





Chapter 2

Walking Through *Spartan*

*This chapter, in the form of a tutorial, introduces a number of basic operations in **Spartan** required for molecule manipulation, property query and spectra and graphics display. This chapter is a must for new **Spartan** users. It shows how to: i) open molecules, ii) view different model styles and manipulate molecules on screen, iii) measure bond distances, angles and dihedral angles, iv) display energies, dipole moments, atomic charges and infrared, NMR and UV/visible spectra, and v) display graphical surfaces and property maps. Spreadsheet operations are not illustrated, no molecules are sketched or built and no quantum chemical calculations are performed.**

1. Start **Spartan**. Click (left mouse button) on **File** from the menu bar that appears at the top of **Spartan's** main window. Click on **Open...** from the **File** menu that appears. Alternatively, click on the  icon at the top of the screen. A file browser appears.

 Tap on  at the top of the screen. If the icon is not available, tap on **File** in the menu bar to bring up a palette of icons and then tap on .

Move to the **Tutorials** directory**, click on **Walking Through Spartan** and click on **Open** (or double click on **Walking Through Spartan**).

* The results of quantum chemical calculations in this chapter have been obtained using the ω B97X-D/6-31G* density functional model.

** For Windows, the **Tutorials** directory is found in **Program Files/Wavefunction/Spartan20**. It needs to be copied to another location available to the user (we recommend Documents or Desktop) prior to opening it in **Spartan**.

For Macintosh, this is located at the top of the **Spartan20** disc image. It needs to be copied to another location available to the user (we recommend Documents or Desktop).

For Linux, the **Tutorials** directory is found in the install directory. Copy the **Tutorials** directory to a location that allows write permission, typically the user's home directory.



Tap on ***Walking Through Spartan*** and tap on **Open** (or double tap on ***Walking Through Spartan***). Note that *click* (left mouse button) and *tap* (one finger) are equivalent as are *double click* and *double tap*. We shall only indicate *click/double click* throughout the text that follows.

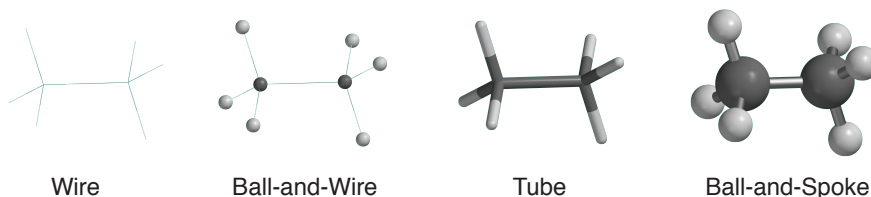
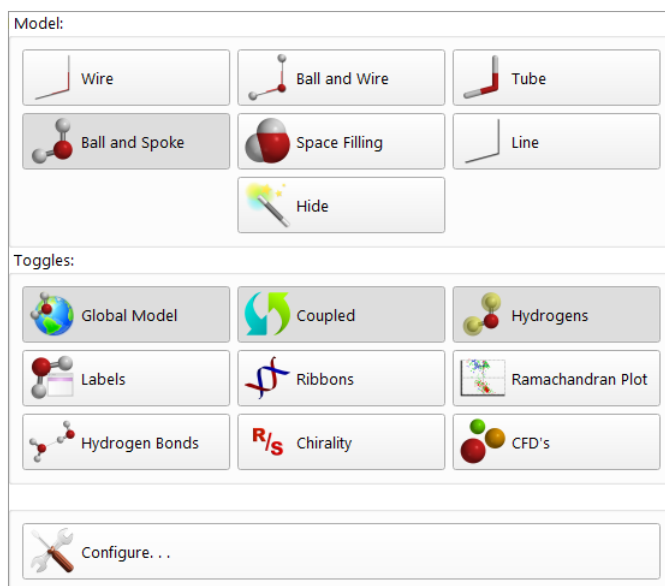
A single file containing ***ethane, acetic acid dimer, propene, ammonia, hydrogen peroxide, acetic acid, water, cyclohexanone, camphor, 3-aminobenzophenone, ethylene, benzene, aniline*** and ***cyclohexenone*** will be opened. A ball-and-spoke model for the first molecule (***ethane***) will be displayed, and its name appears at the bottom right of the screen. The appearance of the name means that the molecule is included in the Spartan Spectra and Properties Database (SSPD).

2. Practice rotating (*move* the mouse while holding down the left button) and translating (*move* the mouse while holding down the right button). Use the scroll wheel to zoom in and out, or alternately move the mouse while holding down both the right button and the **Shift** key.



To rotate, move one finger across the screen. To translate, move two fingers across the screen. To zoom out, pinch two fingers together. To zoom in, move two fingers apart.

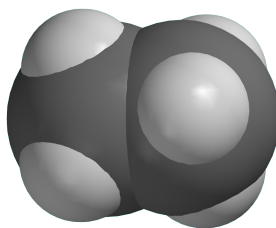
Click on **Model** from the menu bar.



