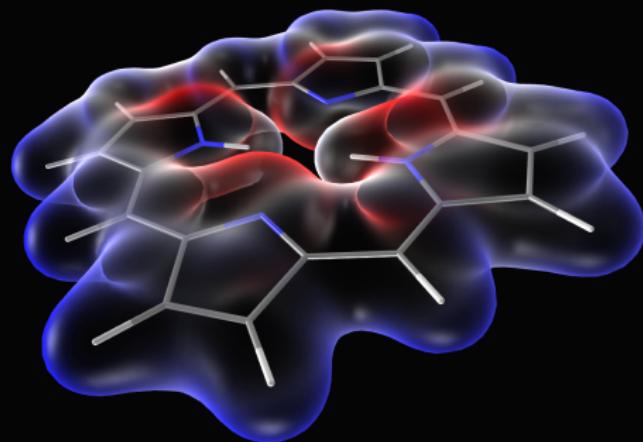


# IQMOL/Q-CHEM Workshop

## Part 2: Applications



RSC - 27 November 2015

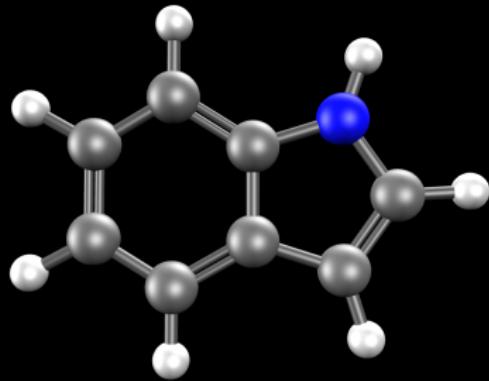
# Outline

This afternoon's session will cover several 'case studies'

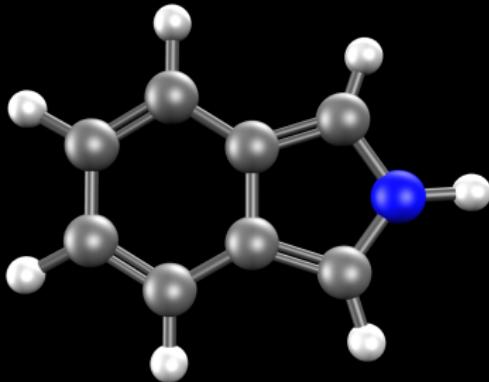
- ▶ Plotting and interpreting molecular orbitals
- ▶ Visualizing potential energy surfaces
- ▶ Vibrational frequency analysis
- ▶ Excited states of transition metal compounds
- ▶ NMR calculations and assignments



# Interpreting Molecular Orbitals



Indole



iso-Indole

Which isomer is more stable?

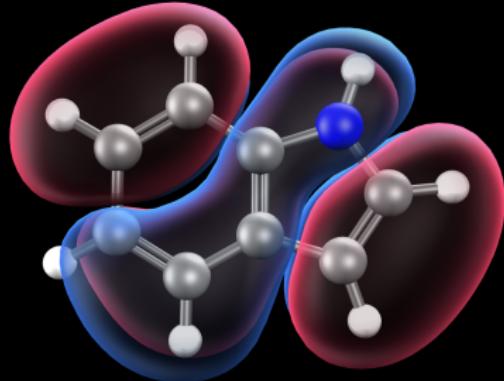


# Exercise

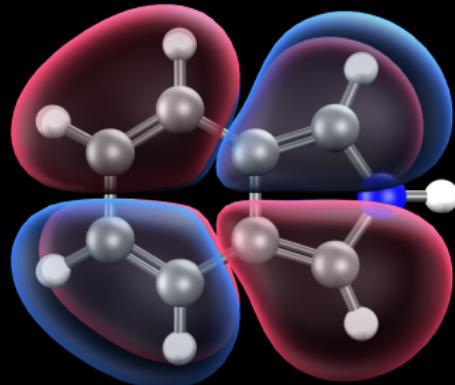
- ▶ Build structures for indole and iso-indole.
- ▶ Run HF/6-31G energy calculations to obtain the MO coefficients.
- ▶ Plot the HOMO of each molecule and predict which isomer is the more stable (hint: consider the nodal structure).
- ▶ Optimize the structures using HF/6-31G and determine the energy difference. Was your prediction correct?



# Results



-361.337412  $E_h$



-361.315424  $E_h$

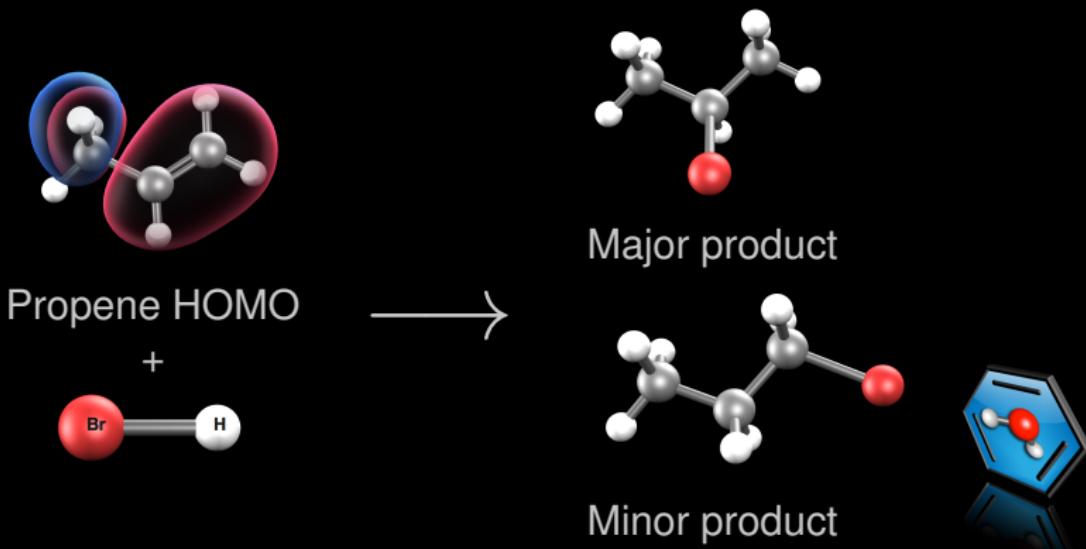
$\Delta E = 58 \text{ kJ/mol} @ \text{HF/6-31G}$



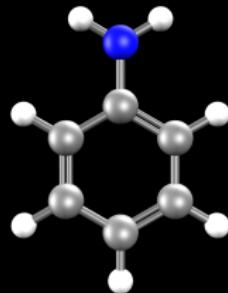
# Electrophilic Attack

In 1952 Kenichi Fukui published his Frontier Molecular Orbital (FMO) theory which provides a qualitative approximation for determining reactivity.

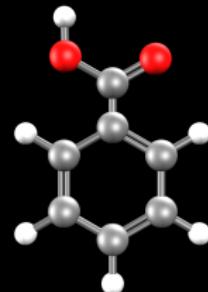
Electrophilic attack is favoured where the HOMO density is largest.



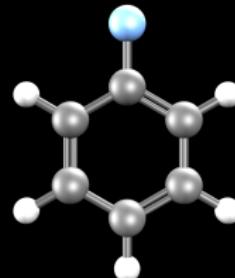
# Exercise



Aniline



Benzoic Acid

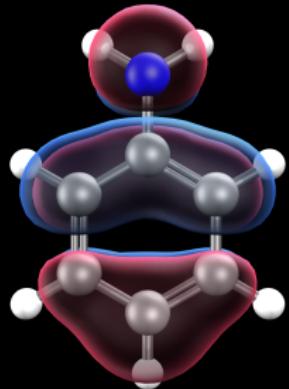


Fluorobenzene

- ▶ Build structures for aniline, benzoic acid and fluorobenzene.
- ▶ Run HF/6-31G energy calculations.
- ▶ For each molecule, plot the HOMO and predict whether the  $\text{NO}_2^+$  electrophile is ortho, meta or para directing.

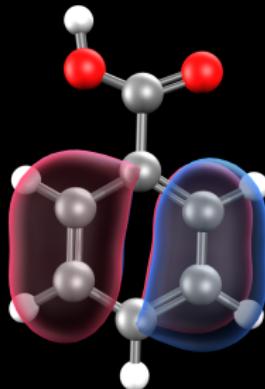


# Results



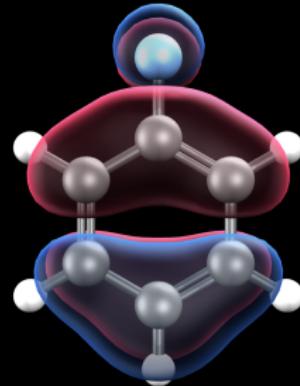
Aniline

Ortho ✓  
Meta ✗  
Para ✓



Benzoic Acid

Ortho ✓  
Meta ✓  
Para ✗



Fluorobenzene

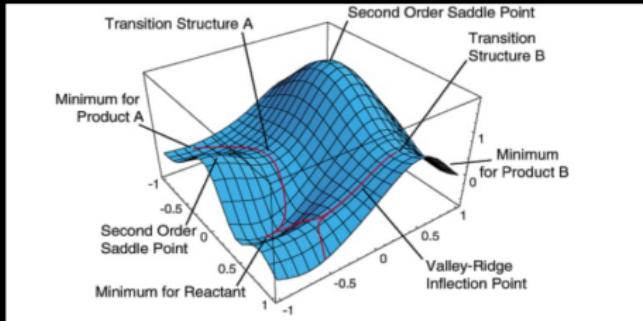
Ortho ✓  
Meta ✗  
Para ✓

Steric hindrance also plays a role.



# Potential Energy Surfaces

Invoking the Born-Oppenheimer approximation gives rise to the concept of a potential energy surface (PES).



Several different types of calculation can be used to explore the PES of a system:

- ▶ PES scan
- ▶ Transition structure search
- ▶ Geometry optimization



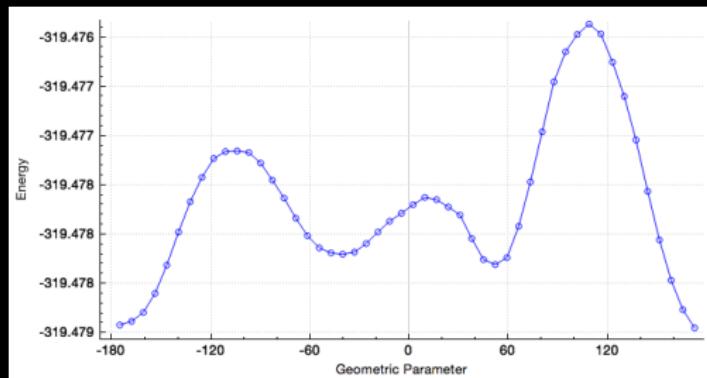
# Exercise

- ▶ Use the Molecule Library to build alanine and optimize the structure using molecular mechanics.
  - ▶ Select the O-C-C-N atoms (in that order!)
  - ▶ Set a dihedral scan coordinate using the Build ▶ Set Geometric Constraint menu option.
  - ▶ Scan between -179 to 155 using 15 steps.
  - ▶ Submit a PES Scan calculation using B3LYP/STO-3G.
- 
- ▶ How many minima do you expect to see on the PES?
  - ▶ What is the barrier to rotation of the C–C bond?
  - ▶ If time permits, you can:
    - ▶ refine your calculation by optimizing the global minimum and maximum
    - ▶ see what effect dispersion has on the results
- (Ask for assistance setting up these calculations)



# Results

- ▶ The PES actually has three minima:

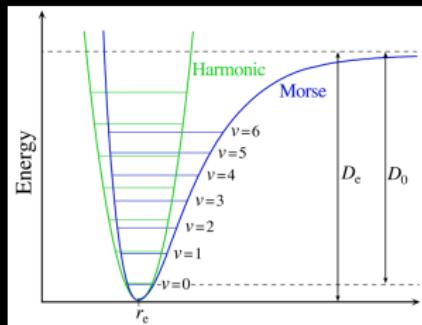


- ▶ The barrier to rotation at B3LYP/STO-3G is about 5.3 kJ/mol ( $\approx 2 \text{ mE}_h$ );
- ▶ The relative stability of the two minima around 0° changes when dispersion is incorporated.



# Vibrational Frequencies

- ▶ Vibrational frequencies can be computed within the harmonic approximation.

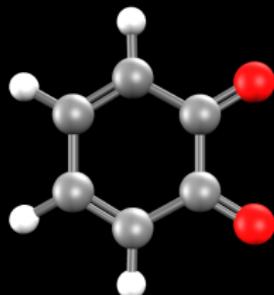


- ▶ Meaningful frequencies must be computed at an energy minimum obtained at the same level of theory.

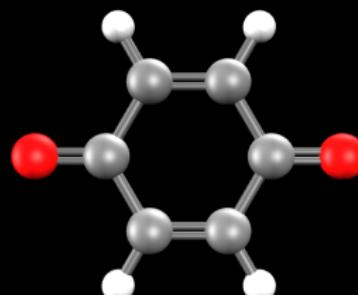


# Exercise

Benzoquinone exists in two isomeric forms:



o-Benzoquinone



p-Benzoquinone

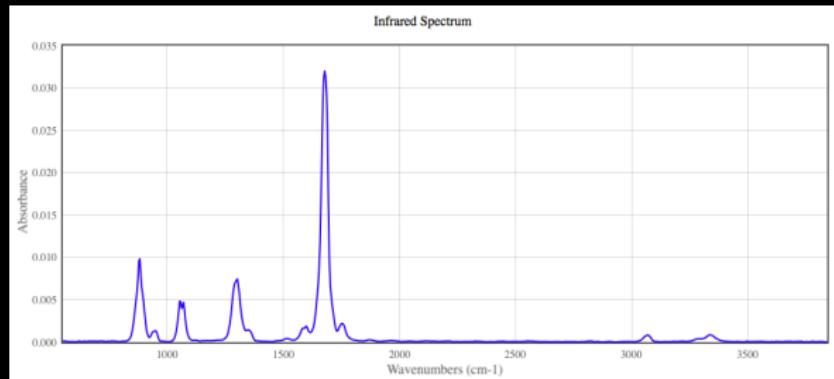
- ▶ Compute the B3LYP/6-31G\* frequencies for these two isomers.

(Remember to optimize the structures first!)



# Exercise

The following IR spectrum of benzoquinone was obtained from the NIST website:

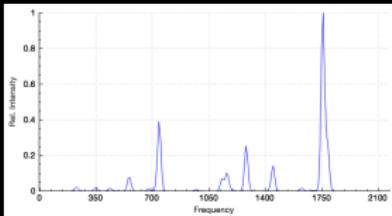


- ▶ To which isomer does this spectrum correspond?
- ▶ Identify the most intense band for each isomer.
- ▶ Characterize the mode that gives the key difference between the isomers.

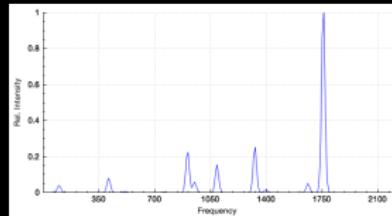


# Results

- ▶ The NIST spectrum is that of p-benzoquinone.
- ▶ The most intense bands both occur at  $1757\text{ cm}^{-1}$  and correspond to the symmetric (o-benzoquinone) and asymmetric (p-benzoquinone) C=O stretches.
- ▶ The out-of-plane wag of o-benzoquinone ( $742\text{ cm}^{-1}$ ) is intense. The corresponding mode in p-benzoquinone is IR silent.



o-Benzoquinone

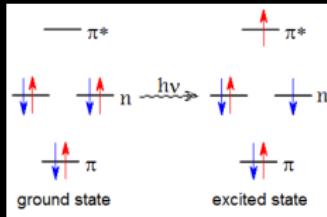


p-Benzoquinone



# Excited States

Electronic excited states are more difficult to compute than the ground state and entail using one of several methods such as CIS or TD-DFT

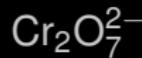
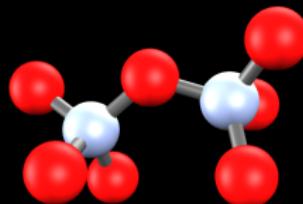


They can be thought of as exciting an electron from an occupied to a virtual orbital, but this picture neglects orbital relaxation.



# Exercise

The chromate and dichromate ions are strongly coloured species. Their colours arise from absorption of photons with energies in the visible part of the electromagnetic spectrum.

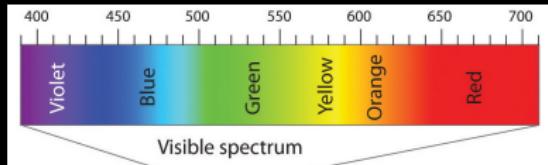


- ▶ Build both ions using the Ghemical force field.
- ▶ Run TD-DFT/SRSC calculations (use 10 roots).
- ▶ Plot relevant MOs to assign any intense transitions in the visible region.
- ▶ Predict what colors you expect the ions to be.



# Results

- ▶ The intense transitions are from the ligands to the metal.
- ▶ Chromate absorbs around 2.1 & 3.1 eV (600 & 400 nm).
- ▶ Dichromate absorbs around 2.2 & 2.4 eV (570 & 530 nm).



$K_2CrO_4$

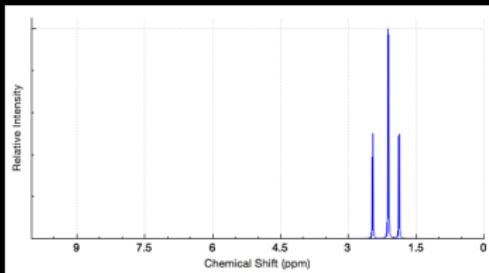


$K_2Cr_2O_7$

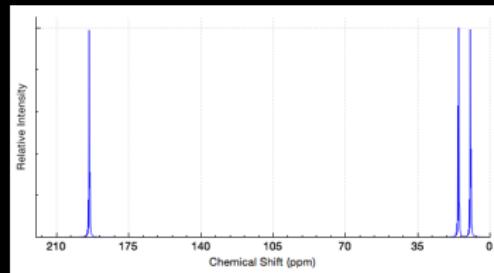


# Exercise

- ▶ Draw as many isomers of  $C_3H_4O$  as you can.
- ▶ Calculate the B3LYP/6-31G\* NMR chemical shifts for each isomer and use these to determine which isomer the following  $^1H$  and  $^{13}C$  spectra correspond to:



$^1H$



$^{13}C$

