

University of Louisville  
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**Dissertation Defense**

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## **COMPUTATIONAL INVESTIGATIONS OF BOND BREAKING PROCESSES USING DFT AND TD-DFT APPROACHES**

### **ABSTRACT:**

The efficient application of DFT and TD-DFT has been harnessed to study bond-breaking processes in some molecules which play a prominent role in some enzymatic reactions and organic synthesis. The first application includes Radical S-adenosyl methionine (SAM) enzymes which are fundamentally important sources of organic radicals to initiate diverse radical reactions. Recently a bio-organometallic intermediate omega ( $\Omega$ )<sup>1</sup> that contains an Fe–C bond has been characterized and shown to be a common feature of radical SAM enzymes. The strength of Fe–C bond in  $\Omega$  has been computed using broken-symmetry density functional theory (BS–DFT).<sup>2</sup> Additionally, Fe–C bond dissociation energy (BDE) in  $\Omega$  has been compared to that with S–C bond in SAM and Co–C bond in adenosylcobalamin (AdoCbl).

The second application includes Ethyl(aqua)cobaloxime (Cbx) which is commonly used as a model compound to study vitamin B<sub>12</sub> derivatives such as AdoCbl and methylcobalamin (MeCbl). The mechanism of Co–C bond photodissociation in Cbx<sup>3</sup> in presence of a benzophenone (acting as photocatalyst, PC) has been investigated by means of time-dependent density functional theory (TD–DFT). The calculation of low-lying singlet and triplet excited states of the substrate and PC reveal that the photodissociation process is mediated by a repulsive triplet state<sup>4</sup> via Dexter energy transfer from PC to Cbx.

Lastly, DFT and TD–DFT have been applied to investigate photo-assisted cleavage of *N, N*-dimethylformamide (DMF).<sup>5</sup> Potential energy surfaces (PES) have been constructed using DFT to investigate the cleavage of C–F bond of perfluoronaphthalene (PFN) and simultaneous attachment of DMF N-atom to C-atom. Excited state PESs, which were calculated using TD–DFT, reveals that the energy barrier for electron transfer from DMF to PFN is significantly reduced in presence of light. This enables a redistribution of the electronic charge between the DMF and PFN leading to accelerated reductive cleavage of the C–F bond and subsequent quick reaction between radical ions to give amination products.

### **REFERENCES:**

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