

HIGHER LEVEL SINGLET-TRIPLET EXCITED  
STATE RELAXATION DYNAMIC PATHWAYS FOR  
ACETOPHENONE AND BENZOPHENONE  
MOLECULAR SYSTEMS

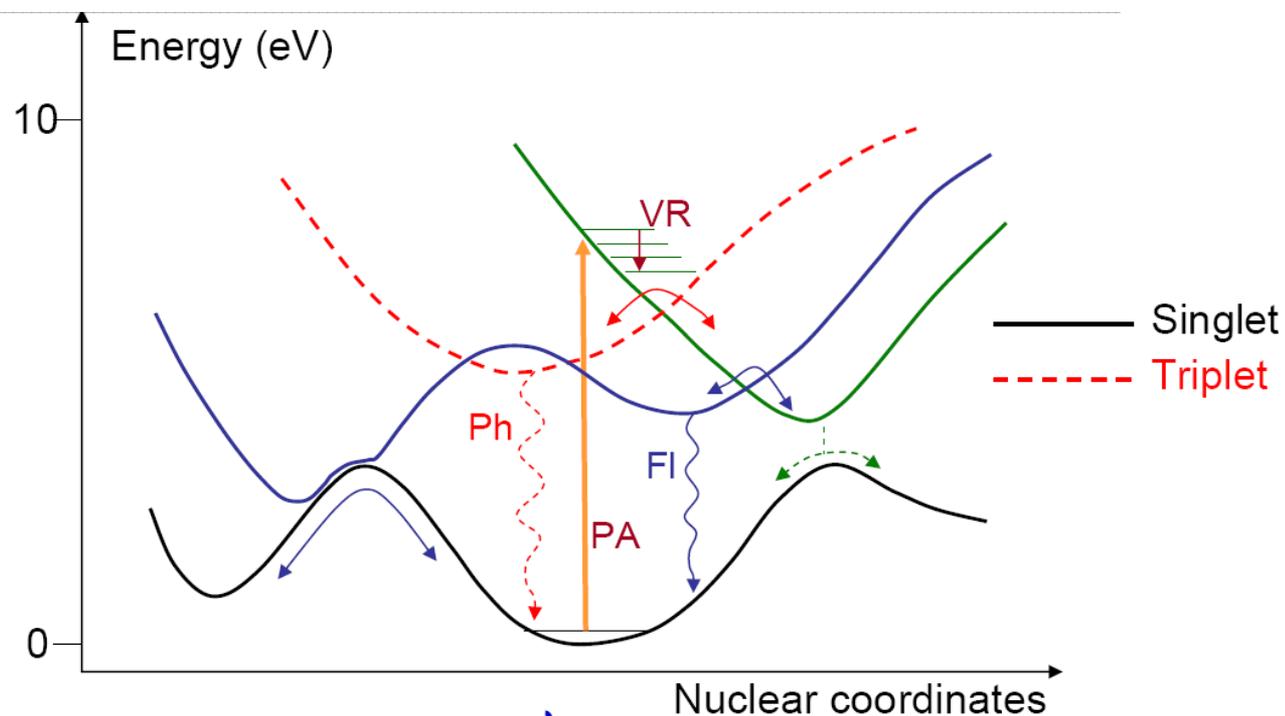
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- 1. Theoretical Background**
- 2. Methods**
- 3. Vertical Excitation Energies**
- 4. Geometry Relaxation**
- 5. Conclusions**

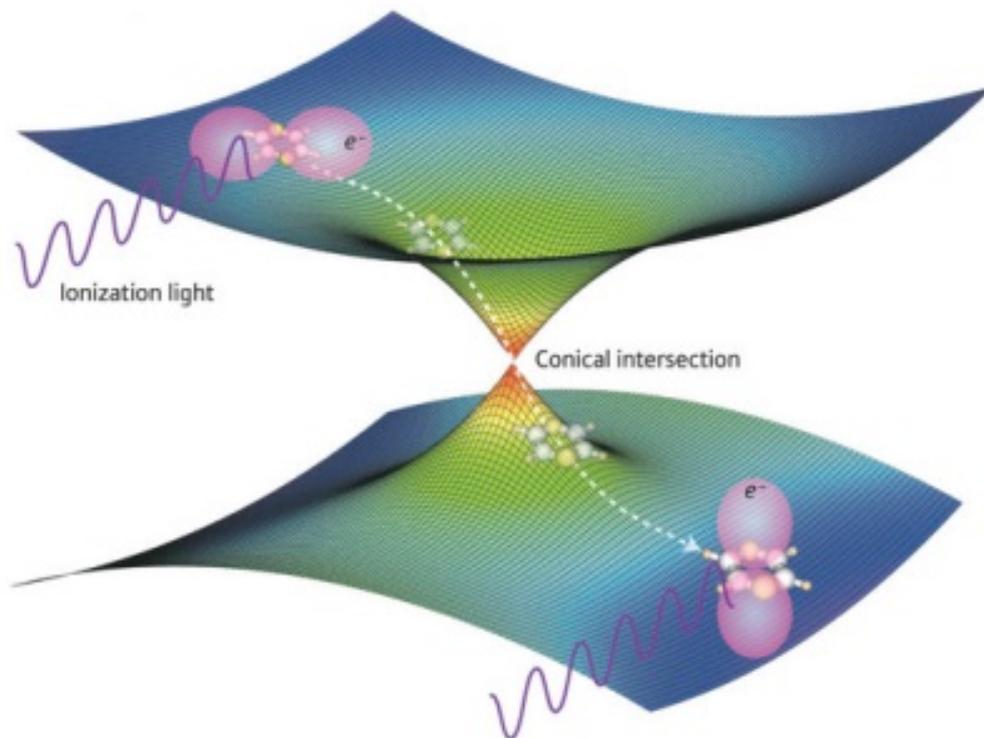
## Excited state Dynamics

## Jablonski-diagram



PA – photoabsorption	1 fs	} <i>ab initio dynamics</i>
conical intersection	10-10 <sup>2</sup> fs	
avoided crossing	10 <sup>2</sup> -10 <sup>4</sup> fs	
VR – vibrational relaxation	10 <sup>2</sup> -10 <sup>5</sup> fs	
intersystem crossing	10 <sup>5</sup> -10 <sup>7</sup> fs	
FI – fluorescence	10 <sup>6</sup> -10 <sup>8</sup> fs	
Ph – phosphorescence	10 <sup>12</sup> -10 <sup>17</sup> fs	

# The topology of potential energy surfaces around the conical intersection point



T. Suzuki – RIKEN Institute

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

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

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

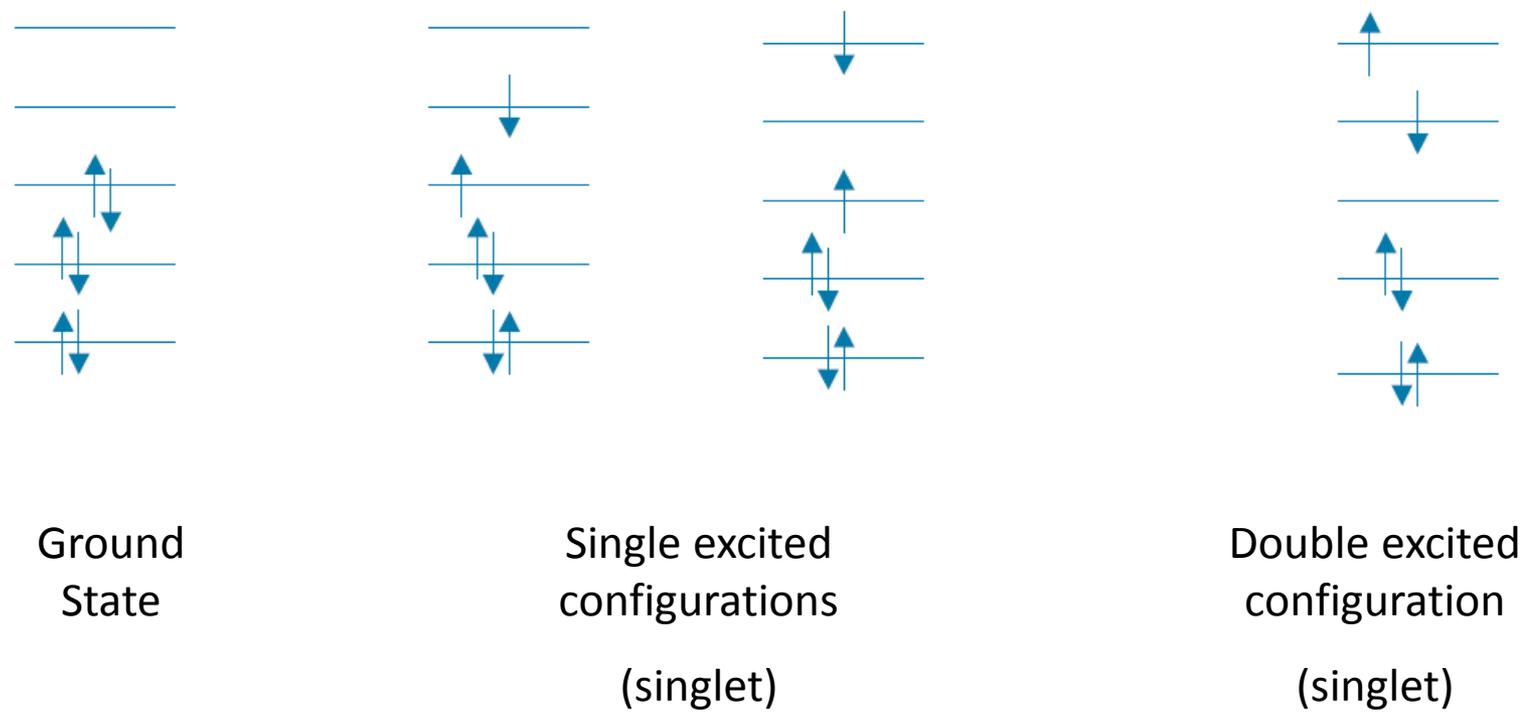
Ground state: Large HOMO-LUMO gap, double occupied states, can be easily treated with **single reference** method

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 !!!

