

SYMPOSIUM CM04

Ultrafast Optical Probes for Advanced Materials Characterization and Development
November 26 - November 29, 2018

Symposium Organizers

Kimberley Hall, Dalhousie University
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Symposium Support

Photon etc.

* Invited Paper

SESSION CM04.01: Hybrid Lead-Halide Perovskites

Session Chair: Carlos Silva

Monday Morning, November 26, 2018

Hynes, Level 2, Room 201

8:30 AM *CM04.01.01

Ultrafast Electron-Phonon Coupling in Emerging Semiconductors Xiaoyang Zhu; Columbia University, New York, New York, United States.

In this lecture, I will briefly introduce out recent efforts in understanding electron phonon coupling in molecular, nano, and hybrid semiconductors. Electron phonon coupling is essential to a broad range of charge carrier processes, such as polaron formation, Auger scattering, and charge carrier recombination. They are also responsible for electronic phase transitions and emergent properties, e.g., charge density waves and superconductivity. Our experimental strategy is to target excited state dynamics in the most direct way possible, using, e.g., femtosecond two-photon photoemission spectroscopy, optical Kerr-effect spectroscopy, and two-dimensional spectroscopies, to directly observe many-body events in the time domain. These experiments have led to recent understanding of coherent and incoherent mechanisms in exciton fission in organic semiconductors, direct and phonon-mediated Auger recombination in a bulk semiconductor, charge separation at van der Waals interfaces of transition metal dichalcogenides, and polaronic screening in lead halide perovskites. Such fundamental understandings are leading to new design principles for nano, molecular, and hybrid semiconductors.

9:00 AM CM04.01.02

Exciton Dynamics in Colloidal Metal Halide Perovskite Nanocrystals and Nanoplatelets Matthew N. Ashner¹, Seung Kyun Ha¹, Katherine Shulenberg² and William Tisdale¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Metal halide perovskites are a promising class of materials for a variety of applications such as solar cells and lasers. In particular, perovskites are highly defect tolerant, an effect that has been attributed to screening of charge carriers due to lattice deformations, among other mechanisms. Like other inorganic semiconductor materials, quantum confinement causes changes in the behavior of excited charge carriers, such as a transition from free carriers to excitons as the dominant excited state. Quantum confined perovskites can be synthesized in a variety of forms, including cubic nanocrystals and nanoplatelets with a thickness of 1-3 unit cells. The nanoplatelets exhibit strong quantum confinement effects, while the cubic nanocrystals are more weakly confined due to the small exciton Bohr radius of ~5 nm. In this work, we use femtosecond transient absorption and femtosecond stimulated Raman spectroscopy to simultaneously investigate ultrafast exciton and lattice dynamics in colloidal perovskite nanocrystals and nanoplatelets. We discuss how exciton formation, energetic relaxation, and the role of lattice interactions in these processes, vary between the weakly and strongly quantum-confined regimes.

9:15 AM *CM04.01.03

Ultrafast Spectroscopy of Semiconductor Nanostructures Tonu Pullerits; Chemical Physics and NanoLund, Lund University, Lund, Sweden.

Nano-size semiconductor structures have a reach spectrum of properties related to quantum confinement which are not available in the corresponding bulk materials. Size-tuneable spectrum is, perhaps, the best known and understood such property. Here we investigate dissipation and transport dynamics of various semiconductor nanosystems and their composites. We have studied colloidal quantum dots, plasmonic metal nanoparticles, hybrid and all inorganic perovskite nanocrystals and Ruddlesden–Popper 2D perovskites. We apply a set of modern ultrafast techniques like photocurrent and fluorescence detected coherent 2D spectroscopy, transient terahertz and absorption spectroscopies revealing detailed information about photoexcitation dynamics.

As an example. Photo-generated charge carrier dynamics in Ruddlesden–Popper 2D perovskites with linear (n-BA) and branched (iso-BA) butylamine as spacing cations were studied by using transient absorption and time-resolved photoluminescence spectroscopies. Both n-BA and iso-BA perovskites consist of mixed-phase 2D quantum wells with various layer thicknesses, where the photo-generated charges undergo inter-phase charge transfer from thinner quantum wells to thicker ones. By shortening the spacer from n-BA to iso-BA, the transfer rates are significantly increased, which can also diminish the charge accumulation in thin quantum wells induced by the unbalanced electron and hole charge transfer rates. Under high excitation intensity, the shorter spacing cation is found to further facilitate transport, which can compete with fast high-order carrier recombination and consequently improve the charge transfer efficiency. Intriguingly, we observe the existence of extra bulk 3D phases embedded within iso-BA perovskites, which can efficiently collect the confined charges within 2D phases and then transport them with faster carrier mobility and slower recombination rates.

9:45 AM BREAK

10:15 AM *CM04.01.04

Ultra-Fast and Ultra-Slow Processes Depict the (Defect) Photo-Physics of Metal-Halide Perovskite Semiconductors [Annamaria Petrozza](#); Istituto Italiano di Tecnologia, Milano, Italy.

Semiconducting metal-halide perovskites present various types of chemical interactions which give them a characteristic fluctuating structure sensitive to the operating conditions of the device, to which they adjust. This makes the control of structure-properties relationship, especially at interfaces where the device realizes its function, the crucial step in order to control devices operation. In particular, given their simple processability at relatively low temperature, one can expect an intrinsic level of structural/chemical disorder of the semiconductor which results in the formation of defects.

Here, first I will present our results on the role of structural and point defects in determining the nature and dynamic of photo-carriers in metal-halide perovskites. Then, I will discuss our understanding of key parameters which must be taken into consideration in order to evaluate the susceptibility of the perovskite crystals (2D and 3D) to the formation of defects, allowing one to proceed through a predictive synthetic procedure. Finally, I will show the correlation between the presence/formation of defects and the observed semiconductor instabilities.

10:45 AM CM04.01.05

Charge Carrier Recombination and Lattice Interactions in Bismuth-Based Perovskites [Lissa Eyre](#), Robert L. Hoye, Tudor H. Thomas, Hannah J. Joyce and Felix Deschler; University of Cambridge, Cambridge, United Kingdom.

A promising class of lead-free perovskites for photovoltaic applications include the bismuth halides, such as $\text{MA}_3\text{Bi}_2\text{I}_6$, BiOI , and $\text{Cs}_2\text{AgBiBr}_6$ [1]. Although these materials have been predicted to display defect tolerance, much like lead-halide perovskites, and already display improved stabilities and long charge carrier lifetimes, the power conversion efficiencies of the corresponding devices have lagged behind the lead-based perovskites. Potential reasons for this are being explored, for example, the disconnected nature of the bismuth halide octahedra in the crystal structure, which limits carrier mobility, and the lower levels of absorption due to indirect bandgaps [2]. We probe the behaviour of excited states in many bismuth-halide compounds with various effective dimensionalities using ultrafast transient absorption, Raman, and terahertz spectroscopy. The importance of phonons in carrier transport and hot carrier cooling is also investigated. Our findings are consistent with previous reports of strong coupling between phonons and electronic states [3]. Overall, this work indicates that bismuth-based materials have the potential to be used in efficient optoelectronic devices, but there is a need to account for the effects of strong carrier-phonon coupling and localisation of electronic states on carrier momentum and scattering rates. We therefore present charge carrier-lattice interaction strength as an important design criterion for efficient next-generation solar cells.

[1] Hoye, R. L. Z. et al. *Adv. Mater. Interfaces*, In Press (2018). DOI: 10.1002/admi.201800464

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11:00 AM *CM04.01.06

Charge-Carrier Dynamics in Metal Halide Perovskites for Photovoltaics [Laura Herz](#); University of Oxford, Oxford, United Kingdom.

Organic-inorganic metal halide perovskites have emerged as attractive materials for solar cells with power-conversion efficiencies now exceeding 21%. Yet the optoelectronic properties underpinning their performance are still the subject of debate. Here, ultrafast optical-pump THz-probe photoconductivity spectroscopy has proven to be an outstanding tool to unravel the dynamics of charge carrier recombination, and probe charge-carrier mobility mechanisms.

Metal halide perovskites (stoichiometry AMX_3) are particularly attractive light absorbers because their properties can be tuned through facile modification in composition and structure, e.g. through substitutions of the organic A cation (e.g. methylammonium versus formamidinium), the metal M cation (e.g. Pb^{2+} or Sn^{2+}) and the halide X anion (I versus Br). Introduction of hydrophobic cations that are too large to be incorporated into the perovskite structure, has also recently been explored, leading to electronic confinement in materials of lowered dimensionality, and better photostability.

We demonstrate how such changes affect parameters essential for photovoltaic operation, discussing the influence of composition, structure, doping and dimensionality on fundamental properties such as electronic bandstructure, charge-carrier recombination and charge-carrier diffusion lengths. We further discuss distinct charge-carrier recombination and scattering mechanisms and their dependences on composition and temperature.

Elizabeth S. Parrott, Thomas Green, Rebecca L. Milot, Michael B. Johnston, Henry J. Snaith, Laura M. Herz, *Adv. Func. Mat.*, ASAP DOI: 10.1002/adfm.201802803 (2018).

D. Wright, R. L. Milot, G. E. Eperon, H. J. Snaith, M. B. Johnston, L. M. Herz, *Adv. Func. Mater.* **27** 1700860 (2017).

C.L. Davies, M. R. Filip, M. R., J. B. Patel, T. W. Crothers, C. Verdi, C., A. D. Wright, R. L. Milot, R. L., F. Giustino, M.B. Johnston, L. M. Herz, *Nature Communications* **9**, 293 (2018).

Z. Wang, Q. Lin, F. P. Chmiel, N. Sakai, L. M. Herz, and H. J. Snaith, *Nature Energy* **2**, 17135 (2017).

SESSION CM04.02: Hybrid Perovskites and Nanostructures

Session Chair: Matt Graham

Monday Afternoon, November 26, 2018

Hynes, Level 2, Room 201

1:30 PM *CM04.02.01

Investigation of Electronic and Structural Dynamics in Metal-Halide Perovskites with Ultrafast Spectroscopy [Felix Deschler](#); University of Cambridge, Cambridge, United Kingdom.

Metal-halide perovskites have emerged as promising solution-processable semiconductors for optoelectronic applications. These materials show

unexpectedly high luminescence yields, long carrier lifetimes under operating conditions. Facile changes in composition during fabrication can be used to control their optical properties, and the nature of electronic states. Recently, the ad-mixture of monovalent cations to the precursor solution has been demonstrated to maximize the luminescence yields and device performance, which harvests photon-recycling effects.

The properties and dynamics of the perovskites' electronic states are controlled by their crystal structure and symmetry. Strong spin-orbit coupling was predicted to introduce Rashba-type state splitting in the electronic band structure. In combination with the soft crystal structure of the perovskite lattice, it is likely that dynamic changes occur in the electronic states during their lifetime. So far, it is not understood how such effects change after optical excitation and how they proceed during relaxation of electronic states.

In this talk I will present how we use spectroscopic techniques to study the dynamics of electronic states and crystal structure in metal-halide perovskites on ultrafast timescales. I will report results on layered and bulk lead-halide perovskites, but also on sustainable lead-free variants. I will discuss how the crystal structure affects the properties of electronic states, and how we can use these changes to create novel optoelectronic devices.

2:00 PM *CM04.02.02

Ultrafast Non-Contact Probes of Carrier Transport and Dynamics within Semiconductor Nanostructures and Interfaces [Matthew C. Beard](#); Chemical and Nanoscience Center, National Renewable Energy Laboratory, Golden, Colorado, United States.

Solar photoconversion in semiconductors is driven by charge generation via photon absorption, charge transport, and charge separation at the interface of the semiconductor and contacting layers. Thus, the carrier dynamics – charge separation and recombination across junctions – represent a key-determining factor in the photoconversion performance. We have developed several non-contact probes based on ultrafast spectroscopy of carrier dynamics within bulk semiconductors, nanostructures and semiconductor interfaces. Isolating spectral signatures and/or the carrier dynamics that are specific to junctions and not just the interface or bulk is challenging. We developed transient photoreflectance (TPR) as an innovative time-resolved spectroscopic probe that can directly monitor carrier dynamics within and across such junctions. In the TPR method, the change in reflectance (of a broadband probe from a specific interface is monitored as a function of pump-probe delay (Fig. 1). The reflectance can be modulated by either photogenerated free-carriers due to band filling, and/or by transient fields due to electro-optic effects when charges are separated. The spectral nature of the reflected beam provides quantitative information about the built-in field; thus, TPR is a non-contact probe of the electric field at that interface. I will present recent studies of Pb-halide perovskites single crystals, thin films, and nanostructures and semiconductor nanostructures.

2:30 PM CM04.02.03

Observation of Multiple Excitonic Dipole Oscillations in Semiconductor Nanocrystals Using Phase-Locked Interference Detection [Hirokazu Tahara](#), Masanori Sakamoto, Toshiharu Teranishi and Yoshihiko Kanemitsu; Kyoto University, Uji, Japan.

Multiple excitons in semiconductor nanocrystals (NCs) are extensively studied for advanced optoelectronic devices such as quantum dot based solar cells, photodetectors, and lasers [1,2]. In particular, carrier multiplication process via multiple excitons is investigated to clarify a fascinating mechanism that enhances the photon-to-current conversion efficiency, i.e., multiple exciton generation. In this process, excitonic coherence is considered to play an important role as predicted in theoretical investigations of the coherent superposition of single and multiple excitons [3]. However, the generation process of multiple excitons still remains unclear. Since multiple excitonic coherence appears only within the ultrafast time regime, the coherent signal is hardly observed by using conventional spectroscopic techniques. Therefore, an advanced spectroscopic technique detecting ultrafast signals is required to observe the multiple excitonic coherence.

In this study, we report on the direct observation of multiple excitonic dipole oscillations in PbS/CdS core/shell NCs by our newly developed spectroscopic technique that employs phase-locked interference detection in transient absorption measurements [4]. Since a stable phase-locked pulse pair was used as pump pulses, transient absorption signals for various time interval between the pulse pair enabled us to monitor the profiles of excitonic dipole oscillations. The transient absorption signals showed the oscillations with higher harmonic orders of the pump photon energy that was set to the single exciton resonance energy. Furthermore, the harmonic dipole oscillations exhibited a clear correlation with the generation probabilities of multiple excitons. These results show that the multiple excitonic coherences, i.e., higher harmonic dipole oscillations, are formed in the NCs. We clarified that the decay profiles of the dipole oscillations are determined as a function of the number of excitons. It is notable that the frequency of higher harmonic dipole oscillations are comparable to that of the dipole oscillation of high-energy hot excitons. This result shows that the harmonic dipole oscillations can also play an important role in the reverse process, i.e., multiple exciton generation from a single hot exciton to multiple excitons in the ground state. Part of this work was supported by JST-CREST (JPMJCR16N3) and JSPS KAKENHI (18K13481).

