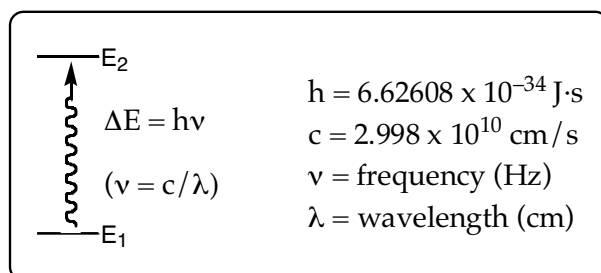


IAP 5.301 Spectroscopy

Chemists use spectroscopy (IR, UV-Vis, NMR) to determine molecular structure.

Spectroscopy: technique that measures the amount of radiation a substance absorbs at various wavelengths (based on the quantization of molecular energy levels)

- Molecules exist in quantized energy states (rotational, vibrational, and electronic quantum states).
 - Molecules absorb discrete amounts of energy (ΔE) and are excited to higher energy states.
 - We can use electromagnetic radiation to excite molecules.



- Molecules have unique absorption spectra that depend on their structure.
 - Specific absorptions provide useful structural information.

How do you know what type of electromagnetic radiation to use?

<u>EM Radiation</u>	<u>Wavelength (cm)</u>	<u>Excitation</u>	<u>Approximate ΔE</u>
cosmic rays	10^{-12} to 10^{-10}	—	—
gamma rays	10^{-10} to 10^{-8}	—	—
X-rays	10^{-8} to 10^{-6}	—	—
ultraviolet	10^{-6} to 3.8×10^{-5}	electronic	70–300 kcal/mol
visible	3.8×10^{-5} to 7.8×10^{-5}	electronic	40–70 kcal/mol
infrared	7.8×10^{-5} to 3×10^{-2}	vibrational	1–10 kcal/mol
microwave	3×10^{-2} to 3×10^2	rotational	~ 1 cal/mol
radio*	3×10^2 to 3×10^5	—	—

* Radio frequency EM radiation is used in NMR spectroscopy.

Infrared Spectroscopy (vibrational energy)

- Chemical bonds are not rigid; they are constantly vibrating.
- Different vibrational modes are of higher energy than others, and complex organic molecules have a large number of vibrational modes (complicated!).
- **A nonlinear molecule containing n atoms has $3n-6$ possible fundamental vibrational modes!**
- Luckily, different functional groups (parts of a molecule) exhibit unique characteristic absorptions.
- This allows us to look at an IR spectrum (% transmission *versus* wavenumber) and determine which functional groups are present based on the absorption bands.
- Wavenumber is the number of waves per centimeter ($1/\lambda$).

Characteristic IR Absorption Bands for Common Functional Groups

Class	Wavenumber, cm^{-1}	Intensity	Assignment
Alkanes	2850–3000	s	C–H stretch
	1450–1470	s	CH ₂ and CH ₃ bend
	1370–1380	s	
	720–725	m	
Alkenes	3080–3140	m	=C–H stretch
	1650	m	C=C stretch
	809–990	s	C–H out-of-plane bend
Alkynes	3300	s	≡C–H stretch
	2100–2140	m	C≡C stretch
	600–700	s	≡C–H bend
Alcohols	3600	var	free O–H stretch
	3400	s	bonded O–H stretch
Ethers	1070–1150	s	C–O stretch
Carbonyls	1540–1870	s	C=O stretch
Aromatic Hydrocarbons	675–900	s	C–H out-of-plane-bend
	1000–1300	m	C–H in-plane bending
	1400–1600	m	C–C stretching

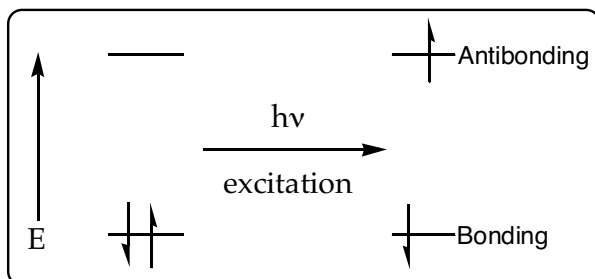
Ultraviolet-Visible Spectroscopy (electronic energy)

- It is easy to think of atoms as tiny little solar systems with the electrons orbiting the nucleus in a similar fashion as planets orbiting the sun. This simplistic picture satisfies our intuition, but it does not correspond with what we know about the atom.

