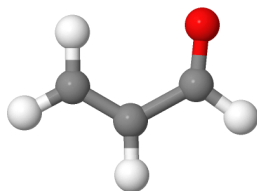
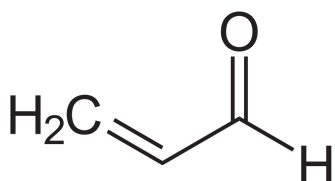


Exercise: UV spectrum of acrolein

Acrolein = 2-propenal ($\text{H}_2\text{C}=\text{CH}-\text{HC}=\text{O}$)



1. Construct the molecule using Molden
 - a. Use the molecular editor
 - b. Save in Gaussian cartesian format

```
source /home/ippoliti/PROGRAMS/modules/molden.sh
molden
```

2. Optimize the molecular structure (keyword `opt`) with Gaussian using the methods (keywords, used in addition to other keywords)
 - a. HF/cc-pVDZ
 - b. B3LYP/cc-pVDZ
 - c. Check the optimization convergence with Molden or directly in the output file
 - d. 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 (a single negative (imaginary) frequency defines a transition state; more than one negative frequency represent higher-order saddle points usually without physical meaning)

Either save the optimized (= final) geometry with Molden or copy it directly from the output file (search for last entry `Standard orientation`)

Keywords for vibrational analysis: `freq=raman`

Gaussian input file format:

```
# HF/cc-pVDZ opt
```

```
Acrolein
Ground state optimization
```

```
0 1
C          0.8232    1.1792    1.6041
C          1.7721    2.2063    1.1241
C          2.8173    1.939   0.3465
O          0.9055    0.       1.339
H          0.       1.5404    2.2419
H          1.5615    3.2308    1.4528
H          3.5029    2.7089    0.0051
H          3.058     0.9365    0.
```

(ends with blank line)

```
source /home/ippoliti/PROGRAMS/modules/gaussian.sh
g09 acrolein.com &
```

```
tail -20f acrolein.log
```

(shows the updated last 20 lines of the file)

Geometry optimization: Look for convergence criteria in the output file:

```
Item                Value      Threshold  Converged?
Maximum Force       0.000195   0.000450   YES
RMS Force           0.000065   0.000300   YES
Maximum Displacement 0.001086   0.001800   YES
RMS Displacement    0.000491   0.001200   YES
Predicted change in Energy=-1.834929D-07
Optimization completed.
  -- Stationary point found.
```

Vibrational analysis: Search for „Harmonic frequencies“

(you can also visualize the normal modes in Jmol or Molden,
see also additional exercise 7)

3. Calculate the molecular orbitals (MOs) at the optimized geometries
 - a. Keywords (instead of `opt`): `pop=full gfprint`
4. Analysis of MOs
 - a. Visualize the MOs with Jmol (either Applet on the course website or stand-alone version on the grs cluster: `jmol`)
 - i. Load up your Gaussian output file
 - ii. If you use the stand-alone version: open a console window of Jmol (right mouse button opens an extended menu) and type: `frame 2`
 - iii. Then you can visualize the MOs
(Surfaces, Molecular orbitals)
 - b. Sketch a qualitative MO diagram (energy levels + MOs for the 4 highest occupied and the 5 lowest unoccupied (virtual) MOs)
 - c. Characterize the MOs (σ , π , n, bonding, antibonding)
5. Calculate the UV (vertical excitation) spectrum (at the respective optimized geometries) using configuration interaction with single excitations (CIS) as well as time-dependent DFT (TDDFT):
Keywords (complete):
 - a. `CIS (nstates=6) /cc-pVDZ`
 - b. `B3LYP/cc-pVDZ TD (nstates=6)`
6. Analysis of UV spectrum
 - a. Characterize the excitations (e.g. $\pi \rightarrow \pi^*$, ...) for the first few excited states
 - b. Compare the results of CIS (based on HF) and TDDFT calculations
 - c. Compare to the experimental UV spectrum

Look for the following entry in the output file:

Excitation energies and oscillator strengths:

```
Excited State 1: Singlet-A 4.7013 eV 263.72 nm f=0.0003 <s**2>=0.000
  14 -> 16      0.63026
  14 -> 20      0.28968
```

This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle
RhoCI density.

...

The notation 14 -> 16 refers to an excitation from MO 14 to MO 16.

The coefficient (here 0.63036) is the contribution of the respective excitation to the CI wave function.

