# Lab 6.  Use of VSEPR to Predict Molecular Structure and IR Spectroscopy to Identify an Unknown

## Prelab Assignment

*Before* coming to lab:

- In addition to reading introduction of this lab handout, read and understand Section 10.2 (Valence Shell Electron-Pair Repulsion Theory and Molecular Shape), pp. 388 – 397, and "*Tools of the Chemistry Laboratory — Infrared Spectroscopy*", pp. 357 – 358 in your text, *Silberberg* 5th ed.
- Answer the ***pre-lab questions*** that appear at the end of this lab exercise and be prepared to hand them in at the start of your lab period.
- This lab exercise does *not* require a report in your lab notebook. The report for this exercise consists of completing the attached Report pages (pp. 7 – 12) as you carry out the procedures on pages 4 – 5.

## Purpose

In this laboratory activity you will gain additional practice predicting the three-dimensional structure of molecules and ions without the use of models. You will also use your knowledge of geometry and bond angles to predict the relative stability of several cyclic compounds, and will compare the structures of some larger drug molecules. Finally, you will collect an infrared spectrum of an unknown compound and, based on an analysis of the spectrum, identify which of six possible unknowns you have been given.

## Introduction

For small molecules the shape or geometry can be accurately predicted using ***Valence–Shell Electron–Pair Repulsion (VSEPR).*** This model is discussed at some length in Section 10.2 of your text, *Silberberg* 4th ed.  Be sure to read this section carefully prior to attempting this activity. Use these pages and table 2 on page 3 of this lab to assist you in completing the prelab questions at the end of this lab exercise.

In this exercise you will begin by predicting the geometry of several molecules and ions. You will then be able to check your work by viewing a computer generated 3–D model of the molecule or ion. Be sure that you complete all work in your lab notebook.

**Infrared Spectroscopy**

The use of electromagnetic radiation to investigate chemical structure, behavior and concentration is a large and important field of chemistry. There are many important instrumental methods of chemical analysis that rely on the interaction between light and matter to probe chemical structure. You have already used visible spectroscopy in a previous lab to determine the concentration of *allura red* in an unknown solution. In this lab you will see how infrared (IR) spectroscopy can be used to give information about the covalent bonds in a molecule. To learn more about spectroscopy, and to prepare for this lab, read the following sections in your text:

- "*Tools of the Chemistry Laboratory — Infrared Spectroscopy,*" pp. 357 – 358(*Silberberg* 5th ed.)

As you will read in your text, ***IR spectroscopy*** relies on the vibrational motion of molecules. The bonds in a molecule act like tiny springs and, like springs, vibrate with a characteristic frequency. These frequencies fall in the infrared region of the electromagnetic spectrum. By passing IR radiation through a sample and observing what frequencies are absorbed, it is possible to deduce what types of chemical bonds are present in the molecule.

To identify your compound you will examine your spectrum for the presence (or absence!) of absorption peaks from the list below. For practice look at the spectrum of acrylonitrile in figure 1 below (it's from p.358 in your text) and find the peaks for the C–H bonds, the C=C bond and the C≡N bond. Note that the typical units for IR absorbance are not nanometers, but wavenumbers, where the unit is cm$^{-1}$.
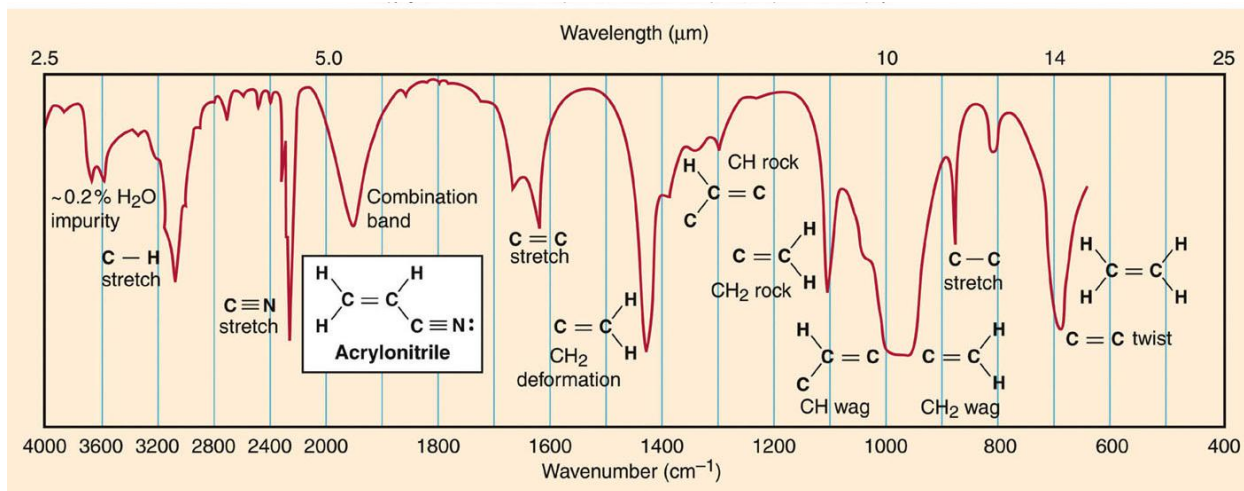


