

LECTURE 25/36

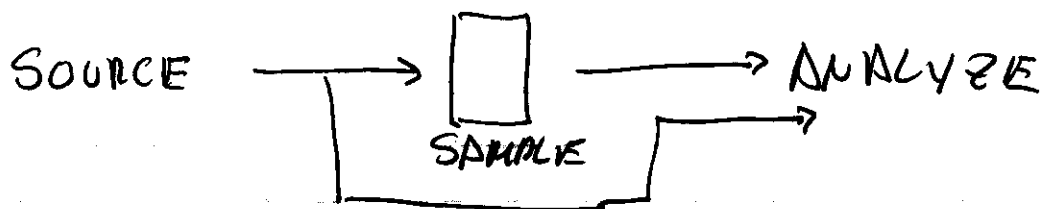
NOV-6-02

SPECTROSCOPY

IR

UV-vis

ABSORPTION



RADIATION \rightarrow WAVE LENGTH λ
 \AA , μ OR nm, $\bar{\nu}$ (cm^{-1})

$$\bar{\nu} = \frac{1}{\lambda} \text{ in } \text{cm}^{-1}$$

PEAKS \rightarrow ABSORPTION \Rightarrow SPECTRA

IR SPECTRUM UNIQUE

FOR UV-VIS



$$\text{ABSORBANCE} \equiv \log_{10} \frac{I_0}{I}$$

$$\text{BEER'S LAW} \Rightarrow A = \epsilon l c$$

$C =$ CONCENTRATION

$\epsilon \equiv$ MOLAR EXTINCTION COEFF.

