The FTIR / Vibrational spectroscopy exercise follows the format of a detective story involving solving a series of problems rather than the normal lab format. The experiment is an adaptation of "Pollution Police" by Profs. Jodye Selco and Janet Beery at the University of Redlands, which was presented at the Division of Chemical Education Regional ACS meeting in Ontario, CA 1999.

Introduction

The theory of FTIR spectrometer operation is discussed in SHN Chapters 16 and 17. The group theory and vibrational quantum mechanics are discussed in McQuarrie and Simon (Chem 110B text) Chapters 12 and 13. The experimental portion of the exercise is problem #10 and problem #11. The computer portion of the exercise is in problems #2, 7, 8, and 9, and is done separately on the computers in room. All four computers are set up to run HyperChem, Gaussian and Spartan.

![FTIR Spectrometer](image)

**Figure 0:** UCD FTIR instruments, both new and old. Track out the light path in the old instrument

Setting the Scene

You have been hired by an environmental testing company to monitor air pollutants. Some of these chemicals are released into the atmosphere from factories, cars, or cattle; others evaporate from agricultural fields. Since most of these chemicals absorb infrared light, we are able to detect them with an infrared spectrometer. A test sample is obtained by taking an evacuated cell to the target location, opening a valve, and allowing the ambient air to fill the cell. A FTIR – Fourier Transform Infrared Spectrometer will be used to take the IR spectra. The final output from the spectrometer, called
an infrared spectrum, is a plot of the intensity of light reaching the detector divided by the initial intensity of light, as a function of frequency (\( \%T = I/I_0 \) vs. frequency in wavenumbers). The goal of this project is to gain a better understanding of group theory and to identify atmospheric pollutants from their infrared spectra.

\[ \begin{align*}
\text{Figure 1: An infrared spectrum of air. The lower, single-beam trace clearly shows the absorption of atmospheric gases.} \\
\text{The top, double-beam trace shows that the reference beam compensates nearly perfectly for the air absorption,}
\end{align*} \]

producing a stable 100% \( T \).

Some of the molecules commonly found in the atmosphere include those in the following list. Water and small amounts of carbon dioxide, methane, and sulfur trioxide are found in “clean” air samples. Large amounts of any of the chemicals other than water usually indicate atmospheric pollution.

1. H\(_2\)O (water): Water is ubiquitous in the atmosphere, even on dry days.
2. CO\(_2\) (carbon dioxide): Carbon dioxide is produced by the combustion of fuels (including the food we eat) and is a major source of greenhouse warming in the atmosphere.
3. CH\(_3\)X (methyl halides): Methyl halides are used as pesticides that are sprayed on agricultural fields. They currently are under strict EPA controls, and are partially responsible for the ozone hole.
4. CCl\(_2\)F\(_2\) (dichlorodifluoromethane): Dichlorodifluoromethane is a refrigerant that is partially responsible for the ozone hole.
5. C\(_2\)H\(_4\) (ethylene): Ethylene is one of the components of natural gas, and is used to ripen bananas.
6. C\(_2\)H\(_2\) (acetylene): Acetylene is a fuel for high-temperature torches.
7. SO\(_3\) (sulfur trioxide): Sulfur trioxide results from the burning of sulfur-containing fuels such as coal; it reacts with water to form acid rain.
8. C\(_6\)H\(_6\) (benzene): Benzene is a component of gasoline, and is carcinogenic.
9. C\(_2\)H\(_2\)Cl\(_2\) and C\(_2\)Cl\(_4\) (dichloroethylenes, or DCEs, and perchloroethylene, or PCE): All three isomers and PCE are air pollutants, due to their use in the dry-cleaning and polymer industries.
10. HOOH (hydrogen peroxide): Hydrogen peroxide is a component of smog.

Examine the three-dimensional ball-and-stick models for these molecules, and compare them with the two-dimensional representations of the molecules in Figure 2. In the drawings in Figure 2, straight lines represent bonds that lie in the plane of the paper; two lines between a pair of atoms represent a double bond; a filled arrowhead indicates a single bond that is angled out of the plane of the paper toward you; and the dashed arrowhead indicates a bond angled into the plane of the paper away from you. Carbon dioxide is an example of a linear molecule; water, ethylene, sulfur trioxide, and benzene are planar molecules.
water

methane

carbon dioxide

methyl bromide

ethylene

allene

sulfur trioxide

sulfur hexafluoride

dichlorodifluoromethane
Problem #1: Center-of-mass and Coordinate Axes

In order to accomplish our goal of identifying a chemical from its infrared spectrum, we must know which infrared frequencies, if any, the molecule absorbs. To decide which molecules absorb infrared radiation and at which frequencies, we will need to examine various properties of the molecules themselves, including their centers of mass, their Cartesian coordinate axes, their vibrations, and their symmetries. Specifically, we will compare the actions of the symmetry operations of a molecule on its Cartesian coordinate axes with the actions of the symmetry operations on its vibrations.

