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DURIP: Four-Dimensional Electronic Raman Spectroscopy for Elucidating Coupled Energy Transfer Processes in Nanomaterials

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Final Report**

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Annual Report for:
**DURIP: Four-Dimensional Electronic Raman Spectroscopy for Elucidating Coupled
Energy Transfer Processes in Nanomaterials**

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AFOSR Grant No. FA9550-18-1-0418 (Start Date: July 15, 2018)

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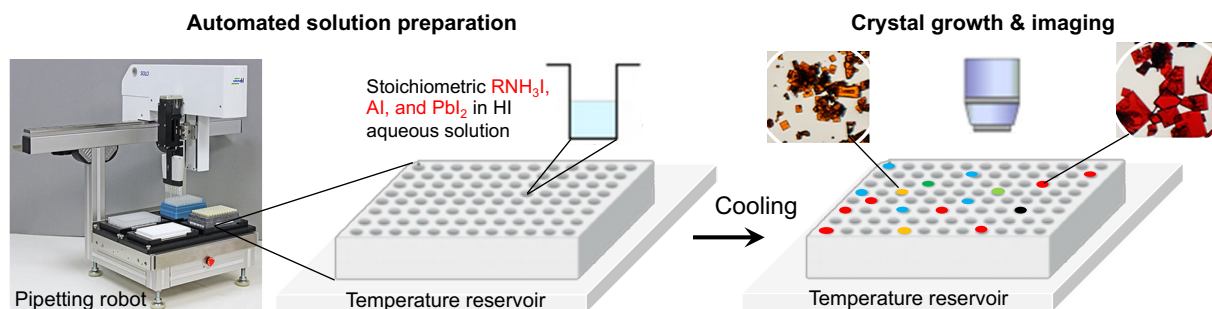
AFOSR PROGRAM MANAGER: Dr. Michael R. Berman

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Objective: The objective of the proposed DURIP grant was to support the development of novel experimental tools that augment our current research capabilities and enable new experiments in support of **AFOSR grant: Multi-dimensional Vibrational-Electronic Spectroscopy to Probe Electronic-to-Vibrational Energy Transfer in Hybrid Materials**. Specifically, our aim is to design high-order nonlinear spectroscopic and nanoscale time-resolved imaging tools that can track local and global changes in structure that accompany strongly perturbative forces acting on condensed phase systems. One major thrust is to study the structure and dynamics of bound and unbound carriers in hybrid organic-inorganic nanostructures. These systems include quantum dots where exciton-phonon interactions play a dominant role and halide perovskite where carriers may be protected by strong interactions with the surrounding lattice. More generally, carrier-environment interactions mediate dynamics in a large class of materials, where both theoretical and experimental tools are lacking to understand these interactions at the appropriate time, energy, and length scale especially in highly heterogeneous materials.

This report documents our progress in developing a combined synthesis-measurement method to study 2D and 3D perovskite materials for use in energy applications. While the focus of the proposed work was to develop characterization methods, we discovered that we needed to simultaneously develop a synthetic approach to create a wider range of materials that could be studied, and where large statistical analysis could be leveraged to uncover cause and effect relationship between the optical and physical properties of these materials. Specifically, we implemented a robotic synthesizer to create a wide range of different perovskite materials using a systematic approach. Transient absorption microscopy was then used to track changes in the optical properties and excited-state dynamics as a function of structural changes in the perovskite cage. This approach allows us to quickly determine structure-property relations and is scalable to more complex materials. In addition, we have greatly improved our multi-dimensional spectroscopic capabilities on the hardware and software side. Rapid scanning methods now allow us to acquire an entire 3D dataset in less than one second, while improved data analysis methods have facilitated physical interpretation of signals. In particular, we have implemented a complex global analysis routine that readily separates coherence and population signals. Coherence signals are then further distinguished by implementing a robust subtraction method that isolated electronic coherence contributions.

