Vibrational Spectroscopy of Polyatomic Molecules

While you have all used vibrational spectroscopy (particularly IR spectroscopy) to identify compounds in organic chemistry, the techniques of vibrational spectroscopy can give you a lot more information than simple fingerprint identifications of compounds. In this lab, you will look at more advanced ways of looking at and understanding vibrational spectra (through the techniques of Group Theory), and you will also be (re-)introduced to a couple of additional vibrational techniques beyond traditional mid-IR spectroscopy that you may have used before (specifically, you will use Raman and far-IR spectroscopy, in addition to mid-IR). You will make extensive use of DFT calculations in your analysis.

The end goal of this experiment is to identify the three unknown samples that you have been given. You will work with your lab partners to take the spectra, but all DFT calculations and all data analysis (including all of your Group Theory work) must be completed on your own. You are also NOT permitted to look up spectra for your potential unknowns. You must identify them based on YOUR analysis of those spectra ONLY.

Introduction

We have talked in class about forbidden and allowed transitions in spectroscopy. For instance, for a harmonic oscillator, the $v_{1→0}$ transition is allowed, but the $v_{2→0}$ transition is formally forbidden (the anharmonicity of the system allows the transition weakly, which is why we sometimes see overtone bands in spectra). Even $v_{1→0}$ transitions are not allowed for every vibrational mode (for instance, we cannot detect vibrations from the N$_2$ or O$_2$ in the air).

Qualitatively, we can identify which bonds will be IR active (their $v_{1→0}$ transitions will absorb in the IR). A vibration will be IR active if and only if the vibration changes the dipole moment of the molecule. The vibrational mode in HCl is IR active because changing the bond length changes the polarity of the molecule. The N$_2$ vibrational mode is not active, because the bond is non-polar, no matter what the bond length.

A similar qualitative rule can be derived for Raman spectroscopy. In that case, a vibrational mode will be Raman active if and only if the vibration changes the polarizability of the molecule. While evaluating a vibrational mode to see if it changes the dipole moment as the bond length changes is relatively simple, seeing whether the polarizability changes is a bit more challenging.

These qualitative measures also will only tell you if a transition is likely to show up in an IR or Raman spectrum. They will not tell you how intense the transition will be. They are relatively easy to apply to diatomic systems, but applying this analysis to vibrational modes involving many atoms is much less obvious.

To quantitatively determine whether a transition is IR or Raman active and what its intensity will be, you need to make use of time-dependent perturbation theory. Rather than go into all of the details, we will only hit the highlights here. Very briefly, the intensity of the transition between states $i$ and $j$ will be related to the integral
\[ M_{i,j} = \int_{all \, space} \psi_j^* \hat{A} \psi_i \, d\tau \]  

Here, \( \psi_i \) and \( \psi_j \) are the wavefunctions for the initial and final vibrational states, respectively. For the case of an IR absorption, the relevant operator is the dipole moment operator, \( \hat{\mu} \), while for Raman it is the polarizability operator, \( \hat{\alpha} \). As you might imagine, solving these integrals is not trivial. To adequately do this, a computer is required (that is one part of the calculations done in the DFT calculations that you will perform).

Luckily for us, there is a middle road between the hand-wavy qualitative statements we started with and the ugly integrals of the full quantitative treatment. The core of this process is a topic known as Group Theory. To a mathematician, Group Theory is a very theoretical topic involving the analysis of sets and operations. To a chemist, Group Theory is the study of molecular symmetry. While it may not be obvious, the chemical version of Group Theory is actually a subset of the mathematical topic, and it relies on many of the theoretical conclusions of Group Theory in general. For our purposes, however, we will skip the theoretical treatment and jump into the more practical applications. For more information on Group Theory, see Chapter 11 of your textbook\(^1\) or Cotton’s Chemical Applications of Group Theory.\(^2\) The idea for this experiment came from McClain et al.\(^3\)

Theory

Symmetry Operations

The starting point for a chemist’s version of Group Theory is to define the symmetry operations available in a molecule. A symmetry operation is any movement of a molecule that, once completed, renders the molecule indistinguishable from its original configuration. In other words, if you took a picture of the molecule, performed the operation, then took another picture, the pictures would look the same. An indistinguishable configuration is not necessarily an identical configuration (an identical configuration is defined as having each atom in exactly the same place as it started with).

There are a total of five possible symmetry operations: the identity operation, rotation, reflection, inversion, and improper rotation.

Identity

This is the simplest of all possible symmetry operations, and it is given the symbol \( \textbf{E} \). It essentially involves doing nothing to the molecule. Obviously, if you do nothing to a molecule, it will remain the same as it was before, so every molecule has the identity operation. While including a “do nothing” operation may seem pointless, it is necessary in order for symmetry to meet the technical requirements of being a “group” in Group Theory.

Rotation
This is probably the next simplest symmetry operation to recognize. The idea here is that you are able to rotate the molecule around an axis to get it into a configuration indistinguishable from the original. Rotations are represented by the symbol \( C_n \), where \( n \) is the number of rotations before bringing the molecule back to its original configuration. This is best shown by example.

