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-tunable spectrums is, perhaps, the best known and understood such property. Here we investigate dissipation and transport dynamics of various semiconductor nanostructures 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.
Ultra-Fast and Ultra-Slow Processes Depict the (Defect) Photo-Physics of Metal-Halide Perovskite Semiconductors

Seminaxing 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.

Charge Carrier Recombination and Lattice Interactions in Bismuth-Based Perovskites

A promising class of lead-free perovskites for photovoltaic applications include the bismuth halides, such as MA$_2$Bi$_4$I$_8$, BiOI, and Cs$_2$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.

References:

Charge-Carrier Dynamics in Metal Halide Perovskites for Photovoltaics

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 (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 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.

Metalloc-x-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, Toshihara 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.

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References

2:45 PM CM04.02.04
Stimulated Emission and Ultrafast Optical Switching in a Nanographene Molecule Giuseppe M. Paterno1, Luca Moretti1, Qiang Chen2, Klaus Muller2, Akimitsu Narita2, Giulio Cerullo3, Guglielmo Lanzani1,3 and Francesco Sciotognella1,3; 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 nanomeshes[1], 1D graphene nanoribbons[2] and 2D graphene quantum dots[3], has paved the way for the development of the promising field of nanographene optoelectronics. In this context, the synthesis of the nanographene 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 dibenzoiridihierstrovalene (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
**Physical Origins of the Transient Absorption Spectra and Dynamics in Thin-Film Semiconductors—The Case of BiVO$_4$**

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.
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 study 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.

References
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.

9:30 AM CM04.04.03
Observation of Chiral Phonons in Monolayer 2D Materials Hanyu Zhu1,2, Jun Yi1, MingYang Li1, Lifa Zhang2, Jun Xiao1, Chih-Wen Yang3, Robert A. Kaindl2, Lam-Jong Li1, Yuan Wang1,2 and Xiang Zhang1,2,1;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.

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Excitonic Quantum Gates

Eric B. 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 Zhang1, Feng Jin1, Xuelian Tan1, Wenbin Wu1, Richard A. 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 La$_2/3$Ca$_1/3$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 Etresses on the Time Dynamics of Photoexcited Charge Carriers in InGaAs Based Superlattices

Arsenii M. Buriakov1, Dinar Khusyainov1, Elena D. Mishina1, Dmitry Ponomarev2, Alexander Yachmenev2, 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 by beryllium atoms, introduction of strained ErAs layers, etc. Another problem of InGaAs is the relatively long lifetime 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: In$_{0.53}$Ga$_{0.47}$As/In$_{0.52}$Al$_{0.48}$As (SL1), In$_{0.53}$Ga$_{0.47}$As/InAs (SL2), In$_{0.53}$Ga$_{0.47}$As/In$_{0.38}$Al$_{0.61}$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 was used to characterize epitaxial deformations. There were no stresses in SL1 sample. In SL2 samples epitaxial...
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.

Influence of Vibrational Coherence on the Excited State Dynamics—Ultrafast Raman Loss Spectroscopy

Siva Umapathy; 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 reorganisation 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 photo-isomerization 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
Levanenia Chabani1,2, Christoph Klieber1, Remi Busselez1, Lionel Guilmeau1, Mathieu Edely1, Vitalyi Gasev2 and Thomas Pezeril1; 1Le Mans Université, JMIMM - 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.


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 (OCS) 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 ISC’s. ESFG is uniquely suited for the study of 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 structure 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 χ(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 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

SESSION CM04.07: Terahertz Spectroscopy
Session Chairs: Ajay Srimath Kandada and Carlos Silva
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.

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 - (1 ps)$^{-3}$ which is in good agreement with the theoretical predictions [2, 4].


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 ultrafast, 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.

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 a 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.
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 $10^{12}$ A/cm$^2$ 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.


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 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 simultaneously 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.


