LOW-LYING EXCITED-STATES OF ACETOPHENONE

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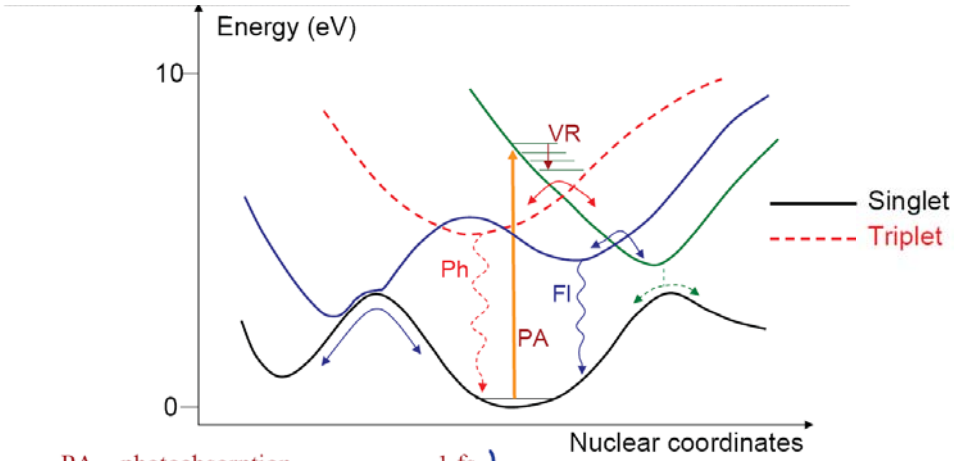
Excited state Dynamics



PA – photoabsorption	1 fs	
conical intersection	$10\text{-}10^2$ fs	*ab initio dynamics*
avoided crossing	$10^2\text{-}10^4$ fs	
VR – vibrational relaxation	$10^2\text{-}10^5$ fs	
intersystem crossing	$10^5\text{-}10^7$ fs	
Fl – fluorescence	$10^6\text{-}10^8$ fs	
Ph – phosforescence	$10^{12}\text{-}10^{17}$ fs	

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

$$\Delta E(ex) = E(ex.s.) - E(gr.s.)$$

This generally can be done:

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

Why do we need to use multiconfiguration reference methods?

The problem of the electron correlation:

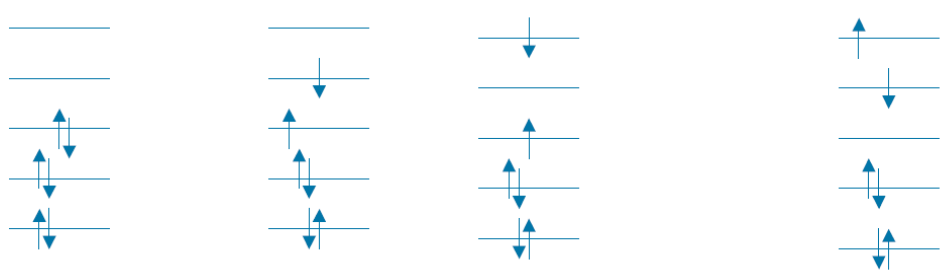
- Static – electronic state degeneracy, long-range effect
- Dynamic – electron pair correlation (exchange effects), short-range effect

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 !!!

Excited state configurations:



Ground State

Single excited configuration (singlet)

Double excited configuration (singlet)

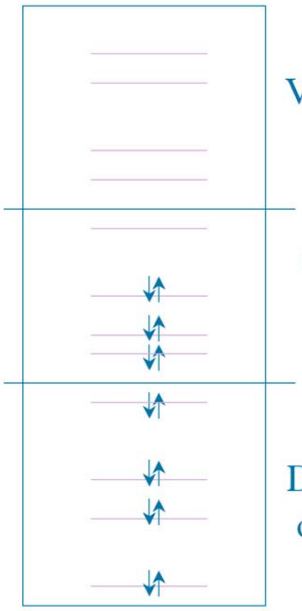
For each electron configuration corresponds a certain Slater determinant

