Molecules of the Day

Isoamyl acetate – *banana*
Benzaldehyde – *almonds*
(R)-Limonene – *lemon, lime*
1,4-Diaminobutane – *a.k.a. putrescine*

Imagine that four unlabelled vials, each containing one of our four "Molecules of the Day", had somehow become mixed up. How could IR spectroscopy (instead of your sense of smell) be employed to identify the contents of each vial?

Molecule structure determination
Three-Stage Strategy for Organic Structure Determination

- Determine the **molecular formula** using **elemental analysis** and **mass spectrometry**

- Identify the **functional groups** using **infrared spectroscopy (IR)** and **nuclear magnetic resonance spectroscopy (NMR)**.

- Elucidate the **connectivity** using $^1$H NMR ("proton NMR") and $^{13}$C NMR ("carbon NMR") spectroscopy.
(Nearly) Foolproof Protocol for Organic Structure Determination

A. Molecular Formula
   1. Determine molecular formula using elemental analysis (EA) and MS.
   2. Determine index of hydrogen deficiency (IHD = # rings + # π-bonds) from molecular formula.

B. Functional Groups
   1. Identify functional groups using IR and $^{13}$C NMR (and $^1$H NMR occasionally)
   2. Determine symmetry (a.k.a. degeneracy) by comparing $^{13}$C NMR to molecular formula.

C. Connectivity
   1. Identify molecular fragments using data from $^1$H NMR:
      a. spin-spin splitting
      b. integration
      c. chemical shift
      d. …and MS fragmentation (can be done earlier in elucidation)
   2. Assemble fragments
   3. Confirm structural assignment – Must be consistent with ALL data.
INDEX OF HYDROGEN DEFICIENCY for the molecular formula $\alpha \beta \gamma \delta$:  
\[
\text{Index} = (z) - (w/2) + (y/2) + 1
\]
Where $\alpha$ represents all *monovalent* atoms (H, D, halogen), $\beta$ *divalent* (O, S), $\gamma$ *trivalent* (N, P) and $\delta$ *tetravalent* (C, Si, Sn).

Example $C_7H_7NO$

<table>
<thead>
<tr>
<th>Mono:</th>
<th>H</th>
<th>$w = 7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di:</td>
<td>O</td>
<td>$x = 1$</td>
</tr>
<tr>
<td>Tri:</td>
<td>N</td>
<td>$y = 1$</td>
</tr>
<tr>
<td>Tetra:</td>
<td>C</td>
<td>$z = 7$</td>
</tr>
</tbody>
</table>

Hydrogen deficiency $= 7 - (7/2) + (1/2) + 1 = 5$

Possibilities:

- ![Possible structure 1](image1.png)
- ![Possible structure 2](image2.png)
- ![Possible structure 3](image3.png)
Raking Leaves
by Shelly Hazard

November, 2010
Print 'n' Play Test
and Table of Results

Alex looked at the fallen leaves blowing around the yard last week and had a great idea. He went around to all the neighbors, offering his raking services to clean up their yards. He got five jobs for this week, a different neighbor each day. The neighbors all lived on different streets and each had a different yard size, so some days he made more than others. Determine the last name of each neighbor who hired him, what street each lived on, what day he worked for each neighbor, and how much each neighbor paid him.

1. Alex worked for the Jones family on Monday afternoon and he earned $10 more than the day he raked for the neighbor on West Street.

2. He earned $4 less working for the Bradley family than he did from the neighbor on School Street.

3. On Friday, he worked on Oak Street but not for the Hayes family. The family on Main Street paid him $10 more than the neighbor he raked for on Wednesday.

4. He got $29 from the May family but it wasn’t on Tuesday.

5. He worked for the Elliot family the day before he worked on Russell Street. He earned $39 on Thursday.

6. Alex raked the Elliot yard two days before the neighbor on Oak Street but one day after the neighbor who paid him $43.