One after another, select **Wire**, **Ball and Wire**, **Tube** and finally **Ball and Spoke** from the **Model** menu. All four models for *ethane* show essentially the same information. The wire model looks the most like a conventional line formula. It uses color to distinguish different atoms, and one, two and three lines between atoms to indicate single, double and triple bonds, respectively.




The ball-and-wire model is identical to the wire model, except that atom positions are represented by small colored spheres, making it easy to identify atom locations. The tube model is identical to the wire model, except that bonds are represented by solid cylinders. The tube model is better than the wire model in conveying three-dimensional shape. The ball-and-spoke model is a variation on the tube model; atom positions are represented by colored spheres, making it easy to see atom locations.

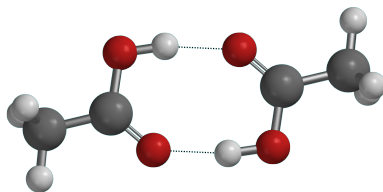
Select **Space Filling** from the **Model** menu.



Space-Filling

The space-filling model is different from the other model styles in that bonds are not shown. Rather, each atom is displayed as a colored sphere that represents its approximate relative size. Thus, the space-filling model for a molecule provides a measure of its size. While lines between atoms are not drawn, the existence (or absence) of bonds can be inferred from the extent to which spheres on neighboring atoms overlap. If two spheres substantially overlap, then the atoms are almost certainly bonded, and conversely, if two spheres barely overlap, then the atoms are not bonded. Intermediate overlaps suggest weak bonding, for example, hydrogen bonding.

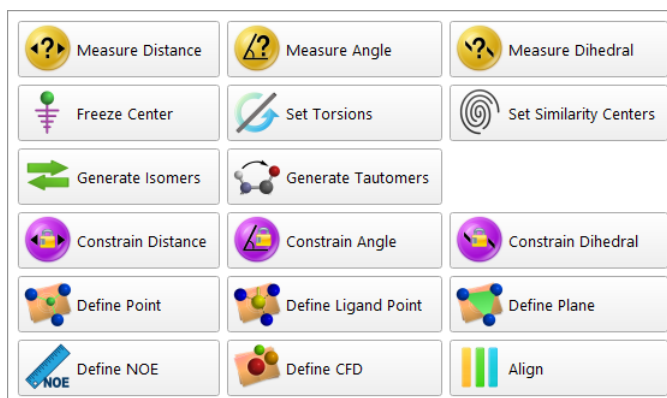
3. Click once on the right arrow key  at the bottom left of the screen. This will move to the next molecule in the document, *acetic acid dimer*. Its name will appear at the bottom of the screen. If you make a mistake, use the backward  or forward  step keys to get to *acetic acid dimer* in the document. From the space-filling model, look for overlap between the (OH) hydrogen on one acetic acid molecule and the (carbonyl) oxygen on the other. Return to a ball-and-spoke model. Click on the **Model** menu and select **Hydrogen Bonds**.






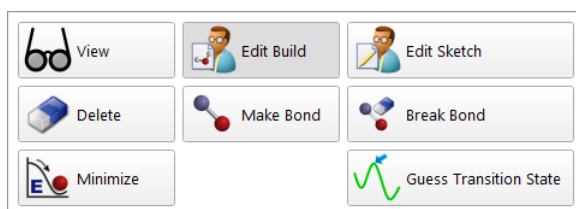
Ball-and-Spoke model for acetic acid dimer
with hydrogen bonds displayed



The two hydrogen bonds, that are responsible for holding the acetic acid molecules together, will be drawn.


4. Distances, angles, and dihedral angles can easily be measured with *Spartan* using **Measure Distance**, **Measure Angle**, and **Measure Dihedral**, respectively, from the **Geometry** menu.






- a) **Measure Distance**: This measures the distance between two atoms. *Click* once on  to move to the next molecule, *propene*. *Click* on the **Geometry** menu and select **Measure Distance** (or *click* on the  icon if it appears at the top of the screen). *Click* on a bond or on two atoms (the atoms do not need to be bonded). The distance (in Ångstroms) will be displayed at the bottom of the screen. Repeat the process for different bonds or pairs of atoms. When you are finished, select **View** from the **Build** menu (or *click* on the  icon at the top of the screen).

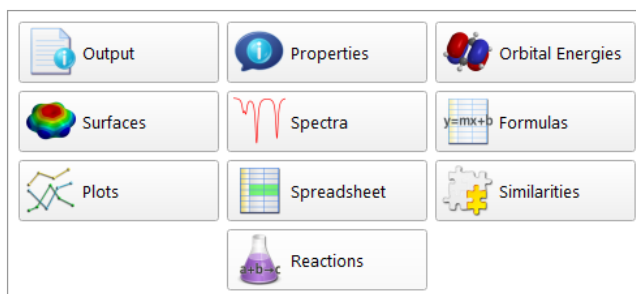




- b) **Measure Angle**: This measures the angle around a central atom. *Click* once on  to move to the next molecule, *ammonia*. *Click* on the **Geometry** menu and select **Measure Angle** (or *click* on the  icon if it appears at the top of the screen). *Click* first on H, then on N, then on another H. Alternatively, *click* on two NH bonds. The HNH angle (in degrees) will be displayed at the bottom of the screen. *Click*

on  when you are finished.

