# The 12th Annual ACSSA Undergraduate Research Symposium


# Abstracts

Department of Chemistry and Biochemistry
University of California, San Diego

Natural Sciences Building Atrium
Thursday, May 17, 2018
5PM – 7PM

# *Keynote Speaker*

## Dr. Valerie Schmidt

Professor Valerie Schmidt, originally from Maryland, earned her undergraduate degree in Chemistry from Towson University. She then pursued graduate studies at the University of North Carolina at Chapel Hill.

As a Burroughs-Wellcome and Venable Fellow she synthesized a series of oxygen-centered radical precursors to achieve olefin difunctionalizations as well as developed an N-haloamide reagent for selective aliphatic C-H bond halogenation. She subsequently studied as a NIH Postdoctoral Fellow at Princeton University. While at Princeton, Valerie synthesized reduced iron and cobalt complexes supported by redox active ligands that catalyze [2+2] cycloadditions of unactivated alkenes. She then joined the Department of Chemistry and Biochemistry at UCSD in July 2016!

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# *Biochemistry Division*

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**Investigating knot motifs in methyltransferase secondary structures**

***Anser Abbas, Tiange Tao (co-presenter), Junkun Zhu (co-presenter),* Dominique Capraro and Patricia Jennings**

Principal Investigator: Dr. Patricia Jennings

Elucidating the relationship between protein structure and function is essential for understanding its role in biological systems. It also yields insight into evolutionary history and may help determine the initial sites for targeted drug design. The discovery of unique backbone knot motifs in protein secondary structures in the last decade has yet to fully reveal the role knots play in final fold and function for these unique proteins. More specifically, a class of proteins, methyl transferases (MTase), contain several knotted backbone proteins. Here we initiate the investigation of the knotted structure in proteins through optimization of purification techniques for MTases from different species. Through affinity and size exclusion chromatography, we are able to isolate protein at 95% purity in unique solution conditions. Furthermore, we attempt to expand our investigation to determine cofactor interactions, as well as to identify the oligomeric state of these MTase proteins.

Biochemistry #1

**Dynamics of E2 Ubiquitin-Conjugating Enzyme**

***Rachel Blake*** **and Ryan Lumpkin**
Principal Investigator: Dr. Ryan Lumpkin

Ubiquitin (Ub) is an 8 kDa post-translational modification that is involved in protein degradation, the immune response, and cellular signaling. Delivery of the ubiquitin tag to the substrate protein depends on activation and transfer by E1, E2 and E3 enzymes. First, the E1 ubiquitin-activating enzyme forms a high energy bond between Mg-AMP and the C-terminus of Ub. The active site cysteine on E1 attacks this bond to form a thioester bond with Ub, from where it is passed onto one of several E2 ubiquitin-conjugating enzymes, exchanging its thioester bond with E1 for another with E2. The E2-Ub complex is then recruited by an E3 ligase that performs the final step of conjugating Ub to an exposed lysine residue on the target protein. While the human proteome contains a single E1 protein, 35 E2 proteins and over 600 E3 proteins have been identified. E3 ligases confer substrate specificity to the process, while the E2 enzymes determine the formation of mono- or poly-ubiquitin modifications. The E2D family (E2D1, E2D2, E2D3) is the most evolutionarily conserved of the E2 proteins, and many E3 ligases associate with at least one protein of the family. In order to probe the interaction between Ub and E2 enzymes, we performed site-directed mutagenesis of E2D2 to replace the active site cysteine with a lysine, resulting in an irreducible isopeptide bond between Ub and E2D2 following activation by E1. We performed Hydrogen-deuterium exchange mass spectrometry (HDXMS), which probes solvent accessibility and protein-protein interactions, on E2D2 and E2D2-Ub to investigate the binding interface and dynamics of E2D2.

**Genome mining for the discovery of potential antibiotics**

***Marvin Chau,* Jie Li and Bradley Moore**
Principal Investigator: Dr. Bradley Moore

The increasing bacterial resistance to antibiotics is an impending crisis. There is a need for new methods in discovering potential antibiotics. Genome mining is a means of sifting through the vast wealth of genetic information available and finding the most promising gene clusters that can lead to novel molecules with biological activities. I am working with a marine Streptomyces sp. CNT360 strain containing a polyketide synthase, nonribosomal peptide synthetase (PKS-NRPS) hybrid biosynthetic gene cluster (BGC). A search through the accessible databases have shown that this BGC has no homologues, suggesting that the compounds produced are likely to be novel. In addition, this gene cluster contains a putative self-resistance gene homologous to heat shock protein 90 (HSP90) which suggests that this BGC product might target HSP90. The BGC was captured by transformation-associated recombination (TAR) cloning and heterologously expressed in Streptomyces coelicolor M1152, which led to an observation of more than 20 compounds separated into 3 types. The isolation and structure elucidation of some of these compounds confirmed their structural novelty as a novel class of compounds, with more compounds under further investigation. The identification of thiazole and sulfur functionalities within isolated compounds have sparked interest in their biosynthesis. Although the isolated compounds were shown to not be HSP90 inhibitors, further biological activity screening have observed cellular membrane activity. Follow-up experiments have shown these compounds to be metal chelators. Further studies on the mechanism of action (MOA) is ongoing.

**Sln10 a peculiar P450 involved in the biosynthesis of Salinamide**

***Ernesto Garibay*, Peter Jordan and Bradley Moore**
Principal Investigator: Dr. Bradley Moore

Salinamides are a rare class of bicyclic depsipeptide antibiotics with a (4-methylhexa-2,4-dienoyl) glycine handle moiety that contributes to its chemical complexity and biological properties. Sln10 is a peculiar P450 enzyme involved in the biosynthesis of these salinamides. Sln10 is involved in the epoxidation of this acylglycine moiety to create the "basket handle" at a tyrosine residue of the depsipeptide. The biochemical mechanism is explored using modified acylglycines.

Biochemistry #4

# Expressing Deuterated W48 Azurin using Minimal Media as a Means of studying Cellular Long-Distance Electron Transfer

***Wanjun Gu*, Joel Rivera, Justine Liange and Judy Kim**
Principal Investigator: Dr. Judy Kim

Despite the simplicity of the transfer of a single negative charge, cellular electron transfer is an essential process for varieties of body metabolism such as ATP decomposition, neuron excitation and gene regulation. For this research, we are specifically focusing on how protein manages to efficiently transfer electrons within a long distance. To better illustrate this complex process deep inside cells, a model protein, Azurin, which can be naturally found in bacteria is used. Based on preliminary work of this research, we are currently working on chemically modify W48(Tryptophan) in Azurin by replacing the original hydrogen atoms on the tryptophan to deuterons. In this way, we are making a difference in terms of charge quenching during electron transfer and resultingly, the spectroscopy of intermediate free radicals formed inside the protein. For the insertion of deuterons in tryptophan, a special kind of growth media, the Minimal Media is used. Minimal Media(MM), unlike Lysogeny broth(LB), is made of inorganic salt and amino acids and it is therefore poor in nutrients. Instead, MM provides only target amino acids to E-Coli, making genetically mutated E-coli express protein only consisted of certain given amino acids pre-engineered into the media. So far, the recipe of MM has already been redesigned to fit certain mutant of E-Coli used to express W48 and potentially WD48 Azurin. And sample spectra of cell growth, Cu-Azurin and Zn-Azurin has already been collected and saved in our database. However, the exact behavior of WD48 Azurin in terms of its possible shift in absorption peak and its influence to electron transfer is yet to be determined.

