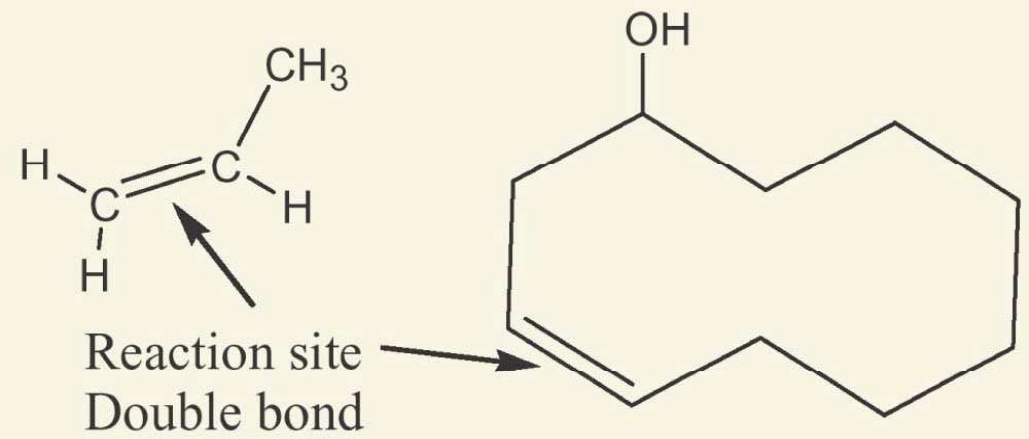
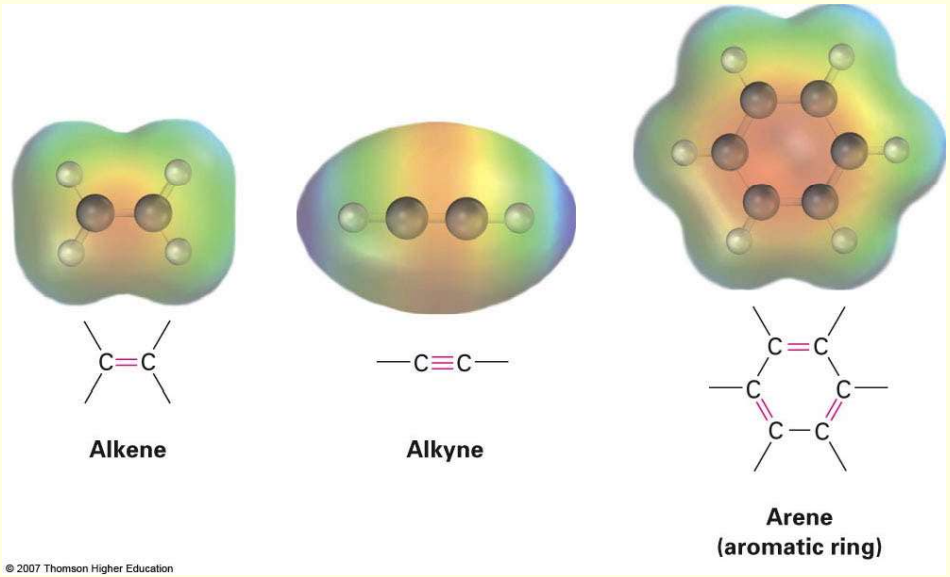
Functional Groups

- **Functional group** - collection of atoms at a site within a molecule with a common bonding pattern
- The group reacts in a typical way, generally independent of the rest of the molecule
- For example, the double bonds in simple and complex alkenes react with bromine in the same way (See Figure 3.1)



Types of Functional Groups: Multiple Carbon–Carbon Bonds

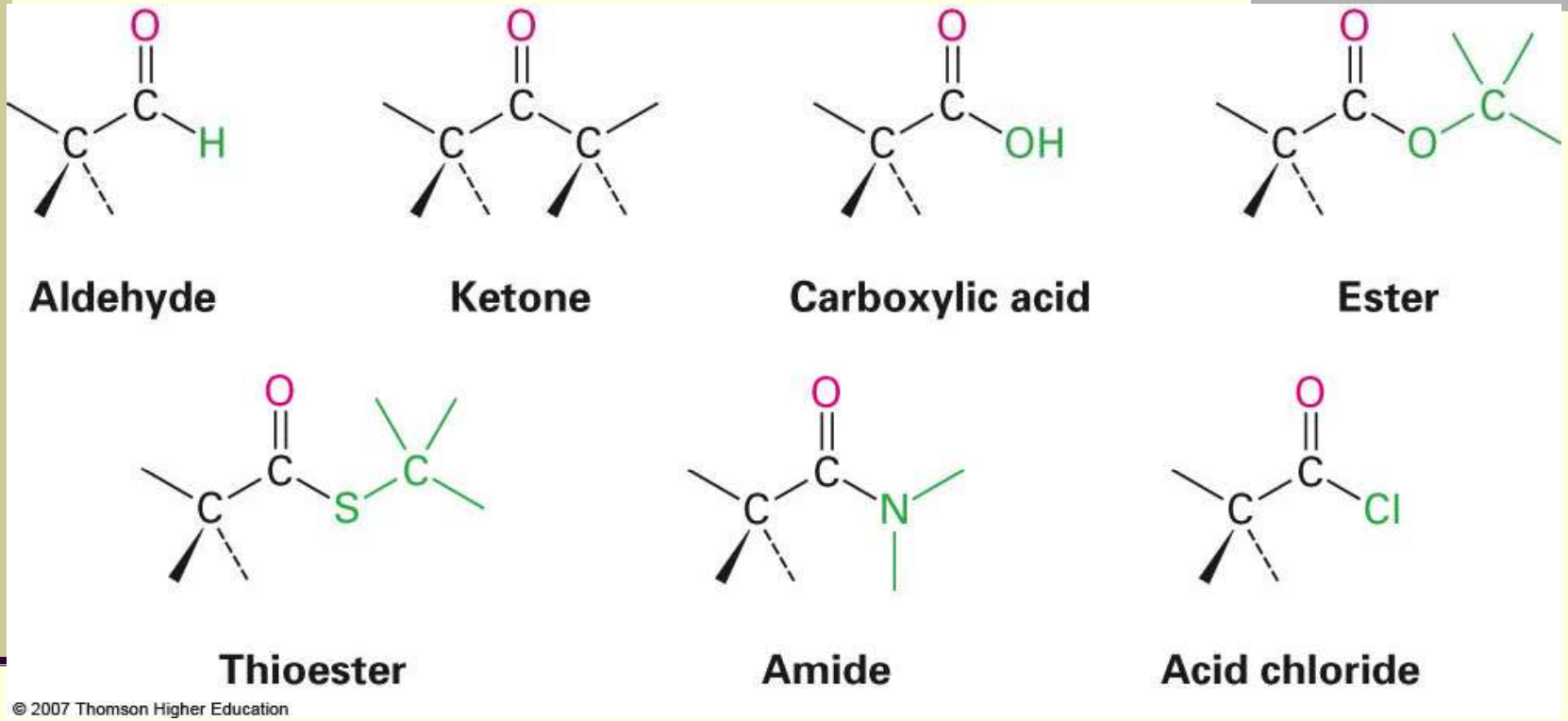
- *Alkanes* have only C-C and C-H single bonds
- *Alkenes* have a C-C double bond
- *Alkynes* have a C-C triple bond
- *Arenes* have special bonds that are represented as alternating single and double C-C bonds in a six-membered ring



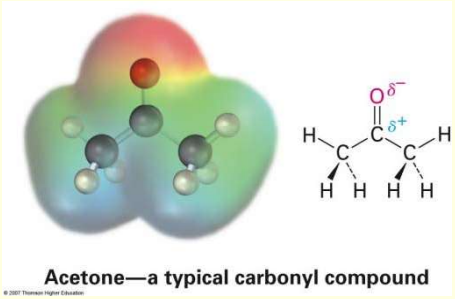
Functional Groups with Carbon Singly Bonded to an Electronegative Atom

- *Alkyl halide:* C bonded to halogen (C-X)
- *Alcohol: C* bonded O of a hydroxyl group (C–OH)
- *Ether:* Two C's bonded to the same O (C–O–C)
- *Amine:* C bonded to N (C–N)
- *Thiol:* C bonded to SH group (C–SH)
- S*ulfide:* Two C's bonded to same S (C–S–C)
- Bonds are polar, with partial positive charge on C (δ+) and partial negative charge (δ–) on electronegative atom

Groups with a Carbon–Oxygen Double Bond (Carbonyl Groups)



Bonds are polar, with partial positive charge on C (δ+) and partial negative charge on O (δ–)



Acetone—a typical carbonyl compound

Table 3.1 Structures of Some Common Functional Groups

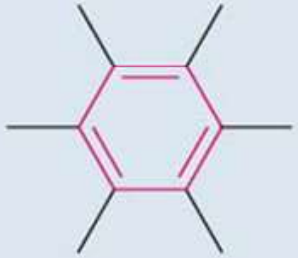
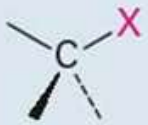
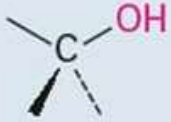
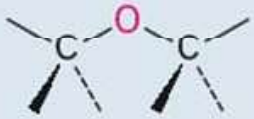
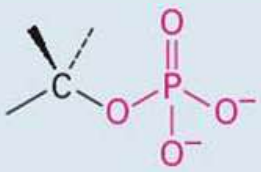
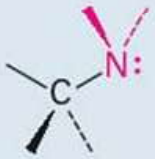
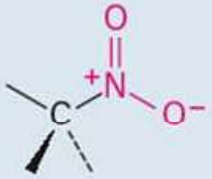
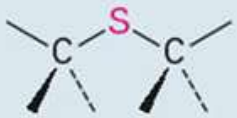
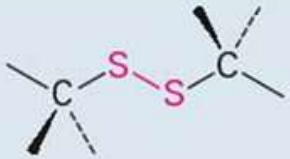
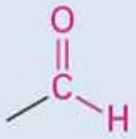
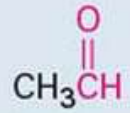
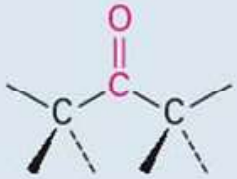
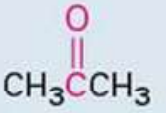
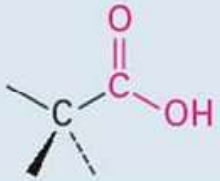
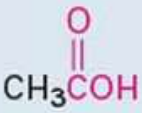
	Name	Structure*	Name ending	Example
**	Alkene (double bond)		*-ene*	$H_2C{=}CH_2$ Ethene
**	Alkyne (triple bond)		*-yne*	$HC{\equiv}CH$ Ethyne
**	Arene (aromatic ring)		None	 Benzene
**	Halide	 (X = F, Cl, Br, I)	None	CH_3Cl Chloromethane
**	Alcohol		*-ol*	CH_3OH Methanol
**	Ether		*ether*	CH_3OCH_3 Dimethyl ether

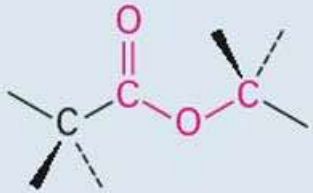
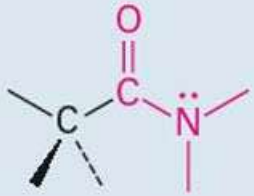
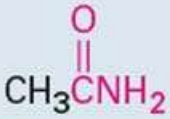
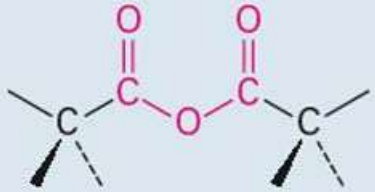
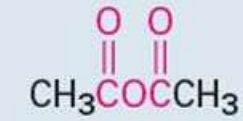
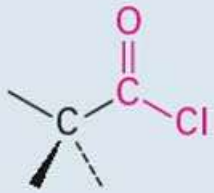
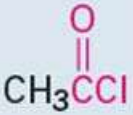
Table 3.1 | Structures of Some Common Functional Groups *(continued)*

	Name	Structure*	Name ending	Example
	Monophosphate		*phosphate*	$CH_3OPO_3^{2-}$ Methyl phosphate
**	Amine		*-amine*	CH_3NH_2 Methylamine
	Imine (Schiff base)		None	CH_3CCH_3 (=NH) Acetone imine
	Nitrile	$-C\equiv N$	*-nitrile*	$CH_3C\equiv N$ Ethanenitrile
	Nitro		None	CH_3NO_2 Nitromethane
**	Thiol		*-thiol*	CH_3SH Methanethiol

*The bonds whose connections aren't specified are assumed to be attached to carbon or hydrogen atoms in the rest of the molecule.

