

VII. IR and NMR

- D. nuclear magnetic resonance
 - magnetic technique
 - magnetism originates from unpaired spin
 - electrons have spin, but most of the time they are paired, so no net magnetism.
 - there is a technique called electron spin resonance (ESR) that can be used to interrogate radicals and other exotic molecules with unpaired electrons.
 - we will be concerned instead with nuclear spins

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- 1. magnetic nuclei
 - nuclei have quantized spins (I)
 - I is an angular momentum like ℓ and s .
 - just like any angular momentum, it has z-component m_I that run from $-I$ to I
 - $I = 1/2$: $m_I = -1/2, 1/2$
 - $I = 2$: $m_I = -2, -1, 0, 1, 2$
 - you cannot predict the value of I , but you can predict whether it will be $1/2$ -integer or whole integer from the number of protons and neutrons

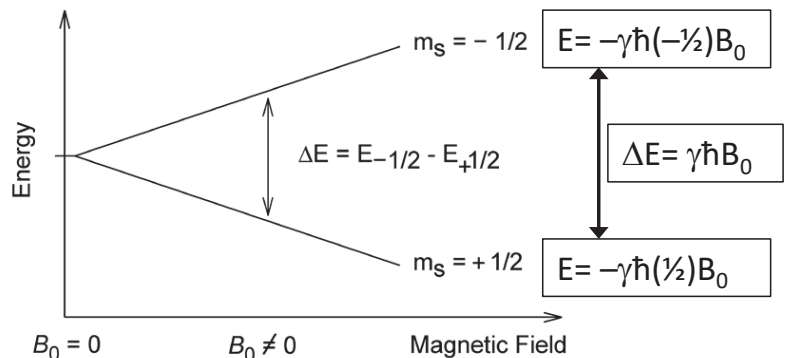
protons	neutrons	I	example
even	even	0	^{12}C , ^{16}O
even	odd	$1/2$ -integer	^1H , ^{13}C
odd	even	$1/2$ -integer	^{19}F , ^{31}P
odd	odd	integer	^2H , ^{14}N

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• 1. magnetic nuclei cont.

- in absence of magnetic field, m_I states are degenerate
- add a magnetic field (B) and the spin magnetic moment interacts with the magnetic moment of the field
- E of state now depends on m_I : $E = -\gamma\hbar m_I B_0$
 - γ = magnetogyric ratio ($\text{rad T}^{-1} \text{s}^{-1}$)
 - isotope dependent
 - scaling factor
 - $\hbar = h/2\pi$ (J s rad^{-1})
 - B_0 = applied field strength (T)
- consider $I = \frac{1}{2}$
 - $m_I = \pm \frac{1}{2}$
 - $+\frac{1}{2}$ stabilized
 - $-\frac{1}{2}$ destabilized

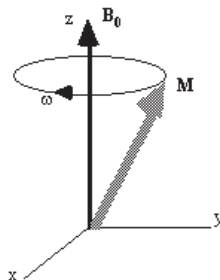


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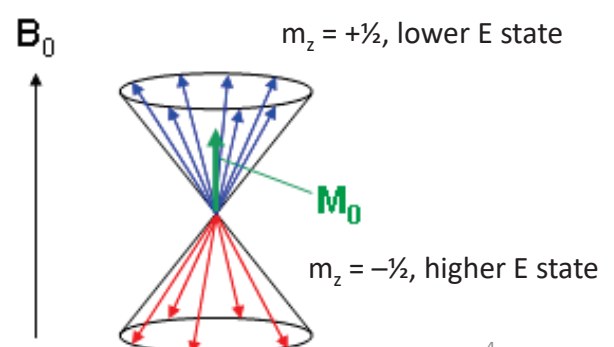
• 1. magnetic nuclei continued

- magnetic moment lines up and precesses around the applied field.



- two states: with the field or against the field

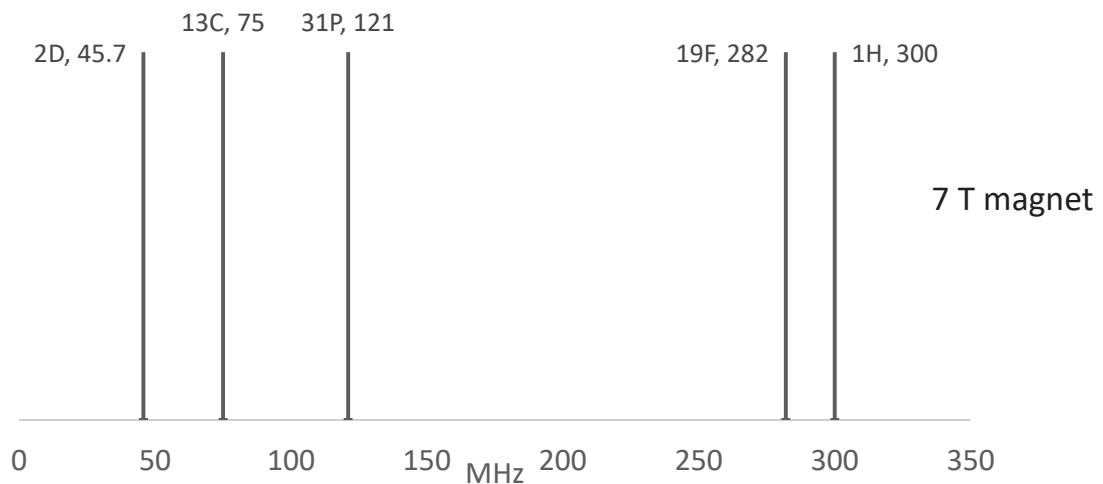
- $\Delta E = \gamma\hbar B_0$
- for 7 Tesla magnet, ^1H
- $\Delta E = \frac{2.675 \times 10^8 \times 6.626 \times 10^{-34} \times 7.0 \text{ T}}{2\pi}$
- $1.97 \times 10^{-25} \text{ J}$
- $\Delta E = h\nu$ gives $\nu = 3 \times 10^8 \text{ Hz}$, 300 MHz



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- 1. magnetic nuclei cont.
 - different nuclei have different γ values and will have different energy gaps.
 - typically one fixed the magnet (B_0) and varies the frequency of applied radiation



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- 1. magnetic nuclei cont.
 - since ΔE is so small, there is only a very small excess in the ground state.
 - $\frac{N_1}{N_0} = e^{-\frac{\Delta E}{k_B T}} = e^{-\frac{1.97 \times 10^{-25} \text{ J}}{1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}}} = 0.99995$
 - this leads to $N_0/N_1 = 1.0000486$, i.e. 49 ppm excess in ground state
 - radio frequency EM radiation is used to promote $\frac{1}{2}$ of the excess ground state spins to the excited state
 - at this point $N_0 = N_1$ and we say that the system is “spin saturated” and no net change in population occurs.
 - once the r.f. pulse is turned off, the excited molecules will “relax” back to the equilibrium populations

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• 2. relaxation

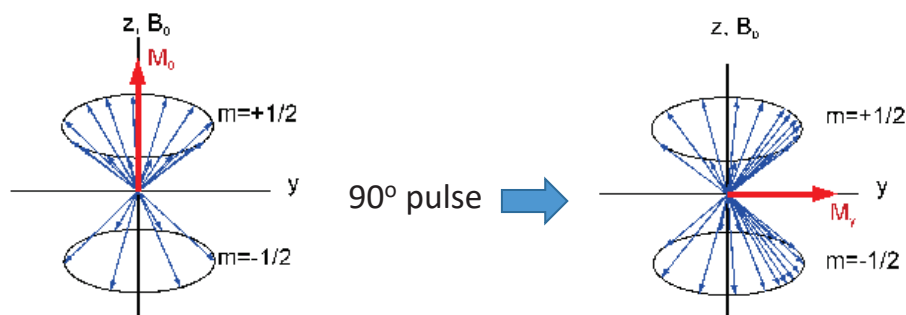
- nuclei that have been excited to their excited states will relax via one of two mechanisms
 - a. spin-lattice (T_1)
 - external conversion-like transfer of excess energy to the solvent
 - also called longitudinal relaxation
 - T_1 is $\frac{1}{2}$ life for relaxation through this mechanism
 - b. spin-spin (T_2)
 - energy transfer to neighboring spins (self quenching)
 - results in a newly excited nuclei that is out of phase (see next slide)
 - T_2 is $\frac{1}{2}$ life for relaxation through this mechanism
- overall relaxation is due to a combination of both mechanisms

