

Chapter 2

Families of Carbon Compounds

Functional Groups,
Intermolecular Forces,
& Infrared (IR) Spectroscopy

Created by

Professor William Tam & Dr. Phillis Chang

About The Authors

These Powerpoint Lecture Slides were created and prepared by Professor William Tam and his wife Dr. Phillis Chang.

Professor William Tam received his B.Sc. at the University of Hong Kong in 1990 and his Ph.D. at the University of Toronto (Canada) in 1995. He was an NSERC postdoctoral fellow at the Imperial College (UK) and at Harvard University (USA). He joined the Department of Chemistry at the University of Guelph (Ontario, Canada) in 1998 and is currently a Full Professor and Associate Chair in the department. Professor Tam has received several awards in research and teaching, and according to *Essential Science Indicators*, he is currently ranked as the Top 1% most cited Chemists worldwide. He has published four books and over 80 scientific papers in top international journals such as *J. Am. Chem. Soc.*, *Angew. Chem.*, *Org. Lett.*, and *J. Org. Chem.*

Dr. Phillis Chang received her B.Sc. at New York University (USA) in 1994, her M.Sc. and Ph.D. in 1997 and 2001 at the University of Guelph (Canada). She lives in Guelph with her husband, William, and their son, Matthew.

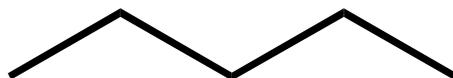
1. Hydrocarbons

❖ **Hydrocarbons** are compounds that contain only **carbon** and **hydrogen** atoms

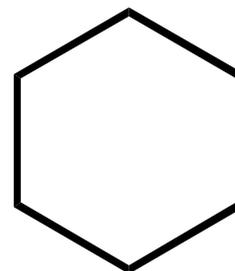
- **Alkanes**

- ◆ hydrocarbons that do not have multiple bonds between carbon atoms

e.g.



pentane



cyclohexane

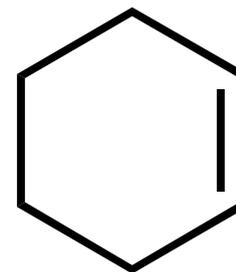
- Alkenes

- ◆ contain at least one carbon–carbon double bond

e.g.



propene



cyclohexene

- Alkynes

- ◆ contain at least one carbon-carbon triple bond

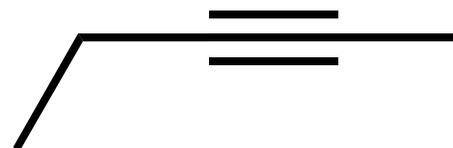
e.g.



ethyne



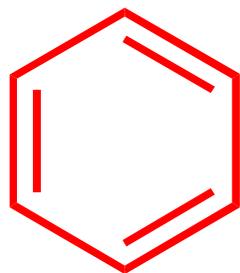
1-pentyne



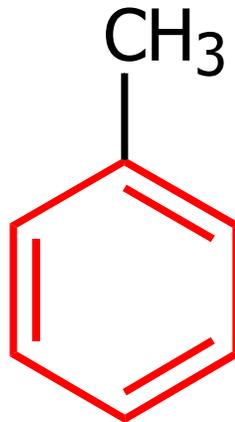
2-pentyne

- Aromatic compound
 - ◆ contain a special type of ring, the most common example of which is a benzene ring

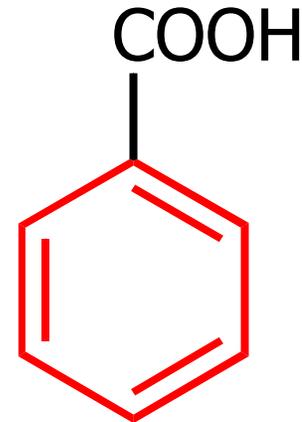
e.g.



benzene



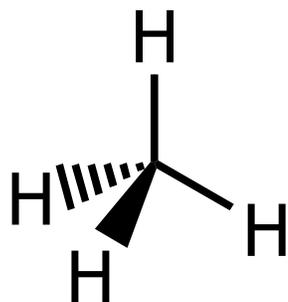
toluene



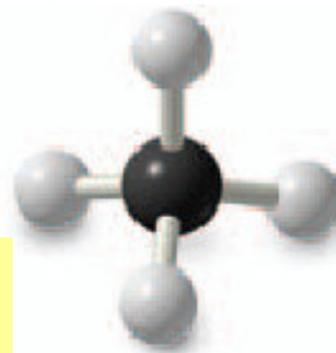
benzoic acid

1A. Alkanes

- ❖ The primary sources of alkanes are **natural gas** and **petroleum**
- ❖ The smaller alkanes (methane through butane) are gases under ambient conditions
- ❖ **Methane** is the principal component of natural gas
- ❖ Higher molecular weight alkanes are obtained largely by refining petroleum

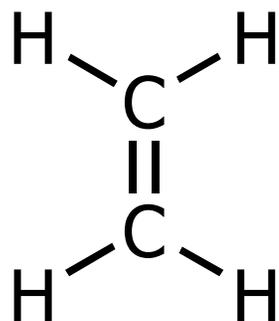


Methane

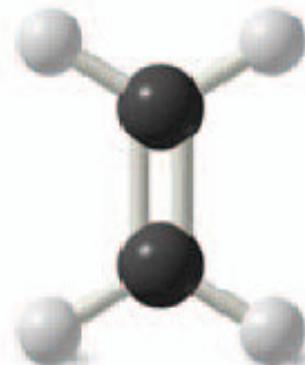


1B. Alkenes

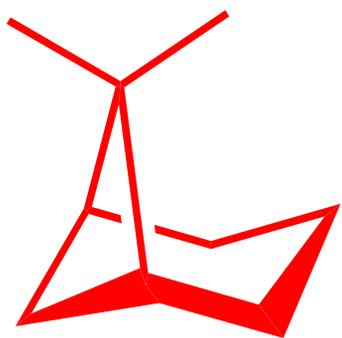
- ❖ Ethene and propene, the two simplest alkenes, are among the most important industrial chemicals produced in the United States
- ❖ **Ethene** is used as a starting material for the synthesis of many industrial compounds, including **ethanol**, **ethylene oxide**, **ethanal**, and the polymer **polyethylene**



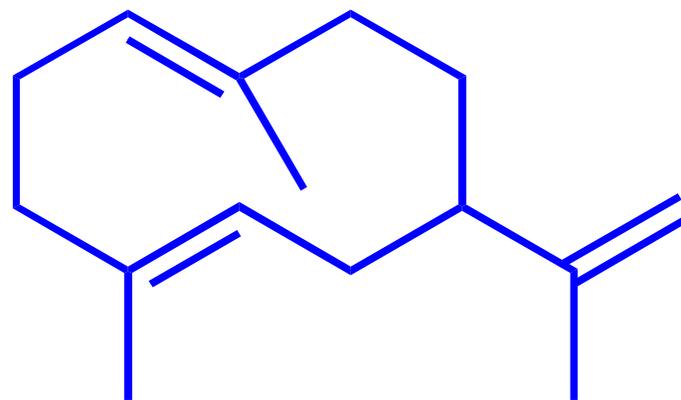
Ethene



- ❖ Propene is the important starting material for acetone, cumene and polypropylene
- ❖ Examples of naturally occurring alkenes



β -Pinene
(a component of turpentine)



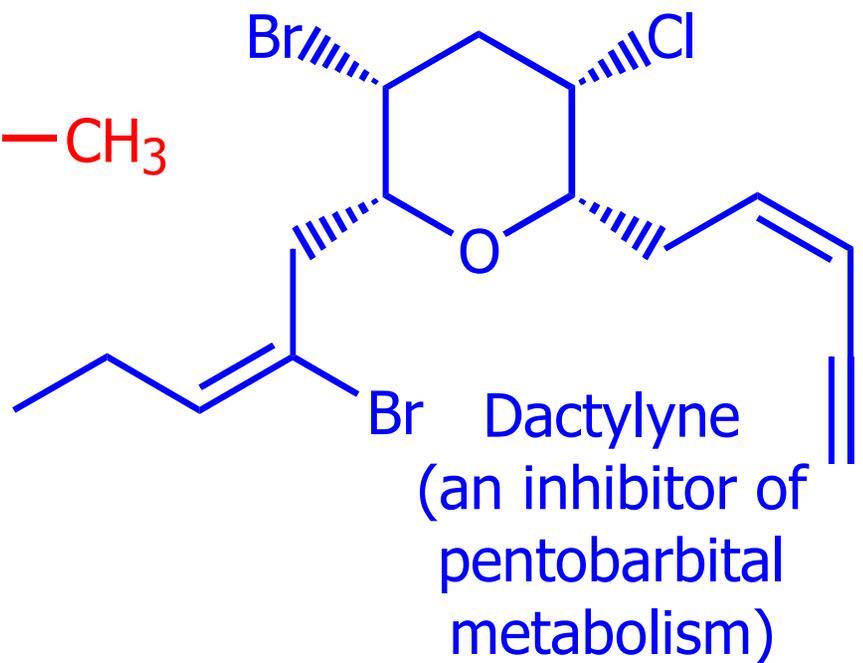
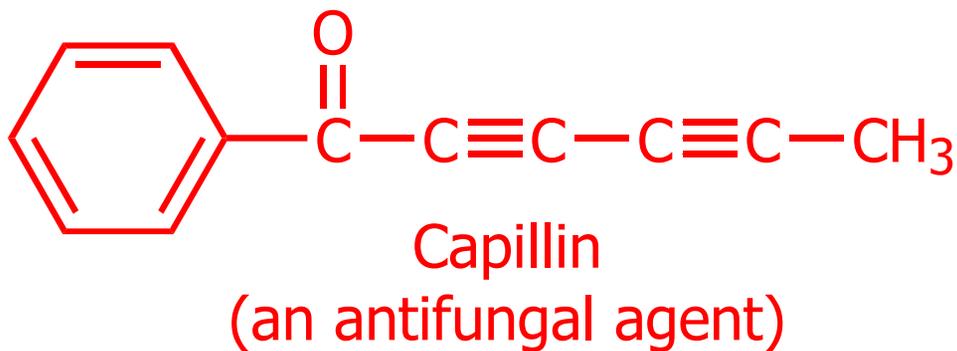
An aphid alarm
pheromone

1C. Alkynes

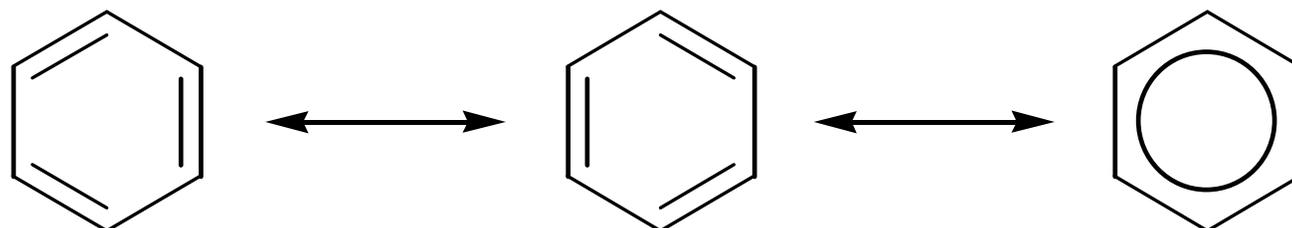
- ❖ The simplest alkyne is ethyne (also called acetylene)



- ❖ Examples of naturally occurring alkynes

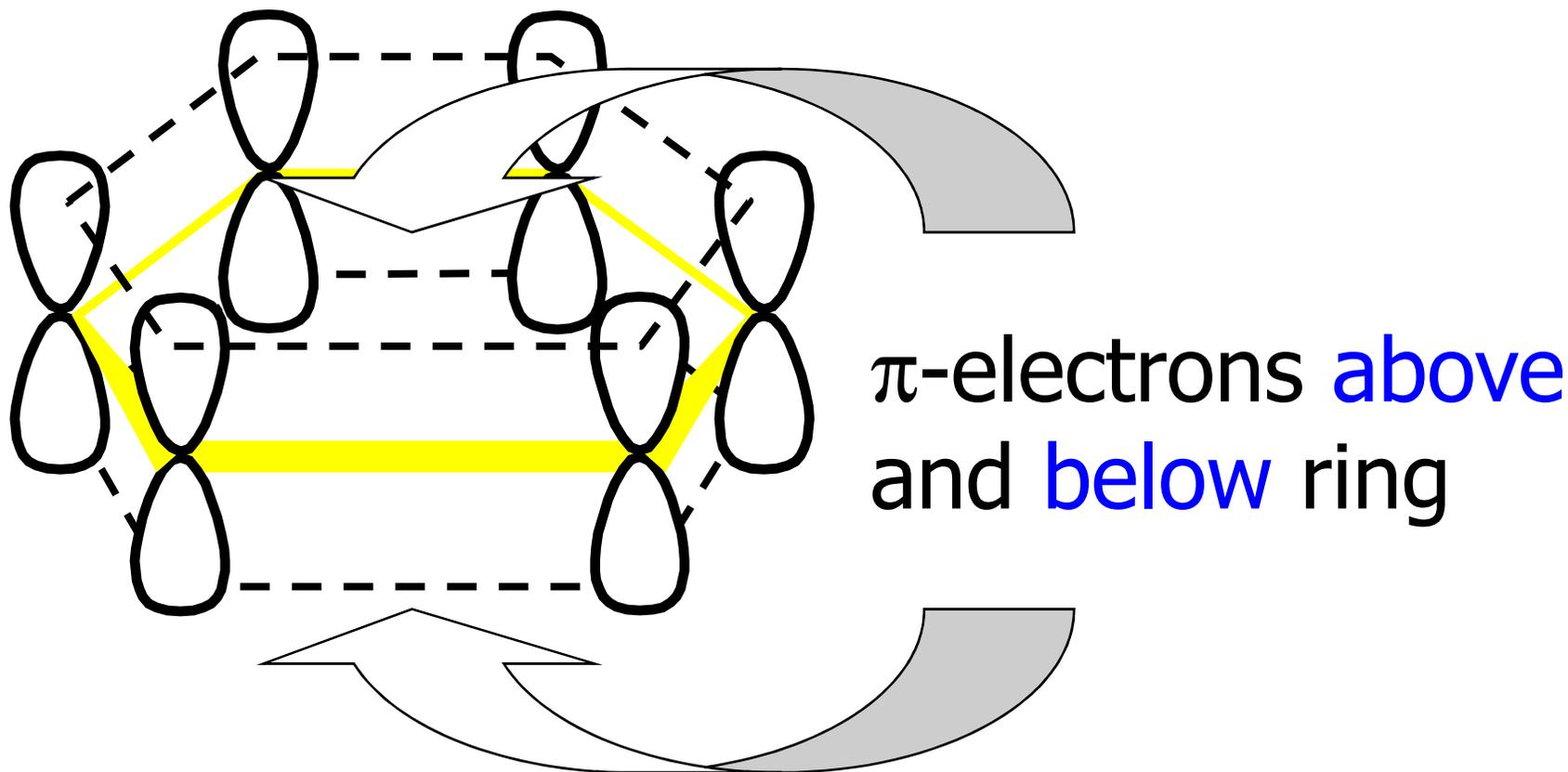


1D. Benzene



- ❖ All $C=C$ bond lengths are the same (1.39 Å) (compare with C–C single bond 1.54 Å, C=C double bond 1.34 Å)
- ❖ Extra stabilization due to **resonance**
⇒ aromatic

