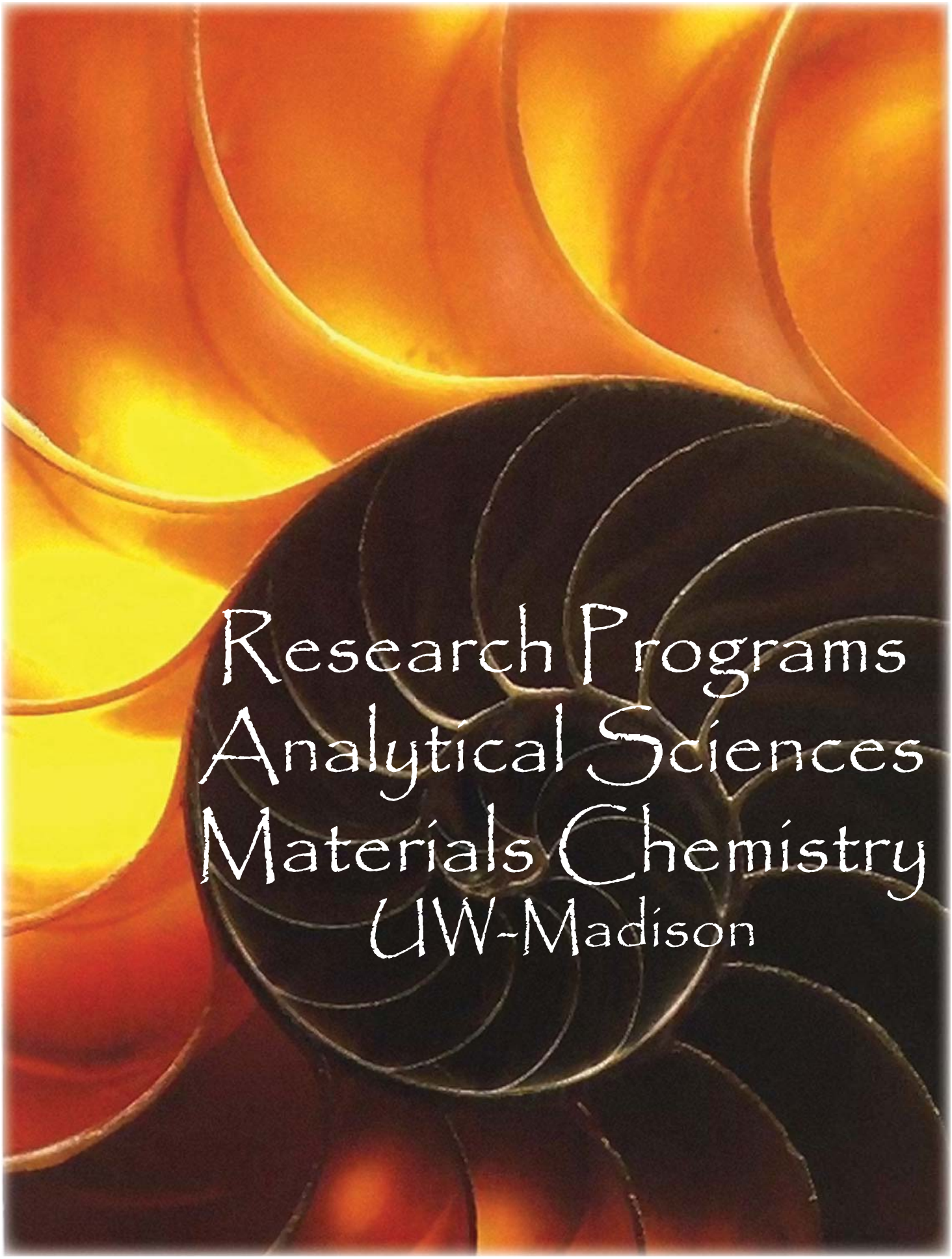
Research Programs
Analytical Sciences
Materials Chemistry
UW-Madison

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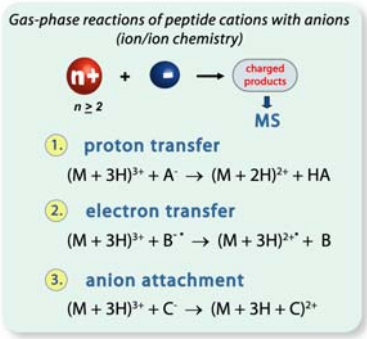
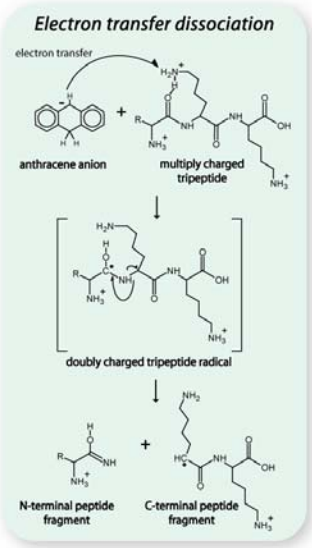
Graduate Students: David Good, Graeme McAlister
Danielle Swaney, April Jue, Jason Keith, Doug Phanstiel
Research Intern: Matthew Wirtala

Research Emphasis: Bioanalytical Chemistry – Mass Spectrometry

Overview. Proteins are involved in nearly every aspect of cellular function. In fact, the characterization of proteins has become such a significant part of modern biology, it has inspired a new discipline: Proteomics – the classification of the protein complement expressed by the genome of an organism. Technology development has, and continues, to drive rapid evolution in this field. We use linear quadrupole ion trap mass spectrometers to perform ion/ion reactions – reactions of small-molecule anions with peptide/protein cations in the gas phase – for protein characterization. In general, these reactions can be classified in three categories: (1) reactions that remove charge from the peptide (proton transfer), (2) reactions that transfer an electron to the peptide (electron transfer dissociation), and (3) reactions that result in the formation of a new covalent complex (anion attachment). We study the first two of these reactions and use them - alone or in sequence - to identify and characterize proteins on a global-scale (proteomics).



Sequencing peptides. The electron transfer reaction results in the attachment of an electron to the protonated peptide. The odd-electron peptide then undergoes very rapid (femtosec) rearrangement with subsequent dissociation of the N – C_α bond. The process occurs efficiently and randomly across the entire sequence of peptides and whole proteins. The aim is to produce a collection of peptide fragment ions that differ in mass by a single amino acid, allowing one to read the amino acid sequence of the peptide. And, by repeating this sequence in a rapid, automated fashion (3- 4 analyses/sec), we can characterize several hundred peptides as they elute from a nanoflow HPLC separation column (~ 2 hour gradient). Most proteomics strategies use enzymes to cleave the analyte proteins into small peptides – peptides that are then sequenced with mass spectrometers. As an alternate method, we are pursuing the use of our technology to directly interrogate intact proteins in the gas-phase. By performing our experiment in the context of the whole protein, we can begin to elucidate important biological events such as global patterns of modification and protein alternative splicing events.



Active projects. Research projects in the Coon lab include: (1) instrumentation development, (2) data analysis software design, (3) fundamental ion chemistry studies, and (4) biological applications of the technology. Biological applications include global identification of protein post-translational modification (specifically phosphorylation), quantitative analysis of protein phosphorylation (i.e., comparative analysis of two cellular states), and cancer biomarker discovery.