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• 3. Fourier transform NMR

- first step in an experiment is called a 90° pulse.
 - short pulse of r.f. radiation that equalizes the population of up and down spins



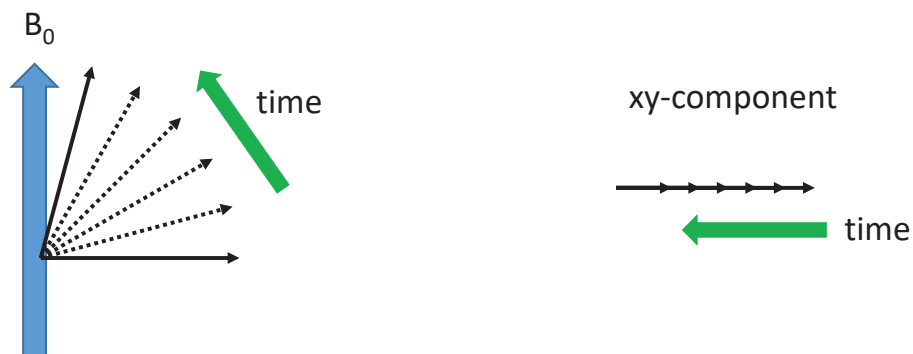
- in addition to equalizing the spin population, the pulse also causes all of the nuclei to precess in phase with each other
 - creates a net moment precessing around the magnetic field
 - this moment can be detected by r.f. coils

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• 3. FT-NMR cont

- precessing magnetic moment is detected as a sine wave at the detector with magnitude proportional to the total number of spins that are “in phase” with each other
- once the r.f. pulse ends, T_1 will cause the xy-component of the moment decrease in magnitude due to fewer excited spins (spin down). tip angle goes from 90° back to equilibrium angle

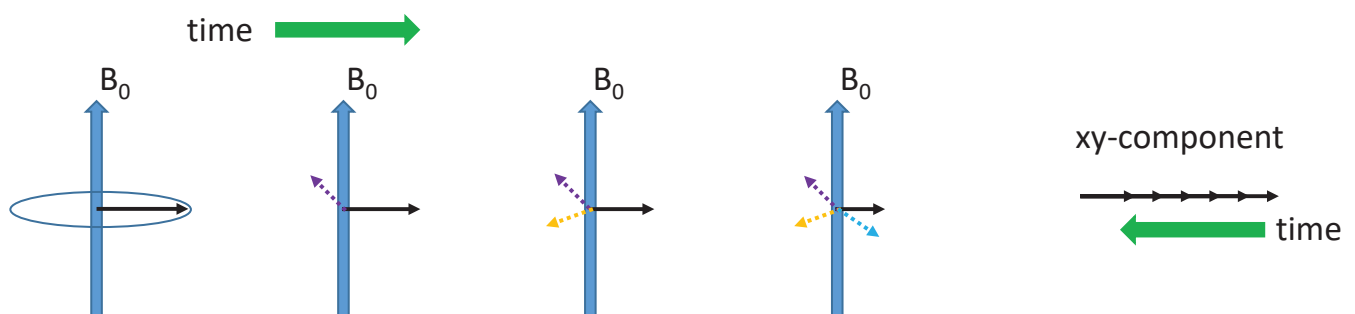


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VII.D IR and NMR

• 3. FT-NMR cont

- precessing magnetic moment is detected as a sine wave at the detector with magnitude proportional to the total number of spins that are “in phase” with each other
- once the r.f. pulse ends, T_2 will cause the xy-component of the moment decrease in magnitude due to spins being out of phase.



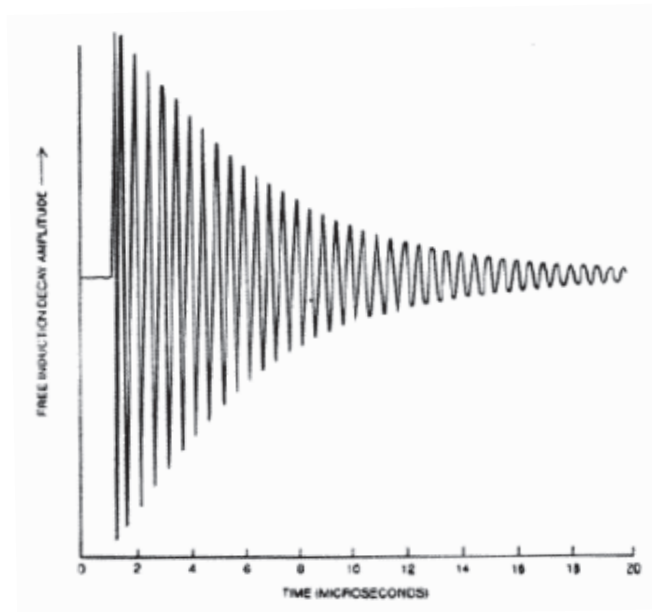
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• 3. FT-NMR cont

- result of T_1 and T_2 relaxation is called a free-induction decay

- exponentially decaying function of time ($e^{-\left(\frac{t}{T_1} + \frac{t}{T_2}\right)}$)

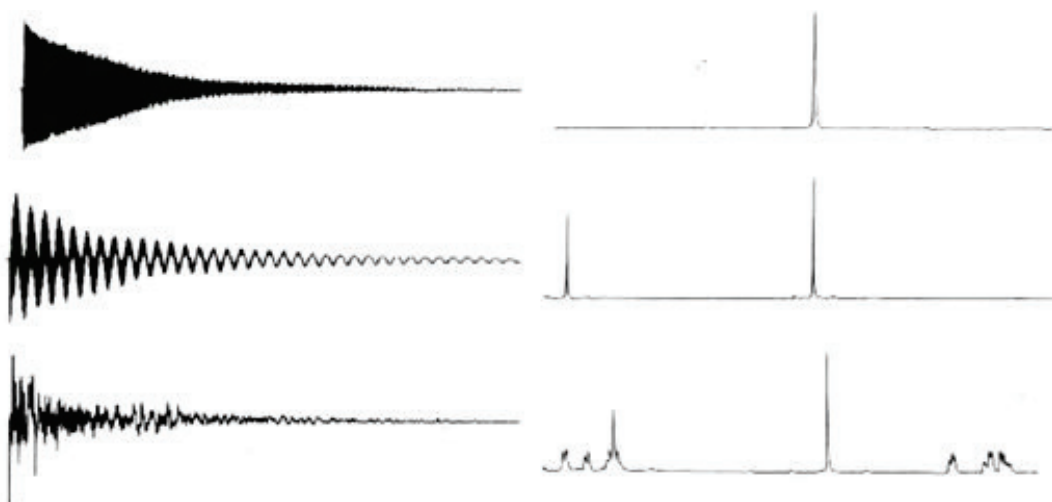


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• 3. FT-NMR cont.

