5.3: Computational Instructions

As shown in Figure 3 the IR spectrum of hexane was acquired using an FT-IR spectrometer. Using the skills that you learned in lecture you should be able to pick out the main functional group stretches. This computational exercise will help you visualize what these vibrational modes look like on a molecular level.

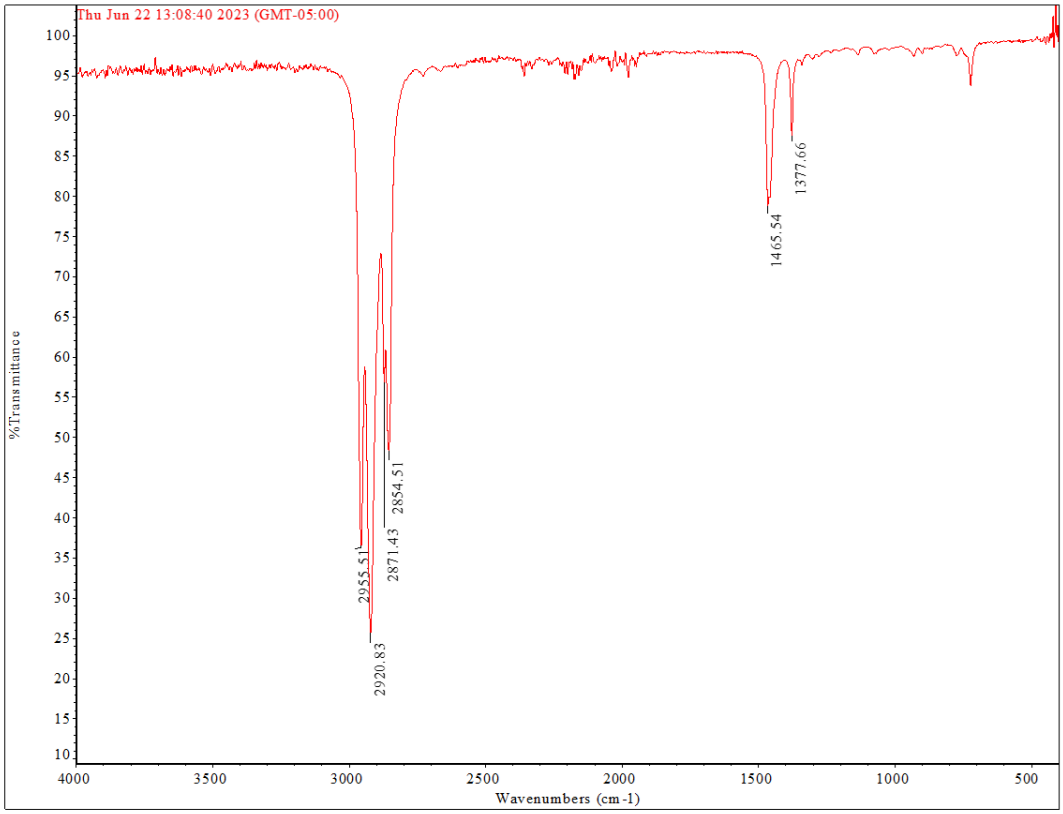

Figure 3. Experimental IR spectrum of n-hexane.

Start by creating a file folder on your local hard drive and name it IR. Next, open Avogadro and draw n-hexane using the drawing mode (Figure 4). After you have drawn this molecule, you should perform a quick preoptimization of the geometry by clicking extensionsà optimize geometry. Save this file in the folder that you created above as hexane_coord.xyz.