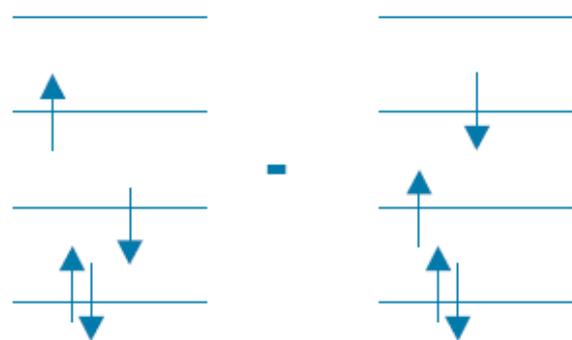
### Excited state configurations:



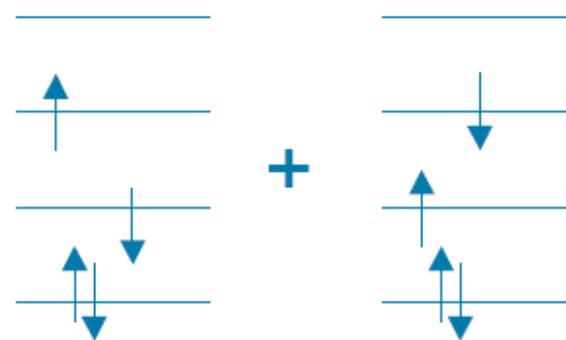
For each electron configuration corresponds a certain Slater determinant

⇒ Needs to consider different Slater determinants for different excited one-electron configuration.

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  $S^2$

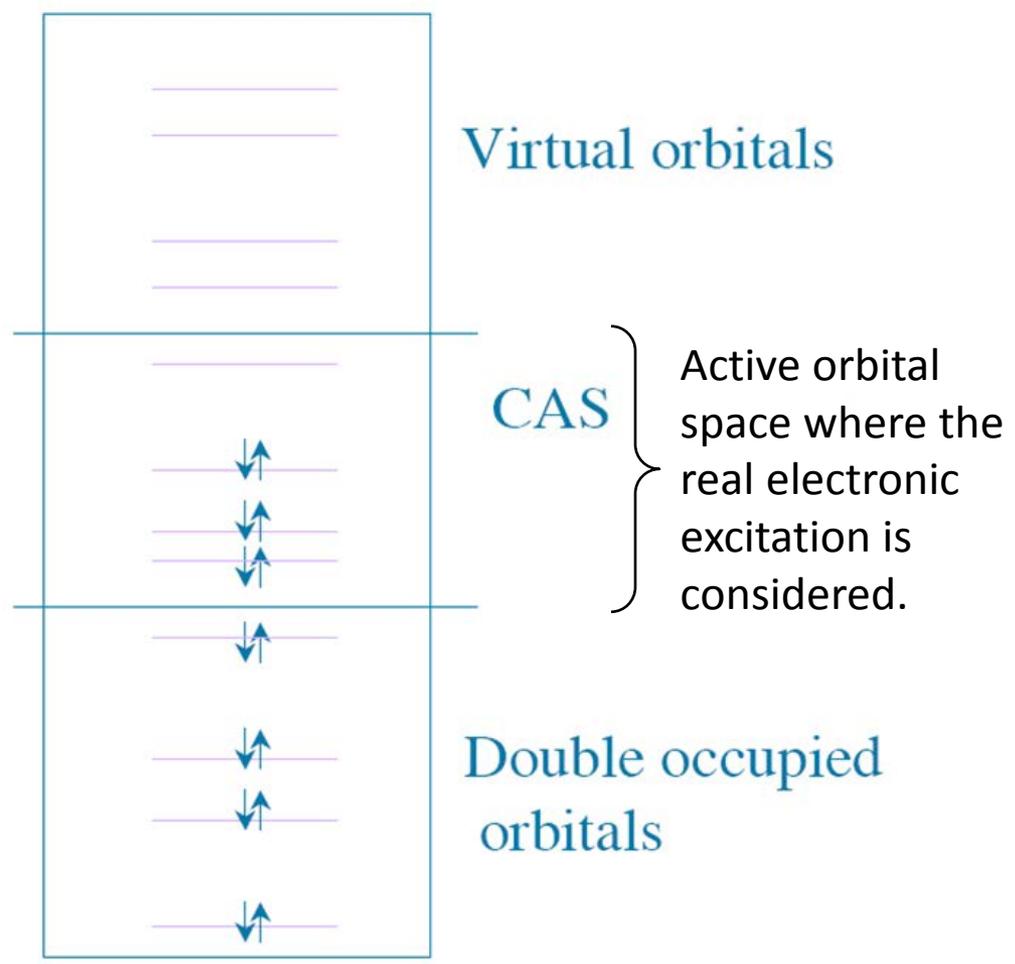


Singlet CSF

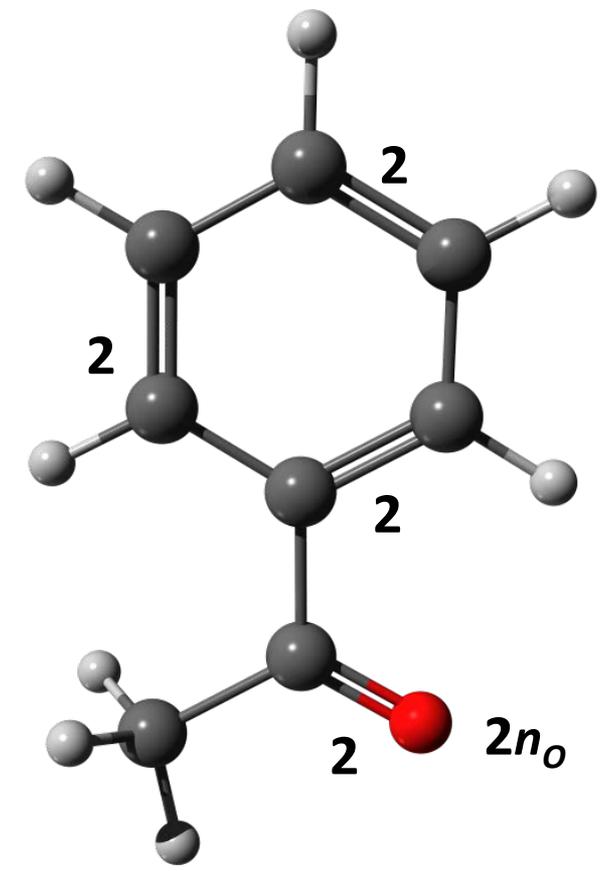


Triplet CSF

# CASSCF



## Choosing the active space:



10 active electrons  
 (8 π + 2 lone pair electrons)  
 5 occupied + 3 virtual orbitals



