

COURSE : SC202 (CHEMISTRY)

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LECTURE-3

DATE: 11.1.2021

Theory of Nuclear Magnetic Resonance

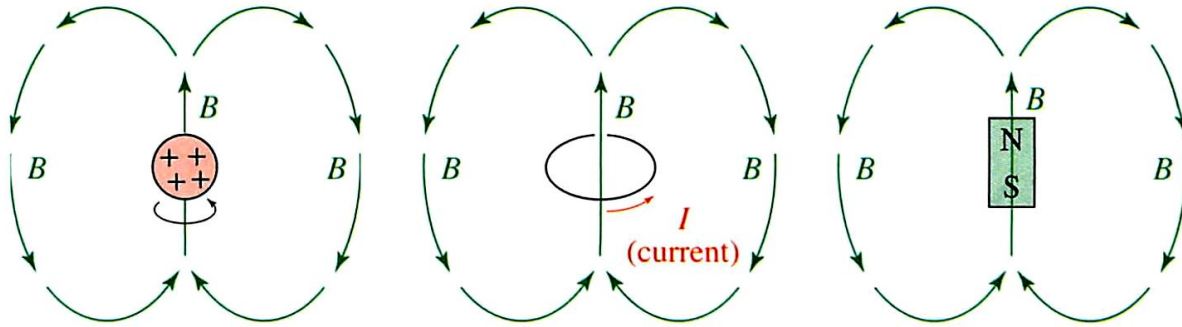


Figure 1

The magnetic moment. A spinning proton generates a magnetic field, called its magnetic moment. This magnetic field (B) resembles that of a small loop of current or bar magnet.

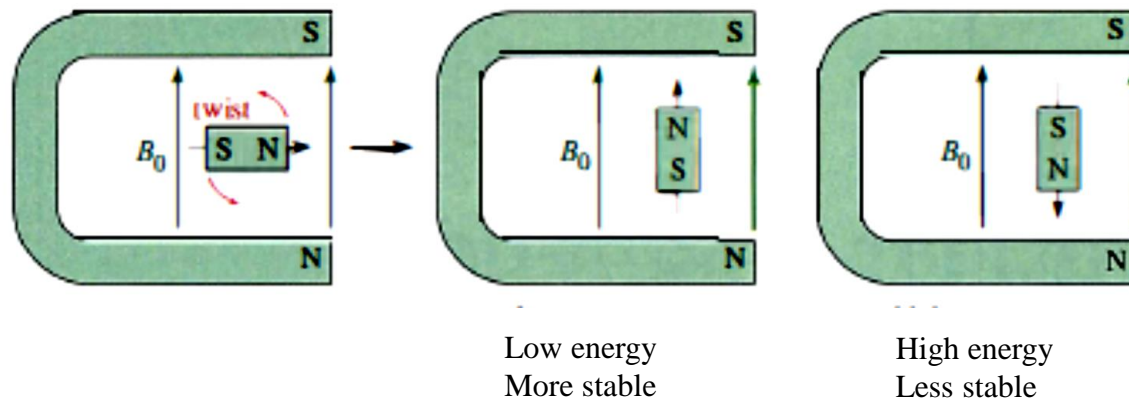
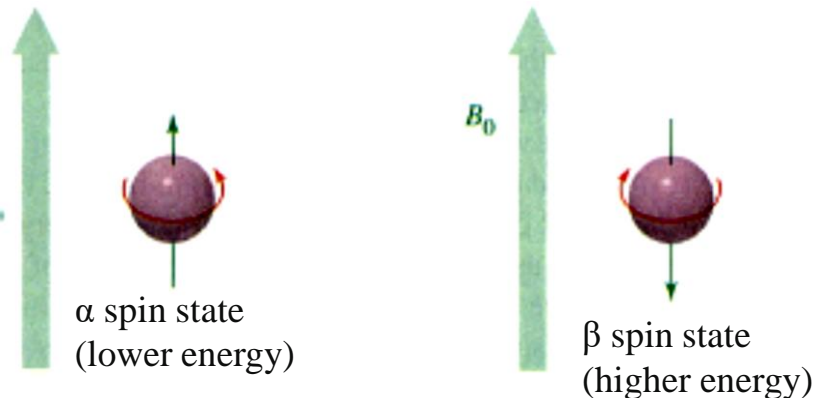
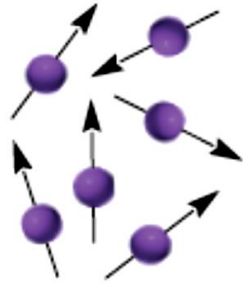


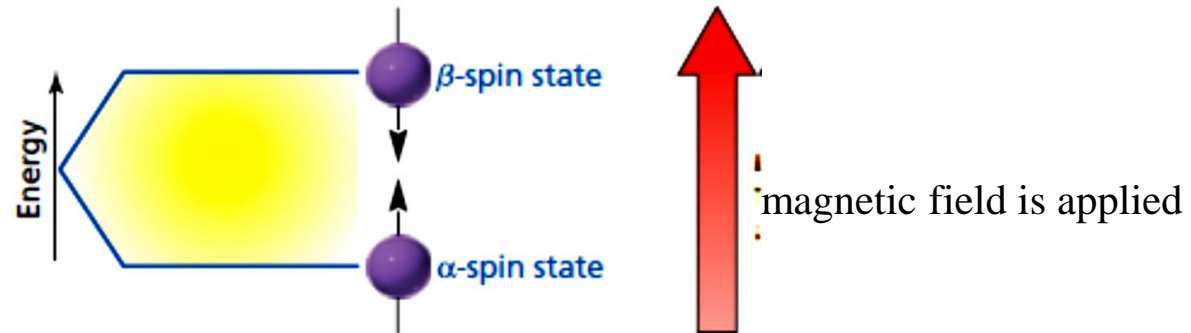
Figure 2

The effect of an external magnetic field. An external magnetic field (B_0) applies a force to a small bar magnet, twisting the bar magnet to align it with the external field. The arrangement of the bar magnet aligned with the field is lower in energy than the arrangement aligned against the field.





No magnetic field is applied



In the absence of an applied magnetic field, the spins of the nuclei are randomly oriented. In the presence of an applied magnetic field, the spins of the nuclei line up with or against the field.

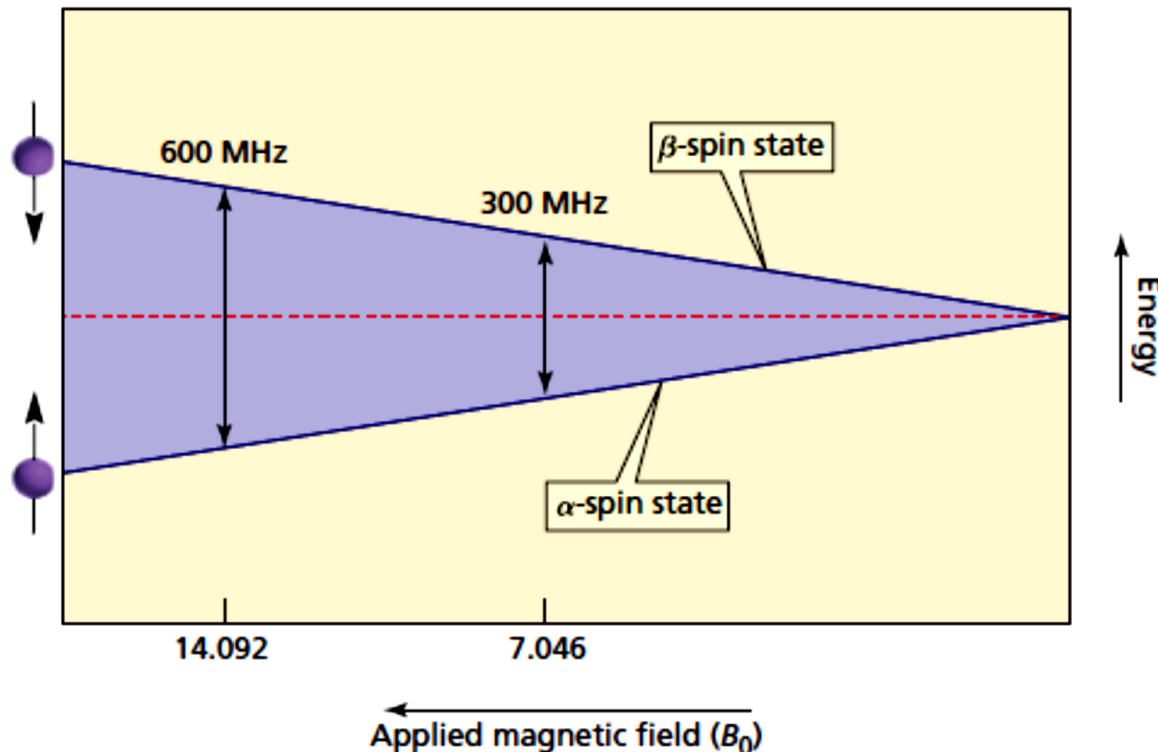


Figure 3 :The greater the strength of the magnetic field to which we expose the nucleus, the greater is the difference in energy between the α and β states.

A photon's energy is given by $E=h\nu$, meaning that the energy, E , is proportional to ν , the frequency of the electromagnetic wave. This equation can be combined with the equation for the energy difference between the spin states:

$$\Delta E = h\nu = \gamma \frac{h}{2\pi} B_0$$

Rearranging to solve for ν shows that the resonance frequency ν is proportional to the applied magnetic field (B_0) and the gyromagnetic ratio (γ):

$$\nu = \frac{1}{2\pi} \gamma B_0$$

For a proton, $\gamma = 26,753 \text{ sec}^{-1} \text{ gauss}^{-1}$, and

$$\nu = \frac{(26,753 \text{ sec}^{-1} \text{ gauss}^{-1})}{2\pi} \times B_0 = (4257.8 \text{ sec}^{-1} \text{ gauss}^{-1}) \times B_0$$

Problem 1 : Calculate the magnetic fields that correspond to proton resonance frequencies of 60 MHz and 300 MHz.