Consider an ammonia molecule (shown in Figure 1). If you look down the axis defined by the lone pair and the nitrogen atom, you can see that a 120° rotation of the molecule will bring it to an indistinguishable configuration. Since there are a total of three such rotations before it comes back to the original orientation, this is denoted a \( C_3 \) rotation. If you rotate it by 240°, you are also left with an indistinguishable configuration. This would be denoted a \( C_3^2 \) rotation, as you are essentially doing the same \( C_3 \) rotation twice.

Rotations of \( C_2 \) and \( C_3 \) are pretty common in molecules. Rotations greater than \( C_6 \) are only rarely found. You should also note that \( C_1 \) and \( C_n^n \) are both equivalent to the identity operation, leaving the molecule in its original configuration.

Reflections

Reflections are another relatively simple symmetry operation. To have a reflection, there must be a plane in the molecule where everything on the left half of the plane identically matches the right half of the plane. Reflections are denoted as \( \sigma_v \), \( \sigma_d \), and \( \sigma_h \) (v stands for vertical, d for dihedral, and h for horizontal). The subscripts refer to the relationship between the plane of reflection and the highest-order rotation in the molecule. A \( \sigma_h \) is perpendicular to the highest-order rotation axis in the plane, while both \( \sigma_v \) and \( \sigma_d \) contain the highest-order rotation axis. Don’t worry too much about the difference between a \( \sigma_v \) and a \( \sigma_d \).

Ammonia has three reflection operations possible, one for each plane containing the nitrogen, lone pair, and one of the hydrogens. Benzene (shown in Figure 2) has a total of seven reflection operations (one \( \sigma_h \), three \( \sigma_v \), and three \( \sigma_d \)).

Inversion

The fourth symmetry operation is an inversion, given the symbol \( i \). An inversion is hard to describe in words, but is relatively easy to see in practice. A molecule has a center of inversion if, for every component of the molecule (atom, bond, etc.) there is a corresponding identical component across from it. In other words, if the coordinates of an atom are \((x, y, z)\) (zero is here assumed to be the center of mass of the molecule), there is another, identical atom at \((-x, -y, -z)\).
While ammonia does not have a center of inversion, a molecule of benzene (shown in Figure 2) does. Another molecule with a center of inversion would be the one shown in Figure 3.

Improper Rotations

The final symmetry operation is that of an improper rotation, denoted $S_n$. An improper rotation combines BOTH a rotation and a reflection through a plane perpendicular to the rotation axis. Thus, improper rotations are sometimes called rotation-reflection operations.

Obviously, any molecule that has both a $C_n$ and a perpendicular reflection will have a corresponding $S_n$ operation, but an improper rotation does not require the existence of each of these separately. Consider the staggered configuration of ethane (shown in Figure 4 in an end-on view). This molecule clearly has a $C_3$ rotation in it, but it does not have a mirror plane perpendicular to the $C_3$. Nor does the molecule have a $C_6$ axis. It does, however, have an $S_6$ operation available. If you rotate the molecule by $60^\circ$ (1/6 of a turn), then reflect through a perpendicular plane, you get an indistinguishable configuration out. Note that neither operation, by itself, gives an indistinguishable configuration.

Point Groups

Finding all of the symmetry operations in a molecule is a bit challenging at first, and it takes quite a bit of practice. Luckily for us, however, symmetry operations naturally form sets of operations with certain properties, known as a group (this is where the Group Theory comes in). Because of this, we don’t have to always find every symmetry operation in a molecule.

There are two different ways of labeling point groups. In this course, we will use the notation called Schönflies symbols. In this notation, a group denoted $C_n$ has only a single $C_n$ rotational axis (and associated symmetry operations such as $C_n^2$, etc.).

If the molecule has a $C_n$ axis plus $n$ mirror planes that contain the rotational axis, the group is denoted $C_{nv}$.

If, in addition to the $C_n$ axis, there is a mirror plane perpendicular to that axis, the group is denoted $C_{nh}$.

Often, molecules will have $n$ $C_2$ axes perpendicular to the main $C_n$ axis. If this is the case, the groups are given a D designation. If all they have are the rotations, the group is $D_n$ (here, the $n$ is the order of the highest-order $C_n$ axis).

If there are $n$ mirror planes containing the $C_n$ axis (in addition to the perpendicular $C_2$ axes), then the group is designated $D_{nd}$.

If there is a mirror plane perpendicular to the $C_n$ axis, the group is given the symbol $D_{nh}$.
Very rarely (as in, there are less than 5 molecules known in these groups), the only symmetry elements will be an $S_{2n}$ operation with a collinear $C_n$ axis. In this case, the group is designated $S_{2n}$.

There are a few special groups worth mentioning, as well. If a molecule is linear, it has an infinite rotational axis, and the group is either $C_{\infty v}$ or $D_{\infty h}$, depending on if there are perpendicular $C_2$’s, as well.