(1) Coon JJ, Ueberheide B, Syka JEP, Shabanowitz J, and Hunt DF. Protein identification using sequential ion/ion reactions and tandem mass spectrometry. Proceedings of the National Academy of Sciences of the United States of America, **2005**, 102, 9463-9468.

(2) Good, DM, Coon JJ. Advancing proteomics with ion/ion chemistry. Biotechniques, **2006**, 40, 6, 783-789.

(3) Swaney, DL, McAlister GC, Wirtala M, Schwartz JC, Syka JEP, Coon JJ. A supplemental activation method for high efficiency electron transfer dissociation of doubly protonated peptide precursors. In press. Analytical Chemistry.

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Research Summary

Our group research interests involve the molecular design, synthesis, and characterization of novel functional organic/polymeric materials directed towards electro-optic, photonic and biological applications. Efforts are targeted towards developing versatile synthetic strategies, which would enable the control of nano- functionality, structure and property. Our current research focus is in three major areas: new synthetic strategies towards organic photonic and electronic materials and interfaces, self-assembly of rod-coil block copolymers with conducting/liquid crystalline segments and directed assembly of biological, mesogenic and nonmesogenic molecules using polymeric brushes.

Our goal is to design novel materials by using the advances made in polymer chemistry and organic chemistry for photonic and biological applications. One such example is elecro-optic materials for high – speed modulators. Compared to lithium niobate based modulators, organic materials have advantages in terms of fast response time, low dielectric constant and low dispersion in index of refraction from dc to optical frequencies hence minimizing the velocity mismatch. Our efforts are too design new dendritic materials with most of the desirable properties using elegant chemistry and demonstrate their viability in photonic devices. Fundamental understanding of the organic-inorganic interface and tailoring these interfaces is a critical component to a successful design of one such material.

The second broad area of emphasis is self-assembly and directed-assembly of block copolymers. Self-assembly of block copolymers can result in organization on length scales ranging from few nanometers to micron size scale. Our interest is in designing block copolymers with nanometer size self-assembled structures. These block copolymers are those containing functional units such as liquid crystalline or conducting domains. Understanding the factors governing the phase separation process in these complex rod-coil block copolymers and predicting the morphologies is the key motivation in this area. Directed-assembly of various organic, inorganic and biological molecules using templates of functional polymeric brushes is another area of interest. In the last few years the area of surface anchored polymeric brushes has grown tremendously. Polymeric brushes provide an uniform, high surface density of the desired functionality which makes them attractive for biosensor applications and as interfaces to impart specific properties such as bio-compatibility,

Selected Publications:

"Chromophore Orientation Dynamics, Phase Stability, and Photorefractive Effects in Branched Azobenzene Chromophores" Campbell, V. E.; In, I.; McGee, D. J.; Woodward, N.; Caruso, A.; Gopalan, P.
Macromolecules 39(3)**,** 957-961, **2006**.

"Synthesis and Characterization of Silicon-containing Block Copolymers from Nitroxide-mediated Living Free Radical Polymerization" Fukukawa, K.; Zhu, L.; Gopalan, P.; Ueda, M.; Yang, S.; *Macromolecules,* 38(2)*,* , 263, **2005**.

"Mesophase Transitions, Surface Functionalization, and Growth Mechanism of Semiconducting 6PTTP6 Films from Solution" Katz, H. E.; Siegrist, T.; Lefenfeld, M.; Gopalan, P.; Mushrush, M.; Ocko, B.; Gang, O.; Jisrawl, N.; *J. Phys. Chem. B.*; 108(25), 8567, **2004.**

"Star-Shaped Azo based Dipolar Chromophores: Design, Synthesis, Matrix Compatibility and Electro-optic Activity". Gopalan, P.; Katz, H. E.; Mc Gee, D. J.; Erben, C.; Zielinski, T., Bousquet, D.; Muller, D.; Grazul, J.; Olsson, Y.; *J. Am. Chem. Soc.* **2004**,*126*, 1741.
"Liquid Crystalline Rod-Coil Block Copolymers by Stable Free Radical Polymerization: Synthesis, morphology, and rheology". **Gopalan,P**.; Yuanming Zhang, Xuefa Li, Christopher K. Ober, Ulrich Weisner, Ober, C. K.; *Macromolecules*, **2003,** *36***,** 3357.

"Broadband Modulation of Light Using an Electro-optic Polymer". Lee, M.; Katz, H. E.; Erben, C.; Gill, D. M.; **Gopalan, P**.; Heber, J. D.; Mc Gee, D. J.; *Science*, **2002,** *298,* 1401.

"Fluorinated Mesogen Jacketed Liquid Crystalline Polymers as Low Surface Energy Materials". **Gopalan, P**.; Andruzzi, L.; Li, X.; *Macromolecular Chem & Physics,* **2002**, *203(10-11)*1573.

"Synthesis, Characterization and Redox Reactivity of Novel Quinone Containing Polymers". Takada, K.; **Gopalan, P**.; Ober, C. K.; Abruna, H. D.; *Chemistry of Materials,* **2001,** *13(9),* 2928.

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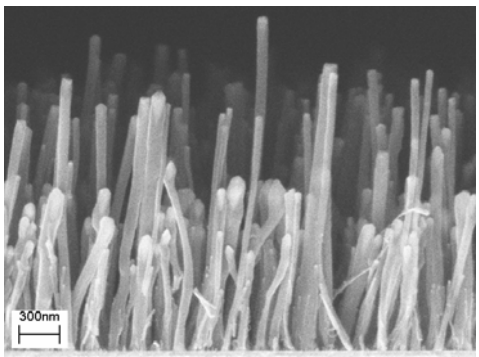
Graduate Students: Ryan Franking, Divya Goel, Stephanie Hogendoorn, Heesuk Kim, Beth Landis, Andrew Mangham, Beth Nichols, Lu Shang, Jeremy Streifer, Bin Sun, Kiu Yuen Tse, Xiaoyu Wang, Patrick Warf

Research Interests:
Surface and interface chemistry, bio-materials interfaces, bioelectronics, nanotechnology, emerging technologies for storage and conversion of electrical energy

Surfaces are important because while for any material most of the atoms are within the bulk, the atoms at the surface often control many of their most important physical properties. Our research is focused on understanding the properties of surfaces and using this information to control interfaces between types of organic and inorganic materials. We refer to this area as "interfacial architecture" because, like an architect designing a building, we are interesting in understanding the physical properties of molecular building-blocks and using this information to design, build, and understand more complex structures with precisely tailored functional properties. Most of our work couples interface chemistry with its effects on electrical/electronic properties.We are especially interested in the use of molecular monolayers to tune the properties of materials such as silicon, diamond, carbon nanotubes, and various types of nanowires, since these materials have especially interesting electrical properties. Hybrid organic/inorganic systems are of increasing importance in emerging areas such as organic and molecular electronics, bio-electronics, biosensing, and emerging technologies for solar energy conversion, fuel cells, and electrical energy storage. Carbon-based materials play particularly important roles because the chemical, electrochemical, and thermal stability of allows it to be used in a wide range of environments.



