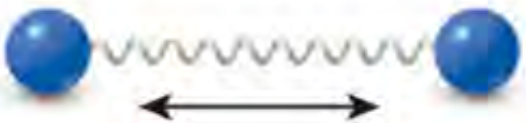
Infrared Spectroscopy

Stretching



A bond can stretch.

Bending

Two bonds can bend.

Bonds and IR Absorption

- **Bonds can be thought of as springs with weights on each end (behavior governed by Hooke's Law).**
  - **The strength of the spring is analogous to the bond strength, and the mass of the weights is analogous to atomic mass.**
  - **For two springs with the same weight on each end, the stronger spring vibrates at a higher frequency.**
  - **For two springs of the same strength, springs with lighter weights vibrate at a higher frequency than those with heavier weights.**

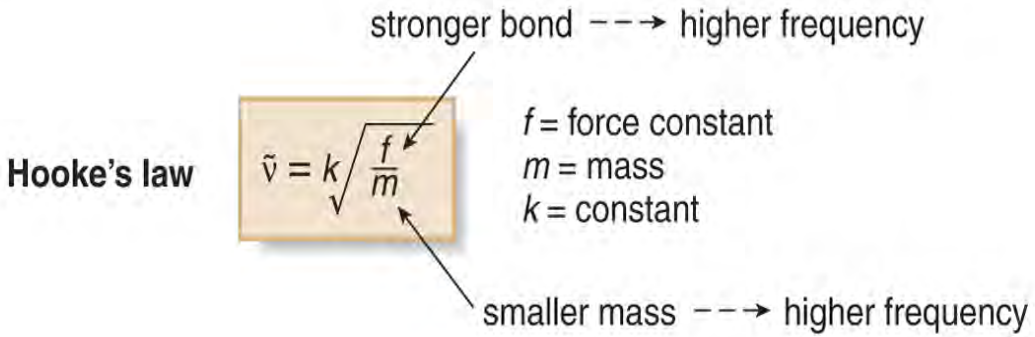
Bonds and IR Absorption

- Where a particular bond absorbs in the IR depends on bond strength and atom mass.
  - Stronger bonds (i.e., triple > double > single) vibrate at a higher frequency, so they absorb at higher wavenumbers.
  - Bonds with lighter atoms vibrate at higher frequency, so they absorb at higher wavenumbers.

Hooke's Law

- Hooke's Law describes the relationship of frequency to mass and bond length.

The frequency of bond vibration can be derived from Hooke's law, which describes the motion of a vibrating spring:

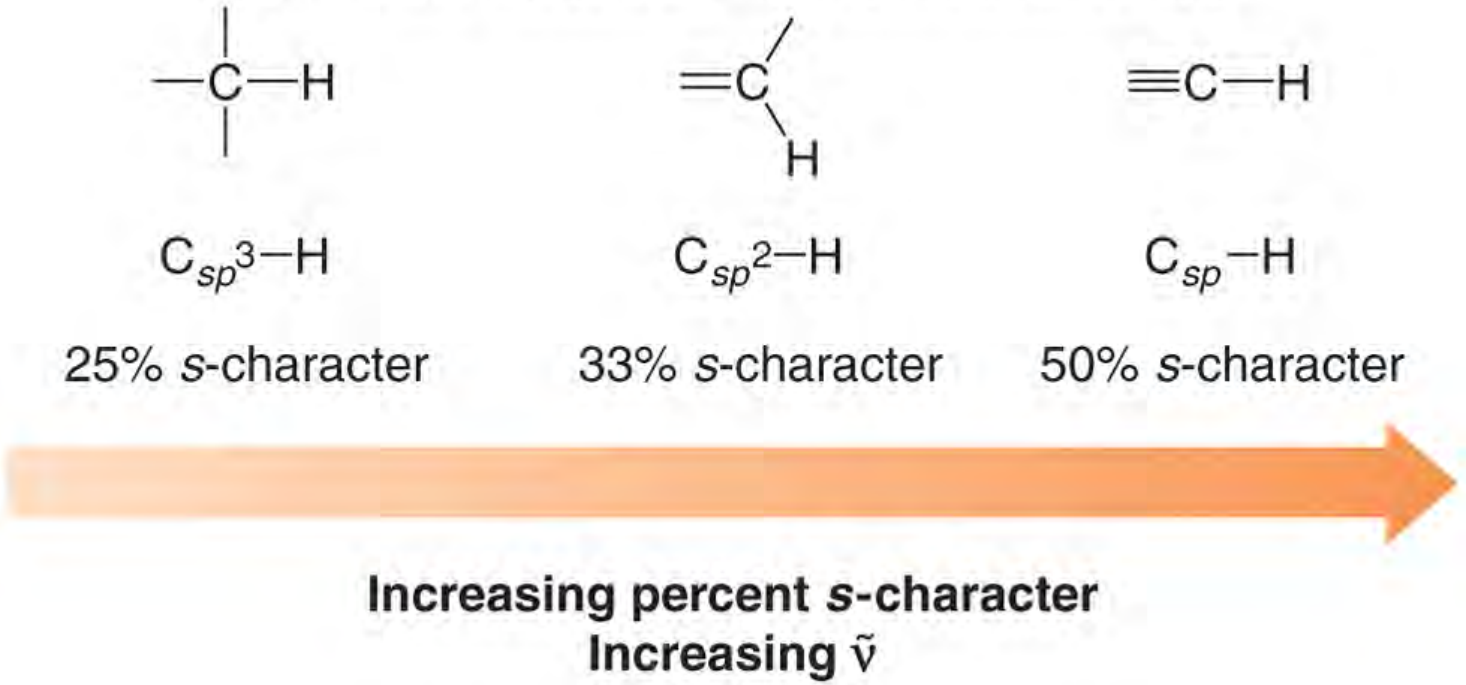


- The force constant (f) is the strength of the bond (or spring). The larger the value of f, the stronger the bond, and the higher the $\tilde{\nu}$ of vibration.
- The mass (m) is the mass of atoms (or weights). The smaller the value of m, the higher the $\tilde{\nu}$ of vibration.

Bond type	Approximate $\tilde{\nu}$ (cm^{-1})	Intensity
O–H	3600–3200	strong, broad
N–H	3500–3200	medium
C–H	~3000	
• C_{sp^3}–H	3000–2850	strong
• C_{sp^2}–H	3150–3000	medium
• C_{sp}–H	3300	medium
C≡C	2250	medium
C≡N	2250	medium
C=O	1800–1650 (often ~1700)	strong
C=C	1650	medium
	1600, 1500	medium

Bond Strength and % *s*-Character

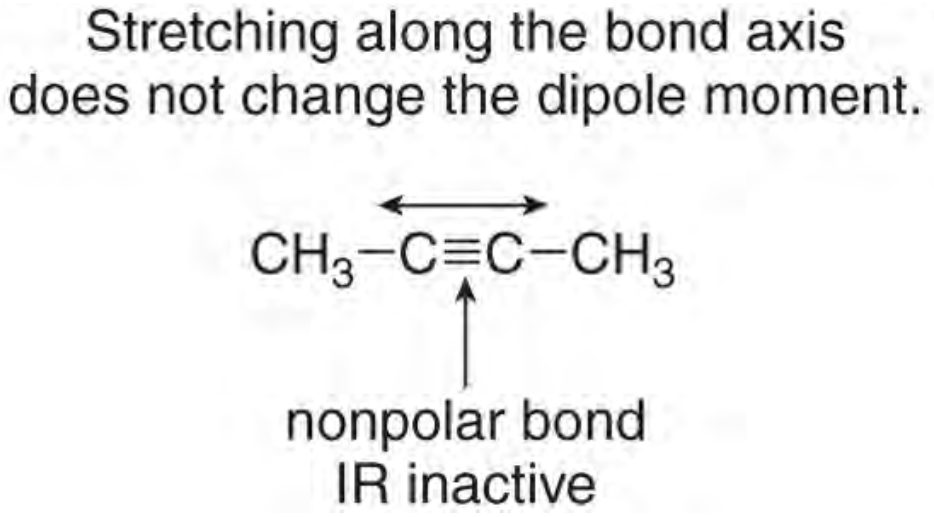
- Even subtle differences that affect bond strength affect the frequency of an IR absorption.



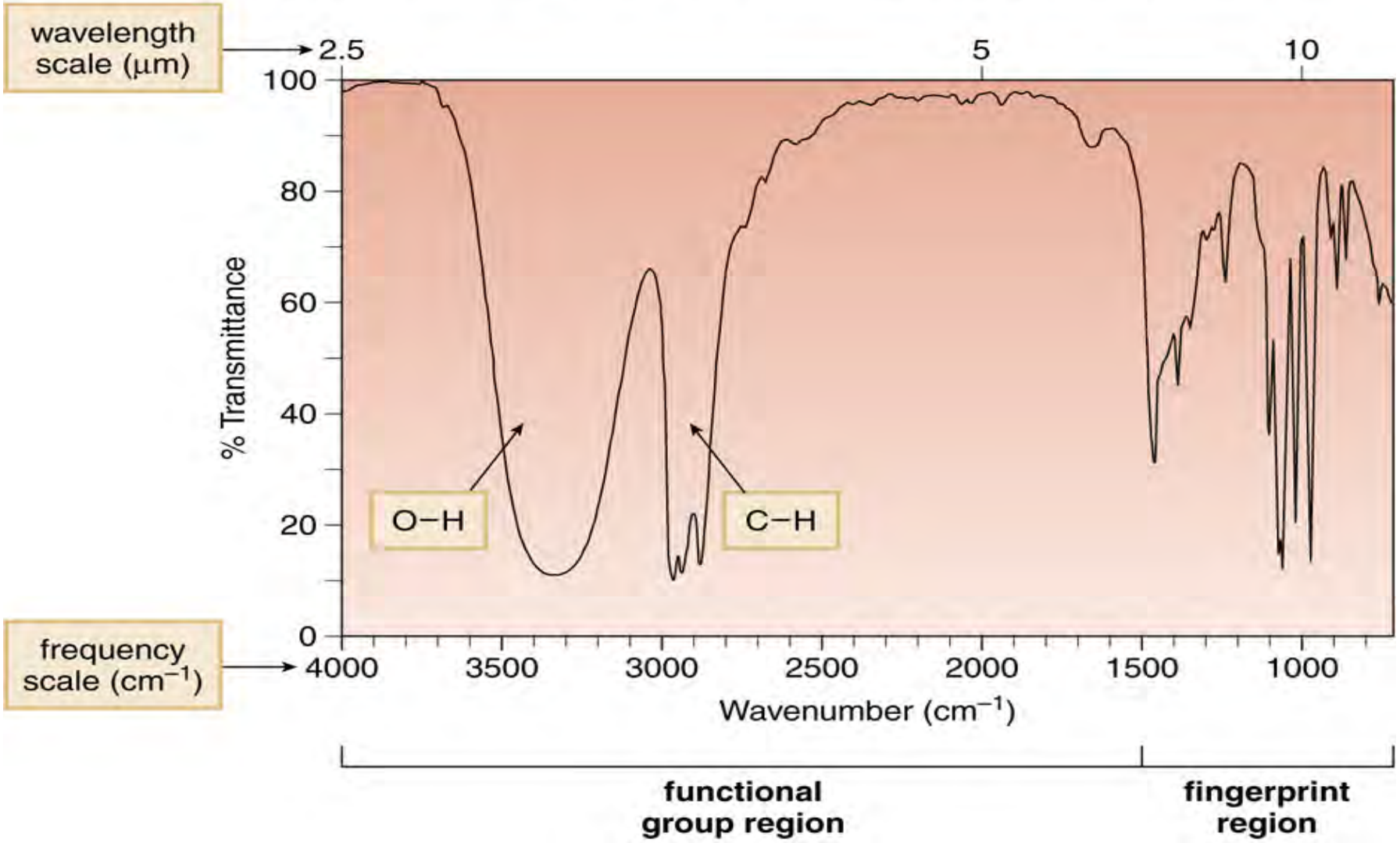
- The higher the percent *s*-character, the stronger the bond and the higher the wavenumber of absorption.

