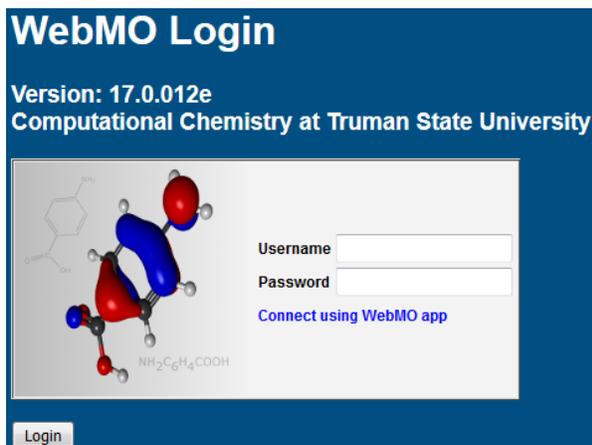


## Using Computational Chemistry to Predict Retention Times for Gas Chromatography

Author: V. M. Pultz

Last Update: June 23, 2018

Go to <https://pyrite2.truman.edu/~webmo/cgi-bin/webmo/login.cgi> by clicking on the link or copy and paste this link in your favorite browser. If one browser does not work, try a different one.



Enter your username and password, and either click the “Login” button or press the Enter key on your keyboard. The **WebMO Job Manager** screen should appear.

Start a calculation on acetone by going to the “New Job” tab (it will show “Create new job”) and click. This will take you to the **Build Molecule** screen. Left-click on the Lookup tab at the top of the screen, move the mouse to *Import by*, click on *Name*, and type “acetone” in the molecule name box. The molecule will appear in the Build Molecule screen. (Verify that the formula of the molecule that is displayed agrees with the formula given in the experiment. The Lookup Molecule feature accesses external data bases which may not be 100% correct all of the time. If the displayed molecule does not agree with the formula, start over for that molecule. In the **Build Molecule** screen put in all C and O atoms, use single or double bonds to connect them as appropriate, and *Comprehensive Cleanup* will enter the H atoms.) Click on the blue right arrow in the lower right corner. You may get a warning that the molecule is nearly (but not exactly) symmetric. You may click on OK to continue. Or you may press Cancel and then click on **Calculate** at the top of the Build Molecule screen. Move the cursor to **Symmetry** and click on **Symmetrize** and press the **Symmetrize** button. (The Point Group will probably be C2, but another possibility is Cs.) Click OK. Click on the blue right arrow in the lower right corner again.

Now you should be at the **Configure Gaussian Job Options** screen. The program gives your job a name based on the molecule that you drew; you might want to add to the name that this is acetone. Choose the type of calculation to do from the *Calculation Pulldown* menu. Select the fourth one down which is “Optimize + Vib Freq” This will tell the program to first do a

“Geometry Optimization” followed by a calculation of the vibrational frequencies which also includes a calculation of the polarizability. Keep the theory as “Hartee-Fock” and choose the basis set “Basic: 3-21G.” Leave the charge as “0” since your molecule is neutral. Leave the multiplicity as a singlet (this means that there are no unpaired electrons). Verify what you have entered and then start the calculation by clicking the right hand blue arrow head or "Submit job." WebMO returns to **WebMO Job Manager** screen which lists all the jobs you have submitted.

While this job is running, start with the next of the molecules listed in the Gas Chromatography experiment. The Lookup Molecule feature should be the fastest way to get the molecules.

For all of these molecules, choose “Optimize + Vib Freq” and “Hartee-Fock” and “Basic: 3-21G.” Once you have started calculations for all of the molecules, the acetone calculation should be finished, and its status will be *Complete* and the "View job" icon () will be displayed to the right of the job. Click on the "View job" icon and, if necessary, accept the risk and Run. Your molecule should be displayed on the screen. At the left side of the screen, click on [Raw output](#) which is immediately below [Job Manager](#). At the very top of the screen, click on Edit and then Find (or press Ctrl and the F key simultaneously). In the box, type **Isotropic polarizability**. Record the value immediately before the units Bohr\*\*3 which stands for Bohr<sup>3</sup> or  $a_0^3$  which is volume in atomic units.

Close the Raw Output tab. Scroll down to the Vibrational Modes section. Click on  to animate a vibrational mode. Watch what happens if you choose one with a frequency over 3000  $\text{cm}^{-1}$  compared to one around 1900  $\text{cm}^{-1}$  compared to one around 1500  $\text{cm}^{-1}$  and finally compared to one with an even lower frequency. These calculated frequencies are higher than experimental frequencies.

Left click on [Job Manager](#) and look at the Raw Output for the other molecules. Record the isotropic polarizability for each molecule. For fun, you may wish to animate the vibrational modes for some of the other molecules, especially for methanol or ethanol, being sure to at least view the highest frequency mode for them.

When molecules are put into a gas chromatography column which has a nonpolar coating, their primary interaction with the column coating will be based on their polarizability. Larger polarizability should lead to longer retention time. In the case of acetic acid, see Figure 12-9 in Petrucci *et al.*, *General Chemistry: Principles and Modern Applications*, 10<sup>th</sup> ed., ©2011 which indicates that acetic acid will primarily exist as a dimer. Since primarily dimers of acetic acid interact with the column coating, multiply the polarizability that you calculated for acetic acid by two to approximate the polarizability of the dimer. Use your polarizability values to predict the order for retention times of your molecules. After gathering experimental values for the retention times in the laboratory, discuss how good your predictions were.