Modeling Photoinitiators – A New Walk for R&D

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Abstract

In this paper, we explore the use of existing quantum mechanical analyses (modeling) software to model commercially available *Type I* and *II* photoinitiators to produce a theoretical initiation pathway replete with theoretical thermodynamic data that can then be compared to experimental values for excited state singlet and triplet energies. Furthermore, theoretical UV-Visible spectra can be calculated and compared to the experimentally determined spectra. The results thereof could provide a new approach to traditional research and development (R&D) of photoinitiators.

1. Introduction

Though photoinitiator development has occurred over the past decades, the development has traditionally been a slow and tedious process involving the use of known photochemical theory coupled with synthesis of potential candidates. Some candidates become viable commercial products while others are abandoned altogether. As the viable candidates are elucidated, the theory expands to allow for a step-wise progression of photoinitiator development.

By applying computational methodologies used for many years in high throughput screening of pharmaceuticals to photoinitiators, the potential for development could be expedited thereby decreasing cost and increasing profits for industrial manufacturers of photoinitiators. Unfortunately, the use of computational methodologies for photoinitiator development has been limited due mostly to the lack of appropriately powerful modeling software. Fortunately, software has become available that will allow for modeling simple *Type I* and *Type II* photoinitiators.

Some of the pertinent photochemical data needed for viability analysis of photoinitiators include the energetics of ground state singlet (S_o), excited state singlet ($S_1{}^*$), and excited state triplet ($T_1{}^*$) species (Figure 1).[1-8]
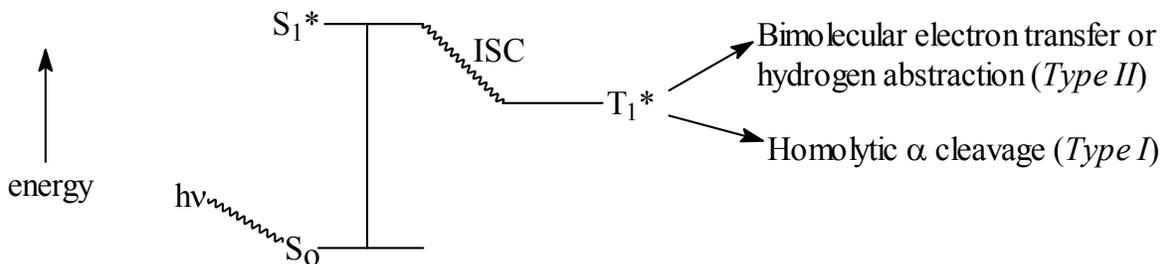

Figure 1. *Abbreviated generic Jablonski diagram for photoinitiators only showing the photochemical pathway known to produce initiating radicals where S_o is the ground state singlet, $S_1{}^*$ is the excited state singlet, $T_1{}^*$ is the excited state triplet, and ISC represents intersystem crossing.*

Other pertinent data include the ultraviolet-visible (UV-Vis) spectra and the location of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). The UV-Vis absorption spectrum of a photoinitiator dictates what radiation wavelengths can and will cause the initial excitation. The HOMO and LUMO determination provides the chemist with the ability to track electron movement before and after irradiation. These will be described in detail for two simple photoinitiators which were chosen based on their relative simplicity and commercial use compared to other commercially available photoinitiators (Figure 2): 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the *Type I* photoinitiator and benzophenone (BP) as the *Type II* photoinitiator. The results of some other common photoinitiators will be examined in the presentation of this paper.
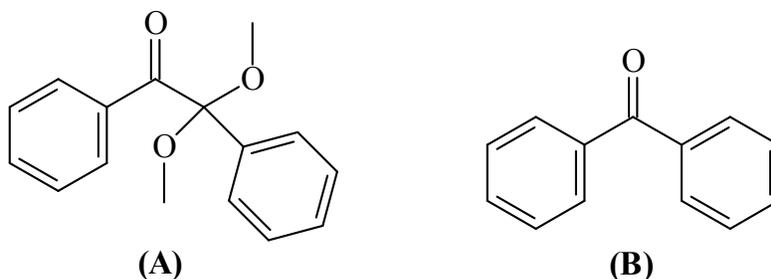

(A)   (B)

Figure 2. *DMPA (A) and BP (B).*

2. Experimental

2.1 Materials

DMPA was acquired from the Albemarle Corporation. Both BP and acetonitrile were purchased from Aldrich.