I. Automated Synthesis using a High-throughput Pipetting Robot



As shown in the figure above, we have implemented a pipetting robot for rapid synthesis of 2D perovskite materials. One major advantage of 2D perovskites is increased chemical stability because of the more hydrophobic cations. In addition, the number of layers in the 2D materials affords additional degree of freedoms that allow for tuning of synthetic knobs such as the identity of the halide anion, metal cation, and organic spacer cation, which act to tune the optical properties of these materials¹⁰. Further, 2D materials exhibit bound states which have fundamentally different properties than unbound states but are affected by carriers through screening effects. A particularly important class of 2D materials that we studied are white-light emitting perovskites (WLEP) with formula $\text{B}_2\text{A}_{n-1}\text{Pb}_n\text{X}_{3n+1}$, where a single cation acts as both A and B⁹. The mechanism of emission is through structural distortions that give rise to transient defects (i.e. STE states), a consequence of relatively strong electron-phonon coupling upon photo-excitation. A particularly important question is how the STE forms, and whether there is an energetic barrier that must be overcome for lattice distortions. The dependence of this barrier on the number of layers, initial carrier temperature, and band structure at and away from the center of the Brillouin zone remain unexplored. Recent work has shown that multilayered 2D perovskites with tunable white-light emission may be obtained by the use of ethylammonium (EA^+) cation in lead-chloride, lead-bromide, and mixed halide perovskite materials¹⁰. The chloride variant, $\text{EA}_4\text{Pb}_3\text{Cl}_{10}$ is heavily distorted with respect to $\text{EA}_4\text{Pb}_3\text{Br}_{10}$, because of the size of the EA relative to the inorganic cage. The mixed halide case allows tuning of this distortion, thereby creating a unique opportunity to study carrier-phonon interactions as a function of bond lengths of the cage structure. While in 3D structures, MAPbCl_3 and MAPbBr_3 have the same Pb-X-Pb structure, with one long and one short Pb-X bond, in the 2D structures, $\text{EA}_4\text{Pb}_3\text{Cl}_{10}$ exhibits long and short Pb-Cl bond lengths in all directions. One can quantify the octahedral distortions of these structures in terms of Pb-X bond lengths, as well as in the extent of octahedral tilting. DFT calculations shows that both 2D perovskite types are direct bandgap, with slight indirect character owing to symmetry breaking. While calculations and measurements on the effect of distortions on the bandgap have been performed and generally understood, the effects of these distortions on the formation of STE states remains unknown. The ability to tune these structures from low- to -high distortions provides a route for detailed study of the kinetics, in particular dependences on initial carrier temperature. Using the robotic synthesizer, we have explored structural distortions through the use of alloying – using mixed cation species (MA and EA) inside the perovskite cage structure as discussed above.

II. Spatially Mapping Carrier Properties in Lead Halide Perovskite Thin Films using Transient Absorption Microscopy

In the last reporting period, we described the use of transient absorption microscopy (TAM) to study grain boundaries and grain interiors in metal halide perovskite thin films (MAPbI₃). These materials have a 3D perovskite structure, and, as we showed in polycrystalline materials, the optical properties strongly depend on the nanoenvironment (e.g. through dielectric screening effects). Another related class of materials are based on a 2D perovskite structure – here, 2D inorganic layers are separated by an organic layer that may be used to influence the electronic structure and optical properties. 2D perovskites have many applications owing to the far larger tunability than their 3D counterparts, including increased stability. However, their efficiency in PV applications remains relatively low. One major challenge to studying these materials is the control of the synthesis and the large parameter space to explore. Even more so than 3D perovskites, 2D perovskites may be strongly influenced by their environment and dynamic disorder from the organic layers. To explore the large parameter space, and to minimize variations in synthesis from human error, we have implemented a robotic synthesis platform that automates the solution-based synthesis of these materials. While many 2D perovskite structures have been explored already by traditional synthesis methods, we focused our efforts on alloyed 2D perovskites, where the organic cation is a mixed ethylammonium (EA), methylammonium (MA) species. The robot was able to synthesize these materials over a wide variety of conditions to produce single crystals, where the EA/MA ratio varied from 1:2, 1:1, 2:1 and pure MA and pure EA species. Further, we obtained crystal structures for each species and verified the stoichiometry using NMR. A detailed structural analysis allowed us to carefully track changes in bond angles and bond lengths (plus cage volume and octahedral tilting angle) of the inorganic cage upon alloying.

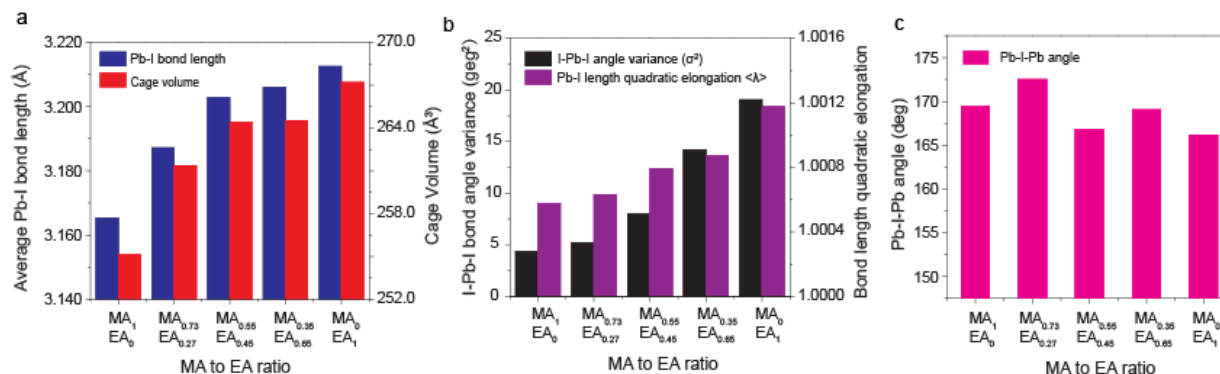


Figure 1. Effects of alloying on the perovskite structure (average Pb-I bond length, I-Pb-I bond angle, and Pb-I-Pb angle).

