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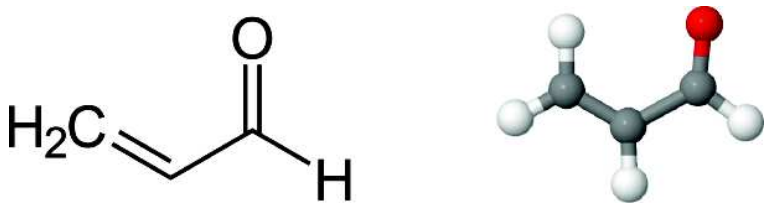
The IR and UV Spectrum of Acrolein



Structure of Propenal (Acrolein)

1. **Geometry of Acrolein**

   Construct the geometry of the acrolein molecule,

   a) by using a Z-matrix.

   b) by using the coordinates given below:

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

2. **Geometry Optimization of Acrolein**

   Optimize the molecular structure with the **Gaussian** program using the following methods:

   a) HF/cc-pVDZ

   b) B3LYP/cc-pVDZ

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

```
%chk=acrolein_opt
# HF/cc-pVDZ opt gfinput gfprint pop=full

Acrolein Ground state optimization

0 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

(ends with a blank line)
```

Check the optimization convergence with the **Molden** program, or directly view the output of the **Gaussian** log file.

3. **Vibrational Analysis of Acrolein**

Verify that the optimization reached a minimum on the potential energy surface by performing a vibrational analysis at the optimized geometry.

```
%chk=acrolein_vib
# HF/cc-pVDZ opt gfinput gfprint freq=raman pop=full guess=read geom=allcheck

Acrolein Vibrational Analysis at the Optimized Geometry

0 1

(ends with a blank line)
```

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.

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4. **Analysis of the IR Spectrum**

   a) Visualize the vibrational normal modes with either **Jmol** or the **Molden** program.

   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 using the **GaussSum** program.

5. **Analysis of Molecular Orbitals (MOs)**

   a) Visualize the MOs with either **Jmol** or **Molden**.

   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.

6. **Analysis of the UV Spectrum**

   Calculate the UV (vertical excitation) spectrum using configuration interaction with single excitations (CIS(nstates=6)/cc-pVDZ) and time-dependent DFT (B3lYP/cc-pVDZ TD(Nstates=6)).

   a) Characterize the excitations ($\pi \rightarrow \pi^*, ...$) for the first few excited states.

   b) Compare the results of the CIS and TDDHF calculations.

   c) Compare the calculated excitation energies with the experimental UV spectrum using the **GaussSum** program.

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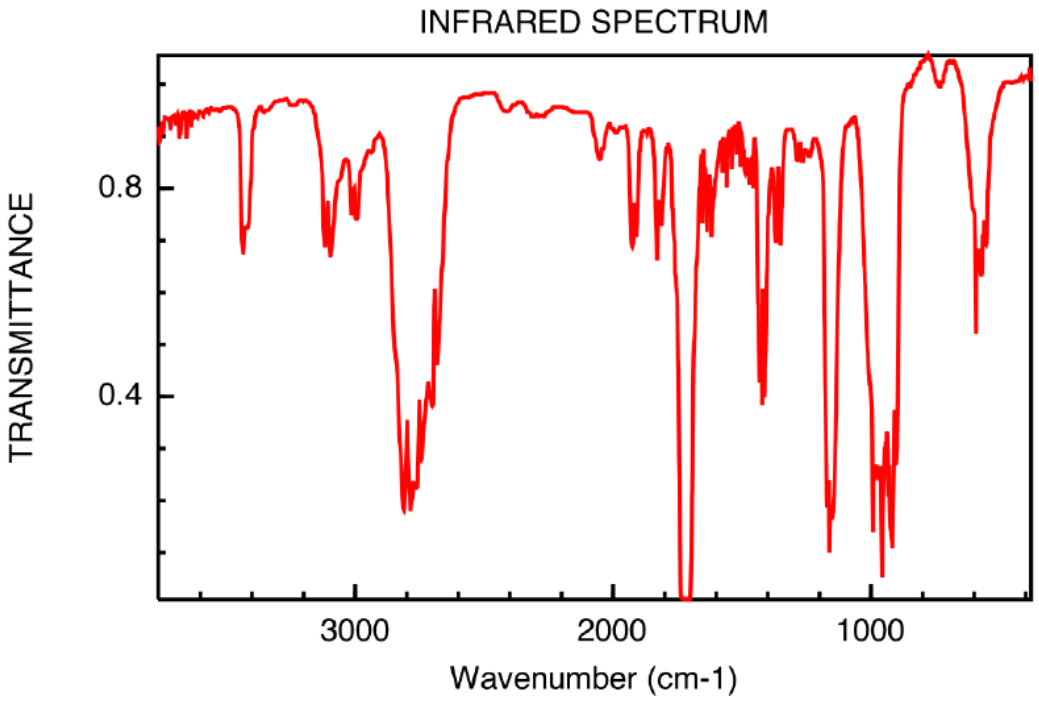
Propenal



