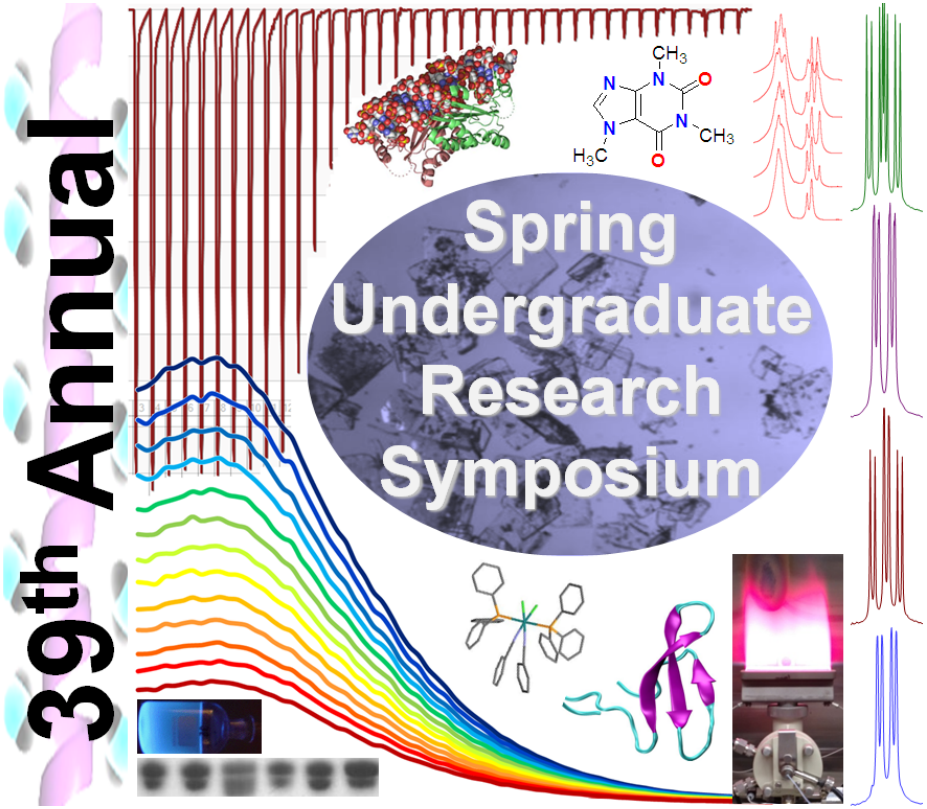
JAMES MADISON UNIVERSITY®

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY



THURSDAY APRIL 3, 2014

ORAL SESSION I: 2:15 – 4:00 PM (ISAT 259)
POSTER SESSION: 4:15 – 5:15 PM (PHYS/CHEM LOBBY)

FRIDAY APRIL 4, 2014

ORAL SESSION II: 1:30 – 3:15 PM (ISAT 259)
KEYNOTE ADDRESS: 3:30 – 4:30 PM (ISAT 259)

See back cover for image description.

Past Keynote Speakers

Each year we feature a keynote speaker for the Department's annual Spring Undergraduate Research Symposium. We are honored to have had speakers who are alumni of the department and are willing to come back and share with our students their experiences of "life after JMU". We thank each of these speakers and look forward to future alumni participation in Spring Symposium.

YEAR	JMU CLASS	SPEAKER	AFFILIATION
2014	1996	**Dr. Dana McGraw Dattelbaum**	*Los Alamos National Laboratory*
2013	1999	**Dr. Christy Vestal Martin**	*Vorbeck Materials*
2012	1994 N/A	**Dr. Melissa C. Rhoten** **Dr. Orde Q. Monro**	*Longwood University* *University of KwaZulu-Natal*
2011	1992	**Dr. Morgan S. Sibbald**	*The Sherwin-Williams Company*
2010	1988	**Dr. Kevin Morris**	*Carthage College*
2009	1988	**Dr. Chris E. Holmes**	*The University of Vermont College of Medicine*
2008	1995	**Dr. Jonathan Dattlebaum**	*University of Richmond*
2007	1987	**Dr. Elizabeth Perry (M.D.)**	*Signature Healthcare, Inc.*
2006	1967	**Dr. Carolyn Abitbol (M.D.)**	*University of Miami (FL) School of Medicine*
2005	1975 1976	**Dr. Daniel Downey** **Dr. Gary Rice**	*James Madison University* *College of William and Mary*
2004	1987	**Dr. James (Dusty) Baber**	*National Institutes of Health*
2003	1984	**Dr. Fred King**	*West Virginia University*
2002	1977	**Dr. Roger Bertholf**	*University of Florida School of Medicine*
2001	1979	**Mrs. Katheryn Lam**	*International Business Machines*
1999	1987	**Dr. Jose Madalengoitia**	*University of Vermont*
1997	1986	**Dr. Fred R. Kinder**	*Novartis Research Institute*
1996	1976	**Dr. Terry O. Trask**	*DuPont Chemicals*
1995	1973	**Dr. Carl Lentz**	*Eastman Fine Chemicals*
1994	1990	**Dr. Michele A. Kelly**	*University of Maryland Baltimore County*
1993	1985	**Dr. Cynthia K. Fallon**	*DuPont Chemicals*
1992	1983	**Dr. Laurie Locascio**	*National Institute of Standards and Technology*
1991	1983	**Dr. Noreen Naiman**	*North Carolina School of Science and Mathematics*
1990	1982	**Dr. Matthew T. Stershic**	*Atomchem North Amercia*
1989	1982	**Dr. Michael Kinter**	*Cleveland Clinic Lerner Research Institure*
1988	N/A	**Dr. Thomas J. Meyer**	*Los Alamos National Laboratory*
1987	1980	**Dr. Steven Davis**	*Naval Research Laboratory*
1986	1980	**Dr. Steven A. Hackney**	*Michigan Technological University*
1983	1978	**Dr. Richard B. Lam**	
1982	1975	**Dr. Daniel Downey**	*West Virginia University*
1981	1959	**Mr. Ronald E. Ney**	*Environmental Protection Agency*
1980	N/A	**Dr. Stanley G. Sunderwirth**	*Metropolitan State College (Denver, CO)*
1979	1973	**Dr. Carl Lentz**	*Eastman Fine Chemicals*

39th Annual Department of Chemistry and Biochemistry

Spring Undergraduate Research Symposium
Keynote Speaker

Dana McGraw Dattelbaum (JMU Class of 1996), Ph. D.