**Figure 1.** The Infrared red (IR) spectrum of Acrylonitrile (from p. 358 Silberberg 5$^{th}$ ed)

**Table 1.** Infrared absorptions of some organic functional groups. See Table 3 on page 6 for a more complete list of organic functional groups and their IR absorptions.
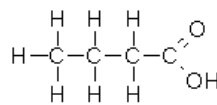
| Bond Type | Absorption in IR Spectrum (cm$^{-1}$) | Notes |
|---|---|---|
| **C–H** | 3000–2850 | All organic compounds will have this peak |
| **O–H** (hydroxyl) | 3600–3400 | Big, very broad obvious peak |
| **C=O** (carbonyl) | 1750–1700 | Very obvious, huge peak |
| **C=C** (alkene) | ~1650 | Not so prominent as some of the others, but obvious in acrylonitrile |
| **C≡N** (nitrile) | 2250 | Also obvious in the acrylonitrile spectrum |

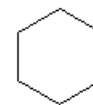Your unknown will be one of the following six compounds:
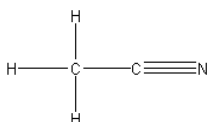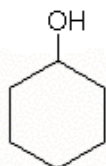
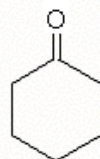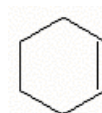**1. Acetonitrile**    **2. Butanoic Acid**    **3. Cylcohexane**

**4. Cyclohexanol**    **5. Cyclohexanone**    **Cyclohexene**
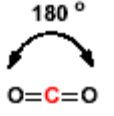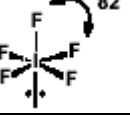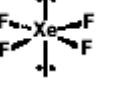


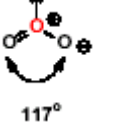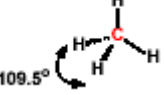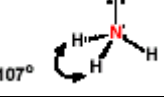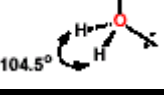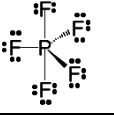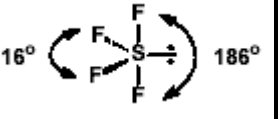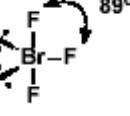**Figure 2.** Structures of the six unknown compounds to be identified in part 3.

**Table 2**. VSEPR formulas, approximate bond angles and 3-D structures for molecules and ions.

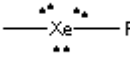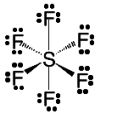| Valence Electron Pairs | Bonding Electron Pairs | Nonbonding Electron Pairs | VSEPR Formula | 3-D Structure & Approx. Bond Angle | Examples | |
|---|---|---|---|---|---|---|
| | | | | | Formula | Image |
| **2** | 2 | 0 | $AX_2$ | Linear; 180º | $CO_2$ |  |
| **3** | 3 | 0 | $AX_3$ | Trigonal planar; 120º | $BF_3$ |  |
| | 2 | 1 | $AX_2E$ | Bent; <120º | $O_3$ |  |
| **4** | 4 | 0 | $AX_4$ | Tetrahedral; 109.5º | $CH_4$ |  |
| | 3 | 1 | $AX_3E$ | Trigonal pyramidal <109.5º | $NH_3$ |  |
| | 2 | 2 | $AX_2E_2$ | Bent; <109.5º | $H_2O$ |  |
| **5** | 5 | 0 | $AX_5$ | Trigonal bipyramidal; 90º, 120º and 180º | $PF_5$ |  |
| | 4 | 1 | $AX_4E_1$ | Seesaw or distorted tetrahedron >90º, <120º, and <180º | $SF_4$ |  |
| | 3 | 2 | $AX_3E_2$ | T-shaped <90º | $BrF_3$ |  |
| | 2 | 3 | $AX_2E_3$ | Linear; 180º | $XeF_2$ |  |
| **6** | 6 | 0 | $AX_6$ | Octahedral; 90º | $SF_6$ |  |
| | 5 | 1 | $AX_5E_1$ | Square pyramidal; <90º | $IF_5$ |  |
| | 4 | 2 | $AX_4E_2$ | Square planar; 90º | $XeF_4$ |  |

