Spartan Instructions

To estimate the IR frequencies of a molecule

The general operating features of Spartan'04 for Windows.

Starting and Quitting Spartan'04

To start, *click* on the **Start** button, then *click* on **Programs**, and finally *click* on **Spartan'04**. To quit, select **Exit** from the **File** menu.

Pull-Down Menus

Program functions may be accessed using pull-down menus under the headings in the menu bar, e.g., the **Setup** menu.

Toolbars

Toolbars provide convenient access to selected functions under the **File**, **Build**, **Geometry** and **Search** menus.

- New
- Open
- Close
- Save As
- View
- Add Fragment
- Delete
- Make Bond
- Break Bond
- Minimize
- Measure Distance
- Measure Angle
- Measure Dihedral
- Freeze Center
- Set Torsions
- Constrain Distance
- Constrain Angle
- Constrain Dihedral
- Define Point
- Define Plane
- Align Molecules
- CSD
- Transition States
- Tautomers

Using the Mouse

The following functions are associated with the two-button mouse.

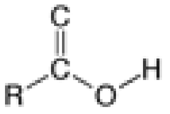
	left button	**right button**
–	picking, X/Y rotate, exchange[a]	X/Y translate
Shift	range picking, Z rotate	scaling[b]
Ctrl	global X/Y rotate[c]	global X/Y translate
Ctrl + Shift	multiple picking, global Z rotate[c]	scaling[b]
Ctrl (build mode)	fragment X/Y rotate, chirality invert[a]	fragment X/Y translate
Ctrl + Shift (build mode)	fragment Z rotate	scaling[b]
Alt	group picking, bond rotation	bond stretching

a	Requires *double clicking*.
b	Scaling is always applied to all open molecules and fragments.
c	Global rotations can be either molecule or screen centered. This is controlled by **Global Rotate** in the **Miscellaneous Preferences** dialog (**Preferences...** under **Options** menu).

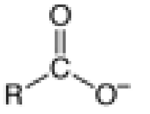
Construction of Molecules and Calculation of IR Spectrum

This section describes the construction of organic molecules from atomic fragments, functional groups and rings. How to carry out quantum chemical calculations and how to calculate and draw infrared spectra wull be addressed later.

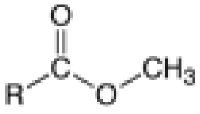
The simplest building blocks incorporated into Spartan'04's entry model kit are "atomic fragments". These constitute specification of atom type, e.g., carbon, and local environment, e.g., tetrahedral. However, much of organic chemistry is organized around functional groups, collections of atoms the structure and properties of which are roughly the same in every molecule. The entry model kit also incorporates a small library of functional groups which can easily be extended or modified. For example, the carboxylic acid group may be modified to build a carboxylate anion (by deleting a free valence from oxygen), or an ester (by adding tetrahedral carbon to the free valence at oxygen).



carboxylic acid

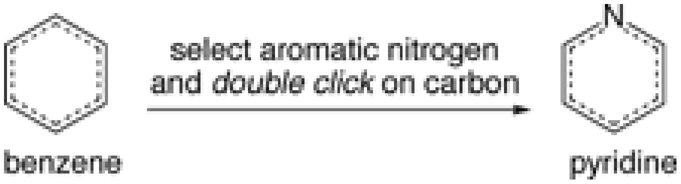


carboxylate anion



ester

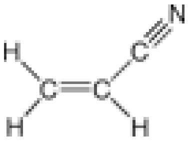
Polyatomic rings are also common components in organic molecules, and the entry model kit incorporates a library of commonly-encountered hydrocarbon rings, which can easily be modified by atom replacement. For example, pyridine can be built starting from benzene by selecting aromatic nitrogen from the list of atomic fragments, and then double clicking on one of the carbons.



Functional groups may also be modified in this manner.

Following example illustrates the construction of some molecules and the setup that would lead to the calculation of the IR spectrum of the energy minimized molecule using HF/321-3G(*) basis functions.

Acetonitrile

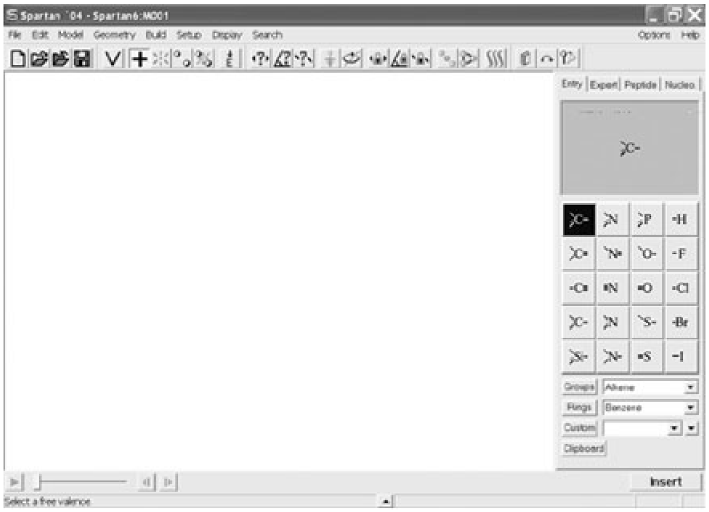


With the program open,

1.Click with the left mouse button on **File** from the menu bar.

