

Project Report for Link Foundation Energy Fellowship 2018–2020: Investigation of Coherent Charge Transfer in Transition Metal Dichalcogenide Heterostructures with Multiresonant Coherent Multidimensional Spectroscopy

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I. INTRODUCTION

Photovoltaic solar cells convert sunlight into electricity by using material heterojunctions to facilitate separation of photo-excited charges in order to generate a current. Understanding and optimizing the efficiency of charge separation at the quantum mechanical level defines the future of the solar energy landscape and its impact on society. In the past decade, new charge separation mechanisms have been researched in heterostructures of layered 2D materials which facilitate ultrafast charge transfer and separation (see Figure 1a).[1, 2] Theoreticians have studied the mechanism of ultrafast transfer in these 2D materials and predict ultrafast transfer occurs by electrons collectively flowing back-and-forth between different layers.[3, 4] The collective/coherent nature of the transfer can lead to a greater efficiency compared to the usual stochastic/incoherent separation accomplished in regular charge separation.[5, 6] These theoretical studies claim that specific lattice vibrations and twist orientations of the heterostructure are important for tuning the efficiency of charge transfer. However, no experimental evidence has been presented for this collective action because conventional, single photon ultrafast probes do not have the quantum mechanical state resolution needed. Specifically, conventional methods lack the ability to determine the affects of lattice modes when coherently coupled to electronic excitations. My dissertation focused on developing new ultrafast probes that are hypothesized to be capable of mapping out ultrafast charge separation at the quantum mechanical level.

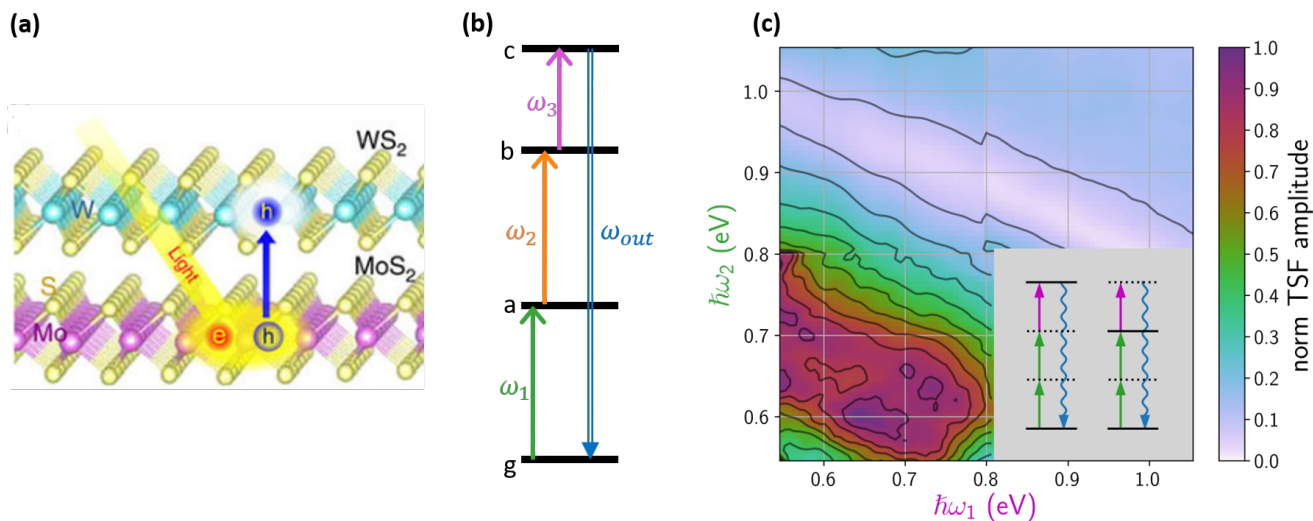


FIG. 1. (a) Cartoon of van der Waals heterostructure showing how a hole can migrate from MoS₂ to WS₂ following photo excitation.[3] (b) Diagram of a triple sum-frequency, TFSF, pulse sequence coupling a ground state, g , to multiple excited states, $\{a, b, c\}$. $\omega_{out} = \omega_1 + \omega_2 + \omega_3$. (c) TFSF spectrum of a MoS₂ thin film.[7]

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Past work in the Wright Group has shown that triple sum-frequency, TSF, spectroscopy is a viable method for probing mixed vibrational-electronic coupling in *molecular systems*.^[8–11] In TSF, three different electric fields (laser beams) collectively excite a charge-density polarization which oscillates at the sum of the input frequencies (see Figure 1b for a diagrammatic representation); this polarization emits an electric field (light) at the triple sum-frequency of the input beams which is then measured. The intensity of output radiation is directly related to how closely the input frequencies match (are in resonance with) the energy differences between quantum mechanical states in the system and how strongly those states are coupled together. Thus, TSF spectroscopy can offer insight into the quantum mechanical structure of a system.

Because TSF can measure how multiple states are coupled together, it is an attractive option for measuring how collective excitations in a semiconductor manifest and evolve. Before I started my graduate work, TSF had not been accomplished on semiconductor systems. The goals of my graduate work were to demonstrate that TSF is a viable semiconductor measurement tool, demonstrate that TSF can measure ultrafast dynamics, and resolve ultrafast charge transfer in layered semiconductor heterostructures. It is hoped that these new measurement techniques will be important tools for rationally designing the next generation of materials used to build more efficient solar cells.