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2:45 PM CM04.02.04

Stimulated Emission and Ultrafast Optical Switching in a Nanographene Molecule Giuseppe M. Paternò¹, [Luca Moretti](#)³, Qiang Chen², Klaus Mullen², Akimitsu Narita², Giulio Cerullo³, Guglielmo Lanzani^{1,3} and Francesco Scotognella^{3,1}; ¹Istituto Italiano di Tecnologia, Milano, Italy; ²Max Planck Institute for Polymer Research, Mainz, Germany; ³Physics, Politecnico di Milano, Milano, Italy.

Quantum confinement of the electronic wave function allows to open a finite band-gap in the graphene electronic structure. For instance, the nanofabrication of 2D graphene nanomesh[1], 1D graphene nanoribbons[2] and 0D graphene quantum dots[3], has paved the way for the development of the promising field of nanographene optoelectronics. In this context, the synthesis of molecular graphene via bottom-up processes permits to obtain monodisperse nanographene, with defined physical and chemical properties[4]. The luminescence features exhibited by molecular graphene[5], in particular, has made these carbon-based materials of great interest for plasmonic and photonic applications, among others.

Here, we demonstrate that the stimulated emission signal of a newly synthesised and very luminescent (absolute PL quantum yield 79%) nanographene molecule, namely dibenzo[hi,st]ovalene (DBOV **1**) can be optically switched in the ultrafast time regime both in solution and in the solid state. We will show that such an effect can be achieved by taking advantage of the overlap between the stimulated emission signal and the absorption of intermolecular polaronic-like species.

References

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3:00 PM BREAK

SESSION CM04.03: Nanostructures
Session Chair: Matt Graham
Monday Afternoon, November 26, 2018
Hynes, Level 2, Room 201

3:30 PM *CM04.03.01

Understanding the Features in the Ultrafast Transient Absorption and Two-Dimensional Electronic Spectra of Colloidal CdSe Quantum Dots Howe-Siang Tan; Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore, Singapore.

We present a model to explain the various features of the transient absorption (TA) and two-dimensional electronic spectrum (2DES) of colloidal CdSe semiconductor quantum dots (QDs). The measured TA and 2DES spectra consist of contributions by the ground state bleach (GSB), stimulated emission (SE) and excited state absorption (ESA) processes associated with the three lowest energy transition of the QDs. We model the shapes of the GSB, SE and ESA spectral components after fits to the linear absorption. The spectral positions of the ESA components take into account the biexcitonic binding energy. In order to obtain the correct weightage of the GSB, SE and ESA components to the TA and 2DES spectra, we enumerate the set of coherence transfer pathways associated with these processes. In 2DES, various other features provide information on the inhomogeneity and homogeneity of the sample under study. We use the nodal line slope (NLS) that separates the positive and negative peaks in the 2DES spectrum to characterize the homogeneous and inhomogeneous linewidths of colloidal CdSe QDs ensembles. With a combination of experimental measurements from linear absorption, transient absorption and 2DES spectra, we devise a simulation process to quantify the ratio between the inhomogeneous and homogeneous contributions to the line-broadening effects of CdSe QDs ensemble.

4:00 PM CM04.03.02

Physical Origins of the Transient Absorption Spectra and Dynamics in Thin-Film Semiconductors—The Case of BiVO₄ Jason K. Cooper^{1,2}, Sebastian Reyes Lillo¹, Lucas Hess², Chang-Ming Jiang², Jeffrey B. Neaton¹ and Ian D. Sharp^{1,3}; ¹Lawrence Berkeley National Lab, Berkeley, California, United States; ²Joint Center for Artificial Photosynthesis, Berkeley, California, United States; ³Walter Schottky Institut and Physik Department, Technische Universität München, Garching, Germany.

Transient absorption spectroscopy offers a unique perspective on the photogenerated carrier lifetimes of materials through the ultrafast evolution of the transient difference spectrum taken in transmission and/or reflection geometries. However, the related spectroscopic features can be challenging to interpret accurately and as such the related kinetics may be convoluted in overlapping signals of unknown origin. By co-collecting both transmission and reflection signals we extract the differential absorption of the material. We use a combination of ground state optical properties and the temperature dependent difference spectra of a model system, bismuth vanadate, to obtain an accurate model of the time dependence of the transient spectrum. From this, we have obtained the temporal evolution of the free carrier density from which a kinetic model was developed enabling a unique perspective on the governing recombination mechanisms. Importantly, the lattice temperature has been shown to play a critical role in the optical response at time delays past 10 ps. Additionally, spectral features related to coherent optical and acoustic phonons have also been identified. This comprehensive approach to analyzing and modeling the TA spectra offers a generalizable basis for understanding the complex pump-probe data, reveals thermal heating artifacts that are frequently erroneously assigned to long-lived photocarriers, and offers a path to eliminating ambiguity in analysis of photocarrier dynamics in solid state systems.

4:15 PM CM04.03.03

Plasmon-Induced Demagnetization and Magnetic Switching in Nickel Nanoparticle Arrays Mikko Kataja¹, Francisco Freire-Fernández², Jorn P. Witteveen², Tommi K. Hakala², Päivi Törmä² and Sebastiaan van Dijken²; ¹CSIC-ICMAB, Bellaterra, Spain; ²Department of Applied Physics, Aalto University, Espoo, Finland.

In heat-assisted magnetic recording (HAMR), a plasmonic noble metal nanoantenna acts as a near-field transducer (NFT) that reduces the switching field of high-anisotropy materials via local heating [1]. Excitation of the NFT at the plasmon resonance frequency efficiently transfers optical energy to a nanoscale region, enabling local switching at a reduced magnetic field. Noble metal nanoantennas placed on ferromagnetic films have been used for nanoscale confinement of all-optical switching (AOS) [2]. Experiments on pure ferromagnetic metals demonstrate that, despite stronger ohmic damping, they also support surface plasmon resonances. This raises the question if one could nanostructure the magnetic medium itself to trigger magnetic switching via local enhancements of the optical field. To study the effect of plasmon resonances on magnetic switching, we considered ferromagnetic nanoparticles of uniform size and shape. Plasmon resonances in single ferromagnetic nanoparticles are rather broad, several hundreds of nanometers [3]. Yet, ordering of the particles into a periodic array significantly narrows the spectral response. In this geometry, hybridization between LSPRs and the diffracted orders of the array produces intense surface lattice resonances (SLRs) that give rise to enhanced optical absorption and light-matter interaction that can be ascertained from their enhanced magneto-optical properties [4]. We report on the manipulation of magnetization by femtosecond laser pulses in a periodic array of cylindrical nickel nanoparticles. By performing experiments at different wavelengths, we show that the excitation of collective surface lattice resonances triggers demagnetization in zero field or magnetic switching in a small perpendicular field. Both magnetic effects are explained by plasmon-induced heating of the nickel nanoparticles to their Curie temperature. Model calculations confirm the strong correlation between the excitation of surface plasmon modes and laser-induced changes in magnetization [5].

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4:30 PM CM04.03.04

Catalyst Metal and Growth Direction-Dependent Carrier Dynamics in Al and Au-Catalyzed Silicon Nanowires Michael R. Williams², Mel Haïney^{1,3}, Joan M. Redwing¹ and Rohit Prasankumar²; ¹Pennsylvania State University, University Park, Pennsylvania, United States; ²Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; ³Materials Process Engineering, Nagoya University, Nagoya, Japan.

Silicon nanowires grown by metal-catalyzed vapor-liquid-solid growth are attractive for photovoltaic, electronic, and sensing applications. However, the impact of catalyst metal incorporation and the effect of nanowire growth direction and sidewall orientation on carrier lifetime have not been fully understood. For instance, Al-catalyzed wires are p-type and should not show deep-level traps usually associated with gold catalysts. Ultrafast optical microscopy (UOM) has previously been used studying carrier dynamics in individual Si NWs, and was applied in this study to observe ultrafast carrier dynamics at specific positions on individual NWs grown in both <111> and <110> directions with Au or Al-catalysts. The results reveal both catalyst and orientation-dependent dynamics for Al and Au-catalyzed silicon nanowires.

For this study, silicon nanowires were grown via low-pressure or atmospheric chemical vapor deposition under conditions promoting either <111> or <110> growth and then transferred to sapphire substrates. Some nanowires were also passivated with ~20nm of Al₂O₃ prior to substrate transfer. The photo-induced change in transmission of the probe beam after 400 nm (3.1 eV) photoexcitation was recorded at specific positions along each NW for probe wavelengths ranging from 750-845 nm (1.47-1.66 eV).

For Al-catalyzed <111> wires, passivation led to a roughly 2x increase in lifetime due to the reduction of surface trap states in the passivated samples, and carrier lifetime in almost all NWs increased with increasing diameter, regardless of passivation (note the NWs studied show some tapering). This trend is consistent with previous results, as the ratio of surface traps to bulk Si states should decrease with increasing wire diameter.

More unexpected is the behavior observed in the <110> Al-catalyzed NWs, which show longer lifetimes with decreasing diameter for both as-grown or passivated wires. This phenomenon appears to be orientation and not catalyst-dependent, since it is also observed in Au-catalyzed <110> NWs. While amorphous silicon (a-Si) was detected on the side walls of some Al-catalyzed <110> wires via micro-Raman, suggesting that the wider diameter regions were simply covered with a-Si, similar behavior was observed for <110> NWs without an a-Si Raman peak as well, suggesting the behavior may be intrinsic to the <110>-orientation. SiNWs.

Wires grown with an Al catalyst also showed increased carrier lifetimes with increasing pump fluence, in contrast to Au-catalyzed wires. This suggests the presence of trap states in Al-catalyzed wires that remain unsaturated, even at higher fluences. These results should prove valuable in tailoring the electrical properties of Si NWs or guiding the selection of individual NWs from an ensemble for use in a particular application. Importantly, our results show that not only do the carrier dynamics in individual NWs vary within an ensemble, but may vary from position to position on the same NW.

SESSION CM04.04: 2D Materials
Session Chair: Ajay Srimath Kandada
Tuesday Morning, November 27, 2018
Hynes, Level 2, Room 201

8:45 AM *CM04.04.01

Excitonic Effects in Single Layer MoS₂ Probed by Two-Dimensional Electronic Spectroscopy Margherita Maiuri¹, Stefano Dal Conte¹, Mattia Russo¹, Junjia Wang², Giancarlo Soavi², Dumitru Dumcenco³, Andras Kis³, Andrea C. Ferrari² and Giulio Cerullo¹; ¹Politecnico di Milano, Milano, Italy; ²University of Cambridge, Cambridge, United Kingdom; ³Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Atomically thin Transition-metal dichalcogenides (TMDs) have promising physical properties [1,2]. Because of the strong quantum confinement effects, Coulomb interaction is poorly screened in single-layer (1L) TMDs, so that the excitons created by photo-excitation have large binding energy, up to several hundred meVs [3].

The spectrum of 1L-MoS₂ is characterized by two peaks of excitonic nature at 1.9 eV and 2.05 eV, the so-called A and B excitons. They arise from optical transitions between the spin-orbit split top valence band and the bottom conduction band, around K and K'. Although, exciton dynamics in 1L TMDs have been largely studied in the last years [4], the complete understanding of the mechanisms leading to the ultrafast excitons formation and coupling is far to understood.

Here we exploit two-dimensional electronic spectroscopy (2DES) to track the sub-ps excitonic interactions within MoS₂. 2DES is an interferometric-based optical technique that allows to fully resolve the non-linear response of a material. It employs a sequence of three delayed short pulses impinging on a sample to provide a series of two-dimensional excitation/detection correlation energy maps at different delays, offering a unique combination of high temporal and spectral resolution. We perform 2DES measurements on a chemical vapor deposition grown 1L-MoS₂ sample, at 77K and room temperature, using sub 20-fs visible (1.75-2.3 eV) pulses, covering both A and B transitions.

In 2DES maps we distinguish two types of contributions: the signals along the diagonal line of the excitation/detection map, and the ones out of the diagonal (cross-peaks). At early times (<20fs), we observe instantaneous positive diagonal peaks appearing at the A/A and B/B excitation/detection energies, reflecting the bleaching of the excitonic transitions, as well as two cross-peaks at the A/B and B/A coordinates, indicating correlations between A and B excitons. At later times (40-60fs) we notice a marked elongation of both A and B diagonal peaks, associated with an ultrafast (100fs) spectral diffusion. For times >200fs a strong decrease of the peaks intensity is observed. While the build-up of the diagonal peaks is instantaneous (within our temporal resolution of 20fs), we can clearly resolve the formation of the lower cross-peak, at A/B excitation/detection point. The dynamic of the lower A/B cross-peak, which is completely masked and thus impossible to observe in transient absorption measurements, cannot be simply explained in term of a phase space filling effect, but it is a strong signature that exciton dynamics in 1L-MoS₂ is dominated by more complex interactions. Our results, combined with theoretical modeling, will shed new light on the origin of exciton dynamics in 1L TMDs.

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9:15 AM CM04.04.02

Ultrafast Dynamics of 2D Materials Studied by Transient SHG Microscopy Hyunmin Kim; DGIST, Daegu, Korea (the Republic of).

Recently, time-resolved pump-probe spectroscopy has been extensively exploited to study ultrafast carrier dynamics of 2D materials in a femtosecond scale time resolution. In this work, we introduce a transient second harmonic generation (tr-SHG) microscopy^{1,2} to study the electron/phonon dynamics of atomically thin MoS₂ materials. A time-dependent sequential tr-SHG imaging on electron/phonon dynamics was monitored using a tr-SHG microscopy composing of a pump beam tuned to the A-exciton (680 nm) and a probe beam (1040 nm) generating a SHG at 520 nm having a submicron scale lateral resolution. We do believe that the tr-SHG microscopy would suggest a new way to study ultrafast carrier physics of low dimensional materials and their hybrids in a more advanced spatiotemporal fashion.

References

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2. Shinde, S.M. †, Dhakal, K.P. †, Chen, X. †, Yun, W.S., Lee, J.D., **Kim, H.***, Ahn, J.-H.* (2018) Stacking-controllable interlayer coupling and symmetric configuration of multilayered MoS₂. *NPG Asia Mater.* 10, e468.

9:30 AM CM04.04.03

Observation of Chiral Phonons in Monolayer 2D Materials Hanyu Zhu^{1,2}, Jun Yi¹, MingYang Li³, Lifa Zhang⁴, Jun Xiao¹, Chih-Wen Yang³, Robert A. Kaindl², Lain-Jong Li³, Yuan Wang^{1,2} and Xiang Zhang^{1,2}; ¹University of California, Berkeley, Berkeley, California, United States; ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ³King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; ⁴Nanjing Normal University, Nanjing, China.

Chirality is often found in systems with structural inversion symmetry breaking. Previously, for bosonic collective excitations in atomic lattices, chirality was only theoretically predicted but never observed. We experimentally show that phonons can exhibit intrinsic chirality in monolayer tungsten diselenide. The chiral phonons have significant implications for electron-phonon coupling in solids, lattice-driven topological states, and energy-efficient information processing. We identified the phonons by the intervalley transfer of holes through hole-phonon interactions during the indirect infrared absorption. The chirality was confirmed by the transient infrared circular dichroism arising from pseudo-angular momentum conservation. From the spectrum we further deduce the energy transferred to the phonons, which agrees with both the first principle calculation and the double-resonance Raman spectroscopy.

