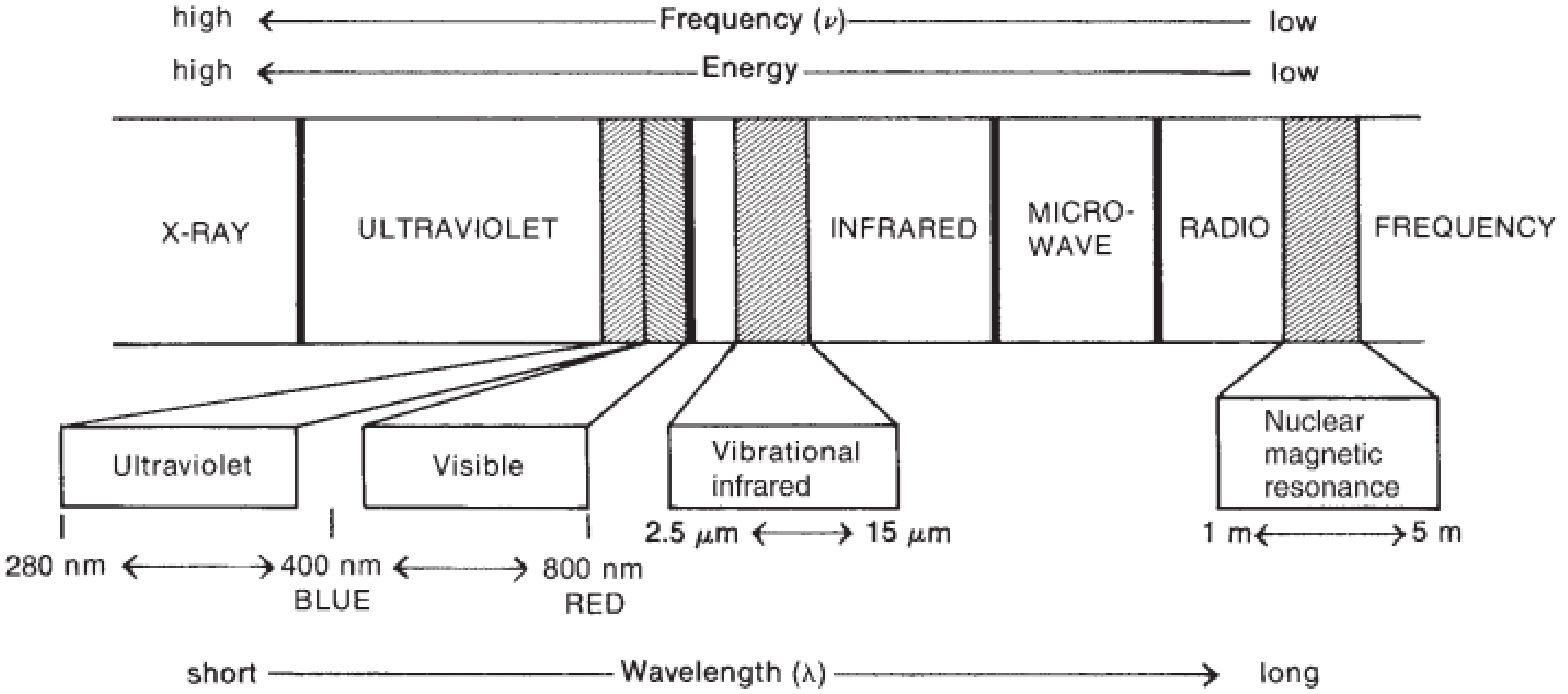
Chapter 6

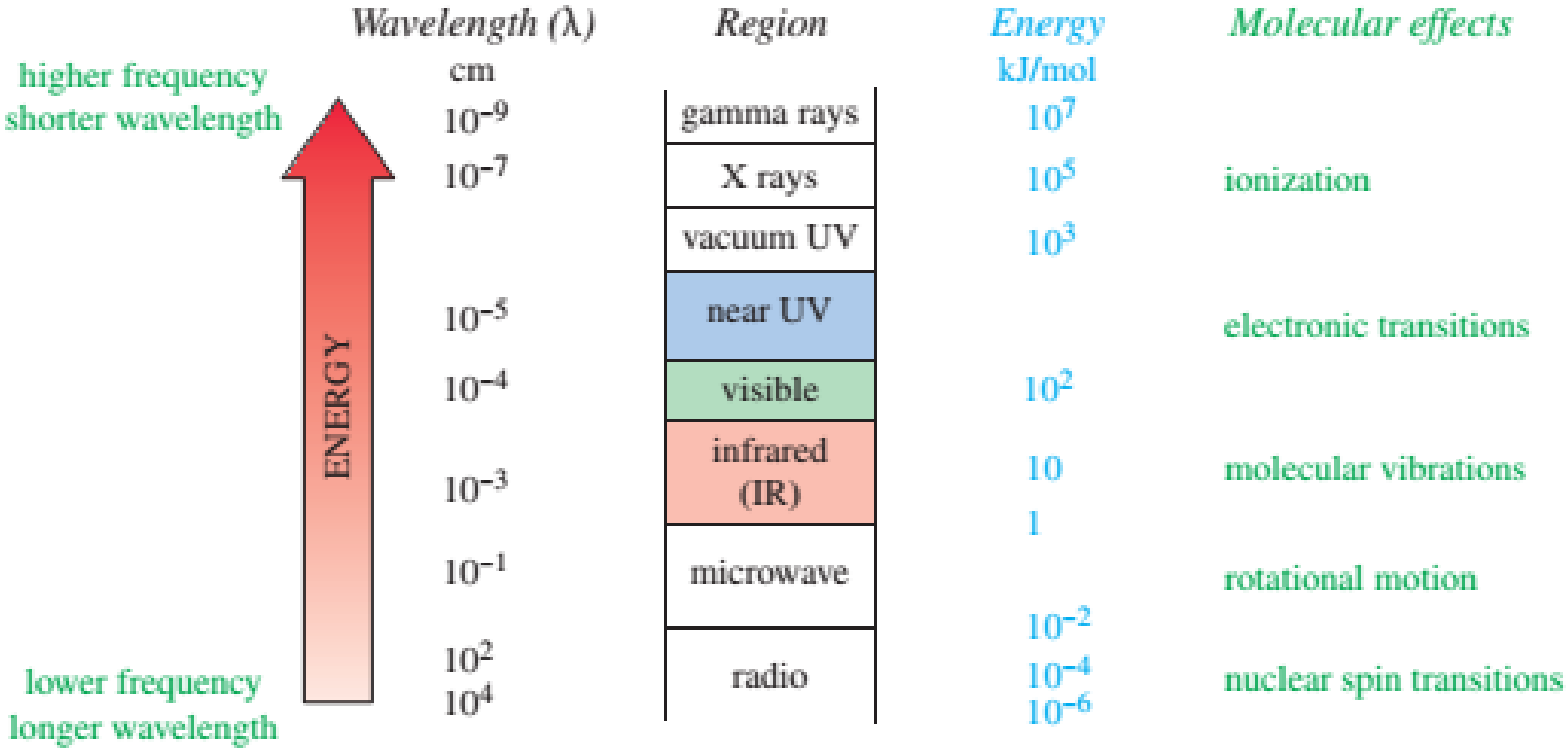
Part I

Infrared Spectroscopy

- The **electromagnetic spectrum** is the range of all possible frequencies, from zero to infinity.
- The spectrum ranges from the very low radio frequencies used to communicate with submarines to the very high frequencies of gamma rays.



The electromagnetic spectrum



The electromagnetic spectrum

- The electromagnetic spectrum is continuous, and the exact positions of the dividing lines between the different regions are somewhat arbitrary.
- Toward the top of the spectrum are the higher frequencies, shorter wavelengths, and higher energies. Toward the bottom are the lower frequencies, longer wavelengths, and lower energies.
- X rays (very high energy) are so energetic that they excite electrons past all the energy levels, causing ionization→ X-Ray diffraction spectroscopic method.
- Energies in the **ultraviolet–visible** (**UV-Vis**) range **excite electrons** to higher energy levels within molecules.
- Infrared (**IR**) energies excite **molecular vibrations**.
- Microwave energies excite rotations.
- **Radio-wave** frequencies (very low energy) excite the nuclear spin transitions observed in **NMR** spectroscopy.

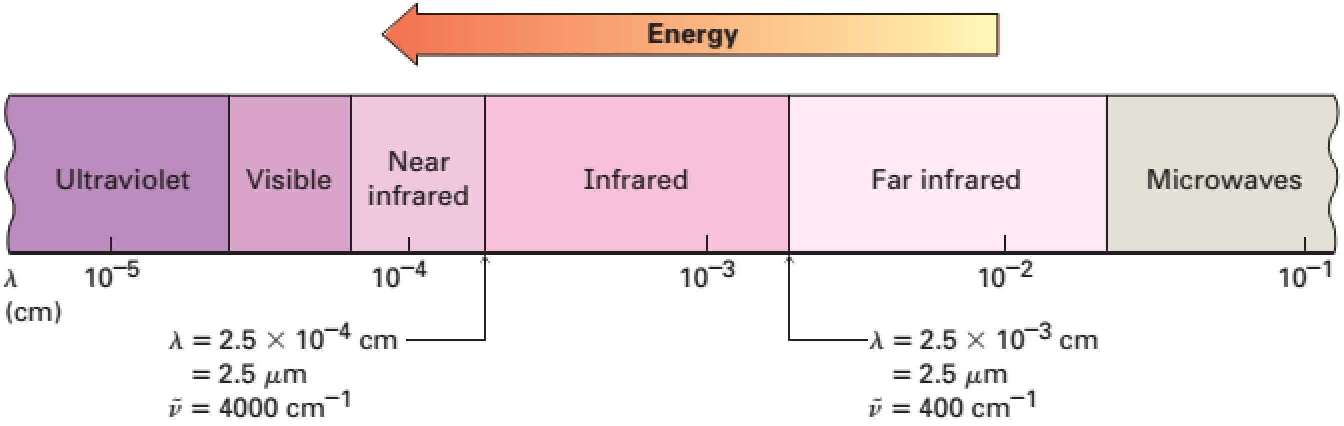
The Infrared Region

- The infrared (IR) region covers the range from just above the visible (7.8×10^{-7} m) to approximately 10^{-4} m, but only the midportion from 2.5×10^{-6} m to 2.5×10^{-5} m is used by organic chemists.

- Wavelengths within the IR region are usually given in micrometers (μm), and frequencies are given in **wavenumbers** rather than in hertz. The wavenumber ($\bar{\upsilon}$) is the reciprocal of the wavelength in centimeters:

$$\text{Wavenumber:} \quad \tilde{\nu}\,(\text{cm}^{-1}) = \frac{1}{\lambda\,(\text{cm})}$$

- Thus, the useful IR region is from 4000 to 400 cm^{-1}.



The Infrared Region

- Infrared photons do not have enough energy to cause electronic transitions, but they can **cause groups of atoms to vibrate** with respect to the bonds that connect them.
- Like electronic transitions, **these vibrational transitions correspond to distinct energies, and molecules absorb infrared radiation only at certain wavelengths and frequencies**.

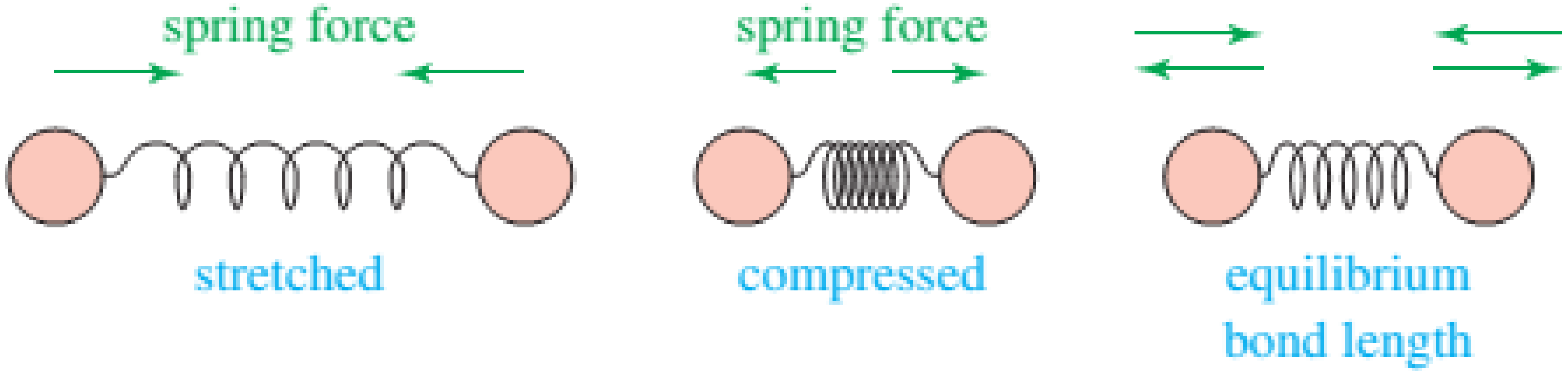
Molecular vibrations

➢ The following drawing shows how a covalent bond between two atoms acts like a spring.

+ If the bond is stretched, a restoring force pulls the two atoms together toward their equilibrium bond length.

+ If the bond is compressed, the restoring force pushes the two atoms apart.

+ If the bond is stretched or compressed and then released, the atoms vibrate.



Molecular vibrations

- The total amount of energy is proportional to the frequency of the vibration.

$$E_{\text{osc}} \propto h\nu_{\text{osc}}$$

- The frequency for a harmonic oscillator is determined by the force constant K of the spring (or its stiffness) and the masses (m_1 and m_2) of the two bonded atoms.
- The natural frequency of vibration of a bond is given by the equation:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

(**IR spectra: 4000 – 400 cm^{-1}**)

Where the **reduced mass** is:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Molecular vibrations

➢ The frequency of the stretching vibration depends on the masses of the atoms and the stiffness of the bond.

+ Heavier atoms vibrate more slowly than lighter ones.

+ Stronger bonds are generally stiffer, requiring more force to stretch or compress them. Thus, stronger bonds usually vibrate faster than weaker bonds.

➢ For example:

+ O-H bonds are stronger than C-H bonds, so O-H bonds vibrate at higher frequencies.

C–H	C–C	C–O	C–Cl	C–Br	C–I
3000 cm^{-1}	1200 cm^{-1}	1100 cm^{-1}	750 cm^{-1}	600 cm^{-1}	500 cm^{-1}

+Triple bonds are stronger than double bonds, so triple bonds vibrate at higher frequencies than double bonds. Similarly, double bonds vibrate at higher frequencies than single bonds.

C≡C	C=C	C–C
2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

← Increasing K

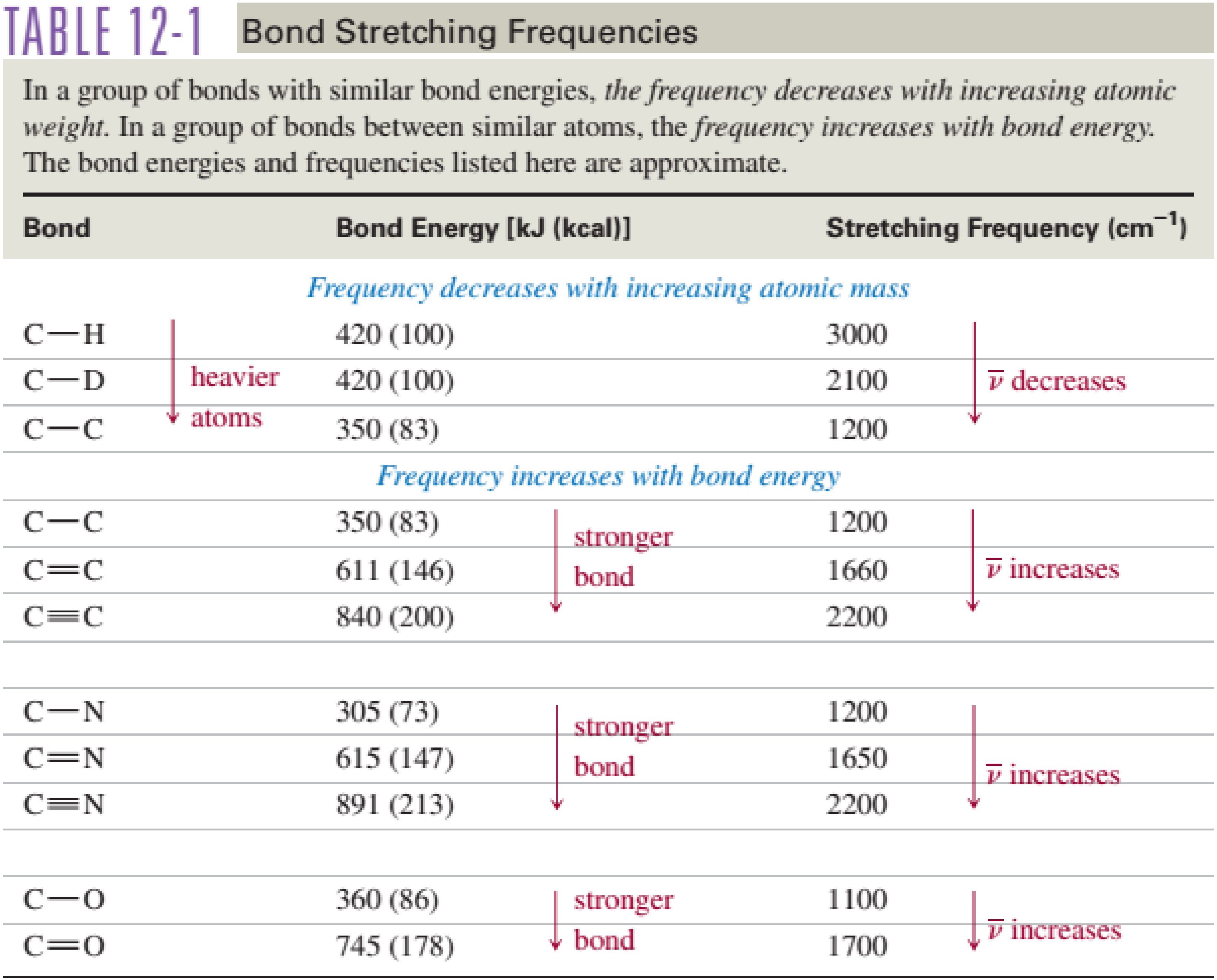


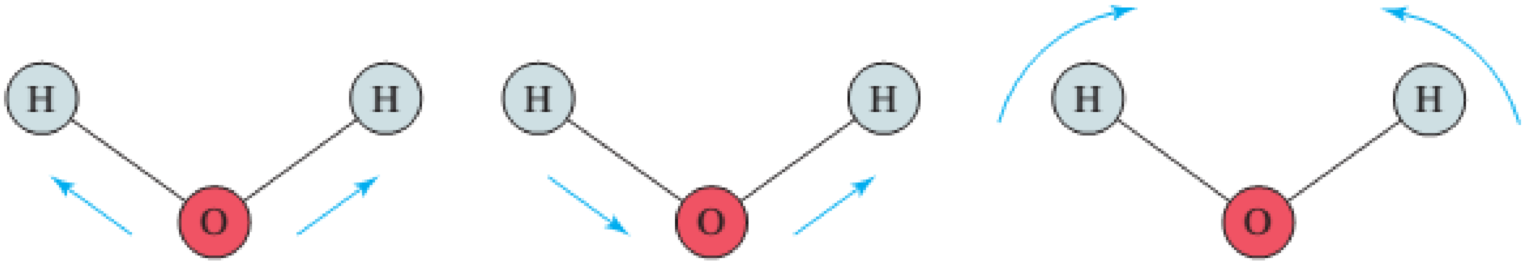
TABLE 12-1 Bond Stretching Frequencies

In a group of bonds with similar bond energies, *the frequency decreases with increasing atomic weight*. In a group of bonds between similar atoms, the *frequency increases with bond energy*. The bond energies and frequencies listed here are approximate.

Bond		Bond Energy [kJ (kcal)]		Stretching Frequency (cm^{-1})	
Frequency decreases with increasing atomic mass					
C—H	heavier atoms ↓	420 (100)		3000	$\bar{\nu}$ decreases ↓
C—D		420 (100)		2100	
C—C		350 (83)		1200	
Frequency increases with bond energy					
C—C		350 (83)	stronger bond ↓	1200	$\bar{\nu}$ increases ↓
C═C		611 (146)		1660	
C≡C		840 (200)		2200	
C—N		305 (73)	stronger bond ↓	1200	$\bar{\nu}$ increases ↓
C═N		615 (147)		1650	
C≡N		891 (213)		2200	
C—O		360 (86)	stronger bond ↓	1100	$\bar{\nu}$ increases ↓
C═O		745 (178)		1700	

Infrared Spectrum

- Consider the fundamental vibrational modes of a water molecule in the following diagram. The two O-H bonds can stretch in phase with each other (*symmetric stretching*), or they can stretch out of phase (*antisymmetric stretching*). The H-O-H bond angle can also change in a bending vibration, making a *scissoring* motion.

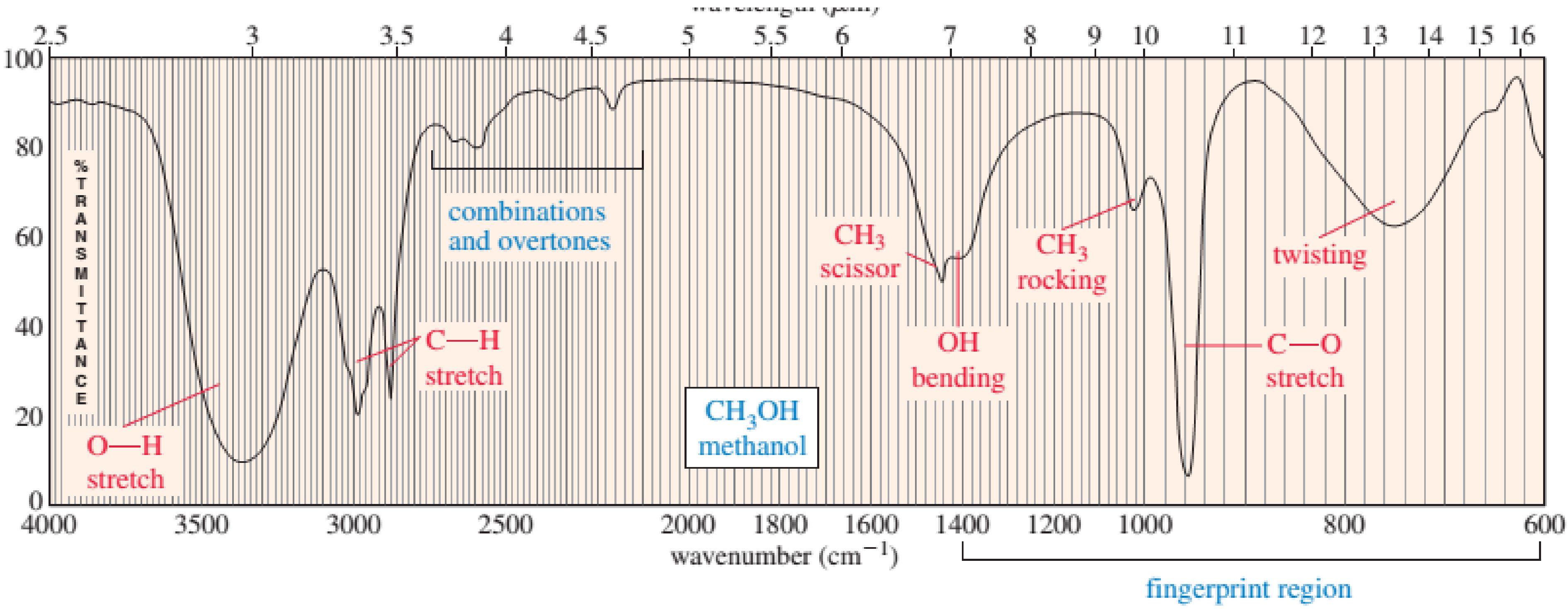


symmetric stretching antisymmetric stretching bending (scissoring)

Infrared Spectrum

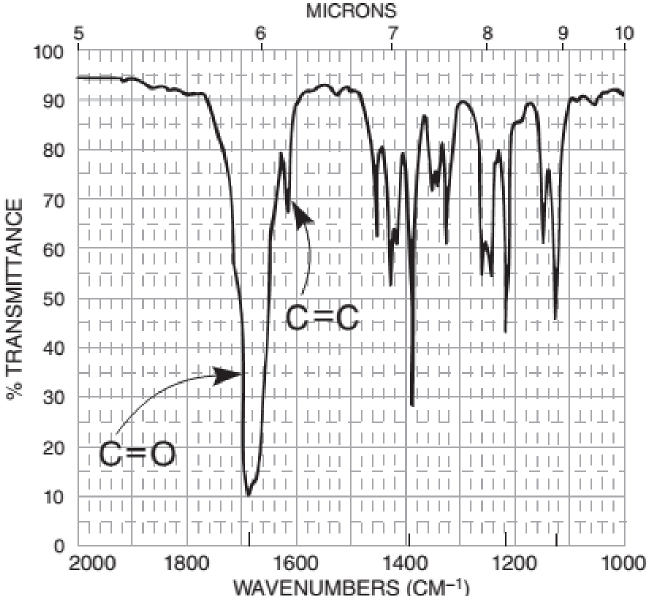
- An **infrared spectrum** is a graph of the energy absorbed by a molecule as a function of the frequency or wavelength of light.

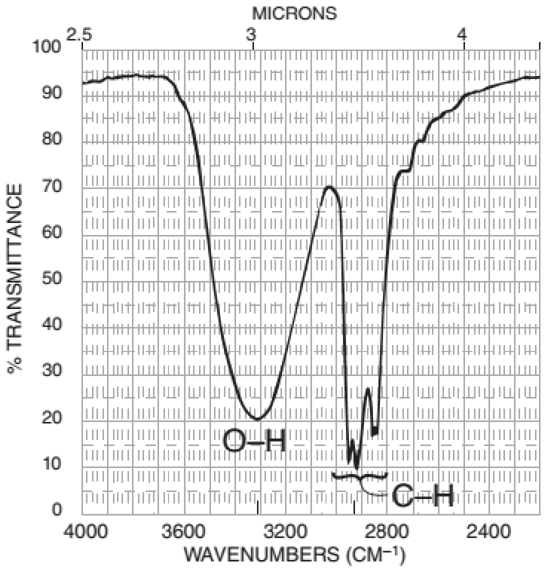
- The IR spectrum of methanol is shown in the figure below. We can see the broad O-H stretch around 3000 cm^{-1}, and the C-H stretch just below 3000 cm^{-1} and the C-O stretch just above 1000 cm^{-1}.

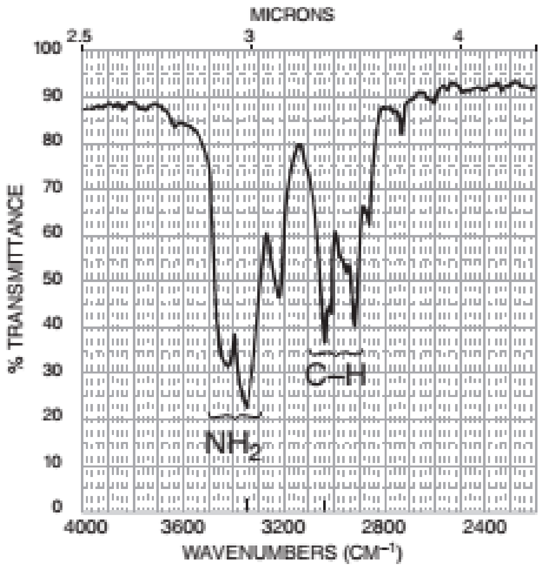


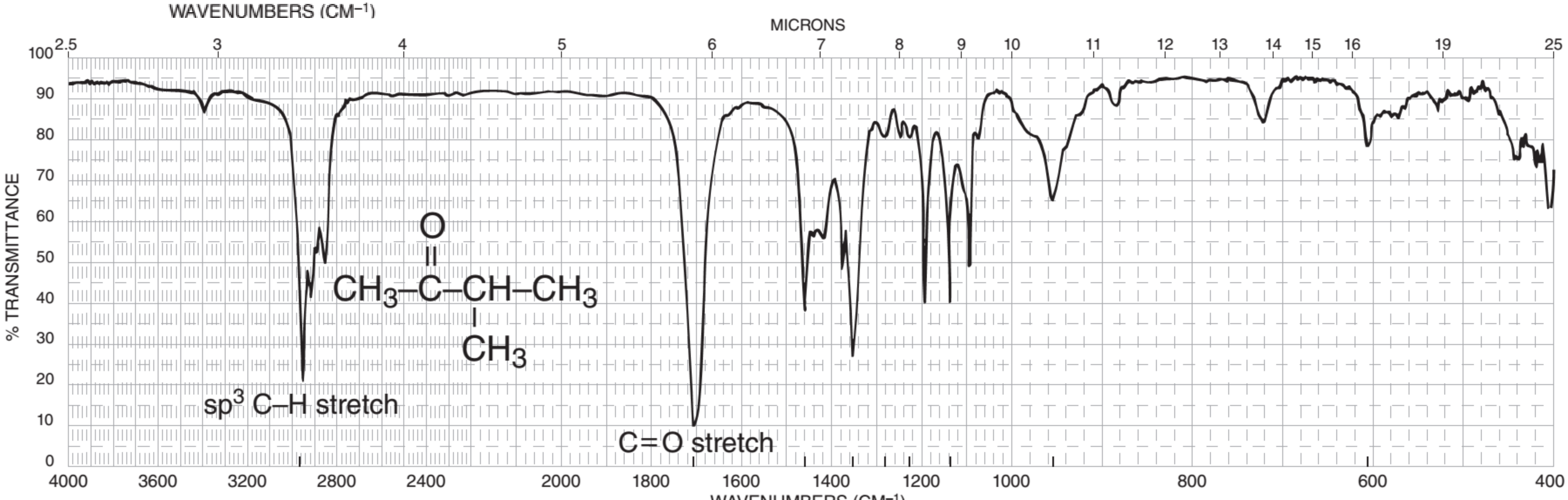
Position – Shape - Intensity

C=O	1850–1630 cm^{-1}
C=C	1680–1620 cm^{-1}
O–H	3650–3200 cm^{-1}
N–H	3500–3300 cm^{-1}









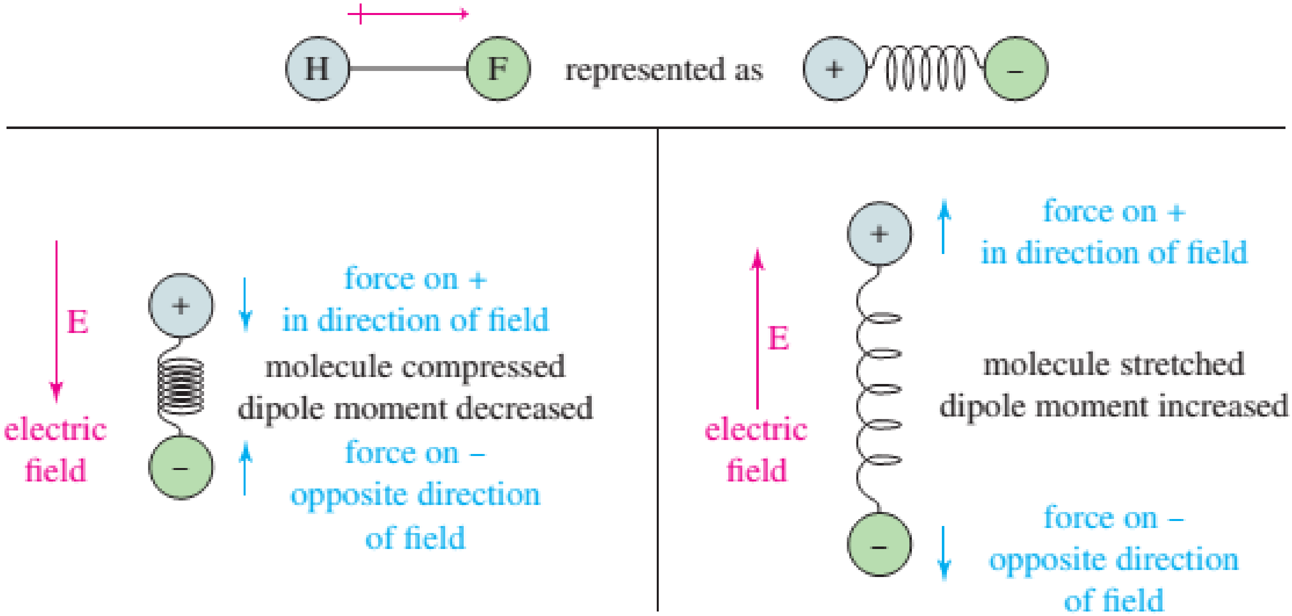
IR-active and IR-inactive vibrations

➢ Not all molecular vibrations absorb infrared radiation:

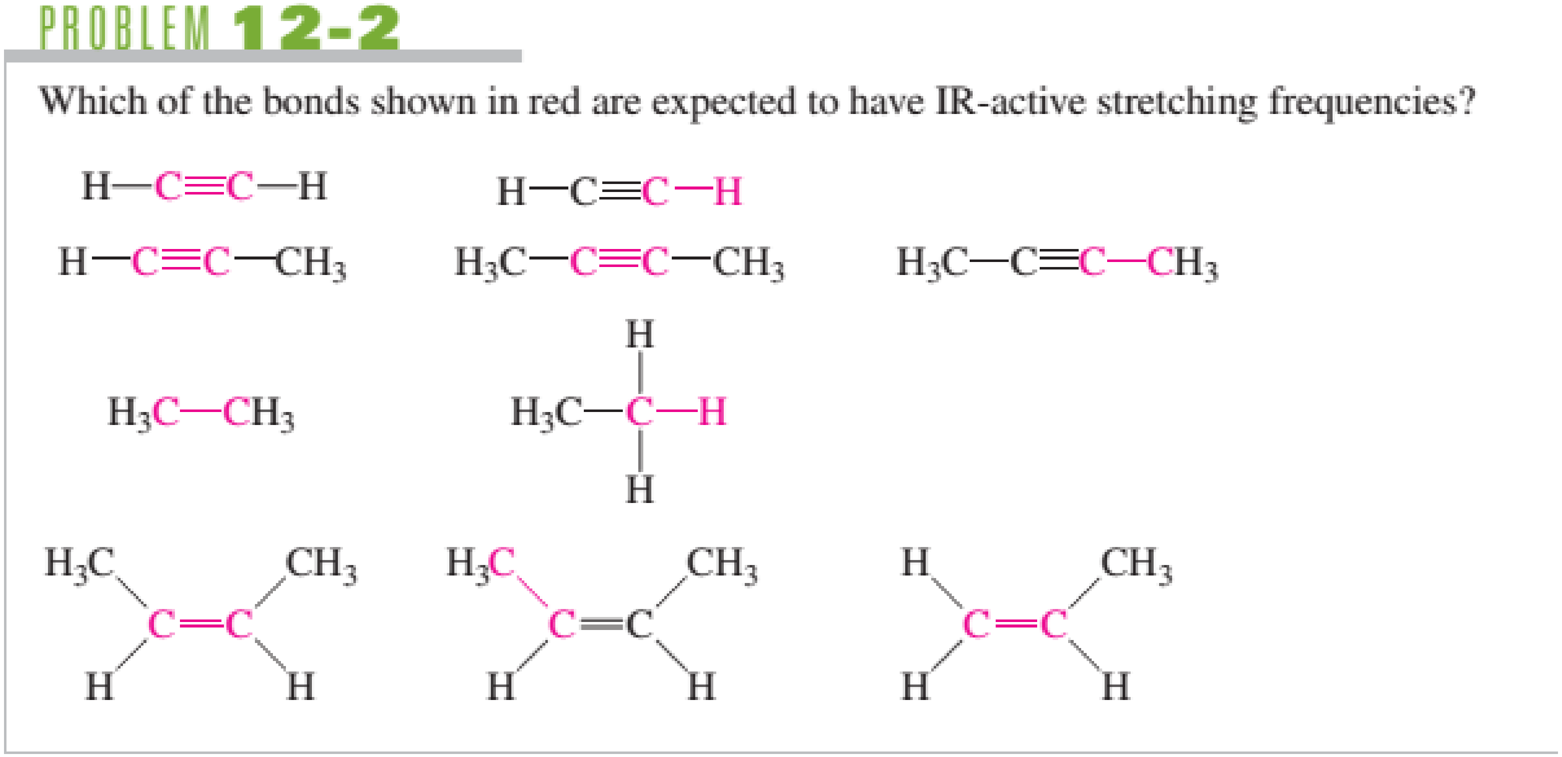
+ In general, if a bond has a dipole moment, its stretching frequency causes an absorption in the IR spectrum.

+ If a bond is symmetrically substituted and has zero dipole moment, its stretching vibration is weak or absent in the spectrum.

➢ For example, the triple bond of acetylene (H-C≡C-H) has zero dipole moment, and the dipole moment remains zero if the bond is stretched or compressed. Because the vibration produces no change in the dipole moment, there is no absorption of energy. This vibration is said to be **IR-inactive,** and it produces no absorption in the IR spectrum.



IR-active and IR-inactive vibrations



PROBLEM 12-2

Which of the bonds shown in red are expected to have IR-active stretching frequencies?

Measurements of IR spectrum

➢ Infrared spectra can be measured using liquid, solid, or gaseous samples that are placed in the beam of infrared light.

\+ A drop of a liquid can be placed as a thin film between two salt plates made of NaCl or KBr, which are transparent to infrared light at most important frequencies.

\+ A solid can be ground with KBr and pressed into a disk that is placed in the light beam. Alternatively, a solid sample can be ground into a pasty *mull* with paraffin oil. As with a liquid, the mull is placed between two salt plates.

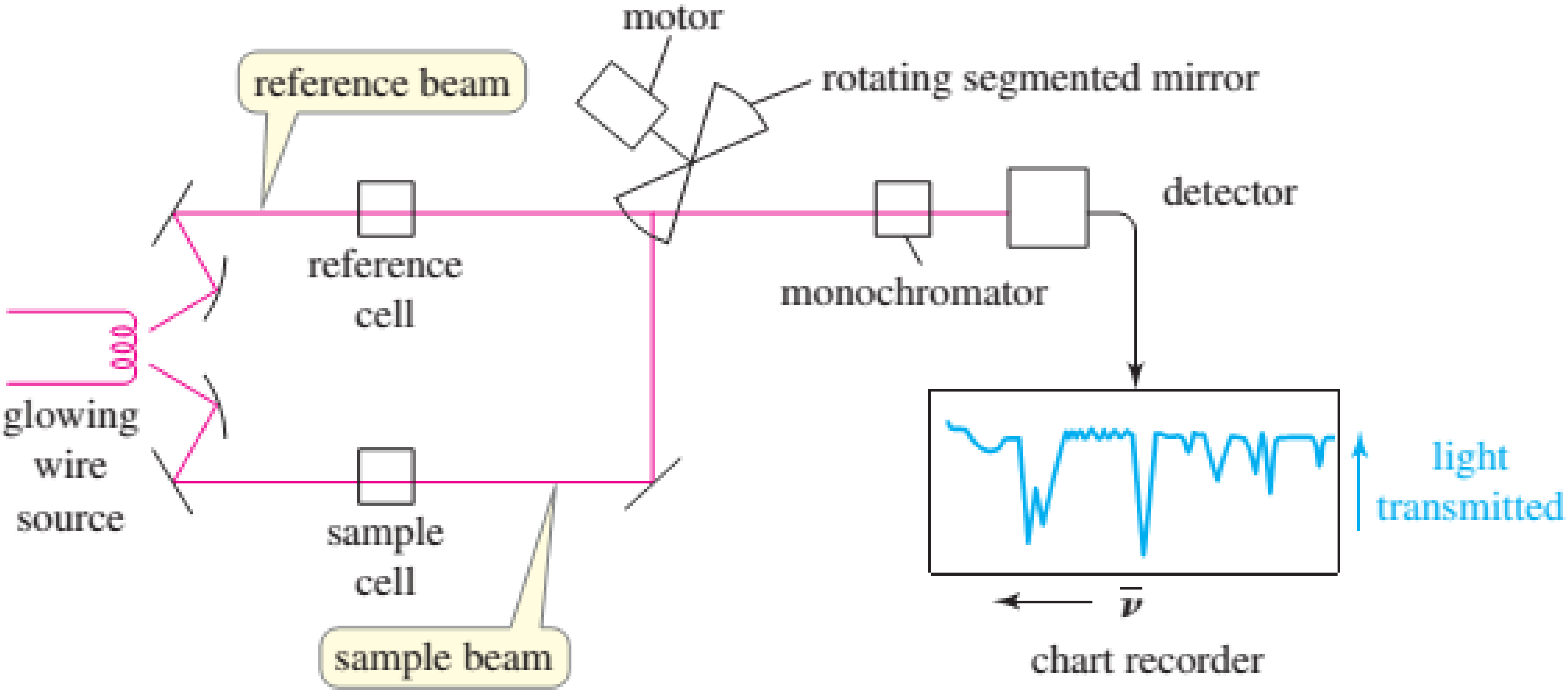
\+ Gases are placed in a longer cell with polished salt windows. These *gas cells* often contain mirrors that reflect the beam through the cell several times for stronger absorption.

Measurements of IR spectrum

- An **infrared spectrometer** measures the frequencies of infrared light absorbed by a compound.
- In a simple infrared spectrometer, two beams of light are used.

+ The *sample beam* passes through the sample cell, while the *reference beam* passes through a reference cell that contains only the solvent.

+ A rotating mirror alternately allows light from each of the two beams to enter the monochromator.



Measurements of IR spectrum

➢ The monochromator uses prisms or diffraction gratings to allow only one frequency of light to enter the detector at a time.

➢ It scans the range of infrared frequencies as a pen moves along the corresponding frequencies on the *x* axis of the chart paper.

\+ Higher frequencies (shorter wavelengths) appear toward the left of the chart paper.

\+ The detector signal is proportional to the *difference* in the intensity of light in the sample and reference beams, with the reference beam compensating for any absorption by air or by the solvent.

\+ The detector signal controls movement of the pen along the *y* axis, with 100% transmittance (no absorption) at the top of the paper, and 0% transmittance (absorption of all the light) at the bottom.

Infrared spectroscopy of hydrocarbons: Carbon-carbon bond stretching

- An infrared spectrum does not provide enough information to identify a structure conclusively but the absorptions of the carbon–carbon and carbon–hydrogen bonds can indicate the presence of double and triple bonds.

- Stronger bonds generally absorb at higher frequencies because of their greater stiffness. Carbon–carbon single bonds absorb around 1200 cm^{-1}, C=C double bonds absorb around 1600 cm^{-1}, and C≡C triple bonds absorb around 2200 cm^{-1}.

Carbon–carbon bond stretching frequencies

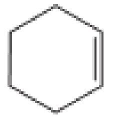
C—C	1200 cm^{-1}
C═C	1660 cm^{-1}
C≡C	<2200 cm^{-1}

- C-C single bond absorptions and most other absorptions in the fingerprint region (below 1500 cm^{-1}) are not very reliable.

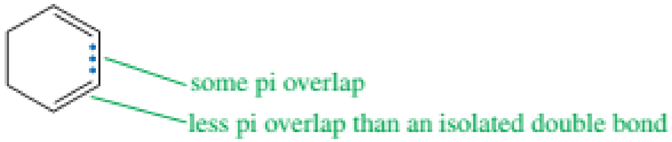
Infrared spectroscopy of hydrocarbons: **Carbon-carbon bond stretching**

- Conjugated double bonds are slightly more stable than isolated double bonds because there is a small amount of pi bonding between them. This overlap between the pi bonds leaves a little less electron density in the double bonds themselves. As a result, they are a little less stiff and vibrate a little more slowly than an isolated double bond.

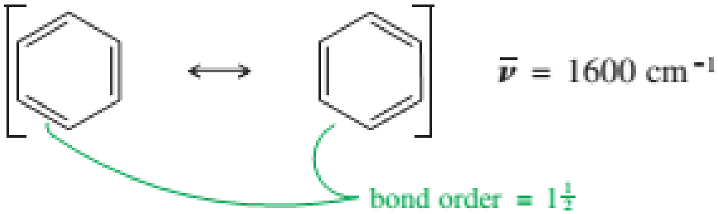
- Isolated double bonds absorb around 1640 to 1680 cm^{-1}, while conjugated double bonds absorb around 1620 to 1640 cm^{-1}.



1645 cm^{-1}
cyclohexene (isolated)



1620 cm^{-1}
cyclohexa-1,3-diene (conjugated)



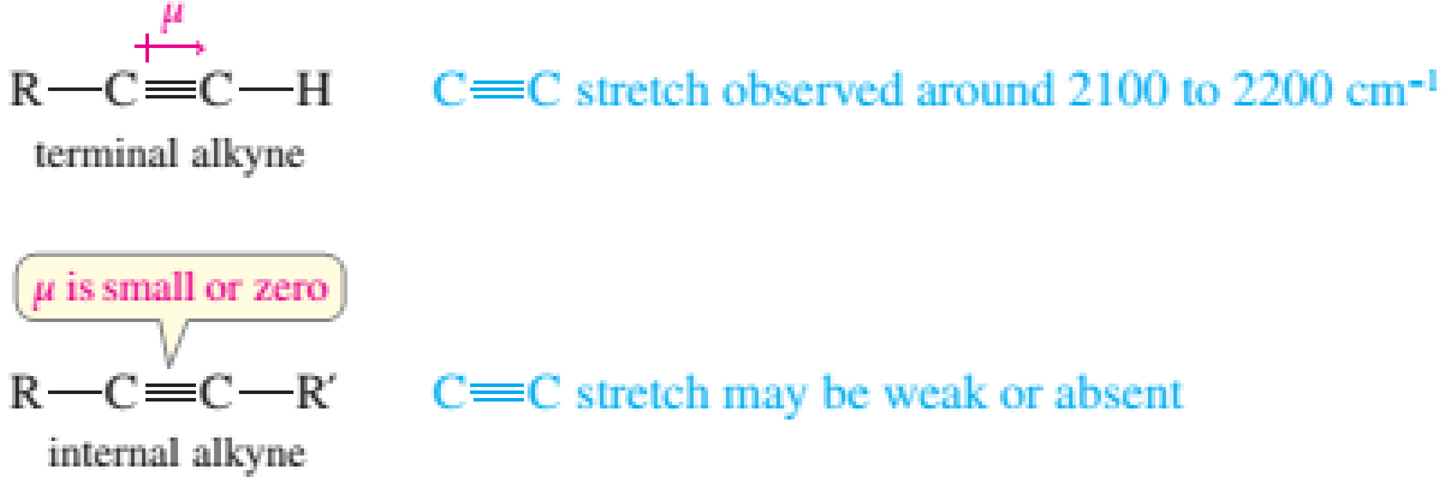
- Aromatic bonds are more like than true double bonds, and their reduced pi bonding results in less stiff bonds with lower stretching frequencies, around 1600 cm^{-1}.

Characteristic C═C stretching frequencies

isolated C═C	1640–1680 cm^{-1}
conjugated C═C	1620–1640 cm^{-1}
aromatic C═C	approx. 1600 cm^{-1}

Infrared spectroscopy of hydrocarbons: Carbon-carbon bond stretching

- Carbon–carbon triple bonds are stronger and stiffer than carbon-carbon single or double bonds, and they absorb infrared light at higher frequencies.
- Most alkyne C≡C triple bonds have stretching frequencies between 2100 and 2200 cm^{-1}.
- Terminal alkynes usually give sharp C≡C stretching signals of moderate intensity.
- The C≡C stretching absorption of an internal alkyne may be weak or absent due to the symmetry of the disubstituted triple bond with a very small or zero dipole moment.



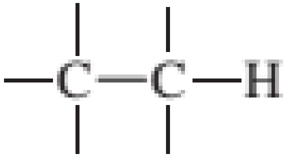
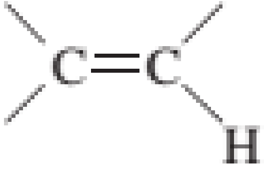
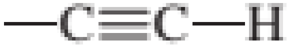
C≡C stretch observed around 2100 to 2200 cm^{-1}

C≡C stretch may be weak or absent

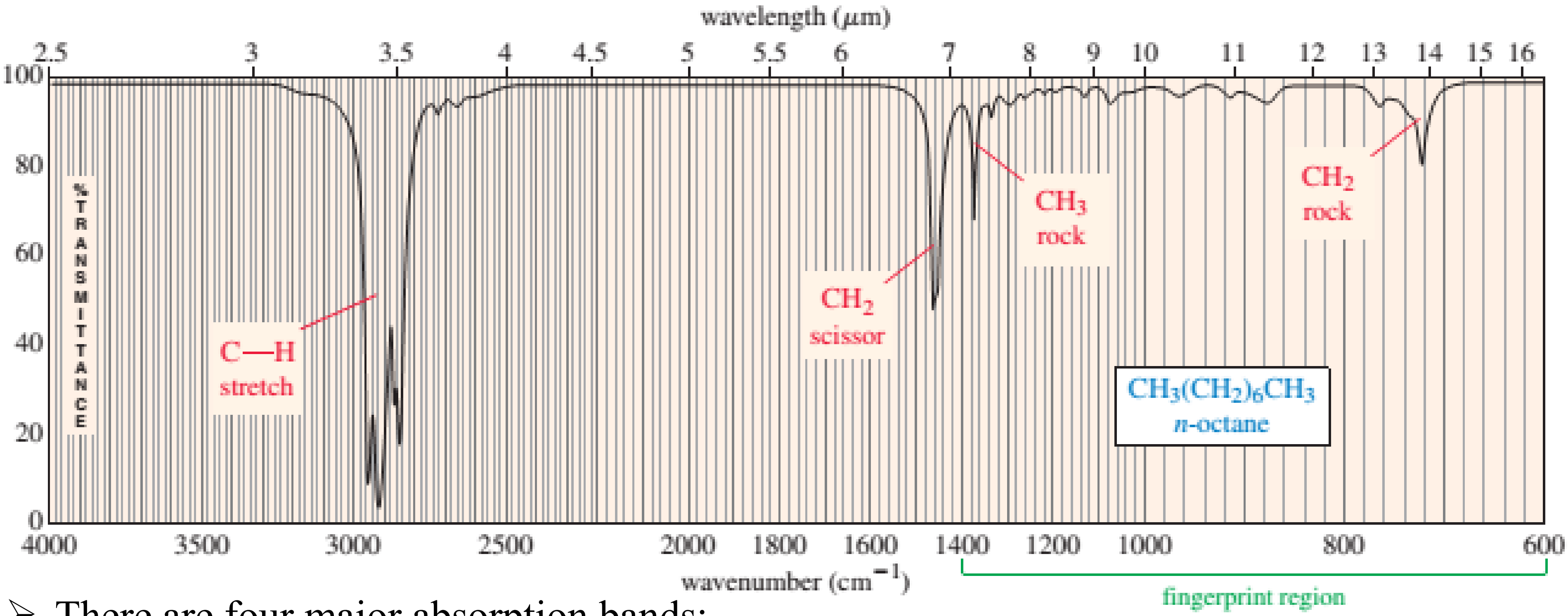
Infrared spectroscopy of hydrocarbons: Carbon-hydrogen bond stretching

- ➢ Carbon–hydrogen bonds involving sp^3 hybrid carbon atoms generally absorb at frequencies just *below* (to the right of) 3000 cm^{-1}.
- ➢ Those involving sp^2 hybrid carbons absorb just *above* (to the left of) 3000 cm^{-1}. We explain this difference by the amount of *s* character in the carbon orbital used to form the bond.
- ➢ The C-H bond of a terminal alkyne is formed using an *sp* hybrid orbital. This bond is stiffer than a C-H bond using an sp^3 or an sp^2 hybrid carbon, and it absorbs at a higher frequency: about 3300 cm^{-1}.

C—H bond stretching frequencies: sp > sp^2 > sp^3

	*sp^3* hybridized, one-fourth *s* character	2800–3000 cm^{-1}
	*sp^2* hybridized, one-third *s* character	3000–3100 cm^{-1}
	*sp* hybridized, one-half *s* character	3300 cm^{-1} (sharp)

Interpreting the IR spectra of hydrocarbons



- There are four major absorption bands:

+ The broad band between 2800 and 3000 cm-1 results from C-H stretching vibrations.

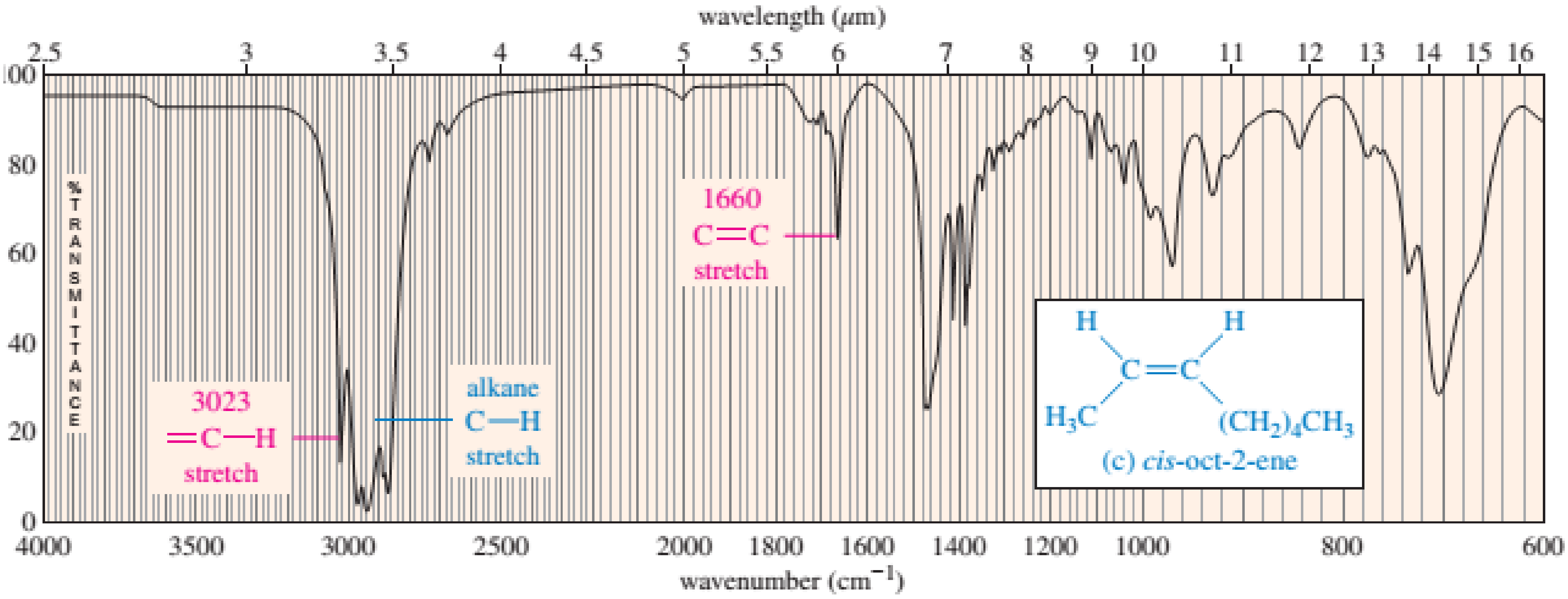
+ The band at 1476 cm^{-1} results from a scissoring vibration of the CH_2 groups.

+ The absorptions at 1378 and 722 cm^{-1} result from the bending vibrations (rocking) of CH_3 and CH_2 groups, respectively.

- In fact, without an authentic spectrum for comparison, *we could not look at this spectrum and conclude that the compound is octane*. However, we could be fairly certain that it is an alkane.

- Although there are seven C-C bonds in octane, their dipole moments are small, and their absorptions are weak and indistinguishable.

Interpreting the IR spectra of hydrocarbons

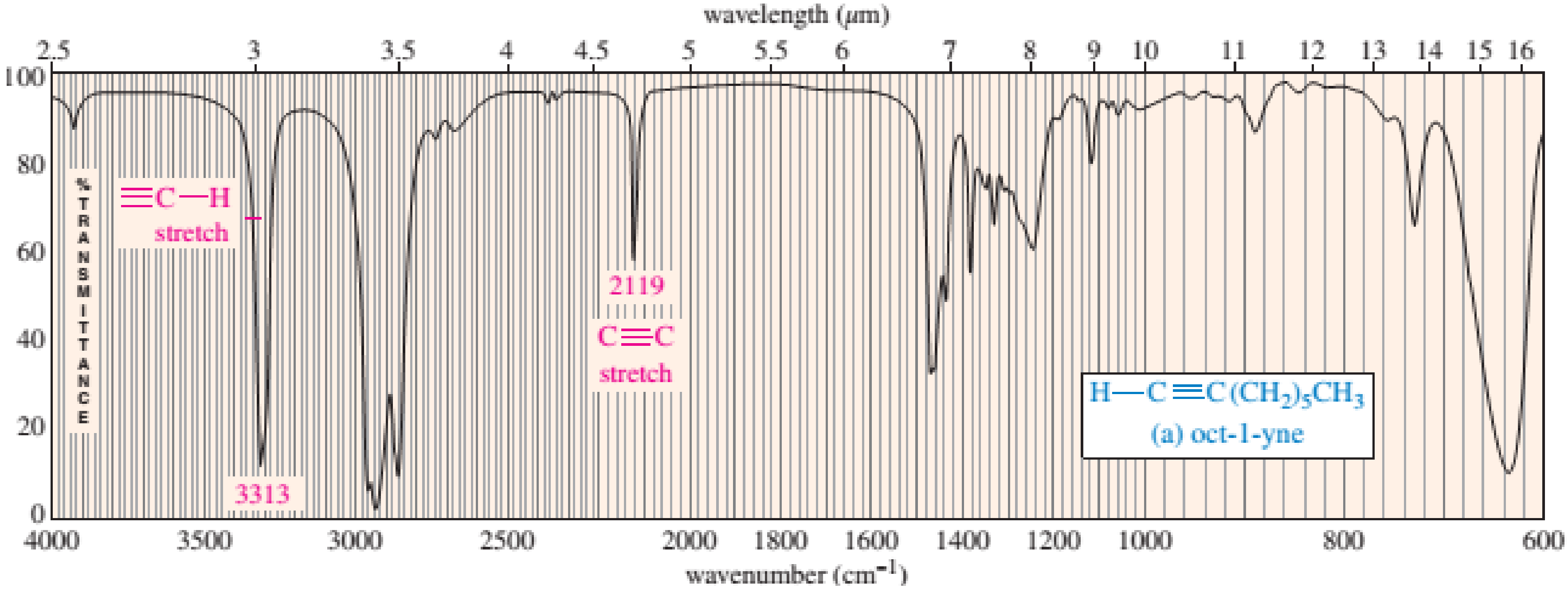


- ➢ The most characteristic absorptions in the hex-1-ene spectrum are:

+ The unsaturated =C-H stretch at 3080 cm^{-1}.