DEPENDS ON THE ABSORBING SAMPLE

$\epsilon \sim 10^3 - 10^5$ ALLOWED

$\sim 10^0 - 10^3$ FORBIDDEN (RAPE) WEAK INT

$\sim 10^5 - 10^0$ SPIN-FORBIDDEN EXT. WEAK INT

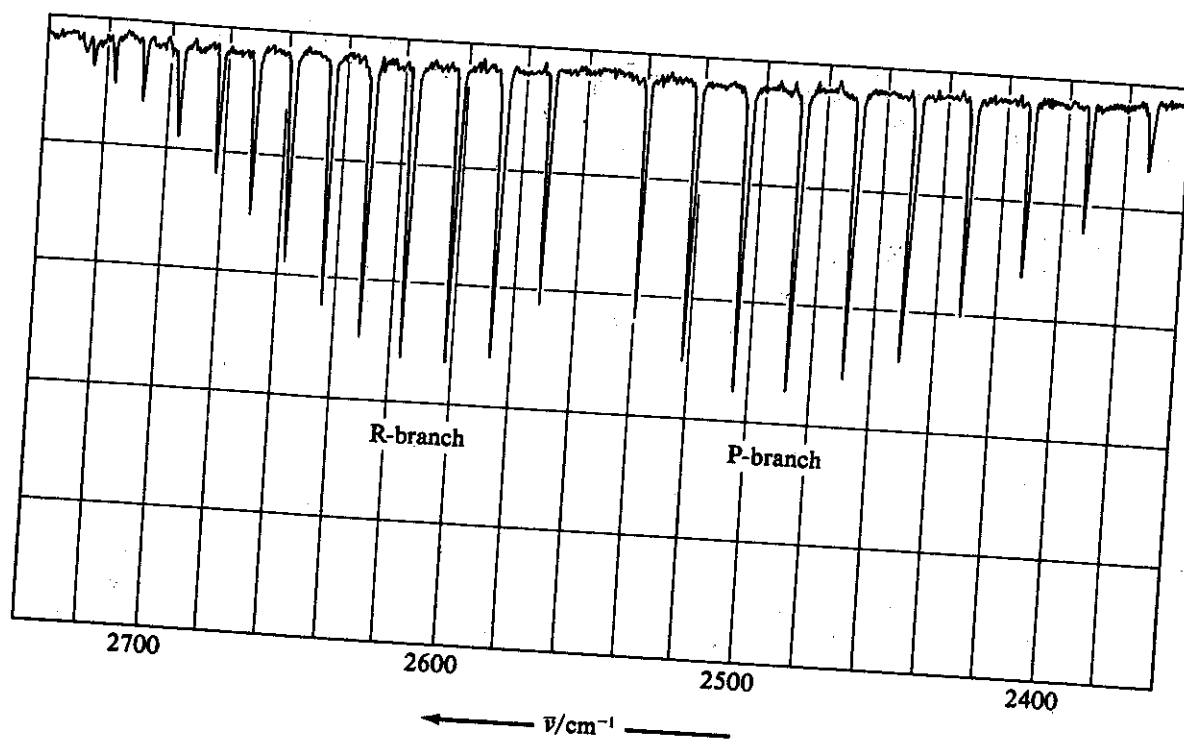
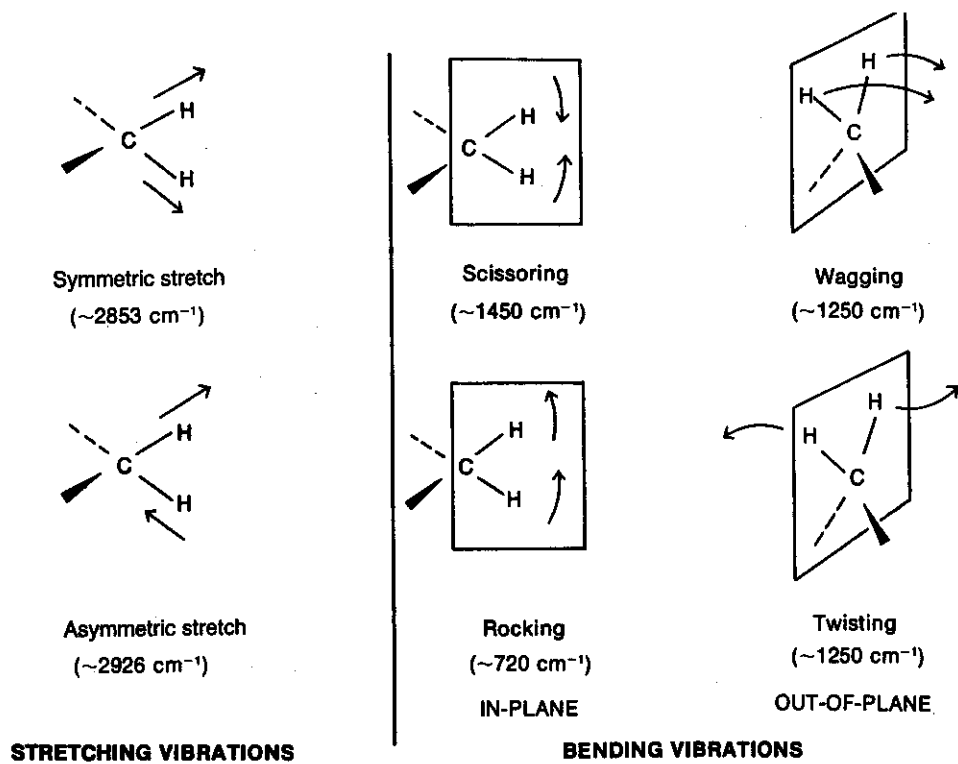


Figure 10-3. The rotational-vibrational spectrum of the $0 \rightarrow 1$ vibrational transition of $\text{HBr}(g)$. The R branch and the P branch are indicated in the figure. (From *Introduction to Molecular Spectroscopy* by Gordon Barrow. Used with the permission of McGraw-Hill Book Company.)



one absorption peak. Amides exhibit similar bands. There are two strong N=O stretch peaks for a nitro group, with the symmetric stretch appearing at about 1350 cm^{-1} and the asymmetric stretch appearing at about 1550 cm^{-1} .

