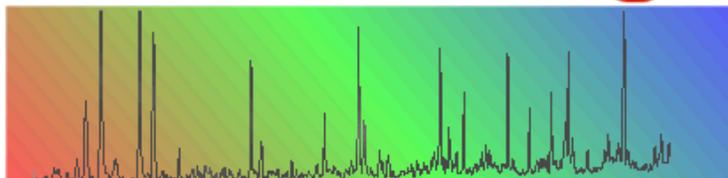# April Meeting
Tuesday, April 7, 2009

The April 2009 meeting will be held at the Student Learning Center in the SES (Science and Engineering South) building on the campus of the University of Illinois at Chicago.

Poster Setup: 5:30 PM   **Buffet Dinner: 6:00 PM**   **Awards: 7:30 PM**

Poster Session on Spectroscopy

1) **Melvin Blaze -** Alginate-chitosan multilayer film with bound antibiotic as a model system for depth profiling by C_{60}^+ ion sputtering **(University of Illinois at Chicago)**

2) **Avi Buchbinder -** Hydrocarbons at Oxide Surfaces Relevant to Catalysis Studied by Vibrational Sum Frequency Generation **(Northwestern University)**

3) **Courtney Cherok -** Acousto-Optic Tunable Filter Hyperspectral Imaging **(Northern Illinois University)**

4) **Alon Danon -** Photo-Catalytic Reduction (PCR) of Carbon Dioxide **(Northwestern University)**

5) **Ali M. Jawaid -** Poly(ethylene glycol) Carbodiimide Coupling Reagents for the Biological and Chemical Functionalization of Water- Soluble Nanoparticles **(University of Illinois at Chicago)**

6) **Prakruti Modi -** Characterization of E22G Pathogenic Mutant of A• (1-40) Peptide by Solid-State NMR and Transmission Electron Microscopy **(University of Illinois at Chicago)**

7) **Sudhakar Partharathy -** Paramagnetic Relaxation-Assisted Condensed Data Collection for Sensitivity Enhancement in Solid State NMR and Copper Binding Studies to Amyloid beta (1-40) Fibrils **(University of Illinois at Chicago)**

8) **Nell Pounder -** Towards Automated Breast Histopathology with FT-IR Spectroscopic Imaging **(University of Illinois at Urbana-Champaign)**

9) **Rohit Reddy -** Advances in Automated Histopathology using Fourier Transform Infrared (FT-IR) Spectroscopic Imaging **(University of Illinois at Urbana-Champaign)**

10) **Dana Sauter -** Study of the Function/Structure Relationship between Iron Clusters within Zeolites **(Northwestern University)**

11) **Bibek Shrestha -** Synthesis and Characterization of Cu(II) (DL-alanine)•H2O and Cu(II) binding studies with Ab(1-40) fibrils using UV-VIS spectroscopy **(University of Illinois at Chicago)**

12) **Sima Singha -** Controlling Material Transformation and Plasma Emission with Trains of Ultrafast Laser Pulses **(University of Illinois at Chicago)**

13) **Grace Stokes -** Reactions of Atmospherically Relevant Organic Surfaces with Ozone Characterized by Sum Frequency Generation **(Northwestern University)**

14) **Aashani Tillekaratne -** Adsorption and Dehydrogenation of Ortho-Carboraneon the Pt(111) Surface **(University of Illinois at Chicago)**

15) **Stephanie Walter -** SFG Studies of the Hybridization of Oligonucleotide-Functionalized Fused Silica at the Aqueous/Solid Interface **(Northwestern University)**

16) **Staci Wegener -** Synthesis and Characterization of Isolated VOx species on q-Al_2O_3 **(Northwestern University)**

17) **Ling Wu -** Peptide Structure Stabilization: A Study Of Aromatic-aromatic Interaction And pH Effect On A b-hairpin Stability **(University of Illinois at Chicago)**

Please make your dinner reservations for the upcoming meeting by email at **sas.chicago@bigfoot.com**, by using the form on our web page < **http://www.sas-chicago.org/Online%20Registration%20UIC%20.htm** > or by calling Slav Stepanovich at **847-421-2056**. Leave **your name, affiliation**, and a **telephone number**. Please register by **noon Monday, April 6th**, so that proper arrangements can be made. If you can't attend, cancel by Monday noon.

Pizza, snacks and beverages will be provided

Dinner Cost <u>Members: $30</u>   **<u>Students and Unemployed Members: $10</u>**   **<u>Non-members: $35</u>**

Poster Abstracts

Alginate-chitosan multilayer film with bound antibiotic as a modelsystem for depth profiling by C_{60}^{+} ion sputtering

Melvin Blaze M.T., Douglas Pleticha, Igor L. Bolotin, and Luke Hanley*
Department of Chemistry, University of Illinois at Chicago
Chicago, IL 60607-7061 USA

C_{60}^{+} polyatomic cluster ion bombardment is known to yield high sputtering rates with minimum beam induced damage on organic, polymeric, and biological materials. This capability allows C_{60}^{+} polyatomic cluster ions to be used in depth profiling in conjunction with secondary ion mass spectrometry and X-ray photoelectron spectroscopy (XPS). An alginate-chitosan polyelectrolyte multilayer is prepared on Au as a model for depth profiling studies of bacterial biofilms and other biological tissue samples. Anionic alginate and cationic chitosan are naturally occurring polysaccharides with good biocompatibility, low toxicity, and biodegradability which, when combined, simulate the extracellular matrix of bacterial biofilms. The formation of these multilayers is confirmed by attenuated total reflectance infrared spectroscopy and XPS. This multilayer system is then sputtered with an 8 kV C_{60}^{+} polyatomic cluster beam, then examined by XPS to reveal little to no beam induced damage in the multilayer. Finally, 3,5-dibromotyrosine is covalently bound to alginate and introduced at different known depths of the multilayer model system by replacing neat alginate with 3,5-dibromotyrosine bound alginate during the formation of the multilayer. This 3,5-dibromotyrosine-alginate-chitosan multilayer system is then analyzed by XPS both before and after C_{60}^{+} ion sputtering to examine the feasibility of using these techniques for depth profiling of bacterial biofilms and other biological samples.

Hydrocarbons at Oxide Surfaces Relevant to Catalysis Studied by Vibrational Sum Frequency Generation

Avram M. Buchbinder
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A variety of heterogeneous reactions are catalyzed by metal oxides. Broadband vibrational sum-frequency generation (SFG) is a highly surface specific technique capable of measuring adsorbate orientation and vibrational transitions on oxide surfaces. Straight chain- and cyclic- alkanes and olefins relevant to catalysis were interrogated at the vapor-oxide and neat liquid-oxide interfaces using SFG with an internal-reflection geometry. These measurements demonstrate that adsorbates on both single crystal sapphire and on powdered zeolite surfaces can be effectively observed with high signal intensity.

Index of Newsletter Sponsors

Acousto-Optic Tunable Filter Hyperspectral Imaging

Courtney Cherok
Department of Chemistry and Biochemistry
Northern Illinois University
DeKalb, IL 60115

Obtaining images of ion and atom emission lines as well as molecular emission bands can be extremely useful in the process of understanding plasma chemistry. Being able to visualize several species of multiple elements and how/where they reside/interact throughout the plasma can help to increase knowledge of plasma chemistry and could allow for the ability to understand observed results found uning other ICP instruments. Using an acousto-optic tunable filter hyperspectral imaging (AOTF-HSI) system can help do just that. This system, with wavelength selected images projected on a CCD camera, allows for the ability to examine plasma images at multiple wavelengths in real time.

In these experiments, a paratellurite AOTF-HSI system was used to observe yttrium atom and ion lines as well as YO molecular bands. A CCD camera was used to take analytical and background images of the plasma to obtain spatially resolved emission images in real time. These species were examined using both the ICP-AOTFHSI system and ICP-OES system with a 1M monochromator. Known Y(I), Y(II), and YO bands were optimized using the 1M monochromator, and were later found using the AOTF-HSI system. Results indicate that this system can be used for yttrium speciation, and with further research, elemental speciation.

Photo-Catalytic Reduction (PCR) of Carbon Dioxide

Alon Danon
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Northwestern University
Evanston, IL 60208

The Photo-Catalytic Reduction (PCR) of CO2 using water as a hydrogen source over semiconductor materials remains a poorly understood photo-catalytic reaction. The process has also been plagued by low yields. An understanding of the process entails elucidating pathways associated with the heterogeneous aspect of the reaction - 1) adsorption of reactants 2) formation of reactive species 3) catalytically induced reactions and 4) desorption of products, as well as understanding photocatalysis aspects of the reaction - 1) absorption of photon 2) excitation e-h pair 3) transfer of excited electron to adsorbed species and 4) hole reaction. Little is known regarding these two dynamics of the process. Knowledge gained from the detailed experiments we perform will help us synthesis the next generation of materials.

We attack this problem using a wide array of synthesis, characterization and mechanistic/spectroscopic techniques. These techniques include – ALD, Chemical Grafting, EXAFS, TPD, TPR, In Situ FTIR, UV-Raman and Homemade Catalysis Setups. Recent accomplishments include synthesized and tested photocatalytically active materials using ALD. Mechanistic studies are being performed.

Poly(ethylene glycol) Carbodiimide Coupling Reagents for the Biological and Chemical Functionalization of Water-Soluble Nanoparticles

Ali M. Jawaid, Hongyan Shen and *Preston T. Snee
Department of Chemistry, University of Illinois at Chicago,
Chicago, Illinois 60607-7061

Quantum dots (QDs) and nanoparticles have size dependent electronic properties in the nanoscale regime. Particularly they are ideal for labeling with biological vectors for imaging because they do not exhibit photoluminescent bleaching. We are interested in designing novel nanoparticle systems and their subsequent functionalization with different moieties. Because these nanoparticles are created via colloidal methods, the materials are hydrophobic. These particles are dispersed into water via amphiphilic polymer encapsulation. The hydrophobic nanoparticles achieve water solubilization via carboxylic acid moieties on the polymer. The subsequent functionalization of these systems to biological vectors through carbodiimide coupling is apparent. However, this also seems to cause permanent precipitation in many cases. To address this precipitation problem, we have developed several novel conjugation vectors to help facilitate these particles to be used ubiquitously. UV-VIS and photoluminescence spectroscopy, in parallel with TEM, are used to characterize QDs. Characterization of our carbodiimide vectors are done via NMR and Mass Spectroscopy; the fecundity of coupling to nanoparticles is analyzed via DLC, UV-VIS absorption, and photoluminescence spectroscopy.

Characterization of E22G Pathogenic Mutant of Aβ (1-40) Peptide by Solid-State NMR and Transmission Electron Microscopy

Prakruti B. Modi, Medhat A. Shaibat, Brian K. Yoo and Yoshitaka Ishii
University of Illinois at Chicago,
Chicago, Illinois 60607

Alzheimer's disease (AD) is a neurodegenerative disease that is identified by the deposition of fibrils of the amyloid •-peptide of 40-42 amino acid residues. Several pathogenic mutations such as Flemish (A21G), Italian (E22K), Dutch (E22Q) and Arctic (E22G), are believed to promote an early onset of AD. Moreover, such mutations of Aβ• peptide often exhibit more neurotoxicity than the wild type. E22G is a mutation in which the amino acid glutamic acid (E) is replaced by glycine (G) amino acid. Previous studies on the Arctic mutation have shown that this mutation promotes the formation of subfibrillar amyloid intermediates preceded by the formation of stable fibrils. Despite the importance of these intermediate and fibril species of Aβ peptide, the structures of amyloid fibrils and intermediate species for the E22G mutant are not well understood. Transmission electron microscopy (TEM) has been the primary method to determine the morphology of the different species of Aβ• peptide and its mutants. Solid-state NMR spectroscopy (SSNMR), on the other hand, has been the main tool to determine the different structures of the wild type of Aβ-peptide.

This poster demonstrates the different morphologies and the structure(s) of the E22G mutants of Aβ• peptide prepared in vitro. Morphological and conformational changes from the E22G monomeric species to its self-assembled fibrils were studied by ThT fluorescence and confirmed by TEM spectroscopy. In addition, SSNMR techniques were used to deduce the structural information of the different species of the E22G peptides, which were prepared by different methods of incubation and captured at different incubation times. Finally, toxicity of the different species of E22G samples were performed on a rat pheochromocytoma (PC-12) cells.

Paramagnetic Relaxation-Assisted Condensed Data Collection for Sensitivity Enhancement in Solid State NMR and Copper Binding Studies to Amyloid beta (1-40) Fibrils

Sudhakar Parthasarathy, Nalinda P. Wickramasinghe, Medhat A. Shaibat and Yoshitaka Ishii
Department of Chemistry, University of Illinois at Chicago,
Chicago, IL 60607

In this study, we present two separate topics on biomolecular solid-state NMR (SSNMR). In the first topic, we discuss the relaxation mechanism and optimum choice of metal chelates for paramagnetic relaxation enhancement (PRE) due to paramagnetic ion dopants in hydrated proteins. One of the main bottlenecks in the field of SSNMR is the limited sensitivity, particularly for biomolecules, which are often available only in minimum amount. To overcome this problem our group recently demonstrated paramagnetic relaxation-assisted condensed data collection (PACC), in which the ^{1}H T_1 of the sample is reduced to 50-100 ms and the spectrum is acquired by rapid recycle delays without compromising the resolution. In the PACC approach, Cu-EDTA has been used as an effective paramagnetic relaxation agent to decrease the 1H T1 for sensitivity enhancement. However, it has not been clear how ^{1}H T_1 PRE is affected by the concentration of the dopants and other factors for various biomolecular systems. In addition, to apply this technique to a wide variety of systems, it is necessary to have different choices of relaxation agents. We address the problem by describing the ^{1}H T_1 relaxation semi-quantitatively with a simple model in which a relaxation sink on the protein surface and the bulk ^{1}H spins inside proteins are coupled. It was found that the model reasonably well reproduced the relaxation behavior for paramagnetically doped proteins. The theoretical analysis presents a guideline in choosing a suitable condition in the PACC approach. We also discuss the ^{1}H T_1 PRE effects and line broadening (^{13}C T_2) for proteins doped with various paramagnetic complexes such as Ni(II)EDTA, Gd(III)DETPA, and Co(II)EDTA complexes. The PACC mechanism due to these metal ions will be explained.

In the second topic, we discuss possibility of site-specific Cu(II) binding with Aβ(1-40) fibrils, which has been considered as probable mechanism that explains the neurotoxicity of Alzheimer's plaques. It has been also reported that the elevated levels of transition metal ions such as Cu(II) (400uM), Zn(II) (1mM) and Fe(III) (1mM) are present in amyloidal •-plaques. The oxidative stress observed in Alzheimer's patients has been related to the production of reactive oxygen species by copper bound forms of Aβ. Although many groups have reported Cu(II) binding to Aβ(1-40), it is still not clear how Cu(II) binds to amyloid fibrils. In this study, we report the use of spectrophotometry and SSNMR to characterize the Cu(II) interaction with the Aβ(1-40) fibrils. The spectrophotometric studies indicate possible binding of Cu(II) ions to the Aβ(1-40) fibrils which could be either site specific binding or non specific superficial absorption on the surface. However, the SSNMR data for fibrils of Aβ(1-40) isotopically labeled at selected residues show site-specific decrease in the signal intensity and relaxation rate enhancement for the Valine residue at position 12 . Further studies are in progress and the data will be presented.

Towards Automated Breast Histopathology with FT-IR Spectroscopic Imaging

F. Nell Pounder
Department: Bioengineering
University of Illinois at Urbana-Champaign

As breast cancer is often treatable at an early stage of diagnosis, most women over forty have a mammogram every other year. Upon observation of an abnormality, a biopsy is conducted to remove tissue for extensive pathology analysis. An estimated 1.6 million patient biopsies are performed each year, and pathology evaluations are expensive and time-consuming. Accurate automated techniques for breast tissue evaluation could improve cancer diagnosis efficiency. Fourier transform infrared (FT-IR) molecular spectroscopy, extensively used in chemical analysis, may be applicable for breast pathology. An IR spectrum gives a quantitative measure of molecular composition, which can be numerically related to histopathology to identify important types of breast tissue. Recent advances in instrumentation permit the combination of FT-IR molecular spectroscopy with optical microscopy to rapidly obtain spatial and spectral information with FT-IR imaging. This technique involves only non-perturbing light, and can be applied directly to fixed tissue sections prepared for conventional staining procedures. FT-IR imaging produces tissue image datasets containing extensive morphological and biochemical information without the use of molecular probes or contrast agents. In this study we employ tissue microarrays (TMAs), which offer a high-throughput approach to collect data and build a prediction algorithm from a large selection of cancer and normal tissue samples. FT-IR TMA datasets are automatically classified by a supervised pattern recognition method to provide false-color images comparable to stains used in breast cancer diagnosis. Classification accuracy is assessed by receiver operating characteristic (ROC) analysis and validated on biopsy surgical resections. After identifying the type of breast tissue associated with each pixel in a FT-IR image, malignant TMA cores are distinguished by epithelium spatial polling. Breast tumors are also identified in metastatic lymph node TMA sections. Results demonstrate exceptionally high accuracy for an automated diagnostic tool and help establish FT-IR imaging as a novel technology for breast cancer diagnosis and research.

Advances in Automated Histopathology using Fourier Transform Infrared (FT-IR) Spectroscopic Imaging

Rohith Reddy
Department of Bioengineering
University of Illinois at Urbana Champaign

Fourier transform infrared (FT-IR) spectroscopic imaging is an emerging technique that provides both chemically and spatially resolved information. Some of the factors that result in the loss of temporal resolution in FT-IR imaging are discussed and the trade-off between signal to noise ratio (SNR) and data acquisition speed are analyzed. A computational method to improve SNR is developed. It has been shown that the Minimum Noise Fraction (MNF) Transform can be effective in improving SNR computationally. However, one of the drawbacks of this method is that the factors to be included in the inverse transformation have to be selected by manually examining spatial features in factor images. An automated factor selection scheme is proposed that uses edge detection as a basis for deciding information content in image factors, removes spectral noise computationally, thereby automating the complete process of noise reduction. This scheme has been used to de-noise over 500 data samples and the SNR results are comparable to those obtained when factors are hand picked. It is also been shown that FT-IR is effective in histopathologic classification of tissues. We elucidate the effectiveness of our algorithm in improving classification accuracy and reducing data collection time.

The uses of Bayesian and genetic-algorithm-based classifiers have been shown to be effective in histological recognition in tissues, yielding an accuracy of 94% to 99%. However, clinical translation of these results requires that the classifiers be robust to factors such as tissue sample preparation and systematic bias introduced by handling of tissues. This poster examines the dependence of classification accuracy on such factors by using independently procured and processed datasets for analysis and validation. The two class histological classification is found to have an accuracy of 92% to 95% even when validation was performed on diverse, independent datasets, thus highlighting the robustness of our technique.

Determining the number of samples (tissue micro-array spots), patients, and pixels required to build a robust classifier are important questions and are discussed thoroughly in the poster. It is shown that a relatively small number of pixels are sufficient to capture information about the entire dataset and a statistical analysis of the intra-person and interperson variance in spectral metrics (features) is presented to understand and explain these results. The number of spectral metrics required for classification and the effects of signal to noise ratio on classification are also discussed.

Study of the Function/Structure Relationship between Iron Clusters within Zeolites

Dana Sauter
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Evanston, IL 60208

Iron loaded zeolites are of particular interest due to its ability to reduce NOx to nitrogen, even in the presence of water. Though the iron-loading concept is commonly used for de-Nox catalyst preparation, the types of complexes formed inside the zeolite pores are not well known and no process yields a single type of complex within the pores. Previous studies have determined a single majority complex within the zeolite, however, characterization has not been thorough and it has been determined that multiple other complexes are able to form within the zeolite pores due to the flexibility of the iron-oxygen bond and the pore width of the zeolite. We are investigating iron-complexes formed within the zeolite pores and comparing the types of iron-oxygen complexes formed using different catalyst loading. This study examines the reproducibility of two common loading methods, chemical vapor deposition (CVD) and atomic layer deposition (ALD), and the formation of the various iron-oxygen complexes formed when the Si/Al and iron precursor were varied. XANES and EXAFS data have produced promising results showing that the oxidation state of the iron complex differs depending on zeolite and catalyst preparation, despite similar amounts of iron within the sample. IR spectra have been used to investigate the bonding relationship between the zeolite Brønsted site and the iron complex. Finally, TEM has been used to estimate the size of the iron clusters between the varying samples. This data lends support to the conclusion that variation in iron precursors and loading technique strongly affect iron cluster size and oxidation state leading to a variety of iron complexes.