9:45 AM BREAK

10:15 AM *CM04.04.04

Optical Multidimensional Coherent Spectroscopy of Exfoliated MoSe₂ Monolayers Steven Cundiff, Eric Martin and Hanna Ruth; University of Michigan, Ann Arbor, Michigan, United States.

Monolayer van der Waals crystals are a class of materials with varying electronic properties that can be stacked into heterostructures with synergistic benefits. A subset of these materials are the semiconducting monolayer transition metal dichalcogenides (TMDCs), which have a direct band gap that makes their electronic transitions optically accessible. TMDCs are known to have widely varying excitonic linewidths that depend on the local environment, excitation source, and sample history (i.e. temperature cycles and exposure to laser radiation).

We use multidimensional coherent spectroscopy (MDCS) to measure the inhomogeneous and homogeneous linewidths of the neutral exciton in molybdenum diselenide (MoSe₂) monolayer samples. Using this method, we study the effects of encapsulation in hexagonal boron nitride, of temperature and of laser power on both linewidths. We observe that both the inhomogeneous and homogeneous linewidths of the encapsulated samples are significantly narrowed in comparison to the non-encapsulated samples. Linewidth narrowing is determined by a thorough power and temperature dependence of the materials' exciton resonances.

10:45 AM CM04.04.06

Visualizing Ultrafast Interfacial Phenomena in 2D Materials William Tisdale; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Dielectric confinement in atomically thin transition metal dichalcogenides (TMDs) leads to excitonic behavior that differs markedly from bulk semiconductors. Using ultrafast SHG microscopy and transient photoluminescence microscopy, we have explored dynamics of charge and energy transfer across TMD interfaces. I will discuss these results and what they teach us about the dominant role of dielectric screening in atomically thin materials.

11:15 AM *CM04.04.07

Probing Ultrafast Interlayer Photocurrent Dynamics in Twisted and Stacked van der Waals Materials Matt W. Graham; Oregon State University, Corvallis, Oregon, United States.

Using time-space resolved ultrafast microscopy on individual 2D crystal grains, we show how long-range interlayer electronic coupling can be selectively enhanced either by applying an *E*-field or by twisting the layer stacking orientation. Considering first twisted bilayer graphene (*t*BLG), we discovered how stacking-angle tunable absorption resonances form a strongly-bound exciton state as a consequence of the symmetrized rehybridization of constrained interlayer *2p* orbitals.[1,2] Using two-photon photoluminescence and intraband-transient absorption microscopies, we have recently imaged the photoemission and exciton dynamics from single-grains of *t*BLG. After resonant excitation, our results suggest the formation of strongly-bound (500-690 meV), stable interlayer exciton states.

Unlike stacked graphene, semiconducting 2D transition metal dichalcogenides (TMDCs) have diffuse interlayer *d*-orbital overlap. To enhance interlayer electronic coupling in TMDCs, we apply an interlayer directed *E*-field, inducing electron-hole dissociation. Our lab [3] and others [4] measure that stacked WSe₂ TMD devices can have both IQE >50% and fast (<50 ps) picosecond electron escape times. Using a first-principle kinetic master equation, our methods analytically extract both the *E*-field-dependent interlayer escape velocity and rate-limiting exciton dissociation time. Remarkably our photocurrent response function produces the same *E*-field-dependent electronic escape and dissociation rates for both the optical and PC addressed ultrafast measurements. As confirmation, the resulting ratio of the electronic rates accurately matches our overall WSe₂ device IQE in the intensity limit of zero Auger recombination. Thus through time-space resolved microscopy, we now obtain a timeline selective to the interlayer electronic dynamics of TMDCs and *t*BLG van der Waals materials. We show how this novel scanning microscopy approach, combines ultrafast photocurrent and transient absorption to identify new long-lived and metastable interlayer electronic states in emerging twisted and stacked 2D materials and devices.

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1:30 PM *CM04.05.01

Ultrafast Momentum-Resolved Phonon Spectroscopy—Direct Observations of Electron-Phonon Coupling and Nonequilibrium Phonon Dynamics in the Time-Domain Bradley Siwick^{1,2,3}, Mark Stern^{1,3}, Martin Otto^{1,3}, Laurent Rene de Cotret^{1,3} and Mark Sutton^{1,3}; ¹Physics, McGill University, Montreal, Quebec, Canada; ²Chemistry, McGill University, Montreal, Quebec, Canada; ³Center for the Physics of Materials, McGill University, Montreal, Quebec, Canada.

The nature of the couplings within and between lattice and charge degrees of freedom is central to condensed matter and materials physics. These interactions are essential to phenomena as diverse as superconductivity, charge density waves and carrier mobility in semiconductors and metals. Despite their fundamental role, detailed momentum-dependent information on the strength of electron-phonon coupling (EPC) and phonon-phonon coupling (PPC) across the entire Brillouin zone has proved elusive. This talk will describe a new technique, ultrafast electron diffuse scattering (UEDS), that provides such information. By exploiting symmetry-based selection rules and time resolution, different phonon branches can be distinguished even without energy resolution. Specific applications of UEDS to 2D materials will be presented, demonstrating that UEDS patterns map the momentum-dependent relative EPC and PPC strength as well as carrier screening effects through their profound sensitivity to photoinduced changes to the phonon system.

2:00 PM CM04.05.02

Probing Lifetimes and Hydrodynamic Transport in Quantum Materials Jennifer Coulter and Prineha Narang; School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

The field of topological materials with strong electron-electron interactions is well established and has been the subject of research over the past few decades. In parallel, the field of photonics has made tremendous progress in connecting spatio-temporal ultrafast measurements of new quantum materials, including 2D plasmonics and Moiré structure localized potentials, to theoretical predictions. The study of the interplay between topological properties, optical properties and ultrafast dynamics in these materials has recently started to receive attention. Experimental demonstrations in a set of Dirac and type-II Weyl semimetals, materials where electrons effectively interact as massless relativistic particles (Weyl fermions) and in 3D the conduction and valence bands touch at isolated points, have shown evidence of a viscous electronic transport regime. In this regime, electron-electron scattering dominates over impurity scattering and other momentum-relaxing processes so that momentum is quasi-conserved and electron flow can be described using the formalism of hydrodynamics. This leads to a variety of surprising behaviors such as breakdown of the Wiedemann-Franz law, appearance of electron vortices, and tunable viscosity via magnetic field. Understanding these physical processes in materials is of both fundamental and practical importance, yet these problems pose unique theoretical and computational challenges. The simultaneous contribution of processes that occur on many time and length scales, not only make direct computational approaches very difficult, they also make comparisons with experimental observations challenging. Here we report a new microscopic model of this behavior using a combination of ab initio scattering methods and fluid dynamics techniques. Our work establishes a connection between the observed hydrodynamic phenomena in Weyl semimetals, crystal structure and symmetry and their experimentally observed dynamical properties.

2:15 PM *CM04.05.03

Excitonic Quantum Gates Eric R. Bittner; University of Houston, Houston, Texas, United States.

Entangled photons offer an exquisite probe to correlated dynamics within a material system. In my talk, I shall discuss some recent experiments and our theoretical investigations into developing an input/output scattering theory approach that connects an incoming photon Fock state to an outgoing Fock state, treating both the internal (material) and photon dynamics on a consistent footing. As proof of concept, we show how entangled photons can probe the inner workings of a model system undergoing spontaneous symmetry breaking.

2:45 PM BREAK

3:15 PM CM04.05.05

Photoinduced Phase Transition in Strained Manganite Films Studied by Ultrafast Optical Single-Shot Spectroscopy Yu-Hsiang Cheng¹, Samuel W. Teitelbaum¹, Jingdi Zhang², Feng Jin³, Xuelian Tan³, Wenbin Wu³, Richard Averitt² and Keith A. Nelson¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²University of California San Diego, La Jolla, California, United States; ³University of Science and Technology of China, Hefei, China.

We performed single-shot pump-probe measurements on strained $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ thin films to study the irreversible photoinduced insulator to metal transition. After resonant excitation of the inter-site d-d transition at 1.55 eV, we observed a persistent change in reflectivity at the same frequency (1.55 eV), i.e. the spectral weight transfer to a Drude component at far-IR due to the insulator to metal transition, as confirmed by THz conductivity measurements. In a 30 nm thin film, the volume fraction of the photoinduced metallic phase grew with laser shots and saturated after ~20 shots. Besides the steady-state reflectivity, the transient reflectivity traces also changed shot-by-shot. There was a fast decay component which decreased with shots and eventually disappeared when a full metallic state was established at high fluences. Comparing with earlier transient reflectivity studies on the insulator to metal transition in other manganites, we believe the fast decay within first picosecond represents the recovery dynamics of the insulating phase from the photoinduced metallic phase. Based on that, we conclude parts of the photoinduced metallic phase stay persistently while other parts return back to the insulating phase in less than a picosecond. We also estimated the ratio of insulating and metallic phase in the thin film shot-by-shot.

3:30 PM CM04.05.06

Effect of Epitaxial Stresses on the Time Dynamics of Photoexcited Charge Carriers in InGaAs Based Superlattices Arsenii M. Buriakov¹, Dinar Khusyainov¹, Elena D. Mishina¹, Dmitry Ponomarev², Alexander Yachmenov², Sergey Pushkarev² and Rustam Khabibullin²; ¹MIREA - Russian Technological University, Moscow, Russian Federation; ²Institute of Ultrahigh-Frequency Semiconductor Electronics, Moscow, Russian Federation.

Epitaxial InGaAs films are promising material for creating photoconductive antennas for the generation and detection of THz radiation. The main disadvantage of such films is the low resistivity. This leads to a high dark current. To increase the resistivity, different approaches are used: ion implantation, epitaxial growth in low-temperature mode with doping with beryllium atoms, introduction of strained ErAs layers, etc. Another problem of InGaAs is the relatively long lifetime τ of the photoexcited charge carriers.

In this work the method of the carrier lifetime decrease was shown via creating of the epitaxial stress in InGaAs films. 3 types of superlattices were grown by molecular beam epitaxy: $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ (SL1), $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InAs}$ (SL2), $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{In}_{0.38}\text{Al}_{0.61}\text{As}$ (SL3). Structure of the superlattices is a 30 period of the photoconductive layer (InGaAs) and insulator layer (InAlAs and InAs) with overall thickness ~ 500 nm. This layered system was selected to create epitaxial stresses in photoconductive layer.

XRD asymmetric scanning method $\omega-2\theta$ was used to characterize epitaxial deformations. There were no stresses in SL1 sample. In SL2 samples epitaxial

deformation value was $\epsilon = -0.0019$, which correspond to compression deformation in InGaAs layer. In SL3 epitaxial deformation value in InGaAs layer was $\epsilon = -0.0053$.

Optical pump-probe reflectivity measurements were used for carrier dynamics investigation. Carrier dynamics was performed in wide power range. Carrier lifetime decrease on picosecond time scale was shown with decrease of the pump fluence. In addition, contribution of the nonlinear processes as two photon absorption and free carrier absorption to carrier dynamics was demonstrated. In SL3 sample with higher epitaxial stresses, decrease of the contribution of the TPA and FCA (characterized by ω parameter on time scale) on carrier dynamics was observed. For SL3 parameter $\omega = 0.15$ ps was minimal, which is contribute to laser pulse duration and carrier lifetime was 2.73 ps. That result shows, that increasing epitaxial stresses decreasing influence of nonlinear processes on carrier dynamics in InGaAs photoconductive layer and decreasing carrier lifetime.

The work was supported by Ministry of Education and Science of Russian Federation (State task no. 3.7331.2017/9.10 and grant no. 14.Z50.31.0034).

3:45 PM CM04.05.07

Microcavity Enhancement of Low-Frequency Raman Scattering from CsPbI₃ at Room Temperature Tal Ben Uliel, Laxman Gouda and Yaakov Tischler; Bar Ilan, Ramat Gan, Israel.

Raman spectroscopy is a powerful laser based nonlinear optical technique for identifying chemicals and characterizing materials that has been adapted for both CW and ultra-fast pulsed excitations. Raman spectra can provide insight into numerous properties, including morphology, stress/strain, crystallinity, doping level, conductivity, local temperature, and polarizability, whether in bulk, thin film, monolayer or nanostructure form. Modern laser filters, based on volume holographic gratings amongst other approaches, now make it relatively straightforward to obtain CW Raman spectra much closer spectrally to the incident laser, in particular in the spectral range of 100 cm^{-1} down to 5 cm^{-1} away from the laser's wavelength. This Low-Frequency spectral range is also accessible with ultra-fast lasers using Impulsive Stimulated Raman Scattering (ISRS). Low Frequency Raman (LFR) scattering is sensitive to the phonon dispersion relation and to the vibrational modes associated with the nanostructural dimensions of the material, with broad applications to chiral purity of organics, biomolecular assemblies, hybrid organo-metal halide perovskites, and semiconductor super-lattices. However, the signal strength from LFR is typically very weak. Here we show that introducing a film of material into a photonic crystal structure, in this case a 1D optical microcavity consisting of two distributed Bragg reflector (DBR) mirrors, greatly enhances the LFR signal. This is the first demonstration of Cavity Enhanced LFR (CE-LFR). In particular, we situated thin films of CsPbI₃, which in some forms are Halide Perovskites, into a microcavity prepared from stacks of ZnS and CaF₂ alternating layers. The resultant microcavities had a Quality Factor $Q = 23$. A TiO₂ layer with a gradient in thickness was also located between the DBRs to enable tuning of the cavity resonance from a wavelength of 490 nm to 545 nm. We investigated the effect of cavity tuning on the LFR intensity. We observed that the width of the cavity peak is sufficiently broad to resonate both the incident laser and the scattered LFR peak from the CsPbI₃ film. This double resonance greatly increased the light-matter interaction and hence the LFR signal. We have achieved a 47-fold increase in the LFR intensity. Our findings suggest CE-LFR is a promising route for sensitive characterization of nanoscale structured materials. We show the CE-LFR is applicable for both CW Raman and pulsed ultra-fast ISRS spectroscopy modalities.

4:00 PM CM04.05.08

Ultrafast Direct Electron Transfer at Organic Semiconductor and Metal Interfaces Yingmin Li¹, Bo Xiang¹, C. Huy Pham², Francesco Paesani^{2,1} and Wei Xiong^{2,1}; ¹Materials Science and Engineering, University of California, San Diego, La Jolla, California, United States; ²Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, United States.

