# Ultrafast Dynamics in Solids: Transient Absorption and Laser Damage

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The proposed program aims to apply concepts and techniques from the fields of femtosecond and attosecond physics, where study has tended to be limited to atoms and small molecules, and extend these techniques to solid-state surfaces. This will enclose two primary directions of research. **Project I** will aim to study attosecond-scale electron correlation dynamic on surfaces and thin films following photoexcitation as well as femtosecond-scale nuclear rearrangement dynamics using techniques of attosecond spectroscopy never before applied to such systems. **Project II** will explore laser damage on surfaces, and will study the properties of structures created by laser fields. My prior expertise with attosecond spectroscopy and ultrafast surface imaging makes me uniquely suitable to approach this highly interdisciplinary program, which extends techniques from AMO physics into materials and surface science.

## I. Femtosecond Transient Absorption Spectroscopy in Solids: Amplitude and Phase

### Project Significance

Charge carrier dynamics on surfaces have inherent relevance to a variety of important processes **[Zuerch]**, including light conversion to energy **[Berera]**, ultrafast optical switching, memory devices, and next-generation electronics. The fundamental understanding of the underlying processes which dictate the first moments of dynamics in these systems will test the fundamental limits in driving electric currents on surfaces and thin films. However, the initial dynamics occur in two forms: electron correlations on the attosecond ($10^{-18}$ s) time scale, and nuclear motion on the femtosecond ($10^{-15}$ s) time scale. Thus, techniques from ultrafast spectroscopy are needed to properly resolve the dynamics and interpret the physical processes involved. Ultrafast transient absorption measurements, which employ optical pump/extreme ultraviolet (XUV) probe techniques, can characterize electronic and structural changes in materials down to the attosecond regime.

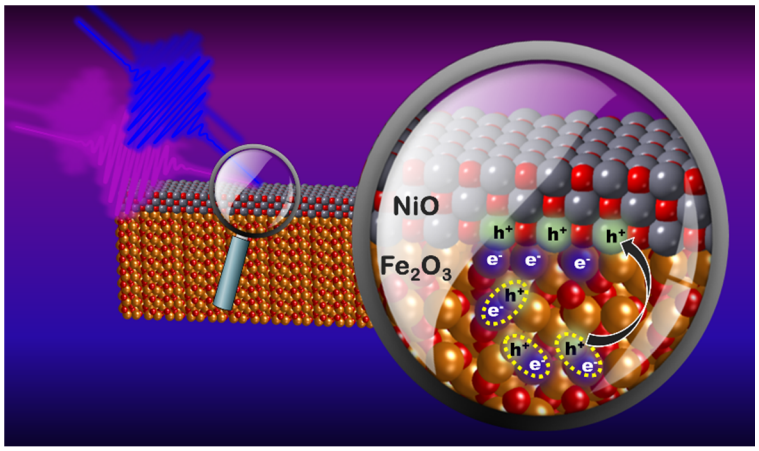


**Figure 1 – Ultrafast transient absorption.** An optical pump pulse (blue) photoexcites a material, inducing electron-hole pairs near the surface. Later, an XUV attosecond pulse (or pulse train) probes the optical response; electron, hole, and nuclear rearrangement dynamics are encoded in the outgoing XUV amplitudes and phases. Figure courtesy of the Robert Baker group at OSU, to be used on the cover of *Phys. Chem. Chem. Phys*.

### Relevant Personal Expertise

While the history of the Zewail group was rooted in exploring femtosecond dynamics in molecules, it was during my time in the group that I learned ultrafast surface science. Working with a first-of-its-kind ultrafast scanning electron microscope, our team identified a previously-unexpected behavior on the surface of a semiconductor junction **[Najafi2015]** and surface acoustic waves in a thin film organic semiconductor **[Najafi2018]**. Further, as my work in attosecond science has evolved, this experience

with surfaces and thin films has allowed me to identify a previously unexplored type of ultrafast spectroscopy on solids.

## Experimental Approach

For systems larger than a few atoms, the application of attosecond spectroscopic methods remains largely unexplored. Recent years have seen developments in ultrafast transient absorption and reflection spectroscopy, but to date, the field has lacked access to the phases imprinted by the associated dynamics. Without measurements of phase, experimental results are heavily reliant on complicated density functional theory (DFT) calculations to interpret the results; however, simultaneous measurement of the phase with absorption/reflection experiments would allow full characterization of the material response.