**Active space: (10,8)**

**Software: Molpro 2012.1**

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

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

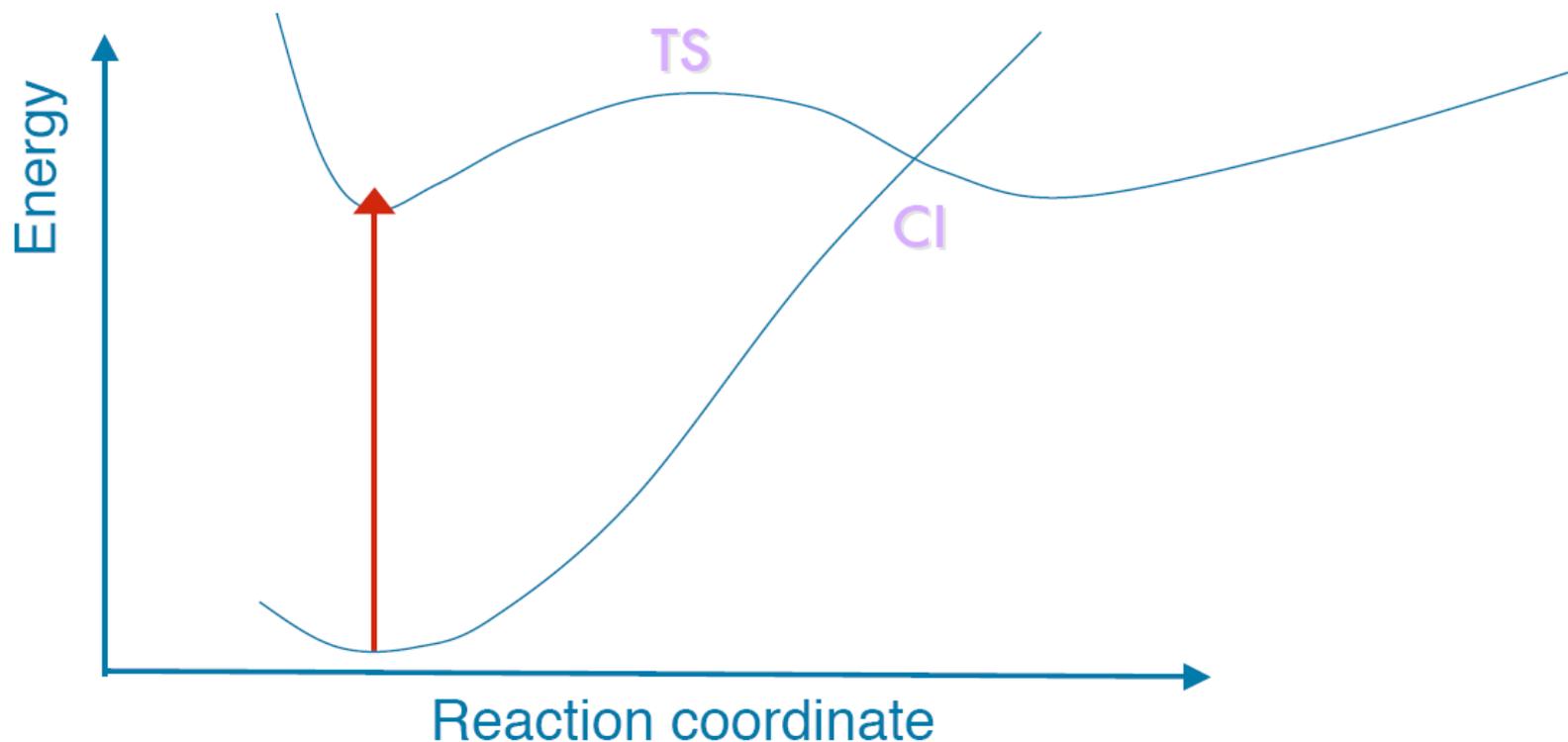
**Multi-State CASPT2**

**MRCI with Davidson correction**

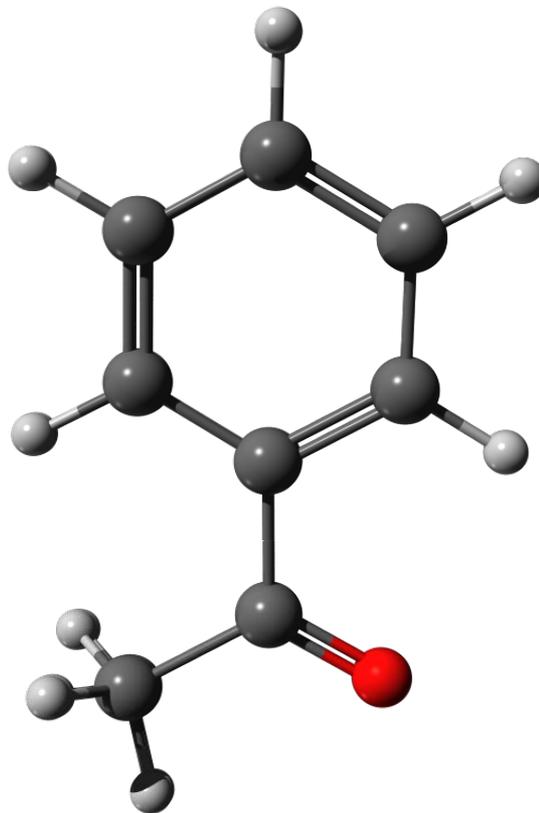
**LT-DF-LCC2**

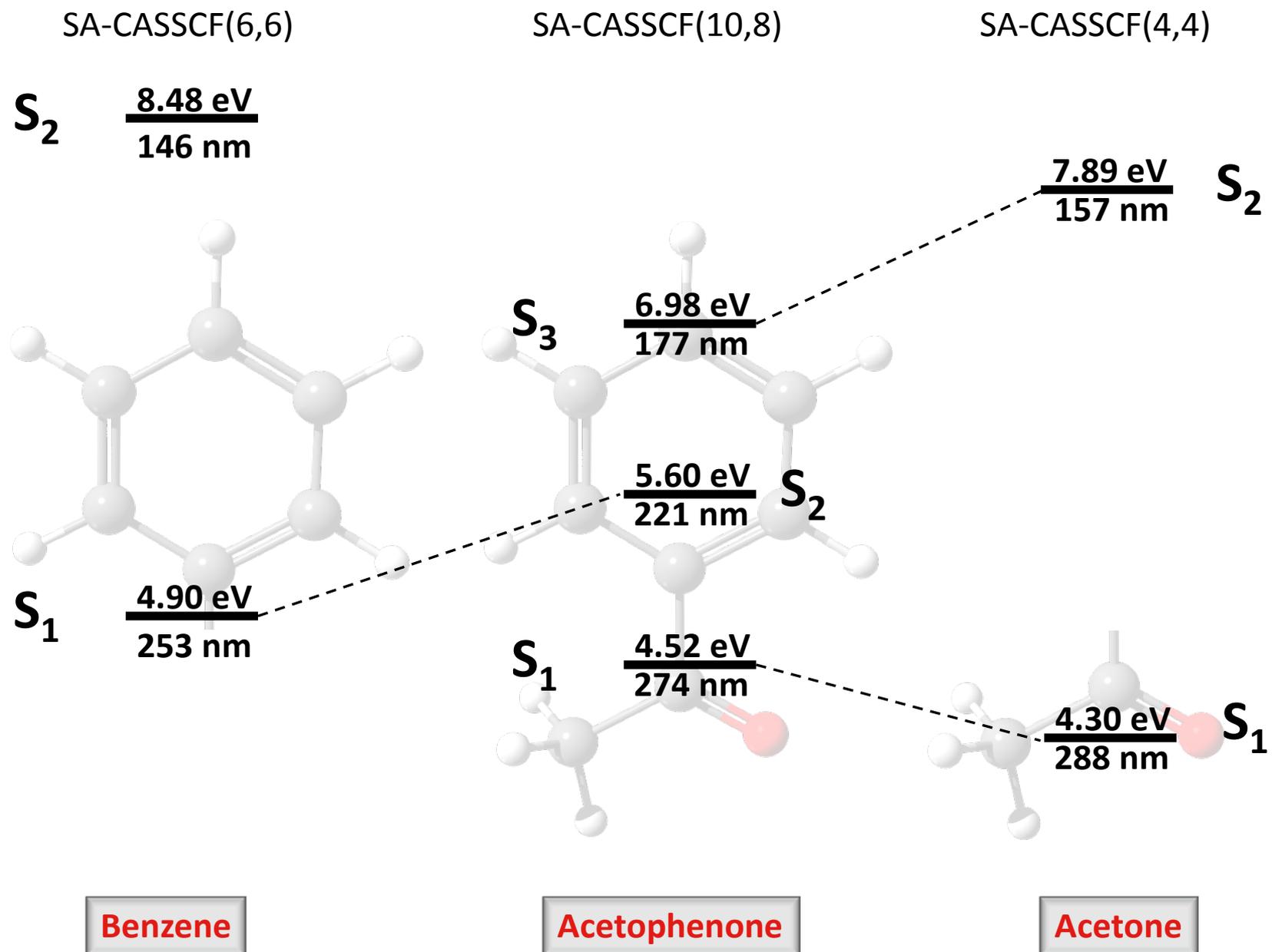
**EOM-CCSD**

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).



