The Effect of Basis Sets on Absorption Spectra

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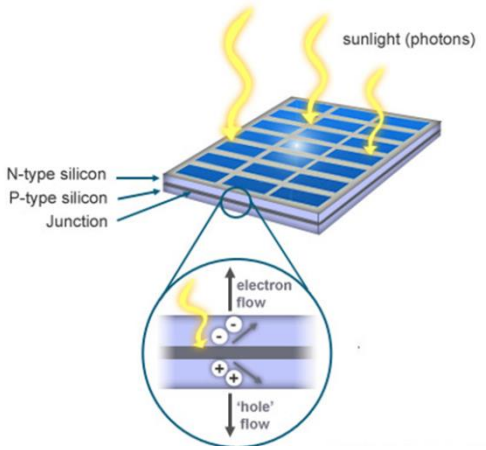
Overview

- Accuracy & prediction
- Design of light absorbing devices
- Density Function Theory (DFT) based approaches
- Basis Set

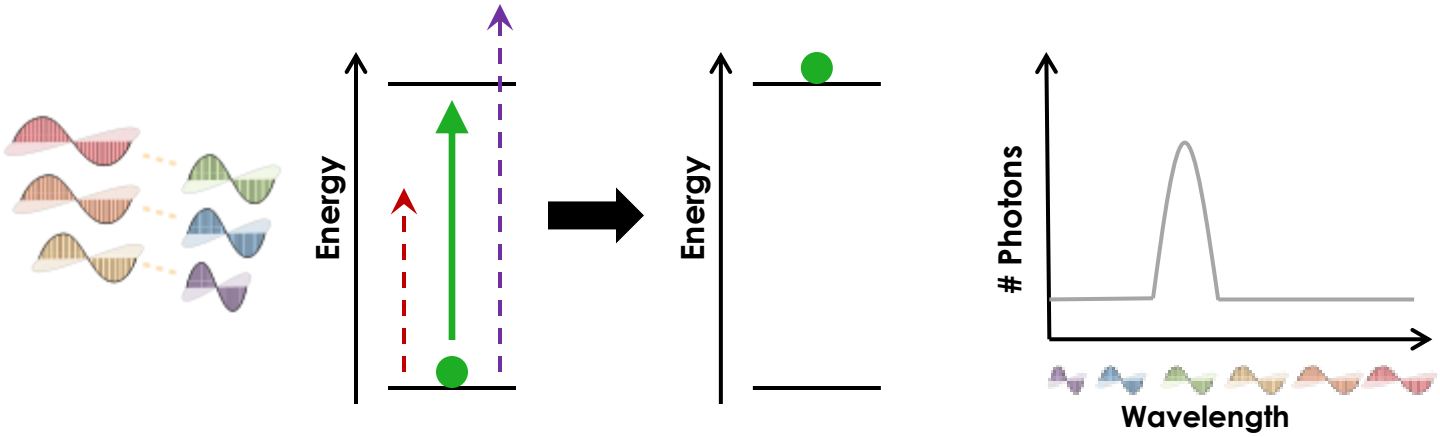


Absorbance Spectra

- A spectroscopic technique that measures the absorption of radiation as a function of wavelength (or energy) of light.