Symmetry and IR Absorption

- For a bond to absorb in the IR, there must be a change in dipole moment during the vibration.
- Symmetrical nonpolar bonds do not absorb in the IR. This type of vibration is said to be IR inactive.

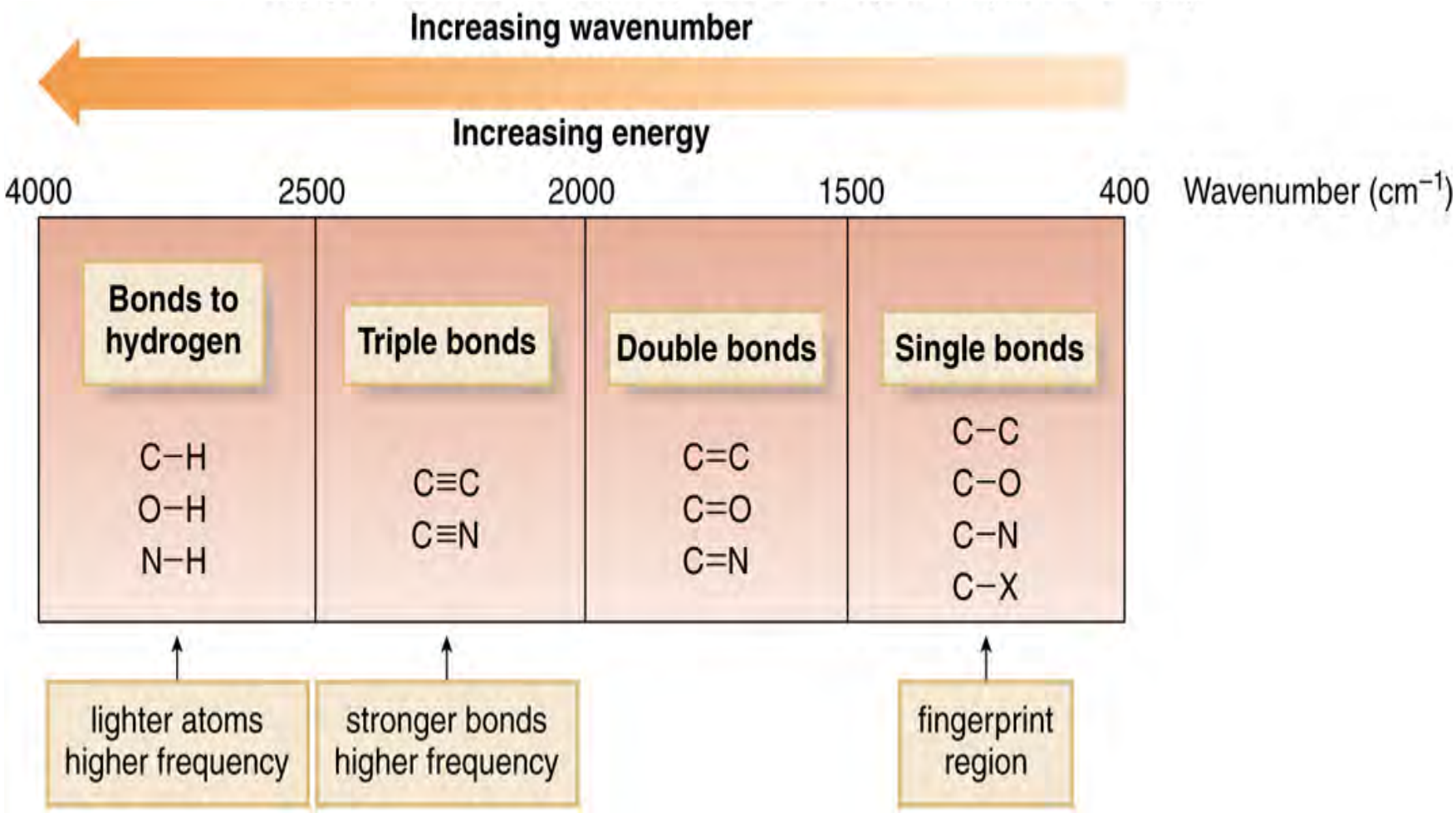


Infrared (IR) spectroscopy is useful to identify what bonds and what functional groups are in a compound.



Four Regions of an IR Spectrum

- Bonds absorb in four predictable regions of an IR spectrum.



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• C_{sp^2}–H	3150–3000	medium
• C_{sp}–H	3300	medium
C≡C	2250	medium
C≡N	2250	medium
C=O	1800–1650 (often ~1700)	strong
C=C	1650	medium
	1600, 1500	medium

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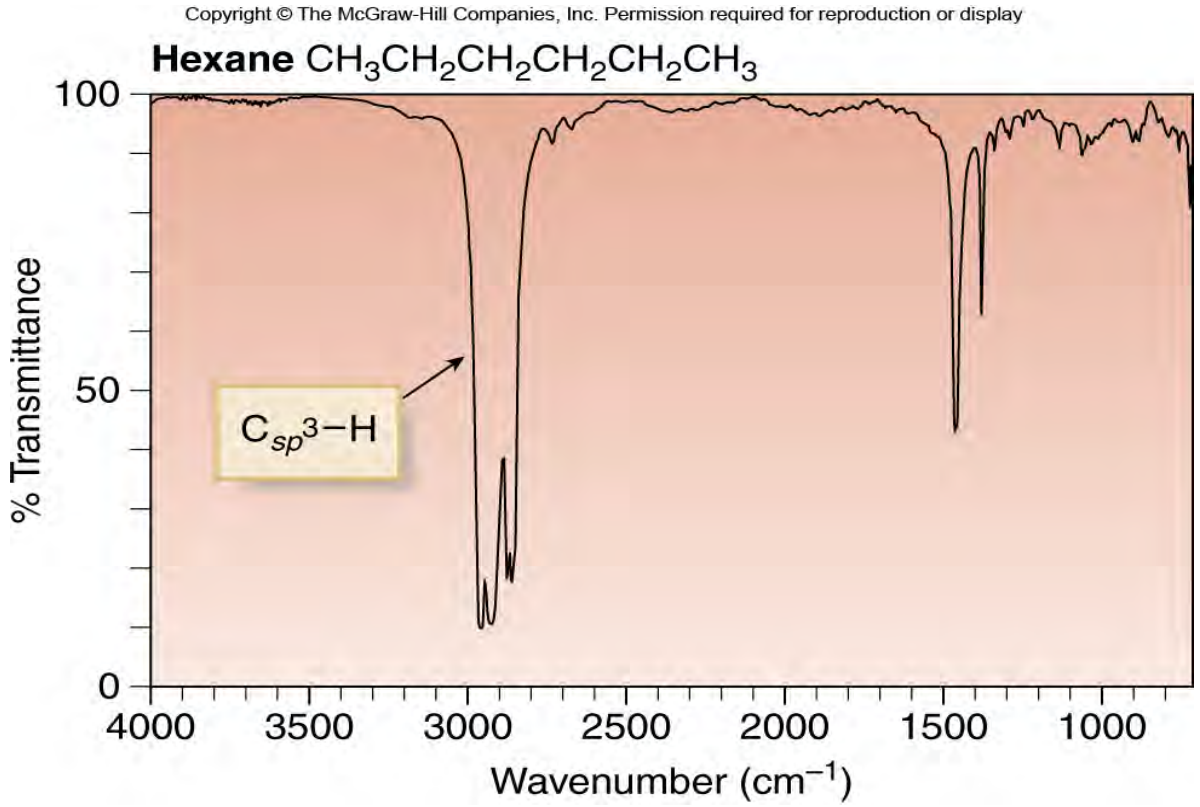
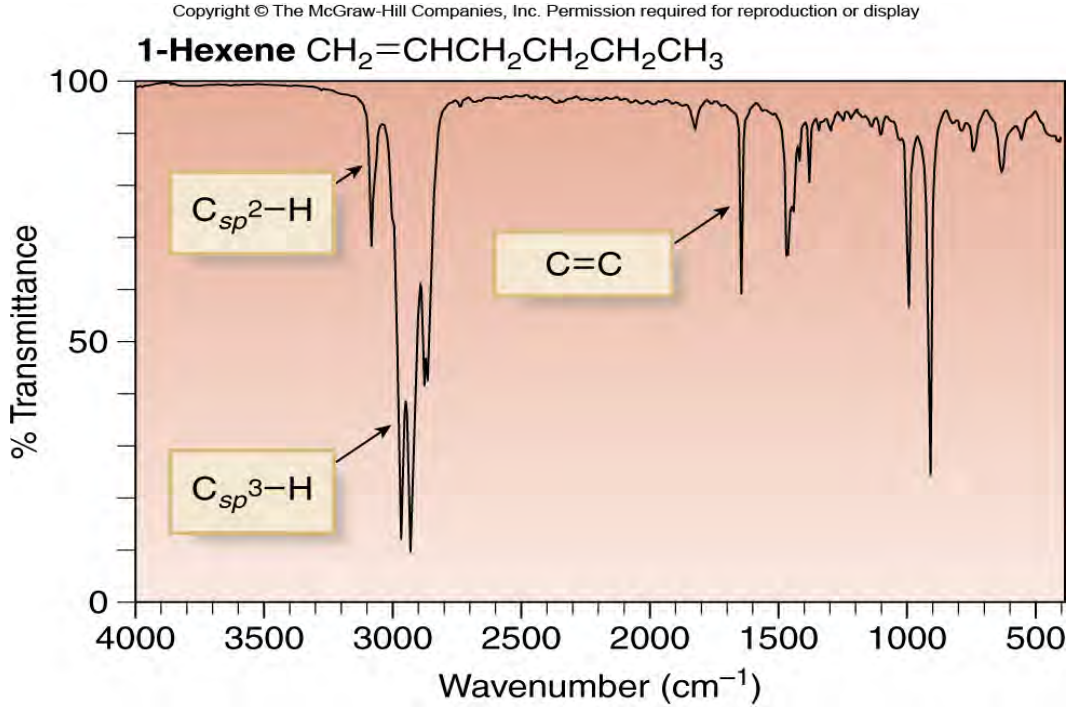
IR Absorptions in Hydrocarbons

- **Hexane has only C−C single bonds and sp^3 hybridized C atoms.**
- **Therefore, it has only one major absorption at 3000-2850 cm^{-1}.**



