DOE Solar Photochemistry Final Report: Accomplishments

Grant DE-SC0018203

Project Period 09/01/2017 - 08/31/2022

1. What are the major goals of the project?

The goals of this project are to develop an understanding of how nuclear motions can be used to drive and control photoinduced charge transfer and singlet fission reactions in molecular crystals and thin films. By following the structural evolution of reacting molecules and nanostructures on the timescale of their nuclear motion, we will determine what interplay of nuclear coordinates is most efficient in driving electron transfers, a necessary first step in most photovoltaic and photocatalytic processes. We identify which nuclear coordinates effectively promote desirable electron transfer processes, or ineffectively dissipate photon energy into unwanted thermal energy, thus guiding the design and implementation of molecular systems tailored for high efficiency processes.

Specifically, we aim to identify which nuclear coordinates are responsible for driving electron transfer and singlet fission reactions at different points along the reaction coordinate, particularly in regimes which deviate from Marcus theory predictions. We do so by investigating systems with electron transfer and singlet fission occurring from non-thermalized states due to strong donor-acceptor electronic coupling. First, we will prove that specific vibrational modes are responsible for charge transfer processes in molecular crystals. Secondly, we will investigate how vibrational coherences and specific nuclear motions can be used to drive high yield singlet fission processes. Finally, we will determine how complex film morphology affects long-range charge transport, a key limiting factor in our ability to make gains in efficiency.

Our target systems are charge transfer molecular crystals and organic thin films which undergo singlet fission. In particular, we will examine tetrathifulvalene-p-chloranil, perylene tetracyanoquinodimethane, pentacene, tetracene, and zeaxanthin. In these materials, condensing all nuclear coordinates down into a single reorganization parameter results in poor theoretical predictions and loses insight as to how the reaction actually proceeds. Potential energy surfaces and reaction pathways are inherently multidimensional, and reducing them into one dimensional reaction coordinates comes at the cost of understanding how exactly the reaction proceeds. However, experiments to obtain time-resolved structural information on the 10-1000 fs timescale of nuclear motion have been difficult due to the experimental challenges associated with high time resolution structural measurements, as well as the solid state and thin film nature of these samples.

We use femtosecond stimulated Raman spectroscopy (FSRS), a vibrational technique capable of obtaining structural information on the femtosecond time scale, to determine the structure, anharmonicity and vibrational wavepacket dynamics of reacting molecules. This enables us to map out reaction coordinates on excited state potential energy surfaces, leading to a complete understanding of how different nuclear coordinates play a role in driving wavepackets, promoting reaction pathways, and dissipating energy. FSRS has previously been used to determine a wide variety of reaction mechanisms, but applications to ultrafast electron transfer and singlet fission in films and solid systems have not previously been possible. We have implemented a variety of unique experimental upgrades to extend the FSRS technique. These advances enable us to examine structural changes in systems not compatible with existing FSRS instrumentation, such as molecular crystals and non-transparent films.

The use of a time-resolved structural technique to probe nuclear changes on the relevant timescale for charge transfer and singlet fission reactions represents a fundamentally new approach to obtaining the step-by-step mechanism. We can follow the rapid structural evolution in systems with strong-donor acceptor coupling in which molecular structure is known to play a significant yet undetermined role in separating and transferring charges. This will lead to a new understanding of the role of molecular structure in intermolecular charge transfer and singlet fission reactions, thus guiding rational molecular design of highly efficient photovoltaic and photocatalytic systems.