❖ 3 Dimensional structure of benzene



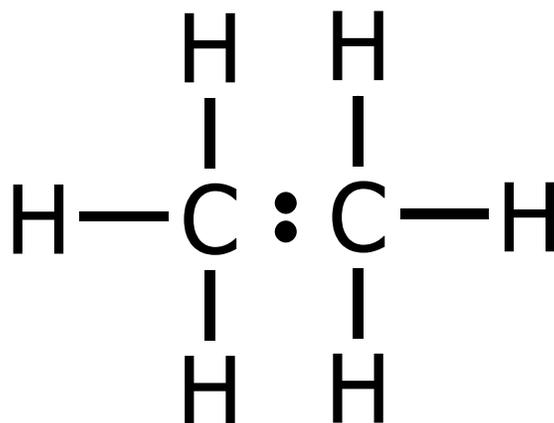
- Planar structure
- All carbons sp^2 hybridized

- ❖ The lobes of each π orbital above and below the ring overlap with the lobes of π orbitals on the atoms to either side of it
- ❖ the six electrons associated with these π orbitals (one electron from each orbital) are **delocalized** about all six carbon atoms of the ring

2. Polar Covalent Bonds



- ❖ Lithium fluoride has an **ionic bond**

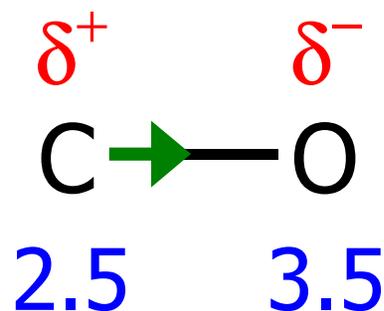


- ❖ Ethane has a **covalent bond**. The electrons are shared equally between the carbon atoms



equal sharing
of e^{-}
(non-polar bond)

electronegativity



unequal sharing
of e^{-}
(polar bond)

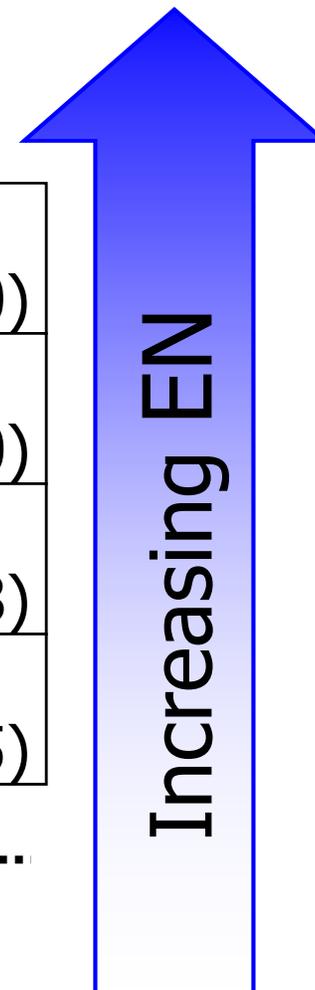
❖ Electronegativity (EN)

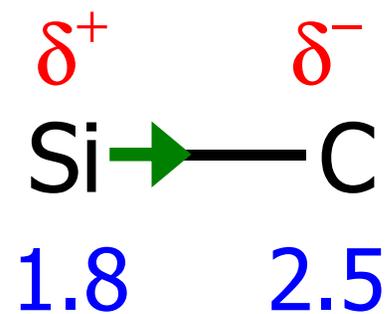
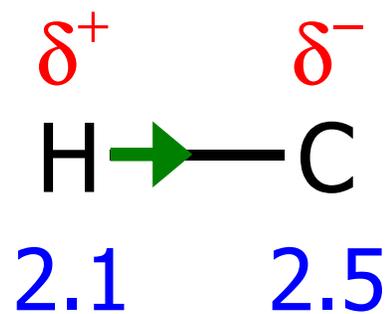
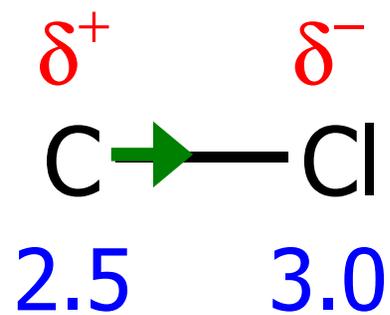
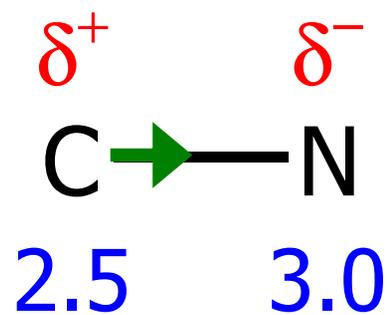
- The intrinsic ability of an atom to attract the shared electrons in a covalent bond
- Electronegativities are based on an arbitrary scale, with F the most electronegative (EN = 4.0) and Cs the least (EN = 0.7)

element
(EN)

H (2.1)

Li (1.0)	Be (1.6)	B (2.0)	C (2.5)	N (3.0)	O (3.5)	F (4.0)
Na (0.9)	Mg (1.2)		Si (1.8)	P (2.1)	S (2.5)	Cl (3.0)
K (0.8)						Br (2.8)
Rb (0.8)						I (2.5)
Cs (0.7)						



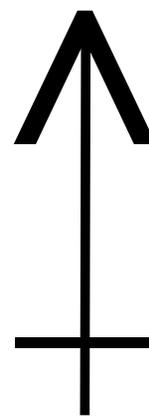
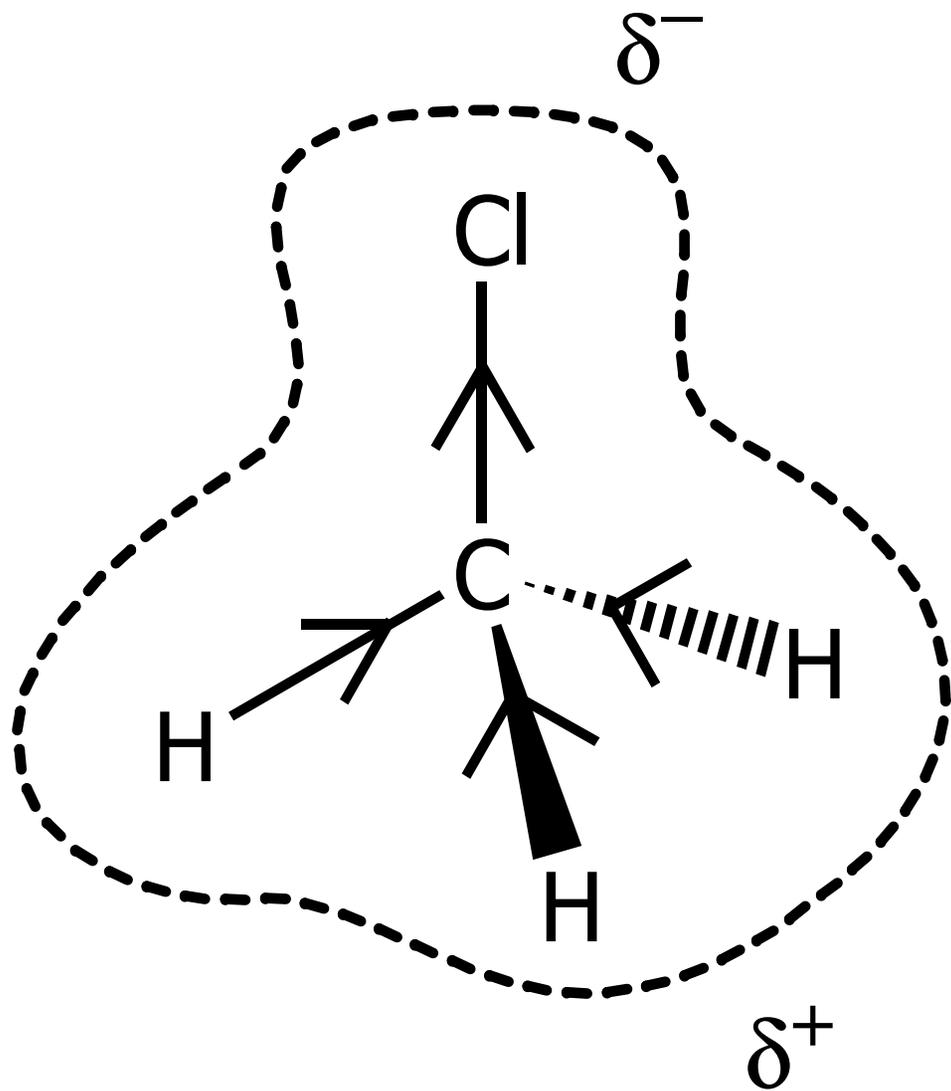


3. Polar and Nonpolar Molecules

$$\text{Dipole moment} = \text{distance between the charges} \times \text{the charge}$$

$$\mu = r \times Q$$

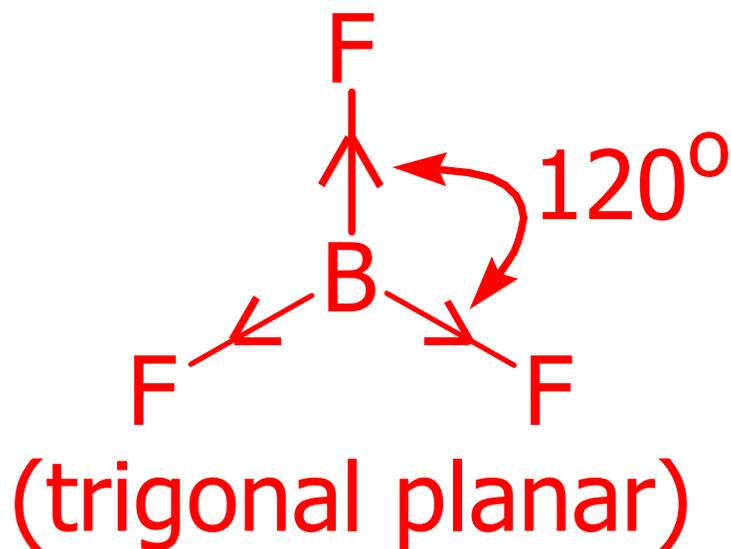
- ❖ **Dipole moments** are expressed in *debyes* (D), where $1 \text{ D} = 3.336 \times 10^{-30}$ coulomb meter (C•m) in SI units



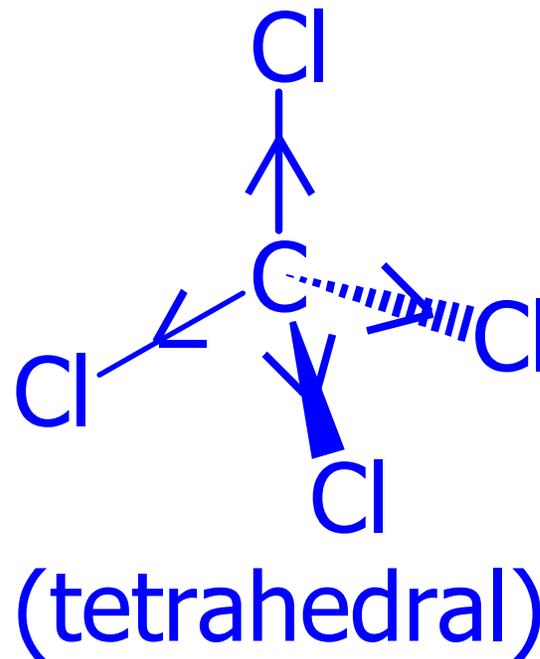
net dipole
(1.87 D)

❖ Molecules containing polar bonds are not necessarily polar as a whole, for example

(1) BF_3 ($\mu = 0 \text{ D}$)



(2) CCl_4 ($\mu = 0 \text{ D}$)



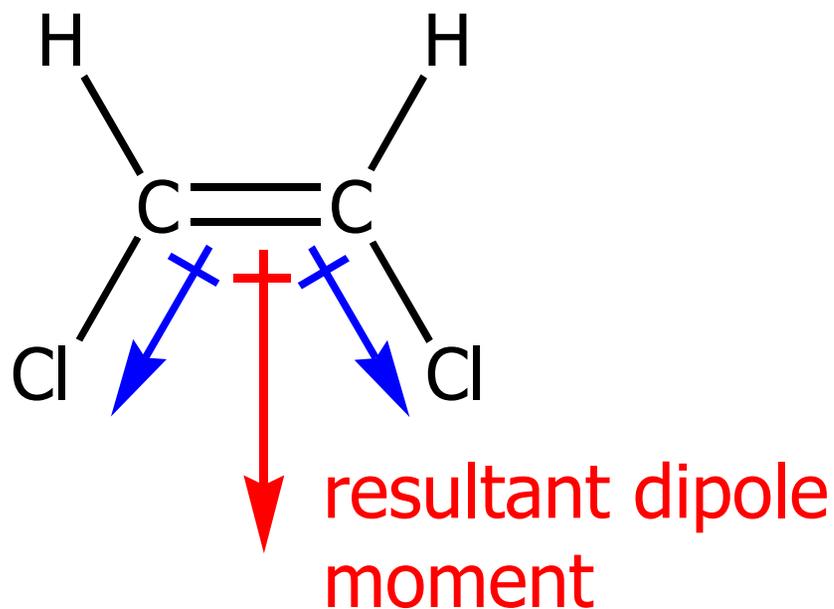
❖ Dipole moment of some compounds

Compound	Dipole Moment	Compound	Dipole Moment
NaCl	9.0	H ₂ O	1.85
CH ₃ NO ₂	3.45	CH ₃ OH	1.70
CH ₃ Cl	1.87	CH ₃ COOH	1.52
CH ₃ Br	1.79	NH ₃	1.47
CH ₃ I	1.64	CH ₄	0
CHCl ₃	1.02	CCl ₄	0

3A. Dipole Moments in Alkenes

cis-

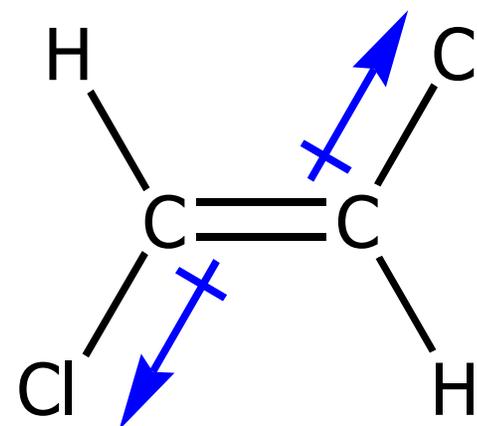
1,2-Dichloroethene



$$(\mu = 1.9 \text{ D})$$

trans-

1,2-Dichloroethene



$$(\mu = 0 \text{ D})$$

❖ Physical properties of some cis-trans isomers

Compound	m.p. (°C)	m.p. (°C)	(μ)
<i>cis</i> -1,2-Dichloroethene	-80	60	1.90
<i>trans</i> -1,2-Dichloroethene	-50	48	0
<i>cis</i> -1,2-Dibromoethene	-53	112.5	1.35
<i>trans</i> -1,2-Dibromoethene	-6	108	0

4. Functional Groups

Alkane	Alkyl Group	Abbrev.	Bond-Line	Model
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$\text{CH}_3\text{—H}$
Methane

$\text{CH}_3\text{—}$
Methyl

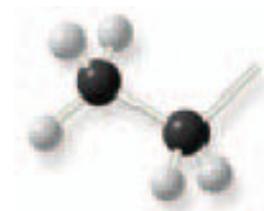
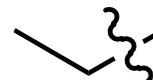
Me-



