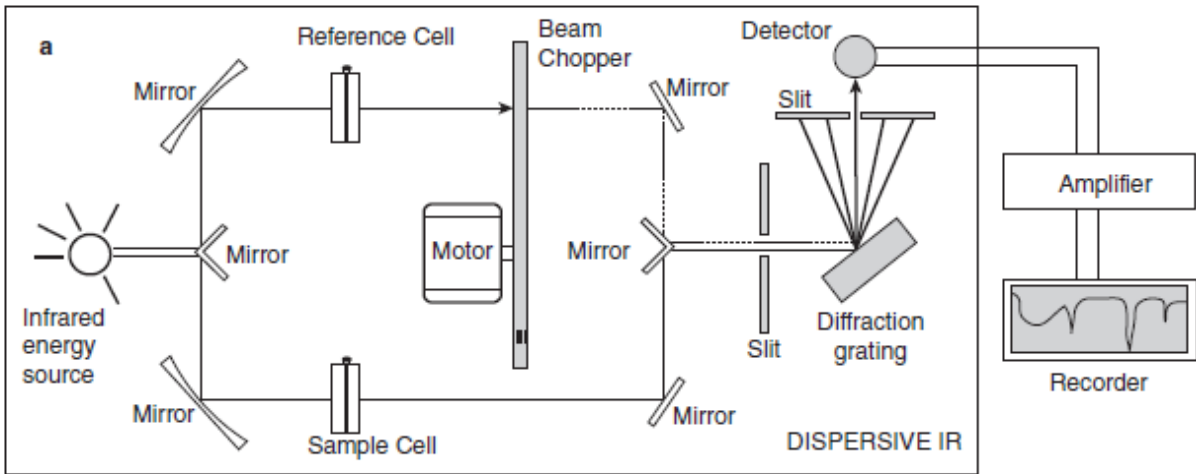


Lecture # 3

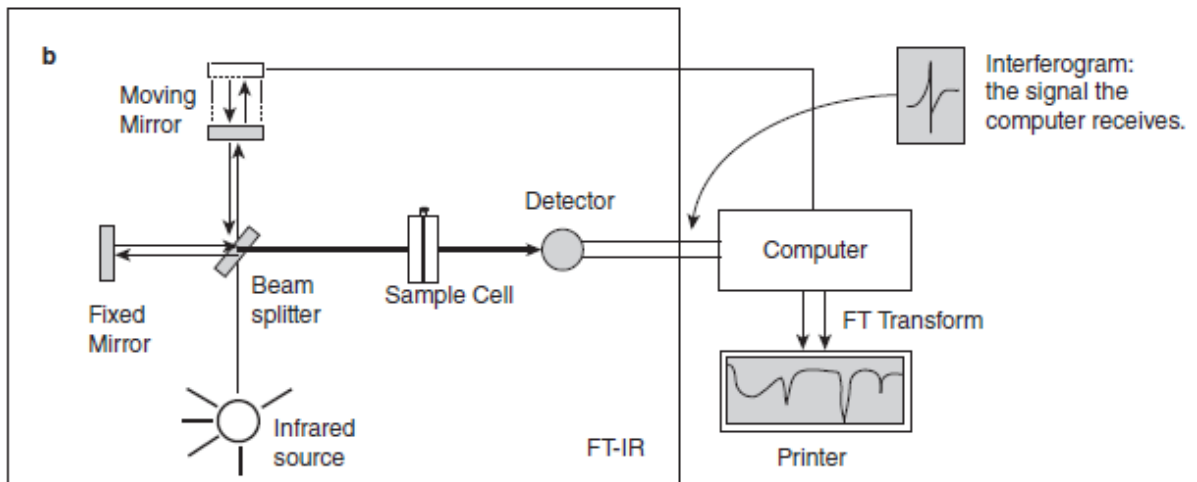
2.5 THE INFRARED SPECTROMETER

A. Dispersive Infrared Spectrometers



$$\text{percent transmittance} = \frac{I_s}{I_r} \times 100$$

B. Fourier Transform Spectrometers

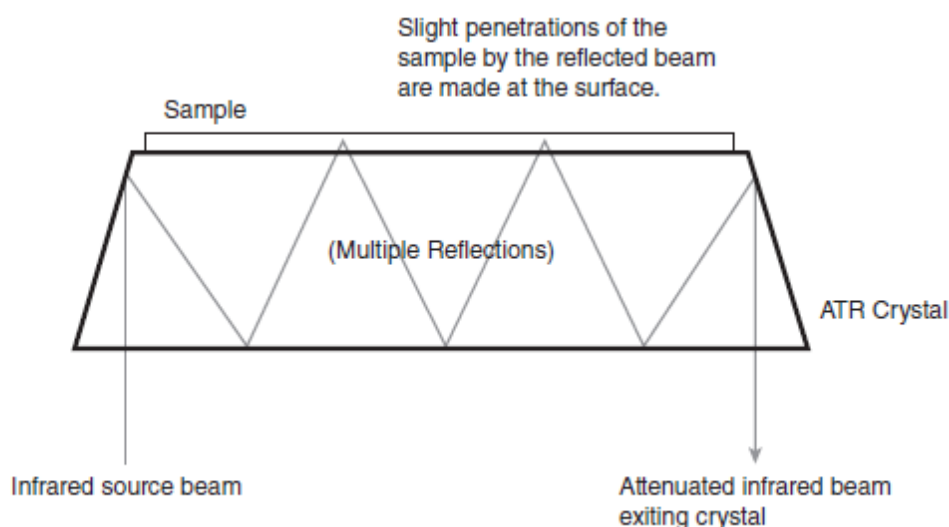


2.6 PREPARATION OF SAMPLES FOR INFRARED SPECTROSCOPY

typically sodium chloride or potassium bromide. Potassium bromide plates are more expensive than sodium chloride plates but have the advantage of usefulness in the range of 4000 to 400 cm^{-1} . Sodium chloride plates are used widely because of their relatively low cost. The practical range for their use in spectroscopy extends from 4000 to 650 cm^{-1} .