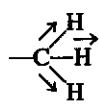
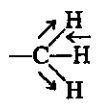
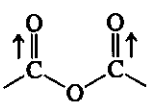
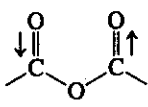
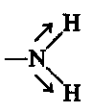
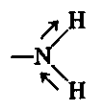
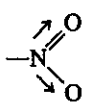
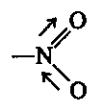
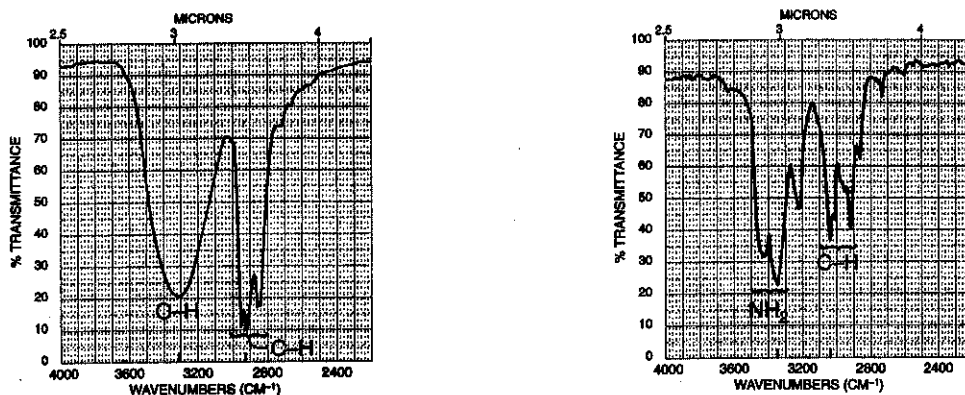
	Symmetric Stretch	Asymmetric Stretch
Methyl	 ~2872 cm^{-1}	 ~2962 cm^{-1}
Anhydride	 ~1760 cm^{-1}	 ~1800 cm^{-1}
Amino	 ~3300 cm^{-1}	 ~3400 cm^{-1}
Nitro	 ~1350 cm^{-1}	 ~1550 cm^{-1}

TABLE 2.3

A Simplified Correlation Chart

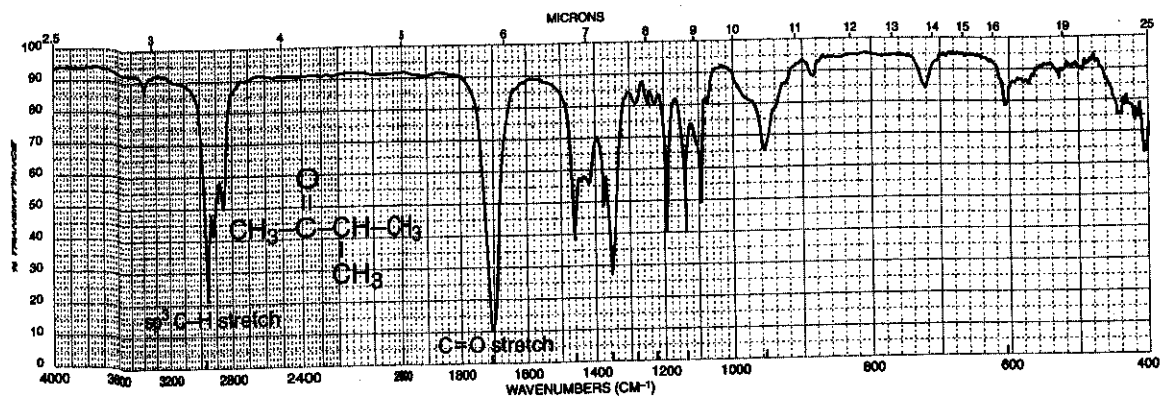
	Type of Vibration	Frequency (cm ⁻¹)	Intensity	
C—H	Alkanes (stretch)	3000–2850	s	
	—CH ₃ (bend)	1450 and 1375	m	
	—CH ₂ — (bend)	1465	m	
	Alkenes	(stretch)	3100–3000	m
		(out-of-plane bend)	1000–650	s
	Aromatics	(stretch)	3150–3050	s
		(out-of-plane bend)	900–690	s
	Alkyne (stretch)	ca. 3300	s	
	Aldehyde		2900–2800	w
			2800–2700	w
C—C	Alkane	Not interpretatively useful		
C=C	Alkene	1680–1600	m–w	
	Aromatic	1600 and 1475	m–w	
C≡C	Alkyne	2250–2100	m–w	
C=O	Aldehyde	1740–1720	s	
	Ketone	1725–1705	s	
	Carboxylic acid	1725–1700	s	
	Ester	1750–1730	s	
	Amide	1680–1630	s	
	Anhydride	1810 and 1760	s	
	Acid chloride	1800	s	
	C—O	Alcohols, ethers, esters, carboxylic acids, anhydrides	1300–1000	s
O—H	Alcohols, phenols			
	Free	3650–3600	m	
	H-bonded	3400–3200	m	
	Carboxylic acids	3400–2400	m	
N—H	Primary and secondary amines and amides (stretch)	3500–3100	m	
	(bend)	1640–1550	m–s	
C—N	Amines	1350–1000	m–s	
C=N	Imines and oximes	1690–1640	w–s	
C≡N	Nitriles	2260–2240	m	
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates	2270–1940	m–s	
N=O	Nitro (R—NO ₂)	1550 and 1350	s	
S—H	Mercaptans	2550	w	
S=O	Sulfoxides	1050	s	
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1375–1300 and 1350–1140	s	
C—X	Fluoride	1400–1000	s	
	Chloride	785–540	s	
	Bromide, iodide	< 667	s	