It is more effective to treat electrons as waves rather than particles!

(This may sound complicated, but you'll have a chance to explore this in great depth during your stay here at MIT.)

- What it boils down to is that electrons occupy discrete **orbitals** that are best described by mathematical functions called **wavefunctions**. Because these orbitals have quantized energy, we can use spectroscopy to investigate the excitation of electrons from lower energy to higher energy orbitals.



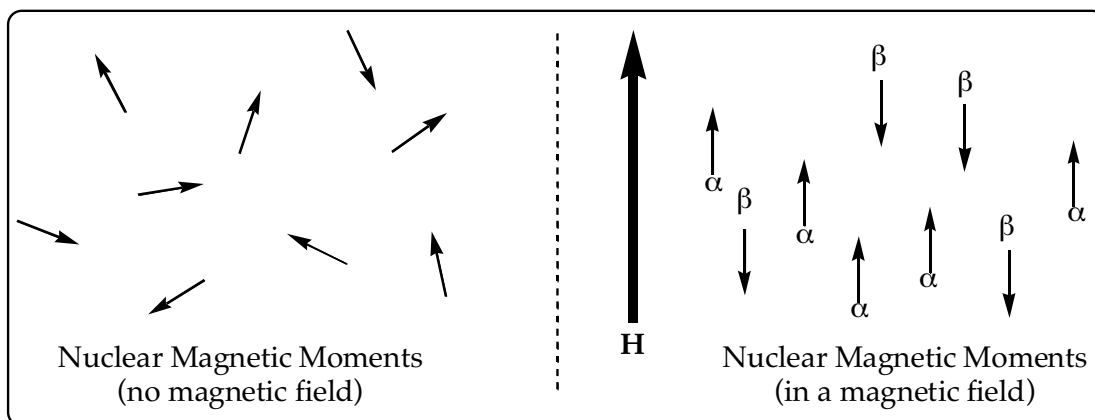
- These excitations usually involve an electron moving from a **low energy bonding orbital** to a **high energy antibonding orbital**.

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- UV-Vis spectroscopy is most frequently used to detect the presence of a specific compound in solution or to measure concentrations very accurately. You will get a chance to do this later this month.

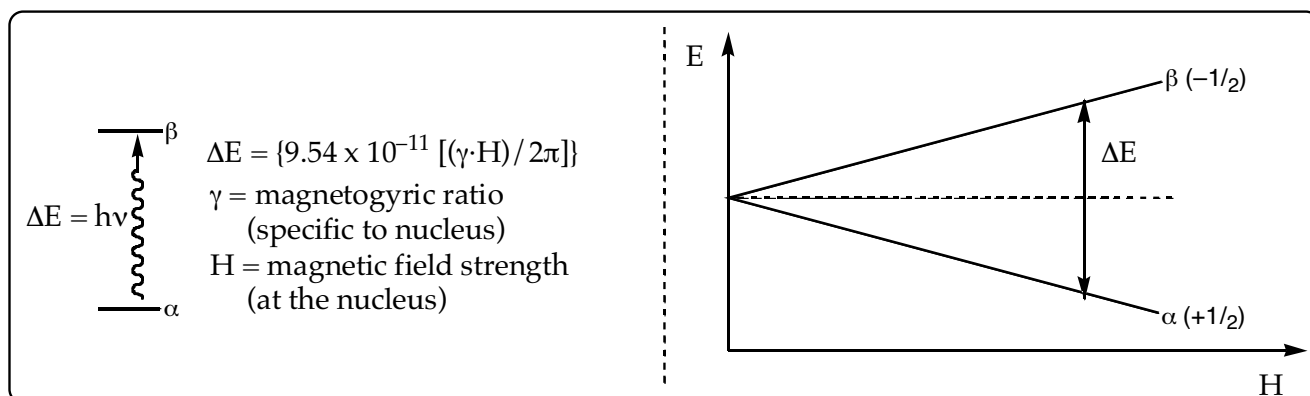
Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR is the most common spectroscopic tool used by organic chemists.