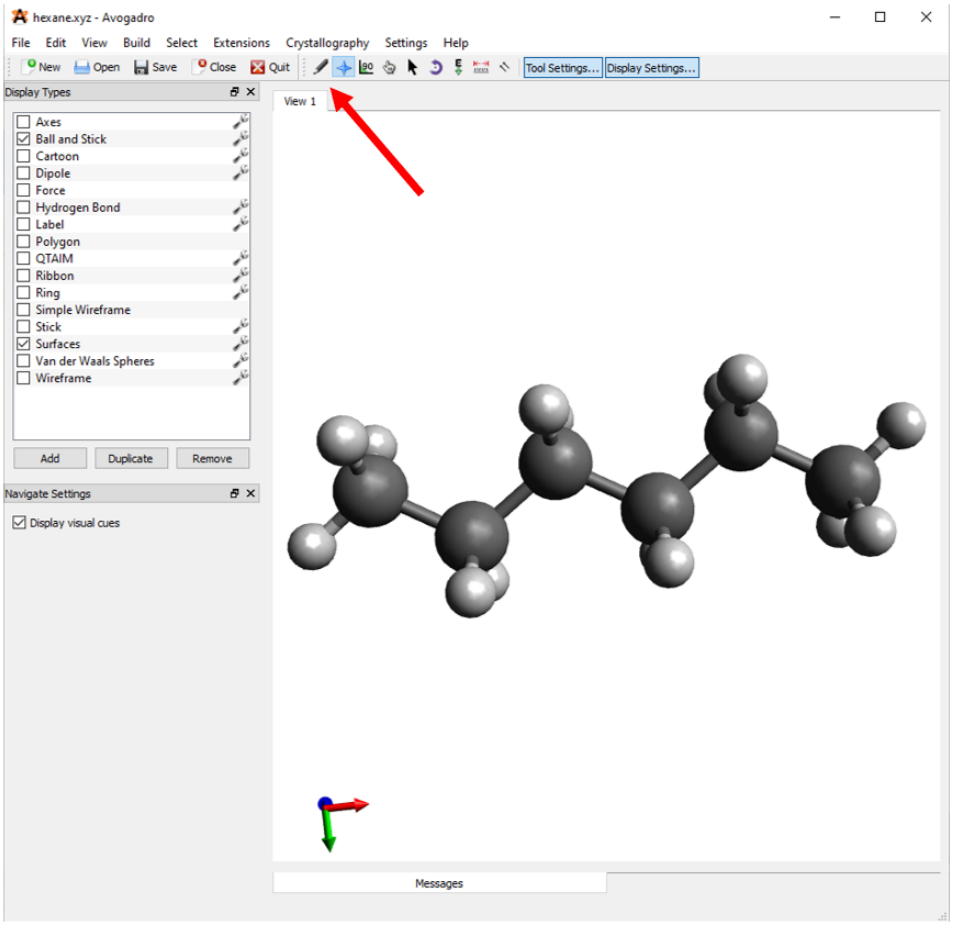

Figure 4. Drawing of n-hexane in Avogadro. The button to access the drawing mode of Avogadro is shown by the red arrow.

Next, you should download the Orca input script from supporting documents and save it in the IR folder as hexane.inp. After this, open this input script in notepad to view its contents. The text of the input file is shown in Figure 5. The first line of the input text (indicated by the blue arrow) tells Orca what calculations to run and how to run them. Specifically, the OPT command tells the computer to optimize the geometry of hexane and FREQ tells the computer to calculate hexane's vibrational frequencies. BP86 and DEF2-SVP tell the computer what functional and basis set, respectively to use in the calculation. The last line of the input script (indicated with a red arrow) tells the computer that we are using an XYZ file in our calculation. The two numbers, 0 and 1, indicate the charge of the molecule and the spin multiplicity of the complex. Finally, hexane_coord.xyz tells the computer what file to run the calculation on. Please check that the filename is exactly the same as the file name of the coordinates file that you created. If they are different, change them so that they are identical (or Orca will give you an error when you try to run the calculation).

```
# hexane IR
!BP86 DEF2-SVP OPT FREQ

* xyzfile 0 1 hexane_coord.xyz
```

Figure 5. Orca input script for the calculation of the IR spectrum of hexane. The line of the input script indicated by the blue arrow indicates the calculations that Orca will run. The line indicated by the red arrow tells orca what coordinates to run the calculation on.