Table 3.1 Structures of Some Common Functional Groups *(continued)*

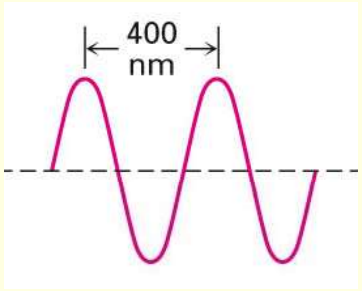
	Name	Structure*	Name ending	Example
**	Sulfide		*sulfide*	CH_3SCH_3 Dimethyl sulfide
	Disulfide		*disulfide*	CH_3SSCH_3 Dimethyl disulfide
	Carbonyl			
**	Aldehyde		*-al*	 Ethanal
**	Ketone		*-one*	 Propanone
**	Carboxylic acid		*-oic acid*	 Ethanoic acid

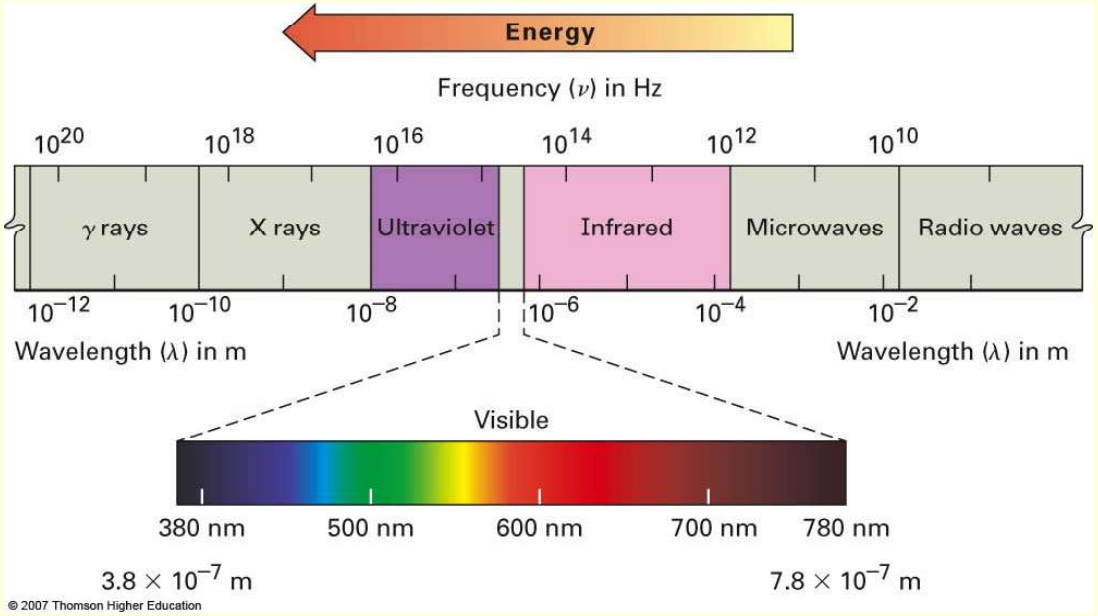
**	Ester		*-oate*	 Methyl ethanoate
**	Amide		*-amide*	 Ethanamide
	Carboxylic acid anhydride		*-oic anhydride*	 Ethanoic anhydride
**	Carboxylic acid chloride		*-oyl chloride*	 Ethanoyl chloride

*The bonds whose connections aren't specified are assumed to be attached to carbon or hydrogen atoms in the rest of the molecule.

Organic Structure Determination

- Spectroscopy = interaction of compounds with light (a form of energy)
- E = hν = hc/λ [ν = frequency, λ = wavelength]
- IR Spectroscopy = used to identify functional groups within a compound



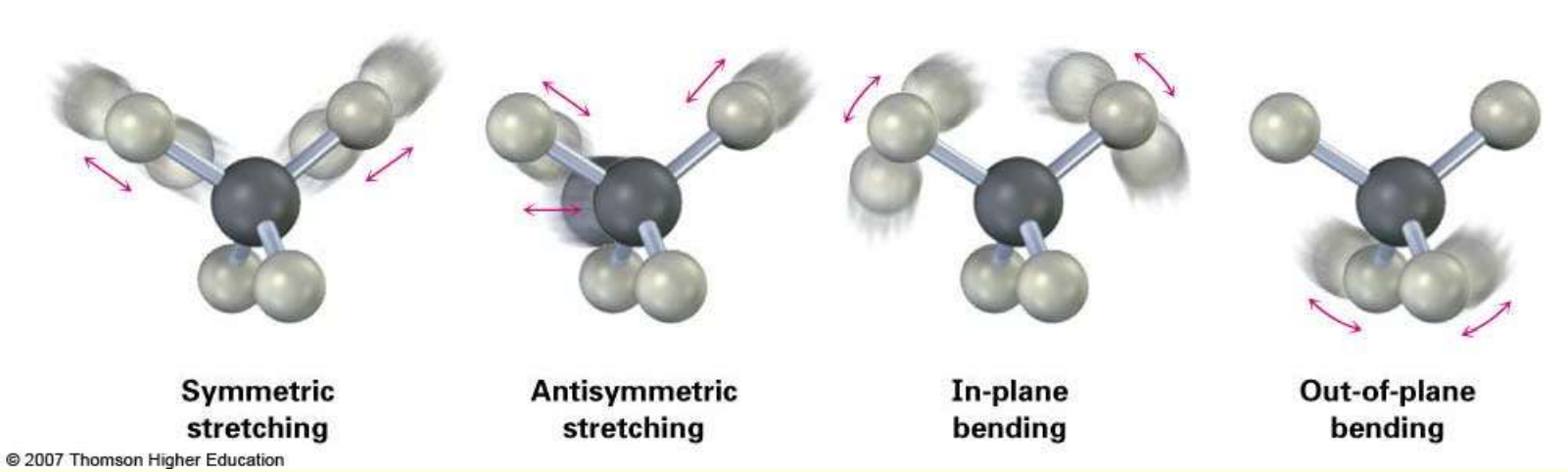


Absorption Spectroscopy

- Organic compound exposed to electromagnetic radiation, can absorb energy of only certain wavelengths (unit of energy)
  - Transmits energy of other wavelengths.
- Changing wavelengths to determine which are absorbed and which are transmitted produces an **absorption spectrum**
- Energy absorbed is distributed internally in a distinct and reproducible way

Infrared (IR) Absorption

- IR energy absorption corresponds to specific vibrational and rotational modes, such as bending and stretching of bonds
- Energy is characteristic of the atoms in the functional group and their bonding



Infrared (IR) Spectroscopy

- IR energy in a spectrum is usually measured as wavenumber (cm^{-1}), the inverse of wavelength and is proportional to frequency and energy
- Specific IR absorbed by organic molecule related to its bonding structure, principally its functional groups
- Wavenumber $\bar{\nu} = 1 / \lambda$ (cm)

- $\bar{\nu} = K \sqrt{\dfrac{f (m_1 + m_2)}{(m_1 m_2)}}$

stronger bonds = higher $\bar{\nu}$
heavier atoms = lower $\bar{\nu}$

Csp^3 - H
vs
Csp^3 - Csp^3

Csp^3 - H
vs
Csp^2 - H

Interpreting IR Spectra

- Most functional groups absorb at about the same energy and intensity independent of the molecule they are in
- Characteristic higher energy IR absorptions in Table 12.1 can be used to confirm the existence of the presence of a functional group in a molecule
- IR spectrum has lower energy region characteristic of molecule as a whole ("fingerprint" region below 1500 cm^{-1})
- Look for "key" absorptions for functional groups, you cannot assign all of the peaks (especially fingerprint region that is unique to a compound)
- Can only tell you what functional groups are in a compound (and what functional groups are not in compound). Cannot tell you how many or what exact structure is.

Regions of the IR Absorption Spectrum

- 4000-2500 cm^{-1} N-H, C-H, O-H (stretching)
  - 3300-3600 N-H, O-H
  - 3000 C-H
- 2500-2000 cm^{-1} C≡C and C≡N (stretching)
- 2000-1500 cm^{-1} double bonds (stretching)
  - C=O 1680-1750
  - C=C 1640-1680 cm^{-1}
- Below 1500 cm^{-1} "fingerprint" region

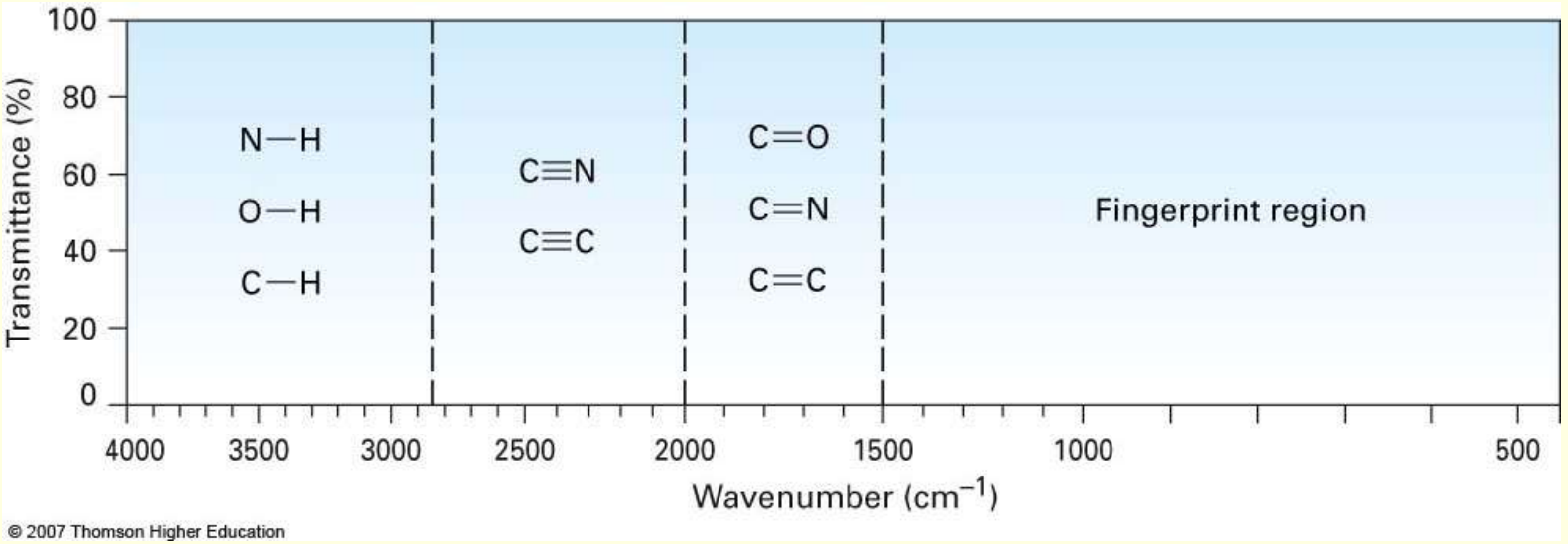


Table 12.1 Characteristic IR Absorptions of Some Functional Groups

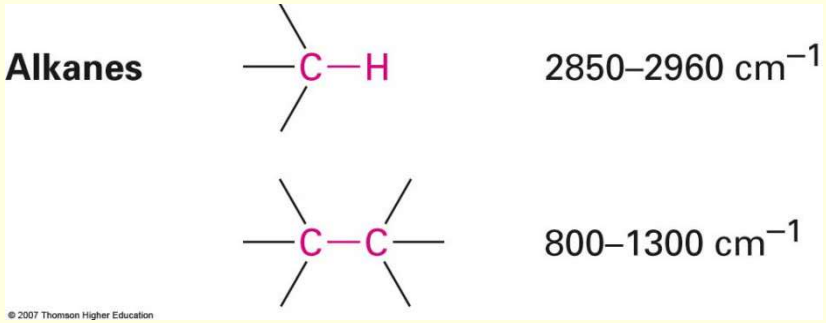
Functional Group	Absorption (cm^{-1})	Intensity
Alkane		
** C–H	2850–2960	Medium
Alkene		
** =C–H	3020–3100	Medium
** C=C	1640–1680	Medium
Alkyne		
** ≡C–H	3300	Strong
** C≡C	2100–2260	Medium
Alkyl halide		
C–Cl	600–800	Strong
C–Br	500–600	Strong
Alcohol		
** O–H	3400–3650	Strong, broad
** C–O	1050–1150	Strong
Arene		
** C–H	3030	Weak
**Aromatic ring	1660–2000	Weak
	1450–1600	Medium

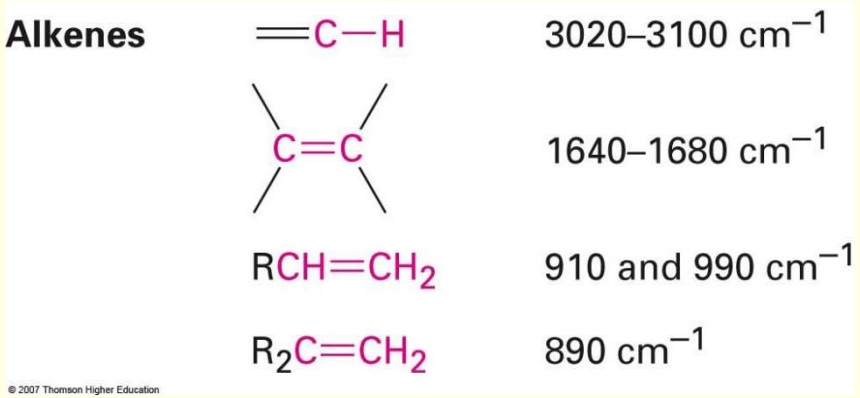
Functional Group	Absorption (cm^{-1})	Intensity
Amine		
** N–H	3300–3500	Medium
** C–N	1030–1230	Medium
Carbonyl compound		
** C=O	1670–1780	Strong
Carboxylic acid		
** O–H	2500–3100	Strong, broad
Nitrile		
** C≡N	2210–2260	Medium
Nitro		
NO_2	1540	Strong
	(two bands 1600 and 1500)	