Weapons Experimentation Division, Los Alamos National Laboratory
Los Alamos, NM

Dana Dattelbaum is an R&D Scientist, and team leader in the Shock and Detonation Physics group at Los Alamos National Laboratory. She received a B.S. in Chemistry from James Madison University in 1996, and performed undergraduate research with Drs. Crowther, DeGraff and Warnaar. She went on to obtain a Ph.D. in Physical Organic Chemistry from UNC-Chapel Hill in 2001 under the direction of Thomas J. Meyer. In Dr. Dattelbaum's graduate research, she developed and applied time resolved optical and vibrational spectroscopies toward the elucidation of excited state electronic structures and electron transfer reactions in transition metal complexes based on Ru, Re, and Os. In 2001, Dr. Dattelbaum joined Los Alamos National Laboratory as a Director's Funded Post-doctoral Fellow in the Materials Science and Technology division, researching the effects of high pressure (compression) on long-chain polymer structures. Dana was hired as a permanent staff member at Los Alamos in 2002, and transitioned to the Dynamic Experimentation Division in 2004. She currently leads nearly 20 scientists, post-docs, students and technicians on the Detonation Physics team. Dr. Dattelbaum's expertise and research interests are in the areas of shock and detonation physics, the shock initiation of explosives, studying materials at high pressure/temperature conditions, and application of static to time-resolved spectroscopies toward understanding material structure and dynamics. She has over 100 publications, and is Past-Chair of the American Physical Society's Topical Group on Shock Compression. Recent awards and honors include 2010 and 2011 Los Alamos Achievement awards, 2004, 2005, and 2012 DOE/NNSA Defense Program Awards of Excellence, and a 2007 LANL Star award. Dr. Dattelbaum is currently the DOE/NNSA Campaign 2 project leader for Polymers and Organic materials at Los Alamos, and a principal investigator on related DOE programs including Nuclear Counterterrorism, Enhanced Surveillance, Surety, Advanced Certification and the DOE/DoD Joint Munitions Program. She serves on several boards and committees within LANL setting strategic directions for the institution, including the Laboratory Directed Research and Development Strategy Team, and the MaRIE Multi-probe Diagnostic Hall Board of Director's for LANL's proposed future free-electron laser facility. In addition to these LANL roles, she is also a steering committee member for the Carnegie DOE Alliance Center (CDAC), reviewer for the DOE/NNSA Stockpile Stewardship Academic Alliance, and is LANL's elector for NSF's COMPRES consortium.

Oral Session I: Thursday April 3rd *(ISAT 259)*		
2:15 - 2:30	Nathan D. Crossland, Dr. Donna S. Amenta and Dr. John W. Gilje	The Study of Supporting Ligands for Ruthenium Complexes
2:30 - 2:45	Kathleen Krist, Dr. Chris Hughes, Dr. Harry Hu and Dr. Brian Augustine	Utilizing Chloroform Post-treatment to Improve the Adhesion of Au Thin Films onto PMMA
2:45 - 3:00	Austin T. Muetterties and Dr. Barbara A. Reisner	Synthesis and Characterization of Sodium Hydrotris(triazolyl)borate·Solvent
3:00 - 3:15	Nicholas D. Cooper and Dr. Thomas DeVore	The Kinetic and Mechanistic Decomposition of Zinc Oxalate
3:15 - 3:30	Kelly E. Du Pont, Aidan M. McKenzie and Dr. Christopher E. Berndsen	Structural Analysis of the Anti-viral Protein, BST-2
3:30 - 3:45	Matthew R. Dent, Alexa M. Vinci and Dr. Barbara A. Reisner	Exploring the Influence of Covalent Modification on Framework Assembly Through the Synthesis and Characterization of Hydrotris(3,5-dimethyl-1,2,4-triazolyl)borates
3:45 - 4:00	Taylor P. Light, Karen M. Corbett, Michael A. Metrick and Dr. Gina MacDonald	Influence of Hofmeister Salts on the Structure, Aggregation, and Backbone Solvation of RecA