When a molecule absorbs infrared radiation of a given frequency, this energy causes the molecule to vibrate in a specific way; the atoms bounce against each other much like balls connected by a spring. The vibrational motions of a molecule that absorb infrared radiation are the ones that exhibit the same behavior as do the Cartesian coordinate axes of the molecule when the atoms of the molecule are permuted in certain ways. This is a result of the orthogonal interaction between the electro-magnetic field of the light and the electric field of the molecule itself. Therefore, you will begin by drawing in a three-dimensional coordinate system for each of the molecules in the set assigned (see table below). The convention for molecules is that the origin of the axis system is placed at the center of mass of the molecule. (This is the weighted average of the positions of the atoms.) First, determine approximately where this should be. (You might want to reexamine the ball-and-stick models.) Remember, the masses of the different atoms are different. To find out how much each atom weighs; consult a periodic table of the elements. The mass number for each type of atom appears at the bottom of the square in which the atomic symbol appears.

By convention, the z-axis is the unique axis, if there is one. This axis is also called the molecular axis, or axis of highest symmetry. In a linear molecule it corresponds to the line formed by the molecule; this is true for carbon dioxide. For benzene, the z-axis is the out-of-plane axis since it is the unique axis. If there doesn’t seem to be a unique axis, then place the heaviest atoms in the molecule along the z-axis (often, there is more than one way to do this). Once the z-axis is assigned, the in-plane axis usually is the y-axis and the out-of-plane axis is the x-axis. In addition, axes should be placed along the molecular bonds whenever possible.

Example 3.1

The y- and z-axes for water and carbon dioxide are shown in Figure 3. The x-axis is out-of-plane from the origin (just below the O atom and pointing straight out at you for water, but centered in the C atom and pointing directly away from you for carbon dioxide).
Figure 3: Cartesian coordinate axes for water and carbon dioxide

Assignment

Assigned molecules for Problem 1:

- For lab groups A and E: dichlorodifluoromethane, hydrogen peroxide, sulfur trioxide
- For lab groups B and F: trans-1,2-dichloroethylene, ethylene, methyl bromide
- For lab groups C and G: gem-1,1-dichlorethylene, dinitrogen tetroxide, ammonia
- For lab groups D and H: cis-1,2-dichloroethylene, perchloroethylene, methyl iodide

Draw in the three Cartesian coordinate axes in a picture of each molecule as outlined in the steps below. (If you do not assign them correctly now, you will have a chance later to re-label them.)

1. Estimate, by eye, the center of mass for each molecule, keeping in mind the atomic masses for each type of atom.
2. Draw in the z-axis using the rules above.
3. Draw in the two remaining axes using the rules above.

Problem #2: Molecular Vibrations

The types of molecular vibrations a molecule has determine whether or not it absorbs infrared light. Hence, you need to determine the types of vibrations your molecules make. To ensure that all of them have been identified, we need to know how many are possible. Consider a molecule that is a collection of N atoms connected together in a specific way by chemical bonds. In order to describe the motions of the molecule, we need to consider the motions of each individual atom. This means that we need 3 degrees of freedom for every atom within the molecule for a total of 3N degrees of freedom. However, the atoms within the molecule have a specific geometric relationship to the other atoms in the molecule; this results in a redistribution of the number of independent degrees of freedom. The motion through space of the molecule uses three degrees of freedom, reducing the 3N degrees of freedom to 3N - 3. Since the molecule also can rotate (like a spinning baton or Frisbee), we require two degrees of freedom to describe the coordinates about which a linear molecule can spin and three degrees of freedom for a non-linear molecule (for a linear molecule there is no concerted rotation about the molecular axis (z-axis). This leaves 3N - 5 degrees of freedom for the linear molecule and 3N - 6 for the non-linear molecule still unaccounted for; each of the remaining degrees of freedom describes a distinct coordinated internal motion, or vibration, of the atoms within the molecule.
For example, when there are only two atoms in the molecule (e.g. O\textsubscript{2}, N\textsubscript{2}, or CO), there is only one vibrational motion: \(3(2) - 5 = 1\). In the case of benzene (C\textsubscript{6}H\textsubscript{6}) there are 12 atoms and \(3(12) - 6 = 30\) vibrational motions possible! As it turns out, not all of these vibrations are capable of absorbing infrared radiation. For the simplest molecules, such as water, it is easy to draw pictures representing the vibrational motions.