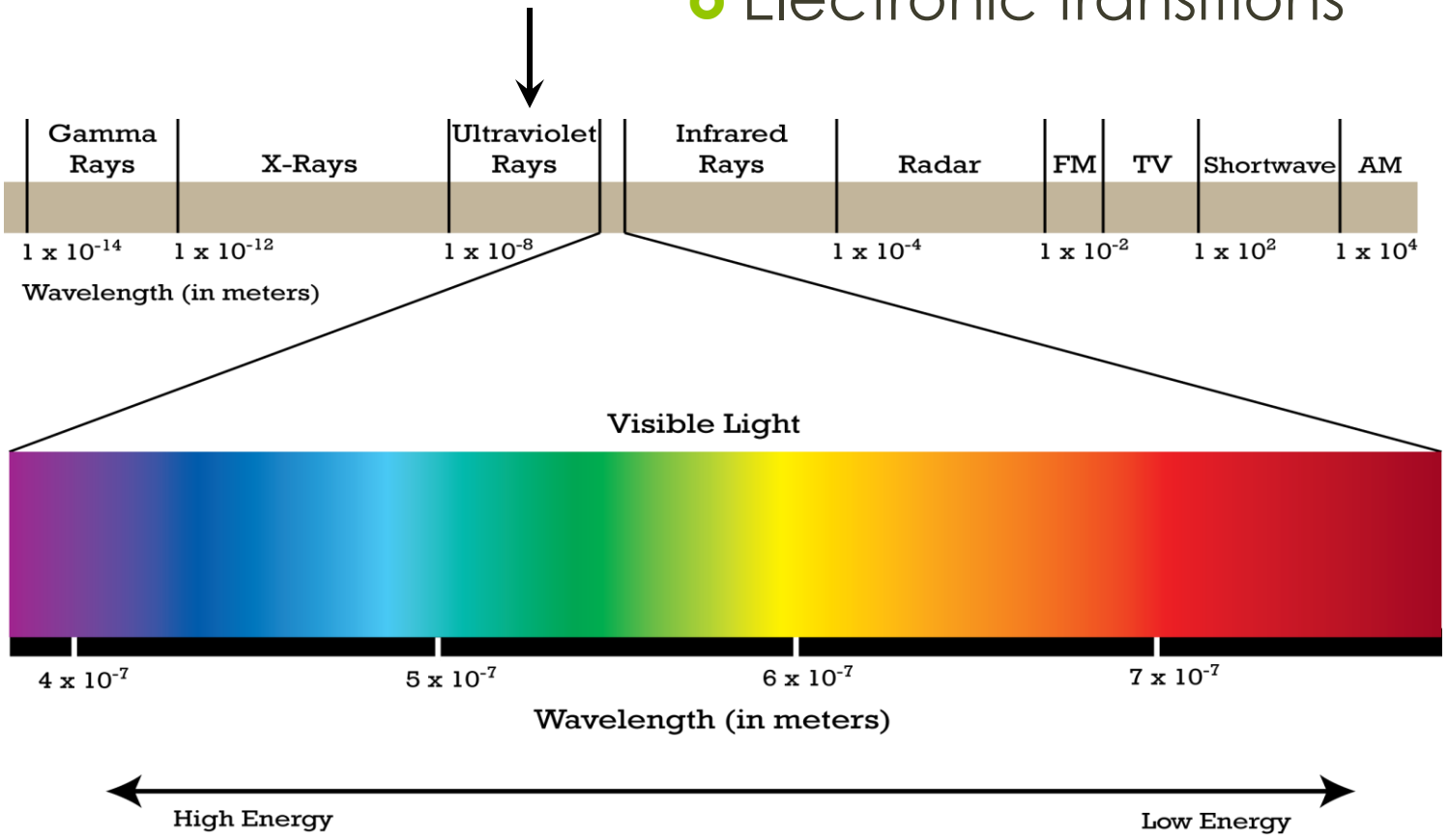
$$A = \varepsilon bc$$

$$E = hv$$



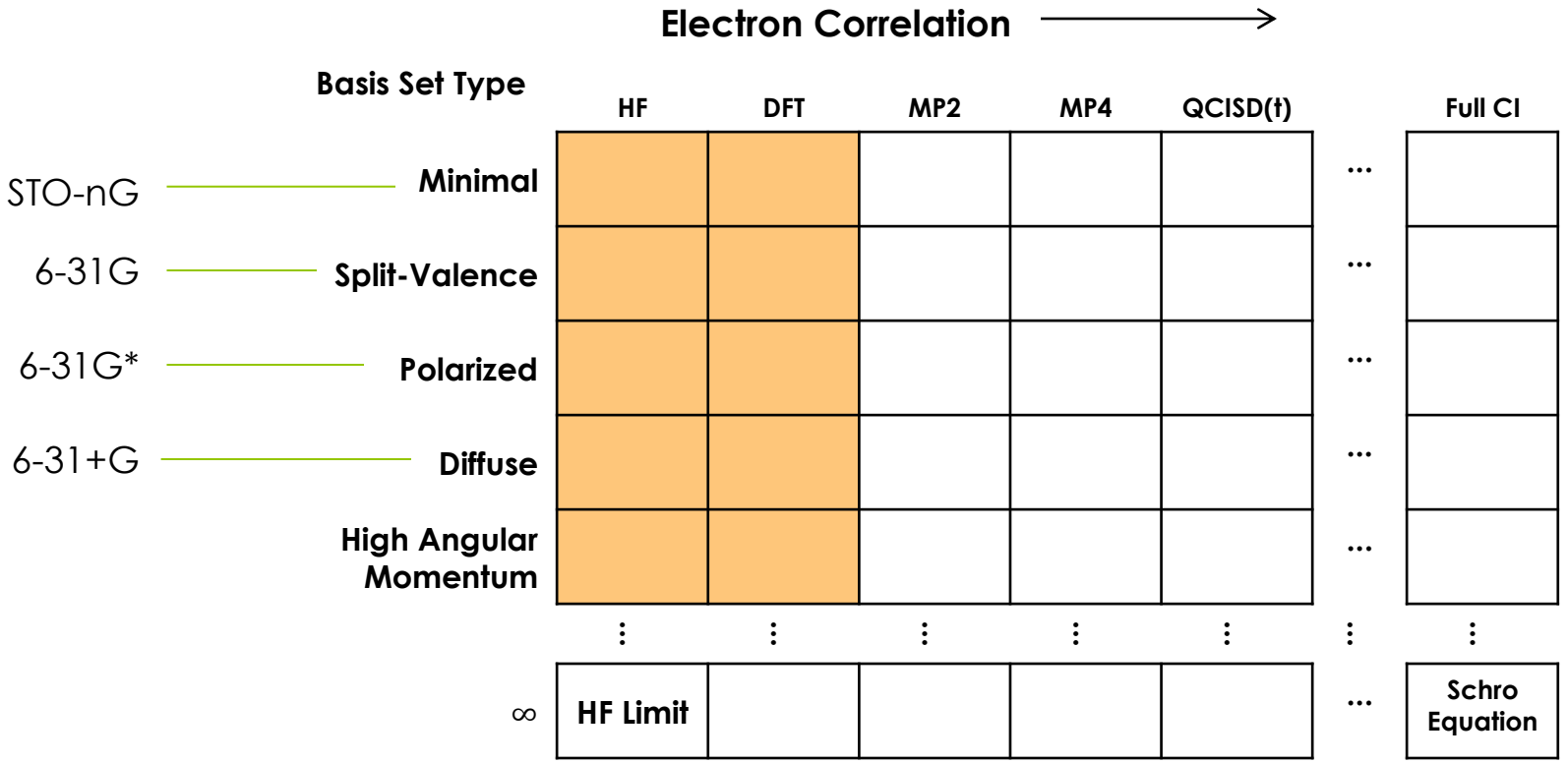
UV-Vis Absorption

- Higher energy
- Electronic transitions



Basis Sets

- A set of functions combined in linear combinations to create molecular orbitals
- Typically atomic orbitals centered on atoms



Types of Basis Sets

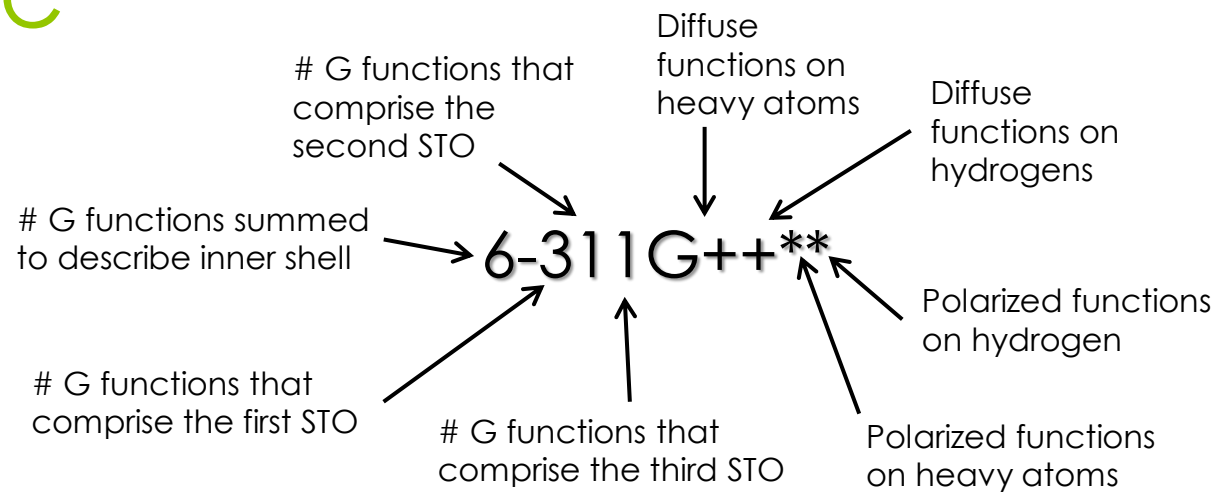
- Minimal (STO-NG)
- Extended Basis Sets
  - Double-Zeta, TZ, QZ