+ The nearly symmetrically substituted double bond in *cis*-oct-2-ene gives a weak C=C absorption at 1660 cm^{-1}.

Interpreting the IR spectra of hydrocarbons

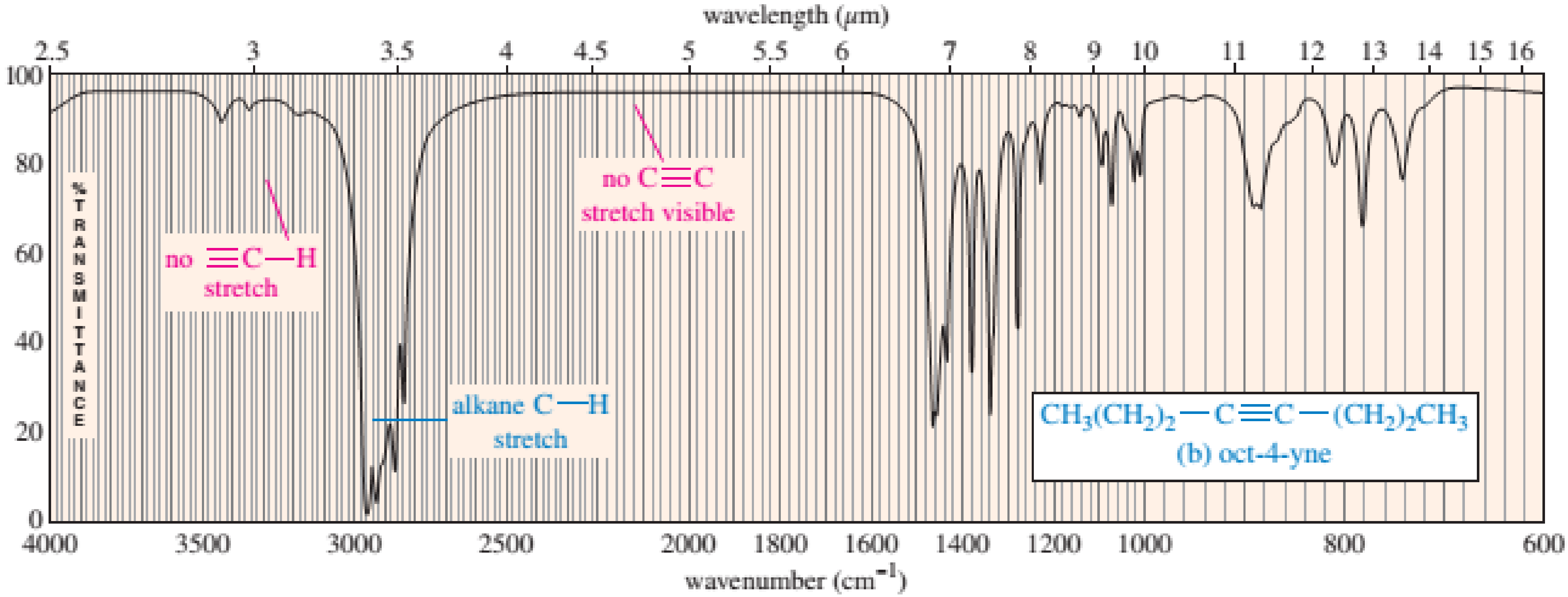


➢ The most characteristic absorptions in the oct-1-yne spectrum are:

+ The absorption at 3313 cm^{-1} results from stretching of the stiff ≡C-H bond formed by the *sp* hybrid alkyne carbon.

+ The 2119 cm^{-1} absorption results from stretching of the C≡C triple bond.

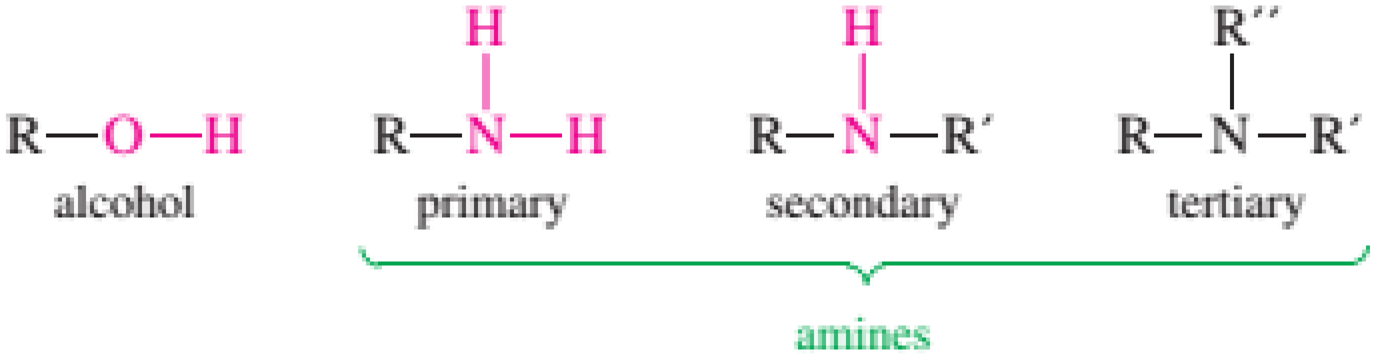
Interpreting the IR spectra of hydrocarbons



- ➢ The spectrum of oct-4-yne is not very helpful.
- ➢ Since there is no acetylenic hydrogen, there is no ≡C-H visible stretching absorption around 3300 cm^{-1}.
- ➢ There is no visible C≡C stretching absorption around 2100 to 2200 cm^{-1} either, because the disubstituted triple bond has a very small dipole moment.
- ➢ This spectrum fails to alert us to the presence of a triple bond.

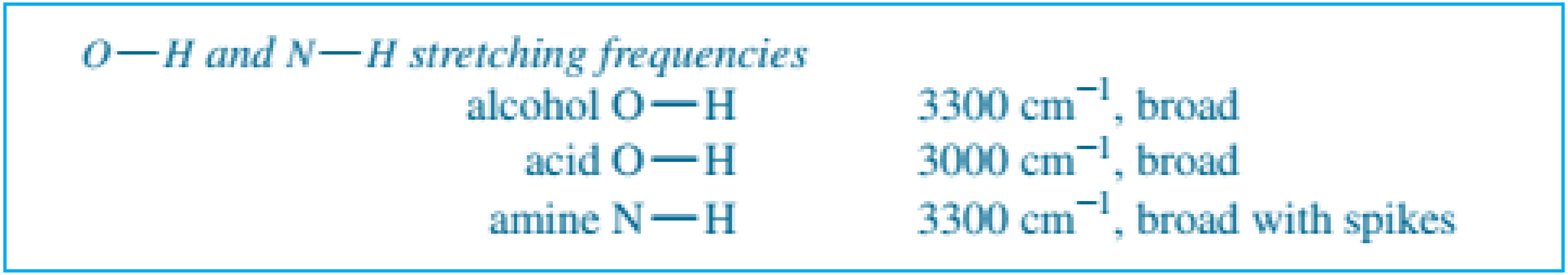
Characteristic absorptions of Alcohols and Amines

- ➢ The O-H bonds of alcohols and the N-H bonds of amines are strong and stiff.
- ➢ The vibration frequencies of O-H and N-H bonds therefore occur at higher frequencies than those of most C-H bonds (except for alkynyl ≡C-H bonds).



Characteristic absorptions of Alcohols and Amines

- Alcohol bonds absorb over a wide range of frequencies, centered around 3300 cm^{-1}.
- Alcohol molecules are involved in hydrogen bonding, with different molecules having different instantaneous arrangements. The O-H stretching frequencies reflect this diversity of hydrogen-bonding arrangements, resulting in **very broad** absorptions.



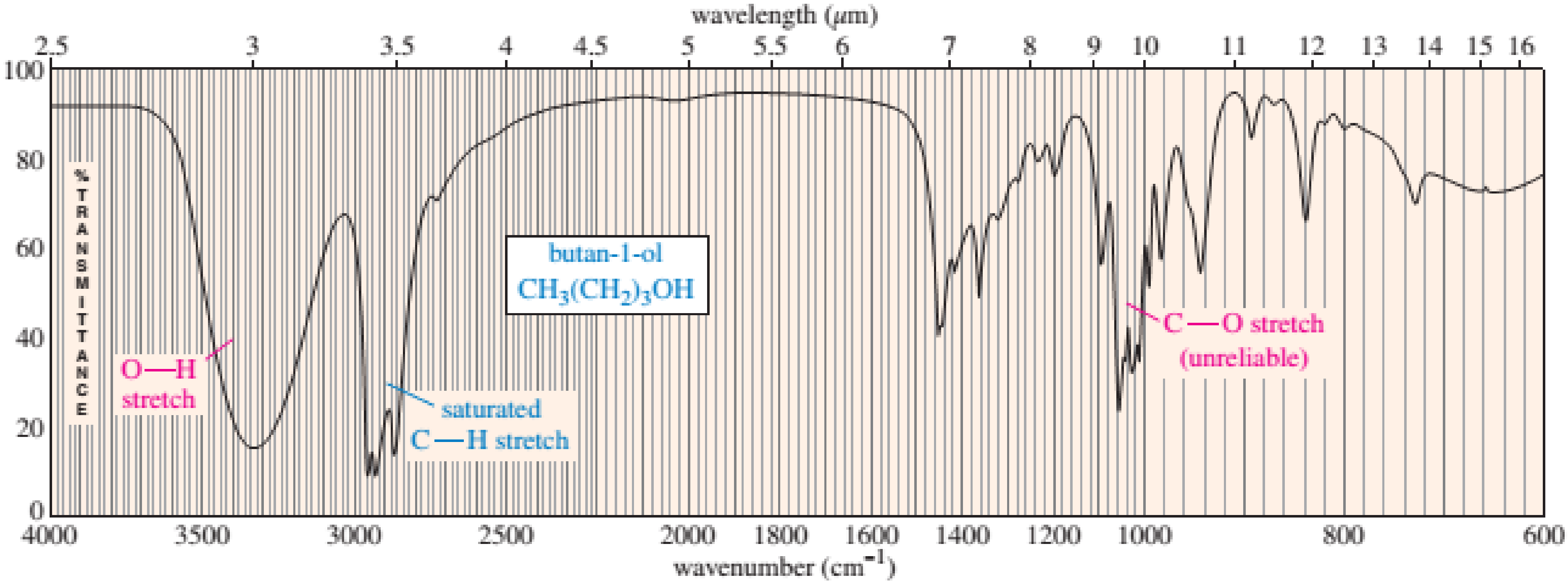
O—H and N—H stretching frequencies

alcohol O—H	3300 cm^{-1}, broad
acid O—H	3000 cm^{-1}, broad
amine N—H	3300 cm^{-1}, broad with spikes

- Like alcohols, carboxylic acids give O-H absorptions that are broadened by hydrogen bonding. However, the broad acid O-H absorption is usually centered around 3000 cm^{-1} (compared with 3300 cm^{-1} for alcohols), because of the stronger hydrogen bonding between acid molecules.

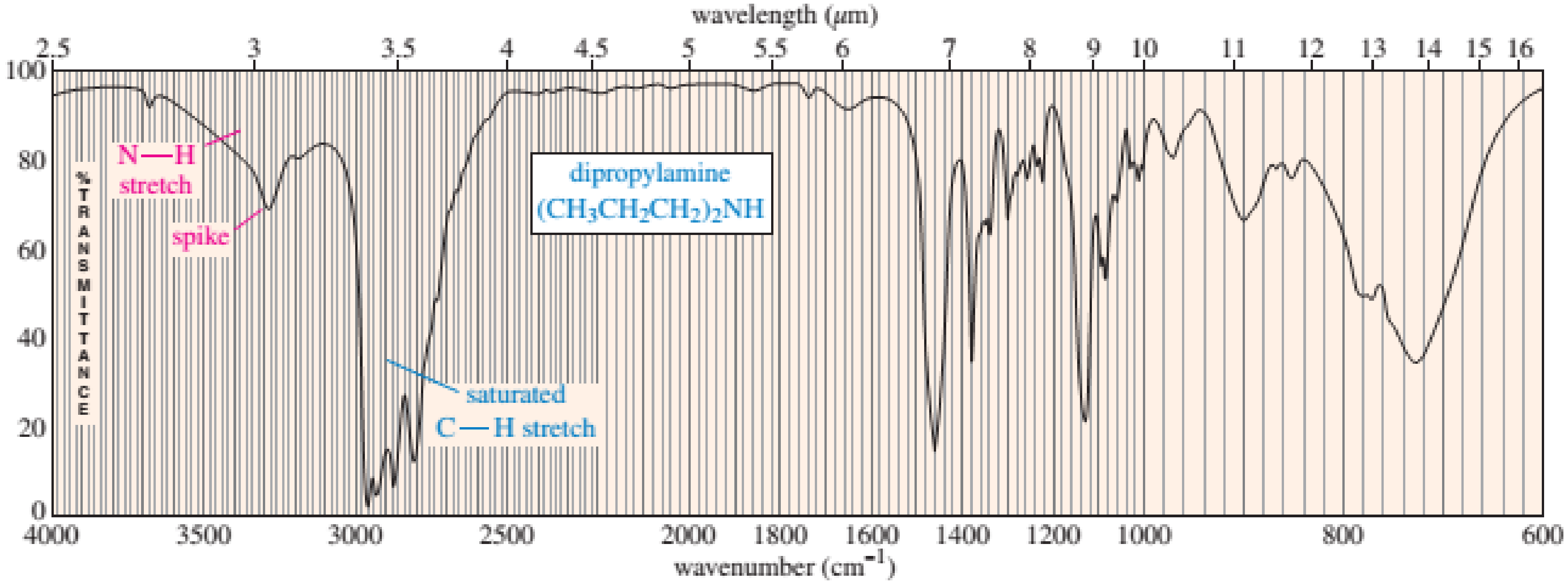
Characteristic absorptions of Alcohols

- The IR spectrum of butan-1-ol shows a broad, intense stretching absorption centered around.
- The broad shape is due to the diverse nature of the hydrogen-bonding interactions of alcohol molecules.



- Compounds with C-O bonds (alcohols and ethers) generally show strong absorptions in the range of 1000 to 2000 cm^{-1};
- However, there are other functional groups that also absorb in this region. Therefore, a strong peak between 1000 and 1200 cm^{-1} does not necessarily imply a C-O bond.
- For simple ethers, this unreliable C-O absorption is usually the only clue that the compound might be an ether.

Characteristic absorptions of amines



➢ Amine bonds also have stretching frequencies in the 3300 cm^{-1} region, or even slightly higher. Like alcohols, amines participate in hydrogen bonding that can broaden the N-H absorptions.

➢ With amines, the absorption is somewhat weaker, and there may be one or more sharp spikes superimposed on the broad N-H stretching absorption:

+ often one N-H spike for the single N-H bond of a secondary amine R_2NH

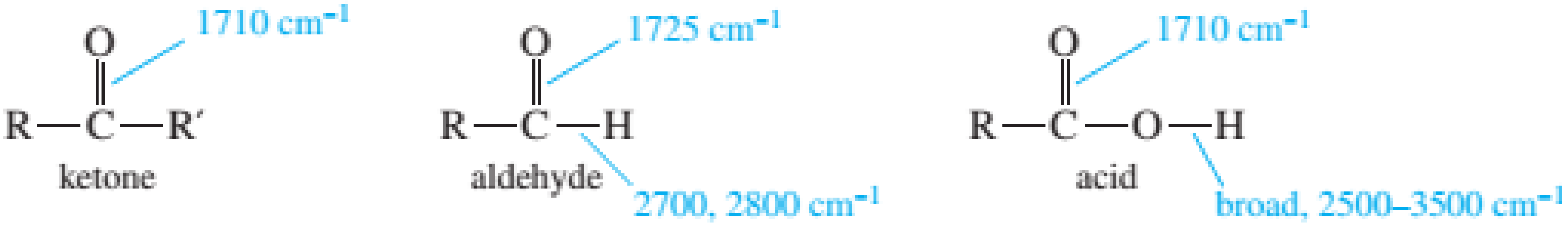
+ and two N-H spikes for the symmetric and anti-symmetric stretch of the two N-H bonds in a primary amine RNH_2. These sharp spikes, combined with the presence of nitrogen in the molecular formula, help to distinguish amines from alcohols.

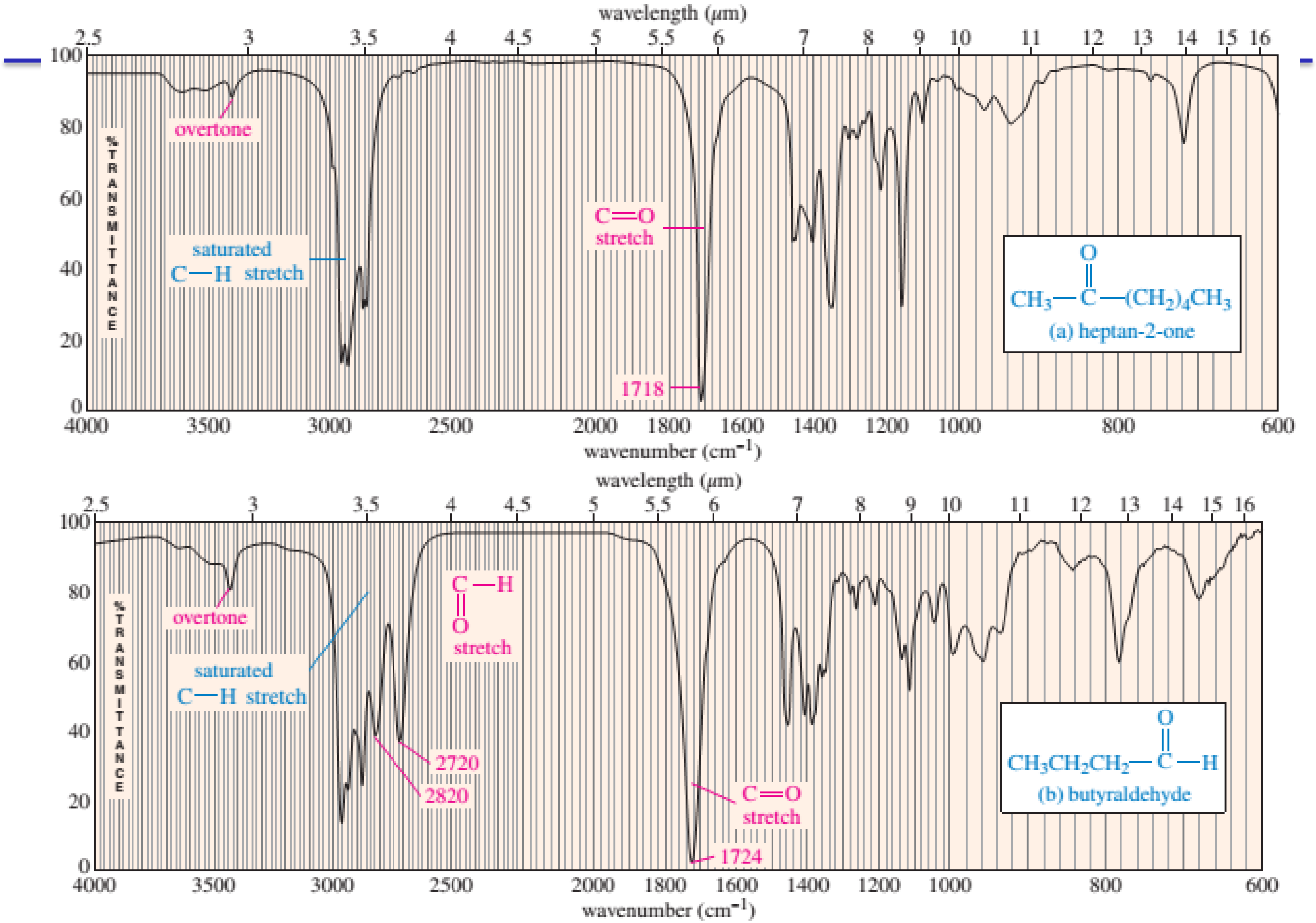
Characteristic absorptions of carbonyl compounds

- Because it has a large dipole moment, the C=O double bond produces intense infrared stretching absorptions.
- Carbonyl groups absorb at frequencies around 1700 cm^{-1}, but the exact frequency depends on the specific functional group and the rest of the molecule.
- Infrared spectroscopy is often the best method for detecting and identifying the type of carbonyl group in an unknown compound.

Simple Ketones, Aldehydes, and Acids

- The C=O stretching vibrations of simple ketones and carboxylic acids occur at frequencies around 1710 cm^{-1}.
- Aldehydes are a little higher, about 1725 cm^{-1}.
- These frequencies are higher than those for C=C double bonds because the C=O double bond is stronger and stiffer.



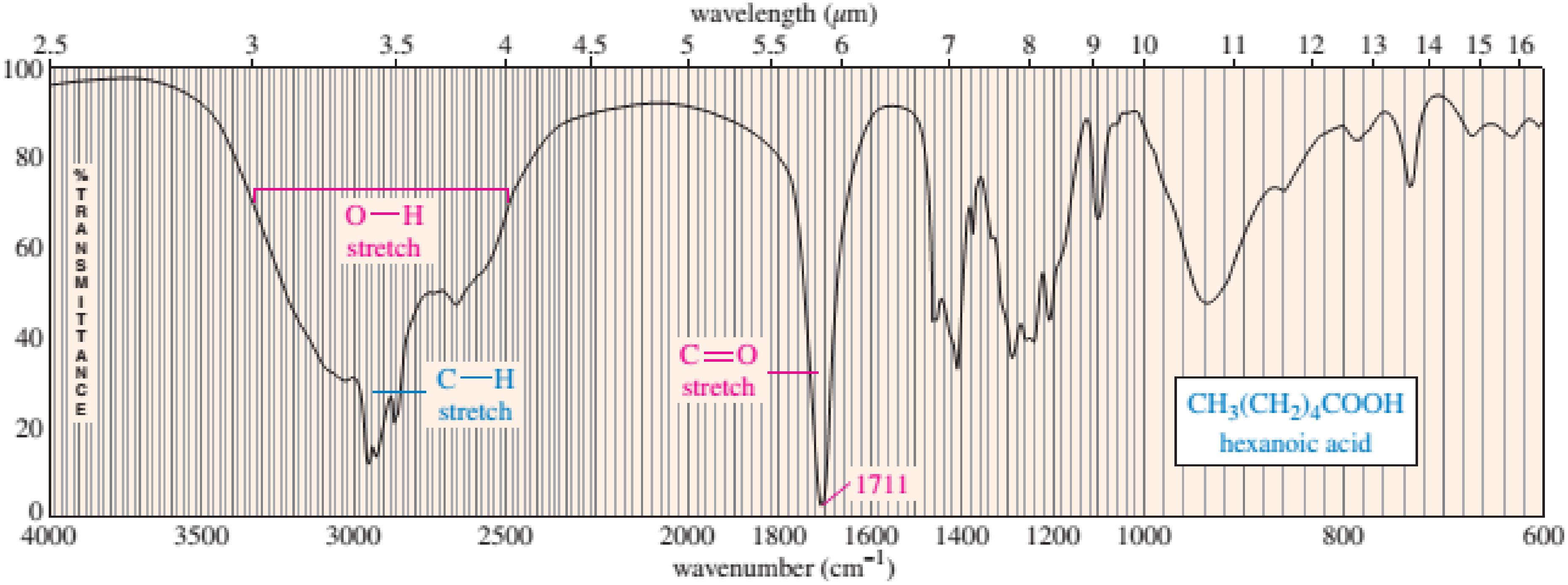


Infrared spectra of (a) heptan-2-one and (b) butyraldehyde. Both the ketone and the aldehyde show intense **carbonyl absorptions near 1720 cm^{-1}**. In the aldehyde spectrum, there are two peaks (2720 and 2820 cm^{-1}) characteristic of the C-H aldehyde stretch.

Measurements of IR spectrum

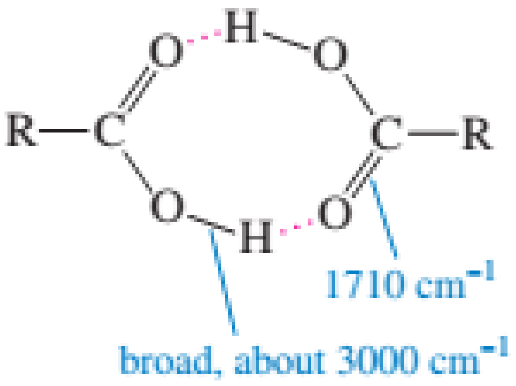
- In addition to the strong C=O stretching absorption, an aldehyde shows a characteristic set of two low-frequency C-H stretching frequencies around 2700 and 2800 cm^{-1}. Neither a ketone nor an acid produces absorptions at these positions.
- The figure above compares the IR spectra of a ketone and an aldehyde. Notice the characteristic carbonyl stretching absorptions in both spectra, as well as the aldehyde C-H absorptions at 2720 and 2820 cm^{-1} in the butyraldehyde spectrum.

Measurements of IR spectrum



$CH_3(CH_2)_4COOH$

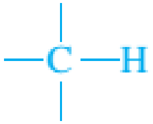
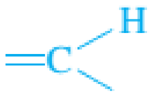
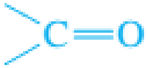
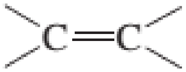
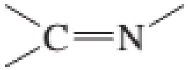
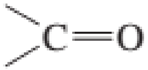
hexanoic acid



1710 cm^{-1}

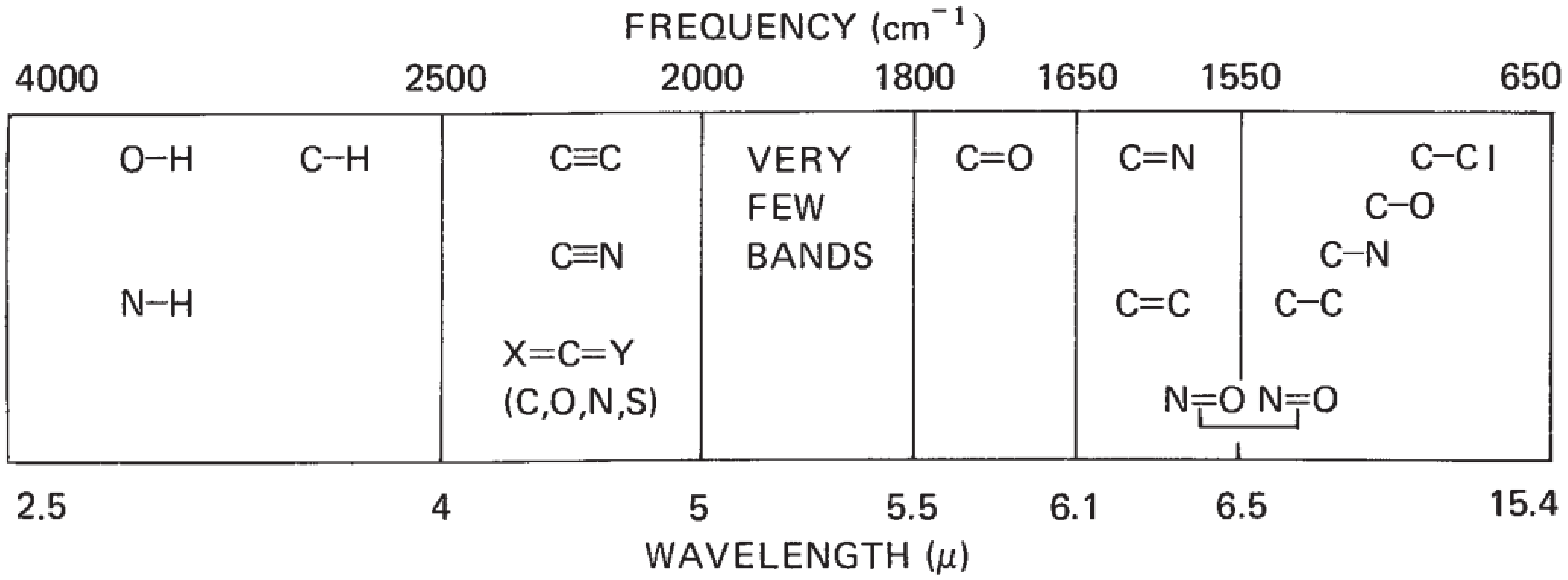
broad, about 3000 cm^{-1}

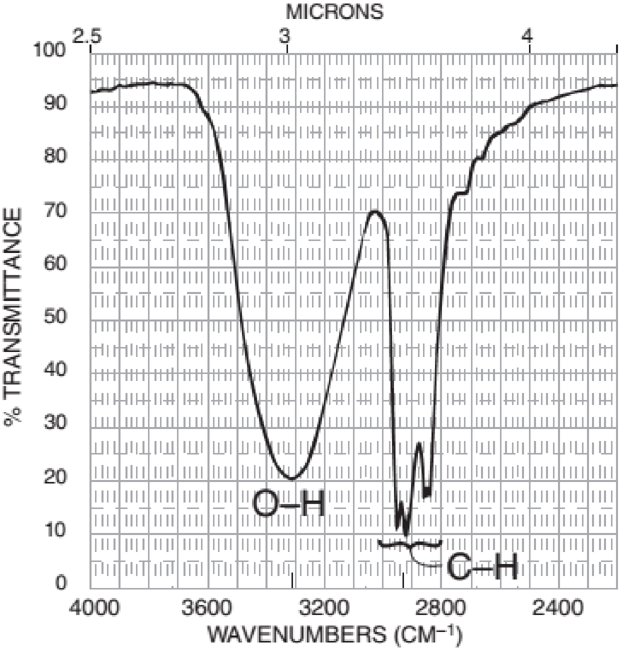
Typical Values of IR Stretching Frequencies

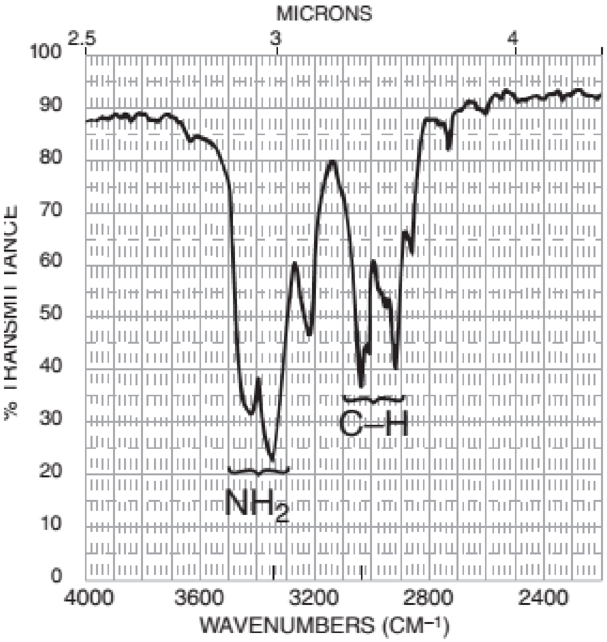
Frequency (cm^{-1})	Functional Group		Comments
3300	alcohol	O—H	always broad
	amine, amide	N—H	may be broad, sharp, or broad with spikes
	alkyne	$\equiv$C—H	always sharp, usually strong
3000	alkane	 $\mathrm{-\overset{\vert}{\underset{\vert}{C}}-H}$	just below 3000 cm^{-1}
	alkene	 $\mathrm{=C-H}$	just above 3000 cm^{-1}
	acid	O—H	very broad 2500–3500 cm^{-1}
2200	alkyne	—C$\equiv$C—	just below 2200 cm^{-1}
	nitrile	—C$\equiv$N	just above 2200 cm^{-1}
1710 (very strong)	carbonyl	 $\mathrm{C=O}$	ketones, acids about 1710 cm^{-1} aldehydes about 1725 cm^{-1} esters higher, about 1735 cm^{-1} conjugation lowers frequency amides lower, about 1650 cm^{-1}
1660	alkene	 $\mathrm{C=C}$	conjugation lowers frequency aromatic C=C about 1600 cm^{-1}
	imine	 $\mathrm{C=N}$	stronger than C=C
	amide	 $\mathrm{C=O}$	stronger than C=C (see above)

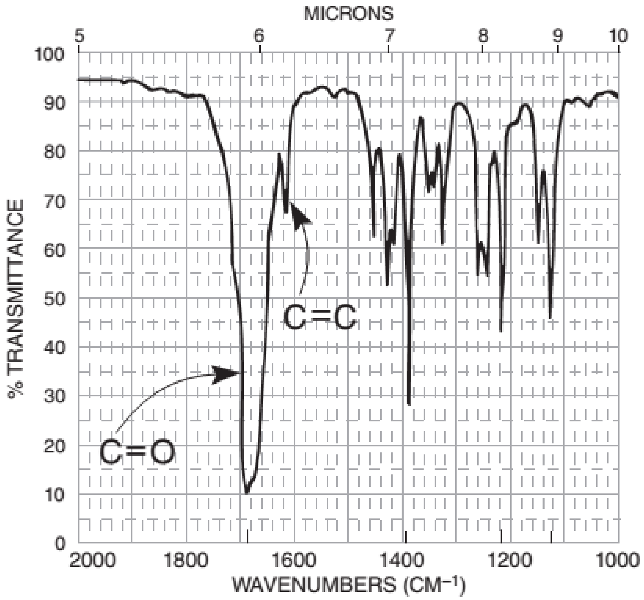
Ethers, esters, and alcohols also show C—O stretching between 1000 and 1200 cm^{-1}.

Try to fix this general scheme in your mind for future convenience!









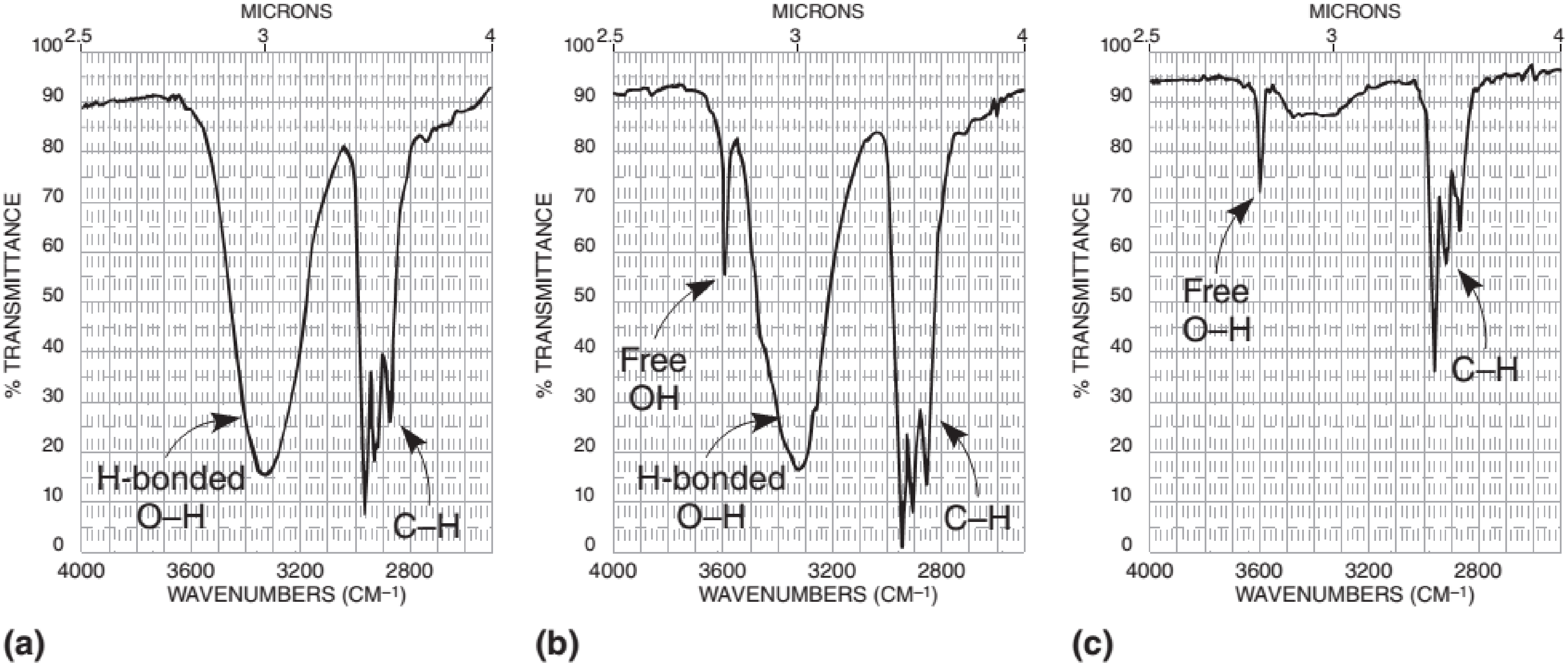


FIGURE 2.32 The O−H stretch region. (a) Hydrogen-bonded O−H only (neat liquid). (b) Free and hydrogen-bonded O−H (dilute solution). (c) Free and hydrogen-bonded O−H (very dilute solution).

2.9 HOW TO APPROACH THE ANALYSIS OF A SPECTRUM (*OR* WHAT YOU CAN TELL AT A GLANCE)

When analyzing the spectrum of an unknown, concentrate your first efforts on determining the presence (or absence) of a few major functional groups. The C=O, O—H, N—H, C—O, C=C, C≡C, C≡N, and NO_2 peaks are the most conspicuous and give immediate structural information if they are present. Do not try to make a detailed analysis of the C—H absorptions near 3000 cm^{-1}; almost all compounds have these absorptions. Do not worry about subtleties of the exact environment in which the functional group is found. Following is a major checklist of the important gross features.

1. Is a carbonyl group present? The C=O group gives rise to a strong absorption in the region 1820–1660 cm^{-1}. The peak is often the strongest in the spectrum and of medium width. You can't miss it.

2. If C=O is present, check the following types (if it is absent, go to step 3):

ACIDS	Is O—H also present? • *Broad* absorption near 3400–2400 cm^{-1} (usually overlaps C—H).
AMIDES	Is N—H also present? • Medium absorption near 3400 cm^{-1}; sometimes a double peak with equivalent halves.
ESTERS	Is C—O also present? • Strong-intensity absorptions near 1300–1000 cm^{-1}.
ANHYDRIDES	*Two* C=O absorptions near 1810 and 1760 cm^{-1}.
ALDEHYDES	Is aldehyde C—H present? • Two weak absorptions near 2850 and 2750 cm^{-1} on right side of the aliphatic C—H absorptions.
KETONES	The preceding five choices have been eliminated.

3. If $C=O$ is absent:

ALCOHOLS, PHENOLS	Check for $O-H$. • *Broad* absorption near 3400–3300 cm^{-1}. • Confirm this by finding $C-O$ near 1300–1000 cm^{-1}.
AMINES	Check for $N-H$. • Medium absorption(s) near 3400 cm^{-1}.
ETHERS	Check for $C-O$ near 1300–1000 cm^{-1} (and absence of $O-H$ near 3400 cm^{-1}).

4. Double bonds and/or aromatic rings

- $C=C$ is a weak absorption near 1650 cm.
- Medium-to-strong absorptions in the region 1600–1450 cm^{-1}; these often imply an aromatic ring.
- Confirm the double bond or aromatic ring by consulting the $C-H$ region; aromatic and vinyl $C-H$ occur to the left of 3000 cm^{-1} (aliphatic $C-H$ occurs to the right of this value).

5. Triple bonds

- C≡N is a medium, sharp absorption near 2250 cm^{-1}.
- C≡C is a weak, sharp absorption near 2150 cm^{-1}.
- Check also for acetylenic C−H near 3300 cm^{-1}.

6. Nitro groups

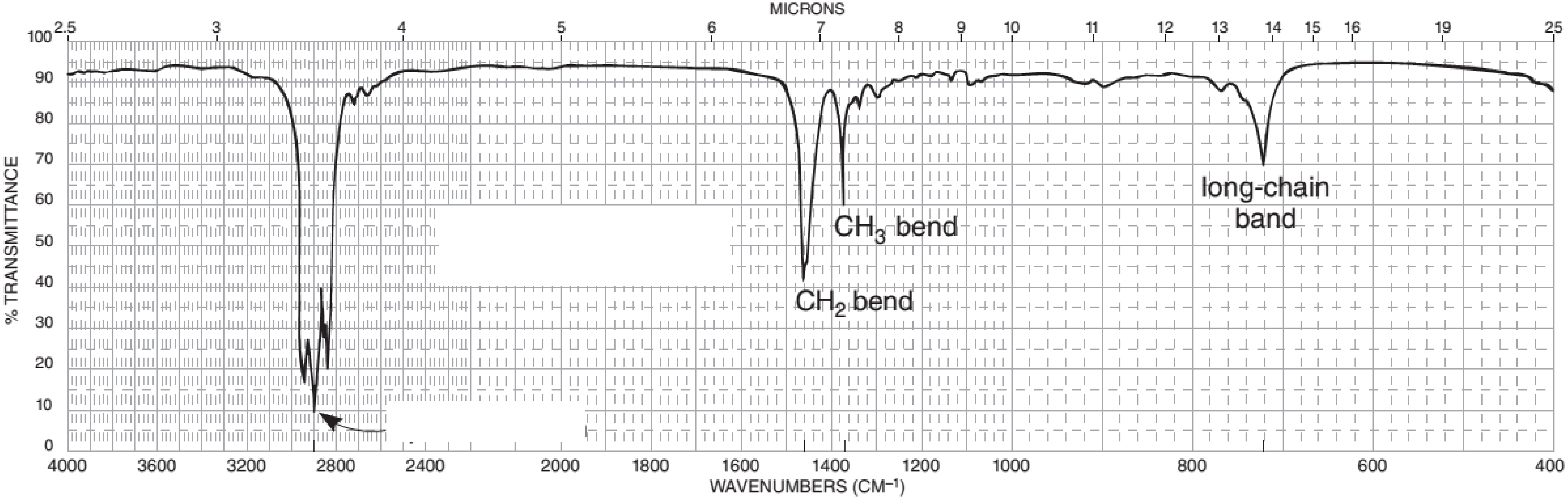
- Two strong absorptions at 1600–1530 cm^{-1} and 1390–1300 cm^{-1}.

7. Hydrocarbons

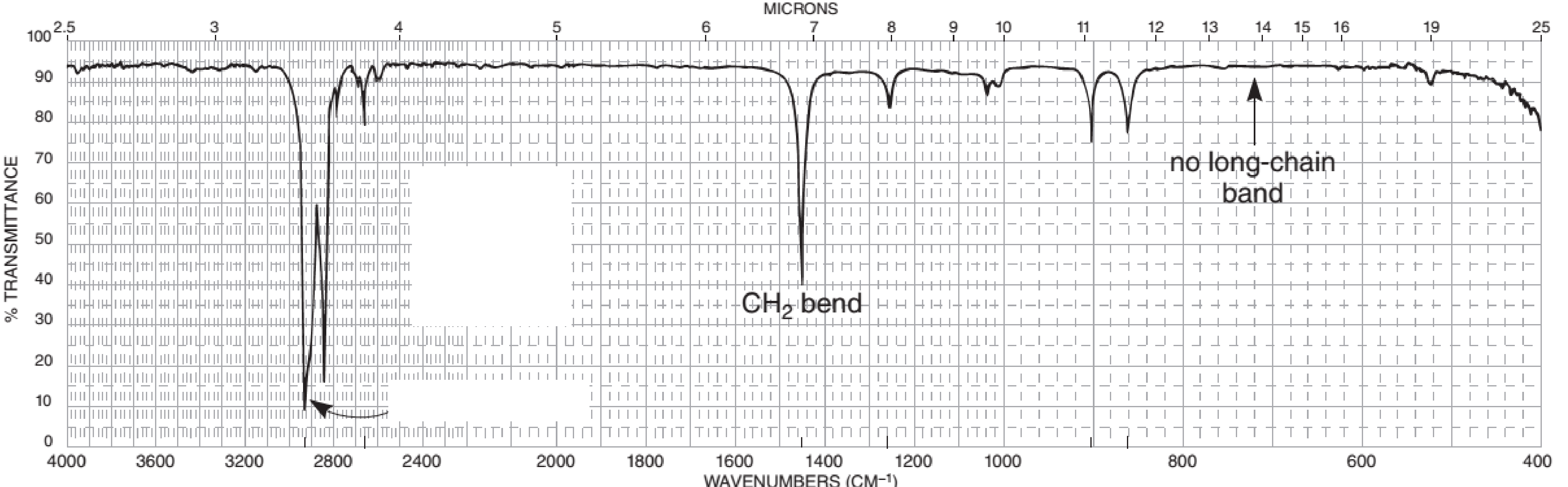
- None of the preceding is found.
- Major absorptions are in C−H region near 3000^{-1}.
- Very simple spectrum; the only other absorptions appear near 1460 and 1375 cm^{-1}.

The beginning student should resist the idea of trying to assign or interpret *every* peak in the spectrum. You simply will not be able to do it. Concentrate first on learning these *major* peaks and recognizing their presence or absence. This is best done by carefully studying the illustrative spectra in the sections that follow.

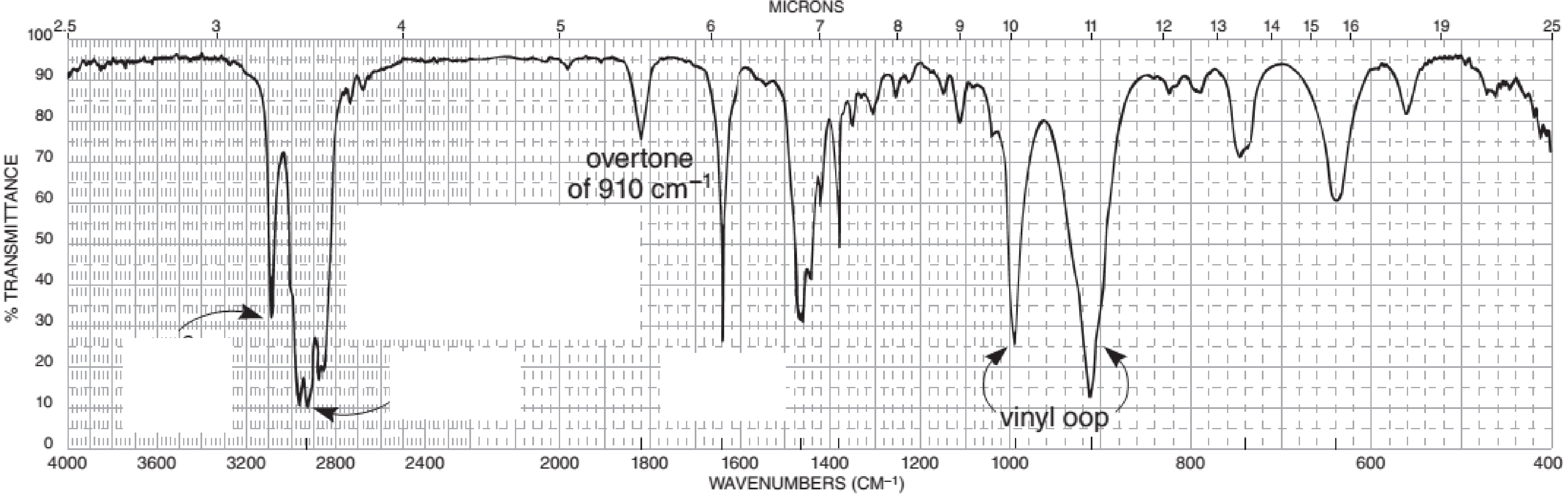
a) $C_{10}H_{22}$



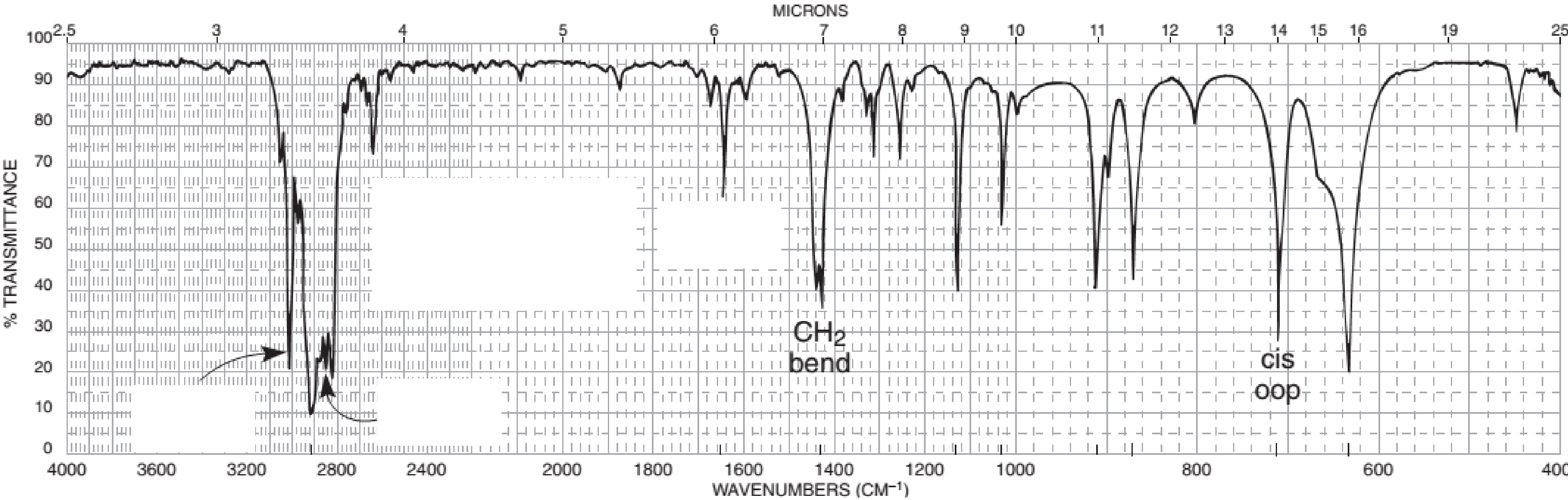
b) C_6H_{12}



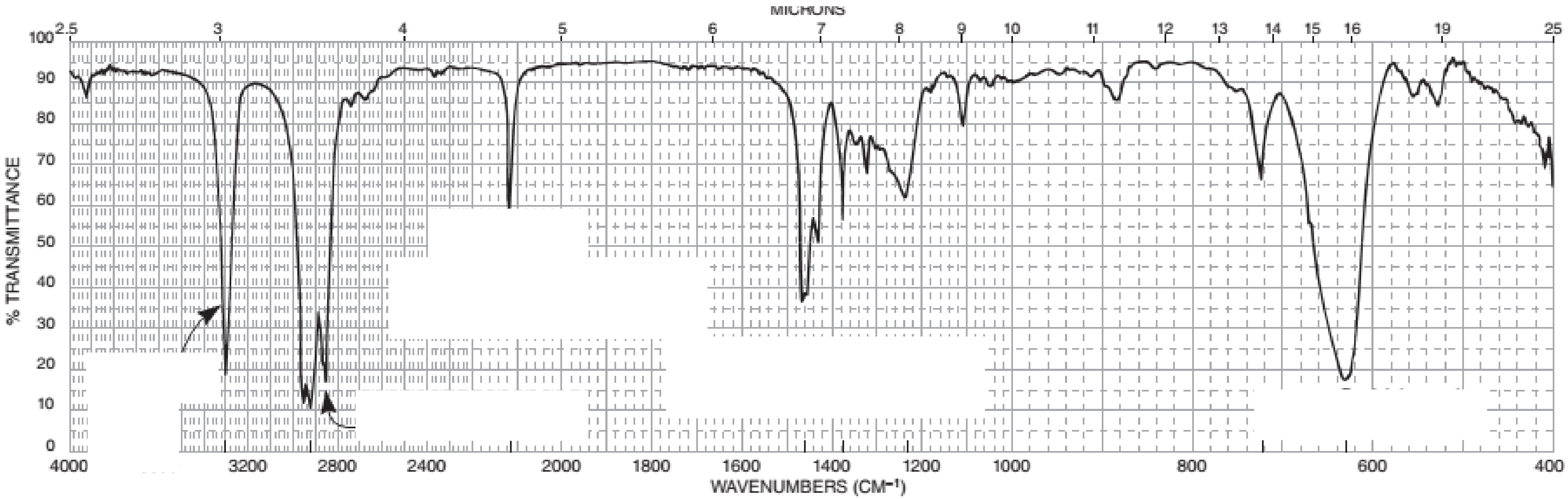
a) C_6H_{12}



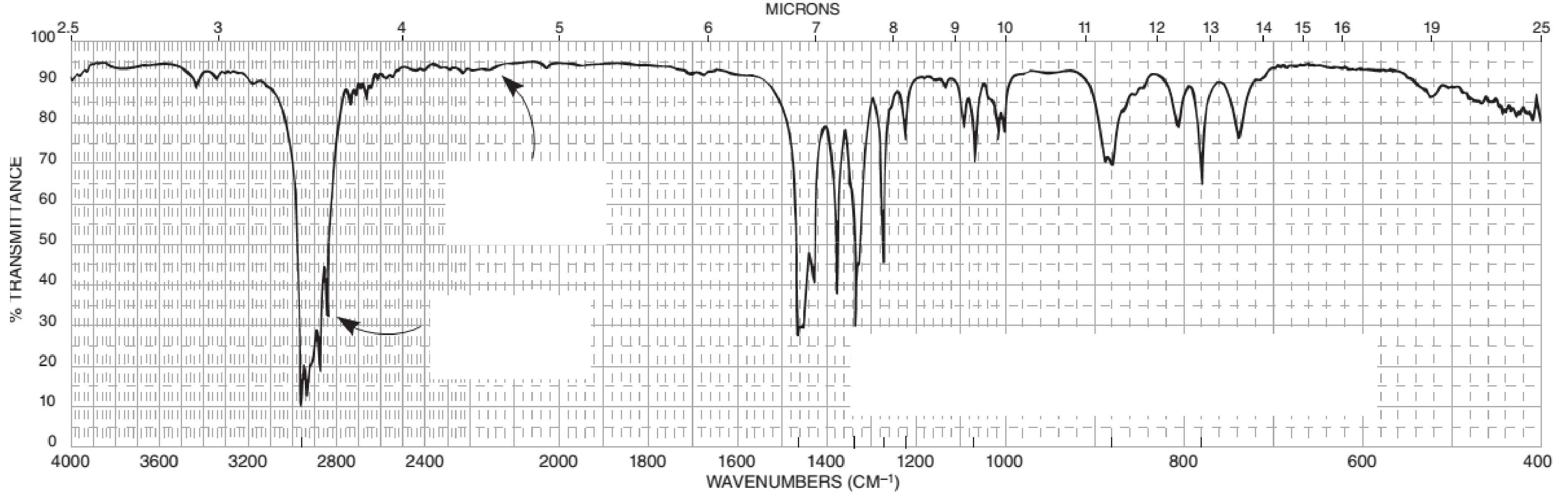
b) C_6H_{10}



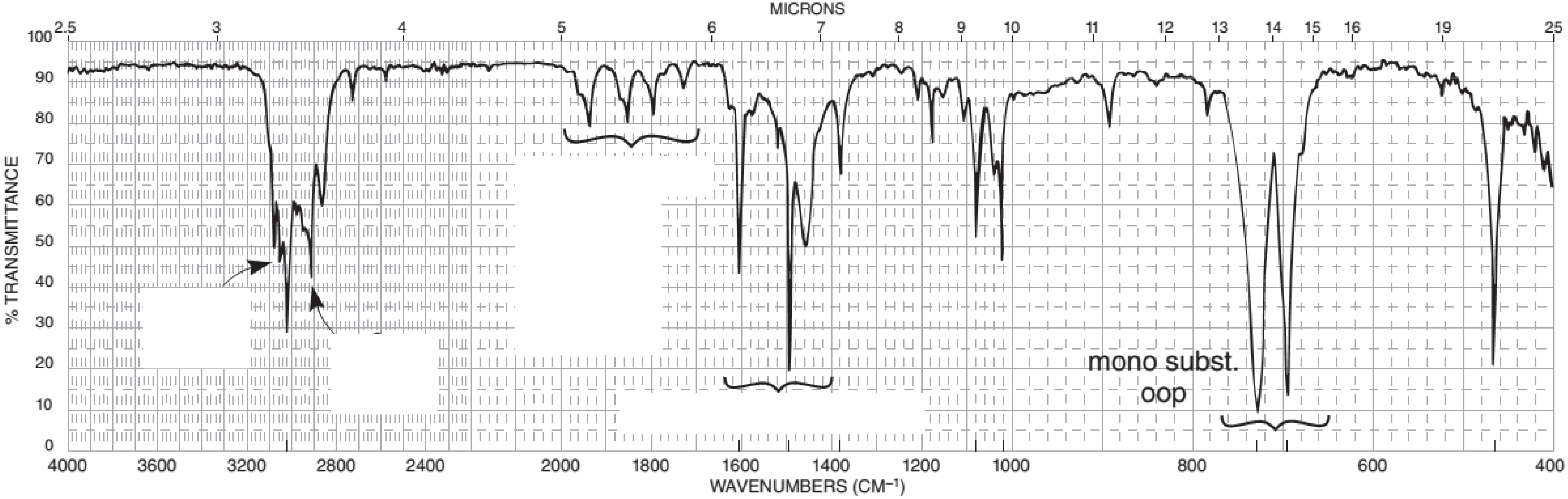
a) C_8H_{14}



b) C_8H_{14}



a) C_7H_8


MICRONS
2.5 3 4 5 6 7 8 9 10 11 12 13 14 15 16 19 25
% TRANSMITTANCE
100 90 80 70 60 50 40 30 20 10 0
mono subst.
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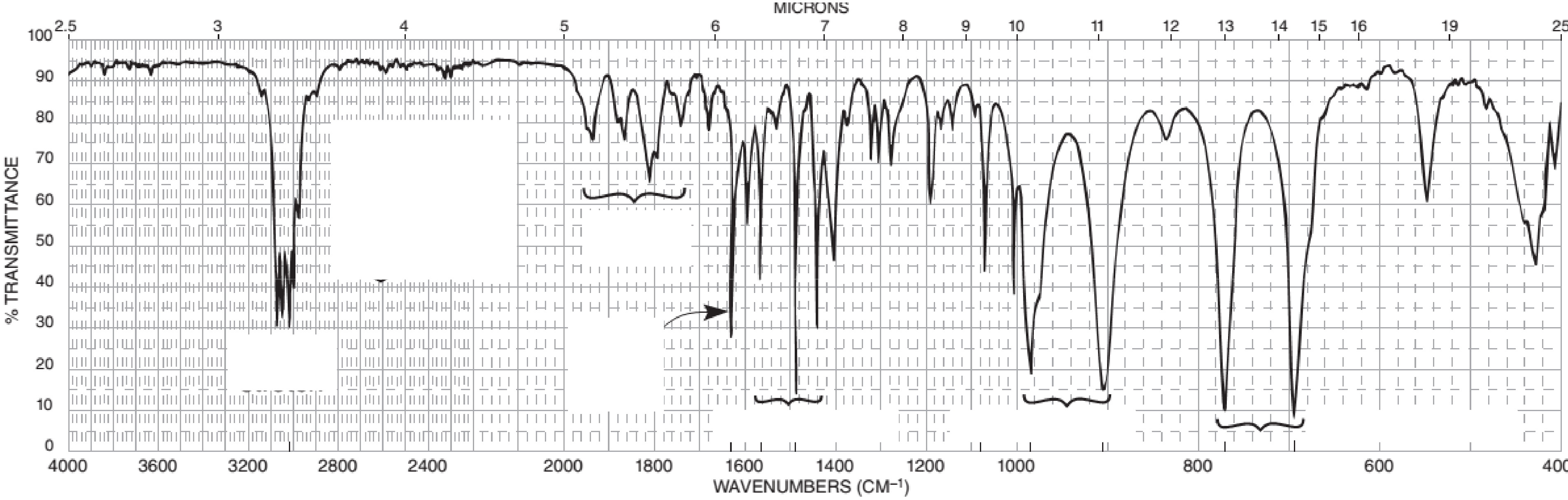
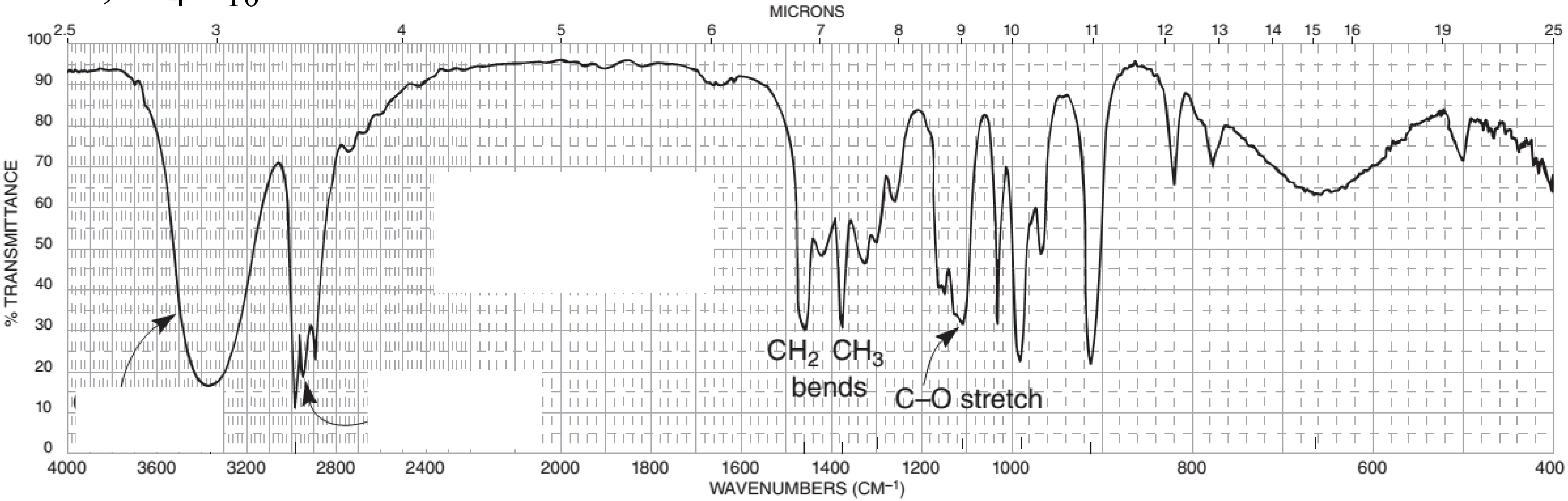
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400
WAVENUMBERS (CM⁻¹)