$\text{CH}_3\text{CH}_2\text{—H}$
Ethane

$\text{CH}_3\text{CH}_2\text{—}$
Ethyl

Et-



$\text{CH}_3\text{CH}_2\text{CH}_2\text{—H}$
Propane

$\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$
propyl

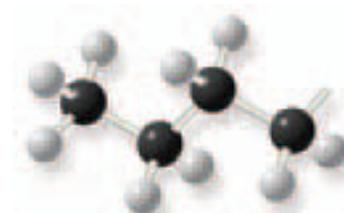
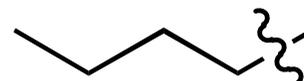
Pr-

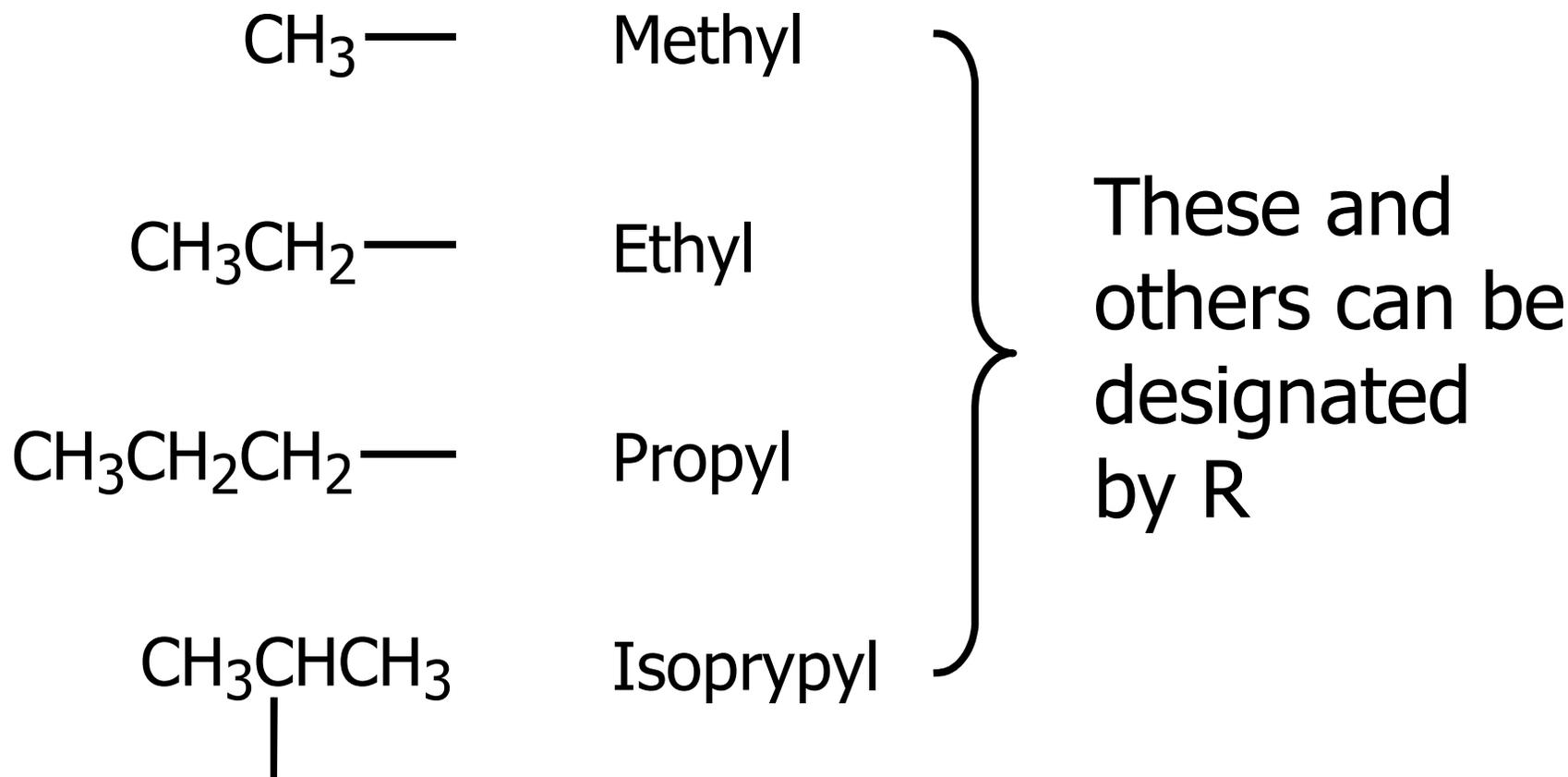


$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—H}$
Butane

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$
Butyl

Bu-

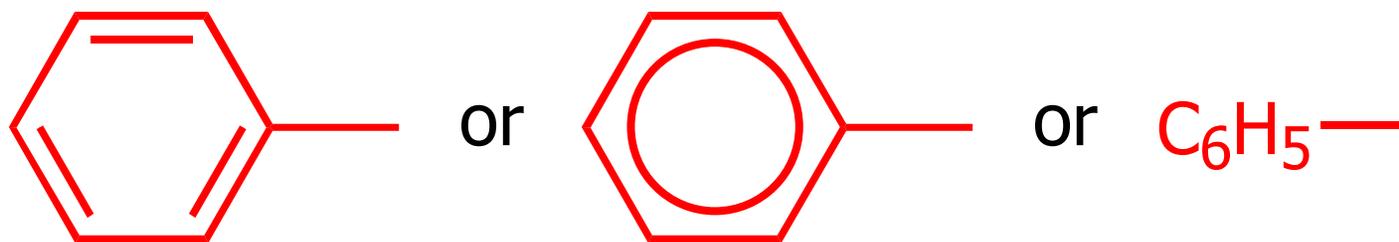




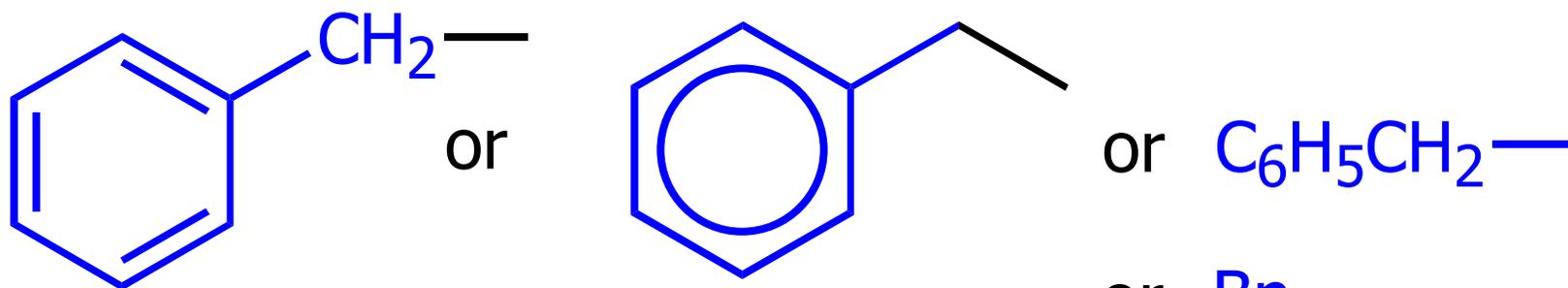
❖ General formula for an alkane is R—H

4B. Phenyl and Benzyl Groups

❖ Phenyl group



❖ Benzyl group

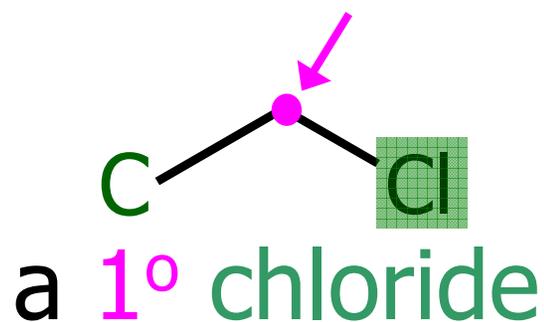


5. Alkyl Halides or Haloalkanes

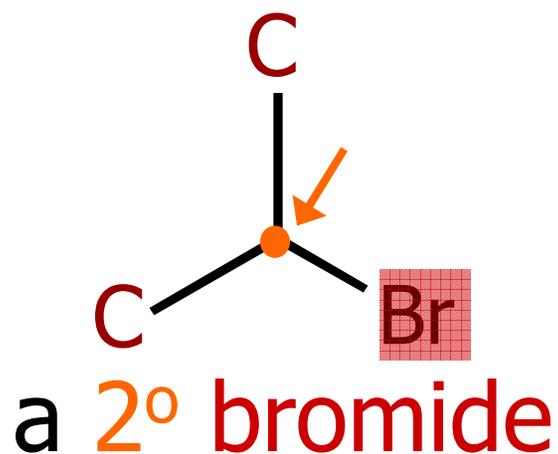


● Examples

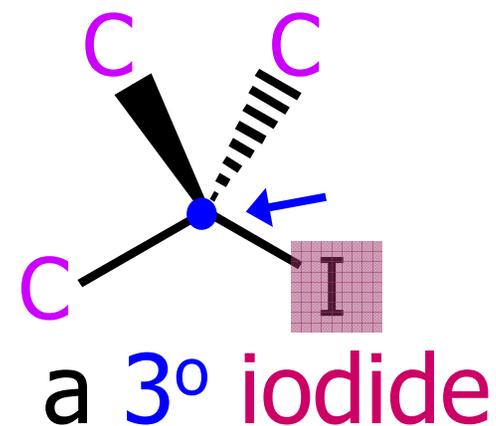
Attached to
1 carbon atom



Attached to
2 carbon atoms



Attached to
3 carbon atoms



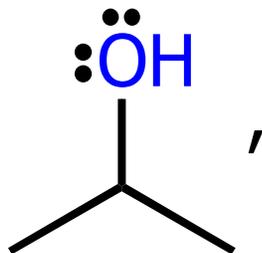
6. Alcohols

❖ R-OH

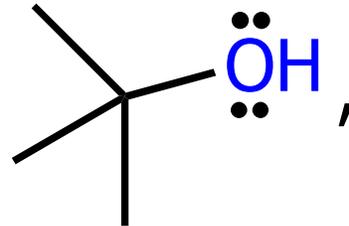
- Examples



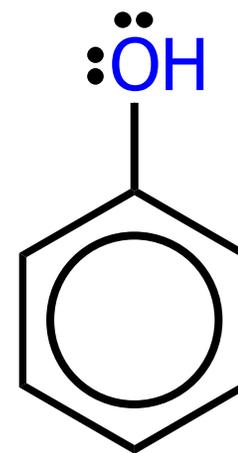
(1°)



(2°)



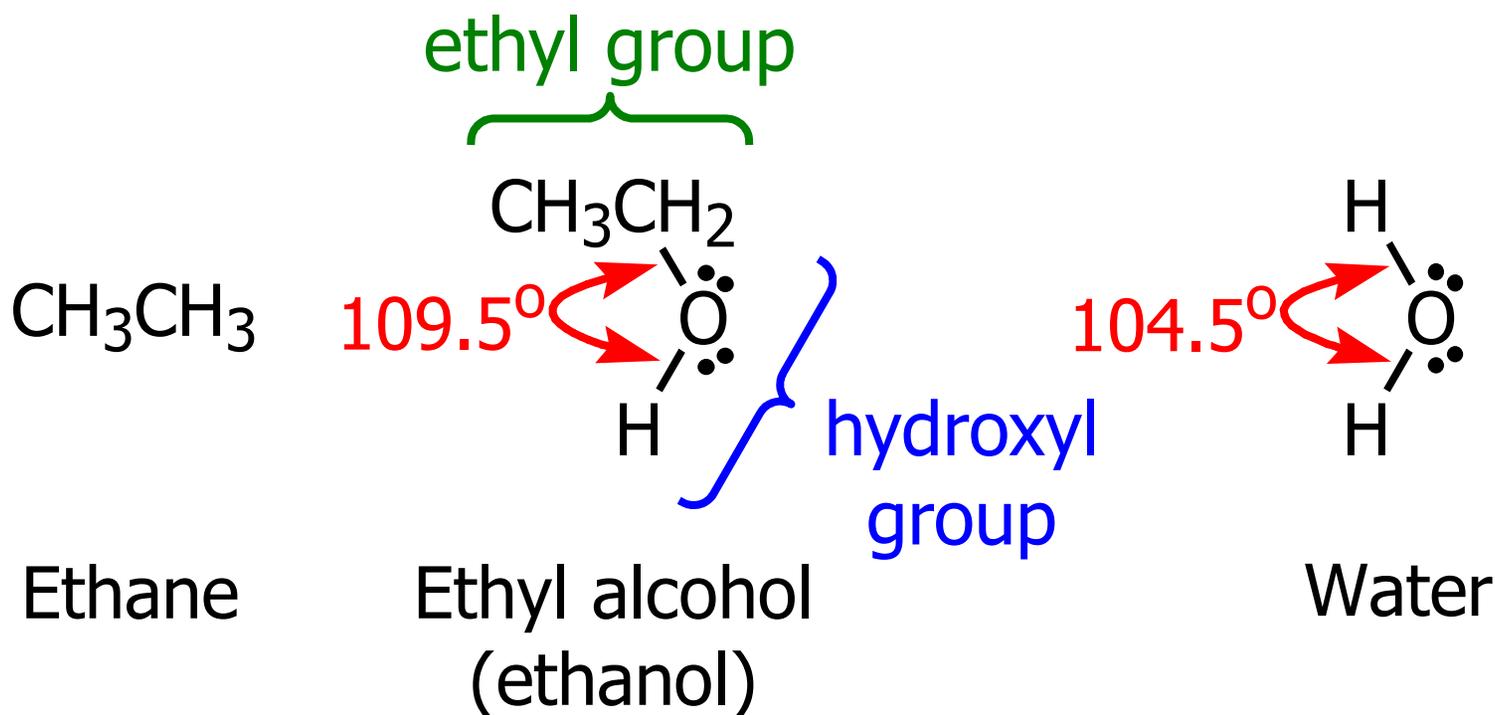
(3°)



(aromatic)
(phenol)

❖ Alcohols may be viewed structurally in two ways:

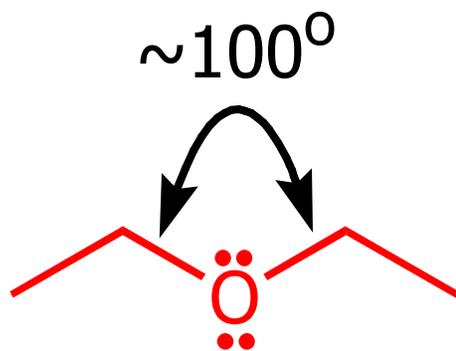
- As hydroxyl derivatives of alkanes
- As alkyl derivatives of water



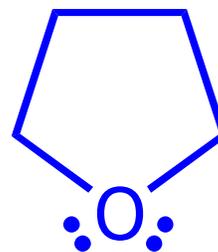
7. Ethers



- Examples



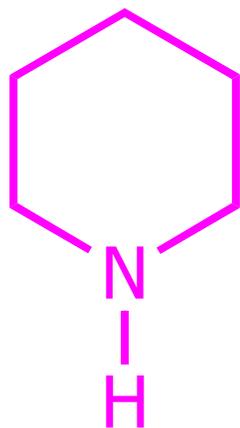
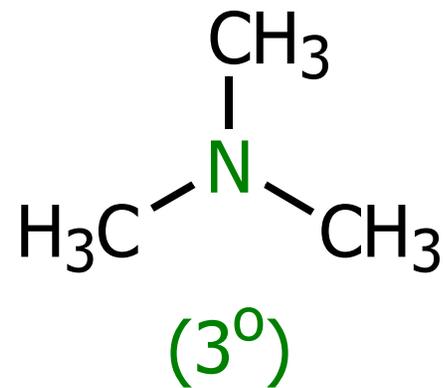
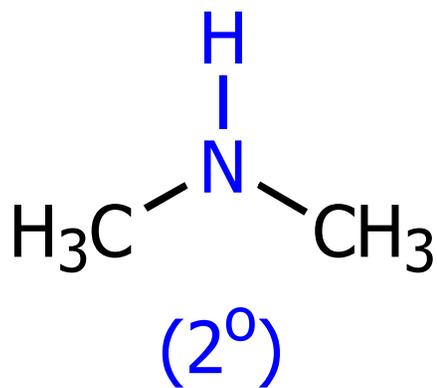
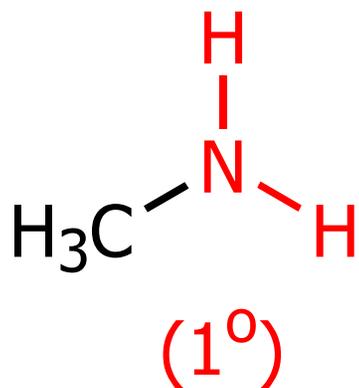
Acyclic