Another method, a **Nujol mull**, involves grinding the compound with mineral oil (Nujol) to create a suspension of the finely divided sample dispersed in mineral oil.

The best method of determining a spectrum of a solid is to make use of an **attenuated total reflectance (ATR)** accessory. Modern FT-IR instruments now offer this accessory



2.7 WHAT TO LOOK FOR WHEN EXAMINING INFRARED SPECTRA

C=O 1850–1630 cm^{-1}

C=C 1680–1620 cm^{-1}

O–H 3650–3200 cm^{-1}

N–H 3500–3300 cm^{-1}

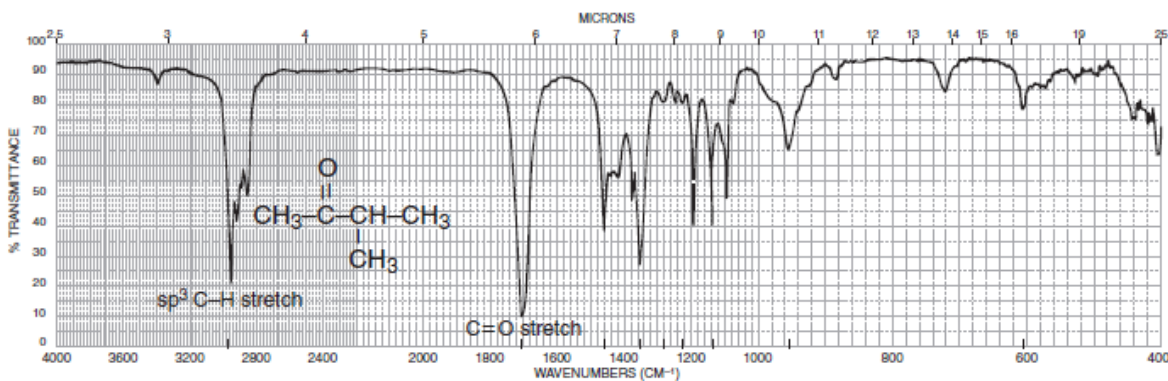


FIGURE 2.4 The infrared spectrum of 3-methyl-2-butanone (neat liquid, KBr plates).