2.2 Computational Analyses

Spartan '06 software (v.1.1.1) designed by Wavefunction was used for all computational analyses. Initial geometry optimizations were performed using Hartree-Fock 6-31G* permutations. The initial 6-31G* geometry was used as a starting point for the Density Functional Theory (DFT) calculations based on B3LYP, the standard for current computational analyses. From these calculations, the theoretical UV-Vis absorption spectra were calculated for the ground state singlet species of the photoinitiators. The electron densities of all species were determined as was the location of the HOMOs and LUMOs. Thermodynamic values were also determined for each species using the conversion of 627.4 hartrees per one kcal/mol.

2.3 UV-Vis Spectroscopy

Absorption was measured at all wavelengths (250-450 nm) simultaneously with a Hewlett Packard Ultraviolet-Visible 8453 Photodiode Array. The desired solutions used acetonitrile as the solvent.

3. Results and Discussion

3.1 BP

The calculations for the S_o of BP produced the electron density, HOMO, and LUMO for the molecule (Figure 3). As expected, the phenyl rings are planar with the carbonyl providing resonance throughout the molecule; however, the phenyl rings do repel one another (steric strain) as evidenced by the increased bond angle of 127.33° (Ph_1–C–Ph_2) which could explain, in part, why BP has a triplet quantum yield of unity. By undergoing the intersystem crossing to the excited state triplet, angle strain could be minimized. The HOMO of BP does predominately reside at the carbonyl with minimal resonance through the ortho carbons on the rings thereby indicating that the electron that would be excited would probably be one of the nonbonding (n) electrons of the carbonyl's oxygen. Likewise, the LUMO, which shows the predicted location of the S_1^* excited electron, also resides on the carbonyl; however, the LUMO resonates to a large degree through the ortho *and* para carbons on the rings. The significant resonance of the LUMO through the ortho and para carbons indicate that the excitation an electron would probably be a π^* transition as π electrons are very capable of resonance stabilization.

Combining the information gathered from the HOMO and LUMO, the computational software seems to correctly predict the n→π* transition of BP.
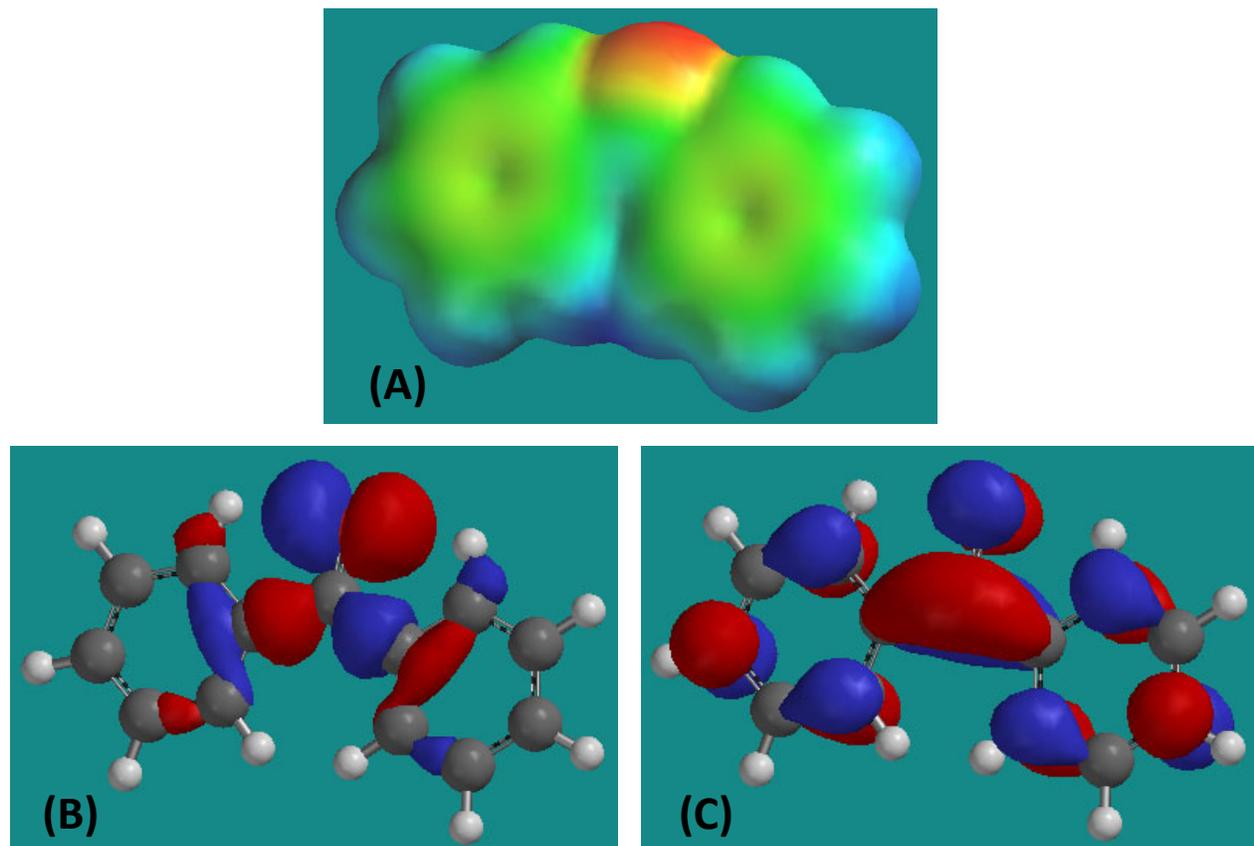

