

POSTER SESSION – Tuesday, June 14 7:00pm-9:00pm

- Doran Bennett** (Harvard University)
“Multiscale Modeling of Light Harvesting and Photoprotection in Plants”
- Kochise Bennett** (UC Irvine)
“Transient Redistribution of Ultrafast Electronic Coherences (TRUECARS)”
- Josiah Bjorgaard** (LANL)
“Nonequilibrium Solvent Effects in Born-Oppenheimer Molecular Dynamics for Ground and Excited Electronic States”
- Carlos Borca** (Purdue University)
“Charge Transfer in the Lithium-Benzene Complex: Understanding the Role of the Hartree-Fock Exchange”
- David Bowman** (University of Minnesota)
“Excited State Absorption in Tetrapyrrolyl Porphyrins”
- Will Bricker** (Massachusetts Institute of Technology)
“Optimization of Energy Transfer in DNA-Dye Excitonic Circuits”
- George Bullard** (Duke University)
“Polymer Wrapped SWNT Hybrid Nanostructures - Exploring the Factors that Give Rise to Efficient Photoinduced Charge Carrier Generation”
- Naveen Dandu** (North Dakota State University)
“Effect of charge and surface defects on the Electronic Structure and Optical Properties of CdSe Quantum Dots”
- Veit Giegold** (LMU Munich)
“Probing and Controlling Optical Coherences in Single Nanostructures and 2D Materials”
- Brendan Gifford** (North Dakota State University)
“Theoretical Insights into End Group Effects on Photophysics of Capped Single Walled Carbon Nanotubes”
- Morgan Hammer** (LANL)
- Nicolai Hartmann** (LANL)
“Photoluminescence Relaxation Dynamics of Covalently Doped Carbon Nanotubes”
- Mohammed Jabed** (North Dakota State University)
“Size Dependent Photophysical and Electrochemical Properties of Silver Clusters Capped by Cytosine”
- Joanna Jankowska** (University of Southern California)
“Understanding the Role of Organic-Inorganic Layer Coupling in Perovskite Materials for Photovoltaics - How the Microscopic Ferroelectric Effect Impacts the Electron-Hole Recombination”
- Souratosh Khan** (University of Arizona)
“Photophysics of Triplet and Triplet-Triplet Singlet States in Acene Dimers and Crystals”
- Evan Lafalce** (University of Utah)
“Optimization and Application of Optical Gain in CdSe/Cd(1-x)Zn(x)Se(1-y)S(y) Core/Alloyed-Shell Quantum Dots”
- Hao Li** (University of Houston)
“Modelling of Charge Carrier Generation in Organic Semiconductors by Photoinduced Absorption-Detected Two-Dimensional Coherent Excitation Spectroscopy”
- Steven Lopez** (Harvard University)
“In Silico Screening of Non-Fullerene Acceptor Materials for Applications of Organic Photovoltaic Devices: A Harvard Clean Energy Project Study”
- Levi Lystrom** (North Dakota State University)

“Understanding Why Pure Ligand Exchange with Dithiocarbamate is Impractical”

- Ben Nebgen** (University of Southern California)
“Simulation of Electron and Energy Transfer Using the Fragment Molecular Orbital Method”
- Tammie Nelson** (LANL)
“Surface Hopping for Extended Molecular Systems: On-the-Fly Limiting of Essential Excited States”
- Amanda Neukirch** (LANL)
“Light Induced Polaron Formation in Perovskite Solar Cell Devices”
- Parmeet Nijjar** (University of Southern California)
“Long-Lived Quantum Coherence in 2D CdSe Nanoplatelets at Room Temperature”
- Whitney Ong** (North Dakota State University)
“Oxidation of PbSe Quantum Dots: Insights from First-Principle Calculations”
- Jacob Pettine** (JILA, University of Colorado)
“Ultrafast Energy-Resolved Studies of Hot Electron Dynamics in Single Gold Nanorods”
- Shahnawaz Rather** (Princeton)
“Ultrafast Photo-induced Electron Transfer Reaction Drives Abrupt Phase Decoherence”
- Benjamin Rudsteyn** (Yale University)
“Strong Binding of CdSe Quantum Dots to Single-Walled Carbon Nanotubes”
- Andrew Sifain** (University of Southern California)
“One- and Two-Photon Absorption in Conjugated Energetic Molecules”
- Hyung-Jun Song** (LANL)
“Ultimate Quantum Dot Luminescent Solar Concentrators Employing Selective Reflector”
- Kyle Throssell** (Wesleyan University)
“Density Corrections for Approximate Molecular Orbital Theory: NDBEBO”
- Roman Vaxenburg** (George Mason University)
“Biexciton Auger Recombination in CdSe/CdS Core-Shell Nanocrystals”
- Dayton J. Vogel** (University of South Dakota)
“Competing Relaxation Mechanisms for Improving Quantum Efficiency in Methylammonium Lead Iodide Perovskite Quantum Dots”
- Zhehui Wang** (LANL)
“Ultrafast High-Energy Photon Imaging, a MaRIE-Driven Technology for and by Mesoscopic Materials”
- Alex White** (LANL)
“Coupled Wavepackets for Non-Adiabatic Molecular Dynamics”
- Tzu-Cheng Wu** (University of New Mexico)
- Hung-Ju Yen** (LANL)
“Bottom-up Synthetic Nanographenes for Highly Efficient Lithium Storage”
- Hyeong-Jin Yun** (LANL)
“Defect Control in CuInSexS2-x Quantum Dots to Enhance Their Electronic Devices Performance”
- Yaxin Zhai** (University of Utah)
“Monitoring Transient Gain-Saturation in Variable Stripe Length Measurements of DOO-PPV”

Multiscale Modeling of Light Harvesting and Photoprotection in Plants

Doran I. G. Bennett¹

Kapil Amarnath¹, Graham Fleming²

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Light harvesting by Photosystem II, the photosynthetic apparatus of plants, depends on both sub-ps exciton dynamics within individual pigment protein complexes and exciton migration across the thylakoid membrane on the >10ps timescale. While the short time dynamics of light harvesting have been extensively studied using non-linear spectroscopy, the long time spatial dynamics across the thylakoid have not been accessible because of the large number of iso-energetic pigments. We have combined information gathered from thylakoid membrane microscopy and non-linear spectroscopic measurements of isolated pigment protein complexes in vitro to describe exciton transport across an intact thylakoid membrane. This model reproduces time-resolved fluorescence measurements of PSII in vivo without free parameters and predicts an exciton diffusion length of ~50 nm, much larger than the typical disordered organic semiconductor (<10 nm). Finally, we explore the relationship between the structure of the antenna array, the exciton diffusion dynamics, and the functional behaviors of PSII as captured by photochemical yield and photoprotection.