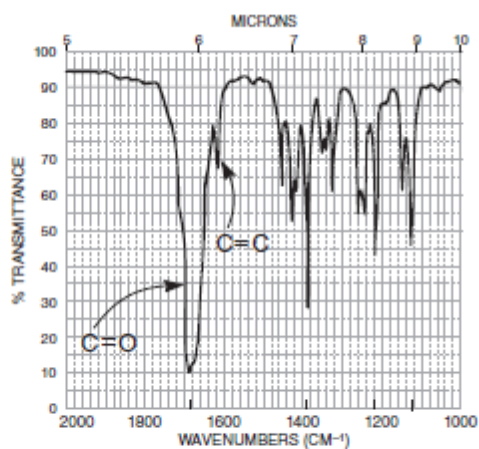


FIGURE 2.5 A comparison of the intensities of the C=O and C=C absorption bands.

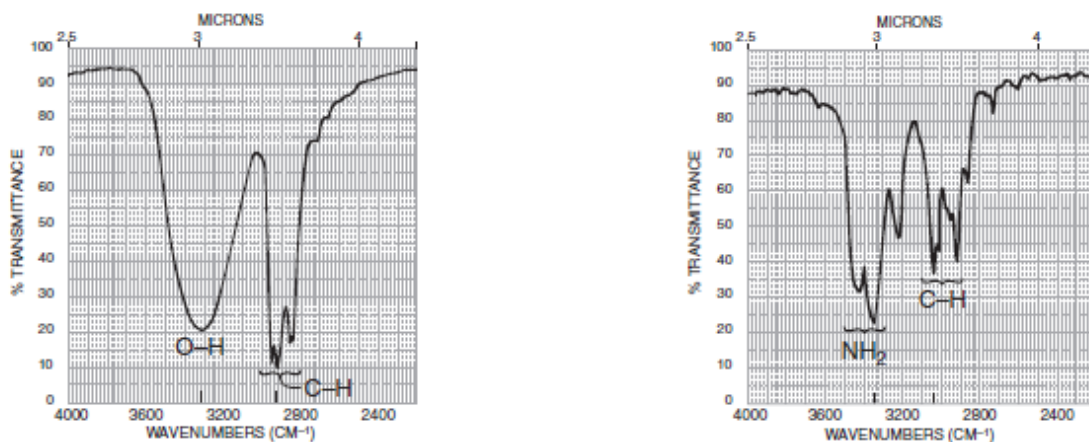


FIGURE 2.6 A comparison of the shapes of the absorption bands for the O-H and N-H groups.

2.8 CORRELATION CHARTS AND TABLES

TABLE 2.3
A SIMPLIFIED CORRELATION CHART

Type of Vibration		Frequency (cm^{-1})	Intensity	Page Reference
C–H	Alkanes (stretch)	3000–2850	s	31
	–CH ₃ (bend)	1450 and 1375	m	
	–CH ₂ – (bend)	1465	m	
	Alkenes (stretch)	3100–3000	m	33
	(out-of-plane bend)	1000–650	s	
	Aromatics (stretch)	3150–3050	s	43
	(out-of-plane bend)	900–690	s	
	Alkyne (stretch)	ca. 3300	s	35
	Aldehyde	2900–2800	w	56
		2800–2700	w	
C–C	Alkane	Not interpretatively useful		
C=C	Alkene	1680–1600	m–w	33
	Aromatic	1600 and 1475	m–w	43
C≡C	Alkyne	2250–2100	m–w	35
C=O	Aldehyde	1740–1720	s	56
	Ketone	1725–1705	s	58
	Carboxylic acid	1725–1700	s	62
	Ester	1750–1730	s	64
	Amide	1700–1640	s	70
	Anhydride	1810 and 1760	s	73
	Acid chloride	1800	s	72