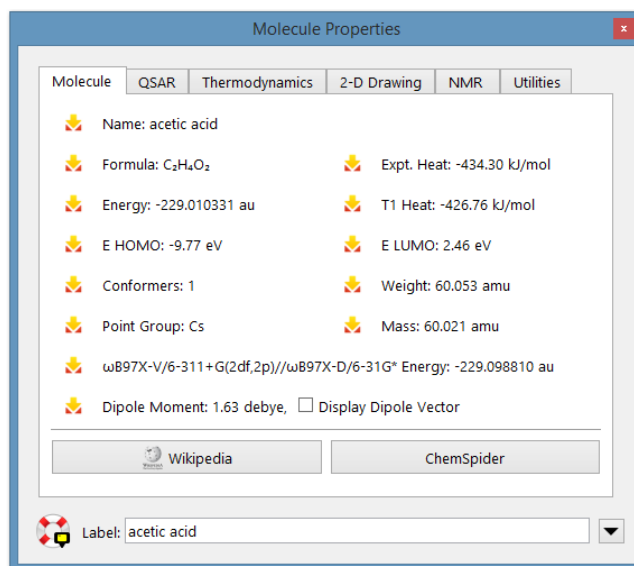
- c) **Measure Dihedral**: This measures the angle formed by two intersecting planes, one containing the first three atoms selected and the other containing the last three atoms selected. Click once on  to move to the next molecule, **hydrogen peroxide**. Click on the **Geometry** menu and select **Measure Dihedral** (or click on the  icon if it appears at the top of the screen) and then click in turn on the four atoms (HOOH) that make up hydrogen peroxide. The HOOH dihedral angle will be displayed at the bottom of the screen. Click on  when you are finished.

5. Energies, dipole moments and atomic charges (among other calculated properties) are available from **Properties** under the **Display** menu.



- a) **Energy**: Click once on  to move to the next molecule, **acetic acid**. Click on the **Display** menu and select **Properties** (or click on  icon if it appears at the top of the screen). The **Molecule Properties** dialog appears. It is divided into six parts designated by tabs. **Molecule** provides the energy and other information relating to the isolated molecule, **QSAR** provides quantities that may be used as QSAR descriptors, and **Thermodynamics** provides the entropy, enthalpy, Gibbs energy, zero-point energy and heat capacity. **2D Drawing** provides a 2D sketch of the molecule, **NMR** relates calculated and experimental NMR chemical shifts and **Utilities** introduces standard atom labels, resets model and atom colors as well as conformational degrees of

freedom to standard values, fixes bond typing, changes absolute configuration adds missing hydrogens and adjusts X-H bond lengths. Note that the last three of these require that calculations need to be repeated. Make certain that the **Molecule** tab is selected.



This provides the energy* for acetic acid in atomic units (**Energy** in au).

- b) **Dipole Moment:** The magnitude of the dipole moment (**Dipole Moment** in Debye) is also provided in the **Molecule Properties** dialog. A large dipole moment indicates large separation of charge. You can attach the dipole moment vector, $\text{+} \rightarrow$ where the + side refers to the positive end of the dipole, to the model on the screen, by *checking* the box to the left of **Display Dipole Vector** to the right of **Dipole Moment**.

The vector will not be displayed if the dipole moment is zero. The dipole moment will not be reported if the molecule is charged because in this case it depends on the location and orientation of the molecule in space.

* The calculated energy depends on a number of factors including computational model, basis set (where applicable) and environment. For a discussion, see **Activities** menu Topics: *Total Energies and Thermodynamic and Kinetic Data*.

- c) **Atomic Charges:** To display the charge on an atom, *click* on it with the **Properties** dialog displayed. **Atom Properties** replaces the currently displayed **Properties** dialog.



The screenshot shows the 'Atom Properties' dialog box for a Carbon atom. The left panel contains basic information: Name: Carbon, Symbol: C, Atomic Number: 6, Mass Number: 12 (selected from a dropdown), Chirality: <none>, and a 'Freeze' checkbox. The right panel displays calculated charges: Electrostatic: -0.706, Mulliken: -0.582, Natural: -0.805, and Chem. Shift: 18.8. Below these are 'Expt. Chem. Shift: Label? +', 'Exposed Area: 19.532 Å²', and a dropdown for 'Experimental Data From: methane'. At the bottom, there is an 'Edit: (Current Molecule)' section with 'Expt. Chem. Shift:' and an 'Edit' button, and a 'Label: C2' field with a dropdown arrow.