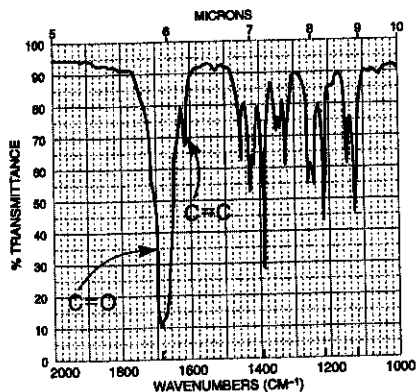
► **FIGURE 2.6** A comparison of the shapes of the absorption bands for the O—H and N—H groups.

A Simplified Correlation Chart

	Type of Vibration	Frequency (cm ⁻¹)	Intensity	
C—H	Alkanes (stretch)	3000–2850	s	
	—CH ₃ (bend)	1450 and 1375	m	
	—CH ₂ — (bend)	1465	m	
	Alkenes	(stretch)	3100–3000	m
		(out-of-plane bend)	1000–650	s
	Aromatics	(stretch)	3150–3050	s
		(out-of-plane bend)	900–690	s
	Alkyne	(stretch)	ca. 3300	s
	Aldehyde		2900–2800	w
			2800–2700	w
C—C	Alkane	Not interpretatively useful		
C=C	Alkene	1680–1600	m–w	
	Aromatic	1600 and 1475	m–w	
C≡C	Alkyne	2250–2100	m–w	
C=O	Aldehyde	1740–1720	s	
	Ketone	1725–1705	s	
	Carboxylic acid	1725–1700	s	
	Ester	1750–1730	s	
	Amide	1680–1630	s	
	Anhydride	1810 and 1760	s	
	Acid chloride	1800	s	
C—O	Alcohols, ethers, esters, carboxylic acids, anhydrides	1300–1000	s	
O—H	Alcohols, phenols			
	Free	3650–3600	m	
	H-bonded	3400–3200	m	
	Carboxylic acids	3400–2400	m	
N—H	Primary and secondary amines and amides (stretch)	3500–3100	m	
	(bend)	1640–1550	m–s	
C—N	Amines	1350–1000	m–s	
C=N	Imines and oximes	1690–1640	w–s	
C≡N	Nitriles	2260–2240	m	
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates	2270–1940	m–s	
N=O	Nitro (R—NO ₂)	1550 and 1350	s	
S—H	Mercaptans	2550	w	
S=O	Sulfoxides	1050	s	



► **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.

However, the C=O bond is a strong absorber, whereas the C=C bond generally absorbs only weakly (Fig. 2.5). Hence, a trained observer would not interpret a strong peak at 1670 cm^{-1} to be a C=C double bond, nor would he interpret a weak absorption at this frequency to be due to a carbonyl group.