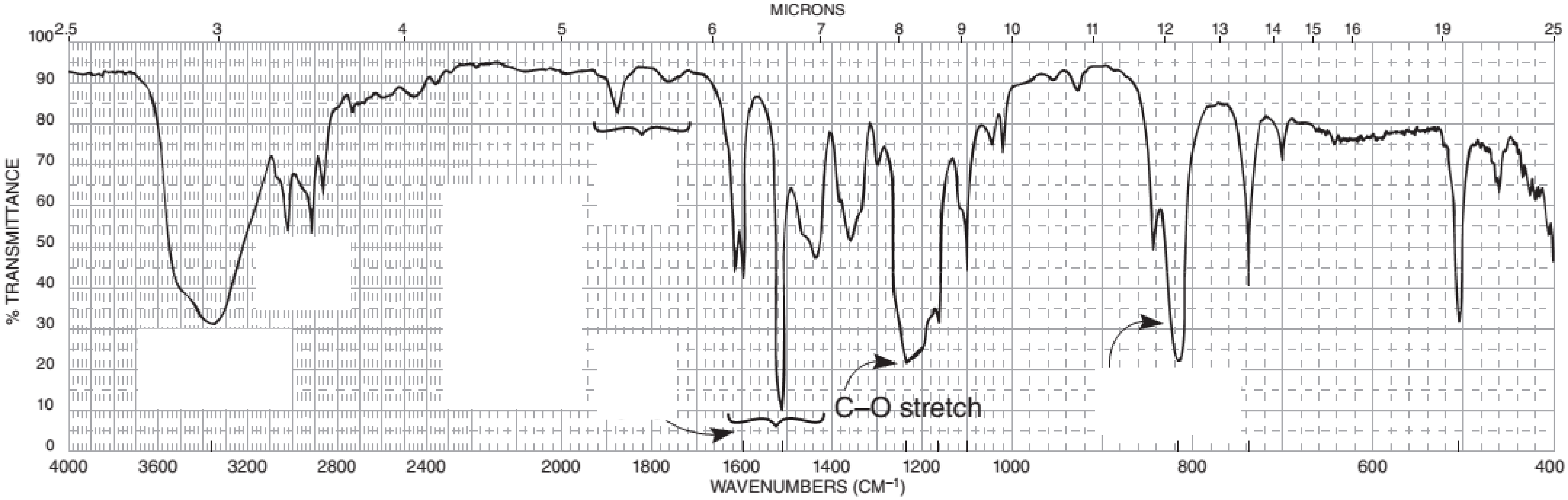
b) C_8H_8


MICRONS
2.5 3 4 5 6 7 8 9 10 11 12 13 14 15 16 19 25
% TRANSMITTANCE
100 90 80 70 60 50 40 30 20 10 0
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400
WAVENUMBERS (CM⁻¹)

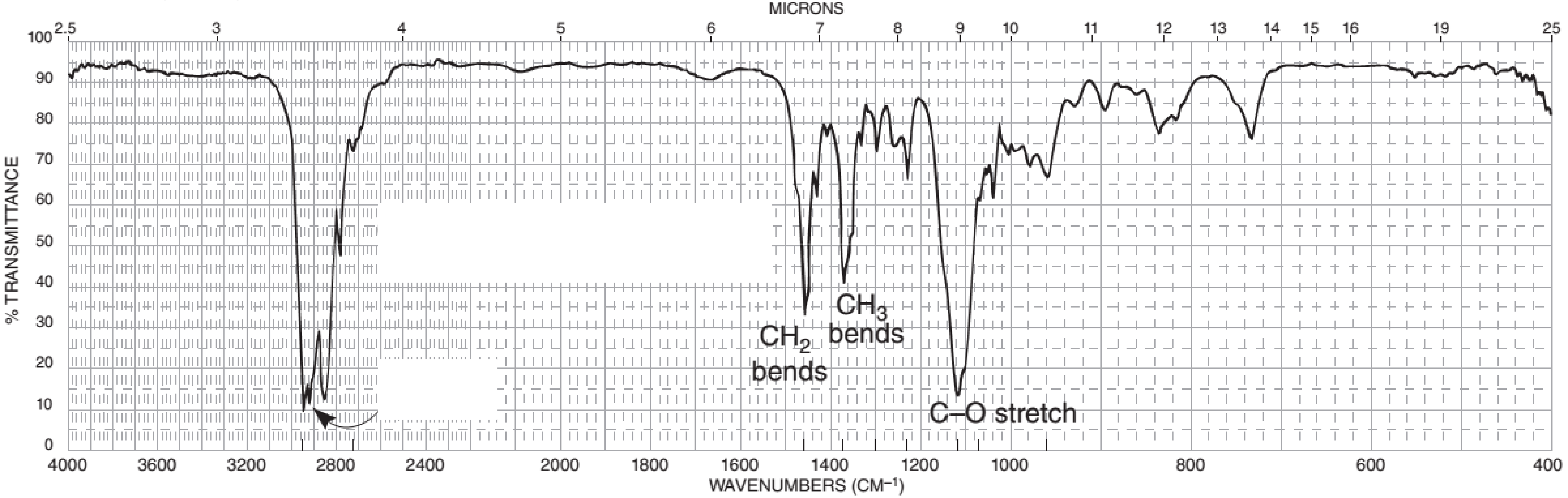
a) $C_4H_{10}O$



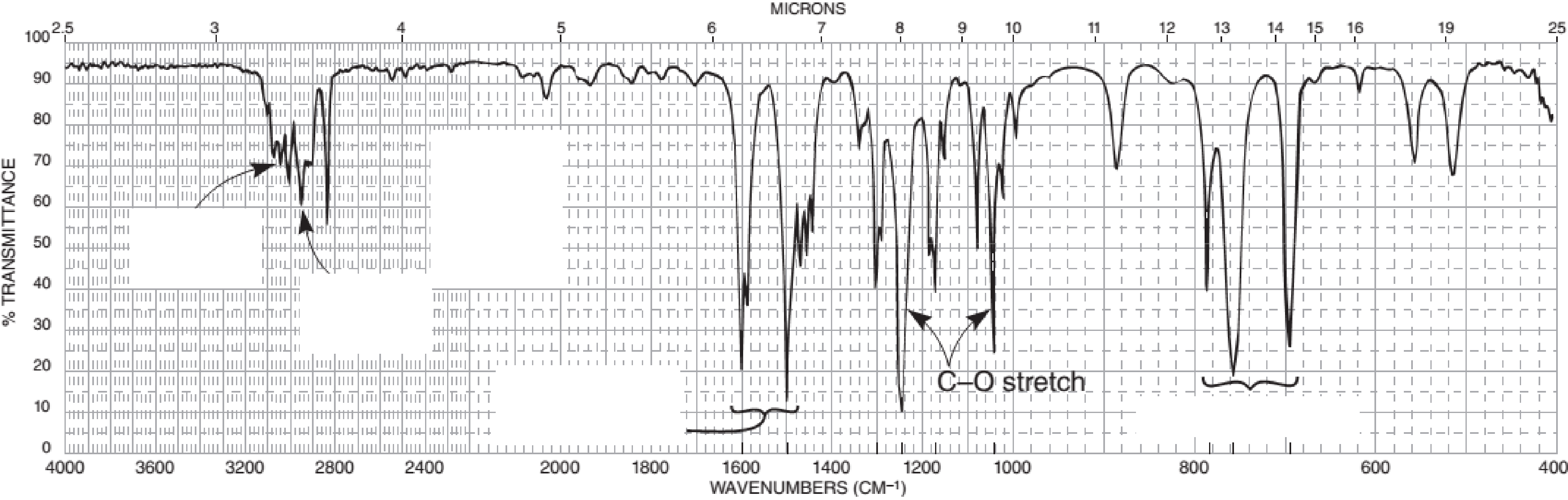
a) C_7H_8O



a) $C_8H_{18}O$



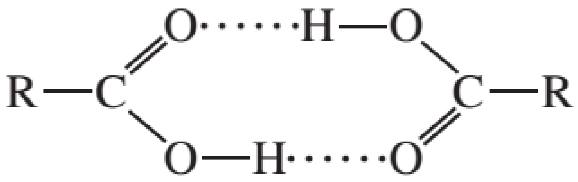
b) C_7H_8O



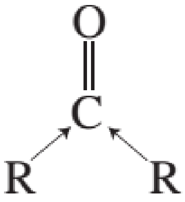
$\longleftarrow$ cm^{-1} $\longrightarrow$

1810	1800	1760	1735	1725	1715	1710	1675
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

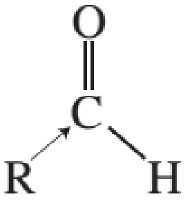
A carboxylic acid exists in monomeric form *only* in very dilute solution, and it absorbs at about 1760 cm^{-1} because of the electron-withdrawing effect just discussed. However, acids in concentrated solution, in the form of neat liquid, or in the solid state (KBr pellet and Nujol) tend to dimerize via hydrogen bonding. This dimerization weakens the C=O bond and lowers the stretching force constant *K*, resulting in a lowering of the carbonyl frequency of saturated acids to about 1710 cm^{-1}.



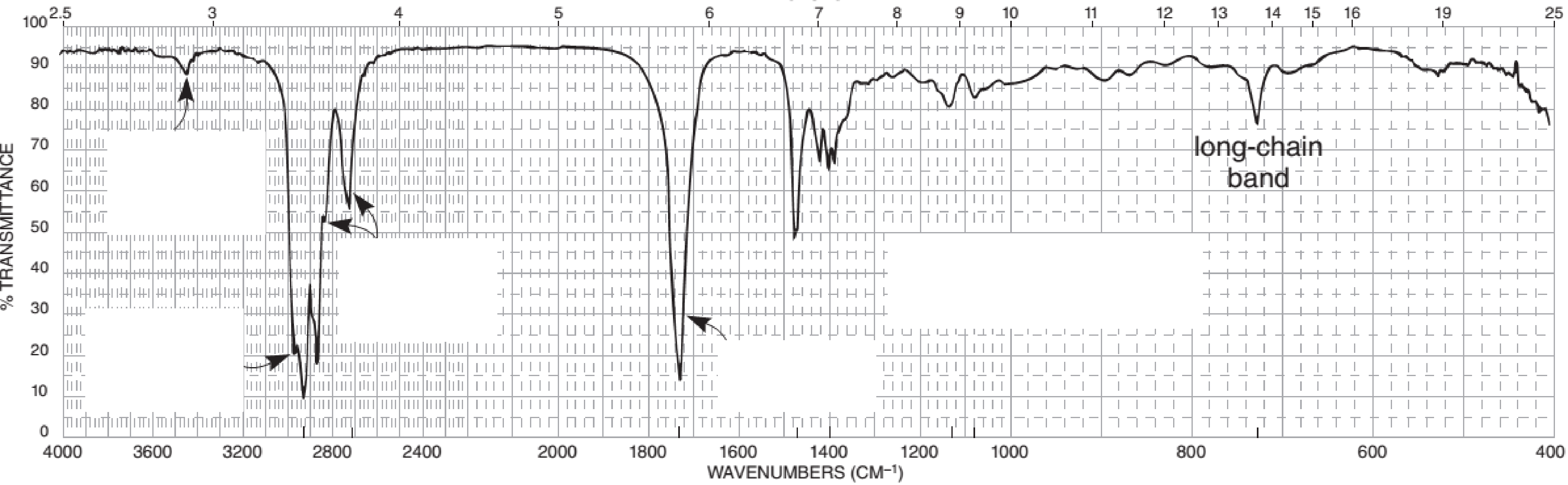
Ketones absorb at a lower frequency than aldehydes because of their additional alkyl group, which is electron donating (compared to H) and supplies electrons to the C=O bond. This electron-releasing effect weakens the C=O bond in the ketone and lowers the force constant and the absorption frequency.



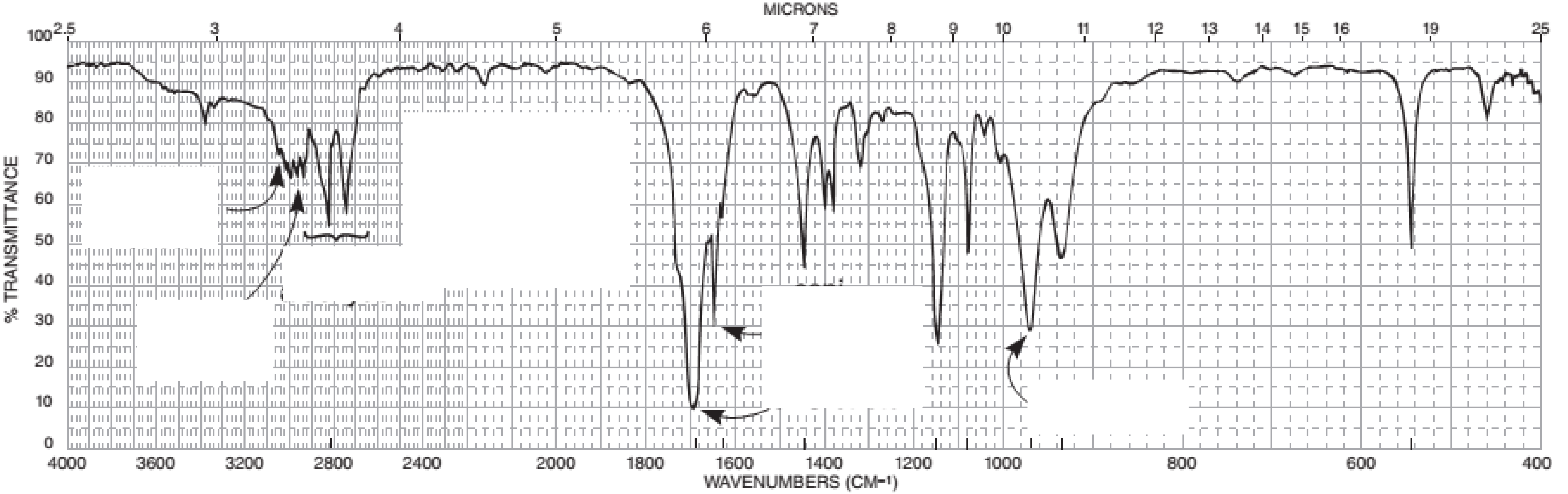
versus



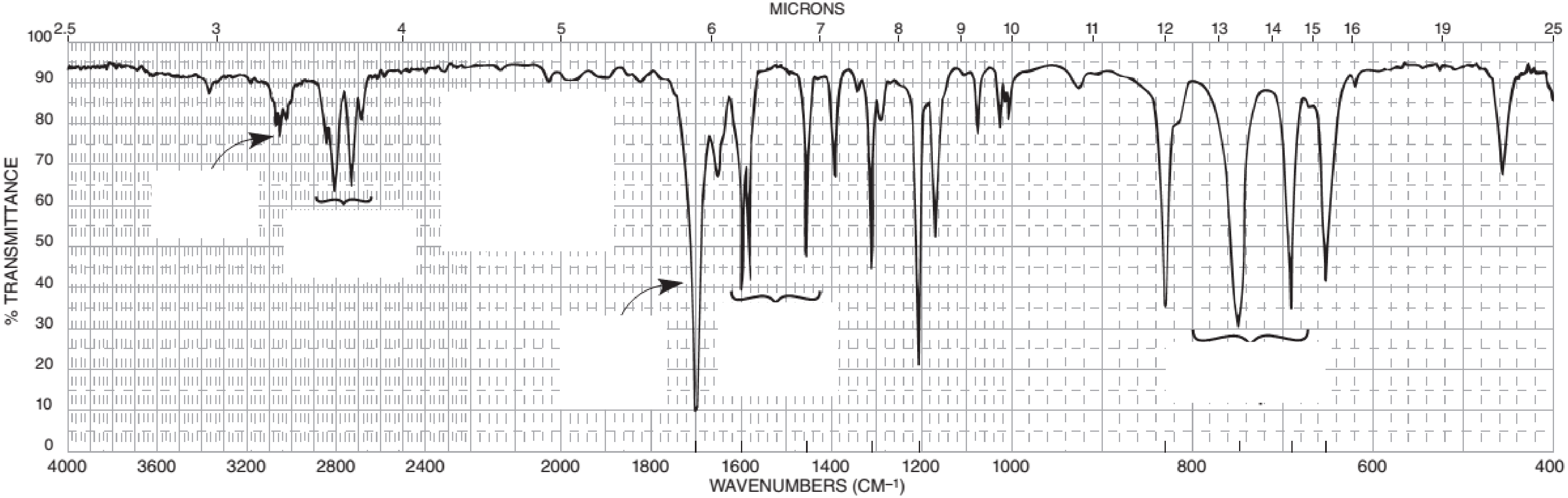
a) $C_9H_{18}O$



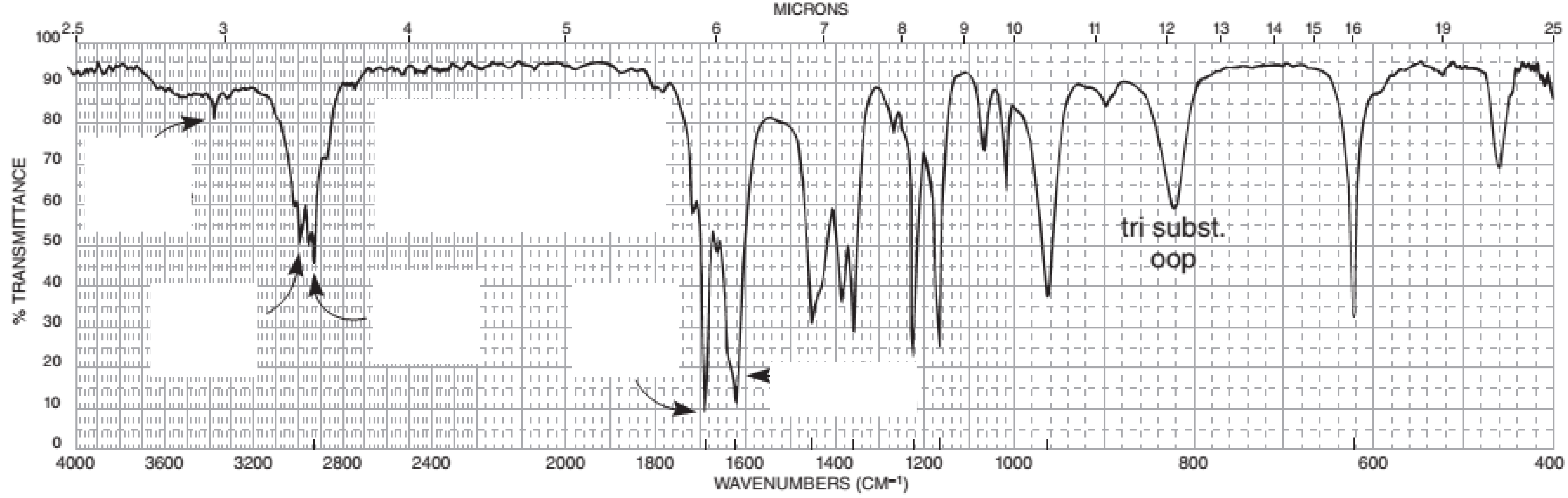
b) C_4H_6O



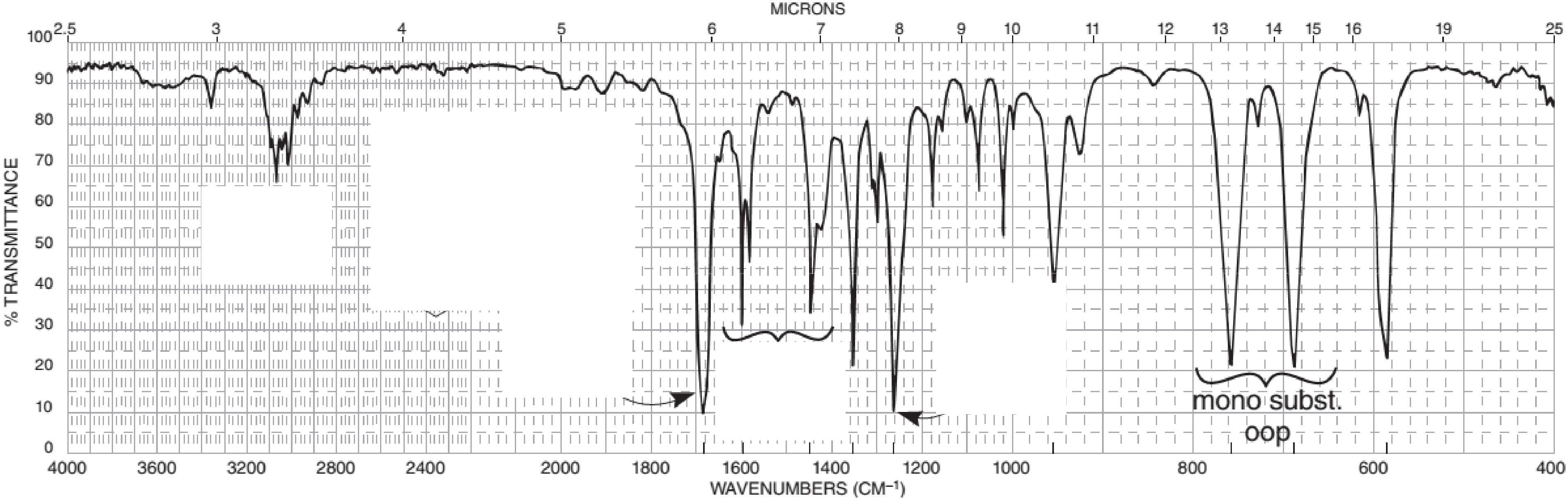
a) C_7H_6O



b) $C_6H_{10}O$



a) C_8H_8O


MICRONS
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% TRANSMITTANCE
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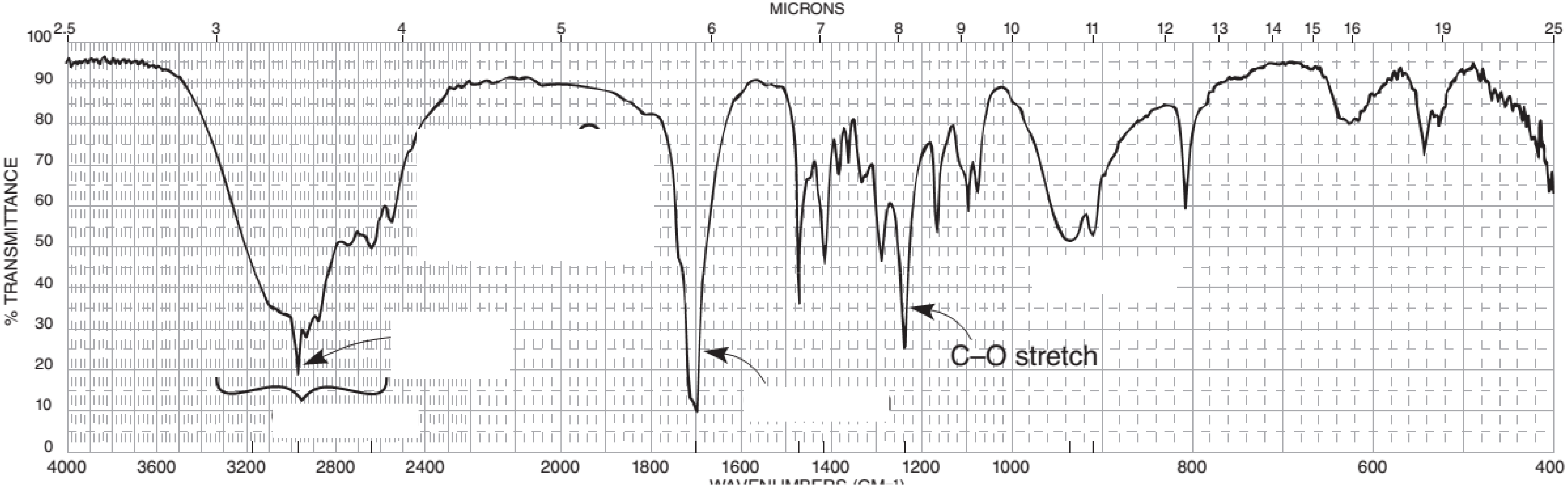
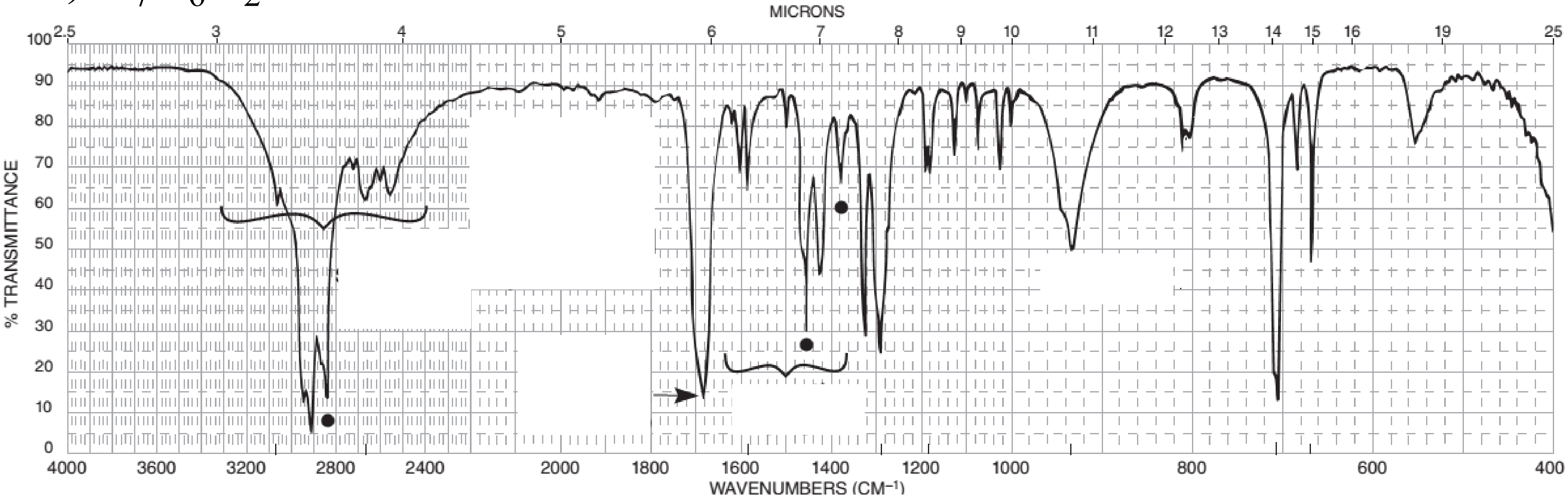
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS (CM⁻¹)
mono subst.
oop

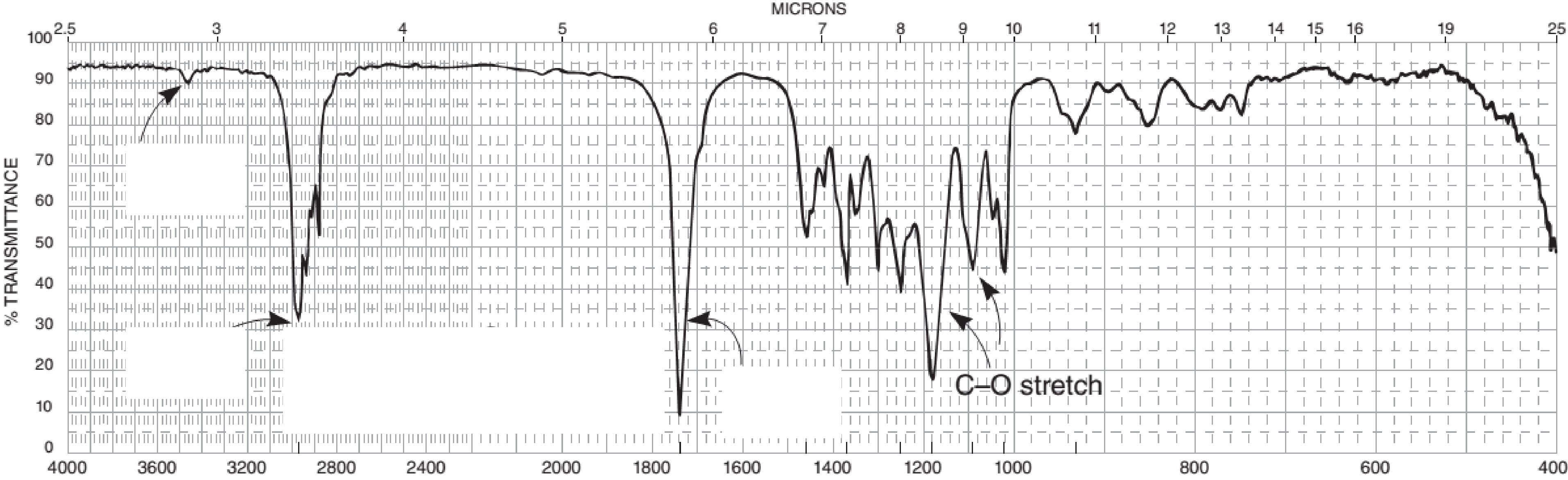
a) $C_4H_8O_2$



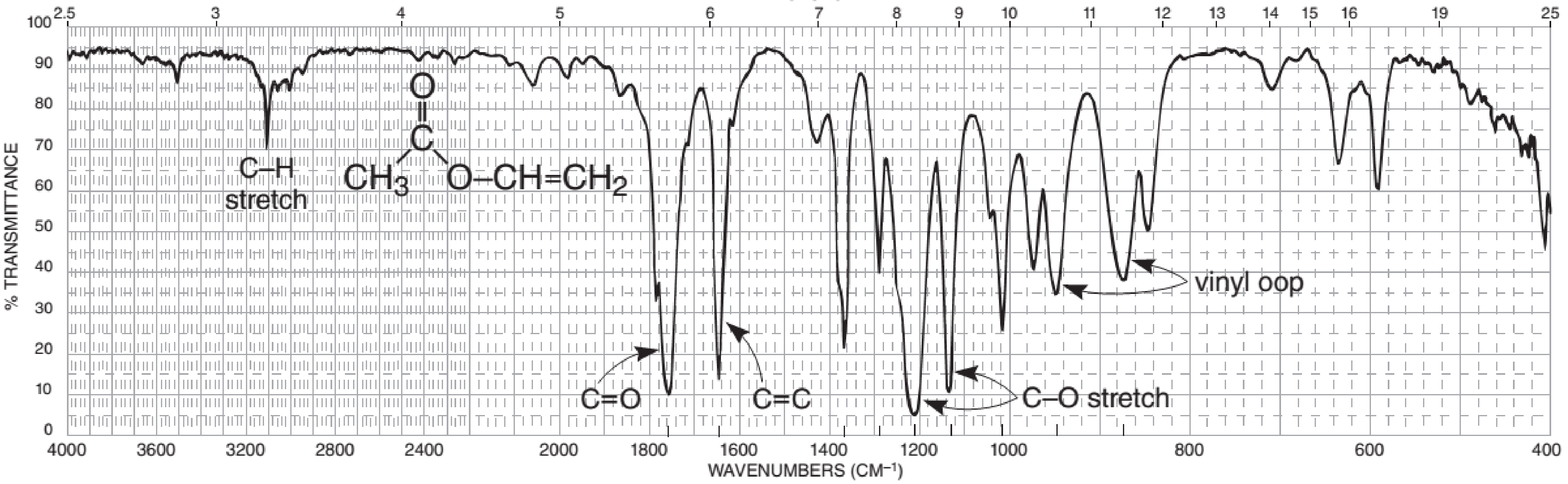
b) $C_7H_6O_2$



a) $C_6H_{12}O_2$

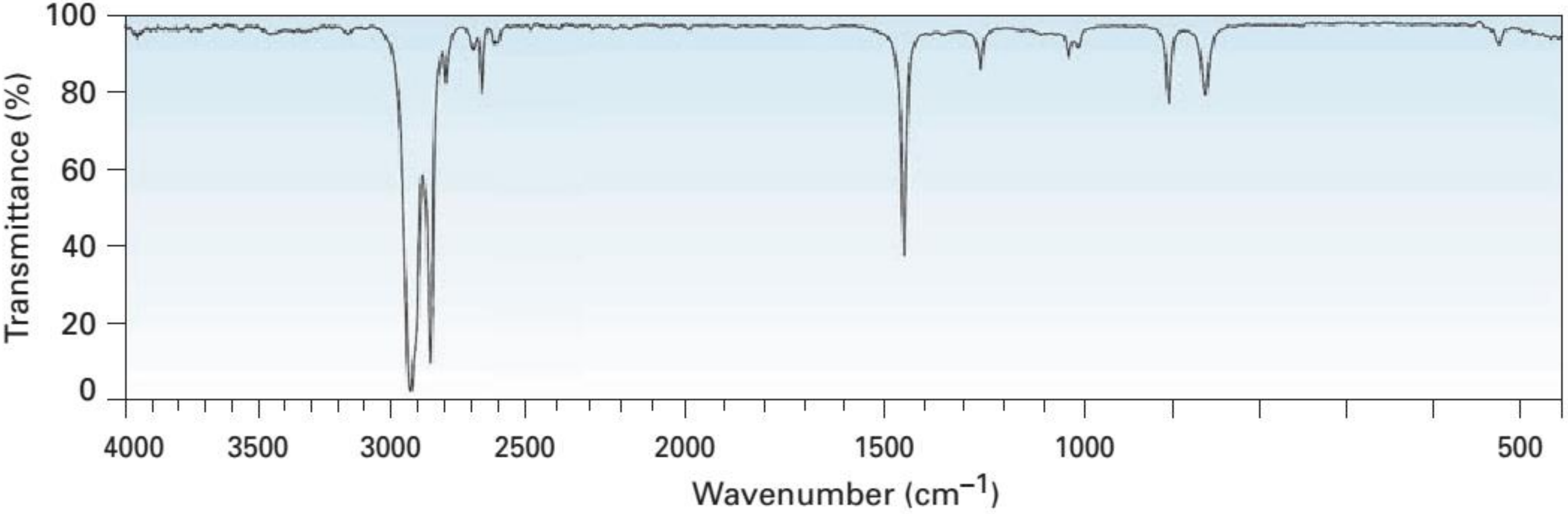


b) $C_4H_6O_2$



12.32 Two infrared spectra are shown. One is the spectrum of cyclohexane, and the other is the spectrum of cyclohexene. Identify them, and explain your answer.

(a)



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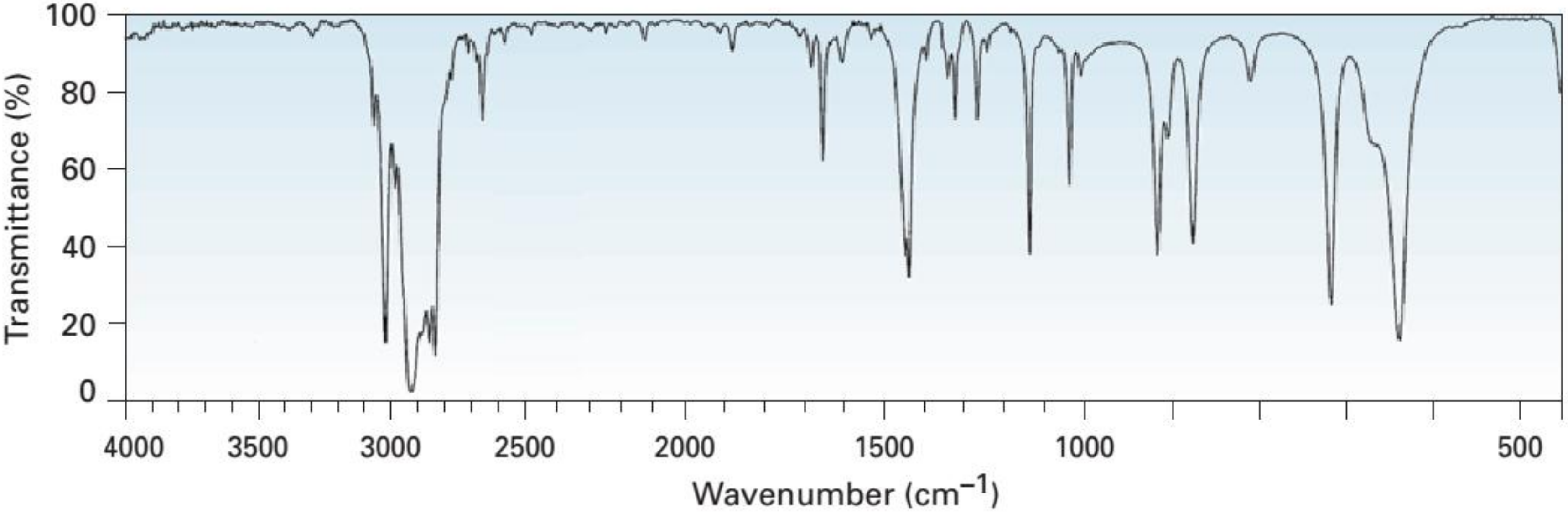
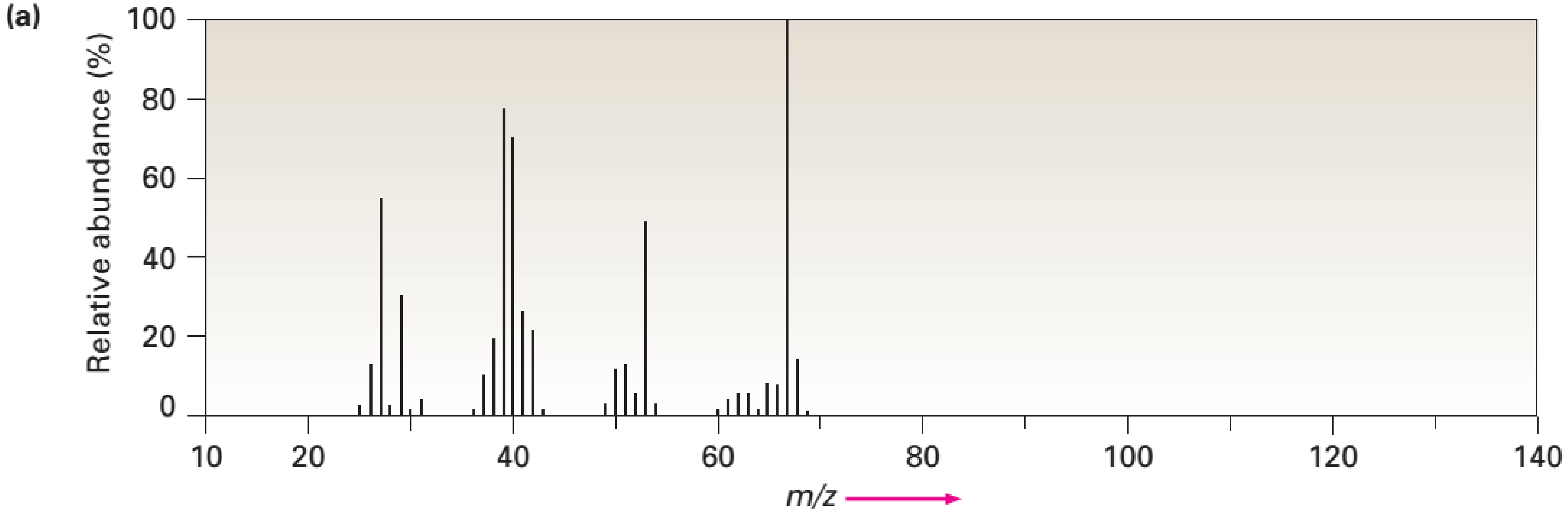
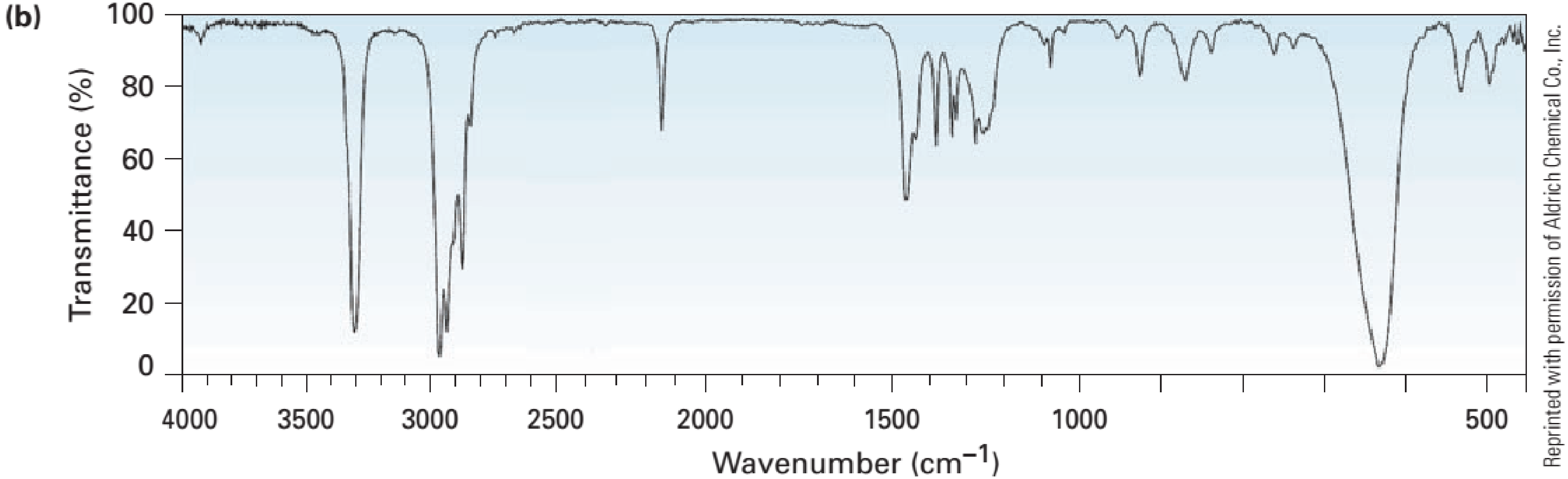
(b)



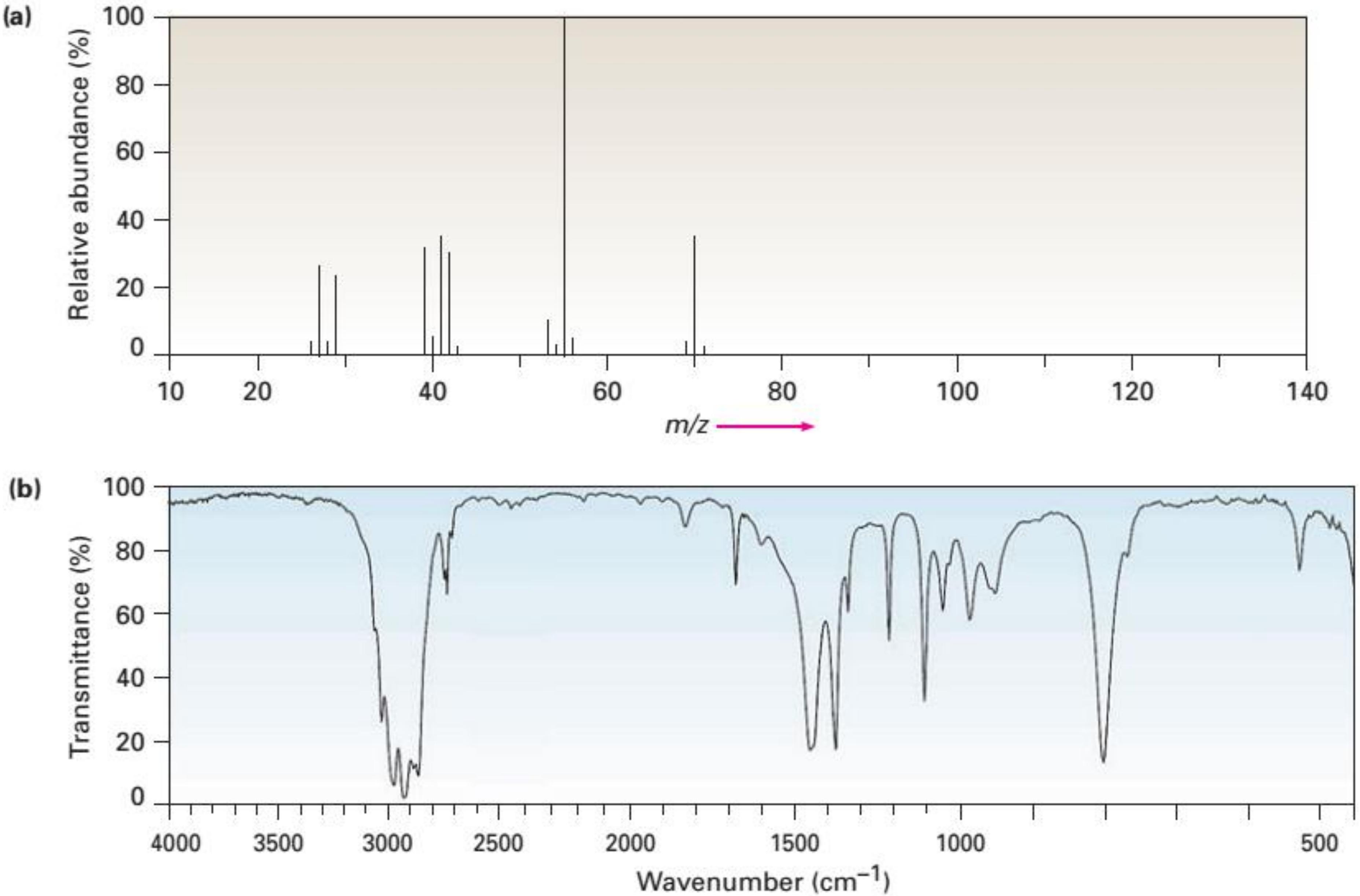
Reprinted with permission of Aldrich Chemical Co., Inc.

12.41 The **(a)** mass spectrum and the **(b)** infrared spectrum of an unknown hydrocarbon are shown. Propose as many structures as you can.





12.42 The **(a)** mass spectrum and the **(b)** infrared spectrum of another unknown hydrocarbon are shown. Propose as many structures as you can.



Chapter 6

Part II

Nuclear Magnetic Resonance Spectroscopy

Introduction

- **Nuclear magnetic resonance spectroscopy (NMR)** is the most powerful tool available for organic structure determination.
- Like infrared spectroscopy, NMR can be used with a very small sample, and it does not harm the sample.
- The NMR spectrum provides a great deal of information about the structure of the compound, and many structures can be determined using only the NMR spectrum.
- More commonly, however, NMR spectroscopy is used in conjunction with other forms of spectroscopy and chemical analysis to determine the structures of complicated organic molecules.
- NMR is used to study a wide variety of nuclei, including and ^{1}H, ^{13}C, ^{15}N, ^{19}F, and ^{31}P. Organic chemists find **proton (^{1}H)** and **carbon-13 (^{13}C)** to be most useful because hydrogen and carbon are major components of organic compounds.

Introduction

Photo of a modern 300-MHz NMR spectrometer:

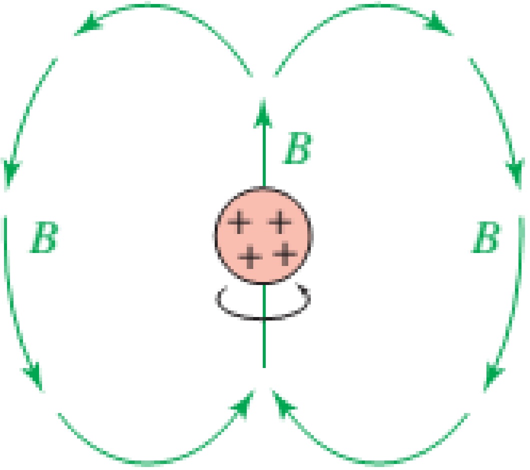
+ The metal container at right contains the superconducting magnet, cooled by a liquid helium bath inside a liquid nitrogen bath.

+ The electronics used to control the spectrometer and to calculate spectra are at left and in the background.

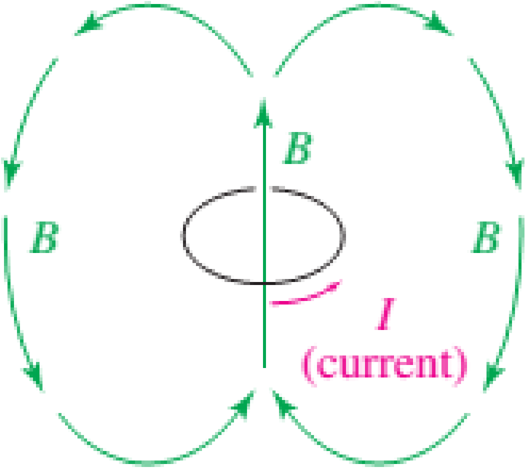
Theory of nuclear magnetic resonance

➢ A nucleus with an odd atomic number or an odd mass number has a *nuclear spin* that can be observed by the NMR spectrometer.

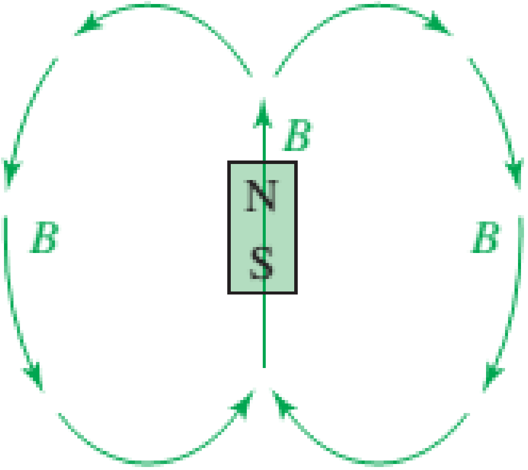
➢ We can visualize a spinning proton as a rotating sphere of positive charge. This movement of charge is like an electric current in a loop of wire. It generates a magnetic field (symbolized by *B*), called the **magnetic moment,** that looks like the field of a small bar magnet.



spinning proton



loop of current



bar magnet

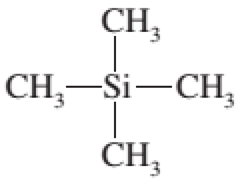
The chemical shifts

- The variations in the positions of NMR absorptions, arising from electronic shielding and deshielding, are called **chemical shifts.**

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

- In practice, it is difficult to measure the absolute field where a proton absorbs with enough accuracy to distinguish individual protons.
- A more accurate method for expressing chemical shifts is to determine the value relative to a reference compound added to the sample.
- The *difference* in the magnetic field strength between the resonances of the sample protons and the reference protons can be measured very accurately.

- The most common NMR reference compound is *tetramethylsilane* abbreviated **TMS.** Because silicon is less electronegative than carbon, the methyl groups of TMS are relatively electron-rich, and their protons are well shielded. They absorb at a higher field strength than most hydrogens bonded to carbon or other elements, so most NMR signals appear *downfield* (to the left, *deshielded*) of the TMS signal. All 12 protons in TMS absorb at exactly the same applied magnetic field, giving one strong absorption.



tetramethylsilane (TMS)

The chemical shift

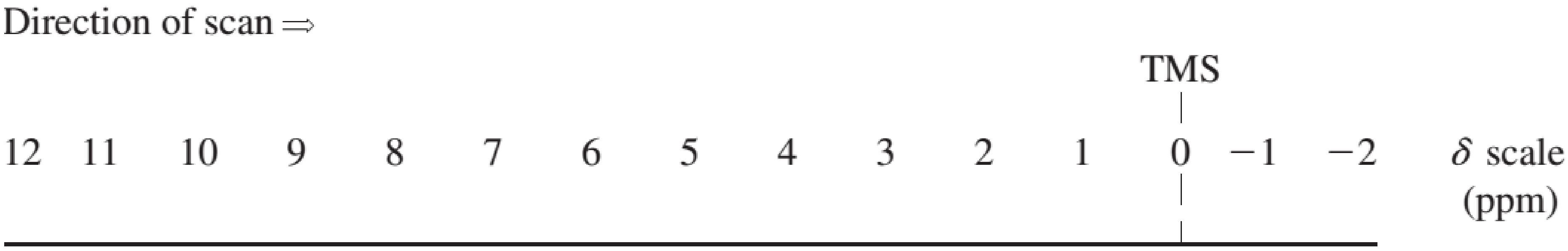
- A small amount of TMS is added to the sample, and the instrument measures the difference in magnetic field between where the protons in the sample absorb and where those in TMS absorb. For each type of proton, the distance downfield of TMS is the chemical shift of those protons.

- Chemical shifts are measured in *parts per million* (ppm).
- A chemical shift in parts per million can be calculated by dividing the shift measured in hertz by the spectrometer frequency measured in millions of hertz (megahertz or MHz).