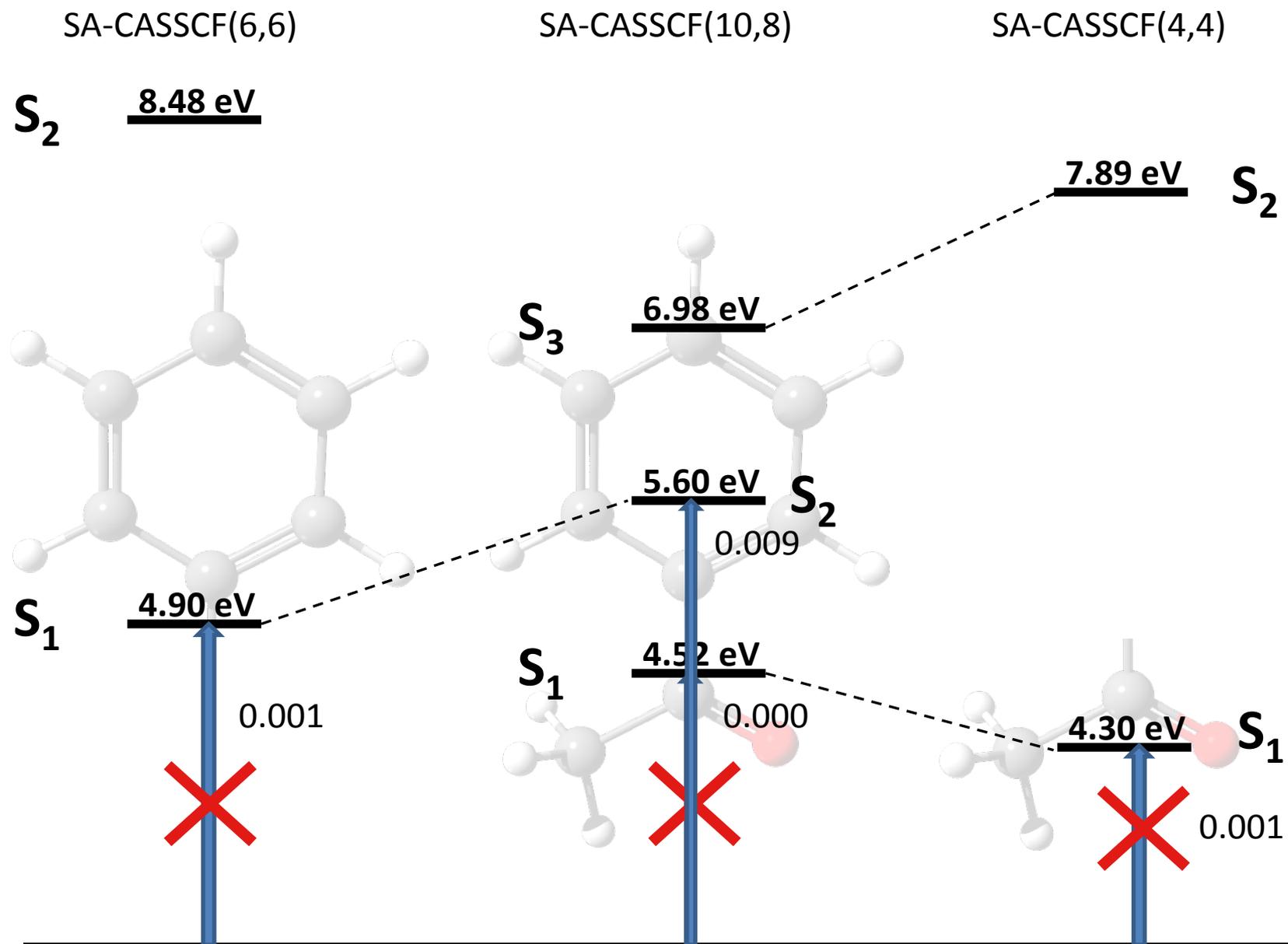
# Acetophenone

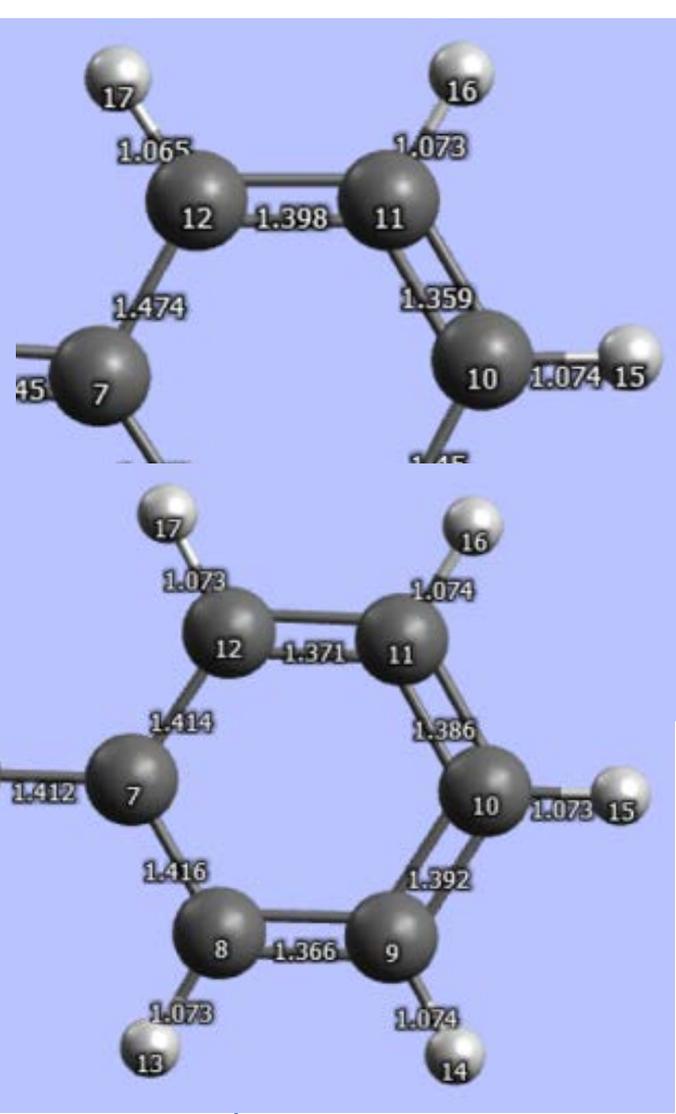
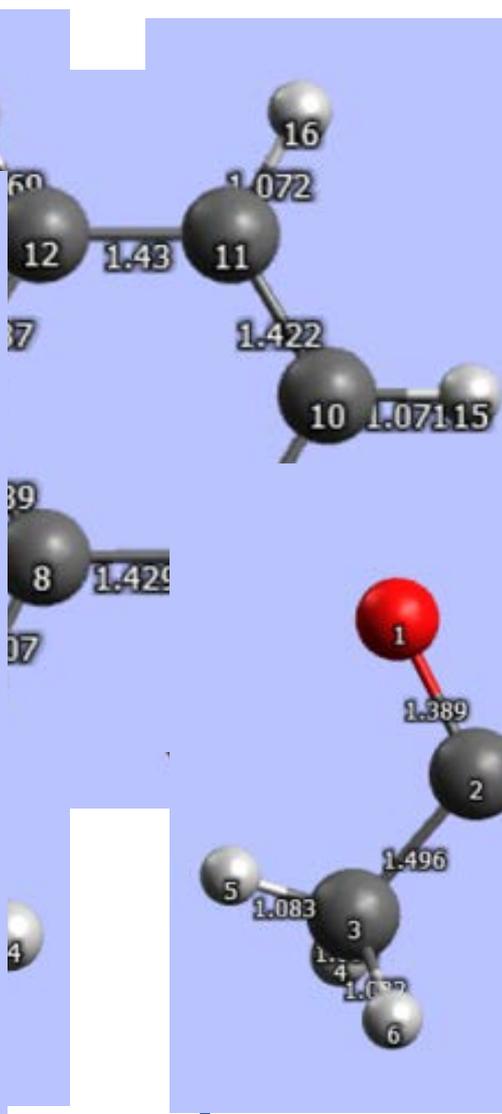
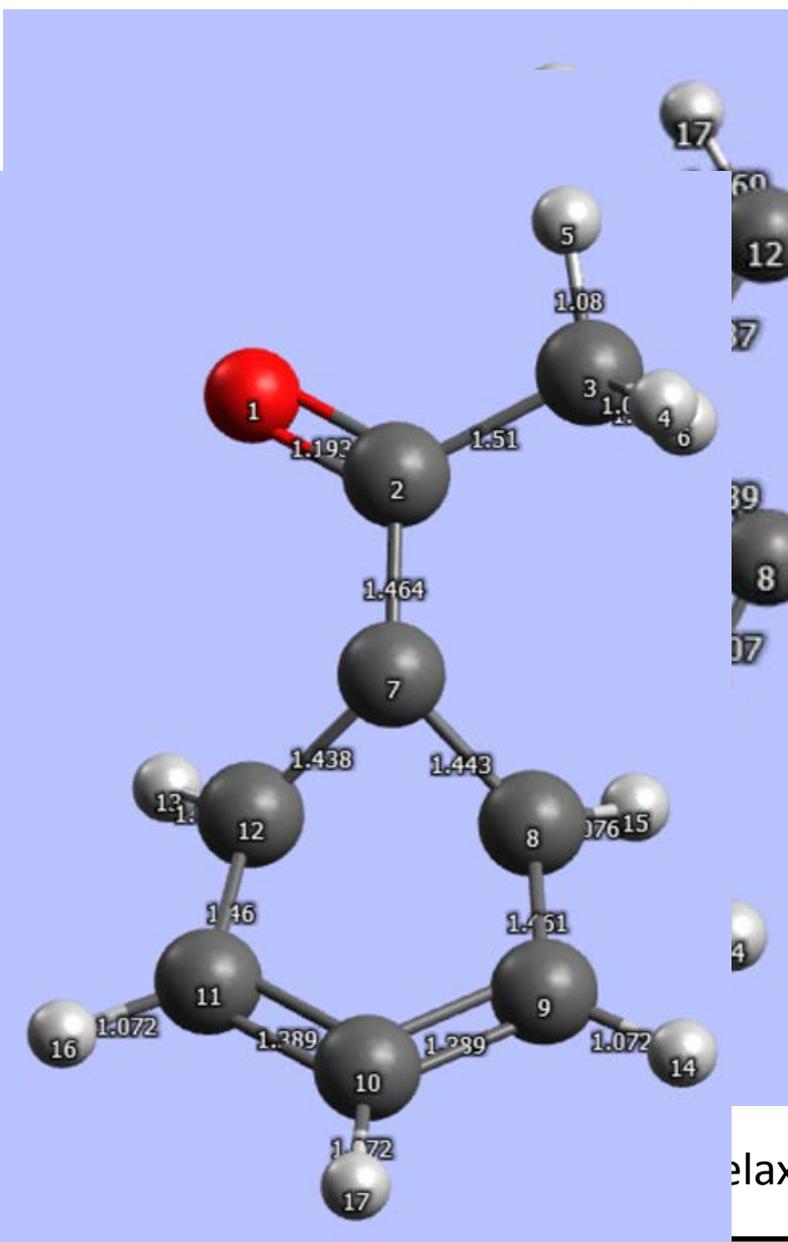