2. What was accomplished under these goals?

We accomplished our goals of identifying key nuclear coordinates driving charge transfer and singlet fission, as well as advanced our experimental design to enable additional measurements. In addition to the research progress described below, we trained a new generation of researchers to work on these projects. All graduates from this project have taken jobs in the STEM workface in the US. Some specific accomplishments include:

1. We published a capstone paper highlighting the use of FSRS to guide the design of photochemical systems (https://doi.org/10.1039/D1SC04251C). This work is a true culmination of a number of efforts funded solely by this DOE award. In this work, we used our previous understanding of structural effects driving singlet fission in crystalline rubrene to design a series of new rubrene derivatives. We hypothesized the by reducing the charge density on the tetracene core, we would effective prime the system to undergo the desired photochemistry. Indeed, we found that the rate and yield of the reaction were positively correlated with electron density withdrawal. This is because the systems undergo less energy loss and less reorganizational energy change, as predicted by our previous work. This study demonstrates the utility and strength of a structurally sensitive spectroscopic technique in providing insights to spectroscopy-guided materials selection and design guidelines that go beyond energy arguments to design new singlet fission-capable chromophores.

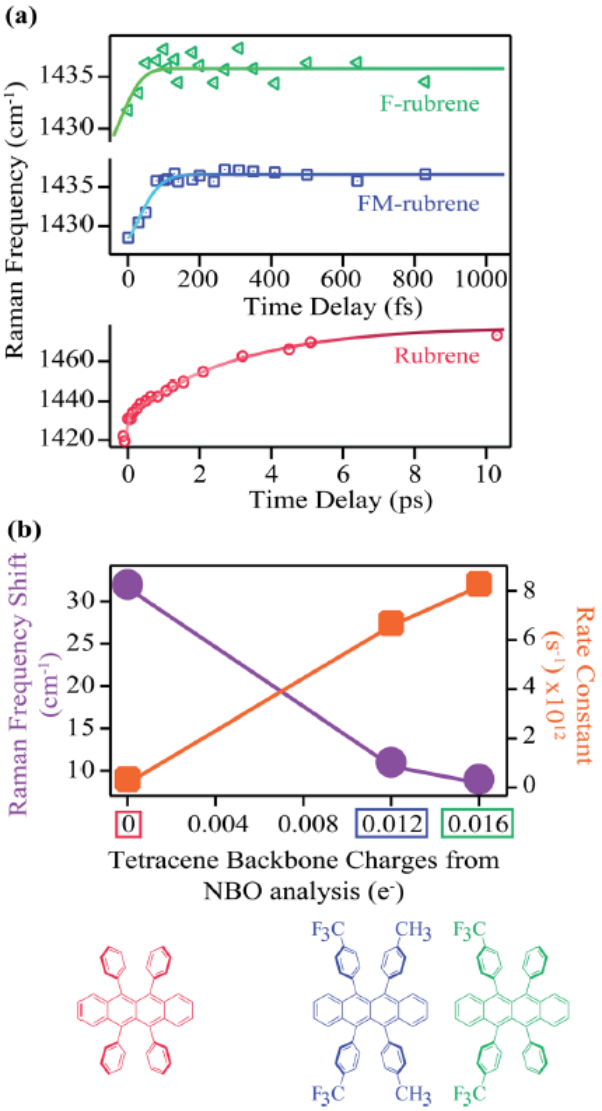

Figure 1. We used insights from FSRS to identify rubrene derivatives that we hypothesized would undergo more efficient photochemistry. We found the rate of the reaction correlated positively with electron density withdrawal from the tetracene core, confirming our spectroscopy-guided prediction.

2. We developed a new approach for quantifying the impact of selective vibrational modes on photoinduced charge transfer (http://dx.doi.org/10.1021/acs.jpclett.0c01834). In this work, we use double-pulse excitation to coherently amplify or suppress the magnitude of individual vibrational motions, and then probe downstream effects on photochemistry. We use a charge transfer molecular crystal, finding that a 50 cm^{-1} vibration drives the charge transfer process, and a 90 cm^{-1} motion drives the subsequent phase transition. This approach should be broadly useful for identifying key nuclear coordinates which drive photochemistry, which can then be used as in accomplishment (1) above to design better molecular systems.