We can now run our calculation using Orca via the command line as we did in previous exercises. Briefly, open the command prompt to your PC by right clicking on the start button and searching for command prompt. First, we need to tell the computer to look on the C drive and we do this by typing C: and hitting enter. Next, we need to tell the computer where the input script and the coordinates file are to run the calculation. We do this by typing cd (space) and pasting the file path. When you hit enter, the computer will paste a new line indicating that the current directory has changed, as shown in Figure 6A. To find the file path of

your input script, right click on the input script (hexane.inp) and select properties. The file path will appear under location, and you can highlight and copy this file path (Figure 6B).

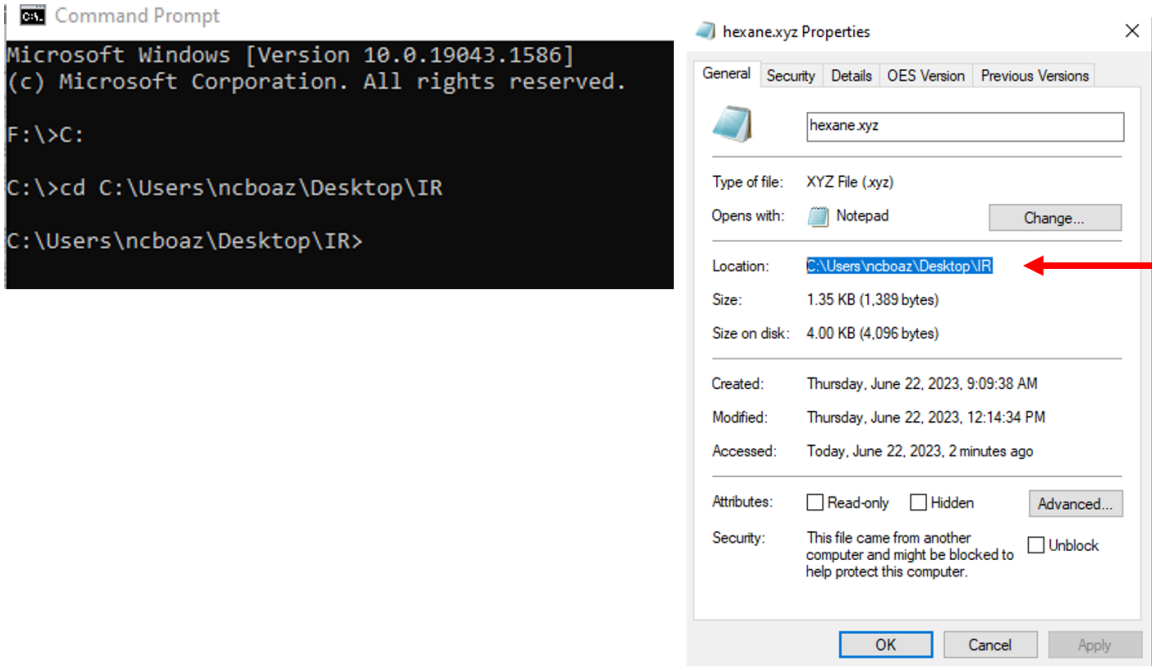

Figure 6A. (**Left**) Changing of the file path in the command prompt to match the location of our input script. **6B. (Right)** Locating the file path on the properties window of the input script (Red Arrow).

Next, we will run the calculation by typing orca hexane.inp > hexane.out and pressing enter. At first it may not appear like anything is happening but the folder on your desktop labeled IR will quickly become populated with the output of your calculation. Depending upon the speed of your computer, the calculation will take about 5-10 minutes, and upon completion the command prompt will print another line indicating that it is ready for the next command (Figure 7).