<table>
<thead>
<tr>
<th>Last Name</th>
<th>Street</th>
<th>Day of the Week</th>
<th>Amount Earned</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bradley</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elliot</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hayes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jones</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>May</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$43</td>
</tr>
<tr>
<td>Monday</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tuesday</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wednesday</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thursday</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Friday</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

There is no “right way” to approach these … just as there is no “right way” to approach spectral interpretation. The best way to build proficiency is to do problems! I will show you what works for me along the way.
<table>
<thead>
<tr>
<th></th>
<th>H-1</th>
<th>C-13</th>
<th>MS</th>
<th>IR/RAMAN</th>
<th>UV-VIS</th>
<th>ORD/CD</th>
<th>X-RAY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation type</td>
<td>RF</td>
<td>RF</td>
<td>Not relevant</td>
<td>IR</td>
<td>UV to visible</td>
<td>UV to visible</td>
<td>X-ray</td>
</tr>
<tr>
<td>Spectral scale</td>
<td>0-15 ppm</td>
<td>0-220 ppm</td>
<td>50-4000 amu</td>
<td>400-4000 cm⁻¹</td>
<td>200-800 nm</td>
<td>185-600 nm</td>
<td>Not relevant</td>
</tr>
<tr>
<td>Average sample</td>
<td>≤ 1 mg</td>
<td>≤ 5 mg</td>
<td>&lt; 1 mg</td>
<td>&lt; 1 mg</td>
<td>&lt; 1 mg</td>
<td>&lt; 1 mg</td>
<td>Single crystal</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>Partial</td>
<td>Partial</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Functional groups</td>
<td>Yes</td>
<td>Yes</td>
<td>Limited</td>
<td>Yes</td>
<td>Very limited</td>
<td>Very limited</td>
<td>Yes</td>
</tr>
<tr>
<td>Substructures</td>
<td>Yes</td>
<td>Limited</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Substituent regiochemistry</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Substituent stereochemistry</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Analysis of isomer mixtures</td>
<td>Yes</td>
<td>Yes</td>
<td>(by GC/MS LC/MS)</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Purity information</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
</tr>
<tr>
<td>What is measured</td>
<td>Peak areas</td>
<td>Chemical shifts Coupling relaxation</td>
<td>Singly or multiple charged ions</td>
<td>Vibrational transitions</td>
<td>Electronic transitions</td>
<td>[α]</td>
<td>Relative atom positions R/S absolute stereochemistry</td>
</tr>
<tr>
<td>Typical units</td>
<td>δ (ppm)</td>
<td>δ (ppm)</td>
<td>m/z</td>
<td>cm⁻¹</td>
<td>nm</td>
<td>nm</td>
<td>ORTEP</td>
</tr>
<tr>
<td>Typical representations</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
</tr>
</tbody>
</table>
Timeline of available techniques

*Elemental analysis (combustion)*
*Melting point, boiling point*
*Chemical reactivity and degradation: derivatives*

*Ultraviolet-visible (UV-vis) - 1930s*
Woodward-Fieser Rules ca. 1941 Circular dichroism 1960s

*Infrared (IR) - 1940s*
Functional groups, molecular fingerprints Raman spectroscopy 1960s

*Mass spectrometry (MS) - 1950s*
Molecular weights, and observation of key fragments Characteristic reactivity ...
... molecular fingerprints

*Nuclear magnetic resonance (NMR) - 1960s*
Fourier Transform NMR 1970s
2-D correlation spectroscopies 1980s
Infrared spectroscopy
Wavelengths, Frequencies, and Energies of Some Regions of the Electromagnetic Spectrum

\[ E = h \nu = \frac{hc}{\lambda} \]
• Frequency is commonly reported in units of:

1. joules
2. nm
3. amu
4. Hz
5. m/z

• Which type of electromagnetic radiation possesses the highest energy?