C–O	Alcohols, ethers, esters, carboxylic acids, anhydrides	1300–1000	s	47, 50, 62, 64, and 73
O–H	Alcohols, phenols			
	Free	3650–3600	m	47
	H-bonded	3400–3200	m	47
	Carboxylic acids	3400–2400	m	62
N–H	Primary and secondary amines and amides			
	(stretch)	3500–3100	m	74
	(bend)	1640–1550	m–s	74
C–N	Amines	1350–1000	m–s	74
C=N	Imines and oximes	1690–1640	w–s	77
C≡N	Nitriles	2260–2240	m	77
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates	2270–1940	m–s	77
N=O	Nitro (R–NO ₂)	1550 and 1350	s	79
S–H	Mercaptans	2550	w	81
S=O	Sulfoxides	1050	s	81
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1375–1300 and 1350–1140	s	82
C–X	Fluoride	1400–1000	s	85
	Chloride	785–540	s	85
	Bromide, iodide	< 667	s	85

TABLE 2.4
BASE VALUES FOR ABSORPTIONS OF BONDS

O–H	3400 cm ⁻¹	C≡C	2150 cm ⁻¹
N–H	3400	C=O	1715
C–H	3000	C=C	1650
C≡N	2250	C–O	1100

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

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⁻¹.
- 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.

2.10 HYDROCARBONS: ALKANES, ALKENES, AND ALKYNES

SPECTRAL ANALYSIS BOX

ALKANES

The spectrum is usually simple, with few peaks.

C–H Stretch occurs around 3000 cm^{-1} .

In alkanes (except strained ring compounds), sp^3 C–H absorption always occurs at frequencies less than 3000 cm^{-1} ($3000\text{--}2840\text{ cm}^{-1}$).

If a compound has vinylic, aromatic, acetylenic, or cyclopropyl hydrogens, the C–H absorption is greater than 3000 cm^{-1} . These compounds have sp^2 and sp hybridizations (see Sections 2.10B and 2.10C).

CH₂ Methylene groups have a characteristic bending absorption of approximately 1465 cm^{-1} .

CH₃ Methyl groups have a characteristic bending absorption of approximately 1375 cm^{-1} .

CH₂ The bending (rocking) motion associated with four or more CH₂ groups in an open chain occurs at about 720 cm^{-1} (called a *long-chain band*).

C–C Stretch not interpretatively useful; many weak peaks.

Examples: decane (Fig. 2.7), mineral oil (Fig. 2.8), and cyclohexane (Fig. 2.9).

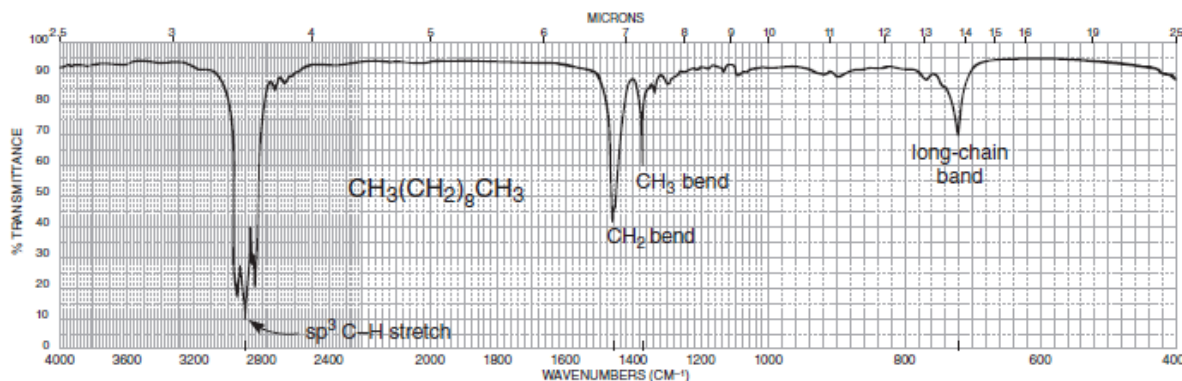


FIGURE 2.7 The infrared spectrum of decane (neat liquid, KBr plates).

