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Investigation of a Molecular Solar Thermal System: Predictions and Insights into Energy Storage, Thermal Dynamics, and Solvent Effects

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ABSTRACT

Using Density Functional Theory (DFT), we investigated the effects of diverse basis sets and solvents. The key parameters studied include changes in energy storage capacity, thermal back-reaction (TBR) barrier, and UV-Vis spectra. The calculations considered five different DFT functionals (B3LYP, B3LYP-D3, CAM-B3LYP-D3, ωB97X-D, and M06-2X) and six different basis sets.

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Introduction

Efficient storage and conversion of solar energy stand as pivotal challenges in advancing renewable energy sources [1]. MOlecular Solar Thermal (MOST) represents a promising avenue, utilizing molecular transformations to capture and release solar energy [2]. MOST systems rely on organic photochromic molecules, that can store solar energy as chemical energy. They do this by using sunlight to trigger reactions that normally would not happen due to thermodynamic constraints [3].

The urgency to establish dependable methods for storing solar energy effectively propels our study. Amid a landscape of evolving solar energy storage innovations, MOST stands out for its potential, yet its precision in forecasting solar conversion efficiency remains a crucial but unverified aspect [4]. Our main motivation is to evaluate how dependable a MOST system is. This is crucial for the advancement of solar energy storage technologies [5]. Photoswitches have been explored in various areas such as at the molecular level, in supramolecular contexts, and in materials applications [6]. The effectiveness of using photoswitches stems from the ability to chemically control a material's properties by manipulating it with light. Our study aims to look into MOST's accuracy in predicting solar conversion efficiency with Density Functional Theory (DFT) [7]. There have been previous calculations where different predicted solar conversion efficiency has shown six molecular structures of the six bicyclic dienes and this study looks further into one of them. There-fore this endeavor seeks to authenticate MOST's ability as a dependable predictive model and contribute empirical insights crucial for shaping the trajectory of solar energy storage technologies [5]. The significance of this work lies in its potential to steer the development of more efficient, scalable, and dependable solar energy storage methods.

Theory and Method

MOST operates on the principle of storing solar energy within molecular bonds, enabling its conversion and release as needed. This process involves molecules capable of reversible transitions between distinct states, capturing solar energy during one state and releasing it in another. The foundation of MOST lies in the photochemical and thermal processes driving these molecular transformations [5]. The molecular structure in question is seen in

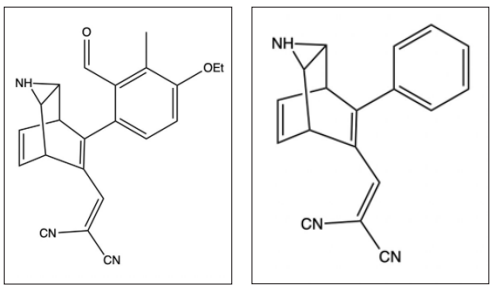

Figure 1: (Left) Molecular Structure with all Substituents. (Right) Simplified version of Molecular Structure without Substituents.

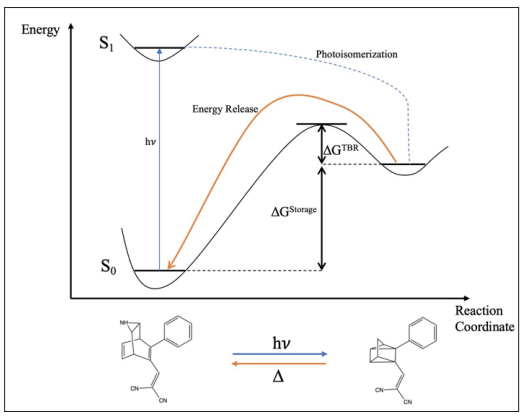

Figure 2: Energy Diagram

Figure 1, here is the full-sized structure that was predicted, but the one that is being focused on throughout the paper is one without its substituents as it is not expected to have large influence into the behavior and can therefore save computational time. In the photochemical step, molecules undergo excitation upon absorbing photons from sunlight, leading to a change in their electronic or molecular configuration. This excitation initiates the storage of solar energy within the molecular structure as pictured in Figure 2. The subsequent thermal process triggers the release of stored energy. Under specific conditions, such as heat or a catalyst, the excited molecules revert to their original state, liberating the stored solar energy either as heat or as another usable form of energy.