Other special groups include those of very low symmetry, such as $C_s$ (only a single mirror plane in the molecule), $C_i$ (only an inversion in the molecule), and $C_1$ (no symmetry).
Finally, there are a number of special groups of very high symmetry. These groups are all identified by the fact that they have more than one rotational axis where $n > 2$. These include tetrahedral, octahedral, and icosahedral groups ($T$, $T_d$, $T_h$, $O$, $O_h$, and $I_h$). The best way to differentiate the high symmetry groups is to identify the highest order rotation (tetrahedral, octahedral, and icosahedral groups will have multiple rotation axes with $n = 3$, 4, and 5, respectively).

Figure 5 gives a shortcut to determining the point group of any molecule. The figure is a decision tree. If you follow through each of the questions, you will end up uniquely determining the point group for any molecule.
Character Tables

Each group has associated with it a collection of information called a character table. The basic information contained in a character table involves what are known as the “irreducible representations” for the particular group. Those irreducible representations indicate the possible ways that a molecular property can vary under the different symmetry operations of the molecule. We will see how to use this information in a little while.

Your textbook has some of the more common character tables in the appendix (pages 943-947). Each source gives character tables a bit differently, but they all contain the same basic information. In general, there are six basic areas to a character table, as shown in Figure 6.

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>III</td>
</tr>
<tr>
<td>V</td>
<td>VI</td>
</tr>
</tbody>
</table>

Figure 6. General layout of a character table.

Section I contains the Schönflies symbol for the group (C₂ᵥ, O₄, D₆h, etc.). Obviously, it’s nice to know what you are looking at. Your book also includes the second name for each of the point groups here, but don’t worry about this too much.

Section II lists the classes of symmetry operations that exist in the point group. A class is a grouping of related symmetry operations. These are identified by a number telling how many operations are in that class followed by a representative operation from that class. For instance, in the C₃ᵥ point group, shown below as Table 1, you have 2 operations in the same class as C₃ (C₃ and C₃) and three operations in the same class as σᵥ (σᵥ, σᵥ’, and σᵥ’’).

| Table 1. Character table for the C₃ᵥ point group. |
|-----------------|-----------------|-----------------|-----------------|
| C₃ᵥ             | E               | 2C₃             | 3σᵥ             |
| A₁              | 1               | 1               | 1               | z, z², x² + y² |
| A₂              | 1               | 1               | -1              |
| E               | 2               | -1              | 0               | (x,y), (xy,x²−y²), (xz,yz) |
|                 |                 |                 |                 | (Rₓ,Rᵧ)      |

If you are ever in doubt about your assignment of a molecule to a point group, the easiest way to check your assignment is to look the character table for the point group and confirm that you find all of the symmetry operations listed and no others.

Section III contains the characters of the irreducible representations of the point group. These characters tell you how that representation behaves under the symmetry operations available in the group. Each irreducible representation is unique in how it behaves, and all molecular properties must behave as one of the irreducible representations (or as some combination of them).
Since the E operation always leaves a molecule unchanged, the character in the E column gives the dimension of the representation.

For 1-dimensional representations, a 1 in an entry denotes that an operation will leave the associated molecular property unchanged, while a -1 indicates that it will invert the sign of the molecular property. One-dimensional representations will never have a zero in them.

The characters for 2- and 3-dimensional characters can have values including 0 and, occasionally, non-integer and even non-real (imaginary) values. Don’t worry too much about those possibilities here.

Section IV contains the Mulliken symbols that identify the different irreducible representations (each row contains one irreducible representation). Each piece of the Mulliken symbols denotes something about the representation. (These are called Mulliken symbols, not surprisingly, because R. S. Mulliken was the one that proposed them.) These symbols actually tell you quite a bit about the items in the table.

1. The letter tells you the dimensionality of the irreducible representation. 1-dimensional representations are given either an A or B, 2-dimensional representations are given an E, and 3-dimensional representations are usually denoted by a T (but an older convention uses F for this).

2. For 1-dimensional representations, those that are symmetric with respect to the $C_n$ rotation (they have a character of +1 under the $C_n$ column) use an A, those that are antisymmetric with respect to the $C_n$ rotation (have a character of -1 under the $C_n$ column) use a B.

3. Subscripts of 1 and 2 for 1-dimensional representations (“A” or “B”) denote those that are symmetric and antisymmetric with respect to the perpendicular $C_2$ (if the molecule is in a D point group) or $\sigma_v$ (if the molecule is in a $C_{nv}$ point group) operations.

4. Primes and double primes are used for representations that are symmetric or antisymmetric with respect to a $\sigma_h$ (if it exists).

5. Inversion symmetry is denoted by g (gerade) for symmetric and u (ungerade) for antisymmetric.

6. Numerical subscripts on 2- and 3-dimensional representations do follow certain rules, but they are complicated. Essentially, you can consider them arbitrary labels.

Now that I have listed these six rules, I am going to quickly back-track and tell you that you don’t really need to memorize these. Rules 1 and 5 will come in handy later, however.