Constant

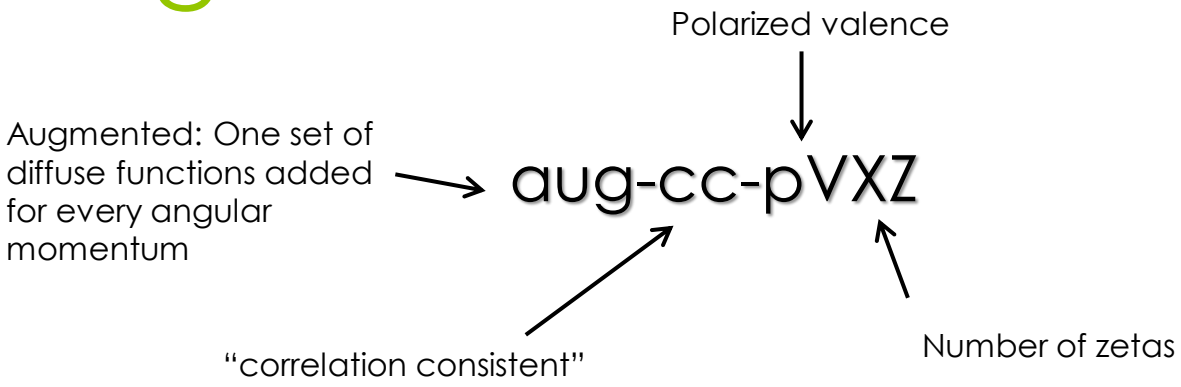
$$\Phi_{2s}(r) = \underbrace{\Phi_{2s}{}^{STO}(r,\zeta_1)}_{\text{Slater Orbital 1}} + \underbrace{d\Phi_{2s}{}^{STO}(r,\zeta_2)}_{\text{Slater Orbital 2}}$$

  - Split-Valence
  - Polarized
  - Diffuse

Pople



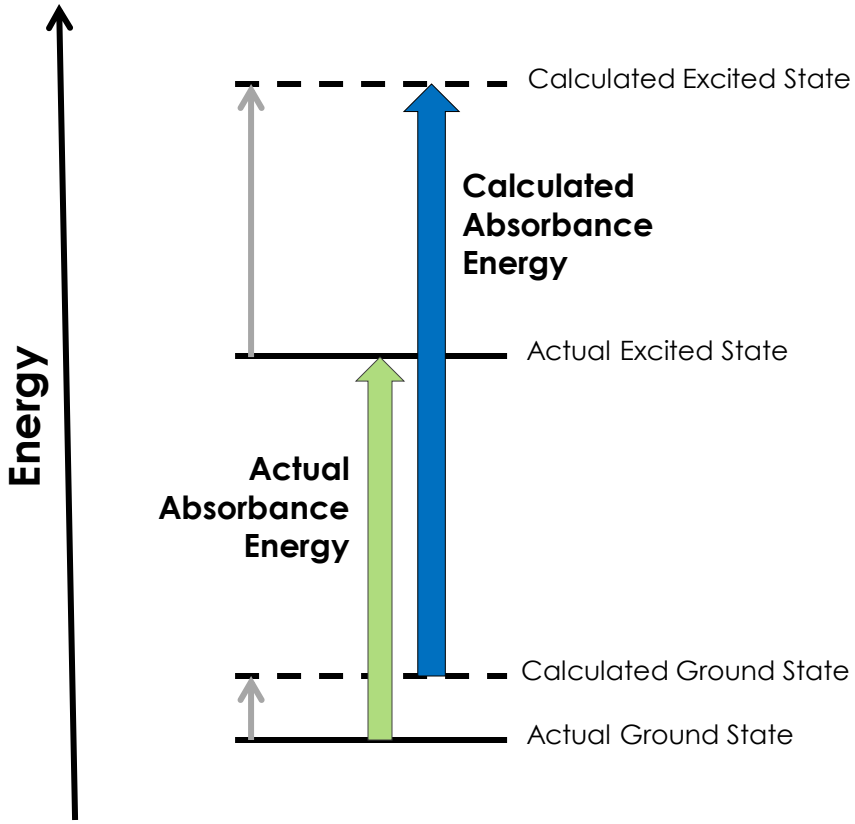
Dunning



Computational Cost

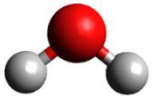
Basis	# of Basis Functions	Relative Time
STO-3G	26	0.05
6-31G	48	0.3
6-31G*	72	1
6-311G*	90	3
6-311G++	264	235
cc-pVTZ	204	82
cc-pVQZ	400	3400
aug-cc-pCVQZ	712	41000

Our Hypothesis

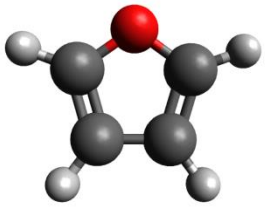


- Calculated state energies are bound (always higher)
- Ground state energies converge faster than excited state energies
- Absorbance energies are the **differences** in energies.