The shape and fine structure of a peak often give clues to its identity, as well. Thus, while the N—H and O—H regions overlap,

$$\text{O—H } 3650\text{--}3200\text{ cm}^{-1}$$

$$\text{N—H } 3500\text{--}3300\text{ cm}^{-1}$$

the N—H absorption usually has one or two *sharp* absorption bands of lower intensity, while O—H, when it is in the N—H region, usually gives a *broad* absorption peak. Also, primary amines give *two* absorptions in this region, whereas alcohols as pure liquids give only one (Fig. 2.6). Figure 2.6 also shows typical patterns for the C—H stretching frequencies at about 3000 cm^{-1} .

TABLE 2.4

Base Values for Absorptions of Bonds			
O—H	3400 cm^{-1}	C \equiv C	2150 cm^{-1}
N—H	3400	C=O	1715
C—H	3000	C=C	1650
C \equiv N	2250	C—O	1100

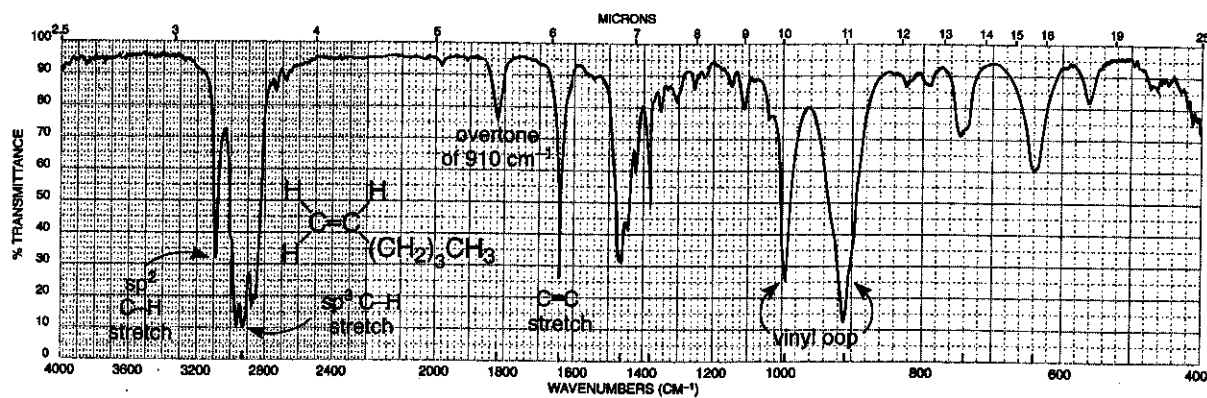
2.9 HOW TO APPROACH THE ANALYSIS OF A SPECTRUM (OR WHAT YOU CAN TELL AT A GLANCE)

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 \equiv C, C \equiv N, and NO₂ 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.

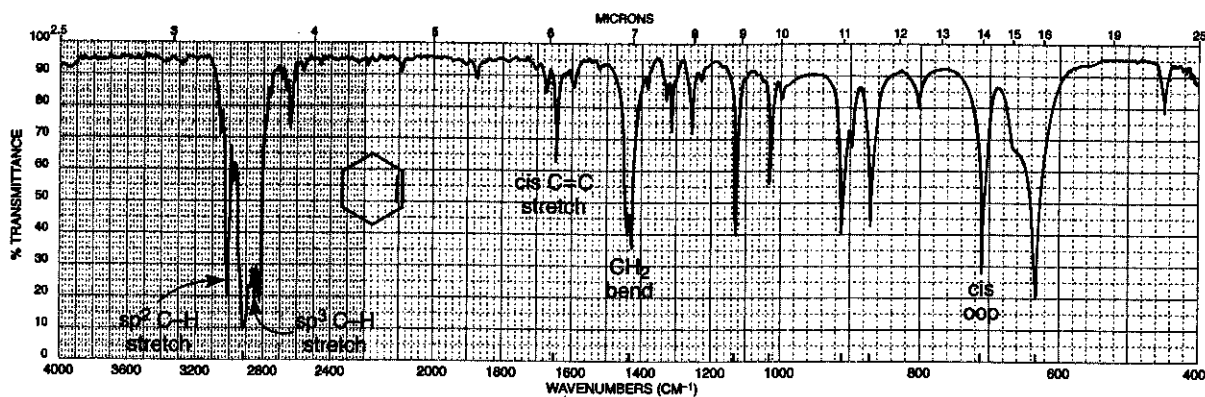
- Is a carbonyl group present? The C=O group gives rise to a strong absorption in the region 1820–1660 cm^{-1} . The peak is often the strongest in the spectrum and of medium width. You can't miss it.
- If C=O is present, check the following types (if it is absent, go to 3).

