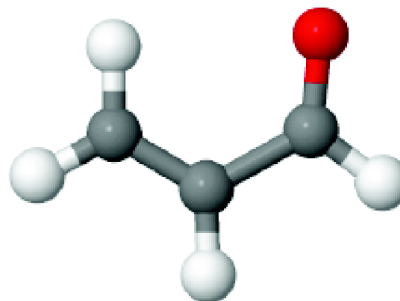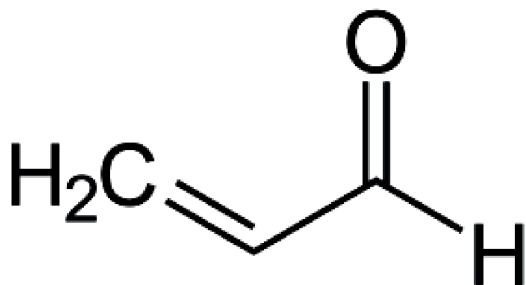# UCONN

Computational Chemistry Workshop

Acrolein: Vibrational and Electronic Spectra Including Solvent Effects

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Exercises

IR Spectrum of Acrolein

Geometry Optimization and Frequency Calculation

A geometry optimization and frequency calcuulation can be combined in one step. A typical **Gaussian** input file for performing this calculation for the acrolein molecule is given below:

Density Functional Theory

```
%chk=acrolein_opt_freq.chk
#P b3lyp/6-31g* opt freq 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
```

Check the optimization convergence with appropriate visualization software, as well as directly viewing the output of the **Gaussian** log file.

Analysis of the Calculated IR Spectrum

- 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.

- Visualize the vibrational normal modes with appropriate visualization software applications.

- Assign the character of the normal modes (e.g. stretching, in-plane bending, out-of-plane bending, other deformations), and assign the symmetry of corresponding vibration.

  Also, look for IR intensity and Raman activity in the **Gaussian** log file.

- Compare the calulated vibrational spectrum with the one experimentally obtained by providing a graph of the two spectra and discussing similarities or differences.

- Explain which normal mode vibrations are allowed or forbidden, as well as whether they are only infrared active, only Raman active, or both active.

UV Spectrum of Acrolein

A **Gaussian** input file for performing a vertical excitation using a restart file is provided below. This results in a UV spectrum of acrolein using configuration interaction with single excitations.

Time Dependent Density Functional Theory (TDDFT)

```
%oldchk=acrolein_opt_freq.chk
%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
```

Analysis of Molecular Orbitals (MOs) and Characterization of Excitations

- Construct an MO excitation diagram for the appropriate highest occupied and lowest unoccupied MOs.

  Visualize the MOs with appropriate visualization software, and include them in the MO excitation diagram.

  Characterize the MOs by $\sigma, \sigma^*, \pi, \pi^*$, and n, i.e. bonding, antibonding, and non-bonding, and assign the symmetry representation for each orbital.

  Both visualized MOs and energy levels should be included.

- Characterize the type of excitations ($\pi \to \pi^*, ...$) for the first few excited states.

- Compare the calulated excitation spectrum with the one experimentally obtained by providing a graph of the two spectra and discussing similarities or differences.

- Which excitations are allowed or forbidden? Why? Use symmetry arguments.

  Why can excitations which are forbidden appear in the experimental spectrum?

- Compare the results of the Wave Function Theory (CIS) and Density Functional Theory (TDDFT) calculations and discuss similarities or differences.

Solvatochromism

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.

