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Imaging and Controlling Energy and Charge Transfer in Nanostructured Materials

Geoffrey Blake
CALIFORNIA INSTITUTE OF TECHNOLOGY

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Air Force Research Laboratory
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Blake, Geoffrey A.

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California Institute of Technology
1200 East California Boulevard, MC
150-21
Pasadena, CA 91125

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14. ABSTRACT

This research was focused on the significant improvements in the imaging and temporal resolution made available with the Caltech ultrafast electron microscopy and crystallography set ups developed by Prof. A. Zewail and his team, and on studies of layered (e.g. graphene) or ordered (MoS2 and related chalcogenides, hybrid perovskite) materials in particular. In addition to the ultrafast optical pump-electron diffraction probe experiments, we also carried out fs-optical pump-THz absorption and emission experiments using techniques pioneered by Prof. Blake's students over the past few years. The latter have experiments have yielded surprising THz emission strengths from two-dimensional, or layered, organolead halide perovskites, including the n=1 version that lacks a center of inversion symmetry. This opens the door to novel studies of patterns films that combine nonlinear optics and solar energy conversion schemes to yield devices with extremely high efficiencies or the possibility of coherent control of the energy flow therein.

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Principal Investigator: Geoffrey A. Blake
California Institute of Technology
Division of Chemistry and Chemical Engineering, MC 150-21
Pasadena, CA 91125
(626) 395-6296 Phone • (626) 585-1917 Fax
Email: gab@gps.caltech.edu

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Highlights from Original Proposal/Grant Summary, Prof. A.H. Zewail, P.I. (CY2015):

In this new grant titled "Imaging and Controlling Energy and Charge Transfer in Nanostructured Materials," which is a continuation of support from the AFOSR, we propose the following new directions of research. First, we shall focus a major effort on the further development of 4D electron microscopy and diffraction for the studies of the structural dynamics of nanoscale materials and the transient structures of complex surfaces following ultrafast optical or heat excitation. Second, of particular interest in applications are the study of composite materials of nanolayers, which are unique carriers of energy and charge transfer. Third, we shall extend the technique of photon induced near-field electron microscopy, PINEM [B. Barwick, D.J. Flannigan, and A.H. Zewail, *Nature* **462**, 902 (2009)] for the study of the nature of electric fields in nanoparticles and their interactions in space and time. Finally, we wish to examine the influence of the length scale, reaching those of quantum dots, on energy and charge transfer phenomena. The current microscopes are equipped with various detectors and geometries to accommodate different studies.

The objective is to build, through imaging in space and time, structural dynamics models of the evolution from a microscopic atomic description to the nanoscale and on to macroscopic observations. These studies offer an opportunity for understanding the nature of forces involved and to answer fundamental questions pertinent to non-equilibrium phenomena, such as diffusionless charge transport and structural changes, cooperativity, friction at interfaces, and nucleation in melting.

Revised General Statement of Work, Prof. G.A. Blake, P.I. (late CY2016):

The originally requested support from the AFOSR has been used in concert with funding from the Gordon and Betty Moore Foundation to enable a broad range of time, space and energy resolved studies of materials and nanoscale patterning that are of interest to the Air Force. In particular, three postdoctoral fellows have been supported by combining the first year of AFOSR funding (12/15/16-12/14/16) with that from the Kavli Nanoscience Institute postdoctoral fellowship program at Caltech. As outlined above, this research is focused on significant improvements in the imaging and temporal resolution available with the Caltech ultrafast electron microscopy and crystallography set ups, and on studies of layered (e.g. graphene) or ordered (MoS_2 and related chalcogenides, hybrid perovskite) materials in particular.

AFOSR-Supported Research Activities in CY2017-2019

Two broad areas of research were undertaken with the 'taper down' support provided by the AFOSR, the first on studies of exfoliated transition metal dichalcogenides (TMDCs) with the Ultrafast Electron Crystallography apparatus, or UEC, and the second on time resolved electron diffraction+photostability and optically pumped THz emission measurements on hybrid lead organohalide perovskite materials using the Ultrafast Electron Microscope (UEM-2) facility and the fs-Ti:Sapphire lasers in the UEC lab. Both areas of research were overseen by the P.I., and carried out by Dr. Tony Karam and Mr. Kyle Virgil, who were supported by AFOSR funds. This work is continuing with graduate students in the group who are supported by the Caltech Resnick Institute for Sustainability and the Division of Chemistry & Chemical Engineering. As outlined below, several papers describing this work are either published or under revision and review in high impact journals, with additional results being prepared for publication in CY2020.

