



**Computational Chemistry Workshops**  
**West Ridge Research Building-UAF Campus**  
**9:00am-4:00pm, Room 009**

Electronic Structure - July 19-21, 2016

Molecular Dynamics - July 26-28, 2016

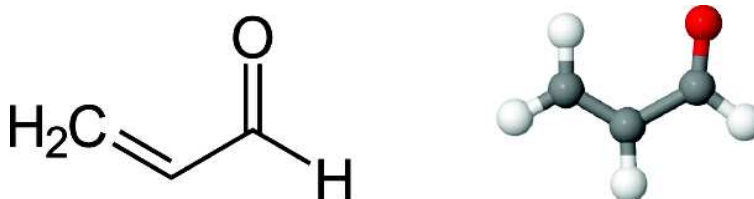


Figure 1: Propenal (Acrolein)

## Structure, Vibrational and Electronic Spectra of Acrolein

## Exercises

### 1. Geometry Optimization of Acrolein

An example **Gaussian** input file for optimizing the acrolein using coordinates is given below:

```
%chk=acrolein_opt
# HF/6-31g* opt ginput gfprint pop=full
```

Acrolein Ground state optimization

```
O 1
O   -1.242755   -1.344192   0.000000
C    0.000000    0.741186   0.000000
C    1.219202    1.332734   0.000000
C   -0.110617   -0.794819   0.000000
H   -0.885875    1.341286   0.000000
H    0.775207   -1.395005   0.000000
H    1.296116    2.400016   0.000000
H    2.105077    0.732634   0.000000
```

- Optimize the molecular structure with the **Gaussian** program using Wave Function Theory: HF/6-31g\* and Density Functional Theory: B3LYP/6-31g\*.
- Check the optimization convergence with appropriate visualization software, as well as directly viewing the output of the **Gaussian** log file.
- Try constructing a Z-matrix for acrolein, and then performing an optimization.

## 2. Vibrational Analysis of Acrolein

An example **Gaussian** input file for performing a frequency calculation by using the data from a restart file is given below:

```
%oldchk=acrolein_opt
%chk=acrolein_vib
# HF/6-31g* opt ginput gprint freq=raman pop=full guess=read geom=allcheck
```

Acrolein Vibrational Analysis at the Optimized Geometry

0 1

- a) Perform a frequency analysis with the **Gaussian** program using Wave Function Theory: HF/6-31g\* and Density Functional Theory: B3LYP/6-31g\*.
- b) Verify that the optimization reached a minimum on the potential energy surface by performing a vibrational analysis at the optimized geometry.  
All calculated frequencies must be positive at the optimized geometry. A single negative (imaginary) frequency defines a transition state. More than one negative frequency represents a higher-order saddle point, usually without physical meaning.

## 3. Analysis of the IR Spectrum

- a) Visualize the vibrational normal modes with appropriate visualization software applications.
- b) Assign the character of the normal modes (e.g. stretching, in-plane bending, out-of-plane bending, other deformations).
- c) Look for IR intensity and Raman activity in the **Gaussian** log file.
- d) Try to assign the vibrational bands in the experimental IR spectrum.

## 4. Analysis of Molecular Orbitals (MOs)

- a) Visualize the MOs with appropriate visualization software applications.
- b) Sketch a qualitative MO diagram for the four highest occupied and five lowest unoccupied MOs. Both visualized MOs and energy levels should be included. Characterize the MOs by  $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$ , and n, i.e. bonding, antibonding, and non-bonding.

## 5. UV Spectrum of Acrolein

Example **Gaussian** input files for performing a UV (vertical excitation) spectrum using the data from a restart file is given below:

### Wave Function Theory

```
%oldchk=acrolein_opt
%chk=acrolein_cis.chk
# CIS(nstates=6)/6-31g(d) 5d gfinput gfprint pop=full guess=read geom=allcheck
```

Acrolein: UV spectrum at the optimized geometry

0 1

### Time Dependent Density Functional Theory (TDDFT)

```
%oldchk=acrolein_opt
%chk=acrolein_tddft.chk
# b3lyp/6-31G(d) td(nstates=6) 5d gfinput gfprint pop=full guess=read geom=allcheck
```

Acrolein: UV spectrum at the optimized geometry

0 1

- Calculate the UV (vertical excitation) spectrum of acrolein using configuration interaction with single excitations using both Wave Function Theory: HF/6-31g\* and Density Functional Theory: B3LYP/6-31g\*.
- Characterize the excitations ( $\pi \rightarrow \pi^*, \dots$ ) for the first few excited states.
- Compare the results of the CIS (wave function theory) and TDDHF (Density Functional Theory) calculations.
- Compare the calculated excitation energies with the experimental UV spectrum using appropriate visualization software.

## 6. Influence of Solvent on Spectra

All of the previous calculations on acrolein have been in the gas phase. However, many molecules are also found in solvents. The interaction between the solvent and the solute impacts the chemical properties of the molecule being studied. The interaction can alter energy, stability, and molecular orientation, and properties relating to energy, i.e. vibrational frequency, electronic spectrum, etc. will also change.

There is a way to model the chemistry of molecules in a solvent-like state which is accomplished using *implicit* solvation models. These models differ from the *explicit* models which attempt to deal with the solvent as individual molecules. In the implicit solvation model, the solvent is treated as a continuous medium that acts upon the solute.

