Chapter 2
Representative Carbon Compounds: Functional Groups, Intermolecular Forces and Infrared (IR) Spectroscopy
♦ Carbon-carbon Covalent Bonds

- Carbon forms strong covalent bonds to other carbons and to other elements such as hydrogen, oxygen, nitrogen and sulfur
  ➔ This accounts for the vast variety of organic compounds possible
- Organic compounds are grouped into functional group families
  ➔ A functional group is a specific grouping of atoms (e.g. carbon-carbon double bonds are in the family of alkenes)
  ➔ An instrumental technique called infrared (IR) spectroscopy is used to determine the presence of specific functional groups
Hydrocarbons: Representative Alkanes, Alkenes, Alkynes, and Aromatic Compounds

- Hydrocarbons contain only carbon and hydrogen atoms
- Subgroups of Hydrocarbons:
  - Alkanes contain only carbon-carbon single bonds
  - Alkenes contain one or more carbon-carbon double bonds
  - Alkynes contain one or more carbon-carbon triple bonds
  - Aromatic hydrocarbons contain benzene-like stable structures (discussed later)
- Saturated hydrocarbons: contain only carbon-carbon single bonds e.g. alkanes
- Unsaturated hydrocarbons: contain double or triple carbon-carbon bonds e.g. alkene, alkynes, aromatics
  - Contain fewer than maximum number of hydrogens per carbon
  - Capable of reacting with $H_2$ to become saturated
Representative Hydrocarbons

- Alkanes
  - Principle sources of alkanes are natural gas and petroleum
    - Smaller alkanes (C<sub>1</sub> to C<sub>4</sub>) are gases at room temperature
  - Methane is
    - A component of the atmosphere of many planets
    - Major component of natural gas
    - Produced by primitive organisms called methanogens found in mud, sewage and cows’ stomachs
Alkenes

- **Ethene (ethylene) is a major industrial feedstock**
  - Used in the production of ethanol, ethylene oxide and the polymer polyethylene

- **Propene (propylene) is also very important in industry**
  - Molecular formula C₃H₆
  - Used to make the polymer polypropylene and is the starting material for acetone

- **Many alkenes occur naturally**
Alkynes

- Ethyne (acetylene) is used in welding torches because it burns at high temperature

Many alkynes are of biological interest

- Capillin is an antifungal agent found naturally
- Dactylyne is a marine natural product
- Ethinyl estradiol is a synthetic estrogen used in oral contraceptives
Benzene: A Representative Hydrocarbon

Benzene is the prototypical aromatic compound

- The Kekulé structure (named after August Kekulé who formulated it) is a six-membered ring with alternating double and single bonds

\[
\begin{align*}
&\text{H} \quad \text{C} = \text{C} \quad \text{H} \\
&\text{H} \quad \text{C} = \text{C} \quad \text{H} \\
&\text{H} \quad \text{C} = \text{C} \quad \text{H} \\
&\text{H} \quad \text{C} = \text{C} \quad \text{H} \\
\end{align*}
\]

Kekulé structure for benzene

or

Bond-line representation of Kekulé structure

Benzene does not actually have discreet single and double carbon-carbon bonds

- All carbon-carbon bonds are exactly equal in length (1.38 Å)
- This is between the length of a carbon-carbon single bond and a carbon-carbon double bond

Resonance theory explains this by suggesting there are two resonance hybrids that contribute equally to the real structure

- The real structure is often depicted as a hexagon with a circle in the middle

\[
\begin{align*}
&\text{Two contributing Kekulé structures for benzene} \\
&\text{A representation of the resonance hybrid}
\end{align*}
\]
Molecular orbital theory explains the equal bond lengths of benzene by suggesting there in a continuous overlap of \( p \) orbitals over the entire ring.

- All carbons in benzene are \( sp^2 \) hybridized.
- Each carbon also has a \( p \) orbital.
- Each \( p \) orbital does not just overlap with one adjacent \( p \) but overlaps with \( p \) orbitals on either side to give a continuous bonding molecular orbital that encompasses all 6 carbons.
- All 6 \( \pi \) electrons are therefore delocalized over the entire ring and this results in the equivalence of all of the carbon-carbon bonds.
Polar Covalent Bonds

- Polar covalent bonds occur when a covalent bond is formed between two atoms of differing electronegativities
  - The more electronegative atom draws electron density closer to itself
  - The more electronegative atom develops a partial negative charge ($\delta^-$) and the less electronegative atom develops a partial positive charge ($\delta^+$)
  - A bond which is polarized is a dipole and has a dipole moment
  - The direction of the dipole can be indicated by a dipole arrow
    - The arrow head is the negative end of a dipole, the crossed end is the positive end

