

Introduction to Infrared Spectroscopy

Created with: Release 2021-3

Prerequisites: working knowledge of Maestro

Files Supplied: IR_worksheet

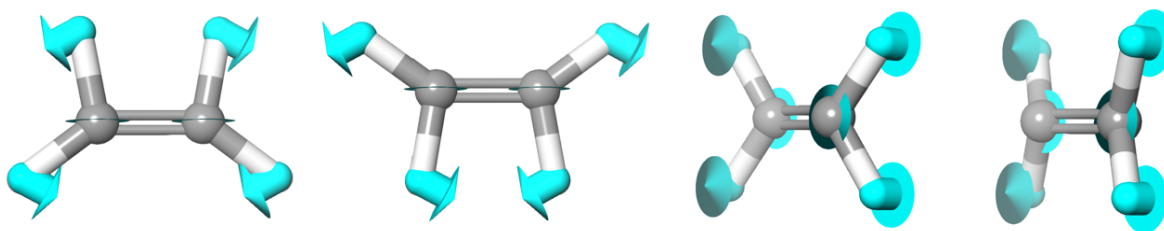
Categories: organic chemistry

About this Lesson

In this lesson, students will learn the fundamentals of infrared (IR) spectroscopy and the many different kinds of vibrational excitation, including stretching and bending. IR spectroscopy can be used to identify which functional groups are present in a compound.

Using Maestro, students will perform frequency calculations and visualize various vibrational modes of small molecules. Students will then generate IR spectra, identify various regions that correspond to particular functional groups, and determine which IR spectrum matches to a given organic compound.

Vibrational Modes of C_2H_4



Learning Objectives

- Visualize vibrational modes of small molecules by performing frequency calculations
- Correspond a given IR spectrum to an organic compound through functional group identification

Standards

- *ACS Guidelines*
 - Deducing structures by interpretation of modern spectroscopic and computational data ([Practical Topics](#))
- *ETS Chemistry GRE*
 - Structure, Bonding and Nomenclature – IR Spectroscopy ([3.A](#))
- *AAMC MCAT*
 - Molecular Structure and Absorption Spectra ([4D](#))

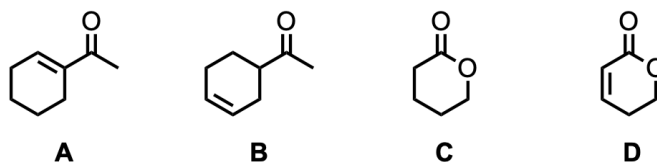
Assessments

The following types of formative assessments are embedded in this lesson:

- Assessment of student understanding through discussion of warm-up questions and filling in any knowledge gaps about functional group identification
- Visual assessment of student-generated IR spectra and correct molecule matching

Warm-Up Questions: To be done on their own or at the beginning of class

Watch the [Khan Academy videos](#) on IR spectroscopy.



All of the molecules shown above absorb IR radiation in the range between 1600 and 1850 cm^{-1} . In each molecule:


- 1) Label the functional groups that are present.
- 2) Identify the specific bond(s) responsible for the absorption(s) and predict the approximate wavenumber of absorption for each of these bonds.

Lesson Outline

1. [What you will need for this lesson](#) - p. 3
2. [Introduction to Infrared Spectroscopy](#) - p. 5
3. [Fundamental Vibrational Modes of Water](#) - p. 6
4. [IR Active versus IR-inactive](#) - p. 9
5. [Functional Groups and Trends](#) - p. 10
6. [Resonance Effects](#) - p. 12
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1. What you will need for this lesson

Before you begin, it is important to note that as you run through each computation, you may find the exact output numbers/CPU time may not be identical to those proposed here. For some types of calculations, the exact numbers are dependent on the starting geometry and operating system and, while the qualitative conclusions are the same, the exact numbers may differ slightly.

	<ol style="list-style-type: none">1. Go to the 'Data' folder and open your Class Folder found on the virtual cluster's desktop.2. Right-click on the folder called "IR_spectroscopy" and copy folder to Desktop<ul style="list-style-type: none">• Here, you will find the lesson plan, worksheet, and any additional resources
 <p>Maestro</p> <p>Figure 1-1. Open Maestro.</p>	<ol style="list-style-type: none">3. Open Maestro<ol style="list-style-type: none">a. See Starting Maestro if you need help