Transient Redistribution of Ultrafast Electronic Coherences (TRUECARS)

Kochise Bennett

University of California, Irvine

Conical intersections (CIs) dominate the pathways that determine the outcomes of virtually all photochemical molecular processes. The vanishing electronic energy gap combined with the fast passage through CIs greatly complicates their direct observation and the experimental evidence is generally inferred from fast reaction rates and vibrational signatures. We show that short X-ray pulses can directly detect the passage through a CI with adequate temporal and spectral sensitivity. The non-adiabatic coupling that exists in the region of a CI redistributes electronic population but also generates electronic coherence. This coherent oscillation can then be detected via a coherent Raman process that employs a composite femtosecond/attosecond X-ray pulse. This technique, dubbed Transient Redistribution of Ultrafast Electronic Coherences (TRUECARS) is reminiscent of Coherent Anti-Stokes Raman Spectroscopy (CARS) in that a coherent oscillation is set in motion and then monitored, but differs in that the dynamics is electronic (CARS generally observes nuclear dynamics) and the coherence is generated internally by passage through a region of non-adiabatic coupling rather than by an externally applied laser.

Konstantin E. Dorfman, Kochise Bennett, and Shaul Mukamel, "Detecting electronic coherence by multidimensional broadband stimulated x-ray Raman signals", *Phys. Rev. A* 92, 023826 – Published 17 August 2015

Markus Kowalewski, Kochise Bennett, Konstantin E. Dorfman, and Shaul Mukamel, "Catching Conical Intersections in the Act: Monitoring Transient Electronic Coherences by Attosecond Stimulated X-Ray Raman Signals", *Phys. Rev. Lett.* 115, 193003 – Published 5 November 2015

Nonequilibrium Solvent Effects in Born-Oppenheimer Molecular Dynamics for Ground and Excited Electronic States

Josiah A. Bjorgaard

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The effects of solvent on molecular processes such as excited state relaxation and photochemical reaction often occurs in a nonequilibrium regime. Dynamic processes such as these can be simulated using excited state molecular dynamics. A new method of simulating nonequilibrium solvent effects in excited state molecular dynamics using linear-response time-dependent density functional theory and apparent surface charge methods is presented. Developments include a propagation method for solvent degrees of freedom and analytical energy gradients for the calculation of forces. Molecular dynamics of acetaldehyde in water or acetonitrile are demonstrated where the solute-solvent system is out of equilibrium due to photoexcitation and emission.

Charge Transfer in the Lithium-Benzene Complex: Understanding the Role of the Hartree-Fock Exchange

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Most approximations to the exchange-correlation functional of Kohn-Sham Density Functional Theory lead to delocalization errors that undermine the description of charge-transfer phenomena. An accurate description of charge-transfer phenomena is crucial in modeling of novel electric energy storage systems such as supercapacitors, which are becoming increasingly used in the development of clean and renewable energy technology. We explore how various approximate functionals and charge-distribution schemes describe ground-state atomic-charge distributions in the lithium-benzene complex. To understand the trends, we compare with Hartree-Fock (HF) and correlated post-HF calculations, confirming that the HOMO-LUMO gap is narrower in semilocal functionals, but widened by hybrid functionals with large fractions of HF-exchange. Calculations with the equation-of-motion coupled-cluster method with single and double excitations for electron attachment provide evidence of a states crossing. When the perpendicular separation between the lithium atom and the benzene plane is closer than 1.465 Å, the long-separation ground state (Benzene + Li[•]), in which the SOMO is mainly localized over lithium, crosses with a charge-transfer state, in which the SOMO localizes exclusively over the benzene molecule. We concluded that, although charge-transfer phenomena are multi-configurational in nature, hybrid functionals with an admixture of HF-exchange are useful in describing charge-transfer in the lithium-benzene model.

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Excited State Absorption in Tetrapyrrolyl Porphyrins

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Screening materials for optical limiting properties is a necessity to drive further design principles. Population of significant amounts of excited states which absorb differently than the ground state, are fundamentally important to this process, and may be useful in design of future photo-optic devices. In this work, we examine a series of 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) compounds for their optical limiting capabilities via DFT/RT-TDDFT methods. Utilization of the real-time propagation of the electron density allows us to model the time dependent observable quantities of the complex. Though costly, this approach can afford the entire excitation spectrum and be used to rapidly screen materials for optical limiting properties.

Optimization of Energy Transfer in DNA-Dye Excitonic Circuits

Will Bricker¹

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In natural photosynthetic systems, quantum coherent effects contribute to a more efficient energy transfer pathway when light-harvesting chromophores are closely packed or aggregated (Scholes, 2011). These effects may be imitated by exploiting the J-aggregation behavior of certain dyes, such as cyanines (Wrthner, 2011). A proof-of-concept study has established that J-aggregated pseudoisocyanine (PIC) dyes can be rationally attached to DNA scaffolding in what has been termed a J-bit (Boulais, In Review). These J-bits are stable and controllable J-aggregated dye units which can self-assemble on DNA circuits in the minor groove of poly-A/T DNA sequences. In this research, we extend the previous study to determine how to optimize the excitonic behavior, and therefore, the energy transfer in these DNA-dye circuits. Since the geometry of the DNA scaffold can be precisely controlled (Dietz, 2009), the geometry of J-aggregated dyes assembled on the DNA scaffold can also be controlled. Several factors are considered in this excitonic optimization study, including the size of J-bit, and geometry factors between J-bits, such as distance and orientational dependence, as controlled by the type of DNA origami scaffold.