Solution: We substitute into the equation $\nu = (1/2\pi) \gamma B_0$.

$$60 \text{ MHz} = 60 \times 10^6 \text{ sec}^{-1} = (4257.8 \text{ sec}^{-1} \text{ gauss}^{-1}) \times B_0$$

$$B_0 = 14,092 \text{ gauss (1.4092 tesla)}$$

$$300 \text{ MHz} = 300 \times 10^6 \text{ sec}^{-1} = (4257.8 \text{ sec}^{-1} \text{ gauss}^{-1}) \times B_0$$

$$B_0 = 70,459 \text{ gauss (7.0459 tesla)}$$

Shielding

In a molecule, the electron cloud around each nucleus acts like a loop of wire, rotating in response to the external field. This induced rotation is a circular current whose magnetic field opposes the external field. The result is that the magnetic field at the nucleus is weaker than the external field, and we say the nucleus is shielded.

$$B_{\text{effective}} = B_{\text{external}} - B_{\text{shielding}}$$

This means that the greater the electron density of the environment in which the proton is located, the greater $B_{\text{shielding}}$ is and the more the proton is shielded from the applied magnetic field. This type of shielding is called **diamagnetic shielding**. Thus, protons in electron-dense environments sense a *smaller effective magnetic field*. They, therefore, will require a *lower frequency* to come into resonance—that is, flip their spin—because is smaller. Protons in electron-poor environments sense a *larger effective magnetic field* and, therefore, will require a *higher frequency* to come into resonance, because is larger.

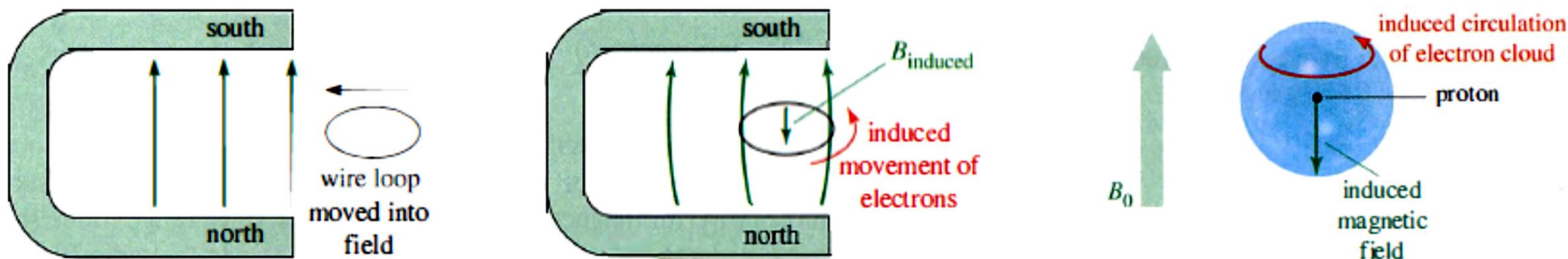


Figure 4: Induced magnetic field. Moving a loop of wire into a magnetic field induces a current in the wire. This current produces its own smaller magnetic field, in the direction opposite the applied field. In a molecule, electrons can circulate around a nucleus. The resulting "current" sets up a magnetic field that opposes the external field, so the nucleus feels a slightly weaker field.

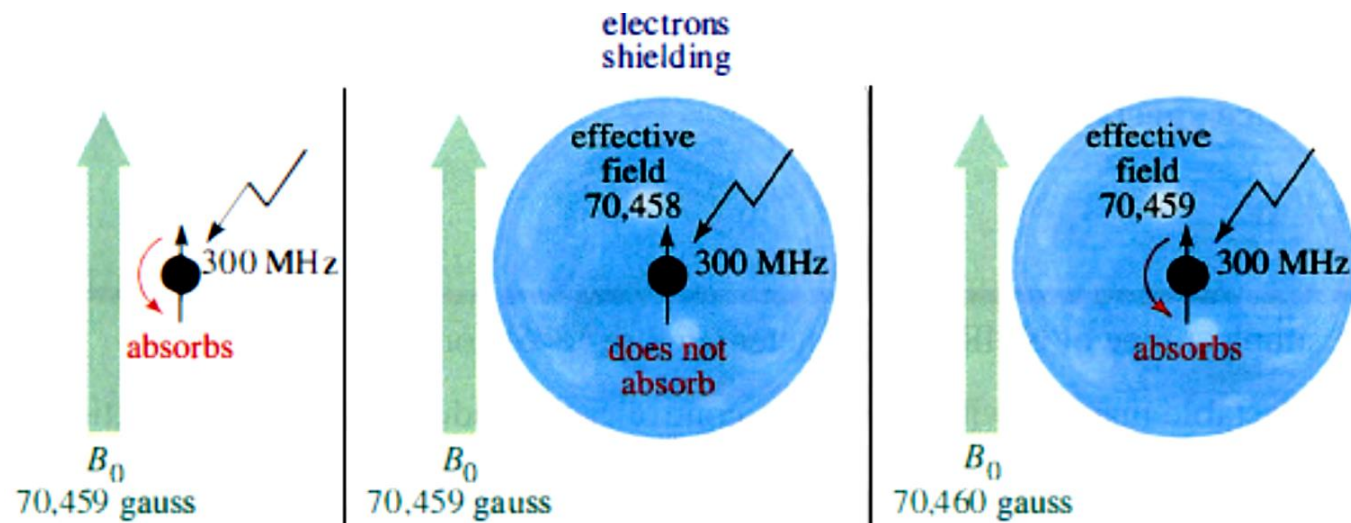
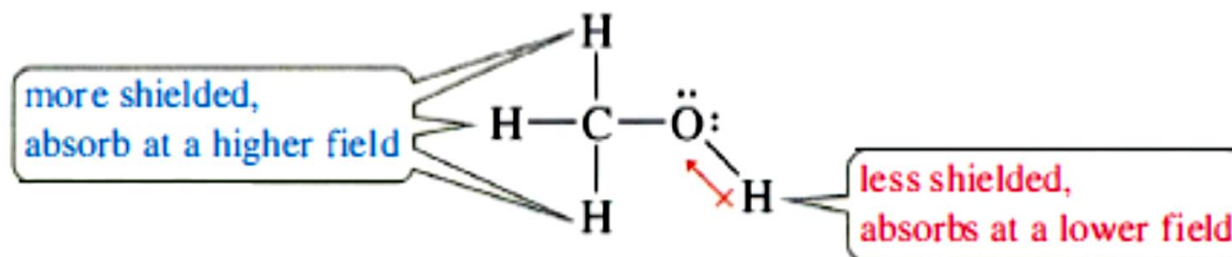


Figure 5

A proton shielded by electrons. The magnetic field must be increased slightly above 70,459 gauss (at 300 MHz) for resonance of a shielded proton.



Protons in different chemical environments are shielded by different amounts. In methanol, for example, the electronegative oxygen atom withdraws some electron density from around the hydroxyl proton. The hydroxyl proton is not shielded as much as the methyl protons, so the hydroxyl proton absorbs at a lower field than the methyl protons (but still at a higher field than a naked proton). We say that the hydroxyl proton is **deshielded** somewhat by the presence of the electronegative oxygen atom.

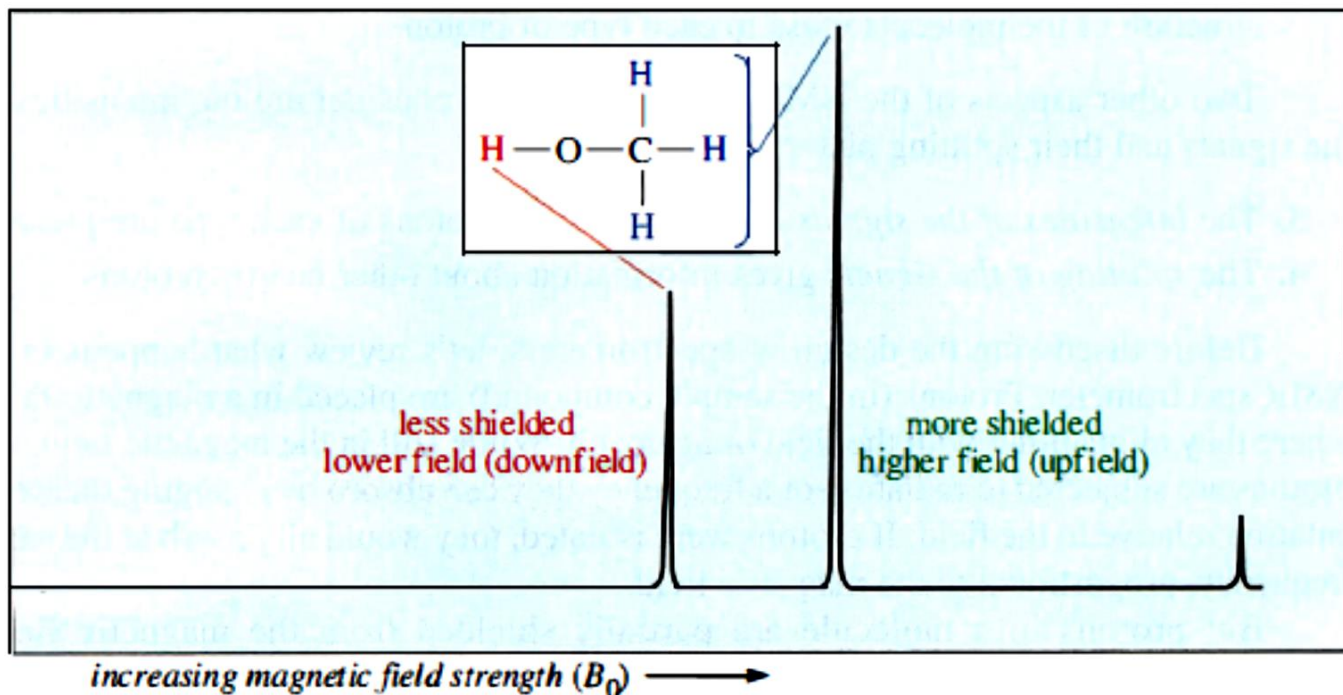
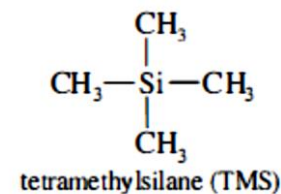


Figure 6: Proton NMR spectrum of methanol. The more shielded methyl protons appear toward the right of the spectrum (higher field); the less shielded hydroxyl proton appears toward the left (lower field)

Chemical shift: The difference (in parts per million) between the resonance frequency of the proton being observed and that of tetramethylsilane (TMS).

A chemical shift in ppm can be calculated by dividing the shift measured in hertz by the spectrometer frequency measured in millions of hertz (megahertz, or MHz).