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

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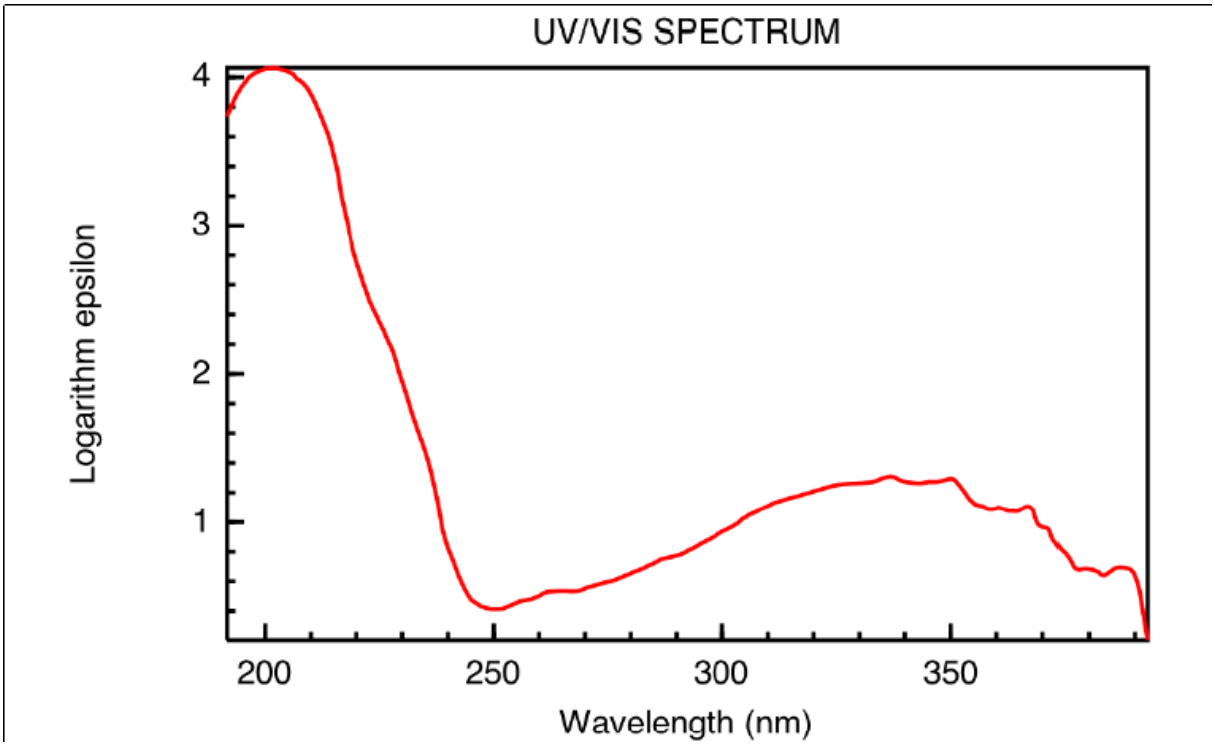
Propenal



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