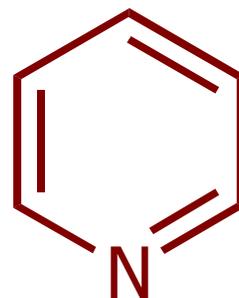
Cyclic

8. Amines

❖ R-NH₂

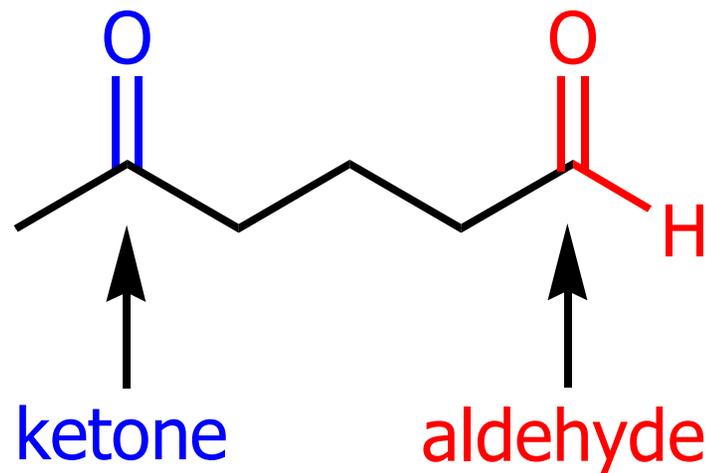
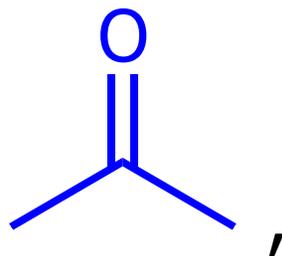
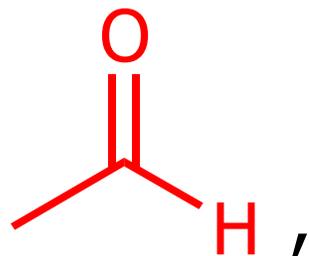
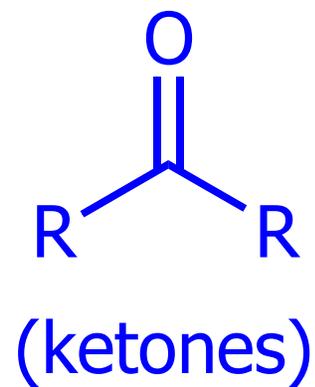
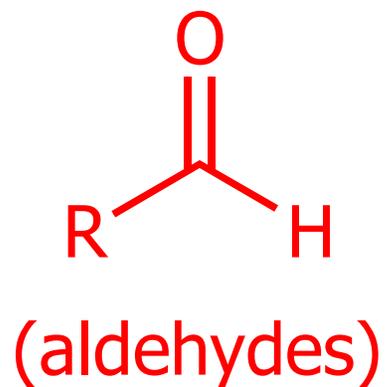


(cyclic)

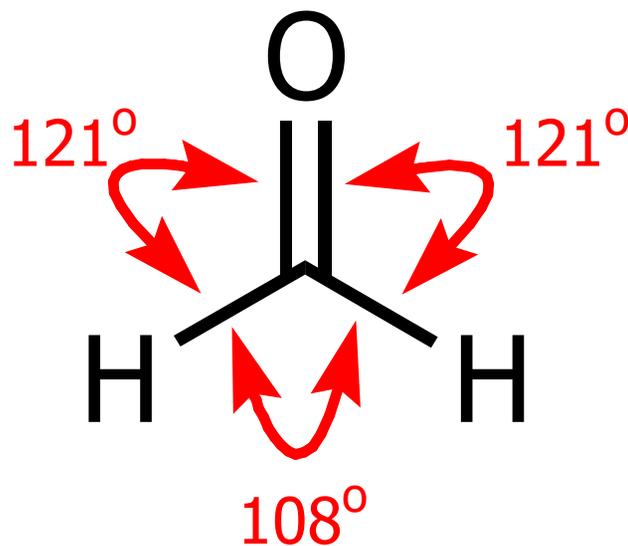


(aromatic)

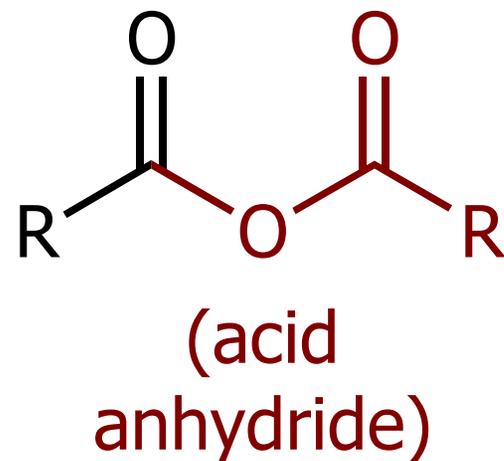
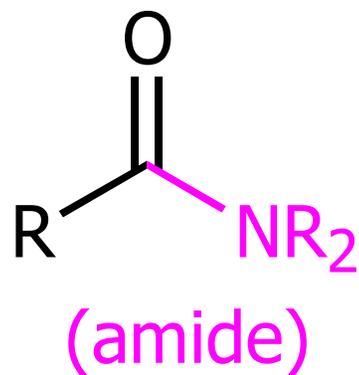
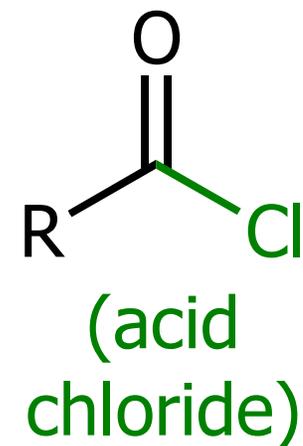
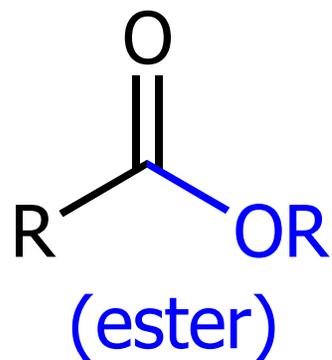
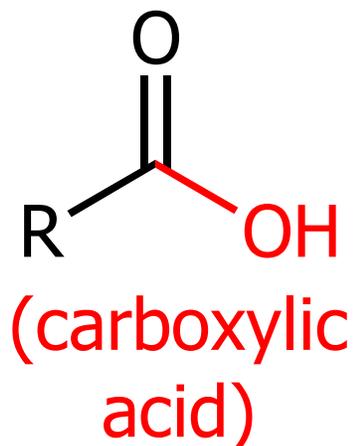
9. Aldehydes and Ketones



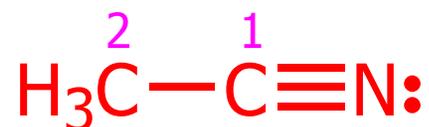
- ❖ Aldehydes and ketones have a trigonal planar arrangement of groups around the carbonyl carbon atom



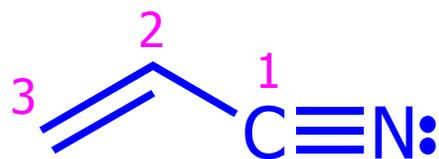
10. Carboxylic Acids, Esters, and Amides



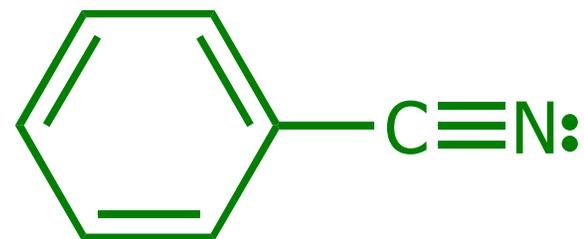
11. Nitriles



Ethanenitrile
(acetonitrile)



Propenenitrile
(acrylonitrile)



Benzenecarbonitrile
(benzonitrile)

12. Summary of Important Families of Organic Compounds

TABLE 2.3 Important Families of Organic Compounds

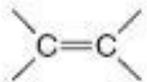
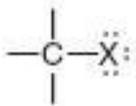
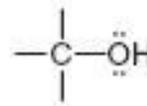
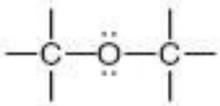
	Family						
	Alkane	Alkene	Alkyne	Aromatic	Haloalkane	Alcohol	Ether
Functional group	C—H and C—C bonds		$\text{—C}\equiv\text{C—}$	Aromatic ring			
General formula	RH	RCH=CH ₂ RCH=CHR R ₂ C=CHR R ₂ C=CR ₂	RC≡CH RC≡CR	ArH	RX	ROH	ROR
Specific example	CH ₃ CH ₃	CH ₂ =CH ₂	HC≡CH		CH ₃ CH ₂ Cl	CH ₃ CH ₂ OH	CH ₃ OCH ₃
IUPAC name	Ethane	Ethene	Ethyne	Benzene	Chloroethane	Ethanol	Methoxymethane
Common name ^a	Ethane	Ethylene	Acetylene	Benzene	Ethyl chloride	Ethyl alcohol	Dimethyl ether

TABLE 2.3

Important Families of Organic Compounds (cont.)

	Family						
	Amine	Aldehyde	Ketone	Carboxylic Acid	Ester	Amide	Nitrile
Functional group							
General formula	RNH ₂ R ₂ NH R ₃ N						RCN
Specific example	CH ₃ NH ₂						CH ₃ C≡N
IUPAC name	Methanamine	Ethanal	Propanone	Ethanoic acid	Methyl ethanoate	Ethanamide	Ethanenitrile
Common name	Methylamine	Acetaldehyde	Acetone	Acetic acid	Methyl acetate	Acetamide	Acetonitrile

13. Physical Properties and Molecular Structure

13A. Ionic Compounds: Ion-Ion Forces

- ❖ The **melting point** of a substance is the temperature at which an equilibrium exists between the well-ordered crystalline state and the more random liquid state

- ❖ If the substance is an ionic compound, the **ion–ion forces** that hold the ions together in the crystalline state are the strong electrostatic lattice forces that act between the positive and negative ions in the orderly crystalline structure
- ❖ A large amount of thermal energy is required to break up the orderly structure of the crystal into the disorderly open structure of a liquid

- ❖ The **boiling points** of ionic compounds are higher still, so high that most ionic organic compounds decompose before they boil

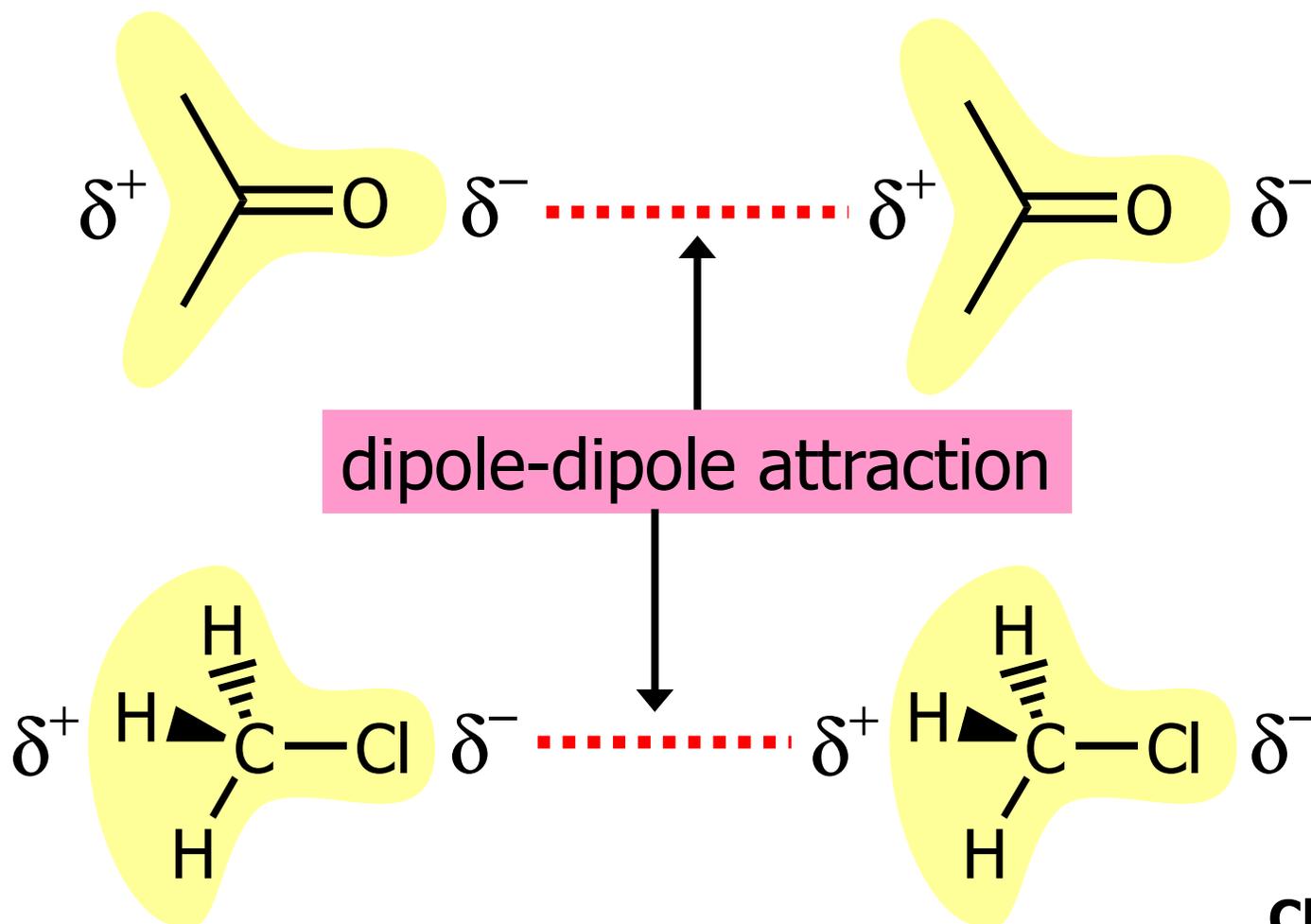
❖ Physical properties of selected compounds

Compound	Structure	mp (°C)	bp (°C) (1 atm)
Ethane	CH ₃ CH ₃	-172	-88.2
Chloroethane	CH ₃ CH ₂ Cl	-138.7	13.1
Ethyl alcohol	CH ₃ CH ₂ OH	-114	78.5
Acetaldehyde	CH ₃ CHO	-121	20
Acetic acid	CH ₃ CO ₂ H	16.6	118
Sodium acetate	CH ₃ CO ₂ Na	324	dec

13B. Intermolecular Forces (van der Waals Forces)