1. IR light
2. UV light
3. Microwaves
4. Visible light
5. FM radio waves
What energies are involved?

\[ E = h\nu = \frac{hc}{\lambda} \]

**Wavelength**

\[ \text{m} \]

**Frequency**

\[ \text{Hz or s}^{-1} \]

We *can* and *will* think of these units as “energies”

---

vacuum

---

\( \sigma^* \)

\( \pi^* \)

\( n \)

\( \pi \)

\( \sigma \)

---

**XPS**

10s-100s
of eV

**UV-vis**

100s
of nm

**IR**

1000s
of cm\(^{-1}\)

---

... to NMR
100s
of ppm
Molecular Spectroscopy

- Study of which frequencies of radiation are absorbed or emitted by a particular substance and the correlation of these frequencies with details of molecular structure

### Table 12.3 Types of Energy Transitions Resulting from Absorption of Energy from Three Regions of the Electromagnetic Spectrum

<table>
<thead>
<tr>
<th>Region of Electromagnetic Spectrum</th>
<th>Frequency (hertz)</th>
<th>Type of Spectroscopy</th>
<th>Absorption of Electromagnetic Radiation Results in Transitions Between</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio frequency</td>
<td>$3 \times 10^7 - 9 \times 10^8$</td>
<td>Nuclear magnetic resonance</td>
<td>Nuclear spin levels</td>
</tr>
<tr>
<td>Infrared</td>
<td>$3 \times 10^{11} - 2.5 \times 10^{14}$</td>
<td>Infrared</td>
<td>Vibrational energy levels</td>
</tr>
<tr>
<td>Ultraviolet-visible</td>
<td>$2.5 \times 10^{14} - 1.5 \times 10^{15}$</td>
<td>Ultraviolet-visible</td>
<td>Electronic energy levels</td>
</tr>
</tbody>
</table>
Relative energies, apologies to a fly

This is IR

This is UV-vis

This is MS
Infrared (IR) Spectroscopy

- Probes **stretching** and **bending** vibrations of organic molecules
- **Vibrational infrared region**: Extends from $2.5 \times 10^{-6}$ (2.5 $\mu$m) to $2.5 \times 10^{-5}$ m (25 $\mu$m)
  - **Wavenumber**: Number of waves per centimeter, with units cm$^{-1}$ (read reciprocal centimeters)
  - Infrared spectrum extends from 4000 to 400 cm$^{-1}$ when expressed in frequencies

\[
\nu = \frac{10^{-2} \text{ m} \cdot \text{cm}^{-1}}{2.5 \times 10^{-6} \text{ m}} = 4000 \text{ cm}^{-1}
\]

\[
\nu = \frac{10^{-2} \text{ m} \cdot \text{cm}^{-1}}{2.5 \times 10^{-5} \text{ m}} = 400 \text{ cm}^{-1}
\]
Infrared Absorption Spectroscopy

**Infrared radiation** - just below the red end of the visible light spectrum. The energy of the radiation is approximately 1–20 kcal/mol. This corresponds to the energy needed to induce bond vibrations.

Energy is related to frequency: \[ E = h\nu \]

And energy is related to wavelength: \[ E = \frac{hc}{\lambda} \]

So high energy vibrations have high frequency and short wavelength.

Bond stretching is higher in energy than...

If we provide the appropriate energy (wavelength or frequency) infrared radiation, the bonds will absorb it, and vibrate/bend more rapidly...
sample absorbs if the wavelength corresponds to a molecular vibration/bending

If we plot wavelength vs. absorption, we will obtain the infrared spectrum characteristic of our sample

Infrared radiation frequency is reported in micrometers (10^{-6} meter) 
**OR** in wavenumbers - cm^{-1} (10^4 divided by wavelength in micrometers)

We will use cm^{-1}

Frequency is proportional to cm^{-1}, and "wavenumber" is often called "frequency"
Molecular Vibrations