- the precession frequency depends on the energy gap, so nuclei in different environments have different frequencies that can be obtained by Fourier transform

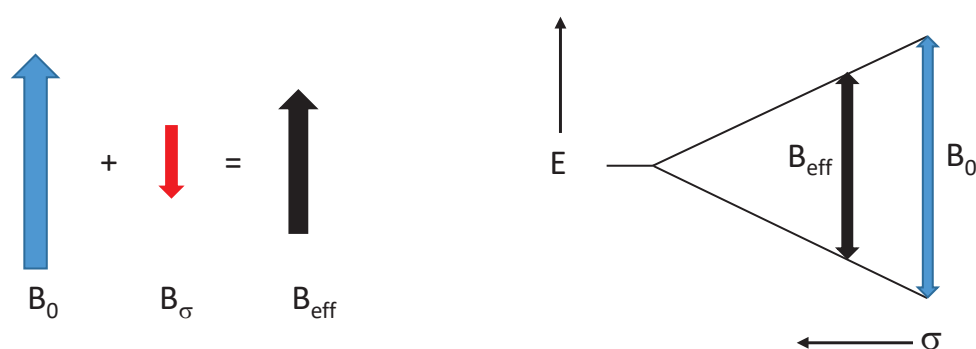


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• 4. chemical shift

- we have been saying that ^1H has an energy gap corresponding to 300 MHz, but that is not strictly true
 - electrons generate a magnetic field (B_σ) that opposes the applied field B_0 creating an “effective” magnetic field (B_{eff})
 - B_σ is said to “shield” the nucleus from the applied field (B_0).
 - we can define a shielding parameter (σ) that describes the amount of shielding
 - large electron density = large σ , shielded nucleus, smaller E gap
 - small electron density = small σ , de-shielded nucleus, large E gap



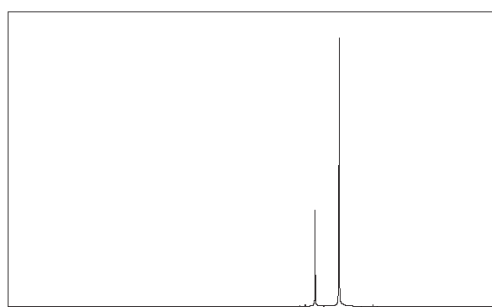
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• 4. chemical shift cont.

- consider CH_3OH
 - two types of proton

	CH_3	OH
e^- density @ H	high	low
shielding (σ)	high (shielded)	low (deshielded)
B_{eff}	smaller	larger
$\Delta E, \nu$	smaller	larger

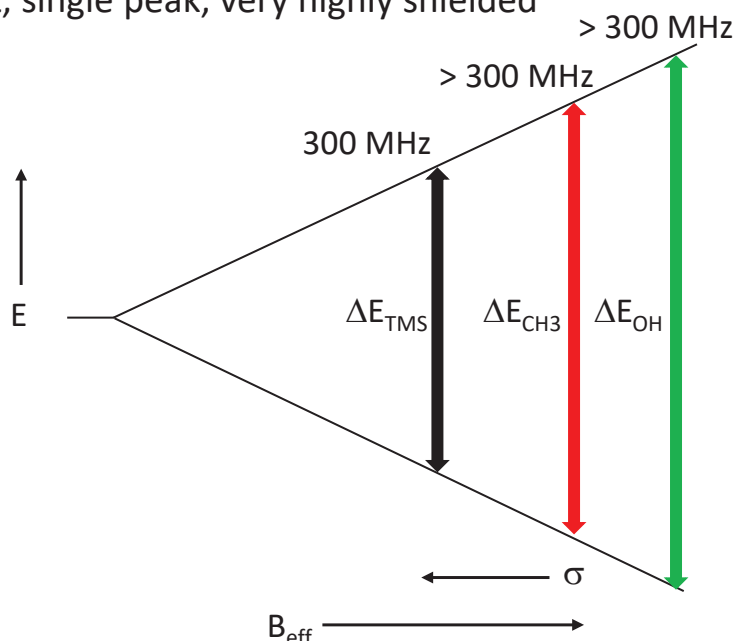


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• 4. chemical shift cont.

- since field strengths vary, we use an internal standard and reference all resonances to it
- tetramethylsilane (TMS) is often used as reference.
 - inert, single peak, very highly shielded



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• 4. chemical shifts cont.

- define: chemical shift (δ) is the amount the resonant frequency for each “sample” nuclei exceeds that of the “reference” nuclei

- usually quite small and measured in parts per million (ppm)

- $$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\nu_{\text{reference}}} \times 10^6$$

- example:

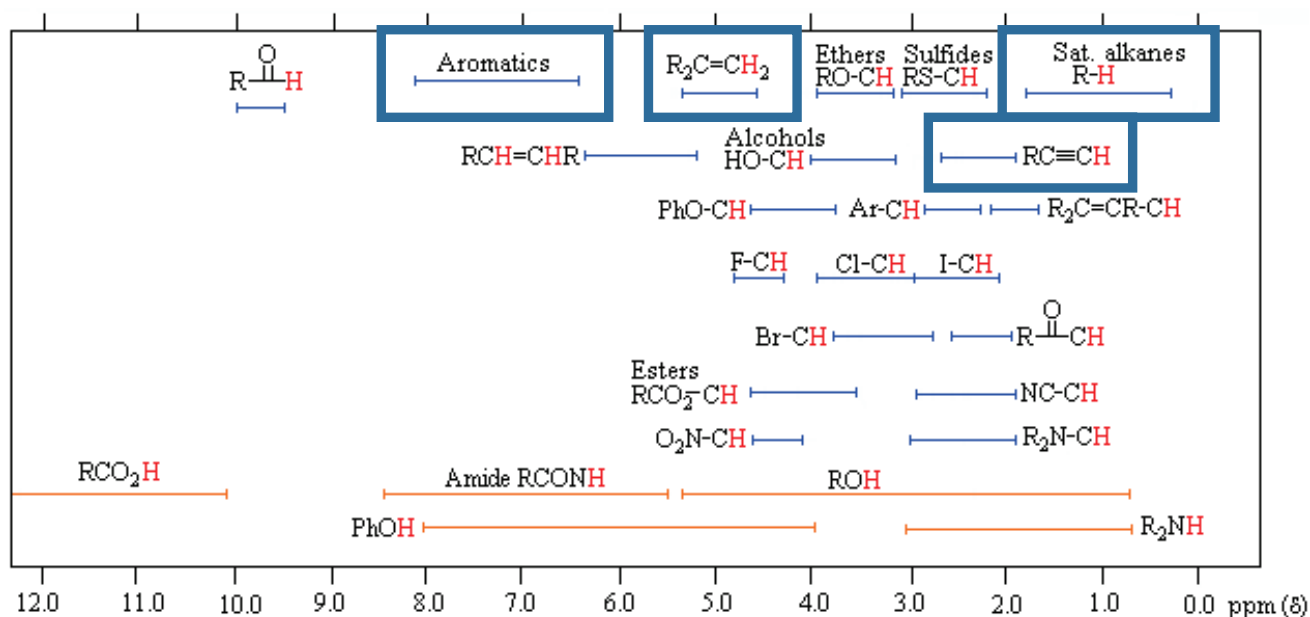
- $\nu_{\text{CH}_3} = 300,001,020 \text{ Hz}$, $\nu_{\text{TMS}} = 300,000,000$
- $\Delta\nu = 1020 \text{ Hz}$
- $\delta = 1020/300,000,000 \times 10^6 = 3.4 \text{ ppm}$

- important: δ is independent of B_0
- CH_3 protons in methanol will always appear at 3.4 ppm regardless of the instrument

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• 4. chemical shifts

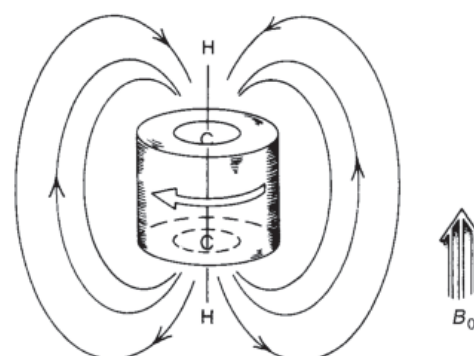
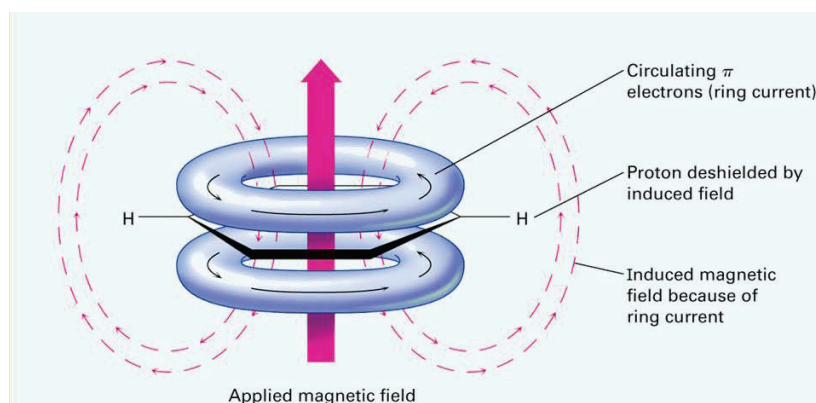


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• 5. magnetic anisotropy

- aromatic and alkyne protons seem out of place
- this is due to magnetic anisotropy
 - p-electrons in circular arrangement can produce a current that interacts with the proton's nuclear spin.