Poster Session: Thursday April 3rd 4:15 – 5:15 pm *(Ph/Ch lobby)*	
Diana Al Husseini, Natalie Trinh and Dr. Yanjie Zhang	Effects of the Hofmeister Anions on Interfacial Tension at the Hydrophobic/Aqueous Interface
Santina Cruz, Dr. Donna S. Amenta, Dr. John W. Gilje and Dr. Glenn P.A. Yap	Do Donor Ligands Displace N-Pyrazolylpropanamide (N-ppa) from $RuCl_2(PPh_3)_2$(N-ppa)? Solution Behavior of $RuCl_2(PPh_3)_2$(N-ppa) & $RuCl_2(PPh_3)_3$ with Nitriles and Dimethylformamide
Louis Damiano, John Marafino, Brenden Wimbish, Irfan (Simon) Ali, Brenna Walsh, Kirstie Thompson, Kristin McKenna, Tara M. Gallagher, Dr. Kyle Seifert, and Dr. Kevin L. Caran	Triscationic Amphiphiles with One or Two Tails
David D'Amico, Dr. John W. Gilje and Dr. Donna S. Amenta	Coordination of Metal Ions with N-Pyrazolylpropanamide Ligands
Andy Heindel and Dr. Nathan Wright	Structural Elucidation of Open Reading Frame 60, ORF-60, in Enteroaggregative *Escherichia coli*
Jacob Roodman and Dr. Daniel Downey	Limestone Analysis for Archeology
Jessica Simpson and Dr. Debra Mohler	Synthesis of Chlororhenium Tricarbonyl Complexes of Substituted Bipyridine Ligands for Interfacial Electron Transfer Studies
Emily Todd, D. Reid Putney, Dr. Christopher Berndsen and Dr. Nathan Wright	Understanding E2 Mechanism using NMR
Colin J. Wallace and Dr. Yanjie Zhang	Phase Behaviors of PEO-PPO-PEO Triblock Copolymer in the Presence of Salts and Alcohols
Brigitte Wendel, Perrin Godbold, Kiara Pontious and Dr. Kyle G. Gipson	The Influence of Synthesis Environments on Fluorescent Nanoparticles

(Student presenters underlined)

Oral Session II: Friday April 4th *(ISAT 259)*		
1:30 - 1:45	Bradley Rogers and Dr. Yanjie Zhang	Specific Anion Effects on Partition Coefficient of Caffeine Between Aqueous and Cyclohexane Phases
1:45 - 2:00	Denise McKaig, Alexandra Iuga and Dr. Isaiah Sumner	Correcting Force-Field Bias in Pin1WW
2:00 - 2:15	Serban Zamfir and Dr. Isaiah Sumner	Molecular Dynamics Studies of the Ubiquitin Conjugation Mechanism
2:15 - 2:30	Dianté Ryals, Jon Clouston, Robbie Hurlbrink, Ziza Machado, James Wooten and Dr. Richard Foust	Water Chemistry Changes in the South Fork of the Shenandoah River and Smith Creek Following Downpours
2:30 - 2:45	Matthew Oehler, Tracy Caldwell, Logan Meyer, Kelly Du Pont and Dr. Nathan Wright	Structural Studies of Obscurin Ig58-59
2:45 - 3:00	Jessica L. Shott, Brian J. Reeves and Dr. Brycelyn M. Boardman	The Synthesis and Characterization of Thienyl Phosphine Derivatives for Polymerizable Metal Complexes
3:00 - 3:15	Irfan (Simon) Ali, John Marafino, Louis Damiano, Brenden Wimbish, Brenna Walsh, Kirstie Thompson, Kristin McKenna, Tara M. Gallagher, Dr. Kyle Seifert, and Dr. Kevin L. Caran	Detergent, the Antibiotic: The Story of Mesitylene-Based Compounds
3:15 - 3:30	-- break --	
Keynote Address: Friday April 4th *(ISAT 259)*		
3:30 – 4:30	Dr. Dana McGraw Dattelbaum	"Shocking" insights into extreme condition chemistry

(Student presenters underlined)

Keynote Address

Friday, April 4, 2014 at 3:30pm
ISAT Room 259

"Shocking" insights into extreme condition chemistry

Dana McGraw Dattelbaum (JMU Class of 1996), Ph. D.
Weapons Experimentation Division, Los Alamos National Laboratory
Los Alamos, NM

Understanding the behaviors of materials in extreme environments is foundational for predicting the response of weapons materials, creating environmentally tolerant properties, and potentially exploiting extreme conditions to tailor materials functionality. For many materials, fundamental physics insights are needed to bridge length scales at the "micron-gap," linking atomic or molecular properties to bulk response. An example is high explosives, where initiation sensitivities and detonation performance characteristics are related to shock-driven chemical reactions, and cannot currently be predicted *a priori*. Significant gaps in our knowledge remain regarding the general principles of shock-induced chemical reactions, and the specifics of bond-changing steps under these conditions. Through *in situ* measurements of shock wave structures and spectroscopic signatures, this project has shed light on the details of chemical reactions behind the shock front in simple chemical structures. These include reaction thresholds/rates and their state sensitivities, as well as electronic changes leading to and perhaps responsible for chemical bond changes. The experimental measurements are matched in length and time scale with a new theoretical reactive molecular dynamics code, LATTE, which allows for computation of reaction pathways under simulated shock conditions for an unprecedented number of atoms. The outcome of this work is a better understanding of how explosives and other weapons materials react under the extreme enviroments created by shock compression.

STUDENT ABSTRACTS

(Student presenters underlined)

Effects of the Hofmeister Anions on Interfacial Tension at the Hydrophobic/Aqueous Interface

Diana Al Husseini, Natalie Trinh and Dr. Yanjie Zhang
Department of Chemistry and Biochemistry, James Madison University

The Hofmeister series is a set of ions in order of their ability to affect physical properties in aqueous solutions. Although Hofmeister series' phenomenon is general, their mechanisms are still not fully understood. An optical tensiometer by pendant drop method is employed to study the Hofmeister anion effects on the surface tension and the interfacial tension at the hydrophobic/ aqueous interface. So far, it has been observed that the surface tension of water increases linearly as chaotropic and kosmotropic salt concentrations increase. They also follow a specific trend with respect to the surface tension increments: $SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^- > Cl^- > Br^- > I^- > NO_3^- > ClO_4^- > SCN^-$. These studies will provide us with some valuable data that would help further investigation and understanding of Hofmeister series mechanisms.