## Procedure

**Part 1.  VSEPR**     (Work with a partner)

1. ***Inorganic Molecules and Ions.*** For each molecule or ion below draw the Lewis structure and record the VSEPR formula using the $AX_mE_n$ notation. Then make a 3–D sketch of the molecule or ion and label the bond angles. Finally, name the 3-D structure of the molecule or ion.

    Record your results in Table 4 of the report sheet for the following inorganic molecules and ions and take note that each substance has only one central atom:

    1.) $BrF_5$     2.) $ClF_3$     3.) $PBr_4^+$     4.) $XeF_2$     5.) $PCl_3$

    6.) $I_3^-$     7.) $SO_3$     8.) $CCl_2O$  9.) $XeF_4$     10.) $PF_5$

2. ***Organic Molecules****:* These molecules all have more than one central atom. After drawing each Lewis structure in Table 5 of the report sheet, again make a 3–D sketch of the molecule and label the geometry and bond angles at *each* of the central atoms. Note that the formulas given below have been written so as to indicate how the atoms are arranged.

    1.) $CH_3CHOHCOOH$          2.) $COOHCH_2COOH$

    3.) $CH_2CHCONH_2$          4.) $CH_3CCCH_2Cl$

3. ***Cyclic Organic Compounds****:* The following compounds are all cyclic, with the atoms arranged in a ring:

    1.) $C_3H_6$     2.) $C_4H_8$     3.) $C_6H_{12}$

    Some cyclic compounds are more stable than others.
    **Analysis Questions**: (Draw the structures in Table 6)
    Given what you know about the possible geometries around carbon, which of these compounds do you think is the most stable? The least stable? To answer these questions first draw the Lewis structures, estimate the bond angles, and then explain your choice.

4. Once you have finished predicting the geometry for each molecule or ion in steps 1 – 3, above, *show your work to the instructor before continuing on to the next step*.

5. Now it's time to check your work. We will do this by venturing off to a website by Dave Woodcock (Professor emeritus, Okanagan University College) to find the correct structures. Go to the Main Index at http://www.molecularmodels.ca/, and then click "Molecular Models," and then click "Inorganic."

    Use this index to look up each of the substances. (Note that the index does not list the charge of an ion.) Each will first appear in a "wire frame" representation. You will probably prefer to view the models in the "ball and stick" view. To change the way the molecule is displayed, *right–click* on the model and choose the desired representation from the "Display" pop-up menu.

    Also, take note that the some of the models displayed on this web site do not show double bonds—if this is the case, then all bonds are shown as if they were single.

**Part 2.  Structural Similarities of Various Drugs**     (Work with a partner)

1.  The three–dimensional structure of a molecule is an essential part of its chemical function and reactivity. Sometimes molecules with similar structures have similar properties. Other times they are vastly different.

    Analysis Question: Consider the following drugs. Two of them have very similar 3–D structures and hence have similar biological effects. Which two are they?

    | Caffeine | Nicotine | Morphine | Cocaine | LSD | Heroin |
    |----------|----------|----------|---------|-----|--------|
    | $C_8H_{10}N_4O_2$ | $C_{10}H_{14}N_2$ | $C_{17}H_{19}NO_3$ | $C_{17}H_{21}NO_4$ | $C_{20}H_{25}N_3O$ | $C_{21}H_{23}NO_5$ |
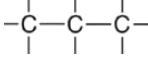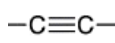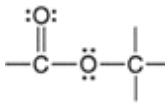
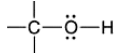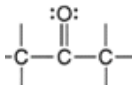2.  To find out, go to the Main Index at http://www.molecularmodels.ca/, and then click "Molecular Models," and then click "Drugs." The drugs are listed in order of the number of carbon atoms in the compound—from fewest to the greatest number of carbon atoms in the compound. It's easiest to compare structures by opening up different "windows" and viewing the structures side by side.
    −   Each structure will first appear in a "wire frame" representation. You will probably prefer to view the models in the "ball and stick" view. To change the way the molecule is displayed, *right–click* on the model and choose the desired representation from the "Display" pop-up menu.
3.  Compare the structures and try to find the two that are most alike. Make a copy of the structure of the structure of these two drugs and include them with the report.