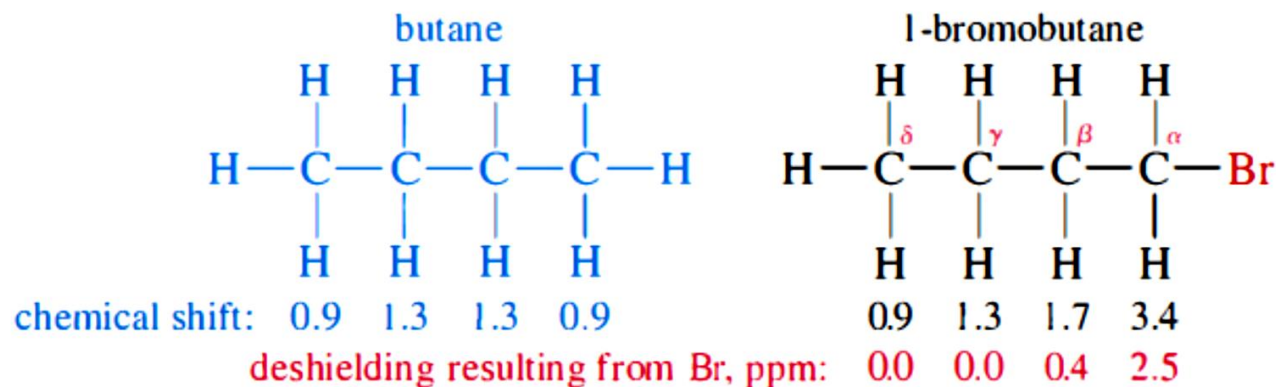
$$\text{chemical shift (ppm)} = \frac{\text{shift downfield from TMS (Hz)}}{\text{Total spectrometer frequency (MHz)}}$$



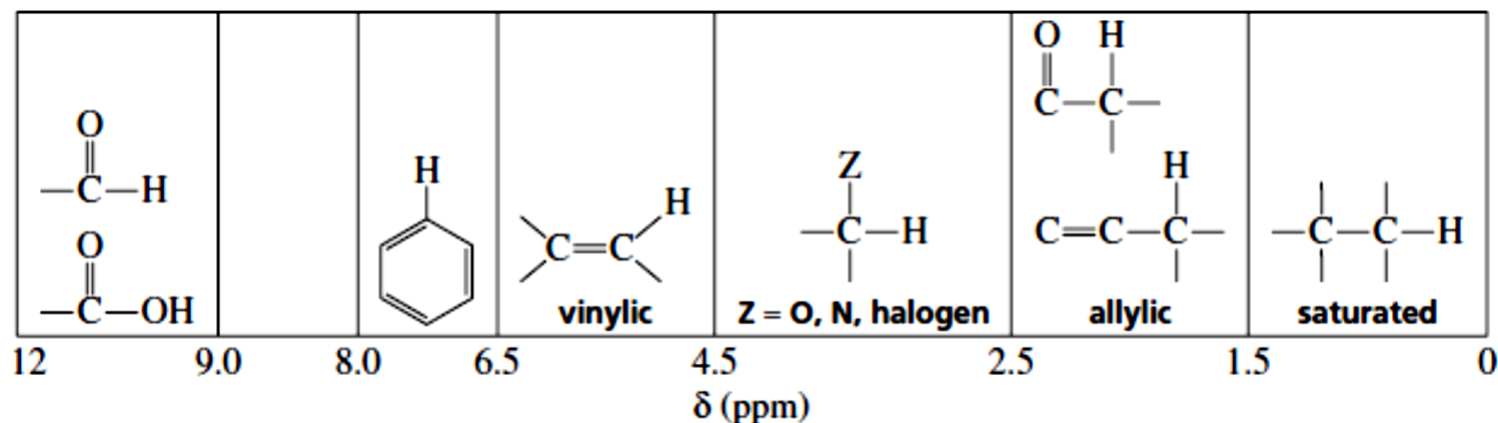
The chemical shift (in ppm) of a given proton is the same regardless of the operating field and frequency of the spectrometer.

TABLE 13-1 Variation of Chemical Shift with Electronegativity

	X in CH ₃ —X				
	F	OH	Cl	Br	I
electronegativity of X	4.0	3.4	3.2	3.0	2.7
chemical shift of CH ₃ —X	δ 4.3	δ 3.4	δ 3.0	δ 2.7	δ 2.2



Characteristic Values of Chemical Shifts



Chemical Shift

- Depends on (1) electronegativity of nearby atoms, (2) the hybridization of adjacent atoms, and (3) diamagnetic effects from adjacent pi bonds
- Hybridization of adjacent atoms

Type of Hydrogen (R = alkyl)	Name of Hydrogen	Chemical Shift (δ)
RCH_3 , R_2CH_2 , R_3CH	Alkyl	0.8 - 1.7
$\text{R}_2\text{C}=\text{C}(\text{R})\text{CHR}_2$	Allylic	1.6 - 2.6
$\text{RC}\equiv\text{CH}$	Acetylenic	2.0 - 3.0
$\text{R}_2\text{C}=\text{CHR}$, $\text{R}_2\text{C}=\text{CH}_2$	Vinylic	4.6 - 5.7
RCHO	Aldehydic	9.5-10.1

Problem 2: A 300-MHz spectrometer records a proton that absorbs at a frequency 2130 Hz downfield from TMS.

- Determine its chemical shift, and express this shift as a magnetic field difference.
- Predict this proton's chemical shift at 60 MHz. In a 60-MHz spectrometer, how far downfield (in gauss and in hertz) from TMS would this proton absorb?

Diamagnetic Anisotropy

The unusual chemical shifts associated with hydrogens bonded to carbons that form bonds are due to *diamagnetic anisotropy*. **Diamagnetic anisotropy** describes an environment in which different magnetic fields are found at different points in space.

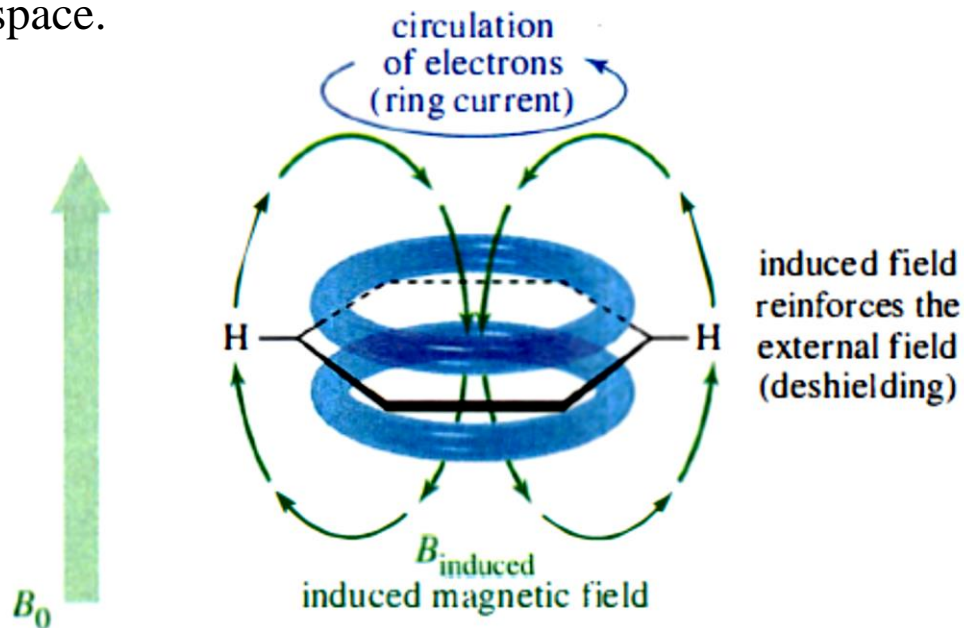


Figure 7

Aromatic ring current. The induced magnetic field of the circulating aromatic electrons opposes the applied magnetic field along the axis of the ring. The aromatic hydrogens are on the equator of the ring, where the induced field lines curve around and reinforce the applied field.

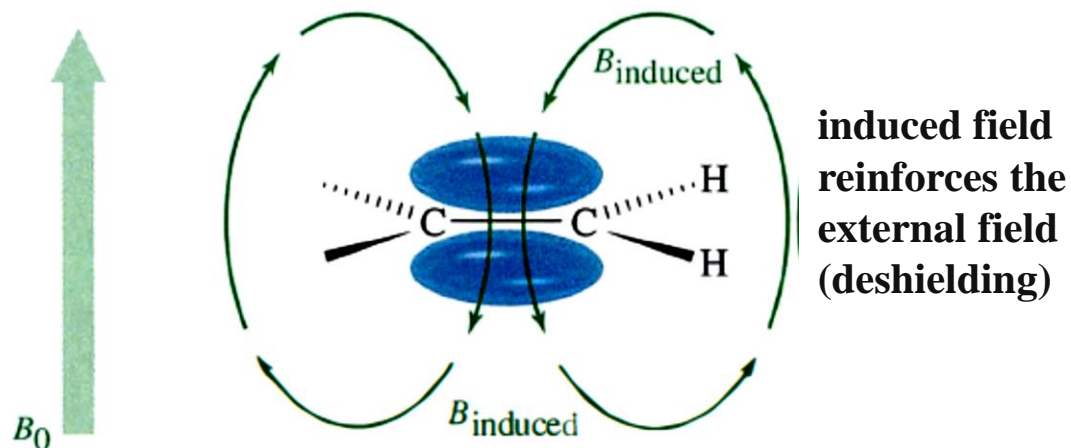


Figure 8

Deshielding by a pi bond. Vinyl protons are positioned on the periphery of the induced magnetic field of the pi electrons. In this position, they are deshielded by the induced magnetic field.

Acetylenic hydrogens absorb around $\delta 2.5$, compared with $\delta 5$ to $\delta 6$ for vinyl protons.