Detergent, the Antibiotic: The Story of Mesitylene-Based Compounds

Irfan (Simon) Ali,[1] John Marafino,[1] Louis Damiano,[1] Brenden Wimbish,[1] Brenna Walsh,[1] Kirstie Thompson,[1] Kristin McKenna,[1] Tara M. Gallagher,[2] Dr. Kyle Seifert,[2] and Dr. Kevin L. Caran[1]

[1]Department of Chemistry and Biochemistry, James Madison University
[2]Department of Biology, James Madison University

Membrane perturbation by polycephalic amphiphiles may have promise in the development of novel antibiotic therapies. These antibiotic compounds likely function, in part, by penetrating biomembranes and thus altering bilayer integrity. The mechanism by which the amphiphiles work is only partially understood; ongoing work by us and other research groups aims to understand this mechanism. Current work in the Caran research lab aims to synthesize polycephalic amphiphiles as potent antibiotics. The current synthetic focus deals with amphiphilic mesitylene derivatives. Molecular architectures in the current study include triple-headed amphiphiles with one or two tails as well as those with three headgroups at either end of hydrocarbon chain (bolaamphipiles). Subsets of compounds containing varying chain lengths are also synthesized. ^{1}H NMR spectroscopy is utilized to confirm structure and purity, while other instrumental techniques provide information on a range of amphiphilic properties including the critical micelle concentration (CMC). The main way that the Caran Group currently measured the CMC is via isothermal titration calorimetry (ITC). The synthesized and analyzed amphiphiles are then delivered for testing by the Seifert Group in the Biology Department at James Madison University.

The Kinetic and Mechanistic Decomposition of Zinc Oxalate

Nicholas D. Cooper and Dr. Thomas DeVore
Department of Chemistry and Biochemistry, James Madison University

The decomposition of zinc oxalate is considered to be a simple one-step decomposition. Careful measurements made early in the decomposition indicate that the products of this decomposition, CO and CO_2, are produced with different rates and follow different rate equations. CO follows the Avrami–Erofeev equation with n≈3 while CO_2 follows the Avrami–Erofeev equation with n≈2. Activation Energies were found for CO and CO_2 where the E_A for CO≈245 KJ/mol while the E_A for CO_2≈257 KJ/mol. These differences suggest that this decomposition follows the mechanism proposed by Boldryve. In this mechanism, the oxalate anion rearranges to produce an intermediate. This intermediate then can lose CO to produce the carbonate. Decomposition of the carbonate then produces the CO_2.

The Study of Supporting Ligands for Ruthenium Complexes

Nathan D. Crossland, Dr. Donna S. Amenta and Dr. John W. Gilje
Department of Chemistry and Biochemistry, James Madison University

The reaction of $RuH(Cl)(CO)(PPh_3)_3$ with N-pyrazolylpropanamide (N-ppa) and $Ru(H)_2(CO)(PPh_3)_3$ with N-ppa were studied under a variety of conditions with the objective of finding a route to substituted ruthenium hydride complexes. Microwave reactions in which the temperature, time, and solvent were varied were the first focus for this study. The range of solvents used included tetrahydrofurane, toluene, methanol, dimethylformamide, and chloroform. The time ranged from 10 minutes to 5 hours and the temperature from 60°C to 190°C. While the starting materials are individually stable under microwave conditions, mixtures of the reactants decomposed in all the microwave experiments. NMR scale studies of $RuH(Cl)(CO)(PPh_3)_3$ with N-ppa at ambient temperature in d-chloroform indicated displacement of a single triphenylphosphine and the formation of $RuH(Cl)(CO)(PPh_3)_2$(N-ppa). Similarly, NMR scale reactions of $RuH(Cl)(CO)(PPh_3)_3$ with bis(diphenylphosphino)propane oxide (dPPPO) were also studied. Both NMR scale reactions showed results indicating the formation of possible product. Larger scale reactions of $RuH(Cl)(CO)(PPh_3)_3$ with N-ppa and dPPPO were conducted. Supporting data will be presented.

Do Donor Ligands Displace N-Pyraolylpropanamide (N-ppa) from $RuCl_2(PPh_3)_2$(N-ppa)? Solution Behavior of $RuCl_2(PPh_3)_2$(N-ppa) & $RuCl_2(PPh_3)_3$ with Nitriles and Dimethylformamide

Santina Cruz,[1] Dr. Donna S. Amenta,[1] Dr. John W. Gilje[1] and Dr. Glenn P.A. Yap[2]
[1]Department of Chemistry and Biochemistry, James Madison University
[2]Department of Chemistry and Biochemistry, University of Delaware

The solution behavior of $RuCl_2(PPh_3)_2$(N-ppa) and $RuCl_2(PPh_3)_3$ with nitriles and dimethylformamide has been investigated. Initially, the reaction of $RuCl_2(PPh_3)_3$ with N-pyrazolylpropanamide was optimized to form $RuCl_2(PPh_3)_2$(N-ppa) in about 75% yield. In an effort to obtain NMR spectra of this compound a variety of solvents were investigated. $RuCl_2(PPh_3)_2$(N-ppa) is insoluble in non-polar solvents, but dissolves in some polar solvents. However, in these cases the N-ppa appears to be displaced. Thus, $RuCl_2(PPh_3)_2$(N-ppa) in excess of CD_3CN produced NMR spectra that are analogous to spectra obtained on solutions of $RuCl_2(PPh_3)_3$ in CD_3CN. This indicates that $RuCl_2(PPh_3)_2(NCCD_3)_2$, the deuterated analog of reported product of the reaction of $RuCl_2(PPh_3)_3$ with CH_3CN, is formed in the RuCl2(PPh3)2(N-ppa) reaction. As a part of these studies the crystal structure of $RuCl_2(PPh_3)_2(NCC_6H_5)_2$ was determined. In many of these reactions, NMR spectra indicate the formation of a species we postulate to be an unsymmetrical chloride bridged binuclear ruthenium species. Attempts are underway to prepare larger quantities of these. Closely related chemistry appears to occur with $HC(O)N(CH_3)_2$.