• Atoms joined by covalent bonds undergo continual vibrations relative to each other
  • Energies associated are quantized, that is, within a molecule, only specific vibrational energy levels are allowed
  • Energies associated with transitions between vibrational energy levels correspond to frequencies in the infrared region
• For a molecule to be infrared active, its vibration must cause a substantial change in the bond dipole moment, and it is observed in the IR spectrum
  • Greater the bond dipole, greater the change in dipole moment caused by a vibration
• Covalent bonds that do not meet this criteria are said to be IR inactive
  • The C=C and C≡C bonds in symmetrically substituted alkenes and alkynes do not absorb IR radiation as vibration does not result in a substantial bond dipole change

\[ \text{H}_3\text{C} \quad \text{CH}_3 \]
\[
\text{C} \equiv \text{C} \\
\text{H}_3\text{C} \quad \text{CH}_3
\]

2,3-Dimethyl-2-butene

\[ \text{H}_3\text{C} \quad \text{C} \equiv \text{C} \quad \text{CH}_3 \]

2-Butyne
Molecular Vibrations

- For a nonlinear molecule containing \( n \) atoms, \( 3n - 6 \) allowed fundamental vibrations exist.
- For even a relatively small molecule, a large number of vibrational energy levels exist.
  - Patterns of IR absorption are complex.
- The simplest vibrational motions that give rise to absorption of IR radiation are bending and stretching.
Characteristic Absorption Patterns

- Consider two covalently bonded atoms as two vibrating masses connected by a spring
  - Total energy is proportional to the frequency of vibration
  - Frequency of a stretching vibration is given by an equation derived from Hooke’s law for a vibrating spring
    \[ \nu = 4.12 \sqrt{\frac{K}{\mu}} \]
  - \( K \) = Force constant of a bond, which is a measure of bond strength
    - Force constants for single, double, and triple bonds are approximately 5, 10, and \( 15 \times 10^5 \) dynes/cm
  - \( \mu \) = Reduced mass of the two atoms, \( \frac{m_1 m_2}{m_1 + m_2} \), where \( m \) is the mass of the atoms

- Hooke’s law predicts that the position of the absorption of a stretching vibration in an IR spectrum depends on:
  - Strength of the vibrating bond
  - Masses of the atoms connected by the bond

- Stronger the bond is and lighter the atoms are, higher the frequency of the stretching vibration will be

- Intensity of absorption depends primarily on the change in dipole of the vibrating bond
Infrared Stretching Frequencies of Selected Functional Groups

<table>
<thead>
<tr>
<th>Bond</th>
<th>Stretching Frequency (cm⁻¹)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H</td>
<td>3200–3650</td>
<td>Weak to strong (strongest when H-bonded)</td>
</tr>
<tr>
<td>N–H</td>
<td>3100–3550</td>
<td>Medium</td>
</tr>
<tr>
<td>C–H</td>
<td>2700–3300</td>
<td>Weak to medium</td>
</tr>
<tr>
<td>C=C</td>
<td>1600–1680</td>
<td>Weak to medium</td>
</tr>
<tr>
<td>C=O</td>
<td>1630–1820</td>
<td>Strong</td>
</tr>
<tr>
<td>C–O</td>
<td>1000–1250</td>
<td>Strong</td>
</tr>
</tbody>
</table>

Calculate the stretching frequency in wavenumbers for a carbon-carbon double bond
Assume that each carbon is the most abundant isotope, namely ¹²C

Solution
Assume a force constant of 10×10⁵ dynes per centimeter for C=C
The calculated frequency is 1682 cm⁻¹, a value close to the experimental value of 1650 cm⁻¹

\[
\bar{v} = 4.12 \sqrt{\frac{10 \times 10^5}{12 \times 12/(12 + 12)}} = 1682 \text{ cm}^{-1}
\]
Fingerprint Region

- Vibrations in the region 1500 to 400 cm$^{-1}$ of IR spectra are complex and difficult to analyze but are **characteristic for different molecules**
- Slight variations in molecular structure and absorption patterns are most obvious in this region

- What functional group is most likely present if a compound shows IR absorption at these frequencies?
  - a. 1705 cm$^{-1}$
  - b. 2950 cm$^{-1}$

