

## Chapter 11: Spectroscopy (Infrared Spectroscopy)

IR is used to identify functional groups. It is particularly useful to distinguish between different functional groups containing C=O, O-H, N-H or NH<sub>2</sub>, triple bonds and double bonds.

### 11.1 Review Functional Groups

Functional groups are common and specific arrangements of atoms that govern reactivity and properties of (organic) molecules.

A table below provides a summary of the most important functional groups:

TABLE 2.3 IMPORTANT FAMILIES OF ORGANIC COMPOUNDS								
	Family							
	Alkane	Alkene	Alkyne	Aromatic	Haloalkane	Alcohol	Phenol	Ether
Functional group	C—H and C—C bonds			Aromatic ring				
Functional group	Amine	Aldehyde	Ketone	Carboxylic Acid	Ester	Amide	Nitrile	

11.1

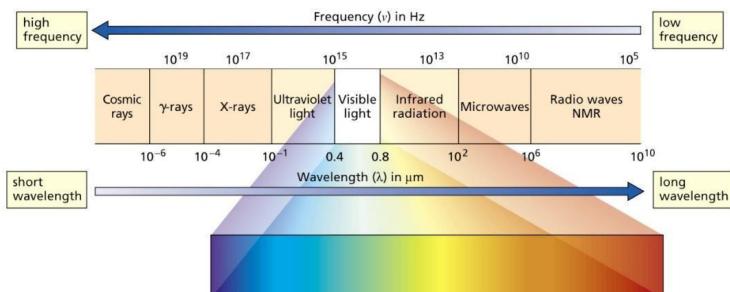
### 11.2 Infrared Spectroscopy: Physical Background

Infrared Spectroscopy (IR) is one of the most useful physical methods to **identify functional groups** in unknown compounds and use their presence or absence to confirm a hypothetical structure.



#### a) The Electromagnetic Spectrum

IR depends on the interaction of molecules with infrared radiation



11.2

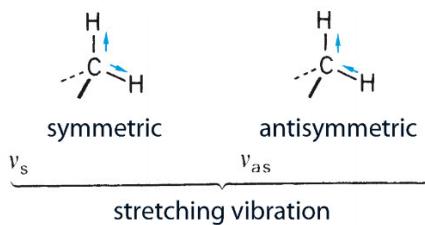
**b) IR Spectroscopy and Energy**

An infrared spectrum is obtained by passing infrared radiation through the sample. The energy of this radiation is

The Wavenumber ( $\bar{\nu}$ ) is another way to describe the frequency of electromagnetic radiation.

Note: High frequencies, large wavenumbers, and short wavelengths are associated with *high energy*.

Because organic molecules are flexible structures, IR radiation can cause their bonds to stretch and contract, atoms to wag, and other motions to occur.

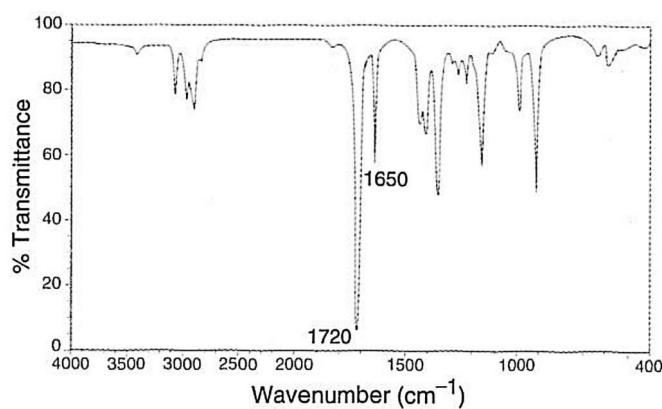


These stretching and bending motions occur with frequency of the IR radiation matches the frequency of the bond vibration. This results in an absorption band (peak) in an IR spectrum.

11.3

**11.3 A typical IR Spectrum**

A typical IR spectrum is shown here



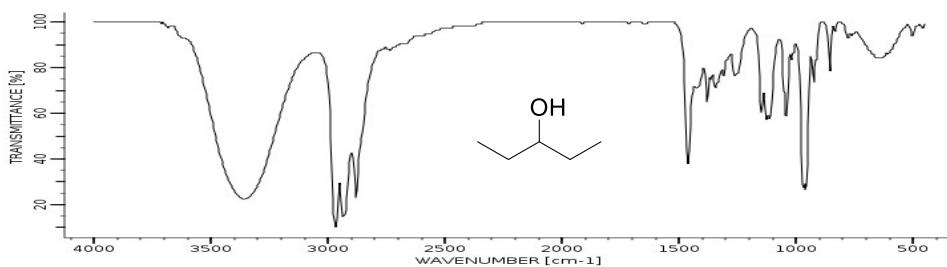
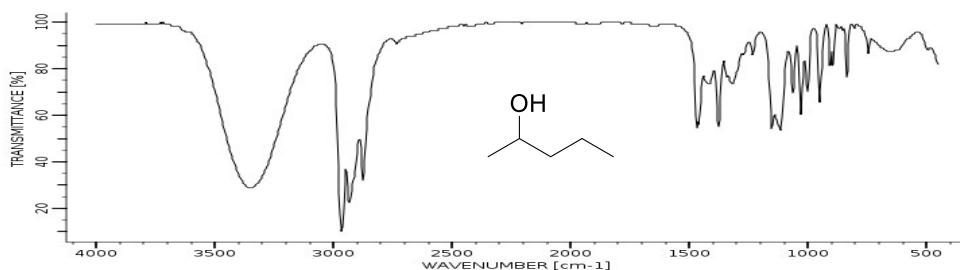
Some points to note:

- IR spectra are plotted as percentage *transmission* versus frequency (in  $\text{cm}^{-1}$ ).
- The frequency is plotted in *wavenumbers* ( $\text{cm}^{-1}$ ).
- Wave numbers are directly proportional to frequency.

11.4

**IR spectra confirm the presence or absence of functional groups within a molecule**

Spectra of compounds containing the same functional groups will differ in the *fingerprint region* ( $1500 - 400 \text{ cm}^{-1}$ ) or by slight changes in frequency of the major functional groups.



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**11.4. Frequencies (wavenumbers) of IR absorptions**

Where a bond absorbs in the IR spectrum depends both on the bond strength (triple>double>single) and the reduced mass.

