**Laboratory Instrumentation: Fourier Transform Infrared Spectroscopy**

**(FT-IR)**

**Operational Theory and Chemical Structure Analysis Using FT-IR**

Refs: (1) Csizmar, C.M.; Force, D.A. and Warner, D.L. *J. Chem Educ.*, **2012**, *89*, 379

(2) McEvoy, J. P. *J. Chem Educ.*, **2014**, *91*, 726

(3) Swartz, J. E. and Schladetzky, K. *J. Chem Educ.*, **1996**, *73(2)*, 188

**Introduction**

Infrared spectroscopy is used to help identify compounds and their structure based on the absorbance of infrared (IR) radiation by the bonds in molecules. Bonds absorb IR if the frequency of radiation is such that it matches the frequency of “vibration” of a bond. While we may think of molecular bonds as static or fixed, this is not true. The atoms connected by bonds are in constant back and forth motion much like two masses connected by a spring. The bond length we reference for a bond is actually an equilibrium bond length that represents a distance where the bond (spring) is neither compressed or expanded but is at an equilibrium position.

A simple diatomic molecule has only two “masses” and one “spring” and so has only one mode or degree of vibration:

Ex: carbon monoxide ⁚C O⁚ one “stretch” vibration

The “C” and “O” atoms are in continuous motion relative to each other depending on whether the bond is compressing or expanding. The frequency of this motion falls in the infrared portion of the electromagnetic spectrum (typically, 2500 🡪 22,000 nm) and so can be used to produce an absorption spectrum of CO. We can calculate the frequency of this vibration using an analysis given by:

where: *k* – Force constant or “strength” of the bond (Nt\*m-1)

*μ* – Reduced mass of the system:

In general, the stronger a bond (*ie*., triple > double > single) the higher the frequency of vibration and so the higher the frequency of absorption. In general, the lighter the masses the lower the values of the reduced mass and the higher the frequency of vibration. So, depending on the nature of the bond each diatomic molecule will have a different frequency of vibration. You should be able to see now how we can use IR spectra to identify molecules.

More complex molecules have even more ways to vibrate that can also be absorb infrared radiation.

Ex: carbon dioxide ⁚O C O⁚ one symmetric “stretch vibration

one “asymmetric” stretch vibration

two “bend” vibrations

Each of these vibrations or “modes” will have a different frequency of IR radiation they will absorb and so will show up as an absorbance at different regions of the spectrum.

The number of vibrational modes in a molecule can be calculated from the following formulas:

Linear molecule: number of vibrations = 3\*N – 5

Non-linear molecule: number of vibrations = 3\*N - 6

N – number of atoms in molecule

Clearly, depending on the molecule, the number of vibrational modes can increase dramatically.

Ex:

Based on the Lewis structure of water, how many vibrational modes do you expect it to have?

⁚ ⁚

H2O O N = 3

Non-linear

H H number of vibrations = 3 symmetric H – O – H stretch

asymmetric H – O – H stretch

H – O – H bend

I’m not getting into the entire physics of this but it is important for you to have an introduction to the theoretical background basis for the absorption of IR radiation by molecules.

An FT-IR instrument is capable of producing an absobance spectrum using infrared radiation. One of the great utilities of an FT-IR instrument, however, is that it can produce a spectrum over a wide range of frequencies with a single scan. The mechanics and mathematics of this process is beyond the scope of this course. However, you should know that it involves obtaining a time based spectrum known as an **interferogram** and converting it to a frequency based spectrum through a mathematical analysis known as a Fourier transform; hence **Fourier Transform-Infrared** or **FT-IR** spectroscopy.

Most infrared instruments do not use wavelength as the x-axis unit. They use a quantity known as a wavenumber, . Wavenumbers are actually represent energy and have unit of one over wavelength or inverse wavelength. Infrared instruments use the unit inverse centimeters or cm-1 for their units. So, your spectrum winds up being recorded as %Transmittance vs wavenumber or Absorbance vs wavenumber.