**Table 1.** Vertical excitation energies (and their oscillator strength in parenthesis) for the two lowest excited states of AP

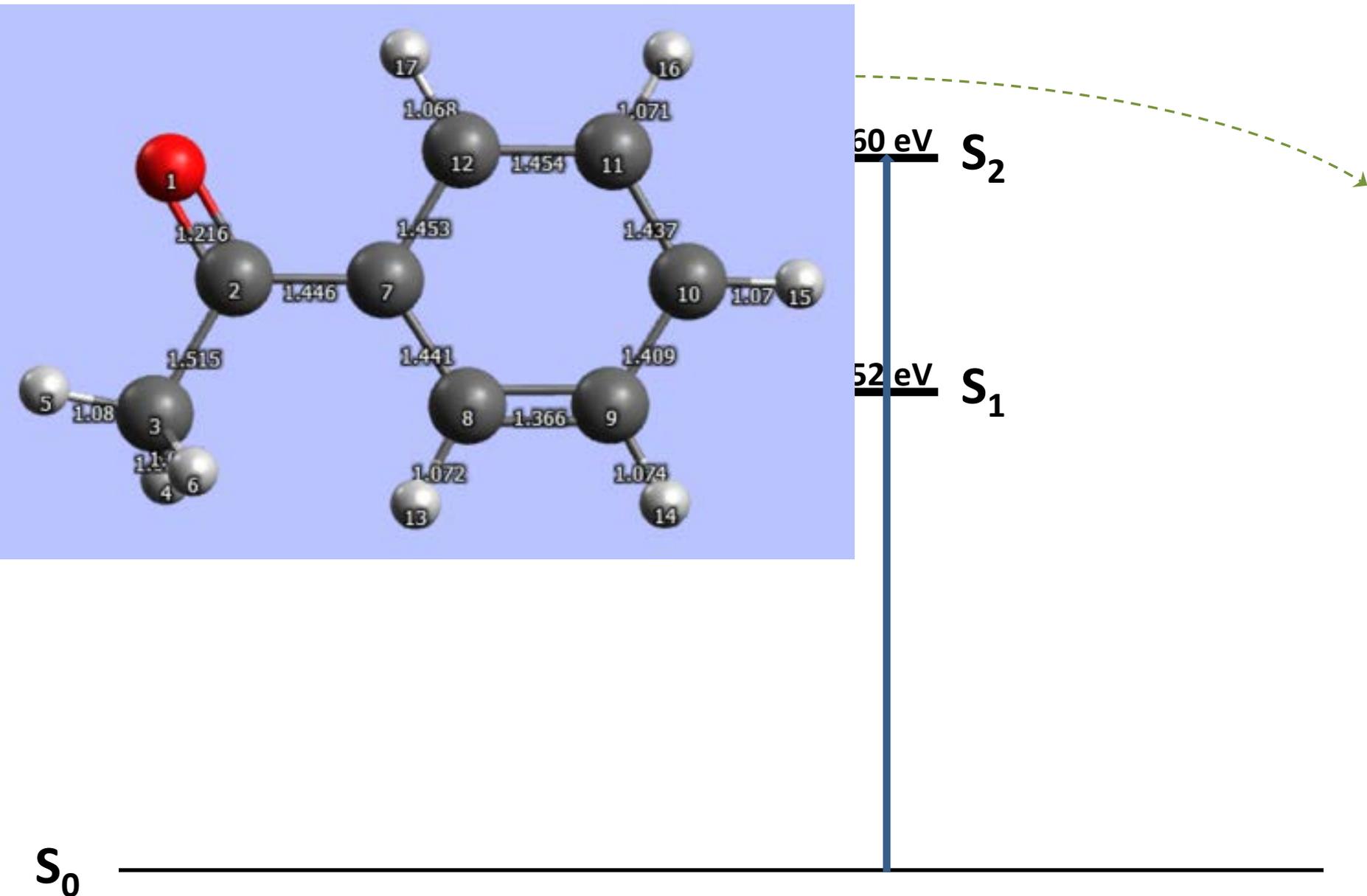
	$S_1$ (eV)	$S_2$ (eV)
<b>AP</b>	$(n\pi^*)$	$(\pi\pi^*)$
SA-CASSCF(10,8)	4.52 (0.0000)	5.60 (0.0091)
MS-CASPT2(10,8)	4.55 (0.0001)	4.85 (0.0068)
MRCI (D) (10,8)	4.65 (0.0001)	4.83 (0.0069)
EOM-CCSD	4.23 (0.0001)	4.97 (0.0077)
LT-DF-LCC2	3.81 (0.0000)	4.90 (0.0088)
Exp.	4.54	5.39





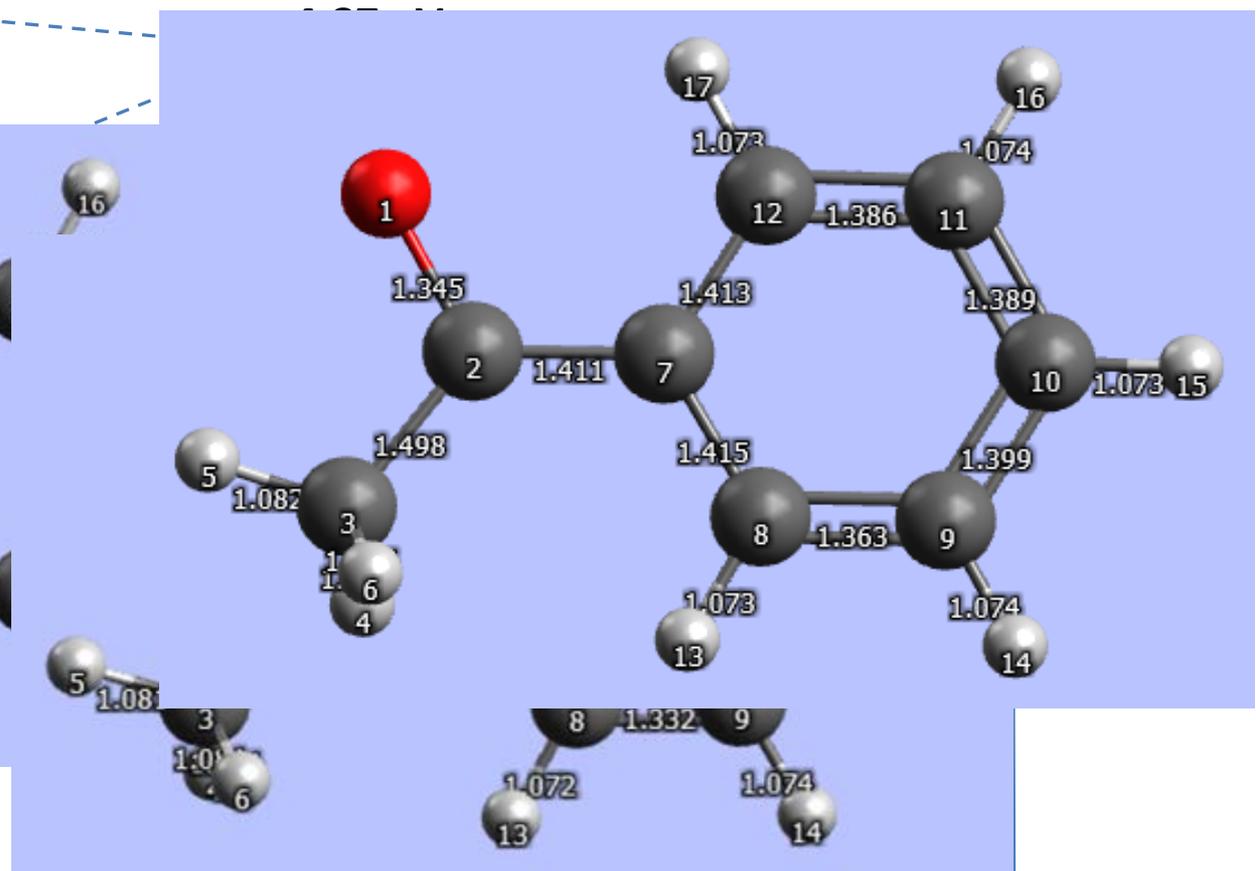
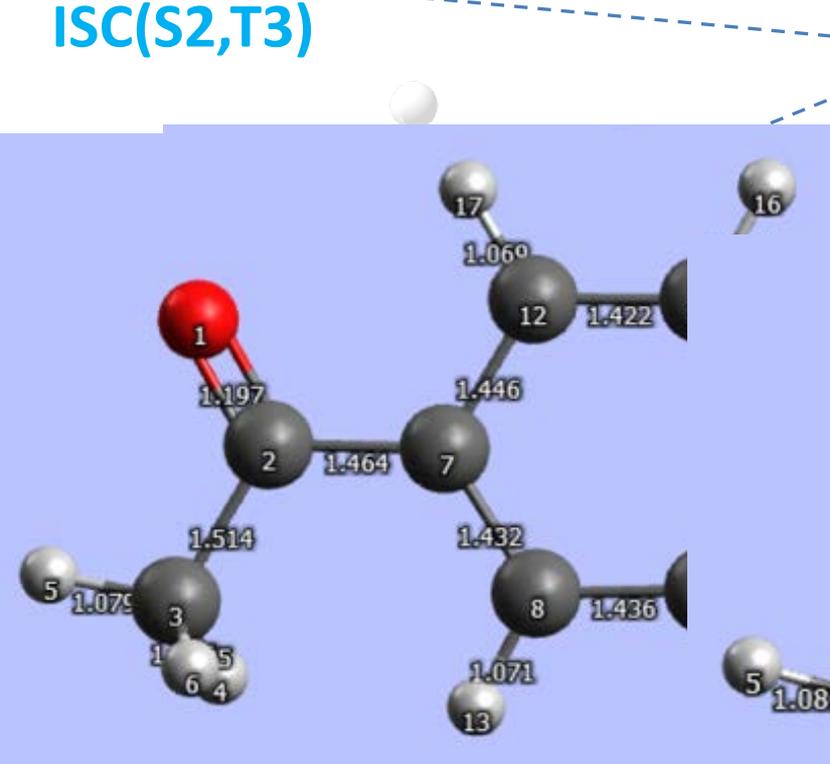
relax