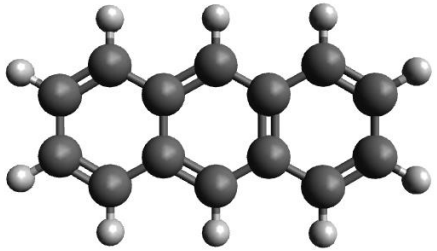
Molecules



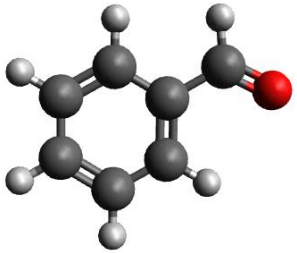
Water



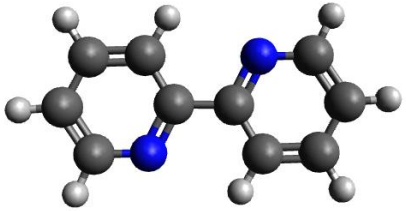
Furan



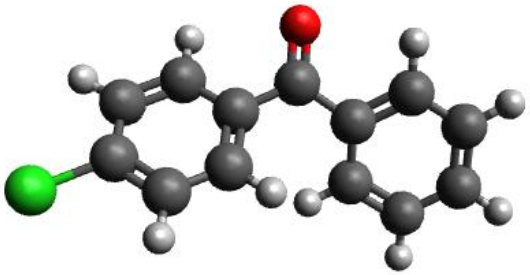
Anthracene



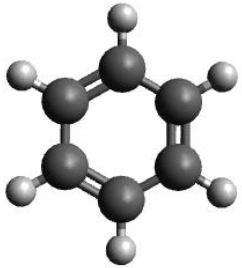
Benzaldehyde



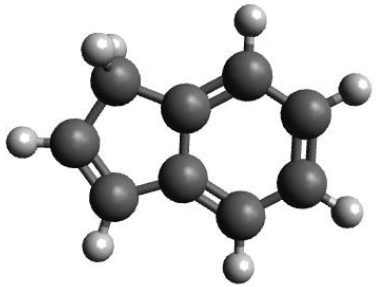
Bipyridyl



Chlorobenzophenone



Benzene



Indene

Parameters

- 6-31G
- 6-31G**
- 6-311G**
- 6-311G++
- cc-pVTZ
- cc-pVDZ
- aug-cc-pVTZ
- aug-cc-pVDZ