The ability to control direct electron transfer can facilitate the development of new molecular electronics, light-harvesting materials and photocatalysis. However, it has been rarely reported and the molecular conformation-electron dynamics relationships remain unclear. Here, we describe direct electron-transfer at buried interfaces between an organic polymer semiconductor film and a gold substrate, by observing the first dynamical electric-field-induced vibrational sum frequency generation (VSFG). In transient electric-field-induced VSFG measurements on this system, we observe dynamical responses (<150 fs) that depend on photon-energy and polarization, evidencing that electrons are directly transferred from Fermi level of gold to LUMO of organic semiconductor. Transient spectra further reveal that, although the interfaces are prepared without deliberate alignment control, a sub-ensemble of surface molecules can adopt conformations for direct electron transfer. DFT calculations support the experimental results and ascribe the observed electron transfer to a flat-lying polymer configuration in which electronic orbitals are found to be delocalized across the interface. The present observation of direct electron transfer at complex interfaces as well as the insights gained into the relationship between molecular conformations and electron dynamics will have implications for implementing novel direct electron transfer in energy materials.

SESSION CM04.06: Ultrafast Probes in Chemistry
Session Chairs: Ajay Srimath Kandada and Carlos Silva
Wednesday Morning, November 28, 2018
Hynes, Level 2, Room 201

8:30 AM *CM04.06.01

Influence of Vibrational Coherence on the Excited State Dynamics—Ultrafast Raman Loss Spectroscopy Siva Umamathy; Indian Institute of Science, Bangalore, India.

Understanding the influence of vibrational coherence on chemical reactions has always been very challenging. The coherence decay is influenced by structural reorganization and collisions with solvent or inter molecular interactions. So, reactions in solution phase differ remarkably from gas phase in terms of rates. To understand the impact of coherence in a chemical reaction, we performed ultrafast Raman loss spectroscopic investigation during photoisomerization of *trans*-stilbene in solution. It has been observed that vibrational coherence influences the reaction rate by coupling the reaction coordinate with optically excited Franck-Condon state of *trans*-stilbene. This presentation demonstrates that the coupling becomes stronger in fast solvent like acetonitrile which helps in efficient energy flow to reaction coordinate and hence results in increased reaction rate. On the other hand, the effect diminishes for relatively slower long chain solvents like butyronitrile and nonane.

Femtosecond transient absorption (fs-TA) and Ultrafast Raman Loss Spectroscopy (URLS) have also been applied to reveal the excited state dynamics of bis(phenylethynyl)benzene (BPEB), a model system for one-dimensional molecular wires that have numerous applications in opto-electronics. It is known from the literature that in the ground state BPEB has a low torsional barrier, resulting in a mixed population of rotamers in solution at room temperature. For the excited state this torsional barrier had been calculated to be much higher. Our femtosecond TA measurements show a multi-exponential behaviour, related to the complex structural dynamics in the excited electronic state. Time-resolved, excited state URLS studies in different solvents reveal mode-dependent kinetics and picosecond vibrational relaxation dynamics of high frequency vibrations. After excitation, a gradual increase in intensity is

observed for all Raman bands, which reflects the structural reorganization of Franck-Condon excited, non-planar rotamers to a planar conformation. The time dependent peak positions of high frequency vibrations provide additional information: a rapid, sub-picosecond decrease in peak frequency, followed by a slower increase (as shown in figure 2), indicates the extent of conjugation during different phases of excited state relaxation. This study expands our understanding of the excited state of BPEB and analogous linear pi-conjugated systems, and may thus contribute to the advancement of polymeric "molecular wires".

We thank the Council of Scientific and Industrial Research (CSIR), the Department of Science and Technology (DST) and the Defence Research and Development Organization for financial assistance. We also acknowledge the DST for a J.C. Bose fellowship.

9:00 AM CM04.06.02

Investigation of GHz Mechanical and Thermal Behavior of Confined Liquids with Molecular Resolution [Ievgeniia Chaban](#)^{1,2}, Christoph Klieber¹, Remi Busselez¹, Lionel Guilmeau¹, Mathieu Edely¹, Vitaliy Gusev² and Thomas Pezeril¹; ¹Le Mans Université, IMMM - UMR CNRS 6283, Le Mans, France; ²Le Mans Université, LAUM - UMR CNRS 6613, Le Mans, France.

The phenomenon of liquid structuring near interfaces is related to the liquid/interface interaction forces at distances of some molecular dimensions [1, 2]. Despite the fact that this universal structuring effect plays a key role in various fields such as heat transport, particle transport through biological membranes, nanofluidics, microbiology and nanorheology, the experimental investigation of liquid structuring remains challenging. In this context, we have adapted the experimental technique of ultrafast time-domain Brillouin scattering (TDBS) [3,4] to investigate high-frequency longitudinal acoustic and thermal properties of ultrathin liquids confined between solid surfaces of different types. We will present results of TDBS used to determine the mechanical properties of ultrathin liquids with a subnanometric resolution of the liquid thickness gap. Fourier analysis of the recorded TDBS signals for different liquid thicknesses yield the value of the longitudinal speed of sound and attenuation at GHz frequencies. The TDBS thermal background recorded at different liquid thicknesses gives insight on the evolution of the thermal properties of the sandwiched liquid structure following a variation of the liquid thickness gap. We will present several results obtained with different types of liquids (glycerol, 8CB liquid crystal, ionic liquids) highlighting in some cases liquid structuring at long distances > 10 nm at the vicinity of the solid interface, as well as thermal frustration linked to the confinement of the thermal phonons in a liquid gap dimensions matching the thermal phonons mean free path.

This pioneering TDBS experimental scheme is a first step towards the mechanical and thermal understanding of confined liquids measured through GHz ultrasonic probing.

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9:15 AM CM04.06.03

Developing Time-Resolved Electronic Sum Frequency Generation to Probe Energy Transfer in Organic Thin Films [Aaron P. Moon](#), Daniel E. Cotton, Jon A. Bender and Sean T. Roberts; University of Texas at Austin, Austin, Texas, United States.

Organic semiconductors (OSCs) represent a broad class of materials for the development of both novel electronics made exclusively from organic materials as well as the augmentation of existing inorganic semiconductors (ISCs). However, incorporation of OSCs into devices on the market has been slow, in part due to a lack of understanding of fundamental processes whose function critically depend on the structure of interfacial junctions between layers in a device. To study these structure-function relationships a technique is needed with the ability to in situ monitor charge and energy transfer between the active layers of a functional device. To this end, we have developed electronic sum frequency generation (ESFG) for study of charge transfer both within purely OSC devices as well as from thin OSC films to ISCs. ESFG is uniquely suited for the study of the inaccessible junctions in such devices given its interfacial selectivity in media containing a center of inversion. ESFG also has the advantage of being a purely optical technique, giving it the ability to study these transfer properties in functioning devices under ambient conditions. By developing heterodyne-detected ESFG (HD-ESFG) for the study of thin films, our group has been able to both resolve the phase of the measured $\chi^{(2)}$ spectrum and greatly increase our detection efficiency. HD-ESFG allows us to add an additional pump beam before our HD-ESFG probe, realizing time resolved ESFG (TR-ESFG) in order to track dynamics of energy and charge transfer at buried interfaces in working devices. Our work demonstrates that TR-ESFG is a strong candidate in the growing list of techniques being developed to answer questions of charge and energy dynamics in OSC-ISC devices.

9:30 AM *CM04.06.04

Ultrafast Electron Solvation Dynamics at the Origin of an Electrochemical Reaction Chain [Julia Stähler](#); Fritz Haber Institute of the Max Planck Society, Berlin, Germany.

The formation dynamics of localized electronic states in molecular films near metal electrodes, including their propensity to act as precursor states for chemical reactions, is for example crucial for a detailed understanding of charge transport and degradation effects in batteries. We investigate the formation dynamics of small polarons and their role as intermediate electronic states in thin films of dimethyl sulfoxide (DMSO) on Cu(111) using time- and angle-resolved two-photon photoemission spectroscopy. Upon photoexcitation, a delocalized DMSO electronic state two monolayers from the Cu surface is initially populated, followed by a dynamic increase in binding energy and electronic state localization. This formation of a small polaron occurs on a 200 fs timescale, consistent with localization due to vibrational dynamics of the DMSO film. This localized state is a precursor state for an extremely long-lived surface-bound electronic state with a lifetime of several seconds and, thus, thirteen orders of magnitude longer than the small polaron. Moreover, experiments in oxygen atmosphere show that these trapped, long-lived electrons react with O₂ at the DMSO surface, likely forming O₂⁻. Our findings highlight the importance of interfacial electronic states near metal surfaces for electrochemical reactions despite their femtosecond lifetimes, as they are crucial precursors for long-lived, reactive states of solvents and electrolytes.

10:00 AM BREAK

Wednesday Morning, November 28, 2018
Hynes, Level 2, Room 201

10:30 AM *CM04.07.01

Nonlinear Terahertz and Optical Spectroscopy of Advanced Materials—Fundamentals and Applications [Keith A. Nelson](#); Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

New developments in nonlinear terahertz spectroscopy have revealed important new insights into quantum material behavior and have opened up new possibilities for practical applications including advanced material characterization and control. Terahertz field interactions with electronic, lattice, and spin degrees of freedom have all been exploited in recent measurements. Terahertz-induced responses including quantum material phase transitions, colossal Stark shifts, and magnetization control will be illustrated. Terahertz-frequency electron paramagnetic resonance (EPR) including two-dimensional terahertz magnetic resonance will be discussed.

Time-resolved transient grating measurements of acoustic and thermal responses, in which crossed optical pulses generate an interference pattern at the sample whose spatial period determines the acoustic wavelength or the thermal transport length scale, have been conducted for some time, with applications already developed including noncontact metrology of thin films in microelectronics. Recently the measurements have revealed nondiffusive thermal transport kinetics, which provides fundamental insight into the phonons that carry thermal energy and which is a key consideration in nanoscale device applications. Experiments with extreme UV pulses from a soft x-ray free-electron laser have enabled the thermal transport length scale to be reduced to tens of nanometers, revealing essentially purely ballistic kinetics. New modes of thermal transport may become possible in some materials.

11:00 AM CM04.07.02

Ultrafast Anharmonic Phonon Scattering in PbTe Probed via Terahertz Emission Spectroscopy [Burak Guzelturk](#)^{1,2}, [Mariano Trigo](#)², [David A. Reis](#)^{1,2} and [Aaron Lindenberg](#)^{1,2}; ¹Stanford University, Stanford, California, United States; ²SLAC National Accelerator Laboratory, Menlo Park, California, United States.

We report on the first direct and real-time measurement of ultrafast anharmonic phonon scattering in PbTe. Among IV-VI semiconductors, PbTe is an important system for infrared (IR) optoelectronics and thermoelectrics. For the latter, low lattice thermal conductivity has been identified as a key for efficient thermoelectric functionality, yet its origin has not been fully understood to date. Theoretical works supported by inelastic neutron scattering measurements pointed to the crucial role played by strong anharmonic phonon scattering between optical and acoustic phonons [1]. Also, ultrafast anharmonic scattering rates were estimated for PbTe underpinning its intrinsic impeded acoustic phonon transport [2]. However, no experimental study to date was able to time-resolve anharmonic phonon dynamics in PbTe.

Here, we observe far-IR electromagnetic radiation within the terahertz (THz) window emitted by PbTe upon ultrafast photo-excitation. This radiation emerges due to buildup of an ultrafast photocurrent close to the surface of the material and leads to the coherent excitation of IR-active optical phonons within the system. In this way, coherent detection of the radiated fields on femtosecond time-scale enables a mode-selective probe of phonon dynamics [3]. We observe that within the first ps following photo-excitation, the bare TO phonon mode (at 0.93 THz) splits into two; a higher energy mode around 1.4 THz and a lower energy mode between 0.4 – 0.8 THz. These new modes develop due to strong anharmonic coupling between TO and longitudinal acoustic (LA) phonons as theoretically predicted before [1, 2]. By monitoring the ultrafast anharmonic phonon scattering processes in real-time, we find the associated scattering rate to be $\sim (1 \text{ ps})^{-1}$ which is in good agreement with the theoretical predictions [2, 4].

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11:15 AM CM04.07.03

Ultrathin THz Waveplate as Characterized by Ultrafast Electron Pulse [Edbert Sie](#), [Clara M. Nyby](#) and [Aaron Lindenberg](#); Stanford University, Stanford, California, United States.

Manipulation of light polarization is indispensable to obtain control over the electronic properties in quantum materials. Here we show that we can change the polarization of light in the THz regime by using an ultrathin, nanometer-thick topological Weyl semimetal. We characterize the change of THz polarization using an ultrafast electron beam streaking that traverses a circular motion with respect to the THz beam. This finding offers a new promising way to enhance control over optoelectronic devices in nanometer scale.

11:30 AM *CM04.07.04

Transient Terahertz Spectroscopy—Femtosecond Dynamics of Low Energy Quasiparticle Excitations [David Cooke](#); McGill University, Montreal, Quebec, Canada.

Terahertz pulses are coherently detected electromagnetic transients with a bandwidth spanning the 1 - 100 meV energy gap. These single cycle, phase stable pulses are powerful tools to examine low energy quasiparticle excitations in materials. Being perfectly synchronized to a fs laser pulse train, they can be used in an optical pump-THz probe geometry to time-resolve the kinetics of these excitations after optical injection or perturbation. The resulting time-energy maps can be used to determine fs dynamics of free charges, phonons, excitons, collective excitations and energy gaps resulting from many-body correlations. In this talk I will review the techniques for transient terahertz spectroscopy, specifically two-color laser plasma based sources capable of continuous coverage of the entire THz band in a single cycle pulse. I will discuss the application of transient terahertz spectroscopy to study a variety of condensed matter systems including semiconductor nanoparticles, organometallic halide perovskites and correlated electron systems. In addition, new methods of generating high field THz pulses have opened the possibility of coherently driving these quasiparticle excitations resonantly. I will discuss the current methods for generation of high field THz pulses, and some applications for controlling electron dynamics. Finally, the prospect of using shaped terahertz fields for quantum control experiments will be discussed, employing a novel pulse shaper demonstrated recently in our group. Proof of principle experiments will be discussed.

1:30 PM *CM04.08.01

Imaging Ultrafast Dynamics on the Nanoscale with Terahertz Scanning Tunneling Microscopy [Frank A. Hegmann](#); University of Alberta, Edmonton, Alberta, Canada.

The ability to directly probe ultrafast phenomena on the nanoscale is essential to our understanding of excitation dynamics on surfaces and in nanomaterials. Recently, a new ultrafast scanning tunneling microscope (STM) technique that couples terahertz (THz) pulses to the scanning probe tip of an STM was demonstrated (THz-STM), showing photoexcitation dynamics of a single InAs nanodot with simultaneous 0.5 ps time resolution and 2 nm spatial resolution under ambient conditions [1]. Operation of THz-STM in ultrahigh vacuum now makes it possible to spatially-resolve subpicosecond dynamics of single molecules [2] and silicon surfaces [3] with atomic precision. Coherent control of THz-pulse-induced tunnel currents in THz-STM has also been demonstrated [3,4]. Even though THz-STM can be performed with THz-induced tunnel currents corresponding to less than 1 electron per THz pulse on average [2], extreme transient tunnel current densities of 10^{11} A/cm² through single silicon atoms on a Si(111)-(7x7) surface have been observed, corresponding to about 500 rectified electrons tunneling in 0.5 ps across the junction [3]. This was attributed to nonequilibrium tunneling dynamics and penetration of the THz field through the metallic-like Si(111)-(7x7) surface. However, more detailed models may be required to better understand the sub-picosecond tunneling dynamics induced in materials by THz-STM. This talk will discuss how THz-STM works and how it can provide new insight into ultrafast dynamics on the atomic scale, which is essential for the development of novel silicon nanoelectronics and molecular-scale devices operating at terahertz frequencies.