Forest of vertically aligned carbon nanofibers

Our group spans a range from very fundamental studies of surface chemical reactions and reaction mechanisms, to the practical applications of these materials to important technologies such as biosensing, energy storage, and solar-to-electrical energy conversion. In our group, we have developed a number of new methods for functionalizing surfaces of carbon and other materials with a range of chemical and biological molecules. By linking molecular and/or metallic catalysts to electrodes, the electron-transfer rates for electrocatalytic reactions (of great importance for fuel cells) can be increased. Electrical signals can also be used to control the behavior of materials on small length scales, and electrical controls signals can be used to to manipulate nanoscale materials and to fabricate new types of nanoscale devices. Our work is interdisciplinary in scope and includes students from analytical, materials, and physical chemistry

Selected Research Publications: (Complete list with pdf-format copies at http://hamers.chem.wisc.edu/)

- B.M. Nichols, J.N. Russell, Jr., J.E. Butler, and R.J. Hamers, "Photochemical Functionalization of Hydrogen-terminated Diamond Surfaces: A Structural and Mechanistic Study", Journal of Physical Chemistry B, **109**, 20938-20947 (2005).
- S.E. Baker, K.-Y. Tse, E. Hindin, T.L. Clare, R.J. Hamers, "Covalent Functionalization for Biomolecular Recognition on Vertically Aligned Carbon Nanofibers", Chem. Materials, **17**, 4971-4978 (2005).
- Jeremy A. Streifer, Heesuk Kim, Beth M. Nichols, and Robert J. Hamers,"Covalent functionalization and hybridization of DNA-modified silicon nanowires", Nanotechnology,16, 1868-1873 (2005).

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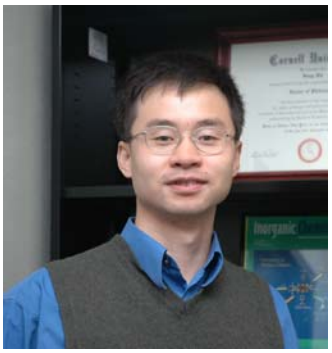


The Lab Group

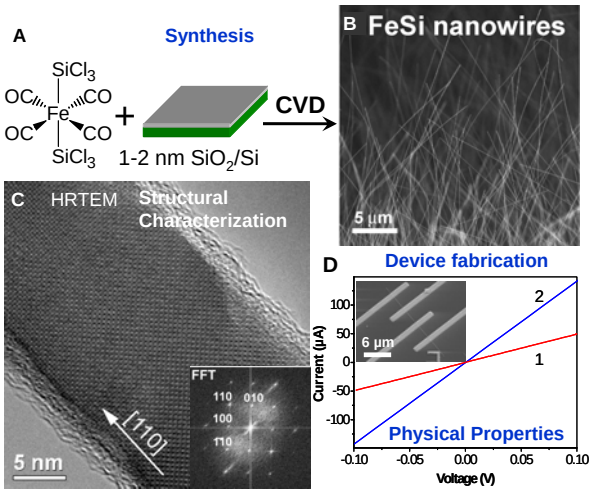
Postdocs: Dr. Fairland Amos, Dr. Yipu Song

Graduate Students: Matthew Bierman, Pinray Huang, Andrew Schmitt, Jeannine Szczech, Stephen Morin, Jeremy Higgins, Rachel Selinsky **Undergraduate Student:** Jonathan Tong

Research Interests:

Chemistry and physics of materials at the nanometer scale.

We not only explore chemical synthesis and carry out the structural characterization of nanomaterials, but also investigate their physical properties, especially through device fabrication and characterization. The emphasis is on developing rational strategies for chemical synthesis, assembly and integration of nanomaterials, and on elucidating fundamental synthesis-structure-property relationships, yet our interdisciplinary endeavors will also lead to applications in nanoelectronics, nanospintronics, optoelectronics, photovoltaic and thermoelectric energy conversion, and biotechnology. Research projects include but not limited to:



Rational synthesis, physical properties, and applications of nanowire materials. A chemist's approach to functional nanomaterials is to build from the bottom up and control the atomic and nanoscale structures drawing from extensive chemical knowledge of the material systems. We apply chemical vapor deposition (CVD), vapor-liquid-solid (VLS) growth, as well as solid-state and solution-phase synthesis, to prepare novel nanowire materials of transition metal silicides and rare earth chalcogenides for spintronic, electronic, photovoltaic, thermoelectric properties and applications. Novel device concepts and applications will arise from these materials, with the ultimate goal of design and engineering of physical properties of nanowire materials with rational chemical strategies.

Biomimetic assembly of functional nanoscale materials. We apply the biomimetic principles derived from biomineralization processes to the assembly of nanoscale functional materials into nanoscale systems. In biomineralization, “matrix” macromolecules can efficiently induce nucleation of inorganic species into crystals at specific locations with controlled size and morphology, and sometimes even with defined growth orientation. We carefully control surface organic molecules to promote heterogeneous nucleation at designated regions while completely suppress homogeneous nucleation elsewhere, therefore enable the controlled bottom-up assembly of inorganic nanomaterials directly from solution. We demonstrate the nucleation and assembly semiconductor arrays on selectively photo-oxidized flexible polymer substrates and exploit them for large-area macroelectronic device applications. Truly nanoscale bottom-up assembly will be realized by using self-assembled nano-structured block copolymers and sequenced biopolymers and as templates.

Biosensing and biotechnological applications of nanomaterials. We are embarking on new projects that aim at using magnetic semiconducting nanowire and nanocrystal materials to enable highly sensitive biological sensing devices and “smart” switchable biological imaging probes. This challenging project will involve molecular and cell biology, biochemistry, surface chemistry, as well as chemistry and physics of nanomaterials.

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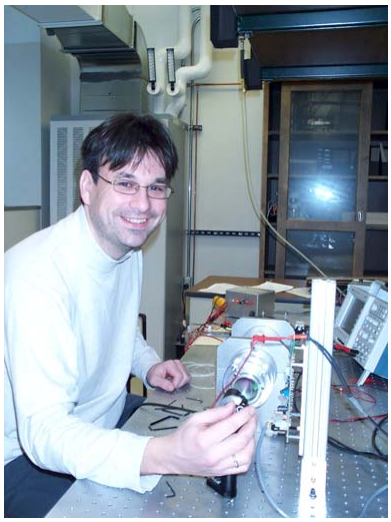

The Keutsch Group:

Graduate Students: Katherine Coens, Joshua DiGangi, Melissa Galloway, John Hottle, Andrew Huisman

Research

Research in the Keutsch Group is highly interdisciplinary and is focused on the tropospheric photochemistry of pollution and the response of greenhouse gas emissions to environmental parameters. To this end we are developing novel highly sensitive *in situ* detection methods:

1. Ground based, robotic, low maintenance and low cost *in situ* instruments that are capable of monitoring important species, such as CH_4 and N_2O.
2. High sensitivity *in situ* instruments for the detection of VOC oxidation products both on the ground and on airborne platforms over a wide range of the lower and middle atmosphere and various regions.
3. Novel techniques and instruments for the *in situ* detection of reactive intermediates.

Research includes laboratory-based investigations into the detailed physicochemical properties of target molecules, with the goal of developing future measurement techniques and instruments.

Biogenic emissions: Measurements of molecules such as CH_4, CO_2 are central to our understanding of carbon sources and sinks and the response of the biosphere to climate change. CH_4, the most abundant hydrocarbon in the atmosphere, is important due to its radiative properties and for the role it plays in the tropospheric chemistry of ozone and the hydroxyl radical. We will be using the new direct absorption technique of off-axis Integrated Cavity Output Spectroscopy (ICOS) in a multi-season analysis of the response of methane emissions from various ecosystems to changes in parameters, such as temperature, water table and CO_2 exchange.