ACIDS	Is O—H also present? • <i>Broad</i> 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} . Two C=O absorptions near 1810 and 1760 cm^{-1} .
ANHYDRIDES	
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.
- If C=O is absent:

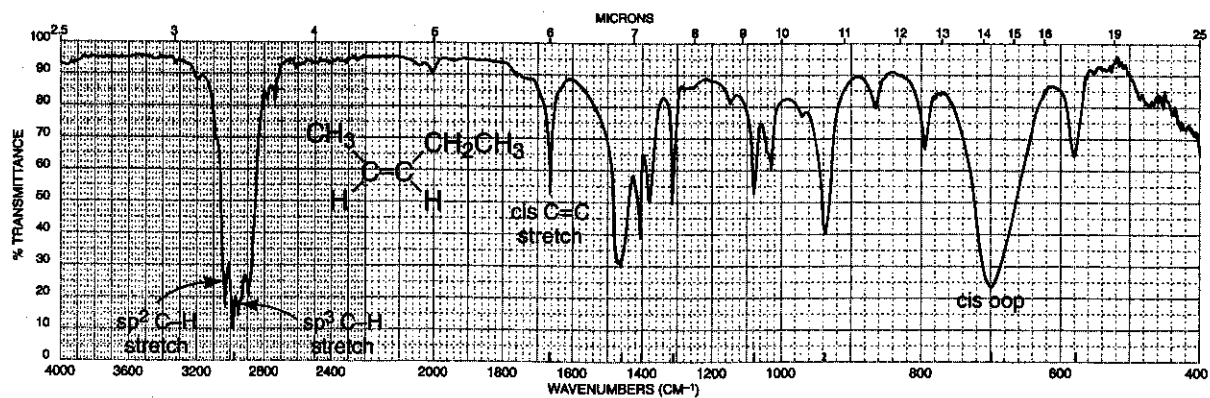
ALCOHOLS, PHENOLS	Check for O—H. • <i>Broad</i> absorption near 3400–3300 cm^{-1} . • Confirm this by finding C—O near 1300–1000 cm^{-1} .
AMINES	Check for N—H. • Medium absorption(s) near 3400 cm^{-1} .



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



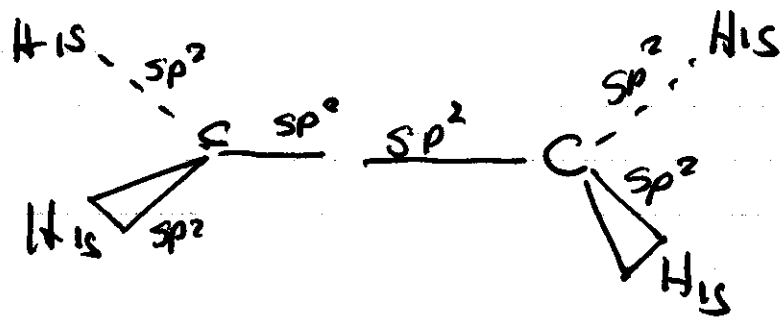
► **FIGURE 2.11** The infrared spectrum of cyclohexene (neat liquid, KBr plates).