(positive end) $\longleftrightarrow$ (negative end)
• Example: the molecule HCl
  ➔ The more electronegative chlorine draws electron density away from the hydrogen
    ➔ Chlorine develops a partial negative charge

\[ \delta^+ \quad \delta^- \]

\[ \text{H : } \overset{\delta^-}{\text{Cl}} : \quad \text{H} \rightarrow \text{Cl} \]

• The dipole moment of a molecule can be measured experimentally
  ➔ It is the product of the magnitude of the charges (in electrostatic units: esu) and the distance between the charges (in cm)
  ➔ The actual unit of measurement is a Debye (D) which is equivalent to \( 1 \times 10^{-18} \) esu cm

\[ \text{Dipole moment} = \text{charge (in esu)} \times \text{distance (in cm)} \]

\[ \mu = e \times d \]
A map of electrostatic potential (MEP) is a way to visualize distribution of charge in a molecule

- Parts of the molecule which are red have relatively more electron density or are negative
  - These regions would tend to attract positively charged species

- Parts of the molecule which are blue have relatively less electron density or are positive
  - These regions would tend to attract negatively charged species

- The MEP is plotted at the van Der Waals surface of a molecule
  - This is the farthest extent of a molecule’s electron cloud and therefore indicates the shape of the molecule

- The MEP of hydrogen chlorine clearly indicates that the negative charge is concentrated near chlorine
  - The overall shape of the molecule is also represented
Molecular Dipole

- In diatomic molecules a dipole exists if the two atoms are of different electronegativity.
- In more complicated molecules the molecular dipole is the sum of the bond dipoles.
- Some molecules with very polar bonds will have no net molecular dipole because the bond dipoles cancel out.

The center of positive charge and negative charge coincide in these molecules.

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\mu$ (D)</th>
<th>Formula</th>
<th>$\mu$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>0</td>
<td>$\text{CH}_4$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Cl}_2$</td>
<td>0</td>
<td>$\text{CH}_3\text{Cl}$</td>
<td>1.87</td>
</tr>
<tr>
<td>$\text{HF}$</td>
<td>1.91</td>
<td>$\text{CH}_2\text{Cl}_2$</td>
<td>1.55</td>
</tr>
<tr>
<td>$\text{HCl}$</td>
<td>1.08</td>
<td>$\text{CHCl}_3$</td>
<td>1.02</td>
</tr>
<tr>
<td>$\text{HBr}$</td>
<td>0.80</td>
<td>$\text{CCl}_4$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{HI}$</td>
<td>0.42</td>
<td>$\text{NH}_3$</td>
<td>1.47</td>
</tr>
<tr>
<td>$\text{BF}_3$</td>
<td>0</td>
<td>$\text{NF}_3$</td>
<td>0.24</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>0</td>
<td>$\text{H}_2\text{O}$</td>
<td>1.85</td>
</tr>
</tbody>
</table>
• Examples

➔ In carbon tetrachloride the bond dipoles cancel and the overall molecular dipole is 0 Debye

➔ In chloromethane the C-H bonds have only small dipoles but the C-Cl bond has a large dipole and the molecule is quite polar

➔ An unshared pair of electrons on atoms such as oxygen and nitrogen contribute a great deal to a dipole

♀ Water and ammonia have very large net dipoles
Some cis-trans isomers differ markedly in their dipole moment

- In trans 1,2-dichloroethene the two carbon-chlorine dipoles cancel out and the molecular dipole is 0 Debye
- In the cis isomer the carbon-chlorine dipoles reinforce and there is a large molecular dipole

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
<th>Dipole Moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-1,2-Dichloroethene</td>
<td>−80</td>
<td>60</td>
<td>1.90</td>
</tr>
<tr>
<td>trans-1,2-Dichloroethene</td>
<td>−50</td>
<td>48</td>
<td>0</td>
</tr>
<tr>
<td>cis-1,2-Dibromoethene</td>
<td>−53</td>
<td>112.5</td>
<td>1.35</td>
</tr>
<tr>
<td>trans-1,2-Dibromoethene</td>
<td>−6</td>
<td>108</td>
<td>0</td>
</tr>
</tbody>
</table>
Functional Groups

- Functional group families are characterized by the presence of a certain arrangement of atoms called a **functional group**.
- A functional group is the site of most chemical reactivity of a molecule.
  - The functional group is responsible for many of the physical properties of a molecule.
- Alkanes do not have a functional groups.
  - Carbon-carbon single bonds and carbon-hydrogen bonds are generally very unreactive.
Alkyl Groups and the Symbol R

- Alkyl groups are obtained by removing a hydrogen from an alkane
- Often more than one alkyl group can be obtained from an alkane by removal of different kinds of hydrogens

