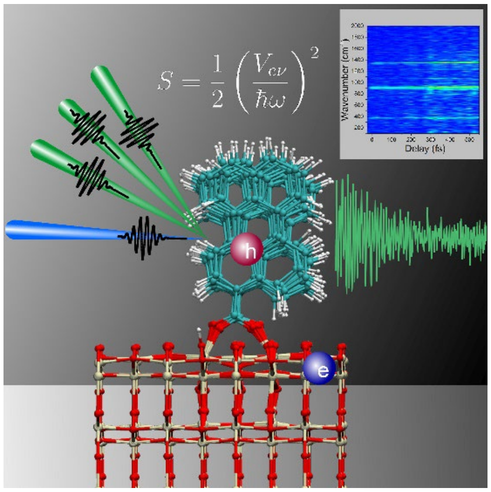
Final Technical Report Cover Page



Recipient Organization:	Lars Gundlach, University of Delaware
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1.0 Executive Summary

Interfacial electron transfer reactions constitute key physical phenomena central to a variety of energy related transport and conversion processes such as catalysis, photocatalysis, photovoltaics, energy storage, molecular electronics, etc. Heterogeneous material systems like organic/inorganic interfaces are of particular interest because they provide great potential to tailor properties according to application specific requirements. While electron transfer dynamics has been studied intensively in heterogeneous systems many questions remain unanswered. The significance of electronic-vibrational coupling and coherence is one aspect that has yet to be fully explored. The objective of this project is to develop and implement new ultrafast spectroscopic techniques based on pump four-wave mixing spectroscopy (pump-FWM) for studying the dynamics of vibrational coupling and coherence in heterogeneous electron transfer (HET) at molecule/semiconductor interfaces. The implementation of the spectroscopic setup allows to explore different four-wave mixing techniques and thus to identify a suitable approach to study the significance of vibrational as well as electronic coherence in HET. The scientific objectives are:

- Evaluating and comparing the capabilities of pump-FWM techniques for identifying coherence.
- Comparing HET induced vibrational modes and vibronic coupling for HET systems with different chromophores, level alignment and coupling strength.
- Uncovering coherence in the product state by comparing TA measurements, pump-FWM signals from the excited state and the cation ground state.

2.0 Background

We are developing and using femtosecond time-resolved spectroscopic and microscopic techniques to investigate excited state dynamics in a wide range of materials systems. Molecular systems, molecule/semiconductor hybrid systems and individual nanoparticles are investigated with a focus on applications in new non-fossil energy resources, non-silicon-based electronics, and novel drug delivery techniques. Condensed matter systems such as 2D materials and magnetic heterostructures are investigated aiming at understanding correlation and coupling of fundamental excitations in these materials. Energy and charge transport on the nanoscale occur on an ultra-short time scale. We are studying these reactions in real time by employing novel time-resolved spectroscopic and microscopic techniques, simultaneously resolving nanoscale dimensions and femtosecond (10^{-15} s) dynamics. The necessary experimental techniques are developed and improved in our group.

3.0 Project Objectives

The goal of this project is to measure and distinguish vibrational excitation, vibrational coherence and electronic coherence in heterogeneous electron transfer (HET) by combining appropriate methods and model systems. This task can be roughly split into three steps: Finding a suitable combination of methods, defining a suitable set of molecule/semiconductor combinations, and uncovering signatures of coherence in the 2D signals. These three steps go hand in hand and overlap strongly.

The following milestones were identified for the funding period:

- Updating the pump-DFWM setup
- Setting up prism spectrometer with 10 kHz CCD

- Improving setup and detection method (pulse compression, additional chopper, etc.)
- First measurements on a dye-sensitized nanocrystalline film in vacuum
- Measuring pump-DFWM or -2DES on Phl, ZnP, and Pe
- Comparing dynamics of HET induced vibrational modes to study donor-acceptor coupling as a function of level alignment and coupling strength. Uncovering vibrational coherence in HET by comparing TA measurements, pump-DFWM signals, and pump-2DES spectra from the excited state and the cation ground state.
- Measuring HET induced structural dynamics via XTA for complementing and extending results from ultrafast spectroscopy.