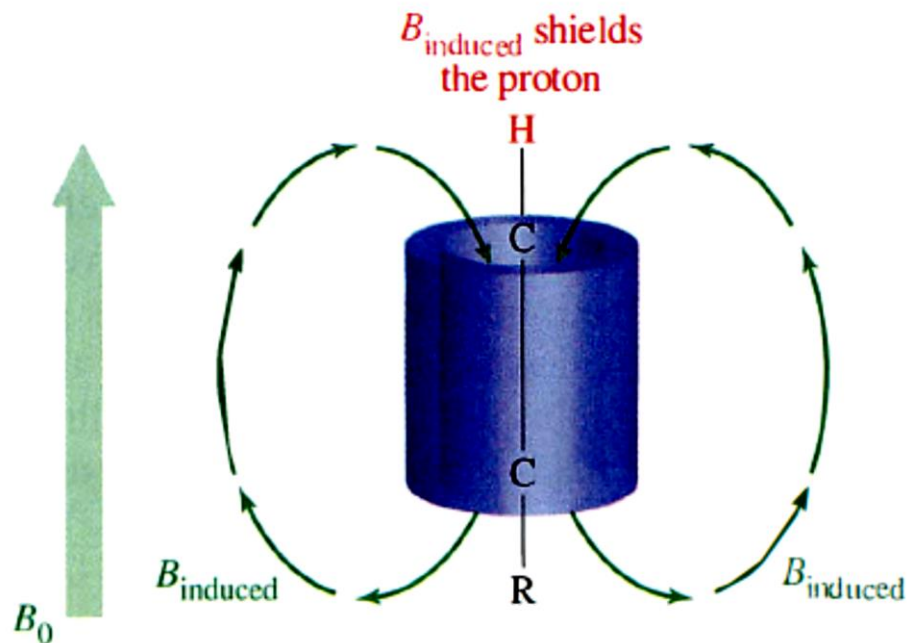


Figure 9

Partial shielding by a triple bond. When the acetylenic triple bond is aligned with the magnetic field, the cylinder of electrons circulates to create an induced magnetic field. The acetylenic proton lies along the axis of this field, which opposes the external field.

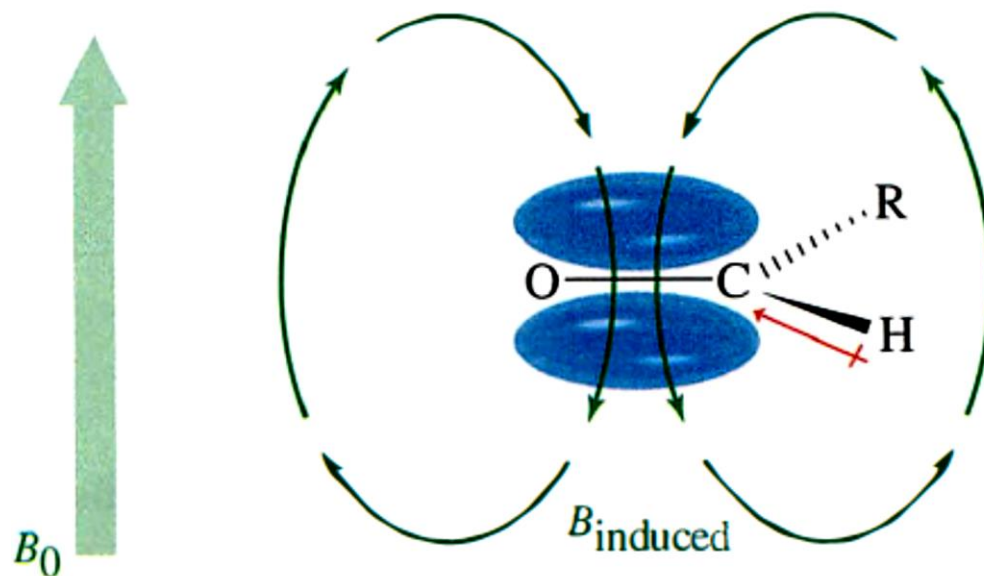
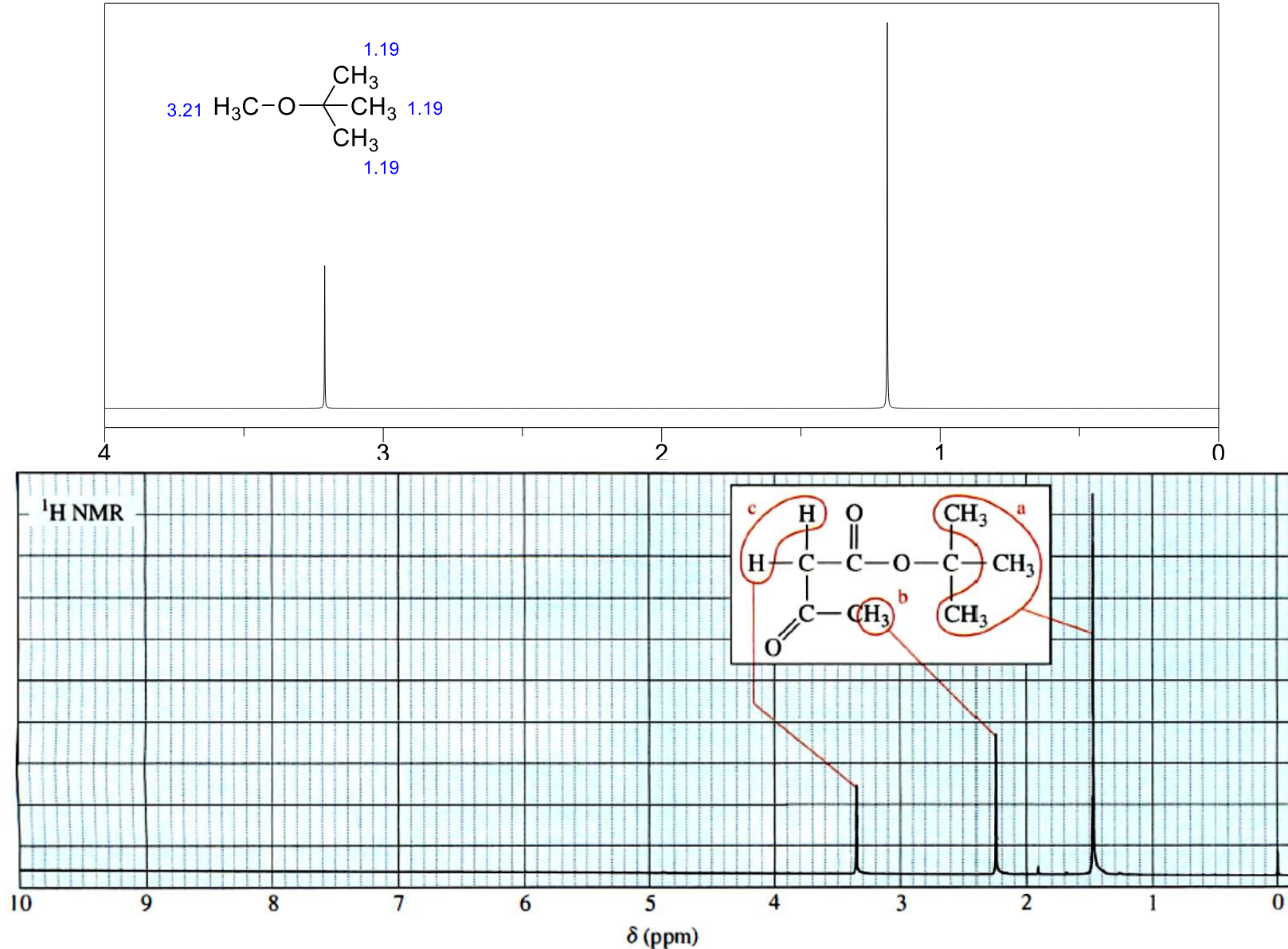


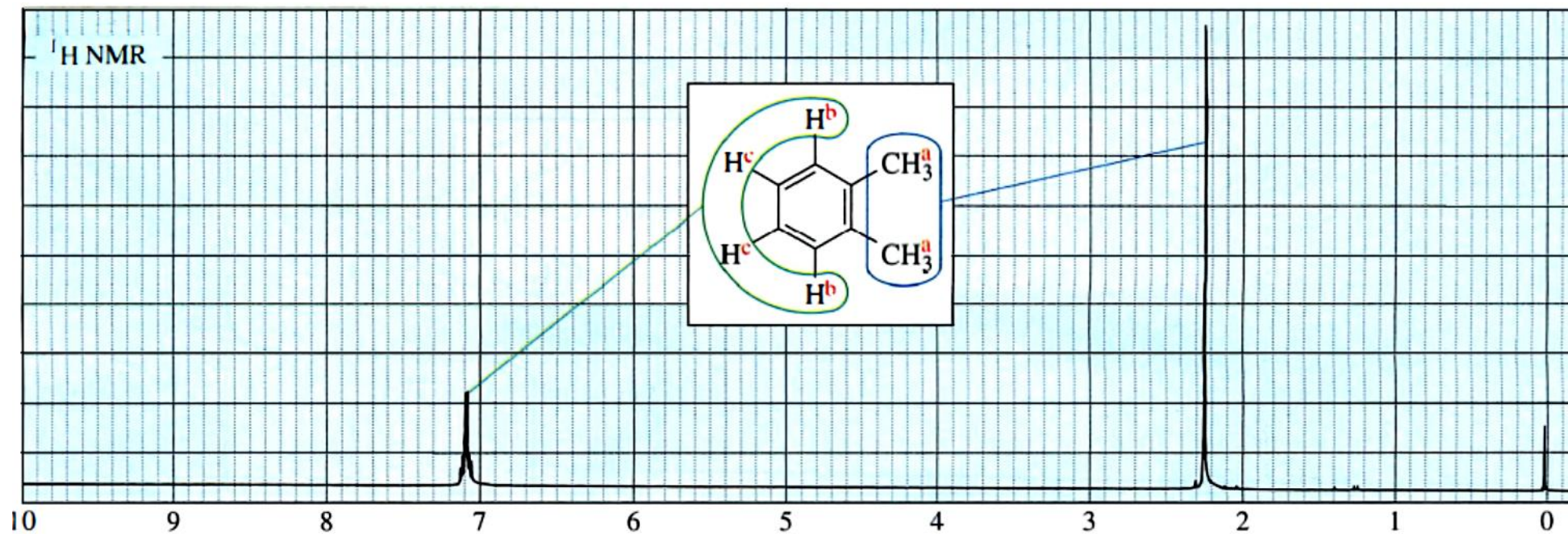
Figure 10

Deshielding of the aldehyde proton. Like a vinyl proton, the aldehyde proton is deshielded by the circulation of electrons in the pi bond. It is also deshielded by the electron-withdrawing effect of the carbonyl ($\text{C}=\text{O}$) group, giving a resonance between $\delta 9$ and $\delta 10$.

The Number of Signals in the NMR Spectrum

Protons in identical chemical environments with the same shielding have the same chemical shift. Such protons are said to be **chemically equivalent**.

