

Determining the Vibrational Frequencies of Water

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1 Introductory Reading

1.0.1 Objective of the lab

The goal of this lab is to learn how to perform a simple quantum chemical calculation using the technologies, techniques, and tools of computational chemistry. In this lab, you will determine the vibrational frequencies of water (H_2O), and compare your results to experimental data.

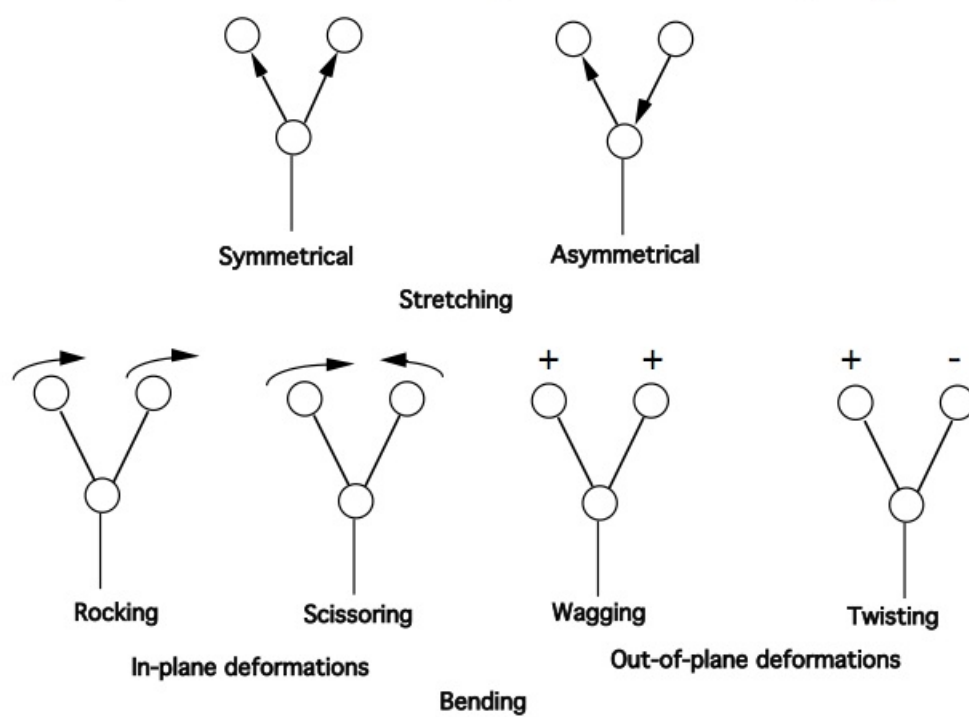
1.0.2 Background Reading:

Unlike the static (non-moving) pictures of molecules that you see in chemistry books, it is a fact that all molecules are constantly moving! They are moving in a variety of ways. One of the ways they move is by vibrating.

There are distinct ways that molecules vibrate, sometimes referred to as vibrational modes. Molecules stretch and bend, and do so symmetrically and asymmetrically. For bending, there are four variations rocking, scissoring, wagging and twisting. The first two bending modes are called "in-plane", and the second two are "out of plane".

The pictures in Figure 1 show the possible vibrational modes. You can imitate these modes with your fingers. Make a "V" or "peace" sign with your hand. To model symmetrical stretching, move both fingertips until they touch your palm. Your knuckles should be bending if you are doing this right. For asymmetrical, move one finger at a time to touch your palm, then the other. This requires a little bit of coordination! For bending, try rocking first. Keep your fingers straight, and simply move both fingers side to side. Scissoring is easiest to do, make your fingers move like a pair of scissors. Your hand is the plane, and notice that with rocking and scissoring, your hand should stay flat. For wagging, don't bend your knuckles, but move both fingers forward then back. For twisting, move one finger forward, then the other.

Figure 1: The six types of vibrations



All of these vibrations happen at specific frequencies. A *frequency* is a measure of how often, or how frequently, the molecule vibrates in a given period of time. Frequencies are measured in units of wavenumber, or in number of vibrations over a distance of centimeters. We write this as vibrations per centimeter, or cm^{-1} . The specific frequencies of a molecule are very much like a fingerprint: every molecule vibrates at very distinctive frequencies.

How many frequencies does a molecule have? There is a rough rule of thumb for calculating the number of frequencies that each molecule will have. For non-linear molecules, the rule is $3N - 6$. N stands for the number of atoms in a molecule. For example, if a molecule has 8 atoms, it will have $(3*8) - 6 = 18$ different vibrations, each one represented by a different frequency number. For linear molecules, the rule is $3N - 5$.

2 Computational Approach

2.1 Option 1: Building the molecule

If you have access to a computational chemistry server running WebMO and Gaussian, follow this procedure. The best option is to use the WebMO Demo Computational Chemistry server, located at <https://webmo.net/demo/index.html>. You can run short jobs, like this one, on that resource. The user name is guest and the password is guest.

1. Log into the chemistry server.
2. In the Job Manager, click on "New Job".
3. A drawing window should open. Under "Build", click on the "O" for oxygen atom.
4. Click once in the drawing window. A red oxygen atom should appear.
5. Under "Cleanup", click on "Comprehensive". This will add the hydrogens automatically. Sweet!
6. Under the Calculate menu item, choose Symmetry and hit the Symmetrize button.
7. To move to the next step, click on the "next" arrow at the bottom right of the window.

2.2 Configuring the Job

To prepare your molecule for calculation, follow these steps:

1. You have a choice of several software packages for this calculation. All of them can calculate water easily. For computational engine, choose Gaussian. For the job type, you want "Optimize+Freq". The theory will be B3LYP, and you want a 6-31G ("Basic") basis set. The combination of the level of theory and the basis set is known as the *model chemistry*.

2. The charge on water is zero, and the number 0 should appear in the Charge window.
3. Multiplicity is a measure of how the electrons are spinning. In the case of water, for every electron spinning "up", there is an electron spinning "down". An electron spinning up cancels out an electron spinning down, so the value of "S", or total spin, is zero (0). The multiplicity rule is $2 * S + 1$, so in this case $S = 0$, so multiplicity = $2 * 0 + 1 = 1$, or a *singlet* condition. Your pull-down should be set at singlet!
4. Click on the "Next" arrow. Once you have done so, you are returned to the Job Manager, and your job is either running, or its in the "queue", or in line! You can hit the "Refresh" button to see how your job is doing in the queue.

2.3 Option 2: Loading the results/log file

For this and all of the labs in this short course, you are provided with a ".log" (dot-log) file. This is the raw data output that is created by software tools such as Gaussian. For this particular lab, you can and should run your own calculation using the WebMO Demo Server, so you have a sense of how to set up a "job" and submit it to the server. For most of the labs in this short course, you may or (more likely) may not have access to tools like Gaussian, so we have run the calculations for you and have provided you with the resulting .log file!

1. Download the .log file to your computer, preferably to your Desktop to make it easy to find!
2. Log into a WebMO-based server, such as the WebMO Demo Server (<https://webmo.net/demo/index.html>).
3. Under "New Job", select the "Import Job" option.
4. The import type is "Job output file". Give your job a name, such as "Water vibrations". Select "Gaussian" as your file type.
5. Click on the "Choose File" button under "2) Local output file". Find and load your water log file. Your file has now been loaded into the "Job Manager".

2.4 Data Analysis

Once your "job" is completed, regardless of which option you followed, click on the name of the job OR the magnifying glass to the right of the window. This will open up your results page. You can now find and download the Student Data Analysis worksheet for this lab on Canvas, or follow instructions from your classroom teacher.