Triscationic Amphiphiles with One or Two Tails

Louis Damiano,[1] John Marafino,[1] Brenden Wimbish,[1] Irfan (Simon) Ali,[1] Brenna Walsh,[1] Kirstie Thompson,[1] Kristin McKenna,[1] Tara M. Gallagher,[2] Dr. Kyle Seifert,[2] and Dr. Kevin L. Caran[1]

[1]Department of Chemistry and Biochemistry, James Madison University
[2]Department of Biology, James Madison University

The past 10 – 15 years has seen a rapid increase in the amount of antibiotic resistant bacteria. This growth is primarily due to the overuse of broad-spectrum antibiotics in both nosocomial and community-based infections. Most outbreaks involving antibiotic-resistant bacteria are nosocomial. However, community-acquired infections are increasing. In the clinical setting, a foundation for infection control lies in controlling bacterial transference. This management becomes crucial as more bacteria become resistant to antibiotics. Thus techniques such as hand washing and surface sterilization are two, of many, important avenues that need to be carefully monitored. Amphiphiles have a number of applications in the medicinal and industrial fields in which they assist in controlling bacteria transference due to their bactericidal activity. This activity is primarily due to their structure. Amphiphiles are comprised of two distinct regions: a hydrophobic tail (typically a fatty hydrocarbon chain) and a hydrophilic head (which can be ionic or non-ionic). Altering the composition, number and juxtaposition of these groups can affect their characteristics, which in turn can alter function. Two novel series of amphiphiles, with either a single or double hydrocarbon tail and three cationic head groups was synthesized. Here, the colloidal and biological properties are presented, including the critical micelle concentration (CMC, as measured by isothermal titration calorimetry), and minimum inhibitory concentration (MIC).

Coordination of Metal Ions with N-Pyrazolylpropanamide Ligands

David D'Amico, Dr. John W. Gilje and Dr. Donna S. Amenta
Department of Chemistry and Biochemistry, James Madison University

The coordination of substituted N-pyrazolylpropanamide ligands to various metallic ions was carried out to obtain crystalline solids. The new ligands; N-3 methyl pyrazolylpropanamide (L1), N-pyrazolyl,N,N dimethyl propanamide (L2), N-pyrazolyl-2-methyl propanamide (L3), and N-pyrazolyl-N-isopropyl propanamide (L4) were synthesized then allowed to react with $MnCl_2$ $4H_2O$, $NiCl_2$ H_2O, and $Ce(NO_3)_3$ $6H_2O$. The ligands were also allowed to react with $Cl_2Ru(PPh_3)_3$ on an NMR scale in various deuterated solvents. In many cases well defined crystals were formed and will be sent for crystal x-ray analysis.

Exploring the Influence of Covalent Modification on Framework Assembly Through the Synthesis and Characterization of Hydrotris(3,5-dimethyl-1,2,4-triazolyl)borates

Matthew R. Dent, Alexa M. Vinci and Dr. Barbara A. Reisner
Department of Chemistry and Biochemistry, James Madison University

Metal-organic frameworks (MOFs) are a class of solid, nanoporous coordination polymers with applications in catalysis and gas separation. Many MOFs possess framework topologies that mimic those of inorganic zeolites by using azole-based organic ligands to connect metal centers. The compound hydrotris(1,2,4-triazolyl)borate is a versatile azole-based ligand that, under solvothermal conditions, can form a diverse array of materials ranging from 0-D coordination complexes to 3-D porous frameworks. This material diversity is achieved by making simple changes to the conditions for framework assembly, such as metal cation, crystallization solvent, temperature, and time. Covalent modification of the ligand is currently being explored as another means to achieve framework diversity within this class of materials. In an attempt to produce new, covalently modified 1,2,4-triazole-based ligands, the compound 3,5-dimethyl-1,2,4-triazole (dmtrz) was synthesized via a two-step condensation reaction. The synthesis and characterization of poly(dmtrz)borates and solvothermal framework assembly will be discussed.

Structural Analysis of the Anti-viral Protein, BST-2

Kelly E. Du Pont, Aidan M. McKenzie and Dr. Christopher E. Berndsen
Department of Chemistry and Biochemistry, James Madison University

BST-2 is a human extracellular transmembrane protein that inhibits the release of viruses such as HIV-1 and Ebola from the cell surface. Viruses can evade this inhibition through antagonistic viral protein interactions with BST-2. The BST-2 is a homo-dimer that forms a coiled-coil connected by three disulfide bonds. Recent cellular studies suggest that the extracellular domain of BST-2 is flexible or structurally dynamic. However, x-ray crystallography suggests the coiled-coil structure is rigid. The goal of this study is to understand the relation between the full-length BST-2 structure and function, and the mechanism of viral protein binding. Through limited proteolysis, protein fluorescence, and small-angle x-ray scattering analysis we show that there is a flexible region and a rigid region in the extracellular portion of BST-2. Cysteine scanning mutagenesis supports these findings in vivo and structural models of the cysteine mutations suggest varying amounts of flexibility. We are beginning studies into HIV-1, Vpu and BST-2. We are purifying both the membrane-bound BST-2 and the viral antagonist protein, Vpu for biochemical and structural characterization. This will help us understand how BST-2 functions and the antagonistic interactions with viral proteins.

