

**Final Report**  
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**Project title: "Applications of Adaptive Quantum Control to Research Questions in Solar Energy Conversion"**

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Sponsoring Office: Department of Energy

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Limitations on public release: none

**Publications List:**

- 12) Carey, T.; Snyder, J. L.; Michael, R. E.; Sammakia, T.; Damrauer, N. H. Synthesis of a Geometrically Well Defined and Electronically Coupled Tetracene Dimer for Singlet Fission *Journal of Organic Chemistry* (2016) Submitted.
- 11) Cook, J. D.; Carey, T.; Damrauer, N. H. Solution-Phase Singlet Fission in Structurally Well-Defined Tetracene Dimers *Journal of Physical Chemistry A.* **120**, 4473–4481 (2016). dx.doi.org/10.1021/acs.jpca.6b04367
- 10) Arias, D. H.; Ryerson, J. L.; Cook, J. D.; Damrauer, N. H.; Johnson, J. C. Polymorphism Influences Singlet Fission Rates in Tetracene Thin Films *Chemical Science*. **7**, 1185-1191 (2016). dx.doi.org/10.1039/C5SC03535J
- 9) Damrauer, N. H.; Snyder, J. L. Symmetry-Directed Control of Electronic Coupling for Singlet Fission in Covalent Bis-Acene Dimers. *Journal of Physical Chemistry Letters*. **6**, 4456-4462 (2015). dx.doi.org/10.1021/acs.jpclett.5b02186
- 8) Alguire, E. C.; Subotnik, J. E.; Damrauer, N. H. Exploring Non-Condon Effects in a Covalent Tetracene Dimer: How Important are Vibrations in Determining the Electronic Coupling for Singlet Fission? *The Journal of Physical Chemistry A.* **119**, 299-311 (2015). dx.doi.org/10.1021/jp510777c
- 7) Vallet, P. J.; Snyder, J. L.; Damrauer, N. H. Tunable Electronic Coupling and Driving Force in Structurally Well- Defined Tetracene Dimers for Molecular Singlet Fission: A Computational Exploration Using Density Functional Theory. *The Journal of Physical Chemistry A.* **117**, 10824–10838 (2013). dx.doi.org/10.1021/jp407426q
- 6) Grumstrup, E. M.; Damrauer, N. H. Modeling and correction of distorted two-dimensional Fourier transform spectra from pixelated pulse shaping devices. *Optics Express* **20**, 20908 (2012). <http://dx.doi.org/10.1364/OE.20.020908>

- 5) Vallet, P. J.; Damrauer, N. H. Computational Exploration of Heterolytic Halogen-Carbon Bond Scission Photoreactions in Ruthenium Polypyridyl Complexes. *The Journal of Physical Chemistry A.* **115**, 3122-3132 (2011). dx.doi.org/10.1021/jp111000d
- 4) Grumstrup, E. M.; Johnson, J. C.; Damrauer, N. H. Enhanced Triplet Formation in Polycrystalline Tetracene Films by Femtosecond Optical-Pulse Shaping. *Physical Review Letters* **105**, 257403 (2010). <http://link.aps.org/doi/10.1103/PhysRevLett.105.257403>
- 3) Montgomery, M. A.; Grumstrup, E. M.; Damrauer, N. H. Fourier Transform Spectroscopies Derived from Amplitude or Phase Shaping of Broad-Band Laser Pulses with Applications to Adaptive Control. *Journal of the Optical Society of America B.* **27**, 2518-2533 (2010). <http://dx.doi.org/10.1364/JOSAB.27.002518>
- 2) Montgomery, M. A.; Damrauer, N. H. A Convenient Method to Simulate and Visually Represent Two-Photon Power Spectra of Arbitrarily Shaped Broadband Laser Pulses. *New Journal of Physics* (Special Issue on Quantum Control Edited by H. Rabitz) **11**, 105053 (2009). <http://iopscience.iop.org/1367-2630/11/10/105053/>
- 1) Grumstrup, E. M.; Shim, S. H.; Montgomery, M. A.; Zanni, M. T.; Damrauer, N. H. Facile Collection of Two-Dimensional Electronic Spectra with Pulse Shaping Technology. *Optics Express* **15**, 16681-16689 (2007). <http://dx.doi.org/10.1364/OE.15.016681>