Tropospheric VOC photochemistry: Oxidation of volatile organic compounds (VOCs) by nitrogen and hydrogen oxide radicals is central to both smog and secondary organic aerosol (SOA) formation. SOAs are implicated in climate change and poor air quality. A concerted effort to understand the kinetics and chemical reactivity of VOC oxidation is necessary to produce accurate models of tropospheric VOC photochemistry. Atmospheric studies are daunting both because of the size of the system and because of the huge number of chemical species involved. Formaldehyde (HCHO) is central to tropospheric chemistry and is included in virtually every tropospheric chemical model, as virtually all VOCs are broken down in part into HCHO, making it a viable proxy for overall VOC oxidation. Glyoxal is the oxidation product of many anthropogenic and biogenic VOCs but, unlike HCHO, has virtually no primary sources. In addition, glyoxal has also been proposed both as an indicator of Secondary Organic Aerosol (SOA) and as a direct contributor to both anthropogenic and biogenic SOA. We will measure atmospheric HCHO and glyoxal concentrations using Laser-Induced Fluoresecence/Phosphorescence instruments with unprecedented sensitivities, which allows for fast measurements over a wide range of concentrations. The scientific analysis of these data will improve our understanding of the VOC oxidation chemistry and SOA formation of anthropogenic and biogenic emissions. An improved understanding of VOC oxidation chemistry and SOA formation will advance our ability to predict future changes in air quality and climate.

Recent Publications

1. E.J. Moyer, D.S. Sayres, F.N. Keutsch, G.S. Engel, N. Allen and J.G. Anderson, "Development of an ultrasensitive mid-IR ICOS instrument for *in situ* detection of HDO, $H_2{}^{18}O$ and H_2O in the stratosphere," in prep. (2007).
2. T.F. Hanisco, E.J. Moyer, E.M. Weinstock, A.E. Dessler, J.M. St.Clair, D.M. Sayres, F.N. Keutsch, J.B. Smith, J.R. Spackman, R. Lockwood, W.B. Read, T.P. Bui, and J.G. Anderson, "Observations of deep convective influence on stratospheric water vapor and its isotopic composition" *Geophys. Res. Lett.* in press (2007).
3. H.A. Harker, **F.N. Keutsch**, C. Leforestier, Y. Scribano, J.-X. Han, and R.J. Saykally, "Refinements in the description of excited VRT states of the water dimer" *Mol. Phys.,* in press (2007).
4. G.S. Engel, W. Drisdel, F.N. Keutsch, and J.G. Anderson, "Ultra-sensitive Near-IR Integrated Cavity Output Spectroscopy (ICOS) Technique for Detection of CO at 1.57 μm: New Sensitivity Limits for Absorption Measurements in Passive Optical Cavities," *Appl. Opt.* 45, 9221-9229 (2006).
5. D.T. Co, F.N. Keutsch, T.F. Hanisco, and J.G. Anderson, "Rotationally Resolved Absorption Cross Sections of Formaldehyde in the 28100-28500 cm-1 (351-356 nm) Spectral Region: Implications for in situ LIF Measurements," *J. Phys. Chem A* 109, 10675-10682 (2005).

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The Li Group:

Postdoctoral Associate: Dr. Junhua Wang

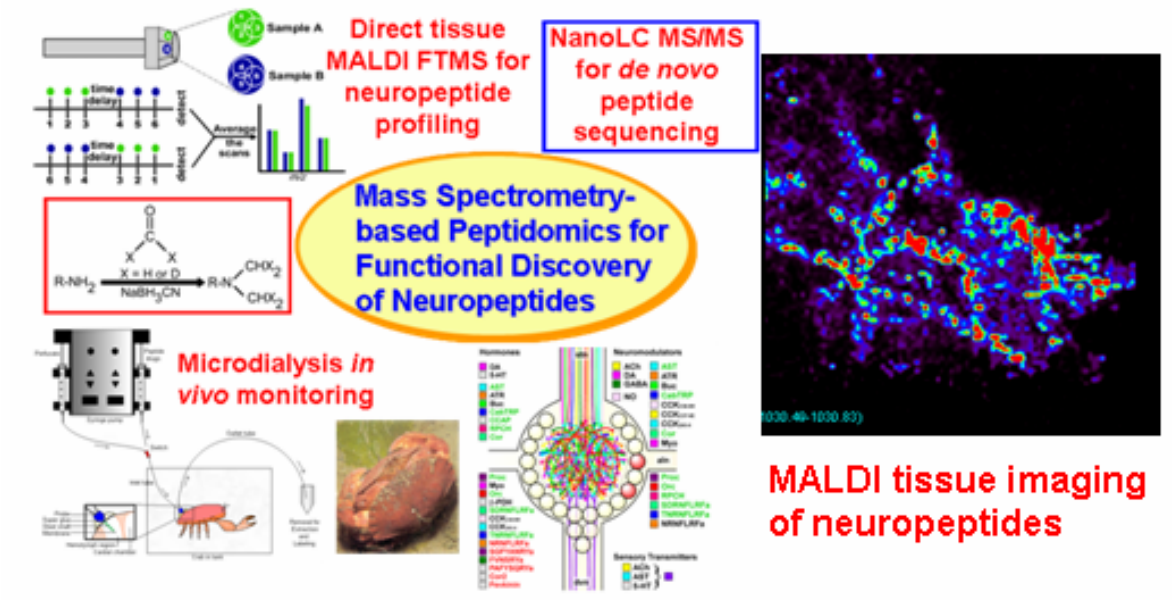
Graduate Students: Heidi Behrens, Weifeng Cao, Ruibing Chen, Christopher Collington, Stephanie DeKeyser, James Dowell, Limei Hui, Mingming Ma, Joshua Schmidt, Xin Wei, Feng Xiang, Jiang Zhang, Yuzhuo Zhang

Undergraduate Students: Dustin Frost, Yuet Fai (Gordon) Tse, Teresa Chiang

Research Interests:

Biological mass spectrometry including MALDI FTMS and ESI QTOF MS; microseparations; peptide *de novo* sequencing and gas-phase fragmentation mechanism, in vivo microdialysis sampling, analytical neurochemistry with special emphasis on neuropeptides and their functional interactions in model nervous systems; neuropeptide distribution and release; neuropeptide and hormone biosynthesis; neuroproteomics; bioinformatics; biomarker discovery and MS-based tissue imaging.

Our research program lies at the interface of analytical chemistry and cellular neurobiology and involves two interlinked aspects. First, we plan to develop and implement an array of enabling mass spectrometric tools coupled with front-end microseparation strategies that are capable of global analysis of peptides and proteins in complex biological matrices in a high throughput and high sensitivity manner. Second, using several well-defined crustacean neuronal networks as model systems and applying the analytical instrumentation and methodology to these nervous systems, we aim to discover a large number of novel neuropeptides and expand our fundamental understanding of cotransmission and neuromodulation at the molecular level.