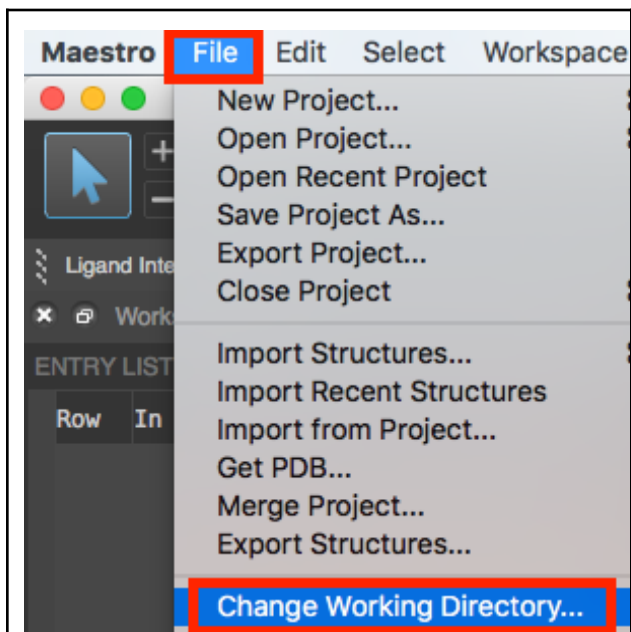


Figure 1-2. Change Working Directory option.

4. Go to **File > Change Working Directory**
5. Find your “IR_spectroscopy” folder that you duplicated to your Desktop, and click **Choose**

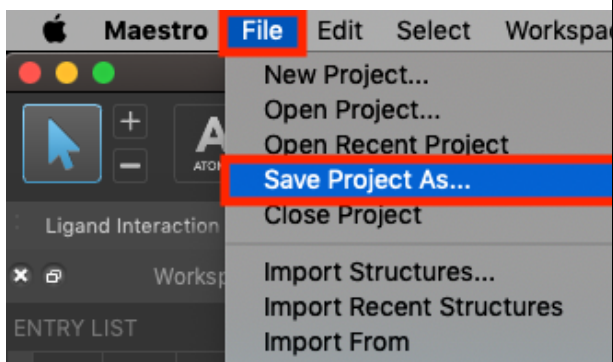


Figure 1-3. Save Project panel.

6. Next, go to **File > Save Project As**
7. Type “IR_tutorial” and click **Save**
 - a. The project will be titled IR_tutorial.prj

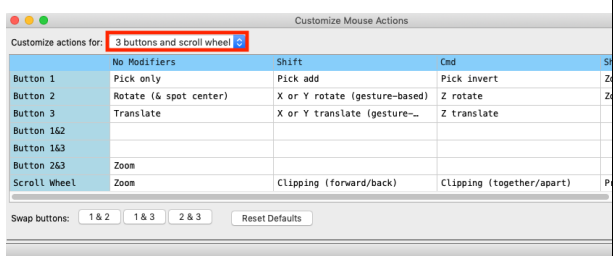


Figure 1-4. Choose the best mouse option for your set up.

8. Finally, check your **Mouse Actions**
 - a. PC : **Edit > Customize Mouse Actions**
 - b. Mac : **Workspace > Customize Mouse Actions**
9. Make sure you have **the best option chosen for your set up**. This lesson was written with a three-button mouse

	with a scroll wheel, meaning the scroll wheel is a button as well as a wheel. If you do not have a mouse, choose Trackpad .
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2. Introduction to Infrared Spectroscopy

Each form of spectroscopy uses a different region of the **electromagnetic spectrum** and involves a different kind of excitation. The interaction between molecules and infrared (IR) radiation promotes **vibrational excitations** of the bonds in a molecule. Each type of bond in a molecule will absorb a characteristic frequency, allowing us to determine which types of bonds are present in a molecule. Chemists irradiate an unknown compound with all frequencies of IR radiation and then detect which frequencies were absorbed. A plot is then constructed showing which frequencies were absorbed by a sample. In this way, **IR spectroscopy** can be used to identify the presence of functional groups in a molecule. IR spectroscopy is commonly used by organic chemists to verify the structures of compounds that are made in a laboratory.

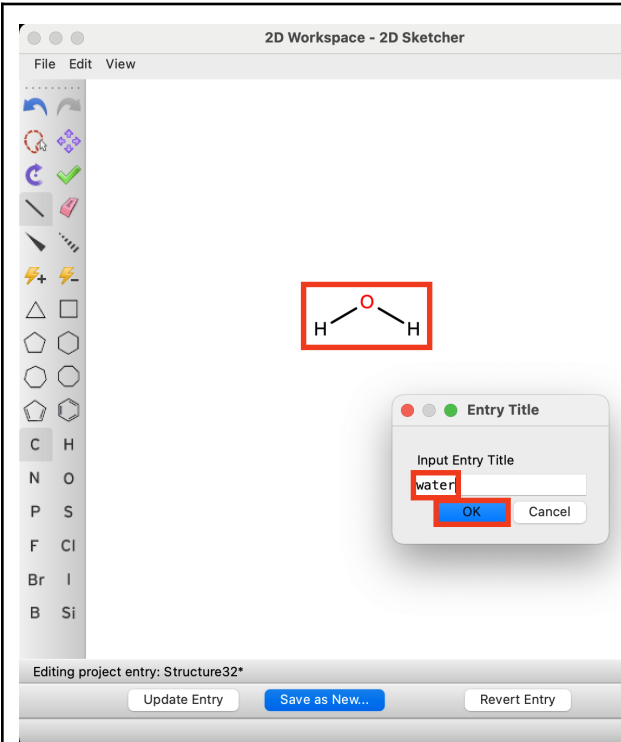
An **IR spectrometer** measures the percent transmittance as a function of frequency. A plot called an absorption spectrum is generated where each signal, called an absorption band, points downwards on an IR spectrum. The position where a signal lies corresponds to a frequency-related unit called a **wavenumber** in units of inverse centimeters (cm^{-1}) where the values can range from 400 to 4000 cm^{-1} . It's important to note that wavenumber is proportional to frequency; therefore, a larger wavenumber represents higher energy. Signals that appear on the left side of an IR spectrum correspond with higher energy radiation, whereas signals on the right side of an IR spectrum correspond with lower energy radiation.