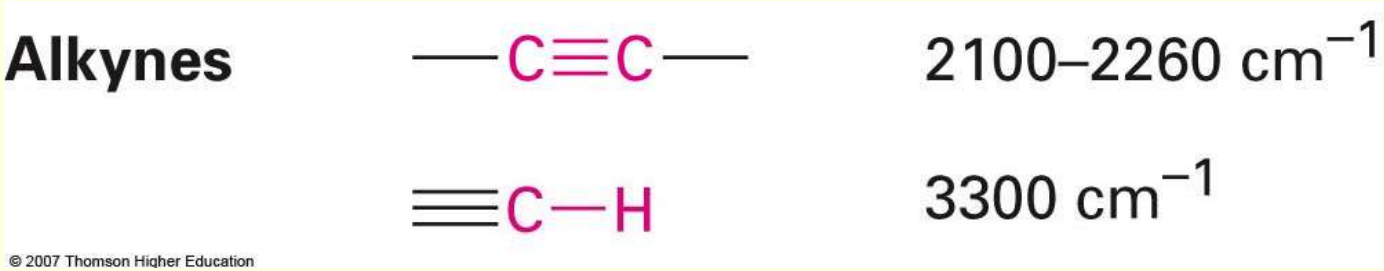
all values listed are for bond stretching

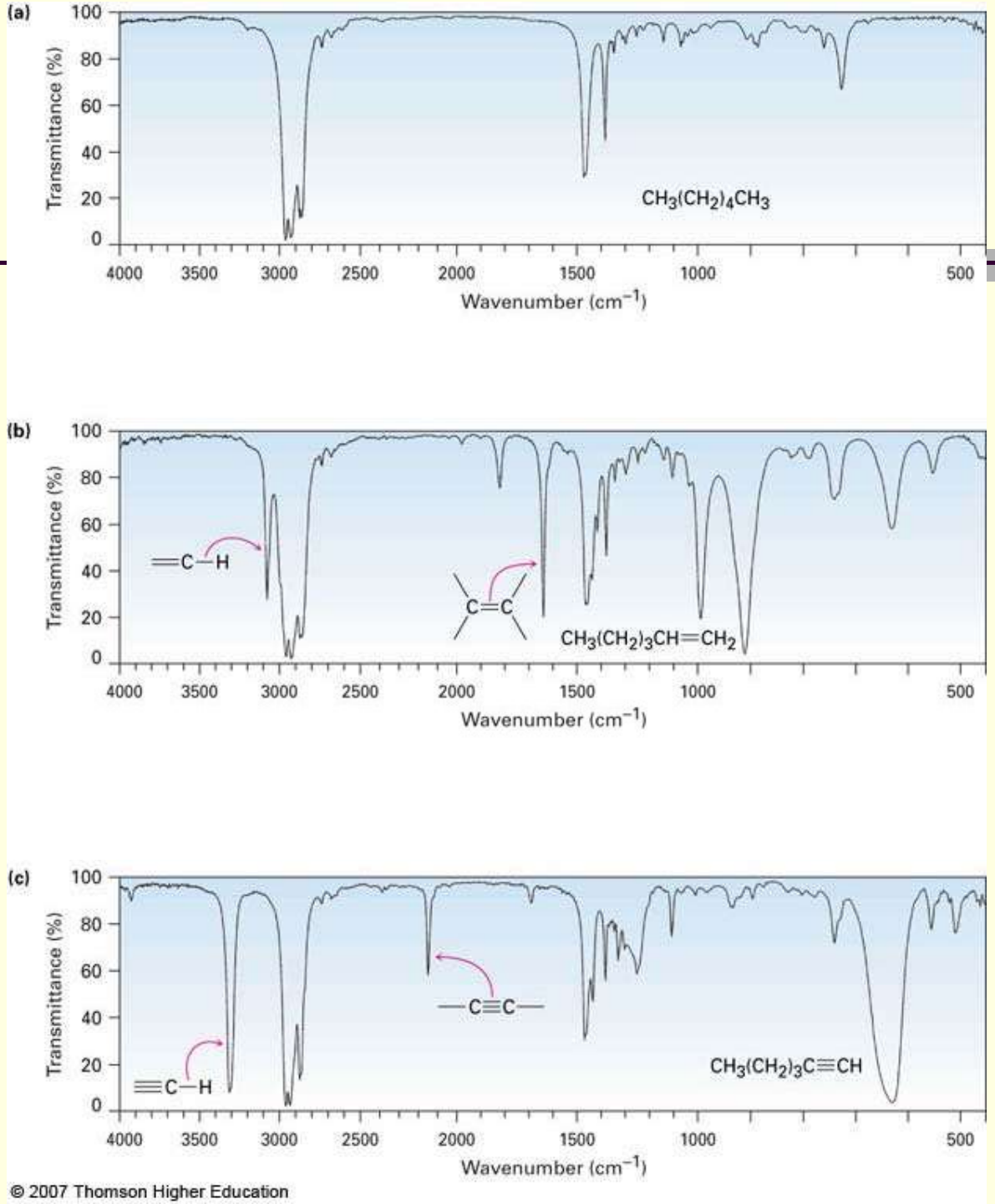
IR of Hydrocarbons

- **Alkanes, Alkenes, Alkynes**
- C-H, C-C, C=C, C≡C have characteristic peaks based on bond strengths
  - absence helps rule out C=C or C≡C



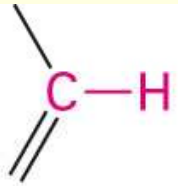






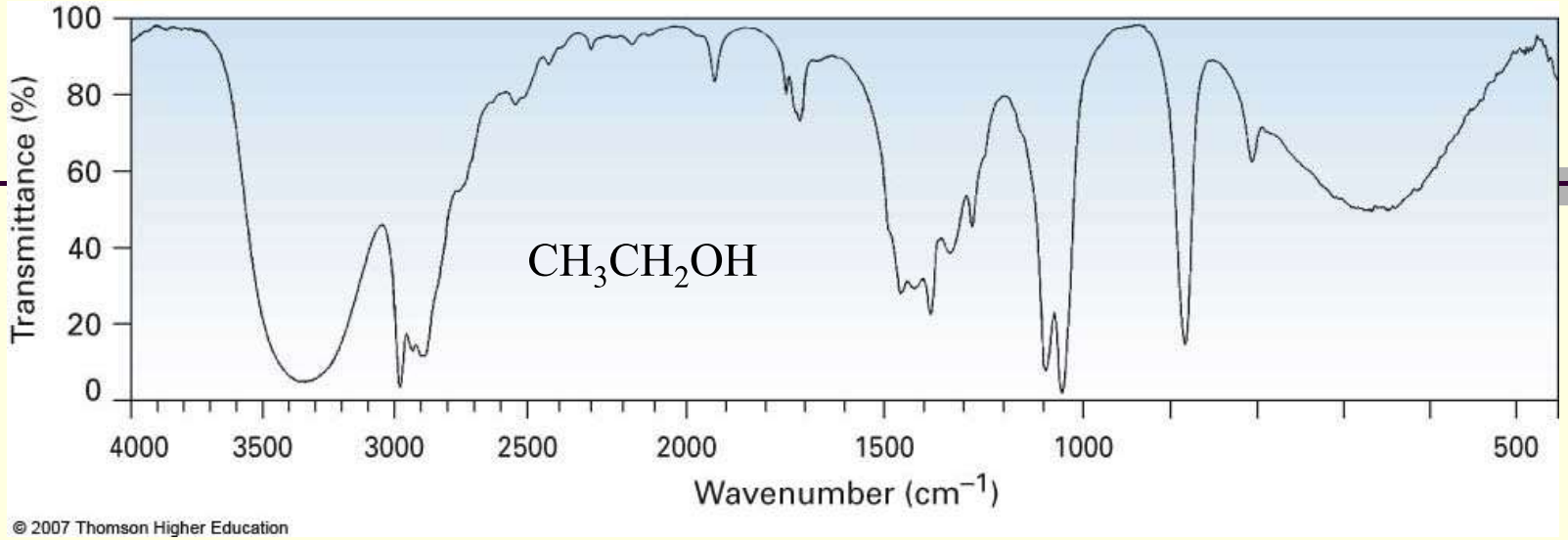
IR of Aromatics

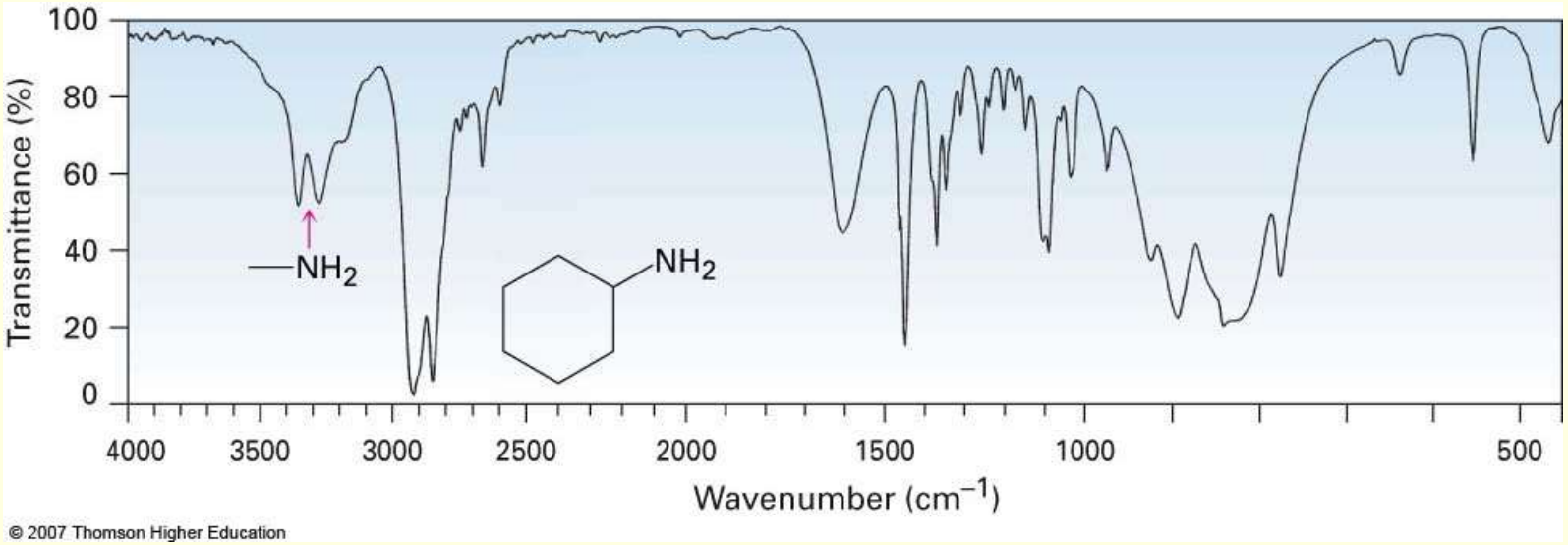
- Weak C–H stretch at 3030 cm^{-1}
- Weak absorptions 1660 - 2000 cm^{-1} range
- Medium-intensity absorptions 1450 to 1600 cm^{-1}

Aromatic compounds		3030 cm^{-1} (weak)
		1660–2000 cm^{-1} (weak) 1450–1600 cm^{-1} (medium)

IR of Alcohols and Amines

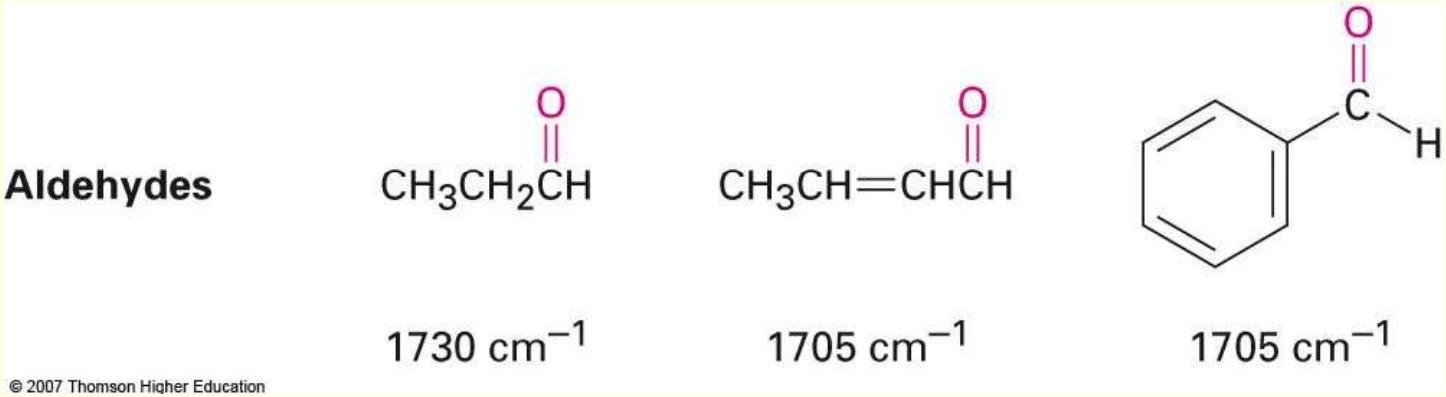
- O–H 3400 to 3650 cm^{-1}
  - Usually broad and intense
- N–H 3300 to 3500 cm^{-1}
  - Sharper and less intense than an O–H

