Evidence for a Vibronic Singlet Fission Mechanism from *Ab Initio* Non-Adiabatic Coupling Calculations of Crystalline Tetracene.

Adrian F. Morrison*, and John M. Herbert†
Dept. of Chemistry & Biochemistry, The Ohio State University, Columbus, OH 43210

The singlet exciton fission process, where a pair of triplet excitons are generated from absorption of a single photon, offers a promising means of overcoming the Shockley-Queisser solar conversion efficiency limit and has been the subject of a great deal of study. Recently, attention has been brought to the, potentially significant, role of the nuclear degrees of freedom in motivating the fission transition. However, due to the complex electronic structure of the key multi-exciton intermediate theoretical treatments remain a challenge, limiting the nascent understanding of the non-adiabatic aspects of the singlet fission mechanism.

Recently, our group developed a novel fragment based method method for computing excited state properties of aggregates, the *Ab Initio* Frenkel Davidov Exciton Model (AIFDEM). The direct product *ansatz* of the AIFDEM provides an elegant way to treat the key multi-exciton intermediate of the singlet fission process as a simple spin-adapted product of two fragment triplet excited states. Analytic derivatives of the AIFDEM Hamiltonian, also recently derived and implemented in our group, provide direct access to the non-adiabatic coupling vector as well as electron-phonon coupling constants, both of which can be used to quantify and characterize the influences of nuclear motion on electronic processes.

We have used this method to investigate singlet fission in crystalline tetracene, where the process is understood to be electronically endoergic. By projecting the non-adiabatic coupling vector onto phonon mode coordinates, we have identified vibrational modes that strongly couple the single and multi-exciton states, finding them to be primarily of localized, intra-monomer character. Furthermore, the phonon frequencies, of 1400-1600 cm^{-1}, are nearly resonant with the electronic energy gap between the single and multi-exciton states. The analogous electron-phonon couplings are primarily of the local, Holstein, type, serving to modulate the site energies. A model Hamiltonian study, utilizing our computed quantities, as well as Redfield dynamics simulations offers qualitative evidence that vibronic coherence can provide the impetus for spontaneous and ultra-fast fission, despite unfavorable electronic energetics.

*morrison.497@osu.edu
†herbert@chemistry.ohio-state.edu