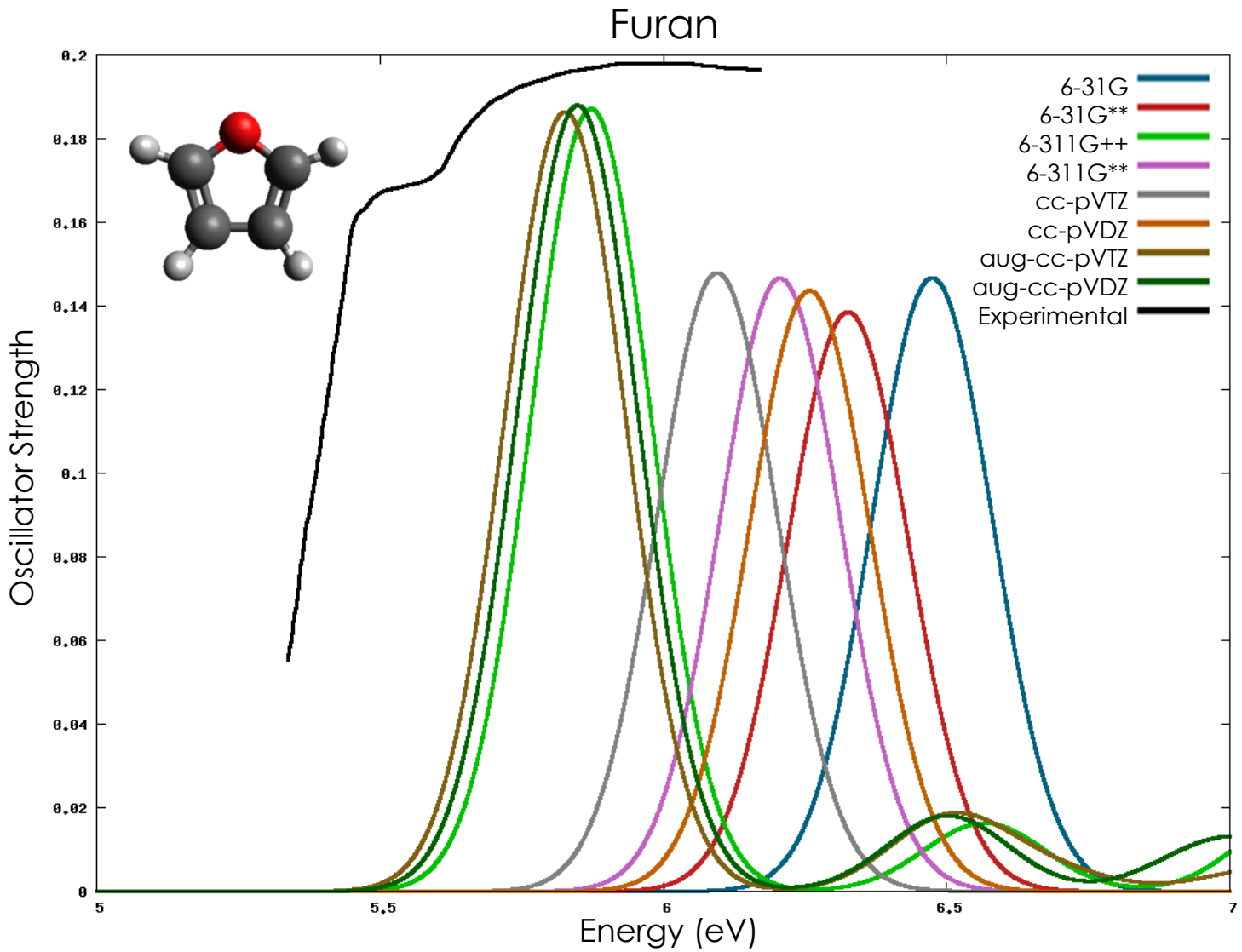
Geometry Optimization

Qchem 4.1
DFT/B3LYP
Basis: LANL2DZ

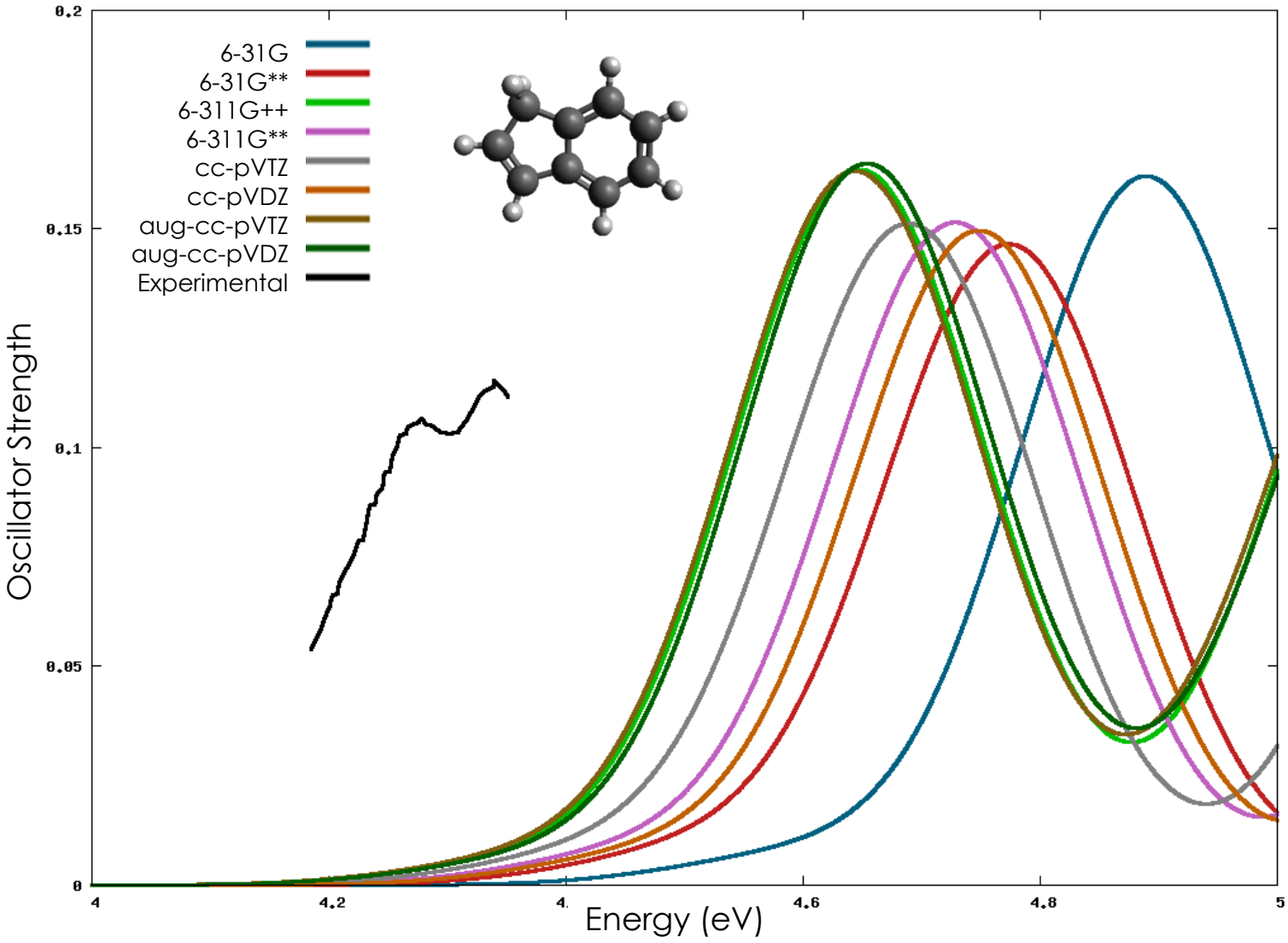
Absorbance Spectra Calculations

Machine: NICS Darter
TD-DFT in NWChem 6.3
DFT/PBE96
Basis Sets: Pople, Dunning

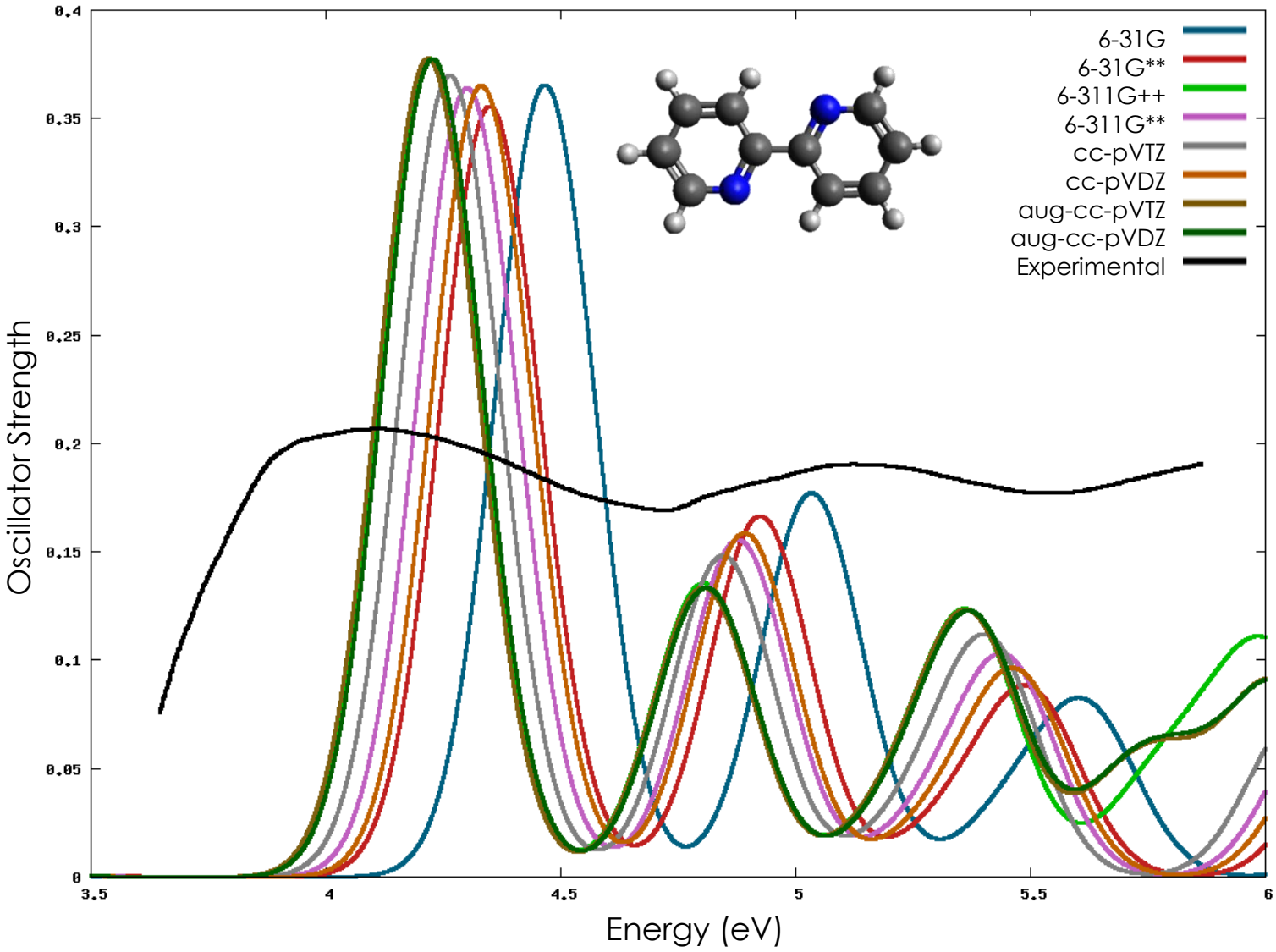
Results


Furan
Oscillator Strength
Energy (eV)