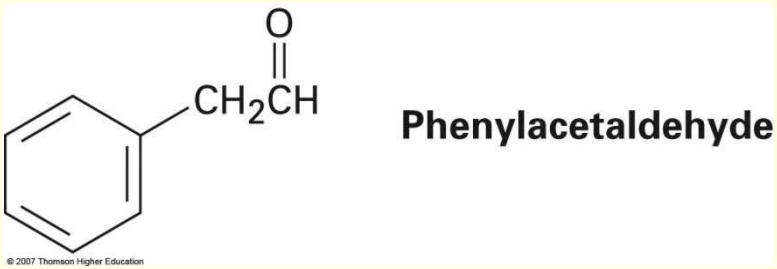




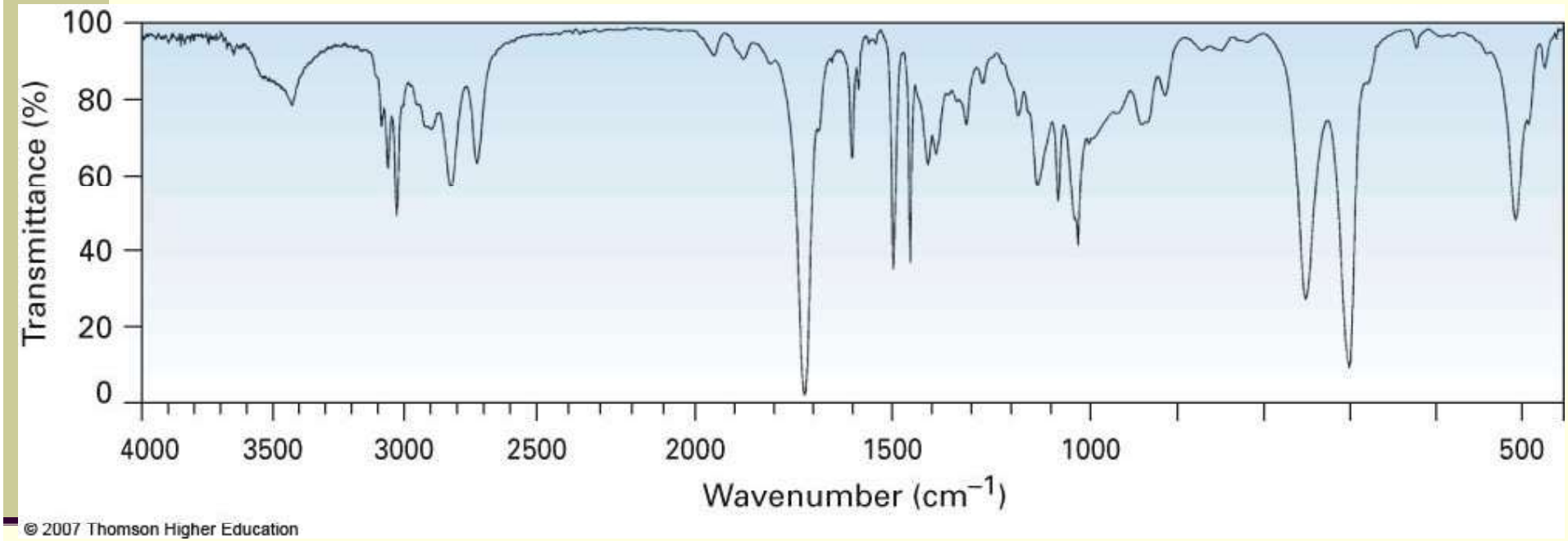
IR of Carbonyl Compounds: Aldehydes

- Strong, sharp C=O peak 1670 to 1780 cm^{-1}
- Exact absorption characteristic of type of carbonyl compound (ald, ket, ester, acid, amide, etc)
  - 1730 cm^{-1} in saturated aldehydes
  - 1705 cm^{-1} in aldehydes next to double bond or aromatic ring





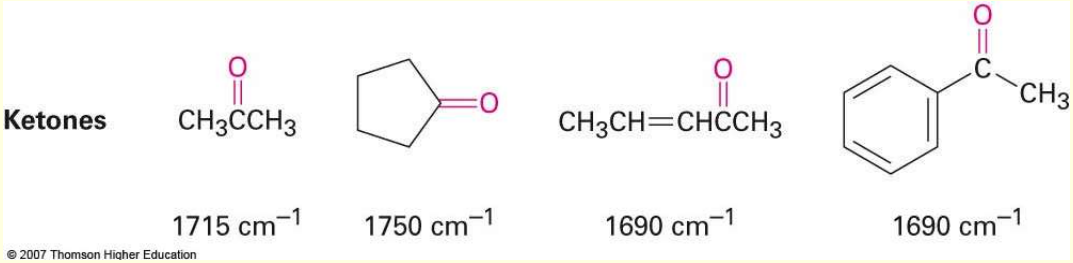
Phenylacetaldehyde



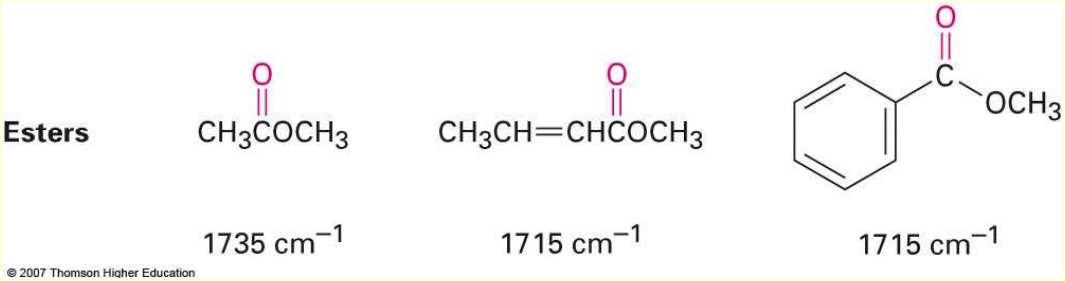
note Aldehyde C-H stretches at 2800-2700 cm^{-1}

IR of Ketones and Esters

- 1715 cm–1 in six-membered ring and acyclic ketones
- 1750 cm–1 in 5-membered ring ketones
- 1690 cm–1 in ketones next to a double bond or an aromatic ring



- 1735 cm–1 in saturated esters
- 1715 cm–1 in esters next to aromatic ring or a double bond



IR of Acids, Amides, Anhydrides, and Acyl Halides

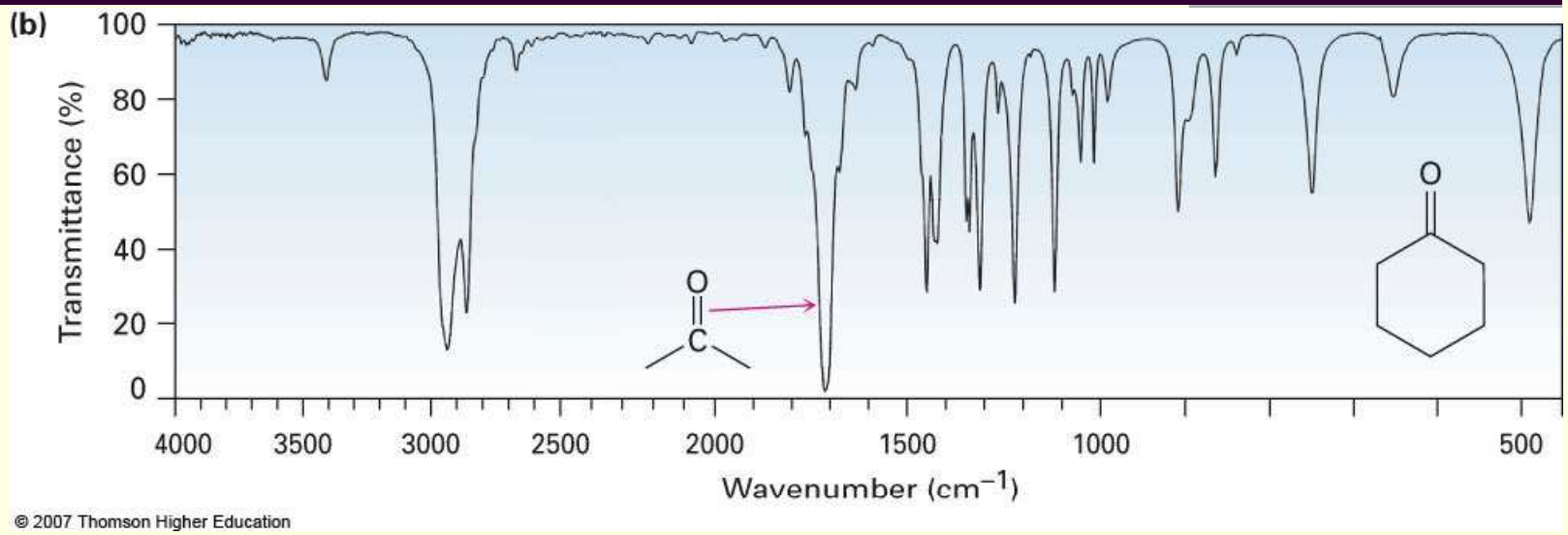
- Carboxylic Acids:
- O-H 2500-3300 cm-1 (very broad, strong)
- C=O 1710-1760 cm–1 (dimers lower, monomers higher $\overline{\nu}$)

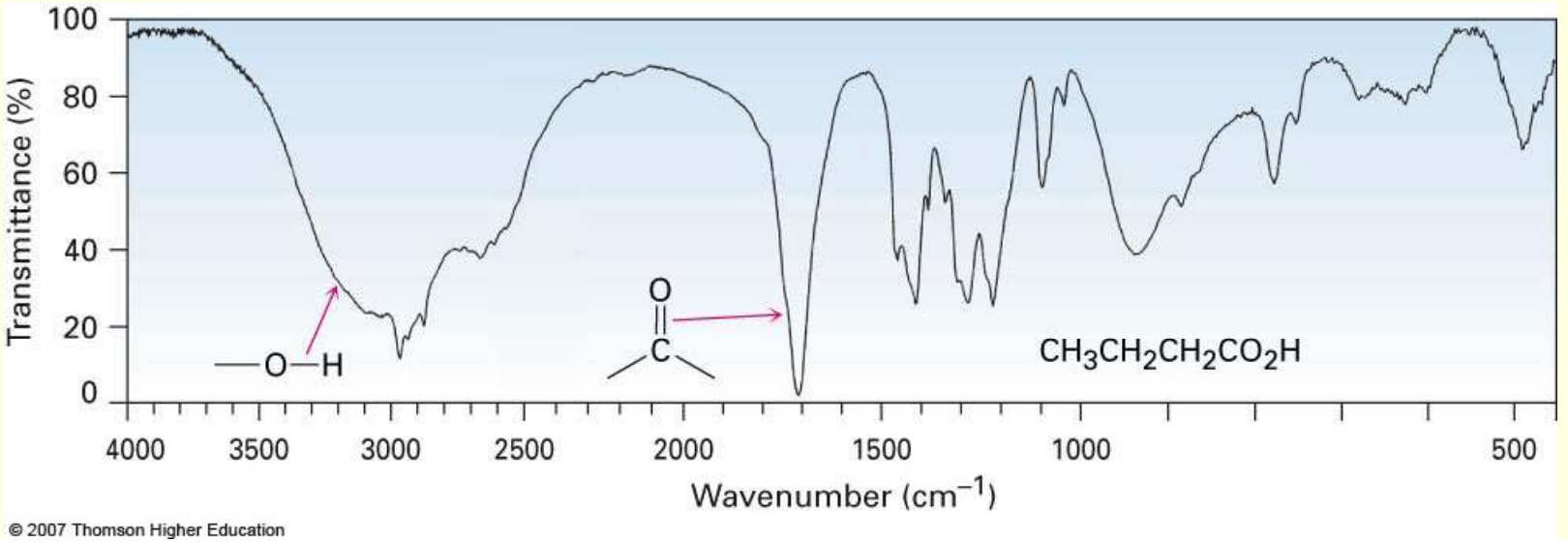
- Amides:
- N-H 3300-3500 cm-1 (sharp, medium, varies with # of H's)
- C=O 1690 cm–1 in saturated amides

- Anhydrides:
- C=O 1820 and 1760 cm-1 (two absorptions)

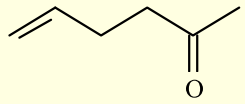
- Acyl Halides:
- C=O 1800cm-1

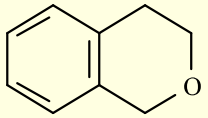
IR of Ketones and Acids

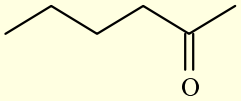


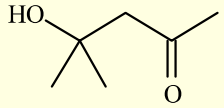


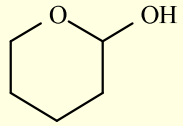
Match a structure from the list below to the IR spectrum

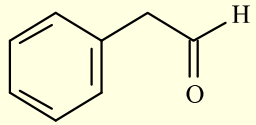
A. 