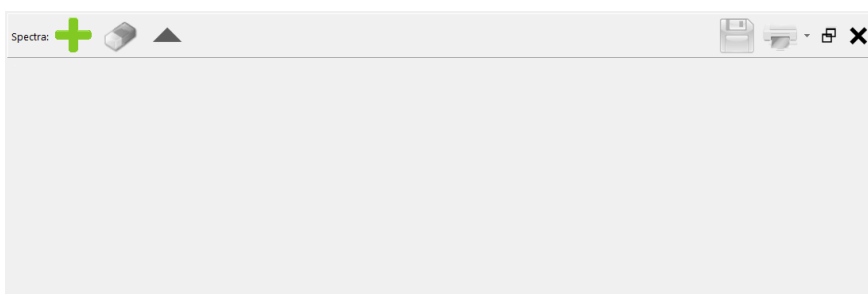
Three different atomic charges, **Electrostatic**, **Mulliken** and **Natural**, are given in units of electrons. A positive charge indicates a deficiency of electrons on an atom and a negative charge, an excess of electrons. Repeat for other atoms. Confirm that the positively-charged atom(s) lie at the positive end of the dipole moment vector. When you are finished, close the dialog by *clicking* on at the top.



The three sets of atomic charges for acetic acid are different, sometimes markedly so. Note that the charge on an atom in a molecule cannot be uniquely defined, let alone measured. While the nuclear charge is equal to the atomic number, it is not possible to say how many electrons “belong” to a particular nucleus. The different calculated charges correspond to different ways of counting the number of electrons associated with an atom.

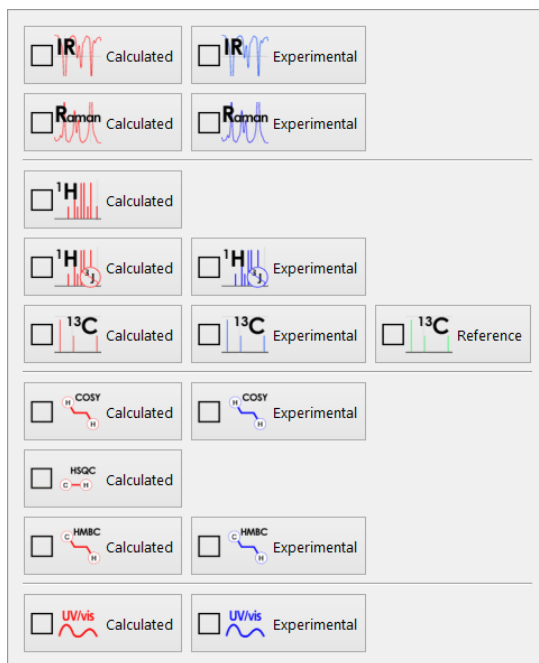
- d) **Infrared Spectra:** Molecules vibrate (stretch, bend, twist) even if they are cooled to absolute zero. This is the basis of infrared (and Raman) spectroscopy, where absorption of

energy occurs when the frequency of a particular molecular motion matches the frequency of the light. Infrared spectroscopy is important for identifying molecules as different functional groups vibrate at noticeably different and characteristic frequencies.

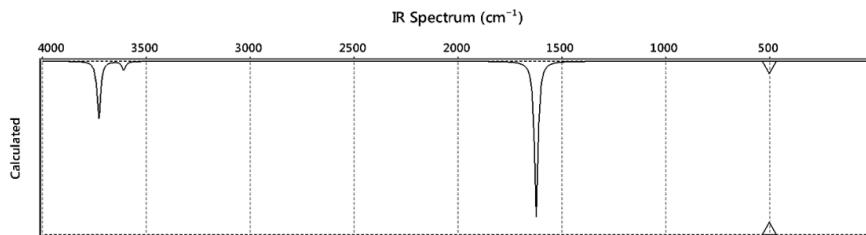
Click once on  to move to the next molecule in the document, *water*. To animate a vibration, select **Spectra** from the **Display** menu (or click on  if it appears at the top of the screen). This leads to an empty spectra pane at the bottom of the screen.



Click on  at the top left of the pane and select  from the available spectra.







The calculated IR spectrum of water from 4000 - 500 cm^{-1} appears in the pane.

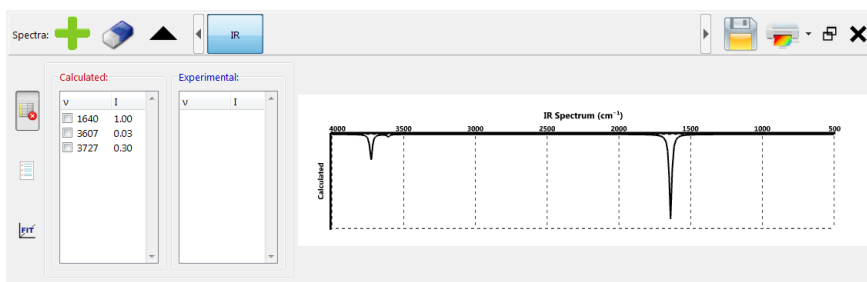




An upward and downward triangle server as a probe indicator, allowing for further inspection of the plot.

There are three lines, one of moderate intensity around 3728 cm^{-1} , one very weak around 3608 cm^{-1} and one very strong around 1623 cm^{-1} . In turn, *click* on each of these peaks. In response, the molecular model will vibrate. The line of moderate intensity corresponds to an asymmetric OH stretching motion, the very weak line corresponds to a symmetric OH stretching motion and the strong line corresponds to the HOH bend.