### **Supported Ph.D. Students:**

Dr. Erik M. Grumstrup (currently an Assistant Professor at Montana State University).  
 Dr. Matthew A. Montgomery (currently a law associate at Hill & Robbins, P.C. in Denver with a practice emphasizing water and natural resource law).  
 Dr. Paul Donohoo-Vallett (currently Technology & Policy Analyst at U.S. Department of Energy)  
 Dr. Jamie L. Snyder (currently Chemistry Lab Coordinator and University Chemical Hygiene Officer at Transylvania University in Kentucky)  
 Jasper D. Cook (still in PhD program)  
 Thomas Carey (still in PhD program)

### **Supported Postdoctoral Associates:**

Dr. Bijan Paul (most recently: Postdoctoral Researcher, Mukherjee Group; Indian Institute of Science Education and Research Bhopal)  
 Dr. Dylan H. Arias (currently: Postdoctoral Researcher, Dr. Justin Johnson's Group; National Renewable Energy Laboratory)

This award supported a broad research effort at the University of Colorado at Boulder comprising synthesis, applications of computational chemistry, development of theory, exploration of material properties, and advancement of spectroscopic tools including femtosecond pulse shaping techniques. It funded six graduate students and two postdoctoral researchers. Four PhDs were earned based on supported research and two more are expected within the year. The first student trained, Dr. Erik Grumstrup, is now a thriving assistant professor at Montana State University and a DOE Early Career Program award winner in 2015. Another student, Dr. Paul Vallet is currently a policy analyst at the Department of Energy.

Manuscripts **1**, **3**, and **6** focused on using phase and amplitude shaping of broadband femtosecond laser pulses to create phase-locked laser pulse pairs. When these are employed as the excitation source in a pump/probe experiment (manuscripts **1** and **6**), one is able to readily implement a Fourier transform multidimensional correlation spectroscopy. Manuscript **1** was the first to show this is possible with an electronic spectroscopy (it had been done with IR) and demonstrated an ease of implementation for two-dimensional electronic measurements that was previously unknown. Manuscript **3** extended the idea of implementing a Fourier transform multidimensional correlation spectroscopy but this time using only phase shaping of femtosecond laser pulses. We argued that this spectroscopic tool was useful for understanding mechanism in adaptive femtosecond pulse shaping quantum control experiments involving two-photon absorption in complex molecules (manuscript **3** and **2**). Although no publications emerged, an ~1.5 year effort sought to use adaptive femtosecond pulse shaping to control product yield signals in nanocrystalline lead salt semiconductor systems implicated in multiple exciton generation (MEG).

Because of challenges with experimental reproducibility in our efforts to control MEG with pulse shaping, we shifted towards a different system with highly related physics. Rather than MEG in lead salts we sought to control multiple exciton generation in organic systems comprised of acene chromophores, where singlet fission is energetically accessible. In this setting, pairs of low-energy triplets are the multiple excitons produced following singlet excitation of the chromophoric system. In manuscript **4** we reported quantum control results for polycrystalline tetracene. Pulse shape families were explored that have a comb-like structure in time; such pulses are produced using a sinusoidal modulation of laser pulse phase in the frequency domain (also explored in manuscript **3**). Optimal pulses were discovered using an adaptive algorithm charged with iteratively increasing a transient absorption signal that could be assigned to triplet yield based on the wavelength of the observation and the time of the observation relative to the shaped excitation pulse. These optimal pulses increase observed triplet yield by ~10-15%. Very interestingly, single wavelength transient absorption signals, which are collected as a function of time following optimal pulse excitation, show a strong enhancement of low frequency vibrational coherences (seen as coherent oscillations) compared to transform limited laser pulses. Our interpretation is that these low frequency modes being coherently stimulated during control correspond to intermolecular lattice vibrations. This work is arguably the first direct experimental support that electronic coupling in the singlet fission reaction can be modulated by inter-chromophore  $\pi$ -interactions.