IR Spectrum of 1-Hexene

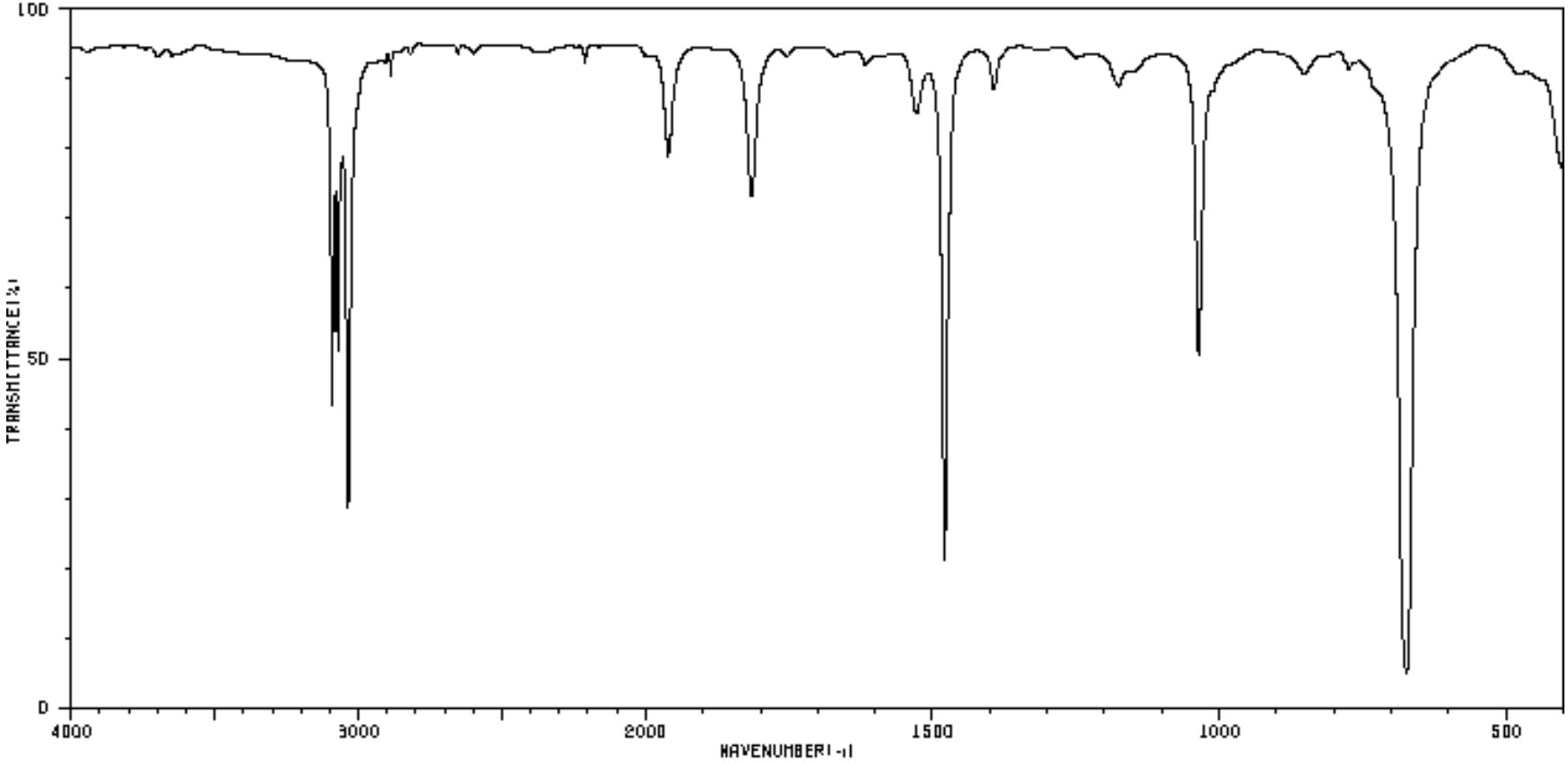
- **1-Hexene has a C=C and C_{sp^2}–H, in addition to sp^3 hybridized C atoms.**
- **Therefore, there are three major absorptions: C_{sp^2}–H at 3150–3000 cm^{-1}; C_{sp^3}–H at 3000–2850 cm^{-1}; C=C at 1650 cm^{-1}.**



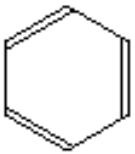
HIT-NO=1237	SCORE= ( )	SDBS-NO=898	IR-NIDA-63541 : LIQUID FILM

BENZENE

C_6H_6

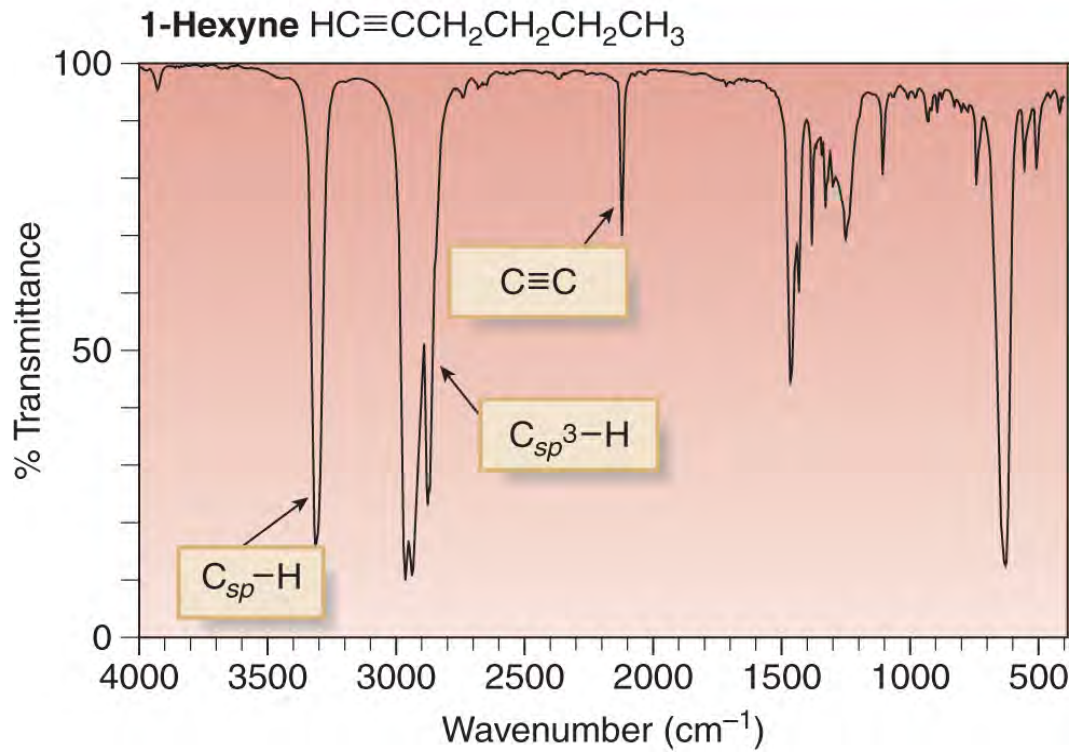


3091	42	1393	84
3072	49	1176	86
3036	27	1038	49
1961	77	674	4
1815	70		
1526	81		
1479	20		



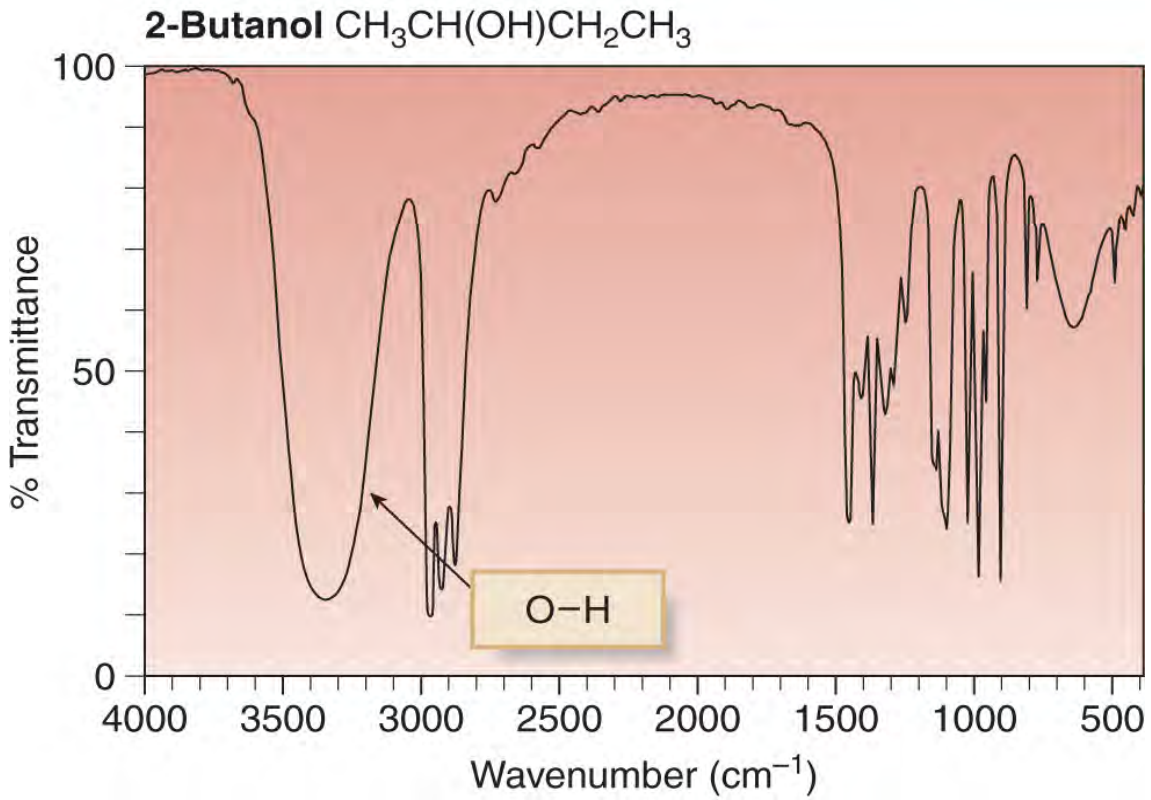
IR Spectrum of 1-Hexyne

- **1-Hexyne has a C≡C and C_{sp}–H, in addition to sp^3 hybridized C atoms.**
- **Therefore, there are three major absorptions: C_{sp}–H at 3300 cm^{-1}; C_{sp^3}–H at 3000–2850 cm^{-1}; C≡C at 2250 cm^{-1}.**



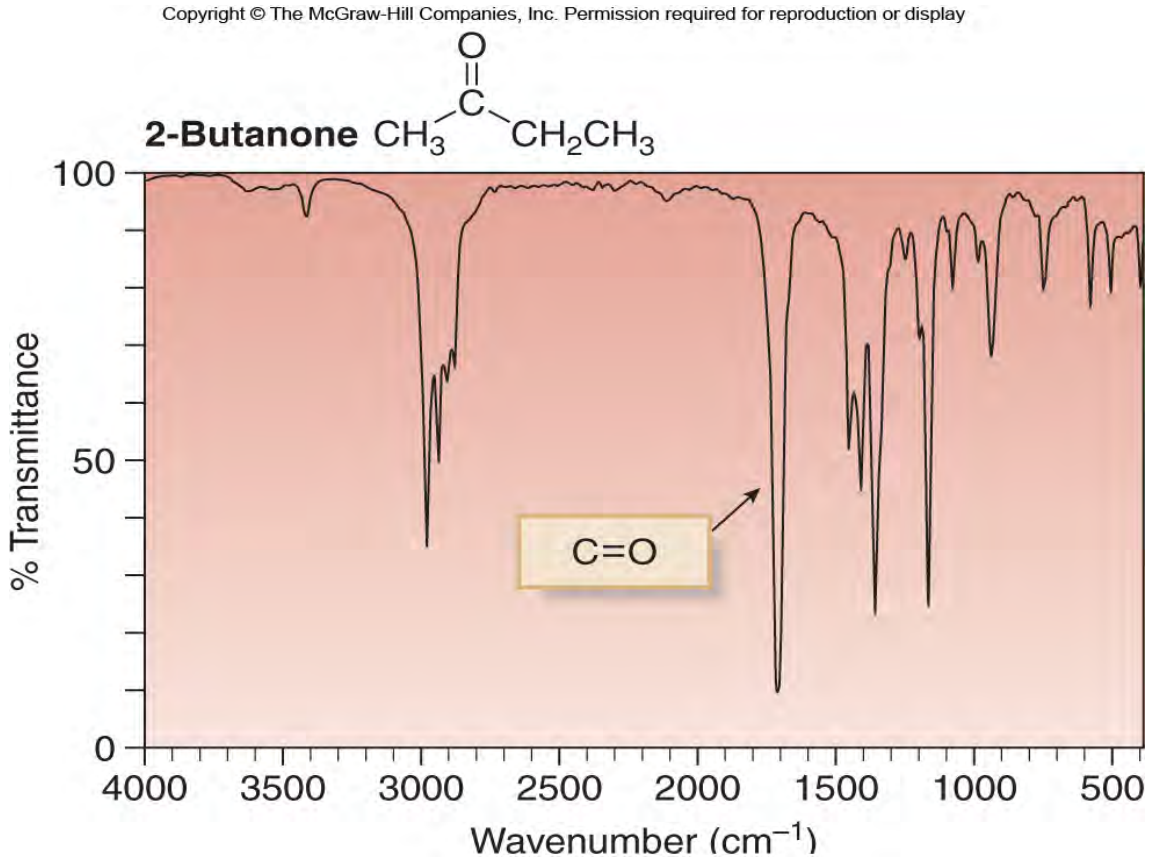
IR Spectrum of 2-Butanol

- **The OH group of the alcohol shows a strong absorption at 3600-3200 cm^{-1}.**
- **The peak at ~ 3000 cm^{-1} is due to sp^3 hybridized C−H bonds.**



