The role of the internal rotation on the 5-benzyluracil excited states

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Theoretical Characterization of Molecular Excited States

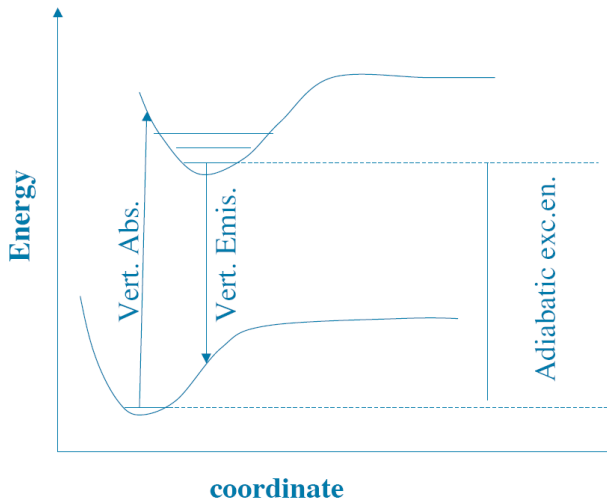– Electronic structure methods for excited states

- **Single reference methods:**
  - TD-DFT
  - EOM-CCSD and EOM-CCSD(T)
  - LT-DF-LCC2

- **Multi configuration reference methods:**
  - MCSCF (CASSCF, RASSCF)
  - MRCI
  - MR-CASPT2

# Potential Energy Surfaces and Excited States

In the simplest case one can calculate excited state energies as energy differences of single-reference calculations.

$$\Delta E = E(excited\ state) - E(ground\ state)$$

This can be done:

1. For states of different symmetry (A', A", etc.)
2. For states of different multiplicity (singlet, triplet)
3. Possibly for states that occupy orbitals of different symmetry

When one is interested in the photochemistry and photophysics of molecular systems the Potential Energy Surface (PES) has to be explored not only in the Franck-Condon (FC) region but also along distorted geometries. Minima, transition states, and conical intersections need to be found (gradients for excited states are needed).
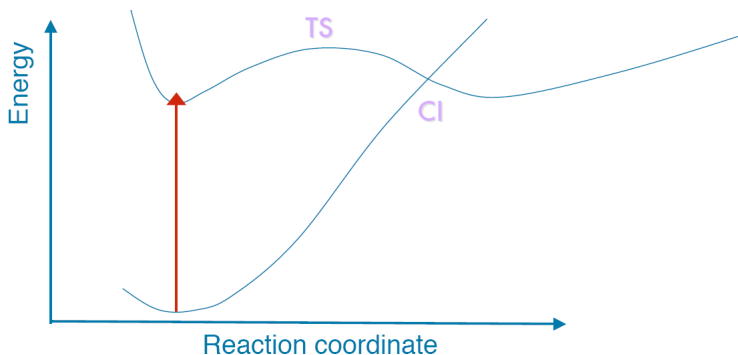
Excited state configurations:

Ground
State

Single excited
Configuration
(Singlet)
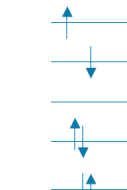
Double excited
Configuration

Why do we need to use multiconfiguration reference methods?

The problem of the electron correlation:

- **Static** – electronic state degeneracy, long-range effect
- **Dynamic** – electron pair correlation (exchange effects), short-range effect

Ground state:

Large Homo-Lumo gap, double occupied states, can be easily treat with single reference method

Excited state:

Small energy difference between electronically excited states (problem of the bond breaking)

Special cases of avoided-crossing or conical intersection, **BUT**

The dynamic correlation is also important !!!

Linear response TDDFT

Consider a small time-dependent external perturbation $\delta V^{ext}(t)$:

$$H'(t) = H + \delta V^{ext}(t)$$

and looking at the linear response of the density

$$\delta\rho(\mathbf{r}t) = \chi(\mathbf{r}t, \mathbf{r}'t')\delta V^{ext}(\mathbf{r}'t')$$

It is possible to derive the excitation energies of the system, as these are simply the poles of the response function:

$\chi(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) =$

$\chi_{KS}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) + \chi_{KS}(\mathbf{r}_1 t_1, \mathbf{r}_2' t_2')(\frac{1}{\mathbf{r}_2' - \mathbf{r}_1'} + f_{xc}(\mathbf{r}_1' t_1', \mathbf{r}_2' t_2'))\chi_{KS}(\mathbf{r}_1' t_1', \mathbf{r}_2 t_2)$

Advantage and Limit of the TDDFT Theory

- TDDFT can predict with much less computational effort the vertical excitation energies.