**Facile Fabrication of HCPT-Backboned Amphiphilic Polyprodrug with Precisely Controlled Drug Loading Content for Controlled Release**

***Qi Hua*, Xiaolong Zhang and Hua Wei**
**Lanzhou Univeristy,China**
Principal Investigator: Dr. Hua Wei

Fabrication of polymeric prodrugs with precisely controlled drug loading content (DLC) as well as promptly intracellular destabilization toward enhanced therapeutic efficacy remains challenge and generally requires complicated chemistry design and manufacture. For this purpose, we accomplished a facile construction of reduction-sensitive amphiphilic polyprodrugs with an anti-cancer drug, 10-hydroxycamptothecin (HCPT) and a hydrophilic poly(ethylene oxide) (PEG) moiety as the alternating building blocks of the multi-block copolymer using Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAc) click coupling between azide-SS-HCPT-SS-azide and alkyne-PEG-alkyne. Adoption of PEGs with two different molecular weights (MWs) of 400 and 1450 Da (PEG400 and PEG1450) afforded two polyprodrugs with different DLCs. Both formulations can self-assemble into spherical micelles with hydrodynamic diameter smaller than 200 nm, and exhibit glutathione (GSH)-triggered degradation for promoted drug release. A further comparison revealed that the PEG1450-based polyprodrug is a better formulation than the analogue constructed from PEG400 in terms of micelle stability, drug loading capacity, in vitro drug release behaviors, cellular uptake, and cytotoxicity. This study thus provides a facile yet efficient strategy toward polymeric prodrugs with precisely controlled DLC and reduction-triggered degradation for enhanced anticancer drug delivery.

**Generating and Characterizing Interfaces in Novel Metalloprotein Assemblies**

***Francis Le,*** **Julian Esselborn and Akif Tezcan**
Principal Investigator: Dr. Akif Tezcan

Azurin is a blue copper protein found in several bacterial genera, known for its fast electron transfer capability. In the infectious bacterium Pseudomonas aeruginosa, it assists in the respiration of nitrates and nitrites via electron donation to reductases such as cytochrome cd1. The protein's stability and tunable redox activity make it a practical and potentially useful building block in the construction of novel metal-mediated assemblies. Our goal is to produce a self-assembling azurin homodimer with a metal-binding β-sheet interface and investigate the assembly's structure, binding constant and electrochemical properties. Using rational design methods, a dimer candidate was selected to maximize interface shape complementarity. We designed a tetrahedral binding site consisting of three histidines and one glutamate. The ligands are distributed across the protein-protein interface, thus making use of strong non-covalent metal bonds to bring together two subunits in a directed configuration. Site-directed mutagenesis PCR and recombinant expression of the protein variants in E. Coli is ongoing. Circular dichroism spectroscopy, potentiometry, and X-ray crystallography techniques will be used to verify the identity, redox activity, and structure of the individual subunits and the overall assembly. In addition, analytical ultracentrifugation will be used to determine the influence of different metals on the strength of the protein-protein interface. These characterizations will provide insight into optimization of the β-sheet interface. Furthermore, successful production of the dimer may allow for additional studies in the formation of metallocluster-mediated azurin dimers and larger metalloprotein networks.

**Improved RNA-hairpin recognition in the RNA-TAG system**

***Dylan Mills*, Kayla Busby, Seth Alexander and Neal Devaraj**

Principal Investigator: Dr. Neal Devaraj

Biochemical modification of RNA substrates could aid in elucidating biological function of RNA and protein, for example by pulling down RNA associated proteins or RNA-imaging in vivo. Previous work has been done on the RNA-TAG system which through use of an enzyme, called TGT, a 17-nucleotide hairpin motif is bound in the active site. A specific guanine in the hairpin is replaced for a functionalized PreQ1 probe. Initial work with this system used E. coli derived TGT. While this enzyme achieves good labeling efficiency in vitro, it also labels endogenous 'off target' mRNA abundant in all cells. We found, using qPCR, increased labeling specificity from a variant of the TGT enzyme from the bacteria Z. mobilis. Zm TGT has nearly 1 order of magnitude greater specificity toward the 'on target' over the 'off target' labeling when compared to E. coli. To explore the structure function relationship in this system we also generated enzyme and RNA-hairpin mutants and characterized their activity in vitro through labeling and gel shift assay.

Biochemistry #8

# Rad9's Role in Suppressing the Sae2Δ Sgs1Δ Synthetic Lethality

***Sarah Moore*, Chris Putnam, and Richard Kolodner**
Principal Investigator: Dr. Richard Kolodner

Synthetic lethality occurs when two mutations, which are viable by themselves, cause cell death (Hengel et al. 2017). Understanding the basis of synthetic lethality provides insight into suppressor mutations and their relationship to DNA repair pathways. The protein Rad9 has two roles in DNA repair regulation; it is involved in the DNA damage checkpoint, which determines whether or not a cell can divide in the presence of DNA damage, and it also forms an oligomer that binds at DNA double strand breaks (DSBs) to aid with repair. This project investigates how the model organism Saccharomyces cerevisiae suppresses the synthetic lethality between deletions of the DNA repair genes SAE2 and SGS1. By further examining Rad9's role in suppressing the sae2Δ sgs1Δ synthetic lethality, one can better understand the molecular pathways involved and their relationship to suppressor mutations. Rad9's first role in the DNA damage checkpoint is currently being tested through its ability to suppress the sae2Δ sgs1Δ synthetic lethality by creating heterozygous sae2Δ/SAE2 sgs1Δ/SGS1 diploid strains. These strains undergo meiosis through sporulation and are genotyped to determine which genetic combinations are viable. Insight into Rad9's role in DNA repair regulation can provide a better understanding of cancer precursors, leading to earlier detection of genetic predisposition towards certain cancers.