Figure 3. The electron density (A) where red is high density and blue is low density, HOMO (B), and LUMO (C) of the S_o of BP.

Of significant interest is the UV-Vis absorption spectrum for any S_o of a prospective photoinitiator. Thus, the computational software was used to determine the theoretical UV-Vis absorption spectrum for BP for comparison to the experimentally determined spectrum (Figure 4). The interest in the absorption spectrum is very important for photoinitiators because it could be used to predict the degree of competitive absorption which would be especially interesting to the formulator. Unfortunately as seen in Figure 4, quantitative data cannot be extrapolated from the theoretical spectrum, but for the purposes of determining the viability *potential* of a photoinitiator, the theoretical spectrum could indeed be useful for some compounds.
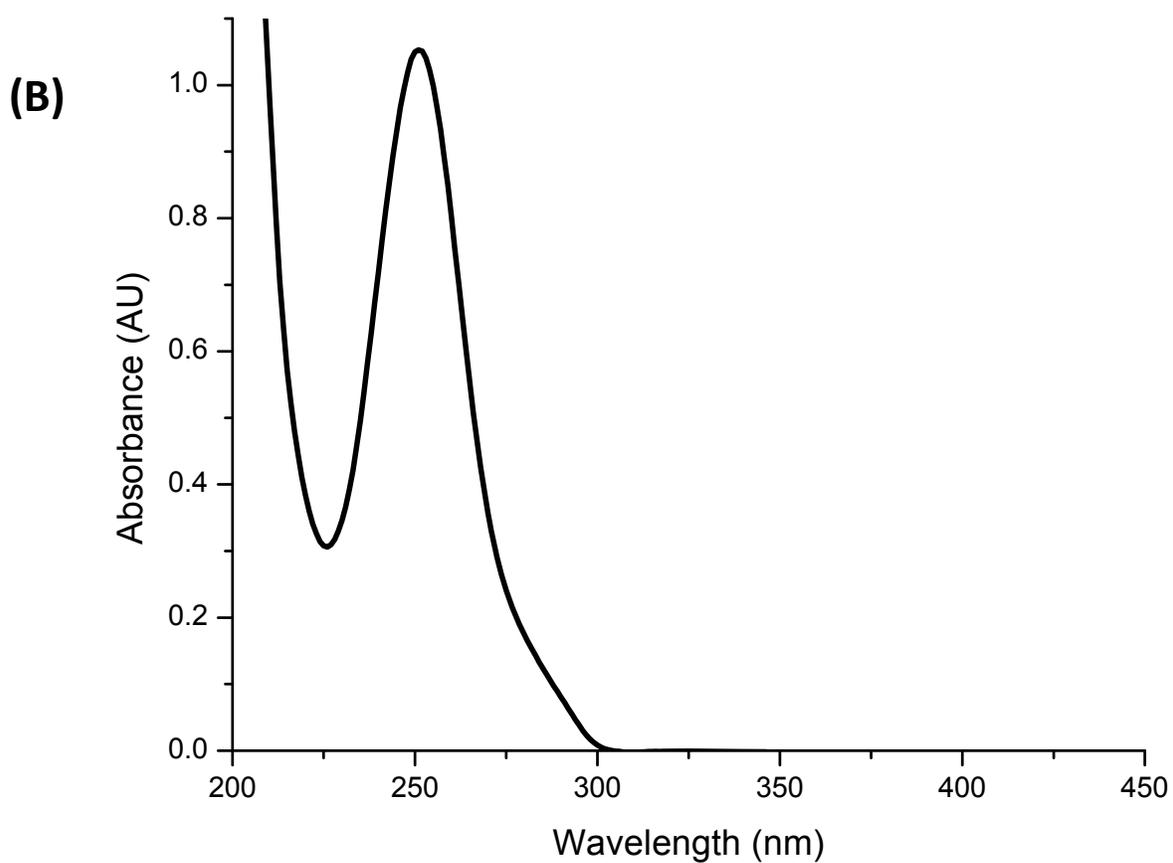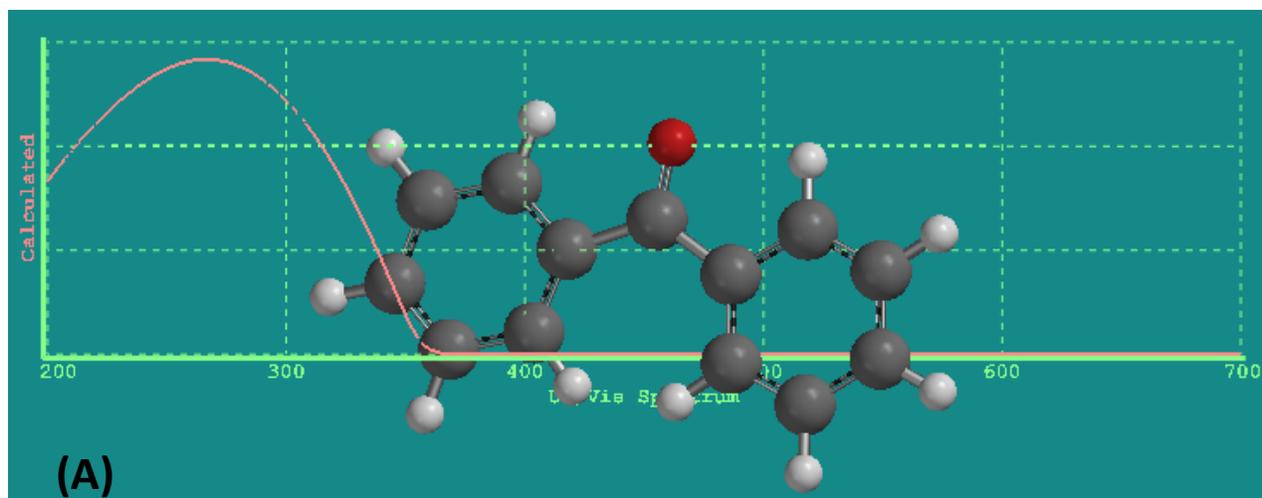
Figure 4. Theoretical UV-Vis absorption spectrum (A) and the experimental UV-Vis absorption spectrum (B) of BP where the experimental spectrum was found for [BP] = 5.04 x 10⁻⁵ M in acetonitrile.