- TDDFT accurately predicts the shape of the PES of singly excited states in the Frank-Condon region.

- TDDFT fails to accurately describe states with significant doubly excited character.

- TDDFT does predict the existence of intersections between states where they exist according to high level ab initio calculations.

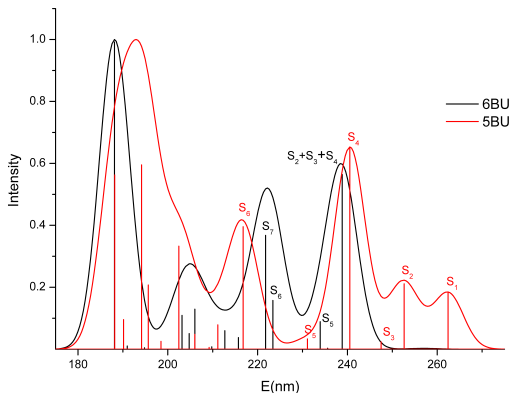## The internal rotation of 5-benzyluracil (5BU)

Rotation of the uracil fragment:
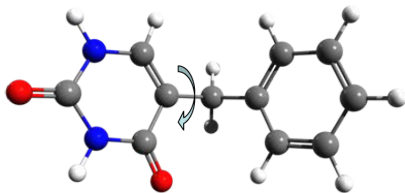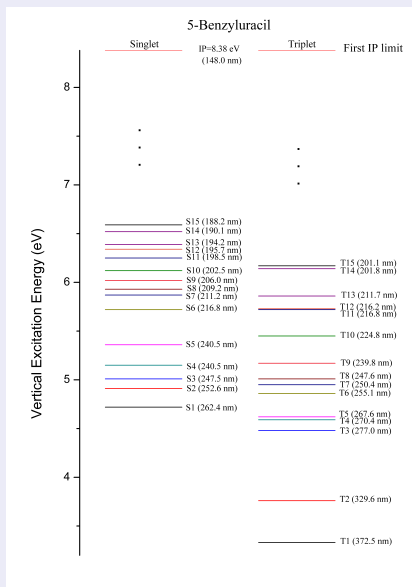

Rotation of the benzene fragment:
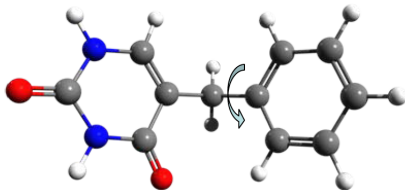
UV – Vis Spectra

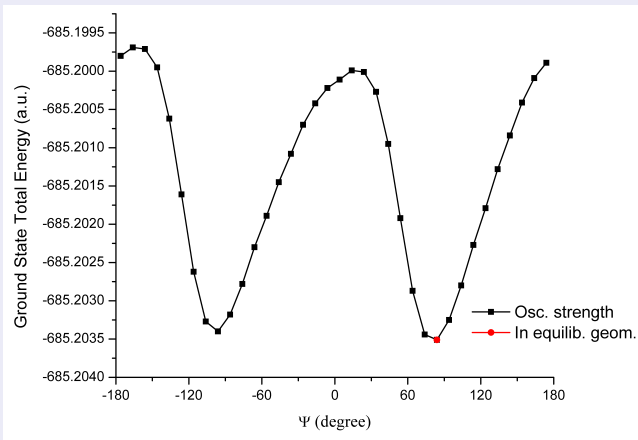

The theoretical UV/Visible absorption spectra for 5-benzyluracil (red line) and 6-benzyluracil (black line).