Sections V and VI contain information on how different mathematical functions relate to the irreducible representations listed. Section V lists the $x$, $y$, and $z$ functions, along with a number of different combinations of these functions ($xy$, $xz$, $yz$, $x^2$, etc.). Knowing what irreducible
representations relate to these functions is very useful for a number of reasons. One of these (that we will not use in this lab but will show up when we talk about bonding in class) is that atomic orbitals relate to different mathematical functions. For instance, the px, py, and pz orbitals relate to the x, y, and z functions, respectively, so each of these orbitals are affected by the symmetry operations in the molecule according to the listed irreducible representations. The dxz, dyz, dxy, and dz2 orbitals correspond to xy, xz, yz, x^2 – y^2, and z^2 functions, respectively.

Section VI contains the symbols Rx, Ry, and Rz. These correspond to rotations around the x, y, and z axes, respectively.

Correlating Molecular Vibrations with Irreducible Representations

The irreducible representations listed in the character tables probably seem rather esoteric at the moment. You will see some applications of these representations in a minute, but remember that every molecular property correlates with one of these irreducible representations.

Molecular vibrations are no exception to this. Every non-linear molecule has 3N – 6 vibrations, where N is the number of atoms in the molecule (a total of 3N degrees of freedom, but 3 of these represent translations and 3 represent rotations, hence the “– 6”). Each of these vibrations can be assigned to one of the irreducible representations in the character table.

This is easiest to show with an example. Figure 7 shows the structure of water, with the associated coordinate system that we will use for this example.

Take a moment to figure out the point group for water and how many vibrations there will be. Hopefully, you find the point group to be C2v, and that there should be 3 vibrational modes. These vibrational modes are shown in Figure 8, and the C2v character table is shown in Table 2.

<table>
<thead>
<tr>
<th>( \text{C}_{2\text{v}} )</th>
<th>E</th>
<th>( \text{C}_2 )</th>
<th>( \sigma_{\text{xz}} )</th>
<th>( \sigma_{\text{yz}} )</th>
<th>( \text{R}_x )</th>
<th>( \text{R}_y )</th>
<th>( \text{R}_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>z, z^2, x^2, y^2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>1</td>
<td>1</td>
<td>–1</td>
<td>–1</td>
<td>xy</td>
<td>Rz</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>1</td>
<td>–1</td>
<td>1</td>
<td>–1</td>
<td>x, xz</td>
<td>RY</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>1</td>
<td>–1</td>
<td>–1</td>
<td>1</td>
<td>y, yz</td>
<td>Rx</td>
<td></td>
</tr>
</tbody>
</table>

If we look at Figure 8a, we can apply the four symmetry operations to this vibrational mode to see how it affects them. Since the E operation leaves the molecule alone, the vibration is symmetric under that operation, giving it a value of 1 in that column. After a C2, the vibration is still indistinguishable, so that also gets a 1. The two reflections also leave the vibration indistinguishable, so each of those gets a 1, as well. That means this vibration has the same symmetry as the A1 irreducible representation.

We can analyze the vibration in Figure 8b the same way. In this case, E leaves the vibration unchanged, but the C2 rotation switches the phase of the vibration (bonds that would be expanding are now compressing after the operation and bonds that were compressing are now...
expanding). Thus, the vibration is anti-symmetric with respect to this operation, and it gets a \(-1\) under the \(C_2\) column. Similarly, the \(xz\) reflection inverts the vibration, so that gets a \(-1\). Finally, the \(yz\) reflection leaves the vibration unchanged, so that gets a value of 1. This means the vibration in Figure 8b must be a \(B_2\).

Finally, the bending motion in 8c gets 1, 1, 1, and 1, respectively, so it must be an \(A_1\).

Reducible Representations

In the previous section, we took known vibrations and assigned them to their appropriate irreducible representations. In many problems, however, we do not know \textit{a priori} the vibrational modes of a molecule. Group Theory is useful in that it can actually be used to FIND the vibrational modes. For our purposes, however, all we will need to know are how many vibrations of each type are in the molecule.

The method for finding the irreducible representations of the vibrational modes closely follows the math we used to find how many vibrational modes there are. We start by considering every degree of freedom in the molecule. We do this by considering an arrow in the \(x\), \(y\), and \(z\) directions on each of the atoms in the molecule. Each arrow represents one degree of freedom in the molecule. From this, we will generate what is known as a reducible representation. A reducible representation is a combination (sum) of irreducible representations.

The reducible representation is found by applying every symmetry operation to the arrows on each of the atoms (3\(N\) total arrows). For any arrow, if the atom it is on moves in the symmetry operation, it does not contribute anything to the reducible representation. If the atom does not move, then the arrow will contribute to the reducible representation an amount equal to its projection on the original arrow. If the arrow is unchanged, it will contribute a +1. If the arrow reverses, it will contribute \(-1\). If the arrow is rotated by an angle \(\theta\), it will contribute \(\cos \theta\).

In our water example, when we do nothing, every arrow is unchanged and therefore contributes a +1 to the \(E\) column (for a total of 9).

In the \(C_2\), both hydrogens move, so their arrows will contribute nothing to the total. On the oxygen, the \(z\) arrow will be unchanged, but the \(x\) and the \(y\) will be reversed. This gives us \(1 - 1 - 1 = -1\).