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

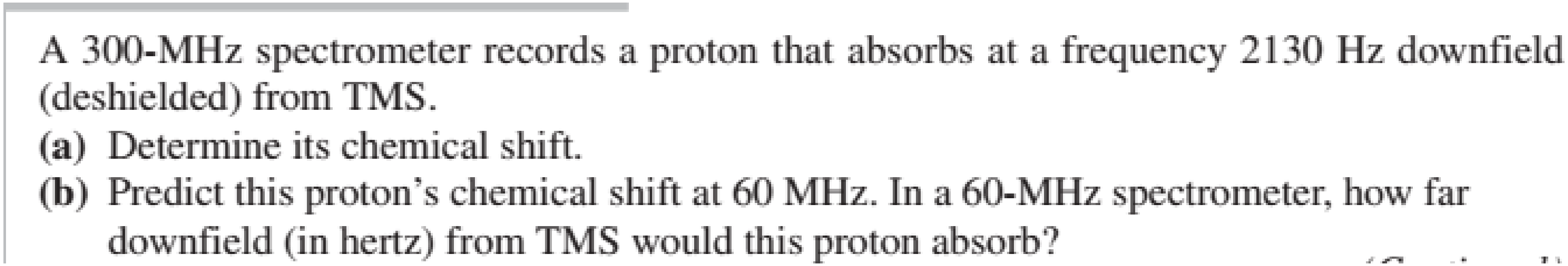
The chemical shift

- ➢ By agreement, most workers report chemical shifts in **delta (δ) units,** or **parts per million (ppm),** of the main spectrometer frequency. On this scale, the resonance of the protons in TMS comes at exactly 0.00 ppm (by definition).
- ➢ The NMR spectrometer actually scans from high values to low ones.
- ➢ Following is a typical chemical shift scale with the sequence of values that would be found on a typical NMR spectrum chart.



- ➢ The signal from tetramethylsilane (TMS) is *defined* as 0.00 ppm on the δ scale. Most protons are more deshielded than TMS, so the δ scale increases toward the left of the spectrum..

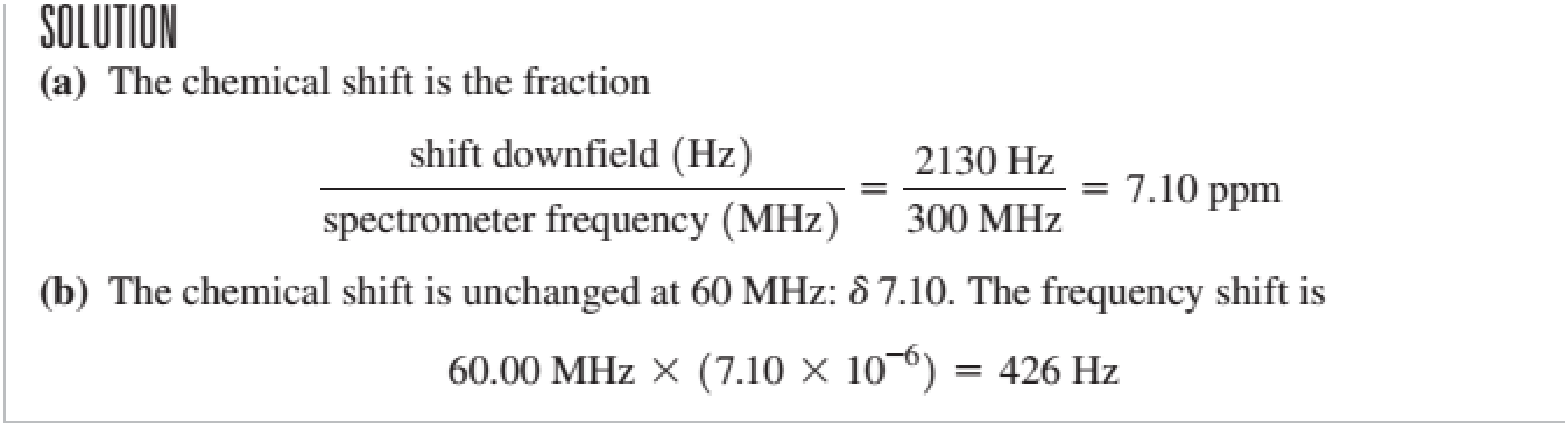
The chemical shift



A 300-MHz spectrometer records a proton that absorbs at a frequency 2130 Hz downfield (deshielded) from TMS.

(a) Determine its chemical shift.

(b) Predict this proton's chemical shift at 60 MHz. In a 60-MHz spectrometer, how far downfield (in hertz) from TMS would this proton absorb?



SOLUTION

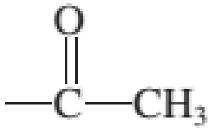
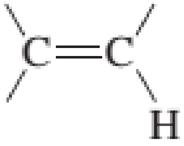
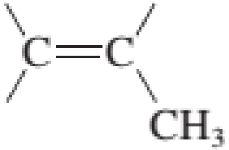
(a) The chemical shift is the fraction

$$\frac{\text{shift downfield (Hz)}}{\text{spectrometer frequency (MHz)}} = \frac{2130\ \text{Hz}}{300\ \text{MHz}} = 7.10\ \text{ppm}$$

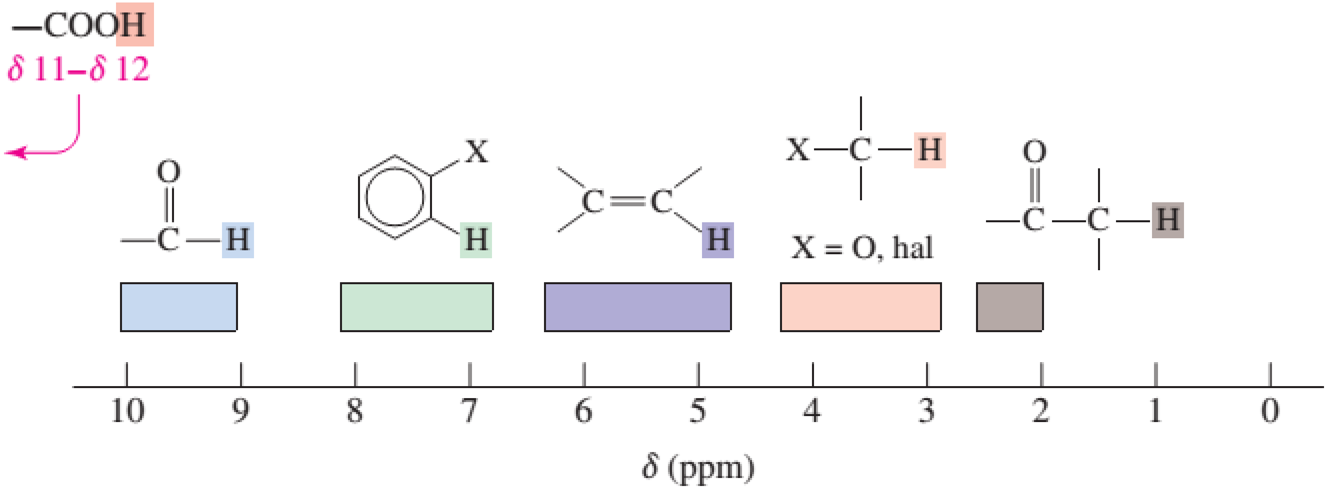
(b) The chemical shift is unchanged at 60 MHz: δ 7.10. The frequency shift is

$$60.00\ \text{MHz} \times (7.10 \times 10^{-6}) = 426\ \text{Hz}$$

Typical Values of Proton NMR Chemical Shifts

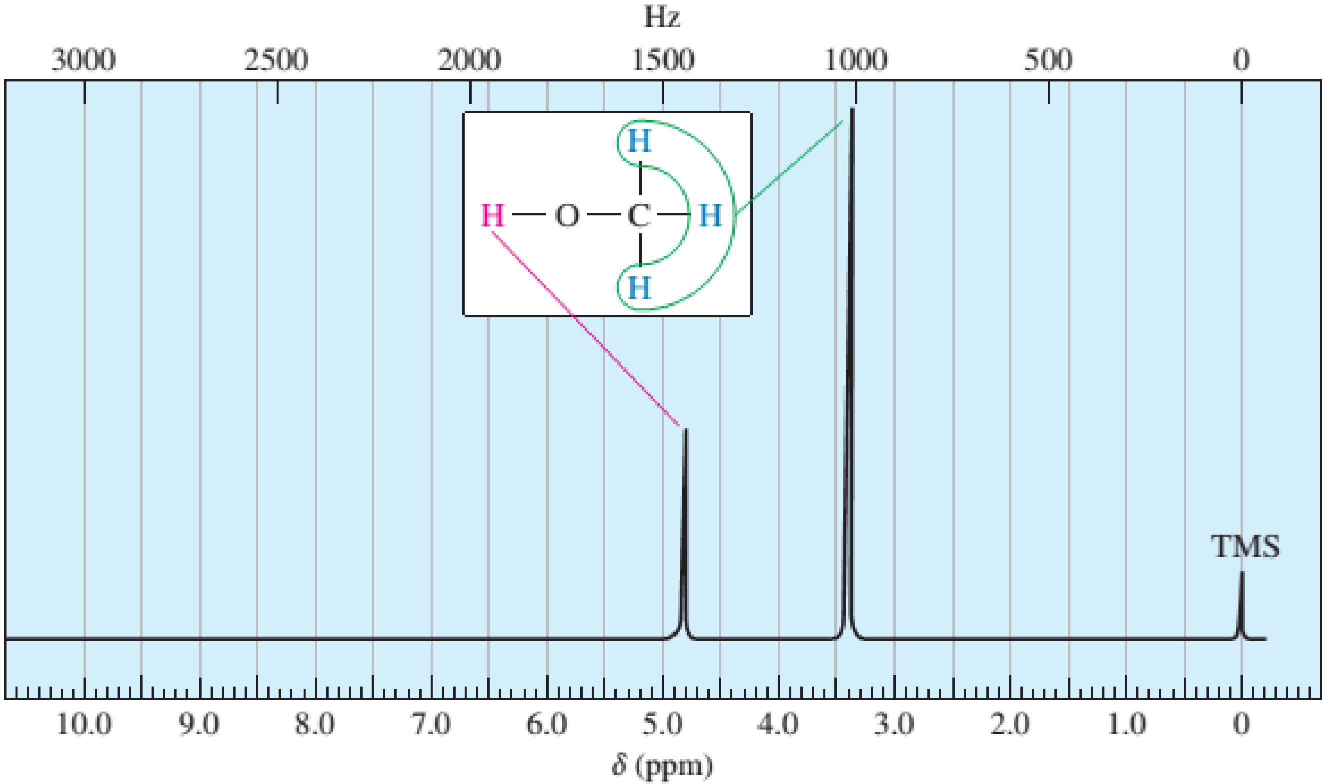
Type of Proton		**Approximate δ**
alkane $(-CH_3)$	methyl	0.9
alkane $(-CH_2-)$	methylene	1.3
alkane $(-\underset{\vert}{CH}-)$	methine	1.4
 $-\overset{O}{\overset{\Vert}{C}}-CH_3$	methyl ketone	2.1
$-C\equiv C-H$	acetylenic	2.5
$R-CH_2-X$	(X = halogen, —O—)	3–4
	vinyl	5–6
	allylic	1.7
Ph—H	aromatic	7.2
$Ph-CH_3$	benzylic	2.3
R—CHO	aldehyde	9–10
R—COOH	acid	10–12
R—OH	alcohol	variable, about 2–5
Ar—OH	phenol	variable, about 4–7
$R-NH_2$	amine	variable, about 1.5–4

These hints are neither exact nor complete. They are simple methods for making educated guesses about the major features of a compound from its NMR spectrum. The hints can be used to draw partial structures to examine all the possible ways they might be combined to give a molecule that corresponds with the spectrum. The figure below gives a graphic presentation of some of the most common chemical shifts.



The chemical shift

- ➢ The NMR spectrum of methanol shows the two signals from methanol together with the TMS reference peak at δ 0.0 ppm. The methyl protons absorbs father downfield; its chemical shift is 3.4 ppm, so we say that the methyl protons absorb at δ 3.4 ppm. The chemical shift of the hydroxyl proton is δ 4.8 ppm.
- ➢ Both the hydroxyl proton and the methyl protons of methanol show the deshielding effects of the electronegative oxygen atom. The chemical shift of a methyl group in an alkane is about δ 0.9.
- ➢ Other electronegative atoms produce similar deshielding effects.



The chemical shift

- The effect of an electronegative group on the chemical shift also depends on its distance from the protons. In methanol, the hydroxyl proton is separated from oxygen by one bond, and its chemical shift is δ 4.8.
- The methyl protons are separated from oxygen by two bonds, and their chemical shift is is δ 3.4.
- **In general, the effect of an electron-withdrawing substituent decreases with increasing distance, and the effects are usually negligible on protons that are separated from the electronegative group by four or more bonds.**

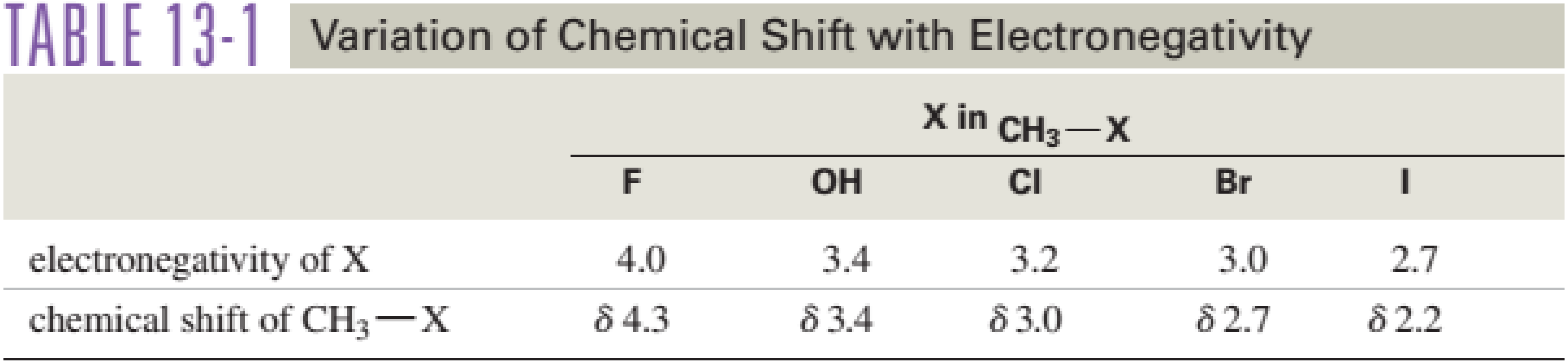
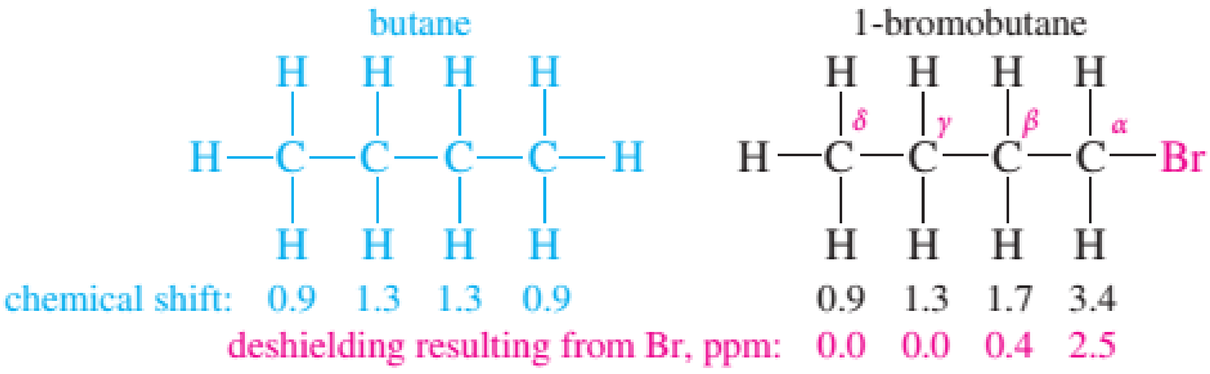


TABLE 13-1 Variation of Chemical Shift with Electronegativity

	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

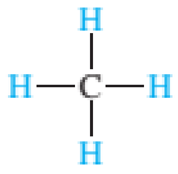
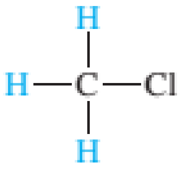
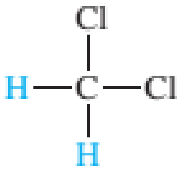
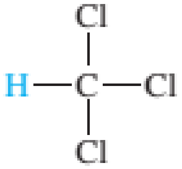
The chemical shift

- The deshielding effect of an electronegative substituent drops off rapidly with distance. In 1-bromobutane, protons on the α are deshielded by about 2.5 ppm, and the β protons are deshielded by about 0.4 ppm.
- Protons that are more distant than the are deshielded by a negligible amount.



- If more than one electron-withdrawing group is present, the deshielding effects are nearly additive.

TABLE 13-2 Chemical Shifts of the Chloromethanes

Compound	Chemical Shift	Difference
	δ 0.2	
	δ 3.0	2.8 ppm
	δ 5.3	2.3 ppm
	δ 7.2	1.9 ppm

Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by 2 to 3 ppm. These changes are nearly additive.

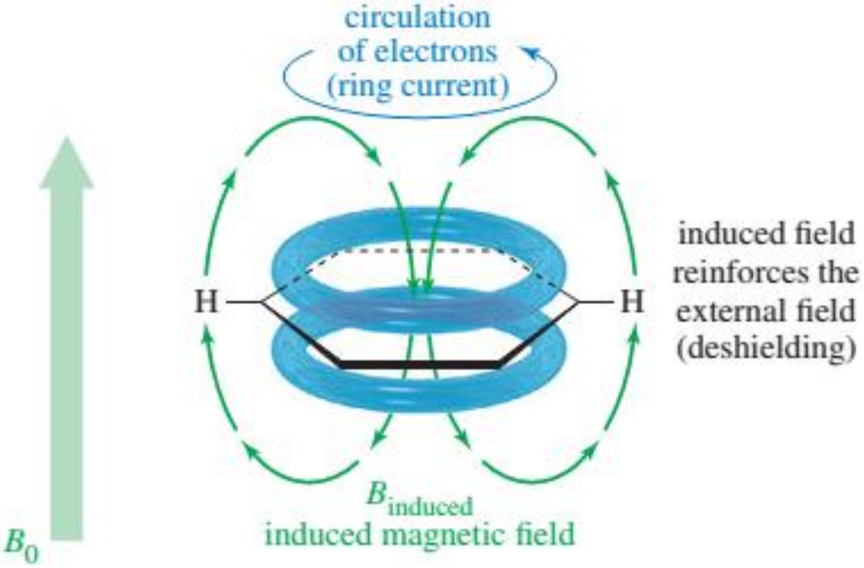
Vinyl and Aromatic Protons

➢ Double bonds and aromatic rings produce large deshielding effects on their vinyl and aromatic protons.

➢ These deshielding effects result from the circulation of electrons that normally shields nuclei from the magnetic field. In benzene and its derivatives, the aromatic ring of pi bonding electrons acts as a conductor, and the external magnetic field induces a *ring current*:

+ At the center of the ring, the induced field acts to oppose the external field. On the edge of the ring the induced field ***adds*** *to* the external field. As a result, the aromatic protons are strongly ***deshielded***, resulting in a large chemical shift.

+ Benzene absorbs at δ 7.2 ppm, and most aromatic protons absorb in the range of δ 7 ppm to δ 8 ppm.

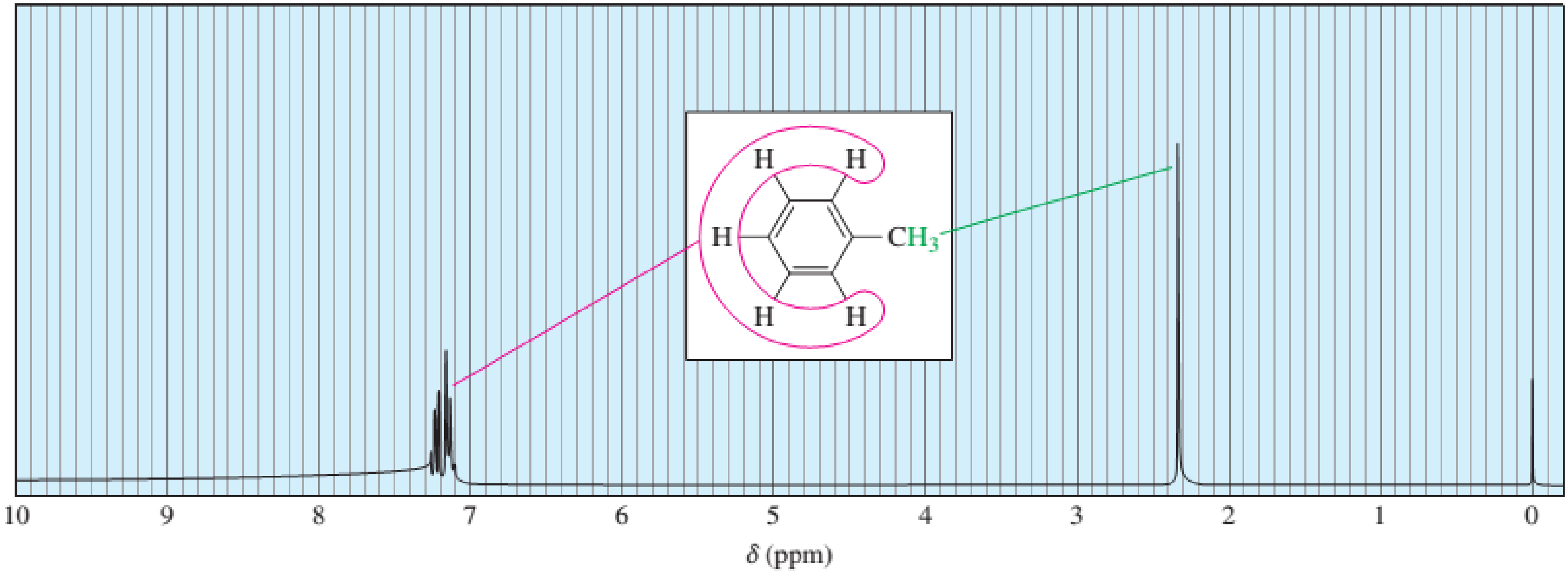


Vinyl and aromatic protons

- NMR spectrum of toluene:

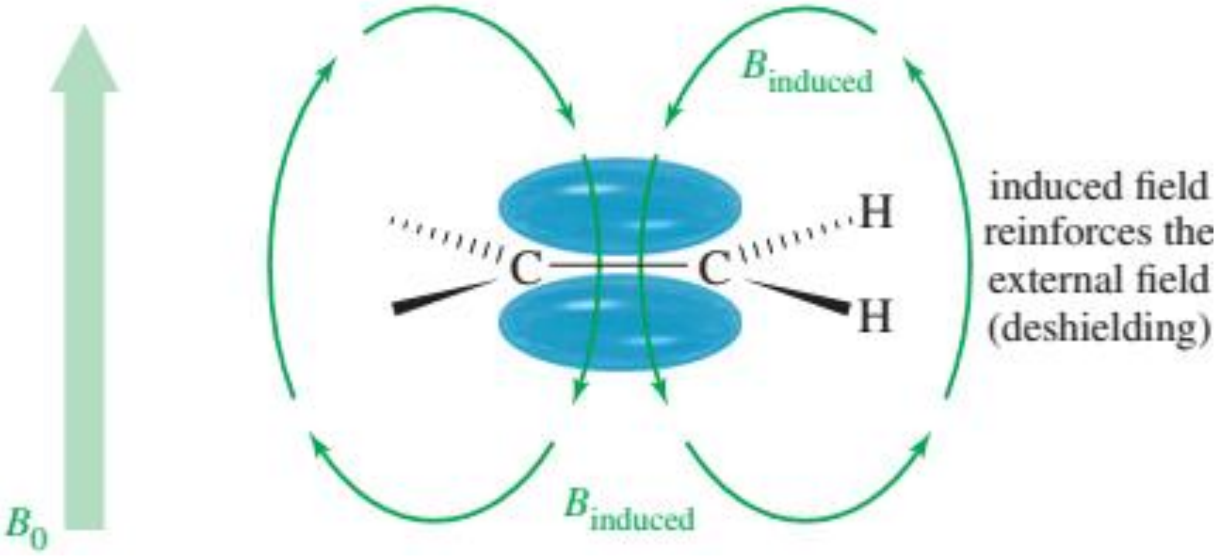
+ The aromatic protons absorb around δ 7.2 ppm.

+ The methyl protons are deshielded by a smaller amount, absorbing at δ 2.3 ppm.



Measurements of IR spectrum

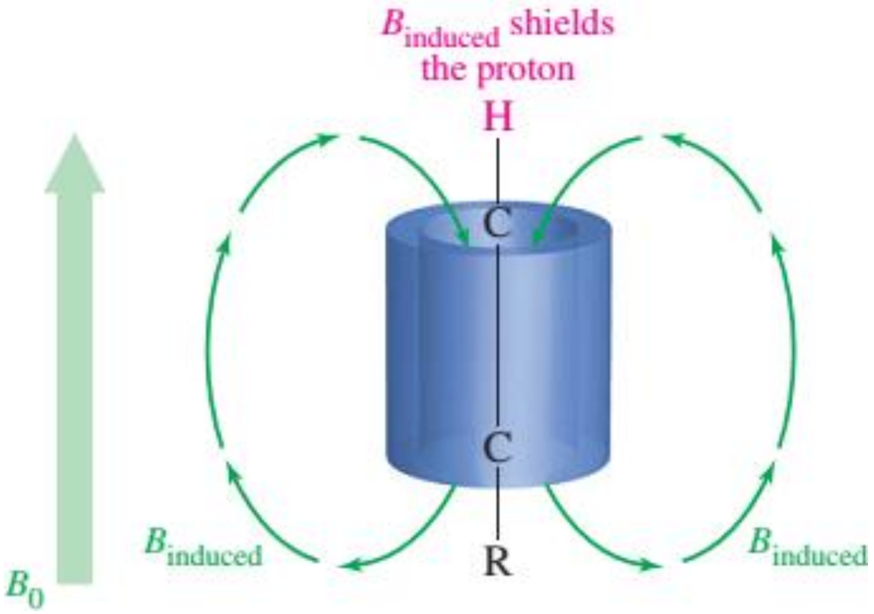
- The pi electrons of an alkene deshield the vinyl protons in the same way that an aromatic ring of electrons deshields the aromatic protons.
- The effect is not as large in the alkene because there is not such a large, effective ring of electrons as there is in benzene.
- As a result of this deshielding effect, most vinyl protons absorb in the range of δ 5 ppm to δ 6 ppm.



induced field reinforces the external field (deshielding)

Acetylenic Hydrogens

- Since the pi bond of an alkene deshields the vinyl protons, we might expect an acetylenic hydrogen -C≡C-H) to be even more deshielded by the two pi bonds of the triple bond.
- The opposite is true: Acetylenic hydrogens absorb around δ 2.5 compared with δ 5 ppm to δ 6 ppm for vinyl protons.
- The triple bond has a cylinder of electron density surrounding the sigma bond. The acetylenic proton lies along the *axis* of this induced field, which is a shielded region.

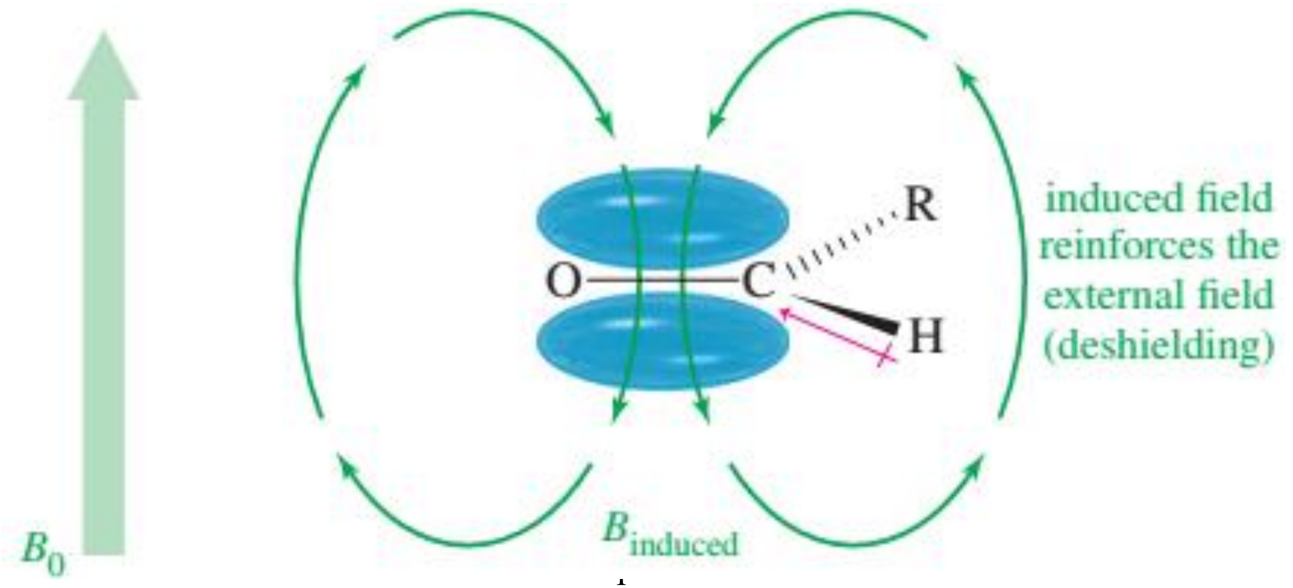


Aldehyde Protons

- Aldehyde protons (-CHO) absorb at even lower fields than vinyl protons and aromatic protons: between δ 9 ppm and δ 10 ppm.
- The aldehyde proton is deshielded both by:

+ the circulation of the electrons in the double bond

+ and by the inductive electron-withdrawing effect of the carbonyl oxygen atom.



Hydrogen-Bonded Protons

➢ The chemical shifts of O-H protons in alcohols and N-H protons in amines depend on the concentration.

+ In concentrated solutions, these protons are deshielded by hydrogen bonding, and they absorb at a relatively low field: about δ 3.5 ppm for an amine and about δ 4.5 ppm for an alcohol.

+ When the alcohol or amine is diluted with a non-hydrogen-bonding solvent such as CCl_4, hydrogen bonding becomes less important. In dilute solutions, these signals are observed around δ 2 ppm.

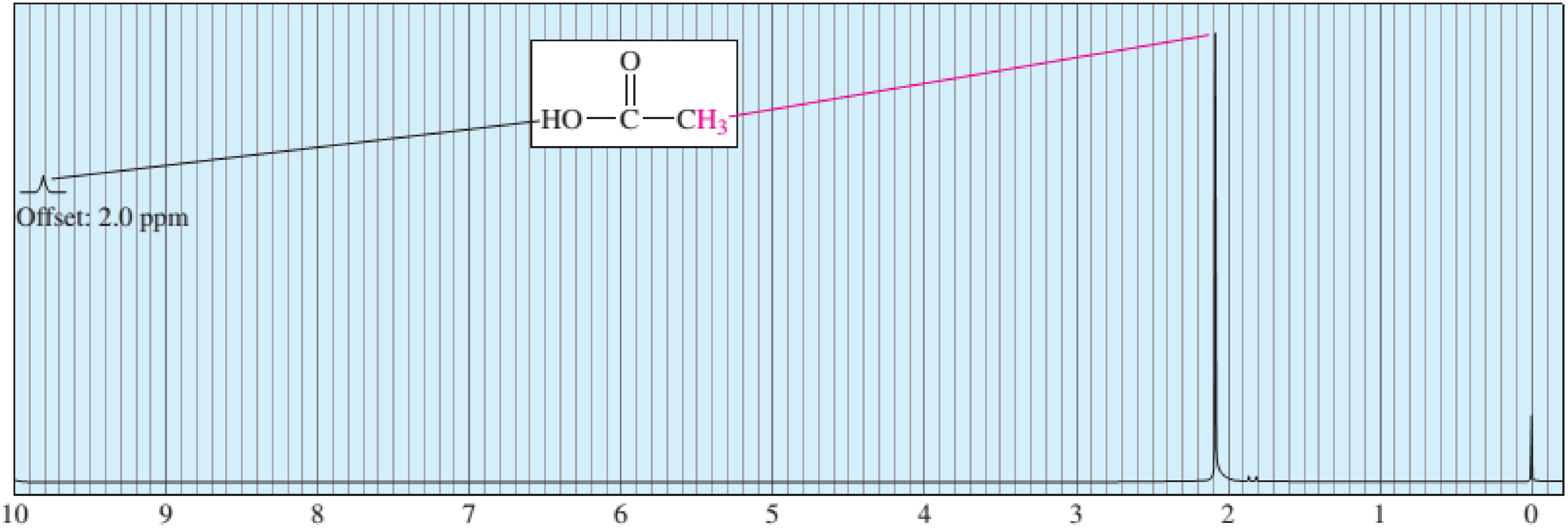
➢ Hydrogen bonding and the proton exchange that accompanies it may contribute to a broadening of the peak from an or proton. A broad peak appears because protons exchange from one molecule to another during the NMR resonance. The protons pass through a variety of environments during this exchange, absorbing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

Carboxylic acid protons

- Because carboxylic acid protons are bonded to an oxygen next to a carbonyl group, they have considerable positive character.
- They are strongly deshielded and absorb at chemical shifts greater than δ 11.8 ppm.
- The proton NMR spectrum of acetic acid.

+ The methyl group next to the carbonyl absorbs at a chemical shift of δ 2.1 ppm.

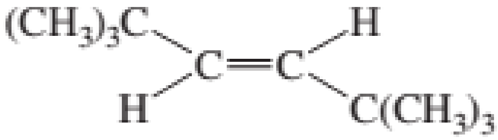
+ The acid proton appears around δ 11.8 ppm.



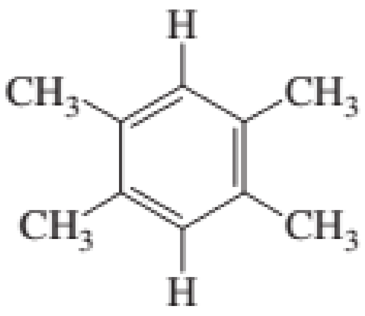
PROBLEM 13-2

Predict the chemical shifts of the protons in the following compounds.

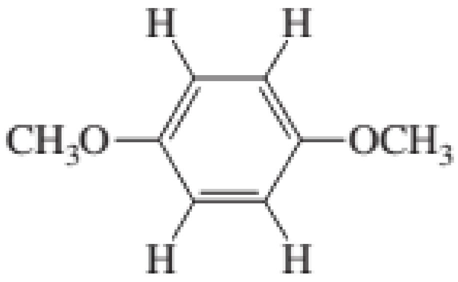
(a)



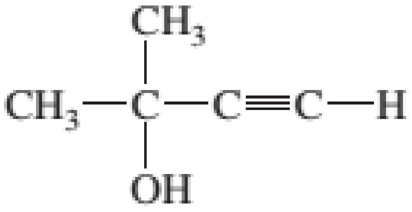
(b)



(c)

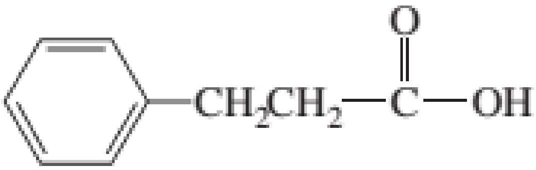


(d)

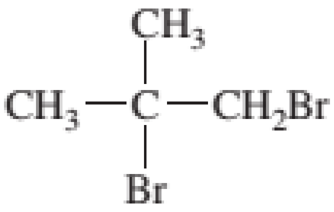


$CH_3-\overset{CH_3}{\underset{OH}{C}}-C\equiv C-H$

(e)



(f)



$CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2Br$

Chemically equivalent protons

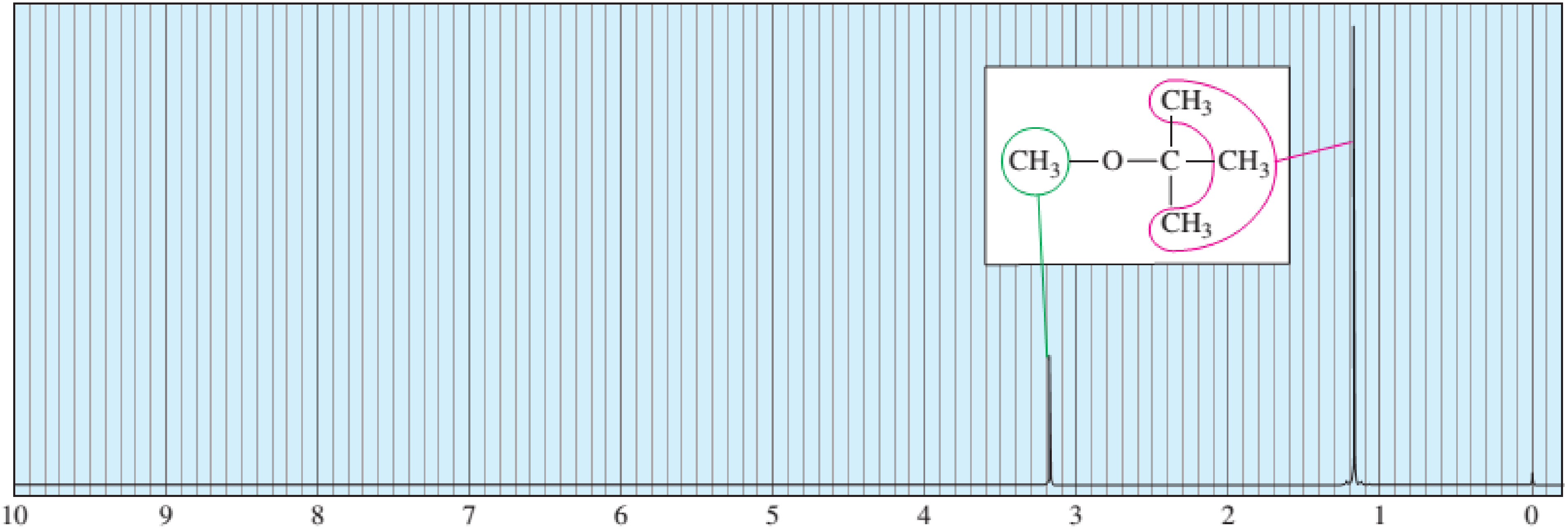
- Protons in identical chemical environments with the same shielding have the same chemical shift. Such protons are said to be **chemically equivalent.**
- This is what is meant whenever we use the term *equivalent* in discussing NMR spectroscopy. In methyl *tert*-butyl ether, the three methoxy protons are chemically equivalent, and the nine *tert*-butyl protons are chemically equivalent.

The number of signals

- In general, the number of NMR signals corresponds to the number of different kinds of protons present in the molecule.
- For example, methyl *tert*-butyl ether has two types of protons:

+ The three methoxy protons are chemically identical, and they give rise to a single absorption at δ 3.2 ppm.

+ The *tert*-butyl protons are chemically different from the methoxy protons, absorbing at δ 1.2.



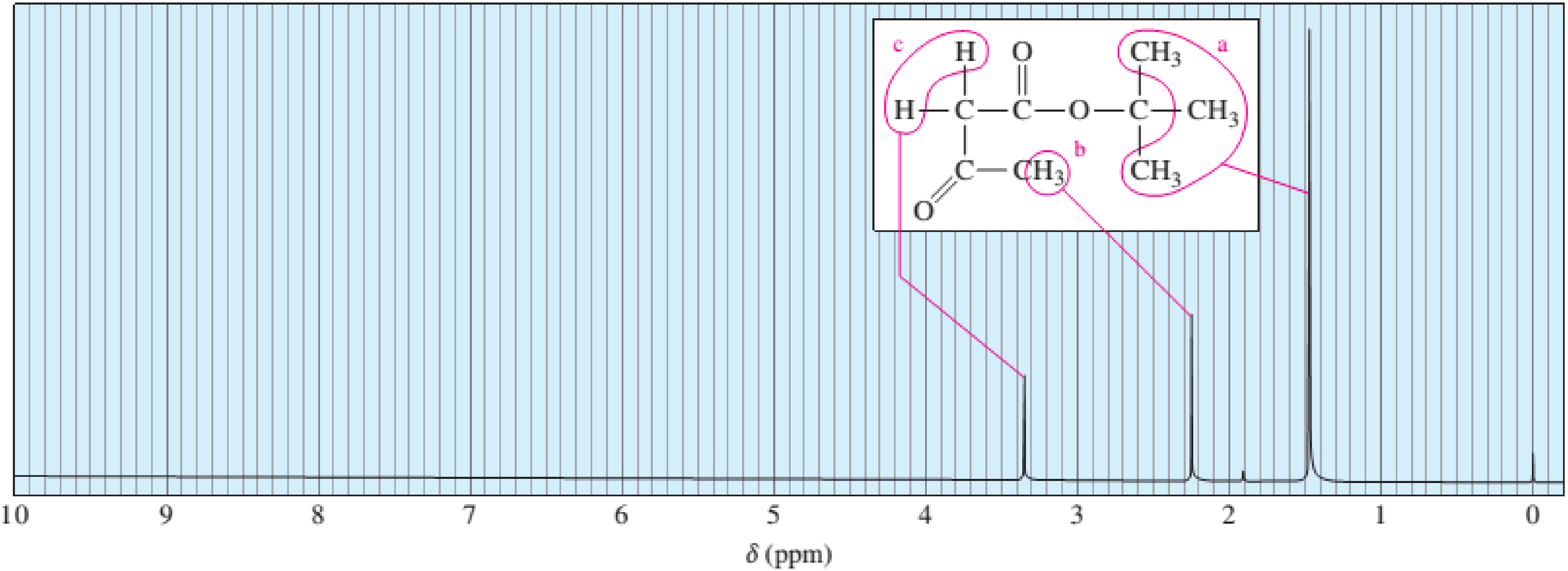
The number of signals

- The spectrum of *tert*-butyl acetoacetate shows three types of protons:

\+ the *tert*-butyl protons (*a*), with a chemical shift of δ 1.5 ppm;

\+ the methyl protons (*b*), deshielded by an adjacent carbonyl group, with a chemical shift of δ 2.25 ppm;

\+ and the methylene protons (*c*), deshielded by two adjacent carbonyl groups, at δ 3.35.



Chemically equivalent protons

- ➢ In some cases, there may be fewer signals in the NMR spectrum than there are different types of protons in the molecule.
- ➢ Spectrum of *o*-xylene (1,2-dimethylbenzene):

\+ There are **three** different types of protons, labeled *a* for the two equivalent methyl groups, *b* for the protons adjacent to the methyl groups, and *c* for the protons two carbons removed.

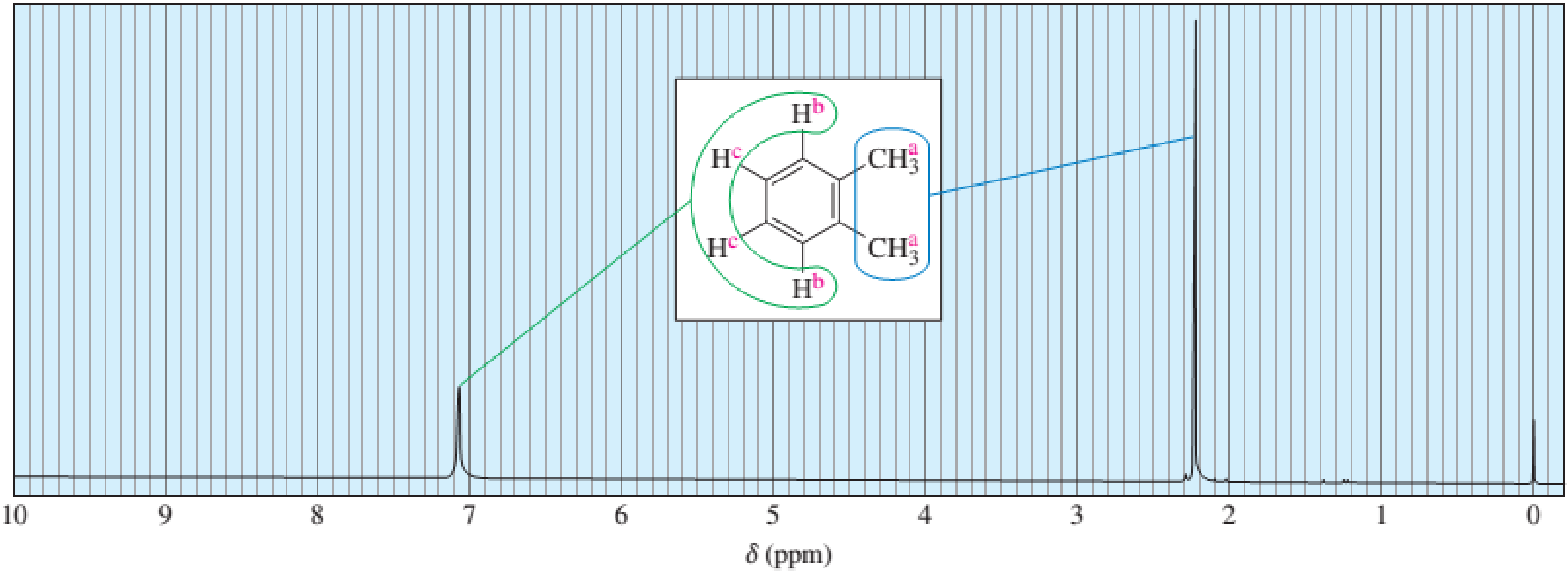
\+ However, the spectrum shows only **two** distinct signals,.

\+ The upfield signal at δ 2.3 ppm corresponds to the six methyl protons, H^a.

\+ The absorption at δ 7.1 ppm corresponds to all four of the aromatic protons, H^b and H^c.

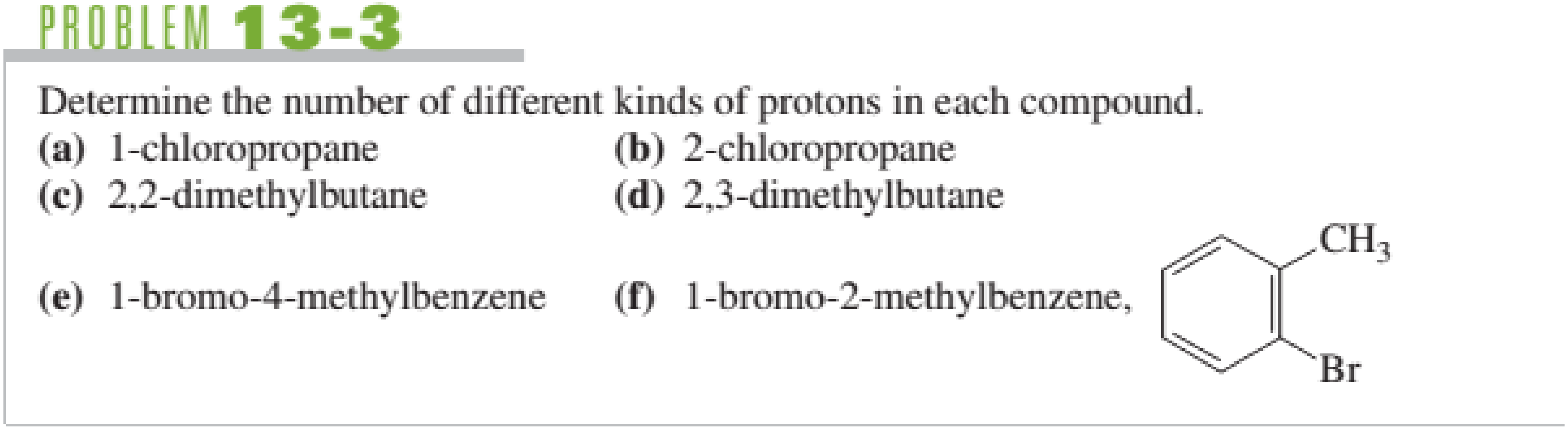
\+ The aromatic protons produce two signals, but these signals happen to occur at nearly the same chemical shift. Protons that are not chemically equivalent but happen to absorb at the same chemical shift are said to be **accidentally equivalent.**

Chemically equivalent protons



Proton NMR spectrum of *o*-xylene. There are three types of protons in *o*-xylene, but only two absorptions are seen in the spectrum. The aromatic protons H^b and H^c are accidentally equivalent, producing a broadened peak at δ 7.1 ppm

Chemically equivalent protons



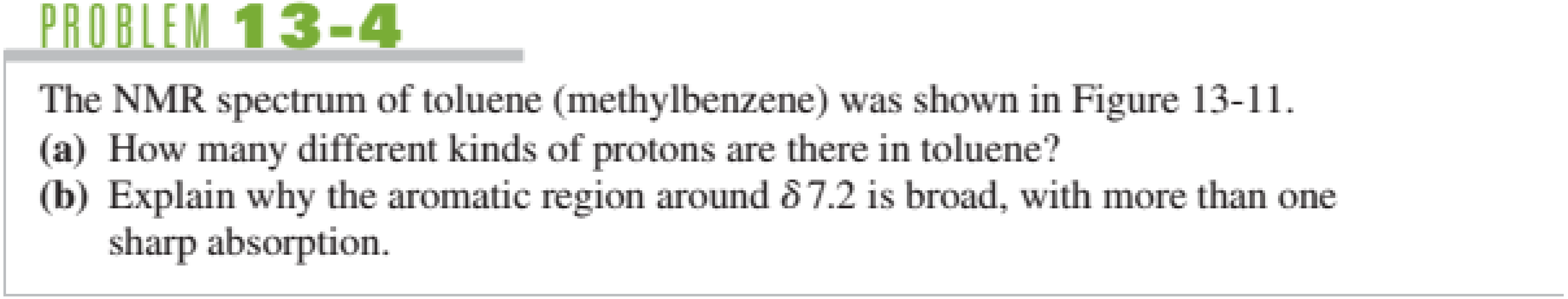
PROBLEM 13-3

Determine the number of different kinds of protons in each compound.

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

(c) 2,2-dimethylbutane **(d)** 2,3-dimethylbutane

(e) 1-bromo-4-methylbenzene **(f)** 1-bromo-2-methylbenzene,



PROBLEM 13-4

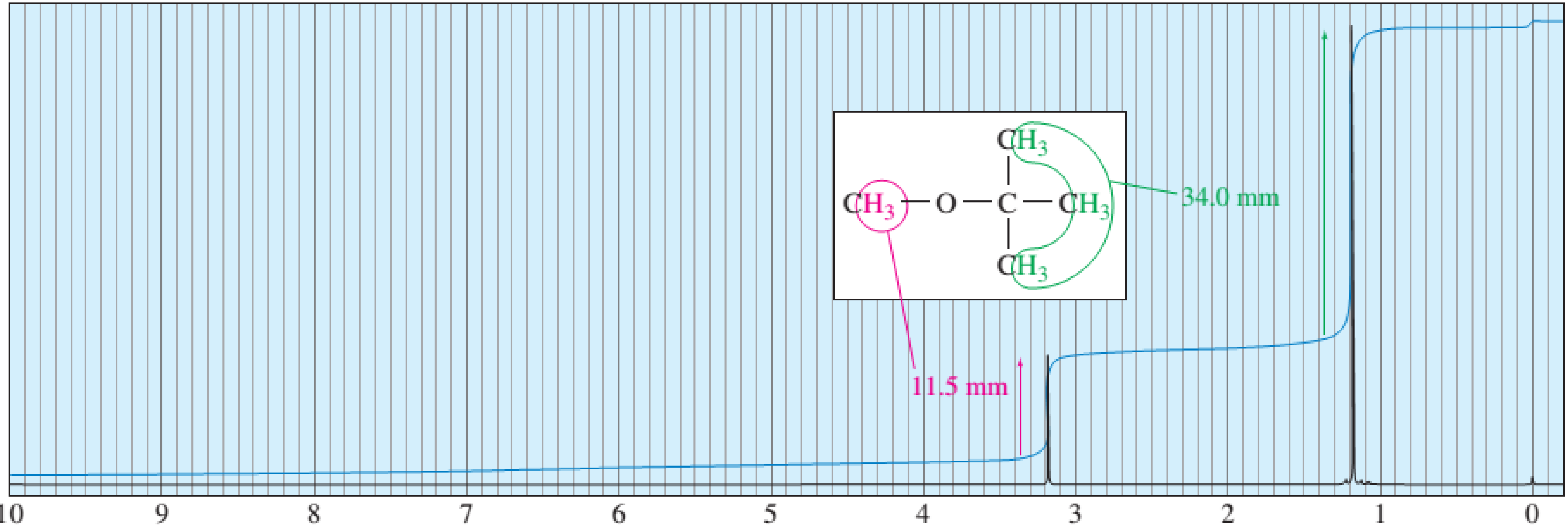
The NMR spectrum of toluene (methylbenzene) was shown in Figure 13-11.

(a) How many different kinds of protons are there in toluene?

(b) Explain why the aromatic region around δ 7.2 is broad, with more than one sharp absorption.

Areas of the peaks

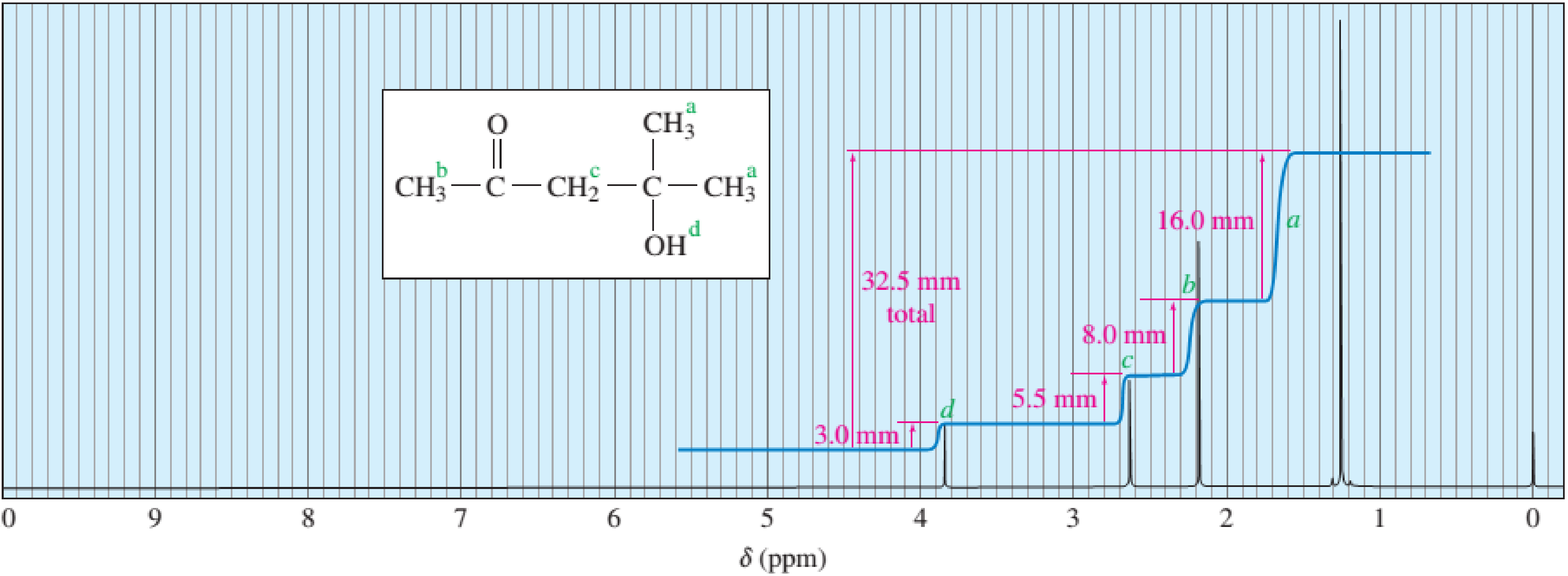
- *The area under a peak is proportional to the number of hydrogens contributing to that peak*.
- For example, in the methyl *tert*-butyl ether spectrum, the absorption of the *tert*-butyl protons is larger than that of the methoxy protons because there are three times as many *tert*-butyl protons as methoxy protons.
- We cannot simply compare peak heights. NMR spectrometers have **integrators** that compute the **relative areas** of peaks. The integrator draws a integral trace that rises when it goes over a peak. The amount the integral trace rises is proportional to the area of that peak. You can measure these integrals using a millimeter ruler.
- Newer digital instruments also print a number representing the area of each peak.

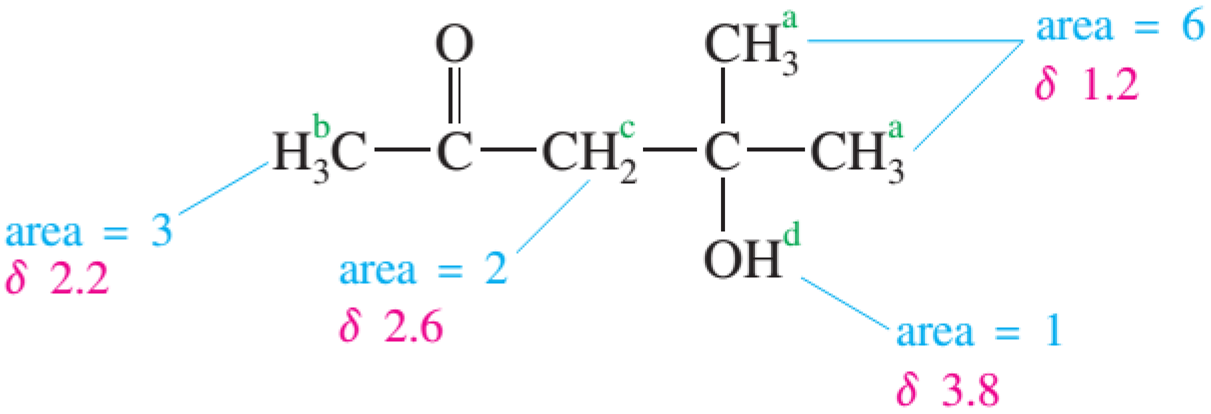


Areas of the peaks

- Neither an integral trace nor a digital integral can specifically indicate that methyl *tert*-butyl ether has three methyl hydrogens and nine *tert*-butyl hydrogens.
- Each simply shows that about three times as many hydrogens are represented by the peak at δ 1.2 ppm as are represented by the peak at δ 3.2 ppm. We must interpret what the **3 : 1** ratio means in terms of the structure.