On the TMDC research, we first got the P.I.'s group up to speed with UEC studies of nanopatterned gold films, work published in a special issue devoted to Prof. Zewail (Hu, Karam, Blake & Zewail 2017, Chem. Phys. Lett. **683**, 258). Next, sub-ps optical pump/electron diffraction probe studies were completed for exfoliates of $TiSe_2$ and WSe_2. For $TiSe_2$ at normal incidence, the suppression of the Bragg diffraction peak intensities following photo-excitation displays strongly bi-exponential behavior. For tilted samples, changes in the diffraction peak positions reveal coherent acoustic vibrations that are dependent on the sample thickness and that further permit a calculation of the Young's modulus. The complex room temperature lattice dynamics observed are attributed to strong electron-phonon coupling and electron-lattice equilibration processes, which provides the first direct experimental support for theoretical simulations that predict a Jahn-Teller origin of the charge density wave (CDW) behavior in $TiSe_2$. These results demonstrate the importance of strongly coupled electron-phonon dynamics in the relaxation of electronically excited room temperature $TiSe_2$, which is expected to impact its applicability in optoelectronics.

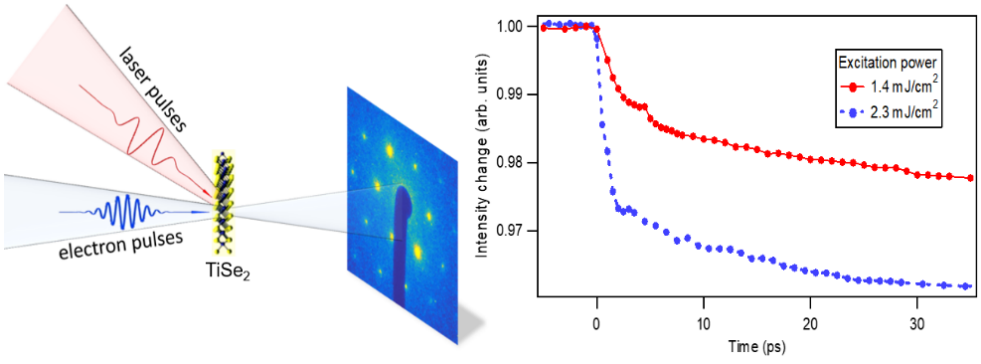

Figure 1. Ultrafast electron diffraction results for monolayer $TiSe_2$. At left is a schematic of the UED setup in the transmission geometry, composed of a laser pump and electron probe, and at right the observed bi-exponential nature of the electron-phonon coupling in this material is displayed (from Karam, Hu & Blake 2018, ACS Photonics **5**, 1228; doi: 10.1021/acsphotonics.7b00878).

For monolayer WSe_2 we find that the change in the intensity of the Bragg diffraction spots is characterized by single-exponential dynamics, consistent with a coherent response of the lattice during electron-phonon and phonon-phonon equilibration. More interestingly, unlike the case for $TiSe_2$, we have discovered a transient and highly anisotropic lattice expansion. These results are

summarized in Figure 2. The nature of the transient anisotropy is in accord with that expected from coherent photocarrier-phonon coupling models and the symmetries of the lowest energy optically active Raman modes of the monolayer. Further detailed modeling of this coupling is underway with the Bernardi group at Caltech, in response to referees comments on the original manuscript. Similar behavior is seen in MoS_2, and so the detailed theoretical work is aimed at explaining the anisotropic expansion in both materials. We expect final publication of these results by summer 2019. The paper will be led by a graduate student in Prof. Bernardi's group.