With the continuum or implicit solent model, the solvent accessible surface (SAS) is traced out by the center of a probe representing a solvent molecule. The solvent excluded surface (SES) is the topological boundary of the union of all possible probes that do not overlap with the molecule.
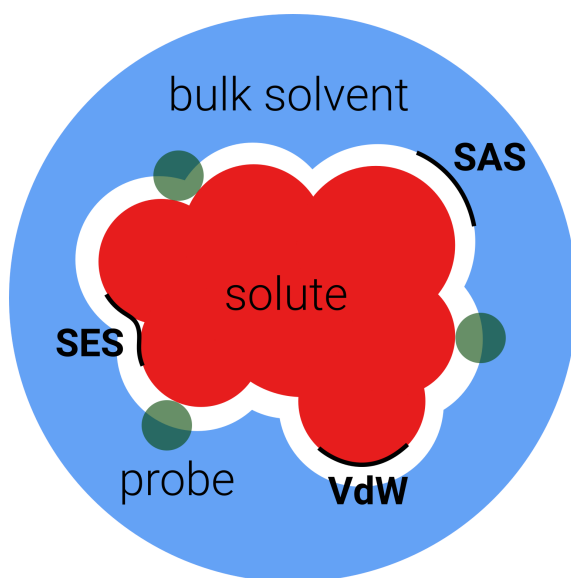
In these models, the solute is placed in a cavity of roughly molecular shape. The solvent is described by a continuum that interacts with the charges on the cavity surface, which are in turn determined by the solute and the problem is solved iteratively. The general picture of the method can be depicted as below:
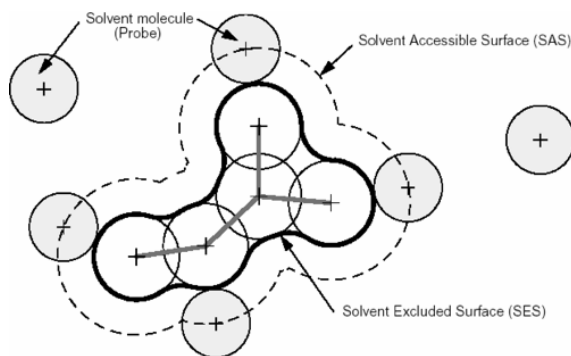
Gaussian input files for the implicit solvation model

Examples of Gaussian input files for implicit polar and non-polar solvent calculations:

Polar Solvent

```
%oldchk=acrolein_opt_freq.chk
%chk=acrolein_tddft_water
#P b3lyp/6-31G(d) guess=read geom=allcheck 5D td(nstates=6) SCRF=(SMD,Solvent=Water)
                 gfinput gfprint pop=full

Acrolein: UV spectrum at the optimized geometry in water

0 1
```

Non-polar Solvent

```
%oldchk=acrolein_opt_freq.chk
%chk=acrolein_tddft_pentane
#P b3lyp/6-31G(d) guess=read geom=allcheck 5D td(nstates=6) SCRF=(SMD,Solvent=Pentane)
                 gfinput gfprint pop=full

Acrolein: UV spectrum at the optimized geometry in pentane

0 1
```

- Calculate the spectra of acrolein in polar and non-polar solvents using the continuum model of solvation, and compare these results with experimental data.

  Look for solvent shifts, and rationalize the results.

Appendix

UV-Visible Absorption Spectra

To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, accurate measurements of light absorption must be performed at different wavelengths in and near the visible part of the spectrum. Commercial optical spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum. The visible region of the spectrum comprises photon energies of 36 kcal/mol ($\sim$ 1.6 eV) to 72 kcal/mol ($\sim$ 3 eV), and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mol ($\sim$ 6 eV). Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.