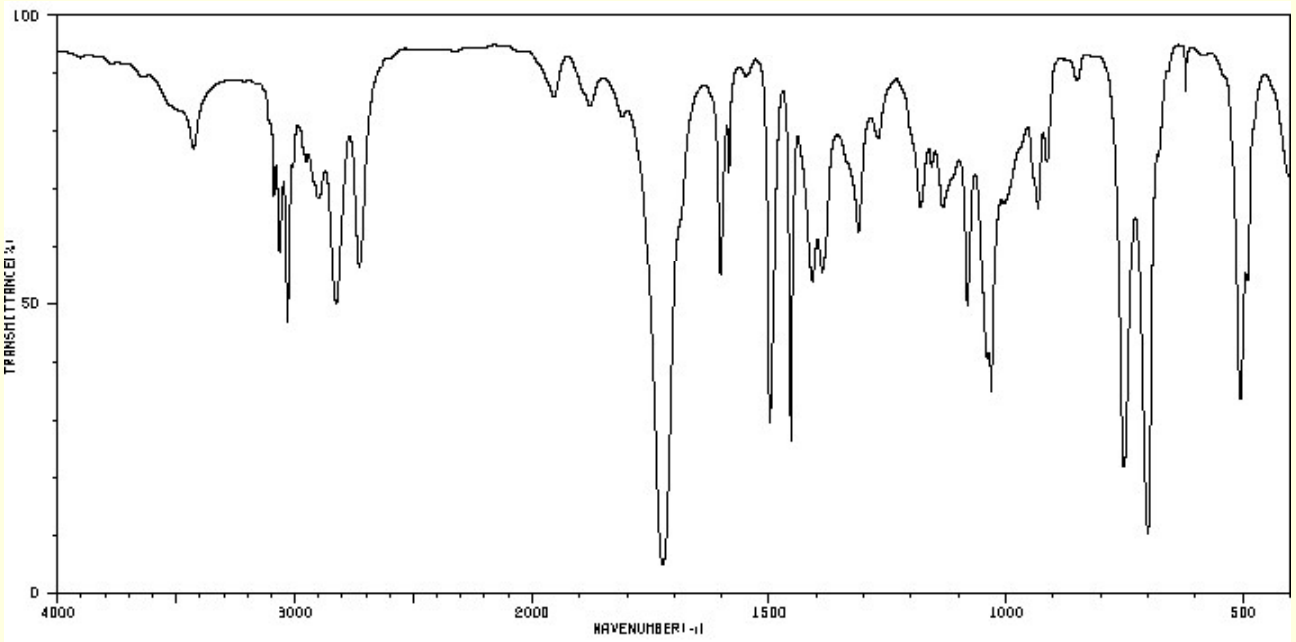
B. 

C. 

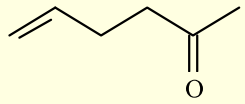
D. 

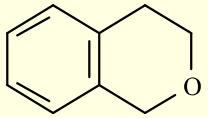
E. 

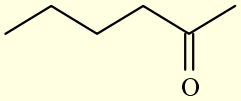
F. 

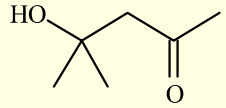


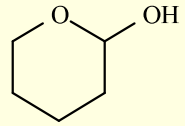
Match a structure from the list below to the IR spectrum

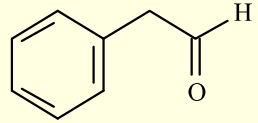
A. 

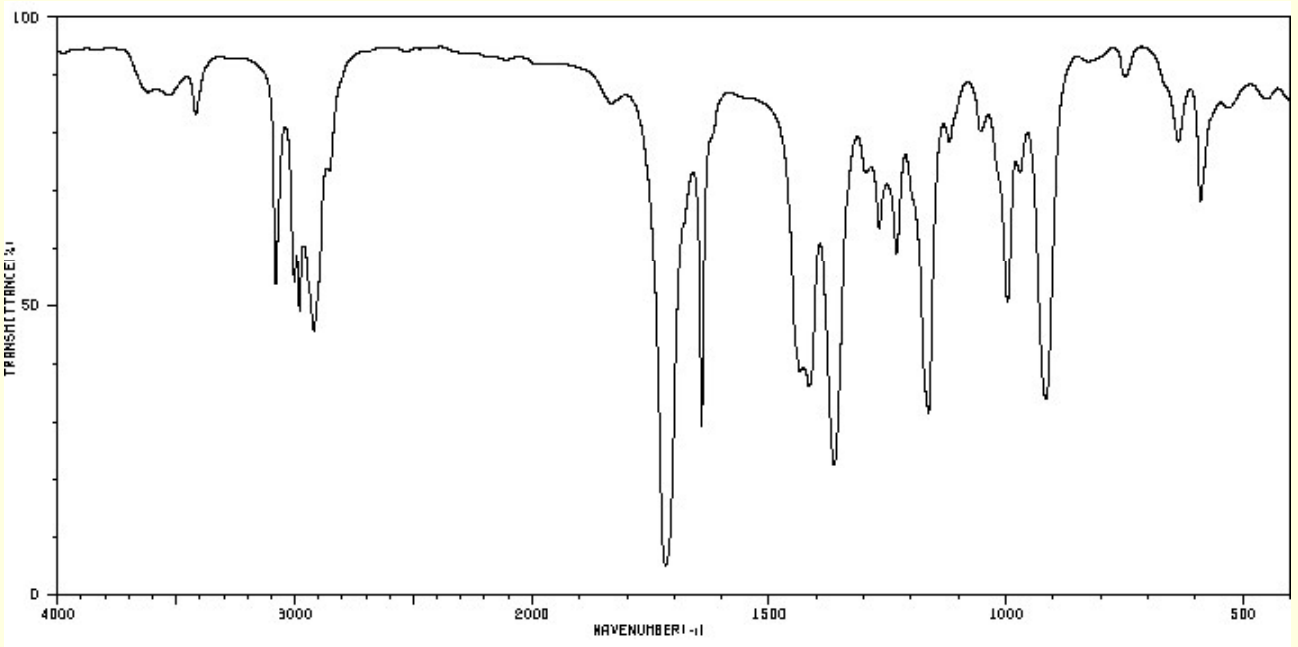
B. 

C. 

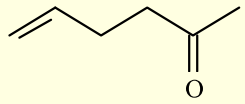
D. 

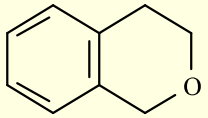
E. 

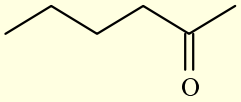
F. 

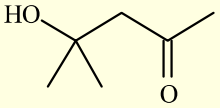


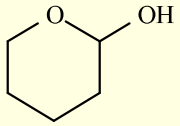
Match a structure from the list below to the IR spectrum

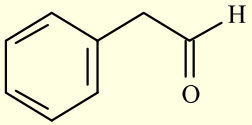
A. 

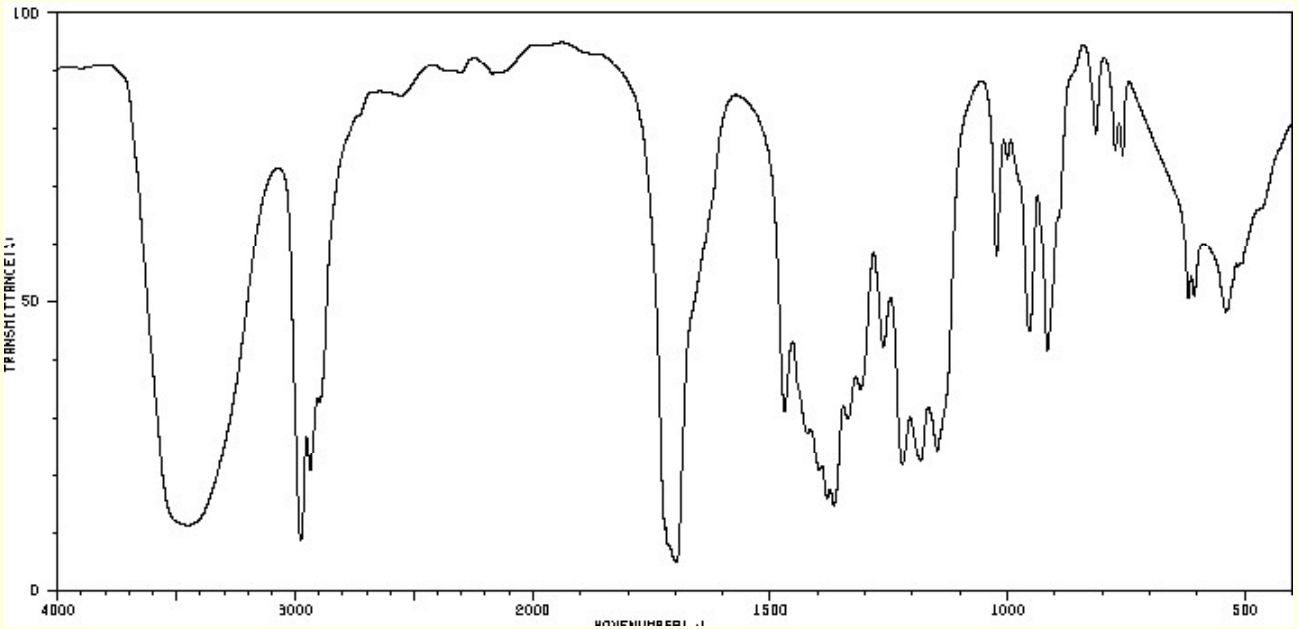
B. 

C. 

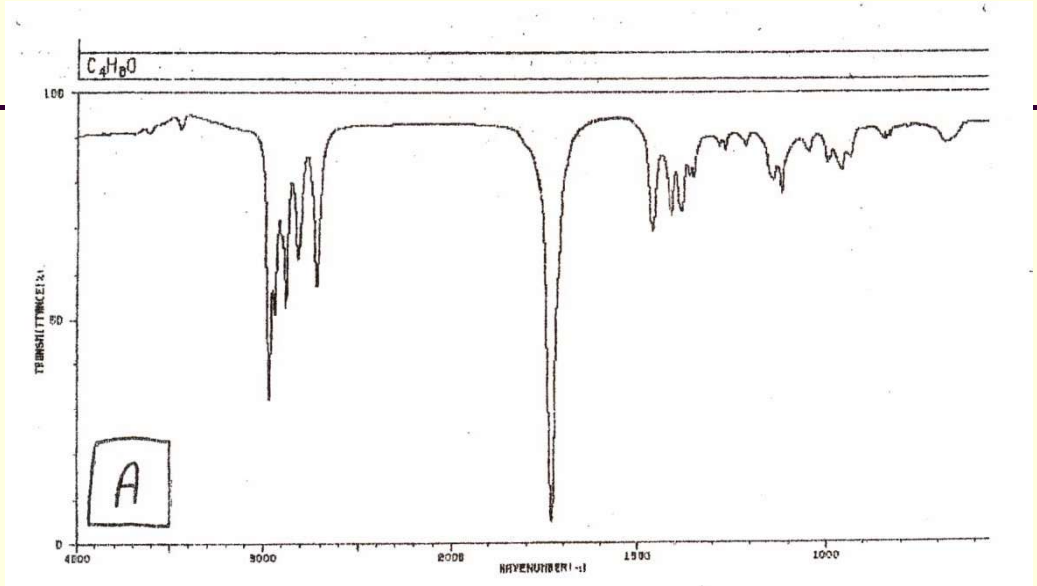
D. 