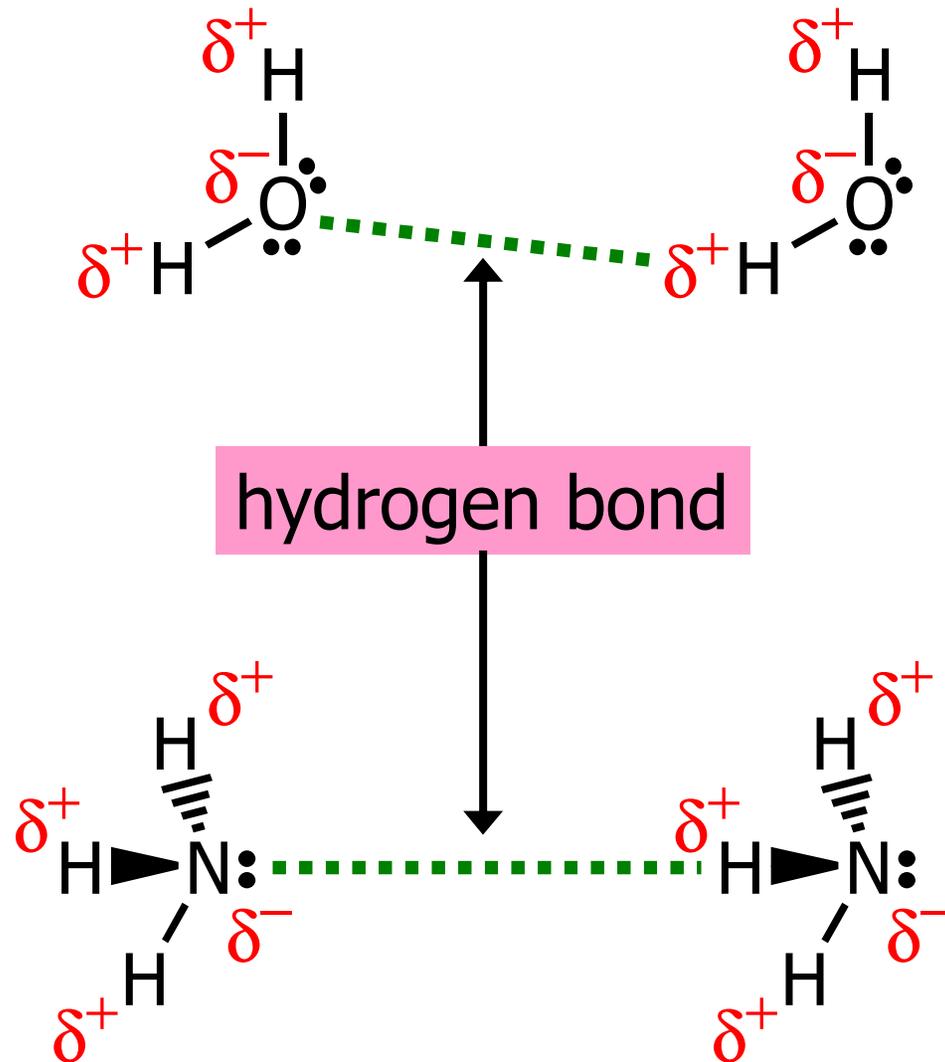
- ❖ The forces that act between molecules are not as strong as those between ions
- ❖ These intermolecular forces, **van der Waals forces**, are all electrical in nature
 - **Dipole-dipole forces**
 - **Hydrogen bonds**
 - **Dispersion forces**

- **Dipole-dipole forces**
 - ◆ Dipole-dipole attractions between polar molecules



- **Hydrogen bonds**
 - ◆ Dipole-dipole attractions between hydrogen atoms bonded to small, strongly electronegative atoms (O, N, or F) and nonbonding electron pairs on other such electronegative atoms
 - ◆ Hydrogen bonds (bond dissociation energies of about $4 - 38 \text{ kJ mol}^{-1}$) are weaker than ordinary covalent bonds but much stronger than the dipole–dipole interactions

- Hydrogen bonds



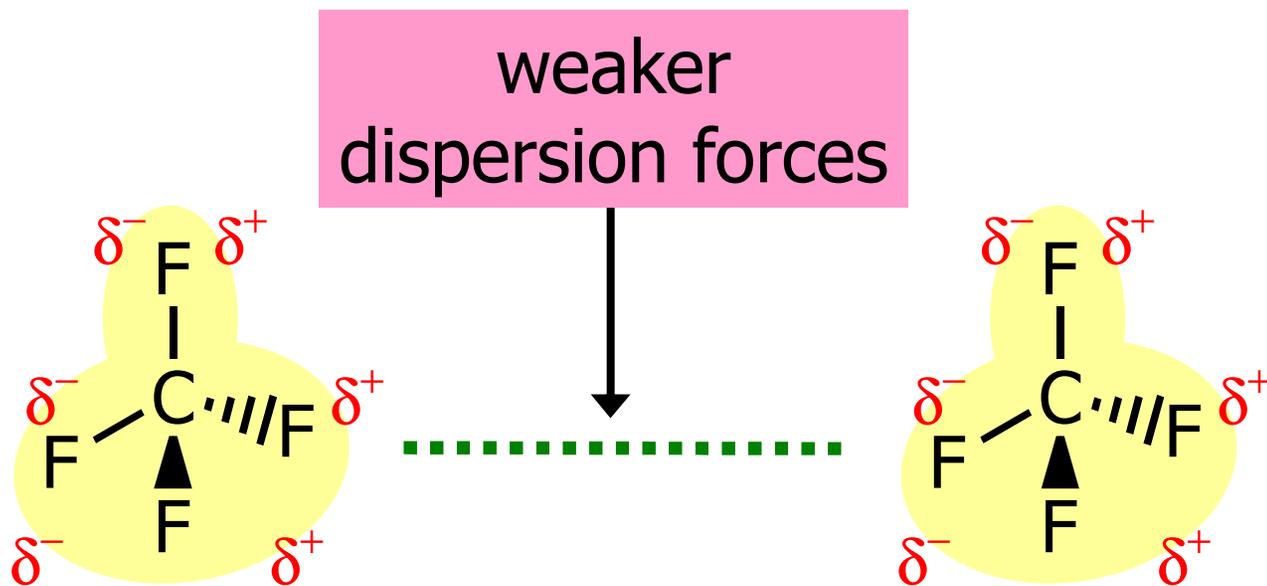
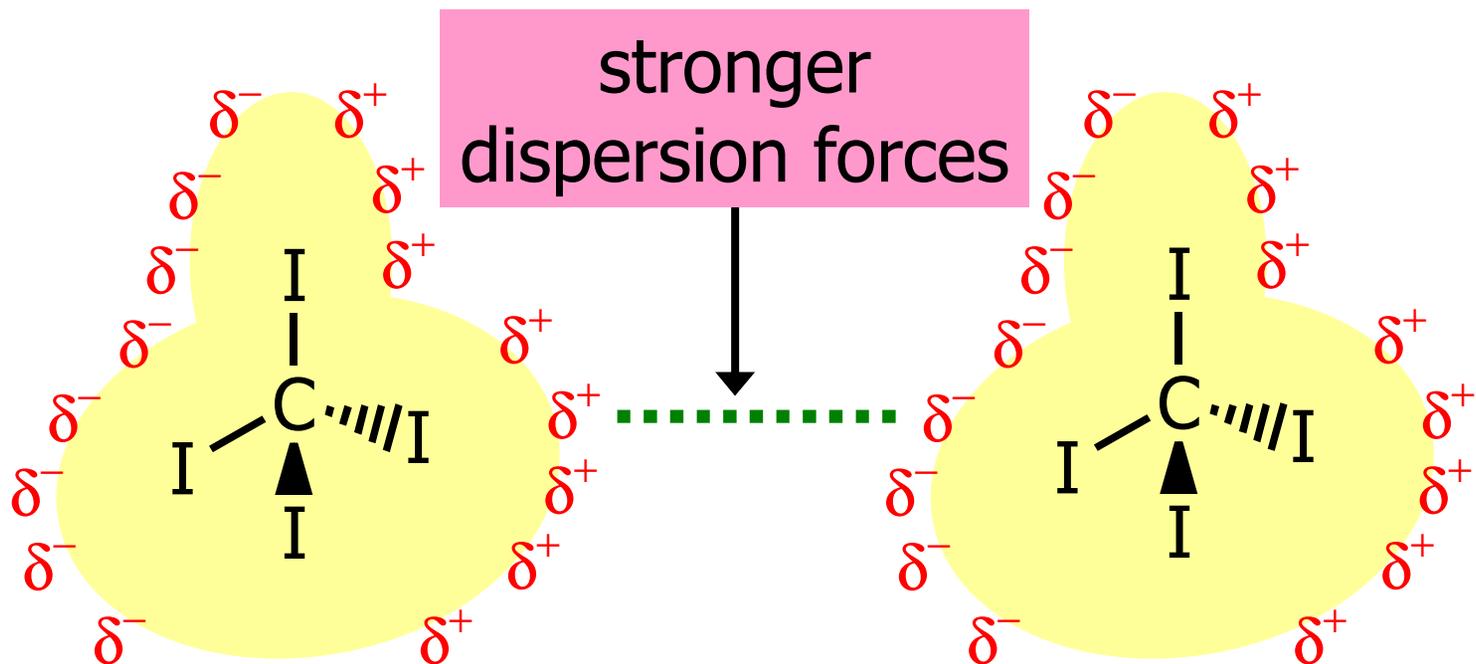
- **Hydrogen bonds**
 - ◆ Hydrogen bonding explains why water, ammonia, and hydrogen fluoride all have far higher boiling points than methane (bp -161.6°C), even though all four compounds have similar molecular weights
 - ◆ One of the most important consequences of hydrogen bonding is that it causes water to be a liquid rather than a gas at 25°C

- **Hydrogen bonds**
 - ◆ Calculations indicate that in the absence of hydrogen bonding, water would have a bp near -80°C and would not exist as a liquid unless the temperature were lower than that temperature

- Dispersion forces (London forces)
 - ◆ The average distribution of charge in a nonpolar molecule over a period of time is uniform
 - ◆ At any given instant, however, because electrons move, the electrons and therefore the charge may not be uniformly distributed
 - ◆ Electrons may, in one instant, be slightly accumulated on one part of the molecule, and, as a consequence, *a small temporary dipole will occur*

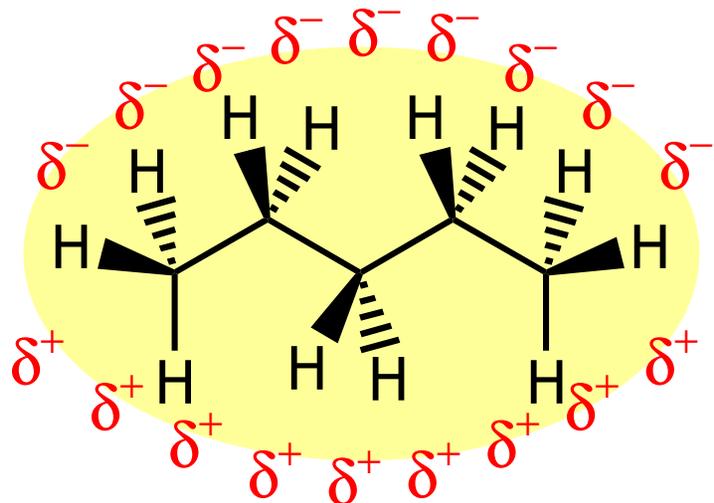
- Dispersion forces (London forces)
 - ◆ This temporary dipole in one molecule can induce opposite (attractive) dipoles in surrounding molecules
 - ◆ These temporary dipoles change constantly, but the net result of their existence is to produce attractive forces between nonpolar molecules

- Two important factors determine the magnitude of dispersion forces
 - ◆ *The relative polarizability of electrons of the atoms involved*
 - The electrons of large atoms such as iodine are loosely held and are easily polarized, while the electrons of small atoms such as fluorine are more tightly held and are much less polarizable

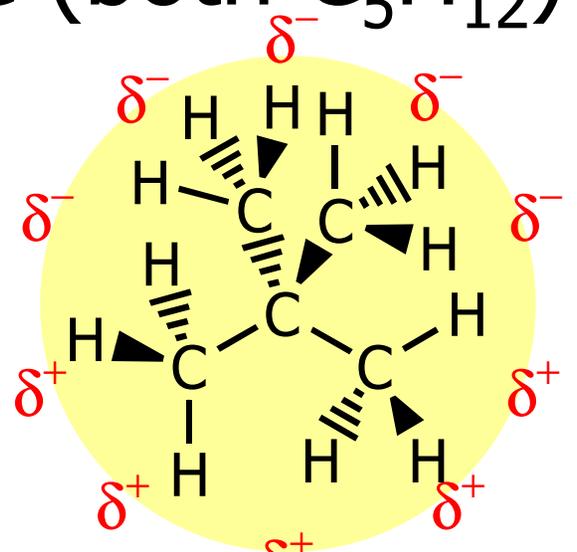


- ◆ *The relative surface area of the molecules involved*
 - The larger the surface area, the larger is the overall attraction between molecules caused by dispersion forces

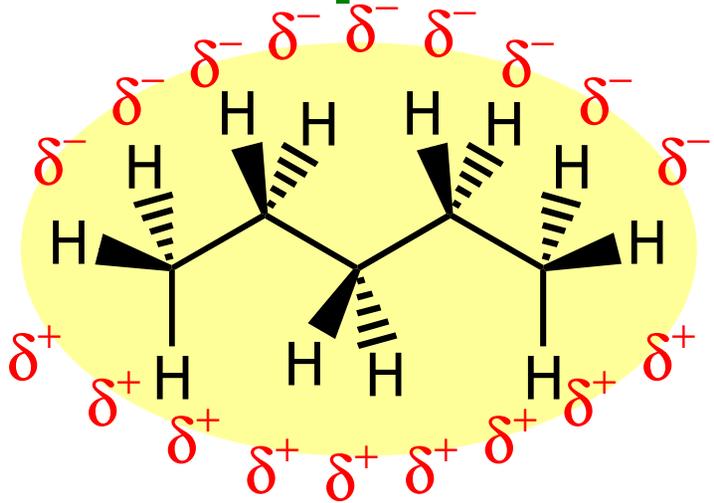
e.g. Pentane vs. Neopentane (both C_5H_{12})



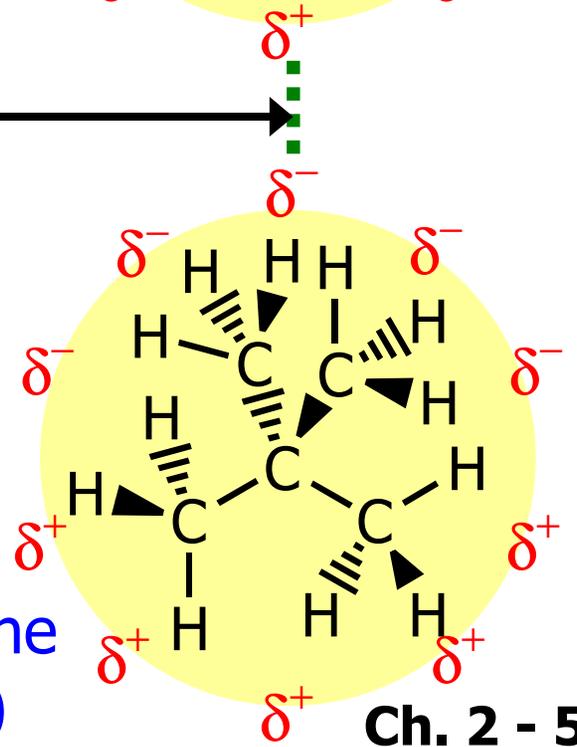
larger surface area
 \Rightarrow stronger dispersion forces



smaller surface area
 \Rightarrow weaker dispersion forces



Pentane (bp $36^\circ C$)

