10A. Bonding and Infrared Radiation

A portion of the electromagnetic spectrum having longer wavelengths than visible light is known as infrared, or IR, radiation (wavelengths between 700 nm and about 100,000 nm). Since the energy of a photon is inversely proportional to the wavelength, infrared radiation is less energetic than visible light. Recall that Planck’s Law states that the energy of a photon is given by $E = h\nu = hc/\lambda$. Lamps designed to emit infrared radiation are often called heat lamps. We may see them in everyday life used in restaurants to warm food or in pet stores to warm a sick bird.

Many molecules absorb infrared light. Recall from your study of the Bohr model that the absorption of a photon of visible or ultraviolet light excites electrons to higher energy levels. In contrast, when lower-energy infrared radiation is absorbed it is not electrons that become excited, but instead vibrations of bonds. We think of bonds as being like springs. These bonds are constantly vibrating in various modes (stretching and bending). When an infrared light photon of the appropriate energy is absorbed by a molecule, a specific "spring" begins to vibrate more energetically. This is a quantum effect; only radiation of a specific energy will excite the vibration of a specific bond. Thus, C-H, C-C, C=O, C-Cl, etc., bonds in a molecule will each absorb infrared light of a particular characteristic frequency as they become vibrationally excited. The infrared spectrum of a substance is a plot of the amount of infrared radiation absorbed by a substance as a function of the frequency of the radiation. The specific pattern of absorptions (frequencies and intensities) may serve as a fingerprint to help identify a given molecule. The spectrum is actually identifying the different types of bonds present in a molecule.

Physics of a Vibrating Spring (Bond): the Harmonic Oscillator

Physicists use Hooke's law to describe the behavior of springs and the forces involved. One form of Hooke's law involves the period of oscillation of the spring (seconds per vibration). Chemists use a variation of Hooke's law which focuses on the frequency of the vibration,

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where $\nu =$ vibrational frequency of the bond, in wavenumbers (cm$^{-1}$). Note that this is actually the inverse of the wavelength, not truly a frequency, but directly proportional to it.

$c =$ velocity of light $= 3.00 \times 10^{10}$ cm/sec  \textbf{NOTE:} cm are used instead of meters, since the frequency is conventionally expressed in wavenumbers.

$k =$ force constant, related to the strength of the bond (N/m). This is the restoring force per meter of elongation. Recall that 1 newton of force $= 1$ kg m/s$^2$. A larger force constant signifies a "stiffer spring."

$\mu =$ reduced mass of the bond, which is given by

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

where $m_1$ and $m_2$ are the masses of the two atoms (in kilograms per molecule).

The vibrational frequency of a bond in Hooke's law will correspond to the frequency of infrared radiation absorbed by that bond.

From Hooke's law one can see that the frequency for an observed vibration would change if one of the atoms were replaced by an atom having a different mass (e.g., an isotope) or if the bond strength is changed. Thus, the bond order (i.e., single, double, or triple) affects the force constant and therefore the vibrational
frequency. Double and triple bonds, with their greater bond strengths, will have absorption bands in the IR that differ in frequency from the related bands for the singly bonded atoms. In this experiment, we will examine the change in vibrational frequency and force constant for C–C, C=C and C≡C bonds. Note that hydrocarbons containing only single C–C bonds are called *alkanes*, those with a C=C double bond are called *alkenes*, and those with a C≡C triple bond are called *alkynes*.

**Procedure**

1. Obtain the IR spectra for hexane, CH₃(CH₂)₄CH₃ (1), 1-hexene, CH₃(CH₂)₃CH=CH₂ (2), and 1-hexyne, CH₃(CH₂)₃C≡CH (3) from the [SDBS website](http://www.aist.go.jp/Riodb/SDBS/menu-e.html). In the case of hexane, use the liquid film spectrum, not the one of a CCl₄ solution of hexane. If you are going to print out the spectra, first use "Page Setup" on the file menu and choose "Landscape." Then click on the spectrum, use "Print Preview" from the File menu and choose "Only the selected frame." Then send the Print command. Fill out the report sheet as follows:

1. Find the frequency for the absorption band due to the C–C, C=C and C≡C bonds (the value at the maximum absorption). Look at the peak tables that accompany the spectra and use the correlation chart below to identify the correct absorption bands. The peak tables list the frequency and intensity (%T) of the major bands in each spectrum. Enter these frequencies in the table on the report sheet. Also, locate the absorption bands (there may be more than one) due to C–H bond stretching modes in each spectrum and enter the frequencies in the table.

### Characteristic Absorption Frequencies

| Bond | Stretching frequency
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H</td>
<td>3000 - 2900 cm⁻¹</td>
</tr>
<tr>
<td>C–C</td>
<td>1200 - 800 cm⁻¹</td>
</tr>
<tr>
<td>C=C</td>
<td>1700 - 1600 cm⁻¹</td>
</tr>
<tr>
<td>C≡C</td>
<td>2300 - 2100 cm⁻¹</td>
</tr>
</tbody>
</table>

2. Calculate the reduced mass of a C–C bond and a C–H bond in the appropriate place on the report sheet. Be sure that the units are *kilograms per molecule* (not per mole).

3. Use these frequencies and reduced masses to calculate the force constants for the three types of carbon-carbon bonds (don't forget units). Show your calculations in detail on a separate page and enter the results in the table. If there is more than one absorption band in the appropriate range, use the one of highest wavenumber to compute the force constant.

4-9. On report sheet

**References**


(Revised 12/05/06)
IR Spectra of Hexane, 1-Hexene, and 1-Hexyne

1. Identify the absorption frequencies from the spectra and fill in the table.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C - C stretch, cm(^{-1})</th>
<th>C=C stretch, cm(^{-1})</th>
<th>C=C stretch, cm(^{-1})</th>
<th>C - H stretch, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1-hexene</td>
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<tr>
<td>1-hexyne</td>
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</tbody>
</table>

2. Calculate the reduced mass of a C - C bond:

Calculate the reduced mass of a C - H bond:

3. Calculate the force constants \(k\) for each type of bond. Show your work on a separate page.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(k) for C - C, N/m</th>
<th>(k) for C=C, N/m</th>
<th>(k) for C=C, N/m</th>
<th>(k) for C - H, N/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-hexene</td>
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<tr>
<td>1-hexyne</td>
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</tbody>
</table>

4. How does the C - C bond order relate to the force constant?

5. Which C-H bond is strongest, that in an alkane, an alkene, or an alkyne? How do you know?
6. Benzene, C$_6$H$_6$, shows an IR absorption around 3050 cm$^{-1}$ that corresponds to a vibrational excitation of a C-H bond, of which benzene has six. Calculate the force constant for this absorption.

7. Isotopic substitution in a molecule will shift the infrared absorption frequency of the affected bond. Deuterium is an isotope of hydrogen, signified by $^2$H or D, with an atomic mass of 2.014 amu (molar mass 2.014 g/mol). Assuming that the force constant for a C-D bond is the same as that for a C-H bond, calculate the expected IR absorption frequency for the C-D vibration of deuteriobenzene, C$_6$D$_6$.

Similarities in IR Spectra

8. Infrared spectroscopy is a powerful method for determining the presence of functional groups in complex molecules. Unfortunately, very different compounds often have similar IR spectra. To illustrate this point visit the SDBS website, type in the compound name, hit the search button, and find the IR spectrum for each of the following compounds. Give the C=C stretching frequency and structure of each of the following compounds.
   a) 2-cyclohexen-1-ol
   b) cholesterol

9. What major absorption bands in common do these two compounds have (agreement to within a few wavenumbers)? List their frequencies.