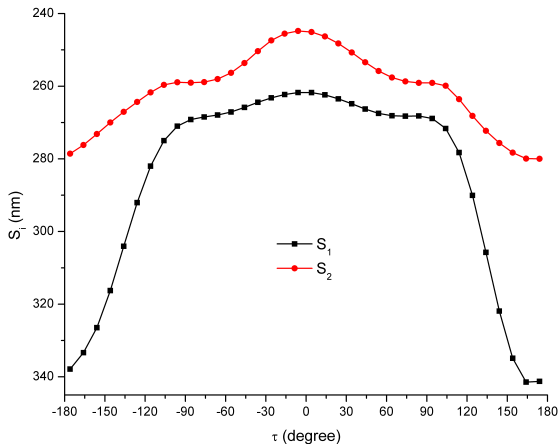# The excitation energy levels of 5BU

5-Benzyluracil

Uracil Rotation

The change of the total energy along the whole internal rotation of the uracil fragment.
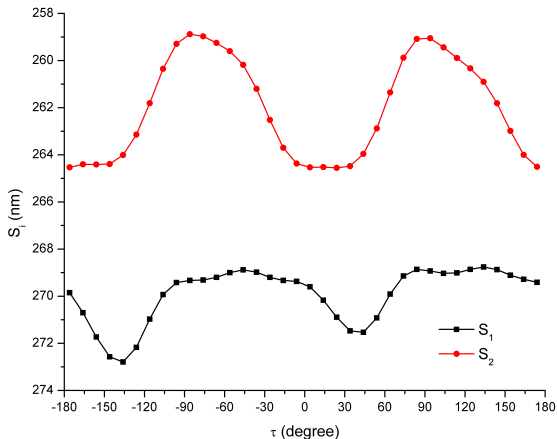
The change of the first and second excited state energies along the whole internal rotation of the $C^4 - C^5 - C - C^a$ axis.
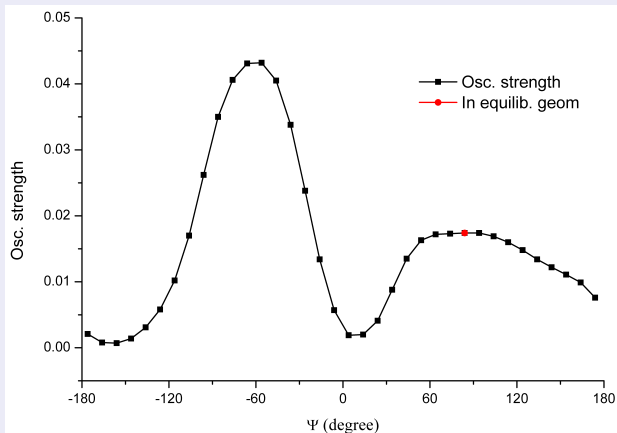
Benzene Rotation

The change of the first and second excited state energies along the whole internal rotation of the $C^5 - C - C^a - C^b$ axis.
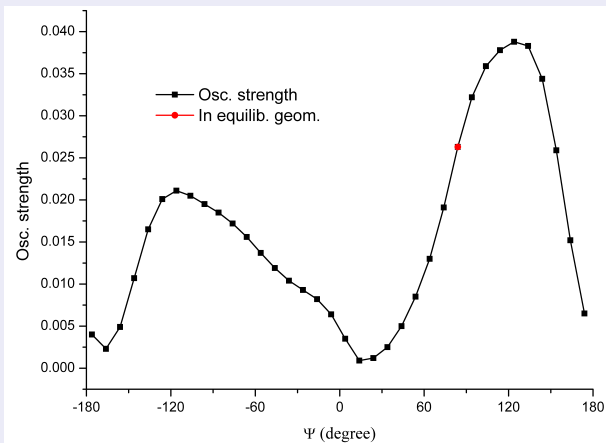
Laser Field Absorption

The change of the laser field absorption at S_1 electronic state during the whole internal rotation around the $C^4 - C^5 - C - C^a$ axis.

Laser Field Absorption

The change of the laser field absorption at S_2 electronic state during the whole internal rotation around the $C^4 - C^5 - C - C^a$ axis.

Conclusions

1. The theoretical UV spectra of the 5-benzyluracil presents significant differences in their absorbtion profile compared to the 6-benzyluracil.

2. The internal rotation of the uracil fragment induces larger spectral shifts than those obtained for the benzene rotation.

3. The equilibrium geometry configuration not always gives the strongest laser field absorbtion, there are other relative conformations obtained by the internal rotation where the absorbtion efficiency is higher.

4. The internal rotation can induce larger bandwidths or line splits for different excited state energy levels.

Thank You for Your Attentions