These factors are optimized via an in-depth computational study, involving molecular docking and molecular mechanics of the DNA-dye assemblies, and quantum dynamics of the excitonic transport behavior due to J-aggregation. Excitonic transport is calculated using a stochastic Schrodinger equation formalism (Ishizaki, 2009). The best DNA-dye candidates for efficient energy transfer are experimentally confirmed using spectroscopic techniques. Modeling these DNA-dye excitonic circuits allows a broader view of the various factors involved in efficient energy transfer, and will lead to quicker optimization and implementation of effective nanophotonic technologies.

G. Scholes, et al. Lessons from nature about solar light harvesting. *Nat. Chem.* 3, 763-774 (2011).

F. Wrthner, et al. J-aggregates: from serendipitous discovery to supra-molecular engineering of functional dye materials. *Angew. Chem. Int. Ed.* 50, 3376-3410 (2011).

E. Boulais, et al. Programming excitonic circuits using DNA scaffolds. (In Review)

H. Dietz, et al. Folding DNA into twisted and curved nanoscale shapes. *Science* 325, 725-730 (2009).

A. Ishizaki, et al. On the adequacy of the Redfield equation and related approaches to the study of quantum dynamics in electronic energy transfer. *J. Chem. Phys.* 130, 234110 (2009).

Polymer Wrapped SWNT Hybrid Nanostructures - Exploring the Factors that Give Rise to Efficient Photoinduced Charge Carrier Generation

George Bullard

Duke University

Progress on the design and construction of perylene diimide (PDI) containing poly(aryleneethynylene) polymers (S-PBN(b)-Ph4-PDI) and the subsequent hybrid nanostructures formed when dispersing single walled carbon nanotubes (SWNTs) is described. Based on established design principles, a control polymer exhibited well defined periodic helical wrapping of individualized [7,5]SWNTs with a pitch length of 8 ± 2 nm. The ability to tune the excited state dynamics of the system through PDI modification is currently being explored. Of particular interest is the ability to generate multiple charge separated states on a single nanoscale object upon photoexcitation to explore: 1) how exciton density affects charge separation (CS) and charge recombination (CR) dynamics; 2) how carrier-carrier and carrier-exciton interactions compete with CS and CR; 3) if there are any unique spectroscopic signatures associated with these processes; and 4) how thermodynamic forces dictate CS and CR dynamics.

Effect of charge and surface defects on the Electronic Structure and Optical Properties of CdSe Quantum Dots

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We investigated the effect of surface defects, such as losing ligands and external charge, on the electronic structure and optical properties in thiols (CH₃SH) passivated Cd₃₃Se₃₃ quantum dots (QDs) in various solvents. Our calculations showed that a non-polar solvent such as chloroform assists in H⁺ transfer from several thiol ligands to surface selenium atoms. This process introduced trap states at the edge of the bandgap resulting in red shifts in their absorption spectra. In another study, where a polar solvent such as acetonitrile was used, we did not observe any H⁺ transfer from the thiol ligands to surface selenium atoms. We have also simulated Cd₃₃Se₃₃ QDs by passivating Se surface atoms by H ligands and Cd surface atoms by thiolate (CH₃S⁻) ligands. For full passivation of all Se surface ions by H⁺ and all Cd surface atoms by thiolate (CH₃S⁻) ligands, absorption spectra are significantly red-shifted with the lowest-energy transitions having partially optically-inactive character (semi-dark). We have also investigated the effect of the charge defects and observed an increase in the bandgap. To further understand the effect of the ligand-QD and QD-QD interactions on their optical properties, Forster Resonance Energy Transfer calculations are performed between two Cd₃₃Se₃₃ quantum dots with and without charge and surface defects providing insights into the energy transfers in these systems.

Probing and Controlling Optical Coherences in Single Nanostructures and 2D Materials

Veit Giegold¹

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Optical detection and coherent control of quantum interferences in nanostructures provide new insight into photo-induced phenomena and could open up novel applications in nanophotonics and optoelectronics [1]. Here, we observe and manipulate the coherent optical response of individual semiconducting single-walled carbon nanotubes (SWCNTs), Graphene and TMDs using femtosecond laser pulse shaping microscopy [2,3].

Single (5,4) SWCNTs with an average length of 400 nm excited with a pair of phase-locked 20 fs laser pulses exhibit beating patterns in their photoluminescence (PL) intensity analogous to Rabi oscillations in a two-level system. We show that light absorption of single SWCNTs can be controlled within their electronic dephasing time, varying between nanotubes from 20 to 65 fs, by tuning the relative carrier envelope phase of the pulses. For longer pulse separation coherent radial breathing mode excitations of the nanotubes with a period of 90 fs are observed. In addition, we determine the oscillator strength on the single nanotube level and estimate the coherence length of the photoexcited state.

For MoSe₂ shorter dephasing times are observed, presumably due to the simultaneous excitation of different excited states.

[1] D. Brinks, F. D. Stefani, F. Kulzer, R. Hildner, T. H. Taminiau, Y. Avlasevich, K. Mollen and N. F. van Hulst, Nature 465, 905 (2010).

[2] R. Ciesielski, A. Comin, M. Handloser, K. Donkers, G. Piredda, A. Lombardo, A. C. Ferrari and A. Hartschuh, Nano Lett. 15, 4968 (2015).