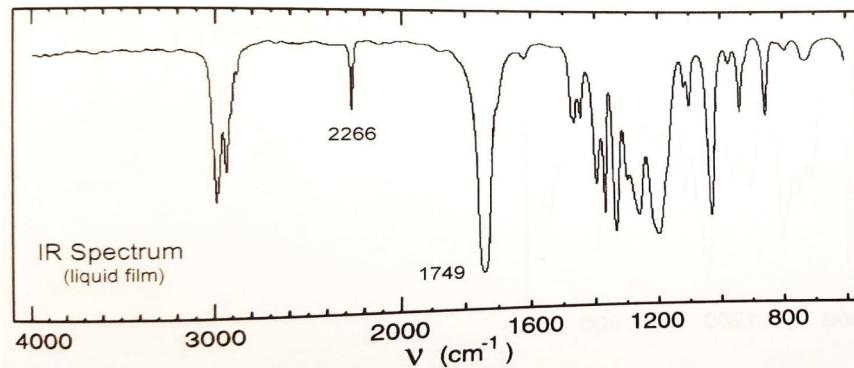
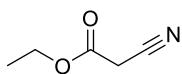
$$k_{\text{C}\equiv\text{C}} > k_{\text{C}=\text{C}} > k_{\text{C}-\text{C}}$$

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} = \text{reduced mass}$$

These are combined in Hooke's law (vibration frequency of a harmonic oscillator):

$$\nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Example:



We can broadly assign four regions to certain types of bonds.

O-H  
N-H  
C-H

C≡C  
C≡N  
C≡O  
X=Y=Z

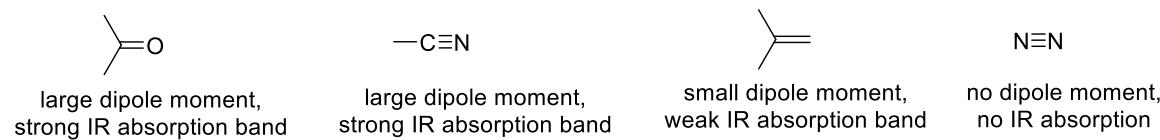
C=O  
C=C  
C=N  
N=O

C-O  
single bonds  
"Fingerprint" region

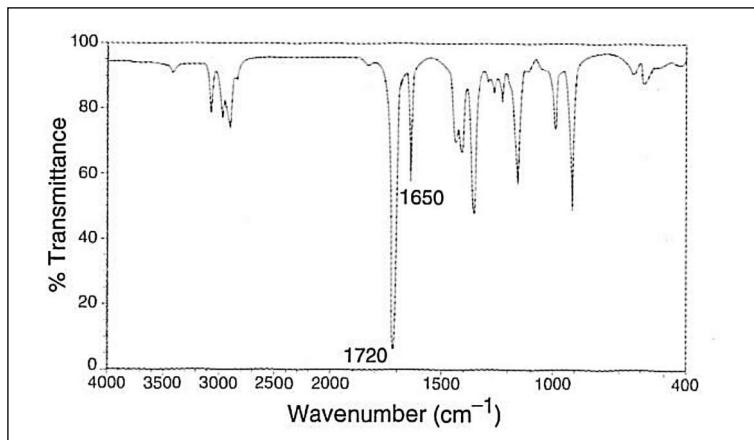
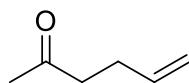
11.6

### 11.5 Strength of IR Absorptions

- The larger the change in dipole moment of the corresponding molecule, the stronger the IR absorption.
- If there is no change in dipole moment for a certain stretching or bending vibration, *no* IR peak will be observed (IR inactive).



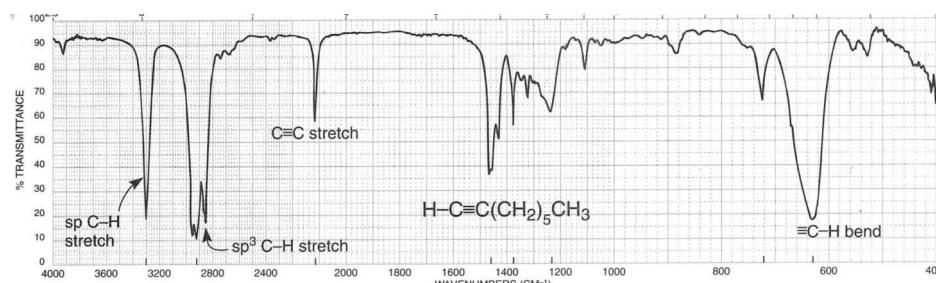
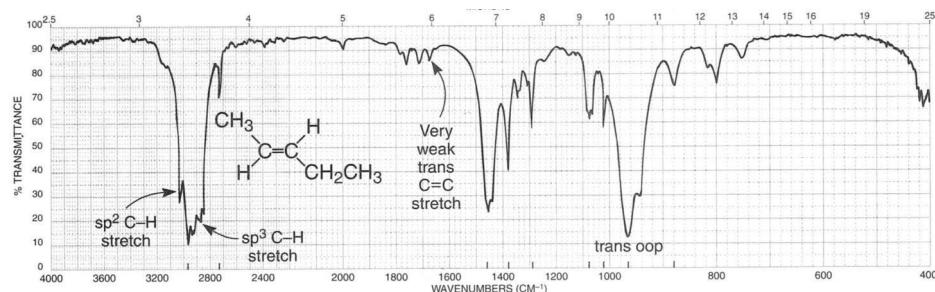
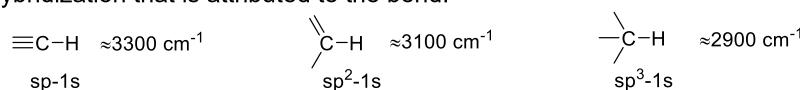
Example:



11.7

### 11.6 The X-H Region (4000-2500 cm⁻¹): N-H, O-H, and C-H bonds

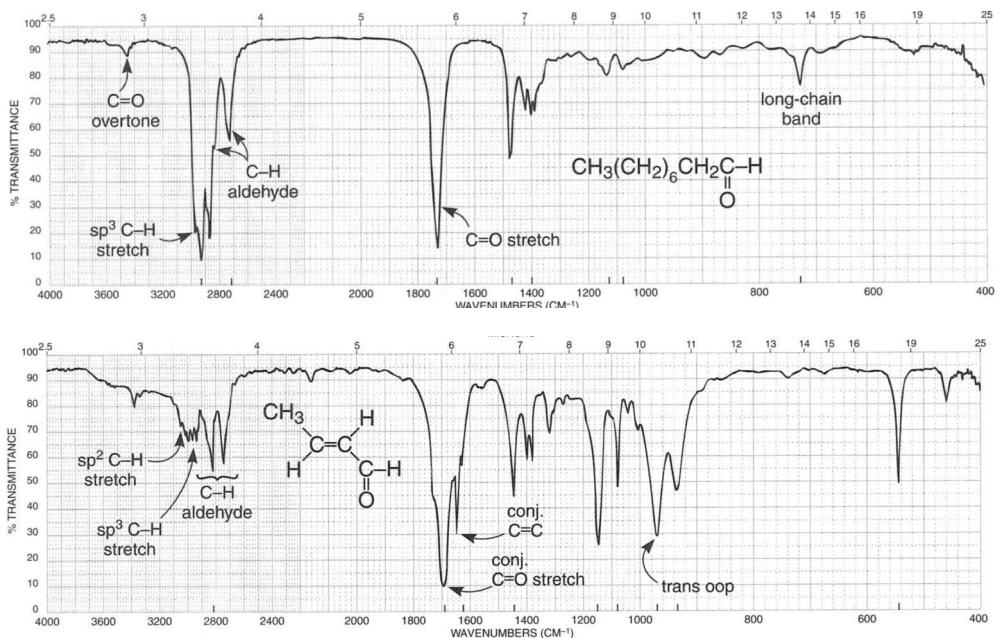
**C-H bonds:** C-H stretching frequencies can range from 3300 to 2750 cm⁻¹ and depend on hydrocarbons mostly on the hybridization that is attributed to the bond.



11.8

**(C–H bonds)**

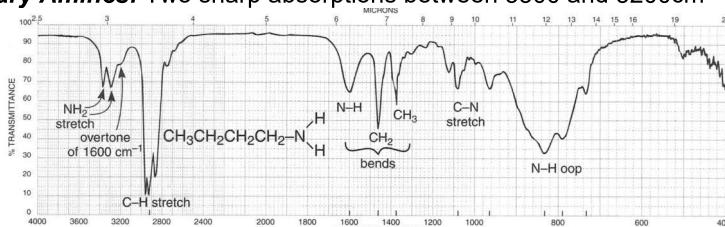
**Aldehydes** (see Chapter 16.14A) show two characteristic weak bands in the 2700–2775 cm<sup>-1</sup> and 2820–2900 cm<sup>-1</sup> regions which differentiates them from other carbonyl containing functional groups.



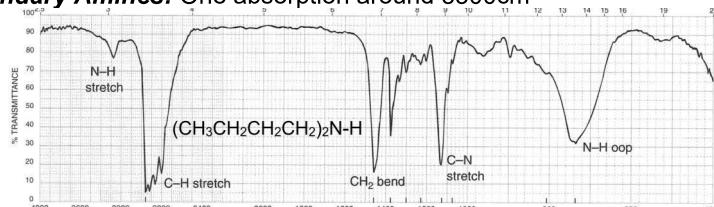
11.9

**N–H bonds:** Primary, secondary, and tertiary amines are easily distinguished from each other by IR spectroscopy (see Chapter 2 and Chapter 20.11B)

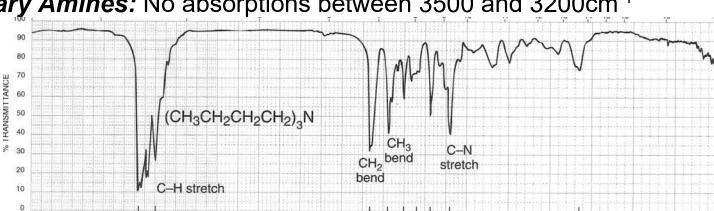
**Primary Amines:** Two sharp absorptions between 3500 and 3200 cm<sup>-1</sup>



**Secondary Amines:** One absorption around 3300 cm<sup>-1</sup>



**Tertiary Amines:** No absorptions between 3500 and 3200 cm<sup>-1</sup>

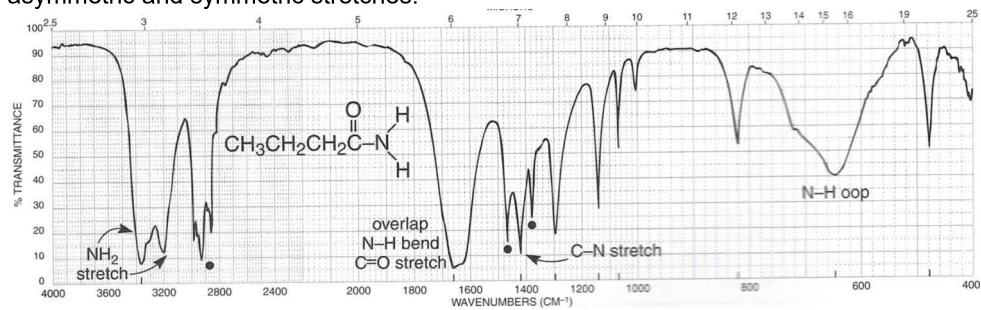


11.10

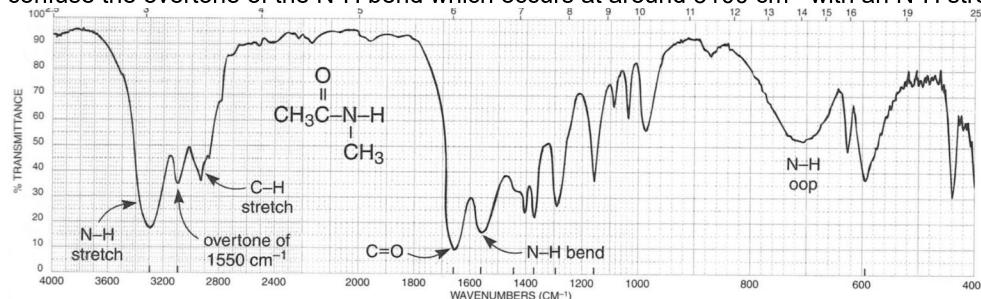
**(N-H bonds)**

N-H bonds are also present in other functional groups.

**Unsubstituted amides ( $\text{R}-\text{CO}-\text{NH}_2$ )** show two bands in the range of  $3500\text{-}3200 \text{ cm}^{-1}$  arising from the asymmetric and symmetric stretches.



Monosubstituted amides ( $\text{R}-\text{CO}-\text{NH}-\text{R}$ ) show as expected only one band in that region. Be careful not to confuse the overtone of the N-H bend which occurs at around  $3100 \text{ cm}^{-1}$  with an N-H stretch.



