CORE-CM SEMINAR
Michigan State University

"Donor-Bridge-Acceptor Biradicals in Ground- and Excited States: Correlation of Exchange and Electronic Coupling with Excited-State Wave Function Mixing"

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Electron donor-acceptor interactions form the basis for controlling electron transfer (ET) and transport at the molecular level. They therefore form crucial, foundational elements in biological and artificial ET and photosynthesis, solar energy conversion and molecular electronics/spintronics (electron spin-based electronics). Chief amongst the variables controlling ET/transport rates is the bridge-mediated donor-acceptor electronic coupling matrix element, H_{DA} – a type of resonance integral.

Photoexcitation of the donor (D) in a donor-bridge-acceptor molecule (D-B-A) yields a D*-B-A excited state which may undergo ET to form a charge-separated, spin singlet ***biradical*** D^+-B-A^- state. A convenient, straightforward way to demonstrate important, fundamental structure-property relationships for nonadiabatic ET rates is to utilize the correlation of H_{DA} with the readily-measured magnetic exchange coupling (J_{DA}) between spin ½ centers in a charge-separated biradical.

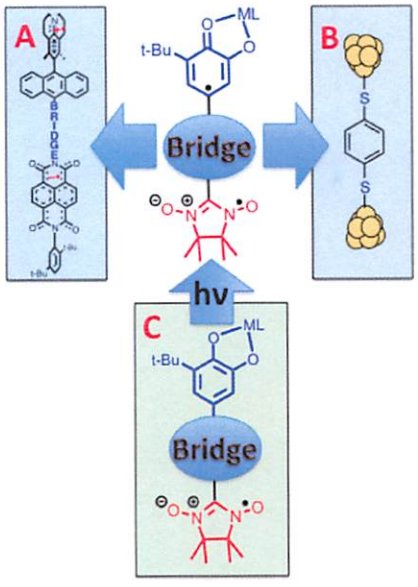

Figure. D-B-A biradical (top center, where D = spin-½ 3-*tert*-butyl-orthosemiquinone and A = spin-½ nitronylnitroxide) complexes serve as models for intramolecular electron transfer (**A**) and nanoscopic electron transport (**B**), as well as novel excited state structures in which SQ-NN exchange might be used to control dynamics (**C**).

Covalently-linked D-B-A biradicals (where D = spin-½ 3-*tert*-butyl-orthosemiquinone, **SQ** and A = spin-½ nitronylnitroxide, **NN**, see Figure) serve as *ground state analogues* of PET-derived charge-separated states as well as models for understanding electronic structure contributions to single-molecule conductance. Given our ability to design strong ferromagnetic bridge-mediated exchange coupling between **SQ** and **NN**, we can use this exchange coupling to control excited state wave function mixing that in turn modulates important excited state photophysical processes.

This talk will show how such biradicals can be used to demonstrate important structure property relationships in the strong-coupling regime and how this strong electronic coupling might be used to control excited state photophysical processes such as intersystem crossings.

Thursday, September 25, 2014
12:00 PM
Room 1400 – BPS
Professor – Ned Jackson - Host