**Part 3.  IR Spectroscopy**    (You will work with everyone at your lab table for this part)

   Your group will select an unknown and run its IR spectrum with the assistance of the instructor. Each student should have a copy of the spectrum attached to the last page of the report. Based on the spectrum and the information provided above, determine the identity of your unknown.

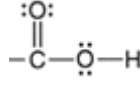1.  Include a copy of your IR spectrum as the last page of the report. *On the spectrum, label the "fingerprint" region of the spectrum and the peaks that you used to identify your unknown*. There will be many peaks on the spectrum; only a few of them will be useful to you in the identification of your unknown. Clearly explain how you identified your unknown. Based on the spectrum, what types of bonds are present (or absent) in your compound?

2.  You may want to compare your unknown with that of others in the class. Each group will receive one of the six unknowns listed above. Therefore, if two groups think they have the same unknown, one of them must be wrong (in fact both may be wrong!). You may also find it interesting to see what the spectra of different compounds looks like.

## Table 3. IR Absorptions for Representative Functional Groups

| Functional Group | Bond Type and its Molecular Motion | Wavenumber (cm$^{-1}$) |
|---|---|---|
| **Alkanes** $C_nH_{2n+2}$ | C-H stretch | 2950-2800 |
| | $CH_2$ bend | ~1465 |
| | $CH_3$ bend | ~1375 |
| | $CH_2$ bend (4 or more) | ~720 |
| **Alkenes** $C_nH_{2n}$ | C=C stretch (isolated) | 1690-1630 |
| | C=C stretch (conjugated: C=C- C=C- C=C) | 1640-1610 |
| | C-H in-plane bend | 1430-1290 |
| **Alkynes** $C_nH_{2n-2}$ | acetylenic C-H stretch | ~3300 |
| | C,C triple bond stretch | ~2150 |
| | acetylenic C-H bend | 650-600 |
| **Alcohols** | O-H stretch | ~3650 or 3400-3300 |
| | C-O stretch | 1260-1000 |
| **Ethers** C-O-C | C-O-C stretch (dialkyl) | 1300-1000 |
| | C-O-C stretch (diaryl) | ~1250 & ~1120 |
| **Aldehydes** | C-H aldehyde stretch | ~2850 & ~2750 |
| | C=O stretch | ~1725 |
| **Ketones** | C=O stretch | ~1715 |
| | C-C stretch | 1300-1100 |
| **Carboxylic acids** | O-H stretch | 3400-2400 |
| | C=O stretch | 1730-1700 |
| | C-O stretch | 1320-1210 |
| | O-H bend | 1440-1400 |
| **Esters** | C=O stretch | 1750-1735 |
| | C-C(O)-C stretch (acetates) | 1260-1230 |
| | C-C(O)-C stretch (all others) | 1210-1160 |
| **Amines** | N-H stretch (1 per N-H bond) | 3500-3300 |
| | N-H bend | 1640-1500 |
| | C-N Stretch (alkyl) | 1200-1025 |
| | C-N Stretch (aryl) | 1360-1250 |
| | N-H bend (oop) | ~800 |
| **Nitriles** | C≡N triple bond stretch | ~2250 |

**Lab 6 Report Sheet**
**VSEPR Theory and IR Spectroscopy**

Name _____

Team No. ____Date _____Section _____

## Experimental Results

### Part 1 — VSEPR

1. **Inorganic Molecules and Ions**

**Table 4.** Structures of simple inorganic molecules and ions

| Formula | Lewis Structure | VSEPR Formula | 3-D Sketch (Label the bond angles) | Name of 3D-Structure |
|---|---|---|---|---|
| 1.  $BrF_5$ | | | | |
| 2.  $ClF_3$ | | | | |
| 3.  $PBr_4^+$ | | | | |
| 4.  $XeF_2$ | | | | |

| Formula | Lewis Structure | VSEPR Formula | 3-D Sketch (Label the bond angles) | Name of 3D-Structure |
|---------|-----------------|---------------|-------------------------------------|----------------------|
| 5.  $PCl_3$ | | | | |
| 6.  $I_3^-$ | | | | |
| 7.  $SO_3$ | | | | |
| 8.  $CCl_2O$ | | | | |
| 9.  $XeF_4$ | | | | |
| 10. $PF_5$ | | | | |