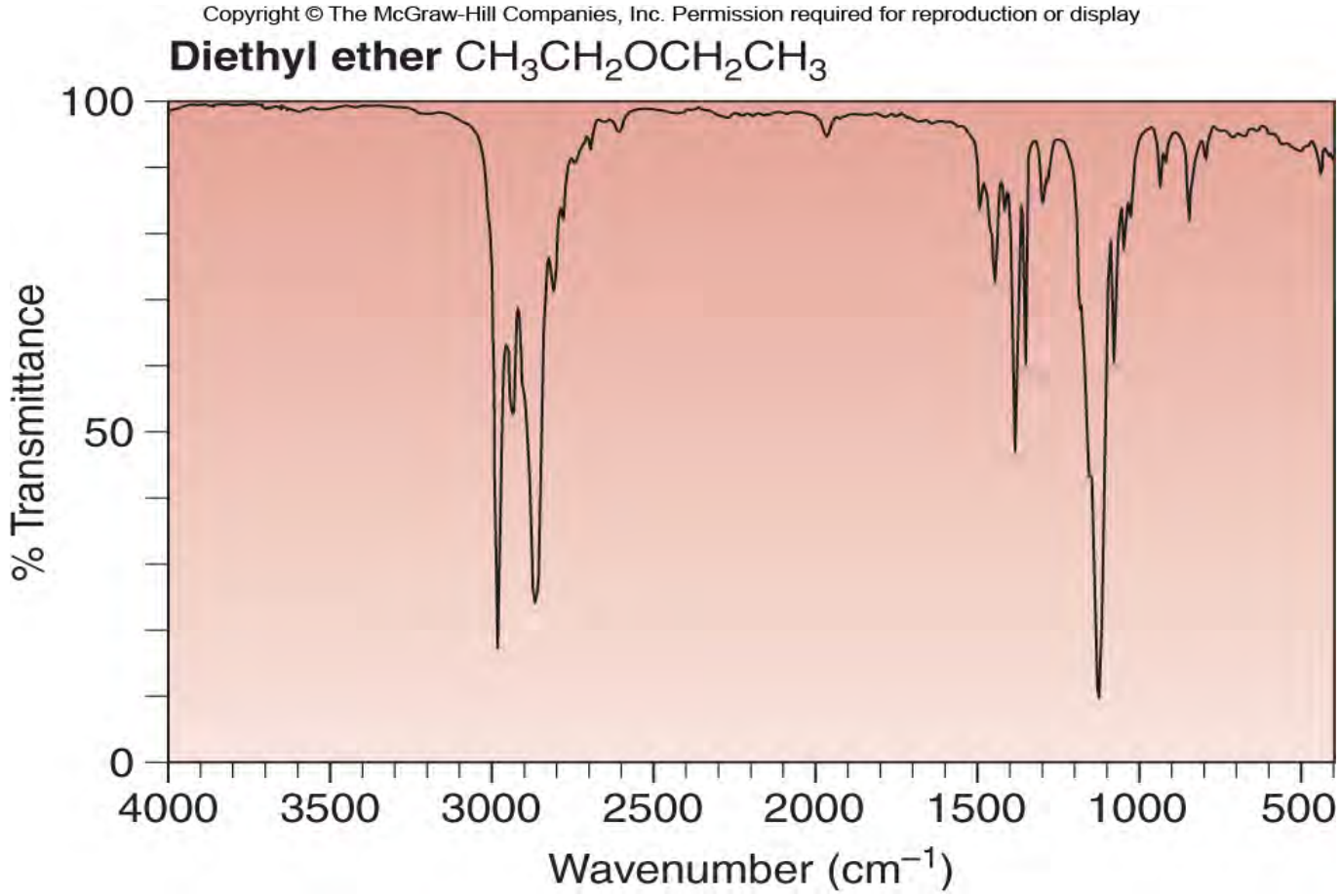
IR Spectrum of 2-Butanone

- **The C=O group in the ketone shows a strong absorption at ~ 1700 cm^{-1}.**
- **The peak at ~ 3000 cm^{-1} is due to sp^3 hybridized C−H bonds.**



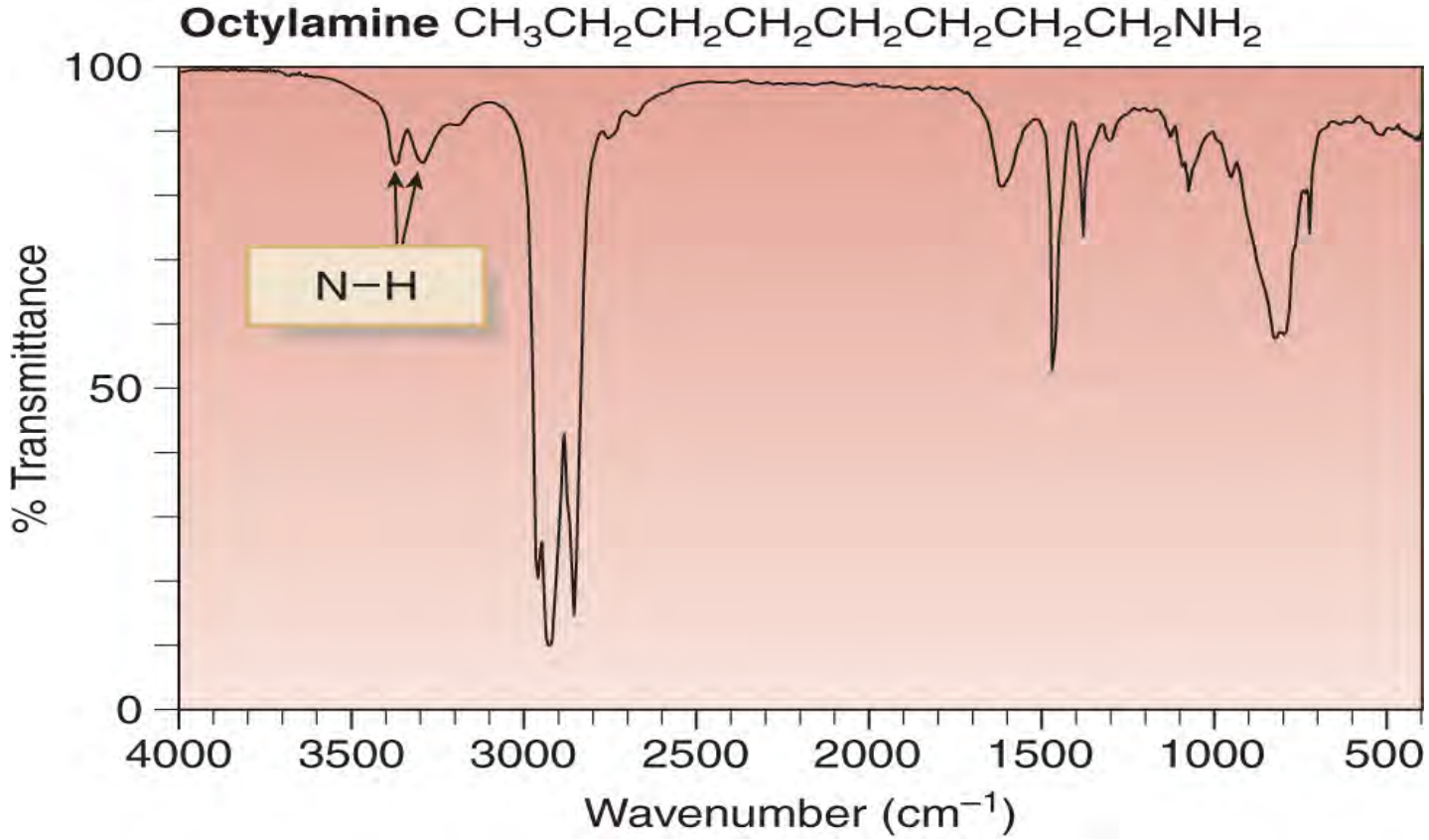
IR Spectrum of Diethyl Ether

- **The ether has neither an OH or a C=O, so its only absorption above 1500 cm^{-1} occurs at ~ 3000 cm^{-1}, due to sp^3 hybridized C−H bonds.**



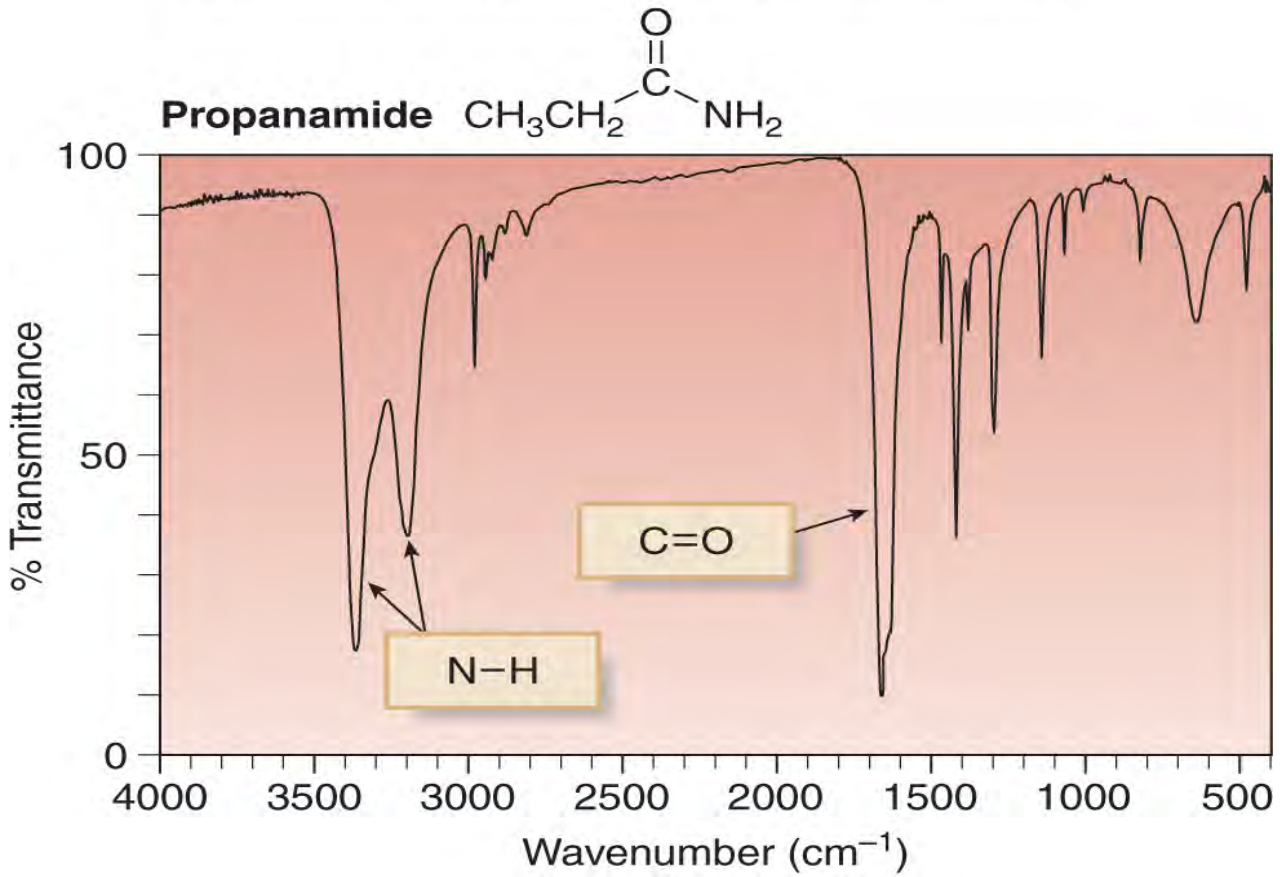
IR Spectrum of Octylamine

- **The N−H bonds in the amine give rise to two weak absorptions at 3300 and 3400 cm^{-1}.**