Biochemistry #9

**Preparation of Neurotensin Receptor 1 in Phospholipid Bilayers for Solid-State NMR Spectroscopy**

***Youjeong Na,* Sangho Park, and Stanley Opella**

Principal Investigator: Dr. Stanley Opella

G protein-coupled receptors (GPCRs) are 7-transmembrane helical proteins that are embedded in the plasma membrane. They recognize various extracellular signals and transduce them to intracellular heterotrimeric G proteins, which further activate cellular responses. Neurotensin receptor 1 (NTR1) interacts with neurotensin, a 13-residue peptide, which plays important roles in the pathogenesis of neurological disorders such as Parkinson's disease and schizophrenia, and in lung cancer progression. To characterize the structure and dynamics of NTR1 in phospholipid bilayers by solid-state NMR spectroscopy, we prepared isotopically labeled receptors using glutathione S-transferase-fusion expression system in E. coli. Optimization of the sample preparation and preliminary NMR results of the receptor in lipid bilayers will be presented.

Biochemistry #10

# Effects of Protein Kinase A (PKA) on Filament Formation in Cells

***Razina Pathan*, Yuliang Frank Ma, and Susan Taylor**
Principal Investigator: Dr. Susan Taylor

Many patients with Parkinson's disease have mutations in LRRK2 (leucine-rich repeat kinase) and a common property of LRRK2 mutants is formation of filaments in cells. It has been suggested that the function of LRRK2 is related to PKA and we are examining the effects of PKA on the filament formation property of LRRK2 in the cells. LRRK2 was stained with flag antibody to visualize the filaments and they were co-transfacted with proteins related to PKA to assess their affects. Cells were co-transfacted with the following: Flag LRRK2 alone, Flag LRRK2- AKAP (A-kinase anchoring proteins that bind to the regulatory subunit of PKA), Flag LRRK2- PKI (PKA inhibitor), Flag LRRK2- RII (regulatory subunit of PKA), Flag LRRK2- RII-R325K (mutant regulatory subunit), and Flag LRRK2- RI. To further induce filament formation, BMPPB-32 (kinase-inhibitor) is added to each set of cells. There seems to be an inverse relationship with filament formation and PKA-RIIB as when there is a high concentration of RII in the cells, there seems to be an absence of filaments. No filaments are observed in the cells co-transfacted with LRRK-RII suggesting that filament formation in the present of RII does not occur. The other co-transfacted cells had filaments present in them, indicating that it does not have as strong of an affect as RII in inhibiting filament growth. Overall, it seems that PKA does have an effect on the filament formation property of LRRK2.

**Determining the binding kinetics of p50/RelA with Transactivation Domain (TAD) with different kB binding sequences**

***Allen Po*, Dominic Narang, and Elizabeth Komives**
Principal Investigator: Dr. Elizabeth Komives

The Nf-κβ family of transcription factors plays an important role in regulating genes involved in eukaryotic immune and inflammatory responses and is regulated and inhibited by the Iκβ family. The canonical and most common form of Nf-κβ is a dimeric complex comprised of p50 and p65 (Rel-A) subunits, the latter of which contains a transactivation domain. All in vitro studies to understand the dynamics of DNA binding and stripping from the RelA/p50 heterodimer have been done with a truncated version of the protein dimer which lacks the transactivation domain (TAD). Previous in vivo studies have shown that upon binding to unique κβ DNA sequences, different coactivators are recruited to the TAD and this is the result of the interactions imparted upon the TAD region by the DNA-binding domain (DBD). These combined results reveal an important allosteric mechanism which exists between the DBD and TAD and can be used to explain the difference in observed binding kinetics when Nf-κβ is bound to different κβ sequences. Recently, however, our lab has been able to purify and express the full length Nf-κβ with the TAD and used it to conduct fluorescence anisotropy and stopped-flow experiments to determine the association and dissociation rates to different κβ sequences. Using this preliminary data, we plan on using the same full-length protein in similar experiments with the inhibitor Iκβα to observe any changes in molecular stripping, the enhanced dissociation rate of Nf-κβ from DNA, with different κβ sequences.

# Uncovering the Role of Oxygen Ligand Position in Conformationally Gated Electron Transfer in Nitrogenase

***Laura Williamson*, Hannah Rutledge, Faith Katz, and Akif Tezcan**

Principal Investigator: Dr. Akif Tezcan

Nitrogenase is the only known enzyme to catalyze dinitrogen reduction, and therefore plays a critical role in the biological nitrogen fixation cycle by breaking the strong, triple bond of dinitrogen to produce ammonia. The P-Cluster -a unique Fe-S cluster consisting of two fused [4Fe-4S] cubes- serves as an electron relay site between FeP (the exclusive reductase of nitrogenase) and FeMoco (the active site of the enzyme). The P-Cluster is therefore responsible for mediating the transfer of multiple electrons between the two subunits in a manner that is believed to be controlled by a conformational gating mechanism. Recent crystallographic studies have revealed that an oxygen-based ligand (either serine or tyrosine) ligates the P-cluster upon 2 oxidation. In both cases, ligation occurred on same cube of the P- Cluster although at different Fe atoms. Such behavior is unusual for Fe-S clusters, and the conservation of the oxygen ligand across nitrogenases indicates that the oxygen-ligand may be functionally relevant to the P-Cluster's role in mediating electron transfer. However, since electron transfer to FeMoco is believed to be regulated by conformational changes that occur upon binding FeP, the question remains of whether the oxygen-ligand's role is to simply donate electron density to the P-Cluster upon oxidation or to donate electron density to a specific region of the P-Cluster. This study therefore seeks to uncover the role of the oxygen-ligand in electron transfer in nitrogenase by creating MoFeP variants where the oxygen-ligand has been moved to the opposite cube of the P-Cluster. To do so, site-directed mutagenesis and homologous recombination techniques were used to create several MoFeP variants where the oxygen-ligand has been repositioned. Once expressed and purified, ligation will be observed using EPR spectroscopy and X-Ray crystallography. Activity assays will then be conducted to determine how the mutations affect the enzymatic activity of the protein.

Biochemistry #13

**Investigating the chemical role of nifM gene in activating Fe-Protein in nitrogenase**

***Wanqing Xu*, Hannah Rutledge, Faith Katz, and Akif Tezcan**

Principal Investigator: Dr. Akif Tezcan

Nitrogenase is the only known enzyme that reduces N2 to NH3. It consists of two proteins: MoFe-protein (MoFeP), which catalyzes the reaction, and Fe-Protein (FeP), which delivers electrons through its 4Fe4S cluster to MoFeP. In Azotobacter vinelandii, the nif gene cluster encodes proteins involved in N2 reduction. NifH codes for the primary structure of FeP, and an accessory gene, nifM, activates FeP to transfer electrons. However, the mechanism of how the nifM and nifH products interact is still unknown, and the structure of nifM is yet to be determined. We are obtaining nifM product from E.coli overexpression followed by affinity-tag purification. Its structure will be solved by protein crystallography, and its function will be tested by chymotrypsin assay and other related assays.

