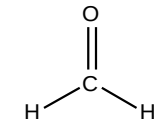
7 Infrared, Thermochemistry, UV-Vis, and NMR

Exercise 1 Method Dependence and Scaling for the Infrared Spectrum of Formaldehyde



Formaldehyde

Build a molecule of formaldehyde. Use Clean-Up > Comprehensive – Mechanics.

Choose Mopac as the computational engine. Type in/Choose the following:

Job Name: CH2O AM1 Geom Opt
Calculation: Geometry Optimization
Theory: AM1
Charge: 0
Multiplicity: Singlet

Click on the blue "continue" arrow. You should now see your job listed. When the calculation is finished, click on New Job Using This Geometry, and Type in/Choose the following:

Job Name: CH2O AM1 IR
Calculation: Vibrational Frequencies
Theory: AM1
Charge: 0
Multiplicity: Singlet

Click on the blue "continue" arrow. You should now see your job listed. When the calculation is finished, open the file and scroll down to the Vibrational Modes window.

How many transitions are shown (count the number of frequencies)? 6 Modes Is this the number expected? Yes

Click on the filmstrip next to one of the frequencies and observe the corresponding vibrational motion. Try to identify the type of motion for each transition. (The molecule can be rotated if needed). In the table on the next page, record the frequencies and type of motion for each.

Repeat the process described above, but use "PM3" in place of "AM1". Observe the vibrational motions, and record the frequency data in the appropriate column on the next page.

Start a New Job, and build a molecule of formaldehyde. Clean up the structure by selecting Clean-Up > Comprehensive – Mechanics.

Choose Gaussian or GAMESS as the computational engine. Type in/Choose the following:

Job Name: CH2O DFT Geom Opt
Calculation: Geometry Optimization
Theory: DFT
DFT Functional: B3LYP
Basis Set: 6-31G(d)
Charge: 0
Multiplicity: Singlet

Click on the blue "continue" arrow. You should now see your job listed. When the calculation is finished, click on New Job Using This Geometry, and Type in/Choose the following:

Job Name: CH2O DFT IR
Calculation: Vibrational Frequencies
Theory: DFT
DFT Functional: B3LYP
Basis Set: 6-31G(d)

Charge: 0
Multiplicity: Singlet

Click on the blue "continue" arrow. You should now see your job listed. When the calculation is finished, open the file and scroll down to the Vibrational Modes window.

As before, click on the filmstrip next to one of the frequencies and observe the corresponding vibrational motion. In the table on the below, record the frequencies.

Which method seems to give the best results? DFT B3LYP

In the "View Job" window, click on Raw Output and investigate the contents of the file.

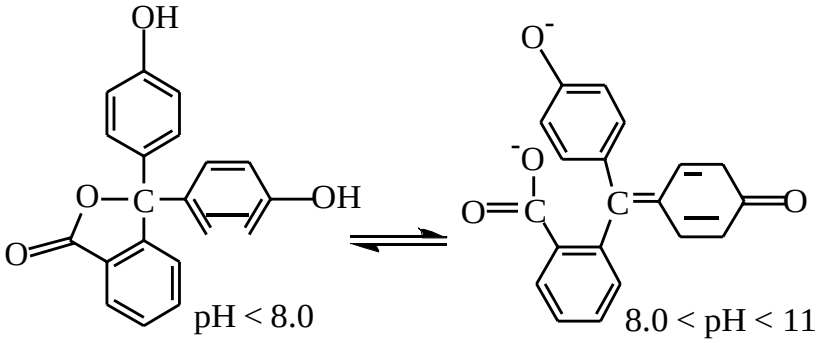
Due to the approximations implicit in these calculations, calculated vibrational frequencies are often higher than the experimental values. For better comparison with experimental results, the calculated frequencies are often multiplied by a scaling factor (fudge factor!). The scaling factors are listed below. Perform the corrections and list the new results in the appropriate columns. Do the scaled values give a better comparison with the experimental values?

Use the scaling factors (AM1 = 0.9532; PM3 = 0.9761; B3LYP/6-31G(d) = 0.9614)

Motion	AM1	Scaled AM1	PM3	Scaled PM3	B3LYP/ 6-31G(d)	Scaled B3LYP/ 6-31G(d)	Experimental values (cm^{-1})
CH_2 Rock	3120.2	2974.175	3025.2	2952.898	2967.923	2853.3612	2843
CH_2 Asymmetric-Strech	3084.1	2939.764	2998.2	2926.543	2916.9059	2804.3133	2782
CH_2 Wag	2052.4	1956.348	1986.8	1939.315	1849.8184	1778.4154	1746
CH_2 Scissor	1443	1375.468	1287.9	1257.119	1563.0872	1502.752	1500
CO Stretch	1176.4	1121.344	1098.3	1072.051	1279.5326	1230.1426	1249
CH_2 Symmetric-Stretch	1164.6	1110.097	1069.6	1044.037	1198.4696	1152.2087	1167

Exercise 3 Electronic Transitions of Phenolphthalein at Various pH

Phenolphthalein is a widely used acid-base indicator. Two forms of the molecule, shown below, will be constructed and the UV-Vis spectrum of each will be calculated. Each optimized structure will be investigated to determine the correlation between structure and absorbance of light. We will be using the PM3 method for geometry optimizations and ZINDO for UV-Vis calculations, so the results will not be *quantitative*. We should see the correct *qualitative* changes in the spectra of the two forms.