DFT offers insights into the electronic structure and properties of materials by solving the quantum mechanical equations governing the behavior of electrons within a material. It provides an efficient means to calculate molecular properties, such as energy levels, structure, and reactivity, crucial for understanding the mechanisms underlying MOST.

In our study, DFT serves as the computational framework to analyze a molecular struc-ture the MOST process has determined to be suitable. By employing DFT calculations, we aim to elucidate the energetics, stability, and electronic properties of the molecule. Re-sults obtained from DFT calculations are analyzed to evaluate the potential of the selected molecule.

Computational Approach

While not comparable in size to proteins, the system under study is considered substan-tial within computational chemistry. In such cases, Density Functional Theory (DFT) stands out for its ability to provide reasonably accurate results while maintaining computational feasibility. Hence, DFT was chosen as the preferred theoretical framework for these calculations. The computations were performed using the Gaussian16 software [8]. The functionals used for the calculations were B3LYP [9], B3LYP-D3 [10], CAM-B3LYP-D3 [11], M06-2X [12], and ωB87X-D [13].

The calculations involved the utilization of six Pople-style basis sets, specifically: 6-31G, 6-31G(d,p), 6-31++G(d,p), 6-311G, 6-311G(d,p), and 6-311++G(d,p) [14-16]. These basis sets were chosen for their established reliability and varying levels of complexity, allowing a comprehensive exploration of the system under scrutiny. The molecule we got to work with was both in its reactant, transition, and product state. To make sure the calculations would not take too long we simplified the molecule by removing some of the substituents as we did not expect them to make as big of a differ-ence to the properties we are trying to investigate. The first calculations were done with the reactant, five different methods, and six different functionals. By increasing the size of the basis set from 6-31G to 6-311G++(d,p) while optimizing the structures and calculating the frequencies for each. It was then determined the best basis sets were either 6-311G(d,p) and 6-311++G(d,p). (See the section on Results and Discussion). When determining what functionals to move forward with, it was decided that CAM-B3LYP-D3, M06-2X, and ωB97X-D was the best options. This was followed up by doing excitation calculations from the optimized structure, but only for the three methods CAM-B3LYP-D3, M062X, and ωB97X-D. These calculations were done for the product and the reactant.

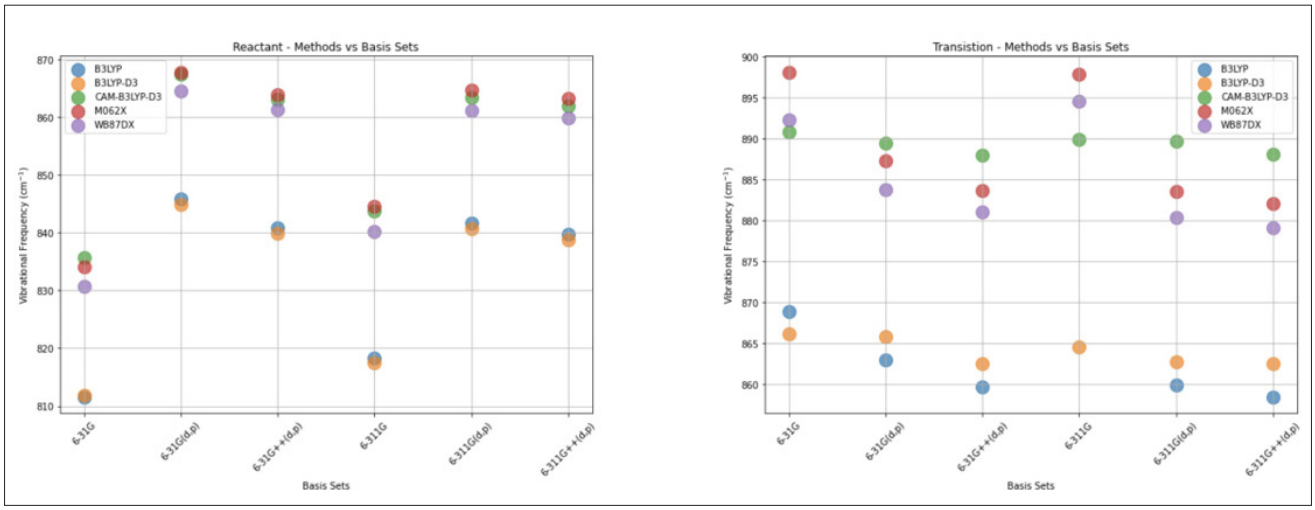

Figure 3: Relevant Vibrational Frequencies as a Function of Functional and Basis Set