- Solution
  - a. A C=O group
  - b. An aliphatic C—H group
• Propanone and 2-propen-1-ol are constitutional isomers
  • Show how to distinguish between them by IR spectroscopy

![Chemical structures of propanone and 2-propen-1-ol]

Propanone (Acetone) \[ \text{CH}_3\text{C}==\text{CH}_2\text{OH} \]
2-Propen-1-ol (Allyl alcohol) \[ \text{CH}_3\text{C}==\text{CH}_2\text{OH} \]

• Solution
  • Only propanone shows strong absorption in the C=O stretching region, 1630–1820 cm\(^{-1}\)
  • Alternatively, only 2-propen-1-ol shows strong absorption in the O—H stretching region, 3200–3650 cm\(^{-1}\)
The higher the wavenumber of a molecular vibration, the lower the energy of the infrared radiation needed to stimulate it

1. True
2. False

Infrared spectroscopy is based on _____ excitation

1. electronic
2. rotational
3. nuclear
4. vibrational

What approximate frequency range is considered the fingerprint region in infrared spectroscopy?

1. 4000–3500 cm⁻¹
2. 3500–3000 cm⁻¹
3. 3000–2000 cm⁻¹
4. 2000–1500 cm⁻¹
5. 1500–500 cm⁻¹
Interpreting Infrared Spectra
<table>
<thead>
<tr>
<th>Region</th>
<th>4000 cm(^{-1})</th>
<th>2000 cm(^{-1})</th>
<th>1500 cm(^{-1})</th>
<th>400 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>X - H Region</td>
<td>2500 - 4000 cm(^{-1})</td>
<td>2000 - 2500 cm(^{-1})</td>
<td>1500 cm(^{-1})</td>
<td>400 - 1500 cm(^{-1})</td>
</tr>
<tr>
<td>X = Y Region</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- C-H, N-H, O-H Stretching
- C≡C
- C≡N Stretching
- C=O
- C=N Stretching
- Single Rond Stretching
- Bond Bending
- Polyatomic Vibrations
### X-H Region

<table>
<thead>
<tr>
<th>Phenols and Alcohols</th>
<th>ROH</th>
<th>3700-3500 sharp or 3200-3600 broad (H-bonded)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids</td>
<td>RCO_2H</td>
<td>2800-3600 very broad</td>
</tr>
<tr>
<td>Amides and Amines</td>
<td>RCONHR</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R_2NH</td>
<td>3300-3500</td>
</tr>
<tr>
<td>C-H bonds</td>
<td>C≡C-H</td>
<td>3100-3300</td>
</tr>
<tr>
<td></td>
<td>C=C-H</td>
<td>3000-3200</td>
</tr>
<tr>
<td></td>
<td>C=C=C-H</td>
<td>2850-3000</td>
</tr>
<tr>
<td></td>
<td>RCHO</td>
<td>2700-2800</td>
</tr>
</tbody>
</table>

### sp Region

| Acetylenes          | C≡C  | 2100                                      |
| Nitriles            | C≡N  | 2200                                      |
| Ketenes             | C=C=O | 2150                                     |
| Allenes             | C=C=C | 1950                                     |

### Double Bond Region

| Alkenes             | C=C  | 1600-1670 weak unless conjugated         |
| Imines              | C=N  | 1600-1700                                |
| Nitro               | -NO2 | 1350-1550 (two bands)                    |
### Carbonyl Groups

Note: subtract ca. 30 cm\(^{-1}\) for conjugation (e.g. with a double bond or aromatic ring)