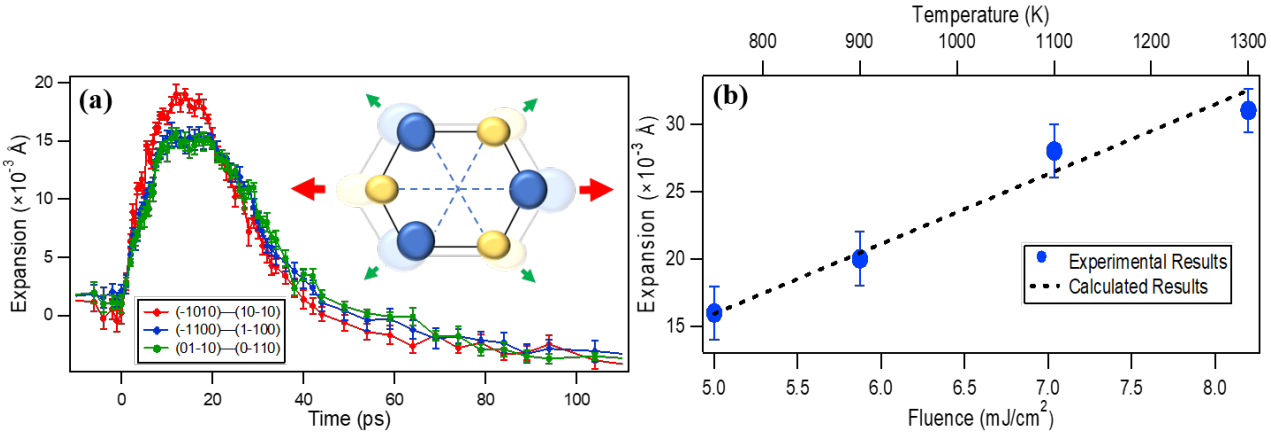

Figure 2. (a) Time-resolved anisotropic expansion of the WSe_2 unit cell, for a monolayer flake, obtained by calculating the change in distance of the diagonals between the Bragg diffraction spots after optical illumination. (b) Plot of the average expansion versus laser pump fluence (which varies the peak temperatures that are reached, also shown). The experimental results are overlapped with the calculated expansion values using a quasi-harmonic empirical model. Detailed simulations are underway with the Bernardi group in Materials Science at Caltech.

Finally, in a last set of optical pump-electron diffraction probes of lead organohalide materials before the UEM-2 facility was closed down for relocation to Prof. Scott Cushing's new laboratories in the Noyes building, we undertook studies on both single crystal perovskites and a variant of the methylammonium halides ($MAPbBr_3$ and $MAPbI_3$) that are derived from mild impulsive force applied to the single crystal precursors. Amazingly, with only 0.5-1 GPa peak pressures, these soft, hybrid materials are found to restructure dramatically under transient force, as the electron diffraction data in Figure 3 show. For the $MAPbBr_3$ perovskite, we have also found that the restructured material is at least an order of magnitude more photostable than the single crystal precursor, *in vacuo* (Figure 4).

We are actively working on understanding both the atomic nature of this restructured phase, and on how the transformation is achieved. From the large area diffraction patterns (obtained over size scales of order 100 μm^2), the patterns are consistent with what are known as 5/3 or higher rational approximates to an aperiodic motif, or a material in which small grained bulk material is strongly twinned. Initially submitted to *Science*, the referees have asked that we provide very high spatial resolution studies of these materials to confirm the twinning (or rational approximate) hypothesis. These materials are quite friable under both photo- and electron-bombardment, and so very low electron beam currents are required. Two days of imaging time scheduled at the Molecular Foundry at the LBNL on March 19th and 20th, for which incredibly sensitive electron detectors are available, went every well, and highlighted the differential

response to electron bombardment versus photo-driven damage. Beam densities of only 1-5 electrons per square nm per second were sufficient to yield demonstrable loss to a lead iodide phase in only a few tens of seconds, for example! We are presently writing these results up for publication, while we work with more rugged (from an electron beam damage point of view) two-dimensional hybrid perovskites generated by the Bakr group at KAUST and the Atwater group at Caltech. These studies have included optical pump-THz probe work using the THz time domain capabilities developed by the P.I.'s group over the past few years.