Selected Publications:

M. Ma et al. (2007) ***Anal. Chem.*** *79*, 673-681; J. Dowell et al. (2006) ***J Proteome Res.*** *5*, 3368-3375; S. DeKeyser and L. Li (2007) ***Anal. Bioanal. Chem.*** *387*, 29-35; C. Zhang et al., ***Science*** *313*, 1291-1294; Q. Fu and L. Li (2006) ***J. Am. Soc. Mass Spectrom.*** *17*, 859-866; S. DeKeyser and L. Li (2006) ***The Analyst***, *131*, 281-290; Q. Fu and L. Li (2006) ***Rapid Commun. Mass Spectrom.*** *20*, 553-562; N. Cruz-Bermudez et al. (2006) ***J. Neurochem.*** *97*, 784-799; Q. Fu and L. Li (2005) ***Anal. Chem.*** *77*, 7783-7795; Fu et al. (2005) ***J. Comp. Neurol.*** *493*, 606-625; Fu et al. (2005) ***Biochem. Biophys. Res. Commun.*** *337*, 765-778; Fu et al. (2005) ***Peptides*** *26*, 2137-2150; Kutz et al.(2004) ***Anal. Chem.*** *76*, 5630-5640.

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Xianghui Liu	Maren Buck
Nathaniel Fredin	Eric Saurer
Chris Jewell	Ryan Flessner
Bin Sun	Shane Bechler

Fields of Interest: Functional Materials
Polymer Synthesis
Gene and Drug Delivery
Biomaterials and Biotechnology

Research Interests:

We use the principles of chemistry, engineering, and biology to address problems in the biomedical, pharmaceutical, and health-related fields. Our research is highly interdisciplinary and provides opportunities for students with interests in chemistry, engineering, biology, materials science, medicine, and the pharmaceutical sciences.

Traditionally, biomaterials research has relied on materials developed for non-biomedical applications. We use new concepts in chemical synthesis and polymer science to design materials specifically for applications such as gene delivery. Within the context of a problem, we seek to understand: 1) how control over structure at the molecular level influences material properties, and 2) how subtle changes in material properties affect interactions with biological systems. The first goal takes advantage of advances in organic chemistry, polymer synthesis, and materials characterization. Toward the second goal, we are engaged in the in vitro evaluation of our own materials and we work closely with members of the biotech industry to identify and explore new design strategies.

How do changes in polymer structure affect the efficiency or mechanism through which cells internalize and process nanoparticles for gene delivery? How does the structure of a material affect the release rates of encapsulated drugs, or influence the attachment, proliferation, and differentiation of different cell types? A fundamental understanding of material properties and the structure/activity relationships that characterize new biomaterials is essential to the design, engineering, and application of new therapeutic systems. While our interests lie broadly at the interface of materials with biological systems, the techniques, materials, concepts, and approaches we use frequently spill over into projects in adjacent areas of chemistry, engineering, and materials science.

Representative Publications:

E. Vázquez, D. M. DeWitt, P. T. Hammond, and D. M. Lynn, "Construction of Hydrolytically-Degradable Thin Films via Layer-by-Layer Deposition of Degradable Polyelectrolytes." *Journal of the American Chemical Society* **2002**, *124*, 13992-13993.

J. Zhang, L. S. Chua, and D. M. Lynn, "Multilayered Thin Films that Sustain the Release of Functional DNA Under Physiological Conditions." *Langmuir* **2004**, *20*, 8015-8021.

C. M. Jewell, J. Zhang, N. J. Fredin, and D. M. Lynn, "Multilayered Polyelectrolyte Films Promote the Direct and Localized Delivery of DNA to Cells." *Journal of Controlled Release* **2005**, *106*, 214-223.

N. J. Fredin, J. Zhang, and D. M. Lynn, "Surface Analysis of Erodible Multilayered Polyelectrolyte Films: Nanometer-Scale Structure and Erosion Profiles." *Langmuir*, **2005**, *21*, 5803-5811.

X. Liu, J. W. Yang, A. D. Miller, E. A. Nack, and D. M. Lynn, "Charge-Shifting Cationic Polymers that Promote Self-Assembly and Self-Disassembly with DNA." *Macromolecules*, **2005**, *38*, 7907-7914.

N. L. Abbott, C. M. Jewell, M. E. Hays, Y. Kondo, D. M. Lynn, "Ferrocene-Containing Cationic Lipids: Influence of Redox State on Cell Transfection." *Journal of the American Chemical Society* **2005**, *127*, 11576-11577.

J. Zhang, N. J. Fredin, J. F. Janz, B. Sun, and D. M. Lynn, "Structure/Property Relationships in Erodible Multilayered Films: Influence of Polycation Structure on Erosion Profiles and the Release of Anionic Polyelectrolytes." *Langmuir*, **2006**, *22*, 239-245.

C. M. Jewell, J. Zhang, N. J. Fredin, M. R. Wolff, T. A. Hacker, and D. M. Lynn, "Release of Plasmid DNA from Intravascular Stents Coated with Ultrathin Multilayered Polyelectrolyte Films." *Biomacromolecules* **2006**, *7*, 2483-2491.

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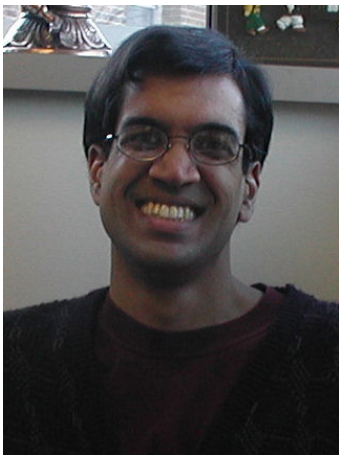

Graduate Students: Rhiannon Carter and David Moody

Research Interests:

Founded upon modern synthetic methods in organic, organometallic, and inorganic chemistry, my research program broadly seeks *to synthesize and to characterize* novel functional organic/polymeric and inorganic materials. The development of functional materials requires two complementary skill sets: (i) the ability to develop and to exploit synthetic methods to achieve precise control over molecular architectures of materials, and (ii) the ability to physically characterize molecular, supramolecular, and bulk materials properties. Traditional molecular characterization methods and physical characterization by a variety of techniques including x-ray scattering, electron microscopy, rheology, and mechanical testing will serve to evaluate the properties and potential utility of newly synthesized materials. Research focus areas include: (i) syntheses of new classes of amphiphilic block copolymers and characterization of their bulk and solution phase behavior, (ii) development of catalytic methods to enable the mild synthesis of polyolefins containing polar functionalities with previously unknown monomer sequence distributions and properties, and (iii) investigations of organometallic strategies for rational syntheses of metal nanoparticles with well-defined shapes. The unique coupling of synthetic methods development and thorough characterization of the resultant materials by our group will facilitate rapid identification of novel materials targets, while enabling swift optimization of their flexible and scalable syntheses.

Selected Research Publications:

1. Mahanthappa, M. K., Lim, L. S., Hillmyer, M. A., and Bates, F. S. “Control of Mechanical Response in Polyolefin Composites: Incorporation of Glassy, Rubbery, and Semicrystalline Components, “ *Macromolecules*, **2007**, ASAP Manuscript #ma0617421.

2. Meuler, A. J., Mahanthappa, M. K., Hillmyer, M. A., and Bates, F. S. “Synthesis of Monodisperse α-Hydroxy-Polystyrene in Hydrocarbon Media Using a Functional Organolithium,” *Macrmolecules*, **2007**, ASAP Manuscript #ma0623338.