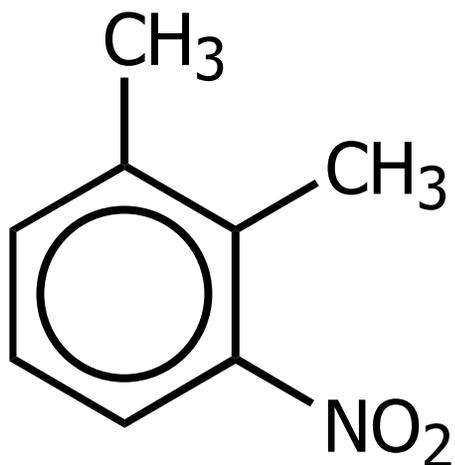


Neopentane (bp $9.5^\circ C$)

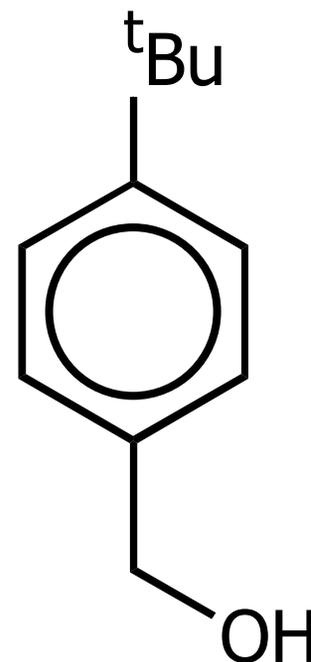
13C. Boiling Points

- ❖ The *boiling point* of a liquid is the temperature at which the vapor pressure of the liquid equals the pressure of the atmosphere above it
- ❖ the *boiling points* of liquids are *pressure dependent*, and boiling points are always reported as occurring at a particular pressure

❖ Examples



bp: 245°C / 760 mmHg
(74°C / 1 mmHg)



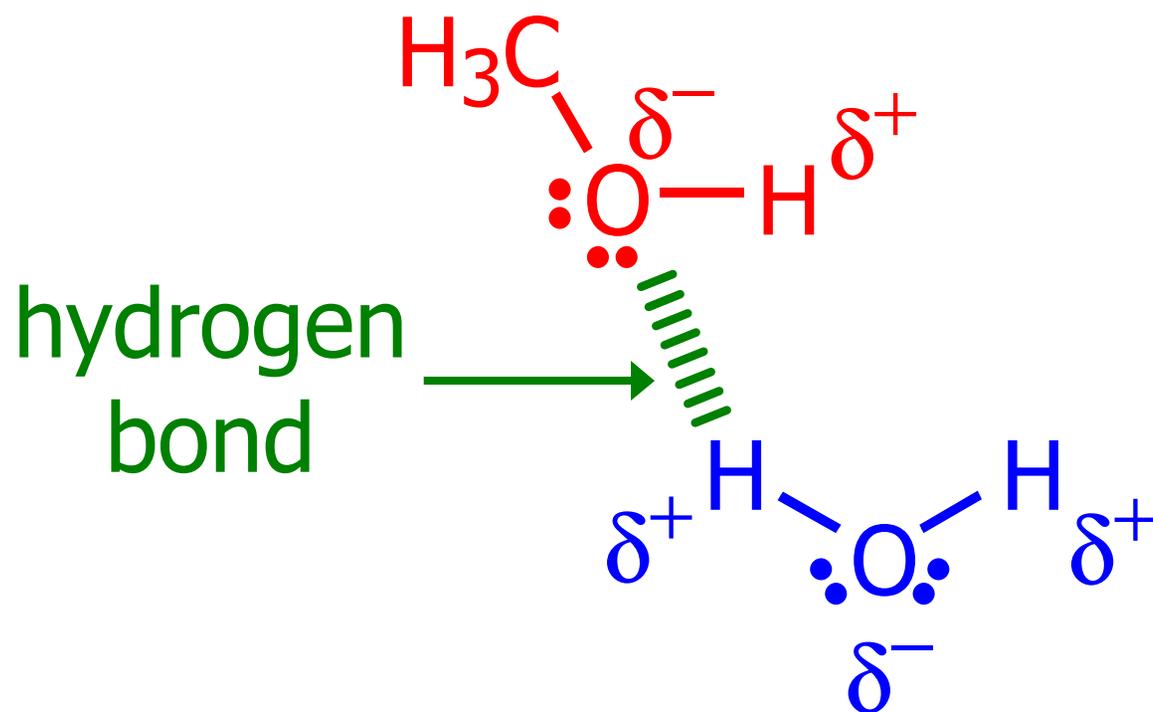
bp: 260°C / 760 mmHg
(140°C / 20 mmHg)

1 atm = 760 torr = 760 mmHg

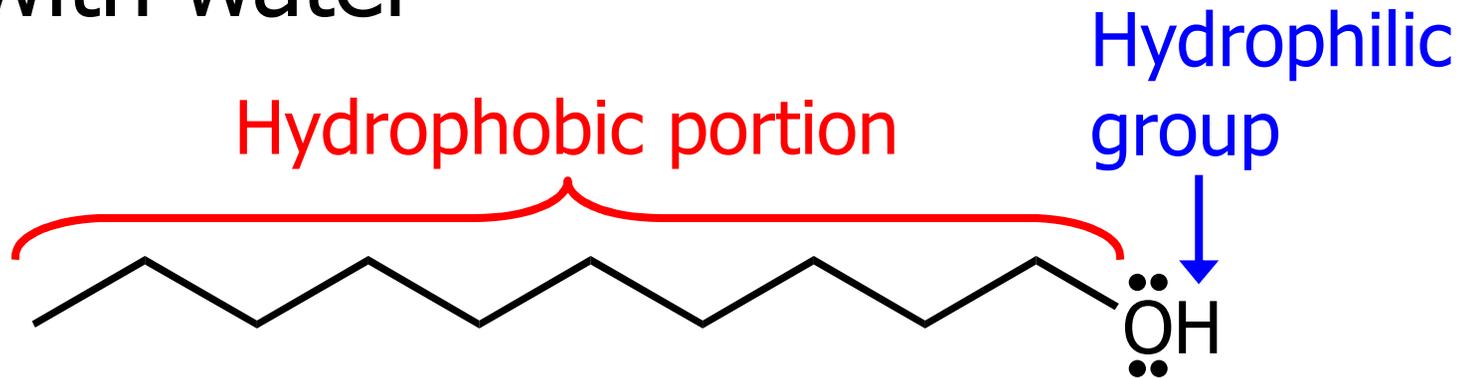
13D. Solubilities

- ❖ A general rule for solubility is that “like dissolves like” in terms of comparable polarities
 - Polar and ionic solids are usually soluble in polar solvents
 - Polar liquids are usually miscible
 - Nonpolar solids are usually soluble in nonpolar solvents
 - Nonpolar liquids are usually miscible
 - Polar and nonpolar liquids, like oil and water, are usually not soluble to large extents

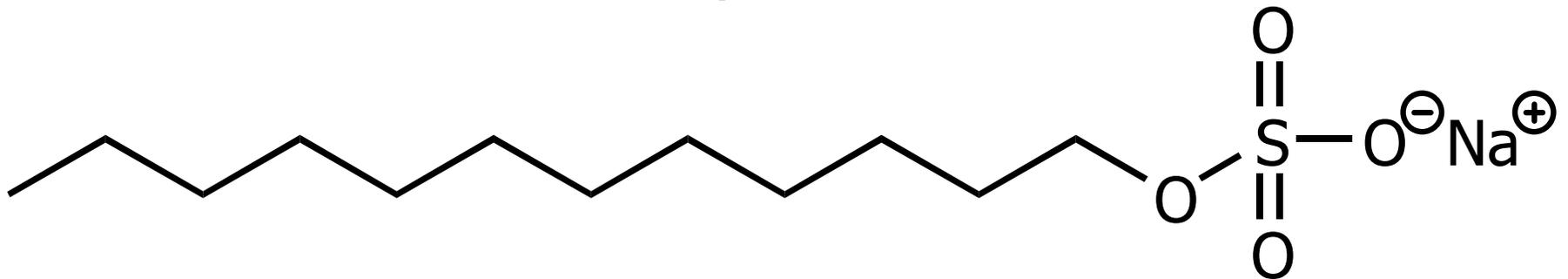
e.g. MeOH and H₂O are miscible in all proportions



- **Hydrophobic** means incompatible with water
- **Hydrophilic** means compatible with water



Decyl alcohol



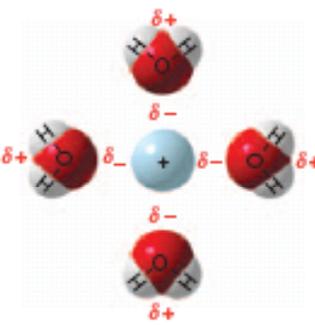
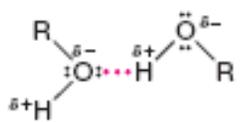
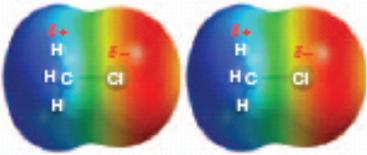
A typical detergent molecule

13E. Guidelines for Water Solubility

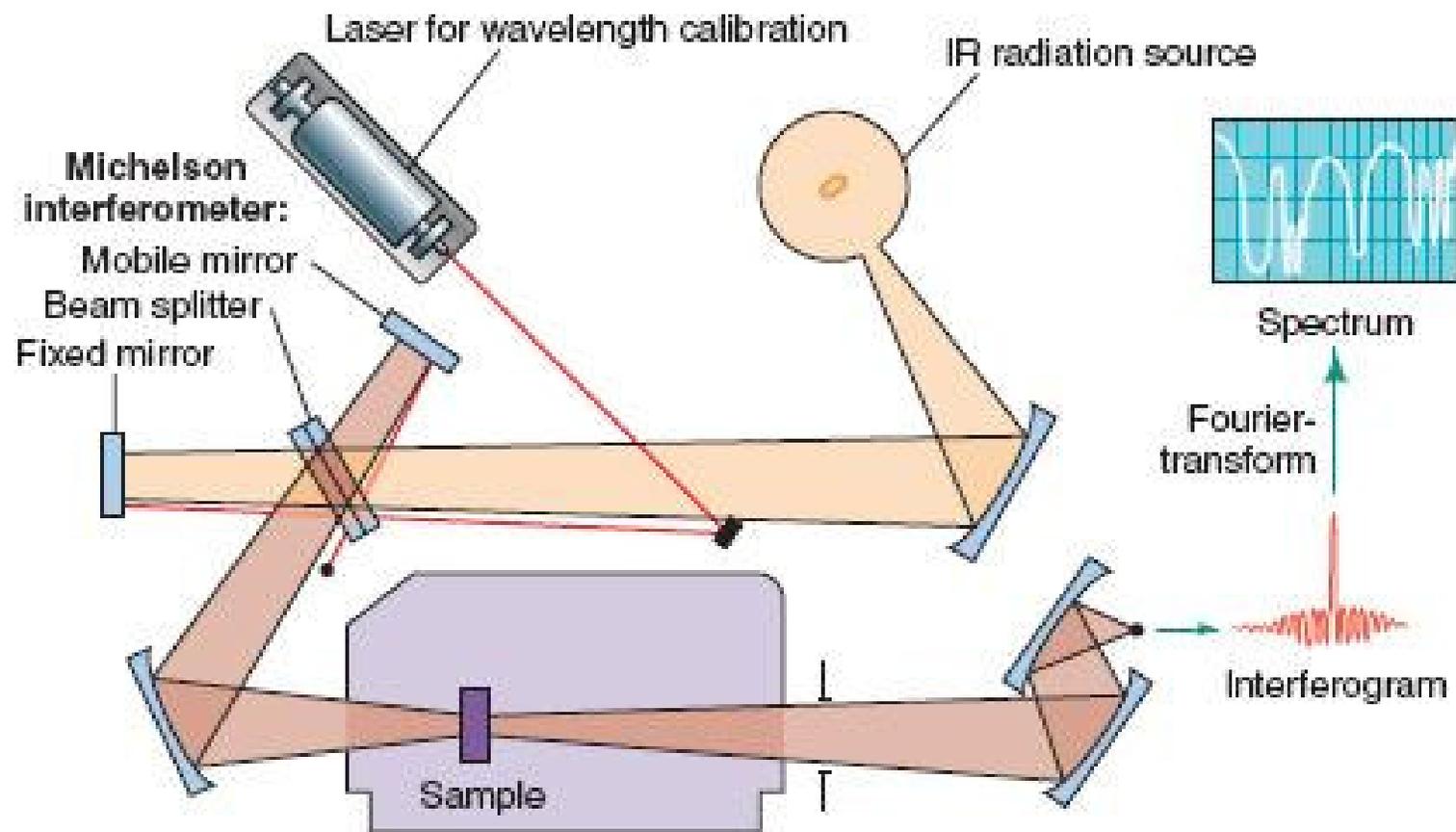
- ❖ Organic chemists usually define a compound as water soluble if at least 3 g of the organic compound dissolves in 100 mL of water
- ❖ Usually compounds with one to three carbon atoms are water soluble, compounds with four or five carbon atoms are borderline, and compounds with six carbon atoms or more are insoluble

14. Summary of Attractive Electric Forces

TABLE 2.6 Attractive Electric Forces

Electric Force	Relative Strength	Type	Example
Cation–anion (in a crystal)	Very strong		Sodium chloride crystal lattice
Covalent bonds	Strong (140–523 kJ mol ⁻¹)	Shared electron pairs	H–H (436 kJ mol ⁻¹) CH ₃ –CH ₃ (378 kJ mol ⁻¹) I–I (151 kJ mol ⁻¹)
Ion–dipole	Moderate		Na ⁺ in water (see Fig. 2.9)
Hydrogen bonds	Moderate to weak (4–38 kJ mol ⁻¹)	$\text{---}\overset{\delta-}{\text{Z}}\text{:}\cdots\overset{\delta+}{\text{H}}\text{---}$	
Dipole–dipole	Weak	$\overset{\delta+}{\text{CH}_3}\overset{\delta-}{\text{Cl}}\cdots\overset{\delta+}{\text{CH}_3}\overset{\delta-}{\text{Cl}}$	
Dispersion	Variable	Transient dipole	Interactions between methane molecules

15. Infrared Spectroscopy



- ❖ The position of an absorption band (peak) in an IR spectrum is specified in units of wavenumbers ($\bar{\nu}$)

$$\bar{\nu} = \frac{1}{\lambda}$$

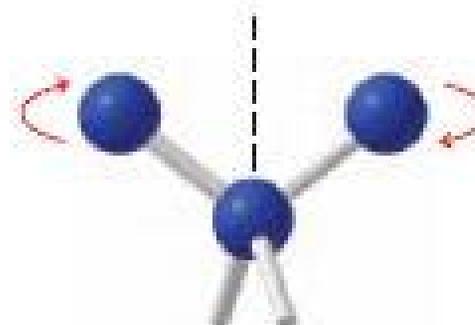
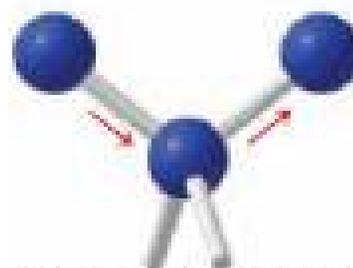
$$\begin{aligned} \therefore \Delta E &= h\nu \\ \therefore E &\propto \nu \end{aligned}$$