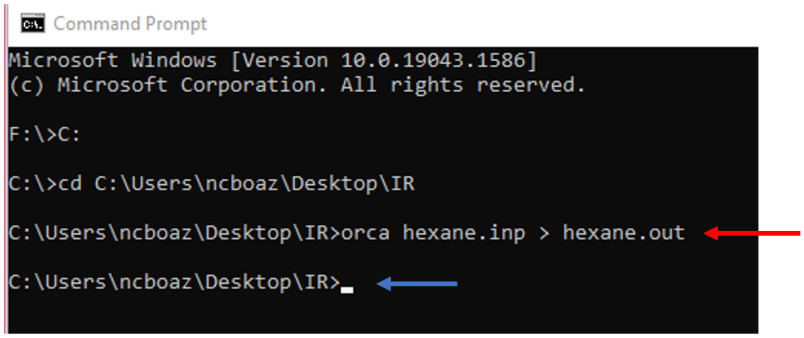

Figure 7. Running the calculation using the command line. The line indicated by the red arrow shows the computer that we want to use Orca to calculate the commands in hexane.inp and that the results of this calculation should be placed in the output file hexane.out. The line indicated by the blue arrow is the computer indicating that the calculation is complete, and the command prompt is ready for the next command.

To visualize the IR spectrum of hexane, you should open the hexane.out file in in Avogadro, which can be found in the folder you created labeled IR. This will open the file showing the vibrational modes in the right-hand corner. If you click on any of these vibrational modes, Avogadro will show you how the molecule vibrates in this mode in the main window. To show the entire IR spectrum please click on the Show Spectra button (Shown in Figure 8). This will open a window that displays the IR spectrum predicted by Orca (Figure 9). You will likely notice that this spectrum looks a little different than the experimental spectrum as shown in Figure 3 above. Specifically, the computational peaks are much skinnier than the peaks obtained experimentally. The reason for this is that the intermolecular interactions between the molecules slightly change the frequency of the peaks, broadening the spectrum. Moreover, the experimental spectrum is limited by the resolution of the spectrometer while the computational spectrum is not.