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2:00 PM CM04.08.02

Time-Resolved (Far-) Infrared Spectroscopy at the Nanoscale Stefan Mastel, Tobias Gokus, Max Eisele and [Andreas Huber](#); Neaspec GmbH, Martinsried, Germany.

Time-resolved optical spectroscopy from the mid- to far-infrared spectral range (0.1 – 100 THz) is a powerful tool to study the dynamics of low-energy elementary excitations in solid state systems, e.g. phonons, plasmons, and excitons on ultrafast timescales. With the development of time-resolved terahertz spectroscopy, ultrafast spectroscopy in the infrared has even reached the ultimate sub-cycle temporal limit [1,2]. In contrast to the achievements regarding the temporal resolution, the spatial resolution of far-field terahertz studies is limited by diffraction to the length scale of the probing wavelength (3 μm – 3 mm), making it impossible to access the intrinsic local response of single nanoparticles, nanodomains, or nanocrystals. To circumvent this fundamental limit, time-resolved infrared and THz spectroscopy has recently been combined with scattering-type Scanning Near-field Optical Microscopy (s-SNOM).

s-SNOM bypasses the diffraction limit, enabling optical measurements with extreme subwavelength spatial resolution down to 20 nm. s-SNOM employs the local field enhancement (hotspot) at the apex of an externally-illuminated sharp metallic atomic force microscopy (AFM) tip. In close proximity to a sample surface, the optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample. Detection of the elastically tip-scattered light yields nanoscale resolved near-field images and spectra simultaneous to topography. By combining s-SNOM and time-resolved IR spectroscopy, for the first time, this approach enables a detailed analysis of charge-carrier dynamics in single layer materials [3,4], semiconductors [5], single nanoparticles [6], and even strongly-correlated materials [7] with femtosecond temporal and nanometer spatial resolution.

This talk will present the recent highlights in the field of ultrafast infrared spectroscopy and time-resolved terahertz time-domain spectroscopy (THz-TDS) in combination with the resolving power of s-SNOM. In addition, we introduce our first commercially available and ready-to-use THz-TDS near-field spectroscopy system and show measurements on various test samples, such as graphene, h-BN and functional SRAM device. We achieve a spatial resolution of < 15 nm at a probe center-wavelength of 300 μm , surpassing the spatial resolution of conventional far-field terahertz spectroscopy by a factor > 20000.

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- [2] R. Huber *et al.*, Nature **414**, 286 (2001).
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- [6] M. Eisele *et al.*, Nature Photonics **8**, 841 (2014)
- [7] M. A. Huber *et al.*, Nano Letters **16**, 1421 (2016)

2:15 PM CM04.08.03

Ultrafast Imaging of Charge Carrier Dynamics on Semiconductor Surfaces [Ebrahim Najafi](#)^{1,2}; ¹California Institute of Technology, Pasadena, California, United States; ²Chemours Co, Wilmington, Delaware, United States.

The spatiotemporal dynamics of nonequilibrium carriers reveal the excitation and relaxation pathways in materials. Here we report the ultrafast imaging of photoexcited carriers generated on the silicon surface by a femtosecond laser pulse. We use the scanning ultrafast electron microscopy (SUEM) technique to investigate the evolution of these carriers in space and time as the semiconductor proceeds to the ground state. We find that carrier transport after optical excitation follows the super-diffusion model with the diffusion coefficient that linearly increases with the laser fluence. However, this trend reverses at high excitation fluences. We attribute this anomaly to the generation of a large electric field by the spatial separation of photoexcited carriers, which strongly opposes carrier super-diffusion. This is evident in the second moment of the carrier distribution, obtained from the SUEM images, which reveals expansions and contractions in the carrier density. The numerical simulation of the drift-diffusion equation supports this interpretation. Our finding shines a new light on the dynamics of hot carriers in highly perturbed semiconductors by directly imaging their progression toward the ground state.

2:30 PM BREAK

3:30 PM *CM04.08.04

Spatial and Temporal Imaging of Multi-Scale Interfacial Charge Transport in Two-Dimensional Heterostructures Libai Huang; Purdue University, West Lafayette, Indiana, United States.

Charge-transfer (CT) excitons at hetero-interfaces play a critical role in light to electricity conversion using organic and nanostructured materials. However, how CT excitons migrate at these interfaces is poorly understood. Atomically thin and two-dimensional (2D) nanostructures provide a new platform to create architectures with sharp interfaces for directing interfacial charge transport. Here we investigate the formation and transport of CT excitons in van der Waals (vdW) heterostructures based on semiconducting transition metal dichalcogenides (TMDCs) employing transient absorption microscopy (TAM) with a temporal resolution of 200 fs and spatial precision of 50 nm.

We have recently imaged the transport of interlayer CT excitons in 2D organic-inorganic vdW heterostructures constructed from WS₂ layers and tetracene thin films. To investigate driving force for exciton dissociation, we perform measurements on heterostructures constructed with different WS₂ thickness ranging from 1 layer to 7 layers. Photoluminescence (PL) measurements confirm the formation of interlayer excitons with a binding energy of ~ 0.3 eV. Electron and hole transfer processes at the interface between monolayer WS₂ and tetracene thin film are very rapid, with time constant of ~ 2 ps and ~ 3 ps, respectively. TAM measurements of exciton transport at these 2D interfaces reveal coexistence of delocalized and localized CT excitons, with diffusion constant of ~ 1 cm²s⁻¹ and ~ 0.04 cm²s⁻¹, respectively. The high mobility of the delocalized CT excitons could be the key factor to overcome large CT exciton binding energy in achieving efficient charge separation.

We have also studied the interlayer charge transfer and recombination in WS₂-graphene and WS₂-WSe₂ heterostructures. We have demonstrated broadband photocarrier generation directly from interlayer CT states in WS₂-graphene heterostructures. Lifetime of the CT excitons has been found to be strongly dependent on interlayer stacking in epitaxial grown AA and AB stacking WS₂-WSe₂ heterostructures.

4:00 PM CM04.08.05

Spatially Localized Electronic Excitation and Carrier Kinetics in Chalcogenide Photovoltaic Materials Using Modern Pump-Probe Microscopy and Spectroscopy Techniques Elham Ghadiri^{1, 2}, Donghyeop Shin³, Ashkan Shafiee⁴, Warren Warren² and David Mitzel^{2, 3}; ¹Chemistry, Wake Forest University, Winston-Salem, North Carolina, United States; ²Chemistry, Duke University, Durham, North Carolina, United States; ³Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States; ⁴Wake forest school of medicine, Winston Salem, North Carolina, United States.

In this paper, we integrate a combination of modern and complementary ultrafast diffuse reflectance based spectroscopy and microscopy techniques to discuss the ultrafast photophysics of efficient photovoltaic materials including Cu₂BaSnS_{4-x}Se_x (CBTSSe) chalcogenides¹ for the first time. CBTSSe is a recently introduced alternative to Cu(In,Ga)(S,Se)₂ and Cu₂ZnSnS_{4-x}Se_x (CZTSSe). Ultrafast diffuse reflectance measurements enable direct examination of charge carrier processes in opaque device-relevant structures², highly light absorbing/scattering materials³ or thin films deposited on metal substrates all of which cannot be studied using conventional transmission based pump-probe spectroscopy schemes. Based on broadband diffuse reflectance transient absorption spectroscopy the fingerprints of photocarrier absorption, GSB bleaching and electronic states in the vis-near IR region are investigated. Moreover, pump-probe microscopic imaging in the diffuse reflectance mode enables to localize the photoexcitation patterns and early charge carrier kinetics within the grains of only a few hundreds of nanometers and localize the kinetics of photogenerated carriers in each grain.

The CBTSSe films deposited on Mo-coated glass substrates, are studied similar to the configuration found in functional devices. We spectrally resolve a sharp ground-state bleaching (GSB) peak for CBTSSe films, formed around the band edge transition. The combination of narrow GSB peak width measured, coupled with the sharp steady state UV-Vis diffuse reflectance band edge, PL emission at the band edge and intensity independent PL shape, all point to a reduction in shallow defects and band tailing in CBTSSe relative to CZTSSe films. Furthermore, we have shown that the unique sensitivity of pump-probe microscopy and sharp electronic transitions allow for detection of small S/Se stoichiometry variations, $\Delta x \leq 0.3$, in Cu₂BaSnS_{4-x}Se_x grains—i.e., features that are largely unresolved for ensemble spectroscopy or luminescence measurements. By noting the sharp band edge transition, we show that the band tailing issue (prevalent for CZTSSe) is largely resolved for CBTSSe. The charge carrier relaxation resolved in CBTSSe single grains, or over an ensemble of grains, however, remains faster compared to CZTSSe, pointing to the need to perhaps better understand deep traps within this absorber family. Such deep defects and fast carriers relaxations, would still impact the photocurrent and open circuit voltage of the CBTSSe devices/films examined.

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4:15 PM CM04.08.06

Ab Initio Predictions of Spatially-Resolved Nonequilibrium Coherent Transport Phenomena George Varnavides^{2, 1}, Adam S. Jermyn³, Polina Anikeeva^{2, 4} and Prineha Narang¹; ¹John A. Paulson School of Engineering and Applied Sciences, Harvard, Cambridge, Massachusetts, United States; ²Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ³Institute of Astronomy, University of Cambridge, Cambridge, United Kingdom; ⁴Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Recent advances in experimental techniques that probe ultrafast dynamics and coherent effects at quantum material interfaces pose a theoretical challenge in predicting such dynamics ab initio with high spatial and temporal resolution simultaneously. Typically, computational predictions of transport phenomena employ either i) stochastic approaches, tracking particle dynamics, or ii) probabilistic approaches, describing the evolution of particle distribution functions. The Boltzmann Transport Equation (BTE), is of the latter kind, and provides the most general description of semi-classical transport. The BTE is a non-linear integro-differential equation in six dimensions which is typically solved either in the time and space-independent form, or using a number of limiting assumptions such as the single-mode relaxation time approximation.

Here, we present a general theoretical and computational framework for carrier transport, which solves the full BTE using all its phase space degrees of freedom (i.e. with both real and reciprocal space resolution). Further, our method allows us to resolve contributions to the carrier distribution as a function of individual scattering events – which is often what ultrafast experimental techniques probe. We extend our framework to capture the dynamics of Peierls' phonon BTE, making it possible to compare our results with picosecond acoustic measurements as well as the more recent coherent phonon spectroscopy techniques. Finally, analyzing the resulting surface fluxes of generated carriers we can draw direct comparisons with techniques probing Surface Acoustic Waves in the GHz range.

4:30 PM CM04.08.07

Deep Analysis of Crystalline Silicon Surface Properties from Gigahertz to Terahertz Microscopy Jonathon Mitchell; Koriyama, Japan.

In monocrystalline silicon, the band-gap and non-linear dispersion of electron and holes are dependent upon material doping, passivation and metallisation materials, which lead to non-trivial features often expressed by high or low carrier mobility and in the band-bending conditions. These can directly influence the overall performance and reproducibility of a photovoltaic devices. In this work, we have studied the ultra-fast properties of photocharges by measurements using pico-second spectroscopy of near-field emissions. Within the GHz domain, free carriers within a semiconductors, like silicon, respond to the incident electric field. Using a microwave interferometer, the free carrier absorption effects were analysed. In the THz domain, the carrier density was determined picoseconds after photoexcitation by Laser Terahertz Emission Microscopy (LTEM), excluding the effects of Auger/Shockley-Read-Hall recombination and carrier injection which are too slow to respond to the laser pulse duration. Emission within the GHz range are shown to be the collective response of high frequency localised states in high electric field; whereas, THz emission results primarily from surface electric field-induced optical rectification with small bulk contributions from two-dimensional monolayering at highly crystalline surfaces. The dielectric response of charge carriers was observed to be strong and dispersive in the THz region, allowing for the influence of various surface features, chemical processing and passivation techniques to be studied for the first time in detail before other longer-term processes become dominant. Within the conjunction of these regimes, detailed photocharge information including the effective binding of photocharge states, phase coordination (including linear and non-linear differences) are determined providing conditions for the saturation of ultrafast processes. Asymmetric phase was apparent for a-Si:H and a-SiC:H dielectric layers, however, not observed in the presence of SiN or SiO layers. Furthermore, material fabrication by microwave plasma exhibited non-sympathetic dampened surfaces, whereas radio-frequency plasma materials were unconstrained offering insight into conditions for reducing network stress and improving favourable conditions for impinging hydrogen.

This work has sort to establish a link between the quasi-steady-state rate equations for Fermi density and the measured THz waveforms on photovoltaic devices. New time-based parameter linkages can now be established for the THz emission analysis, including for intraband scattering and dephasing through cross-analysis of the THz to GHz microscopy emitted spectrums.

4:45 PM CM04.08.08

Tracking Ultrafast Hot Electron Diffusion in Space and Time by Transient Absorption Microscopy [Alexander Block](#)¹, Matz Liebel¹, Renwen Yu¹, Javier Garcia de Abajo¹, Yonatan Sivan² and Niek F. van Hulst¹; ¹ICFO—The Institute of Photonic Sciences, Castelldefels, Spain; ²Ben-Gurion University of the Negev, Beersheba, Israel.

Non-equilibrium dynamics govern the ultrafast response of optically excited materials in both space and time. Transient absorption microscopy, combining femtosecond with nanometer resolution, has recently emerged as a powerful technique to study exciton diffusion in semiconductors, perovskites and 2D materials. While these studies predominantly probed linear diffusion dynamics, non-equilibrium distributions, such as hot electrons in metals or 2D materials, are expected to result in more complex space-time diffusion behavior.

Here, we combine super-resolved imaging with pump-probe techniques to directly visualize non-thermalized carrier diffusion. We track the spatio-temporal hot electron diffusion in a thin gold film, as the carriers move out of the diffraction-limited volume. We observe an initial fast spatial diffusion within the first few picoseconds, followed by an abrupt transition to an orders of magnitude slower diffusion. Theoretical analysis with a two-temperature model identifies two distinct diffusion regimes. Initially, hot electrons dominate the diffusion process, followed by phonon-limited diffusion due to electron-phonon coupling. We compare our spatio-temporal results in gold to silicon and graphene, showing distinct hot carrier dynamics, to test the predictions of non-equilibrium theories.