Although cursory photoinitiator development in terms of the photochemistry, of which the paper is primarily concerned, could be ascertained from the S_o of a molecule such as BP, the

singlet and triplet energies could be calculated by the computational software. Unfortunately, this is a time-intensive process unless computers having fast processors and much random access memory (RAM) are used. Yet, in the conference presentation, both S_1^* and T_1^* for BP were also calculated in order to determine the predictability of the singlet and triplet energies of the respective excited state species. To demonstrate the capability of the software to calculate the singlet and triplet energies, those of DMPA were calculated below.

3.2 DMPA

The photochemical fate of DMPA is well documented and begins with the absorbance of UV radiation by the S_o to form the S_1^*.[9-10] The S_1^* forms the T_1^* via intersystem crossing. The T_1^* then undergoes an alpha cleavage to produce to free-radical species, a benzoyl radical and the 1,1-dimethoxy-1-phenylmethyl radical. For the purposes of this paper which is attempting to provide evidence supporting the use of computational methodologies for photoinitiator development, radical production and the fates thereof will not be addressed since calculations for similar radical species have often been demonstrated in the literature.

Much of the data presented for BP (electron densities, HOMOs, LUMOs, and mechanistic correlations) was previously delineated; however, by way of summary, DMPA was correctly modeled by the computational software.[10]