Then *click* on **New** from the menu which appears (or *click* on the 🗋icon in the **File** toolbar)..

The "entry" model kit appears



Among other things, it contains a library of atomic fragments. *Click* on trigonal planar sp^2 hybridized carbon from the fragment library. The atom icon is shown in reverse video to indicate that it is "active". In addition, a model of the fragment appears at the top of the model kit. Bring the cursor anywhere on screen and click. Rotate the carbon fragment (drag the mouse while holding down the left button) so that you can clearly see both the double free valence ("=") and the two single free valences ("-").

Spartan'04's model kits connect atomic fragments (as well as groups, rings and ligands) through free valences. Any remaining free valences will automatically be converted to hydrogen atoms

2. sp^2 carbon is still selected. *Click* on the double free valence. The two fragments are connected by a double bond, leaving you with ethylene. If you make a mistake and *click* instead on the single free valence, select **Undo** from the **Edit** menu. You can also start over by selecting **Clear** from the **Edit** menu.

Spartan'04's entry model kit allows only the same type of free valences to be connected, e.g., single to single, double to double, etc.

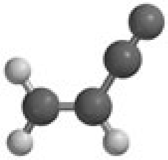
3. *Click* on **Groups** in the model kit, and then select **Cyano** from among the functional groups available from the menu

Click on any of the four single free valences on ethylene (they are all the same). This bonds the cyano group to ethylene, leaving you with acrylonitrile

4. Select **Minimize** from the **Build** menu (or *click* on the icon in the **Build** toolbar).

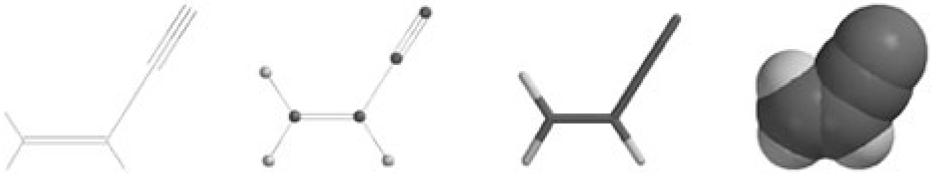
The final molecular mechanics strain energy (8.65 kcal/mol) and symmetry point group (Cs) are provided at the bottom right of the screen.

5. Select **View** from the **Build** menu (or *click* on the V icon in the **Build** toolbar). The model kit disappears, leaving only a ball-and-spoke model of acrylonitrile on screen.



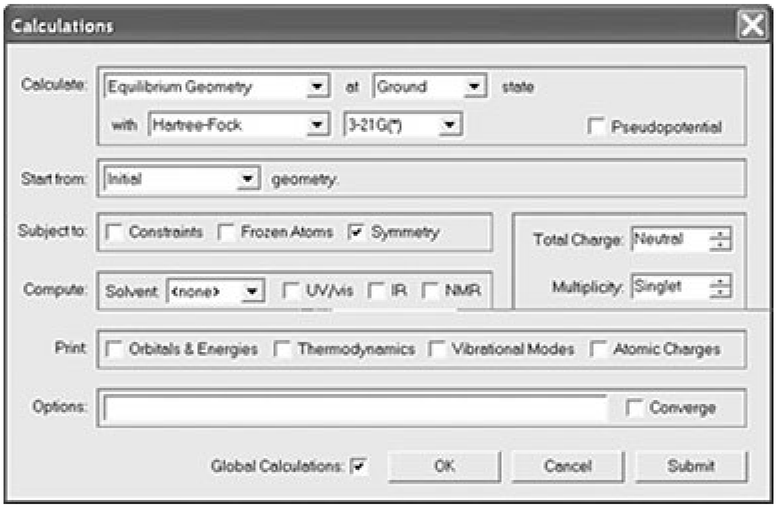
This model can be manipulated (rotated, translated and zoomed) by using the mouse (if necessary, in conjunction with keyboard functions). To rotate the model, *drag* the mouse while holding down the left button; to rotate in the plane of the screen also hold down the **Shift** key. To translate the model, drag the mouse with the right button depressed. To zoom the model (translation perpendicular to the screen), hold down the **Shift** key in addition to the right button while *dragging* the mouse.

6. One after the other, select **Wire**, then **Ball and Wire**, then **Tube** and finally **Space Filling** from the **Model** menu.