Areas of the peaks



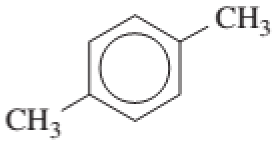


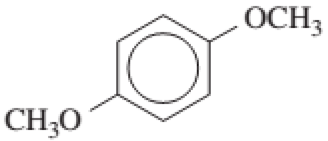
PROBLEM 13-5

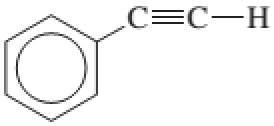
Draw the integral trace expected for the NMR spectrum of *tert*-butyl acetoacetate, shown in Figure 13-17.

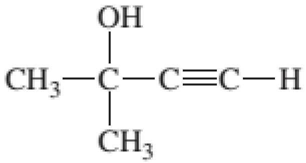
PROBLEM 13-6

Determine the ratios of the peak areas in the following spectra. Then use this information, together with the chemical shifts, to pair up the compounds with their spectra. Assign the peaks in each spectrum to the protons they represent in the molecular structure. Possible structures:

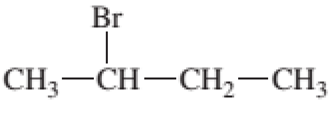




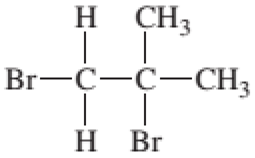




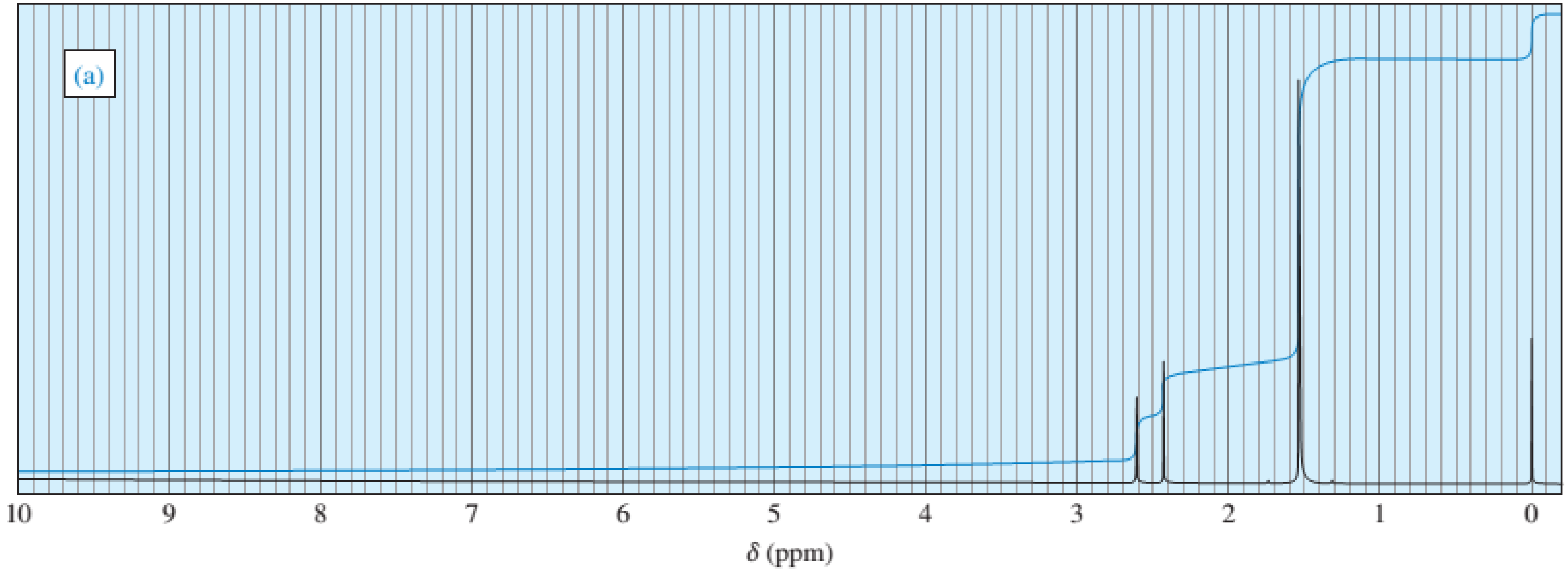
$$CH_3-C(OH)(CH_3)-C\equiv C-H$$



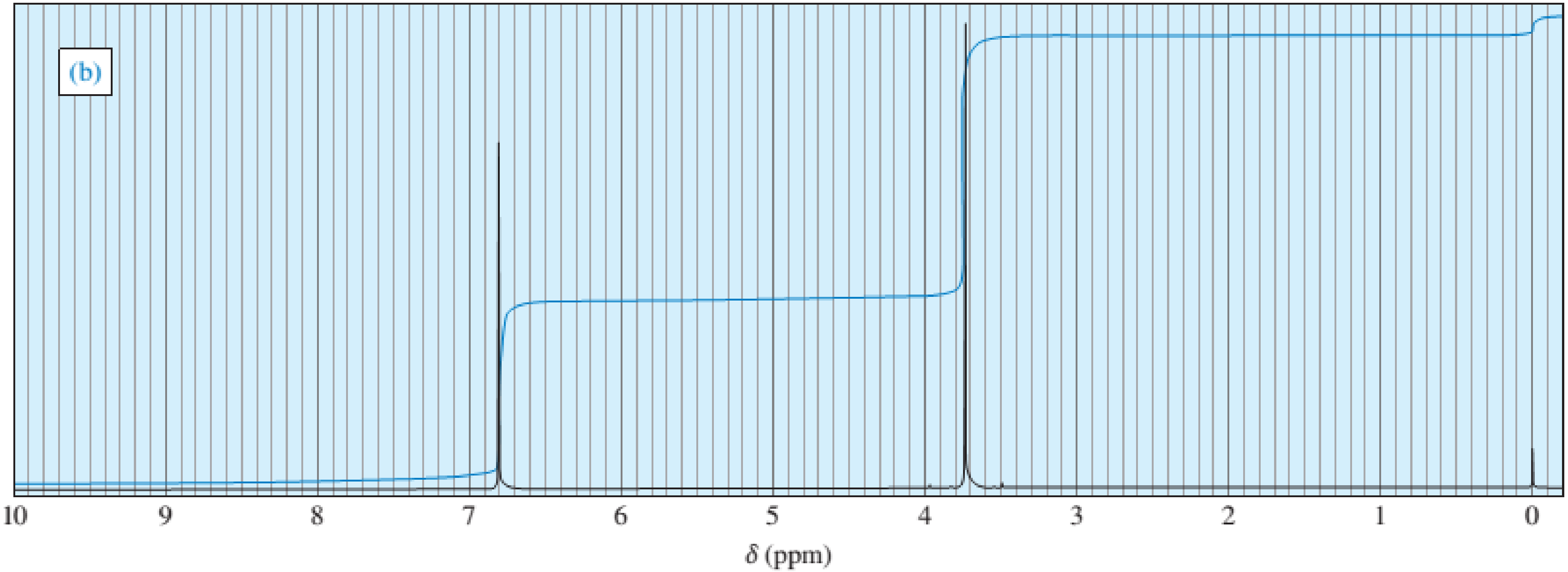
$$CH_3-CH(Br)-CH_2-CH_3$$

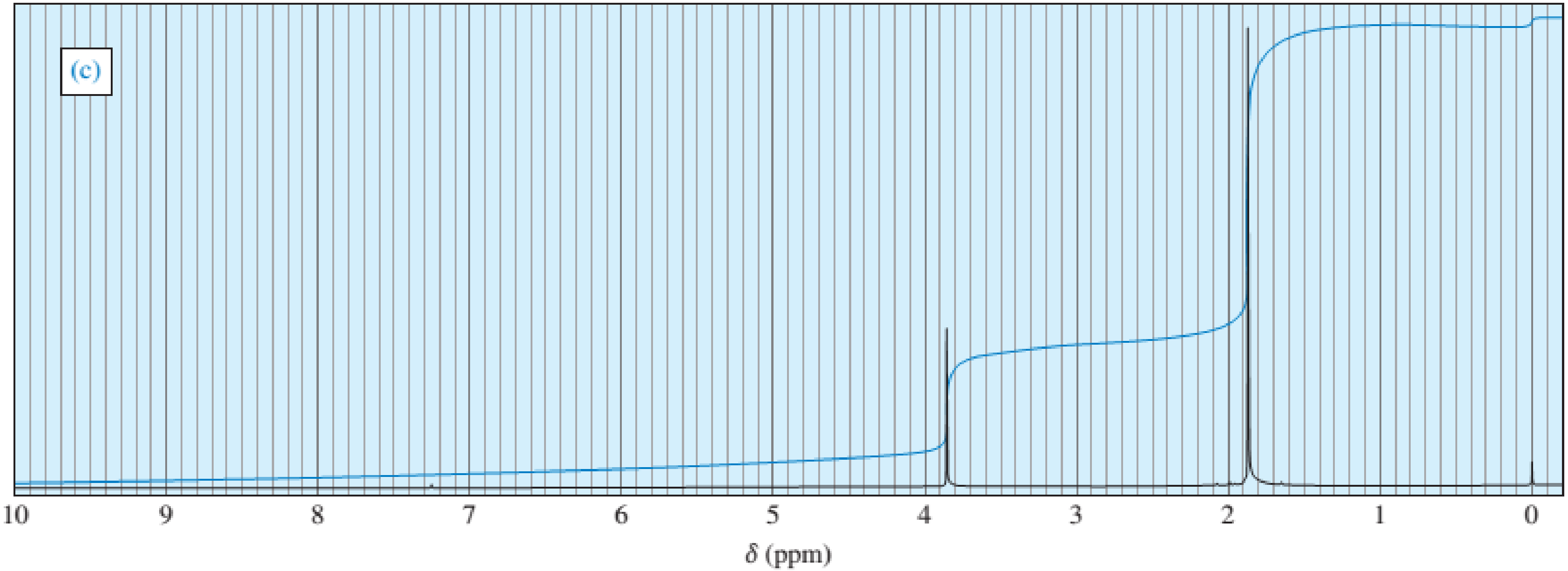


$$Br-CH_2-C(CH_3)(Br)-CH_3$$



Problems 13-6



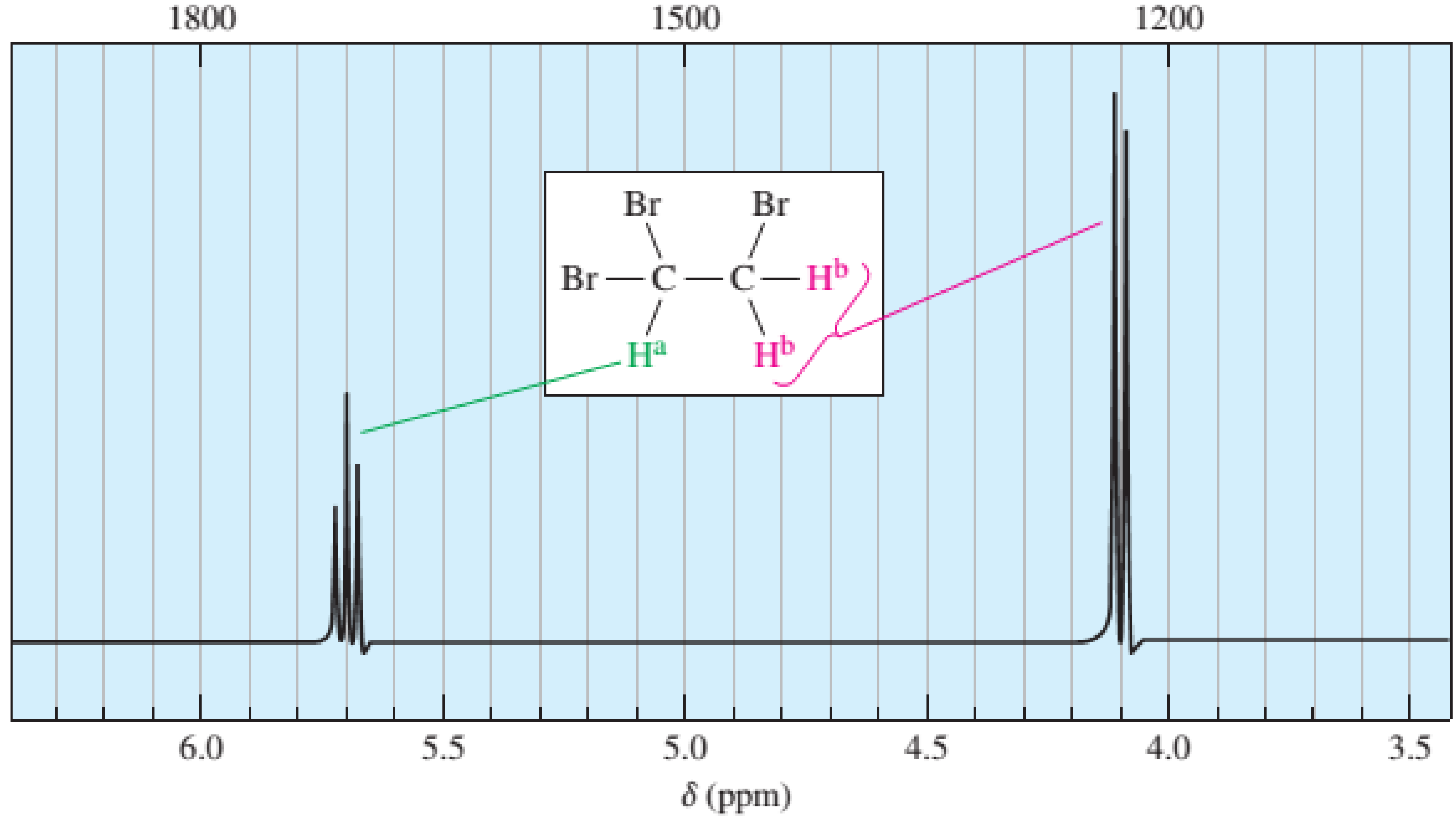


Spin-spin splitting

- A proton in the NMR spectrometer is subjected to both the external magnetic field and the induced field of the shielding electrons. If there are other protons nearby, their small magnetic fields also affect the absorption frequencies of the protons we are observing.
- Consider the spectrum of 1,1,2-tribromoethane.

+ There are two signals with areas in the ratio of 1 : 2.
+ The smaller signal (H^a) appears at δ 5.7 ppm, deshielded by the two adjacent bromine atoms.
+ The larger signal (H^b) appears at δ 4.1 ppm.

- These signals do not appear as single peaks but as a triplet (three peaks) and a doublet (two peaks), respectively.
- This splitting of signals into multiplets, called **spin-spin splitting,** results when two different types of protons are close enough that their magnetic fields influence each other.
- Such protons are said to be **magnetically coupled**.



The proton NMR spectrum of 1,1,2-tribromoethane shows a triplet of area 1 at and a δ 5.7 (-$CHBr_2$) and a doublet of area 2 at δ 4.1 (-CH_2Br).

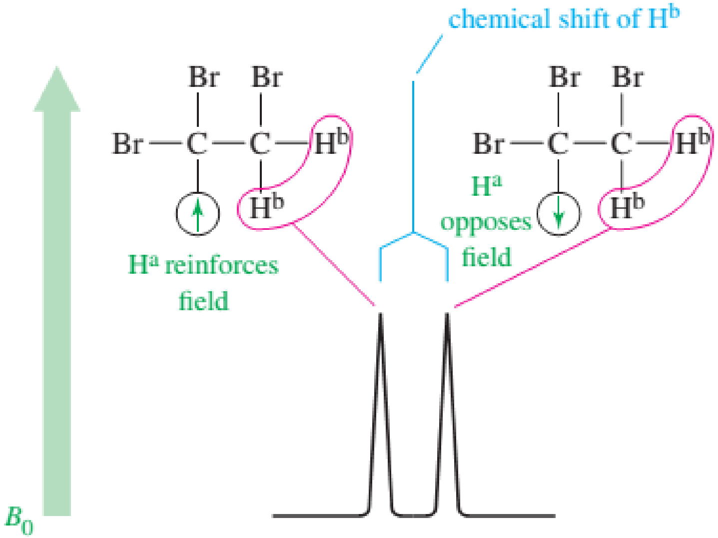
- ➢ Spin-spin splitting can be explained by considering the individual spins of the magnetically coupled protons.

+ Assume that our spectrometer is scanning the signal for the H^b protons of 1,1,2-tribromoethane at δ 4.1 ppm. H^b protons are under the influence of the small magnetic field of the adjacent proton, H^a. The orientation of H^a is not the same for every molecule in the sample. In some molecules, is aligned with the external magnetic field, and in others, it is aligned against the field.

+ When H^a is aligned with the field, the H^b protons feel a slightly stronger total field: They are effectively deshielded, and they absorb at a lower field.

+ When the magnetic moment of the H^a proton is aligned against the external field, the H^b protons are shielded, and they absorb at a higher field. These are the two absorptions of the doublet seen for the H^b protons.

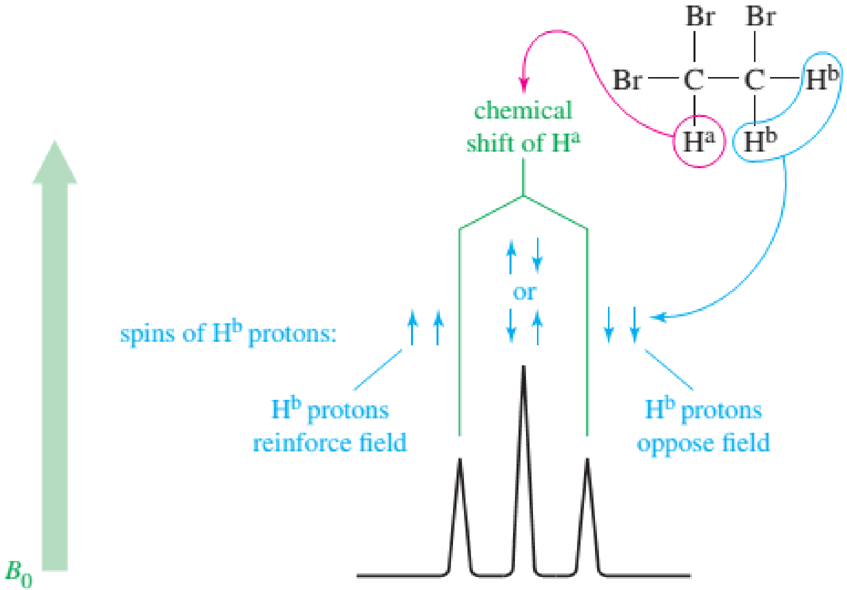
+ About half of the molecules have H^a aligned with the field and about half against the field, so the two absorptions of the doublet are nearly equal in area.



- ➢ Proton *a* in the NMR spectrum of 1,1,2-tribromoethane appears as a triplet (at δ 5.7 ppm) because there are four permutations of the two H^b proton spins, with two of them giving the same magnetic field.

+ when both H^b spins are aligned with the applied field, proton *a* is deshielded;
+ when both spins are aligned against the field, proton *a* is shielded; and
+ when the two H^b spins are opposite each other (two possible permutations), they cancel each other out.

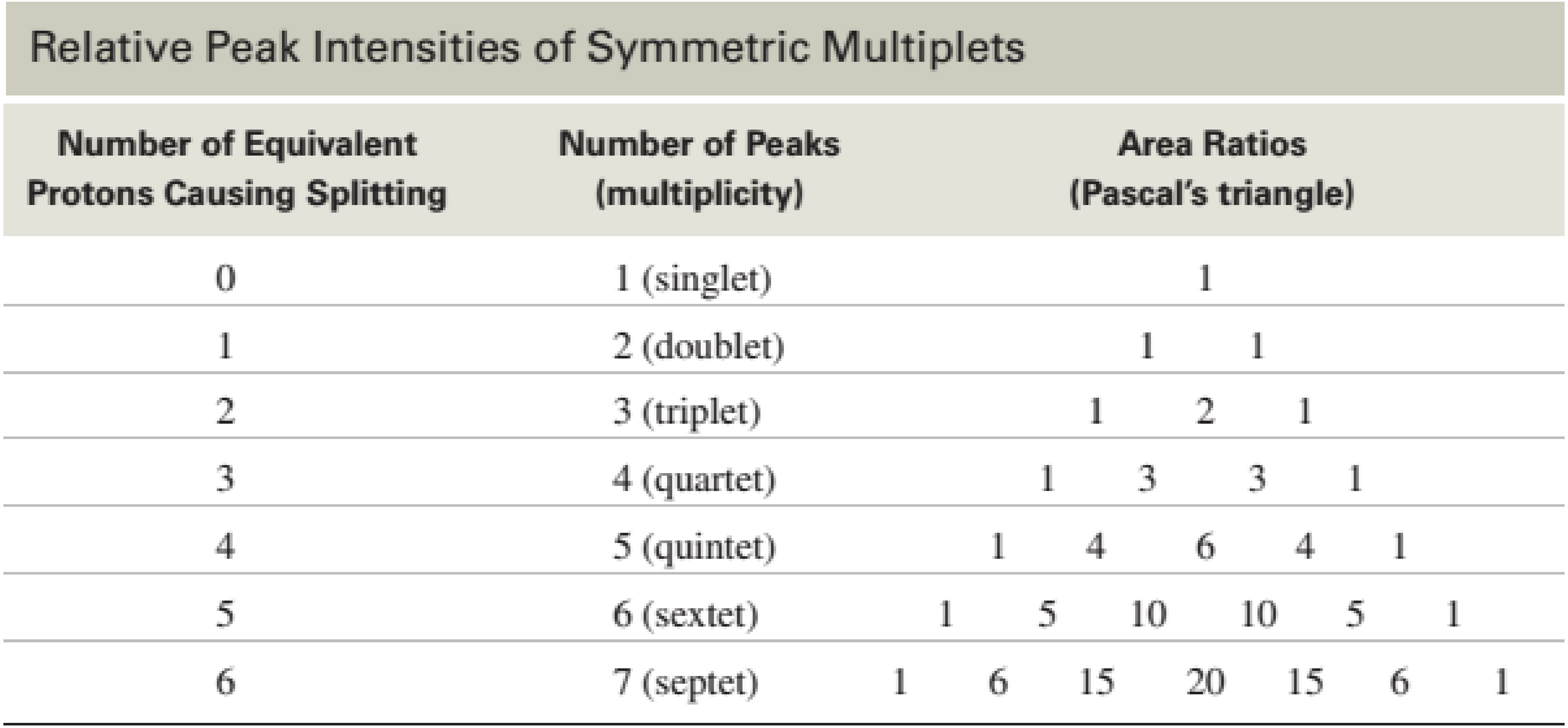
- ➢ Three signals result, with the middle signal twice as large as the others because it corresponds to two possible spin permutations.
- ➢ The two H^b protons do not split each other because they are chemically equivalent and absorb at the same chemical shift.
- ➢ Protons that absorb at the same chemical shift cannot split each other because they are in resonance at the same combination of frequency and field strength.



The $N + 1$ Rule

$N+1$ rule: If a signal is split by N neighboring equivalent protons, it will be split into $N+1$ peaks.

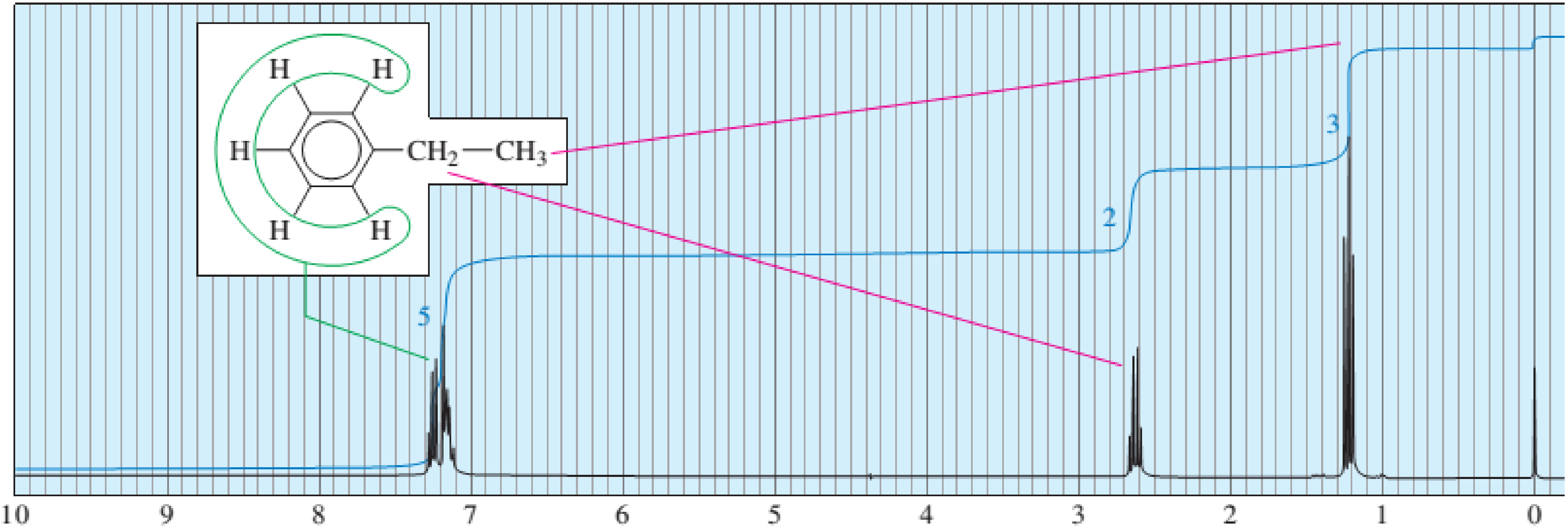
- The relative areas of the $N + 1$ **multiplet** that results are approximately given by the appropriate line of *Pascal's triangle*:



Relative Peak Intensities of Symmetric Multiplets

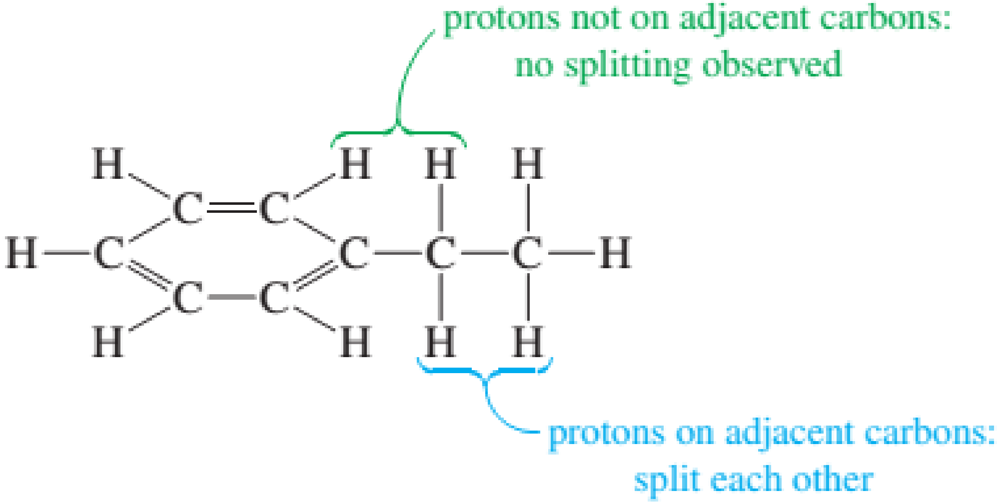
Number of Equivalent Protons Causing Splitting	Number of Peaks (multiplicity)	Area Ratios (Pascal's triangle)
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

- The methyl protons are split by two adjacent protons, and they appear upfield as a triplet of areas 1 : 2 : 1.
- The methylene (CH_2) protons are split by three protons, appearing farther downfield as a quartet of areas 1 : 3 : 3 : 1.
- All five aromatic protons absorb close to 7.2 ppm because the alkyl substituent has only a small effect on the chemical shifts of the aromatic protons. The aromatic protons split each other in a complicated manner in this high-resolution spectrum.



The range of magnetic coupling

- In ethylbenzene, there is no spin-spin splitting between the aromatic protons and the protons of the ethyl group. These protons are not on adjacent carbon atoms, so they are too far away to be magnetically coupled.



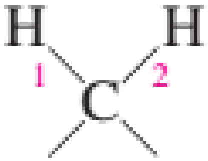
protons not on adjacent carbons: no splitting observed

protons on adjacent carbons: split each other

- The magnetic coupling that causes spin-spin splitting takes place primarily through the bonds of the molecule. Most examples of spin-spin splitting involve coupling between protons that are separated by three bonds, so they are bonded to adjacent carbon atoms (vicinal protons).
- In most cases, protons on the same carbon atom are equivalent, and equivalent protons cannot split each other.

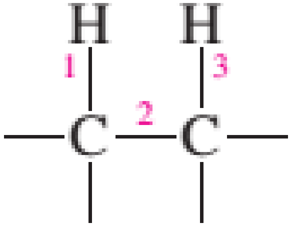
Most spin-spin splitting is between protons on adjacent carbon atoms.

Bonded to the same carbon: two bonds between protons



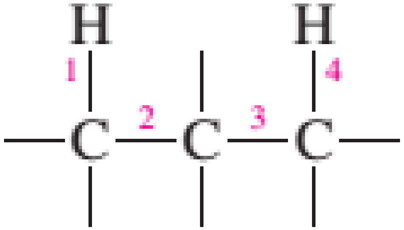
spin-spin splitting is normally observed
(if nonequivalent)

Bonded to adjacent carbons: three bonds between protons



spin-spin splitting is normally observed
(this is the most common case)

Bonded to nonadjacent carbons: four or more bonds between protons



spin-spin splitting is *not* normally observed

- Protons separated by more than three bonds usually do not produce observable spin-spin splitting.
- Occasionally, such “long-range coupling” does occur, but these cases are unusual.
- For now, we consider only nonequivalent protons on adjacent carbon atoms (or closer) to be magnetically coupled.

Roof effect

- The two multiplets in the upfield part of the ethylbenzene spectrum are not quite symmetrical.
- In general, a multiplet “leans” upward toward the signal of the protons responsible for the splitting.
- In the ethyl signal the quartet at lower field leans toward the triplet at a higher field, and vice versa.

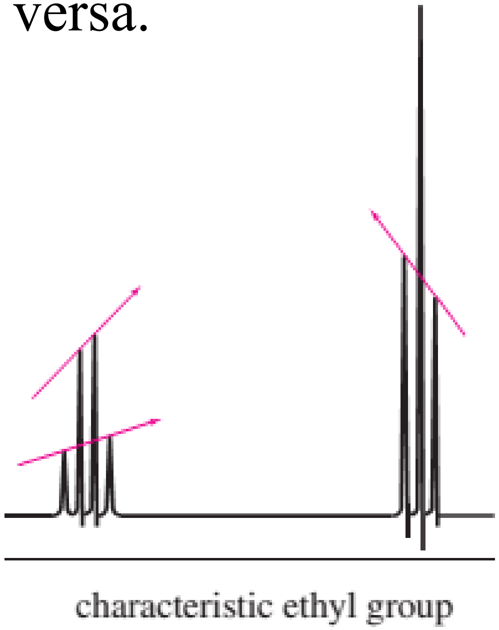
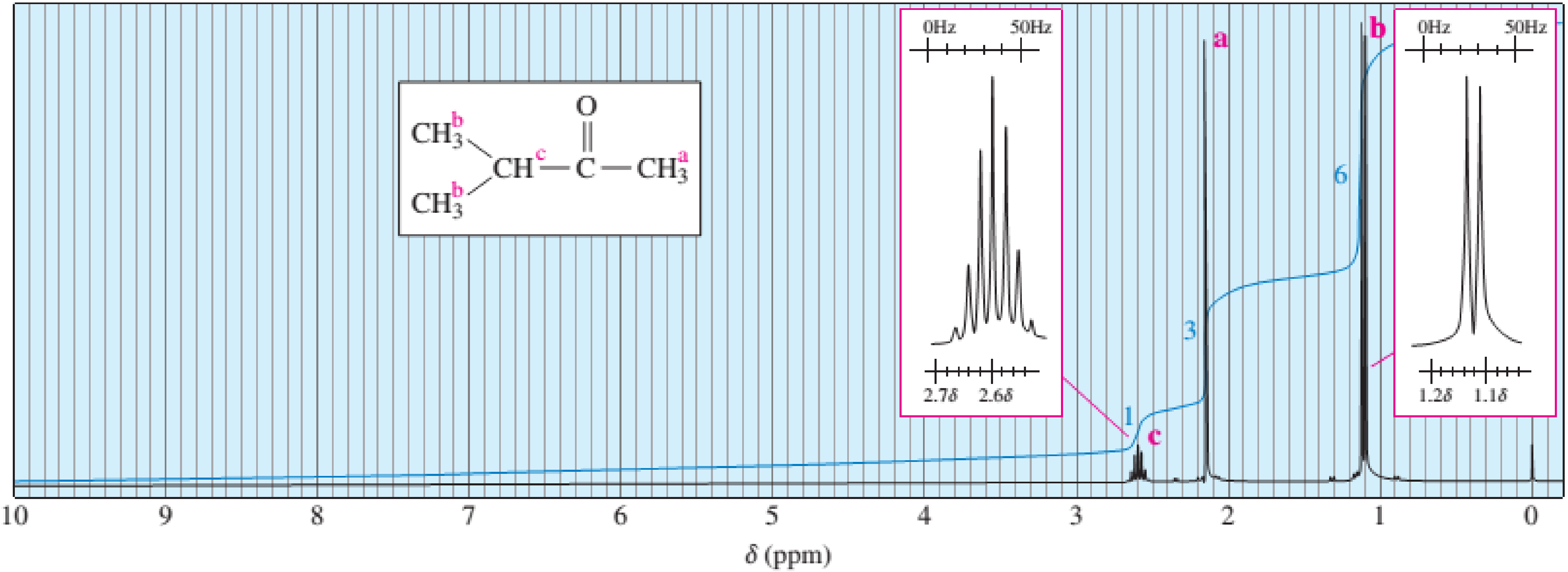


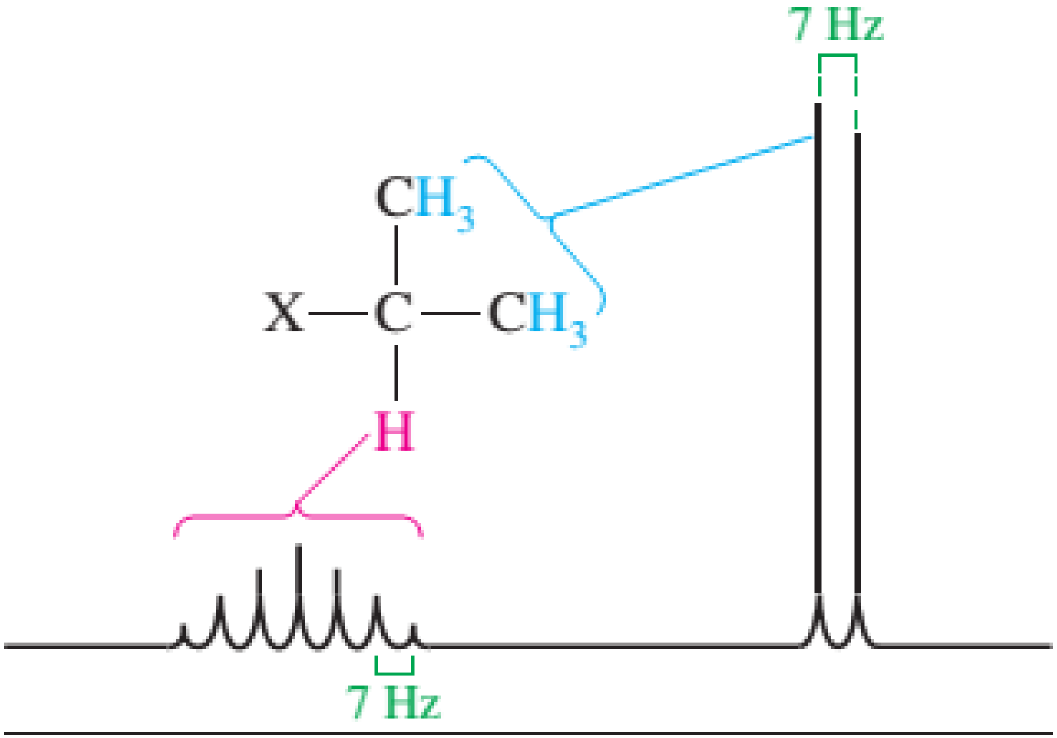
FIGURE 13-25

Leaning of a multiplet. A multiplet often “leans” upward toward the protons that are causing the splitting. The ethyl multiplets in ethylbenzene lean toward each other.

- The six methyl protons (*b*) of the isopropyl group are equivalent.
- They appear as a doublet of relative area 6 at about δ 1.1 ppm, slightly deshielded by the carbonyl group two bonds away.
- This doublet leans downfield because these protons are magnetically coupled to the methine proton (*c*).



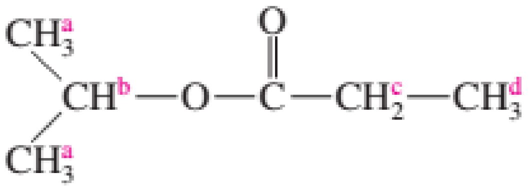
- The methine proton H^c appears as a multiplet of relative area 1, at δ 2.6 ppm.
- This absorption is a septet (seven peaks) because it is coupled to the six adjacent methyl protons (*b*).
- Some small peaks of this septet may not be visible unless the spectrum is amplified, as it is in the expanded insert box.



PROBLEM-SOLVING STRATEGY

Drawing An NMR Spectrum

In learning about NMR spectra, we have seen that chemical shift values can be assigned to specific types of protons, that the areas under peaks are proportional to the numbers of protons, and that nearby protons cause spin-spin splitting. By analyzing the structure of a molecule with these principles in mind, you can predict the characteristics of an NMR spectrum. Learning to draw spectra will help you to recognize the features of actual spectra. The process is not difficult if a systematic approach is used. A stepwise method is illustrated here, by drawing the NMR spectrum of the compound shown here.



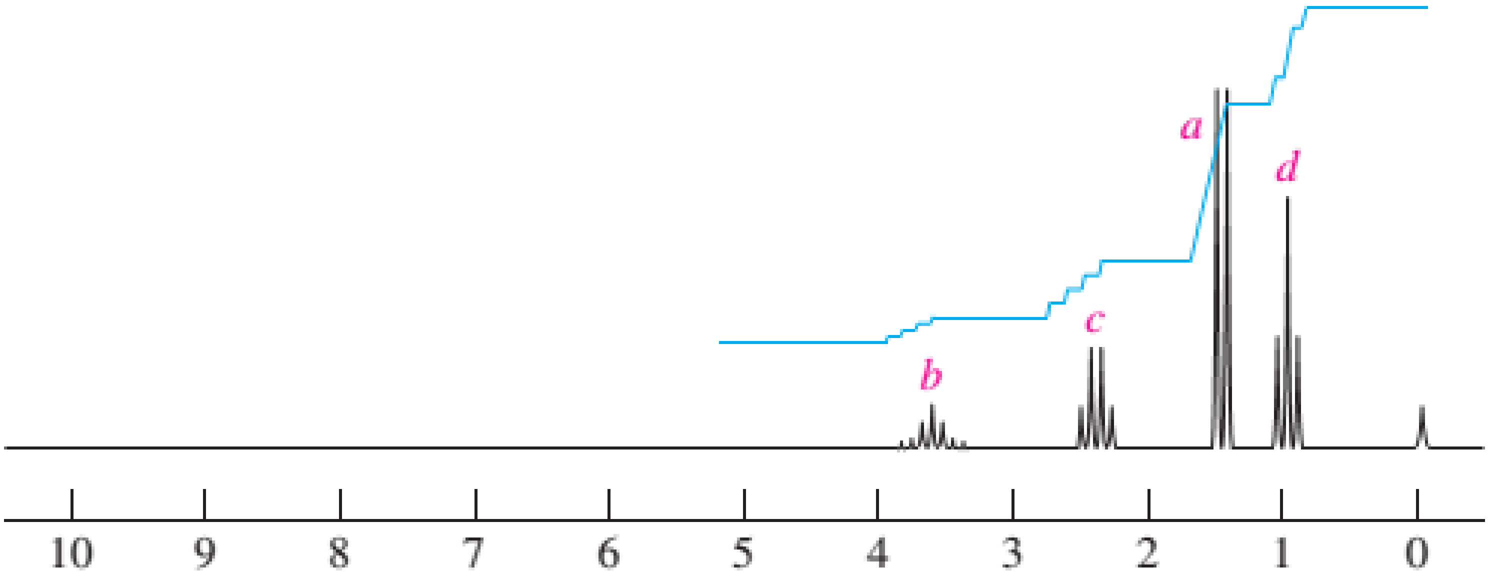
1. **Determine how many types of protons are present, together with their proportions.** In the example, there are four types of protons, labeled *a, b, c*, and *d*. The area ratios should be 6:1:2:3.
2. **Estimate the chemical shifts of the protons. (Table 13.3 and Appendix 1 serve as guides.)** Proton *b* is on a carbon atom bonded to oxygen; it should absorb around δ3 to δ4. Protons *a* are less deshielded by the oxygen, probably around δ1 to δ2. Protons *c* are on a carbon bonded to a carbonyl group; they should absorb around δ2.1 to δ2.5. Protons *d*, one carbon removed from a carbonyl, will be deshielded less than protons *c* and also less than protons *a*, which are next to a more strongly deshielded carbon atom. Protons *d* should absorb around δ1.0.
3. **Determine the splitting patterns.** Protons *a* and *b* split each other into a doublet and a septet, respectively (a typical isopropyl group pattern). Protons *c* and *d* split each other into a quartet and a triplet, respectively (a typical ethyl group pattern).

4. Summarize each absorption in order, from the lowest field to the highest.

	Proton *b*	**Protons *c***	**Protons *a***	**Protons *d***
area	1	2	6	3
chemical shift	3–4	2.1–2.5	1–2	1
splitting	septet	quartet	doublet	triplet

5. Draw the spectrum, using the information from your summary.

Work through the following problem to become comfortable with predicting NMR spectra.

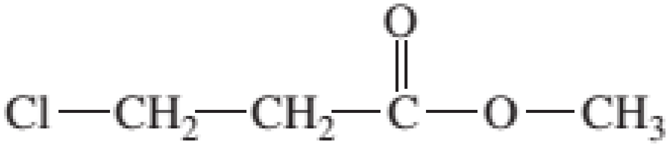


PROBLEM 13-7

Draw the NMR spectra you would expect for the following compounds.

(a) $(CH_3)_2CH-O-CH(CH_3)_2$

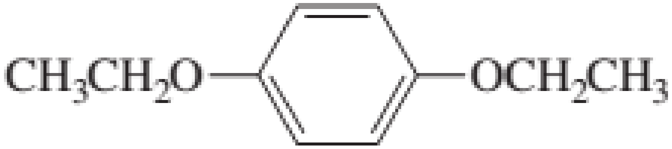
(b)



$Cl-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3$

(c) $Ph-CH(CH_3)_2$

(d)



(e)

$$\begin{array}{l}CH_2-COOCH_2CH_3\\ |\\ CH_2-COOCH_2CH_3\end{array}$$

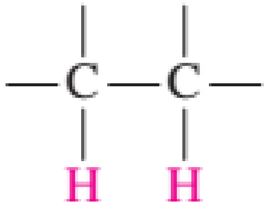
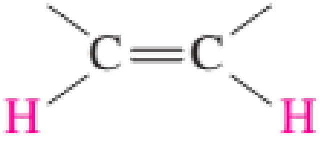
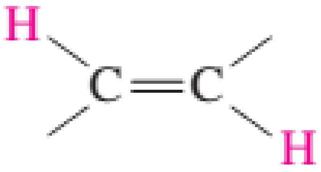
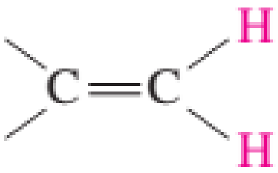
Coupling constants

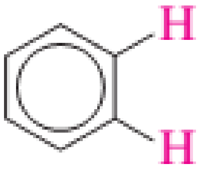
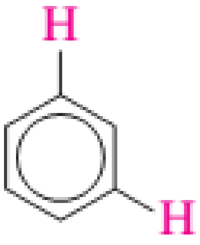
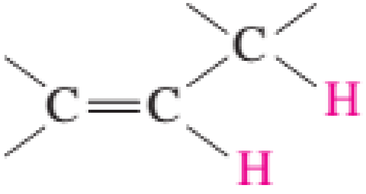
- ➢ The distance between the peaks of a multiplet (measured in hertz) is called the **coupling constant.**

\+ Coupling constants are represented by *J*, and the coupling constant between H^a and H^b is represented by J_{ab}.

\+ Multiplets that have the same coupling constant may arise from adjacent groups of protons that split each other.

- ➢ The magnetic effect that one proton has on another depends on the bonds connecting the protons, but it does not depend on the strength of the external magnetic field.
- ➢ For this reason, the coupling constant (measured in hertz) does not vary with the field strength of the spectrometer.
- ➢ A spectrometer operating at 300 MHz records the same coupling constants as a 60-MHz instrument.

		Approx. *J*
	(free rotation)	7 Hz[a]
	(cis)	10 Hz
	(trans)	15 Hz
	(geminal)	2 Hz

		Approx. *J*
	(ortho)	8 Hz
	(meta)	2 Hz
	(allylic)	6 Hz

The most commonly observed coupling constant is the 7-Hz splitting of protons on adjacent carbon atoms in freely rotating alkyl groups.

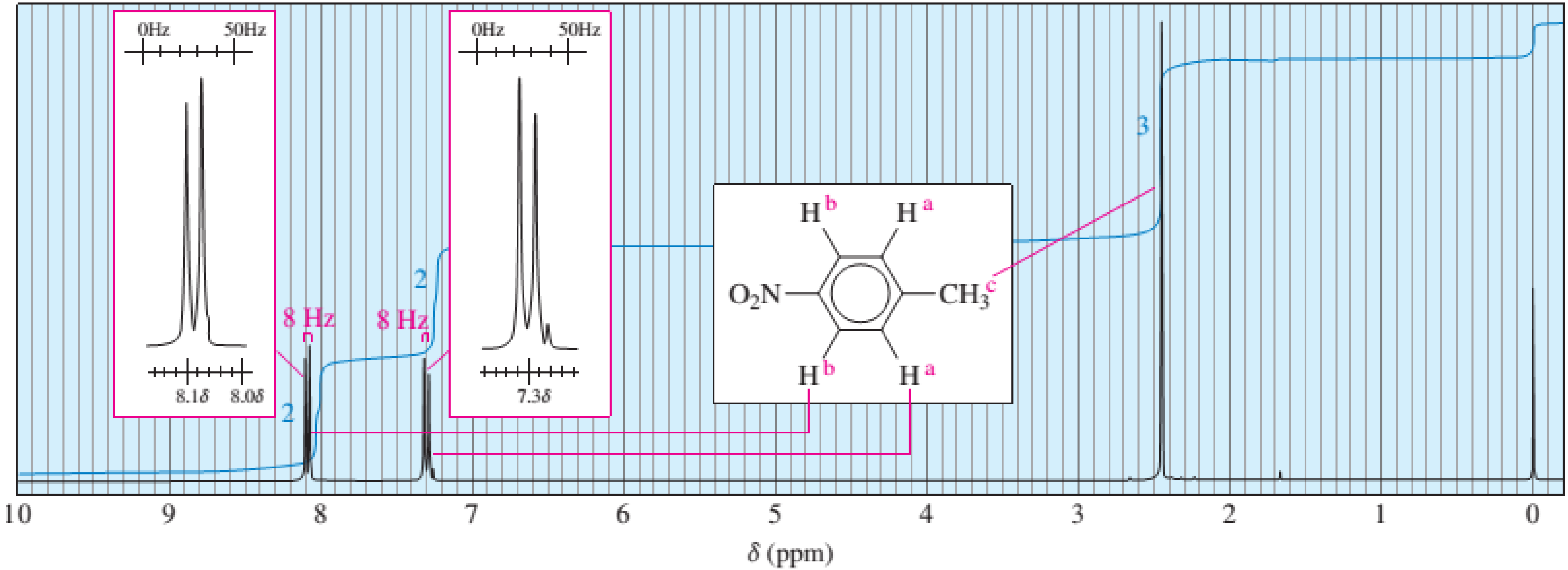
- Splitting patterns and their coupling constants help to distinguish among the possible isomers of a compound, as in the spectrum of *p*-nitrotoluene.

+ The methyl protons (*c*) absorb as a singlet near δ2.5 ppm.

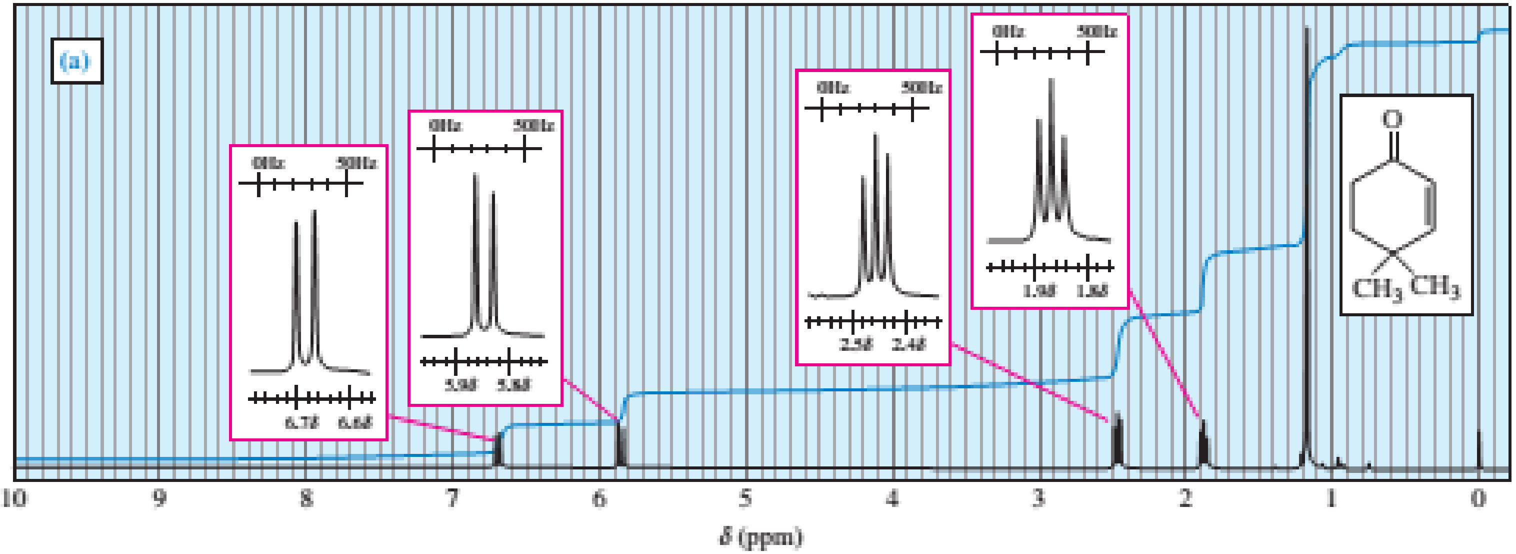
+ The aromatic protons appear as a pair of doublets:

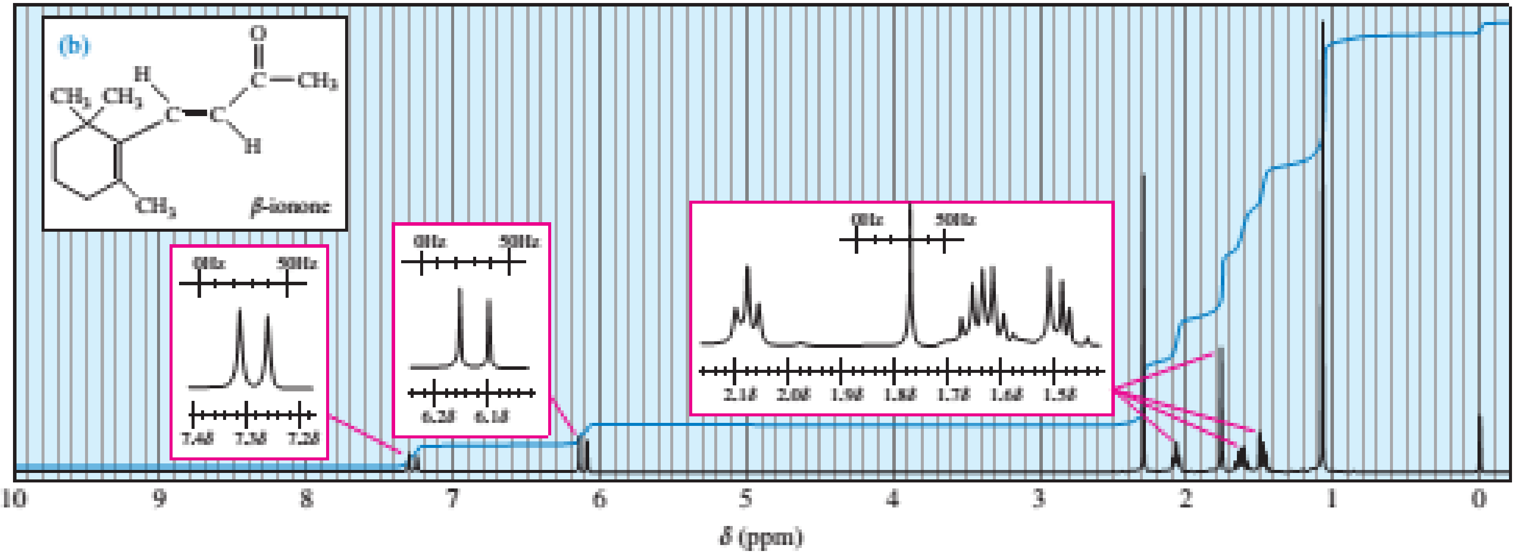
- The doublet centered around δ 7.3 ppm corresponds to the two aromatic protons closest to the methyl group (*a*).
- The doublet centered around δ 8.1 ppm corresponds to the two protons closest to the electron-withdrawing nitro group (*b*).

- Each proton *a* is magnetically coupled to one *b* proton, splitting the H^a absorption into a doublet. Similarly, each proton *b* is magnetically coupled to one proton *a*, splitting the H^b absorption into a doublet.
- The coupling constant is 8-Hz. This 8-Hz coupling suggests that the magnetically coupled protons H^a and H^b are ortho to each other.
- Both the ortho and meta isomers of nitrotoluene have four distinct types of aromatic protons, and the spectra for these isomers are more complex.


0Hz
50Hz
8.1δ
8.0δ
0Hz
50Hz
7.3δ
8 Hz
8 Hz
2
2
3
H^b
H^a
O_2N
CH_3^c
H^b
H^a
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

- ➢ In figure (a), the 9-Hz coupling constant between the two vinyl protons shows that they are cis to one another.
- ➢ In (b), the 15-Hz coupling constant shows that the two vinyl protons are trans.





PROBLEM 13-8

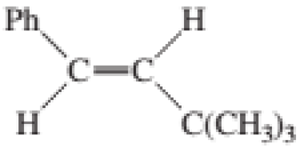
(a) Assign protons to the peaks in the NMR spectrum of 4,4-dimethylcyclohex-2-en-1-one in Figure 13-30(a). Explain the splitting that gives the triplets at δ1.8 and δ2.4.

(b) Assign protons to the peaks in the NMR spectrum of β-ionone in Figure 13-30(b). Explain the splitting seen in the three multiplets at δ1.5, δ1.65, and δ2.1. Explain how you know which of these multiplets corresponds to which methylene groups in the molecule.

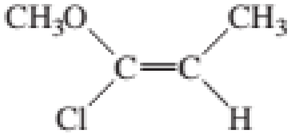
PROBLEM 13-9

Draw the NMR spectra you expect for the following compounds.

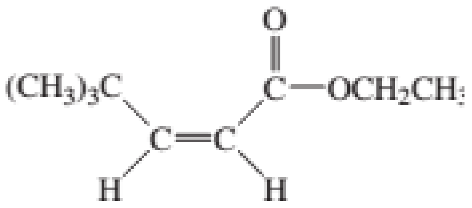
(a)



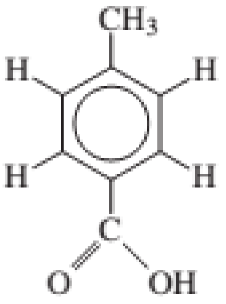
(b)



(c)

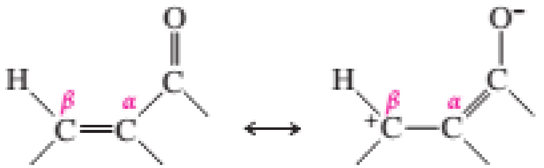


(d)



Problem-solving Hint

Protons on the β carbon of an α,β-unsaturated carbonyl compound absorb at very low fields (about δ7) because of the electron-withdrawing resonance effect of the carbonyl group.