(λ = wavelength in cm)

(E = energy)

(ν = frequency of radiation)

$$\begin{aligned} \therefore \nu &= \frac{c}{\lambda} \\ \therefore \Delta E &= \frac{hc}{\lambda} \end{aligned}$$



❖ Characteristic IR absorptions

Intensity: s = strong, m = medium, w = weak, v = variable

Group	Freq. Range (cm ⁻¹)	Intensity
Alkyl		
C–H (stretching)	2853–2962	(m–s)
Alkenyl		
C–H (stretching)	3010–3095	(m)
C=H (stretching)	1620–1680	(v)
<i>cis</i> -RCH=CHR	675–730	(s)
<i>trans</i> -RCH=CHR	960–975	(s)
Alkynyl		
≡C–H (stretching)	~3300	(s)
C≡C (stretching)	2100–2260	(v)

❖ Characteristic IR absorptions

Intensity: s = strong, m = medium, w = weak, v = variable

Group	Freq. Range (cm ⁻¹)	Intensity
Aromatic		
Ar-H (stretching)	~3300	(v)
- monosubstituted	690–710	(very s)
	730–770	(very s)
- o-disubstituted	735–770	(s)
- m-disubstituted	680–725	(s)
	750–810	(very s)
- p-disubstituted	800–860	(very s)

❖ Characteristic IR absorptions

Intensity: s = strong, m = medium, w = weak, v = variable

Group	Freq. Range (cm ⁻¹)	Intensity
Alcohols, Phenols & Carboxylic Acids		
O–H (stretching)		
- alcohols & phenols (<i>dilute solutions</i>)	3590–3650	(sharp, v)
- alcohols & phenols (<i>hydrogen bonded</i>)	3200–3550	(broad, s)
- carboxylic acids (<i>hydrogen bonded</i>)	2500–3000	(broad, v)

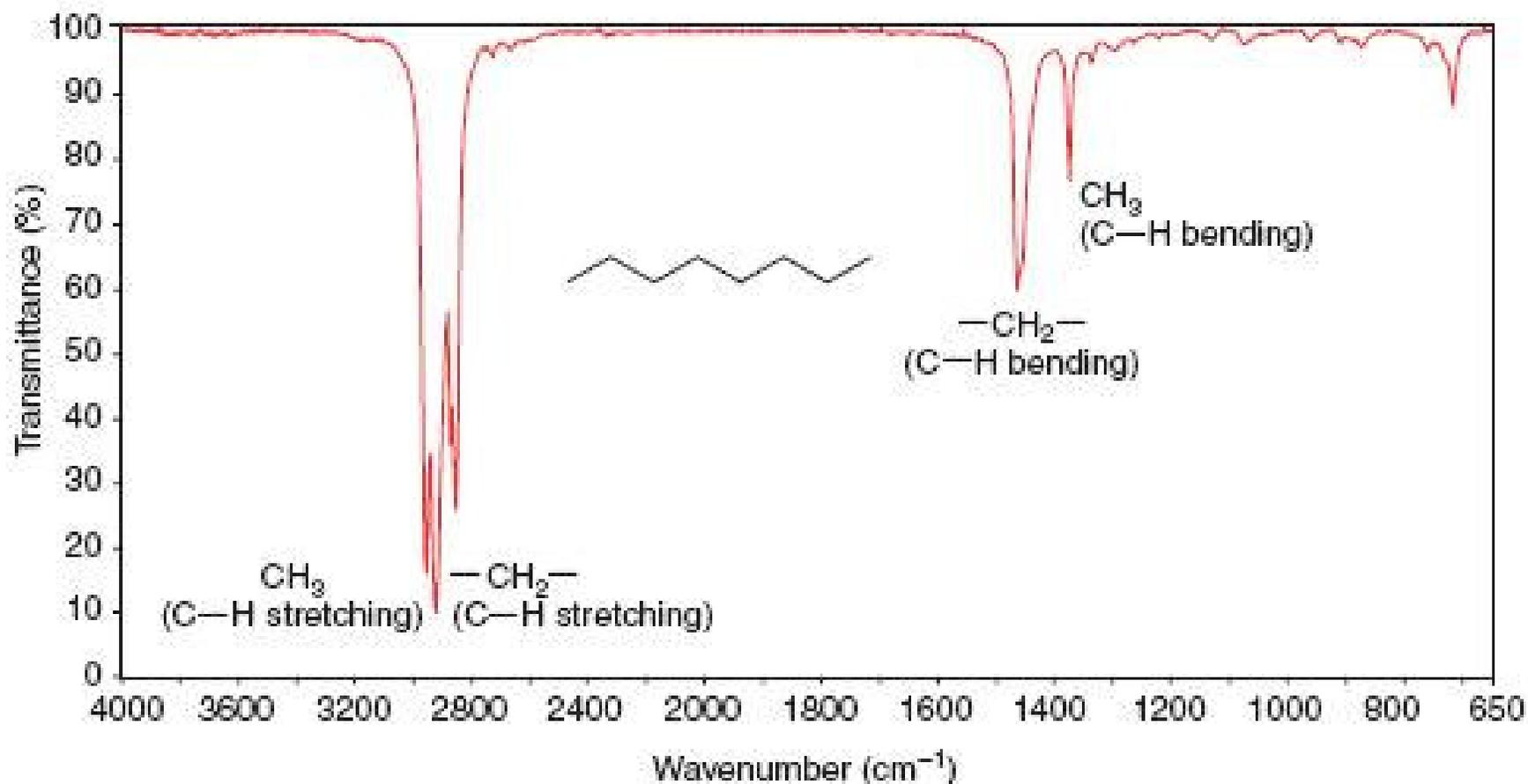
❖ Characteristic IR absorptions

Intensity: s = strong, m = medium, w = weak, v = variable

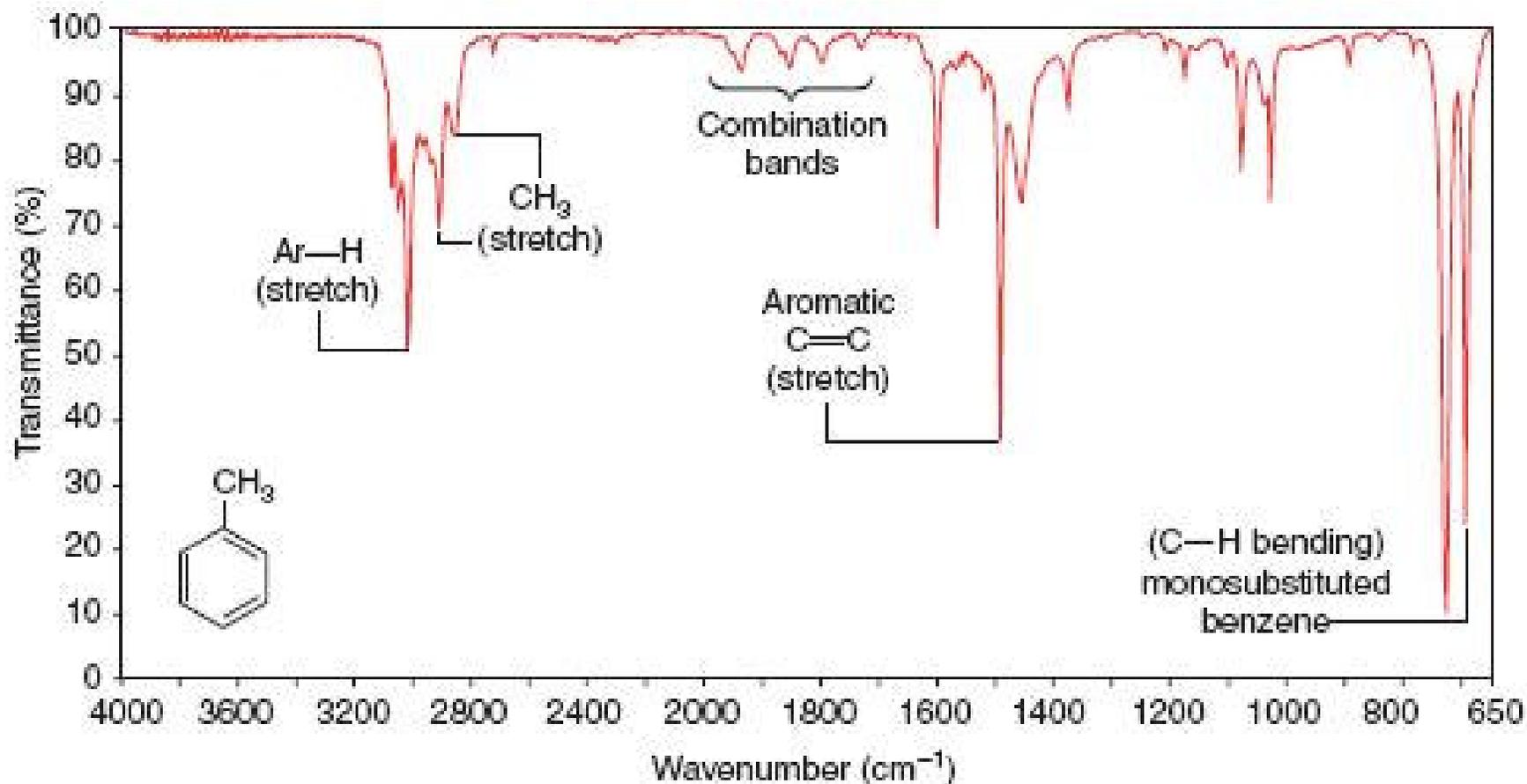
Group	Freq. Range (cm ⁻¹)	Intensity
Aldehydes, Ketones, Esters, Carboxylic Acids, Amides		
C=O (stretching)	1630–1780	(s)
Aldehydes	1690–1740	(s)
Ketones	1680–1750	(s)
Esters	1735–1750	(s)
Carboxylic Acids	1710–1780	(s)
Amides	1630–1690	(s)
Amines		
N–H	3300–3500	(m)
Nitriles		
C≡N	2220–2260	(m)