Results and Discussion

Investigation of Basis Sets

When determining the basis sets and methods that we were going to use for most of the calculations we started by doing 36 calculations for the reactant and 36 calculations for the transition state. Here we set up the five different methods B3LYP [9], B3LYP-D3 [10], CAM-B3LYP-D3 [11], M06-2X, and ωB87X-D [13] and the six basis sets 6-31G, 6- 31G(d,p), 6-31++G(d,p), 6-311G, 6-311G(d,p), and 6-311++G(d,p) [12,14-16]. as seen in Figure 3.

When choosing the basis set, we know that larger basis sets generally enhance calculation accuracy. The 6-311++G(d,p) basis set closely approximates the values obtained with 6-311G(d,p), indicating comparable accuracy, particularly in predicting the geometries of the and therefore 6-311G(d,p) and 6-311++G(d,p) were the chosen basis sets. These are also a favorable compromise between computational precision and efficiency for the specific system in question, supporting its selection within time constraints. When deciding what method to use we decided to go with CAM-B3LYP-D3, M06-2X, and ωB97X-D as they previously have been proved by getting good reliable results [2].

Solvent Effects

When doing the calculations in solvents it was all done with the same basis-set 6-311G(d,p) for the three chosen methods as seen in Figure 4. The solvent calculations were done for the reactant, transition state, and product. Each solvent used had different dielectric constants as seen in Table 1. Then when looking at Figure 4 it is possible to see that when the polarity of the solvent increases the vibrational frequency slowly moves to settle, meaning that when the polarity of the solvent becomes high the vibrational frequency stabilises. This effect is slower for the reactant and the product, but quite rapid for the transition. The stabilizing effect is seen for all three functionals across all solvents.

Table 1: Dielectric constants of Solvents [17].

Solvent	Toluene	Dicholromethane	Acetone	Acetonitrile	DMSO
Polarity	2.4	3.1	5.1	5.8	7.2

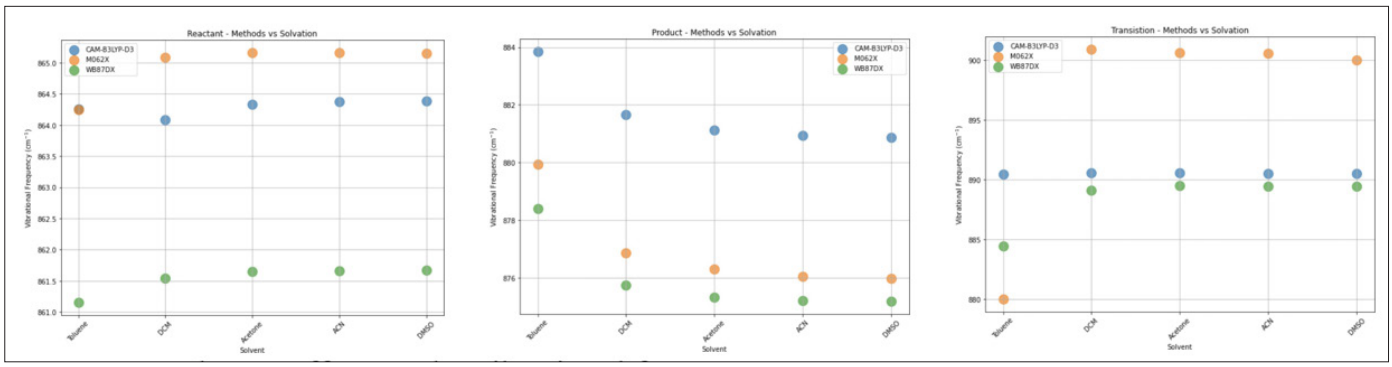

Figure 4: Solvents effect on the vibrational frequency.