<table>
<thead>
<tr>
<th>ALKANE</th>
<th>ALKYL GROUP</th>
<th>ABBREVIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>CH₃—</td>
<td>Me—</td>
</tr>
<tr>
<td>Methane</td>
<td>Methyl group</td>
<td></td>
</tr>
<tr>
<td>CH₃CH₃</td>
<td>CH₃CH₂— or C₂H₅—</td>
<td>Et—</td>
</tr>
<tr>
<td>Ethane</td>
<td>Ethyl group</td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂CH₃</td>
<td>CH₃CH₂CH₂—</td>
<td>Pr—</td>
</tr>
<tr>
<td>Propane</td>
<td>Propyl group</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃</td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂CH₃</td>
<td>CH₃CHCH₃ or CH₃CH—</td>
<td>i-Pr—</td>
</tr>
<tr>
<td>Propane</td>
<td>Isopropyl group</td>
<td></td>
</tr>
</tbody>
</table>

- R is the symbol to represent a generic alkyl groups

The general formula for an alkane can be abbreviated R-H

- CH₃—  Methyl
- CH₃CH₂—  Ethyl
- CH₃CH₂CH₂—  Propyl
- CH₃CHCH₃  Isopropyl

These and others can be designated by R.
A benzene ring with a hydrogen removed is called a *phenyl* and can be represented in various ways

\[
\text{or } \begin{array}{c}
\text{ or } \begin{array}{c}
\text{ or } C_6H_5- \text{ or } \text{Ph}^- \text{ or } \phi^- \text{ or } \text{Ar}^- \text{ (if ring substituents are present)}
\end{array}
\end{array}
\]

Ways of representing a phenyl group

Toluene (methylbenzene) with its methyl hydrogen removed is called a *benzyl* group

\[
\begin{array}{c}
\text{ or } C_6H_5CH_2- \text{ or } \text{Bn}^- \end{array}
\]

Ways of representing a benzyl group
Alkyl Halides

- In alkyl halides, halogen (F, Cl, Br, I) replaces the hydrogen of an alkane.
- They are classified based on the carbon the halogen is attached to:
  - If the carbon is attached to one other carbon, that carbon is primary (1°) and the alkyl halide is also 1°.
  - If the carbon is attached to two other carbons, that carbon is secondary (2°) and the alkyl halide is 2°.
  - If the carbon is attached to three other carbons, the carbon is tertiary (3°) and the alkyl halide is 3°.
**Alcohols**

- In alcohols the hydrogen of the alkane is replaced by the hydroxyl (-OH) group

  An alcohol can be viewed as either a hydroxyl derivative of an alkane or an alkyl derivative of water

  Ethyl group

  ![Chemical structure](image1)

  Ethane

  Ethyl alcohol (ethanol)

  Water

- Alcohols are also classified according to the carbon the hydroxyl is directly attached to

  ![Chemical structure](image2)

  Isopropyl alcohol (a 2° alcohol)

  Menthol (a 2° alcohol found in peppermint oil)
● Ethers

- Ethers have the general formula \( R-O-R \) or \( R-O-R' \) where \( R' \) is different from \( R \)
  - These can be considered organic derivatives of water in which both hydrogens are replaced by organic groups
  - The bond angle at oxygen is close to the tetrahedral angle

- ![General formula for an ether](image)
- ![Dimethyl ether](image)
- ![The functional group of an ether](image)
- ![Ethylene oxide](image)
- ![Tetrahydrofuran (THF)](image)
- ![Two cyclic ethers](image)

● Amines

- Amines are organic derivatives of ammonia
  - They are classified according to how many alkyl groups replace the hydrogens of ammonia
  - This is a different classification scheme than that used in alcohols

- ![A primary (1°) amine](image)
- ![A secondary (2°) amine](image)
- ![A tertiary (3°) amine](image)
• Aldehydes and Ketones
  ➔ Both contain the carbonyl group

  ![The carbonyl group](image)

  The carbonyl group

  ➔ Aldehydes have at least one carbon attached to the carbonyl group

  ![Aldehyde structure](image)

  or $RCHO$  \( R \) may also be $H$

  ➔ Ketones have two organic groups attached to the carbonyl group

  ![Ketone structures](image)

  or $RCOR$;  or $RCOR'$

  ➔ The carbonyl carbon is $sp^2$ hybridized

  \( \hat{\rho} \) It is trigonal planar and has bond angle about $120^\circ$

  ![Bond angles](image)
Carboxylic Acids, Esters and Amides

- All these groups contain a carbonyl group bonded to an oxygen or nitrogen

**Carboxylic Acids**
- Contain the carboxyl (carbonyl + hydroxyl) group

\[ R^*\text{C}=\text{O}H \quad \text{or} \quad R\text{CO}_2\text{H} \quad \text{or} \quad R\text{COOH} \]

A carboxylic acid

\[ \text{The carboxyl group} \]