This leads to a significant reduction in complexity as a uniform continuum, rather than having to calculate multiple molecular interactions between the solute molecule and several surrounding solvent molecules.

Examples of input which perform a calculation using implicit polar and non-polar solvents are given below:

### Polar Solvent

```
%oldchk=acrolein_opt
%chk=acrolein_tddft_water
# B3LYP/6-31G(d) guess=read geom=allcheck 5D td(nstates=6) SCRF=(SMD, Solvent=Water)
      ginput gprint pop=full
```

Acrolein: UV spectrum at the optimized geometry in water

0 1

### Non-polar Solvent

```
%oldchk=acrolein_opt
%chk=acrolein_tddft_pentane
# B3LYP/6-31G(d) guess=read geom=allcheck 5D td(nstates=6) SCRF=(SMD, Solvent=Pentane)
      ginput gprint pop=full
```

Acrolein: UV spectrum at the optimized geometry in pentane

0 1

- Perform calculations to obtain the UV-spectrum of acrolein in both polar and non-polar solvents.
- Plot the calculated spectra in polar and non-polar solvents, compare them, and rationalize the results.
- Plot the calculated spectra in polar and non-polar solvents with the calculated gas-phase spectra, and compare them. Look for solvent shifts, and rationalize the results.

## Experimental Spectra

Figure 2: Infrared Spectrum of Acrolein

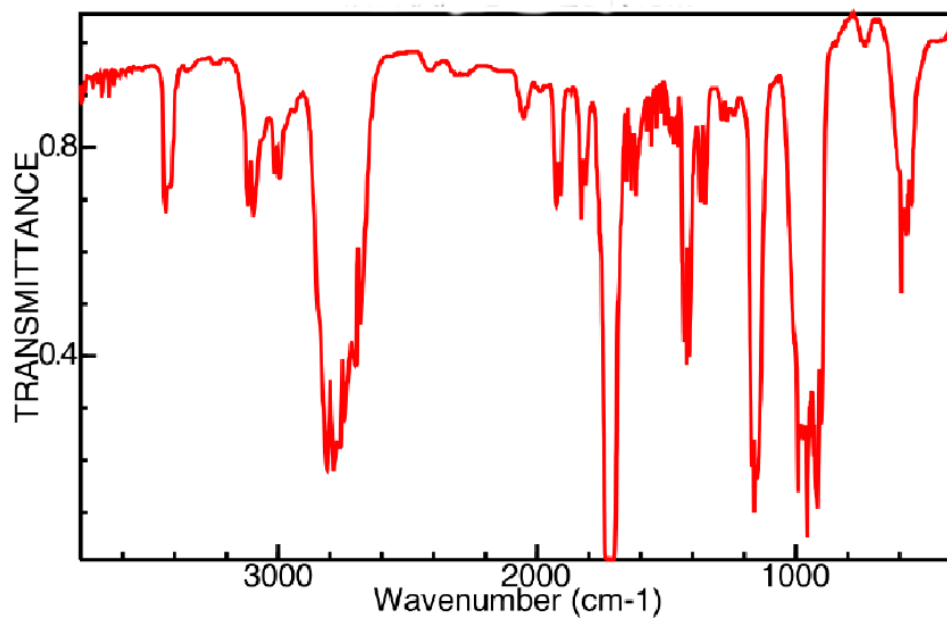
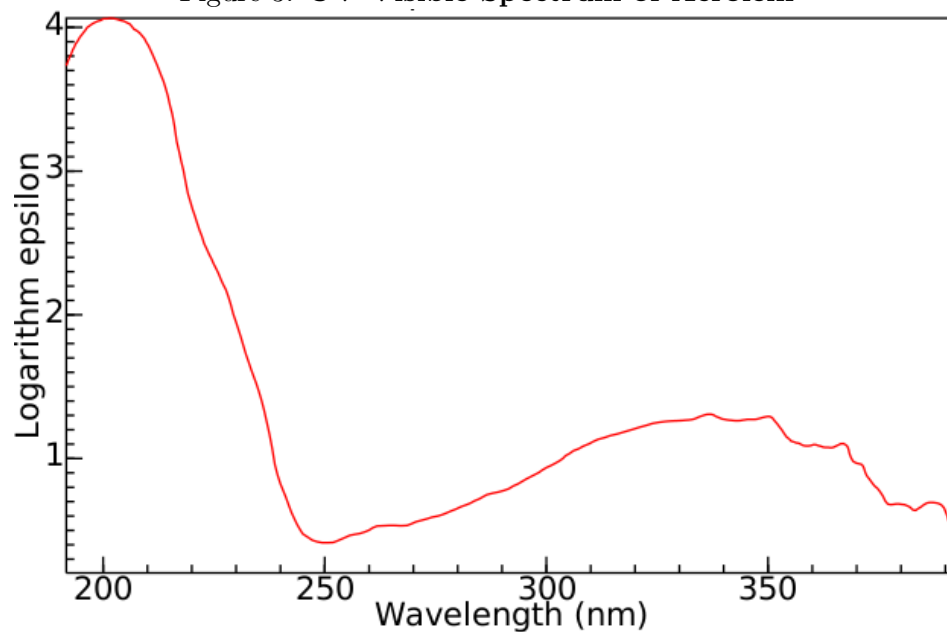


Figure 3: UV-Visible Spectrum of Acrolein



Nist Chemistry Web Book (<http://webBook.nist.gov/chemistry>)