One technique to measure the interaction's phase, is RABBITT spectroscopy **[Paul]**. However, because conventional RABBITT relies on the integration of a harmonic peak to a single data point, fine structures in absorption and reflection measurements can be missed. To combat this, we have developed a color-scanning technique, which is diagrammed in Fig. 2. By changing the wavelength of the fundamental beam which drives HHG, the harmonic comb is shifted in energy; for features which evolve sufficiently quickly or slowly relative to the harmonic spacing, we access the phase or group delay (the phase derivative with respect to energy), respectively.

The first proof-of-principle of this type of phase measurement in a solid is presented in Fig. 3, where RABBITT spectroscopy was used to access the phase of the aluminum $L_{2,3}$ edges using the color-scanning technique mentioned above. This measurement is performed in the same apparatus with which we are studying molecular charge migration. For future studies of dynamics, a pump-probe setup will be instituted into the beamline for

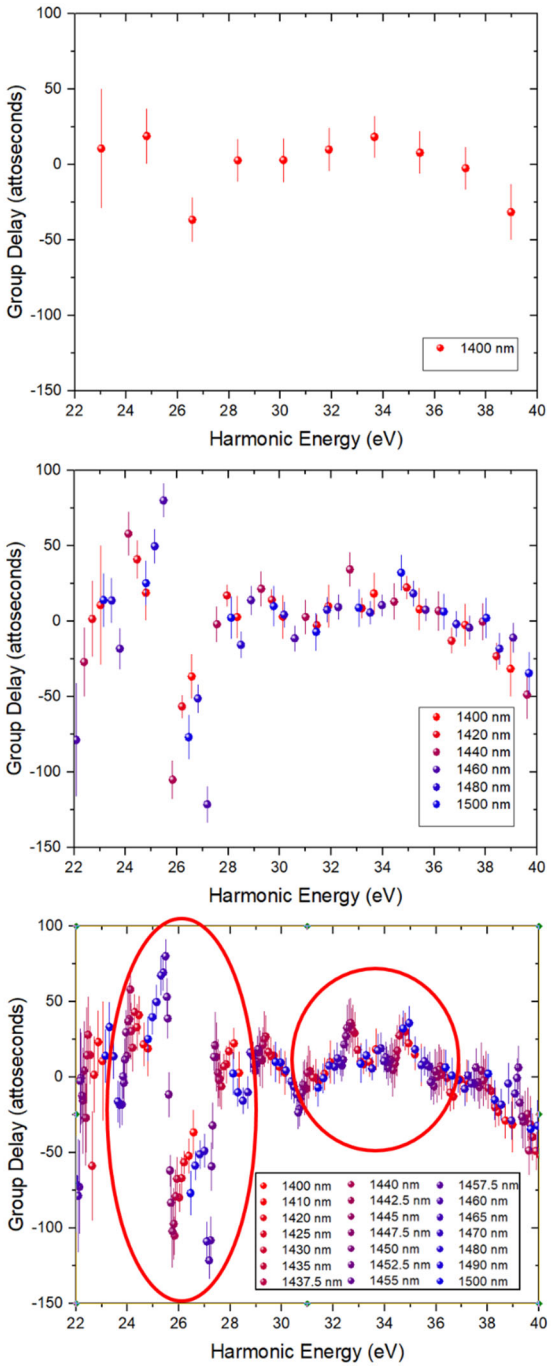


**Figure 2 – Wavelength scanning with RABBITT reveals phase structures.** Where narrow structures such as resonances are present, wavelength tuning of the harmonic generation pulse can be employed. A single scan (top panel) may not reveal sharp features; however, as more scans are included (center panel) structures are revealed, until they are well-defined. The full scan (lower panel) shows a series of autoionizing resonances of argon, with group delay features as small as 25 attoseconds resolved (manuscript in preparation **[Scarborough]**).