Example 3.2

Water has \(3(3)-6=3\) vibrations and carbon dioxide has \(3(3)-5=4\) vibrations as shown in Figures 4 and 5.

<table>
<thead>
<tr>
<th>Molecular Bond</th>
<th>Vibrations of water</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—O—H</td>
<td>antisymmetric stretch</td>
</tr>
<tr>
<td>H—O—H</td>
<td>symmetric stretch</td>
</tr>
<tr>
<td>H—O—H</td>
<td>scissoring bend</td>
</tr>
</tbody>
</table>

**Figure 4: Vibrations of water**

Consider the water molecule as it undergoes the asymmetric stretch; as it reaches its most extreme position, it has one “arm” extended and the other “arm” contracted. The bend is a change largely in angle and not inter-atom distances.

<table>
<thead>
<tr>
<th>Molecular Bond</th>
<th>Vibrations of carbon dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—O—H</td>
<td></td>
</tr>
<tr>
<td>H—O—H</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5: Vibrations of carbon dioxide**

The four vibrations for CO\textsubscript{2} consist of two stretches (one symmetric and one asymmetric) and two bends, that are degenerate (with the same energy) but involve perpendicular motions.

**Assignment**

For each molecule, calculate the number of vibrational motions using the formula given above. Then, use a computer program to view the vibrational motions for water, carbon dioxide and the other molecules assigned. Record the motions of the atoms in the molecule using the symbols from the examples above, and record the frequency calculated for each vibration. Note that some of these motions are out-of-plane motions. Be sure to rotate the molecules on the computer screen so that you examine the motions from many different angles. (Many of the programs calculate the frequencies in cm\textsuperscript{-1}; this is actually the frequency, in s\textsuperscript{-1}, divided by the speed of light \((3.00 \times 10^{10} \text{ cm/s})\). In this exercise, make note
of the frequencies in cm\(^{-1}\) given by the HyperChem program.) Again, you are to complete the following steps for the molecules your instructor assigns you.

1. Determine the number of vibrational motions, \(3N - 6\) or \(3N - 5\), to make sure that you know how many vibrational motions to record.
2. Record the vibrational motions for your molecules, following the notation used in the examples above.
3. Record the frequency for each of these vibrations.

**Spartan ’16 Operation**

1. Double-click “PC Spartan “16” on desktop. Spartan computer located in the TA area of 3475 and has a bright orange name tag.
2. Click the new page icon in the top left corner. Atoms with various bond choices will appear. If you prefer a more advanced setting, click the Expert tab.
3. Draw your molecule by clicking on the atom with the correct number of bonds needed. To join two atoms, repeat this process by touching the mouse arrow to the open bond.
4. Once you are done drawing your molecule, click the Glasses (“View”) icon located just below the Geometry scroll-down. This will finalize your drawing.
5. Next, go to the Setup scroll-down and select Calculations. The following will be your entries:
   1. Calculate: Equilibrium Geometry with Hartree-Fock 3-21G(*)
   2. Compute: IR
   3. Print: Vibrational Modes
6. Go to Setup and scroll down to Submit. Make a new folder with your group's letter in the Chem 115 folder. Label within your folder as you see fit.
7. After you save the file you will be prompted twice that Spartan has started and completed. Press OK both times.
8. Go to Display and scroll to Spectra. Here you will find the frequencies associated with the different vibrations of your molecule. Click on any of the check boxes to view an animation for the vibration associated with that particular frequency.

**Problem #3: Symmetry Elements and Symmetry Operations**

Because the molecules we are examining are very small, the rules of quantum mechanics govern the processes in which we are interested. According to quantum mechanics, not all light absorption processes are allowed; many are "forbidden" by symmetry. If we want to determine which molecular vibrations absorb infrared light, we need to examine the actions of the symmetries of the molecules on the coordinate axes and on the molecular vibrations. We begin by determining the symmetry elements that each molecule possesses.

A symmetry operation on a molecule is an action that moves the molecule into a position that is indistinguishable from the starting position. A symmetry element of a molecule is a geometric feature of the molecule about which a symmetry operation is performed. Symmetry elements include planes and axes; symmetry operations include reflections across planes and rotations about axes. In the case of water, 180° rotation about the z-axis is a symmetry operation, denoted \(C_2\); while the z-axis itself is a symmetry element, a \(C_2\) axis. The symbol \(C_3\) indicates a three-fold axis of symmetry, a symmetry element; while \(C_3\) indicates a 120°rotation about a \(C_3\) axis, a symmetry operation. Rotation by 240° about a
C₃ axis is denoted C₃². Rotation by 360° about a C₃ axis is equivalent to doing nothing; that is, C₃³=E, where E is the identity operation.