3. Mahanthappa, M. K., Bates, F. S., and Hillmyer, M. A. "Synthesis of ABA Triblock Copolymers by a Tandem ROMP-RAFT Strategy," *Macromolecules*, **2005**, *38*, 7890-7894.

4. Koo, C. M., Wu, L., Lim, L. S., Mahanthappa, M. K., Hillmyer, M. A., and Bates, F. S. "Microstructure and Mechanical Properties of Semicrystalline-Rubbery-Semicrystalline Triblock Copolymers," *Macromolecules,* **2005**, *38*, 6090-6098.

5. Mahanthappa, M. K., Cole, A. P., and Waymouth, R. M. "Synthesis, Structure and Ethylene/α-Olefin Polymerization Reactivity of (Cyclopentadienyl)(nitroxide)titanium Complexes," *Organometallics*, **2004**, *23*, 836-845.

6. Mahanthappa, M. K. and Waymouth, R. M. "Titanium-Mediated Syndiospecific Styrene Polymerizations: Role of Oxidation State," *J. Amer. Chem. Soc.*, **2001**, *123*, 12093-12094.

Dr. Robert J. McMahon
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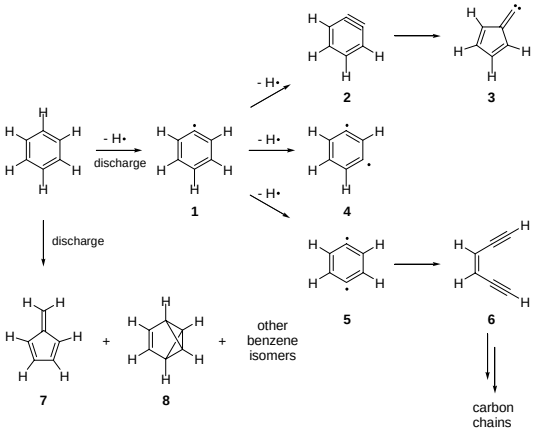
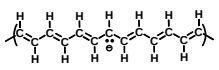
Graduate Students: Nikki Burrmann, Jessica Menke, Caroline Pharr, Phillip Thomas, Katherine Traynor

Research Interests:
astrochemistry; mechanistic organic chemistry of interstellar space; generation and characterization of reactive intermediates; thermal and photochemical rearrangement mechanisms of organic and organometallic compounds; low-temperature matrix isolation spectroscopy; organic materials chemistry

We maintain a longstanding interest in studying highly reactive organic species using both experimental and computational methods. Our recent research efforts focus on elucidating the structure, photochemistry, and spectroscopy of organic species that are postulated to play a role in the chemistry of the interstellar medium. Understanding the chemistry interstellar clouds represents a significant challenge in mechanistic organic chemistry - both in terms of identifying new organic species in the clouds and in terms of investigating the chemical processes that govern the formation and destruction of these organic species. Our study of the electronic structure of conjugated organic compounds is relevant to the spectroscopy of interstellar molecules as well as to the understanding of electronic defects in organic conducting polymers.



Electronic Delocalization in Carbon Chains



defect **in polyene chain**
(soliton)
delocalized and mobile

defect **in polyyne chain**
delocalized? mobile?

With one foot planted squarely in the field of organic chemistry, our group possesses the ability to synthesize all manner of organic compounds. We have used this ability to good result in a number of collaborations within the Department, in which graduate students in my research group have synthesized key materials needed by other groups for important physical or spectroscopic studies.

Selected Research Publications:

Interstellar Chemistry: A Strategy for Detecting Polycyclic Aromatic Hydrocarbons in Space, F. J. Lovas, Robert J. McMahon, Jens-Uwe Grabow, Melanie Schnell, James Mack, Lawrence T. Scott, Robert L. Kuczkowski, *J. Am. Chem. Soc.* **2005**, *127*, 4345-4349.

Ring Opening of 2,5-Didehydrothiophene: Matrix Photochemistry of C_4H_2S Isomers, Yong Seol Kim, Hiroshi Inui, and Robert J. McMahon, *J. Org. Chem.* **2006**, *71*, 9602-9608.

Enediyne Isomers of Tetraethynylethene, Nathan P. Bowling and Robert J. McMahon, *J. Org. Chem.* **2006**, *71*, 5841-5847. [feature article for journal cover]

Reactive Carbon-Chain Molecules: Synthesis of 1-Diazo-2,4-pentadiyne and Spectroscopic Characterization of Triplet Pentadiynylidene (HCCCCCH), Nathan P. Bowling, Robert J. Halter, Jonathan A. Hodges, Randal A. Seburg, Phillip S. Thomas, Christopher S. Simmons, John F. Stanton, and Robert J. McMahon, *J. Am. Chem. Soc.* **2006**, *128*, 3291-3302.

Nita Sahai
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Group Logo, and the Sahai Group (from left: Nianli Zhang, Tim Oleson, Dr. Donald Mkhonto, Mark Stevens, Raj Panneerselvan, Will Welch, Professor Sahai, James Driver, Jie Xu).

Prof. Nita Sahai's research group works in the field of biogeochemistry, which includes biomimetic materials chemistry, bioceramics, medical mineralogy and environmental geochemistry. The unifying theme is an interest in organic and inorganic interactions at mineral surfaces on the molecular- and nano-scale. Specific projects include amine-catalyzed biomimetic nanoporous silica synthesis from organosilicate precursors (Fig. 1), biomineralization of the mineral apatite at protein surfaces to form bone and teeth in humans (Fig. 2), bone growth on silicate bioceramic prosthetic implants, the self-assembly of cell-membranes at mineral surfaces, and the mobility and partitioning of contaminants in the environment such as arsenic in contaminated groundwaters.

In order to determine thermodynamically feasible reactions and to identify kinetic reaction pathways, the group uses theoretical modeling (quantum chemical-molecular orbital calculations and classical thermodynamics), aqueous analytical methods (ICP-OES, AA, etc.), spectroscopic and microscopic techniques to characterize solid, sorbed and aqueous phases (NMR, FTIR/Raman, HRTEM) and thermochemistry (microcalorimetry). We interact closely with other research groups in the Departments of Chemistry, Biochemistry, Chemical and Biological Engineering, Soil Science, and in the Environmental Chemistry and Technology Program.

The ultimate aim in our group is to encourage students to think independently and across the boundaries of traditional scientific disciplines, while maintaining a core chemistry-based expertise.

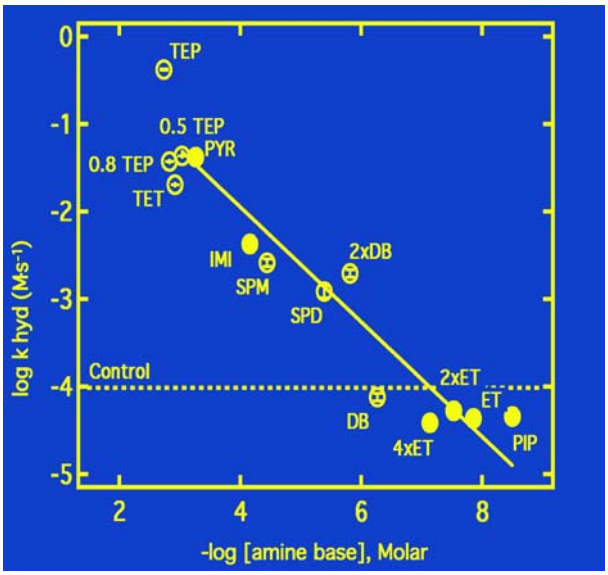

Figure 1. Hydrolysis reaction rates (k_{hyd}) of organosilicate starting compound, measured by ^{29}Si NMR spectroscopy, as catalyzed various amines (Delak and Sahai, 2005, *Chem. Materials*). Rates determine porosity of the silica formed.