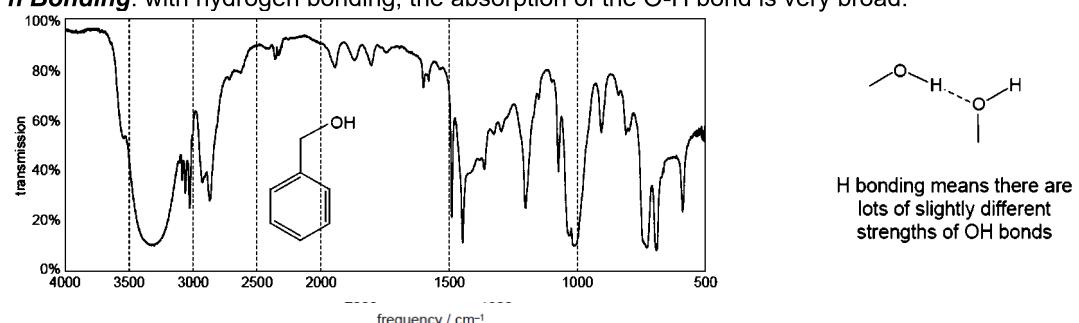
11.11

**O-H bonds**

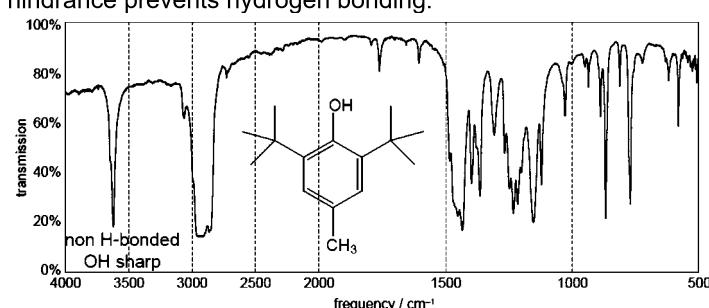
**Alcohols:** The shape of an O-H bond stretch in alcohols depends on whether hydrogen bonding is possible or not.

**O-H with Hydroge**

**n Bonding:** with hydrogen bonding, the absorption of the O-H bond is very broad.

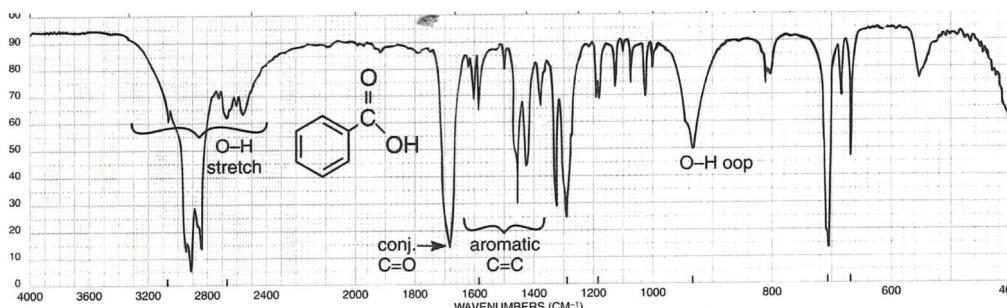
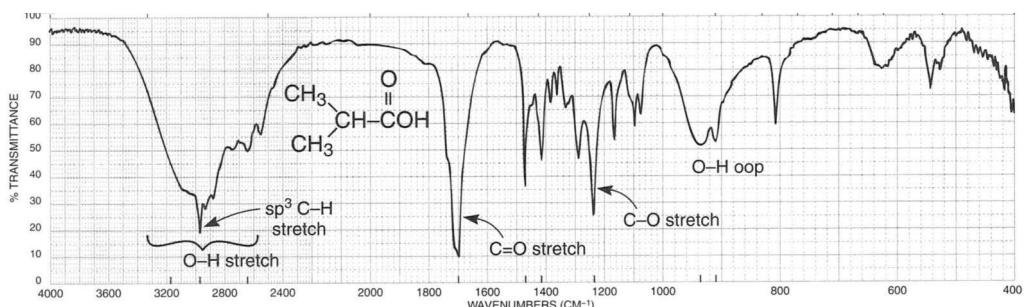


**O-H without Hydrogen Bonding:** Sharp O-H stretches are observed at  $3600 \text{ cm}^{-1}$  when steric hindrance prevents hydrogen bonding.



11.12

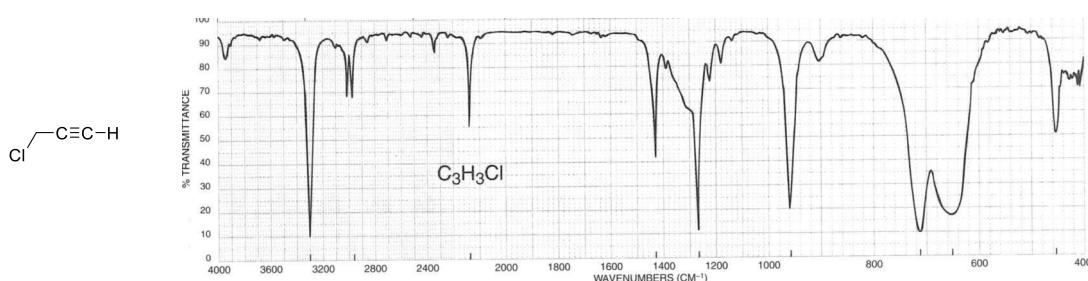
**O-H of Carboxylic Acids:** The V-shape of the O-H stretch in carboxylic acids allows us to distinguish alcohols from carboxylic acids. Carboxylic acid O-H stretches are very broad and can range from 3500-2500 cm<sup>-1</sup>. They can be easily missed if the C-H stretches are strong in comparison!



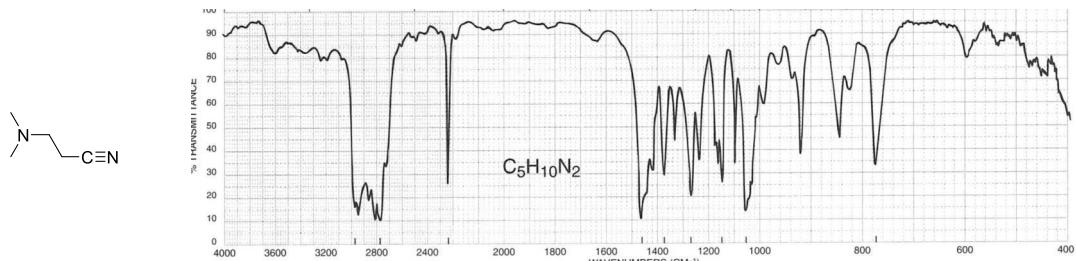
11.13

### 11.7 The Triple Bond Region (2000-2500 cm<sup>-1</sup>)

**Alkynes:** Terminal alkynes will show a clearly visible CC triple bond absorption around 2150 cm<sup>-1</sup>. Internal alkynes generally have a very weak triple absorption which may disappear into the baseline.



