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

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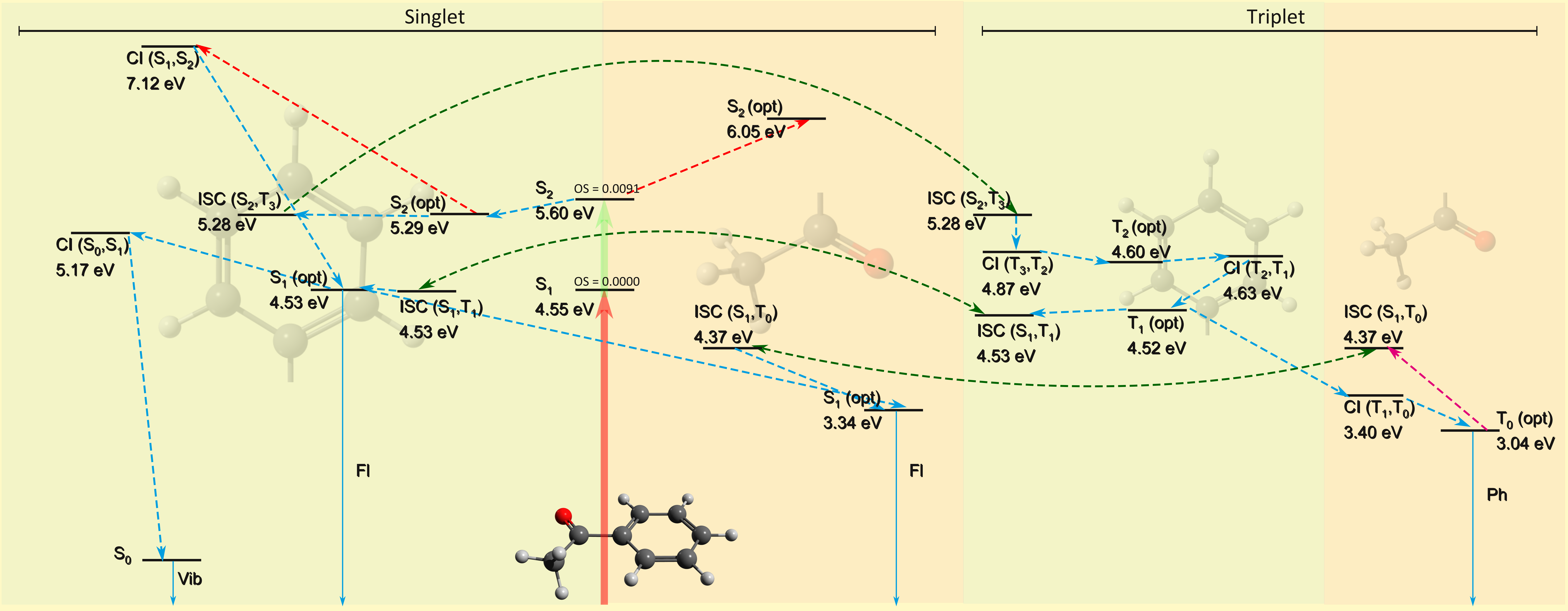
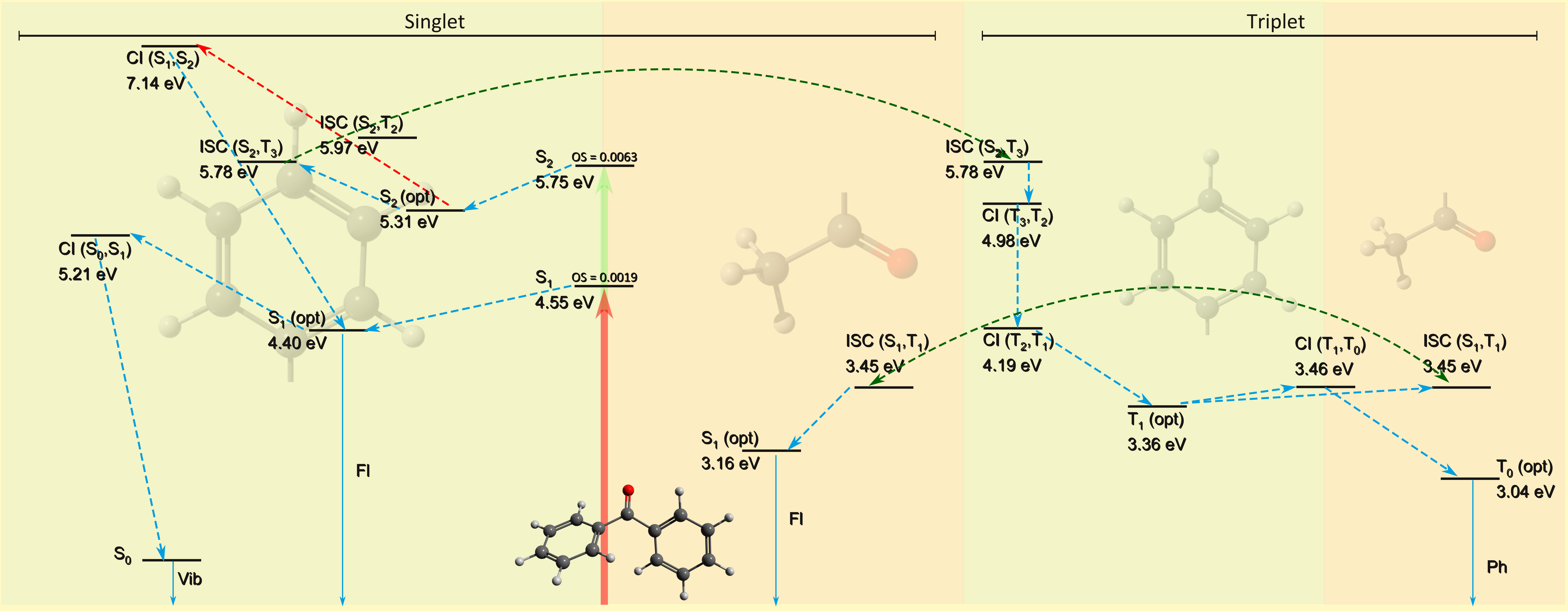
Abstract: New relaxation pathways of the excited state dynamics for acetophenone and benzophenone are presented via conical intersections and singlet-triplet intersystem crossings between the different excited state potential energy surfaces (PES) using the MOLPRO [1] program package. The multireference complete active space and second order perturbation theory methods together with def2-tzvp basis set were used in order to characterize the equilibrium geometries and PES crossing points up to the third excited state level for both singlet and triplet spin states. The results show charge transfer effect either from the carbonyl group to the benzene fragment or contrariwise depending on the given excited state, but in the case of benzophenone this charge transfer phenomena includes one of the benzene rings, the other ring remains only slightly perturbed. After a short geometry relaxation, the relaxation pathways of the second singlet S_2 excited state switch to the third triplet excited state via singlet-triplet intersystem crossing followed by a fast relaxation process over the triplet manifolds down to the first triplet state. Another intersystem crossing between the first singlet and triplet states could draw back the molecule to the singlet state and the molecule will lose its excitation via fluorescence phenomenon, or the molecule could further relax in its ground triplet state and present phosphorescence phenomenon.

Acetophenone:

SO (S_2 , T_3) = 0.32 cm^{-1} SO (S_1 , T_1) = 19.18 cm^{-1}



Benzophenone:



Conclusions

- The vertical excitation has low effiviency (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.

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REFERENCES

[1] MOLPRO, version 2012.1, A package of *ab initio* H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T. B. Adler, *et al.* see http://www.molpro.net.