There are three characteristics in every signal that appears in an IR spectrum: wavenumber, intensity, and shape. The wavenumber of a signal is determined by bond strength and the masses of the atoms sharing the bond. The **intensity** of a signal is dependent on the dipole moment of the bond giving rise to the signal. The **shape** of a signal can either be broad or sharp. Each type of functional group lies within a certain region of an absorption spectrum. Use the IR spectroscopy functional group stretching frequency chart that your instructor has provided you.

3. Fundamental Vibrational Modes of Water

IR radiation causes vibrational excitation of the bonds in a molecule. There are different kinds of vibrational excitation since bonds store vibrational energy in a number of ways. Bonds can **stretch**, similar to how a spring stretches, and bonds can also **bend** in various directions. Even though there are several types of bending vibrations, we will mostly be focusing on various stretching vibrations.

In this section, we will learn the steps for performing a standard frequency calculation. We will also analyze the vibrational modes of a water molecule and view the predicted spectrum.



The screenshot shows the '2D Workspace - 2D Sketcher' window. On the left is a toolbar with various drawing tools. In the center, a water molecule (H₂O) is sketched with a red box around it. Below the sketch, an 'Entry Title' dialog box is open, with 'water' entered in the 'Input Entry Title' field and the 'OK' button highlighted with a red box. At the bottom of the workspace, there are buttons for 'Update Entry', 'Save as New...', and 'Revert Entry'.

1. Go to **Edit > 2D Sketcher**
 - The 2D Sketcher panel opens
2. **Draw** the structure of H₂O

The 2D sketcher functions like many standard 2D molecular drawing tools. For a complete overview of using the sketcher panel, see the [2D Sketcher Panel documentation](#).

3. Click on **Save as New** and for *Input Entry Title* write **H2O**. Click **OK**.

Figure 3-1. Sketching and saving H₂O.

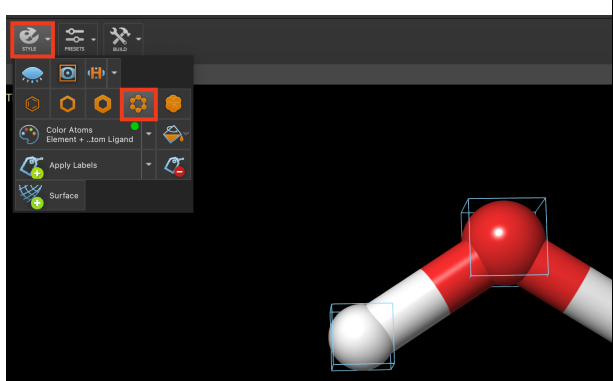


Figure 3-2. Viewing and stylizing H₂O.

4. Close the 2D Sketcher panel
 - The H₂O molecule is selected in the entry list and included in the workspace
5. Change the representation to ball-and-stick by clicking on the **Style** menu and choosing **Apply ball-and-stick representation**