The Storage Energy and the Back Reaction Barrier

In Table 2 we present $\Delta G^{storage}$ in [kJ/mol] and ΔGTBR in [kJ/mol]. These are the two values we also see in Figure 2. The $\Delta G^{storage}$ is the value calculated as the amount of energy that can be stored in the molecule, this number comes from the difference between the lowest energy of the reactant and the lowest corresponding energy of the product. ΔG^{TBR} is the thermal back reaction, which is calculated from the transition state and the product. For these two values we would like to see them both as positives, this means we would be able to store energy when looking at $\Delta G^{storage}$. We would also want the ΔG^{TBR} to be positive because if it was negative, it would reverse back spontaneously, while if positive it may just require an external energy source before reversing meaning it would be controlled. From the ΔG^{TBR} calculations we see a trend that when the polarity increases the ΔG^{TBR} decreases. The calculated values for ΔG^{TBR} are lower than what have been found previously of around 120 kJ/mol [5]. Therefore it would indicate that it would not be able to hold the energy as expected.

Table 2: ΔGstorage and ΔG^{TBR} for Different Methods in Units of kJ/mol

Method	CAM-B3LYP-D3		M062X		ωB97DX	
Solvent	ΔGstorage	ΔGTBR	ΔGstorage	ΔGTBR	ΔGstorage	ΔGTBR
Acetone	152.60	59.00	126.24	68.70	136.48	62.24
ACN	152.35	57.41	133.24	60.02	136.29	60.39
DCM	155.17	63.42	130.04	70.00	137.37	66.55
DMSO	152.27	56.92	125.68	67.02	136.24	59.69
Toluene	154.06	78.25	132.75	84.89	138.30	81.12
Vacuum	155.92	97.01	133.07	104.10	138.68	103.08

Excitation Energies

Table 3: Selected Peaks for Different Methods

Method	CAM-B3LYP-D3		M062X		ωB97DX	
Solvent	Reactant	Product	Reactant	Product	Reactant	Product
Acetone	351.5	313.2	355.1	319.6	350.6	315.6
ACN	351.5	313.2	355.1	319.6	351.5	316.4
DCM	350.6	312.4	354.2	319.6	348.8	315.6
DMSO	352.4	314.0	356.0	320.4	352.4	317.2
Toluene	339.8	310.0	347.0	315.6	341.6	312.4
Vacuum	339.8	297.8	344.3	304.4	338.9	299.9

When looking at Figures 5, 6, and 7, we observe the UV-Vis spectra for the product and reactant in each solvent and with the three different functionals. It is evident at first glance that as the solvent polarity increases, there is a noticeable red shift in the absorption peaks, accompanied by a rise in the absorption intensities. When looking at the wavelengths that are in the more interesting area about 300 nm and up, we see excitation in this area. This does come with spectral overlaps between the reactant and product and this implies that the reactant structures will absorb photons at the same wavelength as the product does, resulting in reduced photochemical conversion. One noteworthy observation is the limited fluctuation in the UV-Vis spectra above 300 nm across the various solvents. The most significant distinction arises when transitioning from a vacuum environment to a solvent, as opposed to transitioning from a nonpolar to a polar solvent. When looking at the peak in UV-Vis spectra from 275nm - 400nm as seen in Table 3 they do in general peak close to each other's wavelength, but here it is also quite clear there is decently sized redshift. A large shift will often also bring a smaller spectral overlap which is good as they will not absorb photons at the same wavelength.

Conclusion

In this study, we examined a molecular structure predicted by a former paper that placed it as a good candidate for solar conversion efficiency. Using Density Functional Theory (DFT), we explored different basis sets and solvent effects on vibrational frequencies. Positive Gibbs free energy for ΔGstorage suggests the potential for energy storage. While the positive ΔGTBR indicates the possibility for control and storage of the energy, the values were low. UV-Vis spectra revealed distinct excitations, supporting the molecule's promise for solar energy conversion. These findings validate MOST's prediction and position the molecular structure as a strong candidate for solar energy technologies, these results contribute to advancing solar thermal energy research, offering both promise and avenues for continued exploration.