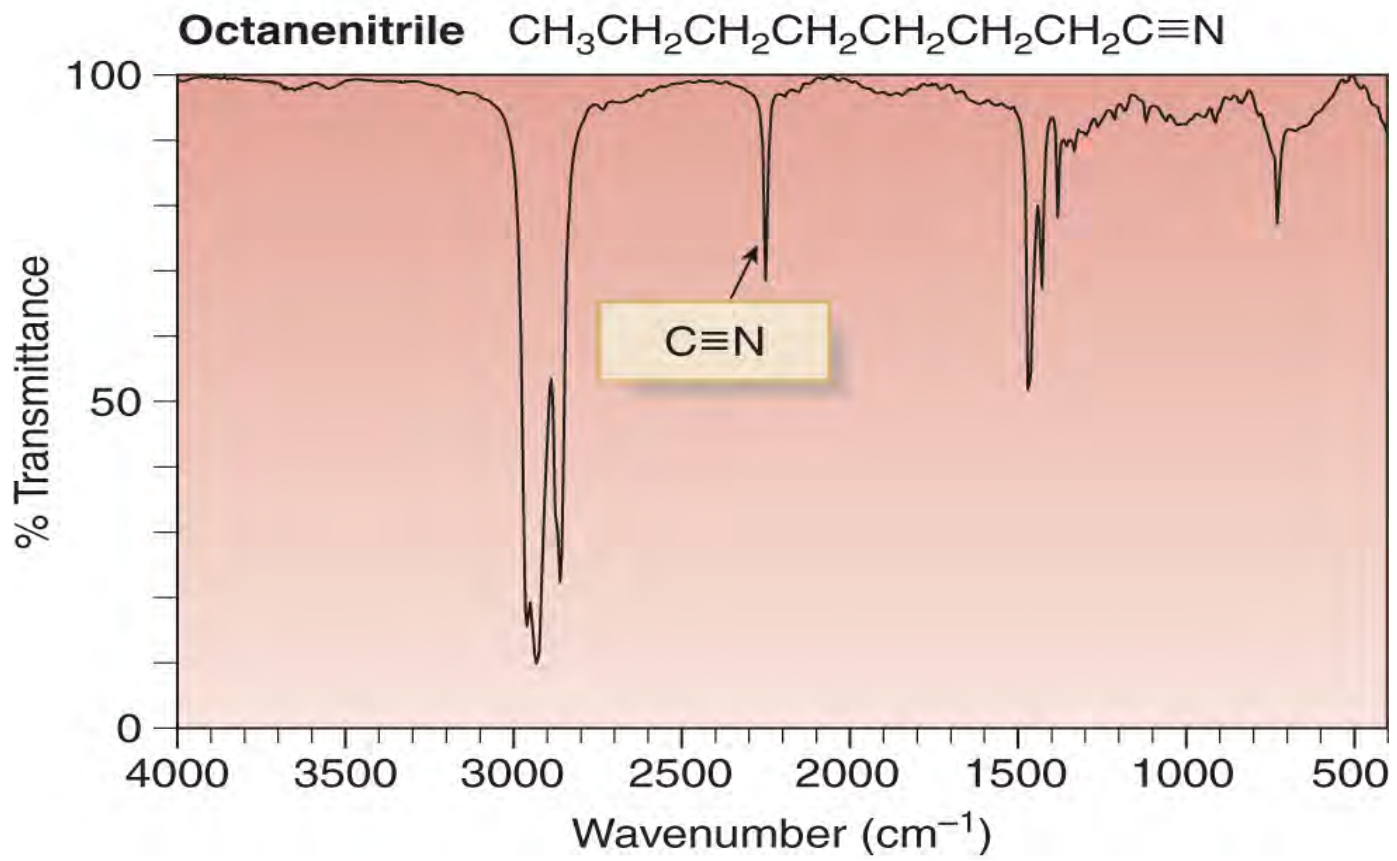
IR Spectrum of Propanamide

- **The amide exhibits absorptions above 1500 cm^{-1} for both its N−H and C=O groups: N−H (two peaks) at 3200 and 3400 cm^{-1}; C=O at 1660 cm^{-1}.**



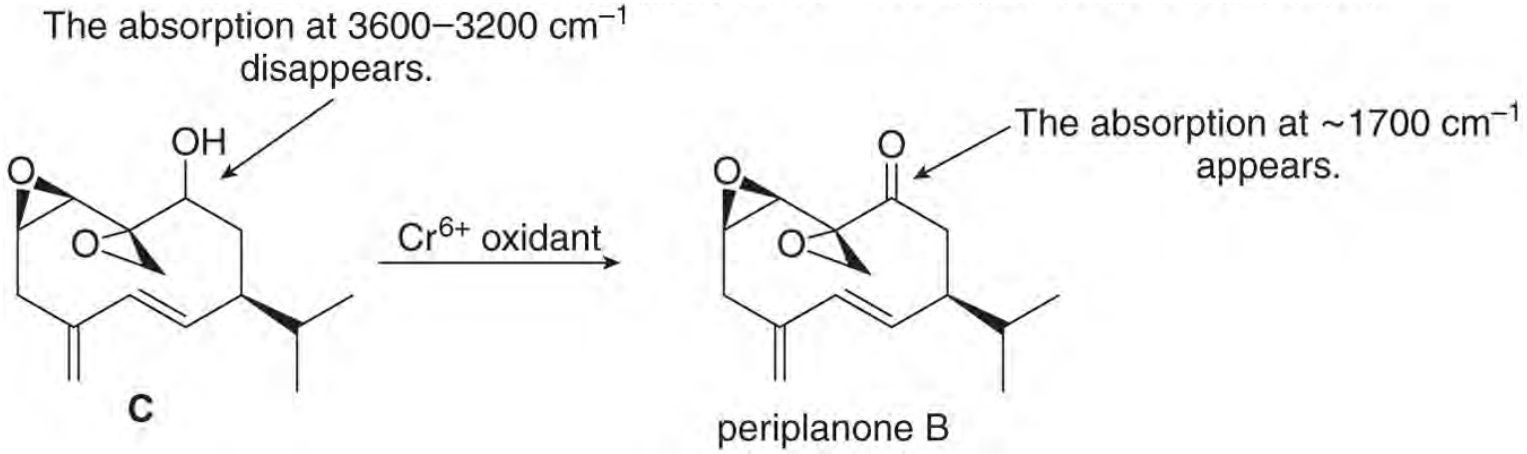
IR Spectrum of Octanenitrile

- **The C≡N of the nitrile absorbs in the triple bond region at ~ 2250 cm^{-1}.**



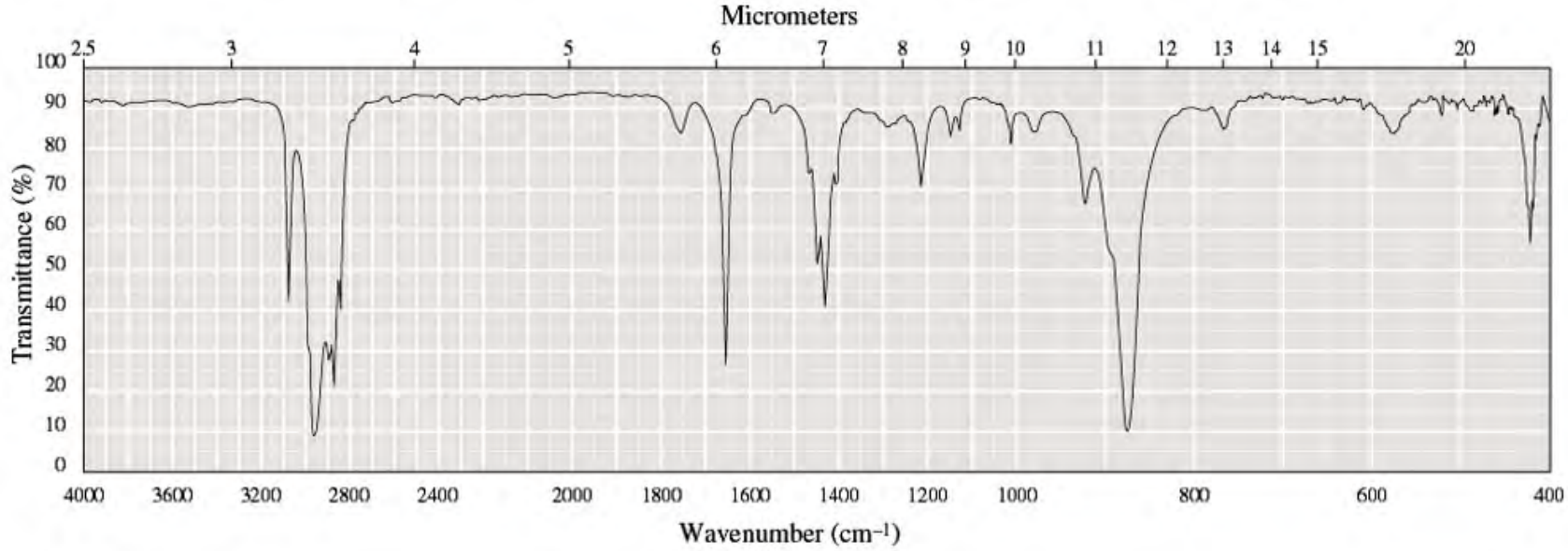
IR and Structure Determination

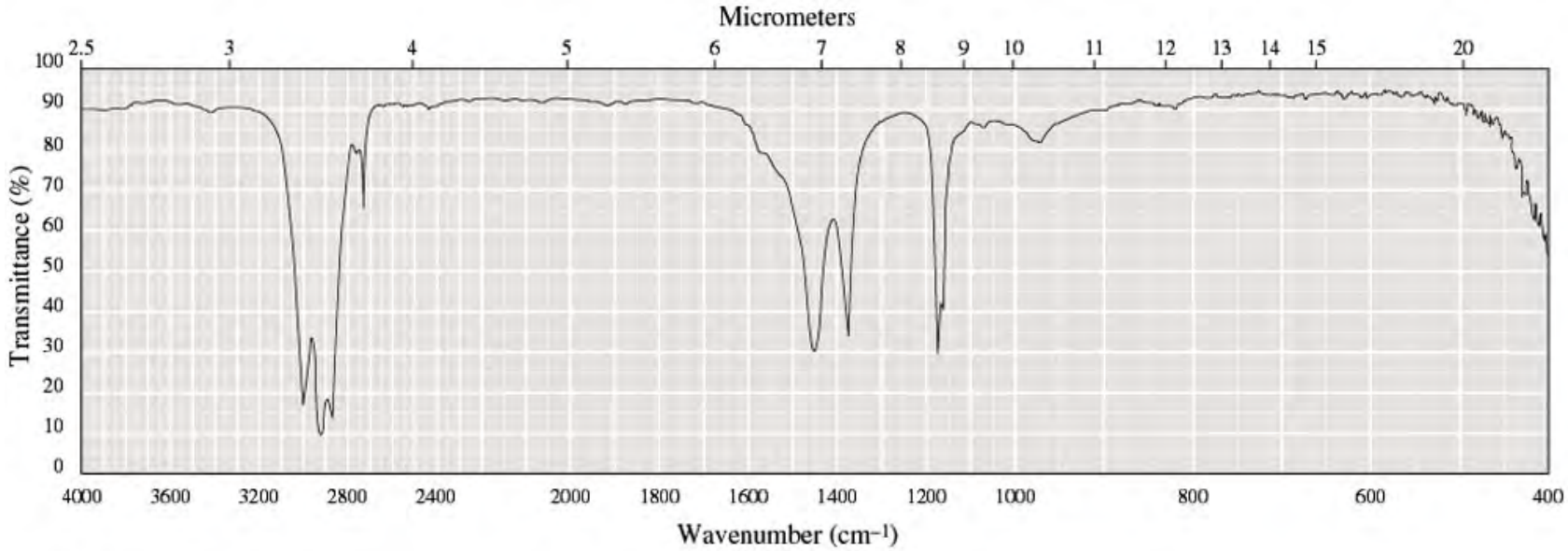
- **IR spectroscopy is often used to determine the outcome of a chemical reaction.**
- **For example, oxidation of the hydroxy group in compound C to form the carbonyl group in periplanone B is accompanied by the disappearance of the OH absorption, and the appearance of a carbonyl absorption in the IR spectrum of the product.**