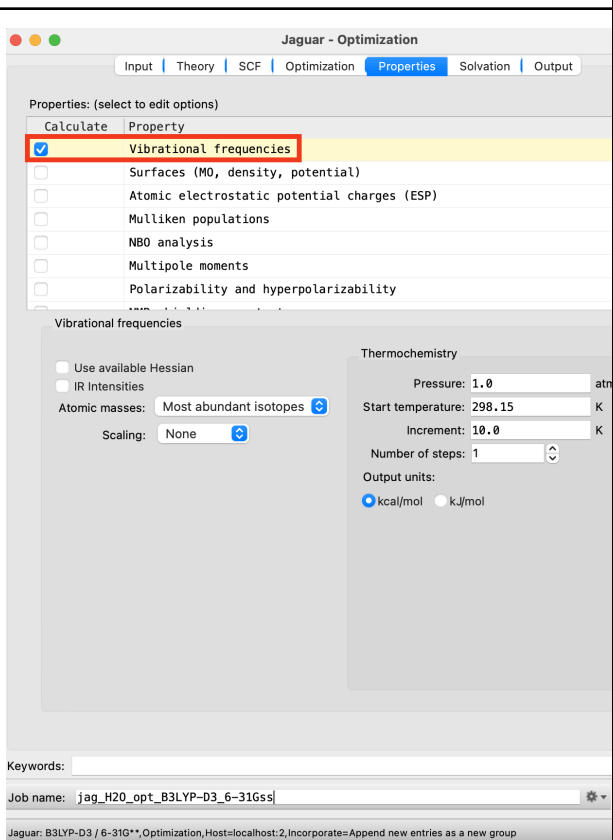


Figure 3-3. Setting the Optimization panel.

Now let us optimize the molecule at the quantum mechanical level and request a frequency calculation.

6. With the H₂O entry selected and included, go to **Tasks > Jaguar > Optimization**
 - The Jaguar - Optimization panel opens
7. Maintain the defaults on the *Input* tab
8. On the *Properties* tab, check **Calculate** for **Vibrational frequencies**
9. **Run** the job

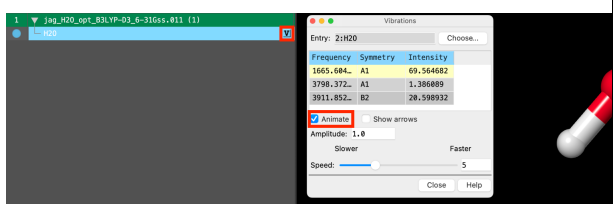



Figure 3-4. Animating the vibrations.

When the job completes, an output group is incorporated into the entry list

10. Select and include the output entry
11. Click the vibration viewer button ()

Three frequencies are shown as well as the symmetry and intensity

12. **Check** Animate and visualize all three modes (bending, symmetric stretching and antisymmetric stretching)
 - Take screenshots of each vibrational mode for the IR worksheet.

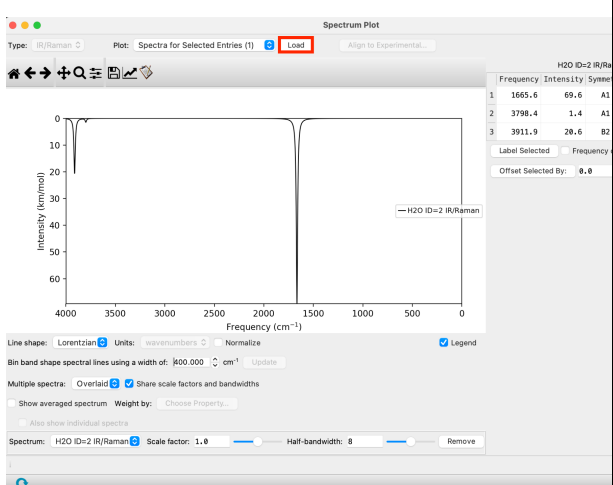


Figure 3-5. Plotting the IR spectrum.

You can plot the spectrum.

13. With the output entry selected and included, go to **Tasks > Jaguar > Plot Spectra**
 - The Spectrum Plot panel opens
14. Click **Load**

The predicted gas phase IR spectrum is shown. Take a screenshot of the IR spectrum for the IR worksheet.

4. IR-active versus IR-inactive

In this section, we will study the frequency output for acetylene to visualize the difference between IR-active and IR-inactive modes.

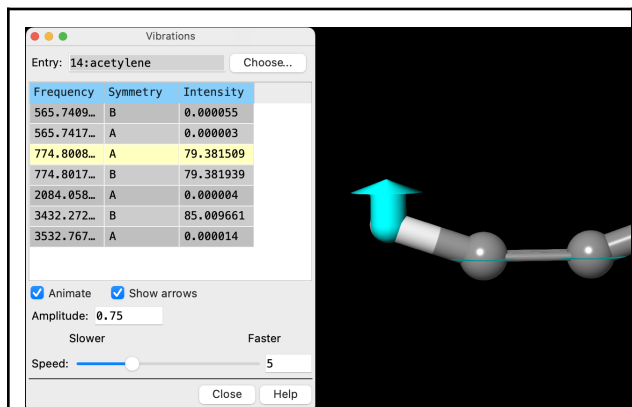



Figure 4-1. Animating the vibrations for C_2H_2 .

1. Repeat the above steps performed for H_2O for an **acetylene** molecule (C_2H_2)
 - Sketch, save, visualize and perform QM calculation
2. Select and include the output entry
3. Click the vibration viewer button ()

Seven frequencies are shown as well as the symmetry and intensity

4. **Check** Animate and visualize all seven modes
 - Take screenshots of each vibrational mode for the IR worksheet.