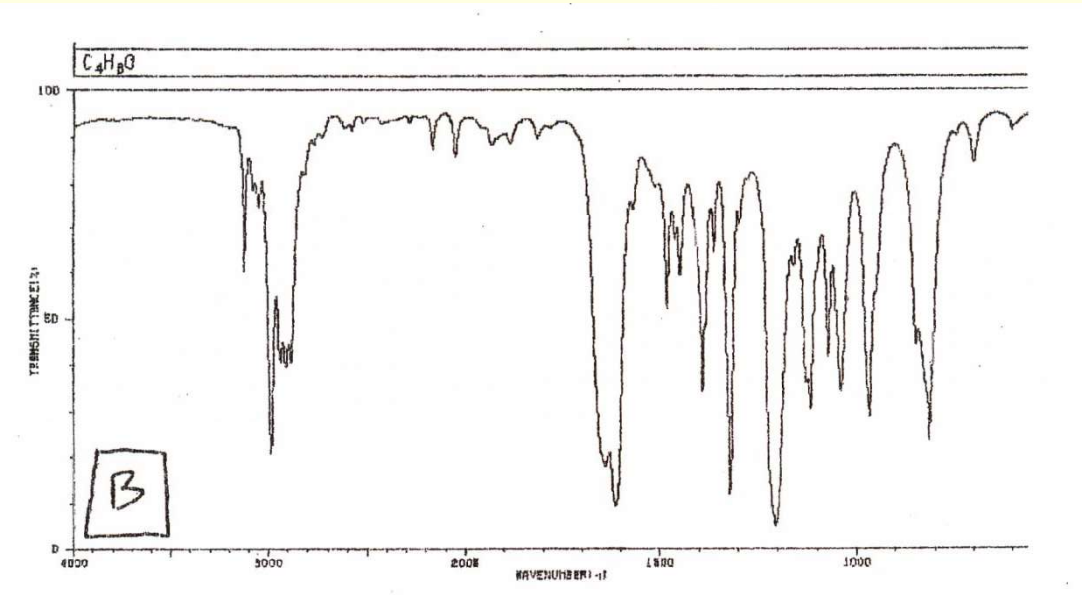
E. 

F. 

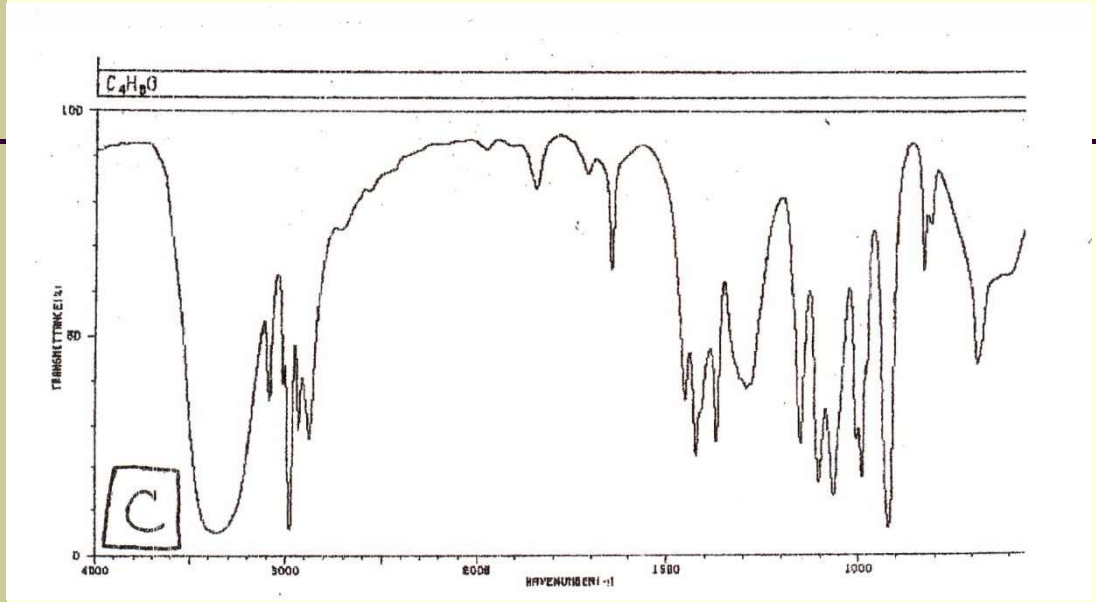


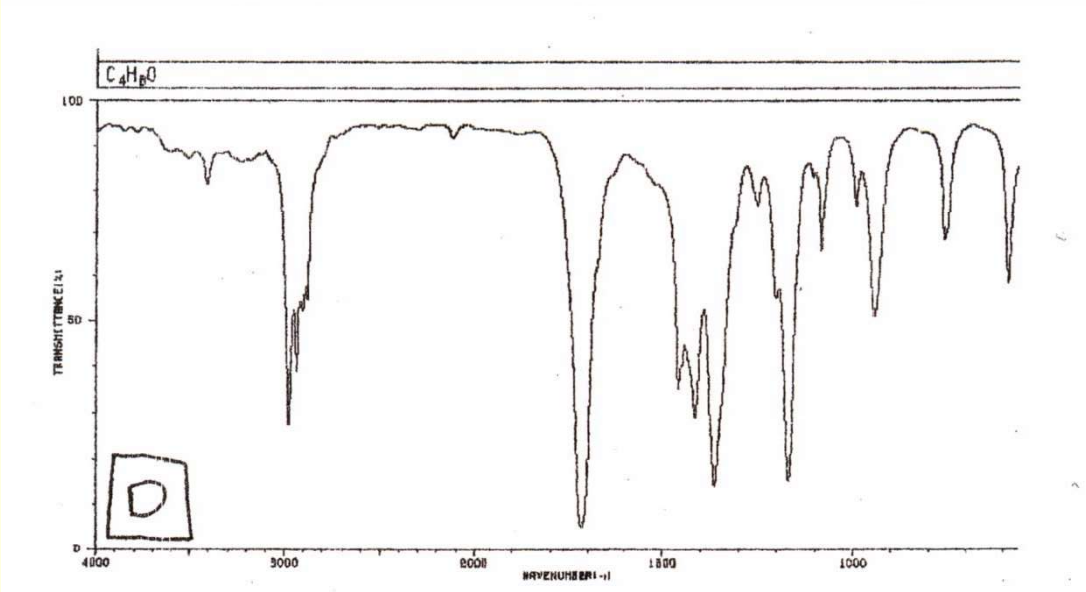
Propose a structure with formula C_4H_8O that fits data



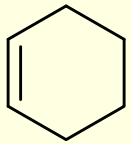
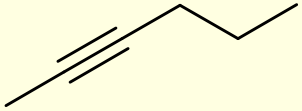


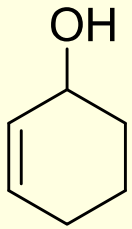
Propose a structure with formula C_4H_8O that fits data

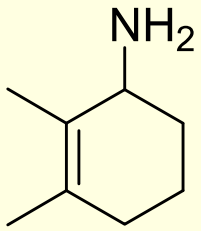


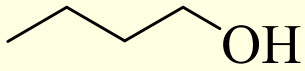


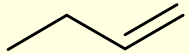
How would you differentiate each pair of molecules below using IR spectroscopy

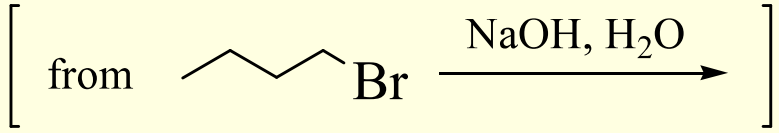
(a)  **and** 

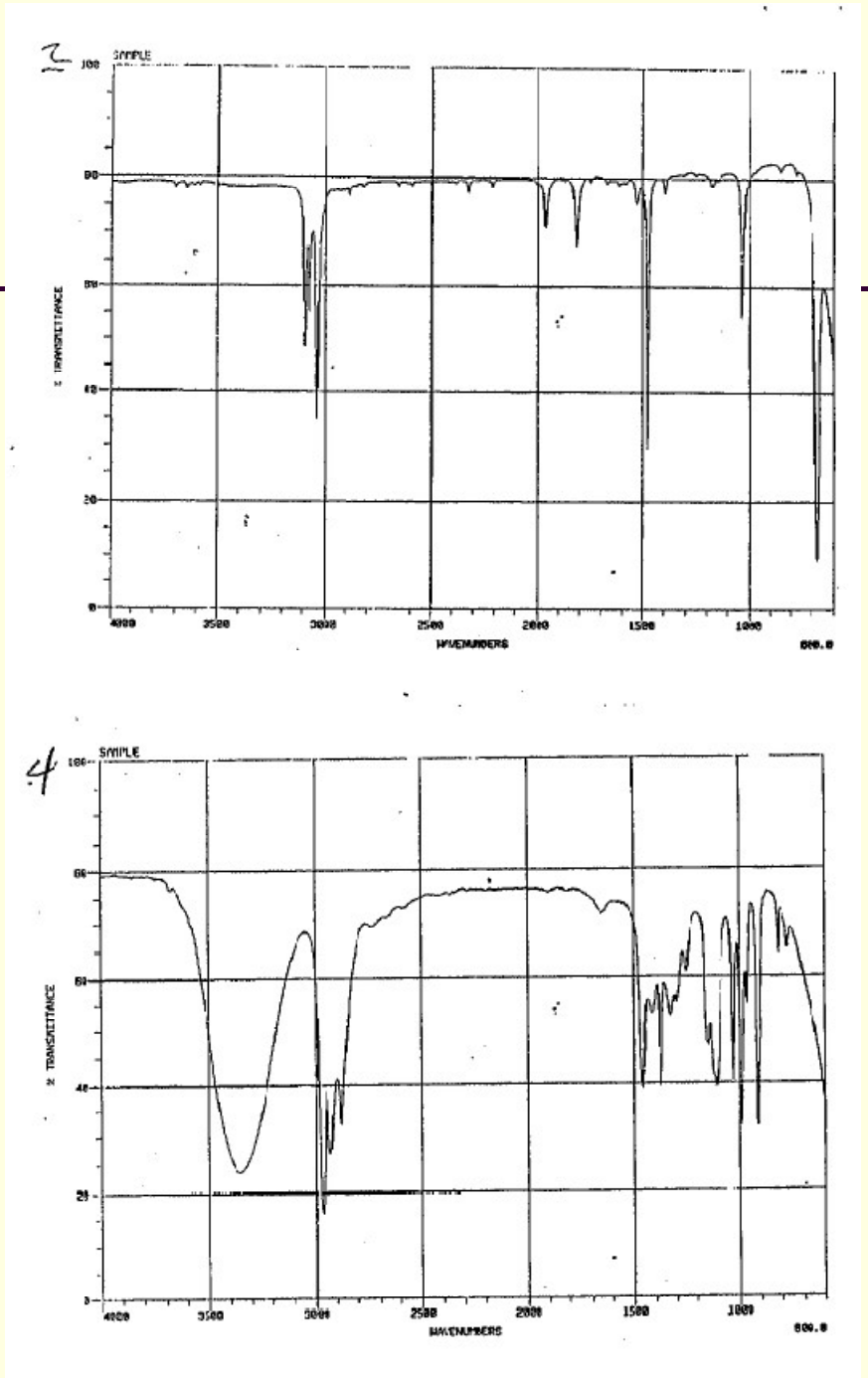
(b) 

and 

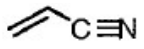
(c) 