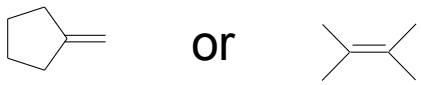


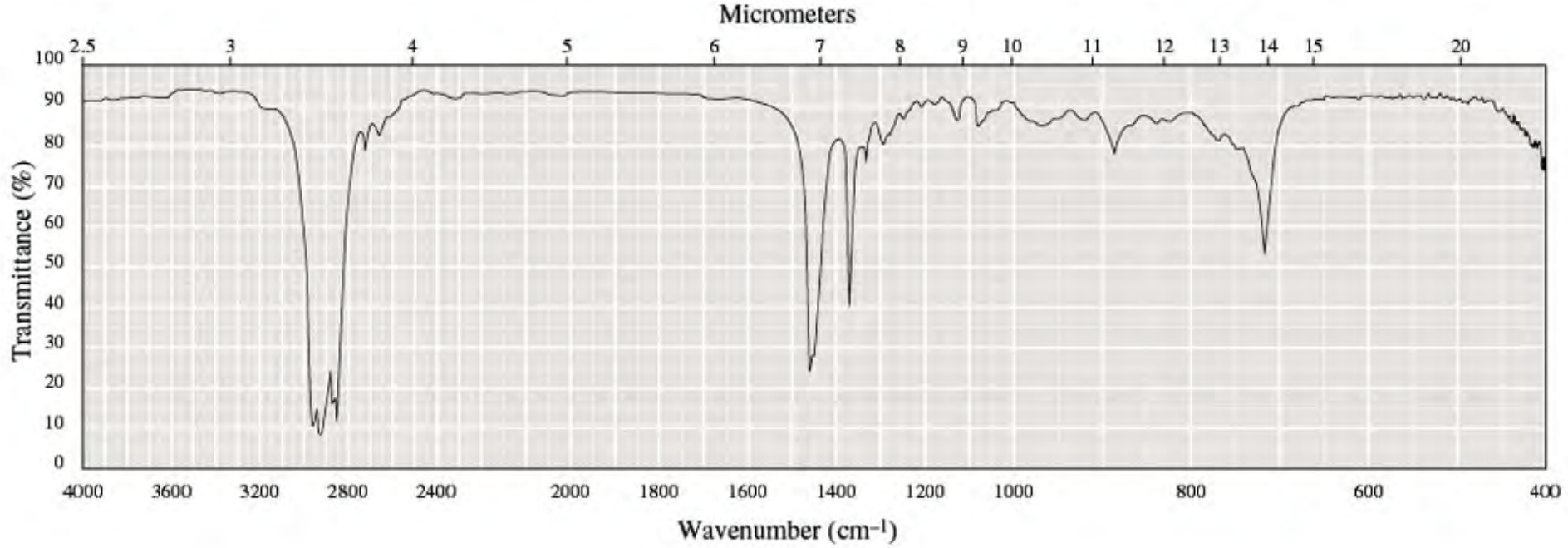
Solving IR problems

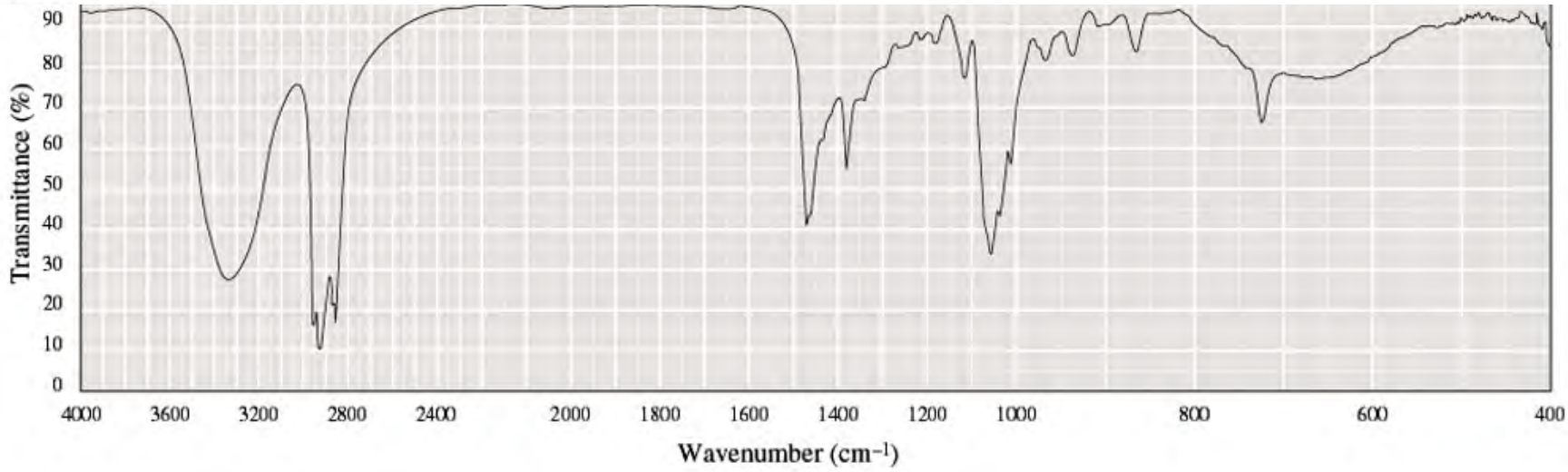
1. Check the region around 3000 cm^{-1}
2. Is there a strong, broad band in the region of 3500 cm^{-1}
   If yes, OH, COOH or NH_2
3. Is there a sharp peak in the region around 1700 cm^{-1}?
   If yes, C=O
4. Is there a peak in the region around 1630 cm^{-1}?
   If yes, C=C
5. Be aware that symmetrical alkynes and alkenes do not give IR absorbance

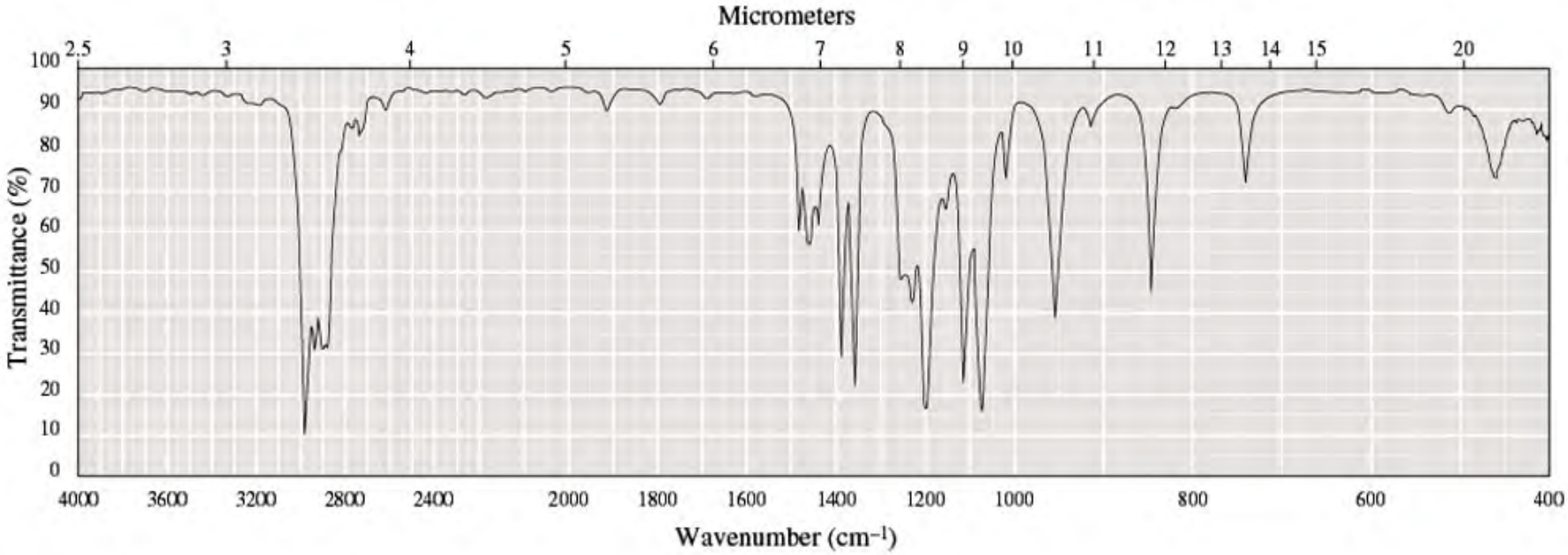


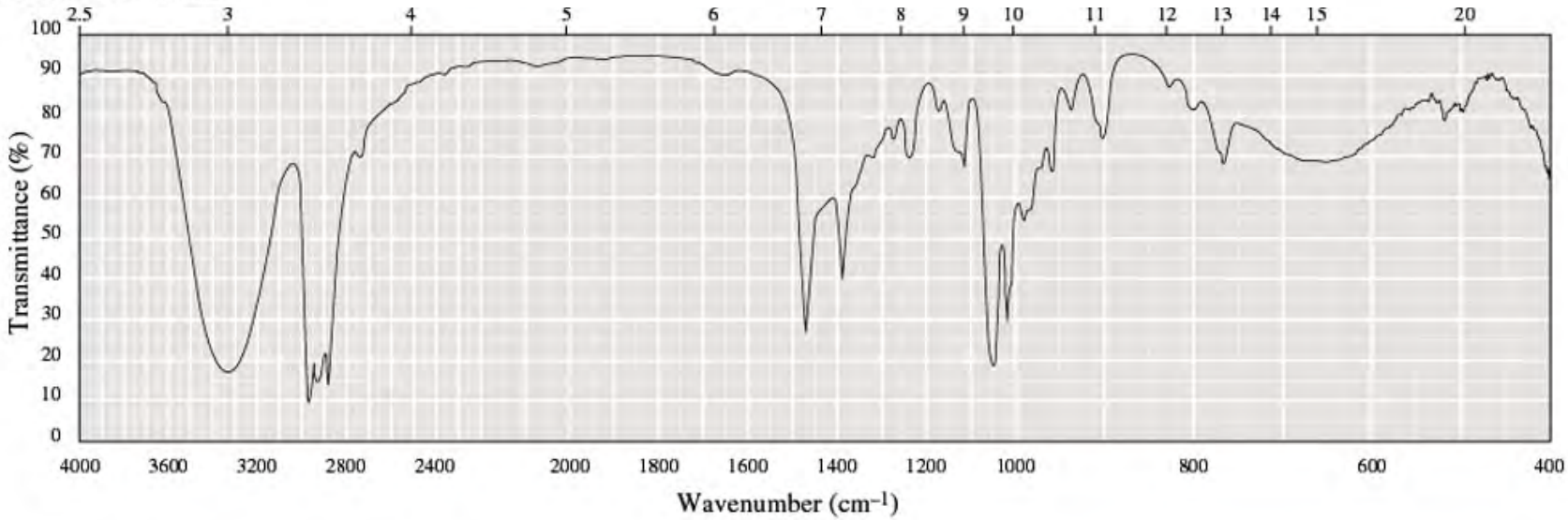












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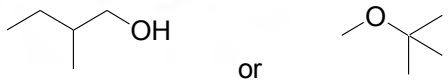
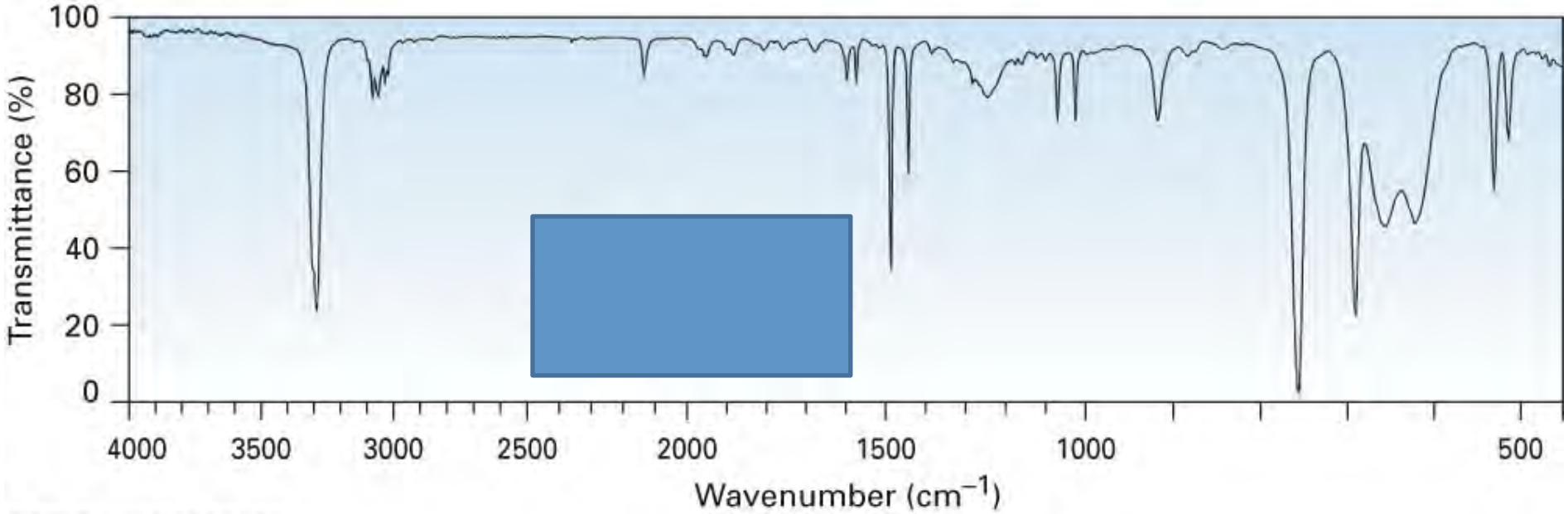