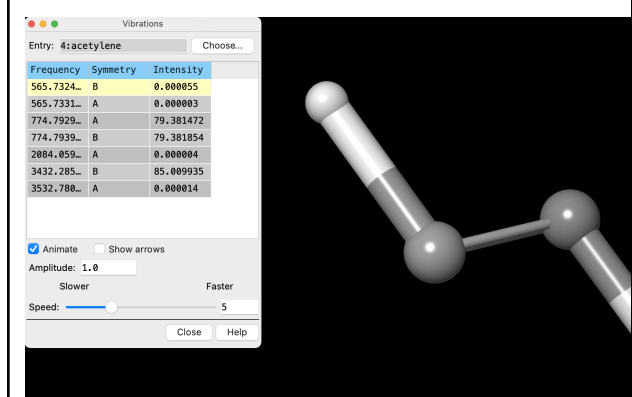


Figure 4-2. Animating the vibrations for C_2H_2 .

Vibrations of bonds with dipole moments generally result in IR absorptions that are 'active,' whereas modes in which the vibration produces no change in the dipole moment are typically 'inactive.'

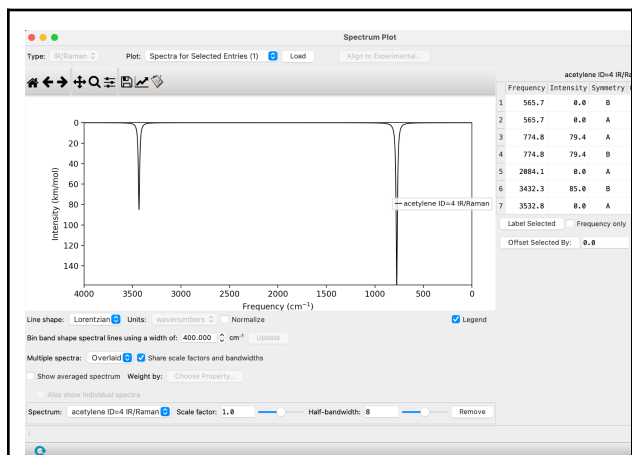


Figure 4-3. Predicted acetylene IR spectrum.

- Plot the IR spectrum following the same steps from Section 2, take a screenshot, and put it in the IR worksheet. Notice that only two peaks appear.
 - Take screenshots of each vibrational mode for the IR worksheet.

5. Functional Groups and Trends

In this section, we will study the frequency output for several organic molecules to familiarize ourselves with the typical shifts associated with different functional groups.

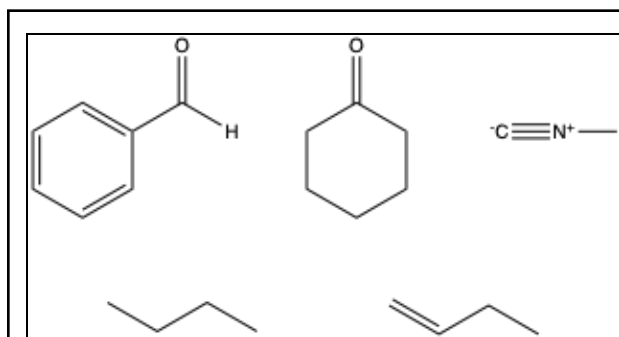


Figure 5-1. Structures to draw.

- Repeat the above steps performed for H₂O for the organic molecules shown in Figure 3-1
 - Sketch, save, visualize and perform QM calculation

Note: Recall that these jobs can be submitted and run simultaneously by selecting all of the entries before opening the Jaguar - Optimization panel

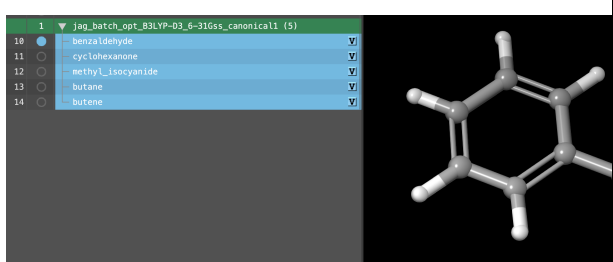


Figure 5-2. Outputs for five organic molecules.

Proceed to analyze the vibrations for the various organic molecules. Can you identify the diagnostic aldehyde C-H stretch, the carbonyl stretch, the CN triple bond? What are the key differences between the butane and 1-butene spectra?