4.0 Description of Activities Performed

A passively phase-stable four-wave mixing setup (pump-DFWM) was built and is producing data. The improved mechanical stability increased the signal-to-noise ratio by about a factor of 2. The phase-stable design will be exploited in the coming month when we start exploring the addition of an external oscillator to the existing pump-DFWM experiment.

A 10 kHz frame rate CCD polychromator based on a pentaprism design was built and commissioned. The camera is synchronized with a 5 kHz chopper and the 10 kHz repetition rate laser system and allows shot-to-shot subtraction of ground state and excited state spectra. Due to the mirrorless prism design the throughput of the polychromator is above 90%.

Different schemes for pulse compression were realized and evaluated. Since we already achieved sub- 10 fs pulses with the previous setup, the goal was to simplify the setup and speed-up the alignment procedure for the DFWM NOPA. We now use a combination of chirped mirrors and a prism compressor to generate sub-15 fs pulses on a daily basis without major realignment.

The first ever pump-DFWM measurement on a solid state sample required a combined effort in nanoparticle synthesis and instrument development. Light scattering is a major issue for measurements on nanoparticle films even more so for background-free techniques like DFWM. We evaluated several schemes for reducing the amount of scattered light in the measurement that were mostly combinations of spatial filtering of the signal beam and post-subtraction of background by including additional choppers. We also strengthened our effort to reduce scattering in the film increasing the homogeneity of particle size and optimizing annealing conditions. We are now able to record ground-state DFWM signals that show Raman active modes of the photosensitizer Zn-TTP on TiO2 colloidal film in vacuum with a signal-to-noise ratio that is only a factor of 2 smaller than measurements in solution. Zn-TTP/TiO2 is not an ideal system for first pump-DFM measurements due to its spectral and dynamic properties. However, a mode at 800 cm-1 that cannot be associated with a ground state Raman mode has been observed from the electronically excited molecule. The Galoppini group at Rutgers University has finished synthesis of DTP-Pe derivatives and we will start measuring on DTP-Pe-CH2-COOH sensitized films shortly. DTP-Pe-CH2-COOH was proposed to be used for first pump-DFM measurements because of its advantageous spectral and dynamic properties.

Major progress has been achieved towards completing the first tasks. TA measurements, pump-DFWM signals from the excited state and the cation ground state of a perylene sensitized TiOs film have been measured as detailed below. The measurements and data evaluation are ongoing.   The first six month were also used to train a new team of students on the instruments and methods that were developed during the first granting period. The students that were involved in the project during the first granting period graduated and moved on to industry and postdocoral positions.

The collaboration with the Galoppini group for molecular synthesis and the Batista and Rego groups for theoretical support was very successful during the reporting period. The measurements performed on a specific sensitizer bound to TiO_2 in vacuum are directly comparable to simulations by the Batista and Rego groups. A manuscript comparing simulations and experiment is under review at the Journal of Physical Chemistry. The collaboration with the groups now allow us to compare directly vibrational excitations that are triggered by electron dynamics with theory. This is expected to be a very valuable input for analyzing our data in terms of electronic-vibrational coupling and coherence. A direct simulation of pump-DFWM signals is planned for the future. One student was trained mainly on the 10 kHz transient absorption setup. Measurements with this setup on the specific perylene/TiO_2 system reveled ultrafast electron transfer of 12 fs. The challenge here is to obtain the very high time-resolution.

Another student was trained mainly on the pump-DFWM setup that is considerably more challenging in instrument use and data analysis. However, first pump-DFWM signals from a perylene dye sensitized TiO2 film in vacuum were measured and showed interesting dynamics including the appearance of a TiO_2 phonon mode that is triggered by electron injection. At the same time the instrument was further improved by employing a new cooled PMT for detection and a new simultaneous-sampling ADC for digitizing the signal was implemented. These steps improved the signal-to-noise ratio by a factor of two.