Biochemistry #14

# *Inorganic Division*

1. Riddhi Ananth
2. Kristine S. Kay
3. Michel Chen
4. Jerika Chiong
5. Gavin Heim
6. Steffen Mevik
7. Josh Richardson
8. Ashley Tamura
9. Junwei Wang

**Facile bench-top procedure to stabilise porous silicon nanostructures**

***Riddhi Ananth*, Hsuan Chang, and Michael Sailor**
Principal Investigator: Dr. Michael Sailor

Production of porous silicon by electrochemical anodization results in the formation of chemically reactive hydrogen terminated surfaces. Grafting of the 5-membered heterocyclic silane, 2,2,5,5-tetramethyl-2,5-disila-1-oxopentane onto mildly oxidized porous silicon surfaces offers a simple and effective method to stabilize mesoporous silicon. Our results suggest that the silane binds to the surface via Si-O-Si bonds, and rapidly polymerizes to form a hydrophobic surface that is stable in alkaline media. The reaction is a 'living polymerization and reaches completion in under 10 minutes while retaining the open pore structure of the original porous silicon substrate, although the porosity is reduced due to partial filling of the pores by the silane polymer product. The porosity of the samples can be regulated by varying the concentration of silane used in the grafting reaction. This chemistry has potential applications in chemical sensor and drug delivery materials.

Inorganic #1

# Synthesis of Carbene Ligands for Cobalt-based Single Molecule Magnets

***Kristine S. Cay*, Alex. J. Mantanona, and Jeffrey Rinehart**
Principal Investigator: Dr. Jeffrey Rinehart

Single molecule magnets (SMMs) exhibit electromagnetic behaviour which is uncommon in molecular species. These properties manifest themselves as bistability of the ground state and magnetic hysteresis - the ability of the molecule to maintain a magnetic moment in the absence of a magnetic field. However, a marked limitation is that their hysteretic behaviour can only be demonstrated at extremely low temperatures.

SMMs can be synthesised by forming transition metal or lanthanide complexes with ligands that would enforce specific geometries on these metals. In this project, 3d transition metals will be bound with various ligands of interest including mesoionic carbenes, triazoles, and bis-N heterocyclic carbenes. These ligands and complexes will be tuned to impart specific geometries on transition metal centres to maximise anisotropy of the single molecule magnets while also optimising ferromagnetic coupling between adjacent metal centres. Data for this project has thus far been collected using a superconducting quantum interference device (SQUID) and single crystal X-ray diffractometry (XRD). Potential future applications of these SMMs include nano-transitors, spin valves, quantum computing, and increased digital storage density of computers.

Inorganic #2

**Photoswitchable Magnetic Properties of a Manganese substituted Keggin-based Extended Polyoxometalate Framework**

***Michel Chen*, Michael Turo, Carl Lemmon, and Alina Schimpf**

Principal Investigator: Dr. Alina Schimpf

Extended polyoxometalate (POM) frameworks have potential application in next generation materials due to the modular assemblies taking on the properties of its POM building blocks. Previous research has shown that a "Keggin-net"{(C4H10NO)40(W72MnIII12O268Si7)} framework consisting of linked Mn-substituted Keggin POM clusters exhibits structural stability when switching from different Mn oxidation states. Additionally, individual POM clusters similar to the "Keggin-net" building blocks exhibit interesting transition metal to POM charge transfer as a photoredox process. By taking advantage of the Mn(II)/Mn(III) redox couple, the magnetic properties of the material can be modulated.

Inorganic #3

# Rational design of metal-organic frameworks from discrete synthetic clusters

***Jerika Chiong,*** **Jake B. Bailey, and F. Akif Tezcan**
Principal Investigator: Dr. F. Akif Tezcan

Metal-organic frameworks (MOFs) are porous coordination polymers comprised of metal ions/clusters (nodes) and metal-coordinating organic ligands (struts). The metal-ligand interactions of these nodes and struts promote self-assembly into organized supramolecular architectures in which the struts control the spatial geometry of the nodes through their size and number of coordination sites. The discrete components of these frameworks can be systematically altered in a predictable manner to produce desired functionalities such as gas storage, catalysis, drug delivery, and molecular recognition. We aim to rationally design highly stable MOFs based on a previously synthesized symmetric cluster. We selected a robust M4L6 cluster with dihydroxamate chelating ligands to act as the node. Replacing this ligand with a symmetric tetrahydroxamate bridging ligand would allow multiple clusters to be chemically linked, leading to the formation of an ordered 3D network instead of a discrete cluster. This could also be achieved by appending a monodentate metal binding group, such as a pyridine ring, in place of one of the dihydroxamate moieties. To this end, we synthesized multiple di- and tetrahydroxamate ligands for MOF assembly. Solvothermal synthesis was employed to facilitate the formation of a crystalline framework. We plan to use both single-crystal and powder X-ray diffraction to characterize the materials that form. The development of these cluster-based MOFs ultimately represents an organized architecture where metal-ligand interactions form highly stable clusters, and the symmetry of the ligands dictates the crystallographic organization of the clusters. The formation of the proposed MOFs allows for precise tuning of the lattice pores while retaining the functionality of the individual clusters.

**Proton-coupled electron transfer between redox non-innocent bridging ligands in hydrogen bonded Ru3O clusters**

***Gavin Heim*, Tyler M. Porter, and Clifford Kubiak**
Principal Investigator: Dr. Clifford Kubiak

The spectroscopic and electrochemical characterization of a hydrogen-bonded, oxo-centered triruthenium cluster of the type Ru3(μ3-O)(OAc)6(CO)(py)(pyrim) (where py = pyridine and pyrim = 4-(3H)-pyrimidone, 1) is reported. Electrochemistry at reducing potentials reveals that the neutral, isovalent cluster is mostly monomer in solution, which then undergoes rapid self-dimerization upon a one-electron reduction to (1[2])-. These results are further supported by Fourier transform infrared spectroelectrochemistry (FTIR-SEC), where upon a one electron reduction, the sudden collapse of the pyrimidone carbonyl (CO) stretch at 1710 cm-1 and small red-shift (< 5 cm-1) of the ruthenium bound carbonyl (CO) stretch, supports an electronic structure that is largely delocalized between the two hydrogen bonded ligands with minimal cluster contribution. The lack of appearance of intervalence charge transfer (IVCT) bands in the near infrared (nIR) indicates that electron transfer (ET) is coupled to a proton transfer event. Spectroelectrochemical studies on the analogous methyl-terminated complex that is incapable of dimerizing, Ru3(μ3-O)(OAc)6(CO)(py)(pyrim-CH3) (2), reveal clear IVCT bands centered about 1200 nm similar to previously reported monomers [1] where intracluster ET is believed to occur. These results have important implications in understanding how non-covalent interactions mediate ET to achieve delocalized electronic structures.

[1] Porter, T.; Heim, G. P.; Kubiak, C. P. Effects of Electron Transfer on the Stability of Hydrogen Bonds. Chem. Sci. 2017, 8 (11), 7324-7329.