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• 6. spin-spin coupling

• similar to spin-orbit coupling

- individual spins interact with each other if they are close to each other

• consider diethyl ether $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

- two types of protons CH_3 and CH_2

- now let's consider just ONE of the methyl protons (\uparrow)

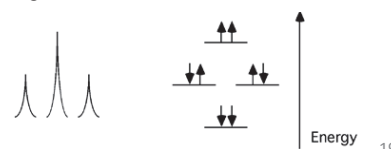
- it is close enough to interact with the two CH_2 protons

- each of those can be either up or down



- the vectors add so the both are up, the CH_3 shifts down-field, when both are down the CH_3 shifts up-field and when one is up and one is down the CH_3 doesn't shift.

- results in a triplet with weight 1:2:1



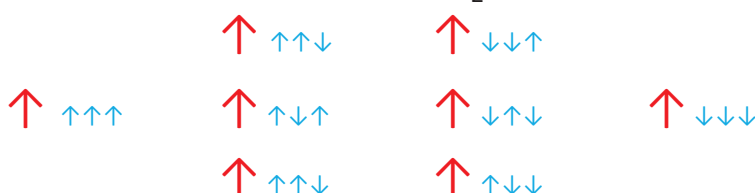
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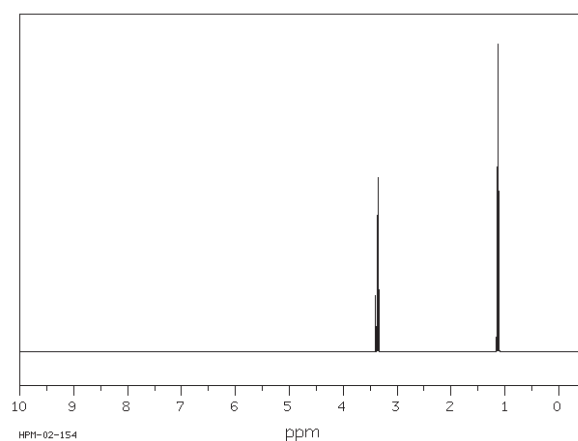
• 6. spin-spin splitting

• $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ continued

- now consider the CH_2 protons



- results in a quartet (1:3:3:1)



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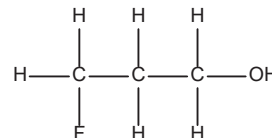
VII.D IR and NMR

• 6. spin-spin splitting rules

- a. equivalent nuclei DO NOT split each other
 - this allowed us to only consider 1 CH₃ or 1 CH₂ proton

- b. significant splitting only observed for:

- geminal (two bonds)
- vicinal (three bonds)



- c. multiplicity of peak given by $(2nI+1)$

- I = spin of splitting nucleus
- n = number of splitting nuclei
- for H, I = $\frac{1}{2}$, so splitting is $(n+1)$
- examples:
 - CHF₃: H will be a quartet ($2 \cdot \frac{1}{2} \cdot 3 + 1$)
 - CH₂F₂: H will be a triplet ($2 \cdot \frac{1}{2} \cdot 2 + 1$)
 - CH₃F : H will be a doublet ($2 \cdot \frac{1}{2} \cdot 1 + 1$)

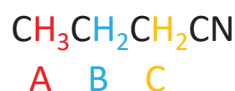
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VII.D IR and NMR

• 6. spin-spin splitting cont.

- d. If more than one different splitting type of proton (A and C), the multiplicity for proton B is given by

$$(n_A + 1)(n_C + 1)$$



example: for CH₃CH₂CH₂CN

H_A: split by 2 H_B = triplet

H_B: split by 2 H_C and 2 H_A = $(2+1)(3+1) = 12$ total peaks (multiplet)

H_C: split by 2 H_B = triplet

compare with CH₃CH₂CH₃

red H: split by 2 blue H: triplet

blue H: split by 6 red H: septet

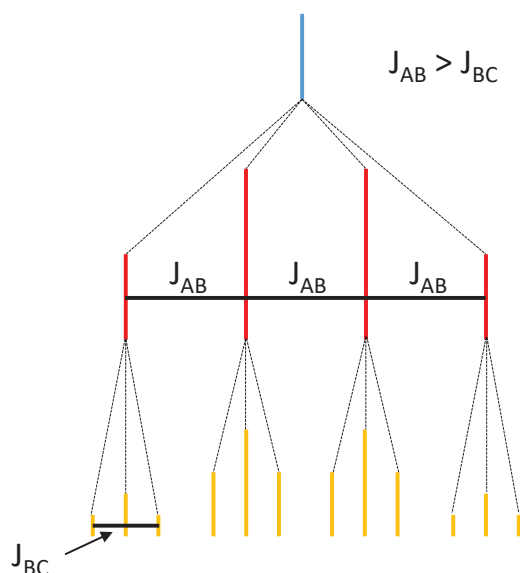
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• 6. spin-spin splitting cont.

• d. continued

- coupling constants J_{XY} give the strength of interaction between two nuclei.
- consider H_B in $CH_3CH_2CH_2CN$ again
- two different coupling constants J_{AB} and J_{BC}

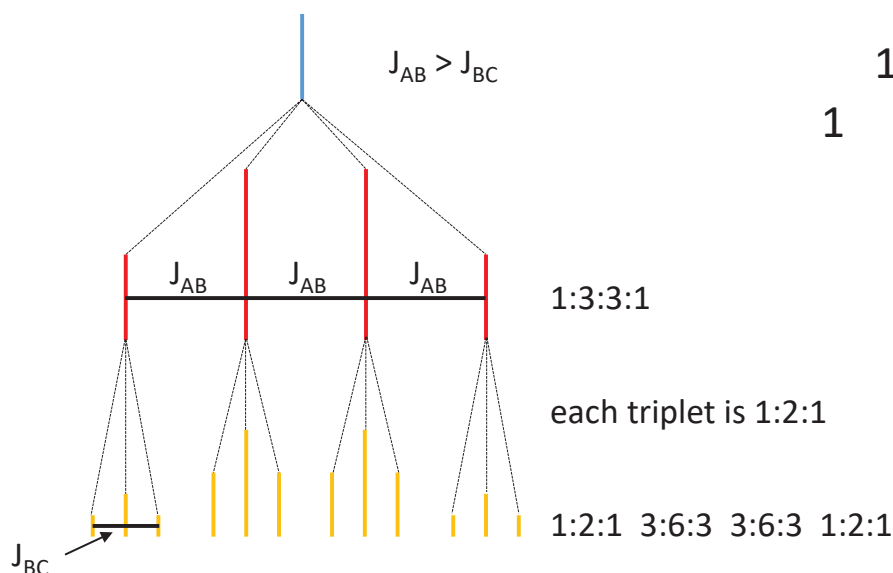


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• 6. spin-spin splitting rules

- e. peak heights within multiplets given by Pascal's triangle



			1				
			1		1		
		1		2		1	
	1		3		3	1	
1		4		6		4	1

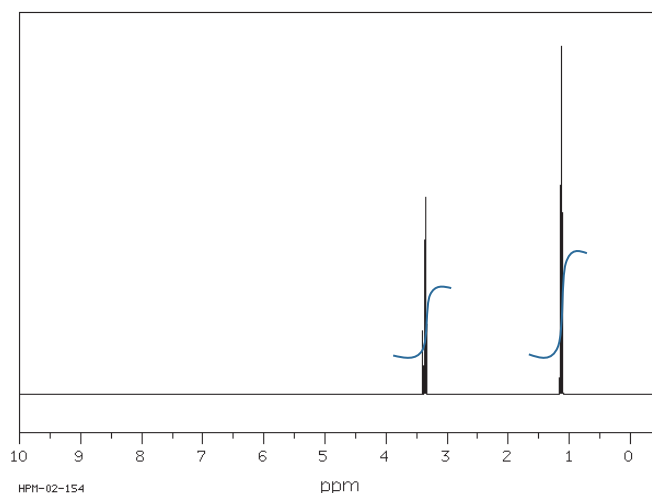
what if you did H_C first?
 H_C triplet 1:2:1
 then H_A quartet and
 each quartet is 1:3:3:1
 gives:

1:2:1 3:6:3 3:6:3 1:2:1

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- 6. spin-spin splitting rules
 - f. coupling constants are always measured in Hz and are independent of B_0
 - allows discernment of J and δ (which will resonate at different Hz value depending on B_0)
 - g. the number of hydrogens contributing to a given multiplet is given by integration of the peak area.