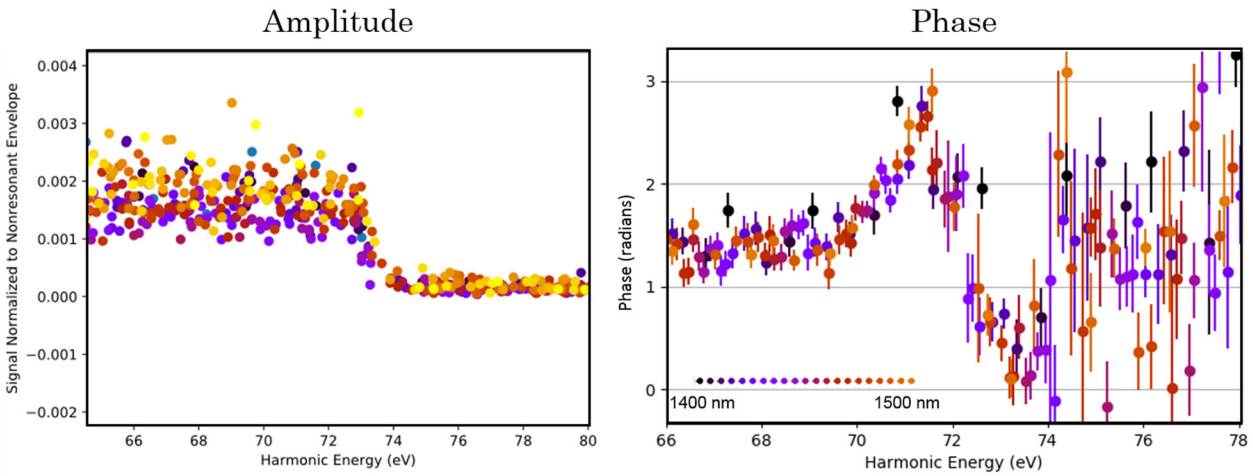


**Figure 3 – RABBITT spectroscopy of solids.** By scanning through a variety of laser wavelengths, we characterize the group delay (and thus phase) structure of the aluminum $L_{2,3}$ edge through high harmonic spectroscopy. In this case, the time delay between pump and probe pulses is fixed due to our experimental setup; in the proposed work, this type of structure will be measured with variable time delay and used to map out the temporal transient absorption dynamics in both amplitude and phase for the first time.

the proposed work, in which a light pulse will photoexcite the sample, and the XUV photons will act as the probe in both absorption and phase in a simultaneous measurement, since the phase is imprinted into the transmitted XUV light, providing a full dynamic reconstruction.

Among the early targets of study, due to the intriguing femtosecond-to-picosecond scale dynamics of photoexcited carriers **[Vanacore]**, will be quantum dots. During my time at Caltech, we attempted ultrafast SEM experiments using GaAs quantum dots grown on a surface of AlGaAs; although early indications were promising, resolving dynamics in the quantum dots (~100 nm in size) were ultimately beyond the capabilities of the microscope when operating in ultrafast mode. Because the quantum dots have a different bandgap than the substrate, one can selectively photoexcite either the dots or their substrate, choosing where to initiate the carrier dynamics. Further, because the size of the dots can be controlled by droplet epitaxy, and is on the order of the mean-free path of high-energy acoustic phonons (~27 nm for GaAs), the structural dynamics of the material can also undergo dynamics on ultrafast timescales. The range and controllability of quantum dots, as well as their applications to optoelectronic, thermoelectric, and energy conversion devices, makes their study an intriguing starting point for transient absorption studies.

## II. Laser-Induced Periodic Surface Structure (LIPSS)

### Project Significance

Laser damage to materials and surfaces can induce a variety of structures, many of which have interesting properties such as bacterial resistance **[Lutey]**. By altering the parameters of the laser pulses, one can induce damage through a variety of processes, and the material responds in different ways to each. Exploring the mechanisms through which the material is changed creates knowledge of how a desired outcome can be reached, and inducing periodic structures on surfaces is a path toward creating novel metamaterials with laser treatment.

## Relevant Personal Expertise

During my undergraduate and graduate career at Nebraska, I was involved in experiments which included laser-etching metals and spatial pulse shaping **[Strohaber]**. The modification of the spatial mode of a laser focus creates an additional degree of control over the surface damage mechanism and character in LIPSS experiments, and laser damage thresholds and mechanisms on surfaces of semiconductors were important to my work in ultrafast scanning electron microscopy at Caltech.

## Experimental Approach

Material damage can be easily explored in a table-top experiment, although high vacuum studies may help to elucidate the underlying results. A variety of regimes can be explored, and these regimes are summarized in Table 1. Long pulses or continuous-wave lasers exchange heat with a target, but do not possess enough intensity to break down the material, whereas shorter pulses may induce dielectric breakdown or cause an avalanche effect of electrons, known as avalanche ionization, in which electron scattering causes further ionization on the surface.