The triplet relaxation pathway

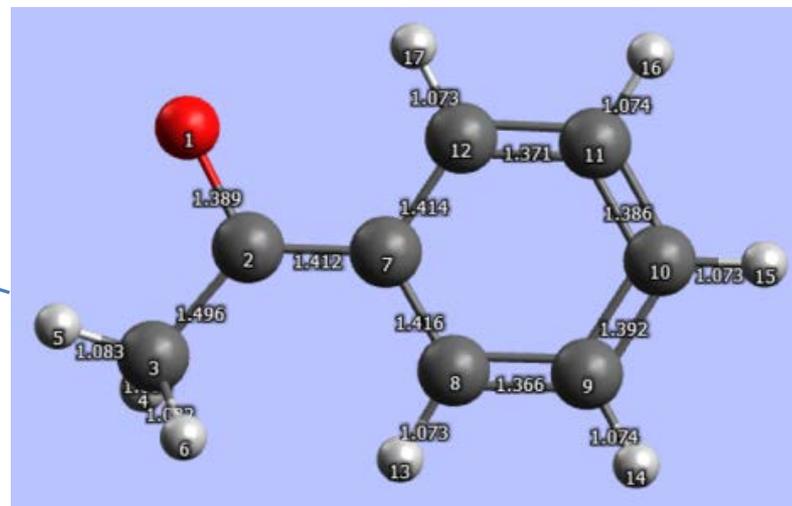
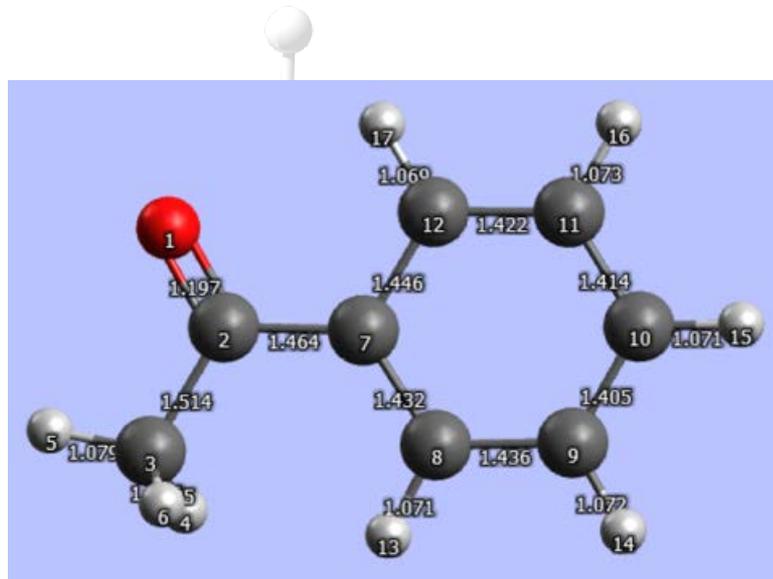
5.28 eV  
ISC(S2,T3)



Phosphorescence



S<sub>0</sub>



Fluorescence



$S_0$



## Experimental evidence for:

A. **Absorption**: M. Berger, C. Steel, *J. Am. Chem. Soc.* **97**(17), 4817 (1975)

$$S_0 \rightarrow S_1 \quad \nu_{exp} = 273 \text{ nm (4.54 eV)} \quad \nu_{theor} = 274 \text{ nm (4.52 eV)}$$

$$S_0 \rightarrow S_2 \quad \nu_{exp} = 230 \text{ nm (5.39 eV)} \quad \nu_{theor} = 221 \text{ nm (5.60 eV)}$$

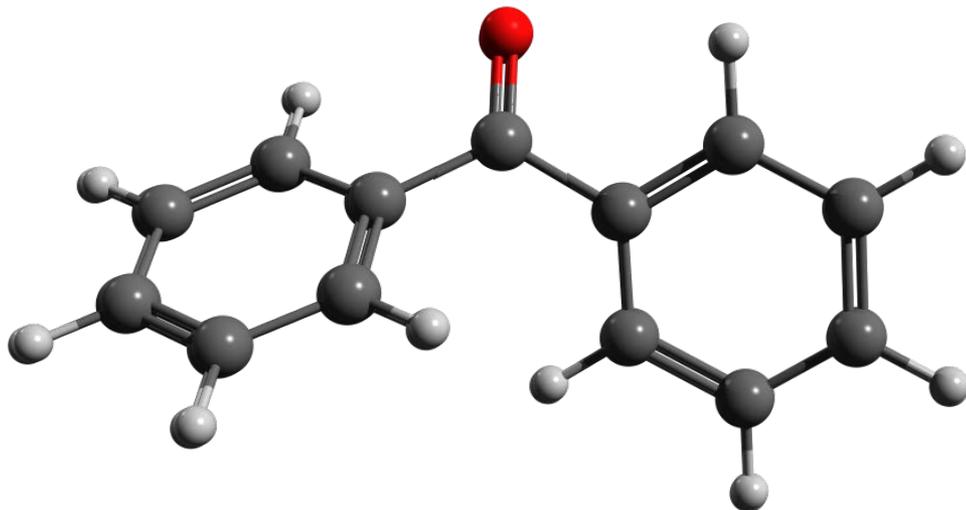
B. **Fluorescence**: R. D. Vanselow, A. B. F. Duncan, *J. Am. Soc. Chem.*, **75**, 830 (1953)

$$\nu_{exp} = 23600 \text{ cm}^{-1} \text{ (2.92 eV)} \quad S_1 \text{ (carbonyl)} = 3.43 \text{ eV}$$