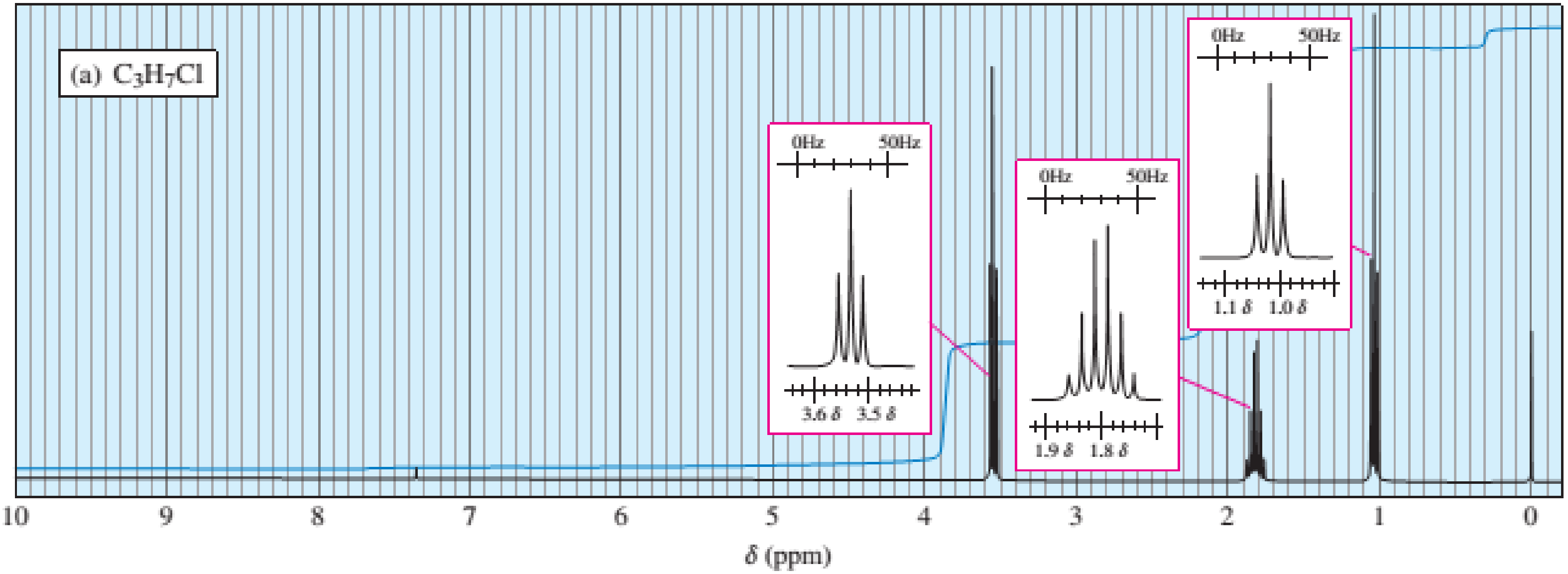


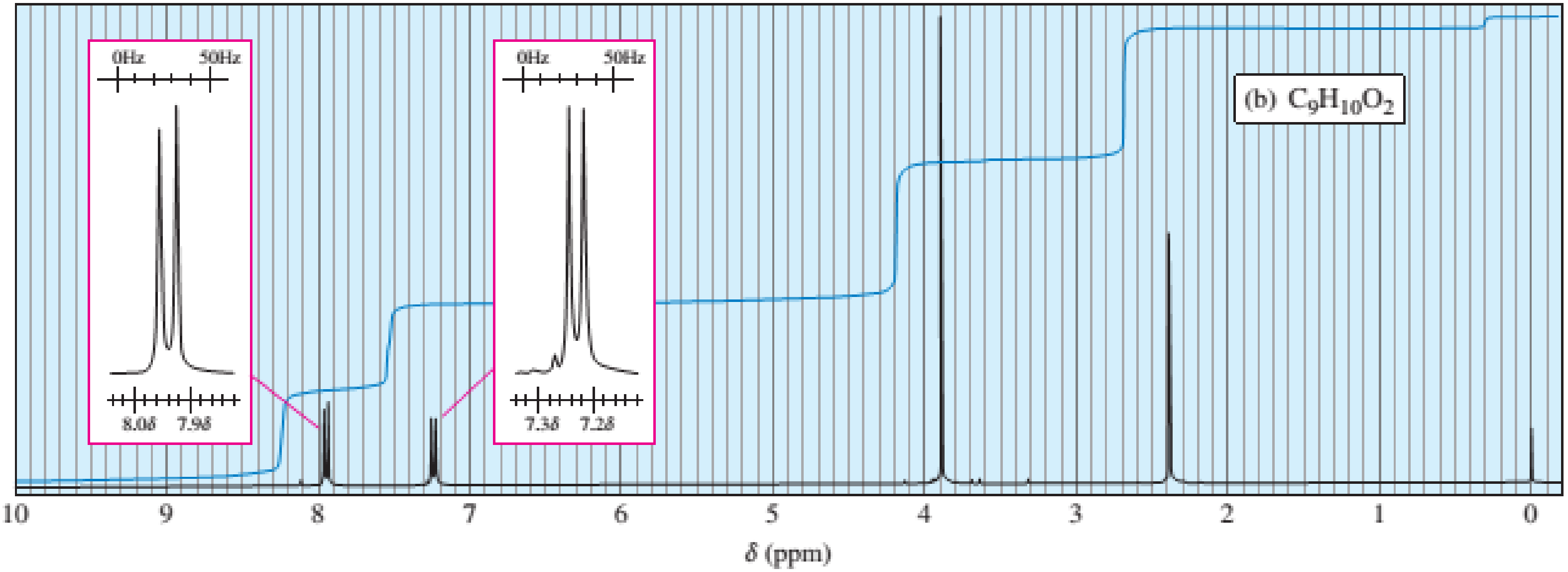
PROBLEM 13-10

An unknown compound (C_3H_2NCl) shows moderately strong IR absorptions around 1650 cm^{-1} and 2200 cm^{-1}. Its NMR spectrum consists of two doublets (J = 14 Hz) at δ5.9 and δ7.1. Propose a structure consistent with these data.

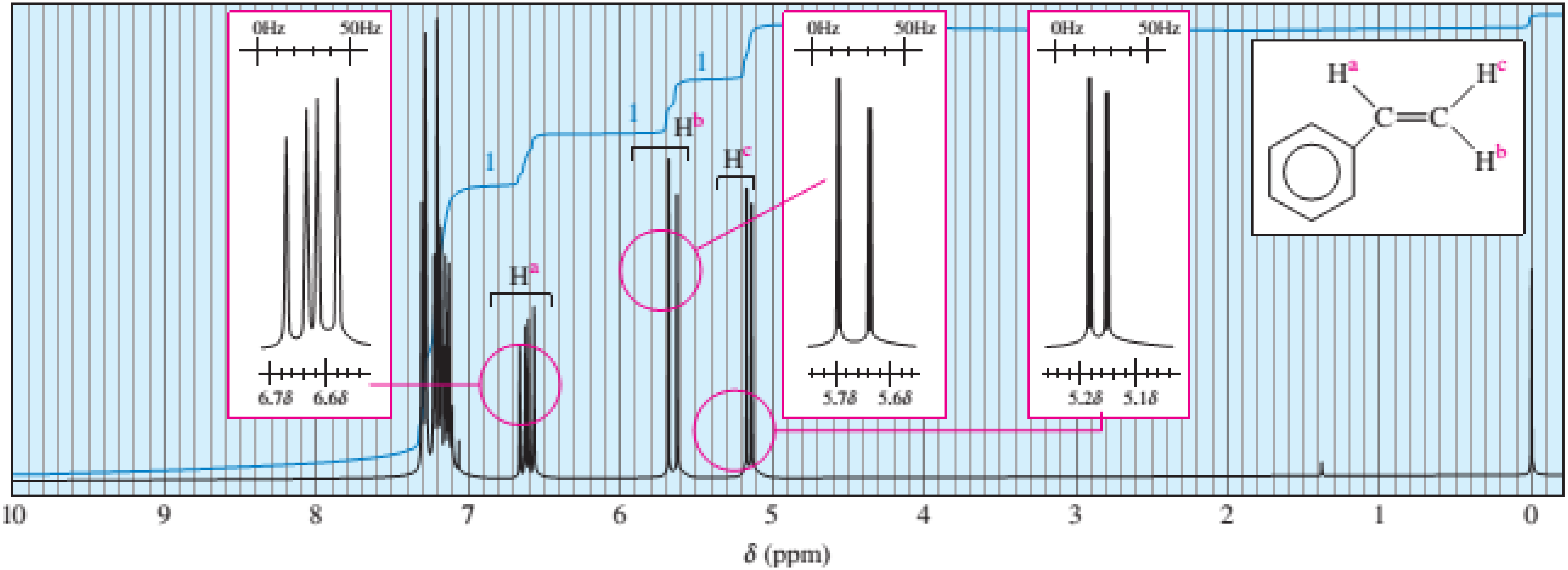
PROBLEM 13-11

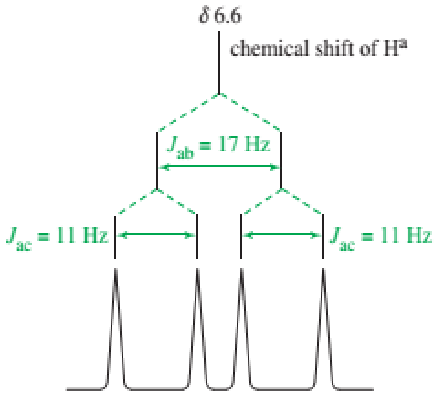
Two spectra are shown. Propose a structure that corresponds to each spectrum.



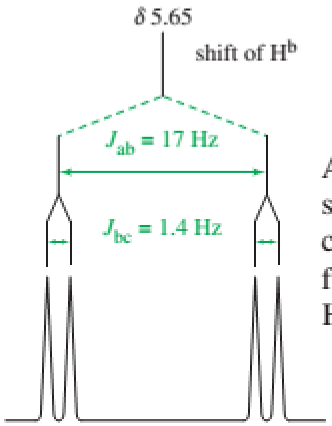


- There are many cases of **complex splitting,** where signals are split by adjacent protons of more than one type, with different coupling constants.
- The proton NMR spectrum of styrene includes several absorptions that show the results of complex splitting. Consider the vinyl proton adjacent to the phenyl ring of styrene.





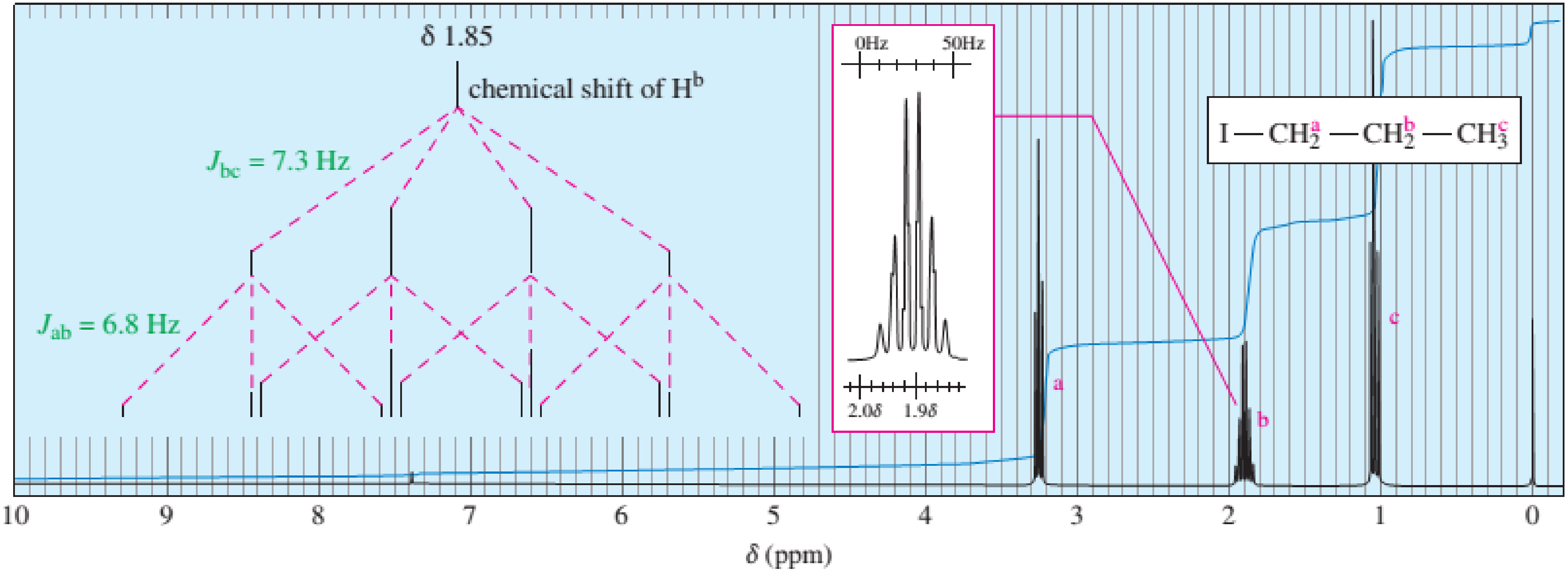
A splitting tree for the H^a proton in styrene. The H^a signal is split (J_{ab} = 17 Hz) by coupling with H^b and further split (J_{ac} = 11 Hz) by coupling with H^c.



A splitting tree for the H^b proton in styrene. The H^b signal is split by coupling with H^a (J_{ab} = 17 Hz) and further split by coupling with H^c (J_{bc} = 1.4 Hz).

- The chemical shift of H^a is δ 6.6 because it is deshielded by both the vinyl group and the aromatic ring.
- H^a is coupled to H^b with a typical trans coupling constant, J_{ab} = 17 Hz. It is also coupled to proton H^c with J_{ac} = 11 Hz. The H^a signal is therefore split into a doublet of spacing 17 Hz, and each of those peaks is further split into a doublet of spacing 11 Hz, for a total of four peaks. This complex splitting, called a *doublet of doublets*, can be analyzed by a diagram called a *splitting tree.*

- Proton H^b is farther from the deshielding influence of the phenyl group, giving rise to the multiplet centered at δ5.65 ppm. H^b is also split by two nonequivalent protons: It is split by H^a with a trans coupling constant J_{ac} = 17 Hz and further split by H^c with a geminal coupling constant J_{bc} = 1.4 Hz.



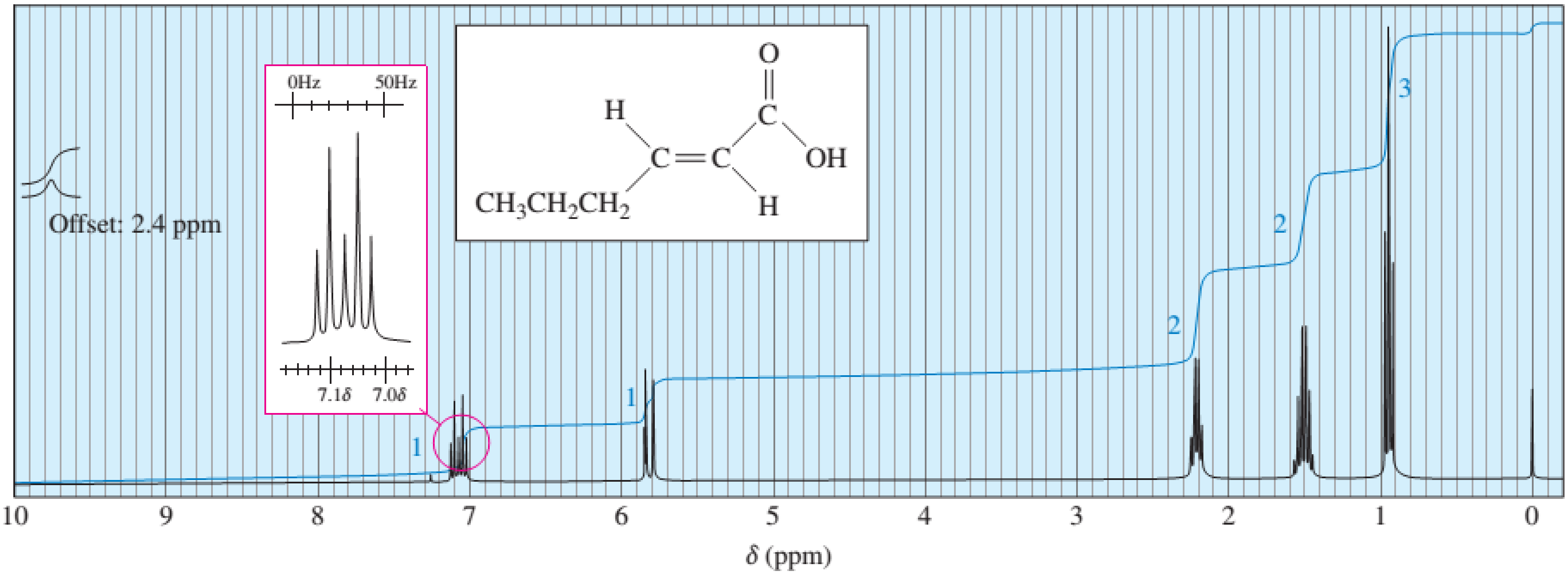
- Sometimes a signal is split by two or more different kinds of protons with similar coupling constants. Consider 1-iodopropane, where the *b* protons on the middle carbon atom are split by two types of protons: the methyl protons (H^c) and the CH_2I protons (H^a).
- The coupling constants for these two interactions are similar: J_{ab} = 6.8 Hz, and J_{bc} = 7.3 Hz. The spectrum shows the H^b signal as a sextet, almost as though there were five equivalent protons coupled with H^b.
- The trace in the insert box, enlarged and offset, shows that the pattern is not a perfect sextet. The analysis of the splitting pattern serves as a reminder that the *N* + 1 rule gives a perfect multiplet only when the signal is split by *N* protons with exactly the same coupling constant.

PROBLEM 13-13

The spectrum of *trans*-hex-2-enoic acid follows.

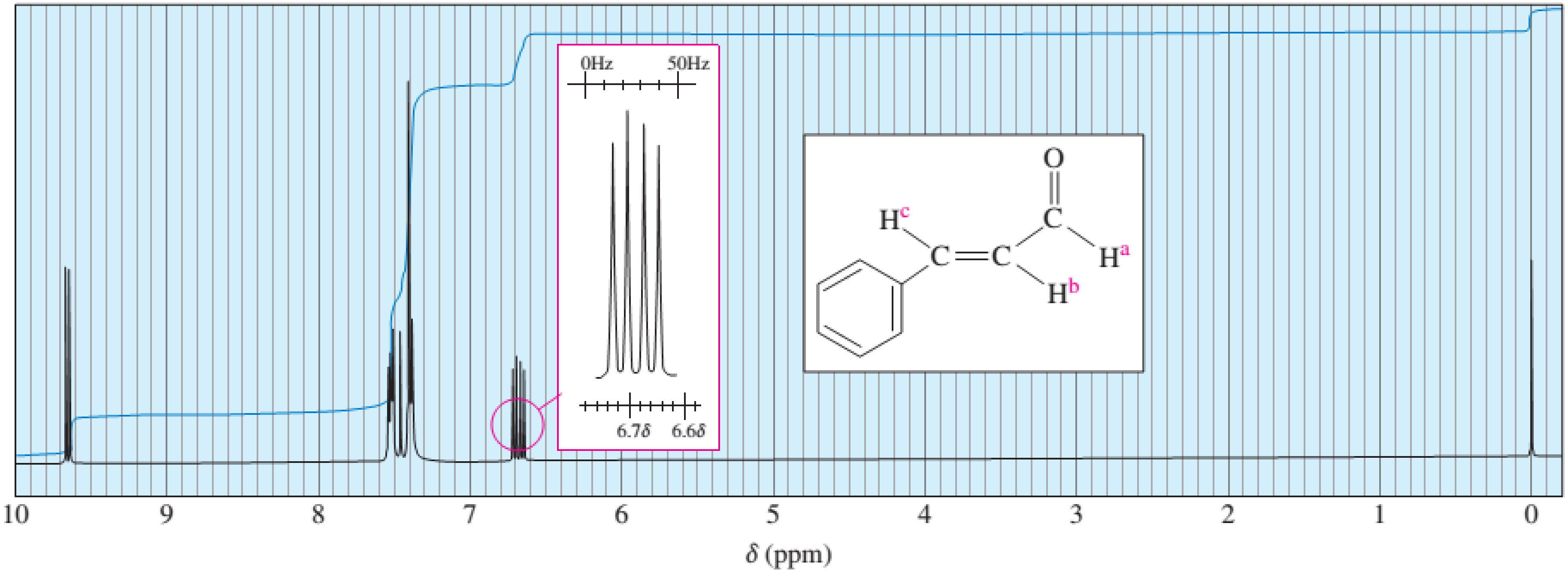
(a) Assign peaks to show which protons give rise to which peaks in the spectrum.

(b) Draw a tree to show the complex splitting of the vinyl proton centered around 7 ppm. Estimate the values of the coupling constants.



PROBLEM 13-14

The NMR spectrum of cinnamaldehyde follows.



(a) Determine the chemical shifts of H^a, H^b, and H^c. The absorption of one of these protons is difficult to see; look carefully at the integrals.

(b) Estimate the coupling constants J_{ab} and J_{bc}.

(c) Draw a tree to analyze the complex splitting of the proton centered at δ 6.7.

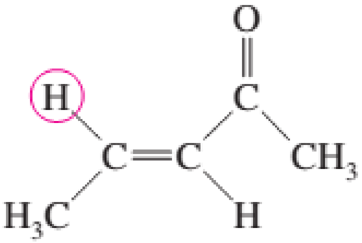
PROBLEM 13-15

Consider the proton NMR spectrum of the following ketone.

(a) Predict the approximate chemical shift of each type of proton.

(b) Predict the number of NMR peaks for each type of proton.

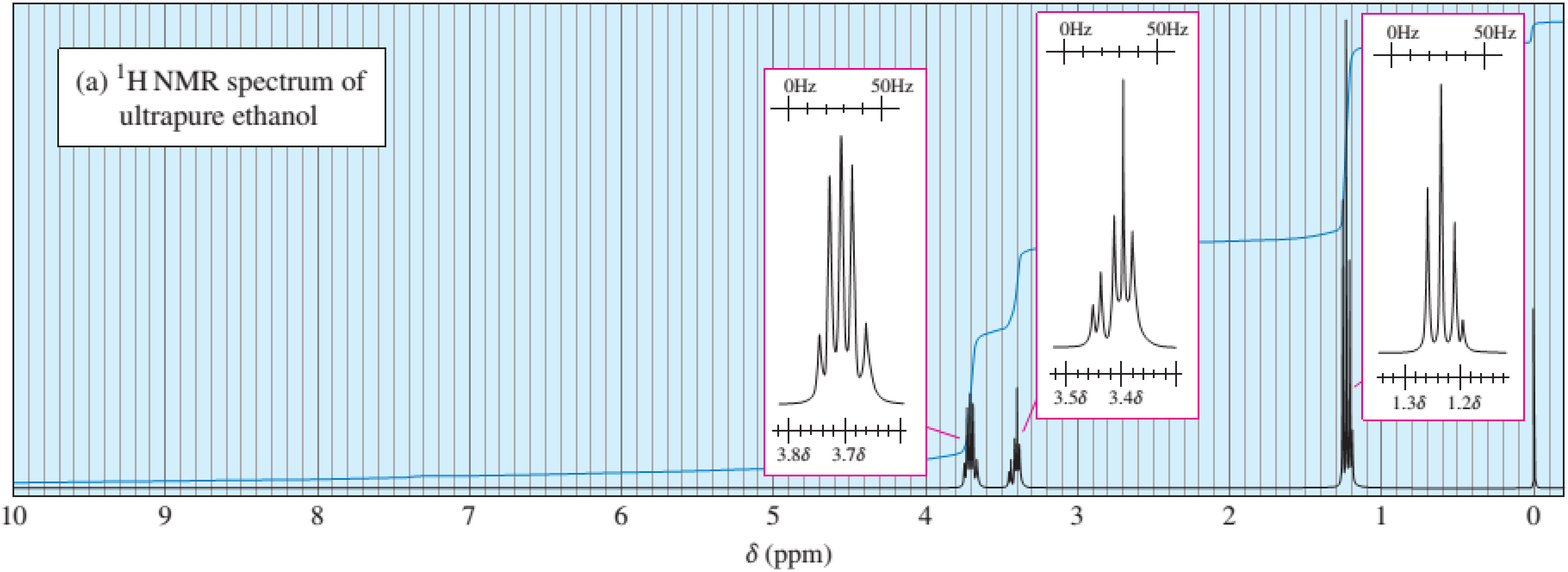
(c) raw a tree to show the splitting predicted for the absorption of the circled proton.



Fast Proton Transfers

Hydroxyl Protons Like conformational interconversions, chemical processes often occur faster than the NMR technique can observe them.

Figure (a) shows coupling between the hydroxyl proton and the adjacent methylene protons, with a coupling constant of about 5 Hz. This is an ultrapure sample of ethanol with no contamination of acid, base, or water.

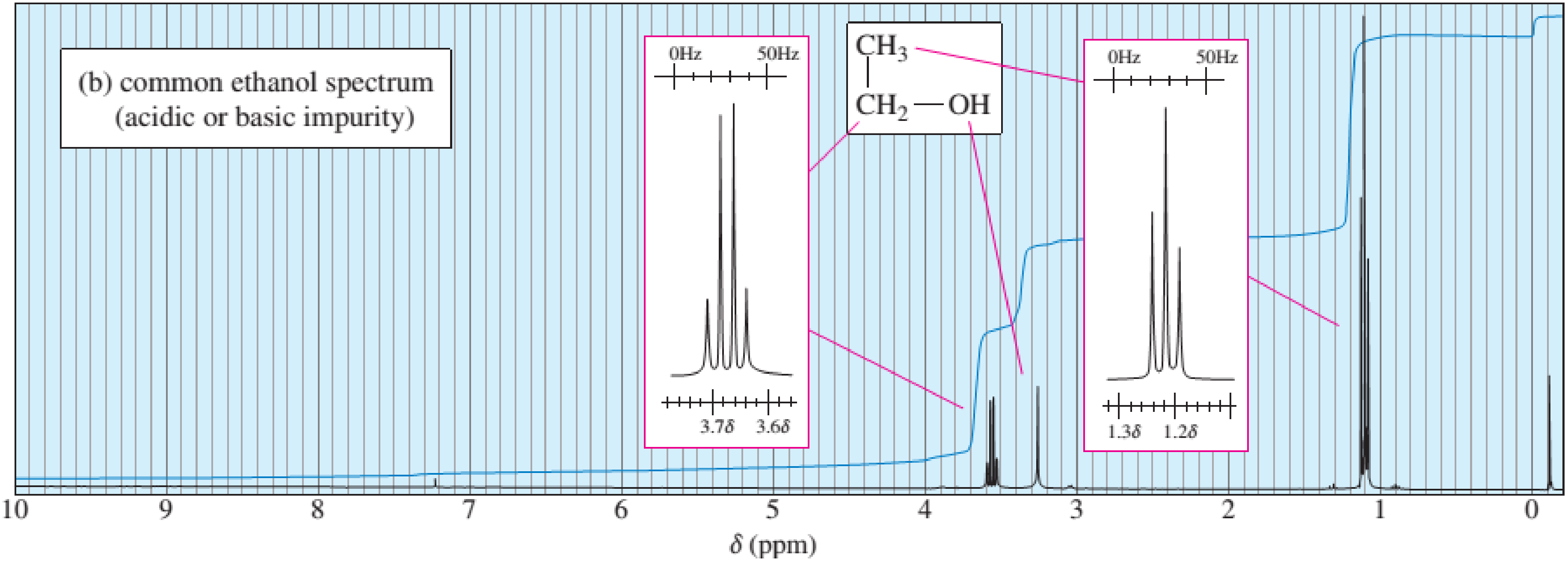


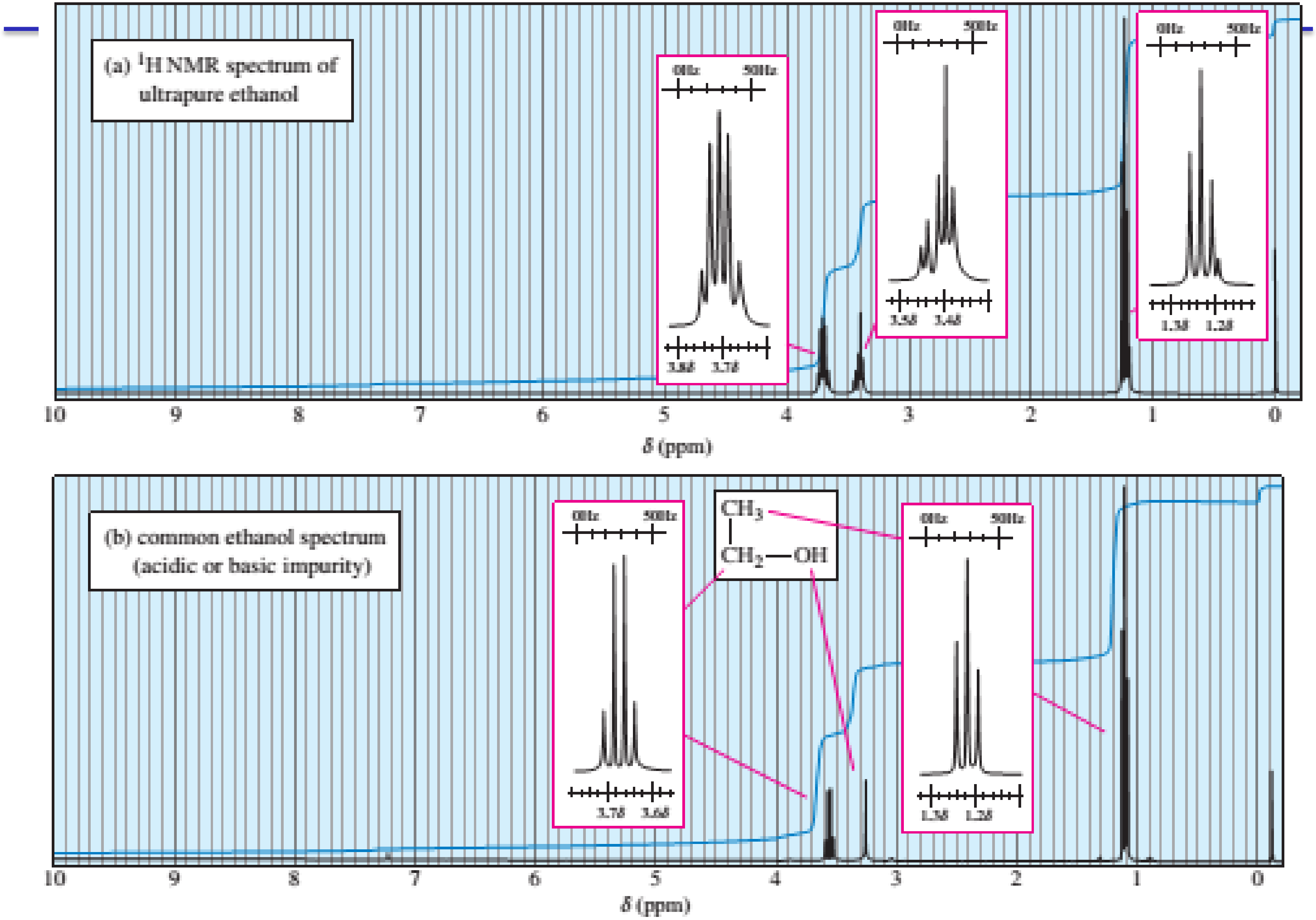
- Part (b) shows a typical sample of ethanol, with some acid or base present to catalyze the interchange of the hydroxyl protons.

+ No splitting is seen between the hydroxyl proton and the methylene protons.

+ During the NMR measurement, each hydroxyl proton becomes attached to a large number of different ethanol molecules and experiences all possible spin arrangements of the methylene group.

+ What we see is a single, unsplit hydroxyl absorption corresponding to the averaged field the proton experiences from bonding to many different ethanol molecules.

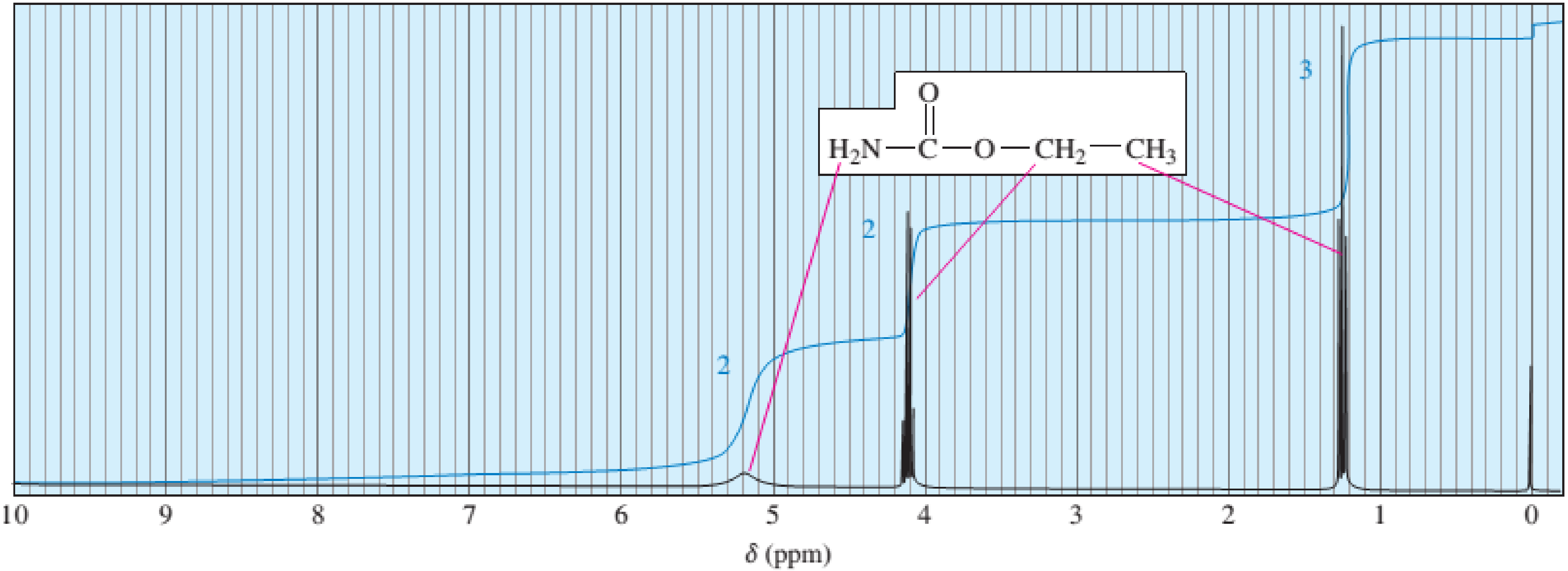




Comparison of the NMR spectrum of unusually pure ethanol and the spectrum of ethanol with a trace of an acidic (or basic) impurity. The impurity catalyzes a fast exchange of the –OH proton from one ethanol molecule to another. This rapidly exchanging proton produces a single, unsplit absorption at an averaged field.

N – H protons

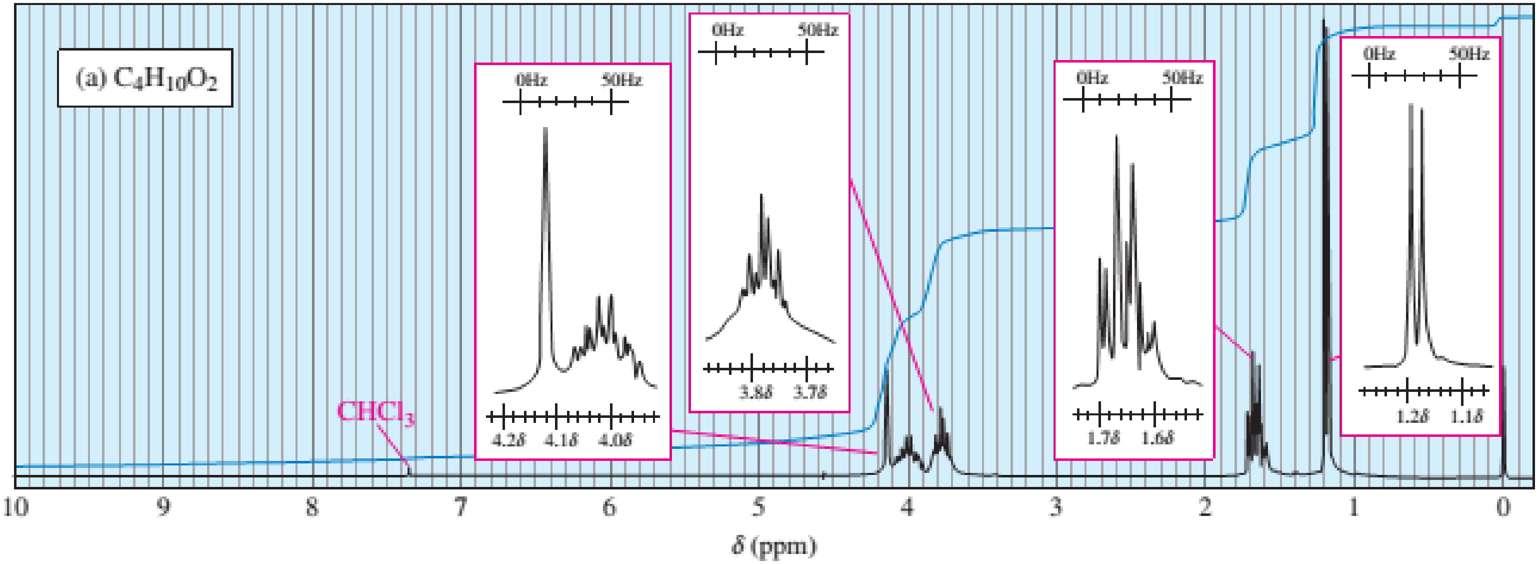
- Protons on nitrogen often show broadened signals in the NMR, both because of moderate rates of exchange and because of the magnetic properties of the nitrogen nucleus.
- Depending on the rate of exchange and other factors, N – H protons may give absorptions that are sharp and cleanly split, sharp and unsplit (averaged), or broad and shapeless.

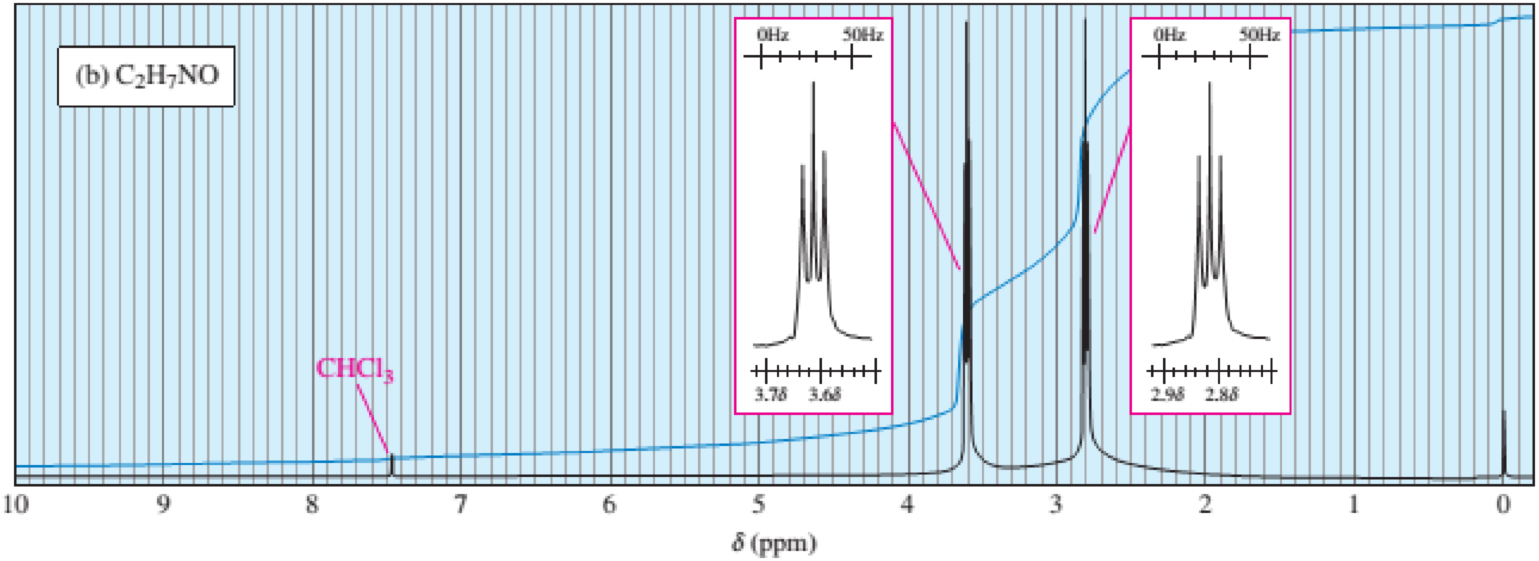


Proton NMR spectrum of ethyl carbamate, showing a broad N-H absorption.

PROBLEM 13-21

Propose chemical structures consistent with the following NMR spectra and molecular formulas. In spectrum (a) explain why the peaks around δ1.65 and δ3.75 are not clean multiplets, but show complex splitting. In spectrum (b) explain why some of the protons are likely to be missed.





PROBLEM-SOLVING STRATEGY

INTERPRETING PROTON NMR SPECTRA

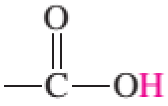
Learning to interpret NMR spectra requires practice with a large number of examples and problems. The problems at the end of this chapter should help you gain confidence in your ability to assemble a structure from the NMR spectrum combined with other information. This section provides some hints that can help make spectral analysis a little easier.

When you first look at a spectrum, consider the major features before getting bogged down in the minor details. Here are a few major characteristics you might watch for:

1. If the molecular formula is known, use it to determine the number of elements of unsaturation (see Section 7-3). The elements of unsaturation suggest rings, double bonds, or triple bonds. Matching the integrated peak areas with the number of protons in the formula gives the numbers of protons represented by the individual peaks.
2. Any broadened singlets in the spectrum might be due to —OH or —NH protons. If the broad singlet is deshielded past 10 ppm, an acid —OH group is likely.

$-\mathrm{O}-\mathrm{H} \qquad -\overset{|}{\mathrm{N}}-\mathrm{H}$

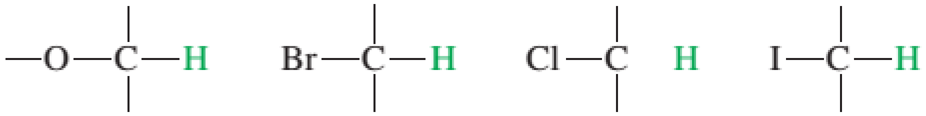
frequently broad singlets



$-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}$

broad (or sharp) singlet, $\delta > 10$

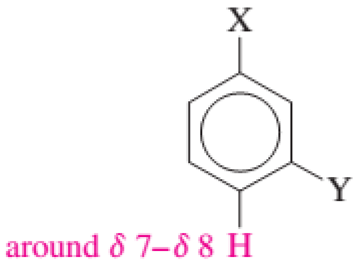
3. A signal around δ 3 to δ 4 suggests protons on a carbon bearing an electronegative element such as oxygen or a halogen. Protons that are more distant from the electronegative atom will be less strongly deshielded.



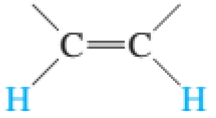
$-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{H} \qquad \mathrm{Br}-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{H} \qquad \mathrm{Cl}-\underset{|}{\overset{|}{\mathrm{C}}}\quad\mathrm{H} \qquad \mathrm{I}-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{H}$

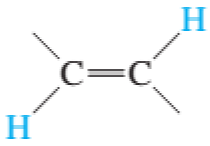
around δ 3–δ 4 for hydrogens on carbons bearing oxygen or halogen

4. Signals around $\delta 7$ to $\delta 8$ suggest the presence of an aromatic ring. If some of the aromatic absorptions are farther downfield than $\delta 7.2$, an electron-withdrawing substituent may be attached.

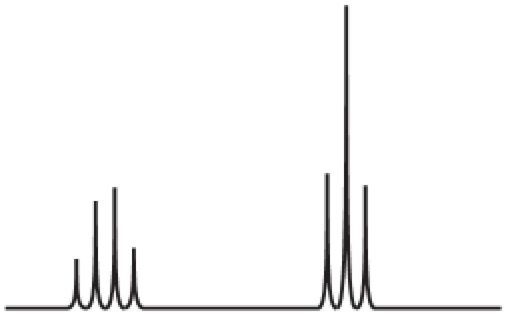


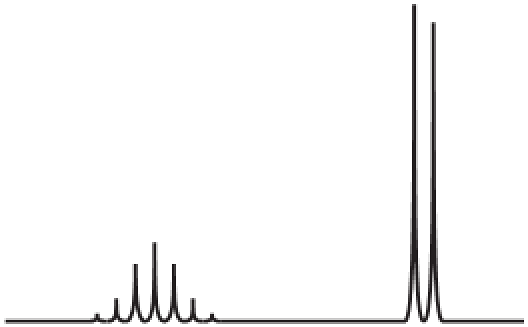
5. Signals around $\delta 5$ to $\delta 6$ suggest vinyl protons. Splitting constants can differentiate cis and trans isomers.


around $\delta 5$–$\delta 6$; $J = 10$ Hz

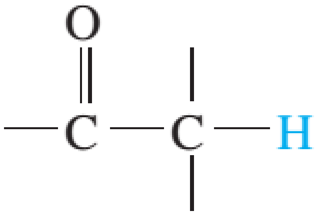

around $\delta 5$–$\delta 6$; $J = 15$ Hz

6. Use the splitting patterns to determine the numbers of adjacent protons, and assemble pieces of the molecule in a trial structure. Learn to recognize ethyl groups and isopropyl groups (and structures that resemble these groups) by their characteristic splitting patterns.

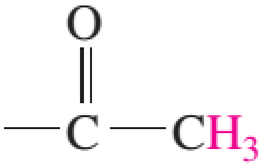

ethyl group


isopropyl group

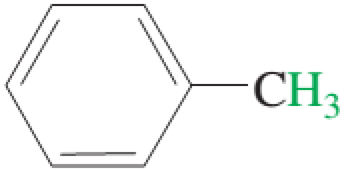
7. Signals around δ2.1 to δ2.5 may suggest protons adjacent to a carbonyl group or next to an aromatic ring. A singlet at δ2.1 often results from a methyl group bonded to a carbonyl group.


$-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{|}{\overset{|}{C}}-H$

around δ 2.1–δ 2.5

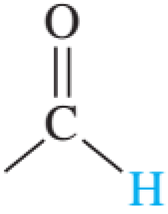

$-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

singlet, δ 2.1



singlet, δ 2.3

8. Signals in the range δ9 to δ10 suggest an aldehyde.



aldehyde, δ 9–δ 10

9. A sharp singlet around δ2.5 suggests a terminal alkyne.

$-C\equiv C-H$

around δ 2.5

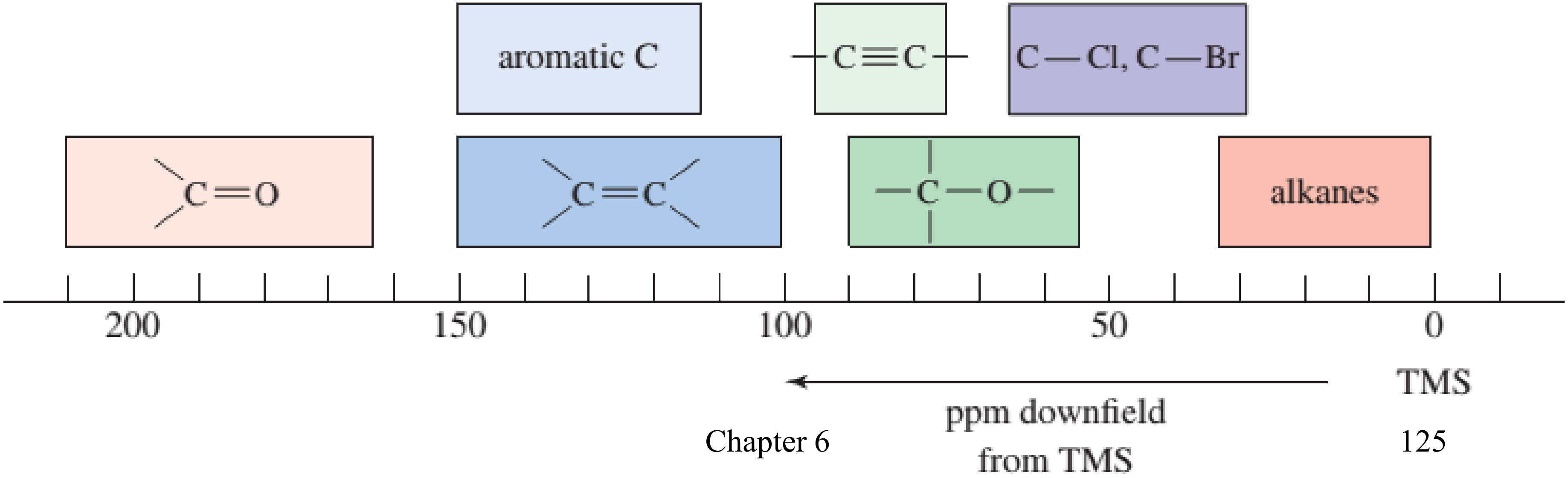
Carbon-13 NMR spectroscopy

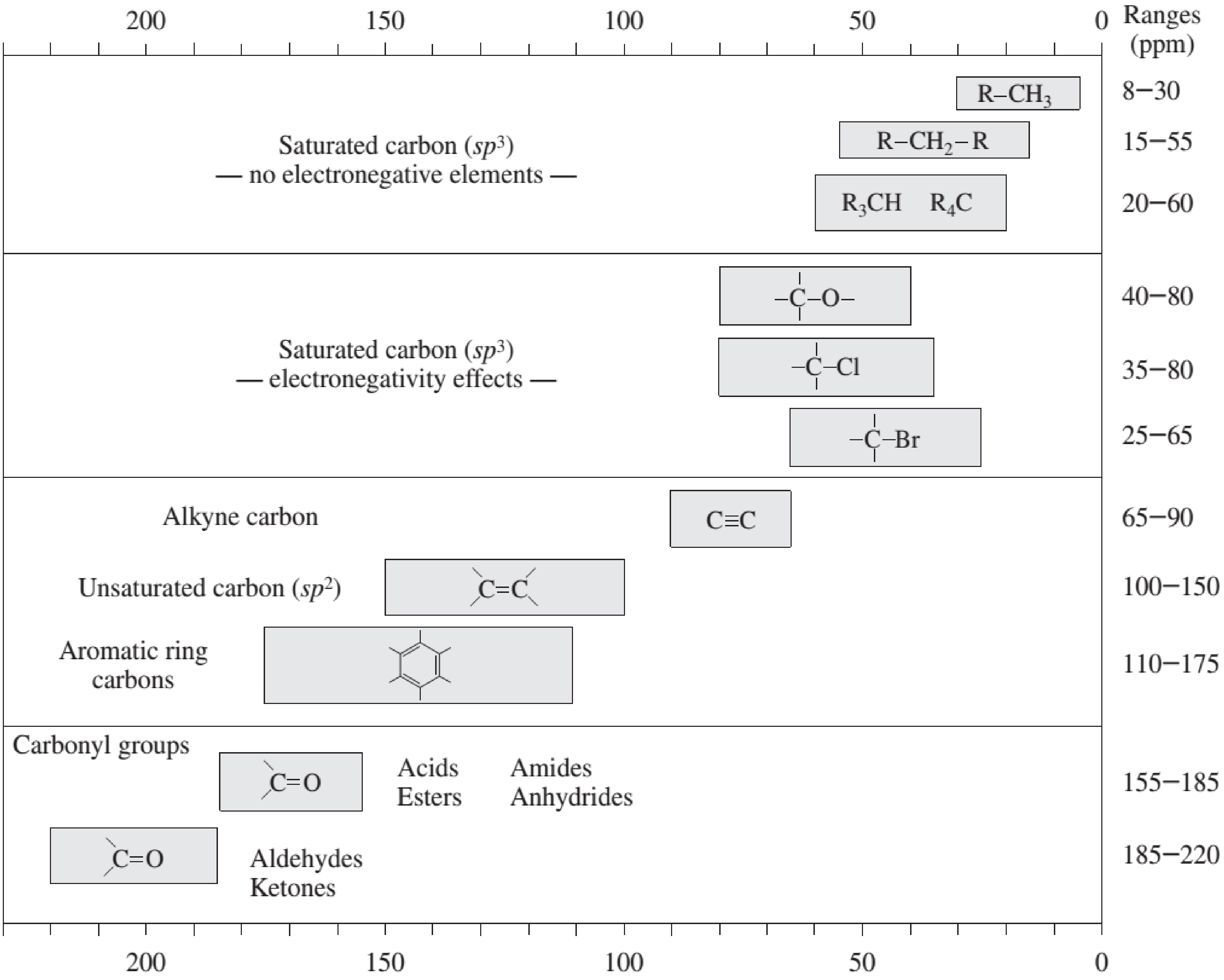
Sensitivity of Carbon NMR

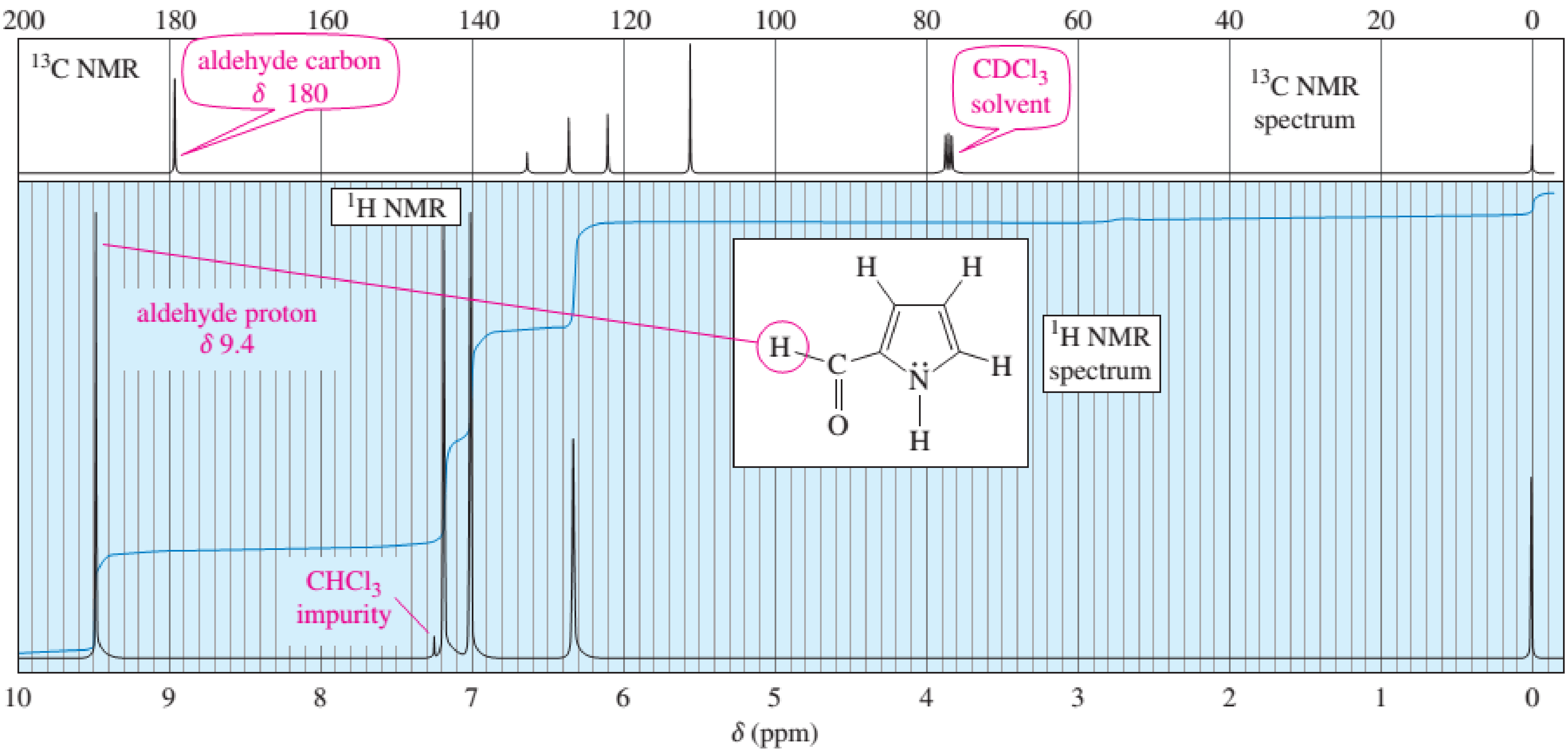
- About 99% of the carbon atoms in a natural sample are the isotope ^{12}C. This isotope has an even number of protons and an even number of neutrons, so it has no magnetic spin and cannot give rise to NMR signals.
- The less abundant isotope has an odd number of neutrons, giving it a magnetic spin of ½, just like a proton.
- Because only **1%** of the carbon atoms in a sample are the magnetic ^{13}C isotope, the sensitivity of ^{13}C NMR is decreased by a factor of 100.
- In addition, the gyromagnetic ratio of ^{13}C is only one-fourth that of the proton, so the ^{13}C resonance frequency (at a given magnetic field) is only one-fourth of that for ^{1}H NMR. The smaller gyromagnetic ratio leads to a further decrease in sensitivity.

Carbon chemical shifts

- As in proton NMR, many ^{13}C signals are deshielded by electron-withdrawing substituents.
- Carbon chemical shifts are usually about 15 to 20 times larger than comparable proton chemical shifts, which makes sense because the carbon atom is one atom closer to a shielding or deshielding group than its attached hydrogen.
- For example, an aldehyde proton absorbs around δ 9.4 ppm in the ^{1}H NMR spectrum, and the carbonyl carbon atom absorbs around 180 ppm downfield from TMS in the ^{13}C NMR spectrum.

