

University of Louisville
Department of Chemistry

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Research Seminar

When: October 27, 2022

Time: 2:30 p.m.

Location: CBLL-16

Computational investigations of bond-breaking processes using DFT and TD-DFT approaches

Abstract:

During my presentation, I will discuss three projects related to bond-breaking that can be summarized as follows:

(a) Radical S-adenosyl methionine (SAM) enzymes are fundamentally important source of organic radicals to initiate diverse radical reactions. Activation of SAM by iron–sulfur cluster to reductively cleave the C–S bond is required to generate the reactive radicals.¹ Recently a bio-organometallic intermediate (Ω) that contains an Fe–C bond has been characterized and shown to be a common feature of radical SAM enzymes.² The strength of Fe–C bond in Ω has been computed using broken-symmetry density functional theory (BS–DFT).³ Finally Fe–C bond dissociation energy (BDE) in Ω has been compared to that with S–C bond in SAM and Co–C bond in adenosylcobalamin (AdoCbl).

(b) Ethyl(aqua)cobaloxime (EtCoX) is used as a model compound to study vitamin B₁₂ derivatives such as AdoCbl and methylcobalamin (MeCbl).⁴ The mechanism of Co–C bond photodissociation in EtCoX has been investigated by means of time-dependent density functional theory (TD–DFT). The low-lying singlet and triplet excited states have been computed along the Co–C coordinate at TD–DFT/BP86/def2-TZVP level of theory. These calculations reveal that the photodissociation process is mediated by a repulsive triplet state.⁵ The feasibility of Dexter energy transfer from benzophenone to EtCoX has been explored using CASSCF/NEVPT2 theory.

(c) Lastly, DFT and TD–DFT have been applied to investigate photo-assisted cleavage of *N,N*-dimethylformamide (DMF).⁶ 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:

1. W. E. Broderick, B. M. Hoffman and J. B. Broderick, *Mechanism of Radical initiation in the Radical S-Adenosyl-L-methionine Superfamily*, Accounts of Chemical Research, 2018, 51, 2611-2619
2. A. S. Byer, H. Yang, E. C. McDaniel, V. Kathiresan, S. Impano, A. Pagnier, H. Watts, C. Denler, A. L. Vagstad, J. Piel, K. S. Duschene, E. M. Shepard, T. P. Shields, L. G. Scott, E. A. Lilla, K. Yokoyama, W. E. Broderick, B. M. Hoffman and J. B. Broderick, *Paradigm shift for Radical S-Adenosyl-L-methionine Reactions: The Organometallic Intermediate Ω is central to Catalysis* Journal of the American Chemical Society, 2018, 140, 8634-8638
3. L. Noodleman and D. A. Case, *Density-Functional Theory of Spin Polarization and Spin Coupling in Iron–Sulfur Clusters*, Advances in Inorganic Chemistry 1992, 38, 423-470
4. Hisham Y. Al-Saigh, and Terence J. Kemp, *Sensitization and Quenching Processes of Alkylcobalt(III) Compounds* Journal of Chem. Soc., Perkin Trans. II, 1983, 615-619
5. P. Lodowski, M. Jaworska, T. Andruniow, M. Kumar and P. M. Kozlowski *Photodissociation of Co-C bond in Methyl- and Ethylcobalamin: An insight from TDDFT calculations* J. Phys. Chem. B 2009, 113, 19, 6898–6909.
6. T. N. Ansari, S. Sharma, P. P. Bora, D. Ogulu, S. Parmar, F. Gallou, P. Kozlowski and S. Handa *Photoassisted charge transfer between DMF and substrate: facile and selective N,N-dimethylamination of fluoroarenes* ChemSusChem 2021, 14, 2704–2709.