**Nitriles:** have a sharp absorption around 2250 cm<sup>-1</sup>. Conjugation with a double bond or an aromatic ring can lower the frequency of absorption.



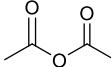
11.14

## 11.8 The Double Bond Region ( $2000\text{-}1500\text{ cm}^{-1}$ ): C=O, C=C, N=O, C=N

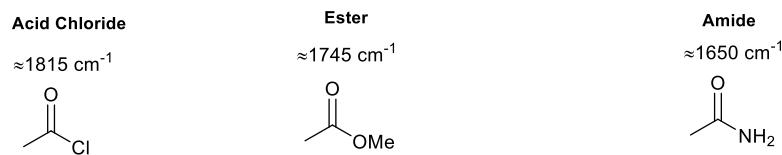
**C=O always has a strong absorption**

It is possible in most cases to identify the specific functional group based on the wavenumber observed.

Typical values for **unconjugated, unstrained carbonyl groups** are:

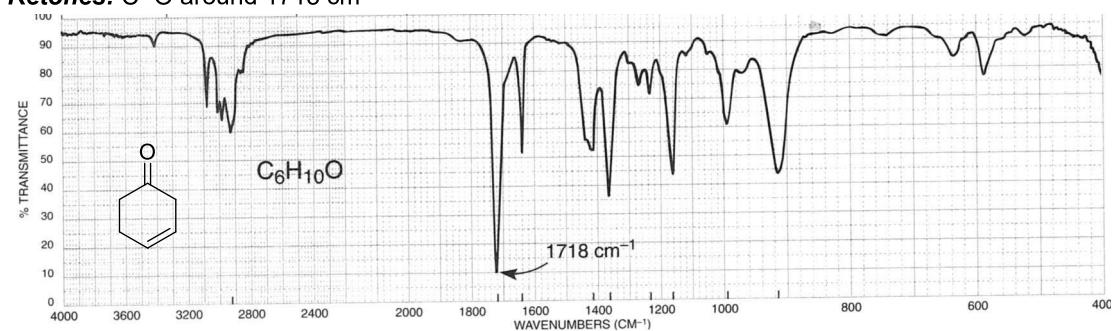
Acid Chloride	Acid Anhydride	Ester	Carboxylic Acid	Aldehyde	Ketone	Amide
						
$\approx 1815\text{ cm}^{-1}$	$\approx 1810\text{ cm}^{-1}$ (band 1) $\approx 1790\text{ cm}^{-1}$ (band 2)	$\approx 1745\text{ cm}^{-1}$	$\approx 1730\text{ cm}^{-1}$	$\approx 1730\text{ cm}^{-1}$	$\approx 1715\text{ cm}^{-1}$	$\approx 1650\text{ cm}^{-1}$

**The C=O IR frequency is a direct measure of the strength of the carbonyl bond.** Electron-withdrawing substituents strengthen the carbonyl bond, electron-donating substituents weaken the carbonyl bond due to resonance.

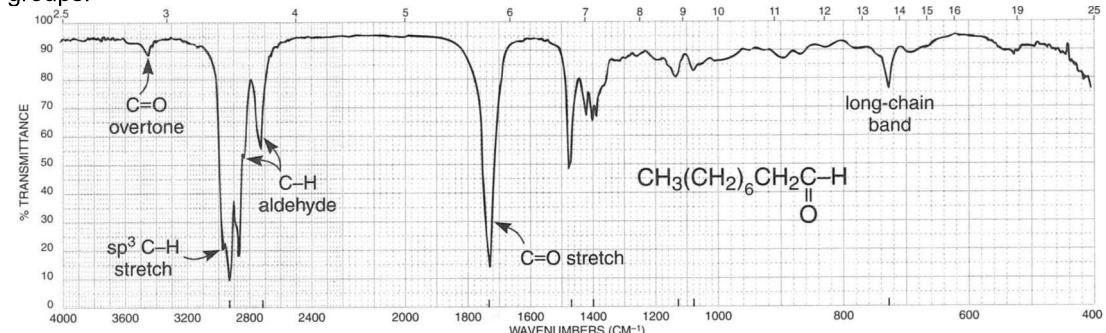


11.15

**Ketones: C=O around  $1715\text{ cm}^{-1}$**

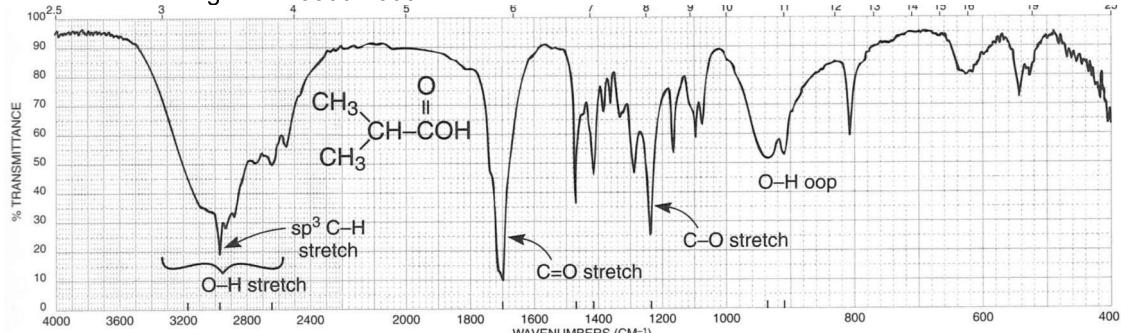


**Aldehydes: C=O around  $1730\text{ cm}^{-1}$ .** Aldehydes have two characteristic weak bands in the  $2700\text{-}2775\text{ cm}^{-1}$  and  $2820\text{-}2900\text{ cm}^{-1}$  regions which differentiates them from other carbonyl containing functional groups.