### Table 1: A list of all symmetry elements and operations

<table>
<thead>
<tr>
<th>Symmetry Element</th>
<th>Symmetry Operation</th>
<th>Symbol</th>
<th>Description</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E)</td>
<td>Identity</td>
<td>(\hat{E})</td>
<td>No change</td>
<td>(\hat{E})</td>
<td>No change</td>
</tr>
<tr>
<td>(C_n)</td>
<td>n-fold axis of symmetry</td>
<td>(\hat{C}_n)</td>
<td>Rotation about the axis by (360°/n)</td>
<td>(\hat{C}_n)</td>
<td>Rotation about the axis by (360°/n)</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Plane of symmetry</td>
<td>(\hat{\sigma})</td>
<td>Reflection through the plane</td>
<td>(\hat{\sigma})</td>
<td>Reflection through the plane</td>
</tr>
<tr>
<td>(i)</td>
<td>Center of Inversion</td>
<td>(\hat{i})</td>
<td>Reflection through the center</td>
<td>(\hat{i})</td>
<td>Reflection through the center</td>
</tr>
<tr>
<td>(S_n)</td>
<td>n-fold rotation-reflection axis of symmetry, also called improper rotation axis</td>
<td>(\hat{S}_n)</td>
<td>Rotation about the axis by (360°/n) followed by a reflection through a plane perpendicular to that axis</td>
<td>(\hat{S}_n)</td>
<td>Rotation about the axis by (360°/n) followed by a reflection through a plane perpendicular to that axis</td>
</tr>
</tbody>
</table>

The plane of symmetry, \(\sigma\), is also referred to as a reflection plane or mirror plane. The symbol \(\sigma_v\) is used to denote a “vertical” plane of symmetry that is parallel to an axis of highest symmetry (z-axis, or \(C_n\) with largest n), while the symbol \(\sigma_h\) is used to denote a “horizontal” plane of symmetry that is perpendicular to the axis of highest symmetry (taken as z-axis). The symbol \(\sigma_d\) denotes a “dihedral” plane of symmetry that bisects an angle between atoms.

**Example 3.3**

Figures 6a and 6b illustrate several of the symmetry elements listed in Table 1.
**Figure 6a:** Symmetry elements for two views of ammonia (NH$_3$). The C$_3$ axis is labeled and the three mirror planes, $\sigma_v$, $\sigma_v'$, $\sigma_v''$ are labeled as gold circles.

**Figure 6b:** Symmetry elements for allene (C$_3$H$_2$). The C$_2$ and S$_4$ axis is labeled and the two mirror planes, $\sigma_d$, $\sigma_d'$ are labeled as gold circles.

Example 4: Figures 7 and 8 show the symmetry elements and operations of water and carbon dioxide, respectively.
In the case of water the symmetry elements are E, C₂ (shown), σᵥ (xz-plane, perpendicular to the plane of the molecule), and σᵥ' (yz-plane, the plane of the molecule). Note that it does not matter whether σᵥ represents the xz- or yz-plane. The corresponding symmetry operations for water are E, C₂, σᵥ, and σᵥ'.

The symmetry elements not shown above are E, σᵥ (yz-plane, the plane of the paper), σₜ (xy-plane, perpendicular to the C₂ axis), and i (center of inversion at the coordinate origin). The symmetry operations for carbon dioxide are E, infinitely many C₂, C∞, infinitely many σᵥ, S∞, σₜ, and i. A subscript of ∞ means that rotation through any angle about that axis results in a valid symmetry operation. Note that σₜ is identical to S₀ and is often omitted.

**Assignment**

Reexamine the ball-and-stick models for your molecules. Determine all of the symmetry elements and corresponding symmetry operations for each molecule. (Hint: At least one molecule on the list contains the symmetry element σₜ and one contains an S₃ symmetry element.)

There are a few things to keep in mind while trying to determine the symmetry elements for chemical compounds. The first is that molecules are three-dimensional objects. This means that we can tell the difference between the “front” and “back” or the “top” and “bottom” of planar molecules. For instance, the σᵥ reflection of the water molecule across the yz-plane is not the same as the identity operation E. Second, since atoms of the same kind (or color) are indistinguishable, you may want to number the atoms in the models in order to keep track of the results of the symmetry operations. Finally, when molecules have hexagonal rings with alternating double bonds, all of these bonds—both single and double—are equivalent (e.g. benzene and toluene). It is only the orientation of the atoms themselves that can be “seen” spectroscopically, and hence needs to be considered here.
After you have determined the symmetries of the molecules, you can double-check your axis assignments. The z-axis should be the axis of highest C_n symmetry. In H_2O, there is only one C_n axis, C_2, so it is the z-axis. In CO_2, there is a C_2 axis and a C_s axis, so the C_s axis is the z-axis. Check the other molecules to make sure that the z-axis you assigned is the one of highest symmetry. Remember that the axis of highest symmetry may not be unique.