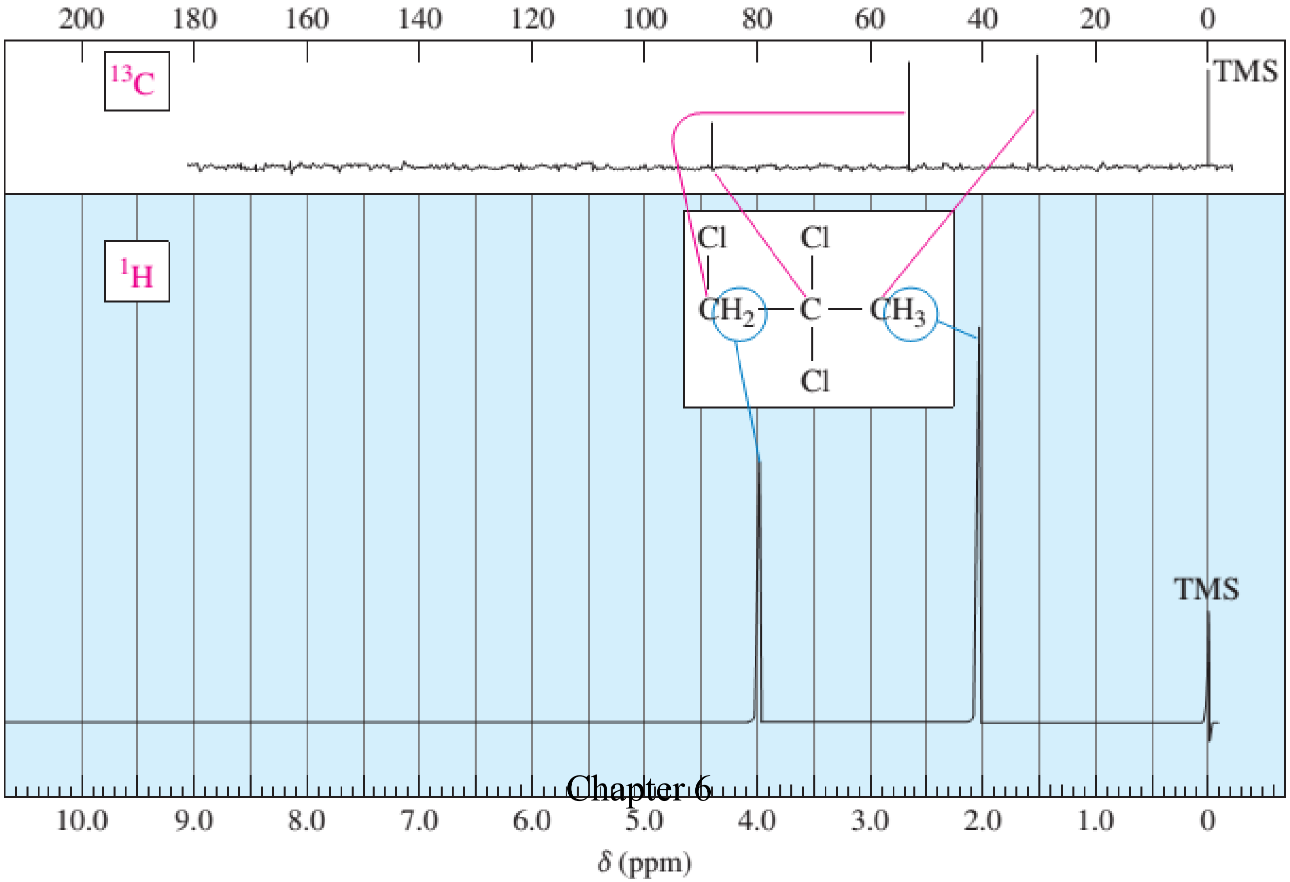



200
150
100
50
0
Ranges (ppm)
$R{-}CH_3$
8–30
Saturated carbon (sp^3)
— no electronegative elements —
$R{-}CH_2{-}R$
15–55
R_3CH R_4C
20–60
–C–O–
40–80
Saturated carbon (sp^3)
— electronegativity effects —
–C–Cl
35–80
–C–Br
25–65
Alkyne carbon
C≡C
65–90
Unsaturated carbon (sp^2)
C=C
100–150
Aromatic ring carbons
110–175
Carbonyl groups
C=O
Acids
Esters
Amides
Anhydrides
155–185
C=O
Aldehydes
Ketones
185–220
200
150
100
50
0



- ^{1}H NMR (*lower*) and ^{13}C NMR (*upper*) spectra of a heterocyclic aldehyde. Notice the correlation between the chemical shifts in the two spectra.
- The proton spectrum has a sweep width of 10 ppm, and the carbon spectrum has a width of 200 ppm.

- Because chemical shift effects are larger in ^{13}C NMR, an electron-withdrawing group has a substantial effect on the chemical shift of a carbon atom beta (one carbon removed) to the group.
- The methyl (CH_3) carbon absorbs at 33 ppm downfield from TMS because the two chlorine atoms on the adjacent $–CCl_2$- carbon have a substantial effect on the methyl carbon. The chemical shift of this methyl carbon is about 15 times that of its attached protons (δ 2.1 ppm) in accordance with our prediction.
- Similarly, the chemical shift of the $–CH_2Cl$ carbon (56 ppm) is about 15 times that of its protons (δ4.0).



Peak Areas

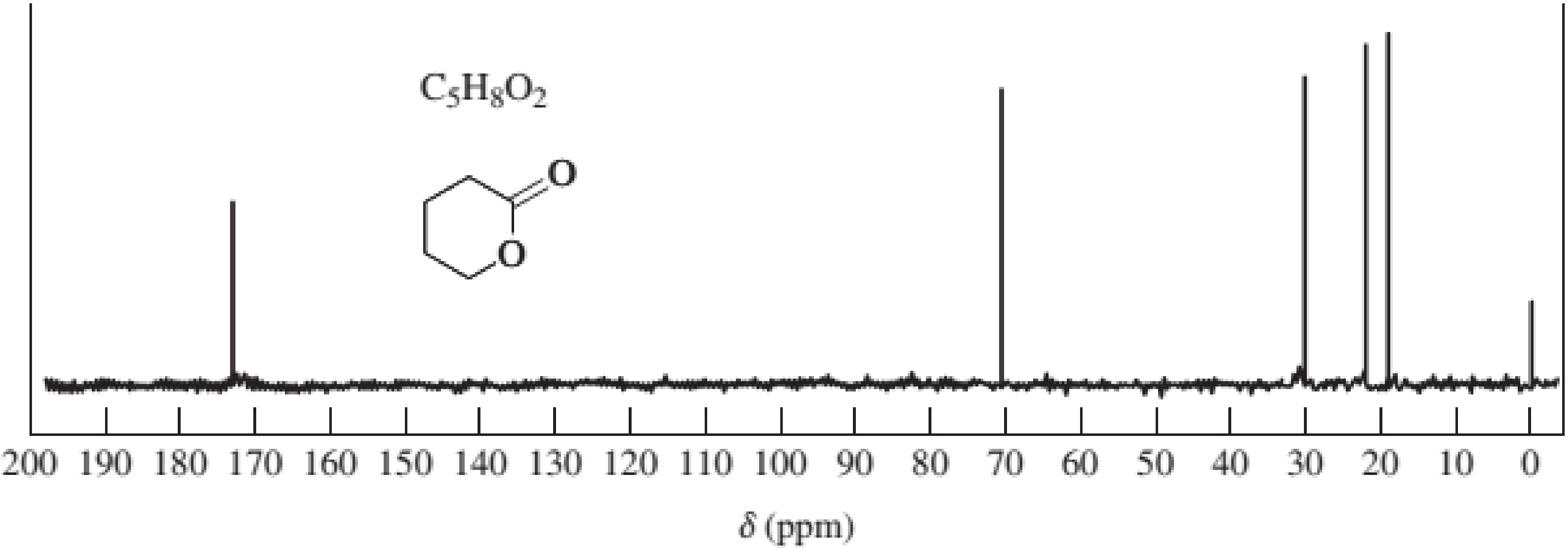
- The areas of peaks are not necessarily proportional to the number of carbons giving rise to the peaks.
- Carbon atoms with two or three protons attached usually give the strongest absorptions, and carbons with no protons tend to give weak absorptions.
- Newer spectrometers have an integrating mode that uses decoupling techniques to equalize the absorptions of different carbon atoms. This mode makes peak integrals nearly proportional to the relative numbers of carbon atoms.

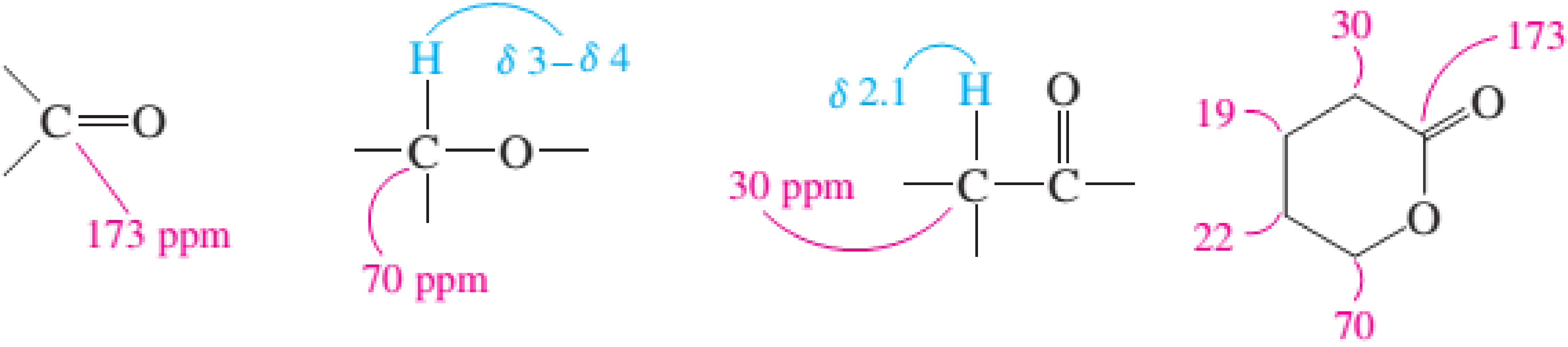
Spin-Spin Splitting

- Only 1% of the carbon atoms in the ^{13}C NMR sample are magnetic, so there is only a small probability that an observed ^{13}C nucleus is adjacent to another ^{13}C nucleus.
- Therefore, carbon–carbon splitting can be ignored.
- However, carbon–hydrogen coupling is common.
- Most carbon atoms are bonded directly to hydrogen atoms or are sufficiently close to hydrogen atoms for carbon–hydrogen spin-spin coupling to be observed.
- Extensive carbon–hydrogen coupling produces splitting patterns that can be complicated and difficult to interpret.

Proton Spin Decoupling

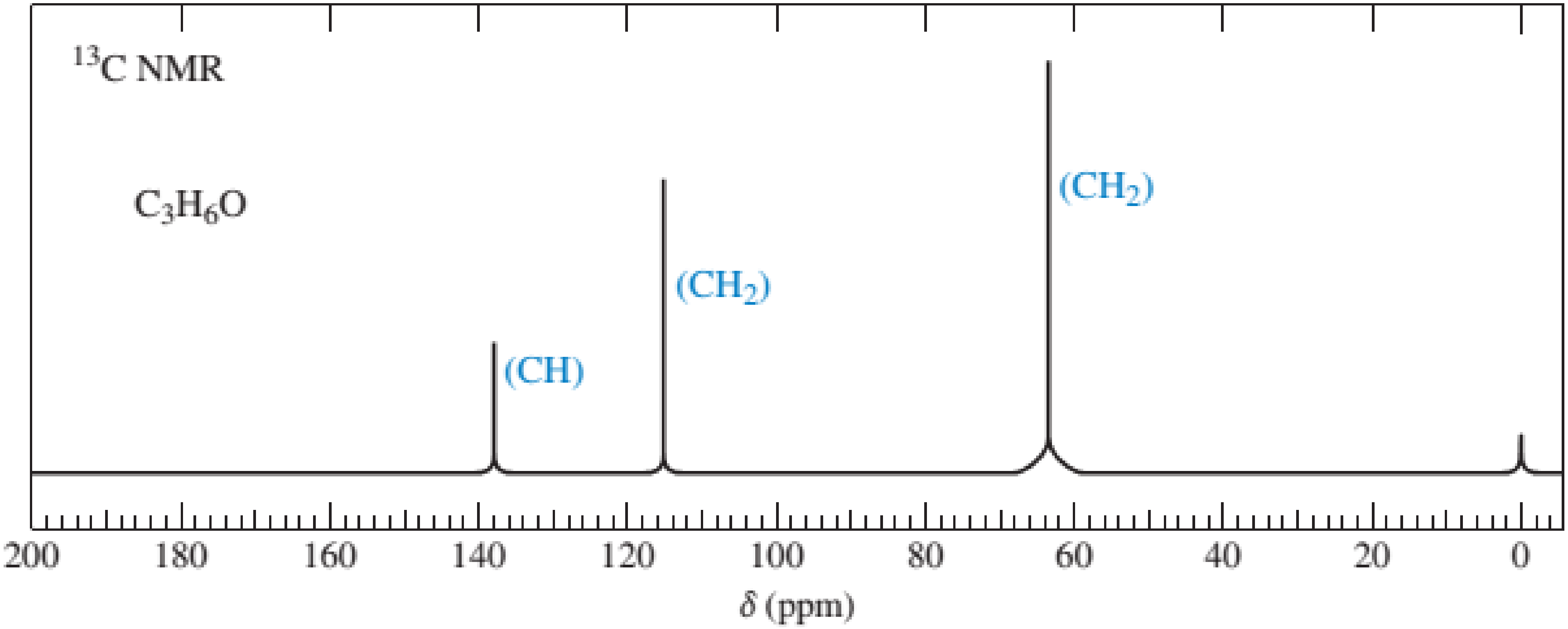
- To simplify ^{13}C NMR spectra, they are commonly recorded using **proton spin decoupling,** where the protons are continuously irradiated with a broadband (“noise”) proton transmitter.
- As a result, all the protons are continuously in resonance, and they rapidly flip their spins.
- The carbon nuclei see an *average* of the possible combinations of proton spin states.
- **Each carbon signal appears as a single, unsplit peak** because any carbon–hydrogen splitting has been eliminated.


C5H8O2
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


C=O
173 ppm
H
δ 3–δ 4
C
O
70 ppm
δ 2.1
H
O
C
C
30 ppm
30
173
19
O
22
O
70

PROBLEM 13-29

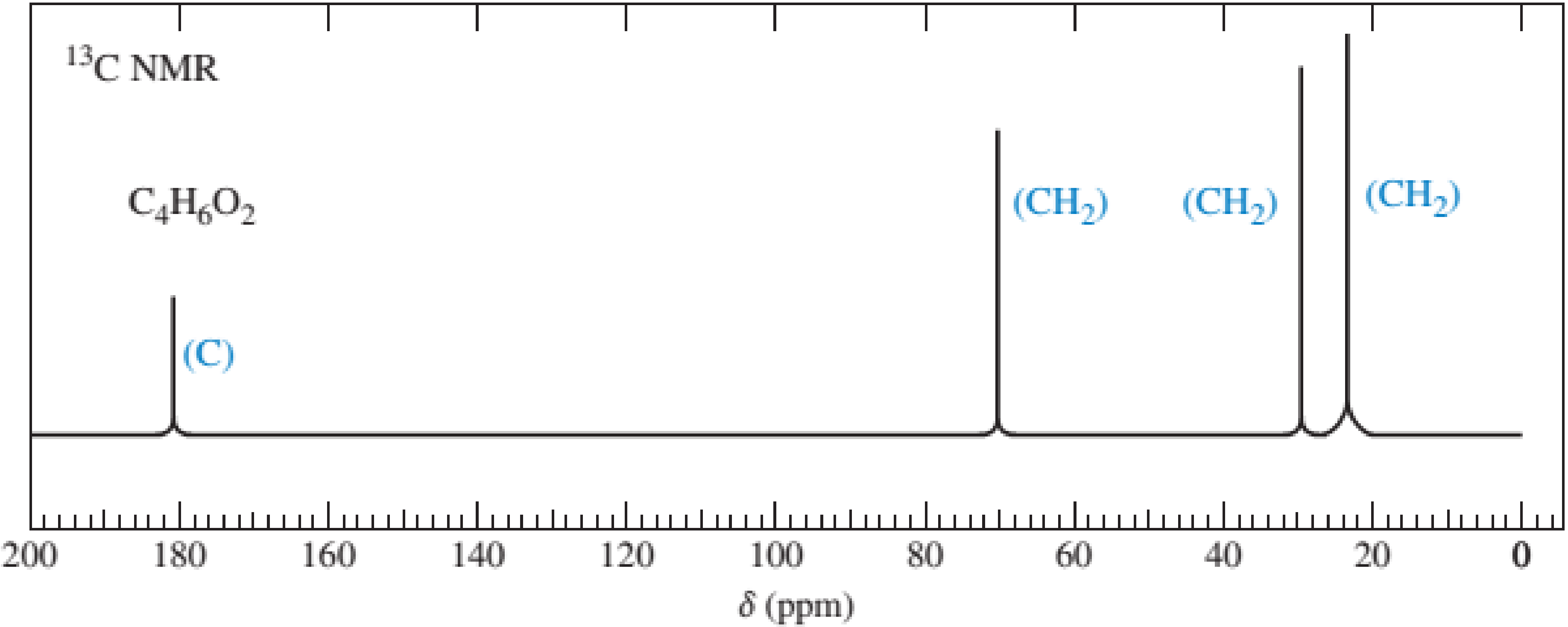
A bottle of allyl bromide was found to contain a large amount of an impurity. A careful distillation separated the impurity, which has the molecular formula C_3H_6O. The following ^{13}C NMR spectrum of the impurity was obtained:



(a) Propose a structure for this impurity.
(b) Assign the peaks in the ^{13}C NMR spectrum to the carbon atoms in the structure.
(c) Suggest how this impurity arose in the allyl bromide sample.

PROBLEM 13-30

An inexperienced graduate student was making some 4-hydroxybutanoic acid. He obtained an excellent yield of a different compound, whose ^{13}C NMR spectrum is shown here.

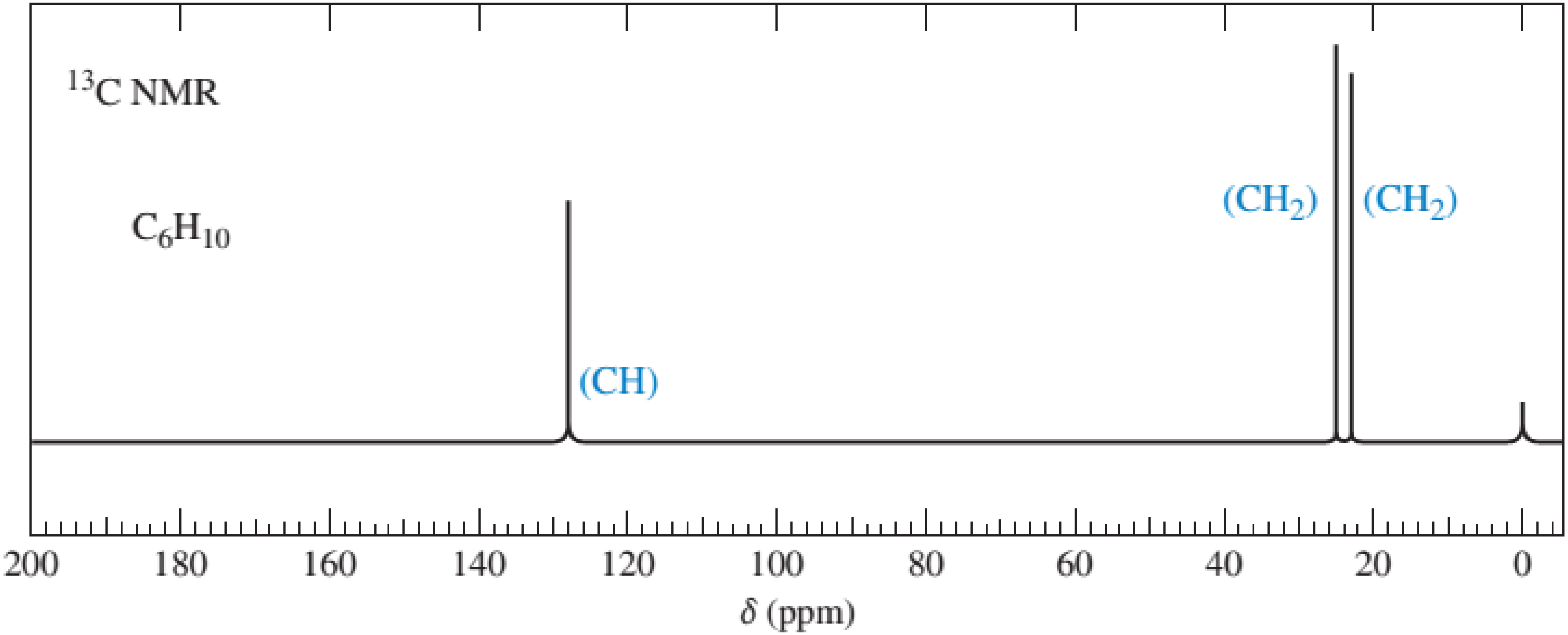


(a) Propose a structure for this product.

(b) Assign the peaks in the ^{13}C NMR spectrum to the carbon atoms in the structure.

PROBLEM 13-31

A laboratory student was converting cyclohexanol to cyclohexyl bromide by using one equivalent of sodium bromide in a large excess of concentrated sulfuric acid. The major product she recovered was not cyclohexyl bromide, but a compound of formula C_6H_{10} that gave the following ^{13}C NMR spectrum:

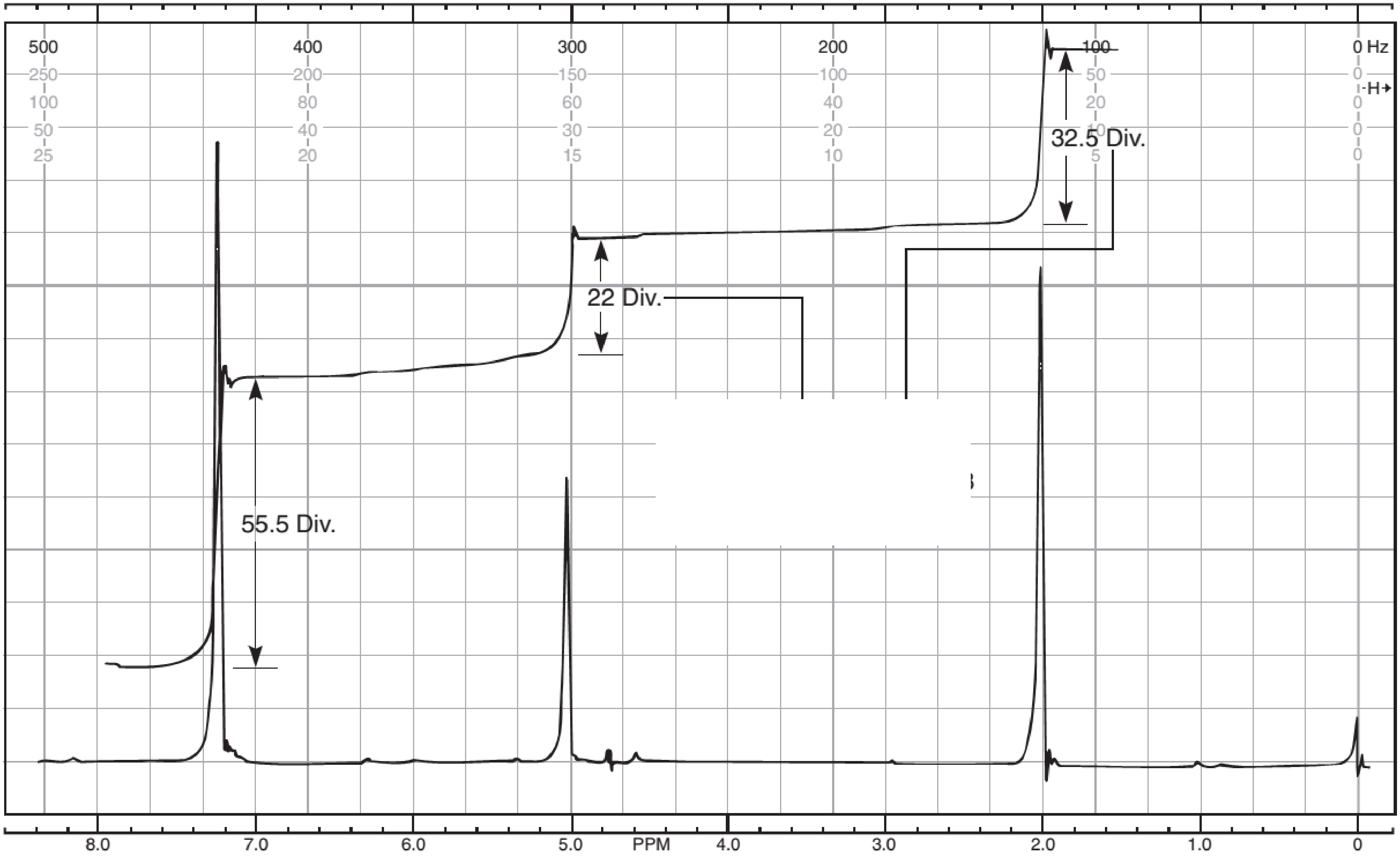


(a) Propose a structure for this product.

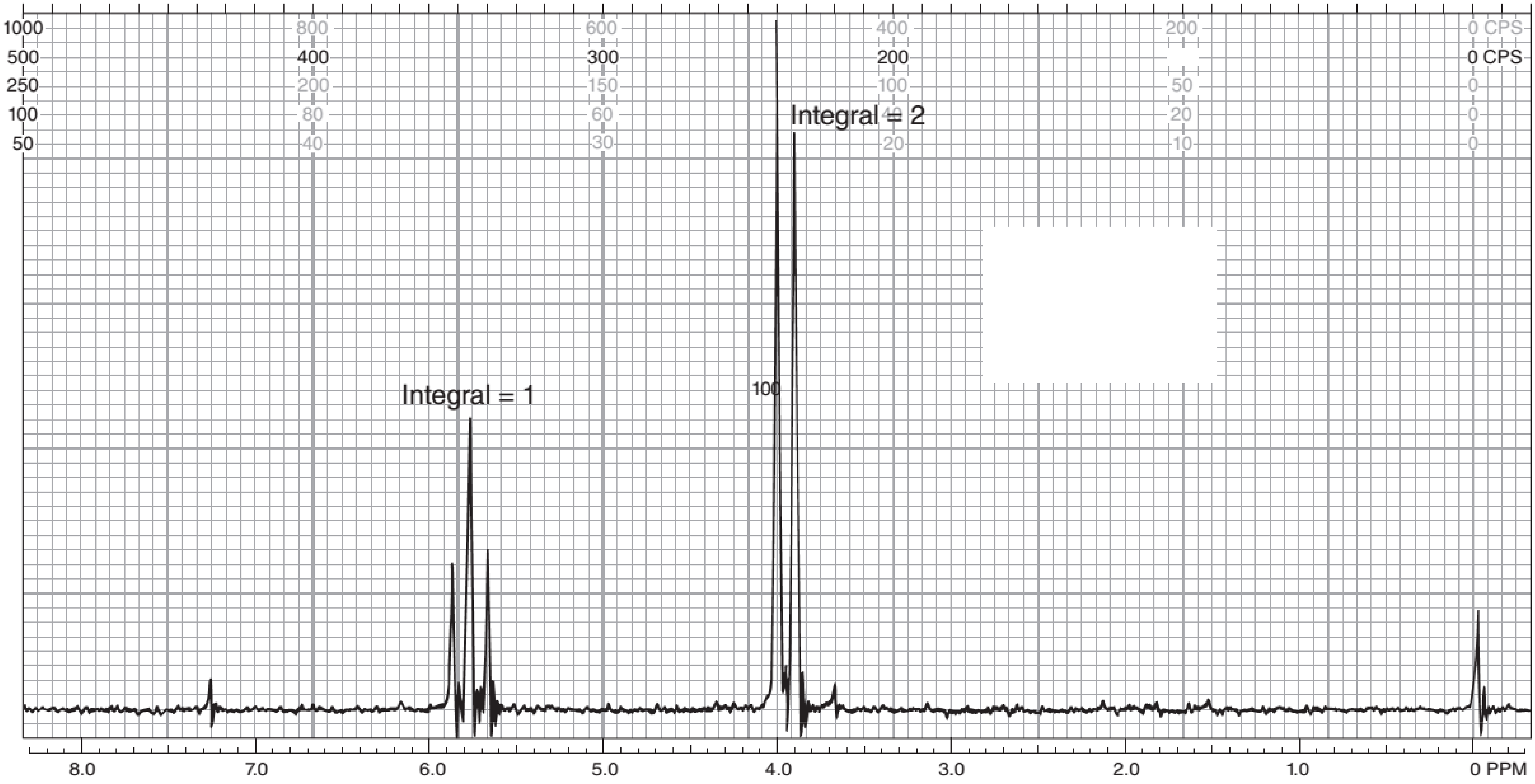
(b) Assign the peaks in the ^{13}C NMR spectrum to the carbon atoms in the structure.

(c) Suggest modifications in the reaction to obtain a better yield of cyclohexyl bromide.

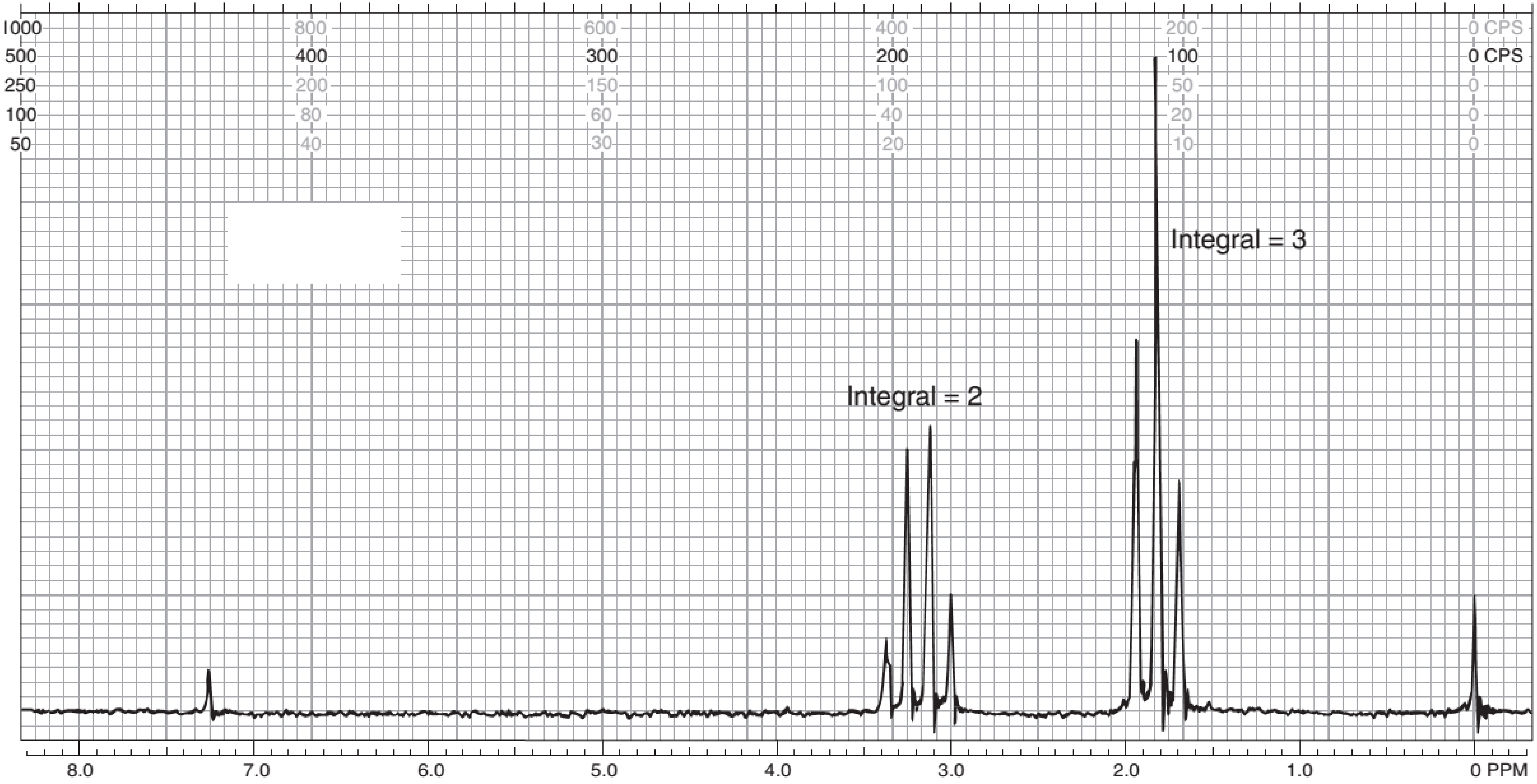
$C_9H_{10}O_2$ (doesn’t decolorize aq. Br_2 solution or aq. $KMnO_4$ solution.



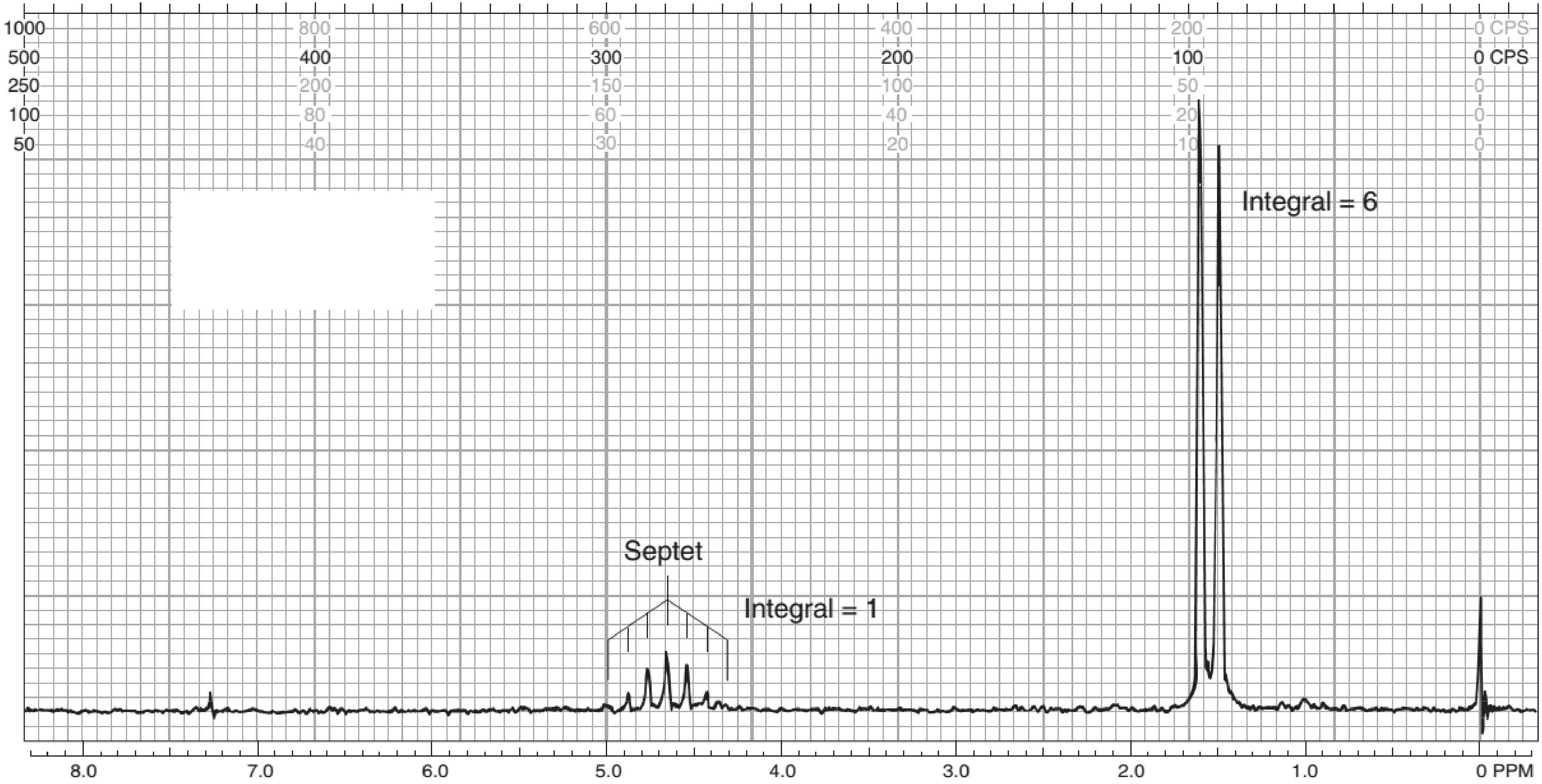
$C_2H_3Cl_3$


1000
500
250
100
50
800
400
200
80
40
600
300
150
60
30
400
200
100
40
20
200
50
20
10
0 CPS
0 CPS
0
0
0
Integral = 2
Integral = 1
100
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 PPM

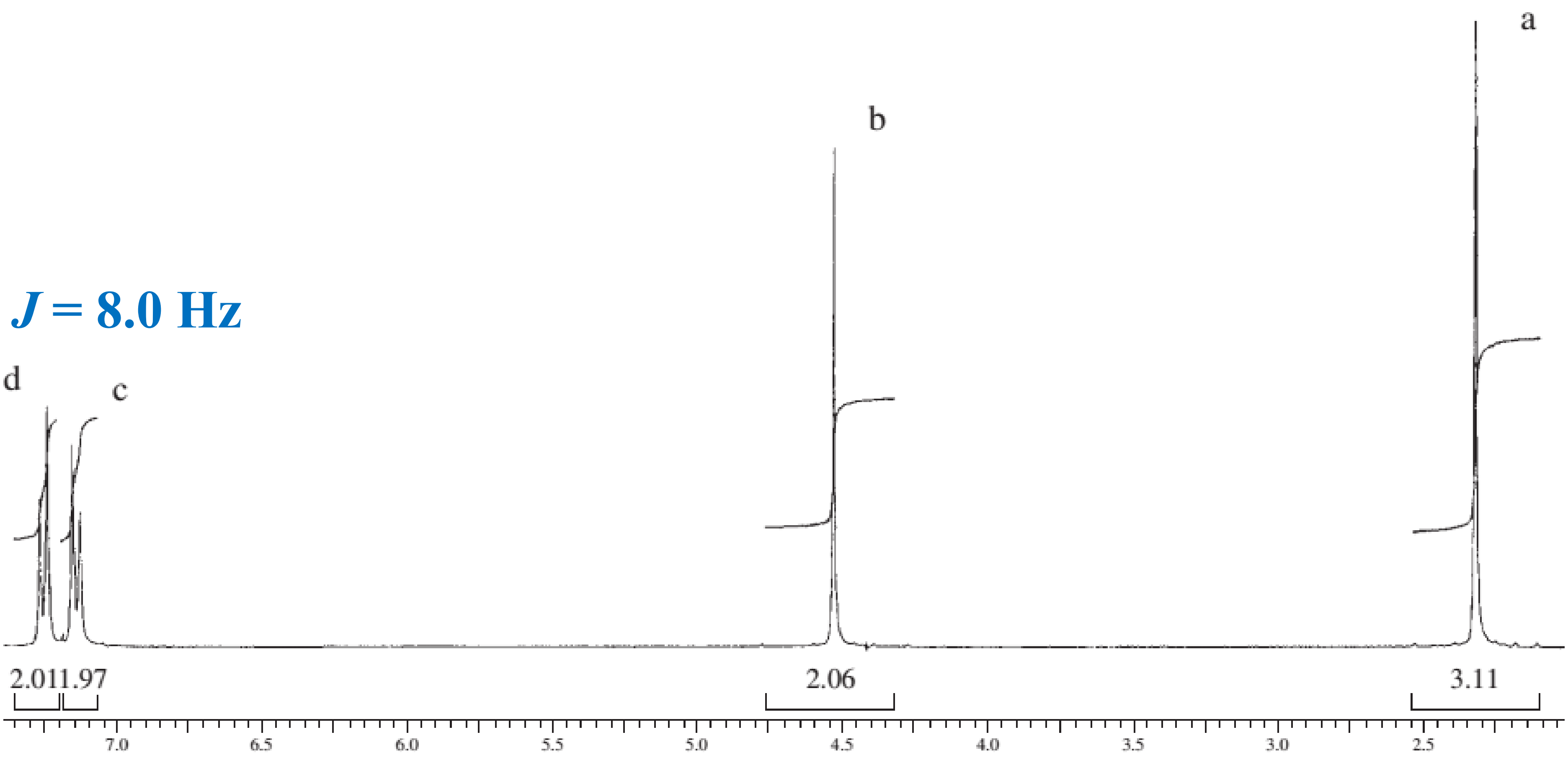
C_2H_5I


1000
500
250
100
50
800
400
200
80
40
600
300
150
60
30
400
200
100
40
20
200
100
50
20
10
0 CPS
0 CPS
0
0
0
Integral = 3
Integral = 2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 PPM

$C_3H_7NO_2$

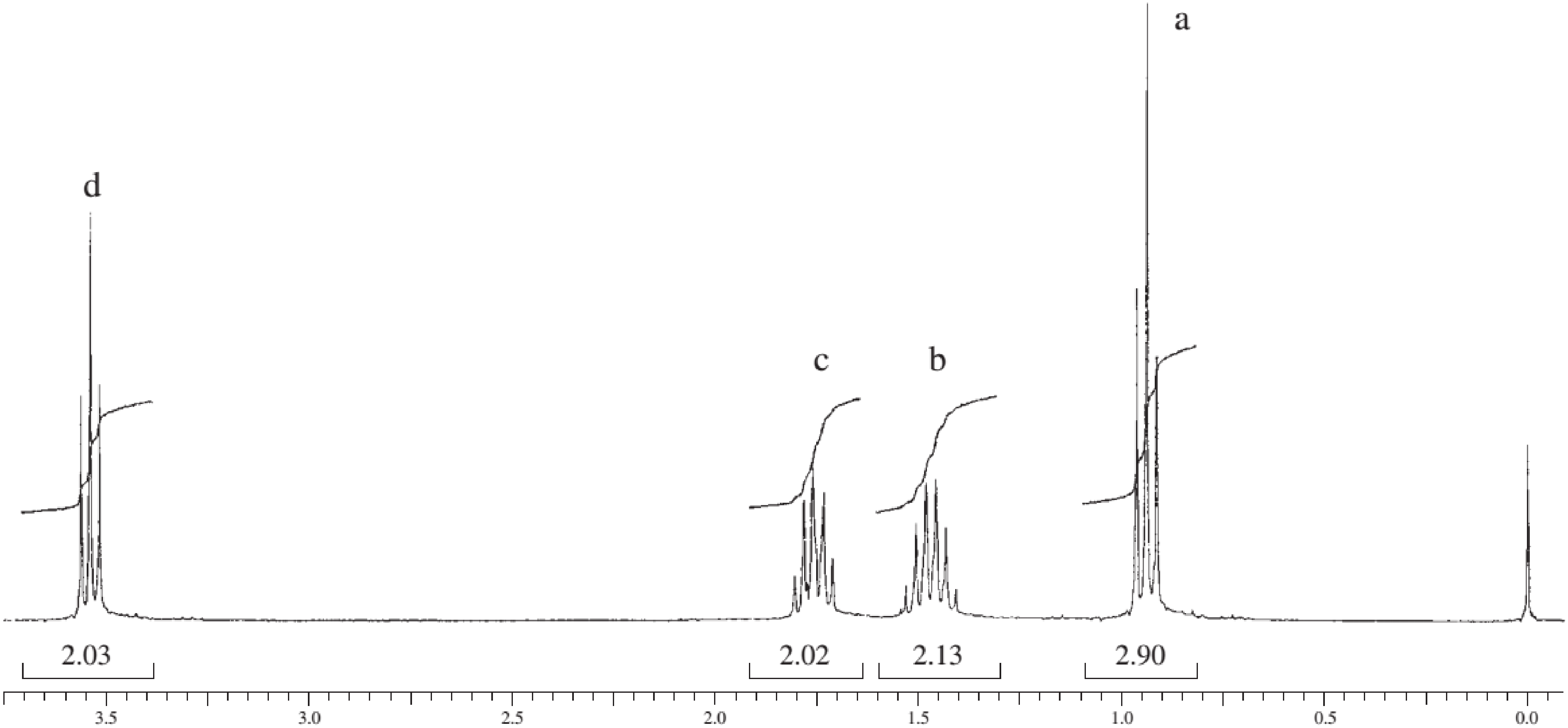

1000
500
250
100
50
800
400
200
80
40
600
300
150
60
30
400
200
100
40
20
200
100
50
20
10
0 CPS
0 CPS
Integral = 6
Septet
Integral = 1
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 PPM

C_8H_9Cl

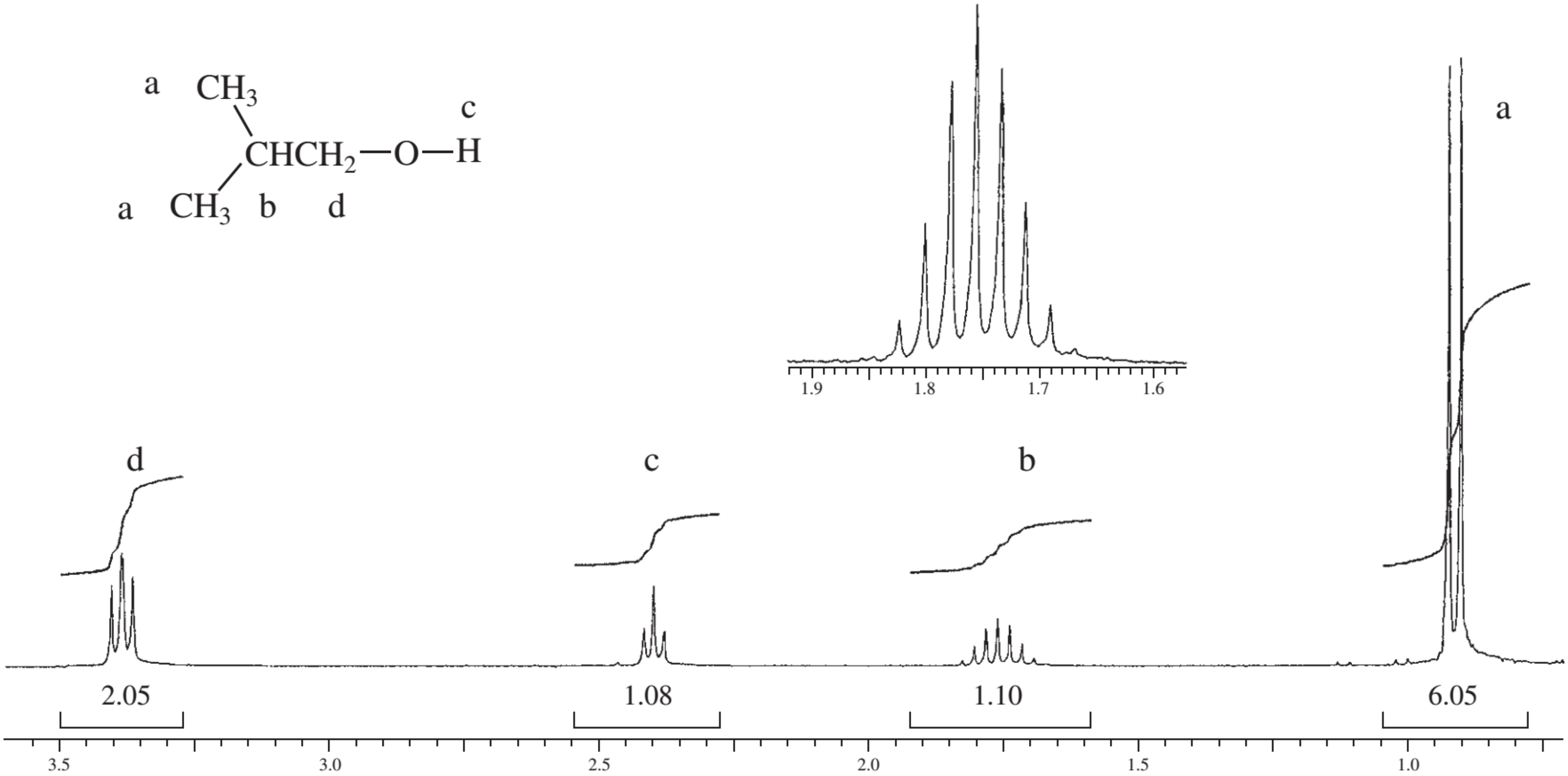


$J = 8.0$ Hz

C_4H_9Cl



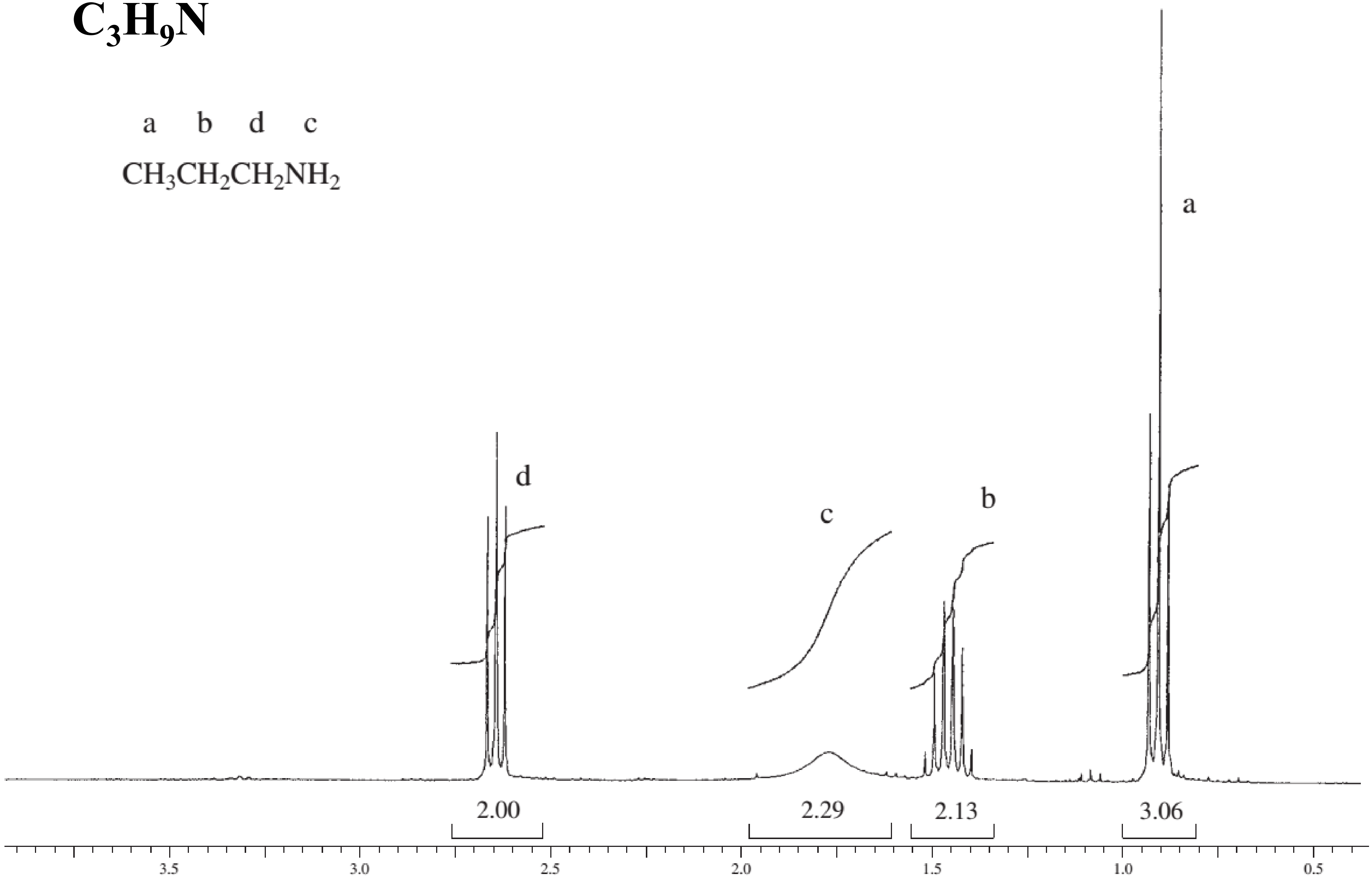
$C_4H_{10}O$ (an alcohol)