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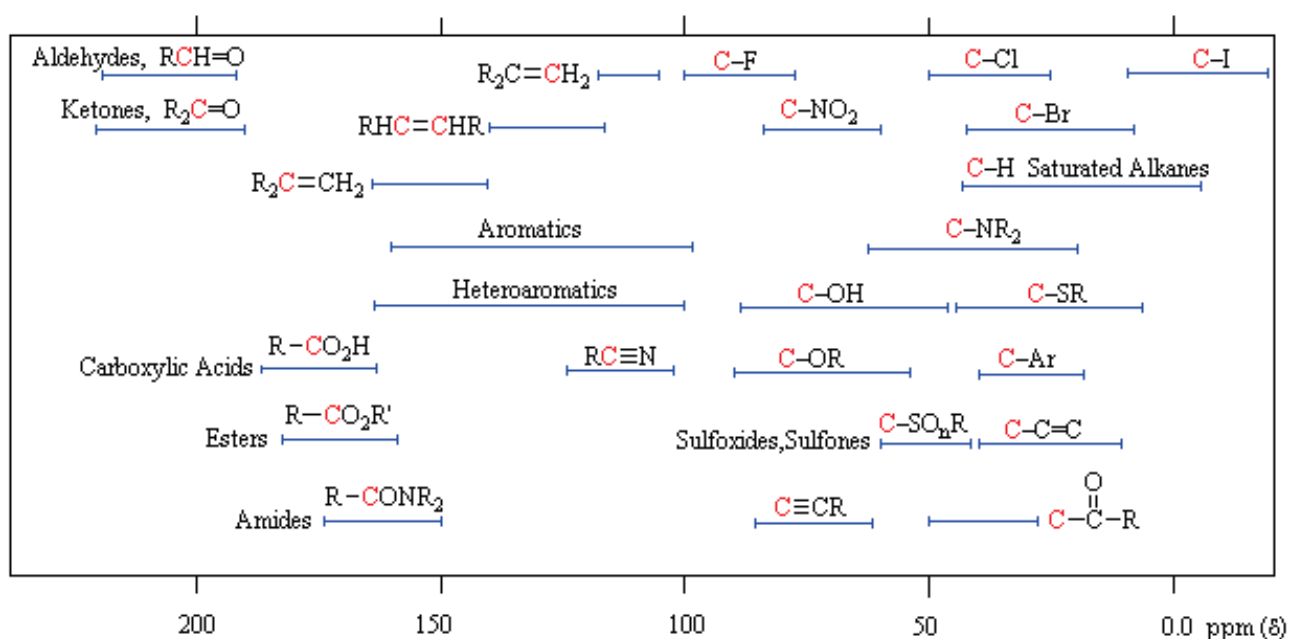
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- 7. ^{13}C NMR
 - ^{13}C is also a spin $\frac{1}{2}$ nucleus
 - gives sharp peaks in NMR
 - but weak signals due to
 - low abundance
 - small γ (~25% of ^1H)
 - much larger chemical shift range (~250 ppm)
 - ^{13}C spectra are broadband decoupled from ^1H
 - sample is flooded with radiation that spin saturates ALL of the protons in the molecule.
 - equal chance of spin up or spin down protons
 - ALL ^{13}C resonances are singlets (unless ^{31}P or ^{19}F present)
 - spin-spin coupling between ^{13}C is negligible due to low abundance
 - integration not useful
 - main use is to tell the number of distinguishable carbons

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• 7. ^{13}C NMR



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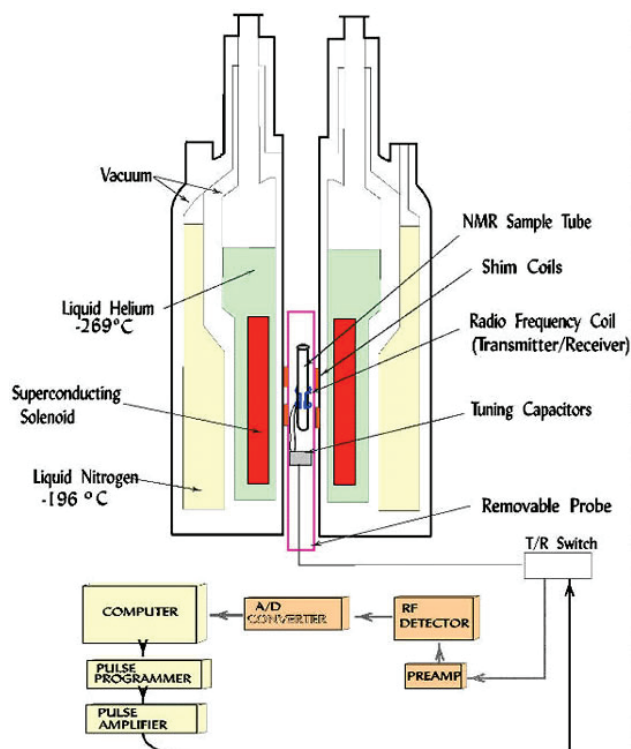
• 8. NMR instrumentation

- powerful but pricey
 - \$300,000 - > \$1,000,000
- most modern instruments are 300 MHz and up
- need magnets > 7 Tesla
- can't get there with permanent magnets or traditional electromagnets
- need to use superconducting materials (next slide)
- which need to be cooled with liquid He to 4.2 K

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• 8. NMR instrumentation

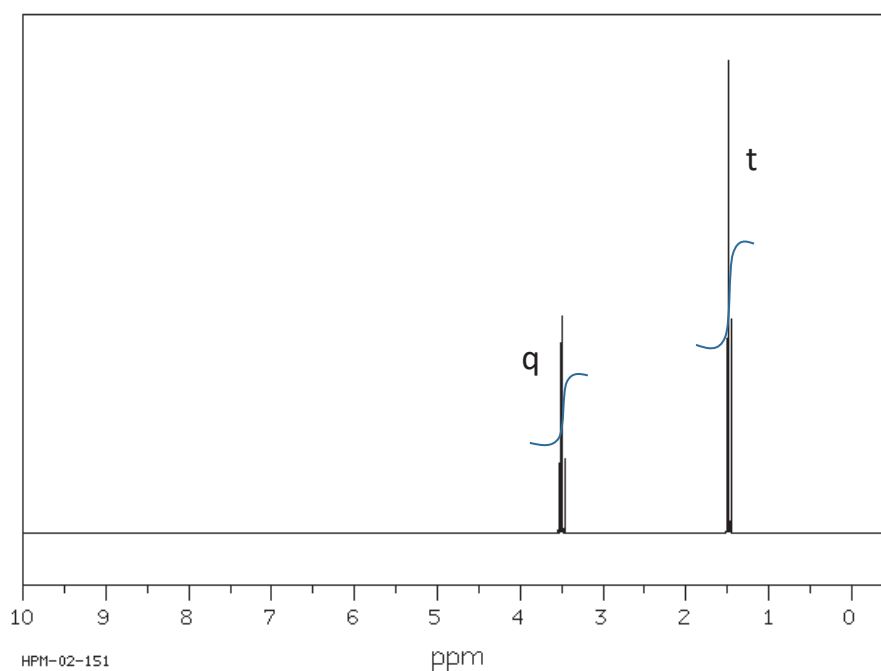


- magnetic field is produced in superconducting coils of wire (Nb-Ti or Nb₃Sn)
- additional coils are used to:
 - shim the magnetic field (shim coils)
 - create pulses of r.f. radiation (excite coils)
 - detect signal from nuclei (detect coils)
 - flood sample with continuous r.f. radiation for de-coupling (de-coupling coils)