The experiment you will perform will demonstrate how different atoms bonded to each other produce absorbance features at different locations (wavenumbers) in an IR spectrum. In addition, you will correlate any trends using Lewis dot structure representations and use a chemical software program *Spartan* to produce an IR spectrum and animated representations of the bond/molecular vibrations.

The FT-IR instrument we use is a *Perkin Elmer Paragon* with the ability to measure infrared spectra of: gas, solid and liquid samples. As noted from lecture, there are two methods of obtaining liquid sample spectra: use of a sample holder between salt windows or use of an Attenuated Total Reflectance (ATR) module. We will use both.

**Hazards**

You will not be using any compound in amounts that are problematic. However, be aware of the following:

* Wear gloves while handling compounds for IR analysis
* Most organic compounds are volatile, flammable and toxic if ingested in large amounts
* Most compounds can be mildly irritating of in contact with skin
* Be sure to close containers of each liquid when not being used for sample evaluation
* Cover any beakers with a watch glass when not under a hood

**Experimental**

The procedural portion of the lab involves three parts:

(i) determination of the Lewis dot structures and model shapes of the compounds

(ii) modelling of the compounds using *Spartan*

(iii) acquire infrared spectrum of the compounds

The experiment will use three related sets of compounds to demonstrate how structural motifs affect the location of various absorption feature in the infrared spectra.

**Compound Set I: CH3OH, CH3CH2OH and H2CO**

The first procedure will demonstrate the location of different bond types as defined by the atoms they connect. You will look at two compounds that have similar structures and should show similar features in an absorbance or %T spectrum.

The compounds you will start with are methanol, ethanol and acetone with structures:

Methanol CH3OH

Ethanol CH3CH2OH

Acetone H2CO

and that have the following bonding types you shall focus on for spectral analysis:

C H ; O H ; C O ; C = O

**Protocol 1: Lewis Dot and Model Kit Structure**

1. Using the model kit, construct 3D models of the compounds. Note the geometry of the

compounds. Keep these available for reference. Based on the models, draw Lewis dot

structures for each compound.

**Protocol 2: *Spartan* Model and Vibrational Modes**

1. This work will be done in the computer lab. You need a USB plug-in key to access the

*Spartan* program. Sign-out a “key” from Ms. Delgado.

2. Begin by plugging the *Spartan* key into an available USB port. A red LED should light

up on the key indicating the computer recognizes the active port. Find the *Spartan ’08* icon in the Start menu and open the program to the following page:

A screenshot of a computer

Description automatically generated

Fig 1(a). Working Window for *Spartan*

3. Click on the *File* dropdown menu and click on “New”. This opens the “Model Kit” menu whose default is the “Organic” tab. Note the other functionality tabs “Inorganic”, “Peptide”, “Nucleotide”, etc. The “Organic” kit provides elements in various hybridized forms to allow for building single- and multi-bonded structures. Note below the table is a series of dropdown menus which provide access to pre- drawn structures such as cyclohexane, benzene, etc.

Functionality tabs

A screenshot of a computer

Description automatically generated

Fig 1(b).

4. Highlight the sp3 hybridized carbon and place it in the working pane by clicking anywhere in the blue/green space. Build methanol selecting an “H” from the “Model Kit” and click on any of the empty valences (yellow sticks) of the “C”-atom. An “H” atom should be added to the “C”. Do this with two additional H’s.

5. Next, select “O” with two open valences from the “Model Kit” and add it to the “C”. Then, add “H” to the open valence on “O” to complete the model build.

6. Energy minimize the structure by clicking on the ***E*** icon of the toolbar menu. Notice that it adds H atoms to each empty valence and gives an energy in the lower right-side of the window. Record this energy.

7. Click on the **“V”** icon to change the program to “View” mode from “Build” mode. Use the dropdown “File” menu to save the structure as Methanol to the desktop.

8. Practice manipulating the structure by doing the following lowing:

(i) click and hold the left mouse key and move the mouse to spin the molecule.

(ii) click and hold the right mouse key and move the mouse to translate the entire molecule on the page.

