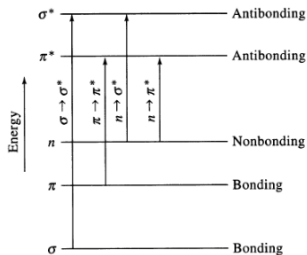


Lesson 12: Calculations of UV/VIS

UV-VIS spectroscopy

- Uses electromagnetic radiation in UV and visible region
- UV light: ~190 to 400 nm
- VIS light: 400 to 700 nm
- Excitations in valence electronic structure
- $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$...

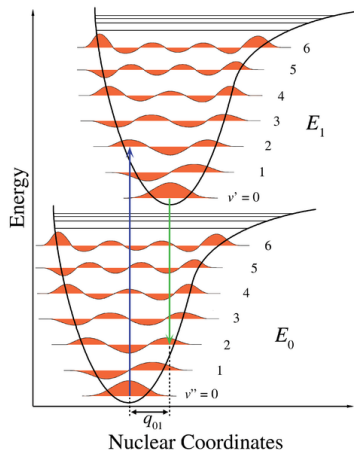


Selection rules

- “Allowed” and “forbidden” transitions
- Nonzero transition dipole moment:

$$\mu_i = \int \Psi_{final} \hat{\mu}_i \Psi_{initial} d\tau \neq 0 \quad (1)$$

- Intensities according to size of TD
- Blue - vertical excitation
- Green - emission



- Vertical excitation energies vs adiabatic excitation energies
- Energy quantum absorbed by molecule
- The time-dependent Schrödinger equation:

$$i \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H}(\mathbf{r}, t) \Psi(\mathbf{r}, t) \quad (2)$$

$$\hat{H} = \hat{T}(\mathbf{r}) + \hat{W}(\mathbf{r}) + \hat{V}_{ext}(\mathbf{r}, t) \quad (3)$$

- Check for low-lying excited states using TDDFT
- Use DFT with caution for molecules with ES lower than ~ 1.5 eV

Gaussian TDDFT output

Excitation energies and oscillator strengths:

Excited state symmetry could not be determined.

Excited State 1: Triplet-?Sym 2.0123 eV 616.12 nm f=0.0000 <S**2>=2.000
35 -> 36 0.70883

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -5142.68752823

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited state symmetry could not be determined.

Excited State 2: Triplet-?Sym 2.0123 eV 616.12 nm f=0.0000 <S**2>=2.000
34 -> 36 0.70883

Excited state symmetry could not be determined.

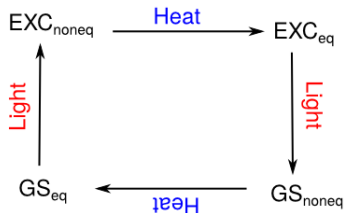
Excited State 3: Singlet-?Sym 2.8399 eV 436.58 nm f=0.0010 <S**2>=0.000
35 -> 36 0.70241

Colors of dihalogens

- Calculate the vertical excitation energies of F_2 , Cl_2 and, Br_2
- Calculate the emission energy from the “allowed” state
- Use PBE1PBE/6-311+G(2d) method

Thermodynamic cycle

- GS - Ground state WF
- EXC - Excited state WF
- eq - equilibrium geometry
- noneq - nonequilibrium geometry



- TDDFT manual page:
- http://www.gaussian.com/g_tech/g_ur/k_td.htm
- Calculate first three excited triplet and singlet states
td=(nstates=3,50-50)
- Select the allowed states and optimize the first excited one:
- opt=readfc td=(nstates=3,{singlets/triplets},root=1,read)
- Excitations/emissions including **solvent effects** are described at Gaussian SCRF manual page

$$\Delta E = \frac{hc}{\lambda} \quad (4)$$