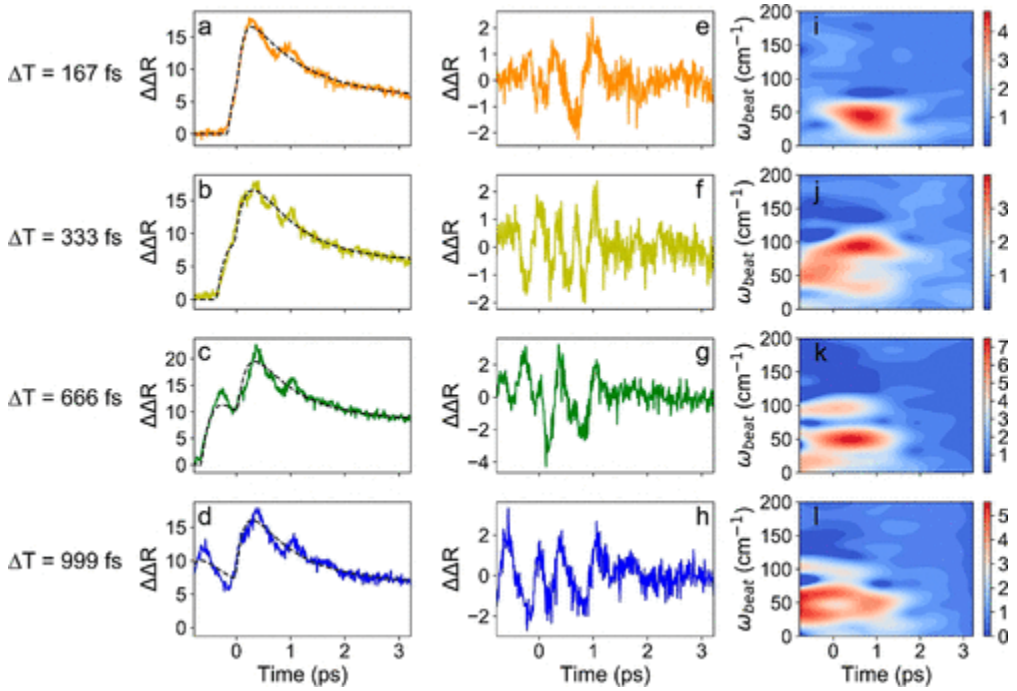

Figure 2. Mode selective chemistry in a charge transfer molecular crystal. We use a double-pulse excitation scheme to quantify the effects of selective nuclear modes on photochemistry.

3. We developed spatially offset FSRS (SO-FSRS) to monitor exciton transport (https://doi.org/10.1021/acs.jpclett.0c01114). y offsetting the photoexcitation beam, we can monitor Raman spectral changes as a function of both time and position. We used SO-FSRS on 6,13-bis(triisopropylsilylethynyl) pentacene, a well-studied organic semiconductor used in photovoltaics and field-effect transistors. We demonstrated that the fast exciton and free charge carrier transport axes are identical and observed that exciton transport is less anisotropic by a factor of ~3. SO-FSRS is the first technique that directly tracks molecular structural evolution during exciton transport, which can provide roadmaps for tailor-making molecules for specific electronic devices.

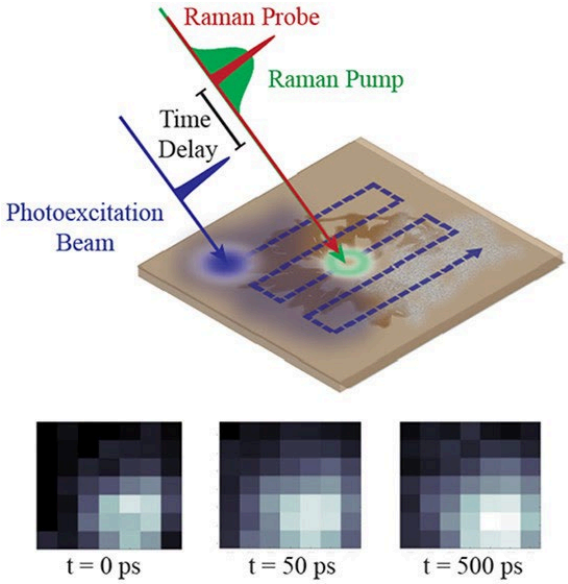

Figure 3. Spatially offset femtosecond stimulated Raman spectroscopy tracks nuclear contributions to exciton transport.