Ultrafast Imaging of Charge Carrier Dynamics on Semiconductor Surfaces

Ebrahim Najafi; 1Califoma Institute of Technology, Pasadena, California, United States; 2Chembours 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.
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 interfaces with sharp architectures for directing interfacial charge transport. Here we investigate the formation and transport of CT excitons in van der Waals (vdW) heterostructures based on semiconductor transition metal dichalcogenides (TMDs) 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 tetraene 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 tetraene 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 cm²/s and ~ 0.04 cm²/s, respectively. The high mobility of the delocalized CT excitons could be the key factor to overcome large CT excitation 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 epitaxially grown AA and AB stacking WS2-WSe2 heterostructures.


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 Cu2ZnSnS4·Se2 (CBTSSe) chalcogenides1 for the first time. CBTSSe is a recently introduced alternative to Cu(In,Ga)(S,Se)2 and Cu2ZnSnS4·Se4 (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, Δx ≤ 0.3, in Cu2BaSnS4·Se4 — 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 carrier relaxations, would still impact the photocurrent and open circuit voltage of the CBTSSe devices/films examined.

References:

Ab Initio Predictions of Spatially-Resolved Nonequilibrium Coherent Transport Phenomena George Varnavides1, Adam S. Jermyn1, Polina Anikeeva2,3 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.

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. The effect of residual field between the carriers and the high mobility and in the band-bending region. These processes 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 its GHZ range was observed as the cumulative 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-Si:C: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 Block1, Matz Liebel1, Renwen Yu1, Javier Garcia de Abajo1, Yanaton 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 and 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 in the THz domain, 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 reflection 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.
Understanding charge generation mechanism in organic solar cells is of great importance to further device optimization. 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 Moretti¹ ², Bryan J. Kudisch³, Yuichi Terazono³, Ana Moore³, Thomas A. Moore³, Devens Gust¹, Giulio Cerullo¹, Greg Scholes² and Margherita Maiuri¹ 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 → Sn); 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 “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.

References:

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:
11:00 AM CM04.09.06

Impact of HOMO-HOMO Offset on Charge Separation in Small Molecule Nonfullerene Organic Solar Cells
Safakath Kanthedath, Julien Gorenflot, RuiZe 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 solar irradiance and low temperature. However, the origin of this superior performance is still not clear. Importantly, the energy offset between donor and acceptor materials, as a key parameter in the design of NFAs, can directly influence the photophysical processes during the charge separation. We report on interfacial charge generation and separation of both electron and hole in 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 (ΔEH: 0.7 eV), O-IDTBR (ΔEH: 0.45 eV), and (ΔEH: 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 charge generation is observed 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

11:15 AM CM04.09.07

Ultrafast Spectroscopy of Loss Processes in Nonfullerene Acceptor Bulk Heterojunction Solar Cells
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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 polydiacetylene (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 broadband electronic sum frequency generation (ESFG), to visualize interfacial states involved in energy transfer between organic and inorganic systems.
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(trisopropylsilyl)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.

In select molecular systems, singlet excitons (S\textsubscript{1}) created from the absorption of a photon can undergo a process where it efficiently splits into two triplet excitons (2T\textsubscript{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 process because of its small T\textsubscript{1} energy (~0.5eV) compared to the S\textsubscript{1} energy (~1.5eV). 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 (~100fs 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.

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 polynye-type systems as singlet fission sensitizes, 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.


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 Liang4, Michael L. Chabinyc2 and Michael F. Toney5; 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 (eg. 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 Nieck F. van Hulse1,2; 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 techniques to investigate the 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].

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References
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 photocconductivity 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  
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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  
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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 spectral 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 melanine 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  
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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 echo 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 bang gap energy. Measurements were carried out in the presence of methanol-N2 saturated atmosphere as a hole acceptor and in presence of N2-Na2S2O8, in an alkaline medium, by using NaOH as electron acceptor. By quenching electrons using Na2S2O8, 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 N2-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 N2-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.