In the \(\sigma_v(xz)\), the two hydrogens move again, so they contribute nothing. On the oxygen, the \(x\) and \(z\) arrows remain unchanged, but the \(y\) arrow reverses, giving us \(1 - 1 + 1 = 1\).

Finally, the \(\sigma_v'(yz)\) operation does not move any of the atoms. On each atom, the \(y\) and \(z\) arrows are unchanged, but the \(x\) arrow reverses. This gives a total of 3 for this column.

The resulting reducible representation is therefore 9, \(-1\), 1, 3. Such a reducible representation is usually denoted by the Greek letter \(\Gamma\) (that is, a capital gamma).
We could, by trial and error, try to figure out what combination of irreducible representations would give us the above reducible representation. Unfortunately, there are $4^9$ possible combinations of these reducible representations, so finding the right one could take a while.

There is, however, a mathematical procedure that tells how many of each irreducible representations exit in any reducible representation. In equation form, this relationship is

$$a_i = \frac{1}{h} \sum n_c \chi_T(C) \chi_i(C)$$

(2)

Here, $a_i$ is the number of times the $i^{th}$ irreducible representation occurs in the reducible representation $\Gamma$. The sum is over each class in the character table. The variable $h$ is the order of the group (the number of symmetry operations in the molecule). Your book is nice enough to give you $h$ in the character table. $n_c$ is the number of symmetry operations in the particular class. $\chi_T(C)$ is the character of the reducible representation for the class, and $\chi_i(C)$ is the character of the $i^{th}$ irreducible representation for the class.

The mathematical form of Equation 2 probably seems a bit opaque to you, so we will use our water example to make it a bit clearer. We already found $\Gamma = 9, -1, 1, 3$ for water. We start with the $A_1$ irreducible representation:

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>C$_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v(yz)$</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>9</td>
<td>-1</td>
<td>1</td>
<td>3</td>
<td>12</td>
</tr>
</tbody>
</table>

For $C_{2v}$, $h = 4$, so there are $12/4 = 3$ $A_1$ terms in $\Gamma$. Looking at $A_2$, we have

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>C$_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v(yz)$</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>9</td>
<td>-1</td>
<td>1</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

This means that only one $A_2$ is included in $\Gamma$. Continuing with $B_1$ and $B_2$, you should find there are two $B_1$ and three $B_2$ irreducible representations contained in $\Gamma$. Since $n_c = 1$ for all of the classes here, this example is a bit trivial, but you will get practice with additional examples later. Just don’t forget to multiply by the number of symmetry operations in each of the classes (the numbers preceding the symmetry operation symbols in the character tables).

This analysis so far gives us nine irreducible representations, each representing one of the degrees of freedom in the water molecule ($3A_1$, $1A_2$, $2B_1$, and $3B_2$). Now, we need to eliminate those that represent translational and rotational motions to leave us with only the vibrational components.
If you look at the \( C_{2v} \) character table (Table 2) again, you will see that the \( x, y, \) and \( z \) functions correlate to \( B_1, B_2, \) and \( A_1 \) representations, respectively. These functions behave in the same way as translation in the \( x, y, \) and \( z \) directions do, so we can subtract these off from our nine degrees of freedom.

Similarly, rotation in \( x, y, \) and \( z \) (\( R_x, R_y, \) and \( R_z \)) correspond to \( B_2, B_1, \) and \( A_2 \), respectively. Subtracting these three off, we have two \( A_1 \) and one \( B_2 \) representations left. These irreducible representations correlate to the three vibrational modes in water (as we saw earlier).

This procedure is general, and it can be done for any molecule. Obviously, the larger the molecule, the more vibrational modes you will have.

Finding IR and Raman Active Modes

Now that we have identified the irreducible representations corresponding to the vibrational modes in a molecule, we can use that information to find out which of these modes are IR active and which are Raman active.

The problem goes back to the integral in Equation 1

\[
M_{i,j} = \int_{all\ space} \psi_j^* \hat{A} \psi_i \, d\tau \tag{1}
\]

For this integral to be something other than zero (and, therefore, for the band to show up in either IR or Raman spectroscopy), the integrand \( \psi_j^* \hat{A} \psi_i \) must have a symmetry corresponding to the totally symmetric irreducible representation (the irreducible representation with all ones, listed at the top of the table and given the symbol \( A_1 \), \( A' \), \( A_g \), etc., depending on the point group of the molecule, but usually just referred to as \( A_1 \)). The argument is similar to integrating even and odd functions over all space. The integral of an odd function over all space MUST be zero, because every positive part has a corresponding negative part. The integral of an even function does not have to be zero (although it may be zero for reasons other than symmetry). All irreducible representations other than \( A_1 \) will have negative parts that cancel out every positive part of the function in an integral, making the integral over all space equal to zero.

Now, all that remains to us is to find the symmetry of the integrand. Each of the three elements in the integrand has symmetry associated with them. Since, at room temperature, essentially all of our molecules will be in the ground vibrational state, \( \psi_i \) is basically always \( \psi_0 \). It turns out (although I will not prove it here), that \( \psi_0 \) has \( A_1 \) symmetry in all cases. Multiplying by something with \( A_1 \) symmetry is very much like multiplying by 1. It doesn’t change the symmetry of the other pieces. Thus, we only need to worry about the symmetries of \( \psi_j \) and the operator ( \( \hat{\mu} \) for IR and \( \hat{\alpha} \) for Raman).