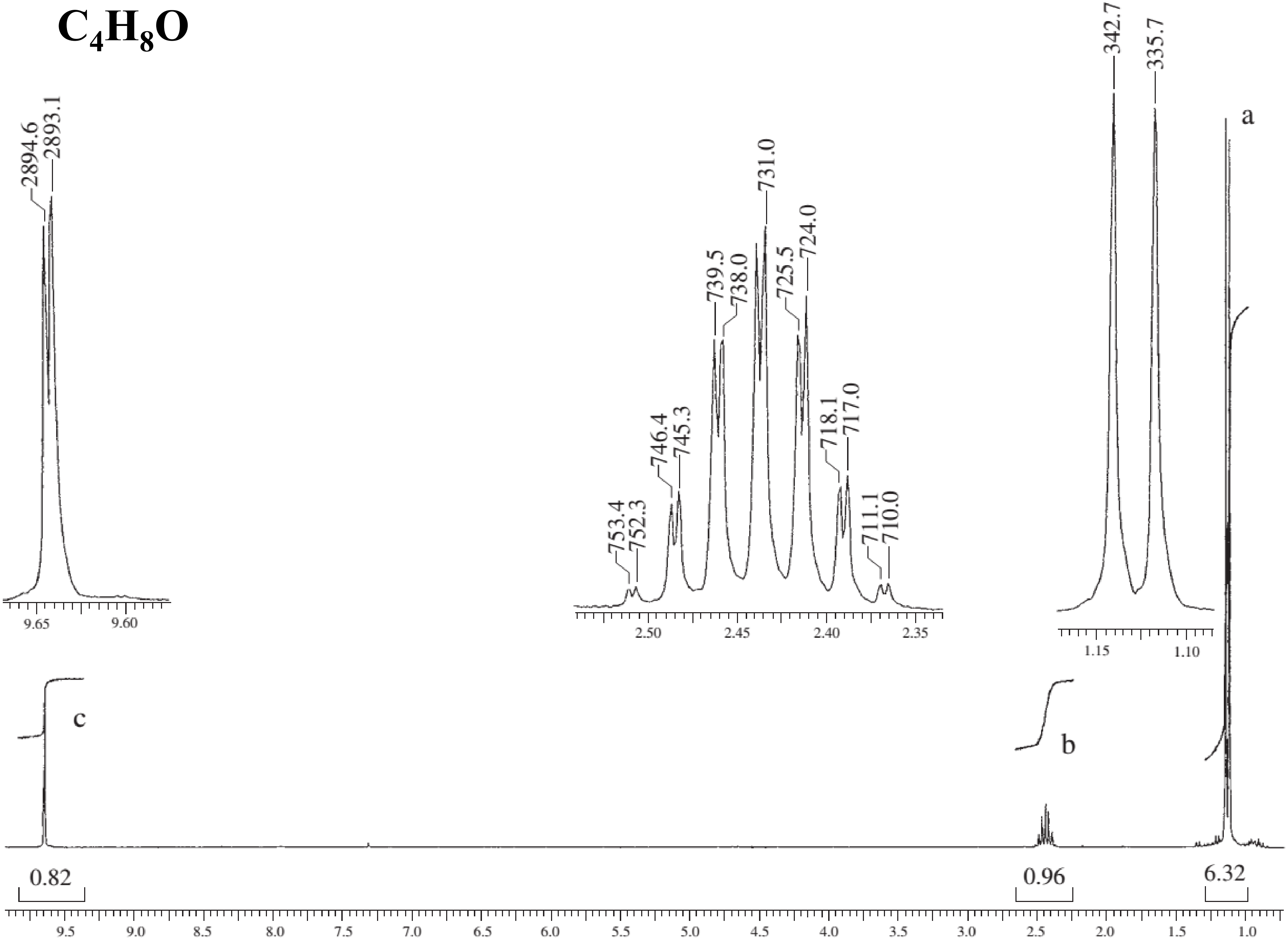
C_3H_9N

a b d c

$CH_3CH_2CH_2NH_2$

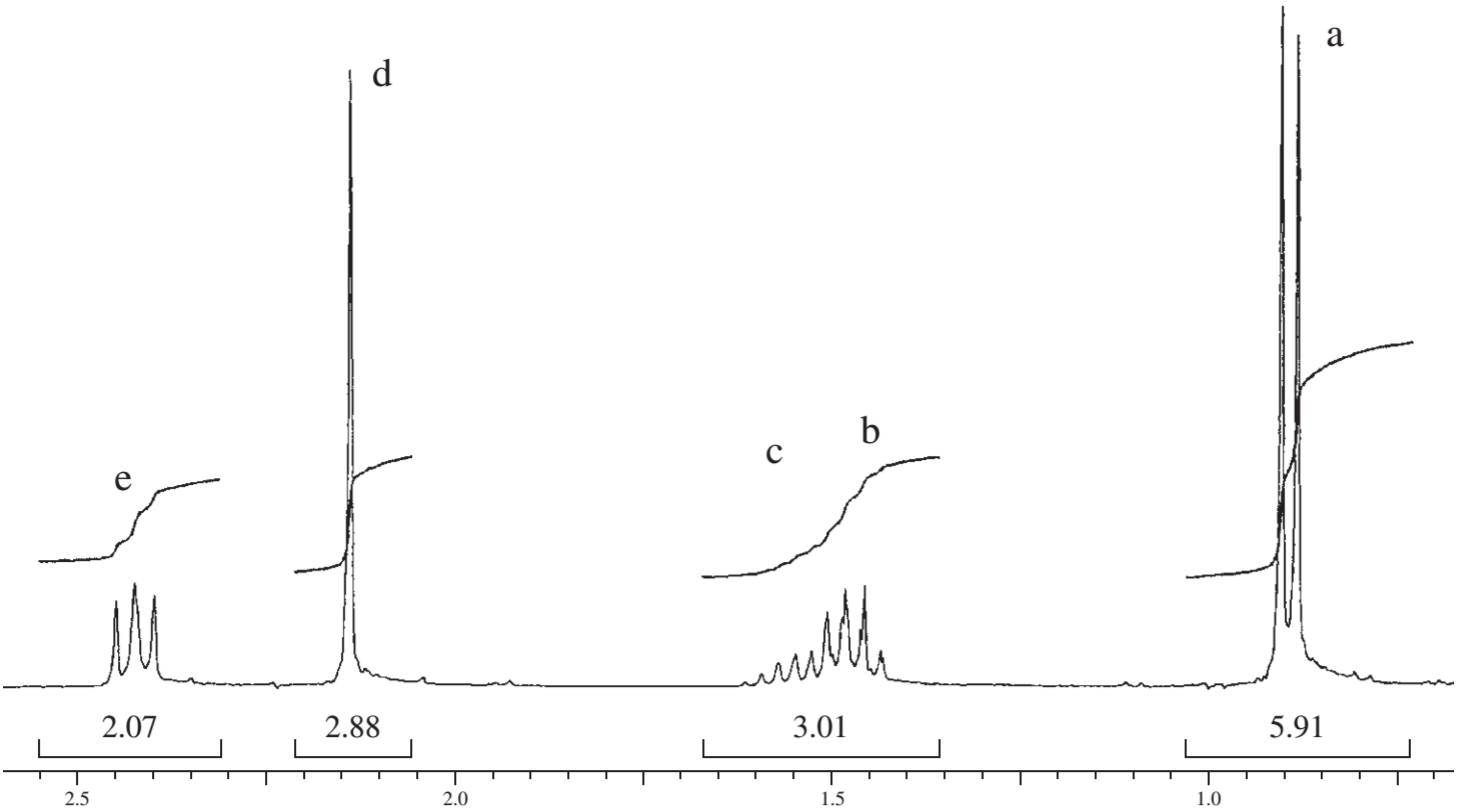


C_4H_8O

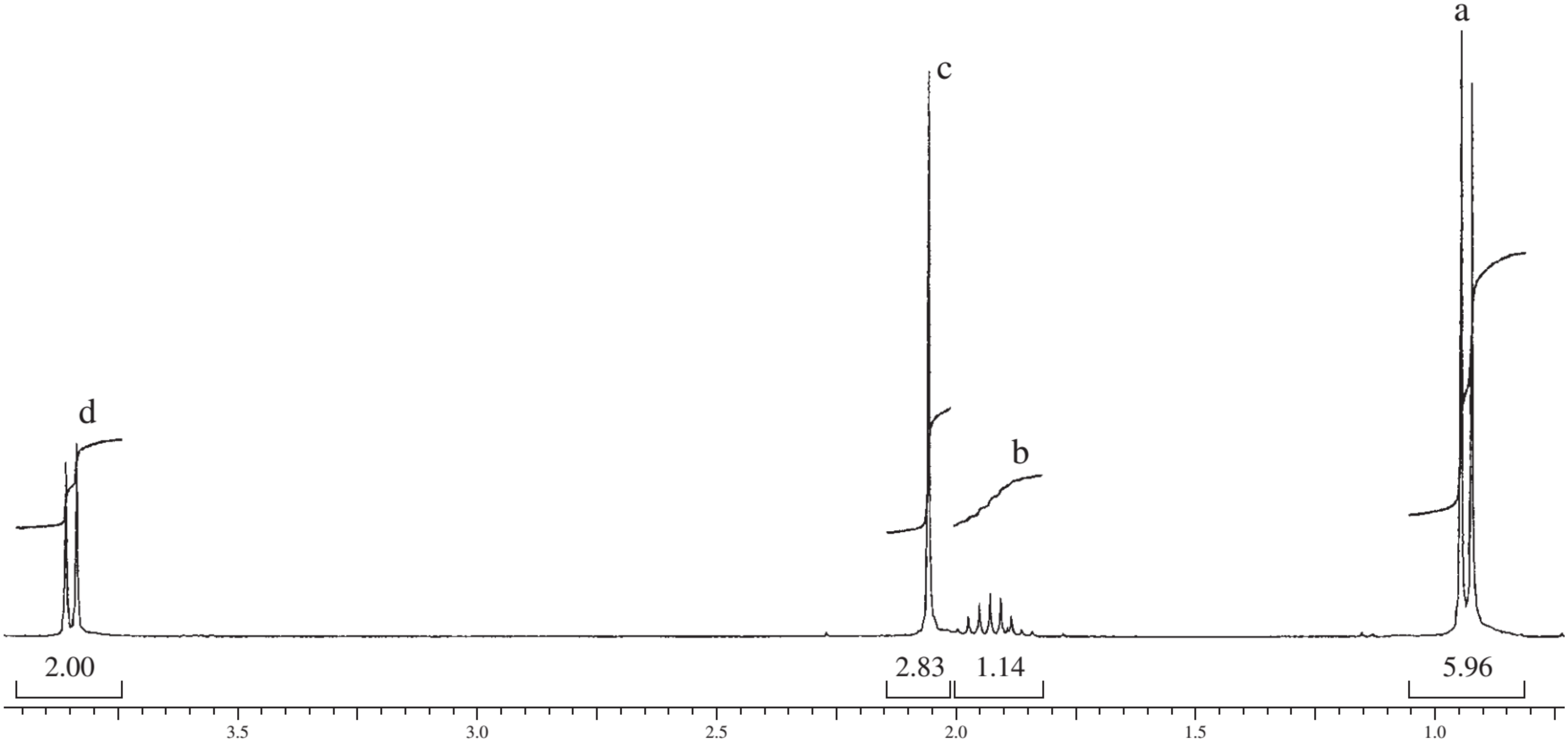


2894.6
2893.1
9.65
9.60
753.4
752.3
746.4
745.3
739.5
738.0
731.0
725.5
724.0
718.1
717.0
711.1
710.0
2.50
2.45
2.40
2.35
342.7
335.7
a
1.15
1.10
c
b
0.82
0.96
6.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

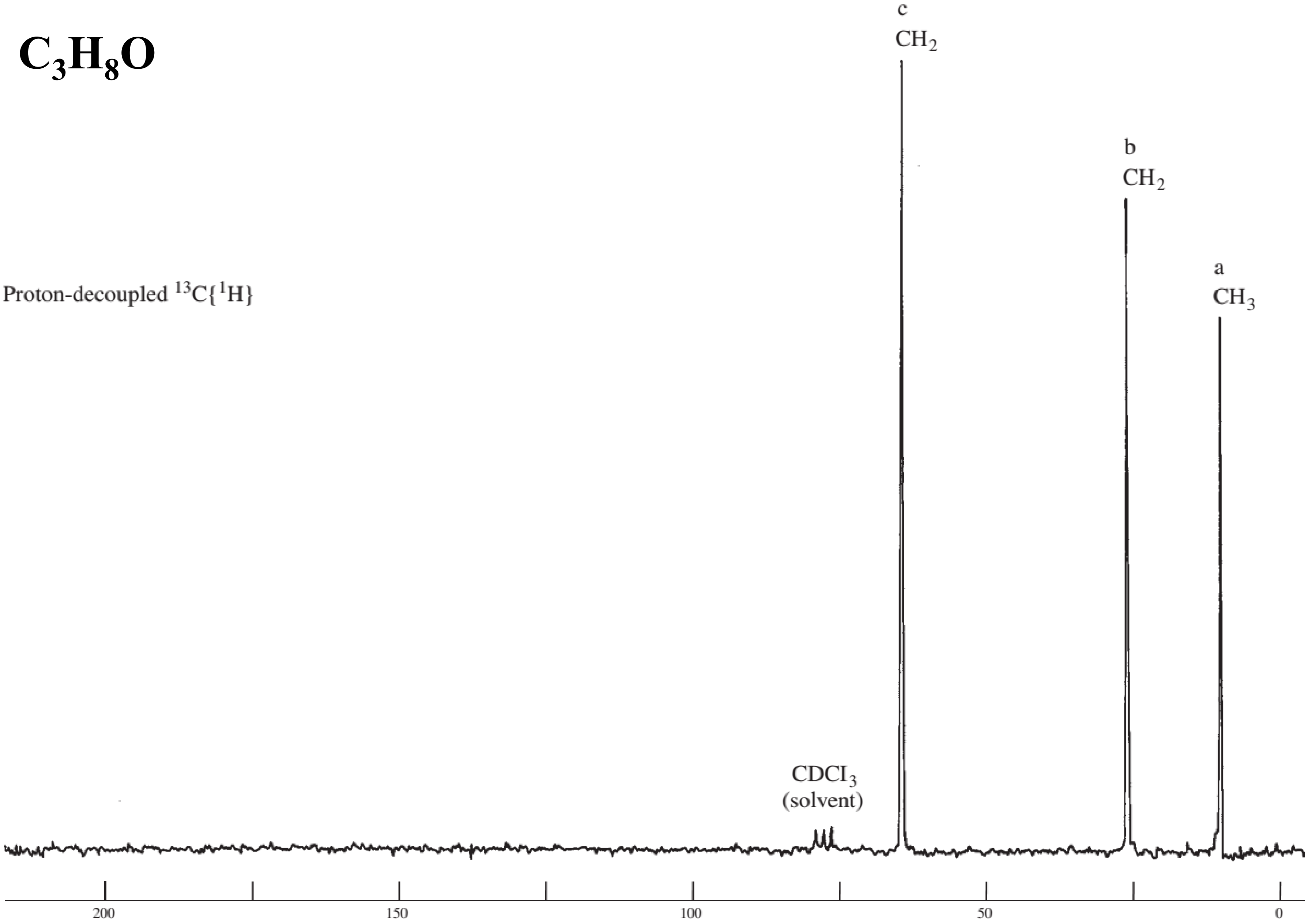
$C_7H_{14}O$



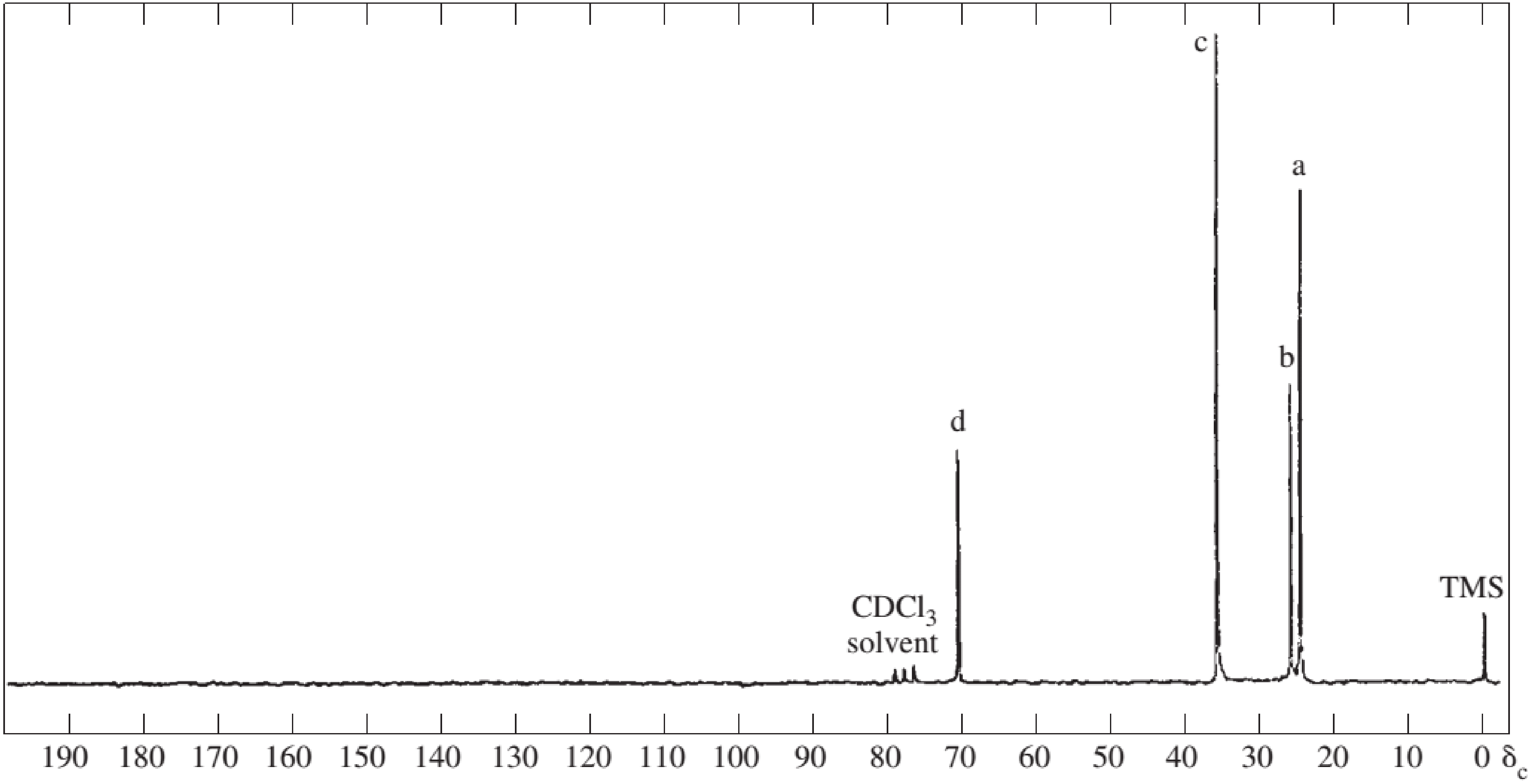
$C_6H_{12}O_2$



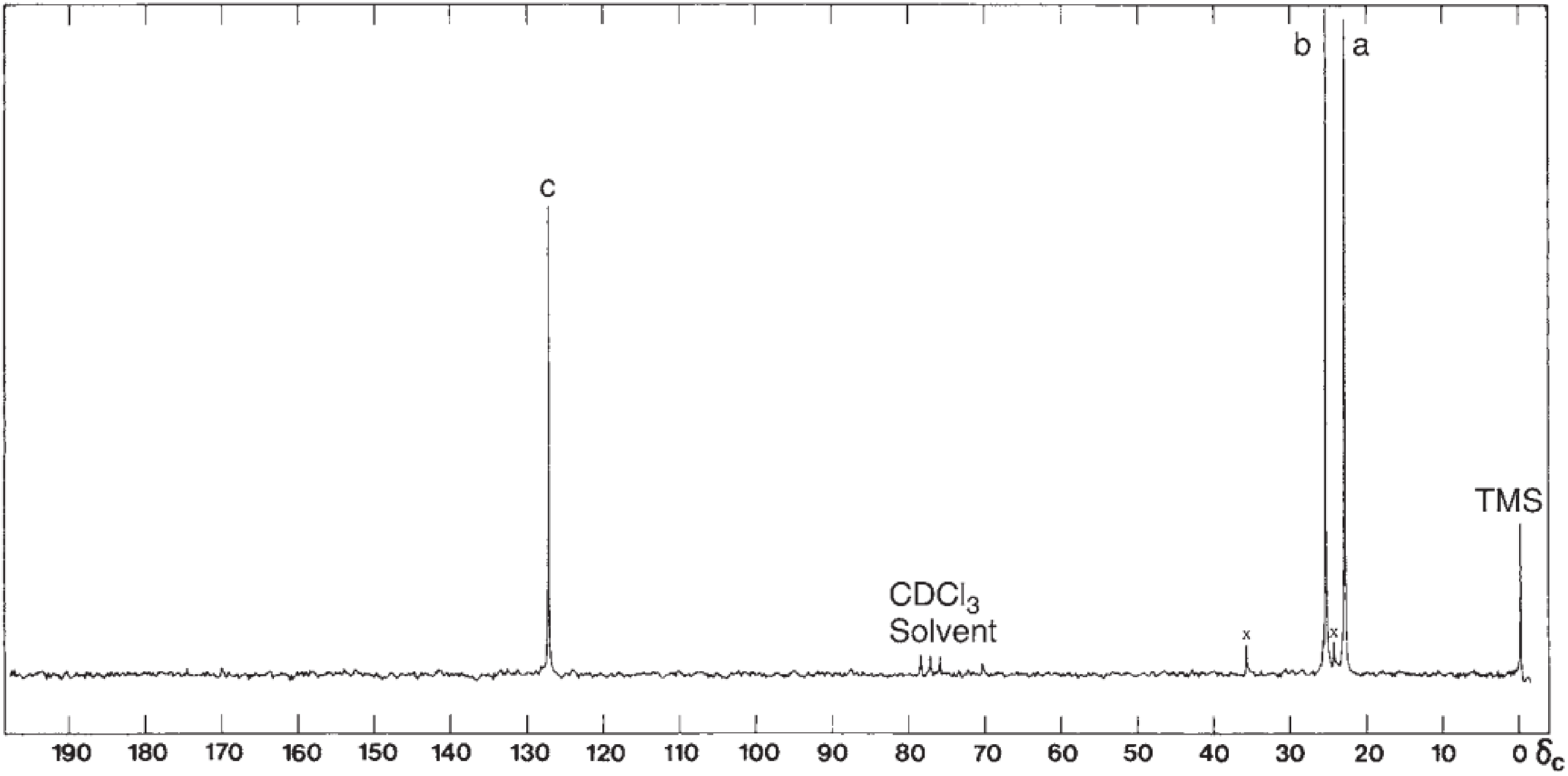
C_3H_8O


c
CH_2
b
CH_2
a
CH_3
Proton-decoupled $^{13}C\{^1H\}$
$CDCl_3$
(solvent)
200
150
100
50
0

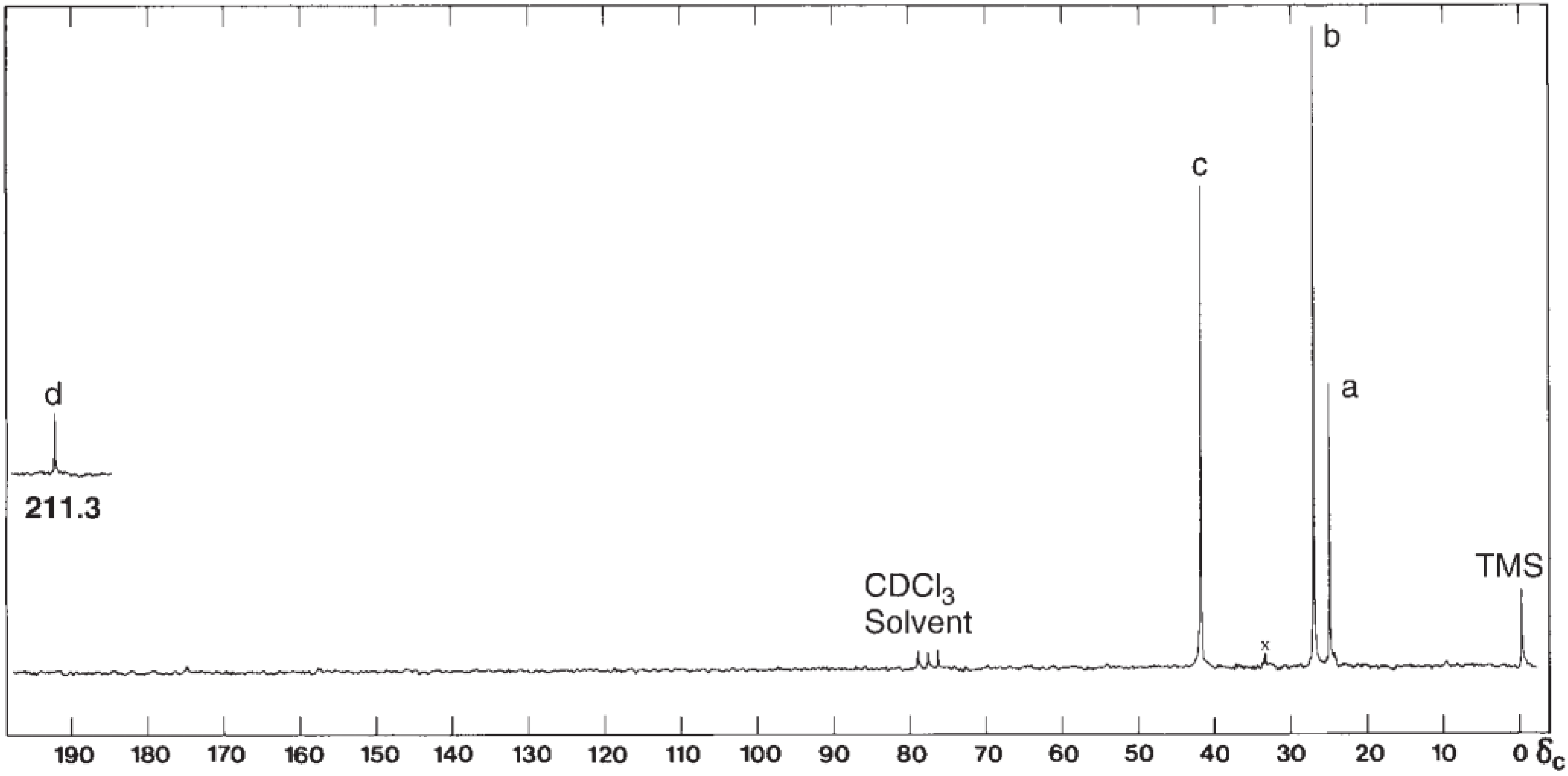
$C_6H_{12}O$


c
a
b
d
TMS
CDCl$_3$ solvent
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 δ$_c$

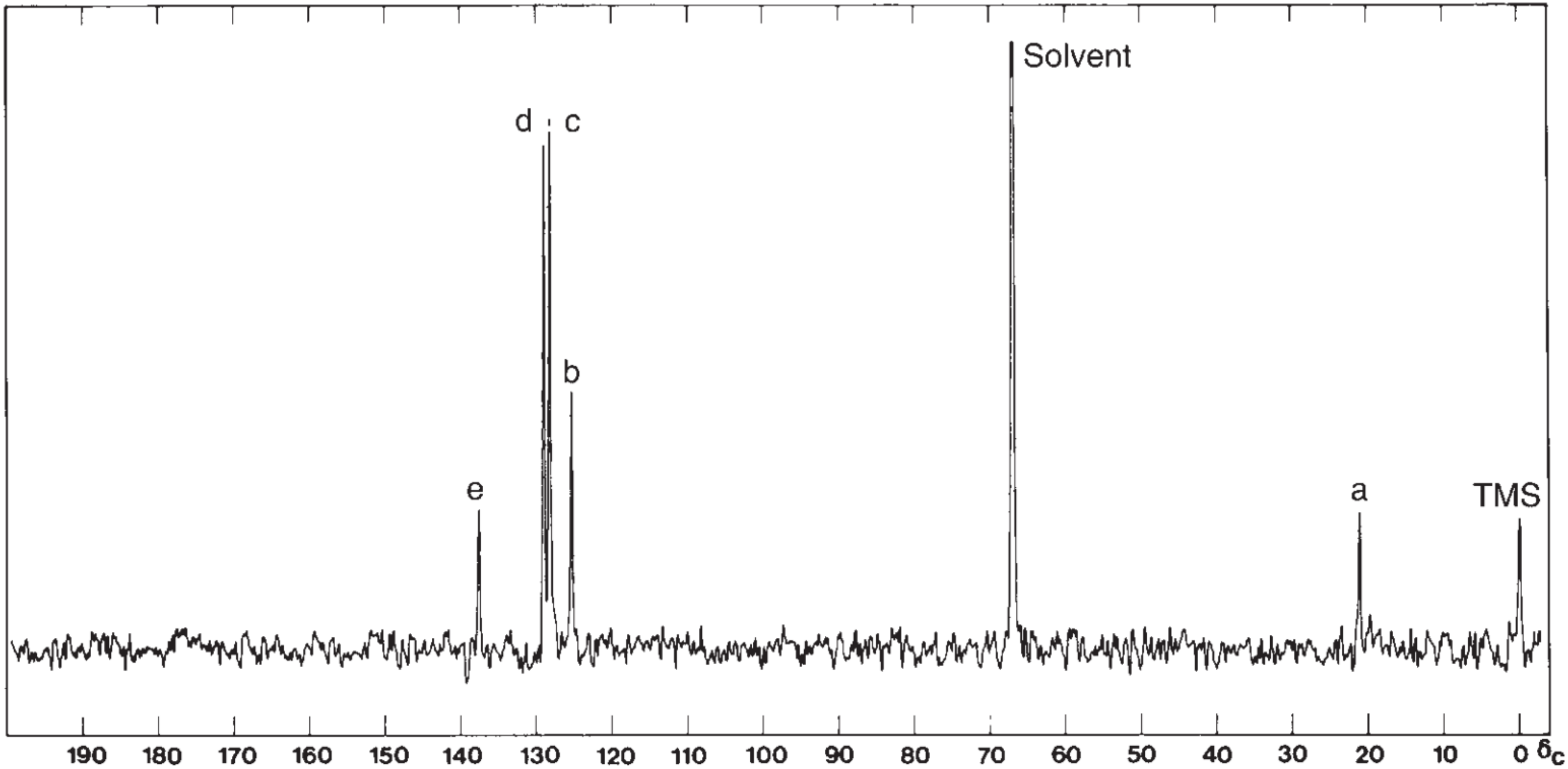
C_6H_{10}

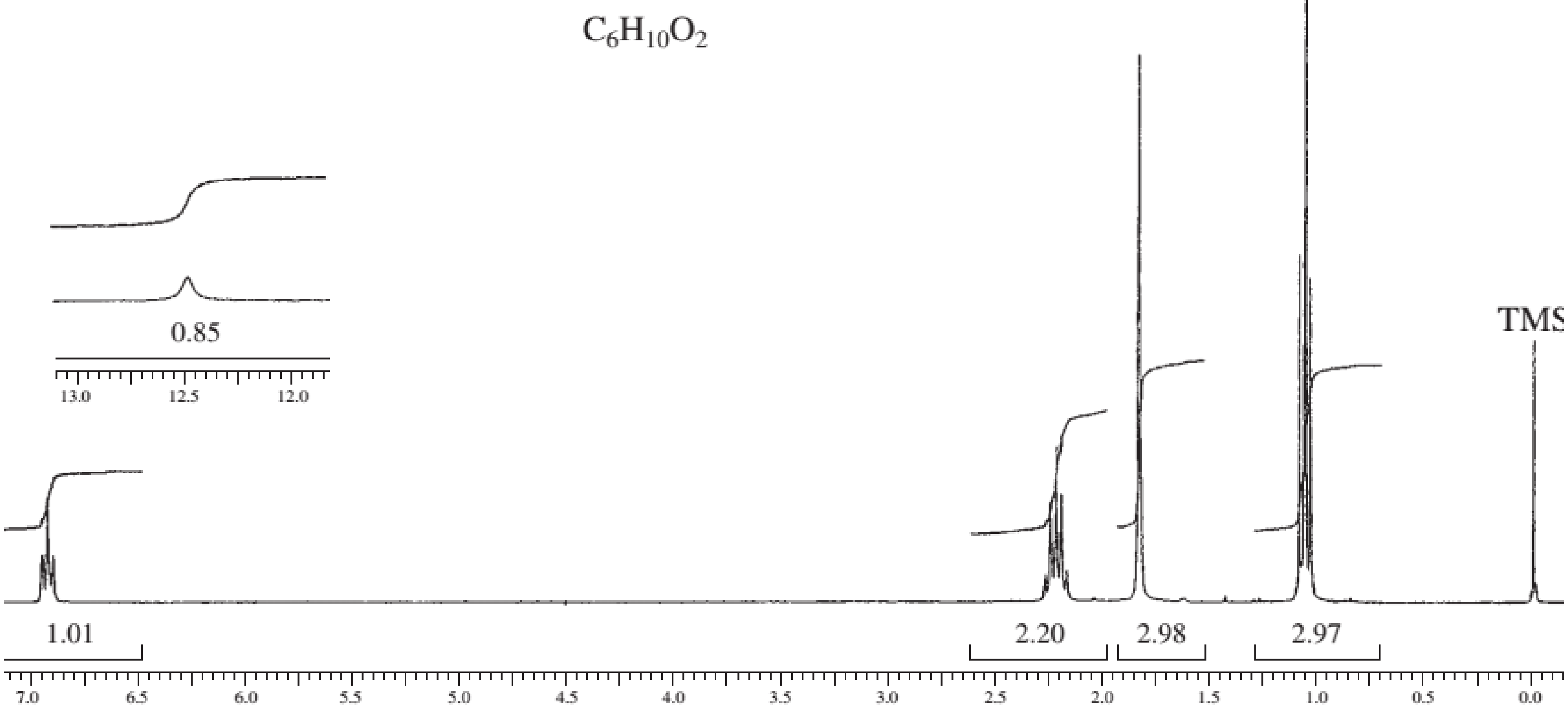

b
a
c
TMS
CDCl$_3$
Solvent
x
x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ_C

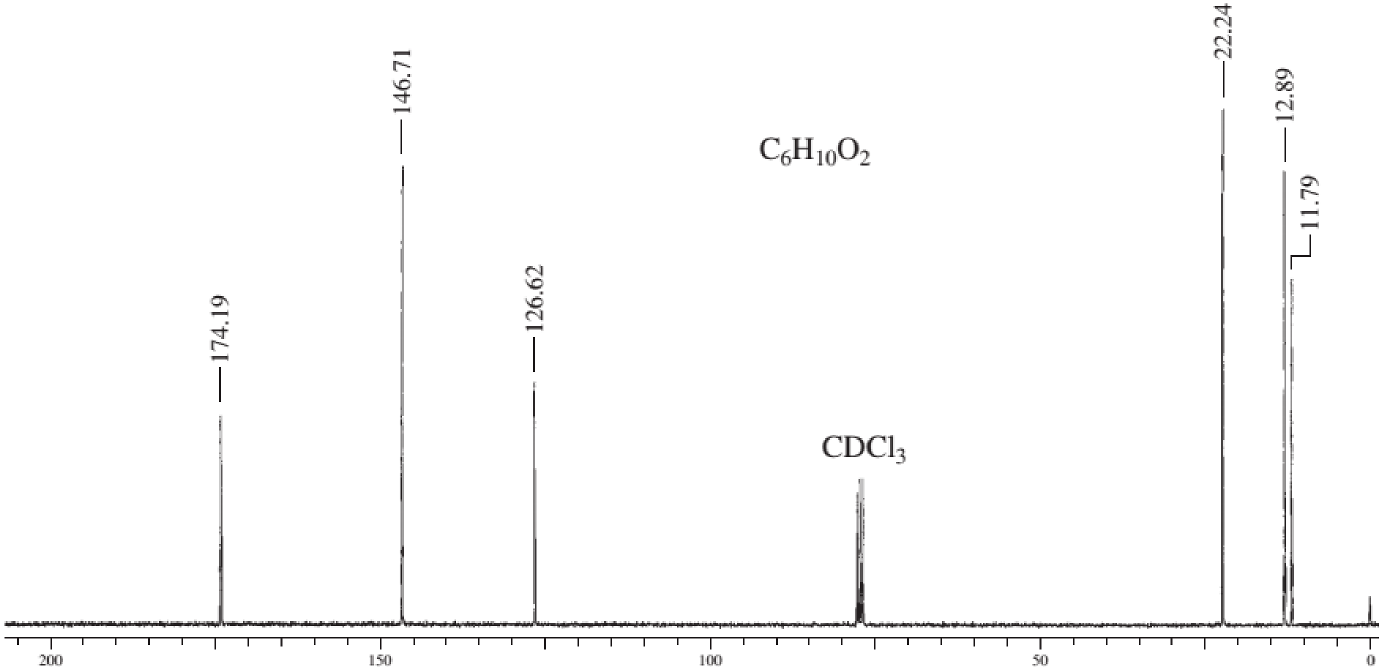
$C_6H_{10}O$


d
211.3
c
b
a
x
CDCl$_3$ Solvent
TMS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ_c

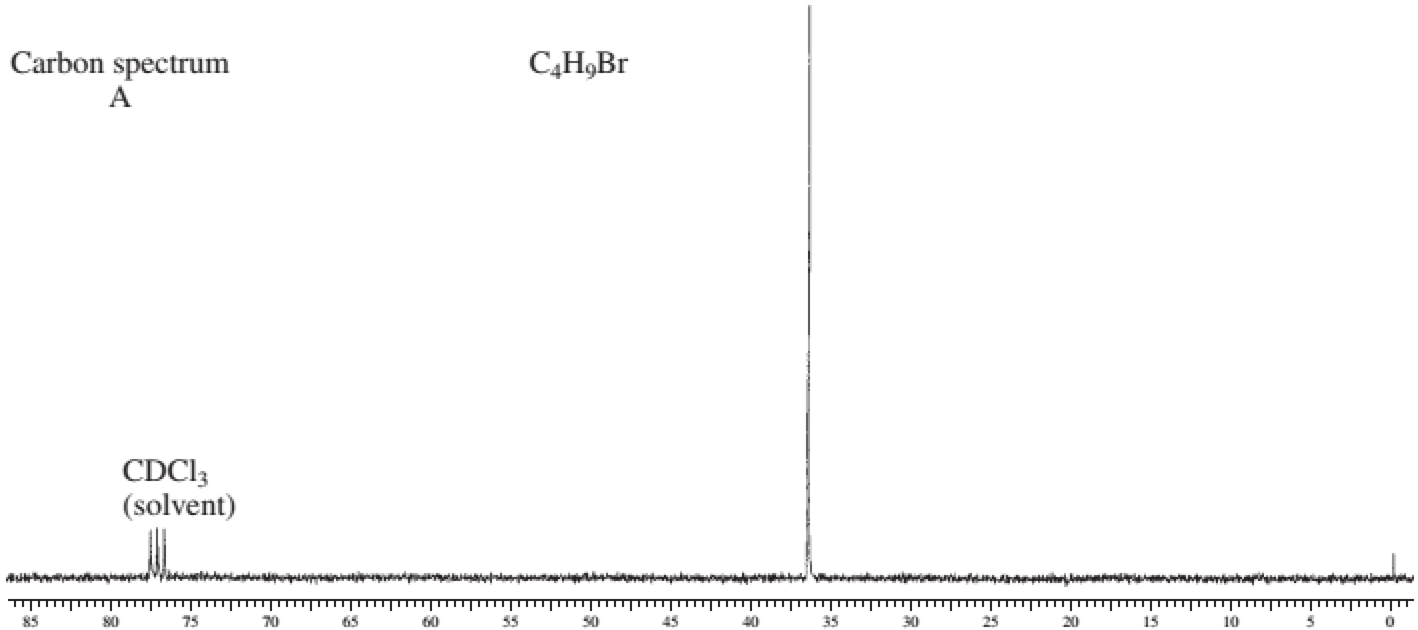
C_7H_8

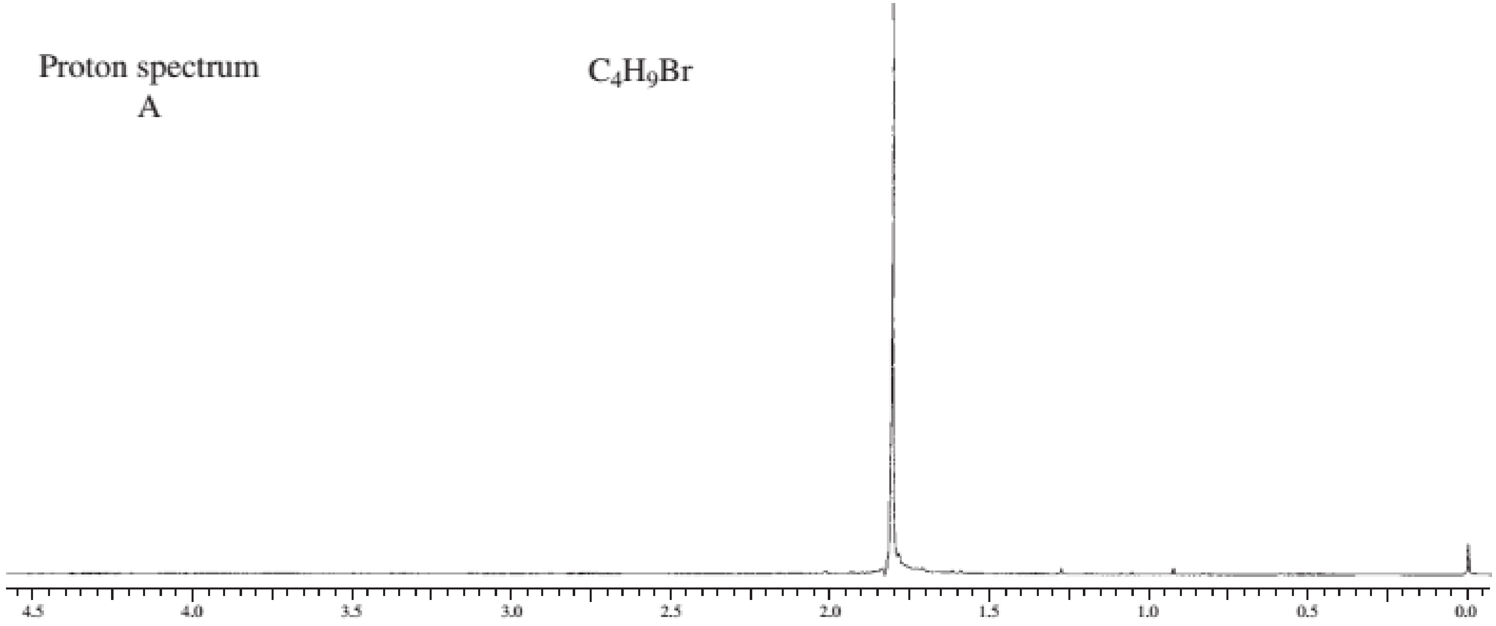

Solvent
d
c
b
e
a
TMS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ_C

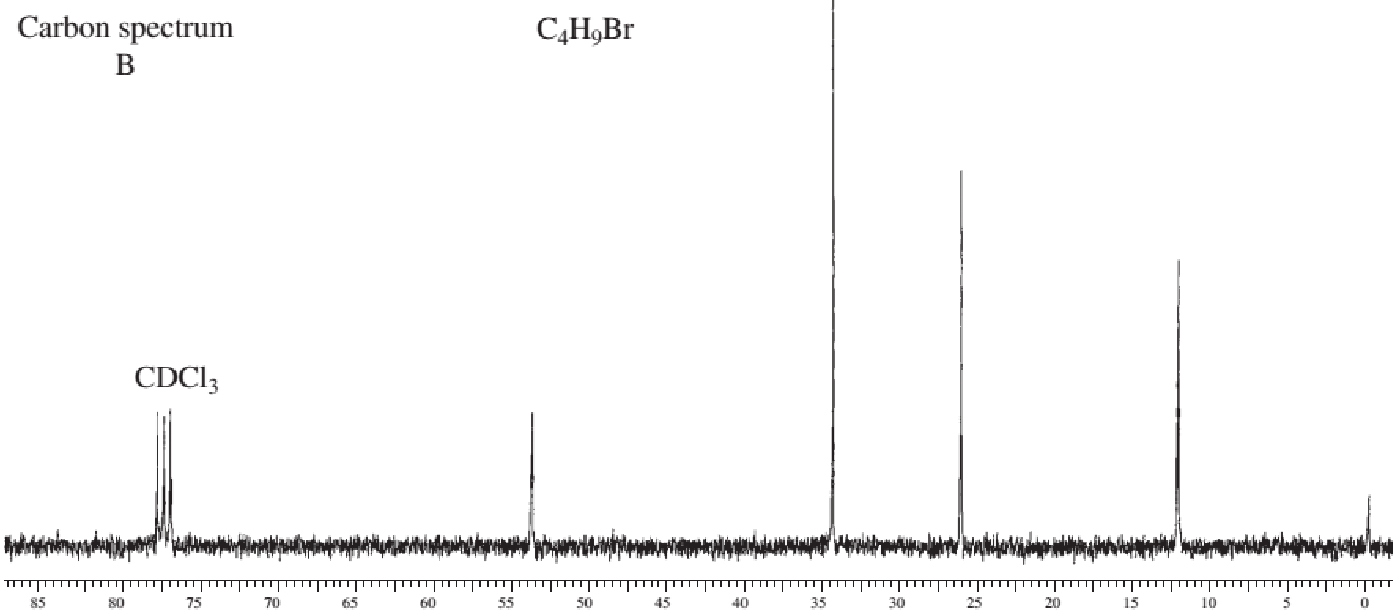

$C_6H_{10}O_2$
0.85
13.0
12.5
12.0
TMS
1.01
2.20
2.98
2.97
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

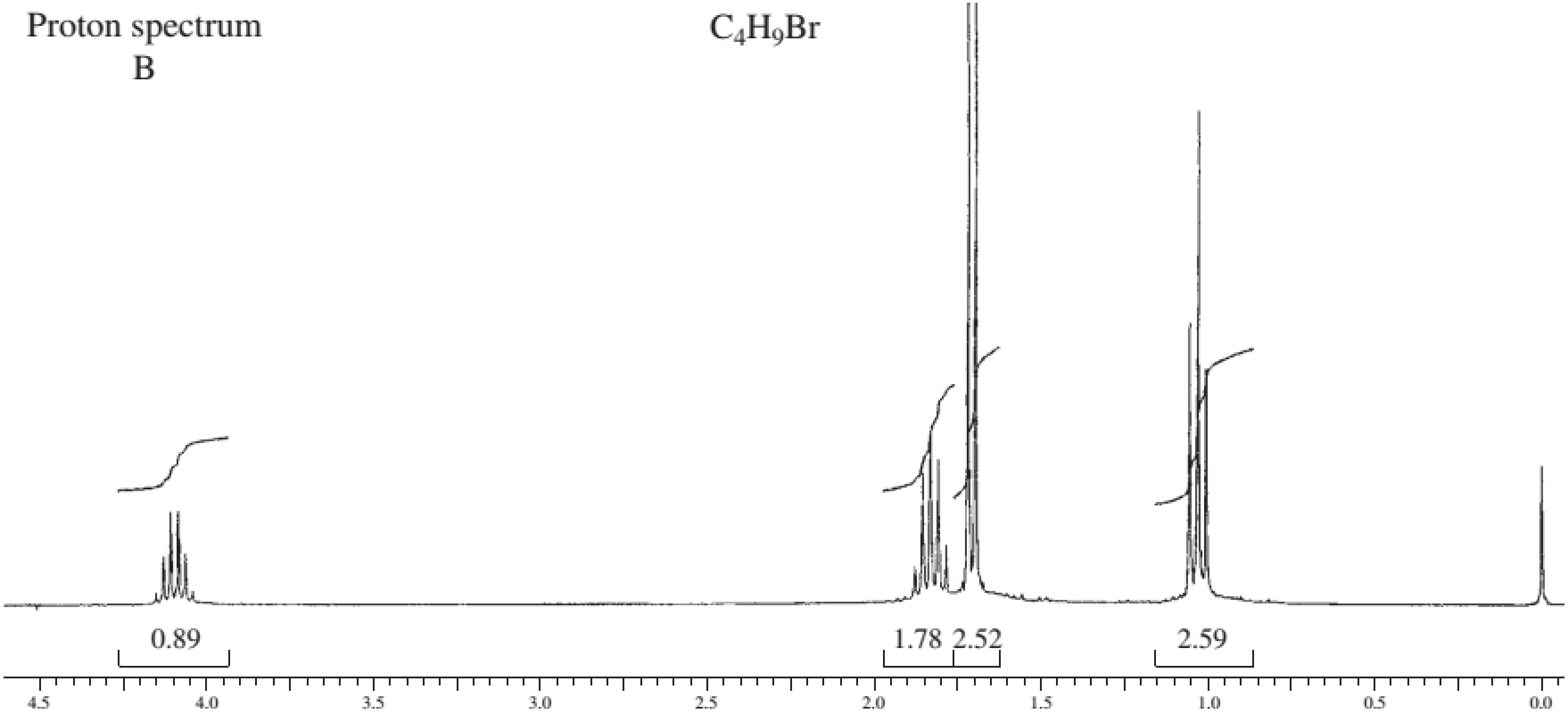

$C_6H_{10}O_2$
174.19
146.71
126.62
CDCl$_3$
22.24
12.89
11.79
200
150
100
50
0

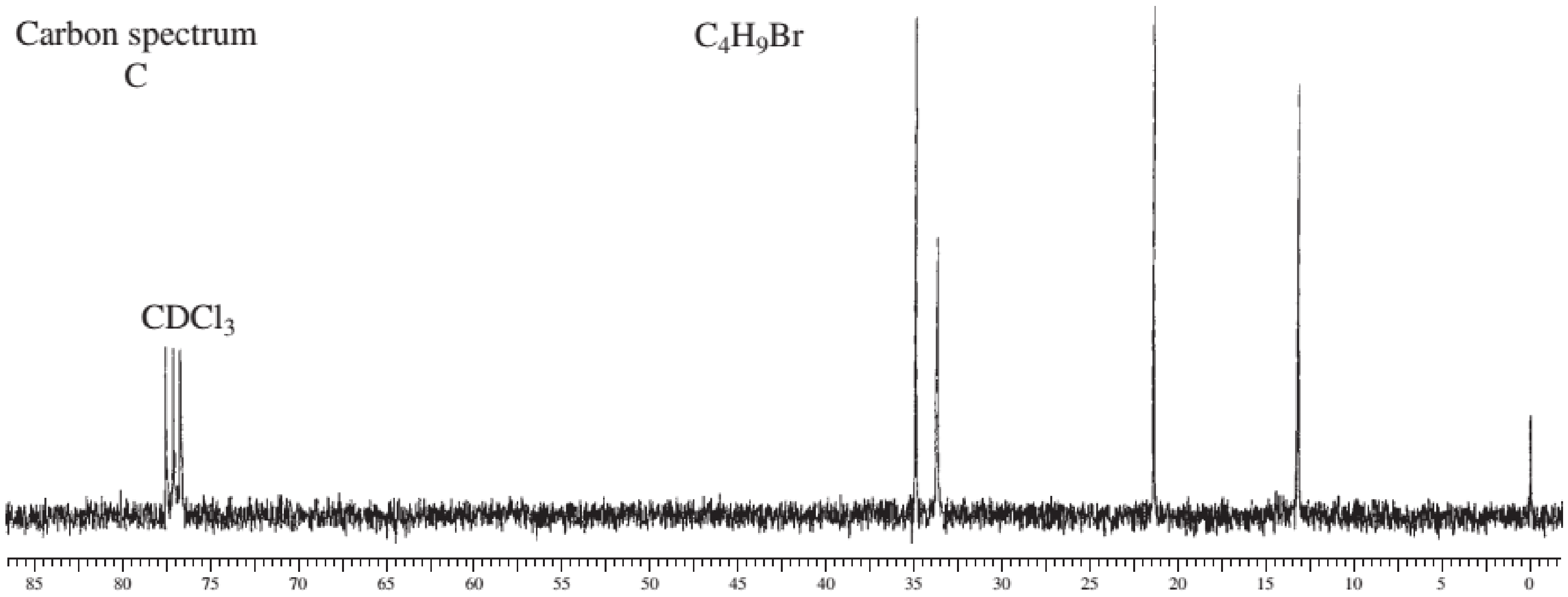
***5.** Following are the ^1H and ^{13}C spectra for each of four isomeric bromoalkanes with formula C_4H_9Br. Assign a structure to each pair of spectra.

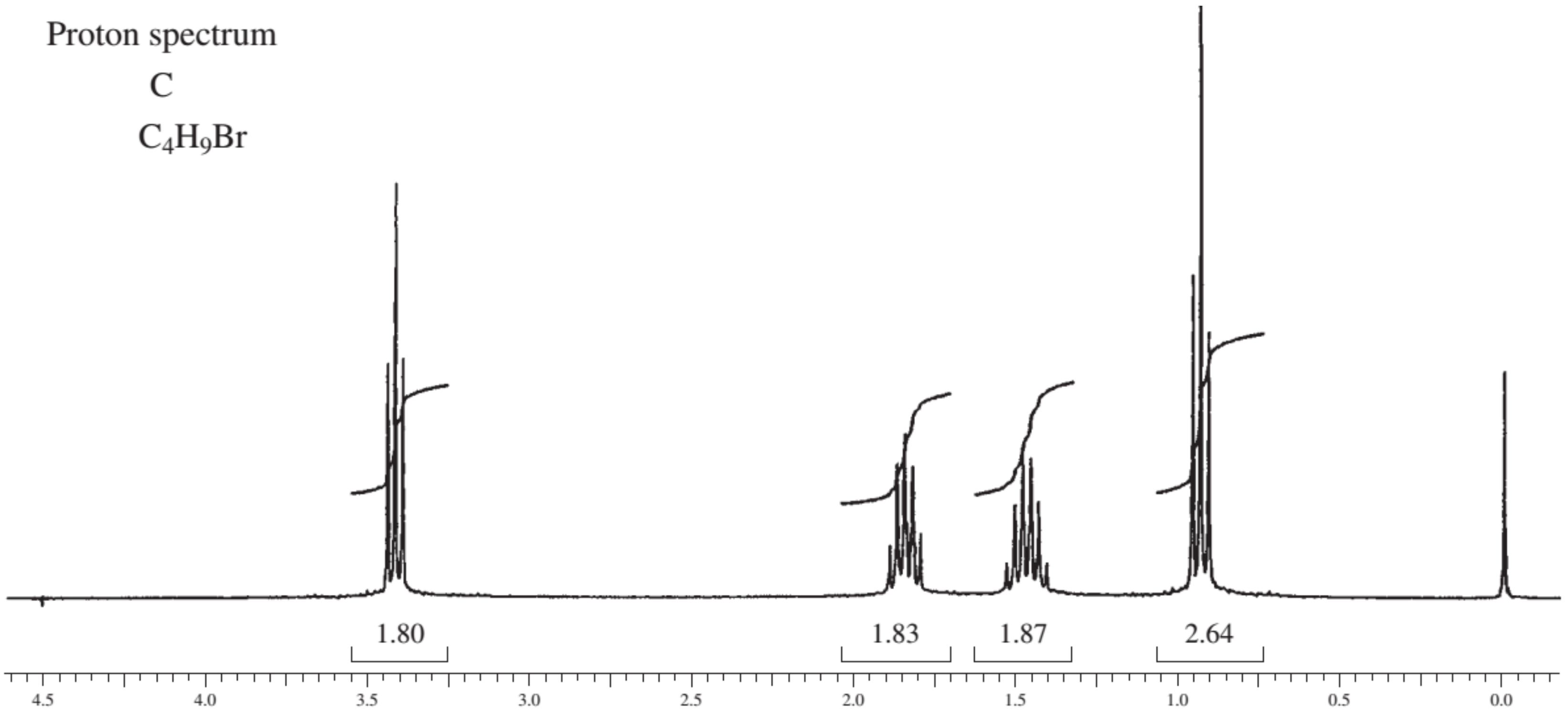


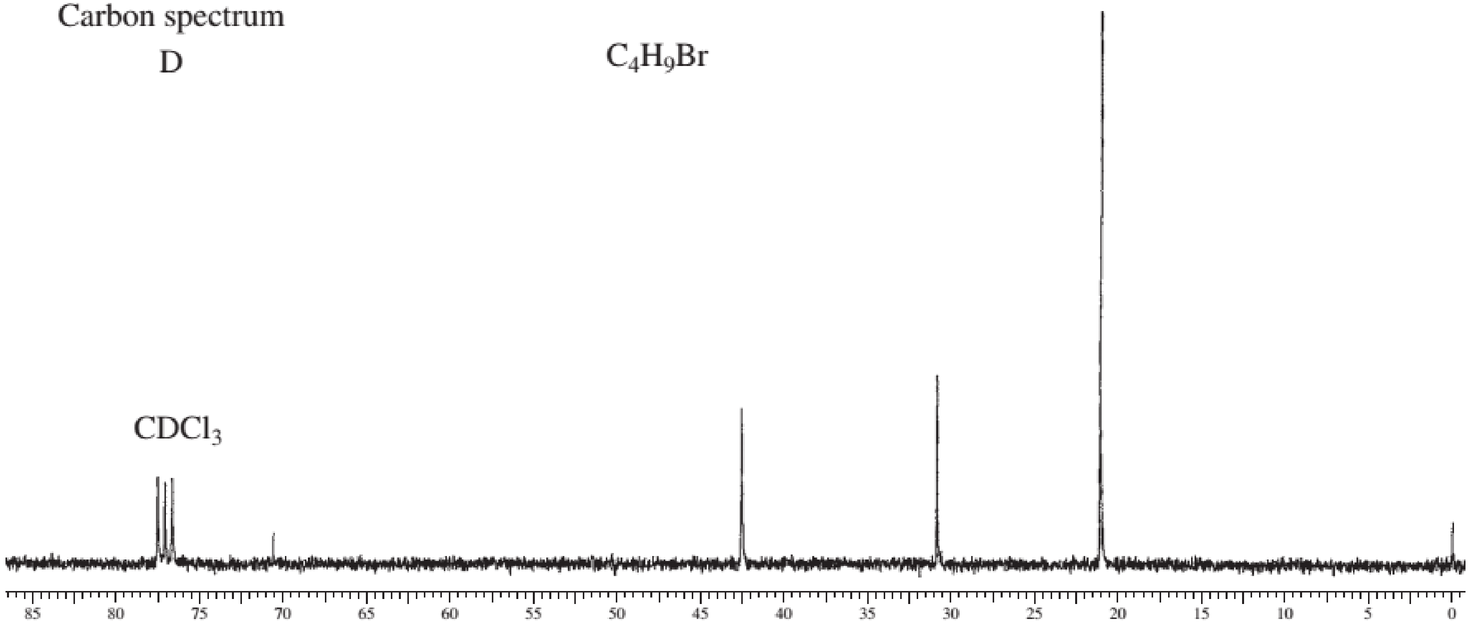


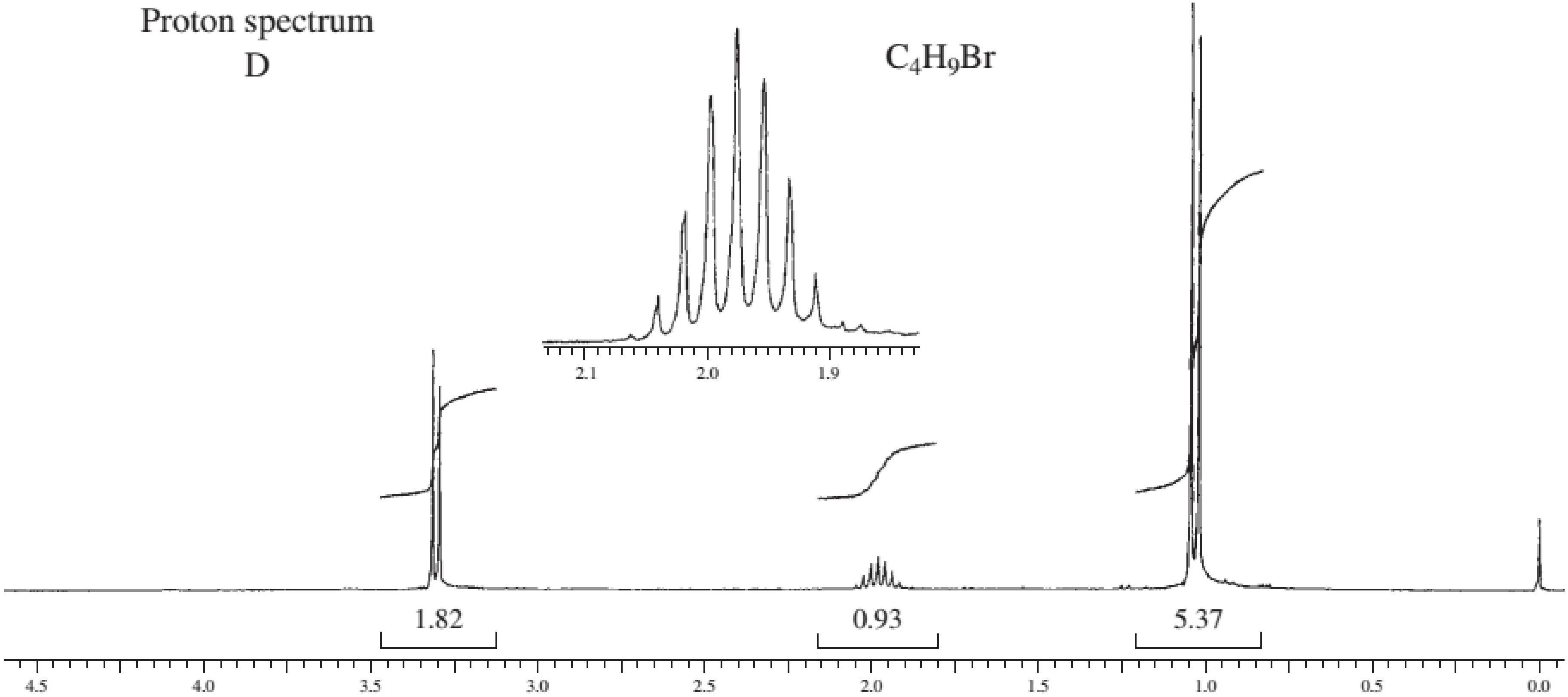

Carbon spectrum
B
C_4H_9Br
$CDCl_3$
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0


Proton spectrum
B
C_4H_9Br
0.89
1.78
2.52
2.59
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Carbon spectrum
C
C4H9Br
CDCl3
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0


Proton spectrum
C
C4H9Br
1.80
1.83
1.87
2.64
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Carbon spectrum
D
C_4H_9Br
$CDCl_3$
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0


Proton spectrum
D
C_4H_9Br
2.1
2.0
1.9
1.82
0.93
5.37
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0