Structural Elucidation of Open Reading Frame 60, ORF-60, in Enteroaggregative *Escherichia coli*

Andy Heindel and Dr. Nathan Wright
Department of Chemistry and Biochemistry, James Madison University

Travelers' Diarrhea is the number one cause of childhood death in the world. Enteroaggregative *Escherichia coli* (EAEC) is one of the main causes of this disease. These bacteria adhere to the surface of the gut and stack in a brick-like pattern. Via an unstudied quorum-sensing mechanism, these bacteria express a variety of virulence factors that lead to diarrhea. The long-term goal of this research is to elucidate the mechanism by which EAEC changes from benign to virulent. A previously-unstudied open reading frame in EAEC, termed Orf-60, has recently been hypothesized to act as one of the major transcription factors influencing virulence. Here, we describe initial attempts to structurally characterize this polypeptide. Orf-60 is highly unstable in solution, and must be bound to a fusion partner in high salt concentrations and in phosphate buffer. Circular dichroism (CD) data suggests a partially α-helical structure. Further tests, including multi-dimensional NMR and X-ray crystallography, are currently being conducted to determine the tertiary structure of the protein.

Utilizing Chloroform Post-treatment to Improve the Adhesion of Au Thin Films onto PMMA

Kathleen Krist,[1] Dr. Chris Hughes,[2] Dr. Harry Hu[1] and Dr. Brian Augustine[3]
[1]Department of Chemistry and Biochemistry, James Madison University
[2]Department of Physics and Astronomy, James Madison University
[3]Department of Chemistry, High Point University

The metallization of Au onto plastics is an important processing step in applications such as the aerospace and automotive industries, the field of microelectronics, and the fabrication of microfluidic devices. While its corrosion resistance and excellent electrical and thermal conductivity make Au a useful choice, its inertness results in poor adhesion to polymer surfaces. Previous studies have indicated that exposing Poly(methyl methacrylate) (PMMA) sheets to chloroform vapor following Au deposition significantly improves adhesion. In this study, we utilized electron-beam evaporation to deposit 60 nm of Au onto 800 micron thick PMMA squares and exposed the samples to chloroform vapor heated on a hot plate set at 70°C. The force required to remove the Au thin films was determined by placing samples on a polisher spinning at 150 rpm. Subsequently, UV-VIS spectroscopy was utilized to measure the transmittance of 800 nm light through the films in order to quantify their removal as a function of applied polishing force. The Au thin films were also characterized using atomic force microscopy (AFM). AFM images demonstrated a progressive roughening of the surface corresponding to an increase in applied force. Additionally, the AFM images support a model in which the chloroform treatment softens the PMMA surface, producing a softened layer that the polisher removes simultaneously with the Au thin film.

Influence of Hofmeister Salts on the Structure, Aggregation, and Backbone Solvation of RecA

Taylor P. Light, Karen M. Corbett, Michael A. Metrick and Dr. Gina MacDonald
Department of Chemistry and Biochemistry, James Madison University

RecA is an *Escherichia coli* protein that catalyzes the strand exchange process involved in DNA repair. Previous circular dichroism (CD) studies in our lab have shown that high salt concentrations stabilize RecA in a reverse anionic Hofmeister series. Here we utilize infrared spectroscopy to further investigate how various Hofmeister salts alter RecA structure, aggregation, and solvation. Infrared studies were performed in water and deuterium oxide. Spectroscopic evidence shows that salts alter the water OH stretch and amide I and amide II vibrations arising from the protein backbone. Our data suggests salt specific influences on RecA aggregation, secondary structure, and unfolding. Additional experiments were performed under various solution conditions known to influence ion-protein and possibly water-protein interactions. These data are compared to those obtained in different Hofmeister salts in efforts to identify changes in solvation and RecA structure.

Correcting Force-Field Bias in Pin1WW

Denise McKaig, Alexandra Iuga and Dr. Isaiah Sumner
Department of Chemistry and Biochemistry, James Madison University

A protein's function is closely related to its structure and proteins that misfold are often implicated in diseases. Therefore, the folding process incredibly important to understand. This project focuses on the folding process of Pin1WW, a fast-folding protein made of three β-sheets connected with two hairpin turns. Understanding the folding process of Pin1WW is critical as it will help us understand the folding process of other β-sheet systems. However, past folding simulations of Pin1WW did not result in the β-sheet structure. Careful analysis showed this was due to a force field that was biased towards helices. Presented in this poster are initial attempts to detect the presence of bias before implementing a full folding simulation. In order to detect the presence of force-field bias, simulations of Pin1WW were created using a helical biased force-field, CHARMM27 and a nonbiased force-field, AmberFF03. These simulations included the native state as well as several nonnative helical structure. Different energy-based functions were used to score each structure. Lower scores indicate that the force-field has a preference for that motif. The initial functions were average energy of the systems and then the free energy of solvation of each system. Neither of these methods proved sensitive enough to detect force-field bias. The functions that were sensitive enough to detect the force-field bias in the CHARMM27 force-field included the conformational entropy of the protein. Hence, it is important that scoring functions include entropy contributions when screening potentially biased force-fields. The ultimate goal for these techniques is to discover any secondary structure bias in density functional theory.

Synthesis and Characterization of Sodium Hydrotris(triazolyl)borate·Solvent

Austin T. Muetterties and Dr. Barbara A. Reisner
Department of Chemistry and Biochemistry, James Madison University

Metal organic frameworks are porous solids known to be capable of gas adsorption and separation. The Reisner group studies porous solids made from the hydrotris(triazolyl)borate anion, $[BH(trz)_3]^-$ (trz=1,2,4-triazole), which is capable of selecting and adsorbing CO_2 gas. Sodium hydrotris-(triazolyl)borate solvate, $Na[BH(trz)_3]$·solvent (solvent = water, isopropanol, dimethylformamide), is a potentially porous framework if the solvent molecule can be removed. Variable temperature PXRD and TGA are being used to study these frameworks, Data show that the three solvates of $Na[BH(trz)_3]$·solvent, are related and vary only by the nature of solvent molecule incorporated. Upon heating, TGA data indicated that the three compounds lose solvent and variable temperature PXRD data shows that they convert into the same phase under vacuum. The desolvated product appears to adsorb water from the atmosphere, which could limit its use as a sorbent for other gas molecules.