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
5
5.5
6
6.5
7
6-31G
6-31G**
6-311G++
6-311G**
cc-pVTZ
cc-pVDZ
aug-cc-pVTZ
aug-cc-pVDZ
Experimental

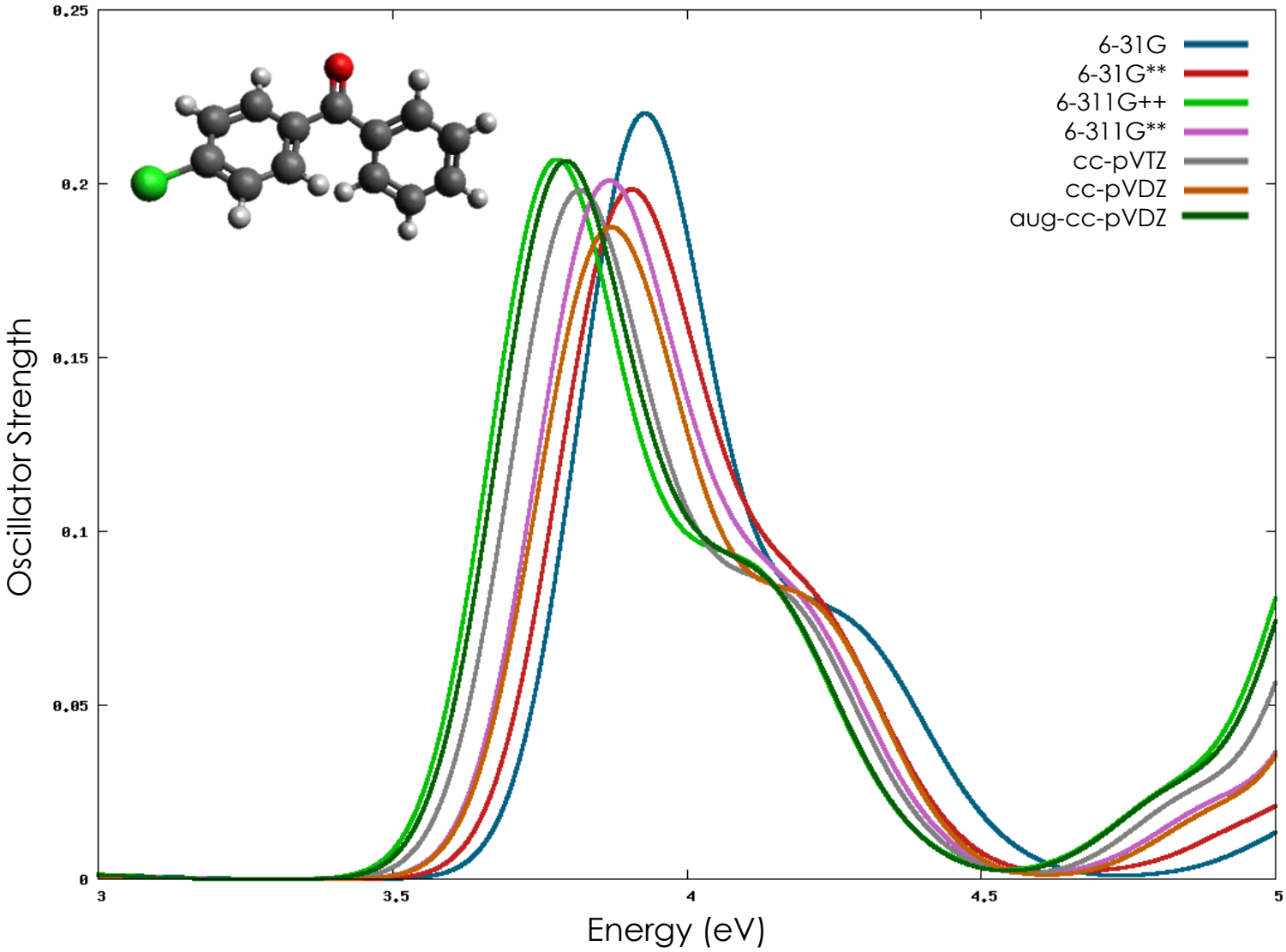
Indene


0.2
0.15
0.1
0.05
0
4
4.2
4.6
4.8
5
Oscillator Strength
Energy (eV)
6-31G
6-31G**
6-311G++
6-311G**
cc-pVTZ
cc-pVDZ
aug-cc-pVTZ
aug-cc-pVDZ
Experimental