The polycrystalline acene system that is controlled in the aforementioned work (manuscript **4**) is complex inasmuch as singlet fission yields are influenced by condensed matter properties such as defect structure that is influenced by polymorphism and crystallite size. Although not chronological, these issues are considered in tetracene systems as described in manuscript **10** (collaborative work with Johnson's group at NREL). There it is found that for larger grain sizes,

singlet fission is significantly faster for films comprised of metastable polymorph II. That work is important in the community for mechanistic reasons but also by way of beginning to explain uncertainties in reported rate constants throughout the literature and highlighting the importance of controlling film deposition conditions. It may also be useful in explaining anomalous temperature dependence that has been observed by others for singlet fission in tetracene. Because of complexities in solid materials, we became interested in studying molecular dimer systems, where in principle, factors influencing singlet fission rates can be carefully controlled using synthesis and where quantum chemistry has a clear opportunity for mechanistic delineation. We were drawn to older work by Paddon-Row and coworkers, who had considered electronic interactions between small acene chromophores derived from naphthalene. Using polycyclic alkyl bridges (conceptually derived from norbornadiene), these workers showed that the electronic coupling between acene chromophores could be tuned by the size of the bridge and that this tuning parameter manifests in the size of Davydov splitting in electronic absorption spectra. Because naphthalene as a chromophore cannot support singlet fission from an enthalpic perspective, we were interested in tetracene analogues and began synthetic efforts as well as computational explorations.

Manuscript 7 falls in the latter category and represents a detailed exploration using density functional theory (DFT) and time-dependent DFT (TD-DFT) of critical state energetics, reaction energetics, and interchromophore couplings in several structurally well-defined tetracene dimers. Coupling is explored through frontier orbital splitting parameters as well as through excited state energy splitting values revealed through TD-DFT. The study shows how bridge structure can be used to tune interchromophore electronic coupling and it quantifies coupling in terms of both interchromophore  $\pi$  interactions as well as through-bond coupling, mediated in part by the  $\sigma^*$  system of the alkyl bridges. The study argues for the first time in the story of these types of systems that diabatic electronic coupling for singlet fission – a quantity that factors into rate expressions like that of Marcus theory – may become small or vanish when there is too much symmetry in the dimers. This is discussed more below. Beyond electronic coupling aspects, an important finding comes from applications of TD-DFT that incorporate energy gradients in order to find geometrical structures of excited states. In this context we find localization of excited state energy at single chromophore sites within dimers, a point that has significant implications in terms of the reorganization energy of the singlet fission reaction in molecular systems, a point that is underappreciated in the literature.

An overall approach to synthesis of dimers in this class is outlined in manuscript 12. Unlike most chromophore dimers that rely on single-bond points of attachment to a bridge or to each other, the structural definition/rigidity of our systems suggests value using a Diels-Alder strategy to simultaneously make two C-C bonds, thereby orienting chromophoric arms about the bicyclic or polycyclic bridge with high regio-specificity. Initial efforts for the smallest norbornyl-bridged dimer (called BT1) sought to use norbornadiene as the dienophile and as such, to install diene moieties in the would-be chromophoric arms. After a significant effort, this route was abandoned, in part due to a severe allergic reaction by one of the graduate students to a key halogenated reactant. We then modified the approach by synthesizing a bicyclic bridging unit containing a pair of oppositely juxtaposed dienes. We can now synthesize this generally useful building block in gram quantities. Dimers are synthesized by sequential Diels-Alder addition of quinone-derived dienophiles that can also be synthesized in large amounts. Both oxidation and reduction steps are also needed and these are interleaved within the synthesis as needed. In work that is ongoing now, the sequential approach to adding chromophore arms is useful for synthesis of heterodimers that

break symmetry. Further, intermediate ketone moieties derived from the quinone Diels-Alder partners prove useful for installation of tri-isopropylsilyl (TIPS) acetylene units for oxidative stability and increased solubility of synthesized dimers. We have synthesized TIPS analogs of BT1 and have recently synthesized a pentacene analogue as well.