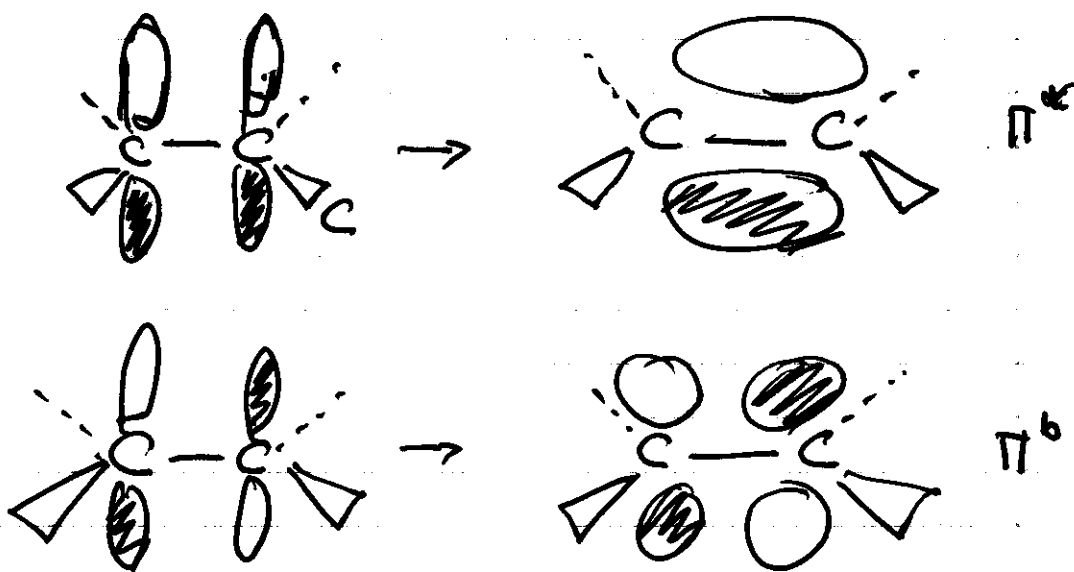
► **FIGURE 2.12** The infrared spectrum of *cis*-2-pentene (neat liquid, KBr plates).

MULTIPLE BONDS IN CARBON

ETHYLENE C_2H_4 sp^2



WE GET π BONDS



PREDICTIONS $\text{H}-\text{C}-\text{C}$ AND $\text{H}-\text{C}-\text{H}$ ANGLES = 120°

EXP: $\angle \text{H}-\text{C}-\text{H} = 117^\circ$

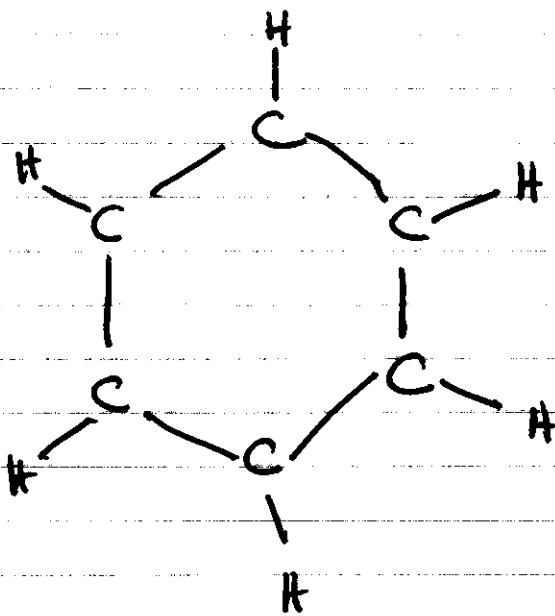
$\angle \text{H}-\text{C}-\text{C} = 121^\circ 31'$

C_2H_4 ABSORBS AT 58500 cm^{-1} $\pi \rightarrow \pi^*$

C_2H_6	$C-C$	1.54 \AA	83 kcal mol^{-1}
C_2H_4	$C=C$	1.35 \AA	125 kcal mol^{-1}
C_2H_2	$C\equiv C$	1.21 \AA	230 kcal mol^{-1}

BENZENE C_6H_6

WE USE sp^2 TO FORM σ BONDS ($1s_H + sp^2$)