[3] T. Winzer, R. Ciesielski, M. Handloser, A. Comin, A. Hartschuh and E. Malic, Nano Lett. 15, 1141 (2015)

Theoretical Insights into End Group Effects on Photophysics of Capped Single Walled Carbon Nanotubes

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Single Walled Carbon Nanotubes (SWCNTs) are pseudo one-dimensional nanostructures with unique chirality-dependent optical and electronic properties. As such, they are promising materials for use as active layers in a wide range of devices including photovoltaics, optoelectronics, and sensors. Chemical functionalization of SWCNTs extends their technological abilities. Due to the chemical inert nature of SWCNTs, their functionalization is expected to occur predominantly near the edges, while precise positions of functional groups is challenging to probe experimentally. We computationally investigate the direct effects on the electronic structure of the SWCNTs from passivation of the edges with various groups. Our studies compare the results of semi empirical techniques and density functional theory to determine the electronic effects of terminating the SWCNTs by functionalizing the edges with groups attached via sp² and sp³ hybridized bonds, while also differ in their electron donating/withdrawing abilities. We have found that precise functional group is not as relevant as the bond order of the connectivity at the edges of the SWCNT for determining the HOMO-LUMO gap and therefore optical properties. For the (10,5) SWCNT, the widest HOMO-LUMO gap is acquired by functionalizing the edges with two groups where the atom bonded to the SWCNT is sp² hybridized. This configuration results in electron density being distributed through the length of the SWCNT, and in contrast to other configurations doesn't result in the introduction of electronic states localized on the edges.

Photoluminescence Relaxation Dynamics of Covalently Doped Carbon Nanotubes

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New red-shifted emitting states in carbon nanotubes, introduced by stable covalently-bound dopants,[1,2] are gaining attention for their potential to boost photoluminescence quantum yields,[1,2] add new functionality,[3] and serve as single photon emitters.[4] Critical to these possibilities is the demonstration of exciton localization or trapping at individual dopant sites.[5] As a consequence of trapping, exciton dynamics are significantly altered, with photoluminescence (PL) lifetimes being extended significantly.[4] We will present a detailed study of the emission dynamics associated with dopant states introduced by aryl diazonium functionalization of semiconducting carbon nanotubes. Dopant-state PL lifetimes are found to increase by around a factor of 10 in comparison to E11 exciton lifetimes. Dependence of lifetimes on nanotube chirality, specific dopant, and dielectric environment will be presented and shown to exhibit a strong dependence on emission energy. Evidence for existence of an associated dark trap state will also be given. The results indicate multiple mechanisms for radiative and nonradiative decay. Of particular interest relevant to PL stability is the relation of PL decay to potential exciton detrapping. Possible contributing factors to detrapping, including detrapping energy, will be discussed.

[1] Ghosh, S. et al., Science 2010, 330, 1656.

[2] Piao, Y. et al., Nat. Chem. 2013, 5, 840.

[3] Kwon, H. et al., J. Phys. Chem. C 2015, 119, 3733.

[4] Ma, X. et al., Nat. Nanotechnol. 2015, 10, 671.

[5] Hartmann, N.F. et al., Nanoscale 2015, 7, 20521.

Size Dependent Photophysical and Electrochemical Properties of Silver Clusters Capped by Cytosine

Mohammed A Javed

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DNA are widely used to bottom-up construction of Silver nanoclusters exhibiting high stability. Understanding the redox and photophysical properties of metal nanocluster is important considering their potential application in sensing, catalysis, photophysical application. Herein, we performed Density Functional Theory (DFT) calculations to optimize silver clusters with varying sizes from 3-9 atoms, passivated by the DNA base, cytosine, in vacuum and water, in their neutral and charged forms. Time dependent DFT (TD-DFT) is used to investigate optical properties of these clusters. We observed that there is a significant difference in the overall absorption spectra between charged and neutral systems. Also, we see a difference in spectra between odd and even number in silver cluster size, with the lowest energy peaks corresponding to the doublet transitions in Si_5 , Si_7 and Si_6^+ , while the second main band originate from singlet transitions in Si_5^+ , Si_7^+ and Si_6 . Natural transition orbital plots show a significant charge transfer behavior between silver and cytosine in their first excited state near 1-2 eV. A strong peak around 3 eV is due to an admix of charge transfer and silver d-d transitions. We also calculate reduction potential which reveal a significant difference of the reduction potential of ground state singlet and doublet multiplicity of odd and even number Ag cluster. It also shows a trend to increase redox potential with increasing size of the silver cluster.

Understanding the Role of Organic-Inorganic Layer Coupling in Perovskite Materials for Photovoltaics - How the Microscopic Ferroelectric Effect Impacts the Electron-Hole Recombination

Joanna Jankowska

Oleg V. Prezhdo

University of Southern California

Hybrid organic-inorganic perovskite materials, since the pioneering reports of Mitzi et al. [1], have been attracting rapidly growing interest as robust active materials for the solar photovoltaics applications [2, 3]. Merging distinct properties of organic and inorganic components within a single molecular composite, hybrid perovskites offer plenteous possibilities for tuning their photophysical and electronic properties. In particular, in a recent experimental study Liao et al. (Nat. Commun., 6, 2015, 7338) showed that these materials may give rise to a new class of room-temperature ferroelectric semiconductors.

Here we report results of a non-adiabatic molecular dynamics investigation of a microscopic ferroelectric effect on hole-electron recombination in a model hybrid ferroelectric perovskite: (benzylammonium)₂PbCl₄. We find that homogenous arrangement of micro-domains originating from interacting polarized C=N bonds enhances the non-radiative hole-electron recombination through coupling with vibrations of the halide network.

[1] D. B. Mitzi, C. A. Feild, W. T. A. Harrison, and A. M. Guloy, Conducting tin halides with a layered organic-based perovskite structure, Nat. 369, 467 (1994)

[2] Z. Fan, K. Sunc, and J. Wang, Perovskites for photovoltaics: a combined review of organic/inorganic halide perovskites and ferroelectric oxide perovskites, J. Mater. Chem. A, 3, 18809 (2015)

[3] T. M. Brenner, D. A. Egger, L. Kronik, G. Hodes, and D. Cahen, Hybrid organic/inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties, Nat. Rev. 1, 15007 (2016)

Photophysics of Triplet and Triplet-Triplet Singlet States in Acene Dimers and Crystals

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Sumit Mazumdar

University of Arizona, Department of Physics

The process of singlet fission (SF), in which a photoexcited singlet exciton dissociates into two triplet excitons has been studied experimentally in aggregates as well as dimers of acene molecules. While ultrafast spectroscopy and time-resolved studies of excited state absorptions are the experimental tools of probing SF, there exist few, if any, theoretical studies of excited state absorptions in these systems. This is particularly true for the triplet-triplet state with overall singlet character, and the singlet excimer, which are believed to be intermediates in the SF process. We present high order configuration interaction calculations of excited state absorptions from the excimer, the spin triplet state, the optical exciton and the triplet-triplet state in acene aggregates and dimers [1], in order to reach understanding of the feasibility and efficiency of the SF process in various cases. Detailed comparisons to experiments are made.