<table>
<thead>
<tr>
<th></th>
<th>Ketones (R_2C=O)</th>
<th>1710 (subtract ca. 30 cm(^{-1}) for conjugation)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anhydrides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(RC(O)OCOR)</td>
<td>1740-1780, 1800-1840 (two bands)</td>
<td>1710</td>
</tr>
<tr>
<td><strong>Acid Chlorides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(RCOCI)</td>
<td>1790-1815</td>
<td>1740</td>
</tr>
<tr>
<td><strong>Esters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(RCO_2R)</td>
<td>1725-1755</td>
<td>1715</td>
</tr>
<tr>
<td><strong>Acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(RCO_2H)</td>
<td>1700-1725</td>
<td>1780</td>
</tr>
<tr>
<td><strong>Amides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(RCONR_2)</td>
<td>1630-1700</td>
<td>1770</td>
</tr>
<tr>
<td><strong>Urethanes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R_2NCO_2R)</td>
<td>1700</td>
<td>1690-1740</td>
</tr>
<tr>
<td><strong>Aldehydes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(RCHO)</td>
<td>1720-1740</td>
<td>1730</td>
</tr>
</tbody>
</table>

6-membered and larger cyclic ketones
Aldehydes and Ketones - Carbonyl Groups

- Position of C=O stretching vibration is sensitive to its molecular environment
  - As ring size decreases and angle strain increases, absorption shifts to a higher frequency

- Presence of an adjacent C=C or benzene ring in conjugation with the carbonyl group shifts the C=O absorption to a lower frequency
Factors That Determine IR Stretching Frequencies

• Why is it that the frequency of vibration is the same as the frequency of the IR light that is absorbed?

• Two main factors that determine the frequencies of IR absorption:
  • 1. the mass of the atoms
  • 2. the strength of the bond
Explain the following comparisons of C=O stretching frequencies:

1. $1735 \text{ cm}^{-1}$ vs $1650 \text{ cm}^{-1}$
2. $1735 \text{ cm}^{-1}$ vs $1720 \text{ cm}^{-1}$
Identifying Functional Groups Using IR Spectroscopy

**Alkane**

**Alkene**

**Alcohol**

**Ketone**

[Images of IR spectra for alkane, alkene, alcohol, and ketone with specific wave numbers marked (e.g., 1620 cm⁻¹ for alkene and 1715 cm⁻¹ for ketone).]
Identifying Functional Groups Using IR Spectroscopy

Identify the functional groups in each of the following IR spectra:
Steps in Solving Infrared Spectral Problems

• Step 1: Check the region around 3000 cm\(^{-1}\)
  • Absorption in this region is caused by C—H stretching

• Step 2: Check for a strong, broad band in the region of 3500 cm\(^{-1}\)
  • If present, the molecule contains an —OH group either of an alcohol or a carboxylic acid
  • Functional group is an —OH group of an alcohol if there is no absorption around 1700 cm\(^{-1}\)
  • Functional group may be carboxyl if there is a peak around 1700 cm\(^{-1}\)
  • One or two peaks in the 3500 cm\(^{-1}\) region at somewhat lower frequency than for —OH may indicate a 2° or 1° amine, respectively

• Step 3: Check for a sharp peak in the region 1630–1820 cm\(^{-1}\)
  • If present, a C=O group is present and the peak will probably be the strongest peak in the spectrum
  • If no peak is present in this region, no C=O is present
• What functional groups are most likely present in a compound whose IR spectrum shows absorbances at 1648 and 2217 cm\(^{-1}\)?

1. Aldehyde and alkene
2. Alkene and alcohol
3. Alcohol and nitrile
4. Alkyne and ketone
5. Alkene and nitrile

• (\(R\))-2-pentanol and (\(S\))-2-pentanol give identical IR spectra

1. True
2. False

• (\(E\))-2-Butene and (\(Z\))-2-butene give identical IR spectra

1. True
2. False

• Which of the following compounds will have its carbonyl absorb at the lowest frequency in IR spectroscopy?

1. \[
\begin{array}{c}
\text{C=O} \\
\text{H} \\
\text{H}
\end{array}
\]
2. \[
\begin{array}{c}
\text{C=O} \\
\text{C=O}
\end{array}
\]
3. \[
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]
4. \[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]
5. \[
\begin{array}{c}
\text{C=O} \\
\text{C}
\end{array}
\]
1-Hexanol

Nonane

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