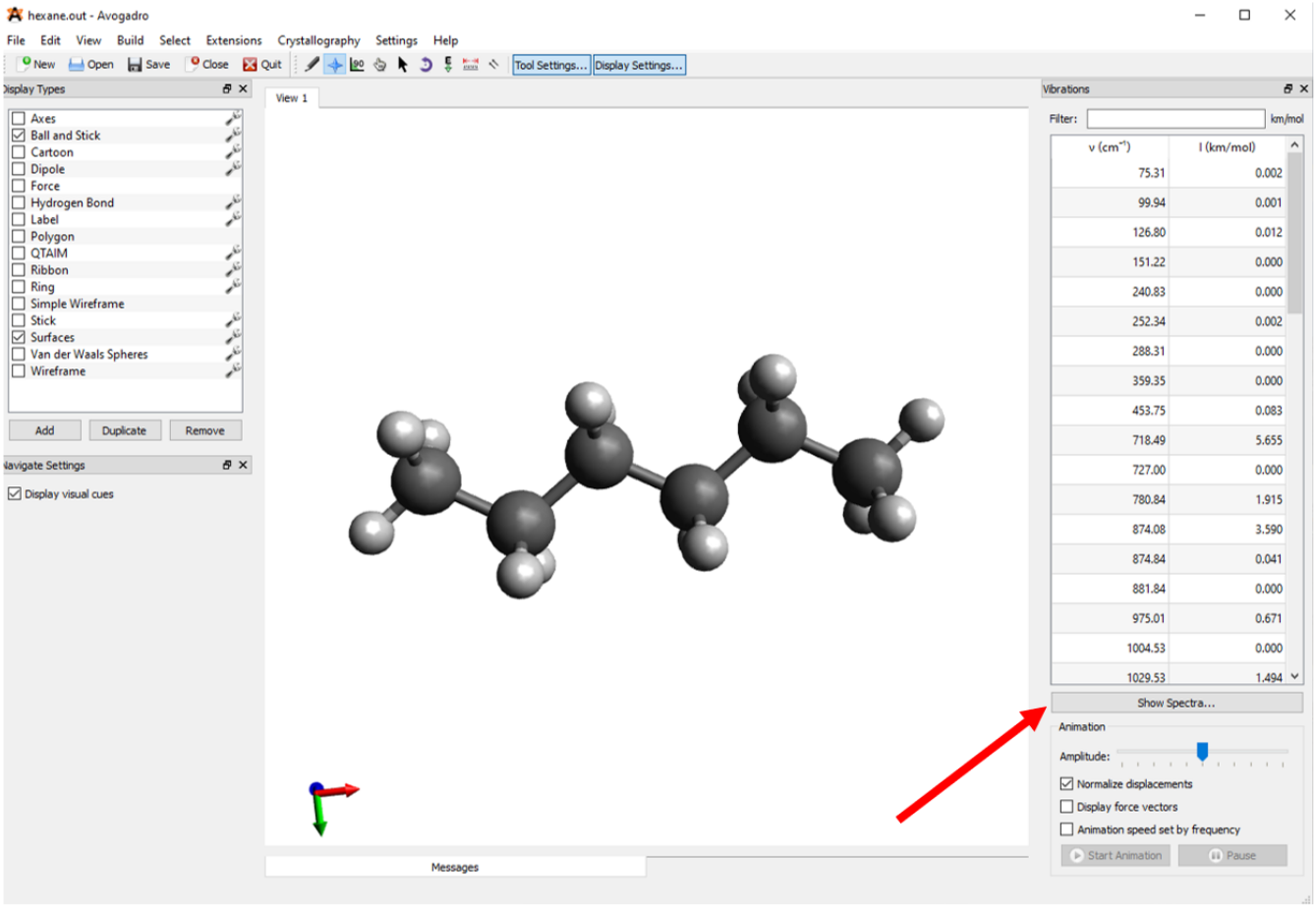

Figure 8. The hexane output file opened in Avogadro. The button to show the IR spectrum is indicated by a red arrow.

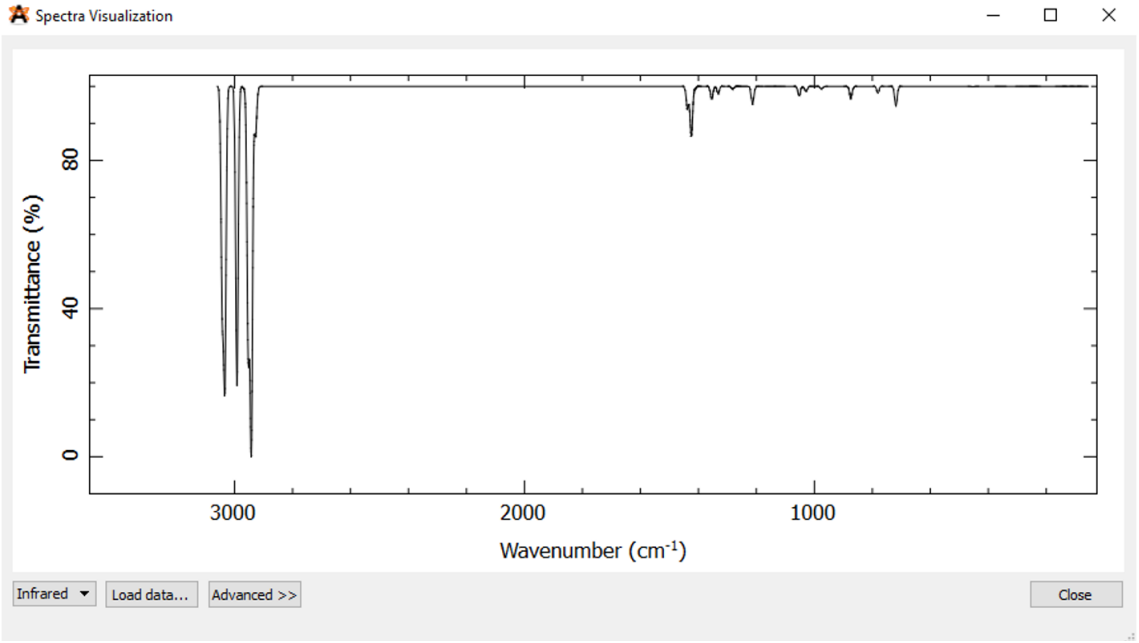

Figure 9. Computed IR spectrum of hexane.