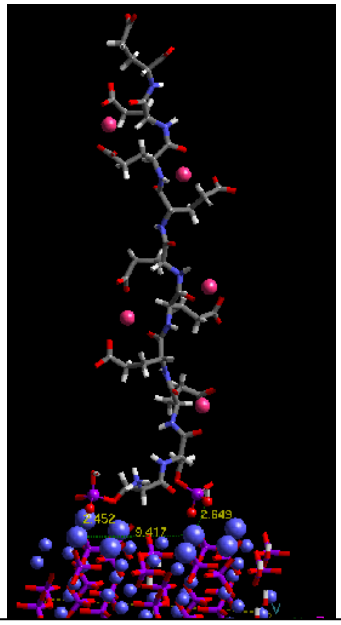

Figure 2. Adsorption of 10 amine-acid peptide from bone sialoprotein on (001) face of the bone-mineral, apatite (Sahai et al., in prep.).

David C. Schwartz

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LMCG:

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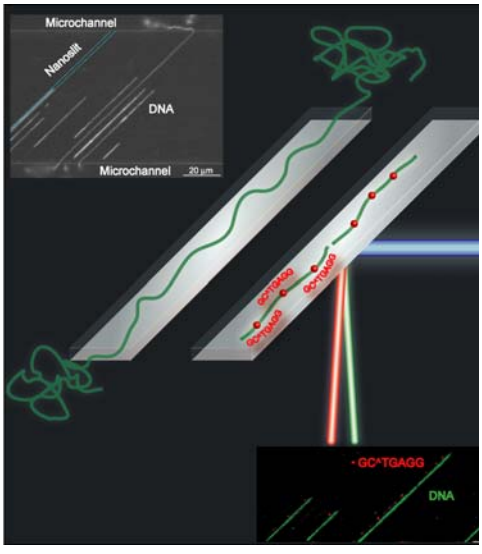
Graduate Students: Dan Abras (Engineering), Gene Ananiev (CMB), Dalia Dhingra (Chem), Jill Herschleb (CMB), Kristy Kounovsky (Chem), Mohana Ray (Chem), Tim Schramm (Chem), Nick Shera (Genetics), Brian Teague (CMB), Hua Yu (Chem)
Computational Staff: Aaron Bergstralh, Chris Churas, Dan Forrest, Rod Runnheim
Instrumentation Innovator: Gus Potamousis
Instrumentation Specialist: Casey Lamers
Research Specialist: Mike Bechner

Research Interests:

Discovery and elucidation of new single molecule effects, and their application to problems in biology and genetics through the creation/analysis of massively large, complex data sets (surface science, imaging, nano/microfluidics, polymer dynamics, nanochemistry, transcription, genome evolution, population genomics, single cell genomics, epigenetics, cancer).

Reduction of experimental scale terminates at the single molecule level. Single molecules are the ultimate analyte, since they represent the pinnacle of miniaturization, and when systematically analyzed as ensembles, offer the greatest advantages for the generation large-scale data sets. Such large and often complex data sets have become the currency of modern biological analysis. In this regard, our laboratory has pioneered the first single molecule system for large-scale genome analysis--Optical Mapping. This system uses automated fluorescence microscopy, and on-line analysis to image and analyze thousands of individual of "biochemically marked" DNA molecules. The analysis files are then directly piped to a database, where further analysis or linking with public resources is enabled. This linkage brings biological annotation into a single molecule context. Downstream systems then allow users to visualize data and analysis as an integral part of their research efforts. Through such integration, the Optical Mapping System has emerged as a general platform for the large-scale analysis of single molecule phenomena, and has made single molecules a practical substrate for chemical and biological research.



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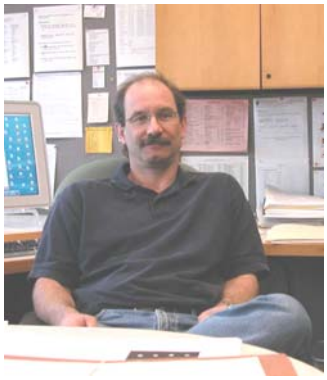
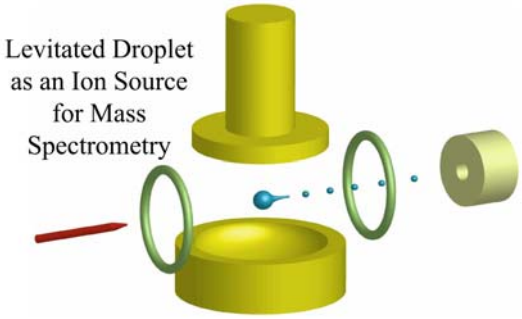
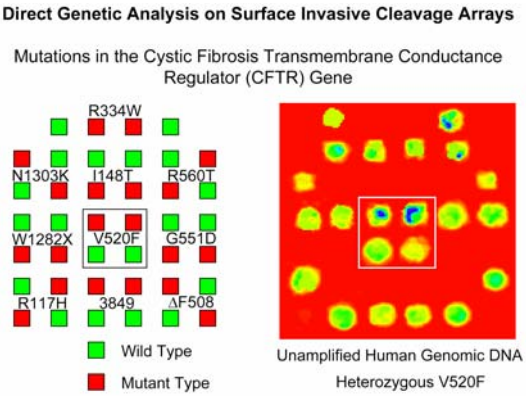


The Lab Group:
Post Docs: Kaveh Jorabchi
Staff Scientists: Brian Frey, Mark Scalf, Michael Shortreed, Michael Westphall
Graduate Students: Siyuan Chen, Ryan Hilger, Suzie Kulevich, Jieun Lee, Joshua Mandir, Matthew Lockett, Margaret Phillips, Xu Zhang

Research Emphasis:
The Smith group is an interdisciplinary group of researchers working on the development of novel methods and approaches for the analysis and manipulation of biomolecules. The group works in two main areas: biological mass spectrometry, and biologically-modified surfaces. A key focus in the area of mass spectrometry is the development of new instrumentation and chemistries for the analysis of complex mixtures of biomolecules. Interest areas include the development of technologies for proteome analysis at the single cell level, single molecule mass spectrometry, levitated-droplet ion sources, high-sensitivity detectors for large ions, and membrane proteomics. We are also engaged in a large number of collaborations using mass spectrometry to analyze for small metabolites (metabolomics) and large proteins (proteomics) to help understand the biology related to such varied topics as plant function, bacterial nitrogen fixation, as well as heart disease and diabetes.



Our surface chemistry and surface detection work is aimed at the development of a new generation of highly robust and reproducible surface attachment chemistries and complementary detection modalities. Chemically reactive surfaces are important, for example, in the fabrication of biomolecule arrays such as DNA or protein chips. The ability to form a covalent bond between a surface and a biomolecule adds control over molecular orientation and presentation that can in turn facilitate hybridization and conjugation. New surfaces that were developed in the course of this research have been successfully implemented in areas such as: oligonucleotide modified gold and diamond chips for parallel determination of single nucleotide polymorphisms in unamplified genomic DNA; lectin modified gold chips for carbohydrate binding assays; protein modified gold chips for measurement of receptors in live cell capture assays; and, oligonucleotide-modified gold chips for DNA computations.



