

Visualizing the Vibrations of Water

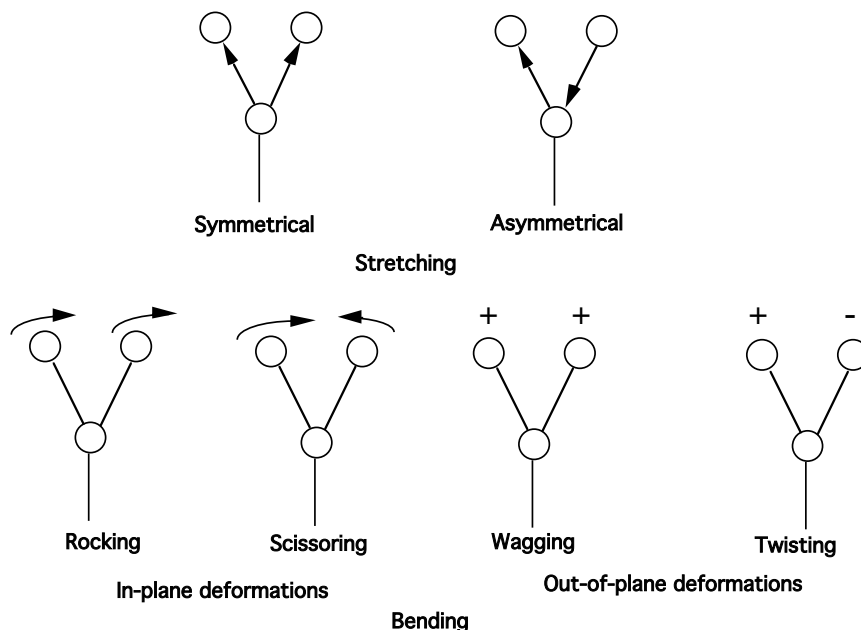
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Introductory Readings

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 below 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. 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

Vibrational modes refers to the way that molecules vibrate.

Symmetric refers to motion in the same direction or motion that is together.

Asymmetric refers to motion that is opposite. One part moves one way while the other part moves a different, usually opposite, way.

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.

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 $(3 \times 8) - 6 = 18$ different vibrations, each one represented by a different frequency number. For linear molecules, the rule is " $3N - 5$ ".

Frequency is a measure of how often the molecule vibrates.

Wavenumber is one measure of a frequency. Wavenumbers are measured in units of "per centimeter", or " cm^{-1} ".

3N-6 Rule is a general rule for calculating the number of different vibrations in a molecule. "N" represents the number of atoms in the molecule.

Objectives of the Case Study

The objective of this case study is to calculate the vibrational modes of a simple molecule – water. Water is a non-linear molecule, meaning it has a bent shape. You should be able to predict, without using a calculator or computer, how many vibrations you expect to see. (Hint: use the $3 \times N - 6$ rule!)

Your objective, therefore, is as follows:

1. Confirm your prediction as to the number of vibrations in water
2. Determine the specific frequencies for each of those vibrations
3. Visualize each vibration to determine the type of vibration – stretching, bending, etc.

Experimental Procedure

Building the molecule

1. Log into the chemistry server.
2. In the Job Manager, click on "New Job".
3. Once the molecular editor opens, click on "Open Editor" at the bottom of the window.

4. A drawing window should open. Under “Build”, click on the “O” for oxygen atom.
5. Click once in the drawing window. A red oxygen atom should appear.
6. Under “Cleanup”, click on “Comprehensive”. This will add the hydrogens automatically. Sweet!
7. Under “File”, click on “Close”. This will close the editor window, and place your molecule in the Viewer window.
8. To move to the next step, click on the “next” arrow at the bottom right of the window.

Configuring the Job

To prepare your molecule for calculation, follow these steps:

1. You have a choice of three software packages for this calculation. All of them can calculate water easily. For this example, choose GAMESS (General Atomic and Molecular Electronic Structure System) for your computational “engine”.
2. Click on the “Next” arrow at the bottom right of the window. You should now see a “Configure GAMESS Job Options” window!
3. Under Job Name, give your job a good title. You might want to call it “Water Vibrational Frequencies”, or perhaps something with your name in it.
4. Under the pull-down menu “Calculation”, select “Vibrational Frequencies”. This is, after all, what we’re looking to calculate!
5. The pull-down menu “Theory” provides you with different options on how the calculation will be done. For this job, we want to use Restricted Hartree-Fock, or RHF. As you learn more about computational chemistry, you will have an opportunity to understand these different theories and how they influence your calculations!
6. Under the pull-down menu “Basis Set”, choose “Minimal: STO-3G”. Again, like the Theory option, as you learn more about computational chemistry, you will learn more about these different options. The Basis Set refers to a built-in set of numbers that will serve as the starting point for your calculation.
7. The charge on water is zero, and the number 0 should appear in the Charge window.
8. 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!
9. Click on the “Next” arrow. Once you have done so, you are returned to the Job Manager, and your job is either running, or it’s in the “queue”, or in line! You can hit the “Refresh” button to see how your job is doing in the queue.

Data Analysis

Once your “job” is completed, follow this procedure:

1. Click on the name of the job **OR** the magnifying glass to the right of the window. This will open up your results page. If you get a “Certificate” window, click on OK to accept the Certificate.
2. Scroll down to the section under “Calculated Quantities” entitled “Vibrational Modes”. How many vibrations do you see? There should be three (3), or $3*3-6=3$, just as you calculated with the $3N-6$ rule!
3. Set your Animation Speed from 10 to 5, then click on one of the filmstrip/movie icons next to one of your three frequencies. Scroll up to the Viewer window, and you should see your molecule vibrate!
4. Scroll back down, and look at each of the three vibrations, one at a time.
5. There are other things you can look at from this run, such as the IR (infrared) spectra of water. Feel free to explore!

Check your answers!

See how you did with your objectives:

1. Confirm your prediction as to the number of vibrations in water
 - a. There are **3 vibrational modes** in water – 3 atoms (one O, 2 Hs), so $3*3-6=3$
2. Determine the specific frequencies for each of those vibrations
 - a. Mode 1: 1766.99 cm^{-1}
 - b. Mode 2: 4157.52 cm^{-1}
 - c. Mode 3: 4269.36 cm^{-1}
3. Visualize each vibration to determine the type of vibration – stretching, bending, etc.
 - a. Mode 1: Scissoring (in-plane bending)
 - b. Mode 2: Symmetrical stretching
 - c. Mode 3: Asymmetrical stretching