You can tell Avogadro to match the resolution of the IR spectrum measured experimentally by clicking on Advanced<< on the Spectra visualization window shown in Figure 9. From here click on Infrared Spectrum Settings and change the Gaussian width toggle to 10 cm^{-1} as shown in Figure 10.

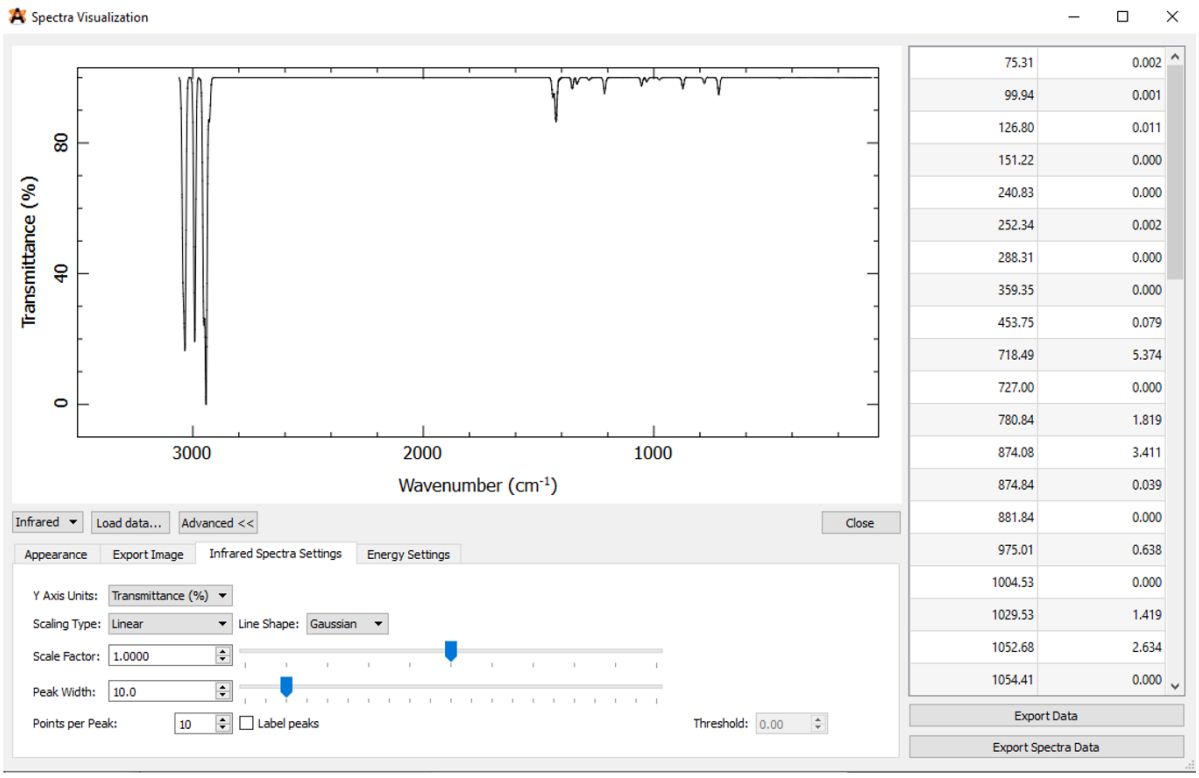

Figure 10. Changing the advanced settings to match the resolution on the experimental IR spectrum of n-hexane.

You now have all the information and computations necessary to complete the questions at the end of this exercise.

References

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