16. Interpreting IR Spectra

❖ IR spectrum of octane

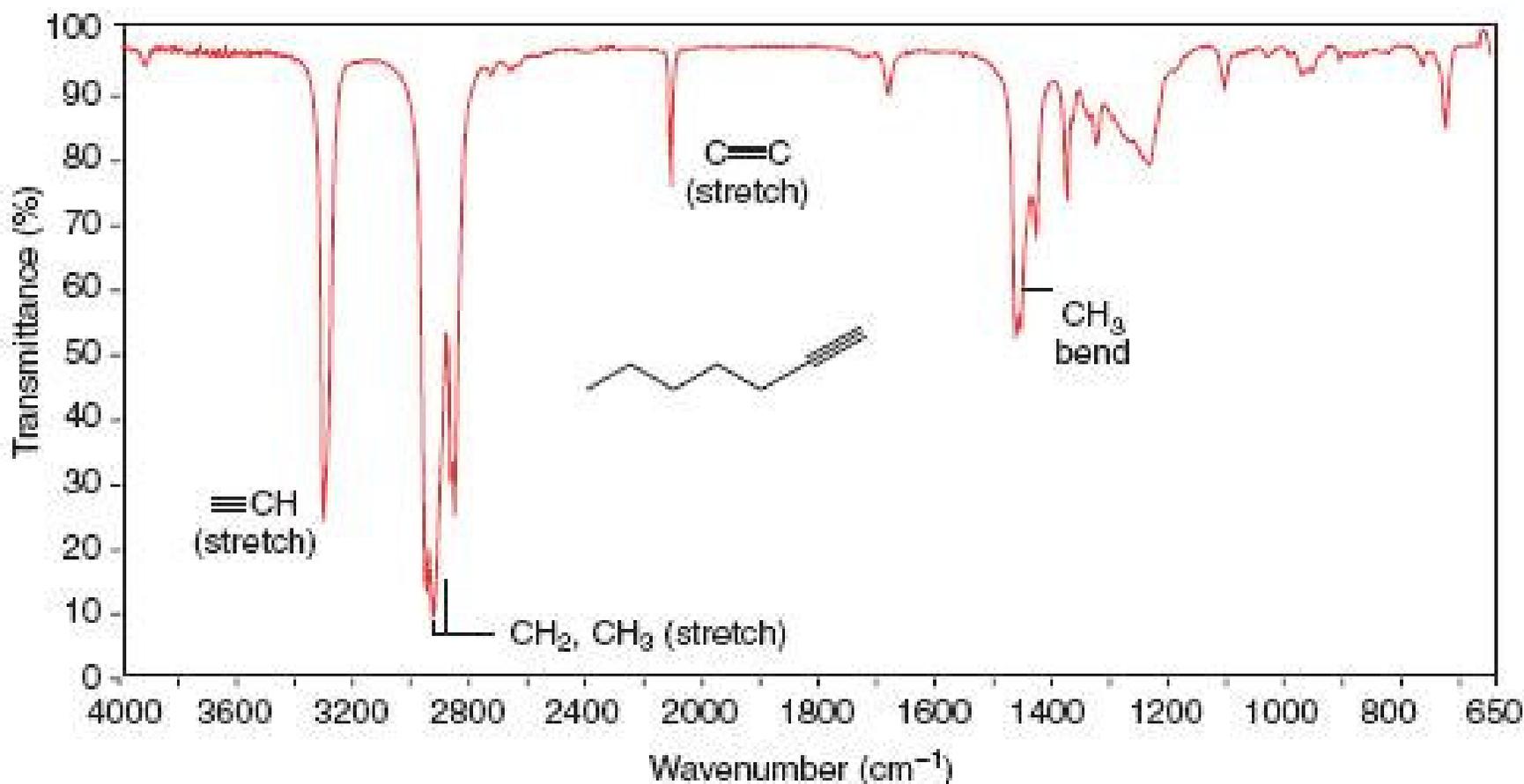


❖ IR spectrum of toluene

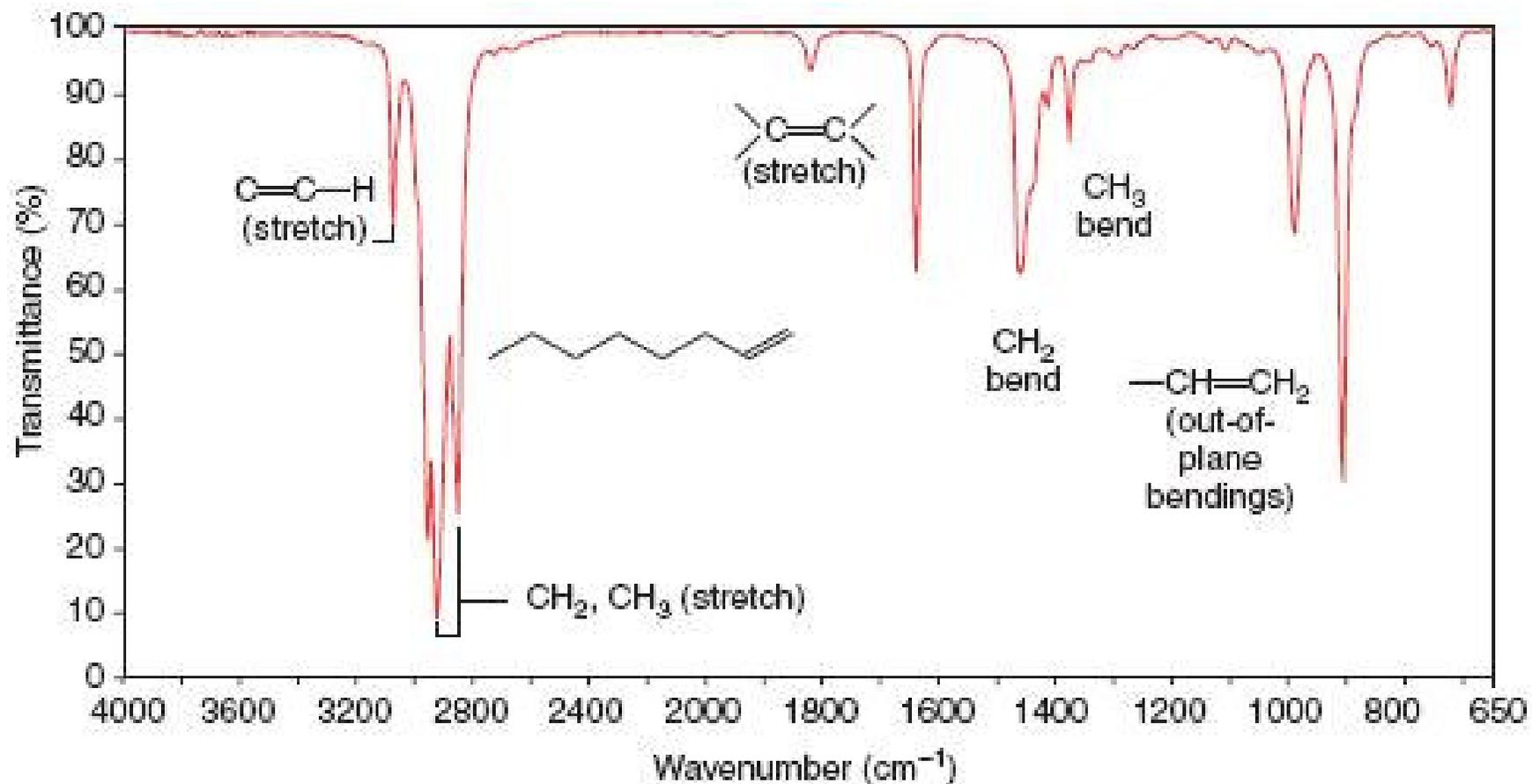


16B. IR Spectra of Hydrocarbons

❖ IR spectrum of 1-heptyne

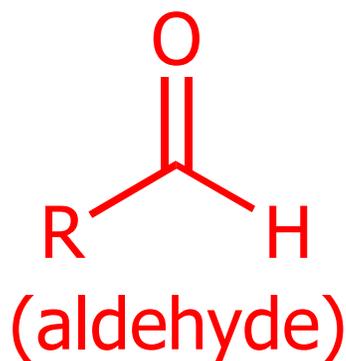


❖ IR spectrum of 1-octene

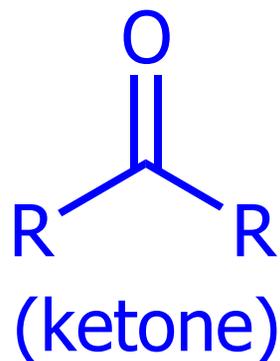


16B. IR Spectra of Some Functional Groups Containing

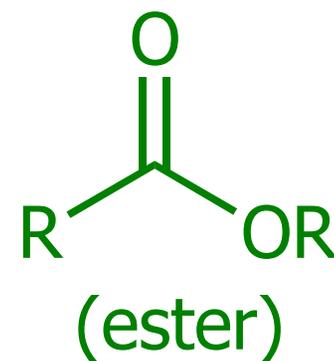
❖ Carbonyl Functional Groups



1690-1740 cm^{-1}



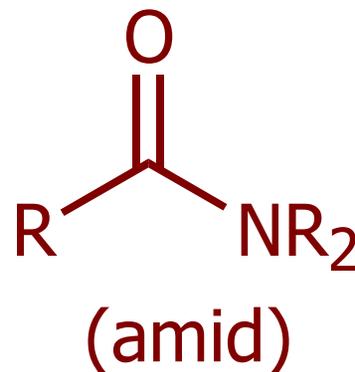
1680-1750 cm^{-1}



1735-1750 cm^{-1}



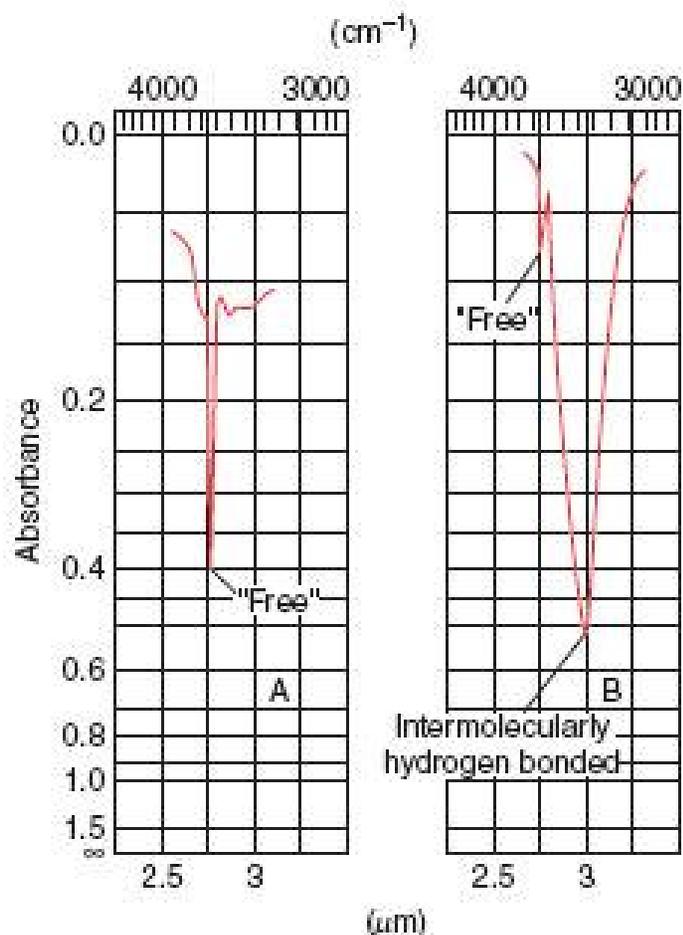
1710-1780 cm^{-1}



1630-1690 cm^{-1}

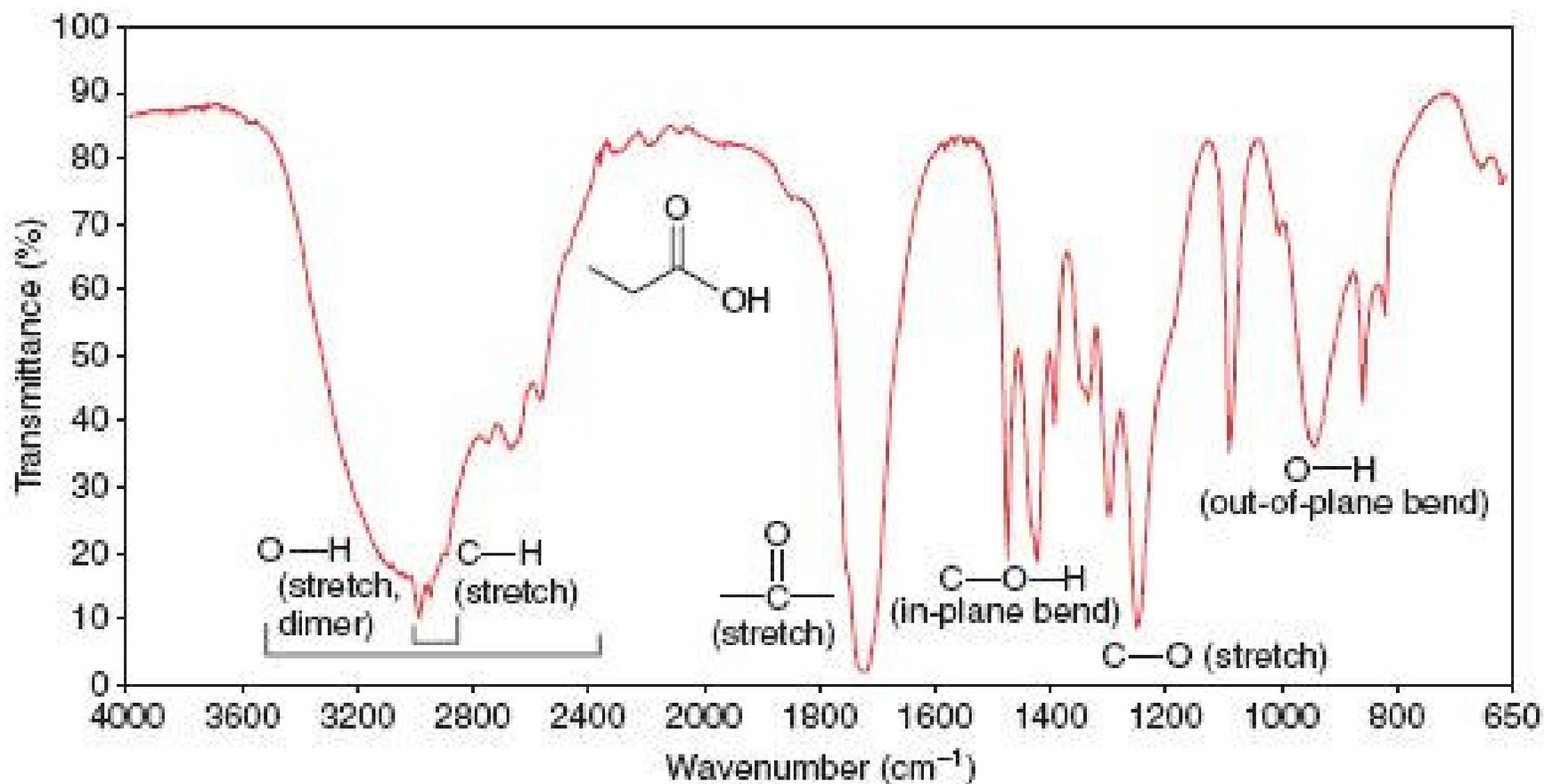
❖ Alcohols and phenols

- The IR absorption of an alcohol or phenol O–H group is in the 3200–3550 cm^{-1} range, and most often it is broad



❖ Carboxylic Acids

- IR spectrum of propanoic acid

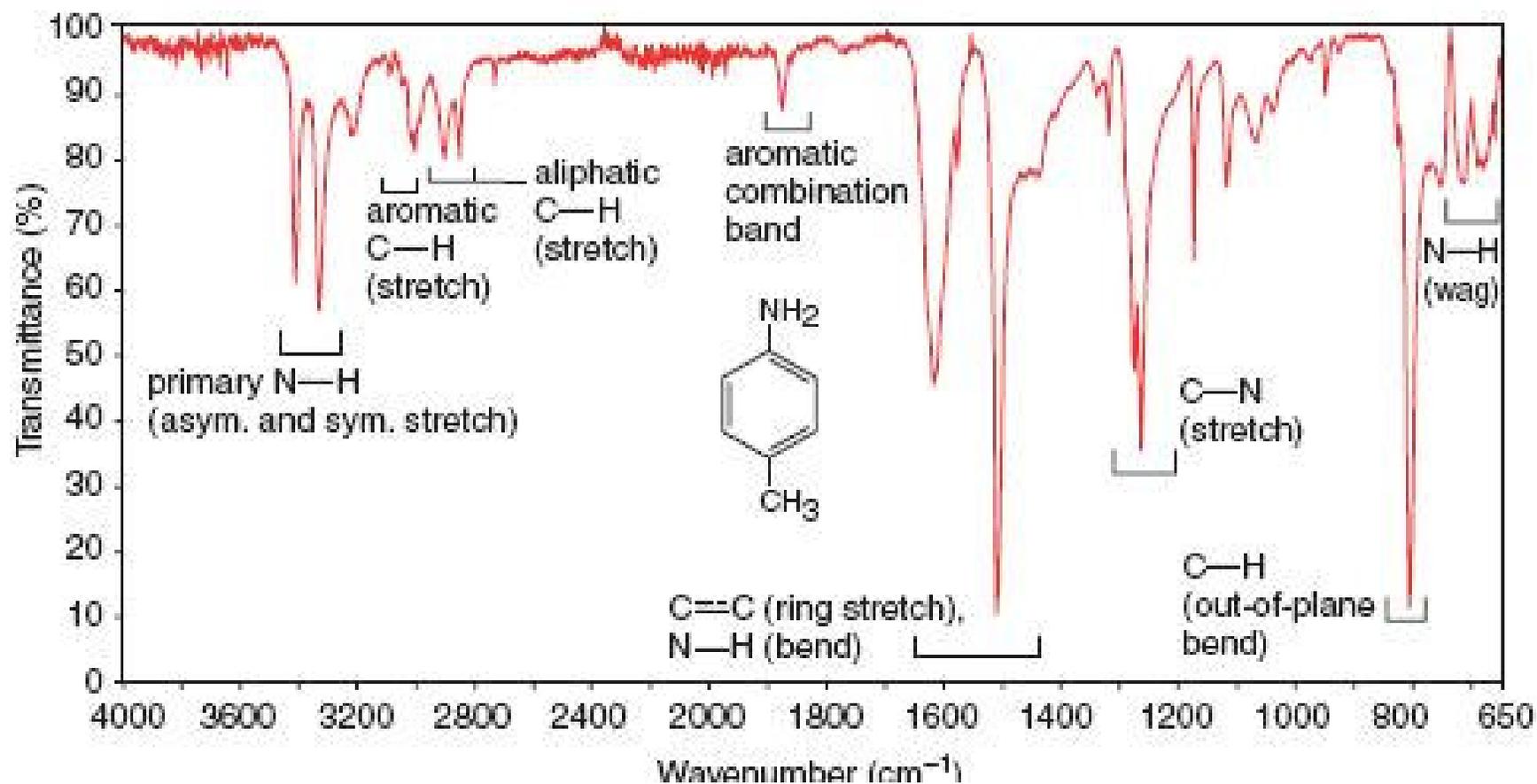


❖ Amines

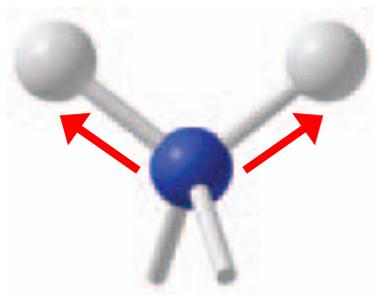
- 1° and 2° amines give absorptions of moderate strength in the 3300–3500 cm^{-1} region
- 1° amines exhibit two peaks in this region due to symmetric & asymmetric stretching of the two N–H bonds
- 2° amines exhibit a single peak
- 3° amines show no N–H absorption because they have no such bond
- A basic pH is evidence for any class of amines

❖ Amines

● IR spectrum of 4-methylaniline

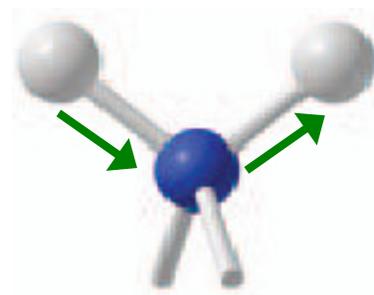


RNH_2 (1° Amine)
Two peaks in
 $3300\text{--}3500\text{ cm}^{-1}$
region

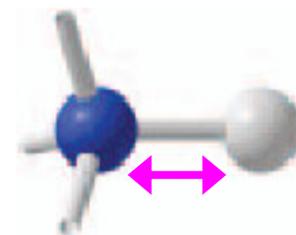


symmetric
stretching

R_2NH (2° Amine)
One peak in
 $3300\text{--}3500\text{ cm}^{-1}$
region



asymmetric
stretching



 **END OF CHAPTER 2** 