**Nickel Supra-Particle Synthesis**

***Steffen Mevik,* Jessica Geisenhoff, Hankyeol Jung, Alexander Rachkov, Mike Turo, and Alina Schimpf**

Principal Investigator: Dr. Alina Schimpf

Supra-particles, particularly magnetic nickel supra-particles are an interesting class of materials because of their possible improvements to previous nickel catalysis, such as dry methane reforming. Our lab has developed a synthesis of nickel supra-particles by dissolving bis(cyclooctadiene)nickel(0) in polarized di-halogenated aromatic hydrocarbon solvents. My research shows that nickel supra-particle formation is dependent on the polarity of the solvent. When dissolved in ortho-dichlorobenzene, nickel nanoparticles agglomerate into monodisperse supra-particle structures, while para-dichlorobenzene affords polydisperse individual particles. Full understanding of this mechanism would yield greater insight into the various possible routes to metallic supra-particle synthesis.

Inorganic #6

**Synthetic Progress Towards Cobalt Chalcogen Isocyanide-Bridged Cluster**

***Josh Richardson*** **and Joshua Figueroa**

Principal Investigator: Dr. Josh Figueroa

It is known that cobalt chalcogen clusters of the form Co6E8(CO)6-x(PR3)x (x=0-6, and R=Me, Et, Ph, and various other common alkyl/aryl phosphines) are redox active and fairly robust, chemically. Moreover, it has also been shown that clusters derived from this parent motif can be used as monomers to create rudimentary polymers that show similar electrochemical activity. Subsequently, we have taken an interest in producing analogous clusters that seek to improve the stability of the parent cluster, while also improving the ability to link monomers into extended polymers. In order to achieve this Co6Se8(PEt3)4L2 (where L=CNAr, and Ar=2,6-(2,4,6-Me3C6H2)-C6H3 also known as dimesitylene m-terphenyl) has been synthesized. This isolobal analog to carbon monoxide allows us to retain the general electronic properties of the molecule, while improving its resistance to chemical attack. Furthermore, we hope to employ a ditopic variant of this ligand (CNAr-ArNC) to achieve higher order polymers, or materials, than the known dimers and trimers.

Inorganic #7

**Synthesis of Nickel Selenide Nanocrystals**

***Ashley Tamura,* Jessica Geisenhoff, and Alina Schimpf**
Principal Investigator: Dr. Alina Schimpf

Layered materials, such as transition metal dichalcogenides (TMDs) have received much attention for their potential as next-generation electronic, optoelectronic, and catalytic materials. The unique properties of these materials stem from their crystallographic structure. Colloidal synthesis of inorganic nanocrystals has been studied extensively due to the control it gives over the electronic, optical, magnetic, and chemical properties of solid state systems. Our project explores a wide range of synthetic parameters in order to obtain size-, shape- and phase-tunable nickel selenide nanocrystals using a colloidal synthesis method. Recently we investigated the use of various selenium precursors and solvents, some of which produced monodisperse, non-sintered nanoparticles. This has furthered our understanding of how to best synthesize these nanocrystals and brings us one step closer to our goal.

Inorganic #8

**Polyoxemetelate Frameworks Composed of Presslyer Anions and Transition-Metal Cations**

***Junwei Wang,*** **Linfeng Chen, and Alina Schimpf**

Principal Investigator: Dr. Alina Schimpf

Polyoxemetelates (POMs) are inorganic polyatomic ions, consisting of transition metal oxyanions linked by shared oxygen atoms. We use transition-metal cations, such as Mn2+, Co2+, Ni2+, and Fe2+/3+, to link a Preyssler POM, K14NaP5W30O110, into an extended framework. This research focuses on determining the best conditions to afford linked structures, and explores the effects of various synthetic conditions on the final structure of the framework. Specifically, we tested different temperatures, concentrations, metal/POM ratios, metal anions and pH conditions. Optimum conditions for linking with various transition metals will be presented.

Inorganic #9

# *Organic Division*

1. Xi Chen
2. Min Cho
3. Emily Eisner
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5. Jacob Hawver Patcher
6. Bryant Lim
7. Richard Niederecker
8. Arthur Rezian
9. Vincent van der Puyl
10. Yifan Wu

**Readily Available Primary Amino-Borane Derivatives as Powerful Reagents for Aldimine Synthesis**

***Xi Chen,*** **Glen P. Junor, Erik A. Romero, Rodolphe Jazzar, and Guy Bertrand**

Principal Investigator: Dr. Guy Bertrand

A new and efficient method for aldimine synthesis from aldehydes and primary amino boranes (RNHBR2) at room temperature has been developed. These primary amino boranes, synthesized from the catalyst-free dehydrocoupling of amines and pinacol borane or 9-BBN, react with aldehydes through a concerted mechanism involving the formation of Bpin-OH or 9-BBN-OH. The synthetic strategy is especially efficient for electron poor and bulky amines, which are reluctant to react with aldehydes under dehydration conditions, even in the presence of pyrrolidine organocatalyst. The high functional group tolerance of this new reaction, as shown by the Glorius robustness screen, open the way for synthesizing previously difficult aldimines in excellent yields. We believe that the simplicity and the scope of this methodology will prove crucial in the synthesis of complex natural products and drug molecules.

Organic #1

**Significance of Analogues of 20-nor-Salvinorin A, a Potent k-Opioid Agonist**

***Min Cho,* Jeremy Roach, and Ryan Shenvi**
Principal Investigator: Dr. Ryan Shenvi

The plant metabolite salvinorin A (SalA) potently agonizes human k-opioid receptors, but does not agonize the k-opioid receptor. Selectivity among opioid receptor types may allow inhibition of pain while limiting risk of addiction – a problem that plagues modern painkillers. However, the hallucinogenic effect of SalA limits its utility as a potent painkiller. Although significant progress has been made in the preparation of SalA analogs with improved properties, chemical syntheses suffer long synthetic routes due to the structural complexity and instability of SalA. The instability of Sal A is due to epimerization at the C8 position, which leads to loss of binding affinity and potency. To minimize scaffold epimerization, we deleted a destabilizing methyl group (C20) through a 10 steps total synthesis. By comparison, prior syntheses of SalA required over 20 or more steps. Additionally, replacement of O6 with CH2 completely suppressed epimerization and maintained activity at the k-opioid receptor. Currently, we are modifying the SalA scaffold to increase metabolic stability and offset hallucinogenic effects.