Additionally, the theoretical UV-Vis absorption spectrum for DMPA was calculated using the computational software for comparison to the experimental UV-Vis absorption spectrum for the selfsame molecule (Figure 5). The general shape of the two spectra are similar; however, comparison of the peak maxima at approximately 250 and 350 nm shows that the theoretical spectrum does not deviate from the experimental spectrum by much. Thus, for DMPA, the theoretical (i.e. calculated) UV-Vis spectrum corroborates the experimentally determined spectrum.
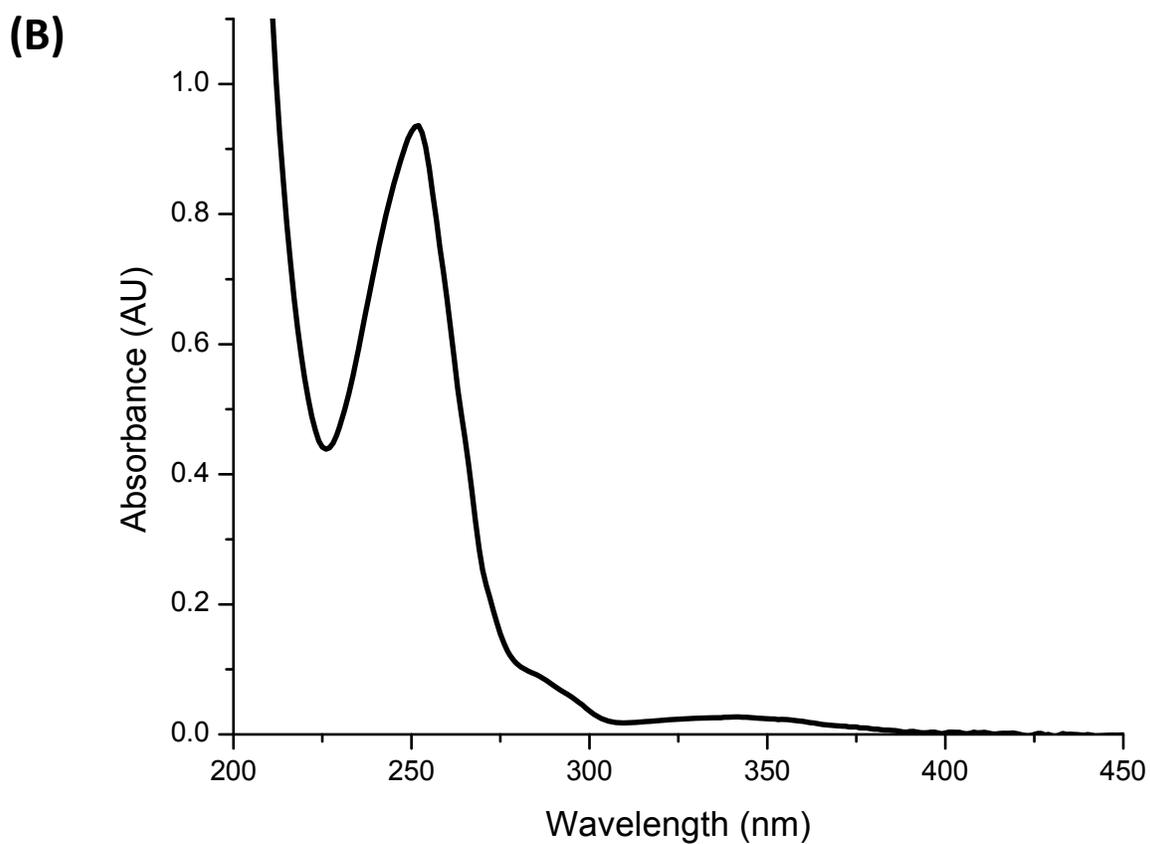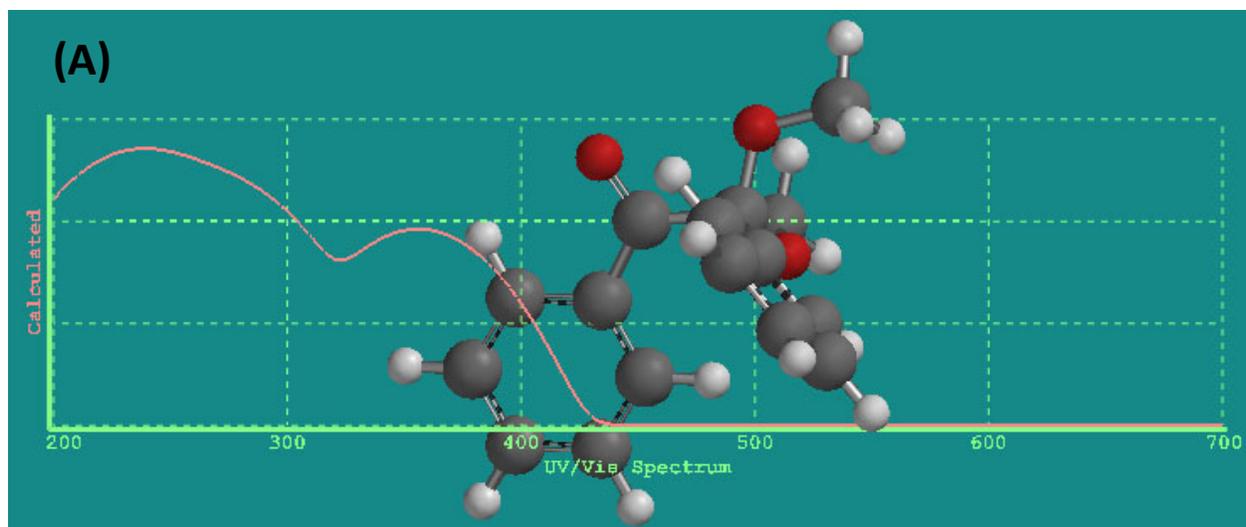
Figure 5. Theoretical UV-Vis absorption spectrum (A) and the experimental UV-Vis absorption spectrum (B) of DMPA where the experimental spectrum was found for [DMPA] = 7.34 x 10^{-5} M in acetonitrile.

Previously unreported, the calculated, theoretical singlet (E$_S$) and triplet (E$_T$) energies were determined to be 76.3 kcal/mol and 107.2 kcal/mol, respectively. The theoretical E$_S$ seems to