Problem #4: Orders of Symmetry Operations

Assignment

The order of a symmetry operation is the number of times the operation must be applied to obtain the identity operation, 1. More specifically, the order of a symmetry operation \( \hat{A} \) is \( n \), if \( n \) is the smallest positive integer such that \( \hat{A}^n = 1 \). For instance, for H_2O, the non-identity symmetry operations each have order 2. The symmetry operation S_4 has order 4 because it must be applied four times in succession to return the molecule to its original orientation when the outside atoms are labeled. (Try it for methane!) Therefore, S_4 generates 4 symmetry operations: S_4, S_4^2 = C_2, S_4^3, and S_4^4 = 1 of orders 4, 2, 4, and 1, respectively. For your molecules, find the order of each symmetry operation.

Problem #5: Symmetry Groups

Assignment

You may have noticed that the set of symmetry operations forms a group under composition of operations, called the symmetry group of the molecule. Consider the groups of symmetries of the molecules in the set assigned in problem #1. The order of a symmetry group is the number of operations which comprise the group. What is the order of each group? Verify by determining the group for your molecules from HyperChem and by examining the character tables in Chapter 12 of McQuarrie and Simon (Chem 110B text) or Chemical Applications of Group Theory, by F. A. Cotton.

Problem #6: Action of Symmetries on Coordinate Axes

Your overall goal is to identify the molecular origins of the infrared peaks observed in a spectrum of contaminated air. Since a molecule’s infrared light absorption depends on how the Cartesian axes transform under the symmetry operations, the next step is to determine what happens to each of the Cartesian axes as the different symmetry operations are performed upon the molecule.

Example 3.5

In Figure 9 and Table 2, we illustrate this process for water. Note that under the identity operation, 1, none of the axes are inverted or reversed. When the molecule is rotated about the C_2 axis, the orientation of the z-axis remains the same but the x- and y-axes are oriented in the opposite direction; each point \((x,y,z)\) is moved to the point \((-x,-y,z)\). In this case, the rotation is equivalent to multiplying the x and y values by -1. For any operation, -1 indicates that there is a reversal in the orientation of the axis relative to the original orientation, whereas +1 indicates that the orientation remains the same.
Figure 9: The coordinate axes and symmetry elements for water

Table 2: How the axes of water transform under the symmetry operations

<table>
<thead>
<tr>
<th></th>
<th>$\hat{E}$</th>
<th>$C_2$</th>
<th>$\sigma_{yz}$ (xz)</th>
<th>$\sigma_{yz}$ (yz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$Y$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$Z$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Assignment

Construct similar tables for the first two molecules that you are assigned. First check with your TA to make sure you have drawn the Cartesian coordinate axes in the standard way for each of these molecules.

Problem #7: Action of Symmetries on Vibrational Motions

The vibrational motions of the molecule that absorb infrared radiation are the ones that transform under the symmetry operations of the molecule in the same way as do the Cartesian coordinate axes of the molecule. Therefore, we need to determine how the molecular vibrations behave under each of the symmetry operations, so that we can compare them to the transformations of the Cartesian coordinate axes.

Example 6: Let us reexamine the vibrations of water.
If we ask how each of the vibrations of water behaves under each of the symmetry operations, we can add more entries to Table 2. When we examine what happens to the vibrating molecules as the symmetry operations are performed, we are interested only in whether or not the geometrical orientation of the molecule has changed. For instance, consider the water molecule as it undergoes the asymmetric stretch. Imagine the molecule (or stop the computer program) when it reaches its most extreme position, with one “arm” extended and the other “arm” contracted. Now perform the $C_2$ operation (rotation by 180°) on this “distorted” molecule. Its orientation after the $C_2$ operation is different from its orientation before. Note that the configuration has been reversed. The fact that its new position is distinguishable from its original position is represented in Table 3 by -1.

Now let’s examine the water molecule as it undergoes the bend or symmetric stretch. If we perform the $C_2$ operation (rotation by 180°) on this vibrating molecule, its geometric orientation is unchanged. Its new position is indistinguishable from its original position. The fact that it appears unchanged is represented in Table 3 by +1.