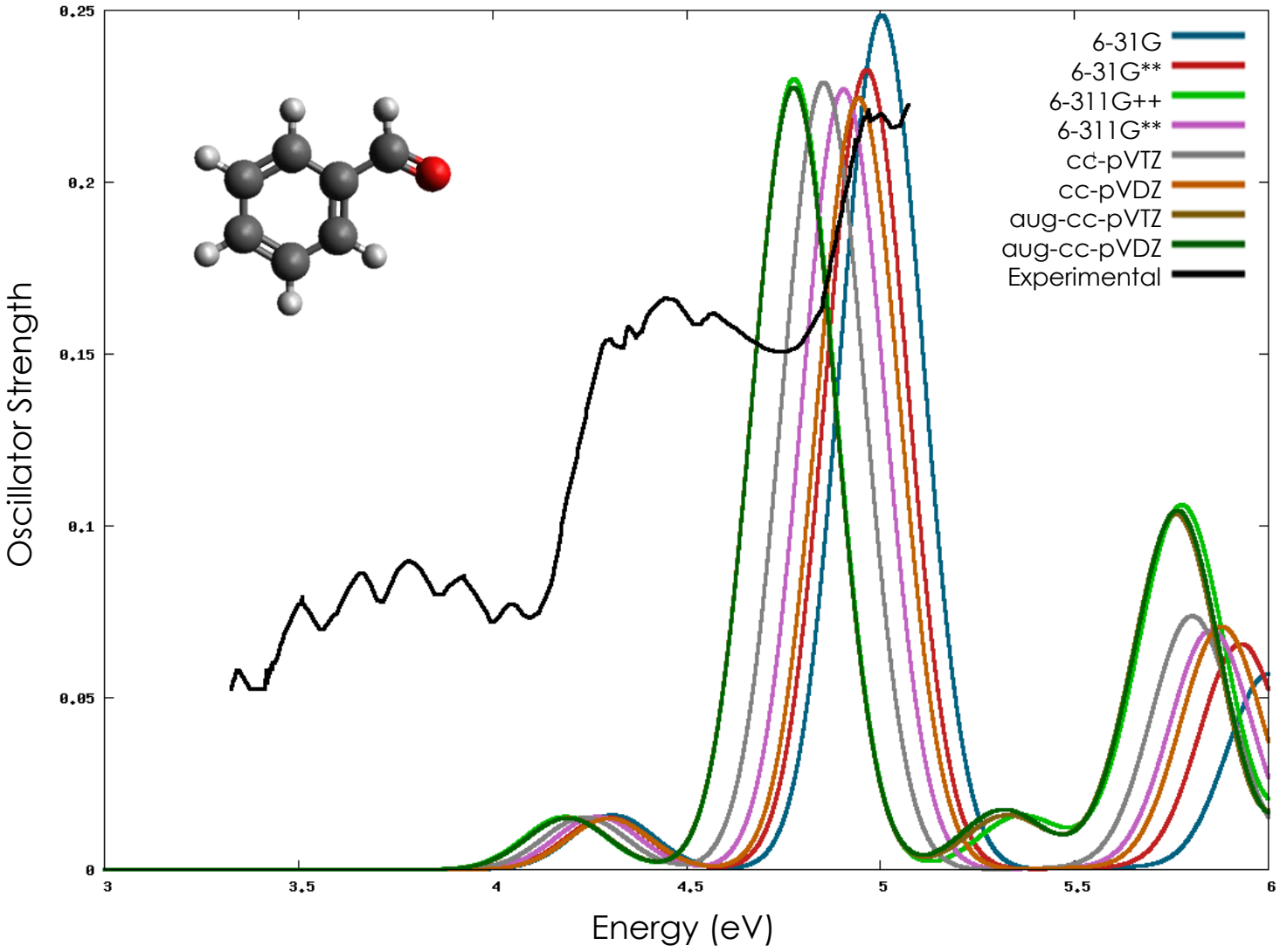
Bipyridyl


Oscillator Strength
Energy (eV)
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
3.5
4
4.5
5
5.5
6
6-31G
6-31G**
6-311G++
6-311G**
cc-pVTZ
cc-pVDZ
aug-cc-pVTZ
aug-cc-pVDZ
Experimental