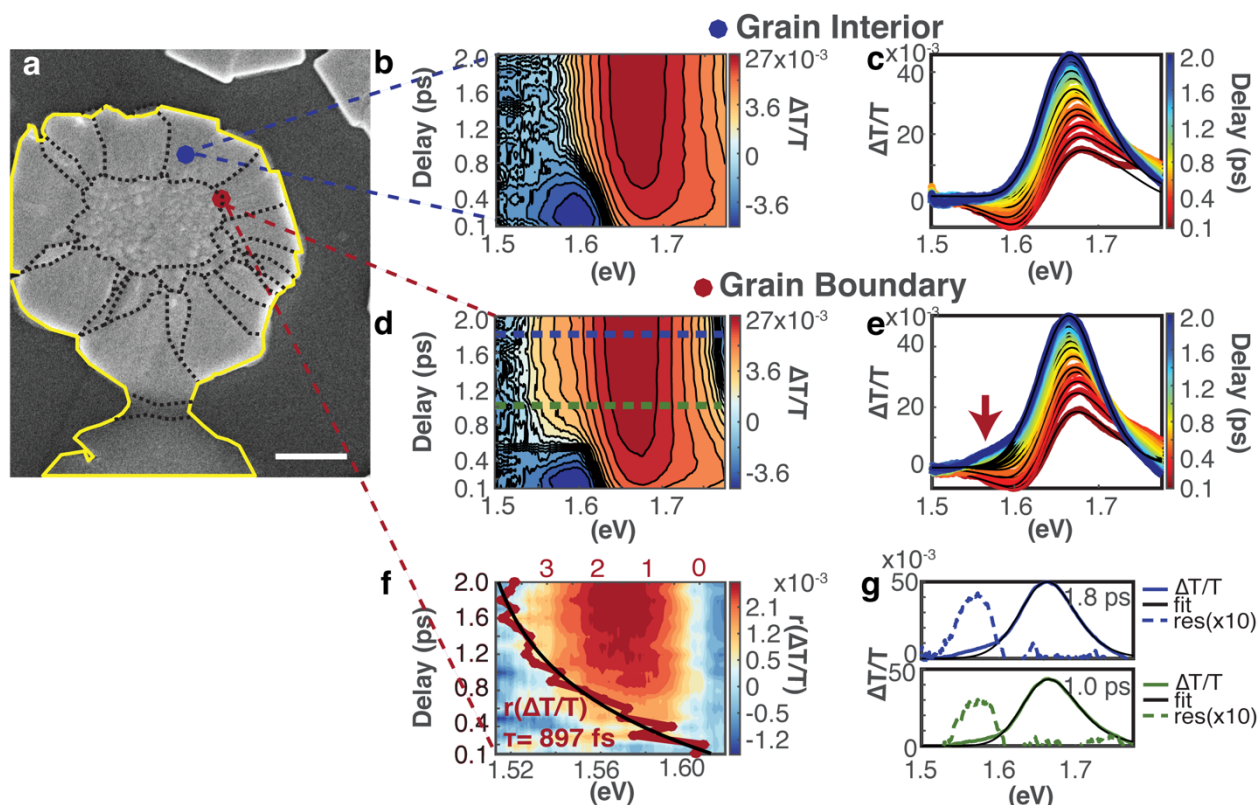
We are currently in the process of correlating these structural changes to quenching of the photoluminescence (which we see as we increase the amount of EA) and to changes in TA (where the ultrafast dynamics are largely immune from structural changes). These results indicate that carrier dynamics are not strongly influenced structural distortions as expected for large polaron formation, while these changes provide a means of non-radiative relaxation back to the ground state (hence, PL quenching). DFT calculations reproduce much of the band gap changes upon alloying, but additional work needs to be done to access the effects on PL.