\( \psi_j \) will have the symmetry of the vibrational mode. It turns out that \( \hat{\mu} \) has three components to it having the same symmetry as \( x, y, \) and \( z \). \( \hat{\alpha} \) has the same symmetry as any quadratic component (\( xy, xz, yz, x^2, y^2, z^2 \), or any combination of these).
The only question remaining is how to combine these symmetries to get our final result. There is a general process for this, but it is not worth covering here. The simple answer is that the product of two irreducible representations will contain the $A_1$ representation if and only if the two irreducible representations are the same. Thus, $B_1 \ast B_1 = A_1$, but $B_2 \ast B_1 \neq A_1$.

As confusing as all of this sounds, it all boils down to two VERY simple rules:

Vibrational modes will be IR active if the mode has the same symmetry as any of $x$, $y$, or $z$.

Vibrational modes will be Raman active if the mode has the same symmetry as any of $xy$, $xz$, $yz$, $x^2$, $y^2$, $z^2$, or any combination of these.

In the IR spectrum of water, then, all three modes should be both IR and Raman active. This gives us no information about the intensities of these absorption bands, but it at least tells us that they will likely be there. There is one complication, however. Just as the integral over all space of an even function can be zero for reasons other than symmetry, the integral in Equation 1 can be zero (or at least very small) for a band that is formally allowed, so an allowed transition does not HAVE to show up in the spectrum.

A Special Case: Molecules with a Center of Inversion

An interesting case shows up when molecules have a center of inversion. If you look at such a character table (for instance, the $C_{4v}$ table), you will note that the $x$, $y$, and $z$ functions ALWAYS correspond to irreducible representations with ungerade symmetry ($u$ subscripts). The quadratic functions will ALWAYS correspond to irreducible representations with gerade symmetry ($g$ subscripts).

This means that, in molecules with a center of inversion, it is IMPOSSIBLE for the same vibrational mode to be both IR and Raman active.

**Procedure**

**Known Compounds: Group Theory**

We will be looking at two sets of molecules in this lab. The first is the series of chlorinated methane molecules shown in Table 3. Using Group Theory:

1. Assign each molecule to a point group.
2. Determine the number of degrees of freedom and the number of vibrational modes in each molecule.
3. Determine the reducible representation given by all of the degrees of freedom.

**Table 3.** Known compounds used in this experiment.

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<thead>
<tr>
<th>Formula</th>
<th>Name</th>
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<tbody>
<tr>
<td>1</td>
<td>CH$_4$ Methane</td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$Cl Chloromethane</td>
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<tr>
<td>3</td>
<td>CH$_2$Cl$_2$ Dichloromethane or methylene chloride</td>
</tr>
<tr>
<td>4</td>
<td>CHCl$_3$ Trichloromethane or chloroform</td>
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<tr>
<td>5</td>
<td>CCl$_4$ Carbon tetrachloride</td>
</tr>
</tbody>
</table>
4. Break this reducible representation down into the component irreducible representations, one for each degree of freedom.
5. Subtract off the degrees of freedom associated with translations and rotations.
6. List which vibrational modes will be IR active and which will be Raman active.

Known Compounds: Spectra

Take the mid-IR, far-IR and Raman spectra of compounds 3-5 (methane and chloromethane are gases, so we will not take these spectra ourselves).

To acquire the Raman data, fill a quartz semi-micro cuvette with a small amount of your sample, and take the Raman spectrum from 80 cm\(^{-1}\) to 4000 cm\(^{-1}\). You will want to take scans using both lasers. Use the 1800 grove/mm grating for the HeNe laser and the 1200 grove/mm grating for the diode laser (these will give you the best resolution covering the entire wavelength range).

Save your Raman data to your user space as a text file. Write the name of the file, the file location, and the parameters in your lab notebook.

For the IR spectra, you will be using both a liquid cell and the ATR cell to take the data. The ATR cell is easier to use, but only the strongest bands will show up (this is because the effective pathlength in an ATR cell is VERY short, only a few \(\mu\)m). The liquid cell is more sensitive, but the strongest bands usually saturate. Using a combination of the two cells will allow you to accurately locate all bands. I will help you switch between the two cells.

To use the liquid cell, ensure that the cell is clean and dry by rinsing with acetone and blowing air through the cell (I will show you how to do this). Take a background scan of the empty cell. This will account for the absorptions from water and CO\(_2\) in the air, as well as any losses from the cell itself. Use a 1 cm\(^{-1}\) resolution (you could take higher resolution, but the bands are generally wider than 1 cm\(^{-1}\), so this would only waste time), and take 8 scans. The range should be 400 cm\(^{-1}\) to 4400 cm\(^{-1}\). These parameters can be found under the Collect|Experiment Setup drop-down options. The resolution and number of scans are set in the “Collect” tab, and the range is set in the “Bench” tab.