Structural Studies of Obscurin Ig58-59

Matthew Oehler, Tracy Caldwell, Logan Meyer, Kelly Du Pont and Dr. Nathan Wright
Department of Chemistry and Biochemistry, James Madison University

Obscurin (800-900 kD) is a giant sarcomeric signaling protein that is an integral component in the arrangement of the basic contractile unit of muscle. Mutations to obscurin and to obscurin binding proteins are linked to human muscle diseases such as hypertrophic cardiomyopathies and muscular dystrophy. These diseases likely occur due to the abrogation of specific interactions. The modular arrangement of independently folding domains of obscurin allows for exclusive study of each of these independent binding events. Here, we study the interaction between obscurin 58/59 and titin Zlg9/10. In a first step to fully characterizing this binding interaction, we have solved the high-resolution structure of the obscurin domain Ig58 to 2.4 Angstroms. This structure is a canonical Ig-like fold, consisting of two beta sheets coming together into a beta sandwich. When combined with previously analyzed SAXS data, a picture emerges where the two domains of obscurin act in a semi-independent manner in a binding platform amenable to zig9-10 binding.

Specific Anion Effects on Partition Coefficient of Caffeine Between Aqueous and Cyclohexane Phases

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The Hofmeister series, discovered in 1888, originally ranked ions in correspondence to their relative effects on protein solubility. The series has shown stunning consistency for the ions' relative effects on physical phenomena that occur in aqueous solution. Protein denaturation, micelle formation, and surface tension comprise some of the aqueous processes of significance for Hofmeister ion discoveries. Despite significant research efforts confirming series' ranking, the mechanisms that explain the observed effects are not well understood. This experimentation investigates the specific anion effects on the partition coefficient of caffeine between aqueous and cyclohexane phases. Correlations between thermodynamic data for caffeine partition and anion physical properties are explored. The presentation will include discussion of the mechanisms that describe anion-caffeine interactions and their ultimate effects on caffeine distribution. The broad-scope implication of these results involves the application of mechanisms describing anion-caffeine interactions to explain observed Hofmeister effects on other behaviors in aqueous solution.

Limestone Analysis for Archeology

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The Shenandoah Valley contains vast amounts of limestone bedrock. Historically, this limestone has been mined and used in the construction of numerous structures around Virginia. Limestone varies in its elemental composition of calcium, magnesium, and various trace elements based on the conditions present at the time of rock formation. This study focuses on developing an analytical technique to match the limestone used in the construction of historic structures to the quarry location the limestone was mined from based on variations in the elemental composition of the limestone. Prior to analysis, the solid rock limestone samples must be digested into solution. Traditional digestion methods are time consuming and tedious, so a new digestion method was developed using a Microwave Accelerated Reaction System (MARS). Samples were analyzed for calcium and magnesium concentrations using Atomic Absorption Spectrometry. Inductively Coupled-Plasma Mass Spectrometry (ICP-MS) was used to determine trace elements present in the limestone samples.

Water Chemistry Changes in the South Fork of the Shenandoah River and Smith Creek Following Downpours

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Water chemistry of the South Fork of the Shenandoah River was compared with the water chemistry of Smith Creek. Water samples were collected at five sites on the South Fork of Shenandoah River and at 3 sites on Smith Creek over the course of four sampling trips (June 12, June 25, July 15, July 19). Field measurements included pH, dissolved oxygen, conductivity, turbidity, and water temperature. Four water samples per site were collected in polyethylene bottles for further analysis in the laboratory. The four samples returned to the lab were: (1) non-filtered, non-acidified, (2) non filtered, acid stabilized with H_2SO_4, (3) non-filtered, acid stabilized with HNO_3, and (4) field filtered (0.45 micron), acid-stabilized with HNO_3. These samples were analyzed for dissolved Ca, dissolved Mg and alkalinity, and reserved for total metals analysis and Chemical Oxygen Demand measurements. The results are interpreted based on water volume, flow rates and the local geology.

The Synthesis and Characterization of Thienyl Phosphine Derivatives for Polymerizable Metal Complexes

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The synthesis of brominated and non-brominated thiophene and bithiophene phosphine ligands were performed by the reaction of thiophene derivatives with n-butyllithium followed by the addition of chlorodiisopropylphosphine. The reactions of 2-bromothiophene and 2,5-dibromo-thiophene under these conditions produced 2-diisopropylphosphinothiophene (1) and 2-diisopropylphosphino-5-bromothiophene (2) respectively. Similarly, 2,2′-bithiophene and 5,5′-dibromo-2,2′-bithiophene yielded 5-diisopropylphosphino-2,2′-bithiophene (3) and 5-bromo-5′-diisopropylphosphino-2,2′-bithiophene (4) respectively. Compounds 1, 2, 3, and 4 were then allowed to react with either cobalt carbonyl or a mixture of cobalt carbonyl and triethylphosphine to form cobalt complexes comprised of polymerizable thienylphosphine ligands covalently bound to the metal center. The intermediates and final products were characterized using ^{1}H and ^{31}P NMR, GC-MS, and FT-IR. The resulting metal complexes were deep blue or green and spectra indicated the formation of cobalt complexes containing phosphine ligands.

Synthesis of Chlororhenium Tricarbonyl Complexes of Substituted Bipyridine Ligands for Interfacial Electron Transfer Studies

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Tricarbonyl rhenium (I) complexes have been found to have very useful applications in chemi- or electroluminescence, chemical and biological sensing, bioconjugation photoredox chemistry and as phosphorescent dopants for organic light emitting diodes due to their luminescent properties. Specifically, this work focuses on the importance of ultrafast electron transport systems, in order to understand the dynamics between ET and molecular structure in ultrafast interfacial processes between metal or semiconductor nanoparticles and molecular adsorbates. By attaching different substituents to the bipyridine ligands it is expected to increase the ET rate by influencing the electronic coupling between the complex and a semiconductor. A molecule of chlorotricarbonyl-rhenium complexed with substituted bipyridine ligands has been synthesized in order to measure their effects on ultrafast electron transport systems.