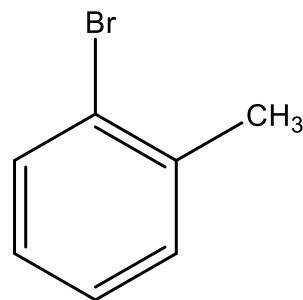
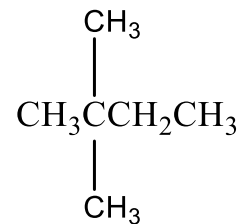
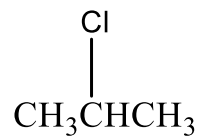
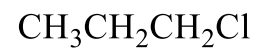




Problem 3: Determine the number of different kinds of protons in each compound.

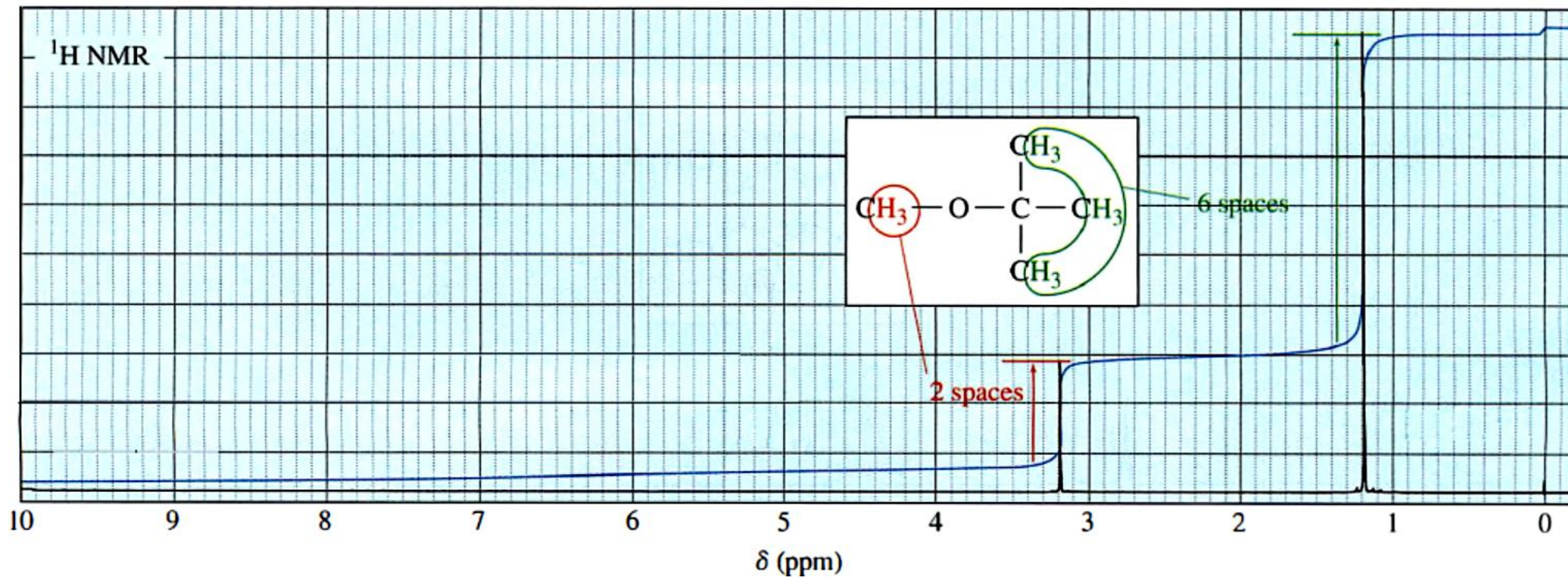
(a) 1-chloropropane (b) 2-chloropropane

(c) 2,2-dimethylbutane (d) 1-bromo-2-methylbenzene

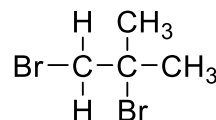
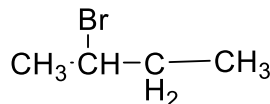
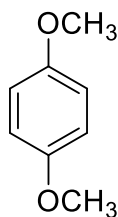
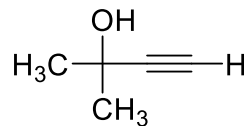
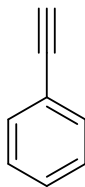
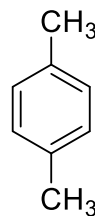


Areas of the Peaks

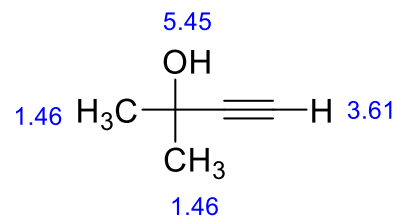
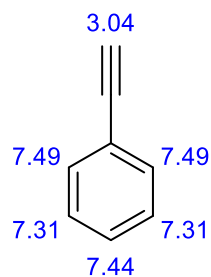
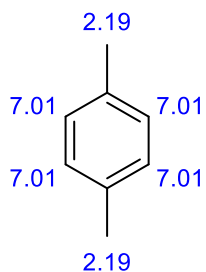
The area under a peak is proportional to the number of hydrogens contributing to that peak.

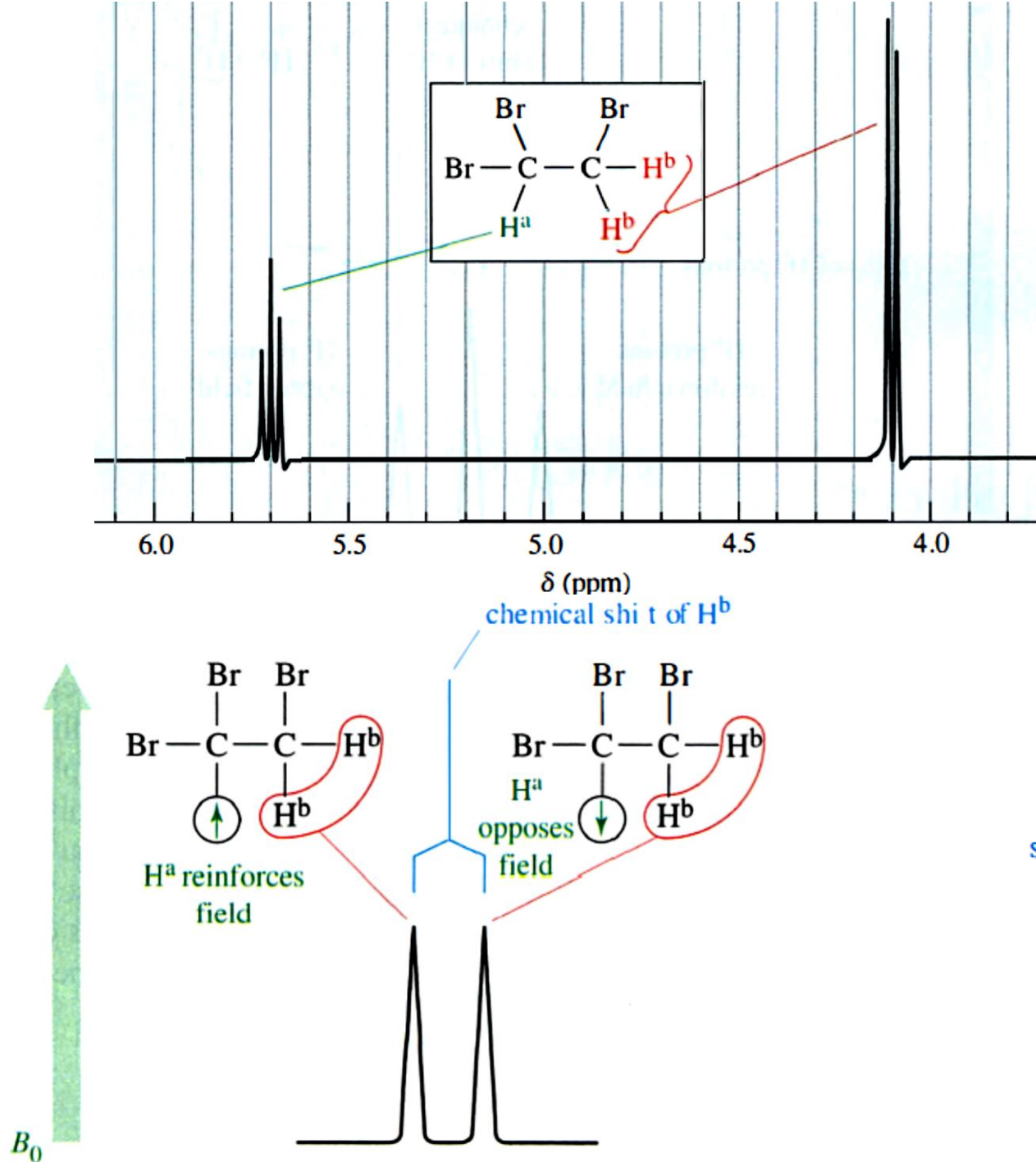


Problem 4: Determine the number of peaks and the ratios of the peak areas in the following spectra.