Configurations can be expressed as Slater determinants in terms of molecular orbitals. Since in the nonrelativistic case the eigenfunctions of the Hamiltonian are simultaneous eigenfunctions of the spin operator it is useful to use **configuration state functions** (CSF-s) – spin adapted linear combinations of Slater determinants, which are eigenfunctions of S^2

Singlet CSF

Triplet CSF

CASSCF

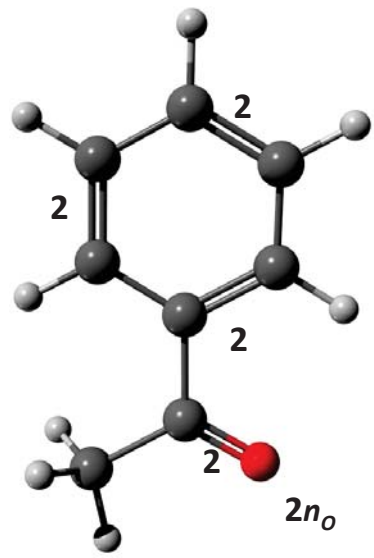


Virtual orbitals

CAS — Active orbital space where the real electronic excitation is considered.

Double occupied orbitals

Choosing the active space:



10 active electrons

5 occupied + 3 virtual orbitals

⇨ **Active space: (10,8)**

Software: Molpro 2012.1

Basis set: def2-tzvp → 4*f* on heavy atoms and 2*p* on H atoms

Methods: State-averaged MCSCF (for geometry, CI)