and 

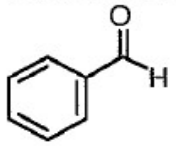




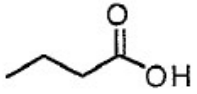
Acrylonitrile



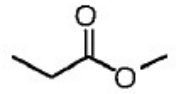
Benzaldehyde



Butyric Acid

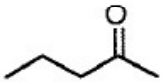


Methyl Propanoate



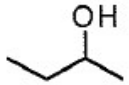
Octane

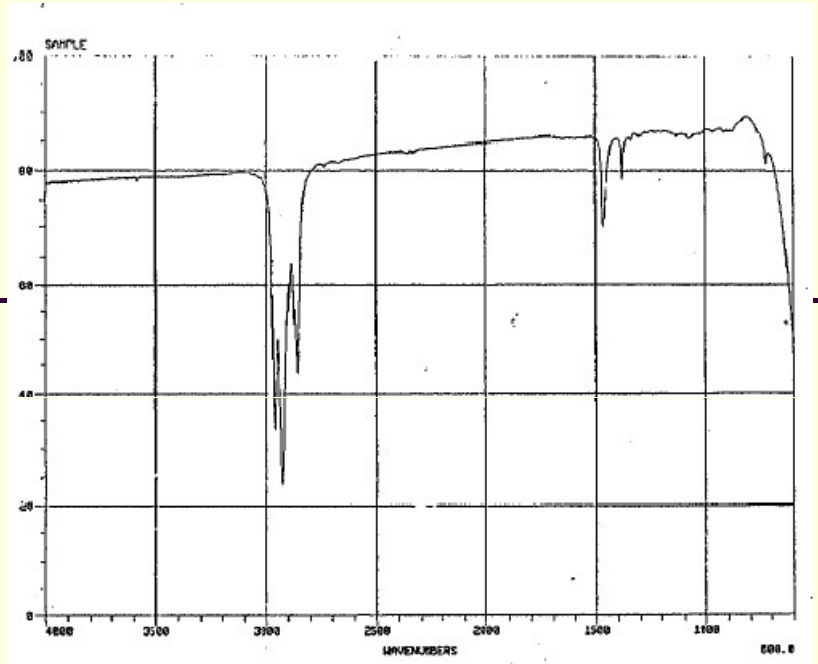
2-Pentanone

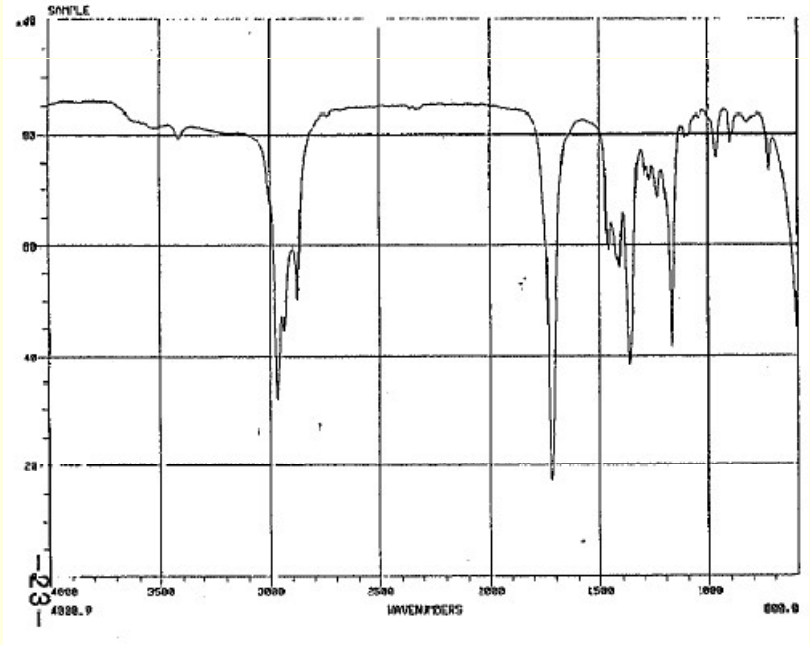


Benzene

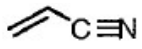
2-Butanol



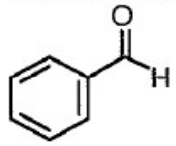




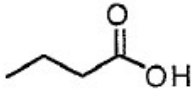
Acrylonitrile



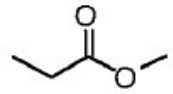
Benzaldehyde



Butyric Acid

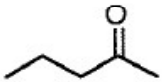


Methyl Propanoate



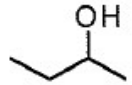
Octane

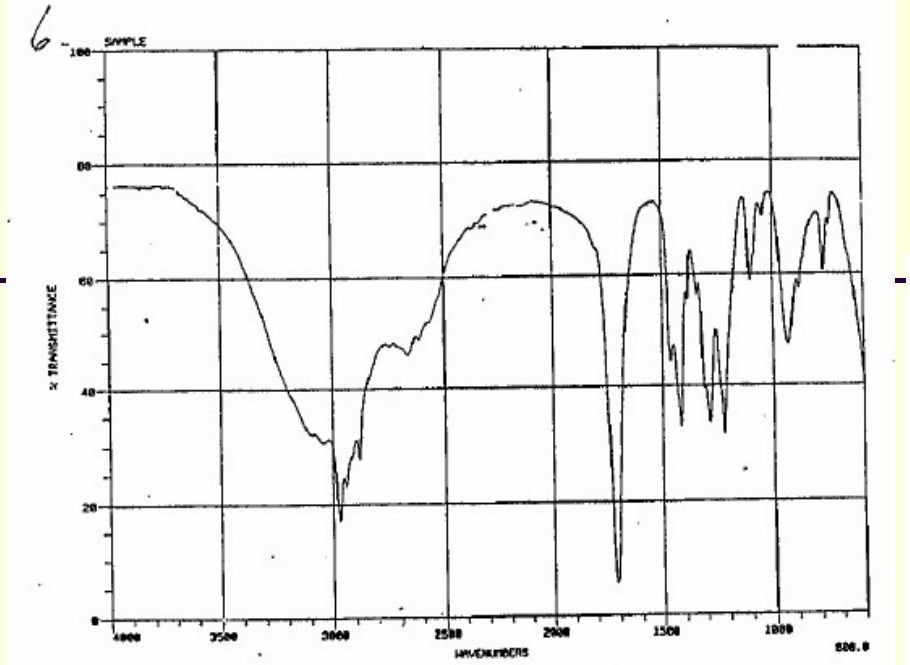
2-Pentanone

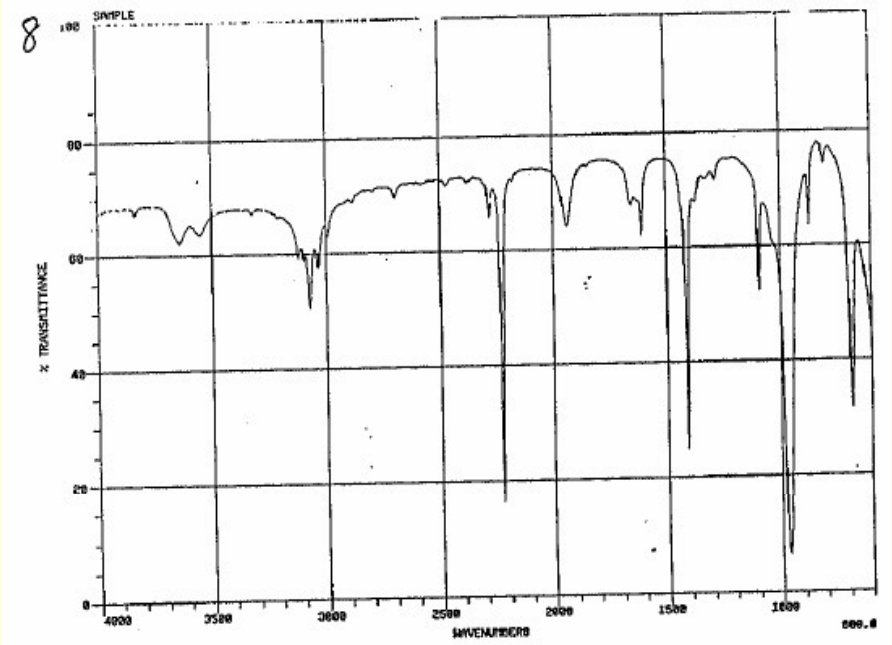


Benzene

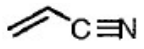
2-Butanol



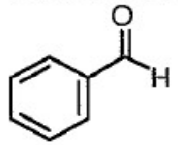




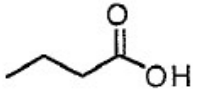
Acrylonitrile



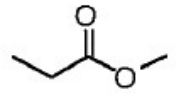
Benzaldehyde



Butyric Acid

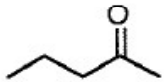


Methyl Propanoate



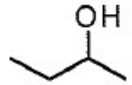
Octane

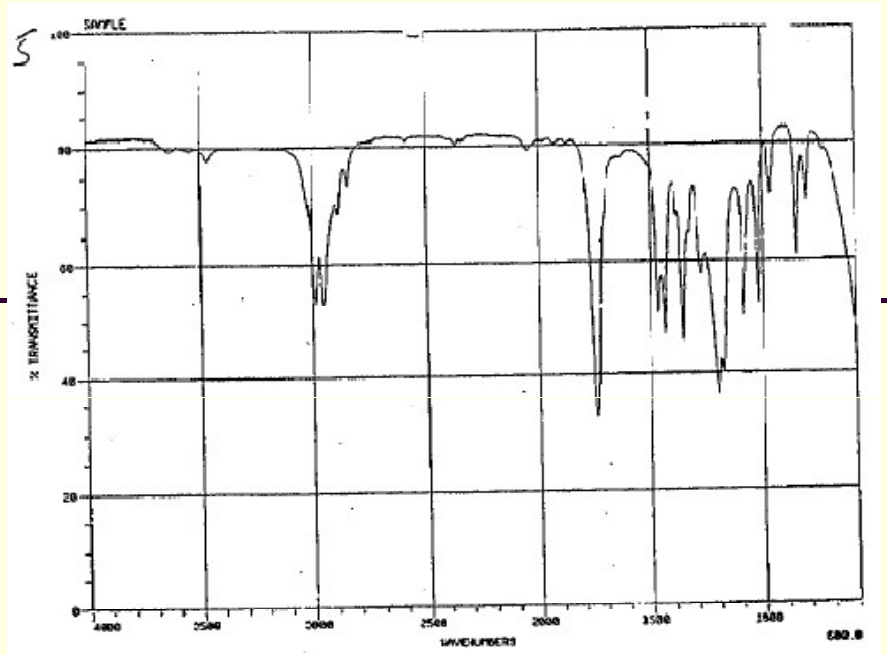
2-Pentanone

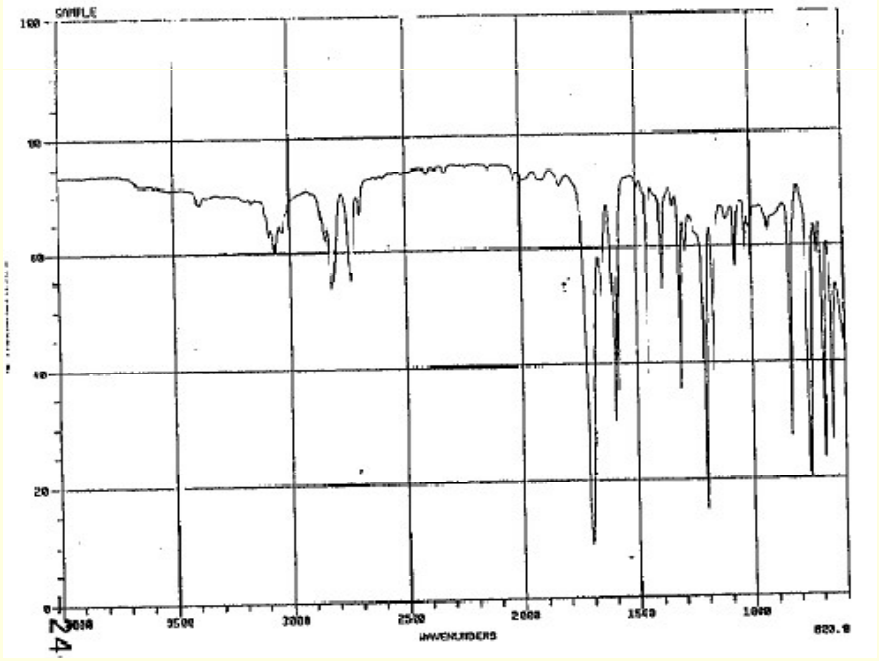


Benzene

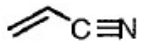
2-Butanol



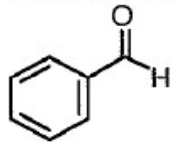




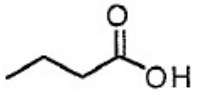
Acrylonitrile



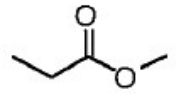
Benzaldehyde



Butyric Acid

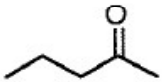


Methyl Propanoate



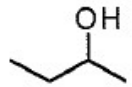
Octane

2-Pentanone



Benzene

2-Butanol

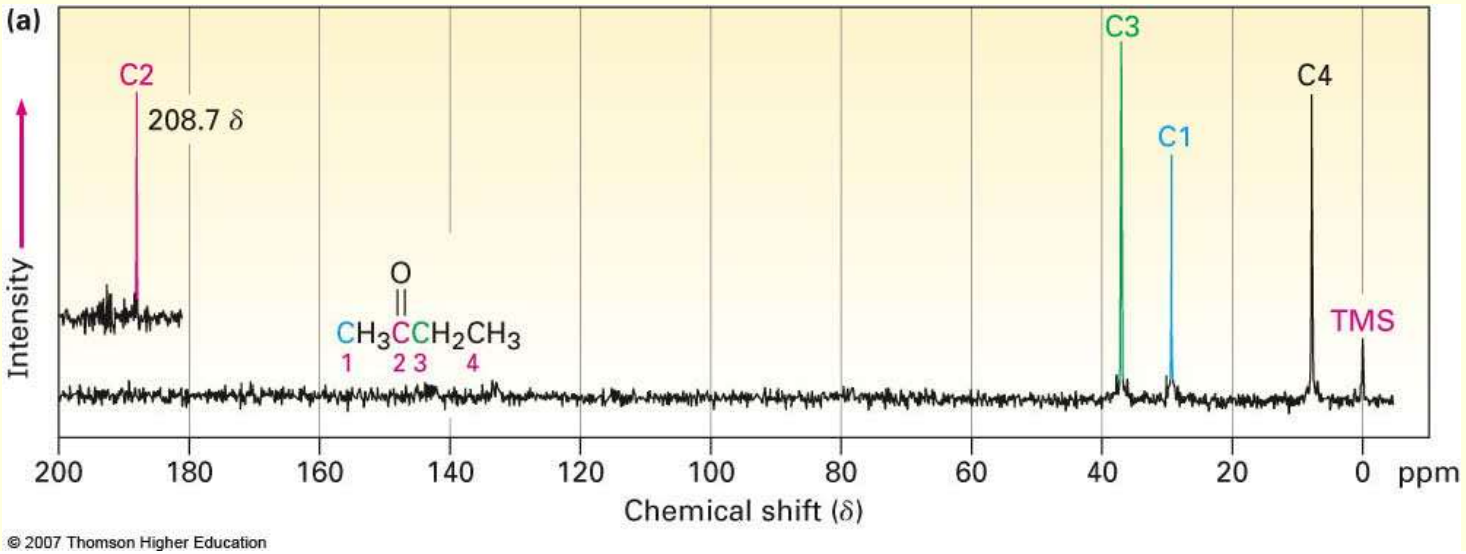


^{13}C NMR Spectroscopy Intro

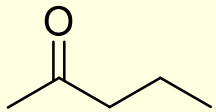
- Provides a method to count the number of different (non-equivalent) carbons in a molecule
- Will also give information about the chemical environment around each carbon atom (ppm scale)