To translate the plot inside the pane, position the cursor over the spectrum and move the mouse left or right while holding down the right button. To expand or contract the scale of the IR plot from its default range, position the cursor over the spectrum and use the scroll wheel on your mouse (or alternatively move the mouse while holding down both the right button and **Shift** key). To reset the spectra plot to the original values, *click* on  in the bar at the top of the spectra pane. To increase (or decrease) the size of the plot, you first need to undock it by *clicking* on () at the upper right. You can then size it as you would any other window. To redock the plot, *click* again on ().





To see a complete listing of frequencies and intensities, *click* on  (**Tables**) at the left of the spectra pane.

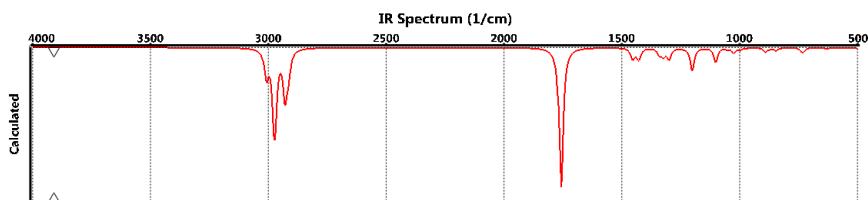


Click on each entry in the table to highlight the frequency in the spectrum and animate the vibration. Click on  to dismiss the table and click on  to remove the spectrum.



Changing the size of the spectrum dialog as well as translating and altering the visible scale are quite simple with touch screen operations. To resize the spectrum, position one finger inside the menu bar at the top of the spectra pane and move up or down. To translate the scale, move two fingers over the spectrum. To alter the scale, pinch two fingers over the spectrum.



Click once on  to move to **cyclohexanone**, the next molecule in the list. The spectra pane is still on screen but should be empty. (If it is not on screen, select **Spectra** from the **Display** menu or click on  if it appears at the top of the screen to restore.) Click on  in the bar at the top of the spectra pane and select  **Calculated**. The calculated infrared spectrum of cyclohexanone appears.

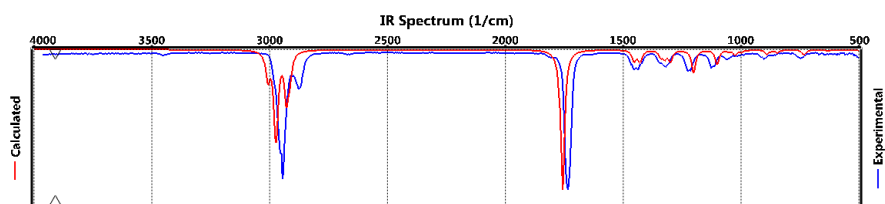


The calculations actually provide a list of frequencies and an associated list of intensities (some of which may be zero or very close to zero). The spectrum that is displayed uses these data but has been broadened (to account for finite temperature) and scaled (to account for the fact that the underlying energy function is assumed to be quadratic as well

as for limitations of different models). The same broadening parameter (temperature) is applied to all molecules and all levels of calculation. The same scaling parameter is used for all molecules but it depends on the theoretical model.

The largest peak appears at 1759 cm^{-1} and corresponds to a CO stretch. The fact that the line is both intense and isolated from other features in the spectrum makes it a very useful indicator of carbonyl functionality. *Click* on this peak and examine the “vibrating” model for cyclohexanone on screen above the spectrum.




Click again on  and this time select . The experimental IR spectrum (from the freely available NIST database) is superimposed on top of the calculated spectrum.

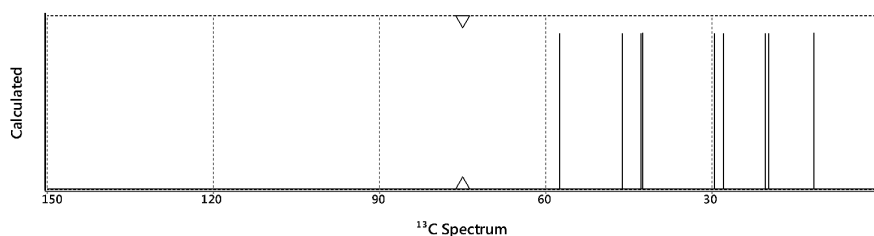


Note that the two spectra are similar but not perfectly matched.

When you are done, select  from the bar at the top of the spectra pane.

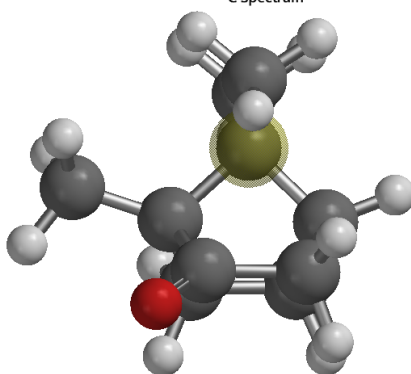
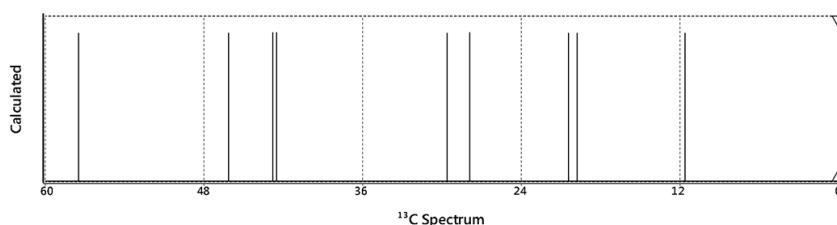
- e) **NMR Spectra:** Along with mass spectrometry, NMR spectroscopy is the most powerful tool available with which to assign molecular structure. Many (but not all) nuclei exhibit NMR spectra, but proton and ^{13}C are by far the most important.