**Esters**
- A carbonyl group is bonded to an alkoxy (OR') group

\[ R\text{C}=\text{O}R' \quad \text{or} \quad R\text{CO}_2R' \quad \text{or} \quad R\text{COOR}' \]

General formula for an ester

\[ \text{A specific ester called ethyl acetate} \]

\[ \text{CH}_3\text{C}=\text{OCH}_2\text{CH}_3 \quad \text{or} \quad \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 \quad \text{or} \quad \text{CH}_3\text{COOCH}_2\text{CH}_3 \]
Amide

- A carbonyl group is bonded to a nitrogen derived from ammonia or an amine

\[
\text{NH}_2 \quad \text{NHCH}_3 \quad \text{CH}_3
\]

Acetamide \hspace{1cm} N\text{-Methylacetamide} \hspace{1cm} N,N\text{-Dimethylacetamide}

Nitriles

- An alkyl group is attached to a carbon triply bonded to a nitrogen

- This functional group is called a cyano group

\[
\begin{align*}
\text{CH}_3\text{C} \equiv \text{N} & : \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{C} \equiv \text{N} & : \\
\text{CH}_2=\text{CH}\text{C} \equiv \text{N} & : \\
\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{C} \equiv \text{N} & :
\end{align*}
\]

Ethanenitrile (acetonitrile) \hspace{1cm} Butanenitrile

Propenenitrile (acrylonitrile) \hspace{1cm} 4-Pentenenitrile
### Summary of Important Families of Organic Compounds

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Alkane</th>
<th>Alkene</th>
<th>Alkyne</th>
<th>Aromatic</th>
<th>Haloalkane</th>
<th>Alcohol</th>
<th>Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—H and C—C bonds</td>
<td>C=C</td>
<td>C≡C</td>
<td>Aromatic ring</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>General formula</td>
<td>RH</td>
<td>RCH=CH$_2$</td>
<td>RCH=CHR</td>
<td>RC≡CH</td>
<td>ArH</td>
<td>RX</td>
<td>ROH</td>
</tr>
<tr>
<td>Specific example</td>
<td>CH$_3$CH$_3$</td>
<td>CH$_2$=CH$_2$</td>
<td>H=CH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IUPAC name</td>
<td>Ethane</td>
<td>Ethene</td>
<td>Ethyne</td>
<td>Benzene</td>
<td>Chloroethane</td>
<td>Ethanol</td>
<td>Methoxymethane</td>
</tr>
<tr>
<td>Common name$^{a}$</td>
<td>Ethane</td>
<td>Ethylene</td>
<td>Acetylene</td>
<td>Benzene</td>
<td>Ethyl chloride</td>
<td>Ethyl alcohol</td>
<td>Dimethyl ether</td>
</tr>
</tbody>
</table>

$^{a}$These names are also accepted by the IUPAC.
### Summary (cont.)

<table>
<thead>
<tr>
<th>Amine</th>
<th>Aldehyde</th>
<th>Ketone</th>
<th>Carboxylic Acid</th>
<th>Ester</th>
<th>Amide</th>
<th>Nitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&lt;sub&gt;N&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>RCH</td>
<td>RCR&lt;sup&gt;′&lt;/sup&gt;</td>
<td>RCOH</td>
<td>RCO&lt;sup&gt;′&lt;/sup&gt;</td>
<td>RCNH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>RCN</td>
</tr>
<tr>
<td>R&lt;sub&gt;2&lt;/sub&gt;NH</td>
<td>R&lt;sup&gt;′&lt;/sup&gt;H</td>
<td>RCO&lt;sup&gt;′&lt;/sup&gt;</td>
<td>RCOR&lt;sup&gt;′&lt;/sup&gt;</td>
<td>RCNHR&lt;sup&gt;′&lt;/sup&gt;</td>
<td>RCNR&lt;sup&gt;′&lt;/sup&gt;</td>
<td>RCN</td>
</tr>
<tr>
<td>R&lt;sub&gt;3&lt;/sub&gt;N</td>
<td>R&lt;sup&gt;′&lt;/sup&gt;H</td>
<td>RCO&lt;sup&gt;′&lt;/sup&gt;</td>
<td>RCNHR&lt;sup&gt;′&lt;/sup&gt;</td>
<td>RCNR&lt;sup&gt;′&lt;/sup&gt;</td>
<td>RCN</td>
<td>RCN</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R&lt;sub&gt;3&lt;/sub&gt;NH&lt;sub&gt;2&lt;/sub&gt;</th>
<th>R&lt;sub&gt;3&lt;/sub&gt;CH</th>
<th>R&lt;sub&gt;3&lt;/sub&gt;CC&lt;sub&gt;3&lt;/sub&gt;H</th>
<th>R&lt;sub&gt;3&lt;/sub&gt;COH</th>
<th>R&lt;sub&gt;3&lt;/sub&gt;COCH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>R&lt;sub&gt;3&lt;/sub&gt;CNH&lt;sub&gt;2&lt;/sub&gt;</th>
<th>R&lt;sub&gt;3&lt;/sub&gt;C≡N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanamine</td>
<td>Ethanal</td>
<td>Propanone</td>
<td>Ethanoic acid</td>
<td>Methyl ethanoate</td>
<td>Ethanamide</td>
<td>Ethenenitrile</td>
</tr>
<tr>
<td>Methylamine</td>
<td>Acetaldehyde</td>
<td>Acetone</td>
<td>Acetic acid</td>
<td>Methyl acetate</td>
<td>Acetamide</td>
<td>Acetonitrile</td>
</tr>
</tbody>
</table>