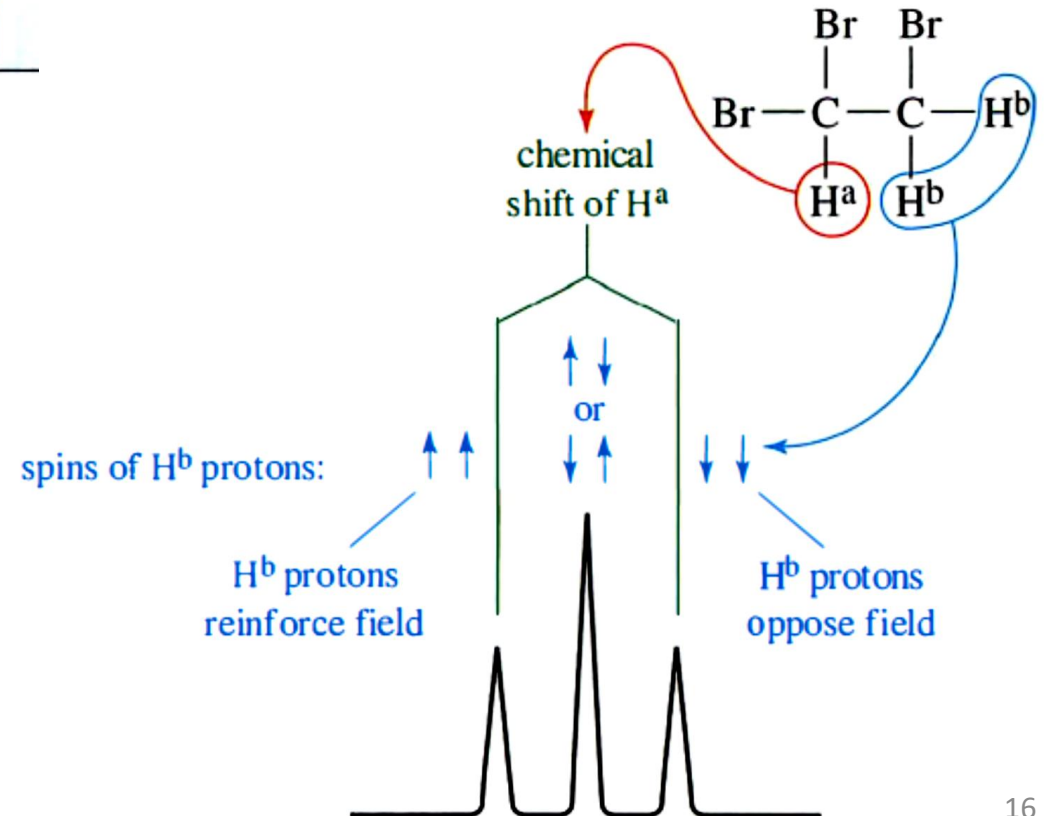


Solution:





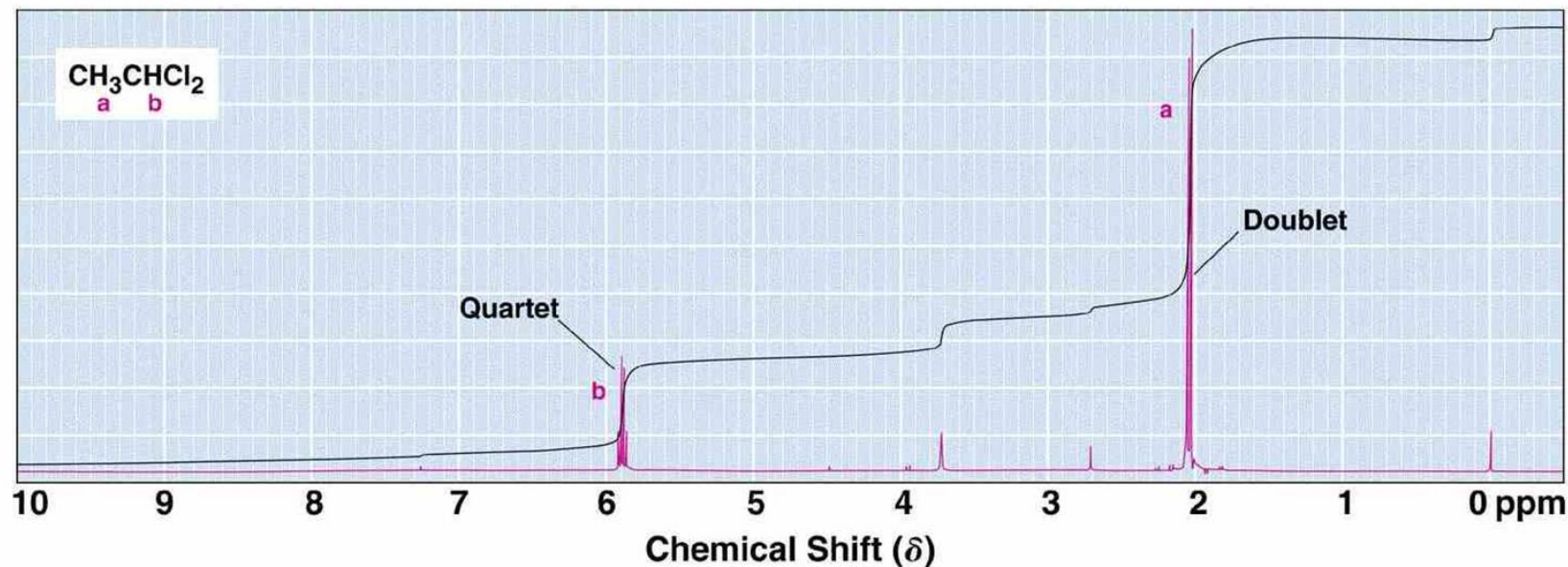
Spin-spin splitting is a reciprocal property. That is, if one proton splits another, the second proton must split the first.



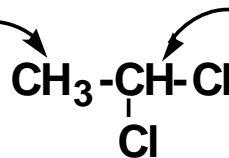
Spin - Spin Splitting

- **Signal splitting:** splitting of an NMR signal into a set of peaks by the influence of neighboring nonequivalent hydrogens
- The number of peaks in a signal is called the **multiplicity** of the signal.
- **(N + 1) rule:** If a signal is split by N equivalent protons, it is split into N+ 1 peaks.

^1H -NMR spectrum of 1,1-dichloroethane



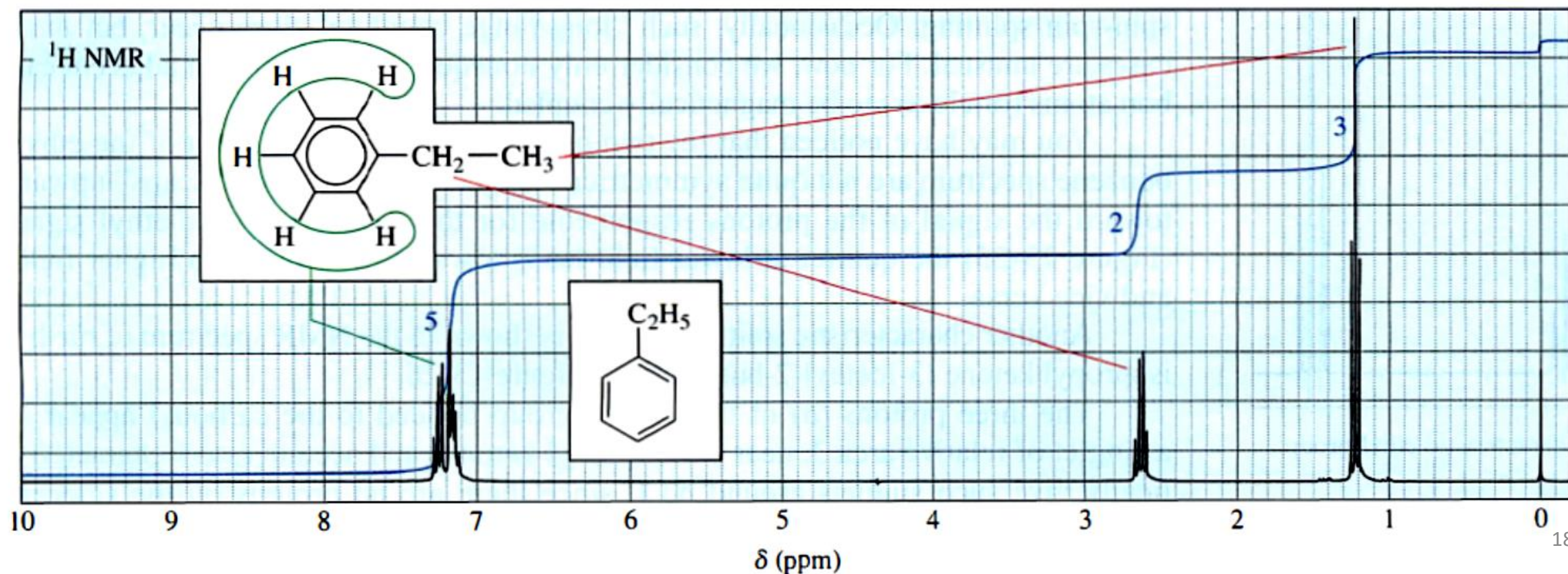
For these hydrogens, $n = 1$;
their signal is split into
 $(1 + 1) = 2$ peaks; a doublet

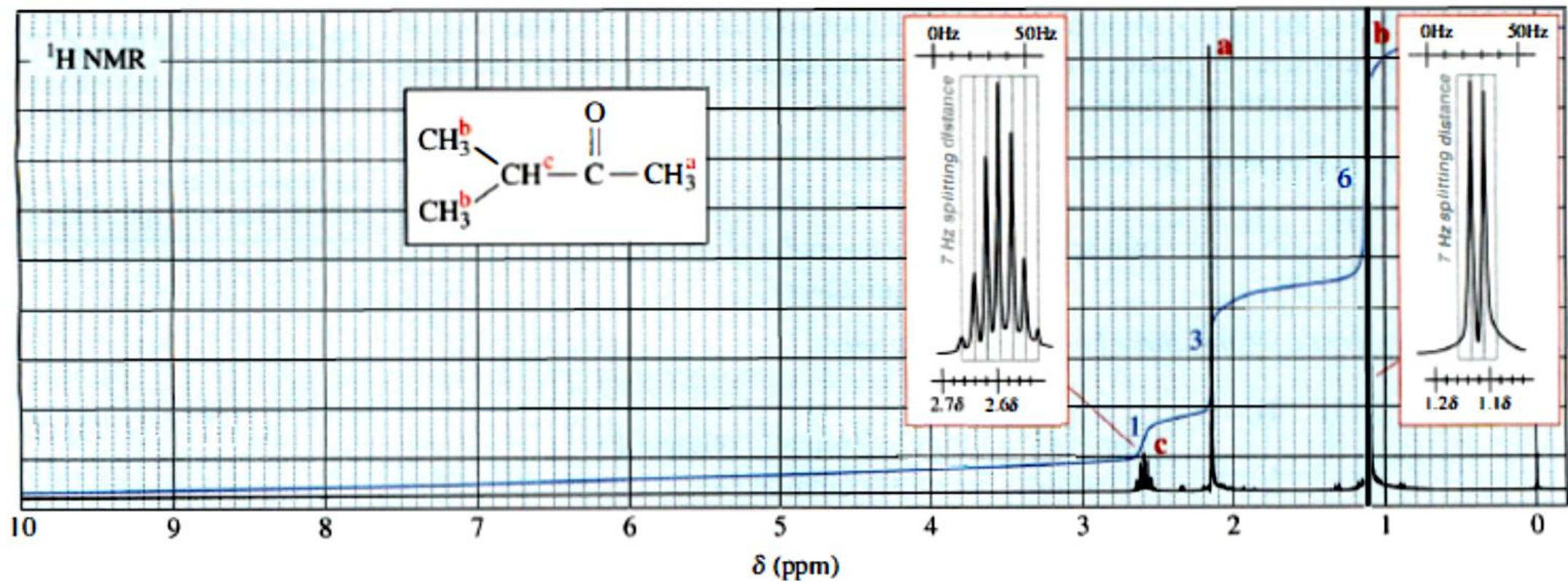


For this hydrogen, $n = 3$;
its signal is split into
 $(3 + 1) = 4$ peaks; a quartet