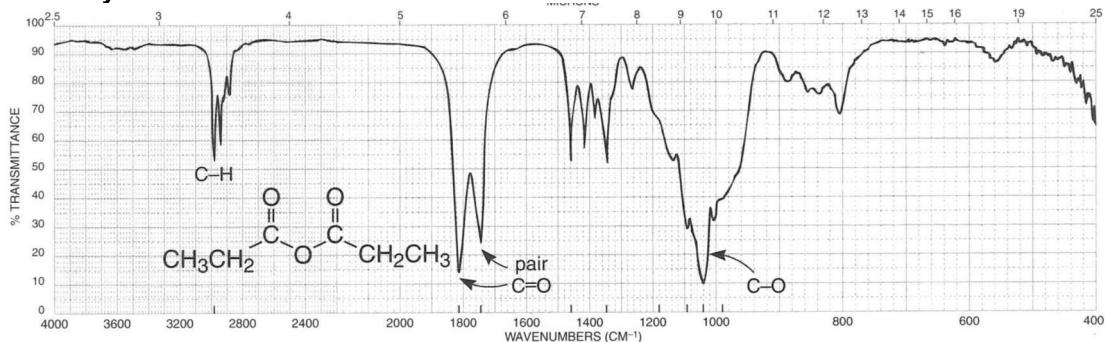


11.16

**Carboxylic Acids:** C=O around  $1730\text{ cm}^{-1}$  but can vary significantly depending on the method of recording the IR spectrum. Carboxylic acids have characteristic V-shaped O-H stretches that are very broad and can range from  $3500\text{-}2500\text{ cm}^{-1}$ .

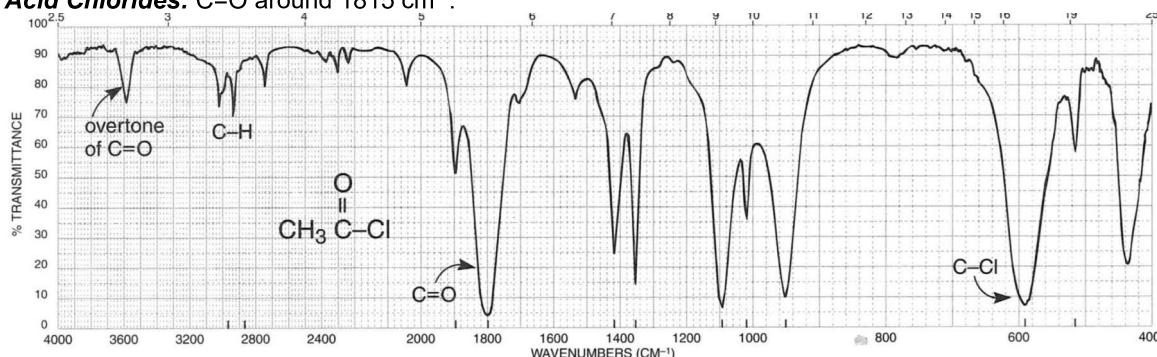


**Acid Anhydrides:** Two C=O bands around  $1810$  and  $1760\text{ cm}^{-1}$ .

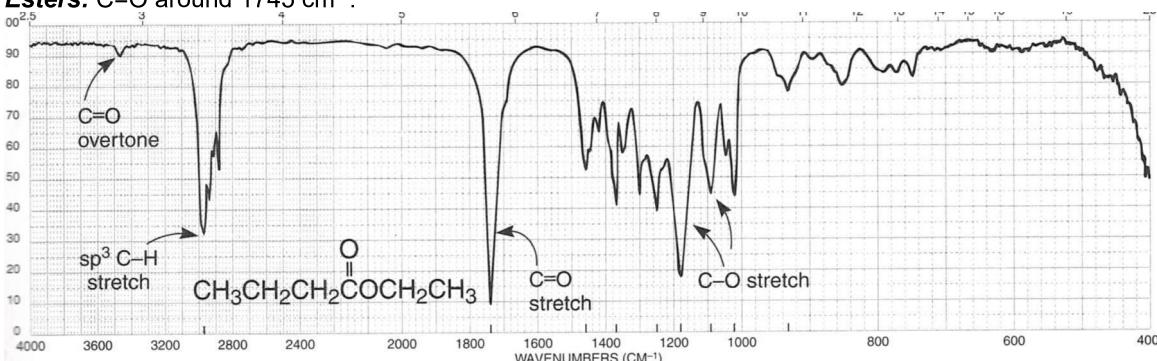


11.17

**Acid Chlorides:** C=O around  $1815\text{ cm}^{-1}$ .

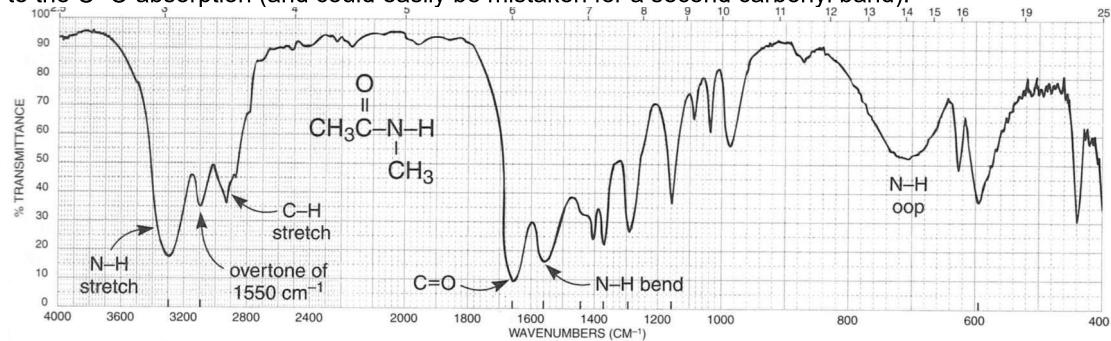


**Esters:** C=O around  $1745\text{ cm}^{-1}$ .



11.18

**Amides:** C=O around  $1650\text{ cm}^{-1}$ . The N–H bending frequency in primary and secondary amides is close to the C=O absorption (and could easily be mistaken for a second carbonyl band).



### Effects of conjugation and ring strain

- Conjugation (with  $\pi$  electrons or lone pairs) weakens the C=O bond and lowers its absorption frequency
- Ring strain strengthens the C=O bond and increases its absorption frequency

11.19

Conjugative effects can significantly lower the IR frequency of the carbonyl group.