- Fill in the Table with diagnostic frequencies in the IR worksheet

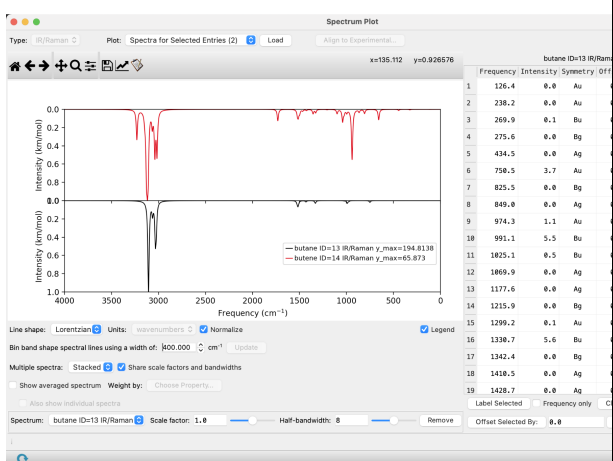


Figure 5-3. Outputs for five organic molecules.

To answer the latter question, let's overlay the spectra from butane and 1-butene in the spectra viewer.

2. **Select** both the output from butane and butene
3. Go to **Tasks > Jaguar > Plot Spectra**
 - The Spectrum Plot panel opens
4. Click **Load**
5. **Normalize** the spectra
6. View in either **Stacked** mode or **Overlaid**

There are two noticeable characteristics that differentiate the butane and 1-butene spectra

6. Resonance Effects

In this section, we will compare the IR frequency output for cyclohexanone and 2-cyclohexen-1-one to demonstrate the effect of resonance on diagnostic modes.

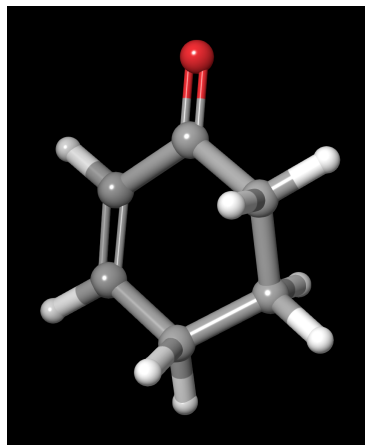


Figure 6-1. 2-cyclohexen-1-one in the workspace.

1. Repeat the above steps performed for 2-cyclohexen-1-one
 - o Sketch, save, visualize and perform QM calculation

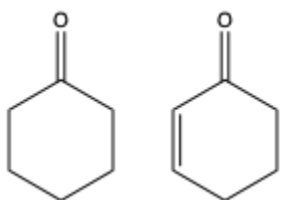
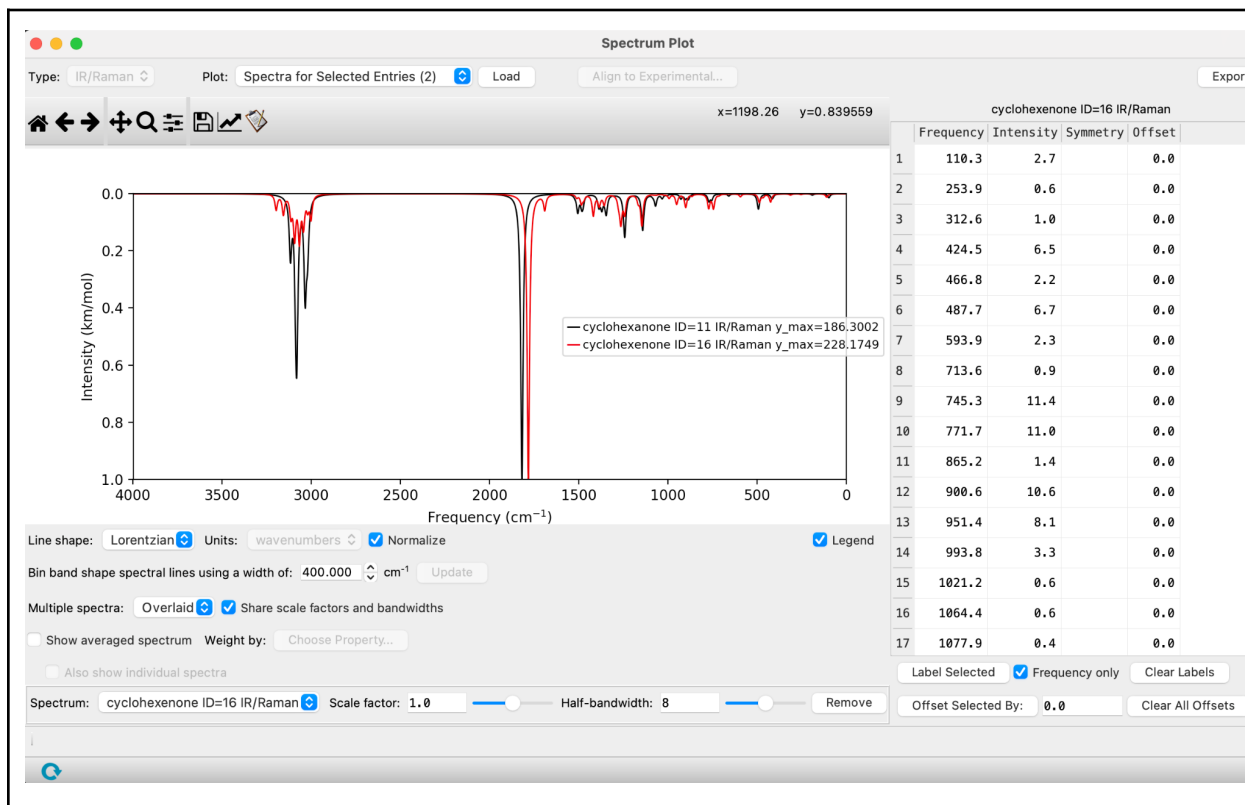