Finally, we extend our transient microscopy to 2D-material devices. Transient refection and even transient photocurrent space-time dynamics give direct insight into the important role of hot electrons for novel applications such as graphene photodetectors and heat management in nanoscale devices.

SESSION CM04.09: Organic Semiconductors

Session Chair: Cathy Wong

Thursday Morning, November 29, 2018

Hynes, Level 2, Room 201

8:30 AM *CM04.09.01

Mapping Atomic Motions with Ultrabright Electrons—Fundamental Space-Time Limits to Imaging Chemistry [Dwayne Miller](#)^{1,2}; ¹The Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany; ²Departments of Chemistry and Physics, The University of Toronto, Toronto, Ontario, Canada.

Watching atomic motions on the primary timescales of chemistry has been a long held objective. It would enable the direct observation of barrier crossing processes related to transition state concepts that link chemistry to biology. There are not only extraordinary requirements for simultaneous spatial-temporal resolution but equally important, due to sample limitations, also one on source brightness. Taking the problem to be an imaging problem, as one makes the shutter speed shorter and shorter, a brighter and brighter source is needed to maintain image contrast. With the development of ultrabright electron and x-ray sources capable of literally lighting up atomic motions, this experiment has been realized and refined to provide a general tool for probing structural dynamics on par with conventional pump-probe spectroscopy. The first studies focused on relatively simple systems. Further advances in source brightness have opened up even complex organic systems and solution phase reaction dynamics to atomic inspection. A number of different chemical reactions will be discussed from electrocyclozation with conserved stereochemistry (Jean-Ruel et al JCP B 2013), intermolecular electron transfer for organic systems (Gao et al Nature 2013; Liu et al Chem Phys Lett 2017), metal to metal electron transfer (Ishikawa et al, Science 2015), to the recent observation of coherently directed bond formation using the classic I₃⁻ system, in a process analogous to a quantum Newton's cradle (Xian et al Nature Chem 2017). New insight into the nuclear motions involved in spin transitions will be similarly related to coupling between electronic surfaces. These studies have discovered that these nominally 100+ dimensional problems, representing the number of nuclear degrees of freedom in the system, distilled down to atomic projections along just a few principle reaction coordinates. Each class of chemistry has different associated time scales, but generally lie between few 10's of femtoseconds to 100 fs time scales. The most dramatic example will be shown for the simplest form of chemistry, electron transfer, which is the heart of redox chemistry. No bonds are made or broken. The reaction coordinate is dictated by medium repolarization that stabilize the charge transfer state. This motion was captured with sub-Å (.01 Å) and 100 fs timescale resolution (Ishakawa, Hayes et al Science 2015) – the fundamental space-time resolution to following the primary processes of chemistry. Without any detailed analysis, the few key large-amplitude modes (basis of 6) can be identified by eye from the molecular movie. This reduction in dimensionality appears to be general, arising from the very strong anharmonicity of the many body potential in the barrier crossing region. We are now beginning to see the underlying physics for the generalized reaction mechanisms that have been empirically discovered over time and the prospect for a new conceptual basis for chemistry.

9:00 AM CM04.09.02

Binding Energy of Charge-Transfer States in Organic Solar Cells Probed by Temperature-Dependent Pump-Push Photocurrent Spectroscopy [Jiangbin Zhang](#)^{1,2}, Yifan Dong², Andreas Jakowetz¹, Akshay Rao¹, Richard H. Friend¹ and Artem Bakulin²; ¹University of Cambridge, Cambridge, United Kingdom; ²Imperial College London, London, United Kingdom.

Understanding charge generation mechanism in organic solar cells is of great importance to further device optimisation. Currently, the nature and magnitude of the binding energy of charge-transfer states (CTS), an intermediate state which is critical for following charge separation process, are still under debate. Here, we demonstrate a new method for determining the dissociation energy of CTSs for a range of devices with various molecular energy levels and disorder using temperature-dependent pump-push photocurrent spectroscopy. We observe that dissociation of CTSs is a temperature-dependent process, from which we determine the binding energy by measuring a single activation energy over a wide temperature range. We propose a simple qualitative picture to explain the observation, based on the direct split between the bound CTSs and free carriers after charge transfer. The activation energy falls within the range of 90 ± 50 meV. Surprisingly, this binding energy does not greatly depend on the material composition or the driving energy (~ 150 meV variation) for charge separation. Such observations in the studied benchmark polymer:fullerene systems as well as polymer:non-fullerene acceptor systems reveal unexpected similarities in the energetics of CTSs formed in different electronic environments. This makes our results of general importance for understanding the photophysics at the heterojunction interface for further development of organic photovoltaics. To a broad aspect, this technique might be used for ultrafast in-operando studies of efficiency-loss states in a variety of optoelectronic devices.

9:15 AM CM04.09.03

Excitonic Effects in Zinc-Porphyrins Arrays Studied by Sub-25-fs UV Pulses [Luca Moretti](#)^{1,2}, Bryan J. Kudisch², Yuichi Terazono³, Ana Moore³, Thomas A. Moore³, Devens Gust³, Giulio Cerullo¹, Greg Scholes² and Margherita Maiuri^{1,2}; ¹Dipartimento di Fisica, Politecnico di Milano, Milan, Italy; ²Chemistry Department, Princeton University, Princeton, New Jersey, United States; ³Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, United States.

Synthetic porphyrins are largely exploited for artificial light-harvesting and optoelectronics due to their efficient role in energy transfer processes as donor or acceptor molecules [1]. Zinc-porphyrins (1Zn) have been used to synthesize arrays of dimers (2Zn) and hexamers (6Zn) to mimic the interactions of photosynthetic pigments [2]. The Zn-arrays revealed evident changes, as splittings and broadening, in the Soret absorption band (ca 415nm, S₂ state) [2]. In porphyrins, an ultrafast S₂→S₁ internal conversion (IC) process occurs on a picosecond timescale due to the strong S₂-S₁ vibronic coupling [3]. In the porphyrins arrays, relaxation within the excitonic manifold should compete with the IC process on similar time scale, however an ultrafast spectroscopic characterization addressing the early steps of the deactivation processes in these complexes is still lacking. Here, we exploit our home-built pump-probe apparatus, which produces UV tuneable sub-25 fs pulses, to resonantly excite the samples at their Soret bands.

For the 1Zn case, our experiments reveal the following signals: instantaneous excited state absorption band (S₂→S_n); instantaneous ground-state bleaching (GSB) of the S₂ and S₁ states; formation of the stimulated emission (SE) from the S₁ state. We fit our data by a global analysis procedure using a sequential model which provides a 300fs decay constant for the fast S₂-S₁ IC. In the arrays we find a faster temporal decay for the dimer 2Zn (150fs) and for the hexamer 6Zn (70fs), preceding the still present 300fs IC. This faster component takes into account a new competing deactivation pathway related to the presence of excitonic manifolds. The π - π "stacked" configuration responsible for this phenomena is a mixed H and J aggregate [2], influenced by the packing in the arrays.

Moreover, thanks to our temporal resolution we observe coherent vibrational oscillations in our pump-probe measurements. In particular, the 350cm⁻¹ vibration observed in 1Zn, assigned to an out of plane mode of the macrocycle, undergoes subtle spectral shifts for the 2Zn and 6Zn cases, which might reflect the slightly different orientation packings.

We complete our ultrafast characterization by extending our measurements up to the nanosecond timescale [4]. For the 1Zn case, the S₁ state undergoes intersystem crossing to long-living triplet states with high efficiency. In the arrays this relaxation pathway is modified by the presence of possible dark states due to the changes in the conformational configuration. Indeed, we observe that the recovery of the GSB for both 2Zn and 6Zn cases is faster with respect to the 1Zn one, thus reducing the yield of the triplet state formation.

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9:30 AM *CM04.09.04

Coherent Exciton-Vibrational Dynamics and Energy Transfer in Conjugated Chromophores [Sergei Tretiak](#); Theoretical Division and Center for Integrated Nanotechnologies (CINT), Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

The role of coherence signifying concurrent electron-vibrational dynamics in complex natural and man-made systems is currently a subject of intense experimental and theoretical studies. Particularly, gaining control of this phenomenon is important for energy and charge transport when designing functional materials for various technologies, ranging from sensing, imaging, solar energy harvesting, to future optoelectronic devices. Using our Non-adiabatic EXcited-state Molecular Dynamics simulations (NEXMD) framework, we study ultrafast dynamics and exciton transport in several distinct molecular systems. These simulations reveal a **ubiquitous pattern** in the evolution of photoexcitation spanning dynamics of multiple electronic states. Symmetries of the excited state wavefunctions define specific form of the derivative non-adiabatic coupling driving non-adiabatic quantum transitions, which leads to a collective asymmetric vibrational excitation coupled to the electronic system. This promotes subsequent wave-like evolution of the excited state wavefunction preserving specific phase and amplitude relations across the ensemble of trajectories, facilitating efficient energy funneling. Proposed simple model explains appearance of coherent exciton-vibrational dynamics due to non-adiabatic quantum transitions, which is universal across multiple molecular systems studied. Observed relationships between spatial extent/properties of electronic wavefunctions and resulting electronic functionalities allow us to understand and to potentially manipulate excited state dynamics and energy transfer pathways in a number of organic molecular materials.

10:00 AM BREAK

10:30 AM *CM04.09.05

The Impact of Coherent and Non-Coherent Delocalisation of Holes and Electrons on Charge Separation [Anna Kohler](#); University of Bayreuth, Bayreuth, Germany.

The mechanisms by which excitons dissociate highly efficiently in some donor-acceptor systems are still not fully understood. In this talk I aim to highlight differences and similarities that exist between the delocalisation of holes along a conjugated polymer backbone and electrons in a more or less ordered (small molecule) acceptor domain, and their impact on the overall dissociation efficiency.

References:

1 Does electron delocalization influence charge separation at donor-acceptor interfaces in organic photovoltaic cells? F-J Kahle, C Saller, S Olthof, C Li, J

Lebert, S Weiß, E M Herzig, K Meerholz, P Strohrig, A Köhler, submitted

2 Efficient Charge Separation of Cold Charge-Transfer States in Organic Solar Cells Through Incoherent Hopping. S Athanopoulos, S Tscheuschner, H Bässler and A Köhler, *J. Phys. Chem. Lett.* 8 (2017) 2093–2098

11:00 AM CM04.09.06

Impact of HOMO-HOMO Offset on Charge Separation in Small Molecule Nonfullerene Organic Solar Cells [Safakath Karuthedath](#), Julien Gorenflot, RuZe Liang, Pierre M. Beaujuge and Frédéric Laquai; King Abdullah University of Science and Technology, Thuwal, Jeddah, Saudi Arabia.

Non-fullerene organic solar cells (NF-OSCs) now outperform fullerene-based solar cells by their higher power conversion efficiency (PCE) at similar photoactive layer thicknesses.¹ However, to compete with other emerging technologies, energy losses after photon absorption need to be minimized. This raises the question: what is the minimum energy difference required to ensure quantitative exciton dissociation at the DA heterojunction? We address this issue in this communication and present the influence of $\Delta E_H = \text{HOMO}_{\text{Donor}} - \text{HOMO}_{\text{Acceptor}}$ for three different small molecule nonfullerene organic solar cells using DR3TBDTT (DR3) as electron donor blended with different small molecule acceptors, namely IC-C6IDT-IC (ICC6), O-IDTBR, and IEICO, which gradually decrease the energy offset. We find a PCE of 8.7%, 6.4%, and 0.5% for ICC6 (ΔE_H : 0.7 eV), O-IDTBR (ΔE_H : 0.45 eV), and (ΔE_H : 0.25 eV) blends under 1 sun condition, indicating a correlation of performance and energy offset. Sub-picosecond to nanosecond (ps-ns) transient absorption (TA) spectroscopy exposes: DR3:ICC6 exhibits charge generation in 20 ps, whereas in DR3:O-IDTBR charges are generated up to 500 ps. In contrast, in DR3:IEICO blends energy transfer (EnT) outcompetes charge transfer, explaining the poor PCE and indicating, the HOMO energy offset is insufficient for charge transfer and separation. In line with the device efficiency, the yield of long-lived carriers remaining at 7 ns after excitation is 65 %, 44 %, and <10 %, respectively, for ICC6, O-IDTBR, and IEICO blends. Our results shine light on the minimum energy offset required for charge separation in all small molecule nonfullerene organic solar cells.

Reference

1. Wencho, Z.; Deping, Q.; Shaoqing, Z.; Sunsun, L.; Olle, I.; Feng, G.; Jianhui, H. Fullerene – Free Polymer Solar Cells with over 11% Efficiency and Excellent Thermal Stability. *Advanced Materials* 2016, 28 (23), 4734-4739.

11:15 AM CM04.09.07

Ultrafast Spectroscopy of Loss Processes in Nonfullerene Acceptor Bulk Heterojunction Solar Cells [Frédéric Laquai](#); King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

The development of novel nonfullerene acceptors has recently boosted the power conversion efficiency of organic bulk heterojunction solar cells beyond an impressive 14%. However, it remains unclear which NFA structures are best to reduce further energy (voltage) and carrier (current) losses, as a precise understanding of the complex interplay between NFA structure and photophysical processes in blends and devices is still lacking. Here, we discuss for selected material systems, how the molecular structure affects the photophysics, specifically the charge separation and energy losses, which we study by ultrafast transient spectroscopy. As one example, we present BHJ systems that systematically vary in the energy offset between donor and acceptor. By using ultrafast transient spectroscopy, we demonstrate that after photoexcitation, singlet energy transfer can compete very efficiently with charge transfer, leading to low free carrier yields, and thus poor device performance. Furthermore, we show that the acceptors' quadrupole moment is an important parameter to consider in the design of NFAs, as it determines the charge separation efficiency and simultaneously affects the open-circuit voltage of devices. Finally, we investigate the bias dependence of the device photocurrent by time-delayed collection field (TDCF) experiments and thereby identify reasons for low fill factors (FF) in polymer and small molecule / NFA systems. Specifically, we demonstrate that the fill factor is determined by two parameters: firstly, the field dependence of interfacial charge separation and secondly, non-geminate recombination of free charges competing with carrier extraction. In fact, depending on the NFA structure, field-independent charge separation is observed and thus high FFs can be achieved, if extraction of carriers kinetically outcompetes non-geminate recombination. However, other NFA structures exhibit low fill factors as charge separation is bias dependent and / or non-geminate recombination of charges competes with carrier extraction. Based on our spectroscopic insights and theoretical modeling of interface energetics and charge separation, we propose general design rules for NFAs that promise further reduction of quantum efficiency and energy losses.

11:30 AM *CM04.09.08

Interfacial Energy and Charge Transfer for Photon Up-Conversion and Down-Conversion Aaron P. Moon, Aaron Le, Jon A. Bender, Daniel E. Cotton, Emily K. Raulerson, Inki Lee and [Sean T. Roberts](#); Chemistry, University of Texas at Austin, Austin, Texas, United States.