It can be challenging to draw chemical structures in three dimensions using tools that only work in two dimensions. In order to avoid overlapping atoms and other troubles, we will use a stepwise approach in constructing phenolphthalein. This approach may serve you well for building other molecules.

Building the low-pH form of Phenolphthalein

In the WebMO Editor window, build the following fragment of phenolphthalein:

Submit the job by clicking on “Submit job” on the left side. Click “OK” in the pop up window. When the job is complete, click on the filename and scroll down to view the “Excited States” table. Near the bottom of the table, click on the magnifying glass to view the calculated spectrum. In the Spectrum Viewer window, use your mouse and place the cursor on the top of the peak and record the wavelength at maximum absorbance (λ_{max} – displayed in the upper right of the “Spectrum Viewer” window) value here: 276.9581 nm.

Building the mid-pH form of Phenolphthalein

Go to “Job Manager” and open the “C20H14O4lowpH” file from above. Click on “New Job Using This Geometry” followed by “Open Editor”.

Use the Rotate tool to position the molecule as shown at the bottom of the previous page.

Submit the job by clicking on “Submit job” on the left side. Click “OK” in the pop up window. When the job is complete, click on the filename and scroll down to view the “Excited States” table. Near the bottom of the table, click on the magnifying glass to view the calculated spectrum. In the Spectrum Viewer window, use your mouse and place the cursor on the top of the most intense peak and record the wavelength at maximum absorbance (λ_{max} – displayed in the upper right of the “Spectrum Viewer” window) value here: 614.2829 nm.

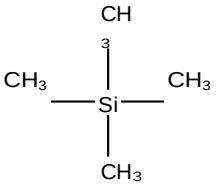
Has the λ_{max} shifted relative to the low pH structure? Yes, Which direction did λ_{max} shift? Towards visible light (To the left of the spectrum)

Which of these two structures is expected to absorb visible light? Mid-pH form

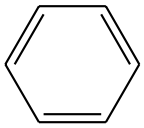
Does the shift in absorption wavelength you calculated make sense? Yes

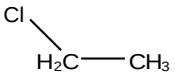
Exercise 4 NMR Chemical Shift Calculations

Build the following molecules, clean up each structure by selecting Clean-Up > Comprehensive – Mechanics, and perform a geometry optimization using Gaussian > B3LYP/6-31G(d).



tetramethylsilane


benzene



1-chloroethane

ethanol

Benzene	**Calc.**	**Exp.**	**CH_3CH_2OH**	**Calc.**	**Exp.**
H's	7.2138	7.16	Methyl H's	1.35	1.16
C's	121.1594	128.4	Methylene H's	3.83	3.59
			Hydroxyl H	0.05	4
CH_3CH_2Cl			Methyl C	17.7	17.6
Methyl H's	1.4	1.48	Other C	59	57
Methylene H's	3.42	3.57			
Methyl C	19.4	18.7			
Other C	44.9	39.9			

Notes:

Most of my colleagues faced failing issues, so in order to avoid it altogether, I tried to set up WebMO on my local machine, I was unable to finish doing that yesterday, unfortunately.

I was able to use MOPAC only, Gaussian is not free and GAMESS takes time to receive the license. So I did a hybrid work, I optimized the geometry -which was the main difficulty- using my local machine then export it to the demo version of WebMO to carry out the remaining calculations. The results were worth it and I did not encounter a single failing job at all. The following pictures show the results:

C20H12O4(-2)	Geometry Optimization - Mopac	3/23/2022 9:26	Complete	9.1 sec	
C20H14O4	Geometry Optimization - Mopac	3/23/2022 9:18	Complete	10.4 sec	
C20H14O4	Geometry Optimization - Mopac	3/23/2022 9:02	Complete	7.6 sec	
C20H14O4	Geometry Optimization - Mopac	3/23/2022 8:54	Complete	0.0 sec	
CH2O	Vibrational Frequencies - Mopac	3/23/2022 8:30	Complete	0.0 sec	
CH2O	Geometry Optimization - Mopac	3/23/2022 8:30	Complete	0.0 sec	
CH2O	Vibrational Frequencies - Mopac	3/23/2022 8:17	Complete	0.0 sec	
CH2O	Geometry Optimization - Mopac	3/23/2022 8:16	Complete	0.0 sec	

Figure 1 My local WebMO

☐	1048382	C20H12O4(-2)	UV-Vis Spectrum - Gaussian	3/23/2022 2:31	Complete	1.7 sec	
☑	1048381	C20H12O4(-2)	Geometry Optimization - Mopac	3/23/2022 9:26	Complete	9.1 sec	
☐	1048380	C20H14O4	UV-Vis Spectrum - Gaussian	3/23/2022 2:23	Complete	1.9 sec	
☑	1048377	C20H14O4	Geometry Optimization - Mopac	3/23/2022 9:18	Complete	10.4 sec	
☐	1048376	C20H14O4	UV-Vis Spectrum - Gaussian	3/23/2022 2:08	Complete	1.8 sec	
☑	1048375	C20H14O4	Geometry Optimization - Mopac	3/23/2022 9:02	Complete	7.6 sec	

Figure 2 Checked ones were imported from local WebMO