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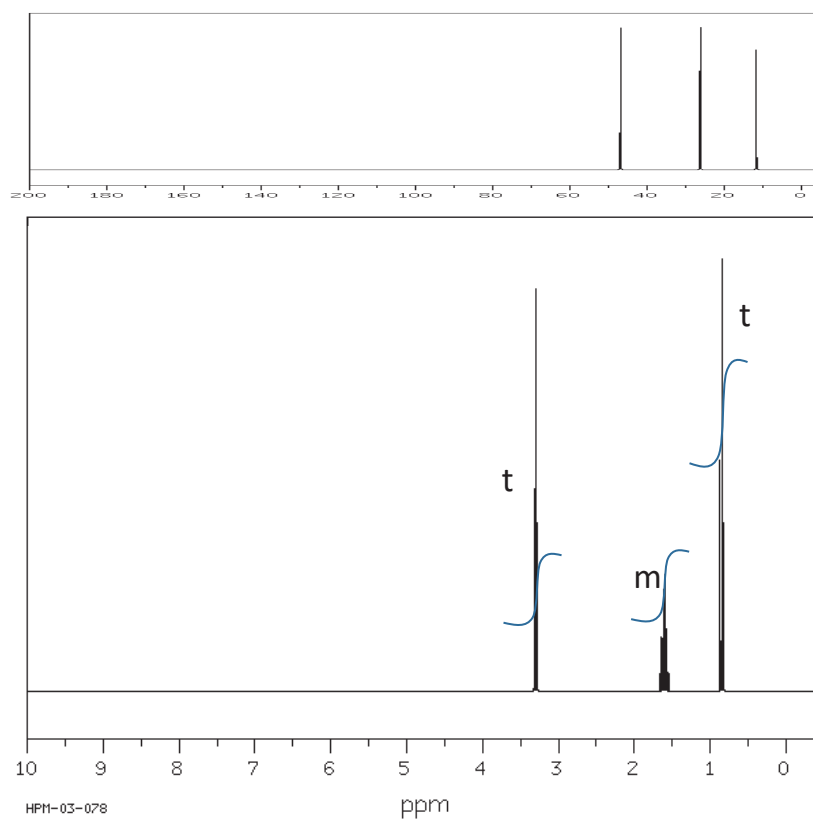
• 9. examples: (CH₃CH₂Cl)



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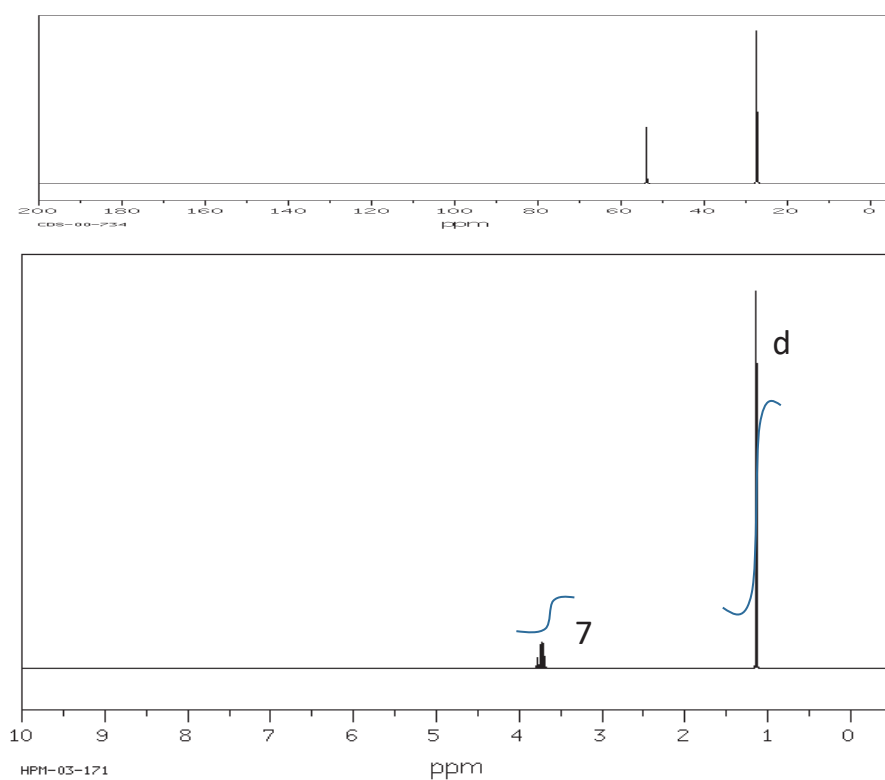
- 9. examples: $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$



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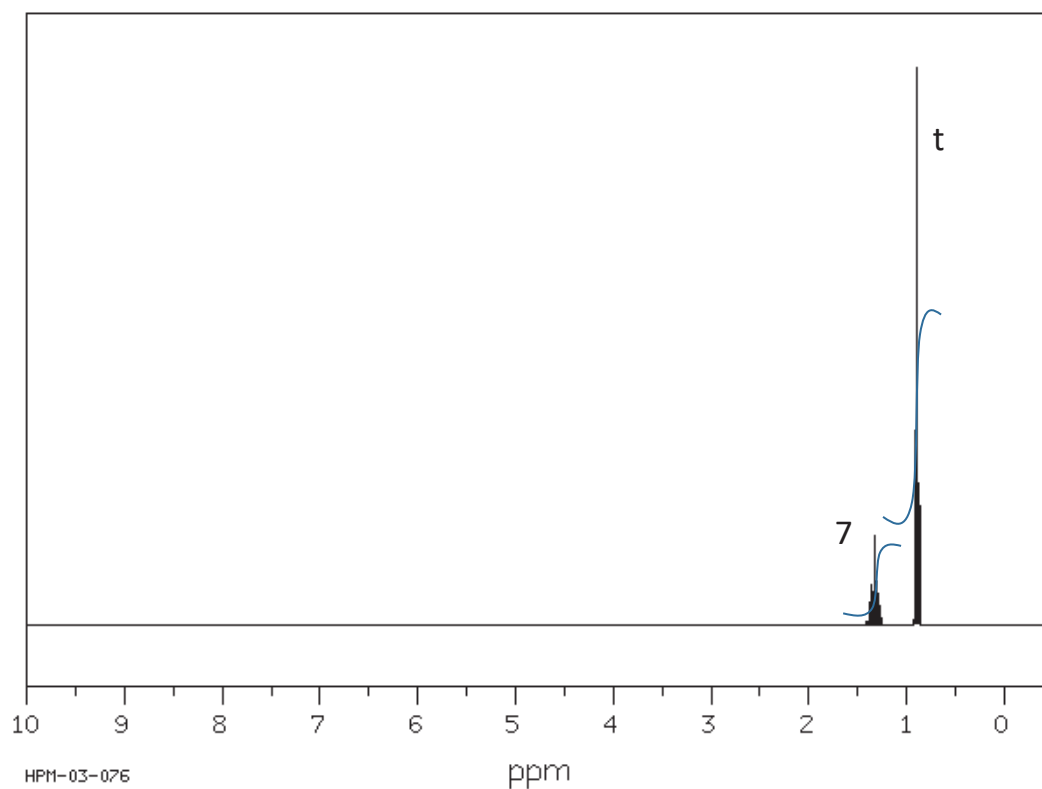
- 9. examples: $(\text{CH}_3)_2\text{CHCl}$



