

Introduction to IQmol: Exploring potential energy surfaces

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Description: Students learn how to build molecules and perform basic electronic structure calculations using *IQmol* and *Q-Chem* while reviewing the key concepts of potential energy surfaces (stationary points, minima, saddle points) and their relation to stable molecular structures and transition states.

Suggested level: Beginning graduate.

Learning objectives: Learn how to build and manipulate molecules; understand concepts of stable molecular structures, transition states, and reaction coordinates; learn basic standards of reporting electronic structure calculations.

I. WHAT MAKES A STABLE MOLECULAR STRUCTURE?

A stable molecular structure corresponds to a minimum on a potential energy surface. At a minimum, the gradient is zero and all frequencies are non-negative. For a given combination of nuclei and electrons, there might be multiple minima; each minimum corresponds to different chemical species. Reaction coordinates connect the minima. The barriers separating different minima control how easily different species can interconvert into each other. Transition states are saddle points of order 1 (one imaginary frequency corresponding to the reaction coordinate).

A. Formaldehyde: Equilibrium structure and frequencies

Launch *IQmol* and build a formaldehyde molecule by activating the ‘Build’ mode and using chemical elements symbols to select desired atom types (see Fig. 1). Optimize this structure using the ω B97X-D/6-31G* level of theory. Verify that the computed structure is a minimum by computing vibrational frequencies at the optimized geometry. Follow these steps to set up this calculation:

1. Activate QUI window by selecting ‘Calculation→Q-Chem Setup’ from the menu.
2. Use ‘Calculate’, ‘Method’, and ‘Basis’ buttons to request ω B97X-D/6-31G* geometry optimization (‘Calculate=Geometry’, ‘Method=Omega-B97X-D’, ‘Basis=6-31G*’). Note the ‘Charge’ and ‘Multiplicity’ settings: ‘Charge=0’ (neutral molecule) and ‘Multiplicity=1’ (singlet state).
3. Use ‘+’ button to add a second job (frequency calculation at the optimized geometry using the same level of theory). Observe the generated input in the right window (see Fig. 2).
4. Use the ‘Submit’ button to submit the job to a preconfigured server.
5. Once the job is completed, *IQmol* will ask whether you want to copy the files from the server. Click yes, and create the directory with *the same name* as the submitted job.