The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called *electronic spectroscopy*. Various types of electronic excitation that may occur in organic molecules is shown in Figure 1.
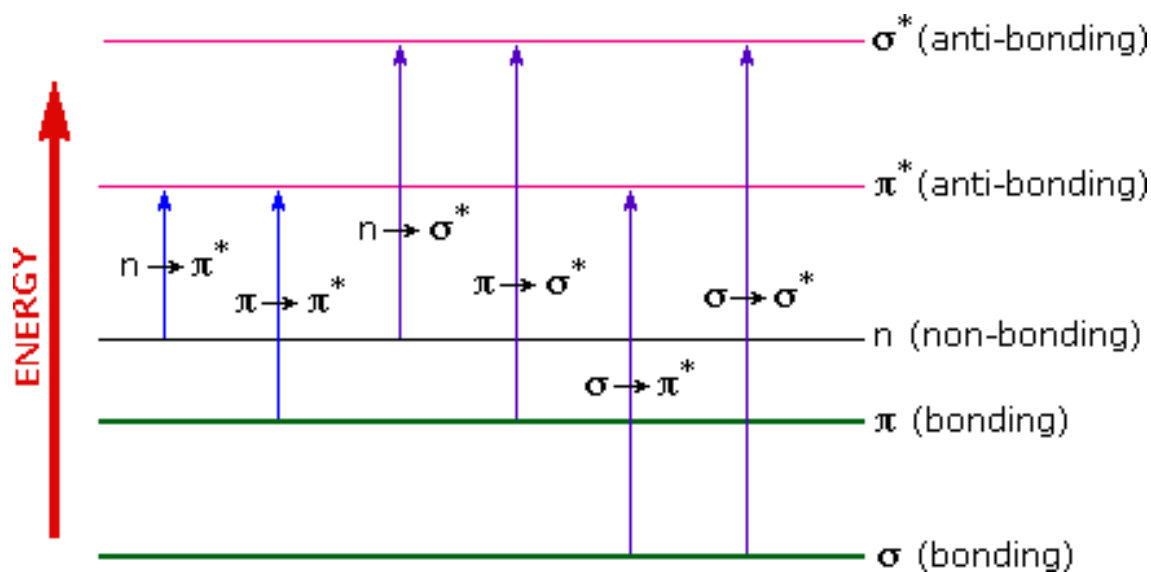

Figure 1: Types of Excitations in Organic Molecules

Of the six transitions outlined, only the two lowest energy ones (colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an excited state. When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital.

Excitation Energies of Common Organic Chromophores

Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	$\pi \longrightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	$\pi \longrightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	$n \longrightarrow \sigma^*$ $n \longrightarrow \sigma^*$	205 255	200 360	hexane hexane

Table 1: Excitation Energies of Common Organic Chromophores

A list of some simple chromophores and their light absorption characteristics is also provided in Table 1.

It should be clear from Table 1 above, that the only molecular moieties likely to absorb light in the 200 - 800 nm region are π-electron functions and heteroatoms having non-bonding valence-shell electron pairs. Such light absorbing groups are referred to as chromophores.

The oxygen non-bonding electrons in alcohols and ethers do not give rise to absorption above 160 nm. Consequently, pure alcohol and ether solvents may be used for spectroscopic studies.

The presence of chromophores in a molecule is best documented by UV-Visible spectroscopy, but the failure of most instruments to provide absorption data for wavelengths below 200 nm makes the detection of isolated chromophores problematic.

Fortunately, conjugation generally moves the absorption maxima to longer wavelengths, so conjugation becomes the major structural feature identified by this technique.

Molar absorptivities (ε) may be very large for strongly absorbing chromophores ($>$10,000) and very small if absorption is weak (10 to 100). The magnitude of ε reflects both the size of the chromophore, and the probability that light of a given wavelength will be absorbed when it strikes the chromophore.

Solvatochromism

Solvent Effects on the Excited States of Molecules

A variety of environmental factors affect excitation of molecules including interactions between the solute molecule and surrounding solvent molecules which is related to solvent polarity, temperature, pH, and the localized concentration of the solute molecule.

In solution, solvent molecules surrounding the solute molecules have dipole moments that can interact with the dipole moment of the solute to yield an ordered distribution of solvent molecules around the solute. Differences between the ground and excited states in the solute molecule produce a change in the molecular dipole moment, which ultimately induces a rearrangement of surrounding solvent molecules.

However, the Franck-Condon principle dictates that, upon excitation, the molecule is excited to a higher electronic energy level in a far shorter time frame than it takes for the solute and solvent molecules to re-orient themselves within the solvent-solute interactive environment.

As a result, there is a time delay between the excitation event and the re-ordering of solvent molecules around the solvated solute as illustrated in Figure 2. which generally has a much larger dipole moment in the excited state than in the ground state.

Solvent Relaxation and Re-orientation

After the solute has been excited to higher vibrational levels of the an excited singlet state S_n, excess vibrational energy is rapidly lost to surrounding solvent molecules as the solute slowly relaxes to the lowest vibrational energy level occurring in the picosecond time scale, as is illustrated in Figure 3.

Solvent molecules assist in stabilizing and further lowering the energy level of the excited state by re-orienting (solvent relaxation) around the excited solute in a slower process that requires between 10 and 100 picoseconds.

This has the effect of reducing the energy separation between the ground and excited states, which results in a red shift (to longer wavelengths) of the fluorescence emission. Increasing the solvent polarity produces a correspondingly larger reduction in the energy level of the excited state, while decreasing the solvent polarity reduces the solvent effect on the excited state energy level.

The polarity of the solute molecule also determines the sensitivity of the excited state to solvent effects. Polar and charged solvent molecules exhibit a far stronger effect than non-polar solvent molecules.
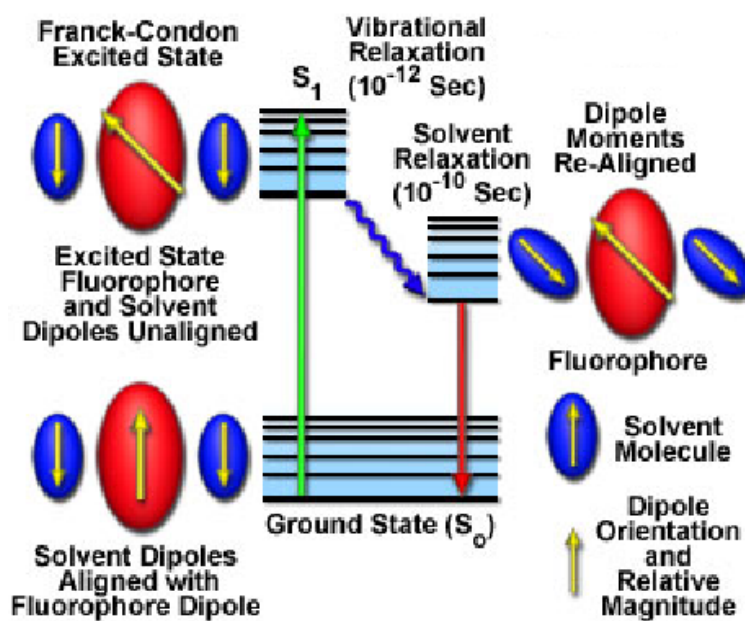
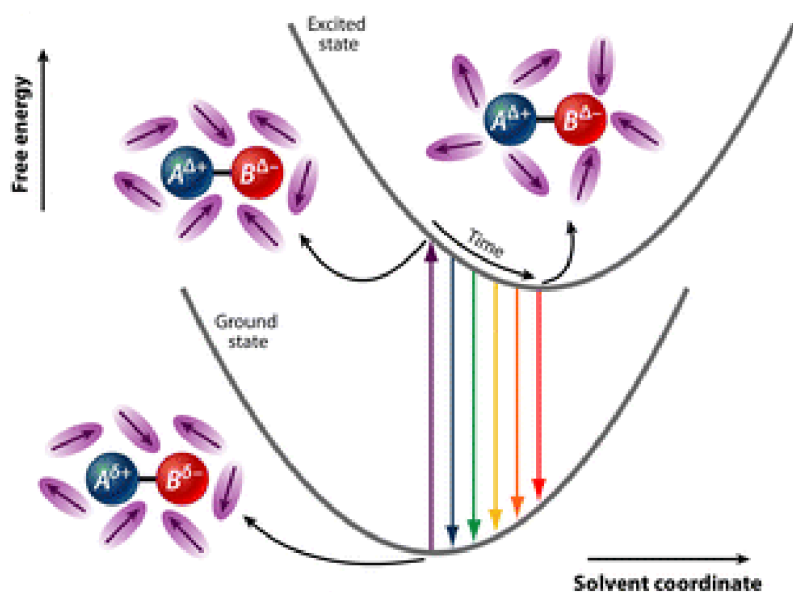Figure 2: Solute-Solvent Excited-State Interactions

