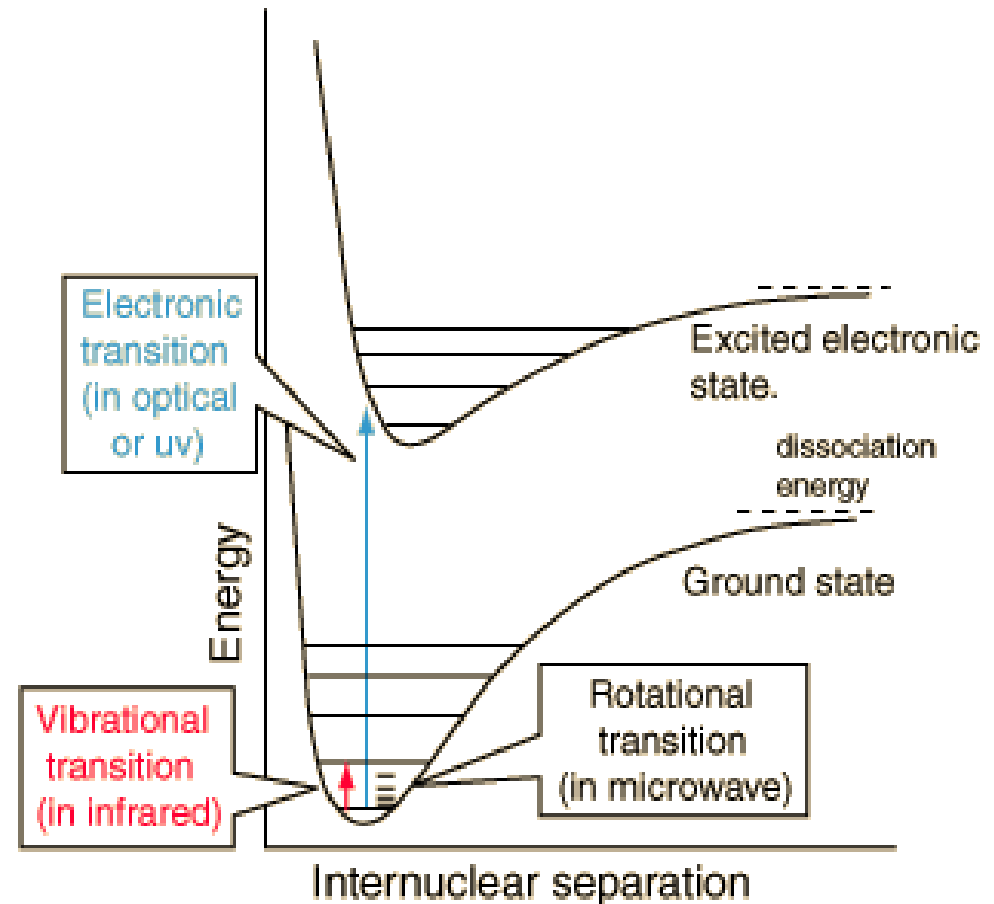


# Calculation of UV-VIS Spectra

# Spectroscopy

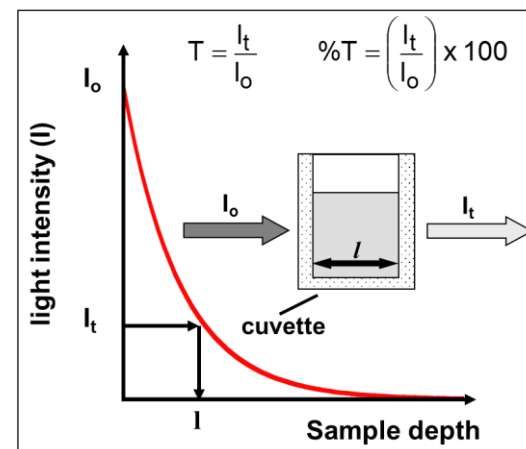
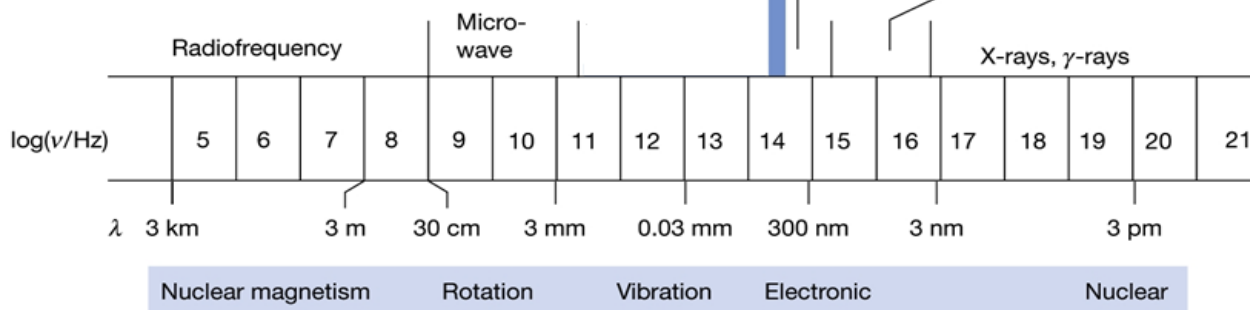
- Atoms and molecules interact with electromagnetic radiation (EMR) in a wide variety of ways and may absorb and/or emit EMR.
- Absorption of EMR stimulates different types of motion in atoms and/or molecules
- The **patterns** of absorption (wavelengths absorbed to some what extent) and/or emission (wavelengths emitted and their respective intensities) are called '**spectra**'.
- The field of **spectroscopy** is concerned with the interpretation of **spectra** in terms of atomic and molecular structure (and environment).



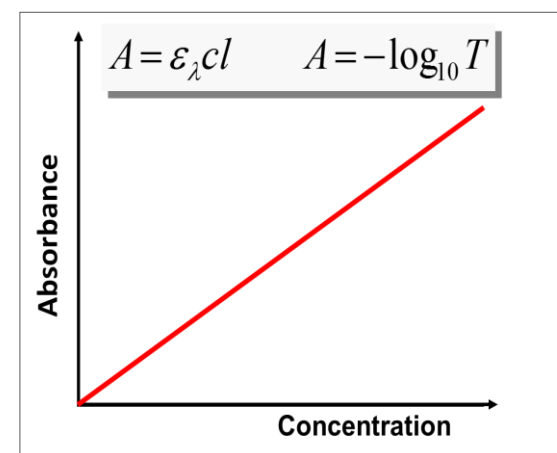
# UV Spectroscopy

- Ultraviolet radiation stimulates molecular vibrations and electronic transitions.
- Absorption spectroscopy from 160 nm to 780 nm
- Identification of inorganic and organic species

Red	Orange	Yellow	Green	Blue	Violet
700	620	580	530	470	420 nm
1.4	1.6	1.7	1.9	2.1	$2.4 \times 10^4 \text{ cm}^{-1}$
4.3	4.8	5.2	5.7	6.4	$7.1 \times 10^{14} \text{ Hz}$



- the BEER-LAMBERT LAW, for a light absorbing medium, **the light intensity falls exponentially with increasing sample conc.**