## Part 1 — VSEPR (cont.)

2. **Organic Molecules**

**Table 5.** Structures of Simple Organic Compounds

| Formula | Lewis Structure | 3-D Sketch (Label the geometry and bond angles of all central atoms) |
|---|---|---|
| 1. $CH_3CHOHCOOH$ | | |
| 2. $COOHCH_2COOH$ | | |
| 3. $CH_2CHCONH_2$ | | |
| 4. $CH_3CCCH_2Cl$ | | |

**Part 1 — VSEPR** (cont.)

3. **Cyclic Organic Compounds**

**Table 6.** Structures Cyclic Organic Compounds

| Formula | Lewis Structure | 3-D Sketch (Label the C-C bond angles) |
|---|---|---|
| 1. $C_3H_6$ | | |
| 2. $C_4H_8$ | | |
| 3. $C_6H_{12}$ | | |

**Analysis Questions**:

Given what you know about the possible geometries around carbon, which the three compounds in Table 6 do you think is the most stable? The least stable? Explain your reasoning fully and use *specific numerical data* from Table 6, above, to support your explanation.

**Part 2. Structural Similarities of Various Drugs**

<u>Analysis Question</u>

Circle the two drugs below that have similar structures and hence similar biological effects. <u>*Explain your choice in a few brief sentences and support your explanation by including the structure of these two drugs below*</u>.

| Caffeine | Nicotine | Morphine | Cocaine | LSD | Heroin |
|----------|----------|----------|---------|-----|--------|
| $C_8H_{10}N_4O_2$ | $C_{10}H_{14}N_2$ | $C_{17}H_{19}NO_3$ | $C_{17}H_{21}NO_4$ | $C_{20}H_{25}N_3O$ | $C_{21}H_{23}NO_5$ |

<u>*Explanation*</u>:

<u>*Structures of the two drugs with similar structures*</u>:

## Part 3. IR Spectroscopy

### Analysis

Attach a copy of your IR spectrum as the last page of this report. *On the spectrum, label the "fingerprint" region of the spectrum and the peaks that you used to identify your unknown*. Clearly explain below how you identified your unknown. Based on the spectrum, what types of bonds are present (or absent) in your compound?

## *Lab 6.  VSEPR, Molecular Structure & IR Spectroscopy*     **Name**_____
**Prelab Questions**                                          **Section** _____   **Team #** _____

1.  a.  Write the Lewis structure for Arsenic trichloride, $AsCl_3$.

   b.  The number of nonbonding electron pairs in $AsCl_3$ is _____.
   c.  The VSEPR formula for $AsCl_3$ is _____.
   d.  The 3-D structure for $AsCl_3$ is _____.

2.  a.  Write the Lewis structure for aluminum chloride, $AlCl_3$.

   b.  The number of nonbonding electron pairs in $AlCl_3$ is _____.

   c.  The VSEPR formula for $AlCl_3$ is _____.

   d.  The 3-D structure for $AlCl_3$ is _____.

3.  A molecule having a bond angle of $90^o$ and an octahedral structure has a _____ VSEPR formula.

4.  As mentioned in the introduction, IR absorbance is measured in wavenumbers ($cm^{-1}$) and not in nanometers or micrometers, μm (see the IR spectra on page 358 in your text, Silberberg 5<sup>th</sup> ed.). Prove that a wavelength of 10 μm is equal to a wavenumber of $1000\ cm^{-1}$. See Table 1.3 on page 19 of your textbook if you don't remember the numerical values of metric prefixes.

5.  Based on the data in Table 3 on page 6 and the structure of Butanoic acid in figure 2 on page 2, predict the wavenumbers (in $cm^{-1}$) of the peaks in the IR absorption spectrum for butanoic acid.

| Wave number  ($cm^{-1}$) | Chemical bond |
|---|---|
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |