

CHEM 865: Chemistry Research Seminars

2013-2014 Spring

Objectives for Chemistry Research Seminars:

- To engage students in research through seminars and interactions with researchers from other universities and industries

This is a 3-credit course.

Times: Thursday 4:30-6:00 PM (possible on Friday on visitors' availability). The following is a tentative schedule, but subject to changes.

Lecturer:

Dr. F. Ji, Chem. Dep. Disqué 507, Phone: 215-895-2562. Email: hj56@drexel.edu

Office hours: Monday 10am-noon.

Grading policy:

Attendance is mandatory. Miss once without documented excuses will result in one letter grade drop, and so on. Your grade will be based on your attendance (50%) and the report /or research discussion (50%).

At the end of the term, you are required to write:

Option 1. One page summary of one seminar. A grade (the best grade is A) will be given based on your writing and your attendance. Single line spacing, font 11, Time New Roman. 6 pt after each paragraph. Including 4-8 references. **The deadline for turning in your writings: 12/07/2013 noon**

Option 2. Ask questions at least twice after seminars (two seminars, not two questions for one seminar) for an A. An A+ will be awarded if any of the questions lead to discussion of a research plan related to the seminar and your research work. This Option is highly recommended. No paper is needed.

Seminars 2013-2014 Fall

Date	Name	From	Title
10/3	Jing Li	U. Rutgers	Microporosity and Functionality: Designing MOFs for Energy Related Applications
10/10	Ritesh Agarwal	UPenn	
10/17	Craig Brown	NIST	Gas adsorption and hydrocarbon separations in microporous materials
10/24	Frank Jordan	Rutgers Univ.	Enzymology of a bifunctional coenzyme: state of ionization/ tautomerization of

		Newark	thiamin-bound intermediates along the reaction pathway.
11/7	John Perdew	Temple	Climbing the Ladder of Density Functional Approximations
11/14	Ann M. Carlton	Rutgers Univ. , New Brunswick	Anthropogenic Water Drives Gas-to-Particle Partitioning of Organic Compounds in the Eastern U.S.
12/5	Gabriel Isaacman	U. Berkeley	Oxygenated Organic Tracers in Ambient Aerosol in Biogenic Environments Provide Insights into Aerosol Formation and Oxidation

10/3

Microporosity and Functionality: Designing MOFs for Energy Related Applications

Jing Li

Department of Chemistry and Chemical Biology

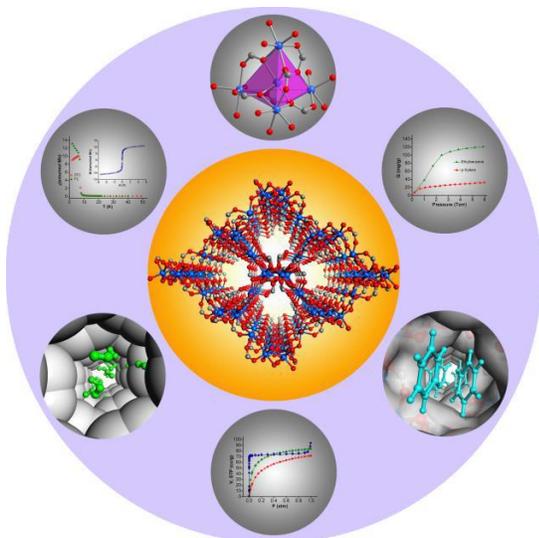
Rutgers, The State University of New Jersey

Piscataway, NJ 08854, USA

jingli@rutgers.edu

Abstract

Metal organic framework (MOF) materials are crystalline coordination polymers having extended network structures. Microporous MOFs (MMOFs) are a subgroup of MOFs that possess permanent and sustainable porosity and have pore dimensions within micropore region (less than 2 nm). Current research on these materials has revealed numerous interesting and unique functionality and porosity-related properties, making them highly promising for practical applications including storage and/or separation of small gases and hydrocarbons, heterogeneous catalysis, guest- and/or pore-induced magnetization, sensing and detection. This presentation will focus on our recent progress in rational designing and systematic tailoring of crystal structures (e.g. dimensionality, connectivity, and topology), chemical compositions (e.g. the type and form of metals and ligands) and pore characteristics (e.g., pore size and shape, pore volume and the chemical functionality of the pore walls) of these materials to enhance targeted properties and achieve improved performance for several important energy related applications.



10/17

Gas adsorption and hydrocarbon separations in microporous materials

Craig M. Brown, NIST Center for Neutron Research.

Adsorption of molecules in functionalized and high surface area microporous materials is of technological importance in a multitude of areas ranging from catalysis, drug delivery, chemical separations and energy storage to personal care products. Over the past several years we have focused our research efforts on understanding the properties of metal-organic frameworks (MOFs) for storage and separations of industrially important small molecules. The properties of metal-organic frameworks can be tuned to optimize electrostatic interactions by exposing open metal cation sites, such as in $\text{Mg}_2(\text{dobdc})$ ($\text{dobdc}^{4-} = 2,5\text{-dioxido-1,4-benzenedicarboxylate}$). A material shown to be highly effective in the capture of CO_2 . The structurally related redox-active $\text{Fe}_2(\text{dobdc})$ allows for the selective adsorption of O_2 over N_2 via an electron transfer mechanism. The same material is demonstrated to be effective for the separation of mixtures of C1 and C2 hydrocarbons, and for the high-purity separation of ethylene/ethane and propylene/propane mixtures. We will explore the details of materials that favor these interactions, and further compare them to zeolites currently employed in industry, detailing how structural features are possible within MOFs, but not in zeolites, so enabling fractionation of hexane isomers according to the degree of branching.

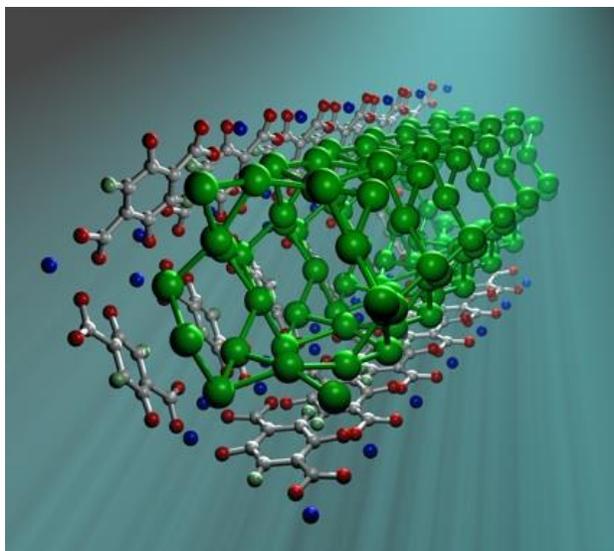


Figure detailing the close packing of hydrogen (green) adsorbed in the pore of a metal-organic framework.

10/24

Enzymology of a bifunctional coenzyme: state of ionization/ tautomerization of thiamin-bound intermediates along the reaction pathway.

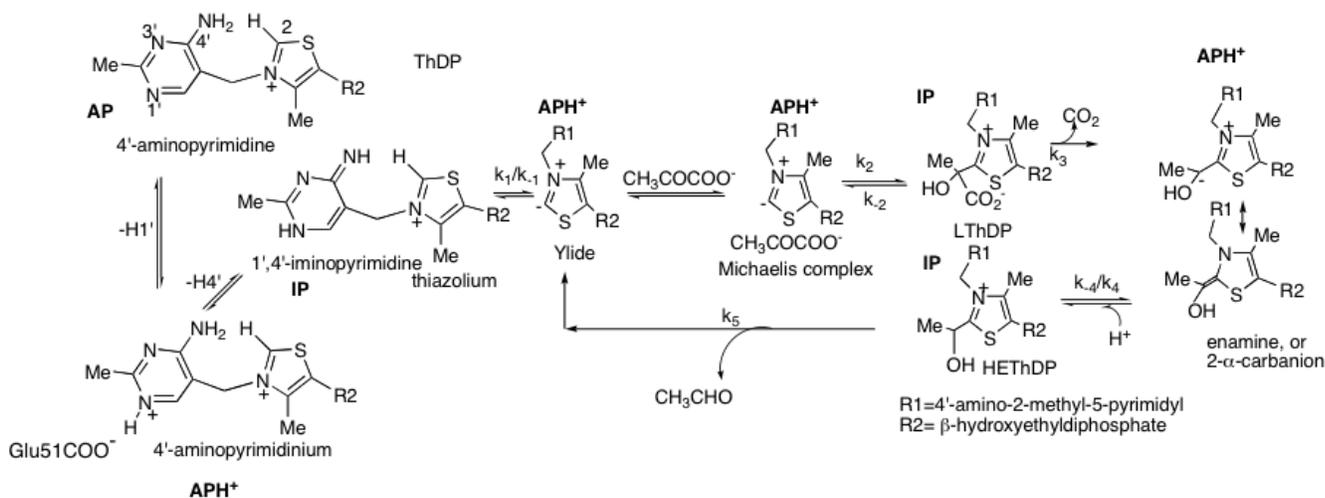
Presented by Frank Jordan, Department of Chemistry, Rutgers University, Newark, NJ USA

E-mail: frjordan@rutgers.edu

Goals of the seminar

1. Introduction to Thiamin enzymes with emphasis on the recently revealed role of the 4'-Aminopyrimidine ring, especially its 1',4'-iminopyrimidine tautomeric form.

Mechanism of yeast pyruvate decarboxylase with tautomeric forms of aminopyrimidine



3. What is the pKa of the enzyme-bound 4'-aminopyrimidinium ring and why should we care?
4. Use CD and NMR spectroscopic signatures to determine microscopic rate constants for time evolution of the various intermediates to further elucidate the mechanism of glyoxylate carboligase and 1-deoxyxylulose-5-phosphate.

11/7

Climbing the Ladder of Density Functional Approximations

John P. Perdew

Department of Physics, Temple University, Philadelphia, PA 19122

Kohn-Sham density functional theory is the most widely-used method of electronic-structure calculation in materials physics and chemistry, because it reduces the many-electron ground-state problem to a computationally tractable self-consistent one-electron problem. Exact in principle, it requires in practice an approximation to the density functional for the exchange-correlation energy. Common approximations fall on one of the five rungs of a ladder, with higher rungs being more complicated to construct but potentially more accurate. The first three or semi-local rungs are important, because (a) they are computationally efficient, (b) they can be constructed non-empirically, and (c) they can serve as input to fourth-rung hybrid functionals. The third-rung meta-generalized gradient approximation can recognize and describe covalent, metallic, and weak bonds, providing a good description of the equilibrium properties of many molecules and solids.

11/14

Anthropogenic Water Drives Gas-to-Particle Partitioning of Organic Compounds in the Eastern U.S.

A.G. Carlton

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ABSTRACT

Gas phase water-soluble organic matter (WSOM_g) is ubiquitous in the troposphere. In the summertime, the potential for these gases to partition to particle phase liquid water (H₂O_{ptcl}) where they can form secondary organic aerosol (SOA_{AQ}) is high in the Eastern U.S. and low elsewhere, with the exception of an area near Los Angeles, CA. This spatial pattern is driven by mass concentrations of H₂O_{ptcl}, not WSOM_g. H₂O_{ptcl} mass concentrations are predicted to be high in the Eastern U.S., largely due to sulfate. The ability of sulfate to increase H₂O_{ptcl} is well-established and routinely included in atmospheric models; however WSOM_g partitioning to this water and subsequent SOA formation is not. The high mass concentrations of H₂O_{ptcl} in the southeast (SE) U.S. but not the Amazon, may help explain why biogenic SOA mass concentrations are high in the SE U.S., but low in the Amazon. Furthermore, during the summertime in the Eastern U.S., the potential for organic gases to partition into liquid water is greater than their potential to partition into organic matter (OM) because concentrations of WSOM_g and H₂O_{ptcl} are higher than semi-volatile gases and OM. Thus, unless condensed phase yields are substantially different (> ~order of magnitude), we expect that SOA formed through aqueous phase pathways (SOA_{AQ}) will dominate in the Eastern U.S. These findings also suggest that H₂O_{ptcl} is largely anthropogenic and provide a previously unrecognized mechanism by which anthropogenic pollutants impact the amount of SOA mass formed from biogenic organic emissions. The previously reported estimate of the controllable fraction of biogenic SOA in the Eastern U.S. (50%) is likely too low.

Oxygenated Organic Tracers in Ambient Aerosol in Biogenic Environments Provide Insights into Aerosol Formation and Oxidation

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² Aerosol Dynamics Inc., Berkeley, CA

³ Environmental Energy Technologies Division, Lawrence Berkeley National Lab, Berkeley, CA

Hourly and bi-hourly time-resolved measurements of organic tracer compounds in ambient aerosols have been successfully used to elucidate sources and formation pathways of atmospheric particulate matter. Using custom in-situ instrumentation in Berkeley, CA and rural Alabama, I measured hourly concentrations and gas-particle partitioning of highly oxygenated organic aerosol tracers that have been inaccessible through traditional measurement techniques. The **Semi-Volatile Thermal desorption Aerosol Gas chromatograph (SVTAG)** desorbs and analyzes ambient aerosol and semi-volatile compounds with hourly time resolution, modified to include on-line derivatization and a second, parallel collection cell that provides simultaneous collection of both particle-phase and particle-plus-gas-phase organic compounds. By introducing a silylating agent upon desorption, SVTAG can measure highly oxygenated compounds that are not easily detected using traditional gas chromatography including most of the previously reported oxygenated tracers for biogenic and anthropogenic secondary organic aerosol. The use of a pair of matched collection cells with parallel sampling and serial analysis provides direct gas-particle partitioning information to yield a check on classical absorption based partitioning theory. Deviations from this theory provide constraints on other driving factors in aerosol formation chemistry, such as oligomerization, salt formation, and acidity. I demonstrate here the utility of the dual cell SVTAG with derivatization, with chemical insights gained from initial tests on ambient Berkeley air and the first results from a rural site in Alabama obtained during the Southern Oxidant and Aerosol Study (SOAS). Tracers for varying isoprene oxidation pathways are used to explore the influence of anthropogenic emissions; concentrations of 2-methyltetrols and 2-methyl glyceric acid provide constraints on the relative importance of NO_x and HO_2 as the fate of the alkylperoxy (RO_2) radical. Measuring these and other known biogenic tracers with hourly time resolution yields detailed diurnal variability patterns of these compounds, elucidating formation timescales and pathways. Gas-particle partitioning of these biogenic oxygenated compounds, as well as oxygenated tracers common in urban environments, are found in many cases to be well-modeled by absorptive partitioning theory. However, for many compounds, the particle-phase fraction is greatly under-predicted by simple absorption. Several commonly used biogenic secondary organic aerosol tracers that are typically considered to exist primarily in the particle phase, such as 2-methyltetrols, are shown to be 20-80% in the gas phase.