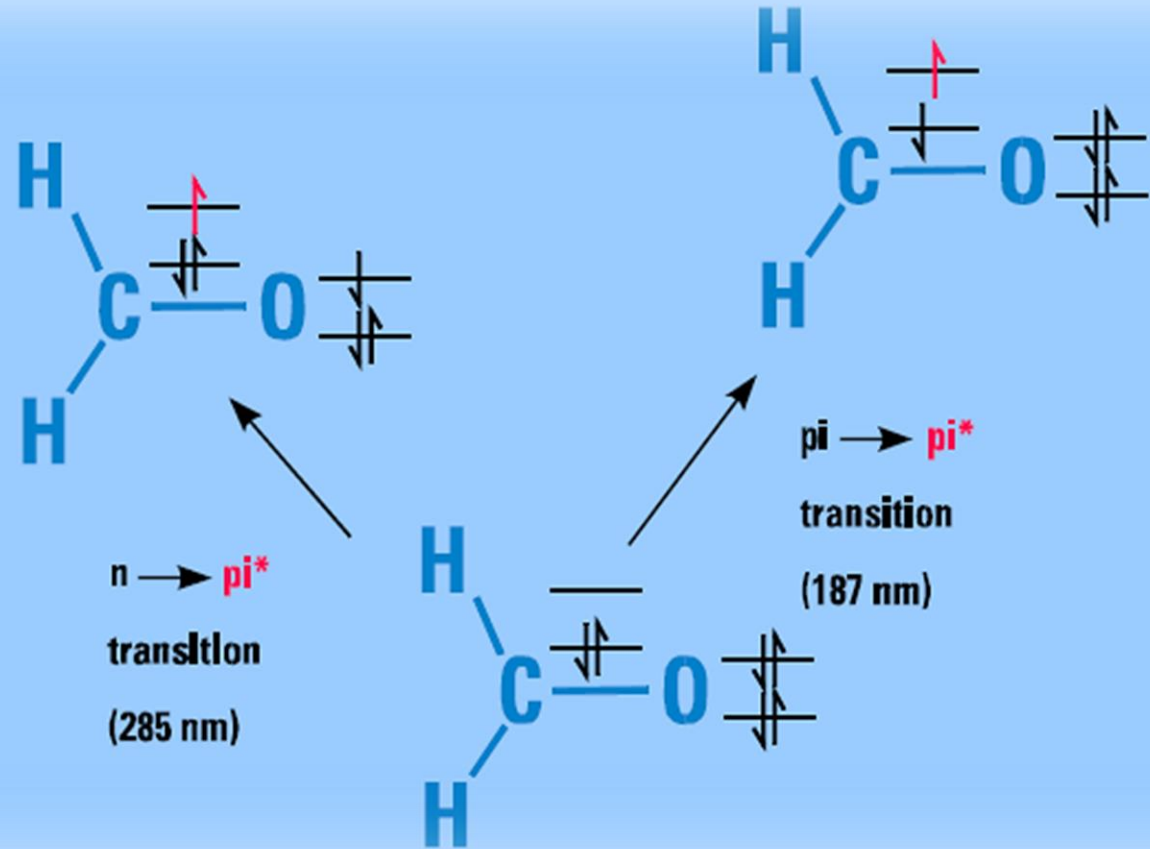
- The negative logarithm of  $T$  is called the absorbance ( $A$ ) and this is directly proportional to sample depth (called pathlength,  $l$ ) and sample concentration ( $c$ ).