Organic #2

**Hands-On Molecules: WebMO and 3D Printing as Interactive Tools for Teaching Sterics and Reactivity in Organic Chemistry**

***Emily Eisner,*** **Scott McAvoy, and Jeremy Klosterman**
Principal Investigator: Dr. Jeremy Klosterman

Success in organic chemistry courses, such as CHEM 40A, requires spatial reasoning that students have not yet developed. Ball-and-stick molecular model kits aid in understanding stereochemistry, but they are limited in representing the physical reality of molecular structure and reaction mechanisms. Three-dimensional printing offers an easy and affordable solution: instructors and students can create 3D models that accurately portray the size and shape of atoms in a molecule, a feature that increases understanding of inherent steric interactions. We present a method for obtaining the atomic coordinates and molecular structure for models via the free online program WebMO. Using Mercury and NetFabb, this information is then converted into the .stl format readable by 3D printers. We printed a series of haloalkanes and alkoxides of varying steric bulk and documented the process in a 3D printing guide. WebMO was also used to calculate an electrostatic potential map for each printed molecule. Students can create and use these maps to color their 3D models, visually representing molecular sites of nucleophilicity and electrophilicity. This interactive process will be incorporated into future CHEM 40A courses to help students develop a spatial understanding of chemical behavior.

# A Radical Approach To anti-Markovnikov Alkene Allyl-Amination

***Kathleen Gundran,*** **Sam Lardy, and Valerie Schmidt**
Principal Investigator: Dr. Valerie Schmidt

Many pharmaceuticals contain N-atom functionality that play vital roles in their biochemical processes. An attractive way to install complex amine functionality is the direct addition of an amine across a C-C double bond. Achieving this type of reactivity through transition metal catalysis is challenging because the amine starting material can "poison" the catalyst. Even when successful, the alkylated amine products are generally more reactive than starting materials, and the innate reactivity only gives access to one possible hydroaminated regioisomer. In hopes to solve and address these issues, we can selectively enforce a desired anti- Markovnikov hydroamination reactivity by creating nitrogen radical precursors that add to alkenes.

Sam Lardy, a graduate student in the Schmidt Group, has developed a direct anti- Markovnikov hydroamination using inexpensive N-hydroxyphthalimide with a variety of olefins using triethyl phosphite. The mechanistic proposal of this project has inspired the development of an analogous amino-allylation reaction. We identified that we can create O-allyl substituted oxyphthalimide derivatives. Our goal is to synthesize O-allyl substituted NHPI derivatives, design, carry out, and analyze the results of these reagents in proposed radical mediated allyl- amination of a variety of alkenes.

Our preliminary studies have shown promising results of successful amino-allylation of one substrate containing vinyl nitrile. There is important information to be gained from investigating the different substituents that we can incorporate on this O-allyl N-hydroxy derivative to fully explore the scope and applicability of this overall amino-allylation reaction.

Organic #4

# Cu-Mediated 2+2 Hetero-Cycloadditions Using Ultraviolet and Visible Light

***Jacob Hawver Patcher,*** **Daniel Flores, and Valerie Schmidt**

Principle Investigator: Dr. Valerie Schmidt

Four-membered heterocycles such as oxetanes and azetidines are prevalent in many biologically active molecules, and are useful as molecular building blocks. The pathways previously developed to synthesize these four-membered heterocycles often have a limited substrate scope, and do not allow for much deviation. There are a number of ways to design three, five, and six-membered rings, but the four-membered ones are scarce. Those that do exist often use two point coordinating Rh or Sc Lewis Acids to alter the absorption wavelength of the substrate, but these methods are expensive, difficult, and dangerous to carry out. We are exploring the prospect of using two point coordinating Cu-based Lewis Acids to shift the absorption wavelengths of the substrate into the UV or visible range. This allows the substrate to be easily excited to its triplet energy state at which point it performs a carbon centered radical 2+2 cycloaddition. We used Cu because it is an inexpensive and abundant metal that will allow us to create a reasonable pathway for the formation of these four-membered rings. We began by experimenting to ensure that the theory was plausible using kinetic studies on known reactions. After proving the concept worked, we began to synthesize a library of molecules on which to practice the conditions. These include various imines to create azetidines, melonal derivatives for oxetanes, and others for cyclobutane rings. As the project moves forward we hope to see Cu-induced carbon centered radical 2+2 cycloadditions move forward on a broad range of substrates.

**Investigation of how the malaria parasite evolves resistance toward various antimalarial compound motifs**

***Bryant Lim,*** **Clare McNerlin, Mitchell Christy, Sabine Ottilie, Elizabeth A. Winzeler, and Dionicio Siegel**

Principal Investigator: Dr. Dionicio Siegel

The evolutionary responses exhibited by P. falciparum to compounds with antimalarial activity have been systematically studied utilizing isogenic clones of the parasite.1 This was done by exposing the parasites to various small-molecule growth inhibitors and sequencing the genome of the clones once resistance had been evolved.1 Through the total synthesis of four molecules, different structural motifs were screened for efficacy as an antimalarial and to identify a correlation between the motif and the genetic alteration that led to resistance. This poster details the synthetic pathways utilized to approach each of these target motifs: diazaspirocycle (1), quinazolinone (2), carbazole (3), and quinoline (4). Between 50 and 100 mg of each antimalarial were synthesized with varying yields (1.6%-80%). Potentially, these molecules will allow for a better understanding of the malaria parasite, its resistance mechanisms, and pave the way for new methods of treatment.

Organic #6

**Development of Protein Loaded Hydrogels for Delivery to Peripheral Nerve**

***Richard Niederecker,*** **John Kim, Wendy Campana, and Jerry Yang**

Principal Investigator: Dr. Jerry Yang

Neuropathic pain is a type of chronic pain resulting from sensory nerve damage in the peripheral nervous system. This condition is untreatable and is expected to rise due to aging of the global population, increased rates of Diabetes Mellitus, and improved survival of cancer patients after chemotherapy. Proposed treatment for this condition includes the use of biologics like the hemopexin domain of matrix metallopeptidase 9 (MMP 9 PEX). MMP 9 PEX is a protein which has been found to promote Schwann cell migration, believed to regenerate damaged nerve fiber, and therefore could potentially be used for treatment of neuropathic pain. To deliver a protein like MMP 9 PEX to a peripheral nerve, alginate hydrogel has been used in the past; however, calcium ions that are used to crosslink the hydrogel have been shown to induce an inflammatory response. One way to circumvent high calcium concentration is to dope alginate gels with agarose to produce composite gels. Here we study the effects of agarose and calcium concentration on the preparation of protein loaded alginate-based hydrogels for MMP 9 PEX delivery to a peripheral nerve. Recombinant glutathione S-transferase (GST), a model protein for MMP 9 PEX, was first produced and chemically modified with a fluorescent tag, 5(6)-carboxyfluorescein. The fluorescent GST was then loaded in alginate and agarose-alginate hydrogels and its release was measured in vitro by monitoring fluorescence. Analysis of GST kinetic release profiles was finally used to identify the optimal hydrogel formulation for in vivo application.

