field accountable to anisotropy.
- 3.) Halogenated hydrocarbon = 3-5 ppm; deshielding occurs based on the electron withdrawing nature of the halogen.
- 4.) Alkene = 5-7 ppm; the  $\pi$  electrons deshield vinylic protons due to anisotropy.
- 5.) Aromatics = 7-8 ppm; the conjugated  $\pi$  electrons of the aromatic ring deshield protons even more due to anisotropy.
- 6.) Aldehydes = 9-10 ppm; combination of an alkene and an electronegative atom = lots of deshielding.
- 7.) Carboxylic Acids = 10-12 ppm; combination of resonance and electronegativity causes lots and lots of deshielding.
- 8.) Hydrogen Bonding = protons that are able to be involved in hydrogen bonding interactions have a chemical shift that is based on concentration, temperature, and the solvent.

Acids	RCOOH	10.5-12 ppm
Phenols	ArOH	4.0-7.0 ppm
Alcohols	ROH	0.5-5.0 ppm
Amines	RNH <sub>2</sub>	0.5-5.0 ppm
Amides	RCONH <sub>2</sub>	5.0-8.0 ppm
Enols	CH=CH-OH	>15 ppm