**Table 3: How the axes and vibrations of water transform under the symmetry operations**

<table>
<thead>
<tr>
<th>H$_2$O</th>
<th>$\hat{E}$</th>
<th>$C_2$</th>
<th>$\sigma_v$ (xz)</th>
<th>$\sigma_v'$ (yz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>Y</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>bend</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>symmetric stretch</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>asymmetric stretch</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>
Assignment

Construct tables as in the water example for the first two molecules in your assigned set. Examine the motions of the atoms for each different vibration. If you were to imagine the molecule (or stop the computer program) when it reaches its most extreme position, consider how that “version” of the molecular shape would behave under each of the different symmetry operations. That the molecule is indistinguishable after the symmetry operation is indicated by a 1, while a distinguishable molecule is represented by a -1. Fill in a line in your table for each vibrational motion. (Note this procedure works for most, but not all simple molecules).

Problem #8: Comparing Symmetry Operations on Axes and Vibrations

For the first two molecules in your assigned set, use the tables you constructed in Problem #7 to determine how the vibrational motions transform under the symmetry operations. List the frequency calculated of the ones that transform as do the x-, y-, or z-axes. (You listed the frequencies you need for this problem in Problem #2.) These are the frequencies that absorb light. Given that infrared spectrometers operate in the range of about 600 cm\(^{-1}\) to 4000 cm\(^{-1}\) (wavenumbers), which vibrational frequencies should you observe in the infrared spectra for your molecules? Make a rough sketch of the infrared spectrum you would expect to see for each of your molecules, labeling peaks with their frequencies. Assume that if peaks are separated by less than 25 cm\(^{-1}\), they will not be resolved and will appear as a single peak.

Example 7: In the case of water, as illustrated in Table 3, the bending vibration transforms under the symmetry operations in the same way as does the z-axis. This is also true for the symmetric stretching motion. On the other hand, the asymmetric stretch transforms in the same way as does the y-axis. In this case, all three of the vibrational motions of water would absorb infrared light since each one of them transforms under the symmetry operations as does one of the Cartesian coordinate axes. All of the vibrations also have frequencies that are in the appropriate frequency range. We would expect the infrared spectrum of water to have three peaks corresponding to frequencies of 1840, 3587, and 3652 cm\(^{-1}\).

Problem #9: Actions of Symmetries on the xy-plane

Now look at your final molecule. For this molecule, some of the symmetry operations move the x- and y-axes to positions that are not 180° from their original orientations. In this case, we describe all movements of the xy-plane using 2 x 2 transformation matrices. For example, the operation C\(_3\) rotates the molecule by an angle of θ=120° in the counterclockwise direction, about its z-axis. Hence, the x- and y-axes are rotated as shown in Figure 11 (but shown for only 45°).
In two-dimensional space (the xy-plane), we can represent any point in that space as a combination of two orthogonal directions, x and y. We can think of the x- and y-axes as two vectors that span the two-dimensional space. Since vectors $i=(1,0)$ and $j=(0,1)$ form a basis for $\mathbb{R}^2$ (2-D space), linear transformations of $\mathbb{R}^2$ are completely determined by where they map those basis vectors. Note that the $120^\circ$ rotation maps vector $i$ to the vector with x-component $\cos 120^\circ (=-\sin 30^\circ)$, and y-component $\sin 120^\circ (=\cos 30^\circ)$; that is, to the vector $(-1/2, \sqrt{3}/2)$. Similarly, vector $j$ is mapped by the transformation to the vector with x-component $\cos 210^\circ (= -\cos 30^\circ = -\sin 120^\circ)$, and y-component $\sin 210^\circ (= -\sin 30^\circ = \cos 120^\circ)$; that is, to the vector $(-\sqrt{3}/2, -1/2)$. Considering the points in the xy-plane as column vectors, note that rotation by $\theta=120^\circ$ is given by left multiplication of each point by the matrix

$$
\begin{bmatrix}
-1/2 & -\sqrt{3}/2 \\
\sqrt{3}/2 & -1/2 \\
\end{bmatrix}
$$

You may recall that rotation of the xy-plane about the origin by an angle $\theta$ in the counterclockwise direction can be described by the matrix

$$
\begin{array}{cc}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta \\
\end{array}
$$

In Figure 12, we have oriented a general tetrahedral molecule AB₃C such that one of the B atoms lies along the positive x-axis.
Figure 12: Oriented general molecule AB₃C

As you can see in Figure 12, the molecule now has B atoms lying along the positive x-axis, at an angle of 120° counterclockwise from the positive x-axis (along the dotted line), and at an angle of 240° counterclockwise from the positive x-axis. The molecule has vertical planes of reflection along each B-A-C angle as symmetry elements. For a reflection such as the one across the vertical symmetry plane through the dotted line, we must determine where the vectors i=(1,0) and j=(0,1) are mapped.