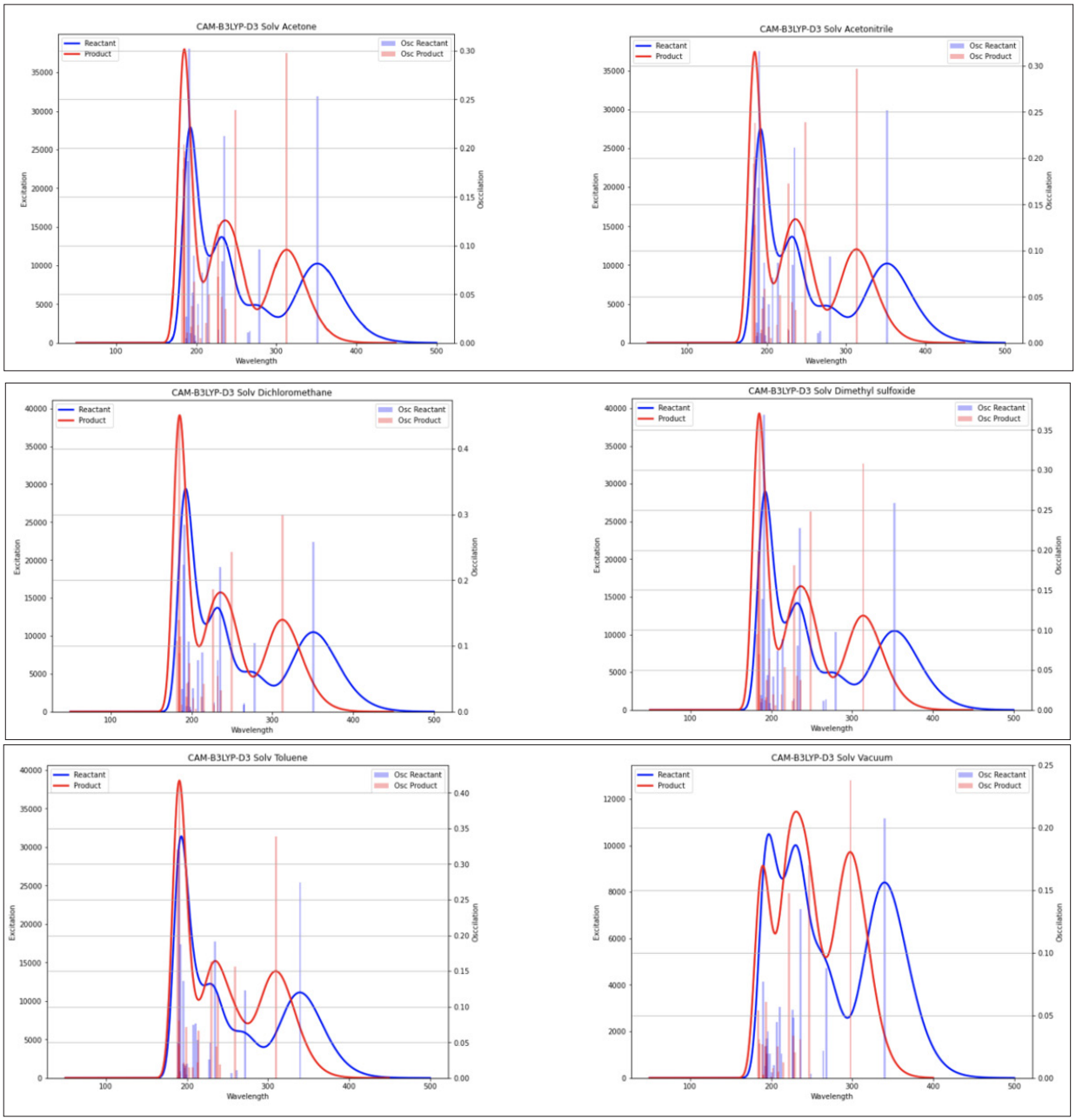

Figure 5: Excitation of product and reactant in solvents calculated with CAM-B3LYP-D3 and 6311++G(d,p) Top left) Acetone Top right) Acetonitrile Middle left) Dichloromethane Middle right) DMSO Bottom left) Toluene Bottom right) Vacuum.