# UV Spectroscopy

➤ Electronic transitions occur when the molecule absorbs energy.

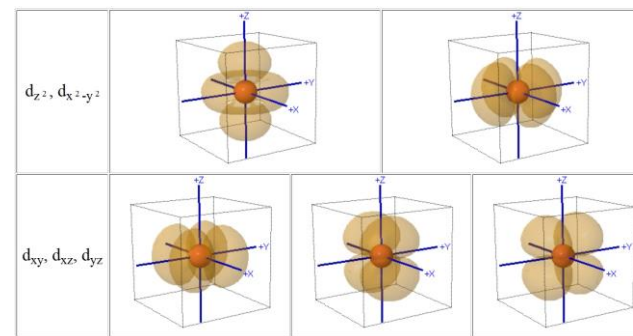
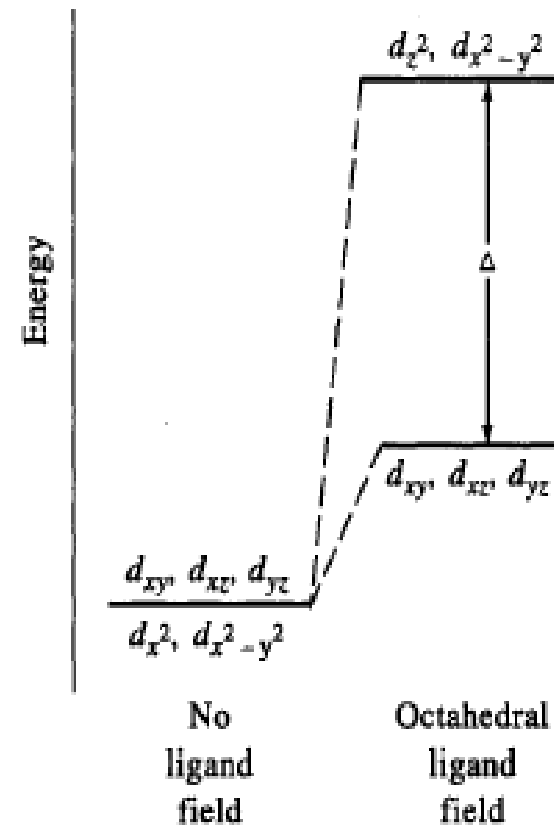
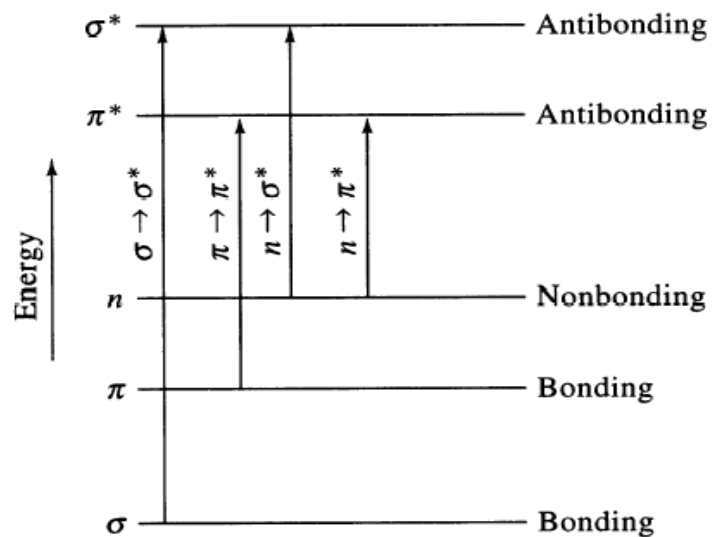
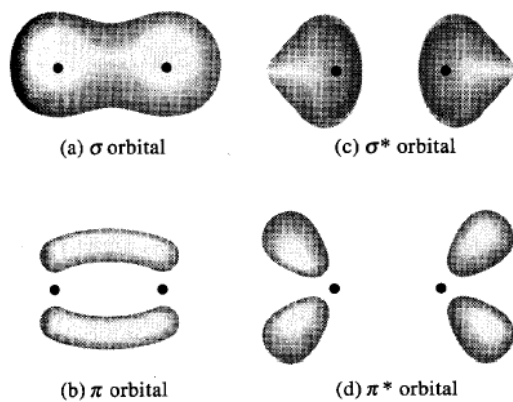
➤ Electronic transitions:

- $\pi$ ,  $\sigma$ , and nonbonding electrons
- d and f electrons
- charge transfer



# UV Spectroscopy

➤ Electronic transitions occur when the molecule absorbs energy.



# Excited States in Computational Chemistry

- basically the Schrödinger equation is written as  $H\Psi = E\Psi$ , However, that obscures the reality that there are infinitely many solutions to the Schrödinger equation, so it is better to write  $H\Psi_n = E_n\Psi_n$
- **Hartree-Fock theory provides us a prescription construct an approximate ground-state wave function** (as a single Slater determinant).
- How do we build from there to **construct an excited state wave function**?

$$\Psi = a_0\Psi_{\text{HF}} + \sum_i \sum_r^{\text{occ. vir.}} a_i^r \Psi_i^r + \sum_{i < j} \sum_{r < s}^{\text{occ. vir.}} a_{ij}^{rs} \Psi_{ij}^{rs} + \dots$$

- The **bigger the CI matrix, the more electron correlation can be captured**. The CI matrix can be made bigger either by increasing basis-set size (each block is then bigger) or by adding more highly excited configurations (more blocks). The ranked eigenvalues correspond to the electronic state energies.
- The higher eigenvalues are treated as the energies of the excited states.

# We will use the Time-Dependent DFT overview

## ➤ Review on Density Functional Theory

$$H = T_e + V_{ee} - \sum \sum \frac{Z e^2}{|\mathbf{r} - \mathbf{R}|}$$

$\rho(\mathbf{r})$  – electron density : the properties (such as energy) of a many-electron system are uniquely determined by an electron density that is a function of spatial coordinates ( $\mathbf{r}$ )

$$\rho(\mathbf{r}) = \sum_{i=1}^n n_i |\varphi_i(\mathbf{r})|^2$$

**DFT** Energy  $[\rho] = T[\rho] + V[\rho]$

: the energy is decomposed into kinetic and potential contributions to the total interactions; this is the “DNA” of density functional theory as well as WF based methods.

$$\left[ -\frac{1}{2} \nabla_i^2 + V_{tot}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

: the potential part is broken down to classical ( $V_{cl}$ ) and nonclassical ( $V_{xc}$ ) part, the “flavor” or type of DFT (e.g. B3LYP, PBE0, etc) represents how the method solves exchange-correlation potential ( $V_{xc}$ ).

$$V_{tot}(\mathbf{r}) = V_{cl}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

# Time-Dependent DFT overview

$$H = T_e + V_{ee} - \sum \sum \frac{Z e^2}{|\mathbf{r} - \mathbf{R}|} + \sum \mathbf{r} \epsilon \cos \omega t$$

- TDDFT : on the other hand is a DFT with time dependent elements, its the most used method to extract features like excitation energies, frequency-dependent response properties, and photo-absorption spectra, particularly for its robustness and versatility.

$$\rho(\mathbf{r}, t) = \sum_{i=1}^n n_i |\varphi_i(\mathbf{r}, t)|^2$$

: the density now has time element, means expectation value of any physical time-dependent observable of a many-electrons system is a unique functional of time-dependent electron density  $\rho(\mathbf{r}, t)$  and of the initial state  $\varphi_i^0(\mathbf{r}, t=0)$

$$\left[ -\frac{1}{2} \nabla_i^2 + V_{tot}(\mathbf{r}, t) \right] \varphi_i(\mathbf{r}, t) = \varepsilon_i \varphi_i(\mathbf{r}, t)$$

: Unknown exchange-correlation time-dependent potential.  $V_{xc}$  functional of the density at all times and of the initial state. This is becoming more complicated and weirder.

$$V_{tot}(\mathbf{r}, t) = V_{cl}(\mathbf{r}, t) + V_{xc}(\mathbf{r}, t)$$

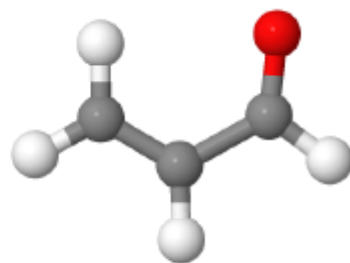
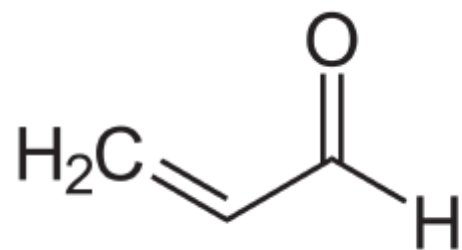


# Time-Dependent DFT overview

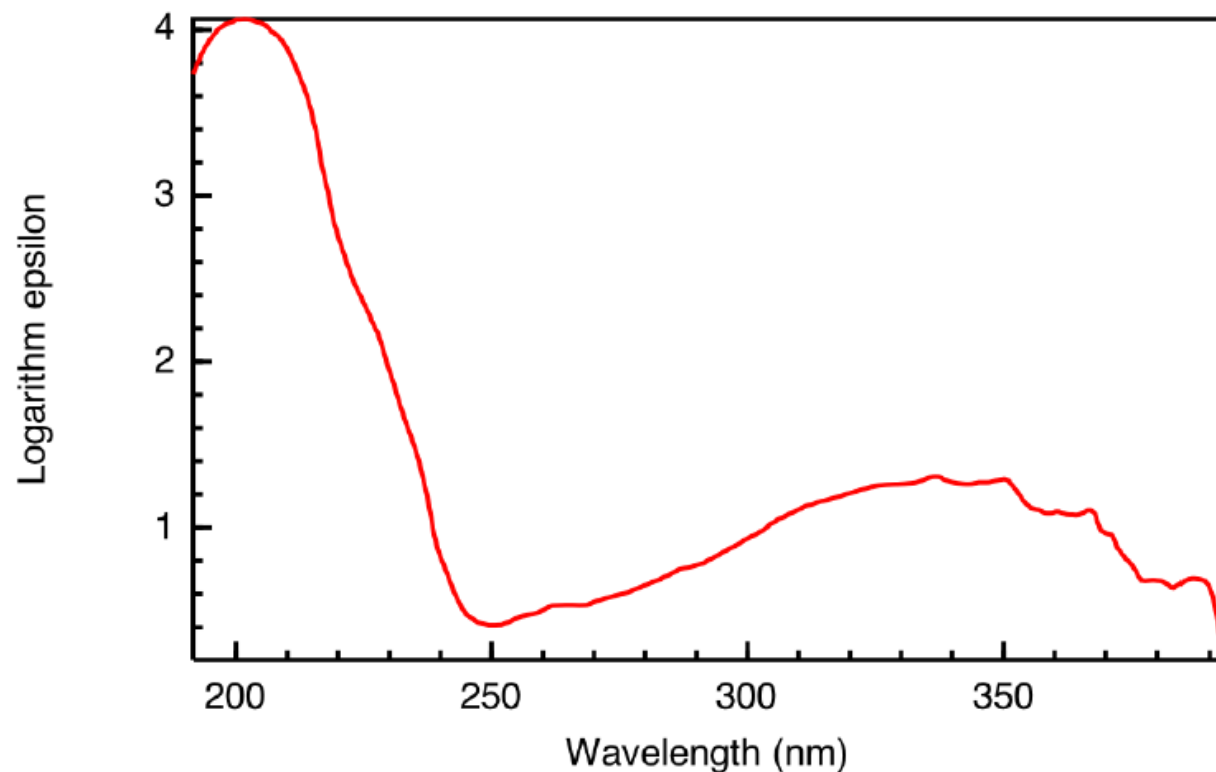
- TD DFT tends to be more accurate than CIS but this is sensitive to choice of functional and certain special situations.
- Charge-transfer transitions are particularly problematic.
- No wave function is created, but eigenvectors analogous to those predicted by CIS are provided.
- There's a Semi-Empirical Method, INDO/S that produces good excitation energy numbers relative to the experiment at least for small not complicated system.

# Exercise

➤ Calculate the UV Spectra 2-propenal



**GEOMETRY**



**UV SPECTRA from NIST**

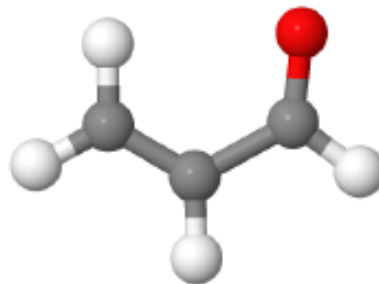
# Exercise

## #1 Construct the molecule

- Draw the molecule using Avogadro
- Create a **Gaussian** input file using “**Extension Menu**”
- Optimized and Calculate the Frequency calculation using Gaussian

**#n pbe1pbe/6-31G(d) opt freq**

- After the successful job, verify that the optimization reached a minimum on the potential energy surface. 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).



## #2 Visualizing the orbitals

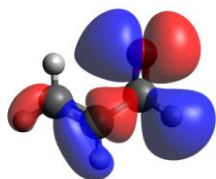
- Calculate the molecular orbitals (MOs) at the optimized geometries

**#n pbe1pbe/6-31G(d) pop=full formcheck**

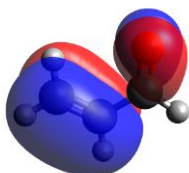
- After the successful job, open the **\*FChk** file in Avogadro
  - Click on **Extensions. Create Surface**. Select “**Molecular Orbital**” as surface type
  - Resolution: **High**, Iso Value: **0.02**, Color Type: **MO**
- Examine the first **2 highest occupied and lowest unoccupied MO's**.

# Exercise

MO#

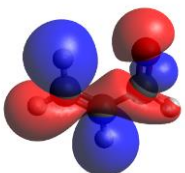


MO#

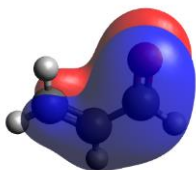


???

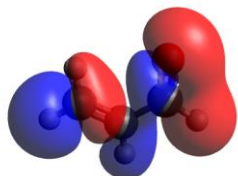
MO#



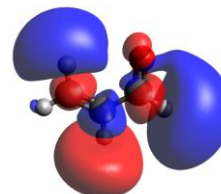
MO#



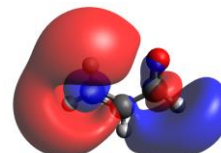
MO#



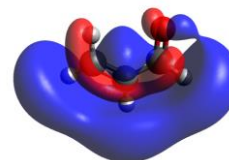
MO#



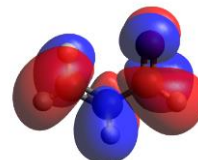
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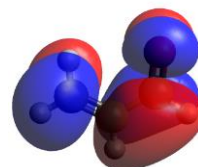
MO#



MO#



MO#



## #2 Visualizing the orbitals (*continuation*)

- Successful run would produce orbitals like this (*left figures*). In the output file, look for the keyword “**Orbital energies and kinetic energies**”, it will report which orbitals are occupied (marked **O**) and virtual (marked **V**) as well as their corresponding energies.
- Which **MO** is the **HOMO** and which is the **LUMO**?
- **Rotate and examine** each orbitals and make a conclusion which orbitals are  $\sigma$ ,  $\pi$ ,  $n$ , **bonding**, **antibonding**, ??

# Exercise

## #3 Calculation of UV Spectra

- Calculate the UV (vertical excitation) at the respective optimized geometry using Time-Dependent Density Functional Theory (TDDFT).

**#n pbe1pbe/6-31G(d) TD**

- If you have done a successful calculation, look for the keyword “**Excitation energies and oscillator strengths**” in the output file
- It will report orbital excitations (e.g. MO14 > MO 16, etc)
- It will report the wavelength where the oscillator strength is strongest; the  $f$  is directly related to intensity of the absorption.
- It will report the energy of the excitations as well as its coefficients; these coefficients refers to the contribution of the respected transition to the wavefunction.

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

\* Identify which orbitals were involved in the excitations?

\* compare the values with exp. excitaitons

E1 3.71 ev

\* What's the nature of the excitation is it singlet or triplet?

E2 6.41 ev

# Exercise

## #3 Graphic Visualizations of the Output File

- You can use various visualization software such as GaussView, Gabedit, Avogadro, etc for UV
- One of the simplest is to use Gabedit

### Module Add Gabedit

In the Gabedit, Menu Bar : **Tools > UV Spectrum > Read energies and intensities from Gaussian output file**

- **It will report the integrated intensity of the absorbance with respect to the wavelength.**
- **Take note once have the figure, you can readjust the range and units to suit your preference.**

# Home Work

Try to calculate Acrolein with CIS and INDO/S methods on the excitations

**GAUSSIAN MANUAL**  
<https://gaussian.com/man/>

- Has the order of orbitals change?
- Are there transitions that were reported that aren't present on the PBE1 method? on the first and second, 3<sup>rd</sup> transitions, etc?
- Which method has closer fit to experimental excitations?

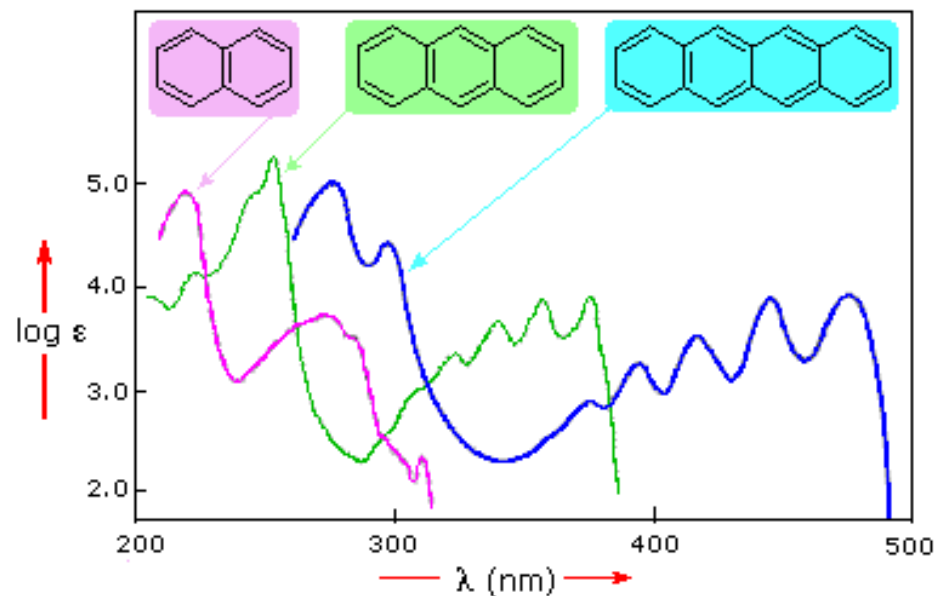
# Home Work

Try to evaluate the peaks of these three ringed systems and judge if they can be reproduced by TDDFT.

Use the same method as stated in this lecture:

Identify which orbital transitions were responsible for these peaks?

What orbital transitions were missing in the experiment if there are?





Happy End