Figure 3: Two Views of Excited-State Solvent Re-Orientation

Solvatochromism Effects in Acetone

UV-Vis spectral properties of many molecules depend on the solvent. One of the best understood examples is provided by the n $\rightarrow \pi^*$ transition in acetone. In the gas phase, this symmetry-forbidden transition is observed as a weak band of peaks near 276 nm (4.49 ev). When dissolved in water, the n $\rightarrow \pi^*$ transition is observed at 265 nm (4.68 eV).

Such changes in the spectrum with solvent are called solvatochromic shifts. When the spectral maximum shifts to longer wavelengths, a red-shift occurred. In case of acetone, a spectral blue-shift occurred when acetone was moved from the gas phase to water.

The solvatochromism in acetone can be understood in terms of dipolar interactions between the polar solute and the solvent. In the gas phase and non-polar solvents, the dipolar interactions are negligible both in the ground and the excited state. In water, the strength of dipolar interactions is significant. More importantly, the ground state and the excited state enjoy different stabilisation by water because the dipole moment of acetone is different in the ground and excited states.
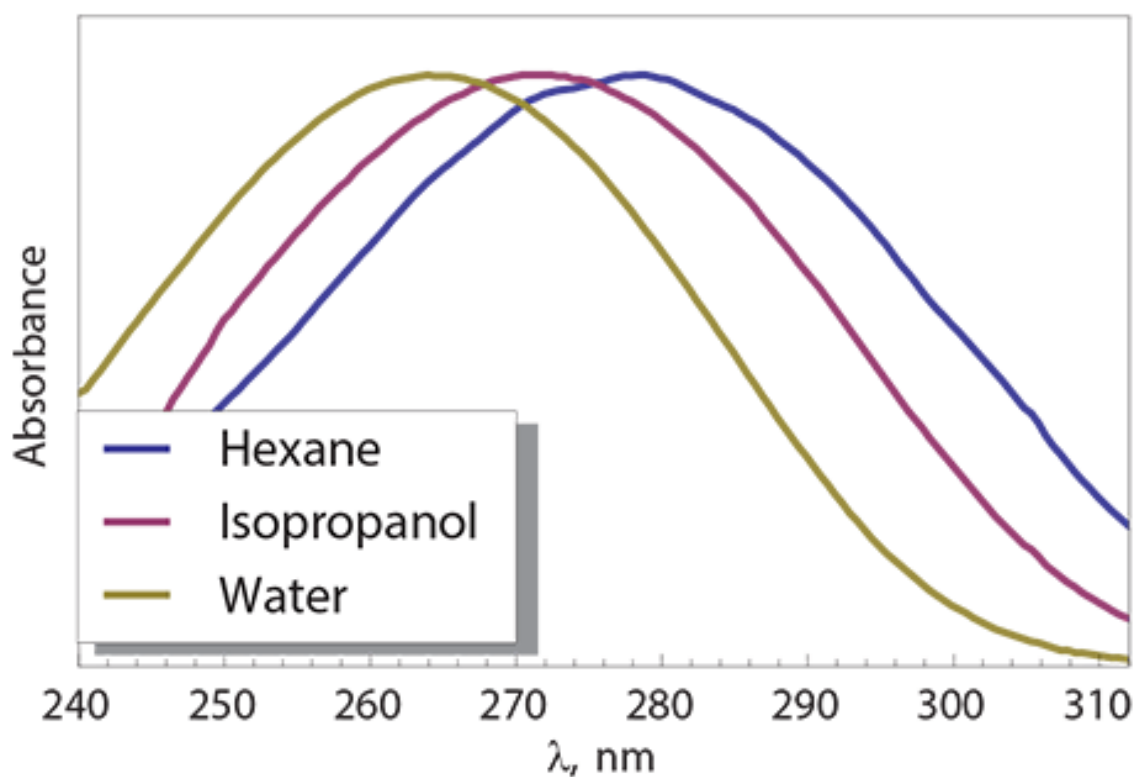