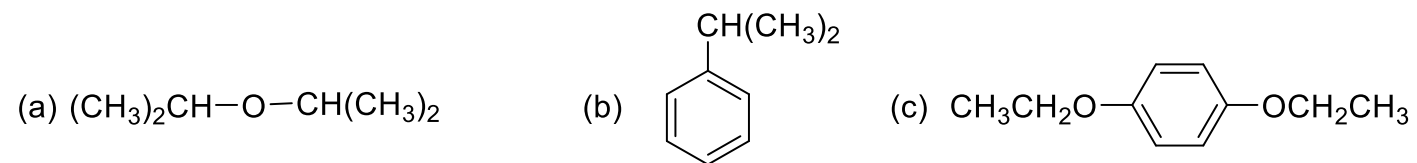
Relative Peak Intensities of Symmetric Multiplets

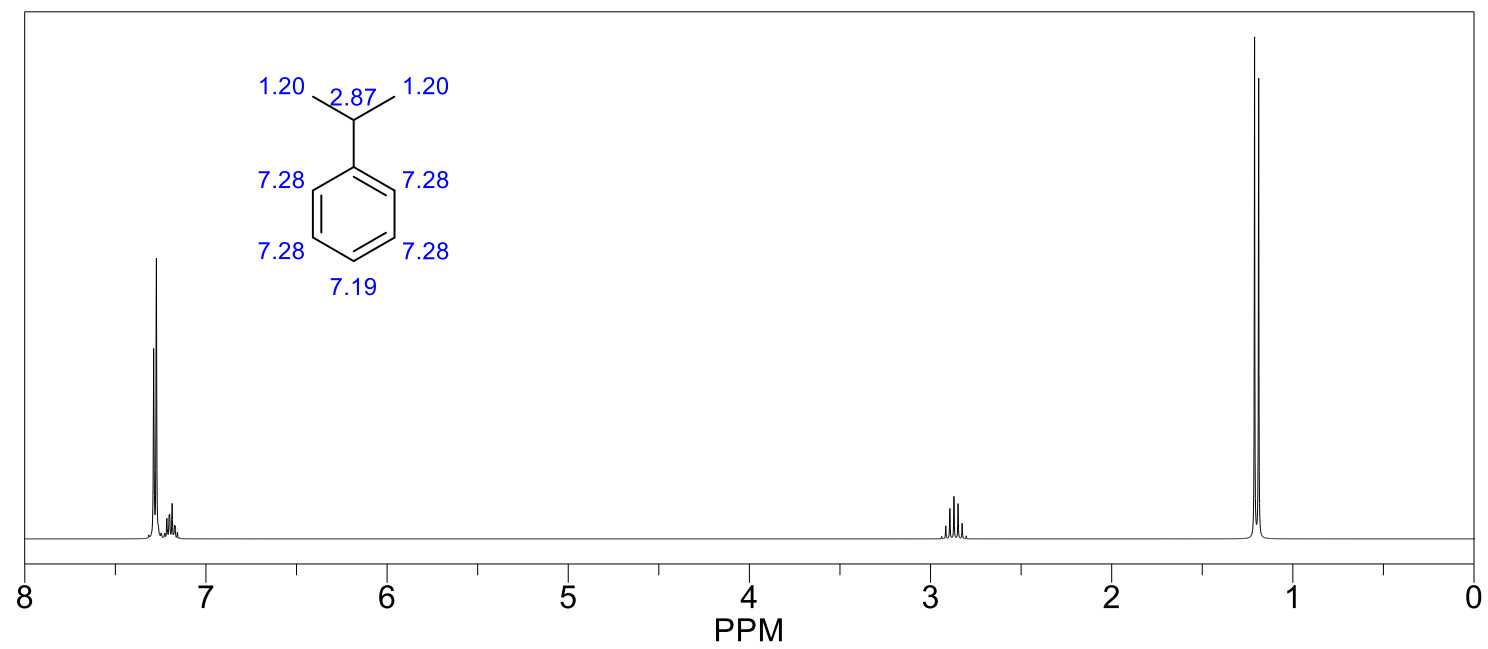
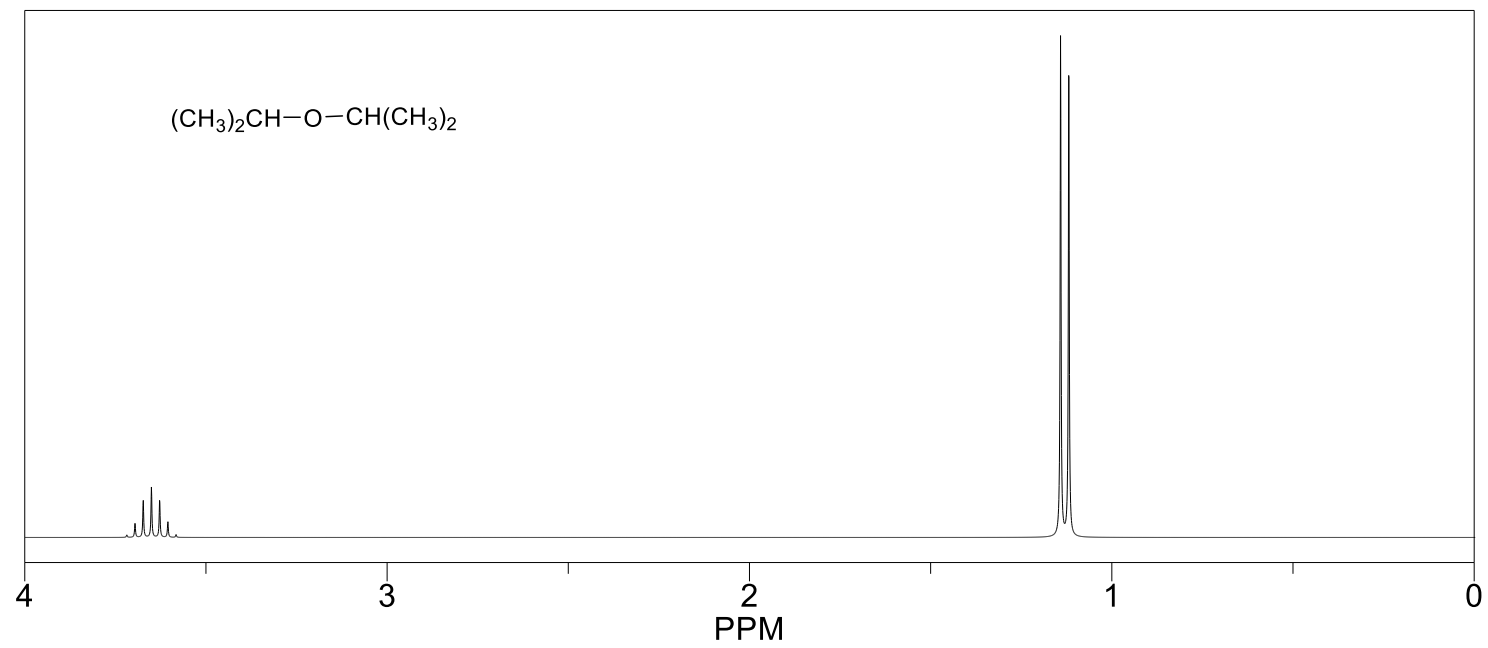
Number of Equivalent Protons Causing Splitting	Number of Peaks (multiplicity)	Area Ratios (Pascal's triangle)
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

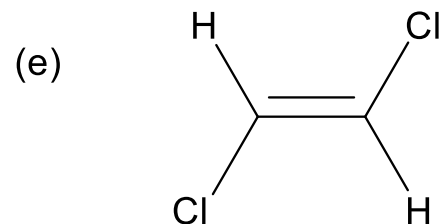
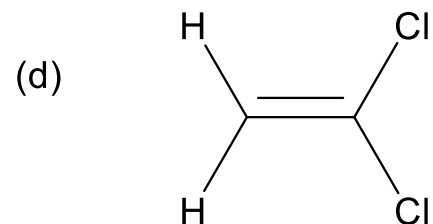
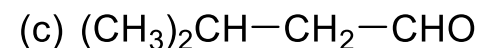
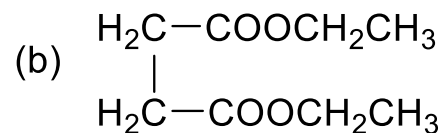
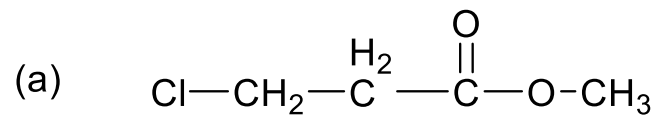
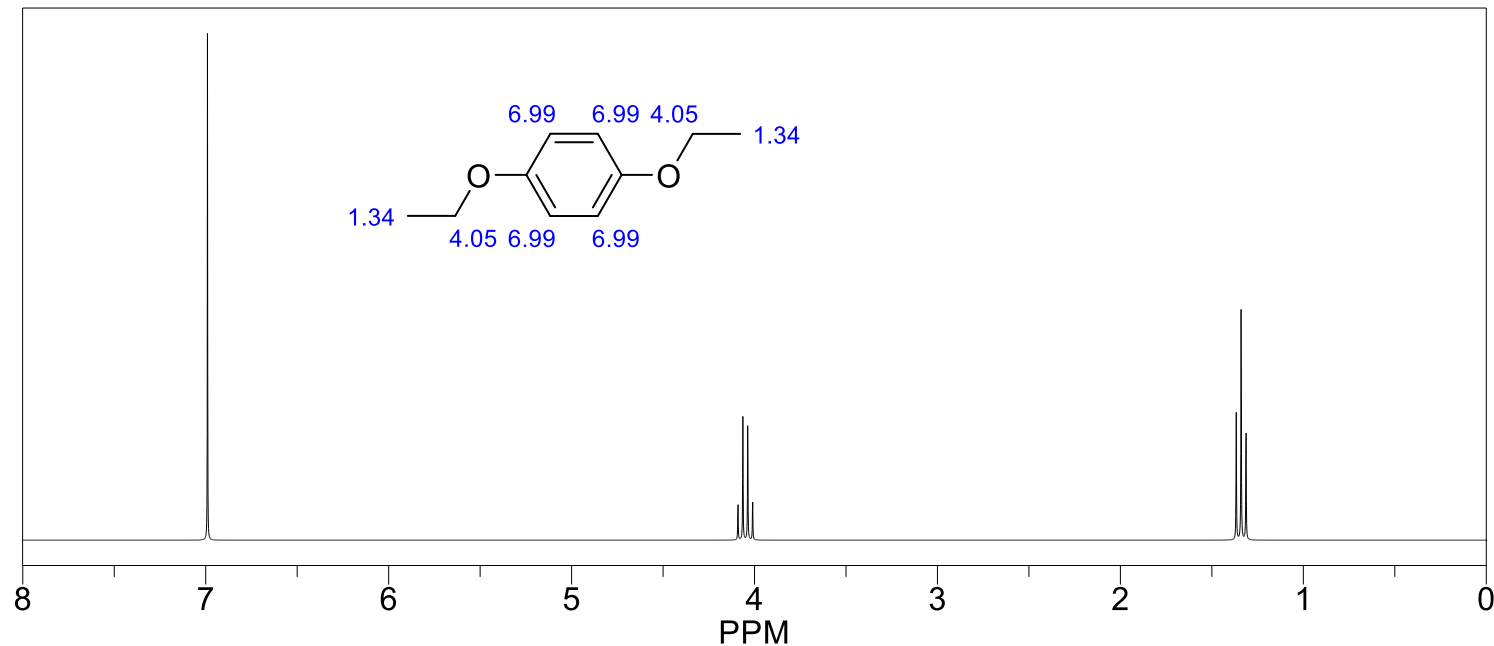