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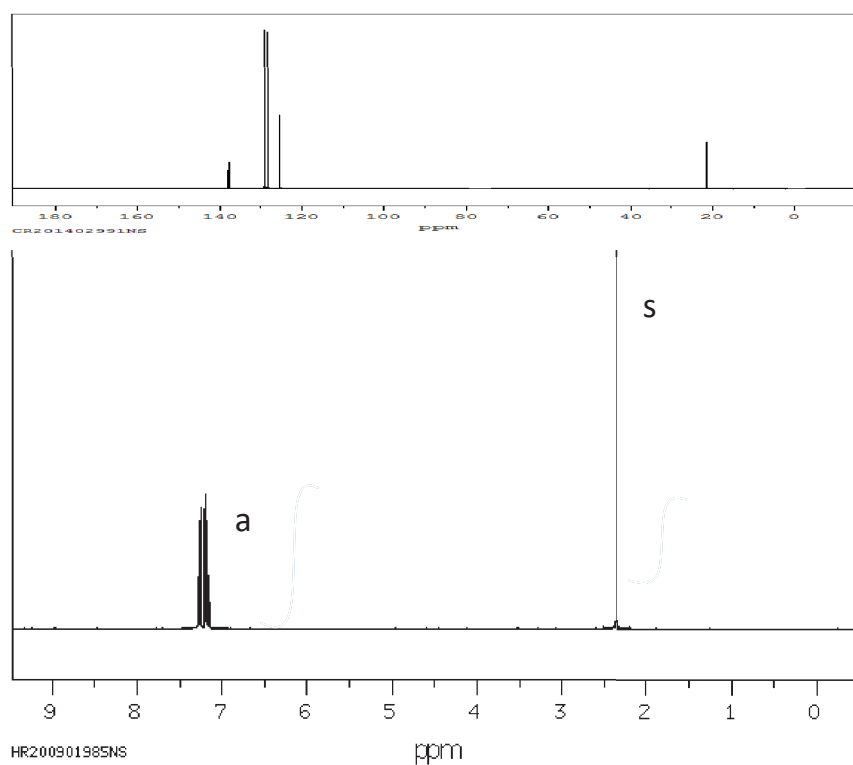
- 9. examples: $(\text{CH}_3\text{CH}_2\text{CH}_3)$



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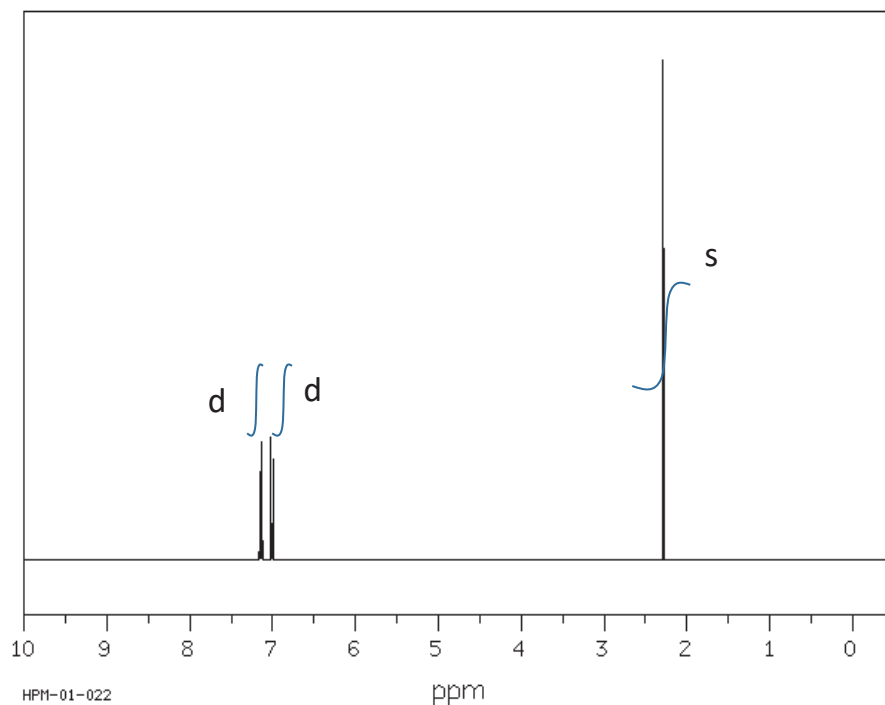
- 9. examples: $\text{C}_6\text{H}_5\text{CH}_3$



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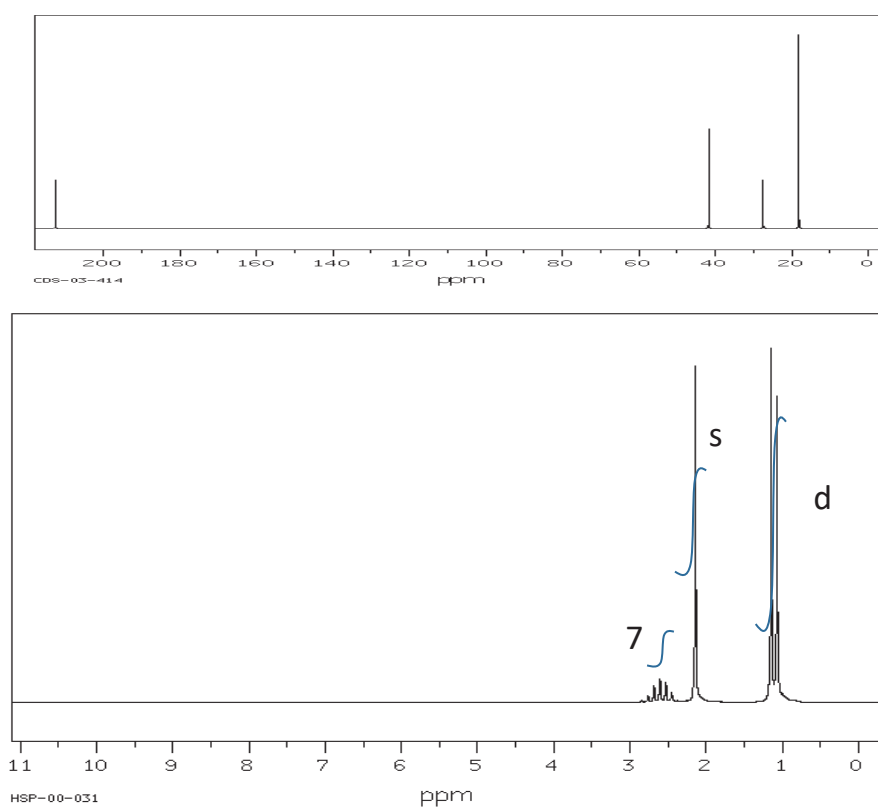
- 9. examples: $p\text{-Cl-C}_6\text{H}_4\text{-CH}_3$