- NMR differs from other spectroscopy because the different energy states (nuclear spin states) exist only in the presence of a magnetic field.
- The nuclei of most (but not all) atoms behave as if they are spinning on an axis (nuclear spin).
- Because nuclei are positively charged, these spinning nuclei create small magnetic moments.
- In the absence of a magnetic field, these magnetic moments are oriented in a random fashion.
- For some nuclei (those having nuclear spin = $\pm 1/2$), the presence of an external magnetic field (H) results in the alignment of each nucleus either with (α) or against (β) the magnetic field.
- ^1H , ^{13}C , and ^{19}F are the three most common nuclei observed using NMR spectroscopy. In this class, we will focus on ^1H (proton) NMR.

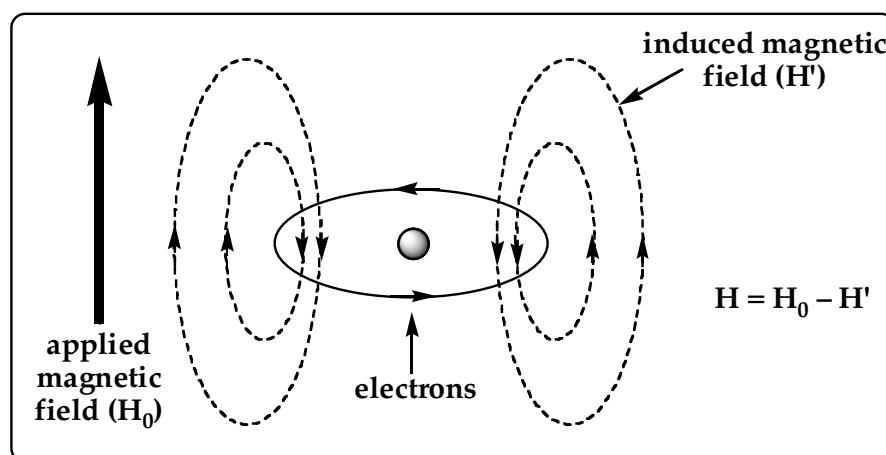


- The energy difference between the α and β states (ΔE) is proportional to the strength of the magnetic field (H) at the nucleus.
- ΔE is relatively small ($\sim 10^{-2}$ cal/mol); radio waves are used to excite (flip) nuclei from α to β .