Functional Group	Approximate Frequency Range (cm <sup>-1</sup> )	1840	1820	1800	1780	1760	1740	1720	1700	1680	1660	1640	1620	1600
Acid chloride	1815–1785 1800–1770 (conj.)					■	■							
Acid anhydride	1820–1750 1775–1720 (conj.)			■				■	■					(Two C=O absorptions)
Ester/lactone	1750–1735 1730–1715 (conj.)						■		■					Also C–O (1300–1000); no O–H absorption
Carboxylic acid	~1760 or 1720–1705 1710–1680 (conj.)						■	(monomer)	■	■				Also C–O (1315–1280) and O–H (~3300, broad)
Aldehyde	1740–1720 1710–1685 (conj.)								■	■				Also C–H (2830–2695)
Ketone	1720–1710 1685–1665 (conj.)								■					
Amide/lactam	1700–1620									■		■	(solid)	(solution)
Carboxylate salt	1650–1550													(Two C=O absorptions)

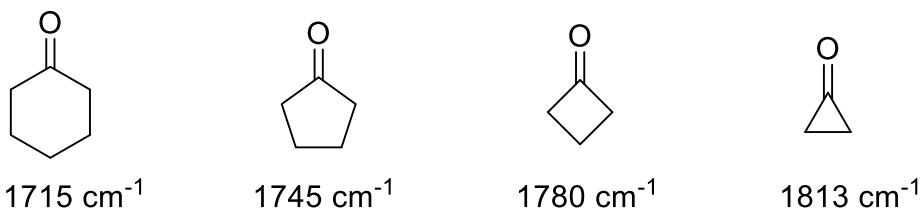
\*Orange bars represent absorption ranges for conjugated species.

**FIGURE 17.2** Approximate carbonyl IR absorption frequencies. (Frequency ranges based on Silverstein and Webster, reprinted with permission of John Wiley & Sons, Inc. from Silverstein, R. and Webster, F. X., *Spectrometric Identification of Organic Compounds*, Sixth Edition. Copyright 1998.)

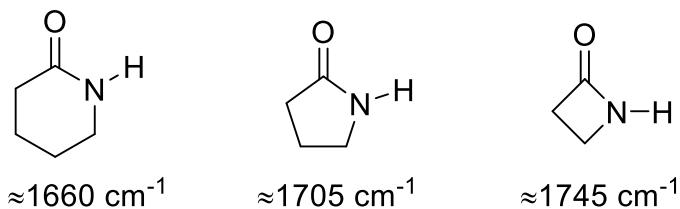
11.20

**Ring strain strengthens the C=O bond and increases its absorption frequency**

**Cyclic ketones**



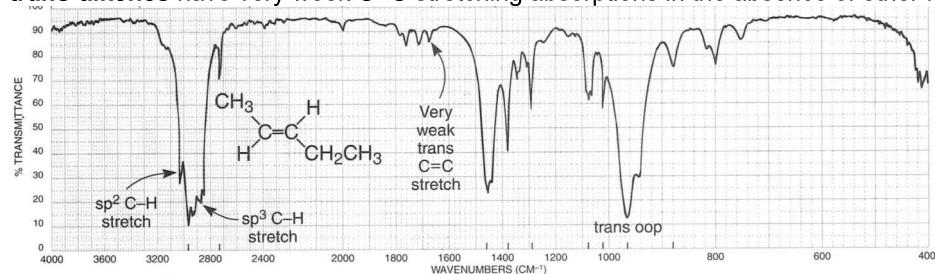
**Cyclic amides (lactams)**



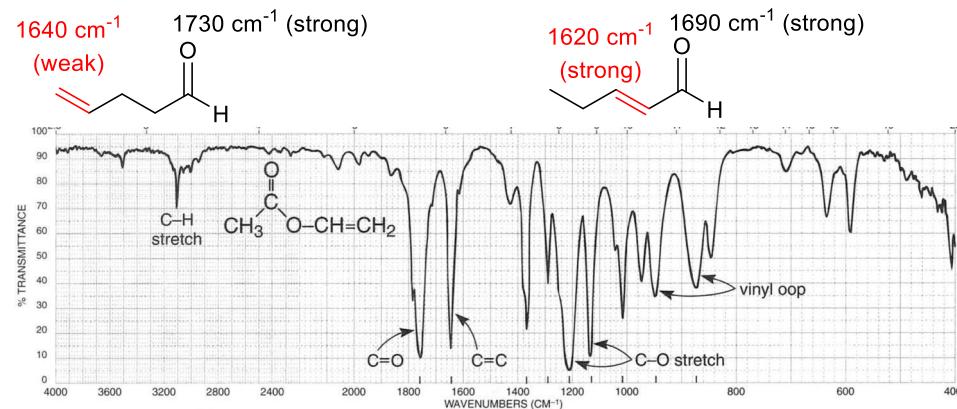
11.21

**C=C bonds: are generally weak unless in conjugation with a polar group**

**trans-alkenes** have very weak C=C stretching absorptions in the absence of other functional groups

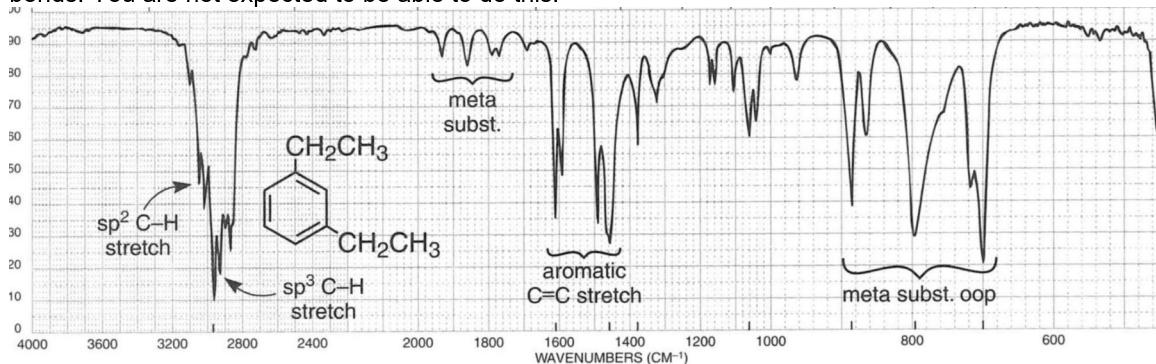


**C=C bonds conjugated with π bonds or lone pairs show strong absorptions (at lower IR frequencies)**



11.22

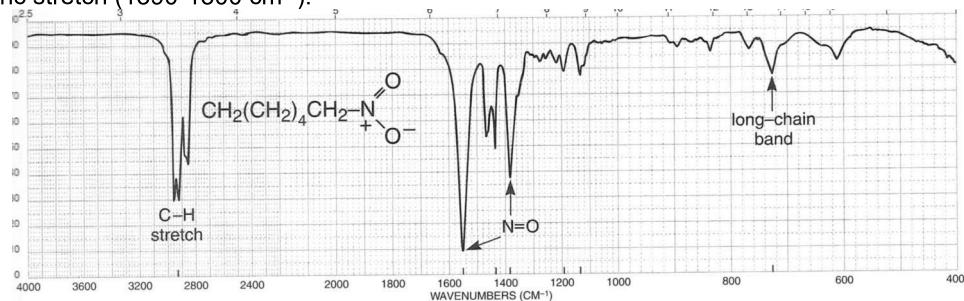
**Aromatic CC bonds** typically show stretching frequencies between 1600 and 1400 cm<sup>-1</sup>. Experts are able to distinguish ortho, meta, and para substitution patterns based on the IR frequencies of the CC bonds. You are not expected to be able to do this.