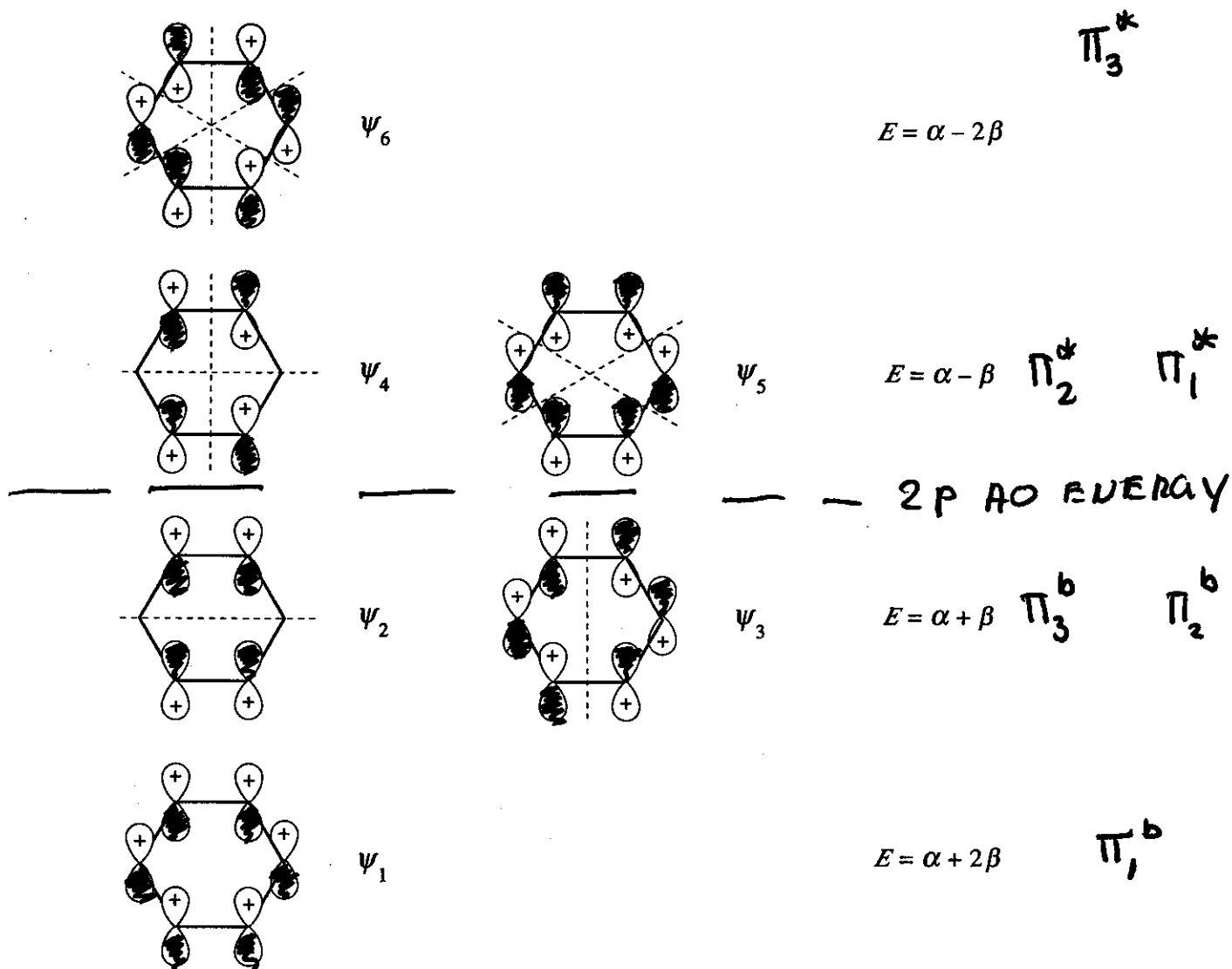


WE HAVE AN EXTRA $2p$ electron

EXAMPLE 10-8

Draw the π molecular orbitals for benzene and indicate the nodal planes.

SOLUTION:



Note that as we found for ethene and butadiene, the energy increases with the number of nodal planes.