[1] K. Aryanpour, A. Shukla, S. Mazumdar J. Phys. Chem. C 2015, 119, 6966-6979

Optimization and Application of Optical Gain in CdSe/Cd(1-x)Zn(x)Se(1-y)S(y) Core/Alloyed-Shell Quantum Dots

Evan Lafalce¹

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Colloidal quantum dots (CQDs) are of considerable interest for lasing applications due to their tunable bandgaps through size and composition, and high optical gains and low lasing thresholds obtained through quantum confinement. We investigated the lasing and gain properties of CdSe/Cd(1-x)Zn(x)Se(1-y)S(y) core/alloyed-shell CQDs. The electronic potential gradient was employed to reduce the energy level mismatch between more typical CdSe/ZnS core/shell CQDs, resulting in a larger Stokes shift of PL, reduced Auger recombination and lower thresholds for laser action. Furthermore, exchange of the native oleic acid ligands with amine groups of different sizes as well as cross-linked ligand networks was used to achieve enhanced QD loading and stability in thin films. Planar waveguides constructed with such films as active layers exhibit gains as high as 650cm⁻¹ as measured by the Variable Stripe Length technique, and thresholds for ASE as low as 60 J/cm² upon optically pumping with pulsed excitation. A detailed characterization of the gain, loss and threshold behavior as a function of the excitation intensity, spectral energy and pulse width was conducted to elucidate the interesting photo-physics of these CQD films that lead to the favorable lasing characteristics and an exceptionally broad gain-bandwidth. In addition to conventional applications for optical gain materials, exotic optical phenomenon based on parity-time symmetric systems has recently been demonstrated in coupled resonators with specific values of optical gain and loss, respectively. We investigated these effects in pairs of coupled micro-disk lasers fabricated from CQDs studied here. The high gain achievable in this material caused PT-symmetry breaking at low thresholds and induced large coupling-mediated nonlinear effects on the observed laser modes.

***In Silico* Screening of Non-Fullerene Acceptor Materials for Applications of Organic Photovoltaic Devices: A Harvard Clean Energy Project Study**

Steven Lopez

Harvard University

Organic Photovoltaics (OPVs) have shown a steady growth in efficiencies since the 1980s, and reported percent conversion efficiencies (PCEs) up to 12% are reported in multi-junction cells. OPVs are lightweight, easy to produce, and feature chemically diverse components. While PCBM is the standard fullerene n-type (acceptor) material, it is not without limitations, which include limited spectral breadth, small range of LUMO energies, and relatively high costs of industrial production. We have undertaken an *in silico* highthroughput screening utilizing the *Harvard Clean Energy Project* to explore the chemical space associated with non-fullerene acceptor materials. A library of 100,000 n-type materials including perylene diimides, tetraazabenzodifluoroanthenes, diketopyrrolopyrroles, and fluoroanthene-fused imides. This work is carried out through a tight feedback loop with experimental colleagues that synthesize target materials and create OPV devices.

Understanding Why Pure Ligand Exchange with Dithiocarbamate is Impractical

Levi Lystrom

Department of Chemistry and Biochemistry North Dakota State University

Rationally designing ligands for quantum dots (QDs) has attracted the attention of the scientific community because the appropriate ligand can tune the optoelectronic properties of QDs for various applications. The ligands used in synthesis are typically carboxylic acid, amine, and phosphine derivatives because they are thermodynamically very stable, but these ligands are not effective in tuning the QD's properties. Ligand exchange therefore is vital and studies have shown that dithiocarbamate (DTC) is one rationally designed ligand. However, these studies have not investigated how stable the DTC is during the exchange; most work had looked at the overall effect in terms of fully exchanging native ligands. The purpose of this study is to gain fundamental knowledge of DTC and its ability to passivate CdSe QDs. Density functional theory calculations have been carried out and have provided insight into the ground state properties. These calculations have shown that DTC is less effective at ligand exchange than previously thought because during exchange methanol is used to precipitate the QDs. The calculated binding of DTC to QDs is unfavorable in methanol and experimentally the rate of decomposition in methanol is significantly higher. The present study indicates that the change in optoelectronic properties of QD's is not due to only exchange of DTC but is complicated by the binding of the products for decomposition of DTC. Future studies will highlight the effects of ligand exchange in terms of several ligands being exchange not only DTC.

Simulation of Electron and Energy Transfer Using the Fragment Molecular Orbital Method

Ben Nebgen
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Modeling electron and energy transport processes in experimental organic photovoltaic systems is challenging due to both the size of the systems as well as the complexity of excited state ab-initio calculations. Here we seek to speed the simulation of electron and energy transport processes using the Fragment Molecular Orbital (FMO) method. This method breaks a single large system into many small fragments which are solved in a self-consistent manner to both intrinsically decrease the difficulty of $O(N^4)$ ab-initio calculations and also allow them to be parallelized efficiently on modern supercomputers. In the FMO method, an ab-initio calculation is performed on each fragment and each fragment pair to obtain gradient information necessary to compute a molecular dynamics trajectory. Using the dimer calculation intrinsic to the FMO method the inter-fragment non-adiabatic couplings for each time step are computed and used to determine the rate of electron and energy transfer between two fragments. This method is applied to variants of Platinum Bipyridine-Fullerene donor chromophore acceptor triads to determine the electron and energy transfer rate from the Platinum antenna complex to the Fullerene acceptor after excitation by a photon. These simulations have proven very accurate at replicating the energy and electron transfer times of these systems as observed by transient absorption spectroscopy.