The Galoppini group at Rutgers University has finished synthesis of DTP-Pe derivatives and we are measuring on Pe sensitized films.

In addition, a proposal for beamtime at Argonne National Lab was scored 1.9 and was not granted. We continue to apply for beamtime to continue our collaboration with the Chen group on Energy Alignment and Structural Dynamics in Heterogeneous Electron Transfer.

Significant result:

- First pump-DFWM spectra of perylene sensitized TiO_2 solid state sample have been measured.
- The detection scheme and the setup has been optimized. Data processing has been automated.

5.0 Conclusions and Recommendations

The project identified electronic-vibrational coupling in heterogenous electron transfer by combining unique model systems and ultrafast spectroscopic techniques. The collaboration with organic synthetic chemists and theoretical chemists resulted in an unprecedented detailed picture of electronic-vibrational coupling. The project also identified the limits of pump-DFWM in the visible for solid state samples.

6.0 Selected Publications

Han Yan, Joseph P Avenoso, Samantha Doble, Ryan Harmer, Luis GC Rego, Elena Galoppini, Lars Gundlach: *Conformational and Binding Effects on Interfacial Electron Transfer from Dual-Linker Sensitizers,* The Journal of Physical Chemistry C **125** (2021) 8667
doi: 10.1021/acs.jpcc.0c11299

Ryan Harmer, Hao Fan, Katherine Lloyd, Samantha Doble, Joseph Avenoso, Han Yan, Luis G. C. Rego, Lars Gundlach, and Elena Galoppini: *Synthesis and Properties of Perylene-Bridge-Anchor Chromophoric Compounds,* The Journal of Physical Chemistry A **124** (2020) 6330–6343
doi: 10.1021/acs.jpca.0c04609

Baxter Abraham, Luis G.C. Rego, Lars Gundlach: *Electronic-Vibrational Coupling and Electron Transfer,* Journal of Physical Chemistry C **123** (2019), 23760-23772, Feature Article
doi: 10.1021/acs.jpcc.9b03849

Robson S. Oliboni, Han Yan, Hao Fan, Baxter Abraham, Joseph P. Avenoso, Elena Galoppini, Victor S. Batista, Lars Gundlach, Luis G. C. Rego, : *Vibronic Effects in the Ultrafast Interfacial Electron Transfer of Perylene-Sensitized* TiO_2 *Surfaces,* Journal of Physical Chemistry C **123** (2019), 12599
doi: 10.1021/acs.jpcc.9b02106

Mahsa Konh, Chuan He, Zhengxin Li, Shi Bai, Elena Galoppini, Lars Gundlach, Andrew V. Teplyakova: *Comparison of ZnO surface modification with gas-phase propiolic acid at high and medium vacuum conditions,* Journal of Vacuum Science **36** (2018), 041404
doi: 10.1116/1.5031945

Baxter Abraham, Hao Fan, Elena Galoppini, and Lars Gundlach: *Vibrational Spectroscopy on Photo-Excited Dye-Sensitized Films via Pump-Degenerate Four-Wave Mixing,* The Journal of Physical Chemistry A **122** (2018), 2039-2045
doi: 10.1021/acs.jpca.7b10652

Chuan He, Baxter Abraham, Hao Fan, Ryan Harmer, Zhengxin Li, Elena Galoppini, Lars Gundlach, and Andrew V. Teplyakov: *Morphology-Preserving Sensitization of ZnO Nanorod Surfaces via Click-Chemistry,* The Journal of Physical Chemistry Letters **9** (2018), p. 768-772
doi: 10.1021/acs.jpclett.7b033880

Abraham B., Nieto-Pescador J., Gundlach L.: *Analyte-Induced Spectral Filtering in Femtosecond Transient Absorption Spectroscopy,* Journal of Luminescence **187** (2017), p. 92-95
doi: 10.1016/j.jlumin.2017.03.003