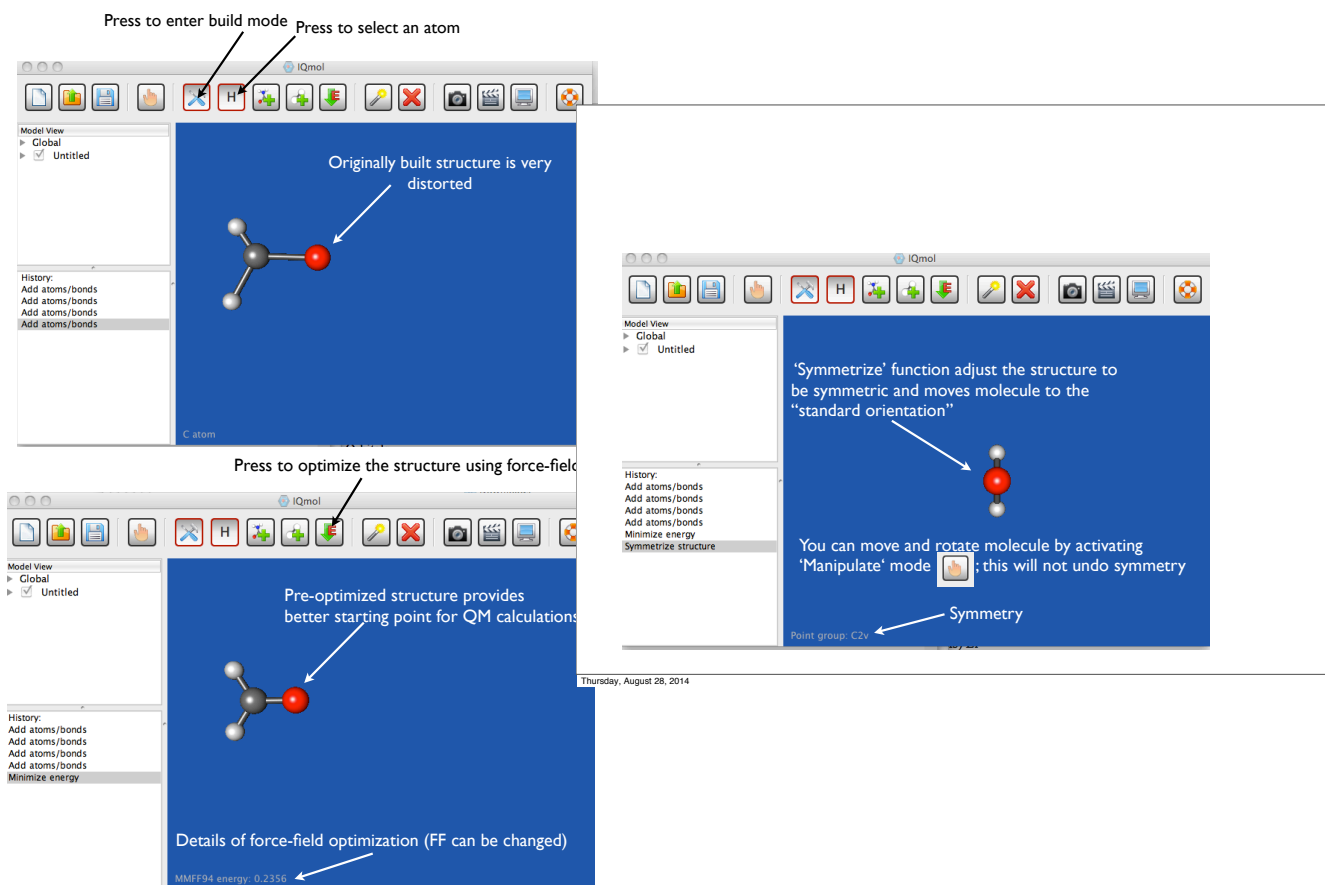


FIG. 1: To build a new molecule, activate the ‘Build’ mode, then select an atom and click in the blue area. To add the second atom, press the left mouse button on the first atom and drag to where you want the second atom to be; release the mouse. After building a structure, use the ‘Minimize Energy’ button to pre-optimize the structure using classical force fields (the choice of the force field is not very important, the default one is good for most cases). To make the structure perfectly symmetric, select ‘Build→Symmetrize Molecule’ menu. Activate the ‘Manipulate’ mode to move and rotate your molecule. If you messed up, use ‘Display→Reset View’ menu. Now your molecule is ready for quantum calculations!

6. Analyze the results. Activate the ‘Select’ mode to select atoms; when 2 atoms are selected, *IQmol* prints the distance between the atoms in the bottom left corner; selecting 3 atoms allows one to see the angle, etc.
7. Analyze the frequencies and observe normal modes (single click on the frequency gives the static picture, whereas double click shows animated motion).
8. Open the raw output by clicking on the ‘yourjobname.out’ file under ‘Files’. Find zero-point energy; take notice of computed IR intensities.

Summarize the results in your report. These are the basic requirements:

- Specify the molecular formula, charge, and multiplicity.
- Specify the level of theory (Method/Basis).