C. **Phosphorescence**: M. Koyanagi, R. J. Zwarich, L. Goodman, *J. Chem. Phys.*, **56**, 3044 (1972)

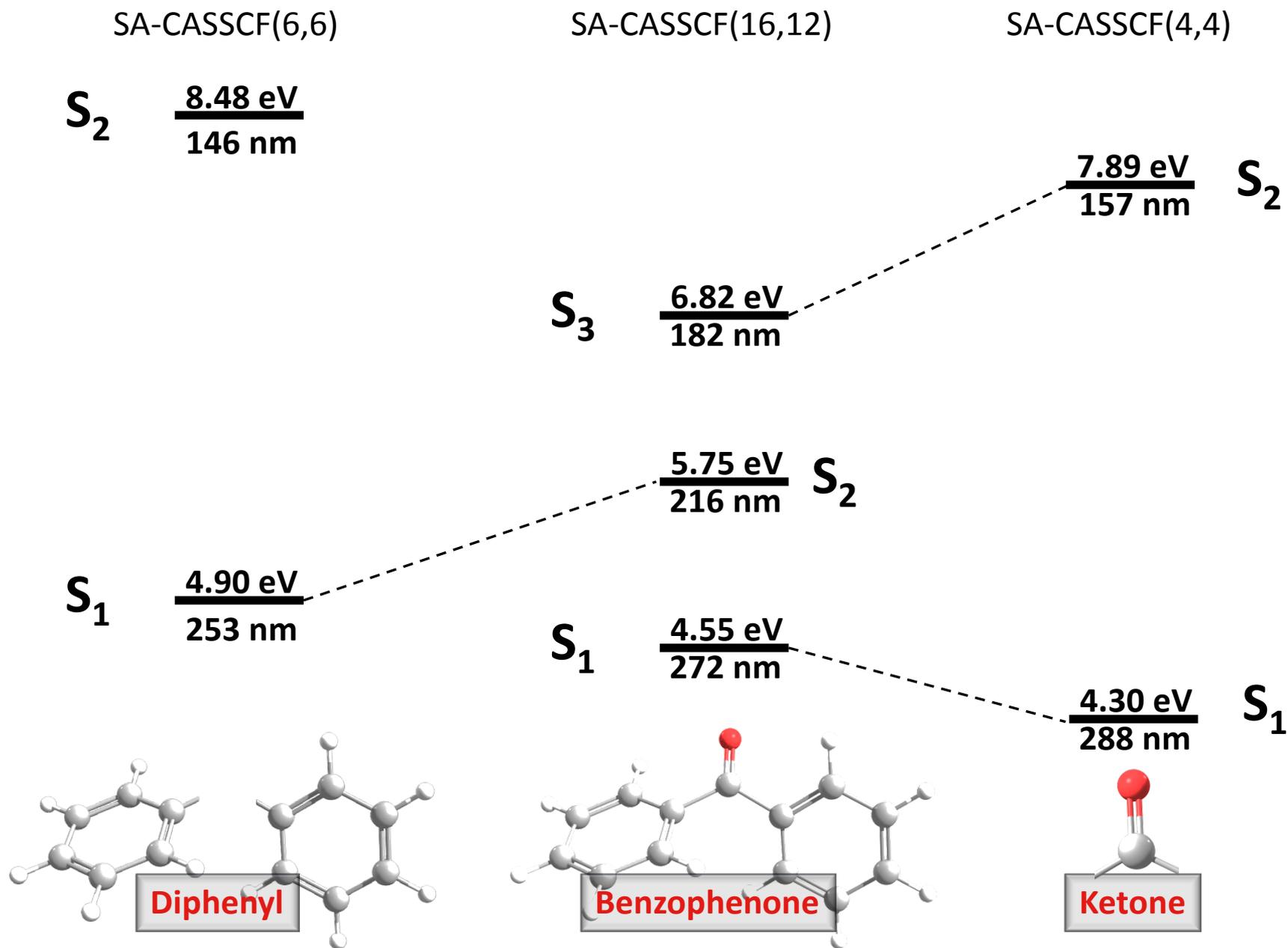
$$\nu_{exp} = 26100 \text{ cm}^{-1} \text{ (3.24 eV)} \quad T_1 \text{ (carbonyl)} = 3.04 \text{ eV}$$

# Benzophenone



**Ketone group**

**Diphenyl group**

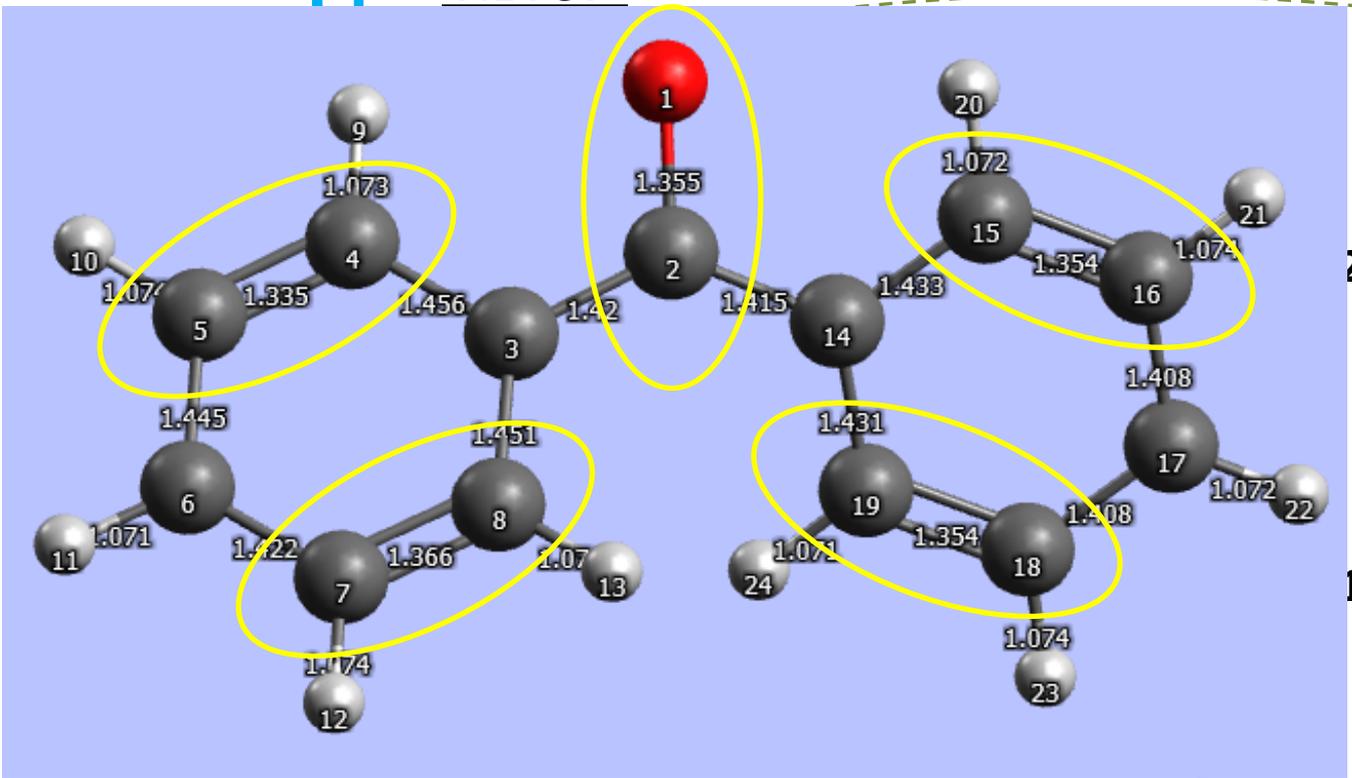


**Table 2.** Vertical excitation energies (and their oscillator strength in parenthesis) for the two lowest excited states of Benzophenone

	$S_1$ (eV)	$S_2$ (eV)
BP	( $n\pi^*$ )	( $\pi\pi^*$ )
SA-CASSCF(16,12)	4.56	5.75
	(0.0019)	(0.0063)
MS-CASPT(16,12)	4.49	4.83
	(0.0009)	(0.0042)
MRCI(D)(16,12)	4.60	5.04
	(0.0014)	(0.0050)
EOM-CCSD	4.11	5.04
	(0.0011)	(0.0086)