Problem 5: Draw the NMR spectra you would expect for the following compounds.





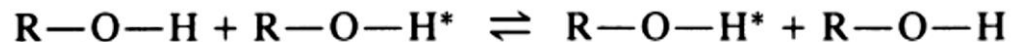


Coupling constant: The distance between the peaks of a multiplet (measured in hertz) is called the coupling constant. Coupling constants are represented by J.

PROTON-EXCHANGE REACTIONS

Why is the OH coupling not observed in the spectrum recorded on the contaminated sample of ethanol?

Exchange of the OH protons among ethanol molecules is normally so rapid that one particular proton does not reside for a sufficiently long time on a particular oxygen atom for the nuclear coupling to be observed:



Rapid proton exchange occurs in carboxylic acids, phenols, amines and thiols, etc

Hydrogen-Bonded Protons

Hydrogen bonding and the proton exchange that accompanies it may contribute to a broadening of the peak from an O-H or N-H proton. A broad peak appears because protons exchange from one molecule to another during the NMR resonance. The protons pass through a variety of environments during this exchange, absorbing over a wider range of frequencies and field strengths.

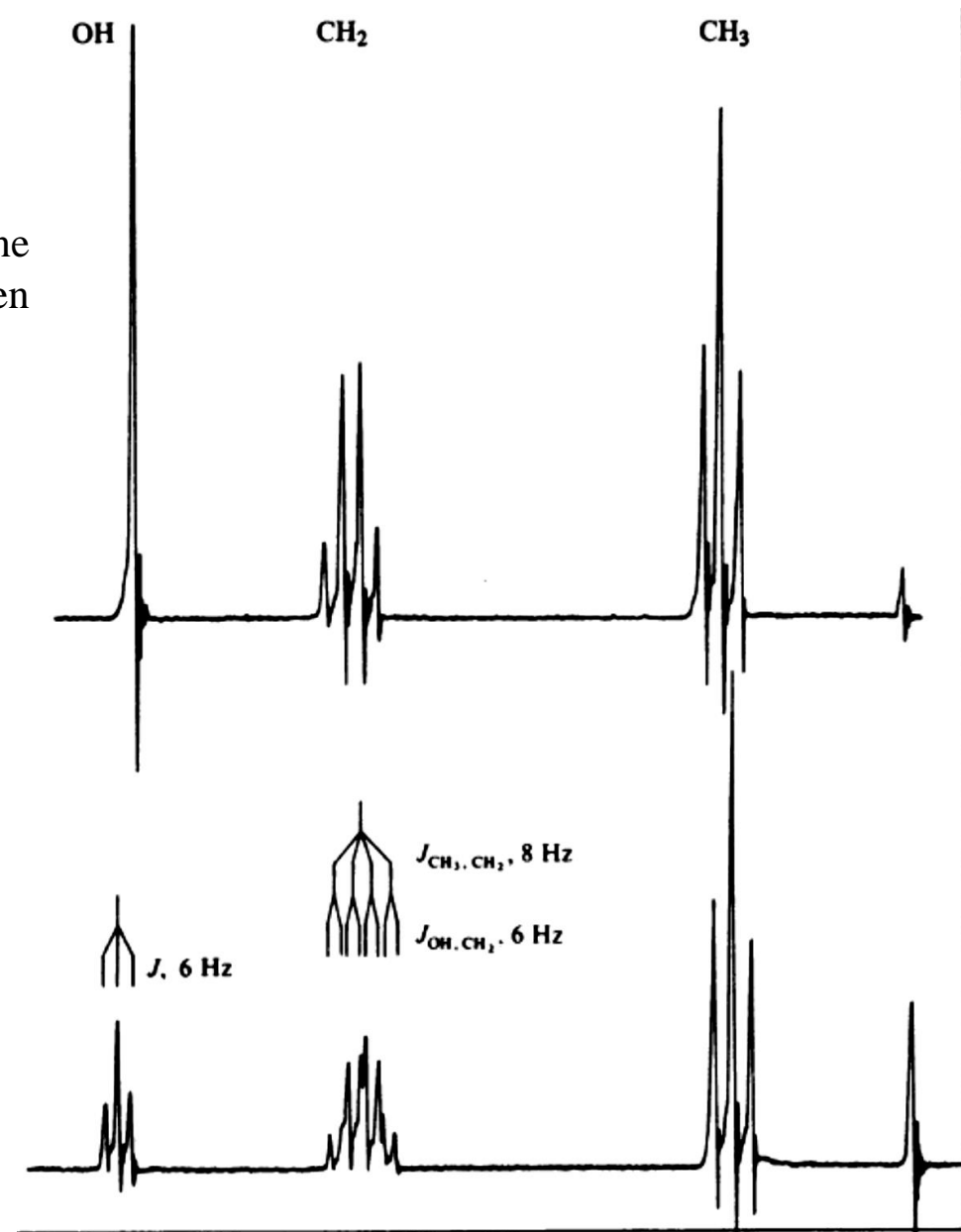


Figure 11: ^1H NMR spectrum of ethanol. Top: sample with acidic impurities. Bottom : pure sample. showing OH - CH_2 coupling

Carboxylic acids frequently exist as hydrogen-bonded dimers, with moderate rates of proton exchange that broaden the absorption of the acid proton.

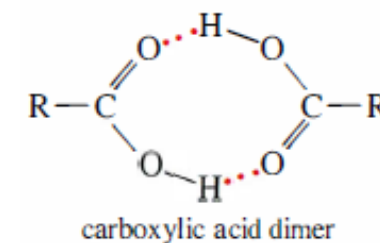
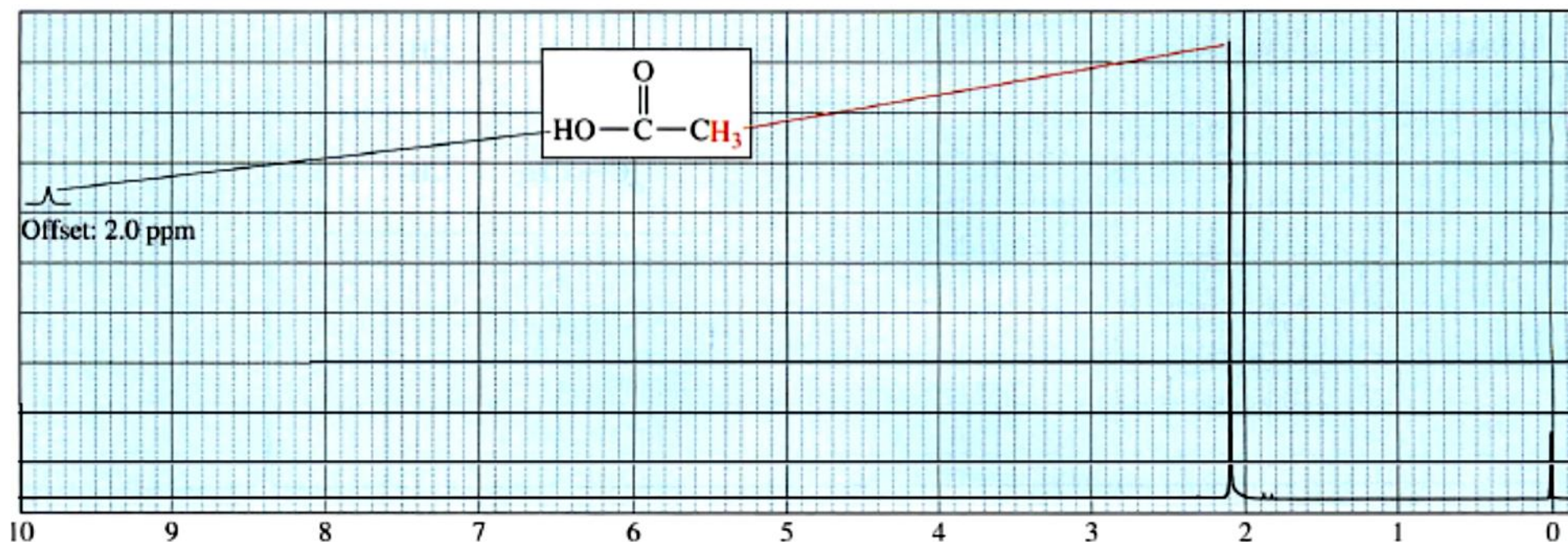


Figure 12: Proton NMR spectrum of acetic acid. The methyl protons of acetic acid are deshielded to about δ 2.1 by the adjacent carbonyl group. The acid proton appears at δ 11.8 shown on an offset trace.