III. Improvements in 3D Spectroscopy and Data Analysis

DURIP funding was also used to improve aspects of our GAMERS methodology for studying energy and charge transfer in hybrid systems, including 2D perovskites and photosynthetic pigment-protein complexes (PPCs). Specifically, we implemented new scanning methods that greatly speed up data acquisition, new optical coatings that increase throughput, and improved detectors that increased sensitivity. One of the topics we addressed was the separation of electronic and vibrational coherences in PPCs, where, over the past decade, intense interests has been directed at the physical interpretation of long-lived coherence signals. While these long-lived signals were originally assigned to electronic coherences, which would have been a surprising and important result, the general consensus now is that these signals are primarily vibrational in origin and do not directly report on long-range energy transfer as originally suggested. However, the time scale of electronic coherences has still not been directly measured, and, in some cases despite the lifetimes being short (< 100 fs), they may still be important in intra-complex transport between certain excitonic states that are close to or overlapping in energy. This is especially true in systems with a large number of chromophores such as the light-harvesting complex II (LH2) from purple bacteria. Here, we have established a means by which to acquire coherence data in a fraction of a second to achieve the highest signal-to-noise possible, giving us the best change to interpret the origin of these signals. By fitting the coherence-only signal only after a few hundred femtoseconds, we were then able to subtract from the full signal (at $T>0$), vibration-only contributions. This then yields the electronic-coherences only without resorting to the Fourier transform which contains no information on time-ordering (when one frequency arrives and another disappears). As a control, we tested this idea on BChl a, where no electronic coherences can exist, and found that no residual coherences remained. On the other hand, for LH2, coherences lasted about ~ 100 fs, which is in line with expectations based on low-temperature single-molecule fluorescence excitation experiments. More importantly, the global analysis scheme found sub-100 fs population transfer components between the B800 and B850 states, which corresponded with the electronic coherence frequencies measured. This indicates that coherences may affect population transfer, although the time scales are in the 100 fs regime and not the picoseconds that was originally postulated.

IV. Using Statistical Analysis to Uncover Dynamics in 3D Perovskite Materials

DURIP funding was used to improve our transient absorption (TA) microscope. Scanning electron microscopy (SEM) correlated to TAM on $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite particles is used to identify a defect state ~ 60 meV into the bandgap at GBs, which accelerates carrier cooling acting as additional energy acceptors. An in-depth statistical analysis performed on a large dataset (806 distinct spatial locations) reveals that the shallow defect state, generally considered to be benign, plays a significant role in accelerating carrier cooling, which is detrimental to hot carrier solar cells.



Spectrally-resolved TA spectra at GI and GB of $\text{CH}_3\text{NH}_3\text{PbI}_3$. (a) SEM image of the perovskite particle. The yellow solid curve traces the edge of the particle and the black dashed curves trace the grain boundaries between grains. The ones in the inner circle are not marked as they are too dense. Scale bar: 1 μm . (b) TA surface and (c) TA spectra with fits (black solid curves) at different pump-probe delays at one position picked in grain interiors. (d) TA surface and (e) TA spectra with fits (black solid curves) at different pump-probe delays at one position picked at grain boundaries. (f) Sub-bandgap feature extracted from fit, with spectrally integrated (1.570 ± 0.015 eV) sub-bandgap intensity (red curve) and single-exponential fit (black solid curve). The population lifetime is labeled. (g) Cuts of TA spectra at grain boundary at 1.0 ps (green) and 1.8 ps (blue), with fits (black solid curve) and residues (dashed curve, scaled). An arcsinh-scaled color map is applied on b, d, f.

The data shown above illustrate that many hundreds of distinct regions of the polycrystalline sample could be studied in a single experiment. The large data set allowed us to perform statistical analysis to isolate the connection between the depth of the sub-bandgap state, its amplitude, the carrier relaxation rate, the Fermi level, and structural features revealed by SEM.

4. Researchers supported by the AFOSR grant this funding period:

None (only equipment funded by DURIP)

5. Journal Publications Funded by this Grant During Reporting Period

S. Irgen-Gioro, K. Gururangan, R. G. Saer, R. E. Blankenship, E. Harel, 'Electronic Coherence Lifetimes of the Fenna-Matthews-Olson Complex and Light Harvesting II', **Chem. Sci.** 2019, 10.1039/C9SC03501J

X. Jiang, J. Hoffman, C. C. Stoumpos, M. G. Kanatzidis, E. Harel, 'Transient Sub-Band-Gap States at Grain Boundaries of CH₃NH₃PbI₃ Perovskite Act as Fast Temperature Relaxation Centers', **ACS Energy Lett.** 2019, 4, XXX, 1741-1747 (2019)

A. P. Spencer, E. Harel, 'Four-Dimensional Spectroscopy of Complex Molecular Systems in Solution', **J. Phys. Chem. C.**, 123, 6303 (2019) COVER ARTICLE

S. Irgen-Gioro, A. P. Spencer, W. O. Hutson, E. Harel, 'Coherences of Bacteriochlorophyll a Uncovered Using 3D-Electronic Spectroscopy', **J. Phys. Chem. Lett.**, 9, 6077-6081 (2018)