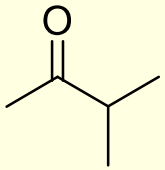
  sp^3 C signal is at δ 0 to 9 sp^2 C: δ 110 to 220

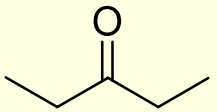
  C(=O) at low field, δ 160 to 220

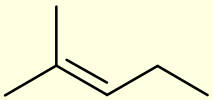


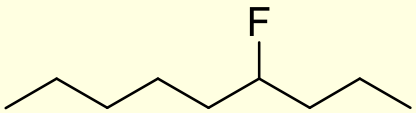
Identify Equivalent Carbons

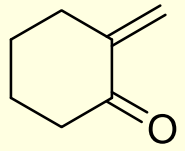


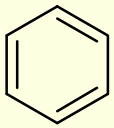


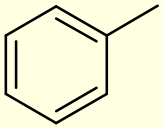


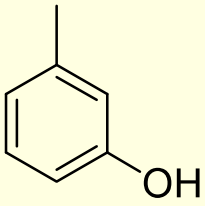


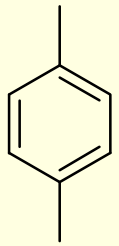






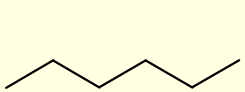


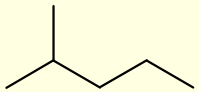


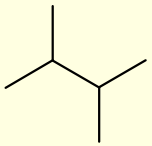


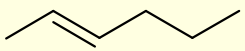
^{13}C NMR Spectroscopy

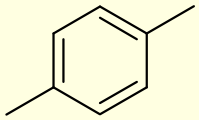
How many signals would you expect to see in the ^{13}C NMR spectrum of each of the following compounds?

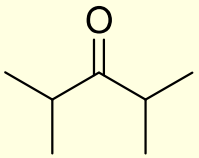


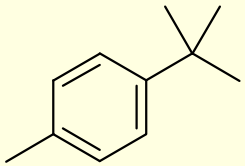


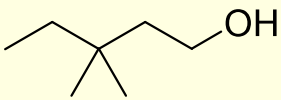


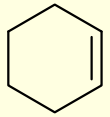






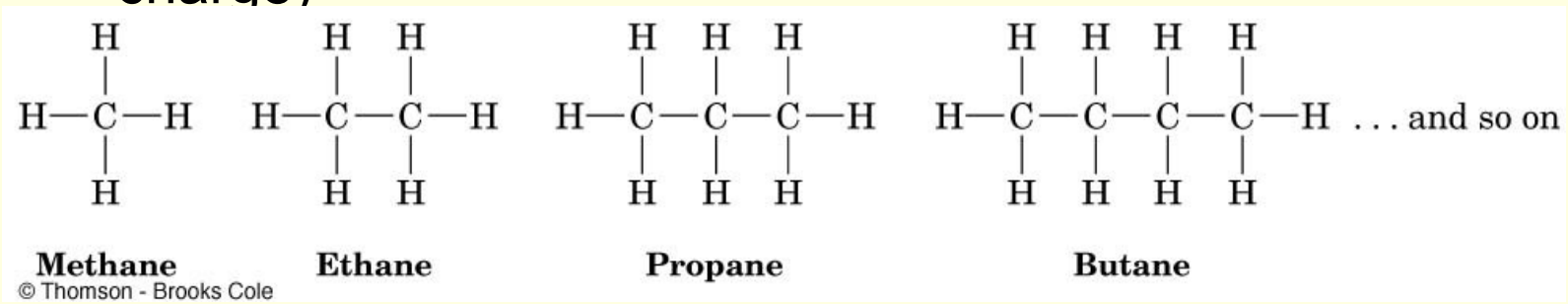






The Simplest FG: Alkanes

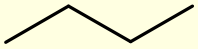
- Alkanes: Compounds with C-C single bonds and C-H bonds only (no other functional groups)
- Connecting carbons can lead to large or small molecules
- The formula for an alkane with no rings in it must be $\mathbf{C_nH_{2n+2}}$ where n is the number of carbon atoms
- Alkanes are **saturated** with hydrogen (no more can be added
- They are also called **aliphatic compounds**
- All C **sp^3** hybridized with **tetrahedral** geometry (if no charge)



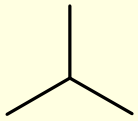
Alkanes & Isomers

compounds with same molecular formula but different arrangement of atoms

- CH_4 = methane, C_2H_6 = ethane, C_3H_8= propane
- The molecular formula of an alkane with more than three carbons can give more than one structure
  - C_4 (butane) = butane and isobutane
  - C_5 (pentane) = pentane, 2-methylbutane, and 2,2-dimethylpropane
- Alkanes with C's connected to no more than 2 other C's are **straight-chain** or **normal alkanes**
- Alkanes with one or more C's connected to 3 or 4 C's are **branched-chain alkanes**



butane



isobutane

Constitutional Isomers

isomers that differ by atomic connectivity

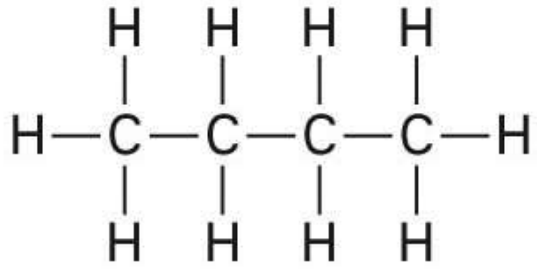
- Isomers that differ in how their atoms are arranged in chains are called **constitutional isomers**
- Compounds other than alkanes can be **constitutional isomers** of one another
- They must have the same molecular formula to be isomers

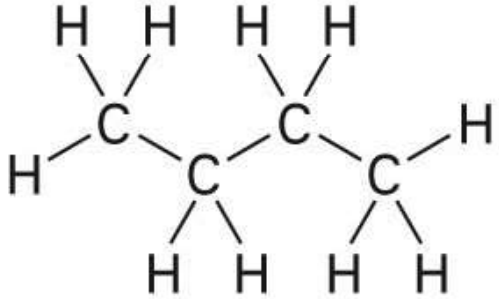
Different carbon skeletons C_4H_{10}	$CH_3CH(CH_3)CH_3$	and	$CH_3CH_2CH_2CH_3$
	2-Methylpropane (isobutane)		**Butane**
Different functional groups C_2H_6O	CH_3CH_2OH	and	CH_3OCH_3
	Ethanol		**Dimethyl ether**
Different position of functional groups C_3H_9N	$CH_3CH(NH_2)CH_3$	and	$CH_3CH_2CH_2NH_2$
	Isopropylamine		**Propylamine**

Names of Normal Alkanes

No. of Carbons	Formula Name	(C_nH_{2n+2})
1	Methane (Me)	CH_4
2	Ethane (Et)	C_2H_6
3	Propane (Pr)	C_3H_8
4	Butane	C_4H_{10}
5	Pentane	C_5H_{12}
6	Hexane	C_6H_{14}
7	Heptane	C_7H_{16}
8	Octane	C_8H_{18}
9	Nonane	C_9H_{20}
10	Decane	$C_{10}H_{22}$

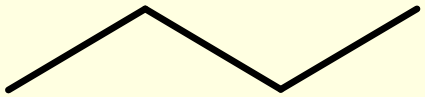
Drawing Alkanes





$CH_3—CH_2—CH_2—CH_3$ $CH_3CH_2CH_2CH_3$ $CH_3(CH_2)_2CH_3$

condensed drawings



skeletal drawing

Alkyl Groups

- **Alkyl group** – remove one H from an alkane (a part of a structure)
- General abbreviation "**R**" (for Radical, an incomplete species or the "rest" of the molecule)
- Name: replace -*ane* ending of alkane with -*yl* ending
  - –CH_3 is "methyl" (from methane)
  - –CH_2CH_3 is "ethyl" from ethane

TABLE 3.4 Some Straight-Chain Alkyl Groups

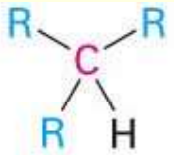
Alkane	Name	Alkyl group	Name (abbreviation)
CH_4	Methane	—CH_3	Methyl (Me)
CH_3CH_3	Ethane	—CH_2CH_3	Ethyl (Et)
$CH_3CH_2CH_3$	Propane	—$CH_2CH_2CH_3$	Propyl (Pr)
$CH_3CH_2CH_2CH_3$	Butane	—$CH_2CH_2CH_2CH_3$	Butyl (Bu)
$CH_3CH_2CH_2CH_2CH_3$	Pentane	—$CH_2CH_2CH_2CH_2CH_3$	Pentyl, or amyl

Types of Alkyl groups

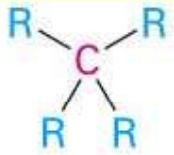
- Classified by the connection site
  - a carbon at the end of a chain (primary alkyl group)
  - a carbon with two other carbons attached to it (secondary alkyl group)
  - a carbon with three other carbons attached to it (tertiary alkyl group)
  - classify hydrogen in same fashion (1° H on 1° C)

Primary **carbon (1°) is bonded to one other carbon.**

Secondary **carbon (2°) is bonded to two other carbons.**



Tertiary **carbon (3°) is bonded to three other carbons.**



Quaternary **carbon (4°) is bonded to four other carbons.**

Types of Alkyl groups

- Some odd examples when non-carbon atoms are part of structure....
- R-CH2-OH is primary C, primary H
- need to fix HW answer key for this!
- RCOH aldehyde is a primary carbon

Naming Alkanes

- Compounds are given systematic names by a process that uses

- Follows specific rules
  - Find parent hydrocarbon chain
  - Carbons in that main chain are numbered in sequence
  - Substituents are identified numbered
  - Write compound name is single word
  - Name a complex substituents as though it were a compound itself
- See specific examples in text

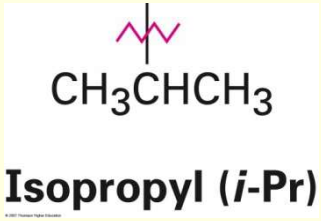
Naming Alkanes (IUPAC Rules)

1. Identify the parent (longest) chain
   - if choice, find one with the most branch points
2. Number atoms in this chain
   - number to give first branching group (substituent)
   - lowest possible number
3. Name and number the substituents
   - if two groups on same C, give same number
   - if same group appears more than once, use di, tri..
   - replace -ane ending with -yl for substituents
4. Write name as a single word
   - use hyphens to separate numbers and letters
   - use commas to separate numbers
   - list subs alphabetically (don't consider di, tri.. sec-, tert-)
   - end name according to priority FG (ane for alkane)

Naming Alkanes

5. Name (complex substituents) by same rules
   number substituent so that first atom connected to main chain is position 1 (put in parenthesis)
6. Learn common names for branched substituents: (when naming, can use common or IUPAC name)

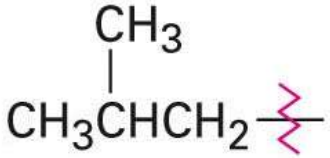
also (1-methylethyl) substituent



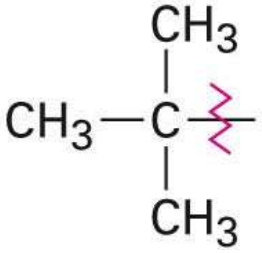
Isopropyl (*i*-Pr)

iso part of name alphabetically, sec- and tert- are not

***sec*-Butyl (*sec*-Bu)**

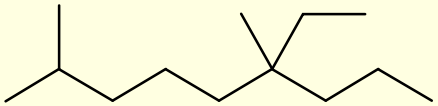


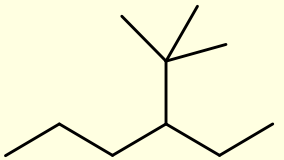
Isobutyl

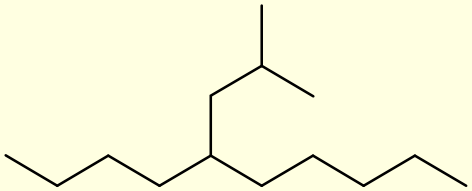


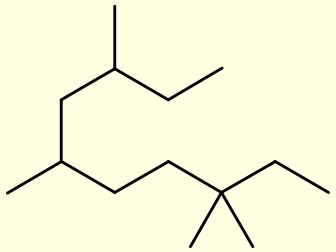
***tert*-Butyl (*t*-butyl or *t*-Bu)**

Examples









Examples

what if same numbers from both ends, go with alpha first lower number

given them some complex subs to name like
#-(2,3-dimethylbutyl)
etc

Physical Properties

- Boiling points and melting points increase as size of alkane increases
- Dispersion forces increase as molecule size increases, resulting in higher melting and boiling points