(iii) zoom in/out by moving the mouse wheel forward/backward.

(iv) hold the “Shift” key and click/hold the left mouse key and move the mouse to rotate the molecule in the plane of the window.

9. *Spartan* has the ability to generate synthetic spectra and animate molecular vibration modes. A specialized energy calculation must first be done in order to access these fearues.

(i) click on the dropdown menu for “Setup” 🡪 “Calculations”. You should see the following:

Graphical user interface

Description automatically generated

Fig 1(c)

(ii) Note the menu in the dialog box labelled **Calculate**. Click the dropdown menu with “Equilibrium Geometry” and select “Energy”. Keep “Ground”

state, and keep the other dropdown boxes as they are.

(iii) In the row labelled “Compute”, check the box beside “IR”. Click “Submit”.

You will be asked for a filename and location. You can once again use

“Methanol” and Desktop as the file location.

10. You should be notified the calculation has begun and very shortly notified that the calculation is complete. If an error window pops up, see your instructor.

Once the calculation has successfully completed, the workspace should now have an image of the methanol molecule superimposed

Choose “Display” 🡪 “Spectra” from the main menu and, if you checked **IR**, you should see a dialog box labelled “Spectra” with all the active infrared spectral modes listed by wavenumber (Fig 8). Check the box beside any value and return to the model on the workspace. You should see an animation of the particular vibrational mode associated with that wavenumber. Record the wavenumbers with an appropriate identifier (*ie.*, “C-H stretch”) in your notebook.

Click the button labelled “Draw Calculated”. You should see the calculated IR spectrum superimposed on the workspace along with the model of methanol. Click on any spectral feature to see the mode associated with that feature in animated vibrational motion.

**Note: The *Spartan* generated wavenumbers will not match exactly with the experimentally recorded spectra. However, they should be close enough to help you to identify spectral features with a particular vibrational mode.**