Click once on  to move to the next molecule in the document, *camphor*. With the spectra pane on screen, *click* on  in the bar at the top of the spectra pane and select . The calculated ^{13}C NMR spectrum appears.

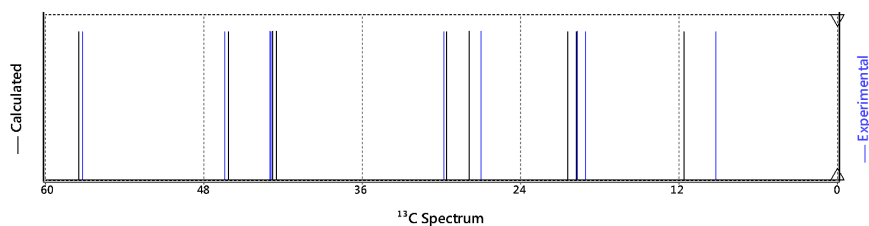


This comprises nine lines, in the range of 150 to 0 ppm (there is a tenth line corresponding to the carbonyl carbon at 216 ppm). You can zoom out to see this line by using the scroll wheel on your mouse. More instructive is to zoom in on the range from 60 to 0 ppm to get a better look at the other lines.


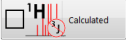
Click on one of the probe triangles to select the probe and move the mouse while holding down the left button over the spectrum. When you come to a line, the chemical shift will appear at the top of the spectrum and the atom (or atoms) responsible for this line will be highlighted on the model displayed above the spectrum.

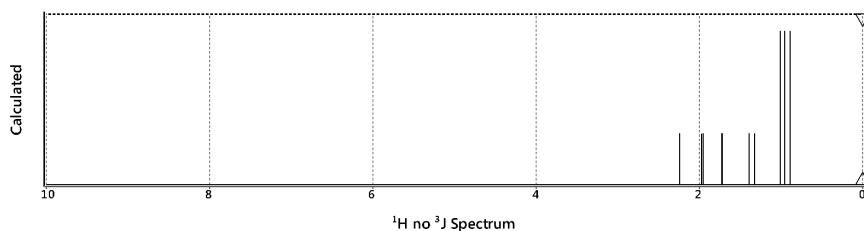


Again, *click* on  in the bar at the top of the spectra pane and select . The experimental ^{13}C spectrum obtained from the freely available nmrshiftdb database will be superimposed on top of the calculated spectrum.





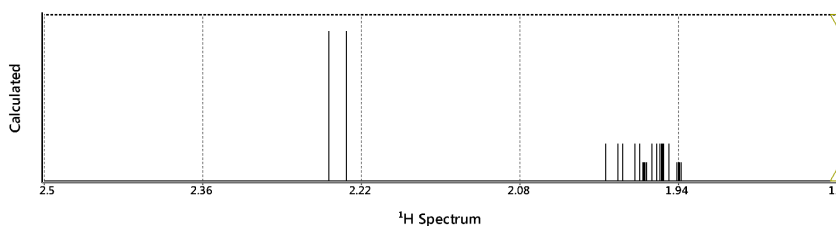
You will see that the overall agreement between calculated and experimental ^{13}C spectra is quite good. As with infrared spectra (see preceding discussion of cyclohexanone), the data resulting from the quantum chemical calculations has been empirically corrected.

Click again on  and select . An “idealized” proton spectrum where three-bond HH coupling constants are set to zero appears.




Spectra manipulations are as before and the hydrogens responsible for selected lines are highlighted in the model. No experimental spectrum is available, but the quality of the match would be expected to be similar to that previously observed with comparison of ^{13}C spectra.




Click again on  and select  from the palette. The spectrum that appears is more complicated and much closer to what would be observed experimentally. In this example, HH coupling constants have not been calculated from quantum mechanics, but they have been estimated based on local environment.

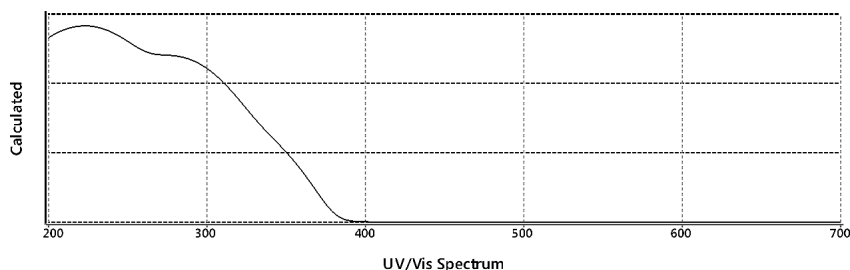




Zoom in on specific lines (scroll wheel) to see the detailed splitting patterns. For example, the two protons at C₃ are both split by the proton at C₄. The doublet at 2.25 ppm shows a much larger splitting than the doublet at 2.0 ppm (you need to zoom in considerably to see that this is a doublet). This reflects the fact that the proton responsible for the line at 2.25 ppm makes a dihedral angle of 43° with the proton at C₄, whereas the proton responsible for the line at 2.0 ppm makes a dihedral angle of 80°.