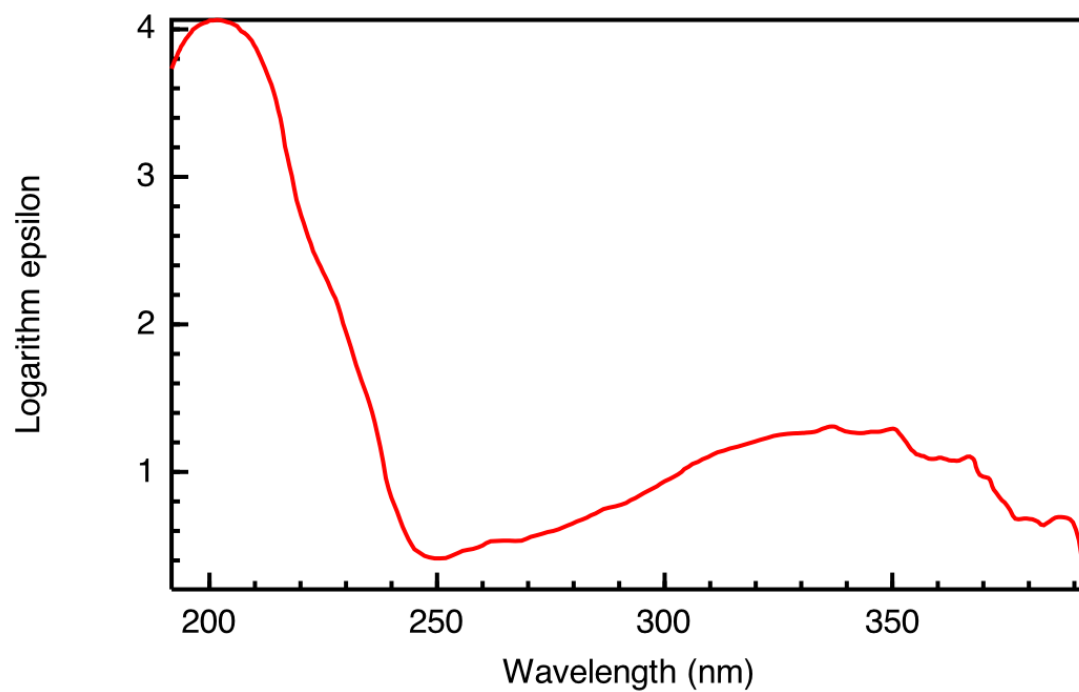
To get a percentage the coefficient needs to be squared and multiplied by 2 ($c \times c \times 2$) to account for 2 contributions in a properly spin-adapted eigenfunction.

f is the oscillator strength which can be compared to the integrated intensity of an experimental absorption band.

7. Additional exercise: Vibrational analysis using the DFT results

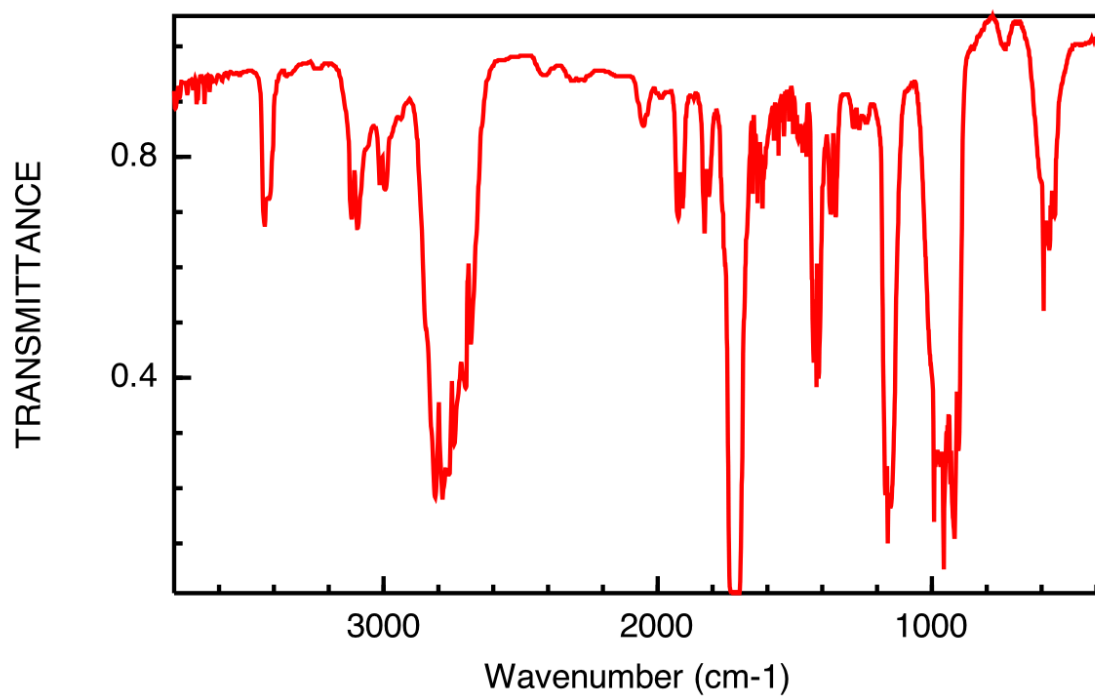
- a. Visualize the vibrational normal modes in Jmol (or Molden)
- b. Assign the character of the normal modes (e.g. stretching, deformation: in-plane bending, out-of-plane bending, ...)
- c. Look for IR intensity and Raman activity in the output file.
- d. Try to assign the vibrational bands in the experimental IR spectrum

2-Propenal
UV/VIS SPECTRUM



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

PROPENAL
INFRARED SPECTRUM



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