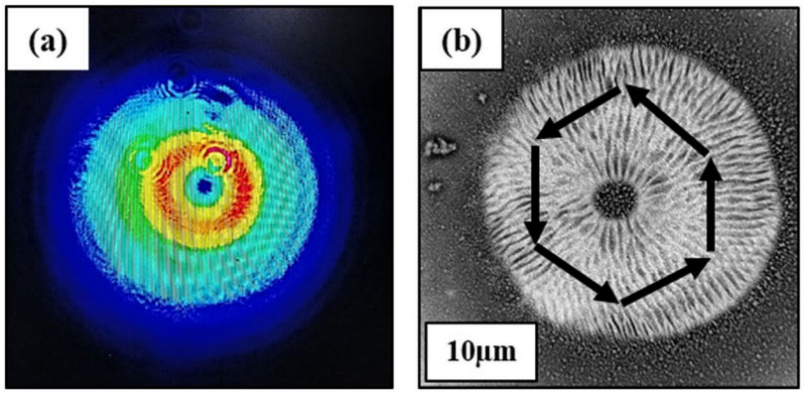


**Figure 4. Antibacterial laser-induced structure.** Periodic surface structures can be induced by a series of many laser pulses. In this case, a pulse with a node in the center (left) and azimuthal polarization (b, black arrows) induces a surface structure similar to the spatial profile of the beam. This structure was shown to have bacteria-repellent properties. Figure is adapted from **[Lutey]**.

There are also strong differences between single-pulse and multi-pulse damage. While single-pulse damage typically leads to ablation or vaporization of material, multi-pulse processes can induce controllable structure; this results in a phenomenon known as laser-induced periodic surface structures (LIPSS). By controlling the laser's pulse energy, polarization, pulse duration, and spatial profile, the experimenter can create designer structures on materials; the study of these structures and how they are made is a significant field of surface science. As a recent example, Fig. 4 shows the resulting LIPSS from a series of pulses with azimuthal polarization (a) which produce LIPSS (b) which mimic the polarization structure of the beam on a steel surface **[Lutey]**. This particular structure was then shown to be resistant to bacteria growing on its surface, and was presented as a way to tailor surface morphology to create a next-generation antibacterial surfaces.

Once interesting surface structures are created, they can be used as targets for the transient absorption experiments. Photoexcitation will cause charge carriers on the LIPSS surfaces to evolve differently than on the unaffected surface regions; as such, even if the absorption is largely in atomic core shells, the temporal evolution of the system will be altered.

| **Pulse Duration** | $t < 10^{-9}$ s | $10^{-9} < t < 10^{-7}$ s | $10^{-7} < t < 10^{-4}$ s | $t > 10^{-4}$ s |
|---|---|---|---|---|
| **Damage Mechanism** | Avalanche Ionization | Dielectric Breakdown | Dielectric Breakdown or Thermal | Thermal |
| **Relevant Damage Specification** | High intensity | Pulsed lasers | Pulsed and CW | CW |

**Table 1. Mechanisms of laser damage.** Laser pulses can cause material through a variety of processes. Many pulsed lasers are too brief to exchange heat energy, instead causing damage through dielectric breakdown or avalanche ionization. Table adapted from **[ThorLabs]**.

## Conclusion

The combination of surface dynamics measurements and laser damage allows for a highly interdisciplinary, collaborative program which will reveal new studies relevant to ultrafast physics, condensed matter dynamics, and materials research. I believe myself to be uniquely positioned based on my prior experience to head such a broadly-based research program, and with the resources of Texas Tech, I will be well-positioned to become a leader in the future of the field. The work in **Project I** will lead to entirely unique, high-impact research and will be ideally suited for graduate students and postdocs; **Project II** is experimentally much less demanding, and will provide a path toward training undergraduate and early graduate researchers.

## Funding

Programs specific to the proposed research, such as the NSF DMR-TMRP, which seeks PIs for electronic and photonic materials, will be highly targeted over the long term. Efforts for more general grants, such as the NSF CAREER program, aimed at providing funding specifically for untenured early-career faculty, will be sought aggressively in the early years upon availability.

Due to the complexity of attosecond physics, the field has been heavily influenced by large teams of PIs performing complementary experiments with a common goal in mind. Thus, in the vein of the grant supporting my current work, I will seek out funding with a collaborative aspect as part of the structure; a joint experiment/theory effort is a sensible way to pursue work of this nature, and the long term goals of the proposed research will benefit from the shared priorities of a team.

## Deliverables

**Project I**

Year 2: RABBITT apparatus built and tested; attosecond temporal resolution in gas phase
Year 4: Pump-probe dynamics measured in GaAs quantum dots

**Project II**

Year 2: LIPSS created with full control of both spatial and temporal pulse shaping
Year 4: LIPSS identified as candidates of interest for transient absorption experiments

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