Organic #7

**Botryococcoene as an Alternative to Petroleum in Polyurethanes**

***Arthur Rezian,*** **Marissa Tessman, Suri Sherman, and Robert Pomeroy**

Principal Investigator: Dr. Robert Pomeroy

Continued production of polyurethanes from petroleum sources has negative environmental implications. Typically, petroleum is converted to polyols through a process of cracking and reformation. Petroleum based polyols are nonrenewable and non-biodegradable and account for 50% of polyurethane, PU, formulations by weight. The PU industry is projected to be a 105 billion dollar market by 2025. Renewable, sustainable and biodegradable algae oils can take the place of petroleum polyols in polyurethane formulations. Botryococcene is an oil produced by the algae Botryococcus braunii and has alkene functional groups which makes it a viable starting material for polyol synthesis. This work outlines the conversion of Botryococcene via oxidation with performic acid in a one-pot synthesis which yielded a polyol required for polyurethane synthesis. Polyurethane cubes were then made by substituting the botryococcene polyol for the polyol component in a standard formulation.

Organic #8

**Directed, nickel-catalyzed carboamination of alkenes**

***Vincent van der Puyl,* Joseph Derosa, and Keary Engle**
Principle Investigator: Dr. Keary Engle

We have developed a regioselective, nickel catalyzed vicinal carboamination of non-conjugated alkenes with O-benzyl hydroxylamine electrophiles1 and organozinc nucleophiles to afford β- and $\gamma$-amino acid derivatives. A variety of secondary amines, including several heterocycle motif, can be installed using this method, along with both alkyl and aryl zinc reagents in good to excellent yields. The reaction is enabled by a tethered 8-aminoquinoline directing group that dictates the regiochemical outcome by the formation of 5 or 6-membered nickelacycle intermediates while suppressing β-hydride elimination and two-component coupling between the electrophilic N-O reagent and organozinc nucleophile.

Organic #9

**Symmetry of the Hydrogen Bonds in Two Enols**

***Yifan Wu* and Charles Perrin**

Principal Investigator: Dr. Charles Perrin

Hydrogen bonding is one of the most widely studied aspects of molecular structure. The distinction of H-bonds is between "symmetric" H-bonds, where the hydrogen is centered between the two donor atoms, in a single-well potential, in contrast to the more usual case of a double well, where the hydrogen may jump from one donor to the other. Although intramolecular H-bonds are often symmetric in crystals, the observed 18O isotope shifts have shown that these H-bonds are double-well in solution. Because bulky substituents that force the oxygens together shorten the O-O distance and may thereby favor a single-well H-bond, we propose to study the enols of nitromalonamide and 3-cyano-2,2,6,6-tetramethylheptane-3,5-dione in solution. Isotopic perturbation will be exerted by mono-18O substitution. Incorporation of 18O into nitromalonamide will be accomplished in the initial hydrolysis of malononitrile in H218O. In preliminary experiments, I have succeeded in converting malonamide to nitromalonamide and in hydrolyzing malononitrile to a mixture of cyanoacetamide and malonamide, but the hydrolysis yield still needs to be improved. Incorporation of 18O into 3-cyano-2,2,6,6-tetramethylheptane-3,5-dione will be accomplished by acid-catalyzed exchange, to produce a statistical mixture with 0, 1, and 2 labels. A mixture of tautomers will be recognized by a splitting of the 13C NMR signals for the carbonyl carbons.

Organic #10

# *Physical/Analytical Division*

1. K Barber, D. Rez and C. Li
2. Brandon Bizzarro
3. Egbert Castro
4. Ivan Cruse
5. Brian Kenney
6. Qin Li
7. Peter Sharp
8. Cynthia Wong
9. D. Zhuang and A. Chen

**Isotopes of Interest in Sulfate Aerosols**

***Kaleb Barber, Donald Rez (co-presenter), Connie Li (co-presenter),* and Robina Shaheen**

Principal Investigator: Dr. Robina Shaheen

Sulfates contribute toward essential physical processes in the atmosphere such as cloud seeding and planetary albedo. Additionally, they have damaging effects on biological systems such as contributing towards cardiopulmonary disease. Anthropogenic emissions have become a major source of the sulfate aerosol. Through measurement of both sulfur and oxygen isotopes, the sources and formation environments of sulfate particles in air samples can be assessed.

Physical/Analytical #1

**Energy Decomposition Analysis for Computational Descriptions of Halide-Water Dimers**

***Brandon Bizzarro,*** **Colin K. Egan, and Francesco Paesani**

Principal Investigator: Dr. Francesco Paesani

An atomic scale description of ion-water systems offers important details for a complete understanding of the role of ion solvation in a number of biological and environmental processes. Unfortunately, an experimental evaluation of the energetics of individual ion-water interactions, which are key to these processes, remains difficult because counterions obscure the measurements of individual ion free energies. However, a number of computational tools can circumvent these complications, providing a unique opportunity to explore the hydration of charged species in aqueous solutions. One such method, molecular dynamics (MD) simulation, can describe the energetics of molecular systems evolving over time, using some form of the Born-Oppenheimer potential energy surface (BO-PES). There are several ways to represent the BO-PES, namely with classical force fields (FFs), density functional theory (DFT), or many-body potential energy functions (PEFs). The quality of an MD simulation description of ion-water interactions depends on the accuracy of a particular BO-PES representation. Although comparing total ion-water interaction energies from these models with high-level electronic structure calculations yields some information regarding respective strengths and deficiencies, decomposing each model's respective interaction energies into terms like polarization and charge transfer can reveal artifacts of the underlying theoretical design. Analysis of the energy decompositions of common models provides valuable insights into the effectiveness of these varied computational approaches.

Physical/Analytical #2

**Empirically-Derived Heuristics for Simulation-Enabled Estimation of Kinetic Rates (SEEKR)**

***Egbert Castro,* Rommie Amaro, and Benjamin Jagger**
Principal Investigator: Dr. Benjamin Jagger

While thermodynamic properties have historically held the focus of compound screening and lead optimization efforts, increasing evidence suggests that kinetic parameters, in particular residence time (1/k-off), are important indicators of in-vivo efficacy. To determine the residence time of a molecule of interest, its binding event must be well characterized through extensive and repeated simulation. However, the simulation of these events using traditional long timescale molecular dynamics simulations becomes computationally infeasible for even relatively simple systems. A novel and modular method of molecular simulation which helps to address this challenge was presented by the introduction of the Simulation Enabled Estimation of Kinetic Rates (SEEKR) package. This suite of scripts utilizes principles from milestoning theory to facilitate the integration of Brownian dynamics and molecular dynamics simulation methods to more efficiently simulate ligand binding and unbinding events for large and complex systems. Here we present developments toward a reliable heuristic for the tailoring of SEEKR to a wide set of systems. To do this, we investigate the accuracy of SEEKR to predict k-on and k-off rates for a set of small and therefore, interpretable systems. The development of empirically-derived best practices for the use of SEEKR will improve accuracy, efficiency, and reproducibility when simulating a diverse range of more complicated biomolecular systems and has the potential to therefore be an informative tool for drug screening and lead optimization.