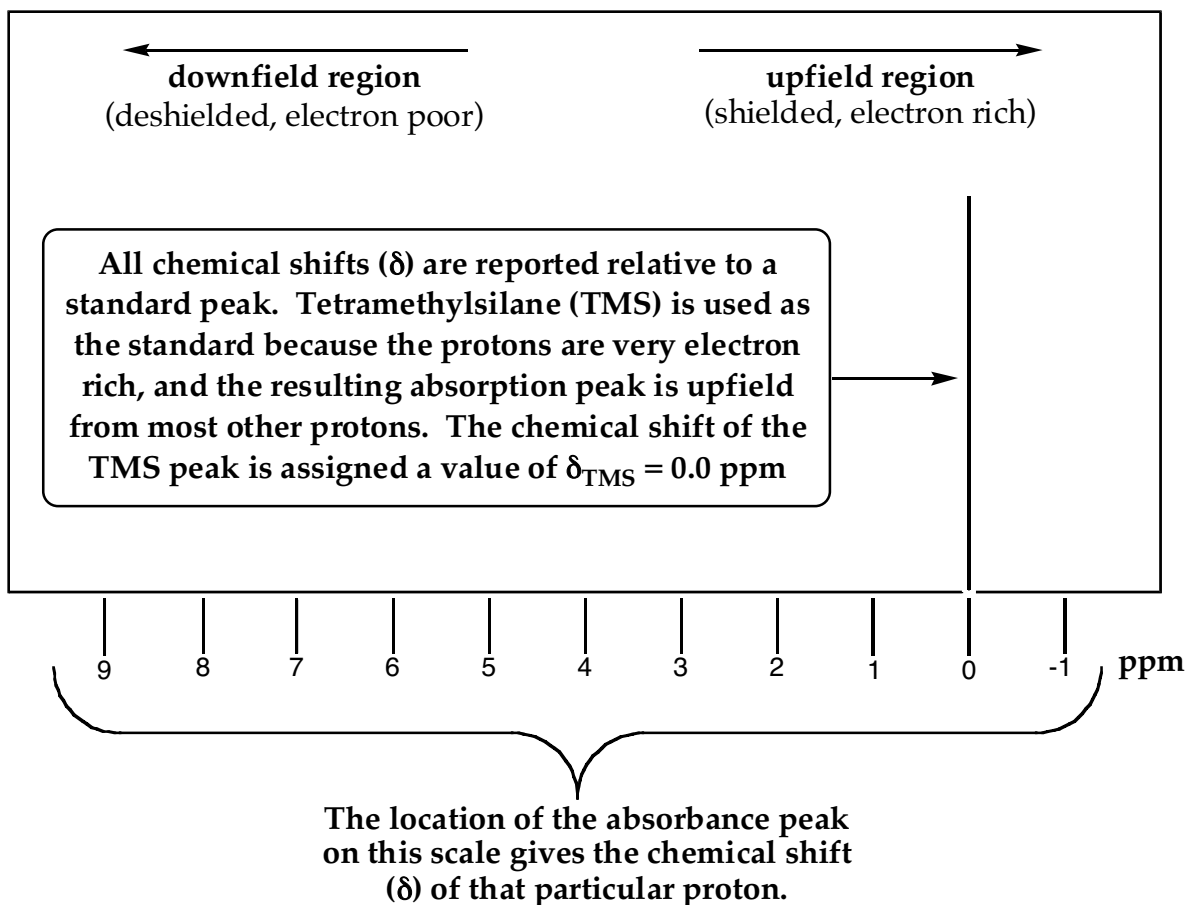
- If the energy difference between the α and β spin states of a proton nucleus (ΔE) depends only on the ^1H NMR magnetogyric ratio ($\gamma = 2.6753 \times 10^4$ radians \cdot sec $^{-1}\cdot$ gauss $^{-1}$) and the magnetic field (H), then won't all of the protons in a molecule absorb radiation of the exact same energy?
- **Luckily, no!** We wouldn't be able to obtain any structural information from a ^1H NMR spectrum if that were the case.

- Remember, nuclei are surrounded by clouds of negatively charged electrons. In the presence of an applied magnetic field (H_0), these electrons move in such a way that their motion induces their own small magnetic field (H').
- At the nucleus, the induced magnetic field (H') **opposes** the applied magnetic field (H_0). Therefore, the nucleus experiences a magnetic field (H) slightly less than the applied magnetic field (H_0).



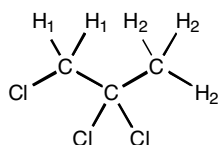
- This phenomenon is called **diamagnetic shielding**. Protons with a lot of electron density around them are well-shielded and experience a reduced magnetic field. As a result, there is a smaller energy difference between the two spin states, and lower energy radiation is required to **flip** the spin from α to β .
- In other words, protons in different electronic environments experience different amounts of shielding and absorb radiation of different frequencies. These differences are referred to as **chemical shifts**.