Figure 4: Effects of Polar and Non-Polar Solvents of n $\rightarrow \pi^*$ Transition in Acetone

Calculational Methods for Excited States

**Wave Function Theory**

CI Singles (CIS) — Acrolein Example

Excited State 1: Singlet-A"   4.8437 eV 255.97 nm f=0.0002
    14 -> 16   0.62380   3.0329   408.79
    14 -> 17   0.30035   3.73

Excited State 2: Singlet-A'   7.6062 eV 163.01 nm f=0.7397
    15 -> 16   0.68354   6.0794   203.94
                                6.41

Excited State 3: Singlet-A"   9.1827 eV 135.02 nm f=0.0004
    11 -> 16   -0.15957   6.6993   185.07
    12 -> 16   0.55680
    14 -> 16   -0.19752
    14 -> 17   0.29331

Excited State 4: Singlet-A"   9.7329 eV 127.39 nm f=0.0007
    9 -> 17   0.19146
    10 -> 16   0.12993
    11 -> 16   0.56876
    12 -> 16   0.26026
    12 -> 17   -0.11839
    14 -> 17   -0.12343
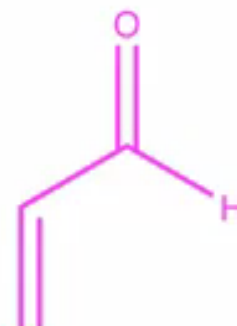
LUMO+1: π_4^*
LUMO: π_3^*
HOMO: π_2
HOMO−1: n_O

The experimental values for the first and second excited states are 3.73 eV and 6.41 eV, respectively

Calculational Methods for Excited States

Density Functional Theory

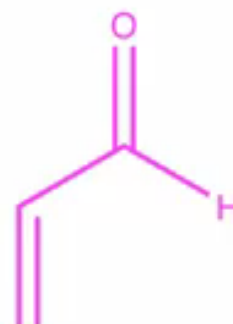## TDDFT — Acrolein Example

Excited State 1: Singlet-A" 3.7829 eV 327.75 nm f=0.0000
   15 -> 16   0.67412
   15 -> 17   0.10545

Excited State 2: Singlet-A' 6.7142 eV 184.66 nm f=0.3785
   14 -> 16   0.60530
   14 -> 17   0.12143

Excited State 3: Singlet-A" 7.2723 eV 170.49 nm f=0.0004
   13 -> 16   0.18077
   15 -> 16   -0.11786
   15 -> 17   0.66306

Excited State 4: Singlet-A" 7.8041 eV 158.87 nm f=0.0006
   13 -> 16   0.67088
   15 -> 17   -0.18640

LUMO+1: π_4^*
LUMO: π_3^*
HOMO: n_O
HOMO−1: π_2

The experimental values for the first and second excited states are 3.73 eV and 6.41 eV, respectively

- TDDFT tends to be more accurate than CIS, but this is sensitive to choice of functional and certain special situations.