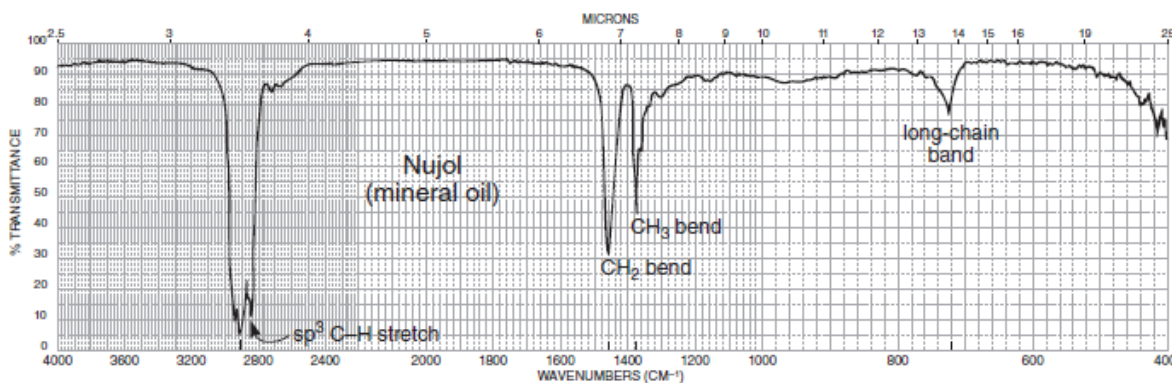


FIGURE 2.8 The infrared spectrum of mineral oil (neat liquid, KBr plates).

SPECTRAL ANALYSIS BOX

ALKENES

=C–H Stretch for sp^2 C–H occurs at values greater than 3000 cm^{-1} ($3095\text{--}3010\text{ cm}^{-1}$).

=C–H Out-of-plane (oop) bending occurs in the range $1000\text{--}650\text{ cm}^{-1}$.

These bands can be used to determine the degree of substitution on the double bond (see discussion).

C=C Stretch occurs at $1660\text{--}1600\text{ cm}^{-1}$; conjugation moves C=C stretch to lower frequencies and increases the intensity.

Symmetrically substituted bonds (e.g., 2,3-dimethyl-2-butene) do not absorb in the infrared (no dipole change).

Symmetrically disubstituted (*trans*) double bonds are often vanishingly weak in absorption; *cis* are stronger.

Examples: 1-hexene (Fig. 2.10), cyclohexene (Fig. 2.11), *cis*-2-pentene (Fig. 2.12), and *trans*-2-pentene (Fig. 2.13).

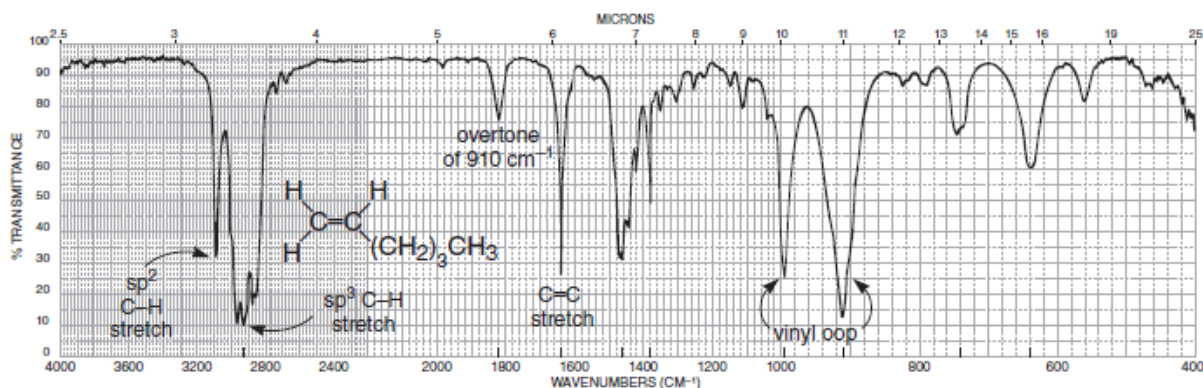


FIGURE 2.10 The infrared spectrum of 1-hexene (neat liquid, KBr plates).