Physical/Analytical #3

**PDI Determination via Orbitrap Direct Injection Mass Spectrometry**

***Ivan Cruse,*** **Marissa Tessman, and Robert Pomeroy**
Principal Investigator: Dr. Robert Pomeroy

The polydispersity index, PDI, is a metric used in the polymer industry to characterize the distribution of molecular weights associated with a polymer sample. PDI is commonly determined by size exclusion chromatography, SEC. While useful, SEC has its drawbacks as it is not only a slow and pricy technique, but also one which has difficulty resolving a 10% difference in mass between components. This project seeks to rectify these shortcomings by using direct insertion mass spectrometry via a high resolution Thermo Fisher Fusion equipped with an Orbitrap which cuts down both the time and cost of analysis while also allowing for differentiation of components with a 5ppm margin of error. A calculator has been developed to compute the PDI from the MS data. The PDI was calculated for four different polyols used in the synthesis of polyurethane foams and is compared to the findings utilizing the industry standard SEC. The comparison will examine figures of merit such as: instrument cost, sample cost, sample run time, and resolution.

Physical/Analytical #4

**Behavior of Nanoparticles in Seawater-Like Conditions**

***Brian Kenney*** **and Natalia Gonzalez**
Principal Investigator: Dr. Natalia Gonzalez

Nanoparticles(NPs) such as TiO2, ZnO, and CuO interact and change in the solution they are suspended in. These metal oxide NPs are used in bandages, ointments, and sunscreen that end up in bodies of water, even in the ocean. Our work focuses on the physicochemical properties of these NPs in seawater-like solutions. In this work, we use solutions with 50mM ionic strength solutions prepared with NaCl, a mixture of salts (synthetic seawater), and sea salt (commercial mixture of salts); in addition, milliQ water is used as a control. In addition to the salt, the effect of other molecules found in seawater are studied, including stearic acid, fulvic acid, and lipase at environmental relevant concentrations of 1mg/L. Nanoparticle dosage is 1 mg of NP per 50ml solution, to simulate the concentrations calculated by environmental fate models. Studies include the changes of the hydrodynamic size of NPs and changes in the surface tension and pH during the solution over a week time period. Our results show that different behavior depends on the nanoparticle. The different trends in the measured surface tension can be explained either by the accumulation of the NPs at the surface or particles aggregate and sedimentation. Furthermore, changes in pH can be correlated to the dissolution of NPs. Overall, this study provides insight in the fate of NPs in seawater.

Physical/Analytical #5

**Water Structure at the Interface of Alcohol Monolayers**

***Qin Li,* Sandeep K. Reddy, and Francesco Paesani**

Principal Investigator: Dr. Francesco Paesani

Our research focused on the interaction of monoalcohol monolayer and water interface at room temperature, with the technique of molecular dynamic simulation and vibrational sum frequency spectroscopy.

Physical/Analytical #6

**Molecular-Level Interpretation of Vibrational Spectra of Ordered ice Phases**

***Peter Sharp,* Daniel R. Moberg, and Francesco Paesani**
Principal Investigator: Dr. Francesco Paesani

When water freezes at ambient conditions, it forms a hexagonal structure known as ice Ih. While this is the most common form of ice on the surface of Earth, on the phase diagram of water there exist 16 other known crystalline phases of ice and several amorphous phases which differ in structure from ice Ih. Due to ice Ih's common occurrence, much research has been done exploring its structure and understanding the underlying hydrogen bonding network and how this effects its vibrational spectra. However, understanding the various ice phases and their occurrences in different environments is now more relevant than before for fields such as atmospheric, planetary and interstellar research. The importance of different ice phases in the involvement of these fields is just beginning to be understood. Currently an unambiguous, coherent interpretation at the molecular level for the proton-ordered ice phases of water and their corresponding vibrational spectra does not exist. We are investigating the various structures of the different proton-ordered ice phases utilizing many-body molecular dynamics (MB-MD) with the MB-pol potential energy function for water, to simulate vibrational spectra and classify the localization and degree of symmetry of the vibrational modes in the OH stretching region. This will paint a clear picture of the subtle forces at play on a molecular level for the different ice phases and how this effects their structures and hydrogen bonding networks.

Physical/Analytical #7

**Multiphase reactions of sulfur oxidation and the influence of organics and iron**

***Cynthia Wong,*** **Ellen M. Coddens, Liubin Huang, and Vicki H. Grassian**

Principal Investigator: Dr. Vicki H. Grassian

Sulfate aerosols, including sulfuric acid and ammonium sulfate aerosol, are some of the most effective radiative-cooling aerosols in the atmosphere as they can scatter radiation back into atmosphere and act as a cloud condensation nuclei. However, current modeling studies underestimate the observed concentration of sulfate in the atmosphere resulting in a need for studies that focus on the various chemical processes and factors that enhance sulfur oxidation. Here, we have investigated the role that aqueous phase Fe3+ and organic compounds play in catalyzing sulfur oxidation and in the formation of organosulfate compounds, respectively. We have done this by quantifying iron in authentic dust samples, spectroscopically monitoring sulfur oxidation in the presence and absence of iron containing dust samples, and identifying inorganic sulfate products via ICP-MS, ATR-FTIR and HESI-HRMS, respectively. In the presence of iron, sulfate concentrations are enhanced indicating a catalytic effect. In addition, in the reaction between sulfite and glyoxal, various organosulfate compounds were formed in the presence of iron. Overall these studies indicate that iron and organics play significant role in sulfur oxidation and the formation of organosulfates in the atmosphere.

Physical/Analytical #8

**Alkali Ion Hydration**

***Debbie Zhuang, Angela Chen (co-presenter),* Marc Riera, Sandeep K. Reddy, and Francesco Paesani**

Principal Investigator: Dr. Francesco Paesani

Ion hydration plays an important role in different fields, from atmospheric chemistry to materials science. An accurate description of these interactions is key to understanding the role of ions in these processes. In this study, we use molecular dynamics simulations (MD) with three different models to understand how the hydration structure changes with the functional form of the model. The three models used are TIP4PEW, a rigid point charge model; TTM-nrg/MB-pol, a classical flexible polarizable model; and MB-nrg/MB-pol, which builds upon TTM-nrg by adding a two-body (2B) short range correction to account for quantum effects such as charge transfer and charge penetration. For each model, the number of water molecules in the first solvation shell, the residence time of a water molecule in the first solvation shell, and the extent of the first solvation shell were computed and compared with available experimental data. As ion size increases, the strength of the coordination structure and the average residence time of water molecules in the hydration shell decreases, while the number of water molecules increases. The TIP4PEW force field showed a more ordered hydration structure compared with TTMnrg and MBnrg. In general, there is a good agreement between TTM-nrg and MB-nrg with available experimental data.

Physical/Analytical #9

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