- Charge-transfer transitions are particularly problematic,

- For TDDFT, no wave function is created, but eigenvectors analogous to those predicted by CIS are provided.
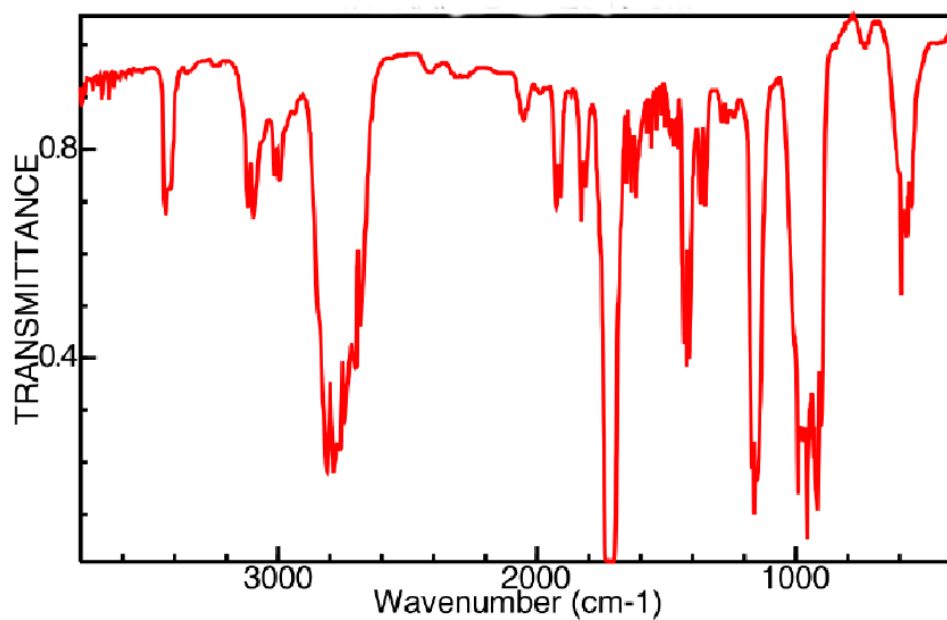
Experimental Spectra
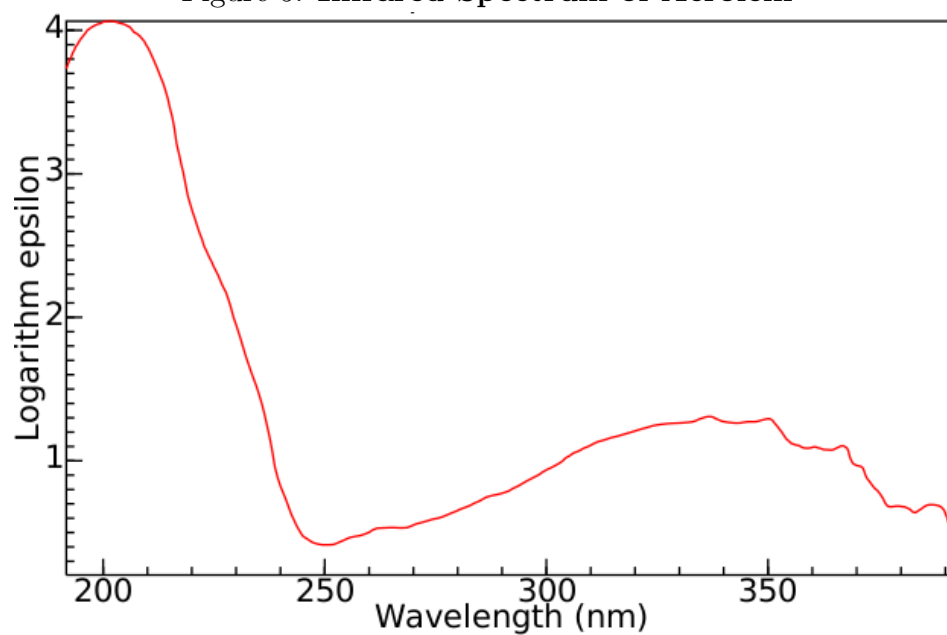

Figure 5: **Infrared Spectrum of Acrolein**

Figure 6: **UV-Visible Spectrum of Acrolein**

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