The negligible spin-orbit coupling in many organic molecules creates opportunities to alter the energy of excited electrons by manipulating their spin. In particular, molecules with a large exchange splitting have garnered interest due to their potential to undergo singlet fission (SF), a process where a molecule in a high-energy spin-singlet state shares its energy with a neighbor, placing both in a low-energy spin-triplet state. When incorporated into photovoltaic and photocatalytic systems, SF can offset losses from carrier thermalization, which account for ~50% of the energy dissipated by these technologies. Likewise, compounds that undergo SF's inverse, triplet fusion (TF), can be paired with infrared absorbers to create structures that upconvert infrared into visible light. However, integrating materials that undergo SF or TF with existing electronics is challenging as this necessitates interfaces that can readily transfer spin-triplet excitations between these materials and bulk semiconductors, such as silicon. In this talk, I will summarize work investigating energy transfer dynamics in two key interfaces for SF and TF devices. First, I will describe work investigating how the local ordering of perylenediimide (PDI) molecules at a silicon surface impacts triplet energy transfer from PDI to silicon. We find small changes in the ordering of PDIs from their bulk structure due to strain at the silicon surface can shift their triplet energy by a few hundred meV, substantially impacting the driving force for triplet energy transfer. Strategies to control the structure of PDI films during growth will be discussed. Second, I will discuss measurements characterizing triplet energy transfer from near-infrared absorbing PbS nanocrystals to TF materials covalently bound to their surfaces. We find PbS nanocrystals are decorated with a number of surface states. While some of these states facilitate triplet energy transfer to surface-bound molecules, others hinder it by trapping excitations. Throughout the presentation, an important theme will be use of key spectroscopic techniques, such as broad-band electronic sum frequency generation (ESFG), to visualize interfacial states involved in energy transfer between organic and inorganic systems.

1:30 PM *CM04.10.01/EP05.13.01

Triplet Energy Transfer Governs the Dissociation of Correlated Triplet Pairs Generated by Singlet Fission Tia S. Lee¹, YunHui L. Lin², Hwon Kim¹, Ryan D. Pensack^{1,3}, Barry P. Rand^{2,4}, Greg Scholes¹ and Kyra Schwarz¹; ¹Department of Chemistry, Princeton University, Princeton, New Jersey, United States; ²Department of Electrical Engineering, Princeton University, Princeton, New Jersey, United States; ³Micron School of Materials Science & Engineering, Boise State University, Boise, Idaho, United States; ⁴Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey, United States.

Singlet fission, a spin-allowed process of spontaneous exciton multiplication, has the potential to enhance the efficiency of photovoltaic devices by utilizing two triplet excitons generated from one singlet exciton. The majority of studies to date have emphasized understanding and optimizing the first step of singlet fission, where the overall singlet intermediate state—the “correlated triplet pair”—is produced from a singlet photoexcitation. Few studies have examined later steps, where the triplet pair may separate and spin correlation may be lost. Here we examine transient absorption of 6,3-bis(triisopropylsilyl)ethynyl)pentacene (TIPS-Pn) films at cryogenic temperatures (78–295 K). We evaluate time constants obtained from global analysis and show that their temperature dependence is inconsistent with an exclusively thermally activated process. Instead, we find that the trends can be modeled by a triplet-triplet energy transfer process involving simultaneous two-electron exchange. The fitted reorganization energy and electronic coupling agree closely with values calculated using density matrix renormalization group quantum-chemical theory. We conclude that the dissociation of the correlated triplet pair to separated (but spin-entangled) triplet excitons in polycrystalline TIPS-Pn occurs by triplet-triplet energy transfer with a hopping time constant of approximately 3.5 ps at room temperature.

2:00 PM CM04.10.02/EP05.13.02

Multiphonon Mediated Singlet Exciton Fission in Hexacene Qifei Gu¹, John Anthony² and Akshay Rao¹; ¹University of Cambridge, Cambridge, United Kingdom; ²Chemistry, University of Kentucky, Lexington, Kentucky, United States.

In select molecular systems, singlet excitons (S_1) created from the absorption of a photon can undergo a process where it efficiently splits into two triplet excitons ($2xT_1$). This process of singlet fission has the potential of realizing high efficiency solar cells that exceed the Shockley-Queisser limit [1]. In this study we investigate a hexacene derivative [2] using pump energy dependent ultrafast transient absorption spectroscopy to study the mechanisms that limit the singlet fission rate and efficiency. Hexacene is a unique system to study the singlet fission processes because of its small T_1 energy ($\sim 0.5\text{eV}$) compared to the S_1 energy ($\sim 1.5\text{eV}$). Therefore, in contrast to other singlet fission systems such as tetracene and pentacene which are close to isoenergetic, singlet fission in hexacene is highly exothermic. The significant degree of electronic coupling compounded with large exothermicity gives the possibility of hexacene to undergo singlet fission from one singlet to either yield three triplets or yield two triplets and phonons.

In this hexacene system we find the singlet fission rate of 470fs which is in line with previous studies [3][4]. Such a short time scale of singlet fission allows it to out-compete other relaxation channels, and hence giving it a high efficiency. Comparing with pentacene, the other system with exoergic singlet fission ($\sim 100\text{fs}$ fission rate), even though hexacene is more exoergic than pentacene the singlet fission rate is observed to be much slower. The proposed phonon bottleneck effect causing this divergence is experimentally explored through transient absorption spectroscopy, yielding corroborative evidence. By inducing more energy into the system through systematically varying the pump excitation to shorter wavelengths, singlet fission mediated by multiple phonon interactions is directly probed. A prolonged singlet fission rate is observed with higher pump energies. Individual singlet and triplet spectra and kinetics are numerically deconvolved through a genetic algorithm method. Thus, the singlet fission rate and the yield can be correlated with respect to the excess energy present in the singlet fission process. Further evidence of the phonon mediated singlet fission process explored through cryogenic transient absorption and through vibrational coherence studies will be discussed.

[1] Smith, Millicent B., and Josef Michl. "Singlet fission." *Chemical reviews* 110.11 (2010): 6891-6936.

[2] Purushothaman, Balaji, et al. "Synthesis and charge transport studies of stable, soluble hexacenes." *Chemical Communications* 48.66 (2012): 8261-8263.

[3] Busby, Erik, et al. "Multiphonon relaxation slows singlet fission in crystalline hexacene." *Journal of the American Chemical Society* 136.30 (2014): 10654-10660.

[4] Pensack, Ryan D., et al. "Exciton delocalization drives rapid singlet fission in nanoparticles of acene derivatives." *Journal of the American Chemical Society* 137.21 (2015): 6790-6803.

2:15 PM CM04.10.03/EP05.13.03

Energetic Driving Force of Singlet Fission in Perylenediimide Thin Films Aaron Le, Sean T. Roberts and Jon A. Bender; University of Texas at Austin, Austin, Texas, United States.

Singlet fission (SF) is a process that can occur in select organic molecules where a singlet exciton splits into two lower energy triplet excitons. While the intersystem crossing of singlets to triplets is typically slow in organic molecules, due to small spin orbit coupling singlet fission does not require a flip in spin and can be exceptionally fast compared to intersystem crossing. The SF process requires two chromophores whose triplet states should be approximately half of the singlet state's energy to conserve energy. This process has applications in photovoltaics where thermalization of high energy excitations accounts for a major loss channel and limits the maximum performance of such devices. Utilizing materials that undergo efficient SF can potentially mitigate the losses these above band gap excitation experience --- high energy excitations can be down converted into lower energy excitations before thermalization can occur. Perylenediimides (PDIs) are a robust class of dye molecule employed as commercial pigments that contain the proper energetics for SF. These molecules form crystalline domains in the solid state that can be readily tuned by functionalization of the molecules, thereby allowing the structure-function relationship of SF and intermolecular geometry in the solid state to be explored. The intermolecular geometry of SF chromophores has been shown to have a strong connection to the SF rate chromophores that undergo SF. A collection of PDIs with different solid state packing structures were evaluated for potential use as SF chromophores in polycrystalline thin films. Employing a combination of ultrafast femtosecond and nanosecond spectroscopy we identify the formation of triplet state spectral features and identify the SF rates for these materials. Extracted experimental rates deviate from theoretical predictions by approximately three orders of magnitude which may be attributed to differences in energetic landscape of the polycrystalline films and the dimer employed in the calculation. A series of temperature dependent spectroscopic experiments were utilized to examine the energetic requirements of SF in these polycrystalline thin films.

2:30 PM *CM04.10.04/EP05.13.04

Singlet Fission in Synthetic Caroteno-Proteins Jenny Clark, Daniel Polak and Andrew Musser; University of Sheffield, Sheffield, United Kingdom.

Singlet fission is the process whereby one photon creates two triplet excited states. If both triplet states could be harvested by a single-junction solar cell, the solar cell efficiency would increase by up to 1/3. There has been much academic and industrial interest in developing new materials for singlet fission,

but to date no material has proved ideal.

Carotenoids are the most widespread of the natural pigments, important for photosynthesis, vision, human health and industry. Work on astaxanthin [1,2] (the pigment which colours lobsters) shows that carotenoids are good candidates for singlet fission sensitizers for solar cells: they have strong absorption and fast (<100fs) singlet fission, independent of energetic driving force. There are hundreds of naturally occurring carotenoids and each of them can form a range of different dimer or aggregate structures (eg H- or J-aggregates).

To determine how carotenoid structure affects singlet fission, and how to exploit carotenoids or other polyene-type systems as singlet fission sensitizers, we use model systems to create identical dimer structures of a range of carotenoids. The model systems are made of synthetic 'maquette' proteins that hold the carotenoids in a specific dimer geometry. I will describe details of the photophysics of singlet fission in polyenes, showing that singlet fission is surprisingly robust to changes in conformation and does not depend on either the aggregate or intramolecular structure.

[1] Musser et al., *Journal of the American Chemical Society*, 137, 5130 (2015)

[2] Musser et al., *Journal of the American Chemical Society*, under review (2018)

3:00 PM BREAK

3:30 PM *CM04.10.05/EP05.13.05

Functional Imaging of Energy Flow in Materials at the Nanoscale Milan Delor, Hannah Weaver, QinQin Yu and Naomi S. Ginsberg; University of California, Berkeley, Berkeley, California, United States.

The ability of energy carriers to move within and between atoms and molecules underlies virtually all biochemical and material function. Understanding and controlling energy flow, however, requires observing it on ultrasmall and ultrafast spatiotemporal scales, where energetic and structural roadblocks dictate the fate of energy carriers. We therefore developed a universal, non-invasive optical scheme that leverages interferometric scattering to track energy transport in four dimensions of spacetime with few-nanometer precision and directly correlate it to material morphology. We visualize exciton, charge, and heat transport in polyacene, silicon and perovskite semiconductors and elucidate, in particular, how grain boundaries impact energy flow through their lateral- and depth-dependent resistivities. We reveal new strategies to interpret energy transport in disordered environments that will direct the design of defect-tolerant materials for the semiconductor industry of tomorrow.

4:00 PM CM04.10.06/EP05.13.06

The Evolving Excitonic Properties of Organic Molecules During Self-Assembly Cathy Y. Wong; University of Oregon, Eugene, Oregon, United States.

The electronic structure and exciton dynamics of organic molecules can change dramatically upon aggregation. The exciton dynamics of molecules in solution and in thin films of aggregates can be measured using transient absorption spectroscopy, but the exciton dynamics of intermediate aggregation states during thin film formation are typically unknown since measurements cannot be performed quickly enough to collect accurate transient absorption spectra of these species. By increasing the speed of data collection, the exciton dynamics of evolving material systems can be measured. A novel implementation of transient absorption spectroscopy is introduced that can measure transients with up to a 45 ps pump-probe time delay in one shot. The exciton dynamics measured during the solution deposition of a thin film is validated by comparing the initial exciton dynamics of the solution and the final exciton dynamics of the dry film to traditional transient absorption measurements. The exciton dynamics of intermediate aggregation states will be presented for the first time. The information gained using this technique can be used to modify environmental parameters during the film formation process to kinetically trap aggregates with exciton dynamics tailored for a particular application.

4:15 PM CM04.10.07/EP05.13.07

Diffraction Before Destruction—Unraveling Structure-Function Relationships in Organic Semiconductors with an Ultra-Fast X-Ray Laser Christopher J. Takacs¹, Kathryn O'Hara², Karsten Bruening¹, Hans-Georg Steinrueck¹, Christopher J. Tassone³, Mengning Liang³, Michael L. Chabinye² and Michael F. Toney³; ¹Stanford Univ, Menlo Park, California, United States; ²University of California, Santa Barbara, Santa Barbara, California, United States; ³SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Charge and ion transport of organic semiconductors depends strongly on both molecular structure and morphology. Our fundamental understanding of structure-function relationships has improved greatly in recent years; however, conventional high-resolution structural probes such as x-ray and electron scattering/microscopy are severely restricted by radiation damage and new structural probes are needed. Towards this end, we present initial results from nano-beam diffraction experiments at the Linac Coherent Light Source (LCLS), a source of high-intensity, ultra-short, and coherent hard x-ray pulses from several molecular and polymeric materials. Known as "diffraction-before-destruction", a single femtosecond x-ray pulses yields useable diffraction images in weakly diffracting and disordered samples before radiation damage can propagate (e.g. sample explosion). This removes the previous limitations of sample damage present in synchrotron and electron microscopy methods. Furthermore, the focused beam (150 nm diameter) is small enough that significant anisotropy in the scattering patterns is observed, yielding insight into polymorphism, strain, and grain-boundaries through statistical analysis of thousands (and eventually millions) of diffraction images. Combined with complementary high-resolution transmission electron microscopy images and atomistic simulations, the results suggest a distribution of packing structures coexist in thin films and that engineering likely packing motifs has the potential to improve both the electronic and ionic transport properties of these materials.

4:30 PM *CM04.10.08/EP05.13.08

Probing Single Molecular Dynamics at Ultrafast Time Scales and in Nanoscale Volumes Niek F. van Hulst^{1,2}; ¹ICFO - Institute of Photonic Sciences, Castelldefels, Spain; ²ICREA - Catalan Institute for Research and Advanced Studies, Barcelona, Spain.