Next, fill the cell using a Pasteur pipet. Hold the cell at an angle and fill from the lower of the two ports. Fill slowly and steadily to avoid introducing air bubbles into the cell. Once you have completely filled the cell, add one or two extra drops to top off the fill ports and cap the ports with the Teflon stoppers. Take the data using the same parameters as the background, and display your data as an absorption scan.

Save your data to your user space as a comma separated text file (CSV Text, *.CSV). Write the name of the file, the file location, and the parameters in your lab notebook. You will want to take all of the samples using the liquid sample cell before switching to the ATR cell (this will reduce the number of background scans you have to take).

To use the ATR cell, first install the ATR cell into the instrument. Place the liquid holder on top of the ATR cell, centered above the crystal. Put the liquid cover and clamp on top of the holder,
and lower the plunger until it seats in the top of the clamp. Take a background scan of the ATR cell using the same parameters as above.

Once you have your background scan, leave the liquid holder clamped down, but slide the rubber cover out. Add one or two drops of your sample to the liquid holder on the top of the ATR crystal, and slide the liquid cover back in place. Use the same parameters as the background, and display your data as an absorption scan. Once the run has finished, clean the ATR crystal gently with a Q-tip to avoid contaminating your next sample.

Again, save your data to your user space as a comma separated text file (CSV Text, *.CSV). Write the name of the file, the file location, and the parameters in your lab notebook.

Once everyone has acquired the mid-IR data, I will convert the instrument to far-IR mode. Converting the instrument from mid- to far-IR operation is not hard, but it involves opening up the instrument. The far-IR region has a lot of interference from water in the air. Thus, the instrument must be purged with N₂ gas for a long time before the far-IR data will be useable. This means that we will need to take the far-IR data during the second week of lab. Thus, we will do all of the mid-IR spectra the first week and the far-IR spectra the second week.

For the far-IR data, you will only use the ATR cell (the windows on the liquid sample cell do not transmit light in the far-IR region). You will take the data in exactly the same manner as for the mid-IR scans.

While you have taken mid-IR spectra before, far-IR spectra are almost certainly new for you. The experiment is nearly the same (in fact, they are done on the same instrument). The only difference is in the range of interest. A standard mid-IR spectrometer like the ones you have used before has a range of about 600 – 6000 cm⁻¹. The far-IR region is lower in energy (wavenumbers), covering approximately 40 – 750 cm⁻¹. The far-IR region is also sometimes called the THz (terahertz) region, as 33 cm⁻¹ = 1 THz.

Look up, from a reliable source, the IR and Raman spectra of methane and chloromethane.

**Unknown Compounds: Group Theory**

You will be given three unknown samples to analyze in this lab. They are all isomers of C₂H₂Cl₂. Figure out the three possible structures of these compounds and do the same analysis as you did for the chlorinated methanes.

**Unknown Compounds: Spectra**

Take mid-IR, far-IR, and Raman spectra of all three unknowns. As these compounds are expensive, you will NOT have a lot of compound to work with (~ 2 mL in each case). This IS enough compound, if you are careful. When you are finished taking the Raman data, be sure to recover the sample from the cuvette, to avoid wasting sample. Be sure to save enough of your compounds to do the far-IR measurements in the second week. Store your samples in the refrigerator in 219 between the two lab periods.
All Compounds: Calculations

Use Gaussian to calculate the vibrational modes of all 8 compounds in this experiment. You should use DFT calculations with the B3LYP method and LanL2DZ basis set. Be sure to run the calculation as Opt+Freq to find the energy minimum AND the vibrational frequencies. Also, set the Raman option to Yes, so that you can calculate the Raman signals, as well. Once the calculation has completed, check to see what symmetry Gaussian assigned to the molecule. Be aware that Gaussian often does not find the highest symmetry group possible.

You can display the vibrational frequencies either of two ways. You can look at the end of the output file, where all of the vibrational frequencies, along with their irreducible representations, are listed. You can also select Results|Vibrations and see the vibrational frequencies, along with their symmetry assignments. Gaussian will also animate the different modes for you. Using these animations, you can assign the symmetry yourself, if Gaussian did not find a correct assignment.

Raman activities calculated using DFT calculations are not exactly the same as Raman intensities measured experimentally, but they can be converted to those intensities using a formula from Keresztury et al.:\(^4\)

\[
I_i = \frac{f(v_0 - v_i)^l S_i}{v_i\left[1 - e^{-hc\nu_i/k_BT}\right]} \tag{3}
\]

where \(I_i\) is the predicted Raman intensity, \(f\) is an arbitrary scaling factor (constant for all bands), \(v_0\) is the Raman excitation frequency (the laser frequency) in wavenumbers (cm\(^{-1}\)), \(v_i\) is the harmonic frequency of the \(i^{th}\) normal mode (from the DFT calculations), \(S_i\) is the predicted Raman activity calculated by DFT, \(h\) is Plank’s constant, \(c\) is the speed of light, \(k_B\) is Boltzmann’s constant, and \(T\) is the temperature.