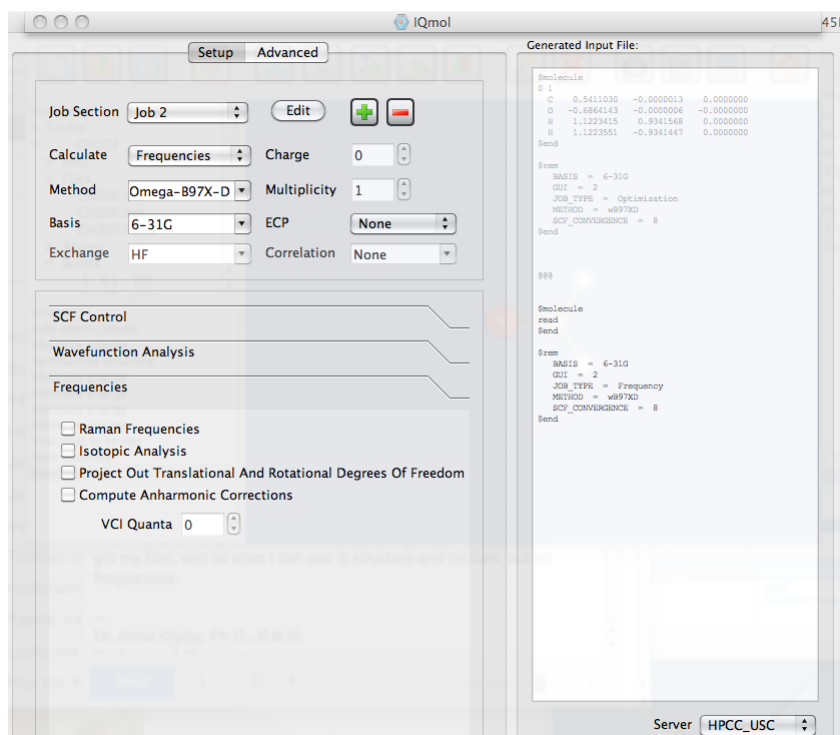


FIG. 2: Basic job setup using *IQmol*. The *Q-Chem* input is displayed on the right; it can be manually edited if desired. This input corresponds to the two consecutive calculations — optimization of the structure followed by the frequencies calculation at the optimized geometry.

- Collect important geometrical parameters of the optimized structure (symmetry-unique bond-lengths and angles) in a table. Give nuclear repulsion energy. Also, give the total energy of the optimized structure.
- Report the frequencies in a table and assign the characters of the respective normal modes.
- For structural parameters, use Angstroms and degrees; give 3-4 decimal points for bond-lengths and 2 for angles. Report total energies in hartrees; give 6 decimal points.
- When reporting energy differences, use eV or kcal/mol.

Answer the following questions:

- How many α and β electrons does your molecule have? How is it related to ‘Charge’ and ‘Multiplicity’?
- Why is it important to report nuclear repulsion energy, in addition to the total energy?
- How does the CO bond-length compare to the experimental one (in formaldehyde)? Compare the computed CO bond-length with a typical single CO bond-length (e.g., experimental CO bond in methanol). Compare the difference between single and double bond-lengths with the differences between the computed and experimental bond-lengths in formaldehyde. Can this level of theory distinguish between double and single bonds?
- Does the optimized geometry correspond to a true minimum? Explain your reasoning.

- How would you describe the highest frequency vibrational mode? What is the frequency of the CO vibration? How many out-of-plane vibrational modes does CH₂O have?

B. Isomers of formaldehyde: cis and trans hydroxycarbenes

Build the HCOH molecule (hydroxycarbene) following the same steps as above. The ‘Symmetrize’ function should give the C_s structure. Optimize the structure and compute frequencies using the same level of theory as above. Summarize the results and answer the following questions.

- How does the CO bond-length in HCOH compare with the CO bond length in formaldehyde? Is it consistent with the bonding pattern?
- Does the optimized structure correspond to a minimum?
- HCOH is an isomer of formaldehyde (there are two isomers, cis and trans). Which one did your optimization find and what is the energy difference between formaldehyde and this HCOH isomer?

To find another isomer, distort the structure accordingly (e.g., if you found the trans isomer, rotate the CH bond into a cis configuration and rerun the optimization). Use ‘Select’ mode to select a hydrogen. Once the atom is selected, use ‘Cntrl’+‘Right mouse button’ (two fingers on Mac track pad, if your Mac has proper settings) combination to drag the selected atom to a desired position. Repeat optimization and frequency calculations. Compare energy differences between the two hydroxycarbene isomers. Which one is the lowest energy isomer?

C. Finding a transition state

Starting from the trans-HCOH structure, locate a transition state (use ‘Calculation = Transition state’), followed by the frequency calculation. Answer the following:

1. How many imaginary frequencies does the optimized structure have? Is it a transition state or an intermediate?
2. Describe the structure of the transition state.
3. What does a vector of molecular displacements for imaginary frequency tell us?
4. Based on the structure and imaginary frequency mode, what product does this transition state lead to?
5. What is the barrier height for that reaction?

Tips for future:

- Transition state optimization converges better if the calculation is preceded by the frequency calculation of the initial structure and the TS job has additional keyword ‘GEOM.OPT.HESSIAN=READ’ (this uses computed Hessians to guide TS search algorithm). To activate this keyword in the second job, go to ‘Advanced→Geometry Optimization’ and select ‘Initial Hessian=Read’).

- Optimization procedure treats the symmetry of the initial structure as a constraint, e.g., if you start with the C_s structure, the optimized structure will also be C_s . If you would like to remove this constraint, start with a slightly distorted structure.
- You can explore different reaction paths (and, consequently, different transition states) by using constrained optimization capabilities (consult Chapter 9 of the *Q-Chem* user manual).