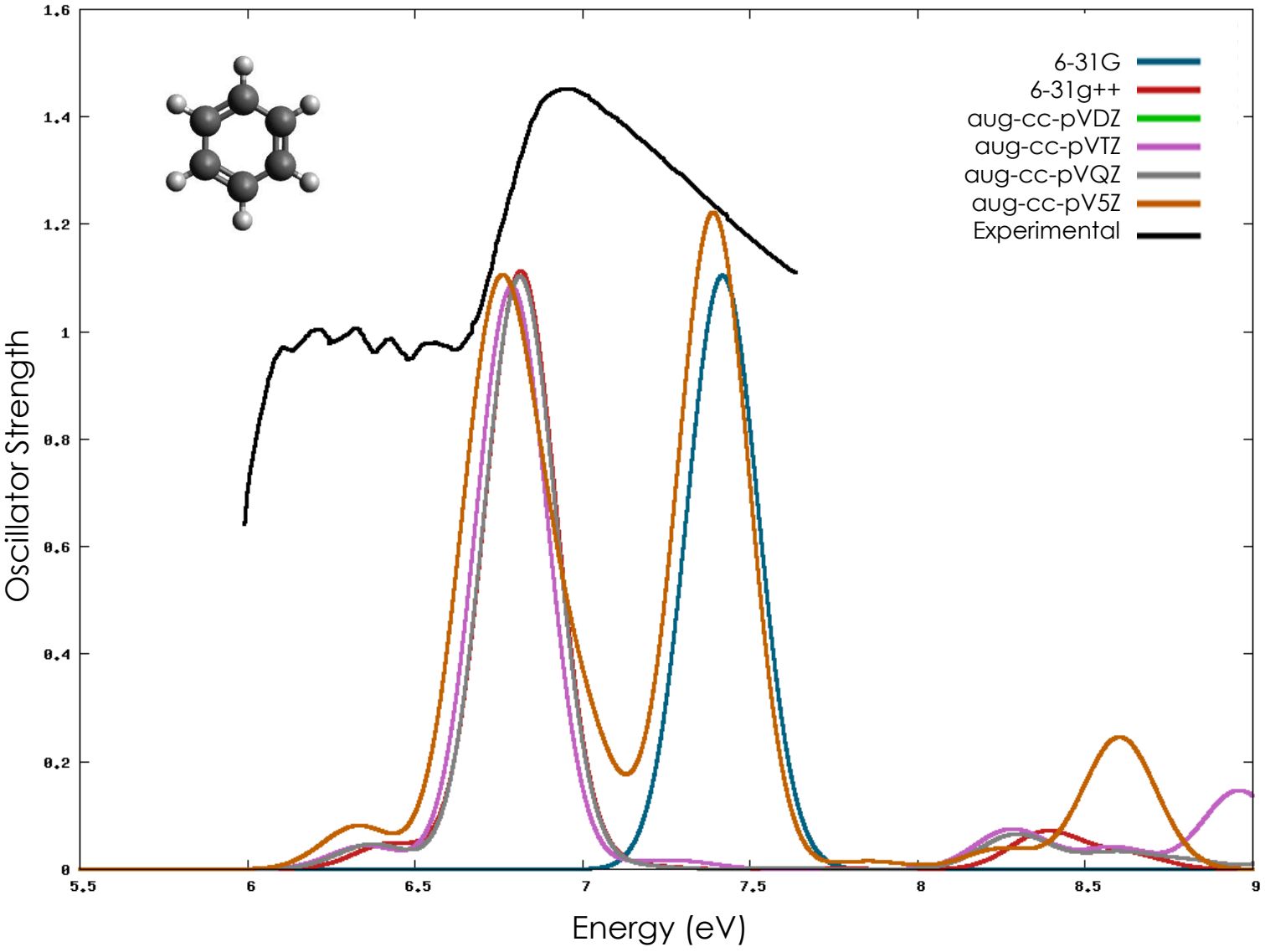
Chlorobenzophenone



Benzaldehyde



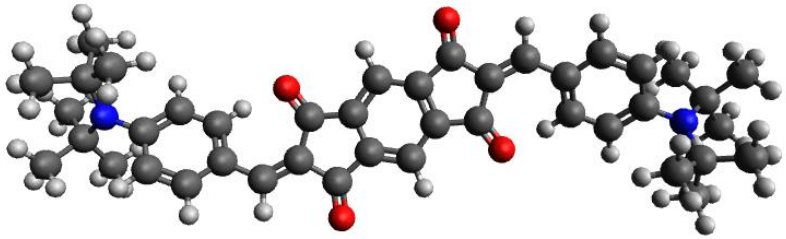
Benzene

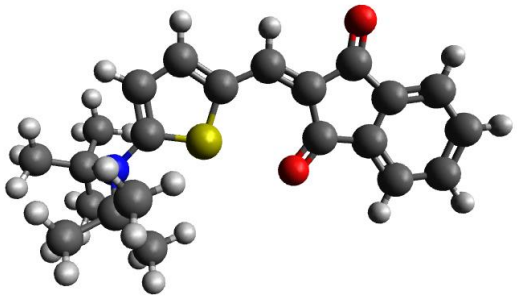

Oscillator Strength
Energy (eV)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
5.5
6
6.5
7
7.5
8
8.5
9
6-31G
6-31g++
aug-cc-pVDZ
aug-cc-pVTZ
aug-cc-pVQZ
aug-cc-pV5Z
Experimental

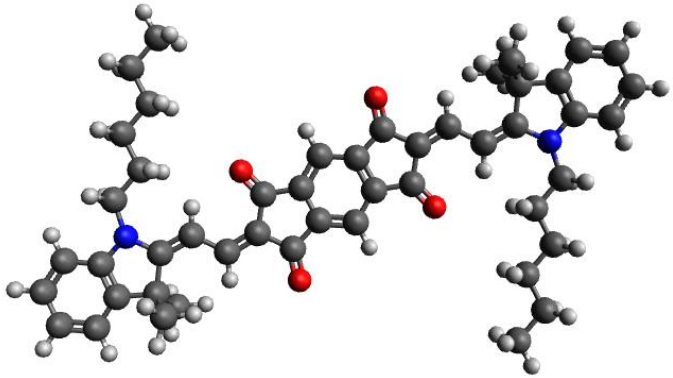
Discussion

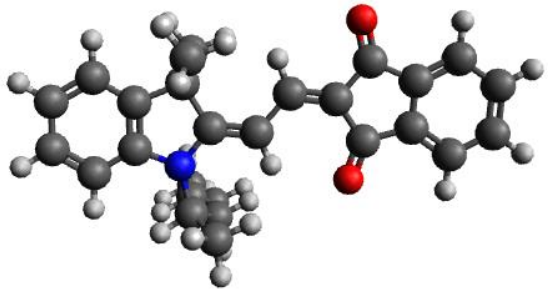
- Red Shifts
- Convergence at augmented polarized basis sets
- Agreeable with UV-Vis experimental data
- cc-pVTZ

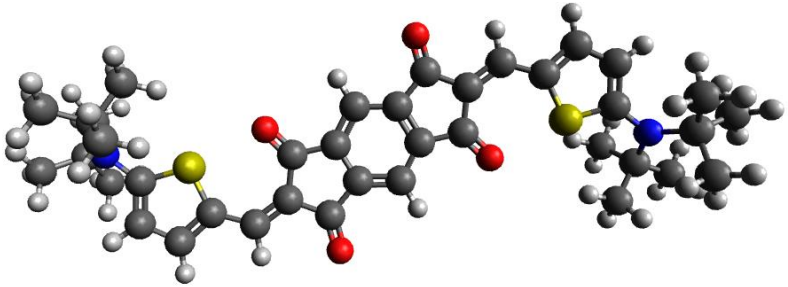
Future Work

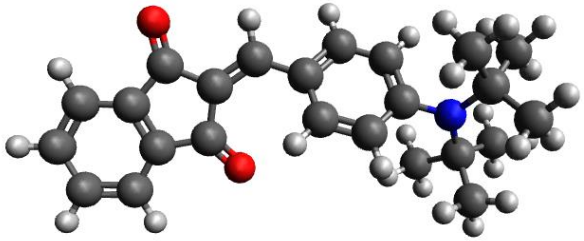












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Acknowledgements

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Questions?