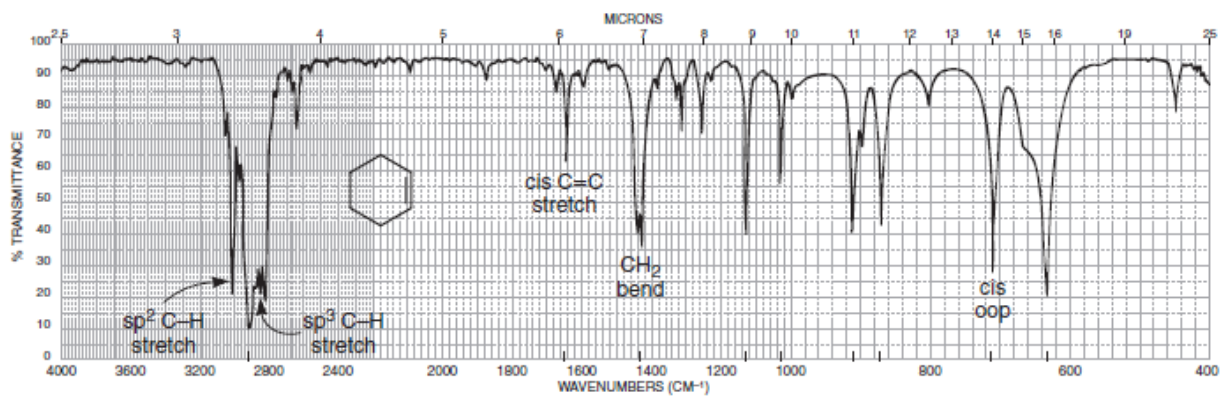


FIGURE 2.11 The infrared spectrum of cyclohexene (neat liquid, KBr plates).

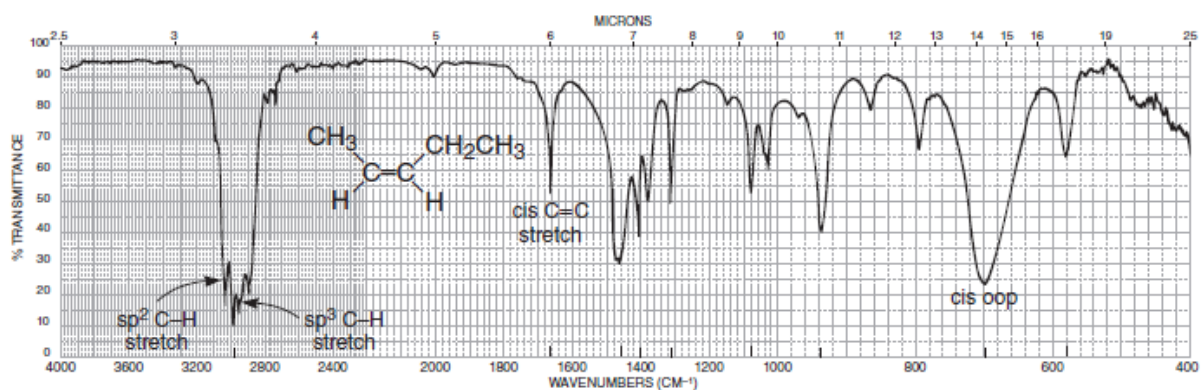


FIGURE 2.12 The infrared spectrum of *cis*-2-pentene (neat liquid, KBr plates).