Surface Hopping for Extended Molecular Systems: On-the-Fly Limiting of Essential Excited States

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The simulation of nonadiabatic dynamics in extended molecular systems involving hundreds of atoms and large densities of states is particularly challenging and computationally demanding. Nonadiabatic coupling terms (NACTs) represent a significant numerical bottleneck in surface hopping approaches. Rather than using unreliable NACT cutting schemes, here we develop “on-the-fly” state limiting methods to eliminate states that are no longer essential for the non-radiative relaxation dynamics as a trajectory proceeds. We propose a state number criteria and an energy-based state limit. The latter is more physically relevant by requiring a user-imposed energy threshold. For this purpose, we introduce a local kinetic energy gauge by summing contributions from atoms within the spatial localization of the electronic wavefunction to define the energy available for upward hops. The proposed state limiting schemes are implemented within the nonadiabatic excited-state molecular dynamics framework to simulate photoinduced relaxation in poly-phenylene vinylene (PPV) and branched poly-phenylene ethynylene (PPE) oligomers for benchmark evaluation. We find that the local kinetic energy threshold combined with the energy-based state limit provides a physically relevant approach that can be extended to any molecular system without requiring a priori knowledge of the excited state manifold. Most importantly, the observed reduction of numerical cost would reach orders of magnitude in larger molecular systems with hundreds of excited states.

Light Induced Polaron Formation in Perovskite Solar Cell Devices

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The need for an affordable, clean, and abundant source of energy has generated large amounts of research in solution processed solar cell materials. The MAPbI₃ has rapidly emerged as a top candidate for the active layer of photovoltaic devices. In the last 6 years, the efficiencies of devices made with this material have increased from 3.5% to over 20%. Despite the remarkable progress associated with perovskite materials, there are still many fundamental questions that need to be addressed regarding their lack of photo-stability over prolonged solar irradiation. Recent experiments on photo-degradation under constant illumination have found fast self-healing by resting the device in the dark for less than 1 minute. Density functional theory and symmetry analysis show that localized charge states couple to local structural lattice distortions and methyl ammonium quasitatic configurations. Once translational symmetry is lost, additional bonding configurations become symmetry allowed, triggering localized charges in the vicinity over time under constant illumination, thus seeding the formation of macroscopic charged domains and preventing efficient charge extraction. Here we present an in-depth study of polaron formation and binding energy at the atomistic level.

Long-Lived Quantum Coherence in 2D CdSe Nanoplatelets at Room Temperature

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Recent experiments on CdSe nanoplatelets synthesized with precisely controlled thickness that eliminates ensemble disorder have allowed measurement of long-lived coherence at room temperature. We have studied the exciton-exciton coherence in two-dimensional CdSe and CdSe/CdZnS core/shell systems at room temperature using atomistic molecular dynamics simulations and electronic structure calculations. We found that the longer dephasing time is a consequence of the small fluctuations in the energy gap between the two excitons. The heavy-hole and the light-hole excitons couple to the same phonon modes causing similar energy fluctuations of the two excitons which lead to the observed longer quantum coherence lifetime.

Oxidation of PbSe Quantum Dots: Insights from First-Principle Calculations

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It is known that quantum dots (QDs) exposed to air commonly demonstrate decrease in their photoluminescence (PL). However, mechanisms of QDs oxidation causing the PL quenching are not fully understood. We use density functional theory (DFT) and time dependent DFT (TDDFT) to investigate the interaction of oxygen in its molecular, atomic, and ionic forms with different surfaces of lead selenide (PbSe) QDs and its effect on the electronic and optical properties of QDs. We found that oxygen concentrations and positions at the QD facets govern an appearance of trap states at the bandgap of QDs. For 2 nm PbSe QDs, as the concentration of oxygen atoms at the surface increases, oxygens attempt to penetrate inside the QD shifting Se ions in the outer shell of the QD. In contrast, oxygen ions attempt to bind and then remove Pb ions from the QDs surface, resulting in Se-enriched QDs of smaller sizes when they are exposed at high concentrations on the QDs surface. In both cases, adsorption of oxygen atoms and ions are accompanied by additional oxygen-associated trap states appearing at the edges of the QDs bandgap. Molecular oxygen shows minor effects on both the geometry and the electronic structure of QDs.

Ultrafast Energy-Resolved Studies of Hot Electron Dynamics in Single Gold Nanorods

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Noble metal nanoparticles and nanostructures are attractive candidates for next-generation devices such as photodetectors and solar cells due to their strong and highly-tunable interactions with visible light. The design of nanosystems for specific applications is best facilitated by single-nanoparticle studies, where ensemble averaging doesn't obscure any of the detailed physics taking place. Using our unique scanning photoemission imaging microscopy (SPIM) technique, we examine the ultrafast thermalization dynamics of nascent electron distributions excited in single gold nanorods. The technique includes time-resolved pump-probe excitation and energy- and angle-resolved velocity map imaging (VMI) detection. By acquiring VMIs at a series of pump-probe delays, the full dynamical information of excited electrons within the probed excitation energy range can be characterized. We find that the lifetimes of individual electronic excitations obey an inverse-quadratic dependence on the excitation energy. While similar energy-dependent lifetimes have been observed in numerous bulk metal studies, and some studies have addressed ensemble and even single-nanostructure electronic lifetimes, this study represents the first definitive characterization of excited electron lifetimes in single nanoparticle systems, to the best of our knowledge. These findings have important implications for any applications involving electron transport out of nanoparticles, such as solar energy conversion, photodetection, and photocatalysis.