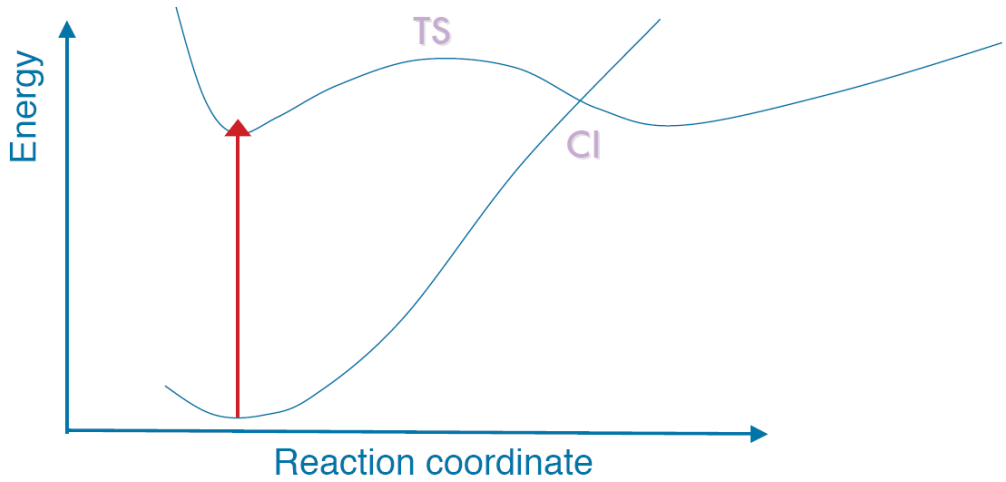
Multi-State CASPT2

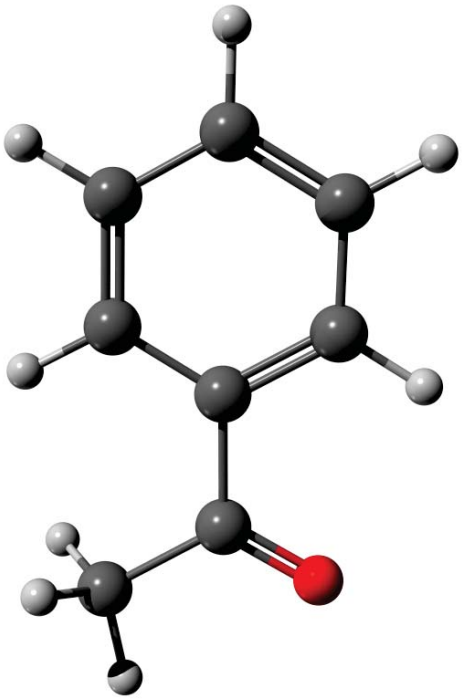
MRCI with Davidson correction

LT-DF-LCC2

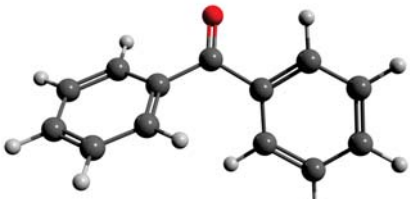
EOM-CCSD

When we are interested in the photochemistry and photophysics of molecular systems the Potential Energy Surface (PES) we have 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).