II. RESULTS

My first project entailed measuring the TSF spectrum (see Figure 1c) of a polycrystalline, MoS₂ thin film. This spectrum has broad, antidiagonal features and resolves the lowest energy spin-orbit split excitonic resonances of MoS₂. Even though Figure 1c has considerably more energetic bandwidth than most multidimensional spectroscopy experiments, the electronic structure of MoS₂ does not have bands close enough together for our laser setup to couple together. Thus, our TSF spectrum is singly-resonant and accesses the same states as absorption spectroscopy. I then developed the theory necessary to compare the TSF results to absorption and second harmonic generation (SHG) measurements. Because absorption, SHG, and TSF all have different scaling rules for transition moments and joint density of states, we were able to extract them from our measurements. Our results conclusively show that certain features seen in the MoS₂ absorption spectrum are due to a singularities in the joint density of states—this had previously been an open question about MoS₂.

Next, I extended TSF to the measurement of carrier *dynamics* by developing pump-TSF-probe spectroscopy. By preceding the TSF pulse sequence with a pump, TSF is able to probe an excited semiconductor. I demonstrated pump-TSF-probe on both MoS₂ and WS₂ thin films and spiral nanostructures. To benchmark this new spectroscopy, I compared the pump-TSF-probe results to conventional transient-reflectance (TR) measurements on the same samples. Pump-TSF-probe and TR recover the same changes in quantum states. However, I found that TR suffers in sensitivity when surface coverage is low, but pump-TSF-probe does not. In short, pump-TSF-probe is most useful when working with samples of diverse morphology and low surface coverage.

While accomplishing the pump-TSF-probe work, it became apparent to me that pump scatter is a major issue when working with micro-structured semiconductors. This pump scatter can saturate the dynamic range of a measurement or obscure important features in the data set. A dual-chopping routine can remove some pump scatter problems, but a dual chopping routine does not remove amplitude-level interference and fails if the detector is saturated. I hypothesized that combining a multiphoton absorption excitation with THG or SHG (optical harmonic generation, OHG) probing would solve the scatter problem. All lasers would be in the near-IR—a color range that the detector used for detecting the OHG output is not able to observe. I was able to demonstrate the utility of this multiphoton pump technique and showed that it gave similar results to one photon pumping, but with no scatter problems. With the support of the Wisconsin Alumni Research Foundation, we submitted a patent on this idea.¹

An aspect of a two-photon-absorption pump which I had not considered involved the affects of the high laser intensities needed to build up a population. These high intensities caused the excitonic resonance to blueshift via the Optical Stark Effect. However, the normal blueshift of the Optical Stark Effect could not explain many of our observations. I discovered a new manifestation of the Stark Effect, brought forth by photon exchange between the pump and probe fundamental fields, which can produce strong modulations of the OHG signal and is thus promising for ultrafast signaling applications.

My final project involved measuring the ultrafast response of monolayer WS₂-MoS₂ core-shell lateral heterostructures. Out-of-plane (vertical) heterostructures have been extensively characterized in the literature using ultrafast spectroscopies, however their in-plane (lateral) counterparts have not had their ultrafast dynamics and energetics characterized. I set out to measure charge transfer dynamics across the 1D junction present in the lateral heterostructures. For a long time I was perplexed by the multidimensional transient-reflectance lineshapes I measured; in some

¹ *U.S. Patent Pending, filed 2019-06-20.* Morrow, D. J.; Kohler, D. D.; Wright, J. C. Ultrafast, multiphoton-pump, multiphoton-probe spectroscopy.

cases these lineshapes were flipped compared to the data I acquired on MoS₂ thin films. However, I was eventually able to reconcile the lineshapes after implementing a Fresnel model which accounts for interference effects from the stratified substrate. Despite the supposed Type-II band alignment, I found no evidence of ultrafast charge separation or coupling between the MoS₂ and WS₂ structures.

III. SIGNIFICANCE, IMPACT, AND WHERE MIGHT THIS LEAD?

The original goal of this project was to develop and apply new nonlinear spectroscopies to interrogate ultrafast charge transfer in heterojunctions of 2D materials. My work demonstrates the viability of using multiple electric fields to probe the ultrafast dynamics of semiconductors. Future work should focus on developing mixed vibrational-electronic multiphoton probe methods. These future methods will offer an exquisite view into how the lattices of a semiconductor heterojunction couple with electronic excitations to facilitate charge separation. I predict that this new family of spectroscopies will give us a better understanding of how specific parameters of a heterojunction's lattice affect charge separation and how these details can be tuned to yield more efficient charge transfer.

IV. HOW DID THE FELLOWSHIP MAKE A DIFFERENCE?

The two years of support afforded by the Link Energy Fellowship allowed me to pursue research avenues which would have been closed if I had to teach each semester for my financial support. For instance, I was able to work on side projects that were started by other researchers, which were able to benefit from my expertise. I was also able to spend an extensive amount of time developing models to explain my measurements. The idea of using a multiphoton probe is common to my research group, but the idea of a pump followed by a multiphoton probe is a new frontier for my research group. The Link Foundation Fellowship allowed me to push my group's work into this new (risky) frontier.

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