Analysis

Known Compounds

For each known compound, create a publication-ready figure for the mid-IR, far-IR, and Raman spectra. For methane and chloromethane, find these spectra from a reliable source (be sure to cite your source). You may not be able to find far-IR spectra for methane and chloromethane.

Using the spectra and the calculations you have, see how many vibrational modes you can assign for each compound. Probably the best place to start is by identifying as many bands as possible in the IR and Raman spectra. When you have multiple IR or Raman spectra for a compound (ATR and liquid cell FT-IR, for instance), use the one with the most bands as a starting point, but use the other spectrum to identify the locations of saturated bands.

There are a number of ways to create a list of bands from your data. You can plot the data using Excel and pick out the bands manually, or you can use the peak-picking functions on the FT-IR
to assist you (note that you will need to come in outside of lab time to use the FT-IR software, as other groups are waiting to collect their data).

If you choose to use the FT-IR software, first zoom into the area of interest, the select the Find Pks button. If you click on the graph, you can adjust where the "Threshold" value is (this is the value that a peak needs to be above in order for it to be considered a real peak). You can also adjust the "Sensitivity" value on the left to try to eliminate noise peaks, as well. You will need to play with these values until you find a reasonable list of peaks. Note that you may have to add a few of the smaller peaks manually, as the automated peak finder may not catch all of them without adding a lot of noise in, as well. Once you have the peaks identified that you want to use, you can copy them to the clipboard by clicking on "Clipboard", then paste them into Wordpad so that you can save them. To exit the Find Pks routine, click "Replace" in the upper right-hand corner of the screen. This will mark all of your peaks on the main window. If you want to save your data with all of the peaks identified, save your data in the native Spectra (*.SPA) format, in addition to the *.CSV format.

You should combine the far-IR and mid-IR data into one list. List these band locations and intensities in an Excel file.

A single vibrational mode may be allowed in both IR and Raman spectra, but if they are, they will show up at (approximately) the same wavenumber. Therefore, once you have both IR and Raman band lists for one compound, line up these lists, matching any bands that have the same location in wavenumbers. Note that, because of imperfect calibration of the instruments, there is some uncertainty here (probably around 5 cm\(^{-1}\) or so), so the wavenumbers may not match exactly, but you should not assign bands that are more than ~5 cm\(^{-1}\) apart to the same vibrational mode.

Finally, using the approximate locations of different types of vibrational modes (C–H stretches versus C–Cl stretches, for instance) and your DFT calculations, assign as many vibrational modes as possible to bands in your spectra.

Label a copy of each spectrum with the frequencies and symmetry assignments for as many bands as possible. Also label, where possible, the type of vibration (C–H stretch, C–Cl stretch, bending mode, torsional mode, etc.).

**Unknown Compounds**

Using your spectra, can you uniquely identify each of your compounds? Remember, you are NOT allowed to look up reference spectra for these compounds. Hint: Use what you know about selection rules to aid in this assignment. Once you have gone as far as you can from the spectra alone, add in your DFT calculations. Does this confirm your assignments? Does it allow you to remove any ambiguity in your previous assignments? Between your spectra and DFT, you should be able to identify all three compounds uniquely.

Go through your spectra and complete the same analysis you completed for your known compounds. This should serve as a double check on your identification of the different molecules.
If your assignments do not work very well, you might want to consider if your identification might be off.

**Suggestions for the Long Report**

Coming up with a motivation for a lab report on this experiment is sometimes challenging. Let me suggest two possible ways to motivate this experiment (one based firmly in reality, the other somewhat more fictional).

1. First, the one based on reality. C$_2$H$_2$Cl$_2$ is an environmental contaminate, but it comes in different isomers. Different processes are necessary to remove each isomer from the environment. You are given three environmental samples to determine which isomer is present as a first step to developing a treatment plan. If you choose this motivation, you will probably want to find papers that discuss how to treat each isomer from an environmental system, if you can.

2. This option is more fictional, but not entirely unrealistic. A synthesis for C$_2$H$_2$Cl$_2$ has been reported that is very green, but it has one major drawback. The product is generated, but with all isomers present. You have managed to separate the isomers, but you need to identify which is which. If you choose this motivation, you can reference a fictional paper reporting the new synthesis, but you should also find references to the ways that the isomers are made currently.

**References**


Attach publication-quality spectra of each of your spectra, including as many vibrational assignments as you can make. Also fill in the tables below with your information.

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### Answer the following questions:

1. Based on your experiences in this lab, give three advantages of IR spectroscopy.

2. Based on your experiences in this lab, give three disadvantages of IR spectroscopy.
3. Based on your experiences in this lab, give three advantages of Raman spectroscopy.

4. Based on your experiences in this lab, give three disadvantages of Raman spectroscopy.

5. Using your spectra, were you able to uniquely identify each of your compounds? What molecular characteristic made one of the compounds easier to identify? How did you resolve the uncertainty between the other two compounds?

6. There are many other ways that these compounds could have been identified. Compare in detail what you did in this lab with at least one other possible method. What are the potential advantages and disadvantages of each technique?

References: ____________________________________________________________

Be sure to label where each reference was used.