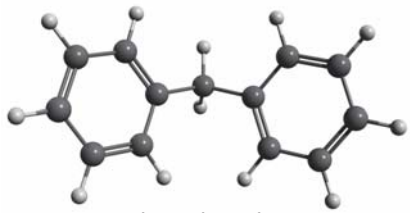




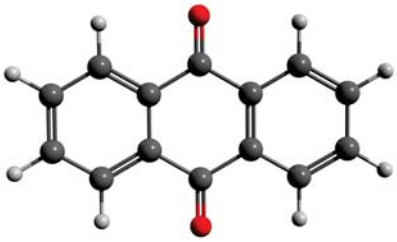
Acetophenone



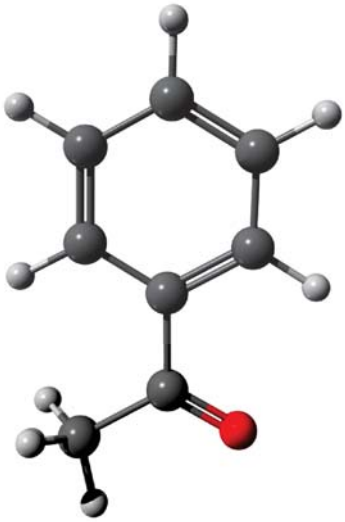
Benzophenone



Diphenylmethane



Anthraquinone



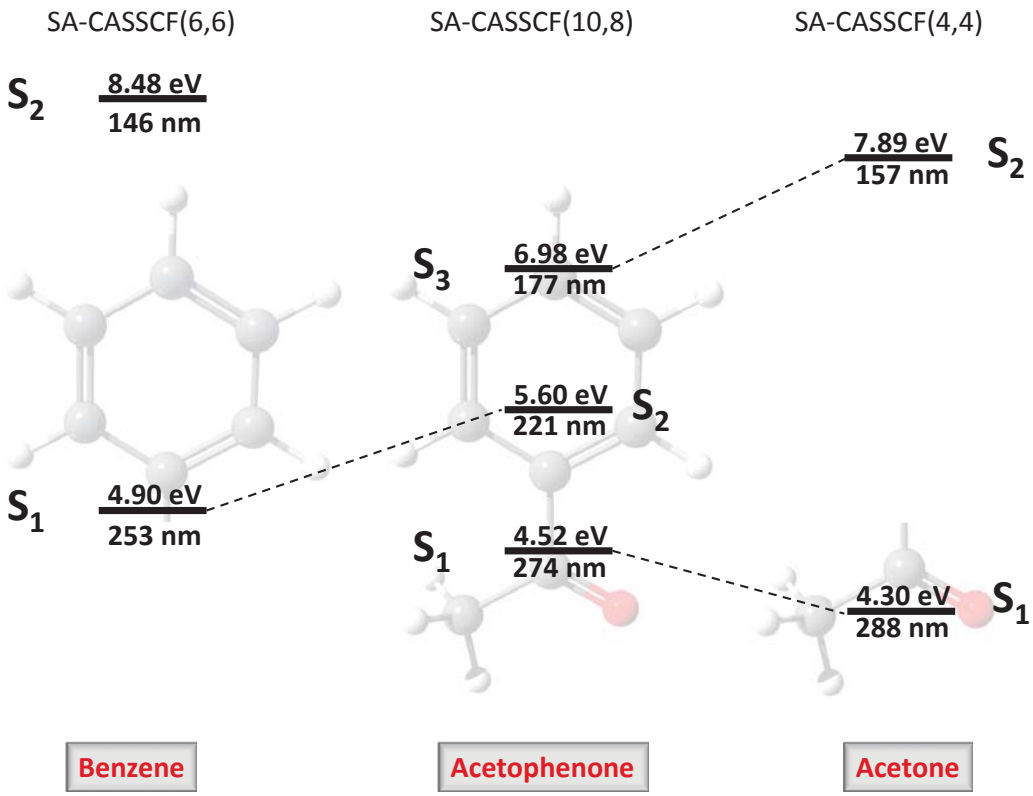
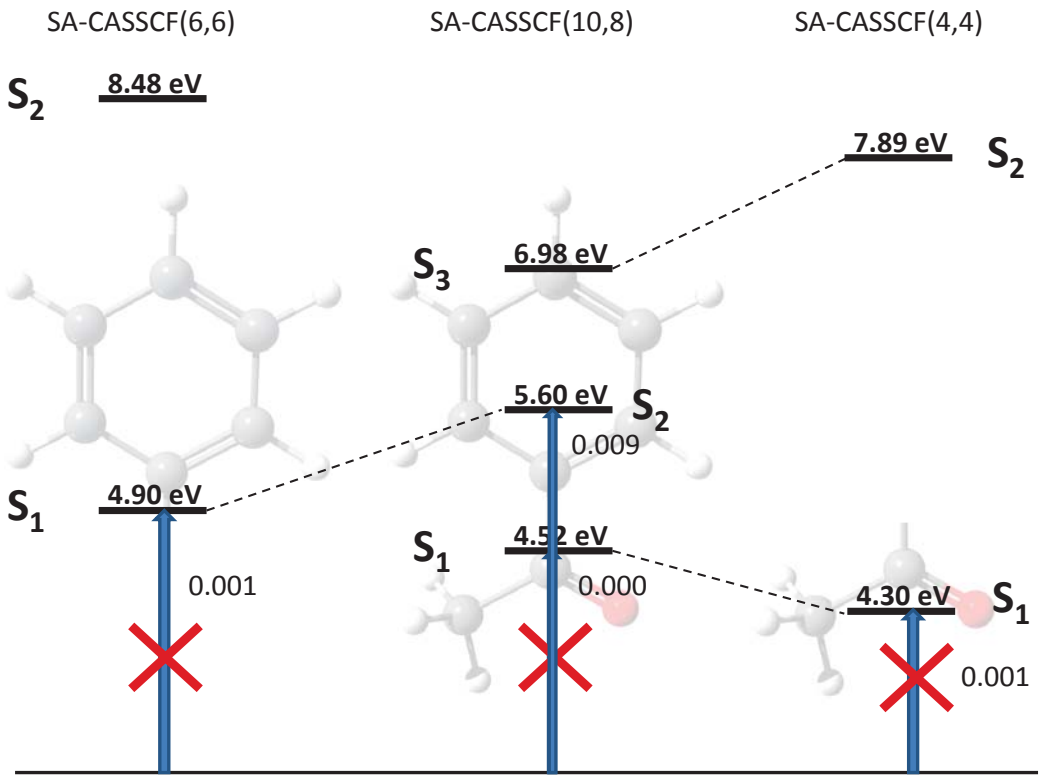
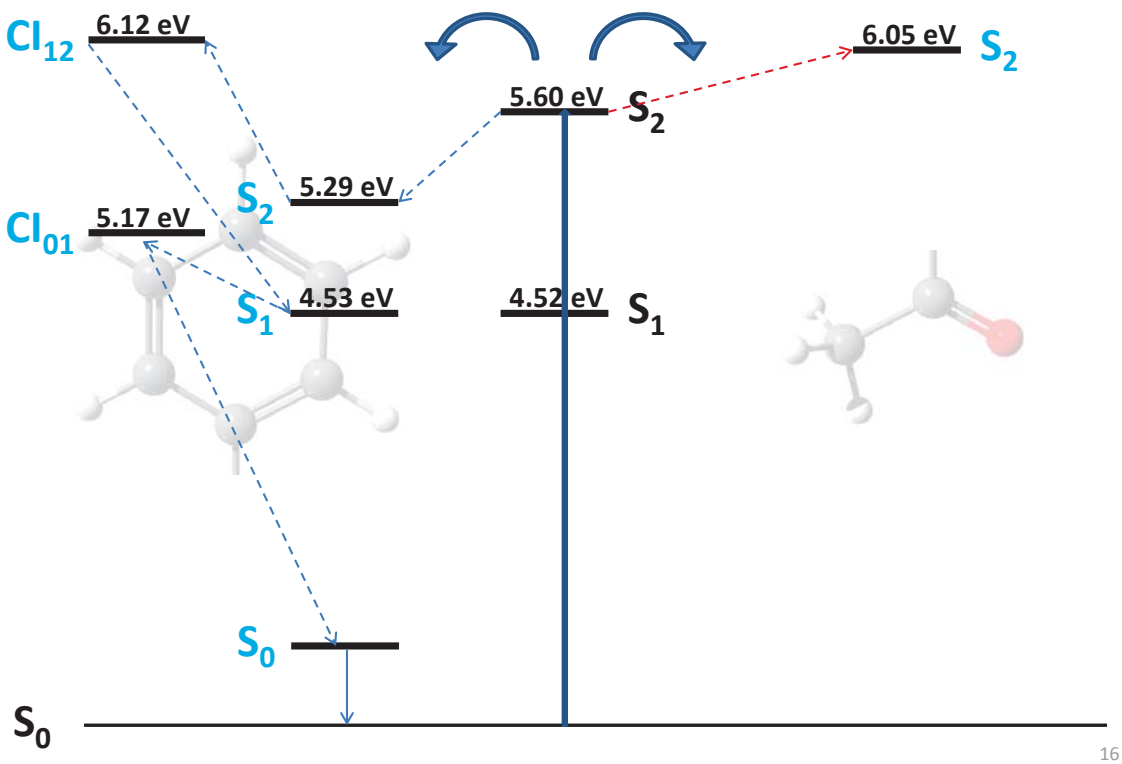