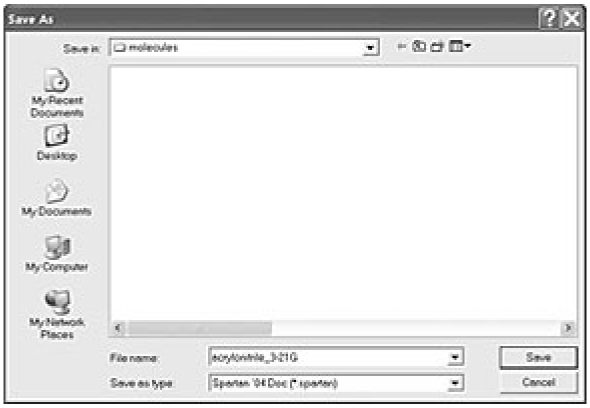
7. Select **Calculations...** from the **Setup** menu.

Perform the following operations in the **Calculations** dialog which appears



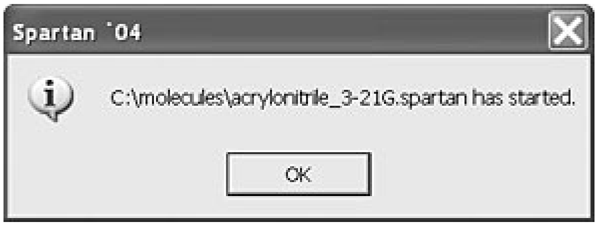
Calculate: Equilibrium Geometry at Ground state
with Hartree-Fock 3-21G(*) ☐ Pseudopotential
Start from: Initial geometry.
Subject to: ☐ Constraints ☐ Frozen Atoms ☑ Symmetry
Total Charge: Neutral
Multiplicity: Singlet
Compute: Solvent <none> ☐ UV/vis ☐ IR ☐ NMR
Print: ☐ Orbitals & Energies ☐ Thermodynamics ☐ Vibrational Modes ☐ Atomic Charges
Options: ☐ Converge
Global Calculations: ☑

a. Select **Equilibrium Geometry** from the top menu to the right of "Calculate". This specifies optimization of equilibrium geometry
b. Select **Hartree-Fock** and then **3-21G(*)** from the two bottom menus to the right of "Calculate". This specifies a Hartree-Fock calculation using the 3-21G split-valence basis set.
c. *Check* **IR** to the right of "Compute" in the center of the dialog. You have requested that an infrared spectrum be computed following optimization of geometry.
d. Select **Submit** from the **Setup** menu. A file browser appears. Provide the name "xxxx" and then *click* on **Save**.



Save in: molecules
File name: acrylonitrile_3-21G
Save as type: Spartan '04 Doc (*.spartan)

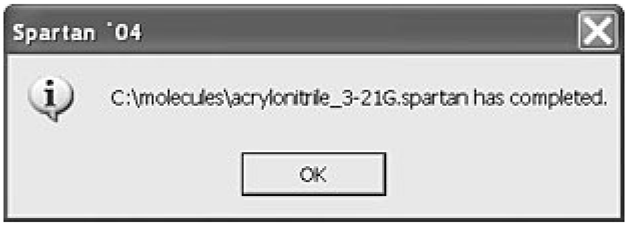
You will be notified that the calculation has been submitted.



C:\molecules\acrylonitrile_3-21G.spartan has started.

Click on **OK** to remove the message from the screen. After a molecule has been submitted, and until the calculation has completed, you are not permitted to modify any dialogs or other information associated with it.

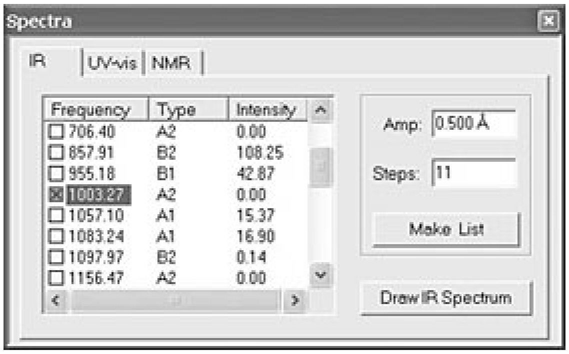
9. You will be notified when the calculation has completed.



C:\molecules\acrylonitrile_3-21G.spartan has completed.

Click on **OK** to remove the message from the screen.

10. Select **Spectra** from the **Display** menu. *Click* on the **IR** tab in the dialog which results to bring up the **IR Spectra** dialog.



Frequency	Type	Intensity
☐ 706.40	A2	0.00
☐ 857.91	B2	108.25
☐ 955.18	B1	42.87
☒ 1003.27	A2	0.00
☐ 1057.10	A1	15.37
☐ 1083.24	A1	16.90
☐ 1097.97	B2	0.14
☐ 1156.47	A2	0.00

Amp: 0.500 Å

Steps: 11

One after the other, *check* the yellow boxes to the left of the frequencies in the dialog. In response, the vibrational motions associated with the frequencies will be animated. Find the frequencies which best fits the description of vibrations, and record its value.

The frequencies should be on the order of 12% larger than the experimental frequency at this level of calculation. Calculate the corrected frequencies by multiplying the calculated frequencies by 0.9026.

Adapted from Spartan 04 Users Manual