That's all well and good, but what does it mean **practically**?



The **chemical shift** of a proton gives us information about its chemical environment, but there's more to be learned!

Let's look at a sample ^1H NMR to get a better idea of the information we can take from it . . .



- The ¹H NMR spectrum of 1,2,2-trichloropropane has two peaks other than the TMS peak.
 - How can you tell which peak corresponds to the two H₁ protons and which is from the three H₂ protons?

Here's a clue: Chlorine atoms are very electronegative and strongly electron withdrawing. This means that they suck electron density away from the atoms close to them.

- The two H₁ protons are attached to a carbon that is also attached to a chlorine atom. As a result, these protons have less electron density around them, are less effectively shielded, and have a chemical shift further downfield than the H₂ protons (H₁ = A, H₂ = B).

Integration

- In addition to chemical shift, the relative size of the peaks provides information.
- When you take a ¹H NMR, you will integrate the different peaks in your spectrum. The relative values of the integrals are proportional to the number of protons absorbing energy at that frequency.
For example (from above):

$$B : A = 75 : 50 = 3 : 2$$

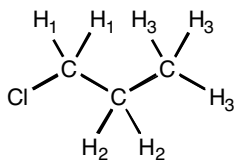
The spectrum tells you that there is a 3 : 2 ratio of different protons in 1,2,2-trichloropropane. Of course you know that there are three H₂ protons and two H₁ protons that fit this criteria.

Spin-Spin Splitting

- Unlike in the ^1H NMR spectrum of 1,2,2-trichloropropane on the previous page, **most peaks are not single lines (singlets).**
- In fact, the **multiplicity** of a peak (singlet, doublet, triplet) provides even more information about the structure of a molecule. This is because **protons on adjacent atoms communicate with each other.**

In simple systems, n adjacent protons cause splitting into $n + 1$ peaks.

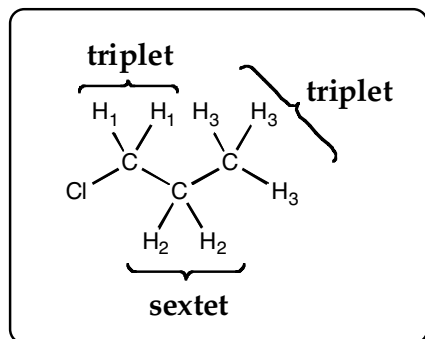
- For example, look at the spectrum of 1-chloropropane:



- There are three inequivalent types of protons in this molecule (H_1 , H_2 , H_3).
- It is easy to assign chemical shifts to the appropriate protons because you already know that chlorine is an electron withdrawing group.
- The protons closest to the chlorine will have the least electron density (deshielded, downfield), and the protons furthest from the chlorine will have the most electron density (shielded, upfield). Using this reasoning, you can assign:

$$A = \text{H}_1, B = \text{H}_2, C = \text{H}_3$$

- Now, let's look at the multiplicity of the three peaks. . .



-
- **Peak A**, corresponding to the two H₁ protons, is a **triplet** (three lines). This is because there are **two adjacent H₂ protons** ($2 + 1 = 3$).
 - **Peak B**, corresponding to the two H₂ protons, is a **sextet** (six lines). This is because there are **five adjacent protons**, two H₁ and three H₃ ($5 + 1 = 6$).
 - **Peak C**, corresponding to the three H₃ protons, is a **triplet** (three lines). This is because there are **two adjacent H₂ protons** ($2 + 1 = 3$).
-

- Spin-spin splitting, also known as **coupling**, can get much more complicated than this, but we'll stick to simple systems for now.
- It is very important to remember that spin-spin splitting and peak integrals **are not related**. **The multiplicity of a peak does not have any correlation to the number of protons absorbing energy at that frequency!**
- There is a useful table on p. 301 of Zubrick that will help you assign the peaks in the ¹H NMR spectra you will be obtaining this month.