Figure 13: Reflection transformation for AB₃C

Note that vector i is mapped by the transformation to the vector (-1/2, -√3/2). Similarly, vector j is mapped by the transformation to the vector (-√3/2, 1/2). The transformation matrix is:

\[
\begin{bmatrix}
-1/2 & -\sqrt{3}/2 \\
-\sqrt{3}/2 & 1/2
\end{bmatrix}
\]

Table 4 shows how the coordinate axes transform under the symmetry operations of the molecule. Find the three remaining 2 x 2 matrices using the method illustrated above.
Table 4: Axis Transformation Table for CH₃Br (matrices)

<table>
<thead>
<tr>
<th></th>
<th>¨E</th>
<th>C₃</th>
<th>C₃²</th>
<th>¨v</th>
<th>¨v'</th>
<th>¨v''</th>
</tr>
</thead>
<tbody>
<tr>
<td>z</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
</tr>
<tr>
<td>x,y</td>
<td>[1 0]&lt;br&gt;[0 1]&lt;br&gt;</td>
<td>[−1/2 −√3/2&lt;br&gt;√3/2 −1/2]&lt;br&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5 is an axis transformation table for AB₃C in which the matrices are replaced by their traces, which is the sum of the numbers along the diagonal of the matrix. Fill in the missing entries in Table 5.

Table 5: Axis Transformation Table for CH₃Br (traces)

<table>
<thead>
<tr>
<th></th>
<th>¨E</th>
<th>C₃</th>
<th>C₃²</th>
<th>¨v</th>
<th>¨v'</th>
<th>¨v''</th>
</tr>
</thead>
<tbody>
<tr>
<td>z</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
</tr>
<tr>
<td>x,y</td>
<td>2</td>
<td>-1</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>0</td>
</tr>
</tbody>
</table>

Reexamine the vibrational motions for your third assigned molecule, whose frequencies are unique (i.e. do not occur in pairs). Which of the vibrations transform in the same way as does the z-axis?

For this molecule, which is three-fold symmetric, it is more difficult to try to determine which motions transform in the same way as do the x- and y-axes. Using the molecular modeling program, orient your third molecule so that you are viewing the xy-plane with the negative z-axis pointing towards you. Observe the motions whose frequencies occur in pairs; these motions are called “degenerate” motions.

If you consider the two motions in each degenerate pair as a set, you will notice that the motions that occur during the vibrations are along either the x-axis or the y-axis.

If you examine one frequency pair, you should notice that one vibrational motion occurs primarily in the x-axis direction. Then (without moving the molecule) switch to the second motion of the pair. You will notice that the motion is now along the y-axis. Try this with all of the paired frequencies. Does the principal motion switch to a different axis?
The atoms within a molecule are held together by their electrons (which have negative charges); the electrons form the chemical bonds. As the atoms in the molecule move during a vibration, so do the electrons. It is this oscillating electron density which interacts with the oscillating electro-magnetic field of the light. For molecules such as AB₃C, in which the x- and y-axes move together under the symmetry operations, we then have electron density oscillation in both the x- and y-directions. In the case of AB₃C, a member of each degenerate pair has electron density oscillation in the x-direction while the other has oscillation in the y-direction. Therefore, these vibrations transform as do the x- and y- axes. The electron density oscillation in the x- and y-directions can interact with the electric field of the light, resulting in absorption of x- or y-polarized electromagnetic radiation.

Assignment

List all the frequencies you should see in the infrared spectrum of your third molecule, then sketch the spectrum you would expect to see, labeling the peaks with their corresponding frequencies.

For the final molecule in your list, all of the degenerate vibrations transform in the same way as do the x- and y-axes. This is not always true, however. Examine the degenerate vibrations for benzene. If you examine the degenerate pairs of vibrations whose frequencies are approximately 1100 cm⁻¹, 1650 cm⁻¹, and 3240 cm⁻¹ (and are labeled E₁u), you should notice that they all have distinct electron density oscillations in the x- and y- directions. Now examine the other 7 pairs of degenerate vibrations. Can you see that they do not have oscillating electron densities along each of the x- and y-axes?

Problem #10: Obtaining Infrared Spectra

Assignment

Now it is time to compare your predicted spectra to real ones. Breathing into the sample compartment of the infrared spectrometer can generate the spectrum of water and carbon dioxide. You will then take spectra of methyl iodide, ethylene, acetylene, trans-DCE, and a sample of contaminated air, which have already been prepared in infrared cells. Do not be overly concerned if the windows on the cells appear to be hazy; they will work fine. Do you observe the predicted absorptions? If not, try multiplying all of your vibrational frequencies by 0.89 (a factor theoretical chemists recommend to compensate for over calculations). Do they come closer to what you observe now?