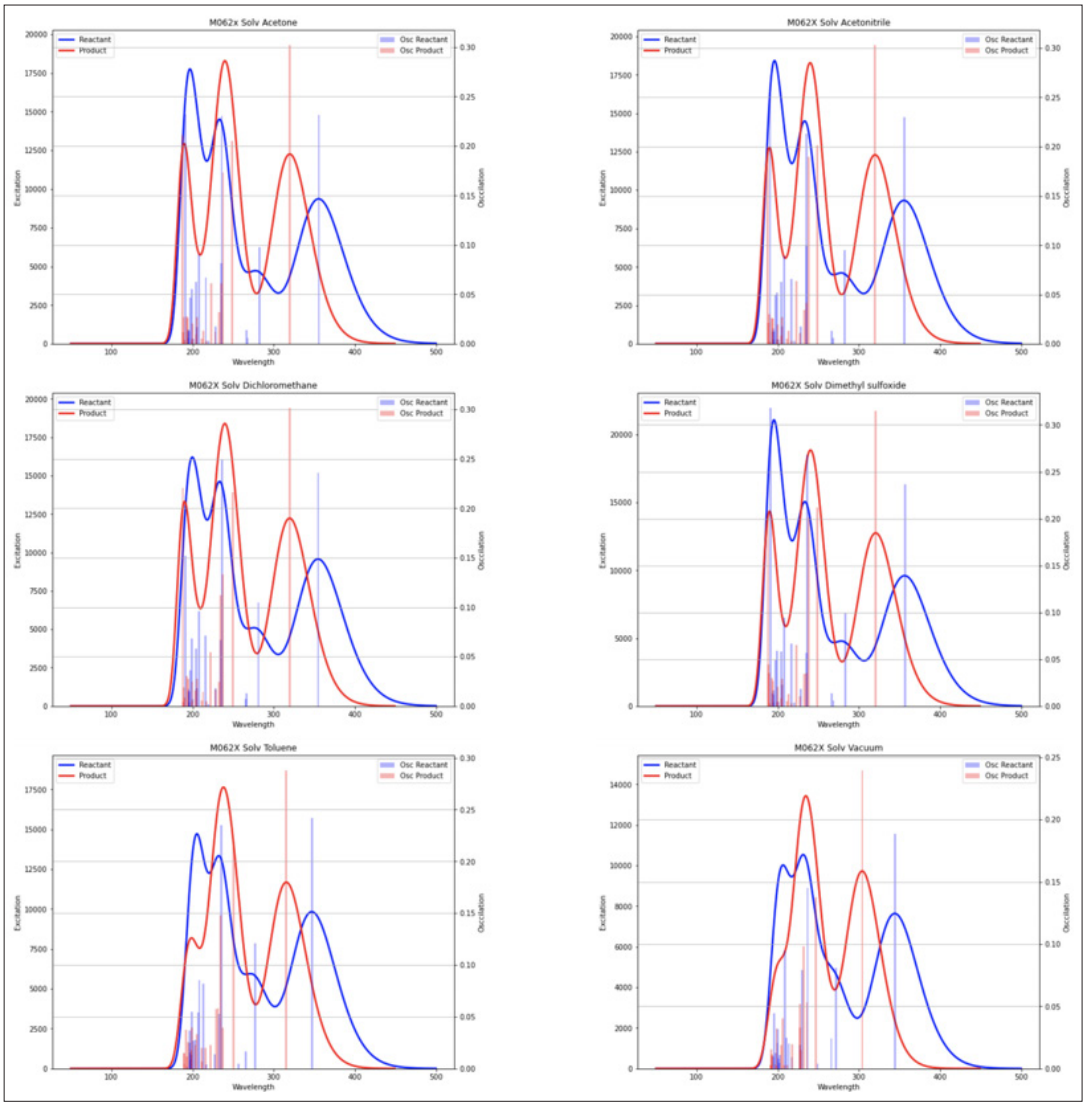

Figure 6: Excitation of Product and Reactant in Solvents Calculated with M062x and 6311++G(d,p) Top left) Acetone Top right) Acetonitrile Middle left) Dichloromethane Mid-dle right) DMSO Bottom left) Toluene Bottom right) Vacuum.