Tracing of individual molecules both in space and in time, provides super-resolution images of intra- and inter-molecular dynamic processes, all beyond the ensemble [1,2]. A host of important dynamic processes occurs on fs-ps timescale, such as electronic relaxation/dephasing, energy & charge transfer, vibrational relaxation, photo-dissociation-ionization, photo-isomerization. Yet capturing fast dynamics is fundamentally limited by the ns lifetime of the detected fluorescence. For the ensemble, fs-ps resolution is conventionally obtained by transient absorption and 2D electronic spectroscopy (2D-ES). Here first, we challenge ultrafast transient absorption of a single molecule and have set out to probe the non-linear ultrafast response of the single molecule using a broadband laser in an effective 3-pulse scheme with fluorescence detection. 2D-ES of single molecules is getting into reach [3]. Next, stimulated emission has the advantage of coherence and unity quantum efficiency, compared to fluorescence. Moreover depleting the excited state rapidly reduces photodissociation. Thus, we have set out to directly detect the stimulated emission from individual molecules and Qdots at ambient conditions, to disentangle ultrafast charge dynamics in the excited state, on fs-ps timescale [4]. Finally, we enhance the sensitivity and resolution using the local optical near-fields of plasmonic nano-antennas. Critical to the optimal coupling and

enhancement is the positioning of the molecule at the local nanoscale hotspot of a resonant antenna. We apply deterministic scanning and stochastic mapping of the nanoscale plasmon-molecule interaction, to optimize the coupling strength and ultrafast interaction [5,6]. We apply the enhancement to photosynthetic complexes, LH2 [7], to detect first single FMO complexes at room temperature and assess their photon correlation. The presented nanoscale ultrafast spectroscopy on individual molecules is of direct importance for pathway-specific detection of energy transfer and charge separation, directly & locally in light-harvesting systems [1].

Acknowledgements

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References

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- [3] M.Liebel, C.Toninelli, N.F. van Hulst, *Nature Photonics* **12**, 45 (2017).
- [4] L.Piatkowski, N.Accanto, G.Calbris, S.Christodoulou, I.Moreels, N.F. van Hulst, under review.
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- [6] J.Hugall, A.Singh, N.F. van Hulst, *ACSPHOTONICS* **5**, 43 (2018).
- [7] E.Wientjes, J.Renger, A.G.Curto, R.Cogdell, N.F. van Hulst, *Nature Commun.* **5**, 4236 (2014)

SESSION CM04.11: Poster Session: Ultrafast Spectroscopy—Methods and Applications
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

CM04.11.02

Generation and Evolution of Excitons and Biexcitons in Layered WS₂—A Time-Resolved Broadband Pump-Probe Study Rup K. Chowdhury¹, Snehashish Nandy¹, Sayantan Bhattacharya¹, Manobina Karmakar¹, Shivakiran B. Bhaktha¹, Prasanta K. Datta¹, Arghya Taraphder¹ and Samit K. Ray^{1,2}; ¹IIT Kharagpur, Krishnagar, India; ²S. N. Bose National Centre for Basic Sciences, Kolkata, India.

Various quasiparticles like excitons, biexcitons are able to co-exist in the exfoliated two-dimensional (2D) stratum of transition metal dichalcogenides (TMDs), which have gained massive attention due to their layer dependent band gap modulations and diverse electro-optical properties^{1,2}. The knowledge about the properties and dynamics of these metastable carriers turn out to be essential for nanofabrication of various optoelectronic components. Therefore, an advanced time-resolved pump-probe spectroscopy has been utilized to investigate these ultrafast processes, as it is beyond the limit of conventional optical studies. In our case, we have explained the transient absorption spectra (TAS) of chemically exfoliated mono-to-few layers WS₂ flakes dispersion. This shows six major features including three saturable absorptions (SA) peaks and three excited state absorption (ESA) peaks for a pump of 405 nm (3 mW). The density functional theory (DFT) calculations predict that the nature of the band structure remains unaffected from mono to few-layers transformation, which has also been independently verified by our TAS analysis. We are able to identify the existence of both the biexcitons in the multi-layered 2D stratum of WS₂ through the cooling process of hot exciton population as well as calculate their corresponding binding energies (AA ~ 69 meV and BB ~ 66 meV) using a new and more robust method. Furthermore, using many-body physics, we demonstrate that the excitons behave like Wannier-Mott excitons and explain their origins via first-principles calculations. Indeed, our results unravel the complex optical response of biexcitons in layered WS₂, which should lead to numerous technological applications for developing biexciton-based valleytronic devices and ultrafast biexciton lasers at room temperature.

Reference:

1. Rup K. Chowdhury et al., *Nanoscale*, **8**, 13429 (2016).
2. Cong Mai et al., *PRB*, **90**, 041414(R) (2014).

CM04.11.03

Measurement of Ultrafast Carrier Dynamics in Graphene/Copper System Cheng Dong, Weigang Ma and Xing Zhang; Department of Engineering Mechanics, Tsinghua University, Beijing, China.

Understanding of ultrafast carrier dynamics between graphene and metals at high frequencies is of great significance in graphene-based devices operating in high frequencies. Hence, we used femtosecond laser pump-probe technique to study the energy coupling between graphene and copper, by monitoring the optical property change of graphene and copper, within 10 picoseconds after excitation of the pump beam. Sample is composed of single layer graphene grown on copper by chemical vapor deposition method. The pump beam of 400 nm is to excite the sample, and the probe beam of 800 nm is to monitor the total reflectivity change of this graphene/copper system. We observed two peaks and two valleys in measured total reflectivity signals, which reflects the graphene optical properties. And then a slow increase in the total reflectivity signals is observed, which is dominated by the copper optical property changes. We developed a four temperature model to calculate the carrier temperature evolution of graphene and copper (phonons and electrons), and considering the energy coupling between graphene and copper is dominated by phonons. The theoretical results modulates the measured signal well. The energy coupling between graphene electrons and phonons, and energy coupling between graphene and copper are extracted from the modulation. These two energy coupling parameters provide understanding of graphene/metal-light interactions in ultrashort time domain, and provide foundation of graphene-based device applications.

CM04.11.04

Carrier Dynamics and Charge Transfer in CdS_xSe_{1-x} Lateral Nanoribbon Heterostructures Freeman Statum, Biswadev Roy and Marvin H. Wu; Mathematics and Physics, North Carolina Central University, Durham, North Carolina, United States.

Ternary CdS_xSe_{1-x} semiconductors exhibit direct continuously composition-tunable bandgaps in the visible region and are thus of interest for applications involving emission and detection of light. Lateral nanoribbon heterojunctions offer large surface areas, short carrier diffusion lengths and lower cost of growth compared to bulk films. We characterize the evolution of photogenerated charge carriers in individual CdS_xSe_{1-x} nanoribbons using ultrafast optical spectroscopy and time resolved millimeter wave photoconductivity. Static confocal photoluminescence (PL) microscopy of these nanoribbons, which are

produced through the vapor – liquid – solid technique using gold nanoparticle catalysts, show variations of 80 – 120 nm in the locations of the PL peaks in adjacent regions due to spatially varying compositions. PL lifetime mapping via time – correlated single photon counting showed shorter lifetimes (< 100 ps) in the central portion of the wider bandgap region, compared to regions near the interface. These shorter lifetimes, combined with wide field static PL measurements that show emission from the narrow bandgap region after excitation in the wider bandgap region, are consistent with transfer of photoexcited carriers. Higher (sub-picosecond) temporal resolution transient absorption (TA) microscopy measurements result in lifetimes matching those obtained via PL. TA and PL measurements with spatially separated excitation and TA probe or PL emission locations show evidence of asymmetric carrier diffusion near the interface. Time resolved photoconductivity decay curves from ensembles of nanoribbons show a system response limited nanosecond lifetime decay consistent with PL measurements, but also show a weak longer lived (~ 50 ns lifetime) component that may correspond to a small population of weakly trapped carriers not observed in PL or TA measurements.

CM04.11.05

Ultrafast Excited State Absorption in Chromophore-Functionalized Chiral Polybinaphthalenes Jonathas Siqueira¹, Marcelo G. Vivas², Cleber Mendonca¹ and Leonardo de Boni¹; ¹Institute of Physics of São Carlos - University of São Paulo, São Carlos, Alabama, United States; ²Instituto de Ciência de Tecnologia, Universidade Federal de Alfenas, Poços de Caldas, Brazil.

The study of ultrafast chirality dynamics in the excited state has received considerable interest over the past years. Chiral polymers show particularly interesting properties for applications in emerging field of chiral photonics. Chromophore-functionalized polybinaphthalenes are an interesting class of chiral polymers given their high chirality in the ground state. Chromophore-functionalized polybinaphthalenes show a tree-like structure: they are composed of a rigid, rod-like backbone to which flexible chromophores are attached. This tree-like supramolecular architecture, the chromophores (branches) are attached to a rigid backbone (trunk), diminishes and even excludes dipolar interactions between the chromophores. In a previous study on donor-embedded polybinaphthalenes, it was demonstrated that they are a very interesting class of polymers since the dipolar interactions between the chromophores are excluded in these materials and chiral contributions are present. The spectral dependence and ultrafast dynamics of excited state absorption of four different chromophore-functionalized polybinaphthalenes, were characterized by femtosecond absorption transient spectroscopy as a first step towards the characterization of their chirality dynamics in the excited electronic state. In order to better understand the origin of chirality in this class of polymers, we aim at studying their chirality in the excited state. An initial study in this direction was the characterization of their excited state absorption and dynamics via femtosecond transient absorption technique for four chiral polybinaphthalenes. Excited state absorption (ESA) spectroscopy at femtosecond time scale was carried out to measure the relaxation times and absorption spectra of their electronic excited states. Femtosecond time-resolved ESA experiment was implemented using 150-fs pulses (775 nm) from a regenerative Ti:sapphire. ESA spectra and dynamics measurements were performed using the pulse at 387.5 nm (second harmonic of 775 nm) as a pump pulse and a white light continuum (400 - 700 nm) as a probe. We obtained excited state characteristic deactivation times shorter than 100 ps and characterized the spectral dependence of their excited state absorption. The data obtained in this study will assist us in the characterization of the chirality ultrafast dynamics on the electronic excited state of this novel class of chiral polymers.

CM04.11.06

High Contrast Photothermal (PT) Phase Imaging in the Mid-Infrared Exceeding Sub-Diffraction Limited Spatial Resolution Panagis Samolis^{1,2}, Shyamsunder Erramilli^{4,5,2} and Michelle Y. Sander^{1,3,2}; ¹Department of Electrical and Computer Engineering, Boston University, Boston, Massachusetts, United States; ²Photonics Center, Boston University, Boston, Massachusetts, United States; ³Division of Materials Science and Engineering, Boston University, Boston, Massachusetts, United States; ⁴Department of Physics, Boston University, Boston, Massachusetts, United States; ⁵Department of Biomedical Engineering, Boston University, Boston, Massachusetts, United States.

Mid-infrared (mid-IR) spectroscopy and imaging has attracted significant interest as a label-free method for material analysis based on the presence of characteristic vibrational resonances in the molecular fingerprint region. However, most mid-IR photothermal (PT) spectroscopic imaging systems so far have mostly focused on extracting amplitude information from the sample. Here, we present how characterization of phase images can result in enhanced spatial resolution and imaging contrast based on the different thermal properties of the imaging target and its surrounding environment. In a heterodyne measurement configuration with a lock-in amplifier, phase details of single particles are resolved below the spatial sub-diffraction imaging limit of the optical system in a spectral window where the amplitude images don't show much contrast.

In the presented PT pump-probe microscopy configuration, a nanosecond pulsed mid-IR beam excites the absorption resonance of the sample while a near-IR beam is used to probe its thermo-refractive response. By detecting the scattered probe intensity in the far field with sensitive detector technology, sub-diffraction limited imaging resolution can be achieved circumventing more complex mid-IR detectors.

In traditional mid-IR imaging, if the surrounding medium and the imaging target feature similar absorption properties, this generally limits the contrast, spatial resolution and chemical specificity. Here, we demonstrate the capabilities of PT phase imaging for highly sensitive detection of weakly absorbing single particles embedded in a medium that is also resonant at the excitation wavelength.

The PT signal of our system is acquired by lock-in detection, which allows background-free detection of small modulations in the probe beam intensity with high signal to noise and enables detection of amplitude and phase signals. We investigated the phase signal of 1 μm melamine beads embedded in an 8CB liquid crystal. We demonstrate that high phase contrast can be obtained due to the different thermal properties of the imaging target and its surrounding environment even in a spectral regime where absorption of the bead and the liquid crystal is similar. By investigating the phase signal, we are able to detect the presence of single absorbers smaller than the diffraction limited spot size with high contrast and enhanced spatial resolution, in an absorbing medium. This method provides a promising pathway to detect weakly absorbing signals in an overcrowded spectral region where high absorptive signals can mask weaker contributions, which is attractive for highly sensitive chemical sensing, detection of hazardous trace materials and biological tissue analysis.

CM04.11.07

Identification of Reactive Species in Photoexcited Nanocrystalline BiFeO₃ Powder by Transient Absorption Spectroscopy Wegdan Ramadan¹ and Detlef Bahnemann^{2,3}; ¹Physics Department-Faculty of Science, Alexandria University, Alexandria, Egypt; ²Institut für Technische Chemie, Leibniz Universität Hannover, Hannover, Germany; ³Laboratory “Photoactive Nanocomposite Materials”, Saint Petersburg State University, Saint Petersburg, Russian Federation.

BiFeO₃(BFO) is a multiferroic semiconductor that combines antiferromagnetic and ferroelectric order well above room temperature. It has a direct band gap energy lies within a range of 2.3 to 2.8 eV hence, it can harvest visible light of the solar spectrum and an indirect band gap around 1.8 eV. The position of the conduction band, E_{CB}, and valence band, E_{VB}, makes it suitable for the oxidation of water and many other organic pollutants. Combining such desired properties in a simple ternary compound that comprises eco friendly and cost effective elements makes it easier to utilize it towards sustainable environment and energy harvesting application. However, fundamental studies about photo charge carrier dynamics of BFO nanoparticles are still lacking.

BFO nanocrystals having particle size ~ 70 nm were synthesised using sol gel method. In this work, charge carrier dynamics of BFO colloid have been investigated by means of diffuse reflectance transient absorption spectroscopy. Nanosecond transient absorption were performed at two excitation wavelengths; 335 nm (3.4 eV) that is higher than the band gap and at 532 nm (2.33 eV) which is around the band gap energy. Measurements were carried out in the presence of methanol- N_2 saturated atmosphere as a hole acceptor and in presence of N_2 - $Na_2S_2O_8$ in an alkaline medium, by using NaOH as electron acceptor. By quenching electrons using $Na_2S_2O_8$ we were able to deal with holes as electrons will be quenched by the persulfate and holes will remain in the particles. Measuring the initial signal height immediately after the laser pulse, two transient absorption maxima can be observed; one sharp maximum centered at around 550 nm and a broad one around 750 nm. To relate the observed transient absorption signals to possible trapped charge carriers, we performed the same measurements in a N_2 -methanol environment to investigate the changes in the transient spectra. In the presence of methanol, the absorption peak at 550 nm significantly decreases, while the absorption at 750 nm remained unchanged. This indicates that the first absorption maximum can be attributed to trapped holes, which react rapidly with N_2 -methanol hence the decrease in the spectrum. The same set of measurements when carried out at excitation wave length of 355 nm and the same behavior was obtained. The observed peak at 750 nm could be related to the indirect band gap which is around the same wave length. This result contradicts what was reported previously by Yasuhiro et. al. who attributed the strong absorption peak at 540 nm to the optical transition of the photoexcited electrons to the higher conduction band. The optical transient absorption of the electrons could not be clearly identified hence, more experiments still need to be carried out.