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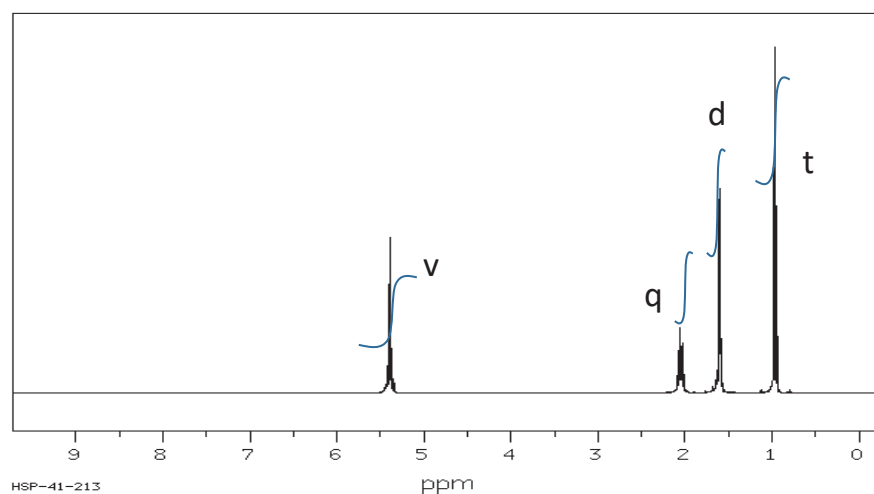
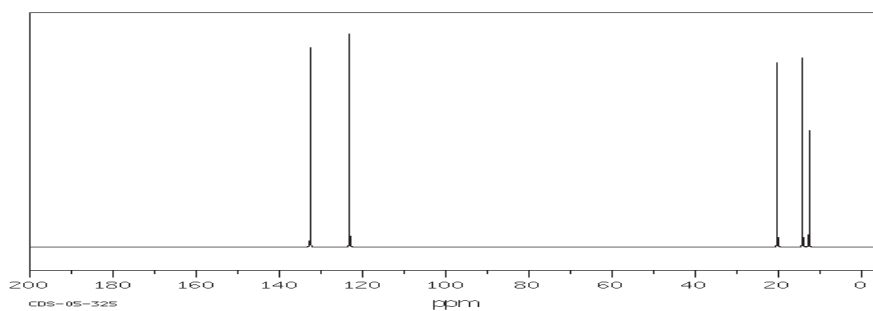
- 9. examples: $i\text{-pr-C(=O)-CH}_3$



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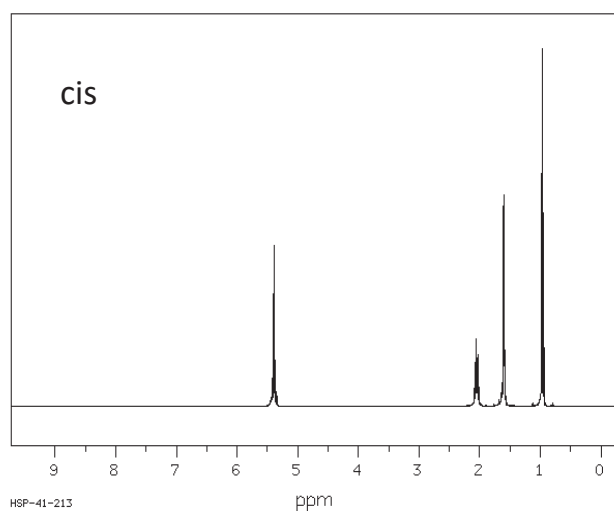
- 9. examples: cis-2-pentene



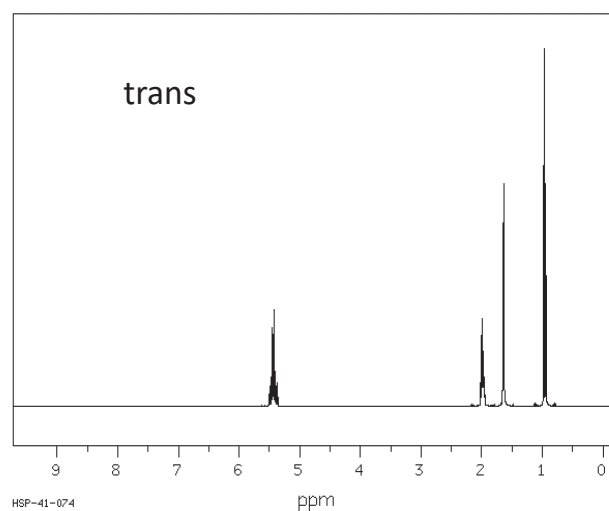
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- 9. examples: trans- vs cis-2-pentene



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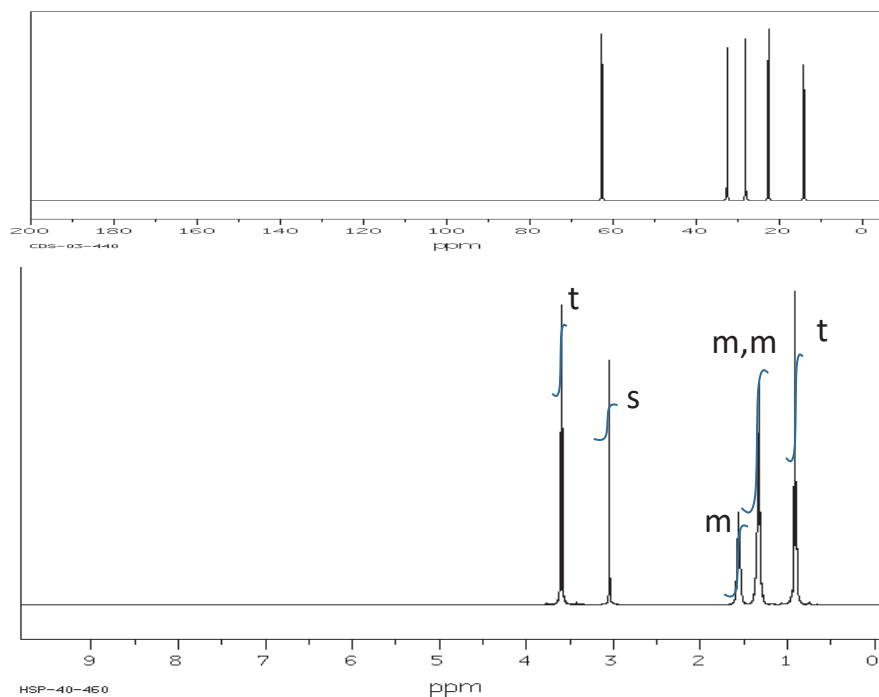
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- 9. examples: pentanol

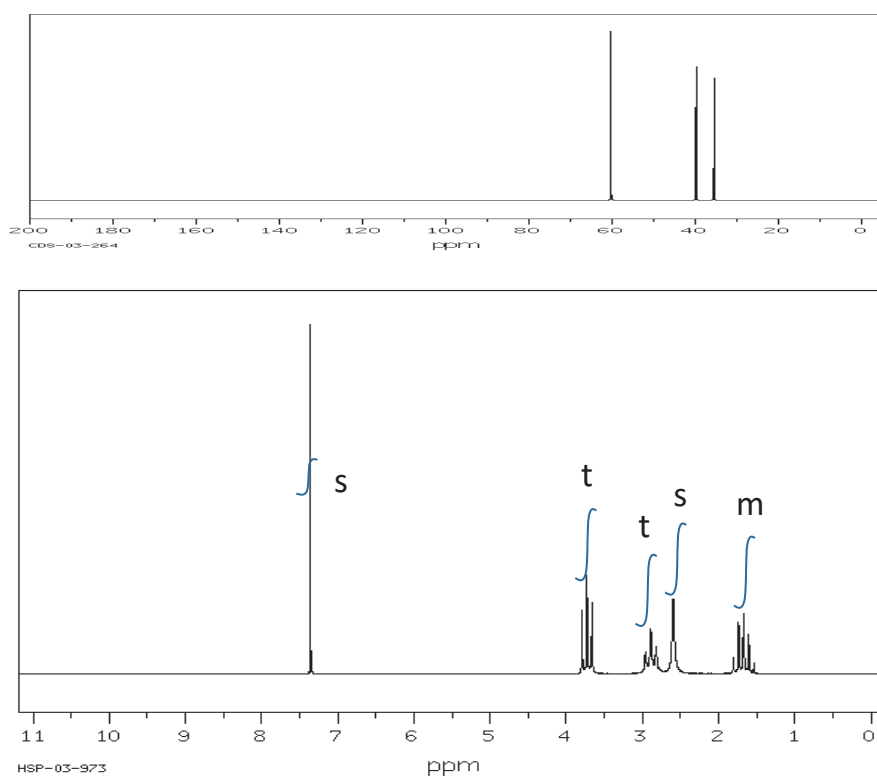
- new splitting rule: H's on OH, NH, do not split and are not split



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- 9. examples: $\text{HO-CH}_2\text{CH}_2\text{CH}_2\text{-NH}_2$



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VII.D IR and NMR

- 9. examples: butanal