**Cl** 7.14 eV

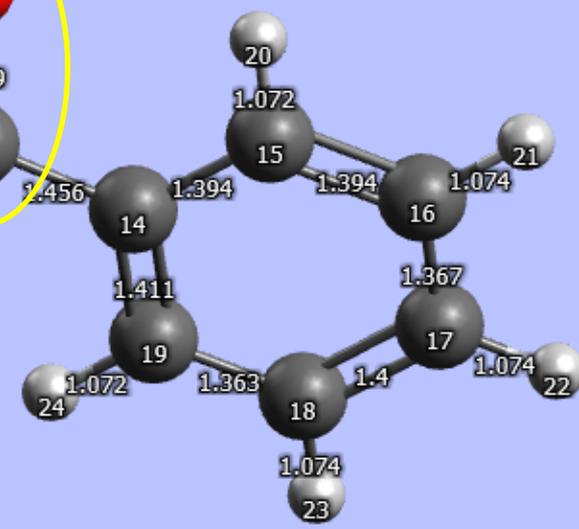
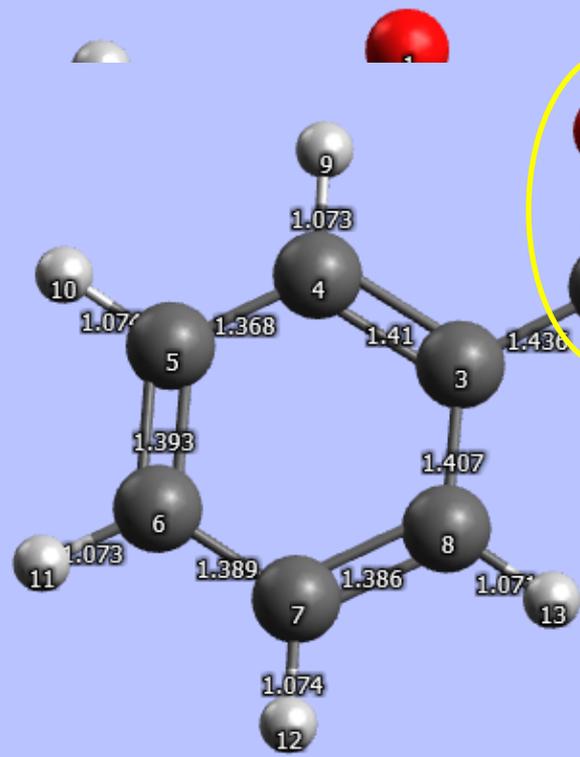
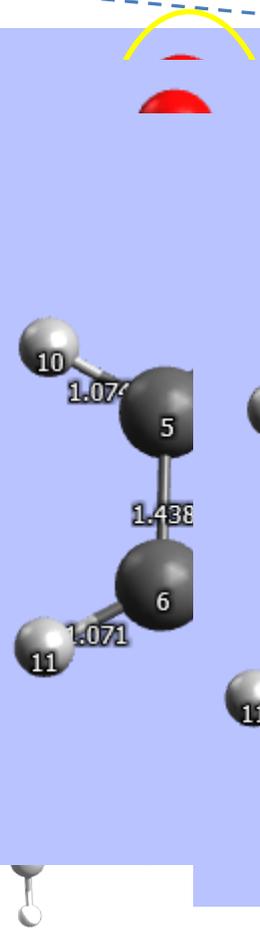
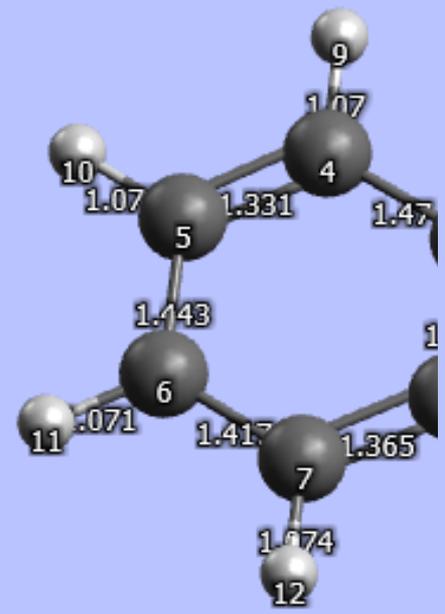


$S_0$

The triplet relaxation pathway

**5.78 eV**  
**ISC(S2.T3)**

**4.98 eV**



Phosphorescence ↓

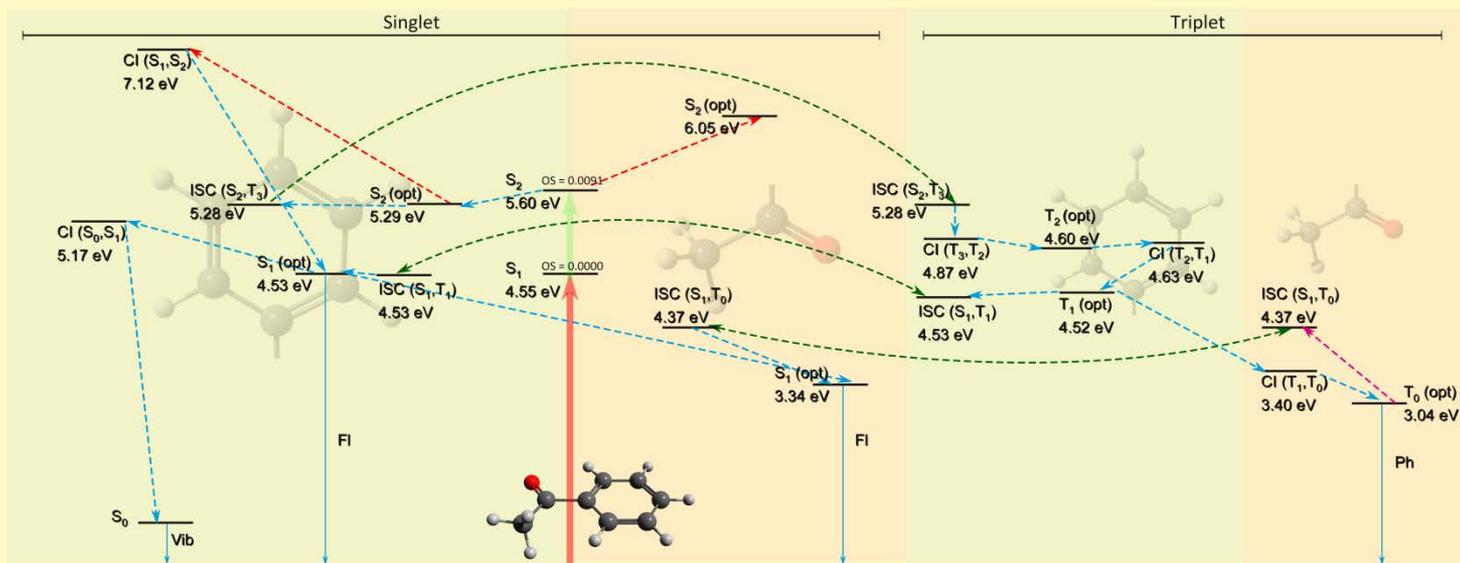
S<sub>0</sub>



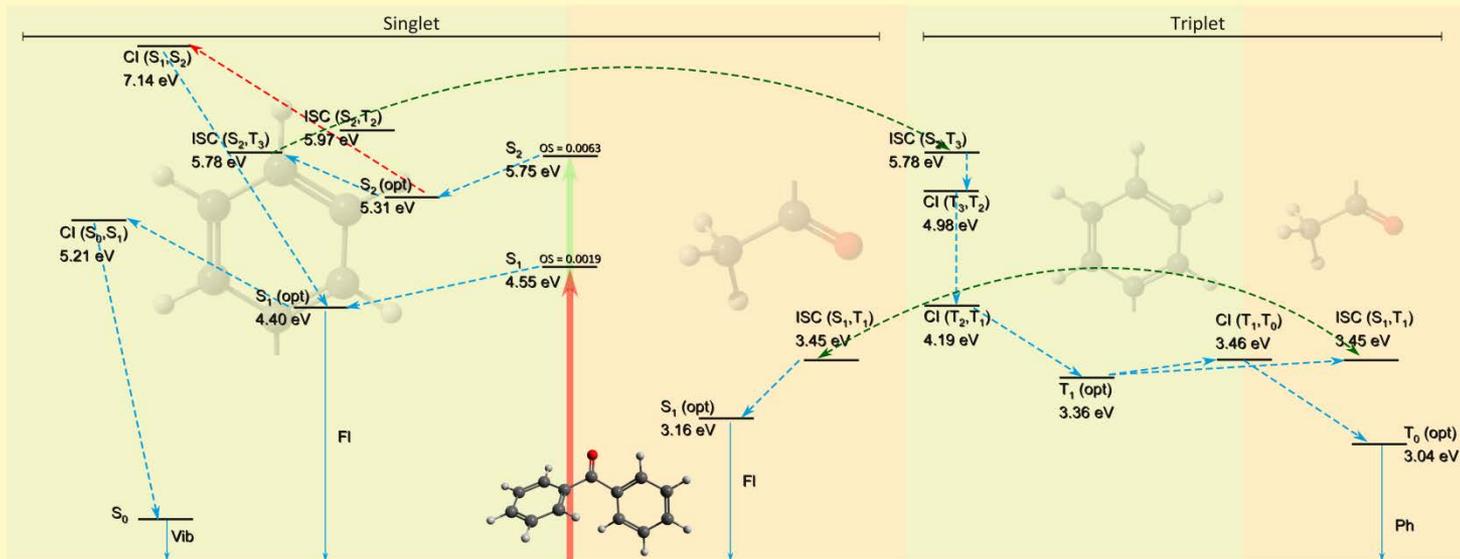
Acetophenone:

$SO(S_2, T_3) = 0.32 \text{ cm}^{-1}$

$SO(S_1, T_1) = 19.18 \text{ cm}^{-1}$



Benzophenone:



- The vertical excitation has low efficiency (with small oscillator strength) in case of  $S_1$  first singlet excited state for both acetophenone and benzophenone molecular structures. → One needs to excite at least to  $S_2$  or  $S_3$  excited state levels.
- The  $S_1 \times S_2$  conical intersection point is difficult to be reached from the  $S_2$  equilibrium structure ( $\Delta E \approx 1.7$  eV).
- The  $S_2 \rightarrow T_3$  intersystem crossing point is energetically close to the  $S_2$  equilibrium structure both for acetophenone and benzophenone molecular structures. => Singlet - triplet transition is a feasible relaxation mechanism.
- The well-known  $S_1 \rightarrow T_1$  intersystem crossing point is also present in the relaxation scheme. → Beyond the pure singlet relaxation pathway the singlet - triplet - singlet relaxation pathway is also feasible.
- While the singlet excited state level is quite similar, there is significant differences between the triplet states of the acetophenone and benzophenone molecular structures.

*Thank you for your attention.*