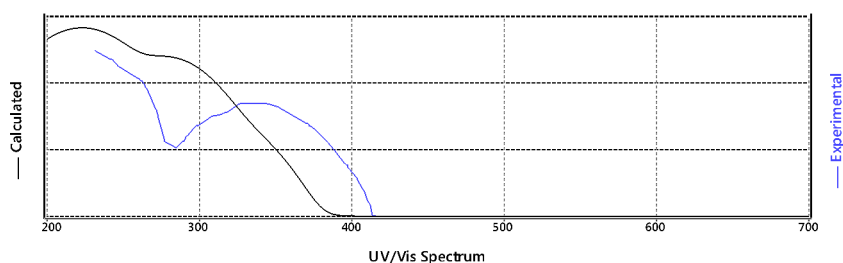
Finally, note that you can switch among the three calculated NMR spectra (as well as the experimental ¹³C spectrum) for camphor by *clicking* on the associated button in the bar above the spectra pane. When you are done, remove all three spectra. Click on  three times in succession to remove the spectra.




- f) **UV/visible Spectra:** Absorption of light in the visible or ultraviolet range of the electromagnetic spectrum leads to electronic excitation from the ground-state to excited-states and (in the case of absorption in the visible), is responsible for a molecule's color. UV/visible spectroscopy not only offers a “fingerprint” but is also an important screen to identify molecules that may be damaged by exposure to light.

Click once on  to move to the next molecule, **3-aminobenzophenone**. The spectra pane should still be on screen. Click on  and select . No empirical corrections have been applied to the calculated spectrum that appears.





Click again on  and select . The experimental UV/visible spectrum from the freely available NIST database will be drawn on top of the calculated spectrum.

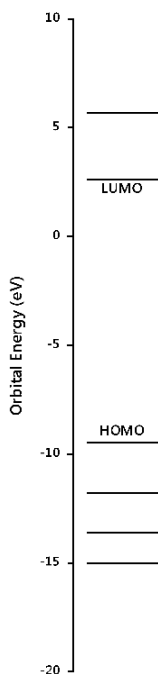


The two spectra are visually similar at least qualitatively. However, calculated and experimental UV/visible spectra are likely to be sufficiently different that the theory will not often be able to account for the “color” of the molecule. Where the theory is likely to be more successful is in anticipating changes in color resulting from subtle changes in structure. Click on  when you are done. Also, remove the spectra pane either by clicking on  at the top right or by selecting **Spectra** from the **Display** menu or by clicking on  if it appears at the top of the screen.


6. *Spartan* permits display, manipulation and query of a number of important graphical quantities resulting from quantum chemical calculations. Most important are the **electron density** or simply **density** as it is commonly referred to (that reveals how much space a molecule actually takes up), the **bond density** (that reveals chemical bonds), and key **molecular orbitals** (that provide insight into both bonding and chemical reactivity). In addition, the **electrostatic potential map**, an overlay of the electrostatic

potential (the attraction or repulsion of a positive charge for a molecule) on the electron density, is valuable for describing overall molecular charge distribution as well as anticipating sites of electrophilic addition. Another indicator of electrophilic addition is provided by the **local ionization potential map**, an overlay of the energy of electron removal (ionization) on the electron density. Finally, an indicator of nucleophilic addition is provided by the **|LUMO| map**, an overlay of the absolute value of the lowest-unoccupied molecular orbital (the LUMO) on the electron density.

Click once on  to move to the next molecule in the list, **ethylene**. Click on the **Display** menu and select **Orbital Energies** (or click  if it appears at the top of the screen). An orbital energy diagram for ethylene will appear at the left of the screen. This provides the energies of all six occupied valence molecular orbitals and two unoccupied molecular orbitals.





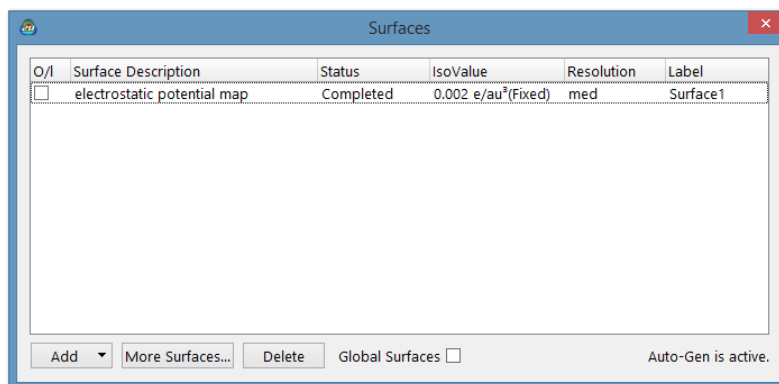
Click on the energy level in the diagram labeled **HOMO**. In a second, the familiar π bond in ethylene will appear. Note that the graphic has “blue and red” regions. These correspond to

positive and negative values of the orbital (the absolute sign is arbitrary). Examine the other occupied orbitals (by *clicking* on their respective energy levels in the diagram) as well as the lowest-unoccupied molecular orbital (the **LUMO**). Note that you can move from one level to the next by moving the mouse up or down while holding down and then releasing the left button. You can also use the up and down arrow keys on your keyboard. *Click* on  when you are done.




