Investigating and Characterizing the Excited States and Energies of [cis-Bis(2-phenylpyridinato) (2,2' bipyridine) cobalt] $^{+}$

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As the search for cleaner, more affordable energy continues, an increasing amount of research has been conducted into solar energy. The conversion of CO_2 gas into its radicals and H_2O into its constituent elements, hydrogen and oxygen, to create solar energy has led to the investigation of different methods to facilitate this reaction.[1]

Metal-based photo-redox catalysts have been at the forefront of these investigations due to their activation through visible light, along with their properties of photoinduced electron transfer, which facilitate the conversion of CO_2.[2,3] While efficient, current metallaphotoredox catalysts, including ruthenium, palladium, and platinum, are costly and non-earth abundant.[2] To further the development of widespread solar energy production, a new, more earth-abundant metal must be identified to act as a metal center for the catalysts.

Our goal over the summer was to demonstrate that a different metal had the potential to serve as an alternative catalyst for the conversion of CO_2 and H_2O. The metal I chose was cobalt, more specifically [cis-Bis(2-phenylpyridinato) (2,2' bipyridine) cobalt] +. Previous research into this molecule has shown significant signs that it could act as a contender for solar energy production, due to energy spikes from light excitation around 500 nm, within the visible light spectrum, along with transfer states that have the potential to prolong excited state lifetimes.[4] Furthermore, cobalt has previously been utilized for water splitting, which strengthens the idea that this molecule could be active in catalysis.[5] However, since the current cobalt molecule is relatively small for a transition metal photo-redox catalyst, its excited-state half-life is too short to catalyze reactions efficiently.[4] Therefore, our goal was to characterize these excited states and confirm that they occur at the wavelength ideal for facilitating the solar energy process.

Since the half-life of the molecule is so short, physical experiments are unable to accurately determine the characteristics of the excited state of my molecule. Therefore, I utilized computational methods, including Complete Active Space Self-Consistent Field (CASSCF) and Density-Matrix Renormalized Group (DMRG), to fully characterize and analyze these excited states.[6,7,8] CASSCF is a highly accurate method that enables me to calculate the multiple excited states of my molecule, along with their corresponding energy levels.[6,7,9] However, while quite accurate, CASSCF only allows for a small number of atoms to be considered. This downside emphasizes the need for a supplementary method. Therefore, to include all the atoms within the molecule, we utilize DMRG. DMRG approximates CASSCF, resulting in less accurate energy levels.[8] To calculate the true energy required to excite my molecule into its excited states, we must make DMRG as accurate as possible, comparable to CASSCF. Results from the DMRG provided evidence that our molecule had the ability to become excited through visible light at 350-440 nm, suggesting its potential to act as a strong catalyst in solar energy conversion. Future steps would focus on examining the lifetimes of my molecule, along with experimenting with ways to prolong these lifetimes through multiple methods including Time-dependent Density Functional Theory.[10] If we could lengthen the excited state half-life of this molecule, it would be one step into a future where solar energy could be much more accessible to all.

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