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Chapter 2  
25
Physical Properties and Molecular Structure

- The strength of intermolecular forces (forces between molecules) determines the physical properties (*i.e.* melting point, boiling point and solubility) of a compound.
- Stronger intermolecular forces result in high melting points and boiling points.
  - More energy must be expended to overcome very strong forces between molecules.
- The type of intermolecular forces important for a molecule are determined by its structure.
- The physical properties of some representative compounds are shown on the next slide.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>mp (°C)</th>
<th>bp (°C) (1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>−182.6</td>
<td>−162</td>
</tr>
<tr>
<td>Ethane</td>
<td>CH₃CH₃</td>
<td>−183</td>
<td>−88.2</td>
</tr>
<tr>
<td>Ethene</td>
<td>CH₂&quot;CH₂</td>
<td>−169</td>
<td>−102</td>
</tr>
<tr>
<td>Ethyne</td>
<td>HC#CH</td>
<td>−82</td>
<td>−84 subl</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>CH₃Cl</td>
<td>−97</td>
<td>23.7</td>
</tr>
<tr>
<td>Chloroethane</td>
<td>CH₃CH₂Cl</td>
<td>−138.7</td>
<td>13.1</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>CH₃CH₂OH</td>
<td>−115</td>
<td>78.5</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>CH₃CHO</td>
<td>−121</td>
<td>20</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃CO₂H</td>
<td>16.6</td>
<td>118</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>CH₃CO₂Na</td>
<td>324</td>
<td>dec</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>CH₃CH₂NH₂</td>
<td>−80</td>
<td>17</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>(CH₃CH₂)₂O</td>
<td>−116</td>
<td>34.6</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>CH₃CO₂CH₂CH₃</td>
<td>−84</td>
<td>77</td>
</tr>
</tbody>
</table>

*In this table dec = decomposes and subl = sublimes.*
• Ion-Ion Forces

- Ion-ion forces are between positively and negatively charged ions.
- These are very strong forces that hold a solid compound consisting of ions together in a crystalline lattice.
  - Melting points are high because a great deal of energy is required to break apart the crystalline lattice.
- Boiling points are so high that organic ions often decompose before they boil.
- Example: Sodium acetate.
• Dipole-Dipole Forces
  
  Dipole-dipole forces are between molecules with permanent dipoles
  
  There is an interaction between δ+ and δ- areas in each molecule; these are much weaker than ion-ion forces
  
  Molecules align to maximize attraction of δ+ and δ- parts of molecules

  Example: acetone
Hydrogen Bonds

- Hydrogen bonds result from very strong dipole-dipole forces
- There is an interaction between hydrogens bonded to strongly electronegative atoms (O, N or F) and nonbonding electron pairs on other strongly electronegative atoms (O, N or F)

\[ \delta^- \quad \delta^+ \quad \delta^- \quad \delta^+ \]

\[ :Z-H \cdots \cdots :Z-H \]

\[ \text{H} \quad \text{H} \]
Example

- Ethanol (CH$_3$CH$_2$OH) has a boiling point of +78.5°C; its isomer methyl ether (CH$_3$OCH$_3$) has a boiling point of -24.9°C
  - Ethanol molecules are held together by hydrogen bonds whereas methyl ether molecules are held together only by weaker dipole-dipole interactions.

- A factor in melting points is that symmetrical molecules tend to pack better in the crystalline lattice and have higher melting points.