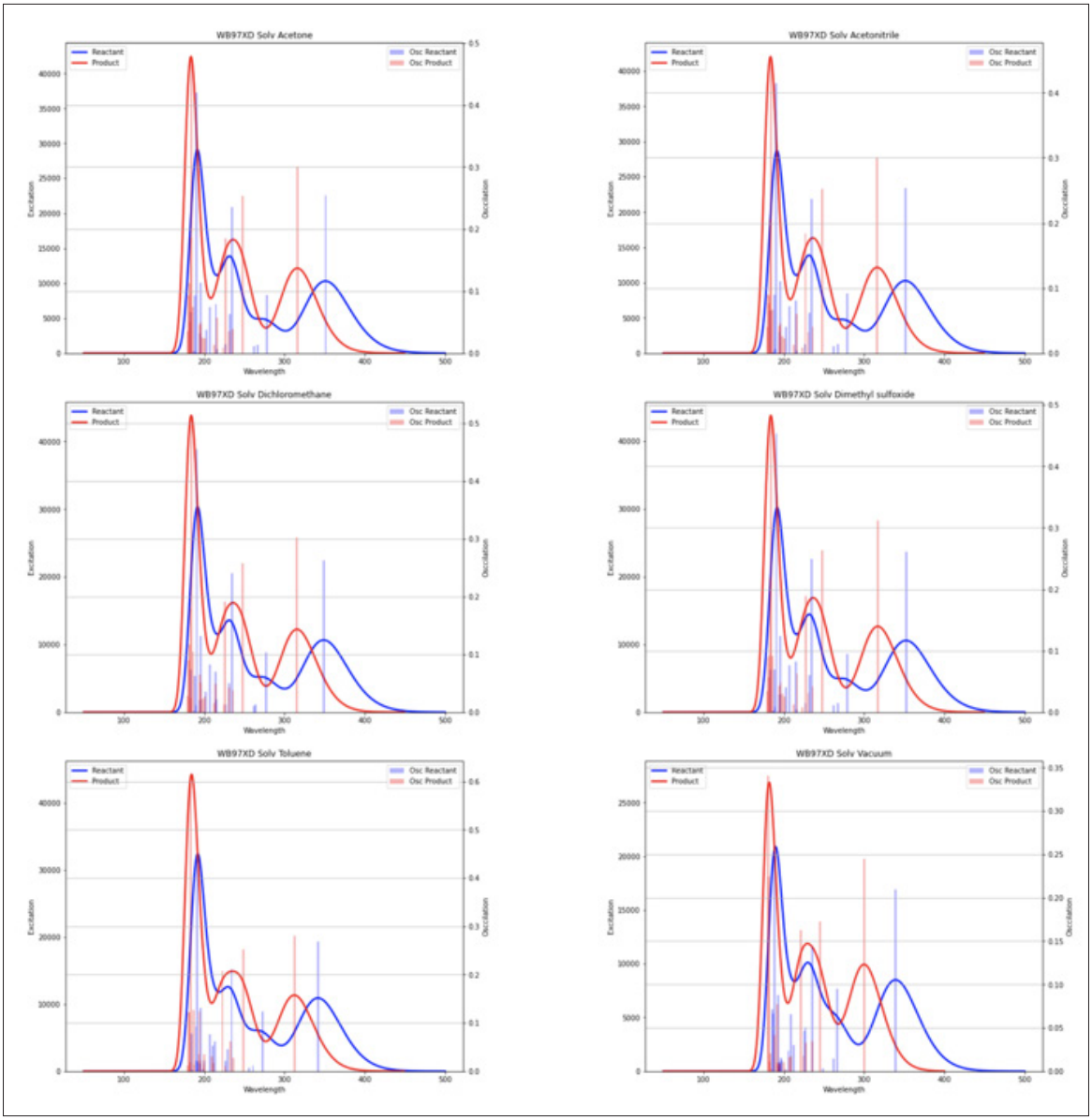

Figure 7: Excitation of Product and Reactant in Solvents Calculated with ωB97DX and 6311++G(d,p) Top left) Acetone Top right) Acetonitrile Middle left) Dichloromethane Mid-dle right) DMSO Bottom left) Toluene Bottom right) Vacuum.

Outlook

Exploring the dynamics of chemical reactions through Intrinsic Reaction Coordinate (IRC) analysis emerges as a promising direction for future investigations. The inclusion of IRC in our methodology can provide a detailed trajectory of the reaction pathway, shedding light on the sequence of molecular rearrangements during the chemical transformation. This approach goes beyond the static view offered by traditional optimization procedures, allowing for a more dynamic understanding of the reaction mechanisms.

Moreover, an expanded examination of the entire molecular structure is warranted in our future endeavors. While the current study has provided valuable insights into specific regions of interest, a comprehensive analysis of the full molecule is essential. This holistic perspec-tive can uncover hidden intricacies and interdependencies within the molecular framework, contributing to a more nuanced comprehension of the system under study.

In terms of computational methods, transitioning from Density Functional Theory (DFT) to advanced Coupled Cluster (CC) methods holds the potential to refine the accuracy of our predictions. CC methods, known for their high accuracy in capturing electron correlation effects, may offer a more precise description of the electronic structure and energetics of the studied reactions. This switch in methodology could enhance the reliability of our results and provide a solid foundation for making quantitative comparisons with experimental data.

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