“Swipe” one finger up or down over the orbital energy diagram to move to the next higher or lower energy level.

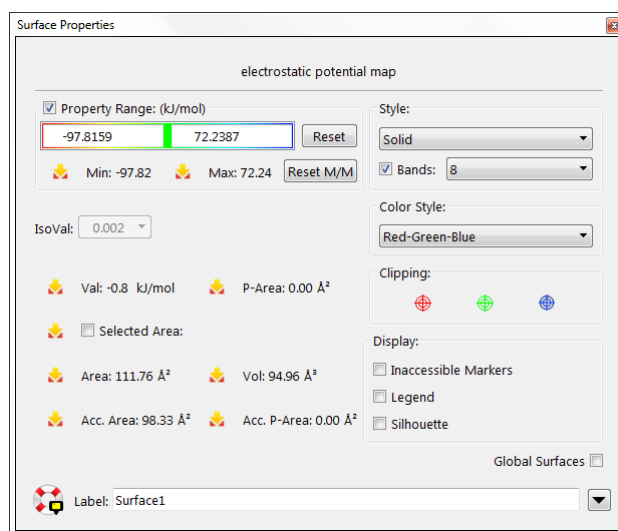
Click once on  to move to the next molecule in the list, **benzene**. *Click* on the **Display** menu and select **Surfaces** from the palette (or *click* on  if it appears at the top of the screen). The **Surfaces** dialog appears.





Select **electrostatic potential map** inside the **Surfaces** dialog (*check* the box to the left of the name). An electrostatic potential map for benzene will appear.* *Click* on the map. The **Style** menu will appear at the bottom right of the screen. Select **Transparent** from this menu. This makes the map transparent and allows you to see the molecular skeleton underneath. Go back to a **Solid** display (**Style** menu) in order to clearly see color differences. The default color scheme follows a rainbow,

* Discrete displays are the default. You can change the default to continuous displays by turning off the **Bands** checkbox in the **Molecule** tab of the **Preferences** dialog (**Preferences...** under the **Options** menu; **Chapter 25**).

red → orange → yellow → green → blue, where by convention red indicates a negative potential (the benzene π system) or attraction to a positive charge while blue indicates a positive potential (the σ system) or repulsion by a positive charge. An alternative scheme with only three colors (red, white and blue) may be selected. *Click* on the **Display** menu and select **Properties** (or *click* on  if it appears at the top of the screen) and *click* on the surface.

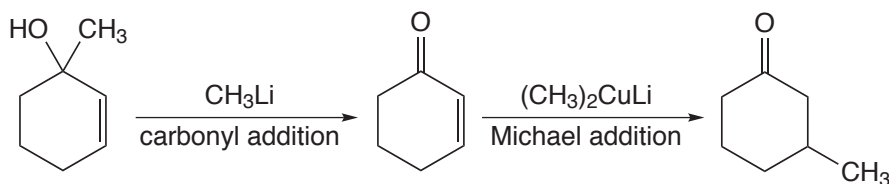



Click once on  to move to the next molecule in the list, *aniline*, and select **local ionization potential map** inside the **Surfaces** dialog. By convention, red regions on a local ionization potential map indicate areas from which electron removal (ionization) is relatively easy, meaning that they are subject to electrophilic attack. These are easily distinguished from regions where ionization is relatively difficult (by convention, colored blue). Note that the *ortho* and *para* ring carbons are more red than the *meta* carbons, consistent with the known directing ability of the amino substituent.

Click once on  to move to the last molecule in the list, *cyclohexenone*, and check **LUMO** inside the **Surfaces** dialog. The resulting graphic portrays the lowest-energy empty molecular orbital (the LUMO) of cyclohexenone. This orbital

is delocalized onto several atoms and it is difficult to tell where exactly a pair of electrons (a nucleophile) will attack the molecule.

A clearer portrayal is provided by a LUMO map that displays the (absolute) value of the LUMO on the electron density surface. By convention, the color blue is used to represent maximum value of the LUMO and the color red, minimum value. First, remove the LUMO from your structure (*uncheck **LUMO*** in the **Surfaces** dialog) and then turn on the LUMO map (*check **|LUMO|map*** in the dialog). Note that there are two blue regions, one directly over the carbonyl carbon and the other over the β carbon. This is entirely consistent with known chemistry. Enones may either undergo carbonyl addition or conjugate (Michael) addition.



7. When you are finished, close the document by selecting **Close** from the **File** menu or alternatively by *clicking* on the  icon if it appears at the top of the screen.