![Chemical structures](image)

tert-Butyl alcohol (mp 25°C)  Butyl alcohol (mp -90°C)  Isobutyl alcohol (mp -108°C)  sec-Butyl alcohol (mp -114°C)
• van der Waals Forces (London or Dispersion Forces)

Van der Waals forces result when a temporary dipole in a molecule caused by a momentary shifting of electrons induces an opposite and also temporary dipole in an adjacent molecule

- These temporary opposite dipoles cause a weak attraction between the two molecules
- Molecules which rely only on van der Waals forces generally have low melting points and boiling points
Polarizability predicts the magnitude of van der Waals Interactions

- Polarizability is the ability of the electrons on an atom to respond to a changing electric field
- Atoms with very loosely held electrons are more polarizable
- Iodine atoms are more polarizable than fluorine atoms because the outer shell electrons are more loosely held
- Atoms with unshared electrons are more polarizable (a halogen is more polarizable than an alkyl of similar size)

All things being equal larger and heavier molecules have higher boiling points

- Larger molecules need more energy to escape the surface of the liquid
- Larger organic molecules tend to have more surface area in contact with each other and so have stronger van der Waals interactions
- Methane (CH₄) has a boiling point of -162°C whereas ethane (C₂H₆) has a boiling point of -88.2°C

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Dipole Moment (D)</th>
<th>Dipole–Dipole</th>
<th>van der Waals</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>1.85</td>
<td>36°</td>
<td>8.8</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>NH₃</td>
<td>1.47</td>
<td>14°</td>
<td>15</td>
<td>-78</td>
<td>-33</td>
</tr>
<tr>
<td>HCl</td>
<td>1.08</td>
<td>3°</td>
<td>17</td>
<td>-115</td>
<td>-85</td>
</tr>
<tr>
<td>HBr</td>
<td>0.80</td>
<td>0.8</td>
<td>22</td>
<td>-88</td>
<td>-67</td>
</tr>
<tr>
<td>HI</td>
<td>0.42</td>
<td>0.03</td>
<td>28</td>
<td>-51</td>
<td>-35</td>
</tr>
</tbody>
</table>

*These dipole–dipole attractions are called hydrogen bonds.*
Solubilities

Water dissolves ionic solids by forming strong dipole-ion interactions

These dipole-ion interactions are powerful enough to overcome lattice energy and interionic interactions in the solid.
Generally like dissolves like

- Polar solvents tend to dissolve polar solids or polar liquids
- Methanol (a water-like molecule) dissolves in water in all proportions and interacts using hydrogen-bonding to the water

A large alkyl group can overwhelm the ability of the polar group to solubilize a molecule in water

- Decyl alcohol is only slightly soluble in water
- The large alkyl portion is hydrophobic (“water hating”) and overwhelms the capacity of the hydrophilic (“water loving”) hydroxyl
Generally one hydrophilic group (e.g. hydroxyl) can make a compound with 3 carbons completely soluble in water

- One hydrophilic group can make a 5 carbon compound at least partially soluble
- A compound is water soluble if at least 3g of it will dissolve in 100 mL water

♦ Summary of Attractive Electric Forces

<table>
<thead>
<tr>
<th>Electric Force</th>
<th>Relative Strength</th>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation–anion (in a crystal)</td>
<td>Very strong</td>
<td>[image]</td>
<td>Lithium fluoride crystal lattice</td>
</tr>
<tr>
<td>Covalent bonds</td>
<td>Strong (140–523 kJ mol⁻¹)</td>
<td>Shared electron pairs</td>
<td>H–H (436 kJ mol⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH₃–CH₃ (378 kJ mol⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>I–I (151 kJ mol⁻¹)</td>
</tr>
<tr>
<td>Ion–dipole</td>
<td>Moderate</td>
<td>[image]</td>
<td>Na⁺ in water (see Fig. 2.9)</td>
</tr>
<tr>
<td>Dipole–dipole (including hydrogen bonds)</td>
<td>Moderate to weak (4–38 kJ mol⁻¹)</td>
<td>[image]</td>
<td>[image]</td>
</tr>
<tr>
<td>van der Waals</td>
<td>Variable</td>
<td>Transient dipole</td>
<td>Interactions between methane molecules</td>
</tr>
</tbody>
</table>
Infrared Spectroscopy: An Instrumental Method for Detecting Functional Groups

- Electromagnetic radiation in the infrared (IR) frequency range is absorbed by a molecule at certain characteristic frequencies
  - Energy is absorbed by the bonds in the molecule and they vibrate faster
  - The bonds behave like tiny springs connecting the atoms
    - The bonds can absorb energy and vibrate faster only when the added energy is of a particular resonant frequency
  - The frequencies of absorption are very characteristic of the type of bonds contained in the sample molecule
  - The type of bonds present are directly related to the functional groups present
  - A plot of these absorbed frequencies is called an IR spectrum
Infrared Spectrometer

- An infrared spectrometer detects the frequencies absorbed by the sample molecule.
- Light of all the various IR frequencies is transmitted to the molecule and the frequencies absorbed are recorded.
- The absorption frequencies are specified as wavenumbers in units of reciprocal centimeters (cm\(^{-1}\)).

\[ \bar{v} = \frac{1}{\lambda} \]  (with \( \lambda \) in cm)  or  \[ \bar{v} = \frac{10,000}{\lambda} \]  (with \( \lambda \) in \( \mu \text{m} \)).