Ultrafast Photo-induced Electron Transfer Reaction Drives Abrupt Phase Decoherence

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A coherent superposition of vibrational states generated in the reactant state of an electron transfer (ET) system carries quantum information about the transfer in the form of phase correlations. Rapid loss of phase coherences in the vibrational wavepacket is witnessed during the transition to the ET product state on a 200 fs time scale, in model system of Oxazine in electron-donating solvent. Contrarily, vibrational coherences of the excited state in a nonreactive solvent dephase at a much slower rate (>1 ps). Such an observation is in contrast to the conventional theory, that ET is a mere jump from one chemical species to the other, enabling coherences to survive when following a crude adiabatic Born-Oppenheimer approximation. This rapid phase decoherence suggests, that the population transfer from the reactant to the product state occurs strictly via curve crossing enabled by collective vibration of the modes. The created anharmonicity in the mixing region leads to wavepacket broadening and disperses it into the product potential with significantly faster dephasing. This indication of strong mode mixing or pathway interference results in decoherence of all the Franck-Condon modes in contrast to the specificity in the number of modes involved in conical intersections, an alternate curve crossing pathway.

Strong Binding of CdSe Quantum Dots to Single-Walled Carbon Nanotubes

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Experimentally monitored transient absorption of CdSe quantum dots (QDs) before and after attachment to single-walled carbon nanotubes (SWNTs) show considerably shorter lifetimes with direct covalent binding of the CdSe on SWNTs. This observation may indicate faster deactivation of charge-separated states in CdSe QDs via ultrafast electron transfer from CdSe QD to the SWNTs or formation of strongly coupled nanocomposites. The latter explanation is supported by quantum dynamics simulations of interfacial electron transfer in a fully atomistic model of the molecular assembly that matches the experimental EXAFS spectra and direct comparisons to transient absorption measurements.

One- and Two-Photon Absorption in Conjugated Energetic Molecules

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Initiating an explosive with light has been an active field of research. Common methods for optical initiation require high laser intensities that proceed through indirect mechanisms such as thermal or shock processes. Conjugated energetic molecules (CEMs), however, open the possibility for controlled and direct optical initiation using conventional lasers. CEMs combine the optical properties of carbon-based, conjugated organic molecules with high nitrogen content. Recent progress has been made to strategically alter the molecular structure of CEMs to influence their heat of formation and oxygen balance, two factors that contribute to the sensitivity and strength of an explosive material. The optical range and intensity of excitation are also affected by molecular structure. The extent to which CEMs can be used for optical initiation needs a thorough theoretical investigation. Using time-dependent density functional theory, one- (OPA) and two-photon absorption (TPA) spectra are calculated for a series of CEMs. Vertical excitation energies are compared to experimental spectra for several molecules in the study and are in good agreement. Moreover, TPA peaks are calculated to be on the order of 100 Gs. Our results were computed using the B3LYP functional and a 6-31G* basis set.

Ultimate Quantum Dot Luminescent Solar Concentrators Employing Selective Reflector

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Luminescent solar concentrators (LSCs), comprising fluorophores embedded waveguide slab and edge or side mounted photovoltaic cells (PVs), can concentrate solar light on PVs with low cost. Especially, colloidal core/shell structure quantum dots have drawn much attention due to their large stoke shift, leading to reduced re-absorption losses in LSCs. However, the optical losses during the waveguide to the PVs strikingly increase, as the size of LSC is enlarged. Hence, the attainable concentration of LSC is limited. In this work, we investigate the relationship between optical properties of selective reflector and performance of LSC to find out the way for realizing ultimate LSCs. Monte-Carlo simulation indicates that the average path length of photons elongates three times when highly reflective film ($R > 96\%$) is incorporated to the top window of large sized LSCs (geometric factor = 2000) compared to the case without it. Moreover, escaping photons from the slab are suppressed in the case implementing highly reflective film, originated from recycling them into LSCs. Thus, three times higher concentration and waveguide efficiency are expected in the device surrounded by highly reflective film that those of uncovered case. This result is verified by empirical data using same structured LSCs, which is consistent to theoretical expectation. Consequently, the implementation of LSC allow us to break the attainable concentration limit of LSC. We believe that this work will be a guideline to design highly efficient LSCs.

Density Corrections for Approximate Molecular Orbital Theory: NDBEBO

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Approximate Molecular Orbital theory must overcome the problems inherent in minimum basis set Hartree-Fock in addition to the reduction of terms included in the Fock matrix. We are using a density based correction derived from Mayer Bond orders to account for these problems and improve semi-empirical methods.

Biexciton Auger Recombination in CdSe/CdS Core-Shell Nanocrystals

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We present a theoretical study of positive and negative trion channels of the nonradiative Auger recombination of band-edge biexcitons in CdSe/CdS core/shell nanocrystals. The theory takes into account the biexciton fine-structure produced by the nanocrystal asymmetry and hole-hole exchange interaction. The calculations show that the growth of CdS shell upon CdSe core suppresses the rate of the Auger recombination via negative trion channel, while the more efficient positive trion channel shows much weaker dependence on the shell thickness. We find a strongly oscillatory dependence of the positive and negative trion Auger rates on core and shell sizes. These oscillations can be qualitatively explained in terms of overlap of the ground and excited carrier wavefunctions. Also, the calculations show that increase of temperature accelerates the Auger recombination in CdSe/CdS nanocrystals due to the decrease of the bulk energy gaps of CdSe and CdS. An additional effect of temperature via changes in the population of biexciton fine-structure states can be observed.

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Competing Relaxation Mechanisms for Improving Quantum Efficiency in Methylammonium Lead Iodide Perovskite Quantum Dots

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Many methods for increasing quantum efficiencies (QE) within photovoltaic and optoelectronic processes have been developed such as material interfacing, modified device architecture, and physical constraints to the photoactive material. One such process harnessed by size confinement of the light absorbing material is multi-exciton generation (MEG). This process applied to small bandgap semiconductor quantum dots (QD) has achieved QE over 1.1. Methylammonium lead iodide perovskite (MAPbI₃) materials have successfully been applied in photovoltaic devices with high solar energy conversion efficiencies driving research to reach and understanding of material behavior.² Here we provide a computational approach to studying electronic relaxation processes within a MAPbI₃ QD. Understanding which electronic relaxation mechanisms and their corresponding timescales will allow for a clearer picture into which relaxation processes are of greatest importance and can be harnessed for maximum efficiency. Non-radiative (NR) relaxation rates calculated by nonadiabatic dynamics and density matrix formalism produce rates on the scale of 1ps. Radiative (R) relaxation rates computed by estimating oscillator strengths in the independent orbital approximation³ are on the scale of 10ps. MEG relaxation rates computed with many-body perturbation theory are found to be on the scale of 10fs. From the computed relaxation rates, the mechanism timescales trend in the order of MEG>NR>R. From these results one expects MEG to be a highly probable relaxation process in the MAPbI₃ QD.