4. We developed a new approach for FSRS which reduces issues with baseline subtraction (http://dx.doi.org/10.1021/acs.jpca.9b02473). This approach is based off of shifted excitation Raman difference spectroscopy. By adding two mirrors to a conventional FSRS system, we generate a dual frequency Raman pump pulse, which can be used to easily discriminate between true FSRS signals and narrowband background or baseline signals. We automated the data analysis for this approach and shared our code on github.

5. We performed FSRS measurements on crystalline pentacene, finding clear evidence of a hotly debated charge transfer intermediate state (http://dx.doi.org/10.1039/C7SC03496B). This work identified the mechanism of singlet fission in this system, settling a long debate regarding the role of intermolecular charge transfer. We used these results to build towards accomplishments (1) and (4) as described above.

6. We performed FSRS measurements on crystalline betaine-30, a canonical intramolecular charge transfer molecule, identifying key nuclear coordinates that change during the charge transfer process (http://dx.doi.org/10.1039/C5CP06195D). This work was helpful in training new graduate students on this technique, as well as providing valuable insights regarding the interpretation of polarization-dependent effects in ultrafast crystal studies.

7. We wrote two invited review articles on our approaches and the general use of ultrafast vibrational techniques to probe singlet fission and photoinduced chemical reaction dynamics (https://doi.org/10.1021/acs.jpcc.0c06725, https://doi.org/10.1063/5.0009976).

3. What opportunities for training and professional development has the project provided?

The PI is passionate about mentoring, including performing annual individual development plan meetings, encouraging researchers to present their work at conferences, organizing and attending professional development meetings and mentorship training events, and encouraging students and postdocs to achieve their professional goals. This project supported the following personnel with current positions as indicated:

Dr. Christopher Rich was a postdoc working on this project, and is now a Chemistry Lecturer at Binghamton University.

Dr. Siu Yi Kwang was a graduate student working on this project, and is now a Laser and Light Delivery Engineer at Seagate.

Dr. Kajari Bera was a graduate student working on this project, and is now at Dow Chemical.

Dr. Alyssa Cassabaum was a graduate student working on this project, and is now Scientist at the Center of Science and Industry in Columbus, Ohio. She recently won an Emmy for her work on developing an online science show!

Dr. Margaret Clapham was a graduate student working on this project, and was also a recipient of a SCSGR fellowship that allowed her to perform neutron scattering work at Oak Ridge. She is now a Senior Scientist at Dupont.

4. How have the results been disseminated to communities of interest?

We published papers as described above. We shared our code for running FSRS experiments as well as analyzing data on Github. A number of researchers gave presentations at conferences over the reporting period. Additionally, PI Frontiera gave over 90 invited seminars and conference presentations on these projects over the past reporting period.

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Femtosecond stimulated Raman spectroscopy – guided library mining leads to efficient singlet fission in rubrene derivatives. Bera, K., Douglas, C. J., Frontiera, R. R. *Chemical Science*, 2021. https://doi.org/10.1039/D1SC04251C

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Plasma-driven solution electrolysis. Peter J. Bruggeman, Renee R. Frontiera, Uwe R. Kortshagen, Mark J. Kushner, Suljo Linic, George C. Schatz, Himashi Andaraarachchi, Stephen Exarhos, Leighton O. Jones, Chelsea M. Mueller, Christopher C. Rich, Chi Xu, Yuanfu Yue, and Yi Zhang, *Journal of Applied Physics*, 2021 https://doi.org/10.1063/5.0044261

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Orientation and Polarization Dependence of Ground- and Excited-State FSRS in Crystalline Betaine-30. Cassabaum, A. A., Silva, W. R., Rich, C. C., Frontiera, R. R. *The Journal of Physical Chemistry C*, 2019, articles ASAP. 10.1021/acs.jpcc.9b01023

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