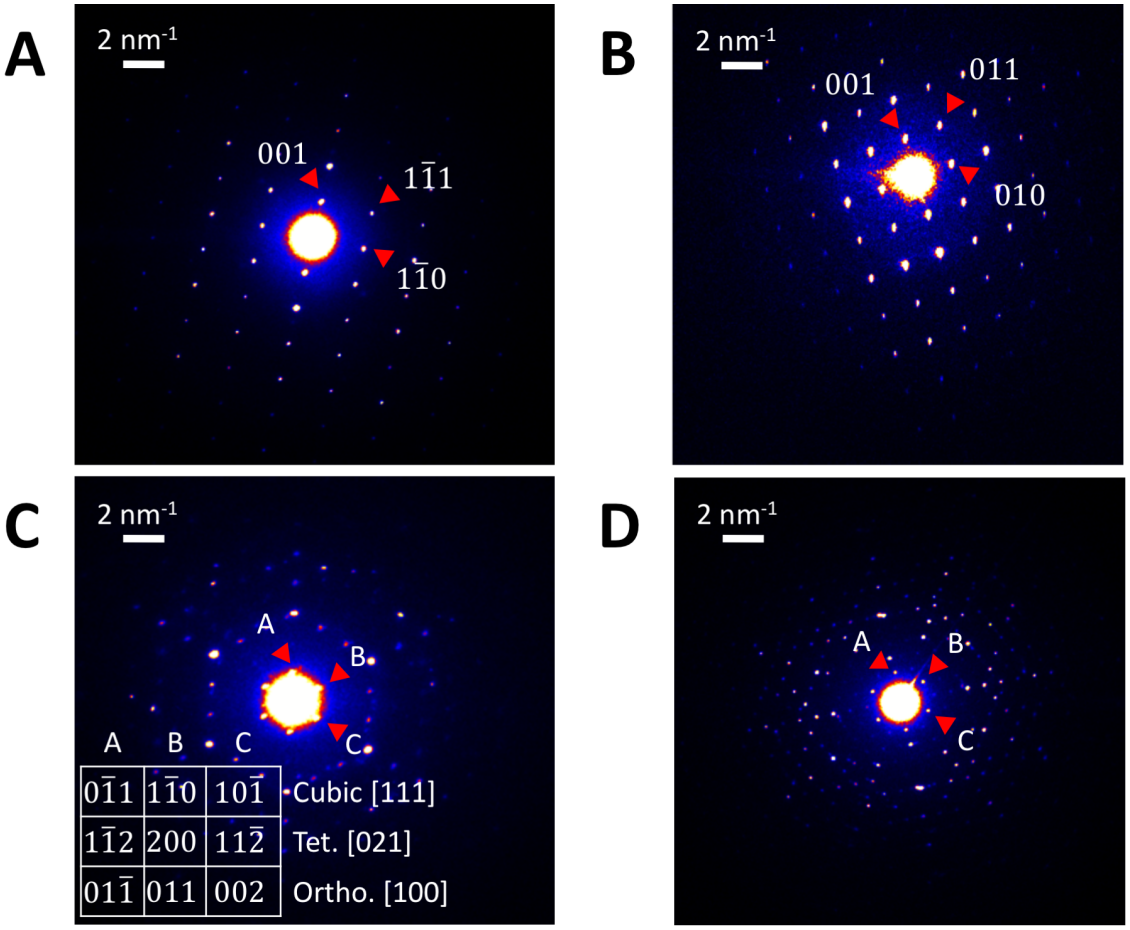

Figure 3. Single crystal $MAPbBr_3$ diffraction patterns along the [110] (A) and [100] (B) zone axes, obtained with the UEM-2. Approximant-like diffraction patterns used in the photostability measurements (panels C/D, photostability data presented in Figure 4) were analyzed to determine if the pattern could be produced by diffraction along a single crystal zone axis. Measurements along the labeled reciprocal lattice vectors failed to reproduce literature values for $MAPbBr_3$ single crystal lattices by large factors.