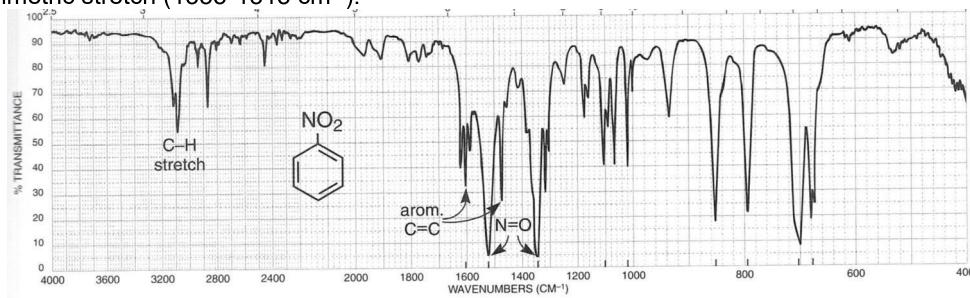
11.23

### N=O bonds

**Aliphatic nitro compounds** show a strong asymmetric stretch (1600-1530 cm<sup>-1</sup>) and a medium symmetric stretch (1390-1300 cm<sup>-1</sup>).



**Aromatic nitro compounds** show two strong IR absorptions: asymmetric stretch (1550-1490 cm<sup>-1</sup>) and symmetric stretch (1355-1315 cm<sup>-1</sup>).



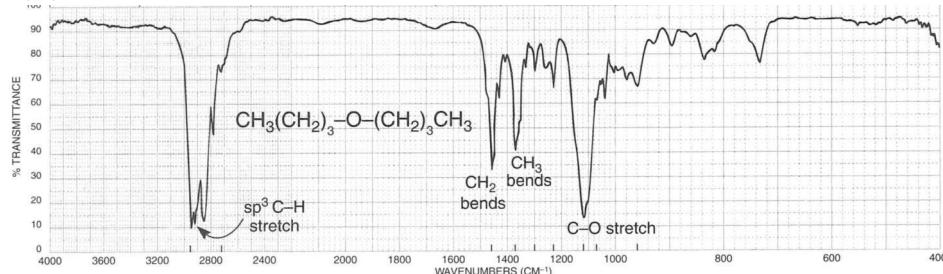
11.24

### 11.9 The Fingerprint Region (< 1500 cm<sup>-1</sup>)

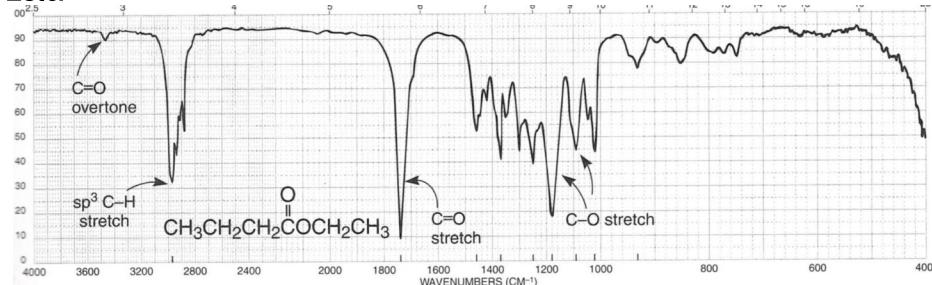
With exception of the C-O single bond, absorptions in the fingerprint region are not used for primary identification of functional groups.

**The C-O single bond** shows strong absorptions in the region between 1260-1000 cm<sup>-1</sup> and indicates the presence of one of the following groups: **Ether, alcohol, ester, or carboxylic acid.**

#### Example Ether



#### Example Ester



11.25

### 11.10 Tables and Useful Tools for solving IR problems

#### Characteristic IR Absorptions

##### CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES

Bond	Compound Type	Frequency range, cm <sup>-1</sup>
C(sp <sup>3</sup> )-H	<b>Alkanes</b>	2960-2850 (strong)
C(sp <sup>2</sup> )-H	<b>Alkenes, Aromatic Rings,</b>	3100-3000 (medium)
C(sp)-H	<b>Alkynes</b>	3333-3267 (strong)
C(sp <sup>2</sup> )-H	<b>Aldehydes</b>	2850 and 2750 (weak)
C=C	<b>Alkenes</b>	1680-1640 (medium, weak)
C≡C	<b>Alkynes</b>	2260-2100 (weak, sharp)
C=C	<b>Aromatic Rings</b>	1600 and 1500 (weak)
C-O	<b>Alcohols, Ethers, Carboxylic acids, Esters</b>	1260-1000 (strong)
C=O	<b>Aldehydes, Ketones, Carboxylic acids, Esters</b>	1760-1670 (strong)
O-H	<b>Alcohols, Phenols</b>	3600-3200 (broad, U-shaped)
	<b>Carboxylic acids</b>	3300-2500 (very broad, V-shaped)
N-H	<b>Amines</b>	3500-3300 (medium)
C≡N	<b>Nitriles</b>	2260-2220 (varies)

11.26

**Suggested strategy for IR spectrum interpretation**

1. Look first at the high-frequency end of the spectrum ( $> 1500 \text{ cm}^{-1}$ ) and concentrate initially on the major bands.
2. For each band, short list the possibilities by using a correlation chart.
3. Use the lower-frequency end of the spectrum for the confirmation or elaboration of possible structural elements.
4. Do not expect to be able to assign every band in the spectrum.
5. Keep cross-checking wherever possible. For example, an aldehyde should absorb near  $1730 \text{ cm}^{-1}$  and also in the region  $2900\text{-}2700 \text{ cm}^{-1}$ .
6. Exploit negative evidence as well as positive evidence. For example, if there is no band in the  $1850\text{-}1600 \text{ cm}^{-1}$  region, it is most unlikely that a carbonyl group is present.
7. Band intensities should be treated with some caution. Under some circumstances they may vary considerably for the same group.