- The spectrum is a plot of frequency on the horizontal axis versus strength of absorption on the vertical axis.
There are different types of stretching and bending vibrations induced by the absorption of infrared energy. The actual relative frequency of vibration can be predicted, with bonds containing lighter atoms vibrating faster than those with heavier atoms.

<table>
<thead>
<tr>
<th>GROUP</th>
<th>BOND</th>
<th>FREQUENCY RANGE (CM⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl</td>
<td>C—H</td>
<td>2853–2962</td>
</tr>
<tr>
<td>Alcohol</td>
<td>O—H</td>
<td>3590–3650</td>
</tr>
<tr>
<td>Amine</td>
<td>N—H</td>
<td>3300–3500</td>
</tr>
</tbody>
</table>
Triple bonds (which are stiffer and stronger) vibrate at higher frequencies than double bonds

- Double bonds in turn vibrate at higher frequencies than single bonds

<table>
<thead>
<tr>
<th>BOND</th>
<th>FREQUENCY RANGE (CM⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡C</td>
<td>2100–2260</td>
</tr>
<tr>
<td>C≡N</td>
<td>2220–2260</td>
</tr>
<tr>
<td>C≡C</td>
<td>1620–1680</td>
</tr>
<tr>
<td>C=O</td>
<td>1630–1780</td>
</tr>
</tbody>
</table>

The IR spectrum of a molecule usually contains many peaks

- These peaks are due to the various types of vibrations available to each of the different bonds
- Additional peaks result from overtone (harmonic) peaks which are weaker and of lower frequency
- The IR is a “fingerprint” of the molecule because of the unique and large number of peaks seen for a particular molecule
<table>
<thead>
<tr>
<th>Group</th>
<th>Frequency Range (cm(^{-1}))</th>
<th>Intensity*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. Alkyl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C—H (stretching)</td>
<td>2853–2962</td>
<td>(m–s)</td>
</tr>
<tr>
<td>Isopropyl, –CH((CH_2))(_2)</td>
<td>1390–1385</td>
<td>(s)</td>
</tr>
<tr>
<td>and</td>
<td>1385–1370</td>
<td>(s)</td>
</tr>
<tr>
<td>tert-Butyl, –C((CH_3))(_3)</td>
<td>1385–1395</td>
<td>(m)</td>
</tr>
<tr>
<td>and</td>
<td>~ 1385</td>
<td>(s)</td>
</tr>
<tr>
<td><strong>B. Alkenyl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C—H (stretching)</td>
<td>3010–3095</td>
<td>(m)</td>
</tr>
<tr>
<td>C=(\equiv)C (stretching)</td>
<td>1620–1680</td>
<td>(v)</td>
</tr>
<tr>
<td>R—CH=CH(_2)</td>
<td>985–1000</td>
<td>(s)</td>
</tr>
<tr>
<td>and</td>
<td>905–920</td>
<td>(s)</td>
</tr>
<tr>
<td>(R_2C\equiv CH_2)</td>
<td>880–900</td>
<td>(s)</td>
</tr>
<tr>
<td>cis-RC\equiv CHR</td>
<td>675–730</td>
<td>(s)</td>
</tr>
<tr>
<td>trans-RC\equiv CHR</td>
<td>960–975</td>
<td>(s)</td>
</tr>
<tr>
<td><strong>C. Alkynyl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(=\equiv)H (stretching)</td>
<td>~ 3300</td>
<td>(s)</td>
</tr>
<tr>
<td>C≡C (stretching)</td>
<td>2100–2260</td>
<td>(v)</td>
</tr>
<tr>
<td><strong>D. Aromatic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar—H (stretching)</td>
<td>~ 3030</td>
<td>(v)</td>
</tr>
<tr>
<td>Aromatic substitution type</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C—H out-of-plane bendings)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monosubstituted</td>
<td>680–710</td>
<td>(very s)</td>
</tr>
<tr>
<td>α-Disubstituted and</td>
<td>730–770</td>
<td>(very s)</td>
</tr>
<tr>
<td>(n)-Disubstituted</td>
<td>735–770</td>
<td>(s)</td>
</tr>
<tr>
<td>and</td>
<td>680–725</td>
<td>(s)</td>
</tr>
<tr>
<td>(p)-Disubstituted</td>
<td>750–810</td>
<td>(very s)</td>
</tr>
<tr>
<td>and</td>
<td>900–860</td>
<td>(very s)</td>
</tr>
<tr>
<td><strong>E. Alcohols, Phenols, and Carboxylic Acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O—H (stretching)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohols, phenols (dilute solutions)</td>
<td>3590–3650</td>
<td>(sharp, v)</td>
</tr>
<tr>
<td>Alcohols, phenols (hydrogen bonded)</td>
<td>3200–3550</td>
<td>(broad, s)</td>
</tr>
<tr>
<td>Carboxylic acids (hydrogen bonded)</td>
<td>2500–3000</td>
<td>(broad, v)</td>
</tr>
<tr>
<td><strong>F. Aldehydes, Ketones, Esters, and Carboxylic Acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O (stretching)</td>
<td>1630–1780</td>
<td>(s)</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>1680–1740</td>
<td>(s)</td>
</tr>
<tr>
<td>Ketones</td>
<td>1680–1750</td>
<td>(s)</td>
</tr>
<tr>
<td>Esters</td>
<td>1735–1750</td>
<td>(s)</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td>1710–1780</td>
<td>(s)</td>
</tr>
<tr>
<td>Amides</td>
<td>1630–1690</td>
<td>(s)</td>
</tr>
<tr>
<td><strong>G. Amines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N—H</td>
<td>3300–3650</td>
<td>(m)</td>
</tr>
<tr>
<td><strong>H. Nitriles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡N</td>
<td>2220–2260</td>
<td>(m)</td>
</tr>
</tbody>
</table>

*Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.
Interpreting IR Spectra

Generally only certain peaks are interpreted in the IR
Those peaks that are large and above 1400 cm\(^{-1}\) are most valuable

- Hydrocarbons
  - The C-H stretching regions from 2800-3300 cm\(^{-1}\) is characteristic of the type of carbon the hydrogen is attached to
  - C-H bonds where the carbon has more s character are shorter, stronger and stiffer and thus vibrate at higher frequency
    - C-H bonds at sp centers appear at 3000-3100 cm\(^{-1}\)
    - C-H bonds at sp\(^2\) centers appear at about 3080 cm\(^{-1}\)
    - C-H bonds at sp\(^3\) centers appear at about 2800-3000 cm\(^{-1}\)
  - C-C bond stretching frequencies are only useful for multiple bonds
    - C-C double bonds give peaks at 1620-1680 cm\(^{-1}\)
    - C-C triple bonds give peaks at 2100-2260 cm\(^{-1}\)
    - These peaks are absent in symmetrical double and triple bonds
• Example: octane

[Diagram showing the infrared spectrum of octane with labeled peaks for \( \text{CH}_3 \) (C-H stretching), \( \text{CH}_2 \) (C-H bending), \( \text{CH}_2(\text{CH}_2)_n\text{CH}_3 \), and \( \text{CH}_3 \) (C-H bending).]

• Example: 1- hexyne

[Diagram showing the infrared spectrum of 1-hexyne with labeled peaks for \( \text{C}==\text{C} \) (stretch), \( \text{CH}_3(\text{CH}_2)_n\text{CH}_2==\text{C}==\text{CH} \), \( \text{CH}_3 \) (bend) and \( \text{CH}_2, \text{CH}_3 \) (stretch).]
Alkenes

The C-H bending vibration peaks located at 600-1000 cm\(^{-1}\) can be used to determine the substitution pattern of the double bond.
Example: 1-hexene
• Aromatic Compounds
  ➔ The C-C bond stretching gives a set of characteristic sharp peaks between 1450-1600 cm\(^{-1}\)
  ➔ Example: Methyl benzene
Other Functional Groups

- Carbonyl Functional Groups

- Generally the carbonyl group gives a strong peak which occurs at 1630-1780 cm\(^{-1}\).
  - The exact location depends on the actual functional group present.

![Chemical Structures]

- Aldehyde: 1690–1740 cm\(^{-1}\)
- Ketone: 1680–1750 cm\(^{-1}\)
- Ester: 1735–1750 cm\(^{-1}\)
- Carboxylic acid: 1710–1780 cm\(^{-1}\)
- Amide: 1630–1690 cm\(^{-1}\)
Alcohols and Phenols

The O-H stretching absorption is very characteristic

- In very dilute solutions, hydrogen bonding is absent and there is a very sharp peak at 3590-3650 cm\(^{-1}\)
- In more concentrated solutions, the hydroxyl groups hydrogen bond to each other and a very broad and large peak occurs at 3200-3550 cm\(^{-1}\)
- A phenol has a hydroxyl group directly bonded to an aromatic ring
Carboxylic Acids

The carbonyl peak at 1710-1780 cm\(^{-1}\) is very characteristic.

The presence of both carbonyl and O-H stretching peaks is a good proof of the presence of a carboxylic acid.

Example: propanic acid
• Amines
  ➔ Very dilute solution of 1° and 2° amines give sharp peaks at 3300-3500 cm\(^{-1}\) for the N-H stretching
    ➔ 1° amines give two peaks and 2° amines give one peak
    ➔ 3° have no N-H bonds and do not absorb in this region
  ➔ More concentrated solutions of amines have broader peaks
  ➔ Amides have amine N-H stretching peaks and a carbonyl peak