A

or

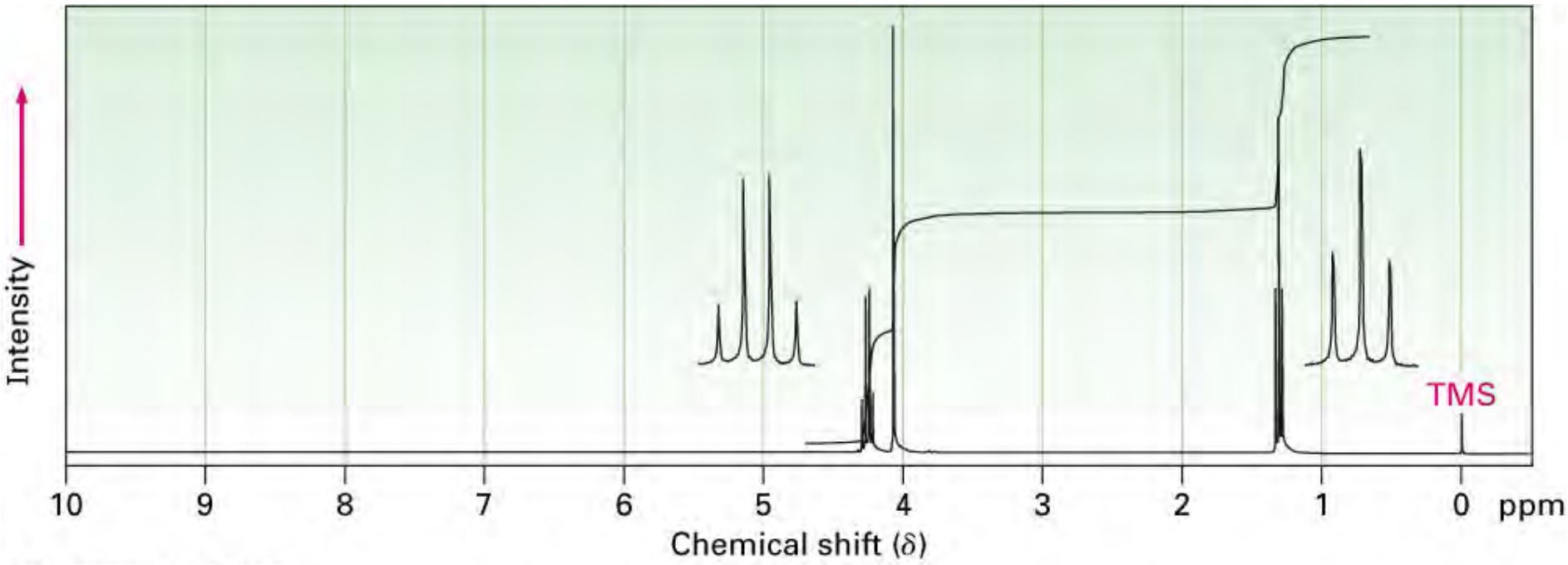
B

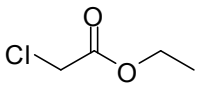


How to determine structures of compounds from their spectra?

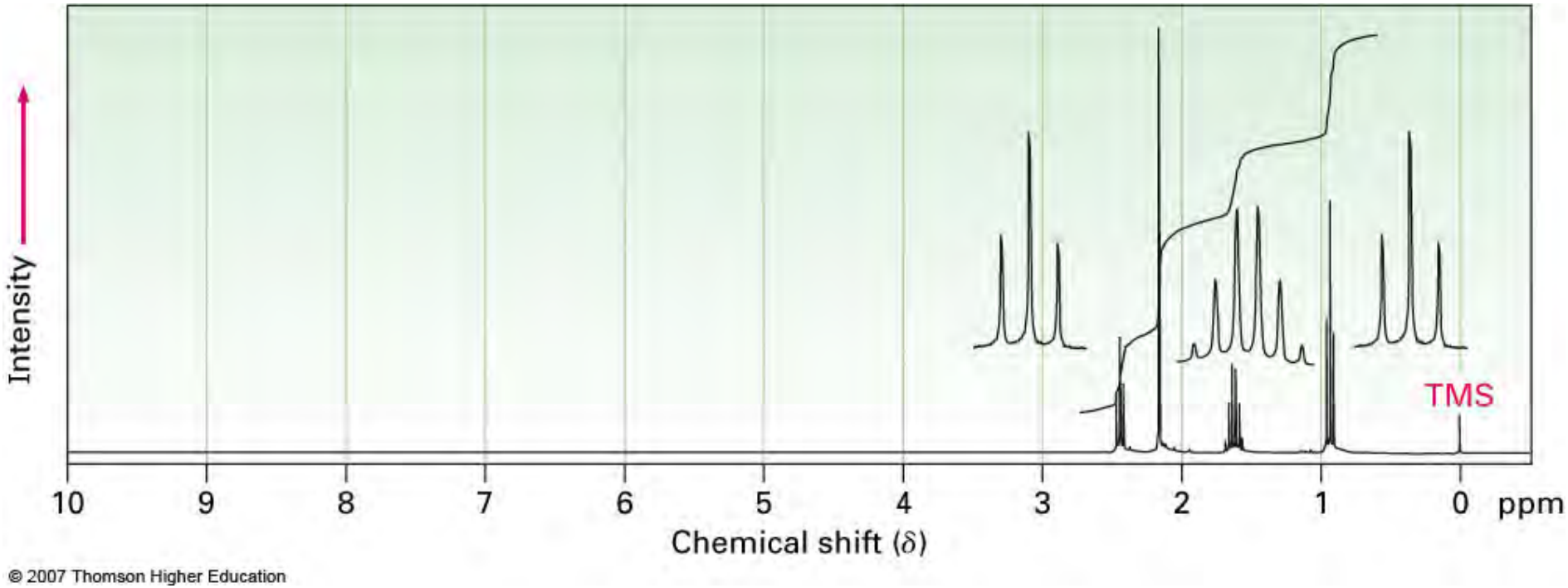
1. Determine the molecular formula and degree of unsaturation
2. Determine the functional group present from IR
3. From ^{13}C-NMR, determine # of signals and chemical shifts
4. From ^{1}H-NMR, determine # of signals, # of protons in each signal, peak splitting patterns and chemical shifts

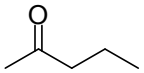
Molecular formula: C4H7O2Cl, IR absorption peak at 1740 cm^{-1}