be reasonable given that the E_S of acetophenone approximates 79 kcal/mol.[11] As shown in Figure 6, the S_o HOMO shows the highest energy electrons residing principally on the carbonyl with some distribution among the substituents anti-planar to the carbonyl.
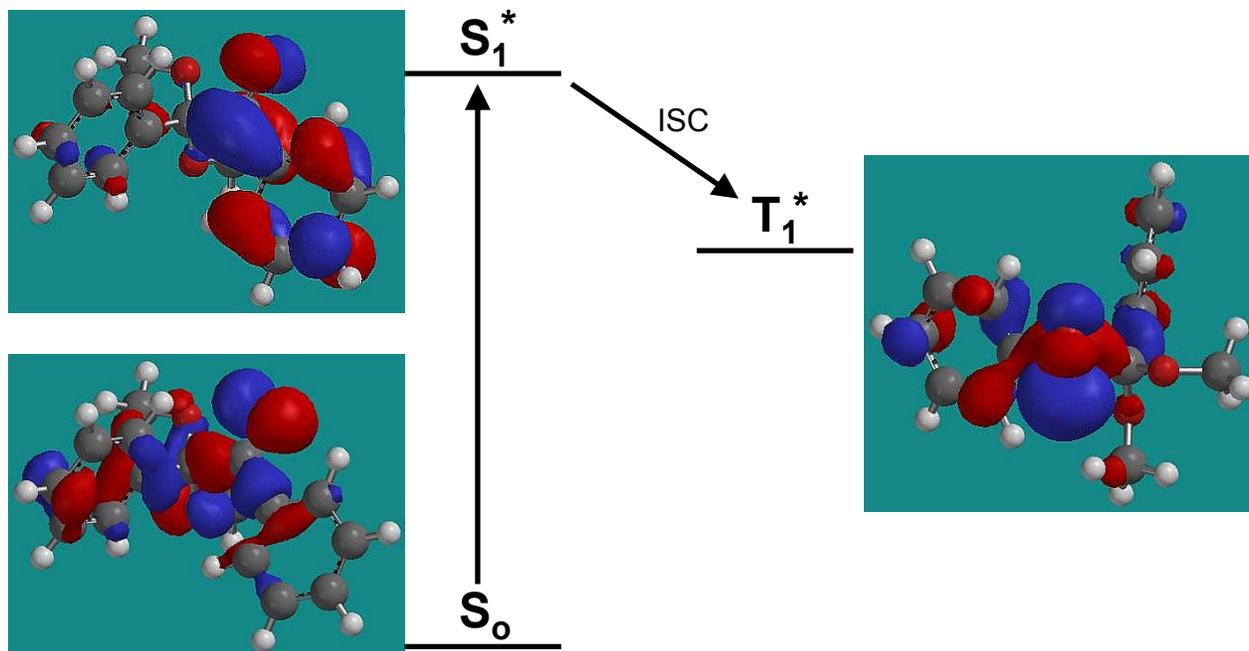

Figure 6. Jablonski diagram for DMPA only showing the photochemical pathway to produce T_1^* where S_o is the ground state singlet, S_1^* is the excited state singlet, T_1^* is the excited state triplet, and ISC represents intersystem crossing.

This phenomenon would raise the ground state energy somewhat compared to acetophenone given that the electrons populating the HOMO would not be able to resonate through the substituents though they would theoretically prefer the resonance. However, the S_1^* does allow for resonance of the HOMO thereby stabilizing the S_1^*. Therefore, the lower singlet energy for DMPA seems to be reasonable. Furthermore, the $\pi \rightarrow \pi^*$ transition is observed in the diagram. Unfortunately, the theoretical E_T for DMPA does not follow the accepted theory by being lower than that of the E_S. Thus, for DMPA, the calculated E_S is reasonable whereas the E_T is not.

4. Conclusions

The photochemical behavior of BP and DMPA were both modeled based on the ground state singlet (S_o), the singlet excited state (S_1^*), and the triplet excited state (T_1^*). The results corroborated the known photochemical behavior of each species based on the determination of the highest occupied molecular orbital and the lowest unoccupied molecular orbital (i.e. electron density). The singlet (E_S) and triplet (E_T) energies for DMPA were also found using computational methodologies. The E_S for DMPA seems to correlate well after applying known

thermodynamic theory and comparing the E_S of DMPA to that of acetophenone. Therefore, the authors conclude that computational chemistry could be used as a screening methodology to examine the potential viability of novel *Type I* and *Type II* photoinitiators as a substitute to expensive syntheses and characterizations of potential photoinitiators.

5. Acknowledgements

6. References

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