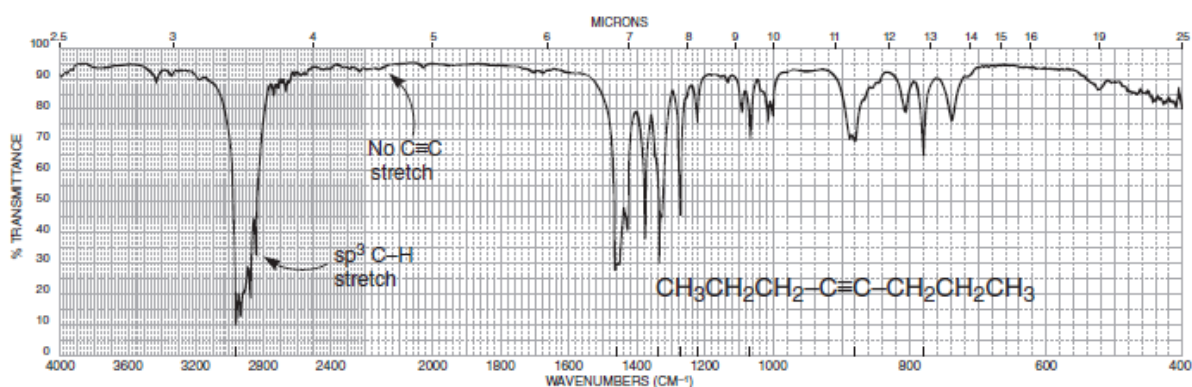


FIGURE 2.13 The infrared spectrum of *trans*-2-pentene (neat liquid, KBr plates).

SPECTRAL ANALYSIS BOX

ALKYNES

- $\equiv\text{C}-\text{H}$ Stretch for sp C-H usually occurs near 3300 cm^{-1} .
- $\text{C}=\text{C}$ Stretch occurs near 2150 cm^{-1} ; conjugation moves stretch to lower frequency. Disubstituted or symmetrically substituted triple bonds give either no absorption or weak absorption.

Examples: 1-octyne (Fig. 2.14) and 4-octyne (Fig. 2.15).

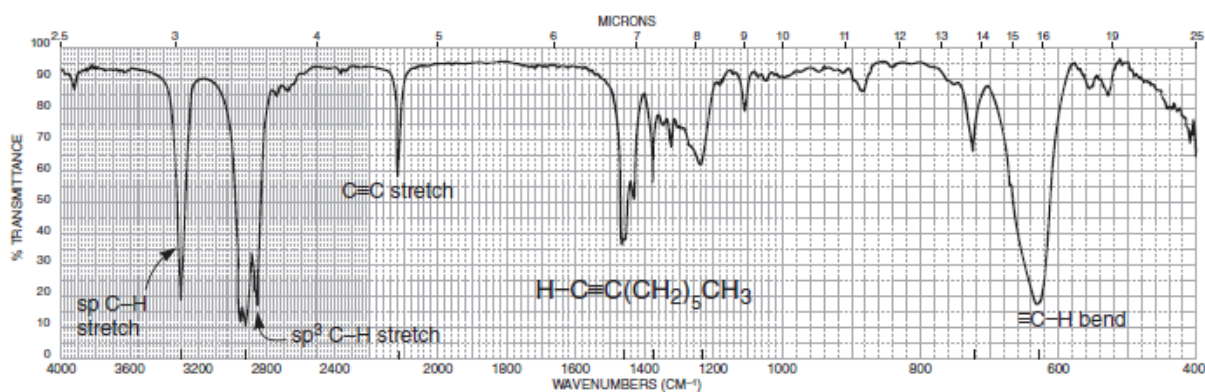


FIGURE 2.14 The infrared spectrum of 1-octyne (neat liquid, KBr plates).