In manuscript **8**, we developed theoretical tools that enable calculation of diabatic coupling matrix elements for the singlet-fission reaction. We sought tools based on one-electron orbital couplings that would approach accuracy but at the same time enable rapid prediction and foster mechanistic understanding based on orbital symmetry and orbital coefficients. Traditional electronic structure methods do not suffice because calculated orbitals (generally delocalized about both chromophores of the dimer) are eigenfunctions of the Hamiltonian and therefore uncoupled to each other. The tools we put in place exploit a frontier-orbital active space and apply a unitary transformation based on methodology developed by Boys, to localize orbitals on chromophore arms. Following a diagonalization procedure, a Fock matrix is generated that allows one to directly read off one-electron orbital couplings that contribute to singlet fission diabatic coupling when it occurs via charge-transfer mediated pathways (the dominant source of diabatic coupling for singlet fission in acene dimers). These calculations are rapid and do not meaningfully add computational time to what is needed for single-point DFT. Applications to BT1 indeed show that diabatic coupling for singlet fission vanishes at the  $C_{2v}$  symmetry of the ground state. The source of this effect is a plane of symmetry in the molecule that passes through both chromophores and the fact that highest occupied chromophore-localized molecular orbitals are anti-symmetric to the operation of reflection through this plane whereas lowest unoccupied chromophore-localized molecular orbitals are symmetric.

Continuing in manuscript **8**, we then sought to study the effect of molecular vibrations for turning on diabatic coupling for singlet fission in these dimer systems. For a  $C_{2v}$  dimer structure in BT1, there are four types of motions classified in terms of the irreducible representations of the point group symmetry. Two of these are motions that break the aforementioned plane of symmetry and it is through these that diabatic coupling can emerge. Within this exploration, a fascinating discovery emerged that has to do with these two types of motion. For one of these – so-called  $B_2$  vibrations where the  $\sigma_v$  reflection plane symmetry element passing between chromophores is preserved throughout the motion – the two quantum mechanical pathways that contribute to charge transfer mediated diabatic coupling *destructively* interfere. These two interfering pathways include a hole-transfer pathway mediated by occupied orbitals and an electron-transfer pathway mediated by unoccupied orbitals. For the other of the two coupling-inducing motions – so-called  $A_2$  vibrations where the  $C_2$  rotation symmetry element is preserved throughout the motion – the two quantum mechanical pathways *constructively* interfere. The work shows that low-frequency  $A_2$  motions play an important role in establishing finite diabatic coupling for singlet fission at room temperature in symmetrical dimers such as BT1.

In manuscript **11**, we studied the ground state absorption spectroscopy and excited state dynamics of BT1 as well as a one-chromophore-armed model complex that contains the bicyclic bridging unit. These studies were undertaken in non-polar solvent at room temperature and are the first to consider singlet fission in a structurally well-defined system. A comparison of features in the UV, in a region associated with a monomer long-axis  $S_3 \leftarrow S_1$  transition, shows clear Davydov splitting in BT1 signaling interchromophore electronic coupling. Intramolecular singlet fission is demonstrated but it is slow (70 ns) and low yielding (6%). These results confirm our predictions about symmetry control of diabatic coupling as well as the importance of reorganization energy in

the photophysical reaction. Both issues must be factored in future designs and this is an active area of research in the group now.

In manuscript **9**, we show in a computational/theoretical exploration that symmetry can be exploited to achieve remarkable control over singlet fission rate constants. This work draws on the vibrational symmetry results described above (manuscript **8**) and considers three systems where ground state structures maintain either  $C_2$  symmetry or  $C_s$  symmetry. Those species with  $C_2$  symmetry are shown to exhibit constructive interference of electron transfer and hole transfer quantum mechanical pathways towards diabatic coupling. This is in contrast to  $C_s$  analogues where the pathways destructively interfere. Calculations were made to determine reaction energetics, reorganization energy, and the energy of virtual charge transfer states. All of this allows for a comparison of predicted rate constants. The degree of predicted control is, in our view, extremely compelling. For example, in a comparison of aza-substituted tetracene dimers, a  $C_2$  and  $C_s$  pair have identical reaction energetics and reorganization energy, and no differences in the energy of the charge transfer state. Yet the symmetry has a profound impact on diabatic coupling such that the  $C_2$  molecule is predicted to have a rate constant for singlet fission  $\sim 300$  times larger than the  $C_s$  analogue. Control of dimer symmetry is the current focus of our synthetic efforts in this work.