Table 1. Vertical excitation energies (and their oscillator strength in parenthesis) for the two lowest excited states of AP

	S_1 (eV)	S_2 (eV)
AP	$(n\pi^*)$	$(\pi\pi^*)$
SA-CASSCF(10,8)	4.52 (0.0000)	5.60 (0.0091)
MS-CASPT2(10,8)	4.55 (0.0001)	4.85 (0.0068)
MRCI (D) (10,8)	4.65 (0.0001)	4.83 (0.0069)
EOM-CCSD	4.23 (0.0001)	4.97 (0.0077)
LT-DF-LCC2	3.81 (0.0000)	4.90 (0.0088)
Exp.	4.54	5.39


SA-CASSCF(6,6)
SA-CASSCF(10,8)
SA-CASSCF(4,4)
S2
8.48 eV
7.89 eV
S2
S3
6.98 eV
5.60 eV
S2
0.009
S1
4.90 eV
S1
4.52 eV
0.001
0.000
4.30 eV
S1
0.001


Cl12
6.12 eV
6.05 eV
S2
5.60 eV
S2
5.29 eV
S2
Cl01
5.17 eV
S1
4.53 eV
4.52 eV
S1
S0
S0

Conclusions

- The vertical excitation energy levels of the Acetophenone are combinations of benzene and acetone vertical excitation energy levels.
- The first excited state of the Acetophenone is a dark state → we need to include the second excited state.
- The geometry relaxation most probably happens at the benzene branch, reaching the acetone branch relaxation is more difficult.
- The excited state relaxation between S_2 and S_1 state is also difficult to be reached because of the high position of the S_1S_2 conical intersection point
- The singlet → triplet transition could also be a solution.