Understanding E2 Mechanism using NMR

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The ubiquination pathway controls human cellular processes such as cell cycle division, DNA transcription and repair, and immune responses. In these processes, ubiquitin is covalently attached to a substrate protein by the combined efforts of an E1 activating enzyme, an E2 conjugating enzyme, and an E3 ubiquitin ligase. We are concerned with investigating the catalytic mechanism of ubiquitin transfer onto the substrate protein. The structure of yeast Ubc13, an E2 conjugating enzyme, has been solved using nuclear magnetic resonance (NMR). The study of the structure of Ubc13 compared to that of Ubc13 bound to ubiquitin in the active site will show the changes in the active site upon binding. Through the use of kinetic isotope effects, mutagenesis, and transition state mimics of ubiquitin conjugating reaction we will completely describe the mechanism of Ubc13 and the functional elements of the active site of Ubc13.

Phase Behaviors of PEO-PPO-PEO Triblock Copolymer in the Presence of Salts and Alcohols

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The phase behaviors of a poly(ethylene oxide)-b-poly-(ethylene oxide) (PEO-PPO-PEO) triblock copolymer in the presence of salts and alcohols were investigated by using an Optimelt automated melting point system. In solutions with low concentrations of alcohols, the polymer underwent a two-step phase transition while at high concentrations of alcohols there was a one-step phase transition. Introduction of salts into the methanol-polymer mixture did not influence the effects of methanol on the phase behaviors of PEO-PPO-PEO significantly. On the other hand, addition of methanol into salt-polymer mixture enhanced the effects of salts on PEO-PPO-PEO phase behaviors. The mechanisms of interactions between the anion, methanol, and the polymer that affect the phase behaviors of the polymer were discussed.

The Influence of Synthesis Environments on Fluorescent Nanoparticles

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Currently, in the field of optical materials silica glass is the dominant matrix. Polymers are being studied as an alternative to silica glass. To address the limitations of polymer matrices due to attenuation caused by high vibrational energy, fluorescent nanoparticles are added into the polymer. Inorganic crystals doped with luminescent rare-earth ions are formed to produce those light emitting nanoparticles. Attenuation limits the effectiveness of the fiber optic cables and reduces the emissions of the rare-earth ions if dispersed without a protective polymer. This research explores the factors that impact the luminescent properties of rare-earth ions when the rare-earth ions are a part of low vibrational energy structure (nanocrystal) within the polymer matrix. Rare earths ions (La^{3+}, Tb^{3+}, Eu^{3+}) and acetylsalicylic acid (an organic ligand which aids in dispersing the nanocrystals within the polymer matrix) were synthesized to create nanoparticles in polymethyl methacrylate (PMMA). This research focuses on varying synthesis environments for rare-earth doped nanoparticles. The main objective is to use rheology to determine the viscosity of the synthesis environments. The information collected will give better understanding as to how the viscosity impacts the luminescent properties of the polymer matrix.

Molecular Dynamics Studies of the Ubiquitin Conjugation Mechanism

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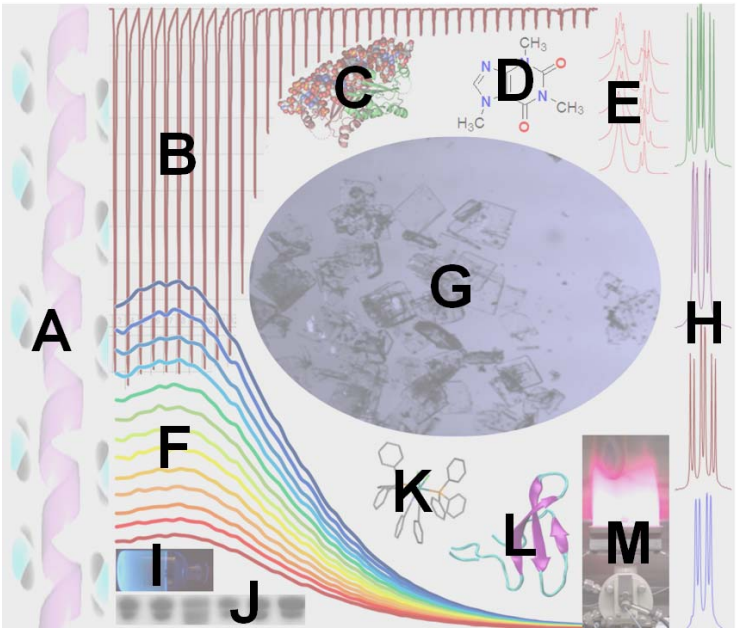
One of the main functions for ubiquitin is to signal proteins for cellular degradation. Ubiquitination of proteins occurs in three enzymatic steps. In the second step, ubiquitin transfers to a conjugating enzyme, called E2, which then transfers ubiquitin to a lysine in the target protein. However, the mechanistic details for this final transfer remain obscured. Although it is clear that ubiquitin does bind, there are no studies that show exactly how this happens. The most favored proposal involves a step-wise mechanism with a tetrahedral oxyanion intermediate. This work probes the accuracy of the oxyanion hypothesis. In particular, the oxyanion is conjectured to be stabilized by forming hydrogen-bonds with a nearby asparagine residue. This is called an oxyanion hole. By using molecular dynamics (MD), combined with umbrella sampling, a free energy profile of the formation of the oxyanion hole is constructed to see if its creation is thermodynamically favorable. Furthermore, information about the hydrogen-bonding environment in the active site is extracted.



The image on the front cover is a collage of images from the research labs of:

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