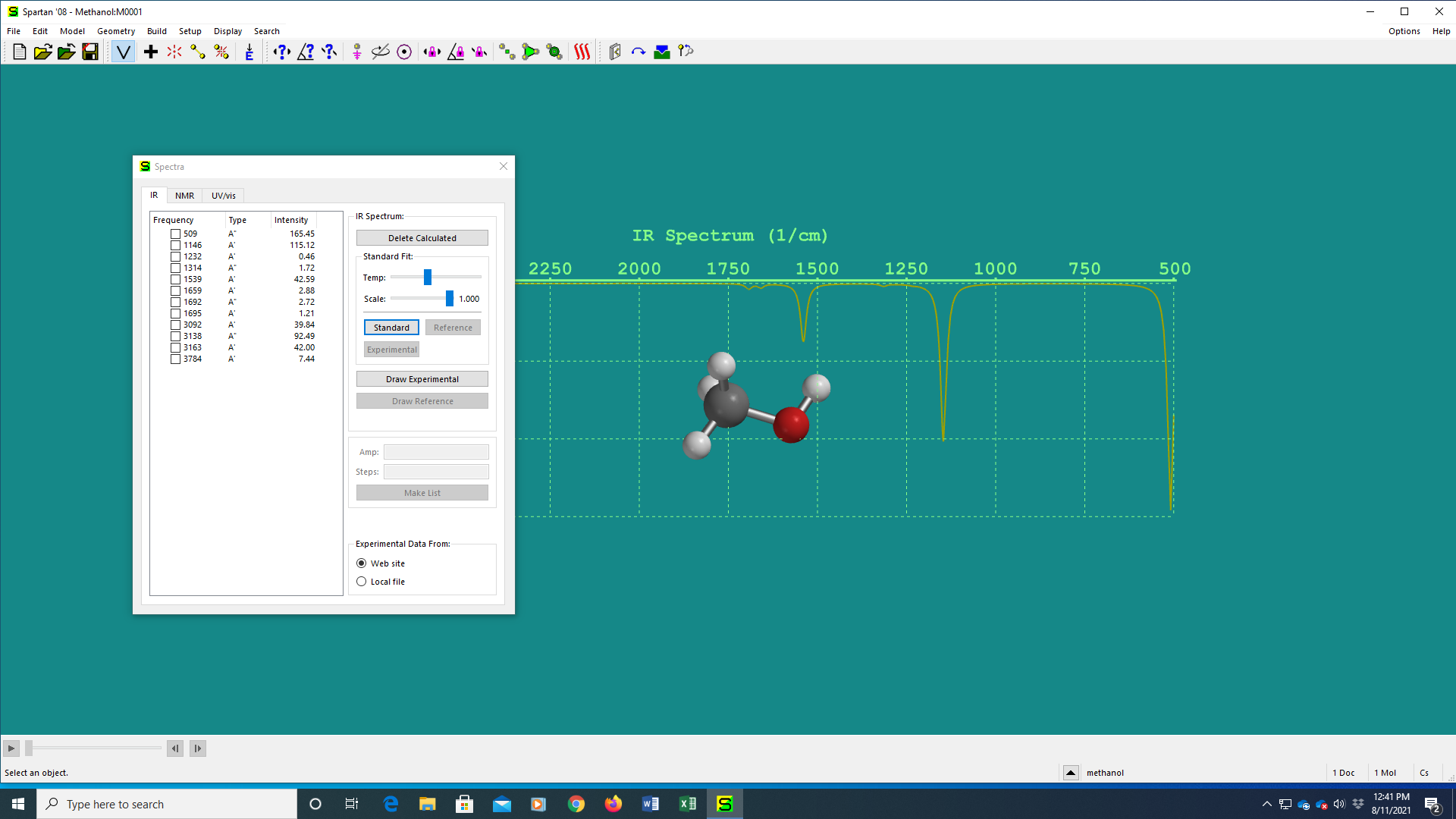


Fig. 8

11. Repeat the calculational process for ethanol, CH3CH2OH and H2C = O.

**Protocol 3: FT-IR Infrared Spectrum**

1. Make sure the spectrometer is powered off and, if necessary, attach the ATR module.

Ask for help from the instructor if you are unsure of what to do.

2. After successfully attaching the module, power up the spectrometer.

3. Access the *SpectrumOne* software program on the control computer. It should

automatically recognize the ATR attachment and default to the control program for ATR.

4. Remove the crystal surface cover and gently wipe the crystal face with a small amount of isopropanol and a Kimwipe.

5. Identify the scan with an appropriate filename.

6. The first “scan” will be a background of the empty crystal. Establish the scan parameters and maintain these for all samples. If you change scan parameters, you will need to scan a new background.

7. Once the “Background” is complete, you will be in the mode for the sample “Scan”.

8. Place one or two drops of sample on the crystal and cover with the plate. Click “Scan”.

**Note: when scanning acetone, you may have to continuously refresh the sample due to its volatility.**

9. Once the first compound is completed, wipe the crystal clean with isopropanol and scan the next compound. You do not have to redo “Background”.

10. When finished with all compounds, be sure to clean and cover the crystal.

**ATR Crystal ‐ Liquid Samples:**

1. Open the “Spectrum” program on the desktop. Accept the username of “analyst” and the instrument of “Spectrum 100.”

2. From the “Instrument” menu, select “Scan.” Enter a sample name in the pop‐up menu and select “Scan.” You will be prompted to acquire a background scan.

3. Clean the surface of the ATR crystal with fresh isopropanol and make sure nothing is covering it. Select “Scan.”

4. Once your background spectrum is completed, you will be prompted to begin acquiring your sample spectrum.

5. Place one or two drops of your sample on the surface of the crystal and click “Scan.” **Note:** The surface of the crystal must remain saturated with your sample at all times throughout the scan. Therefore, **it is useful to continually drip your sample onto the crystal throughout the entire scanning process**.