[1] Nozik, A.J., Multiple Exciton Generation in Semiconductor Quantum Dots, *Chem Phys Lett* 2008, 457, 3-11. [2] Nie, W., et al., High-Efficiency Solution-Processed Perovskite Solar Cells with Millimeter-Scale Grains. *Science* 2015, 347, 522-525.

[3] Vogel, D.J.; Kilin, D.S., First-Principles Treatment of Photoluminescence in Semiconductors. *J. Phys. Chem. C* 2015, 119, 27954-27964.

Ultrafast High-Energy Photon Imaging, a MaRIE-Driven Technology for and by Mesoscopic Materials

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To advance manufacturing on mesoscale will require both XFEL illumination above 30 keV (MaRIE) and high-performance imaging technologies. The existing detectors and cameras, which rely mostly on electrons or light as signals, are rather primitive on the mesoscale, i.e., dominated by random processes. Mesoscale highways for light (\sim wavelength) and electrons (\sim collection distance) will be revolutionary.

Coupled Wavepackets for Non-Adiabatic Molecular Dynamics

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Understanding and control over light-induced dynamics is critical for efforts to design functional optoelectronic materials for many applications (e.g. solar-energy harvesting). Current simulation methods for such complex non-adiabatic molecular dynamics (NAMD) are either too inefficient to be used for large-scale molecular systems, or are based on approximations that breakdown even in simple systems, especially when quantum coherence and interference are important. Quantitative and predictive simulation of NAMD requires proper treatment of coupled quantum (electrons) and semiclassical (nuclei) subsystems. Coupled Wavepackets (CW) is a novel method that extends Heller's Thawed Gaussian wavepacket dynamics to include non-adiabatic coupling between potential energy surfaces. By studying several standard test problems we demonstrate that the accuracy of the method can be systematically improved while maintaining high efficiency. The method is suitable for investigating the role of quantum coherence in the non-adiabatic dynamics of many-atom molecules.

Bottom-up Synthetic Nanographenes for Highly Efficient Lithium Storage

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Traditional graphene anodes in lithium ion batteries (LIBs) suffer significant performance loss due to the restacking of graphene layers. In this work, we have demonstrated a facile synthesis of preparing a series of graphene-derived nanomaterials. Among other potential applications, these nanomaterials achieved an excellent cyclic durability with much enhanced capacity as novel anode materials in LIBs. These exceptional metrics observed within the novel assemblies is primarily due to the robust structure along with the optimal d-spacing allowing for facilitated Li adsorption/desorption and diffusion. Furthermore, the significantly enhanced rate performance was achieved after optimizing the structure of the self-assemblies. Development of nanomaterials anode suggests that the optimal design of graphene materials with robust structures is very important for next generation LIBs with high-energy storage efficiencies.

Defect Control in CuInSexS2-x Quantum Dots to Enhance Their Electronic Devices Performance

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Colloidal copper indium selenide sulfide (CuInSexS2-x) quantum dots (QDs) are non-toxic alternatives to Cd- or Pb-based QDs for sustainable solar energy applications. The key to using QD thin films in opto-electronic devices such as solar cells is understanding their carrier transport properties. The carrier transport behavior is strongly influenced by various kinds of defects that can serve as carrier traps. To improve the electronic device performance, it is important to control the defect with reducing the number of carrier traps. In this research, we combine field effect transistor (FET) and ultrafast transient photocurrent (u-TPC) measurements to obtain a more complete picture of the nature and role of trap states in CuInSexS2-x QD thin films. Pristine FET devices employing indium contacts exhibit n-type transport with decent electron mobility ($3.95 \times 10^{-3} \text{ cm}^2/\text{Vs}$), but they also indicate high concentrations of free carrier in the films. Early-time dynamical signatures revealed in u-TPC studies suggest that this high carrier density arises from the presence of trap states in CuInSexS2-x QDs. In order to reduce the density of trap states that might be related to surface defects, atomic layer deposition (ALD) technique was used to infill the CuInSexS2-x QD film with amorphous Al2O3. This process results in both higher FET mobilities ($2.0 \times 10^{-2} \text{ cm}^2/\text{Vs}$), and an elimination of trap-related decay signatures in u-TPC measurements. In addition, ALD infilling provides long term air stability of CuInSexS2-x-based devices.

Monitoring Transient Gain-Saturation in Variable Stripe Length Measurements of DOO-PPV*

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The variable stripe length (VSL) technique is a simple and useful technique for determining the optical gain of thin films of novel semiconductors. However, the occurrence of gain-saturation causes deviations from the expected exponential rise in emission intensity with increasing stripe length and a subsequent underestimation of gain. We present a straightforward experimental methodology to determine the pre-saturation gain, g_0 , as well as the saturation length, LS , above which the emission intensity measured from the stripe is affected by propagation through a medium of non-constant gain in the π -conjugated polymer, DOO-PPV. By simultaneously performing transient photo-induced absorption spectroscopy (TAS) to measure the stimulated emission dynamics while measuring the emission from the stripe pump beam, we observe exciton depletion through stimulated emission at precisely the same stripe length at which gain-saturation begins to affect the VSL measurement. Meanwhile, the change in exciton population is unaffected at stripe lengths below LS but above the threshold length, LTH , for observing amplified spontaneous emission. The measured dynamics are consistent with simulations of the coupled rate-equations for the exciton and photon densities as function of position through the stripe. Furthermore, we describe how g_0 and LS may be determined from analysis of the VSL data alone, when TAS is not available.

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