Operating the Bruker FTIR Spectrometer (room 3475)

1. Start the OPUS 6.0 software on the computer next to the instrument.
2. In the Measure Menu, go to the Advance tab to set the parameters for the experiment
   - Scans: 16 for sample and 16 for background
   - Resolution: 2.0
   - Signal Gain: 1
   - IR Data Type: Transmittance
   - Go to Path: and select the Chem115 directory for data storage
     - Name your sample in the Filename: field
3. Close the sample compartment and wait 2-3 minutes for sample compartment to be purged of air.
4. In the **Measure Menu**, go to the **Basic tab**. Click the “Background Single Channel” button, the instrument will start scanning the background. The progress status will be shown on the bottom of the screen.

5. Open the chamber, and load your sample in. Close the chamber.

6. To acquire your sample scan. Give your sample a description under the **Basic tab**. Run the sample spectrum by clicking on the “**Sample Single Channel**” button. The progress of the scan can be seen in the bottom of the screen.

**Operating the FTIR Spectrometer (room 3480)**

1. Start the **OPUS 7.2 software** on the computer next to the instrument.

2. In the **Toolbar Menu**, find the **Advance Measurement** tab to set the parameters for the experiment
   - Scans: 16 for sample and 16 for background
   - Resolution: 2.0
   - Signal Gain: auto
   - IR Data Type: Transmittance
   - Go to **Path**: and select the Chem115 directory for data storage
     - Name your sample in the **Filename**: field

3. Close the sample compartment and wait 2-3 minutes for sample compartment to be purged of air.

4. In the **Measure Menu**, go to the **Basic tab**. Click the “Background Single Channel” button, the instrument will start scanning the background. The progress status will be shown on the bottom of the screen.

5. Open the chamber, and load your sample in. Close the chamber.

6. To acquire your sample scan. Give your sample a description under the **Basic tab**. Run the sample spectrum by clicking on the “**Sample Single Channel**” button. The progress of the scan can be seen in the bottom of the screen.

**2017-An Agilent 630 FTIR might be available, ask Paul**

**Collect a spectrum of water and carbon dioxide:**

1. Open the sample compartment.
2. Exhale into the sample compartment.
3. Collect the spectrum by clicking on the “**Sample Single Channel**” button on the **Basic Tab**.

**Collect spectra of the four reference samples and your unknown:**

1. Open the sample compartment.
2. Put the cell holder with the cell into the sample compartment. Align the holes in the bottom of the holder with the holes in the plate in the bottom of the compartment.
3. Wait 2-3 minutes for the compartment to purge.
4. Name the file.
5. Acquire the spectrum by pressing **Sample Single Channel** button.
To pick peaks

Click on the peak picking icon

Select Peak Picking from the Evaluate menu.

• The peak picking screen will show up. Choose the Interactive mode. Sliding the Threshold square up or down so that all the peaks are below it.
• Each peak above the threshold will be labeled with its frequency and the peak list will be written to a report file that you must save by selecting Save Report from the File pulldown menu.
• You can annotate the plot by selecting the annotator options from the Tools pulldown menu.
  • The file path and name are the default title for your plot. You can change this by selecting Title under the Display pulldown menu.
  • Once you have picked your peaks and annotated your plot, save the window as before by selecting Save Sample from the File pulldown menu.
  • Select Plot from the File pulldown menu. In the Plot menu select the window you wish to print. Check that the size of the plot is correct and then click on the “plot”. This will take 1-2 minutes. Be patient. You can then select another window to print or click on the “done” button.

Problem #11: Identifying the Pollutant

Assignment

Examine the spectrum from your sample of unknown, contaminated air. Note that it is a very different spectrum from that of carbon dioxide and water, which is shown in Figure 1. The spectrometer automatically purges the cell cavity with N₂, which is transparent in infrared. This removes water and carbon dioxide, which exhibit strong IR absorptions. The sample was taken in a location 20 m away from an open farm field where strawberries were growing. In the field on one side there were cows grazing; on the other side there was a natural gas pumping station. Across the street there was a gas station with an auto repair shop specializing in air conditioner repair and a dry cleaner. This information narrows the list of suspected chemicals to six. Which ones remain on the list? (Remember, there may be trace amounts of water and carbon dioxide in the sample.) Which of the chemicals that you studied is responsible for this spectrum? To which potential polluter would you attribute this pollution?

Outside Links

• http://symmetry.otterbein.edu/index.html
  • Point group symmetry character tables

References


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