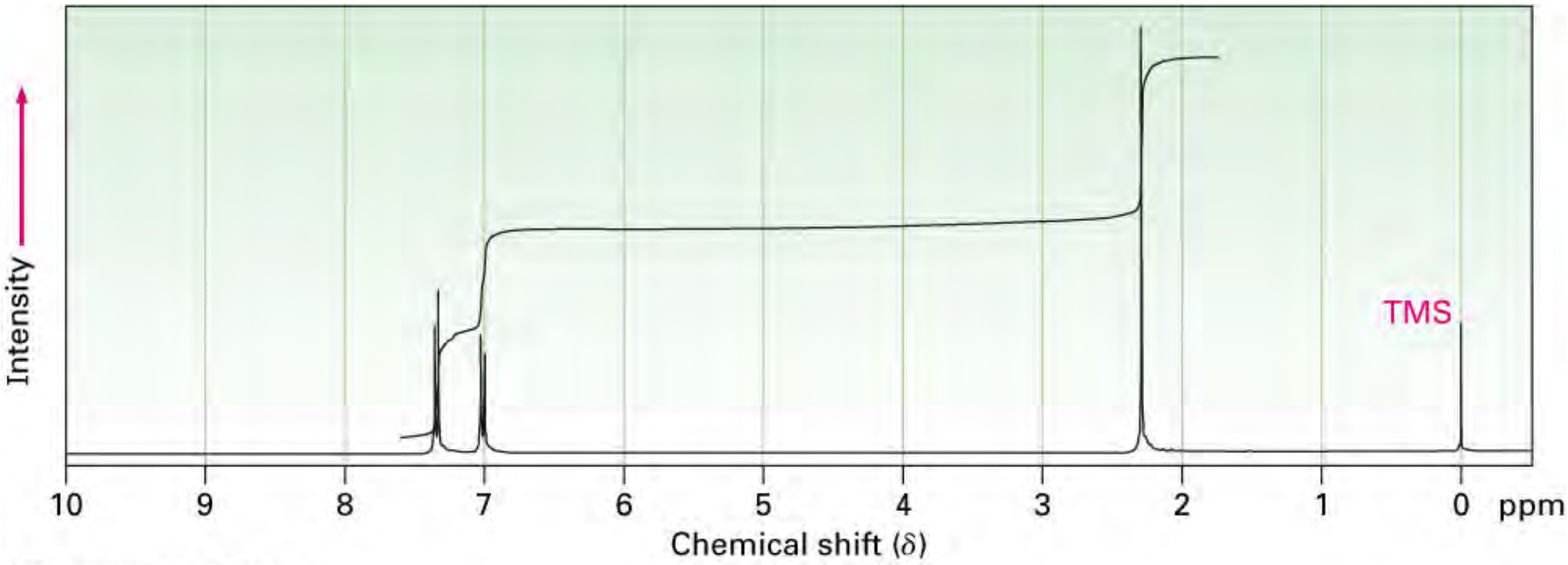


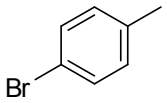
Molecular formula: C5H10O

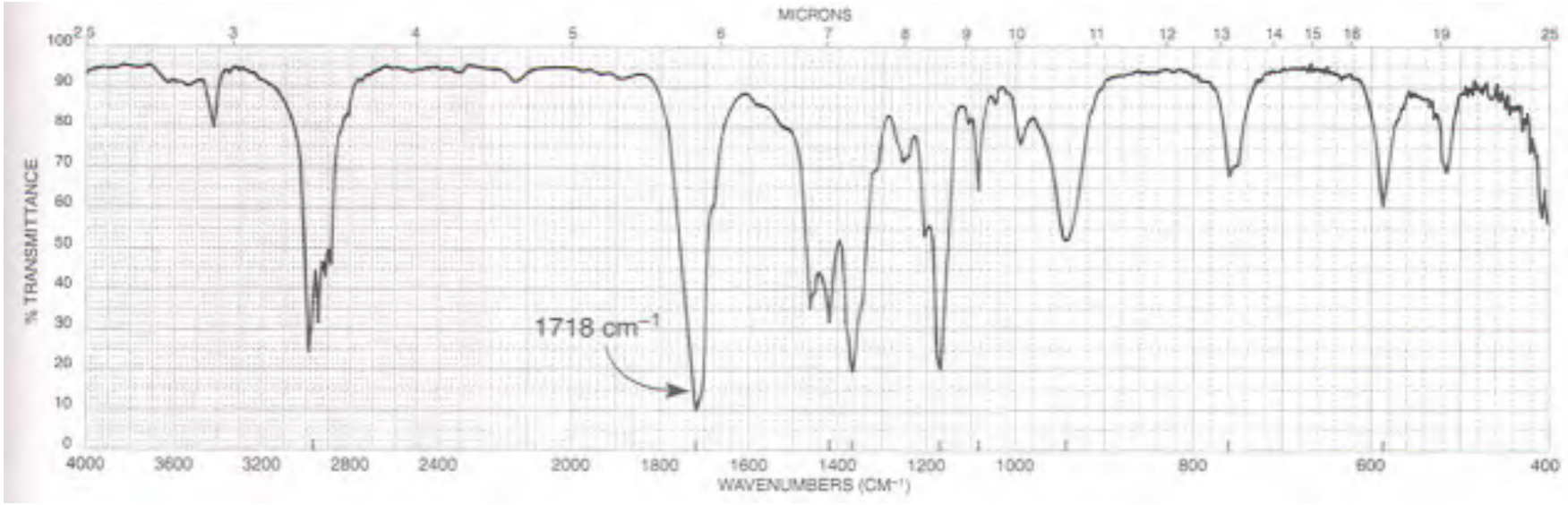




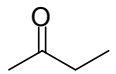
Molecular formula: C7H7Br

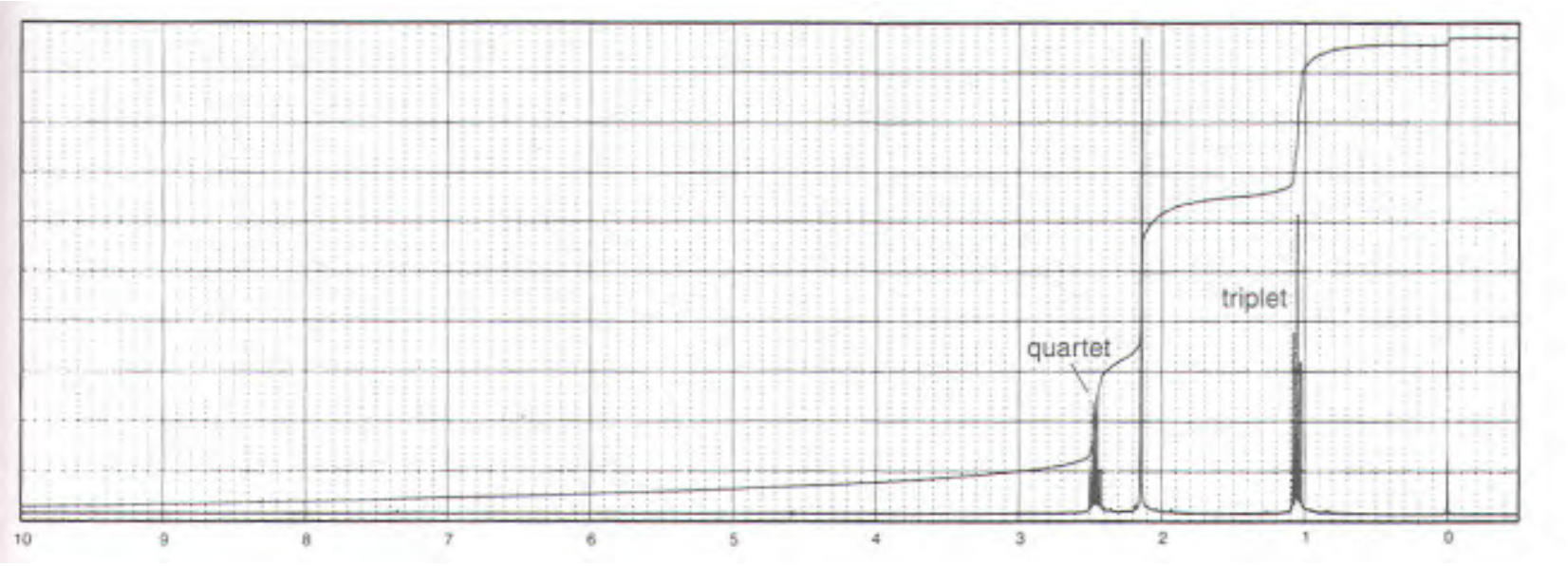


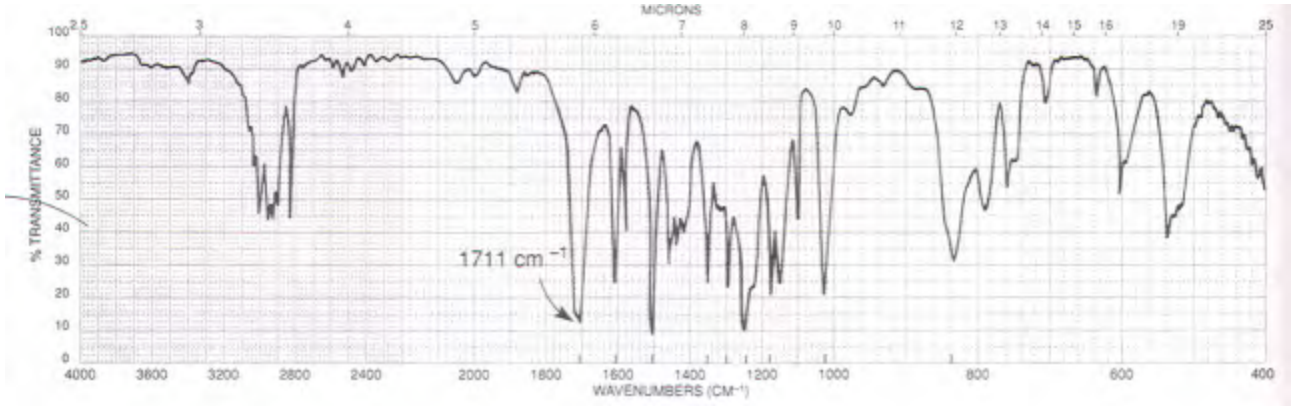


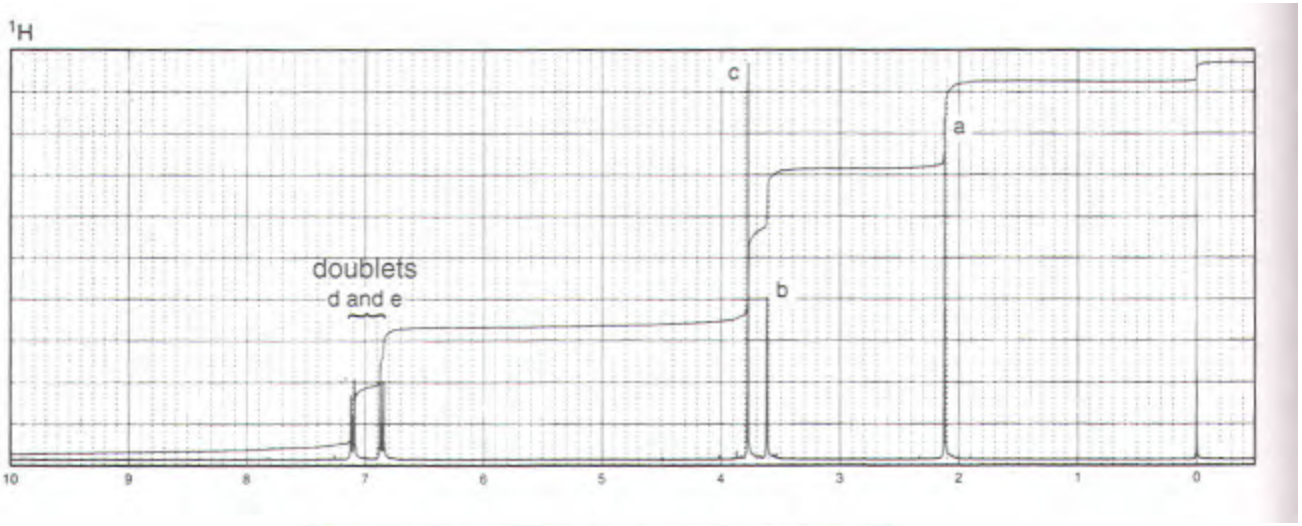


Formula
C4H8O

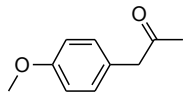




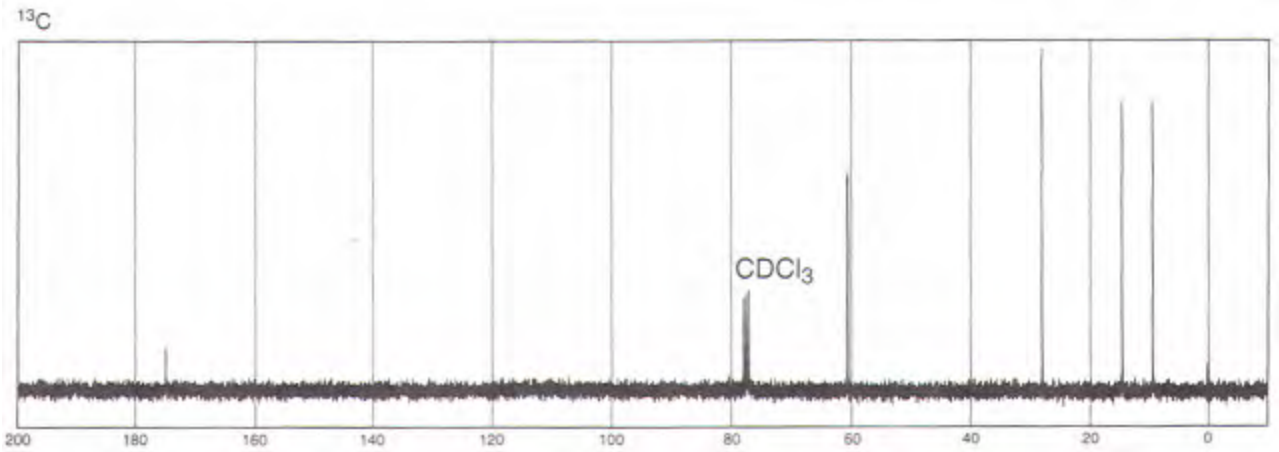


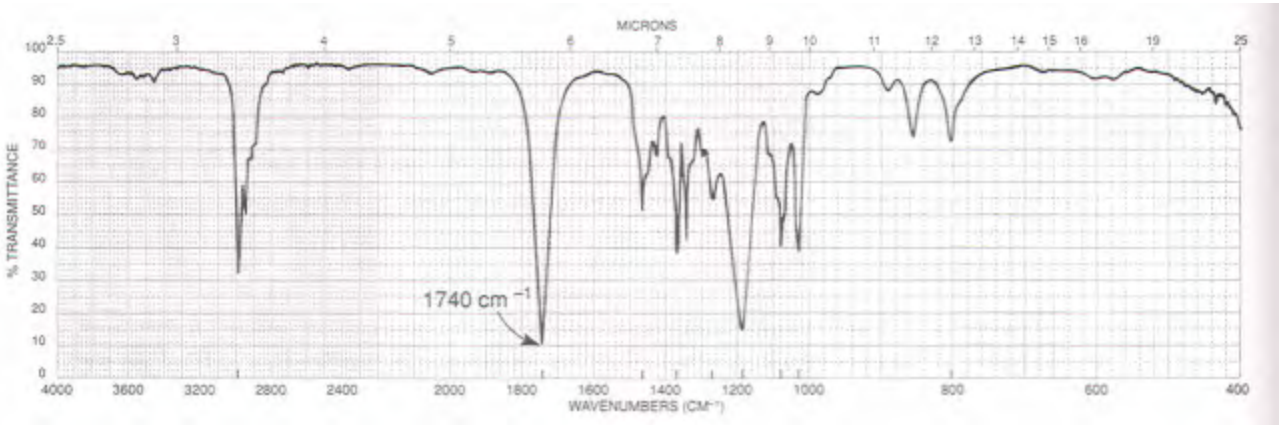


Formula
C10H12O2



Normal Carbon	DEPT-135	DEPT-90
29 ppm	Positive	No peak
50	Negative	No peak
55	Positive	No peak
114	Positive	Positive
126	No peak	No peak
130	Positive	Positive
159	No peak	No peak
207	No peak	No peak





Formula
C5H10O2