Figure 6-2. Structures.

Compare the key carbonyl vibrations for the two compounds. Which stretching frequency is lower? Can you explain why based on a simple Lewis structure approach? Answer these questions in the IR worksheet.



7. Mass Effects

In this section, we will compare the IR frequency output for acetylene and acetylene-d₂ to demonstrate the effect of mass on diagnostic modes.

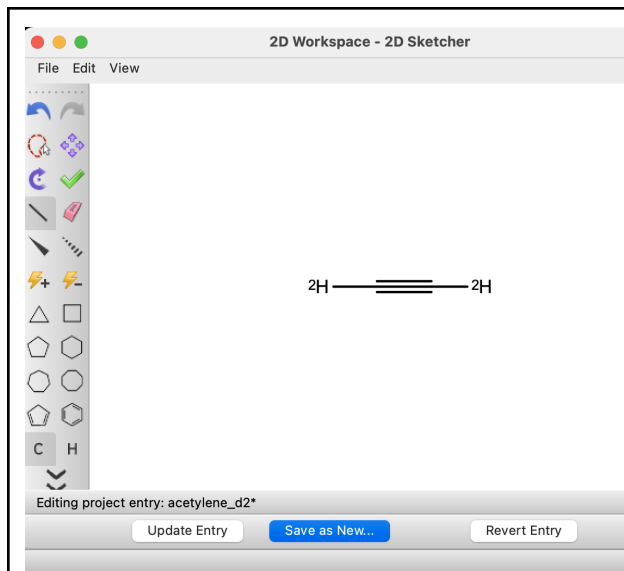


Figure 7-1. Adding deuterium to the acetylene model.

1. Repeat the above steps for acetylene-d₂
 - Sketch, save, visualize and perform QM calculation

Note: In the 2D sketcher, hover over a hydrogen with your mouse and type 'd' on your keyboard to change the hydrogen to a deuterium atom. Alternatively, right-click the hydrogens in the workspace and adjust the isotope.

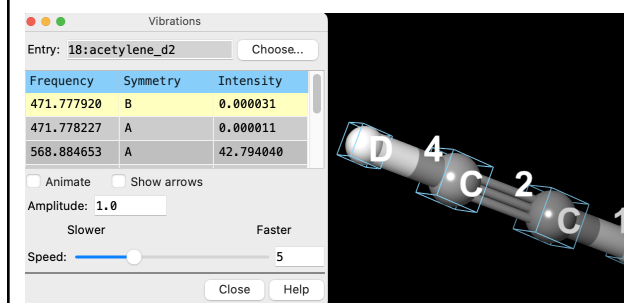


Figure 7-2. Vibrations for the acetylene-d₂ structure.

Compare the IR spectra of acetylene and acetylene-d₂.

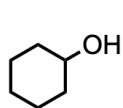
What do you notice about the spectrum of the non-deuterated molecule as compared to the deuterated molecule? Why do you think this difference is observed? How can this be useful for a synthetic chemist?

8. Individual Exercises

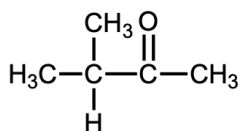
Two infrared spectra are shown, corresponding to two of the following compounds. Match the corresponding structure to each IR spectrum by:

- 1) Identifying how the major peaks (above 1500 cm^{-1}) in each spectrum correspond to the structure you have chosen
- 2) Using molecular modeling to perform a vibrational analysis with Maestro to confirm your answers

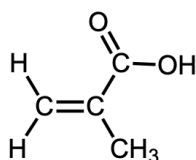
Structure Bank:



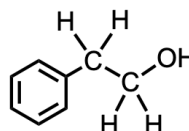
1



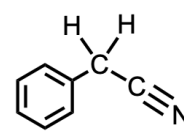
2



3

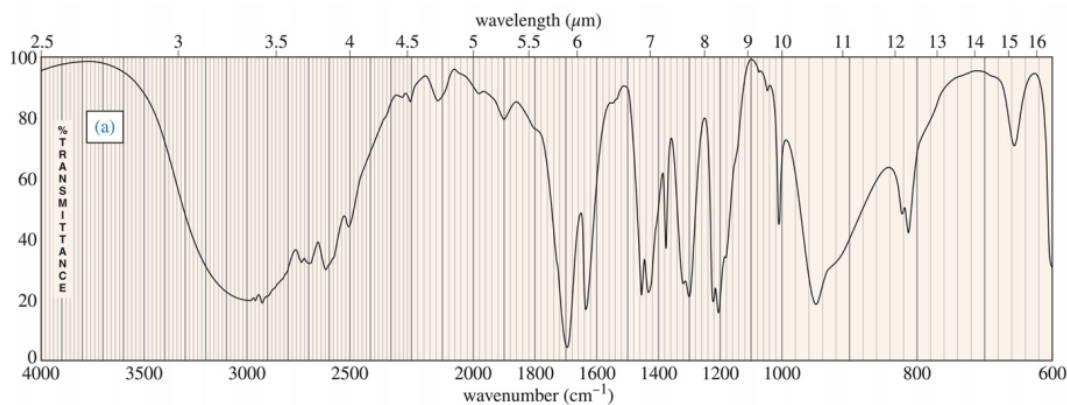


4

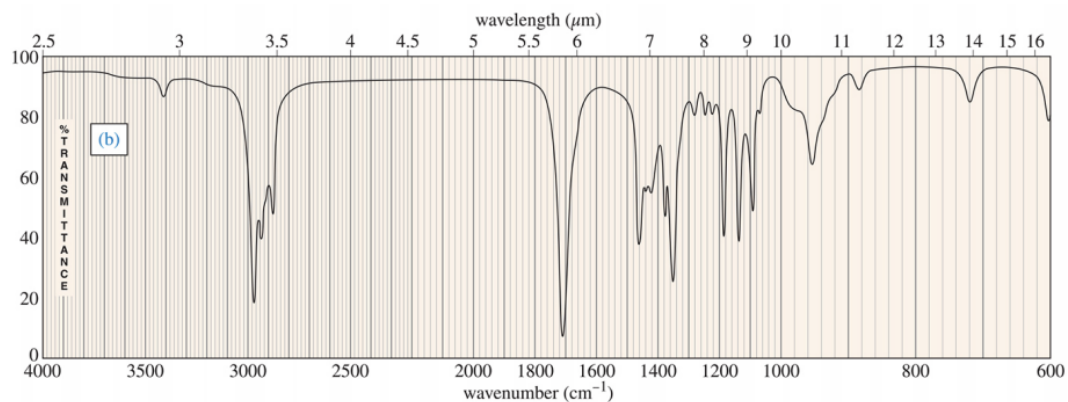


5

IR Spectrum A:



IR Spectrum B:



9. Conclusion and References

For further learning:

For introductory content, focused on navigating the Schrödinger Materials Science interface, an [Introduction to Maestro for Materials Science](#) tutorial is available.

For some related practice, proceed to explore other relevant tutorials:

- [Introduction to Multistage Quantum Mechanical Workflows](#)
- [Locating Transition States](#)
- [Optoelectronics](#)
- [Band Shape](#)
- [pKa Predictions with Jaguar pKa](#)
- [Computing Atomic Charges with Jaguar](#)
- [Reaction Workflow with Polyethylene Insertion](#)

For further reading:

- [Introduction to Computational Chemistry, 3rd Edition](#)
- [Essentials of Computational Chemistry: Theories and Models, 2nd Edition](#)
- [Molecular Modelling: Principles and Applications, 2nd Edition](#)
- See the Jaguar help [documentation](#)

10. Glossary

Entry List - a simplified view of the Project Table that allows you to perform basic operations such as selection and inclusion

Included - the entry is represented in the Workspace, the circle in the In column is blue

Project Table - displays the contents of a project and is also an interface for performing operations on selected entries, viewing properties, and organizing structures and data

Recent actions - This is a list of your recent actions, which you can use to reopen a panel, displayed below the Browse row. (Right-click to delete.)

Scratch Project - a temporary project in which work is not saved. Closing a scratch project removes all current work and begins a new scratch project

Selected - (1) the atoms are chosen in the Workspace. These atoms are referred to as "the selection" or "the atom selection". Workspace operations are performed on the selected atoms.

(2) The entry is chosen in the Entry List (and Project Table) and the row for the entry is highlighted. Project operations are performed on all selected entries

Working Directory - the location that files are saved

Workspace - the 3D display area in the center of the main window, where molecular structures are displayed

2D Workspace - the 2D panel that opens from the “edit” dropdown that allows for the construction of molecules using a 2D sketcher

Tile - if multiple entries are included, included entries are displayed side by side in individual boxes rather than being overlaid in the same space