Chen, Y., Shortreed, M.R., Peelen, D., Lu, M. and Smith, L.M. 2004. Surface amplification of invasive cleavage products. *J. Am. Chem. Soc.*, **126** (10), 3016-3017.
Liu, Q., Wang, L., Frutos, A.G., Condon, A.E., Corn, R.M. and Smith, L.M. 2000. DNA computing on surfaces. *Nature*, **403**, 175-179.
Scalf, M., Westphall, M.S., Krause, J., Kaufman, S.L. and Smith, L.M. 1999. Controlling charge states of large ions. *Science*, **283** (5399) 194-197.

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Postdoc: Michael Konopka

Research Interests: Tracking biomolecular motion in real time by fluorescence microscopy, including single-molecule detection. *Neurochemistry*: secretory vesicle trafficking and exocytosis in live cells. Dynamics of docking and fusion of v-SNARE-containing vesicles with t-SNARE-containing planar lipid bilayers *in vivo*. *Membrane protein dynamics*: self-assembly of 'rafts' of Syt, Ca^{2+}, and phosphatidylserine. *Crowding effects in vivo:* effects of external osmotic shifts on diffusion of GFP in the cytoplasm and periplasm of *E. coli.*

The work of the cell is carried out by assemblies of specific proteins with coordinated moving parts that operate in precise sequence—protein machines! While x-ray crystallography and NMR provide critically important "snapshots" of stable structures, new techniques in fluorescence microscopy allow us to directly observe *single and multiple proteins and nucleic acid oligomers in action in real time.* The Weisshaar group studies the self-assembly and internal motion of proteins and DNA in live cells and in model lipid bilayers. We can count constituents of a protein machine as it assembles in a model membrane. We can observe conformational changes, such as the bending of DNA by a protein at a special recognition site. By engineering fluorescent constructs into live cells, we can follow the motion of specific biomolecules *in vivo*. Single-molecule and single-vesicle trajectories can reveal inhomogeneities that are obscured in bulk measurements. The goal of all this work is a better understanding of how biomolecular machinery functions. This is inherently interdisciplinary research, combining the skills of physical and analytical chemists, molecular biologists, and theorists.

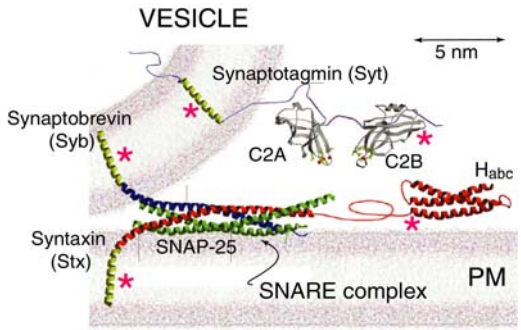

Fig. 1. Secretory vesicle bound to the plasma membrane by a SNARE complex. Ca^{2+}-triggered binding of synaptotagmin to the PM, to SNAREs, and to each other may result in vesicle fusion, releasing neurotransmitter to the synapse.

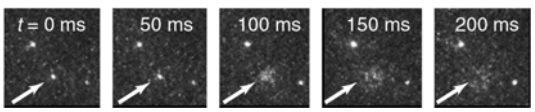

Fig.3. Vesicle containing v-SNARE protein Syb (Fig. 1) and labeled lipids docks and quickly fuses on a planar lipid bilayer containing t-SNARE proteins (Stx/SNAP-25). Our fast fusion rate constant of 40 s^{-1} begins to mimic the speed of neuronal exocytosis *in vivo.*

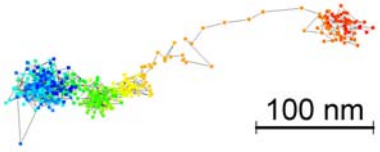

Fig. 2. Experimental trajectory of a single secretory vesicle in a live PC12 cell. Spatial accuracy is 5-10nm. Note motor protein activity (fast, directed motion).

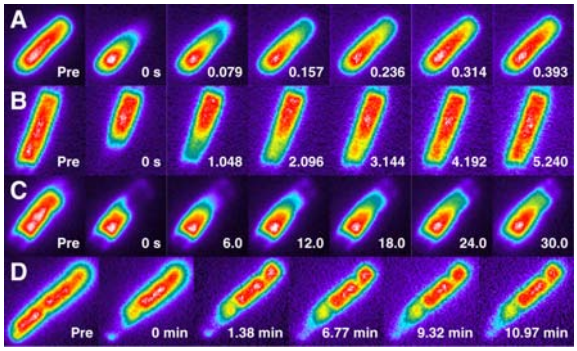

Fig. 4. Gallery of *E. coli* expressing GFP, whose diffusion coefficient is measured by fluorescence recovery after photobleaching (FRAP). As increasing external osmolality extracts water from the cytoplasm (A through D), diffusion slows down dramatically (note time scale of recoveries).

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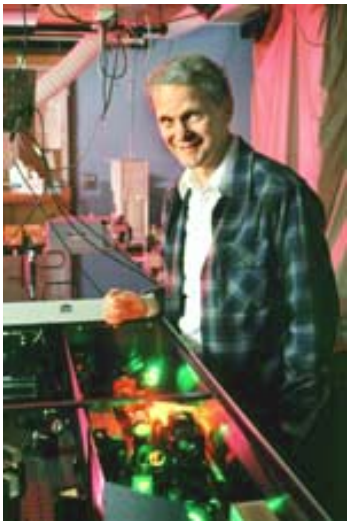

The Lab Group
Postdoc: Andrei Pakouley
Graduate Students: Kathryn Kornau, Nathan Mathew, Mark Rickard, Stephen Block, Lena Yurs
Undergraduate Student: Tom Mueller

Research Emphasis:
Ultrafast lasers and modern laser technology have opened new opportunities for probing and manipulating matter. The intensity of focused laser beams allows one to excite multiple transitions before a molecule has time to forget about the previous transition. One can therefore create new quantum entangled mixtures of vibrational and electronic states that were previously impossible to achieve. Our research focuses on using these new multiple quantum coherences to probe and control the structural dynamics of condensed phases. Excitation of multiple states reveals the intermolecular and intramolecular interactions that couple them. The intensity is sufficiently high that the very high electric fields of the electromagnetic radiation can actually perturb and control the electron distributions in molecules so electron transfer or molecular rearrangements can occur. This new approach offers many dimensions of controllable variables- the laser and detector frequencies and the time delays between excitation pulses. It permits examination of coherent and incoherent processes, much as modern NMR methods probe nuclear spins. Our work is directed towards exploring and understanding these new capabilities of lasers for analytical measurements and electron transfer in materials.

The diagrams show examples of 2D slices through the multidimensional variable space. Below is a 3D plot of the four wave mixing intensity as a function of two laser frequencies along with 1D infrared spectra. Peaks appear when the lasers are resonant with states in the molecules. One can set the lasers on a specific peak and scan the delays between the lasers as shown on the right. The top right diagram shows the various nonlinear processes that occur for different delay times and the bottom right diagram shows the experimental implementation with lasers tuned to the bottom right cross-peak in the lower spectrum.