6. Once your spectrum is finished, wipe your sample from the surface of the crystal and clean it with fresh isopropanol.

7. Repeat steps 5‐6 for the remainder of your compounds.

8. With all three of your spectra on the same screen, click the “Split/Overlay Display” button on the upper toolbar. This should separate and stack your three spectra.

9. From the menu bar, choose “View” and then “Label Peaks.” If the tallest peak is not labeled in this process, click the “Cursor” button and place the cursor over the tallest peak. Then return to “View” and choose “Label Cursor.”

Print your stacked spectra.

**Compound Set II:**

These compounds will demonstrate a new set of bonding types.

CH3 CH3 CH3

Di-isopropylethylamine H C N C H

CH3 CH3

2-methyl-1-pyrroline

Acetonitrile H3C – C N

and that have the following bonding types you shall focus on for spectral analysis:

C N ; C = N ; C N

**Repeat “Protocols” as given above for Compound Set II.**

**CH411 Fall 2021**  **Name : \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

**Laboratory Instrumentation: FT-IR**

**Partner : \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

**1. FT-IR Data Results**

Compound Set I

(i) Lewis Dot Structures

|  |  |
| --- | --- |
| **Compound** | **Lewis Dot Structure** |
| CH3OH |  |
| CH3CH2OH |  |
| H2CO |  |

(ii): Vibrational Data

CH3OH: Number of Vibrational Modes:

|  |  |  |  |
| --- | --- | --- | --- |
| **Vibrational Motion** | **Spartan**  **Wavenumber** | **FT-IR**  **Wavenumber** |  |
| C – H Stretch |  |  |  |
| C – H Stretch |  |  |  |
| O - H Stretch |  |  |  |
|  |  |  |  |

CH3CH2OH: Number of Vibrational Modes:

|  |  |  |  |
| --- | --- | --- | --- |
| **Vibrational Motion** | **Spartan**  **Wavenumber** | **FT-IR**  **Wavenumber** |  |
|  |  |  |  |
| C – H Stretch |  |  |  |
| C – O Stretch |  |  |  |
| O - H Stretch |  |  |  |
|  |  |  |  |

H2CO: Number of Vibrational Modes:

|  |  |  |  |
| --- | --- | --- | --- |
| **Vibrational Motion** | **Spartan**  **Wavenumber** | **FT-IR**  **Wavenumber** |  |
| C – H Stretch |  |  |  |
| C – O Stretch |  |  |  |
| O - H Stretch |  |  |  |
|  |  |  |  |

Compound Set II

(i) Lewis Dot Structures

|  |  |
| --- | --- |
| **Compound** | **Lewis Dot Structure** |
| Di-isopropylethylamine |  |
| 2-methyl-1-pyrroline |  |
| Acetonitrile |  |

(ii): Vibrational Data

Di-isopropylethylamine: Number of Vibrational Modes:

|  |  |  |  |
| --- | --- | --- | --- |
| **Vibrational Motion** | **Spartan**  **Wavenumber** | **FT-IR**  **Wavenumber** |  |
| C – H Stretch  ( - CH3) |  |  |  |
| C – H Stretch |  |  |  |
| C - N Stretch |  |  |  |
| C = N Stretch |  |  |  |
| C N Stretch |  |  |  |

2-methyl-1-pyrroline: Number of Vibrational Modes:

|  |  |  |  |
| --- | --- | --- | --- |
| **Vibrational Motion** | **Spartan**  **Wavenumber** | **FT-IR**  **Wavenumber** |  |
| C – H Stretch  ( - CH3) |  |  |  |
| C – H Stretch |  |  |  |
| C - N Stretch |  |  |  |
| C = N Stretch |  |  |  |
| C N Stretch |  |  |  |

Acetonitrile: Number of Vibrational Modes:

|  |  |  |  |
| --- | --- | --- | --- |
| **Vibrational Motion** | **Spartan**  **Wavenumber** | **FT-IR**  **Wavenumber** |  |
| C – H Stretch  ( - CH3) |  |  |  |
| C - N Stretch |  |  |  |
| C = N Stretch |  |  |  |
| C N Stretch |  |  |  |