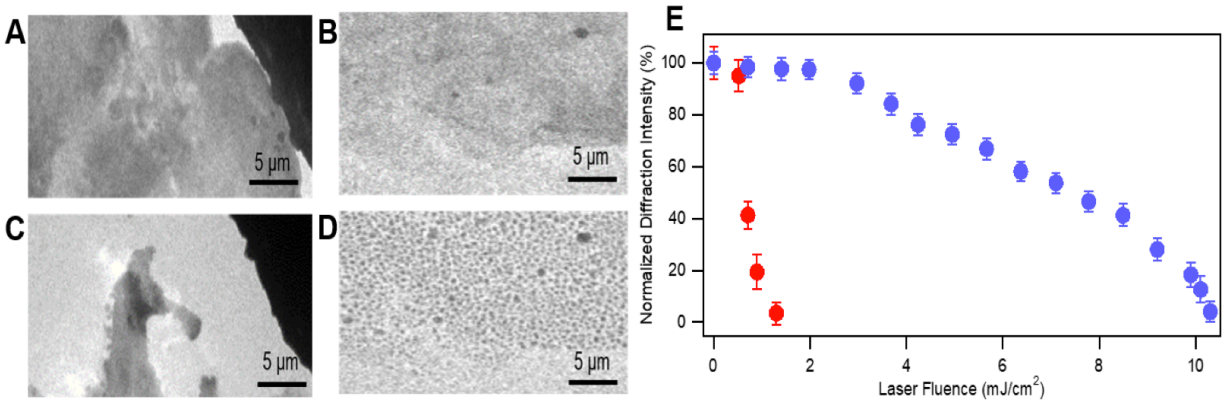

Figure 4. Photostability measurements, *in vacuo*, of the $MAPbBr_3$ impulse-derived material and its single crystal precursor. UEM-2 TEM images of the single-crystal perovskites before (A) and after (C) irradiation, and of the new structures before (B) and after (D) irradiation. (E) Bragg diffraction spot intensities of the single-crystal (red circles) and impulse-reconstructed samples (purple circles) after successive 5 min. irradiations by 519 nm/200 fs pulses at 500 kHz and increasing fluence (adapted from Mead et al. 2020, in preparation).

Our initial THz emission results from bulk and various 2D perovskite thin films are shown in Figure 5. The heterodyne detection schemes we have developed have greatly improved the sensitivity compared to results in the literature, and demonstrate that both Photo-Dember and surface field depletion effects must operate in these films, even for the n=1 hybrid material. With no center of inversion symmetry, the latter displays intense nonlinear characteristics, and so the discovery of THz emission will enable a range of novel experiments on the mechanism of charge transport in hybrid perovskites and the possibility of creating integrated device architectures that can readily exchange between photon transport and carrier transport as best suites the applications at hand. We are presently making even high quality materials and adding polarization manipulation and detection schemes so that the Photo-Dember and surface field depletion contributions can be disentangled quantitatively. And, we can now run the temperature of the samples from 10-500 K, and so can investigate the role of phase changes in the remarkable photonic and charge carrier behavior of these direct bandgap, solution processed semiconductors. Initial papers are presently being written up by the P.I.'s group in collaboration with the Atwater team, and will be forwarded to the program officer upon submission.

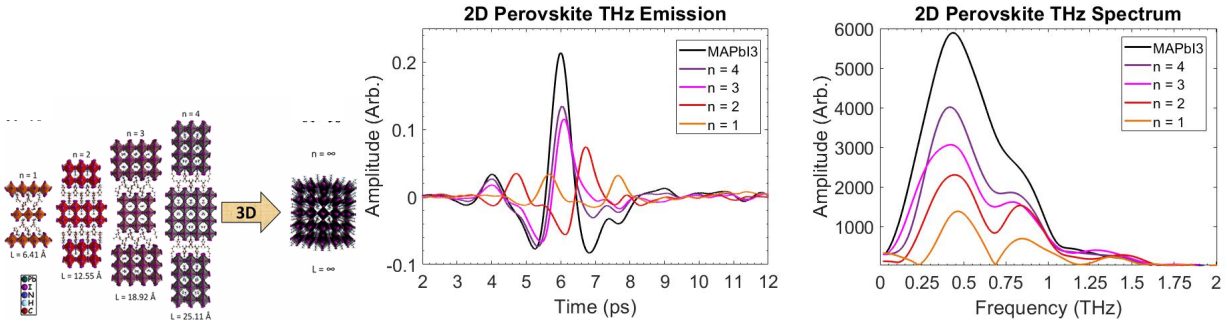

Figure 5. Optically pumped THz emission from 2D, or 'layered,' lead organohalid perovskites. The general structure of these materials is shown at left. The middle panel plots the observed THz emission from $MAPbI_3$ materials following excitation at 400 nm. As can be seen, weaker but readily detectable signals can be seen from the n=1 material, which lacks inversion symmetry.