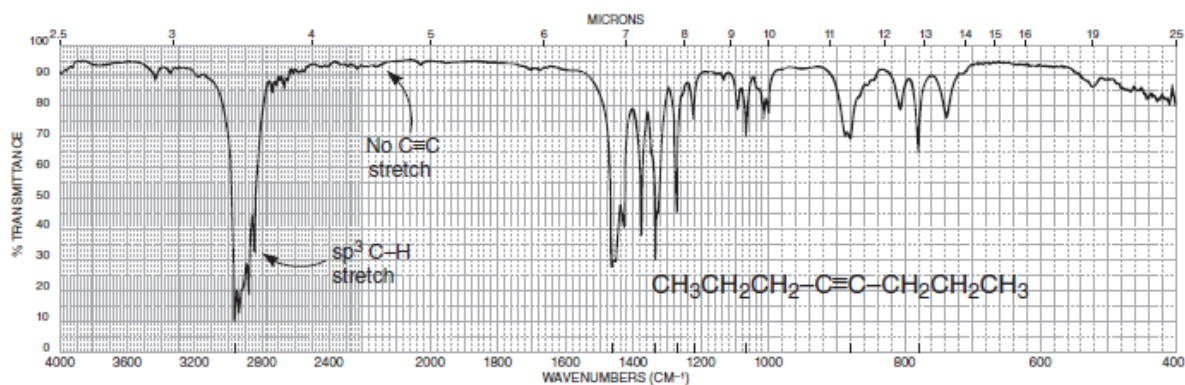


FIGURE 2.15 The infrared spectrum of 4-octyne (neat liquid, KBr plates).

TABLE 2.5
PHYSICAL CONSTANTS FOR sp -, sp^2 -, AND sp^3 -HYBRIDIZED CARBON AND THE RESULTING C–H ABSORPTION VALUES

Bond	$\equiv\text{C}-\text{H}$	$=\text{C}-\text{H}$	$-\text{C}-\text{H}$
Type	$sp-1s$	sp^2-1s	sp^3-1s
Length	1.08 Å	1.10 Å	1.12 Å
Strength	506 kJ	444 kJ	422 kJ
IR frequency	3300 cm^{-1}	$\sim 3100 \text{ cm}^{-1}$	$\sim 2900 \text{ cm}^{-1}$

TABLE 2.6
STRETCHING VIBRATIONS FOR VARIOUS sp^3 -HYBRIDIZED C–H BONDS

Group		Stretching Vibration (cm^{-1})	
		Asymmetric	Symmetric
Methyl	CH_3-	2962	2872
Methylene	$-\text{CH}_2-$	2926	2853
Methine	$\begin{array}{c} \\ -\text{C}- \\ \\ \text{H} \end{array}$	2890	Very weak

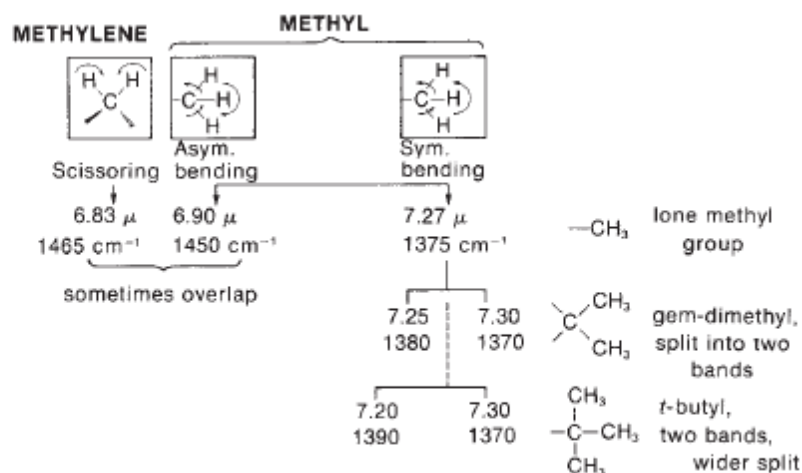


FIGURE 2.17 The C–H bending vibrations for methyl and methylene groups.

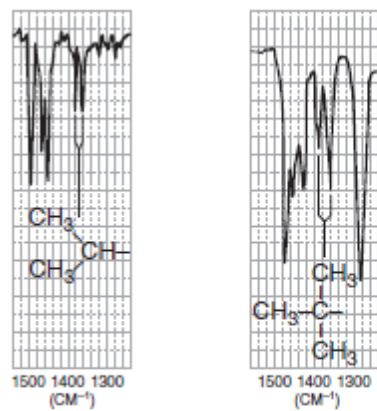


FIGURE 2.18 C-H bending patterns for the isopropyl and *tert*-butyl groups.