Synthesis and Characterization of Cu(II) (DL-alanine)•H2O and Cu(II) binding studies with Ab**(1-40) fibrils using UV-VIS spectroscopy**

Bibek Shrestha
Department of Chemistry, University of Illinois at Chicago,
Chicago, IL 60607

In this study, two separate topics involving paramagnetic Cu(II) are discussed. In the first topic, we examine incubation-time dependence of amyloid fibril formation for 40-residue Alzheimer's peptide (Aβ(1-40)) and Cu(II)-binding properties of Aβ(1-40) fibrils using ThT fluorescence and UV-VIS spectroscopy. Alzheimer's disease is a neuro-degenerative disease that disrupts memory and learning. Amyloid fibrils of A•(1- 40) are believed to be the primary component of the Alzheimer's plaques, which possess neurotoxic characteristics. The deposition of these insoluble amyloid beta aggregates found in the neural human brain cells are target of Alzheimer's disease researchers. There were several hypothesis describing the neurotoxicity of amyloid fibrils one of them could be high concentration of Cu(II) ions found in the amyloid plaques. Hence it is highly important to study and understand the Cu(II) binding with Aβ(1-40) peptide. The spectrophotometric studies of Cu(II) binding with Aβ(1-40) fibrils showed specific/non specific interaction of Cu(II) with Aβ(1-40) fibrils. We also discuss potential to uncover the binding pattern of Cu(II) with Aβ(1-40) fibrils using solid-state NMR (SSNMR). In the second topic, characterization of a paramagnetic compound, Cu(II) (DLalanine)• H$_2$O by infrared (IR) and SSNMR spectroscopy is discussed. . It was shown that IR spectroscopy is an ideal technique for the characterization of Cu(II) (DL-alanine)•H$_2$O, since the compound has vibrational transitions associated with periodic changes in its dipole moments. We also show that SSNMR is a powerful technique to characterize paramagnetic compounds that could not be analyzed using solution NMR methods due to signal quenching.

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Controlling Material Transformation and Plasma Emission with Trains of Ultrafast Laser Pulses

Sima Singha, Zhan Hu, Yaoming Liu, and Robert J. Gordon
Department of Chemistry, University of Illinois at Chicago

Laser transformation of materials is a highly complex process involving multiple time and length scales. One way of separating and possibly controlling such processes is to excite the material with trains of sub-ps pulses separated by the characteristic times of the processes of interest. Here we describe experiments performed on two such time scales. In the first experiment, we irradiated a crystal in air with a pair of 50fs, 800nm pulses having delays of up to 100ps. The ratio of the plasma fluorescence produced by the pulse pair to that produced by a single pulse of the same total energy from Si(111) was found to increase monotonically with pulse delay, reaching an asymptotic value at approx. 100ps. At constant fluence, the enhancement ratio grows to a plateau with a time constant of 30-40ps, whereas at a fixed delay the ratio passes through a maximum and falls off at high fluence. We interpret this as an incoherent effect in which the first pulse melts the surface and the second pulse interacts more strongly with the liquid phase, as the melt front propagates into the bulk In a second set of experiments, trains of three or more pulses were generated with a spatial light modulator, with separations on the order of 1.5 ps. The peak spacing of the fluorescence signal from GaAs corresponds approximately to the LO phonon period of the crystal and is highly suggestive of a coherent effect.

Reactions of Atmospherically Relevant Organic Surfaces with Ozone Characterized by Sum Frequency Generation

Grace Stokes
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Evanston, IL 60208

Terpenes emitted from vegetation can become oxidized and form molecular films on tropospheric aerosols. These greasy olefinic coatings can be oxidized by ozone and may influence the microphysics of cloud formation and the earth's climate. Using a laboratory approach that combines organic synthesis with nonlinear optical spectroscopy, we utilized vibrational broadband sum frequency generation (SFG) to survey a number of terpene-modified silica surfaces (including cyclohexene, cyclopentene,1-pentene, and limonene) and track their interactions with ozone in real time. Our organosilane-functionalized surfaces were also characterized with XPS, AFM, ellipsometry and contact angle measurements. Exposure of these surfaces to atmospherically relevant ppb levels of ozone at 1 atm and 300 K yields initial reactive uptake coefficients that are significantly higher than those measured in corresponding gas phase reactions and correlate with the accessibility of the C=C double bonds at the surface. We found that reaction rates for cyclohexene-functionalized silica are pseudo-first order and follow Langmuir-Hinshelwood dependence on gas-phase ozone levels over two orders of magnitude. The changes in the olefinic =C-H stretch and aliphatic C-H stretches in our SFG spectra were used to characterize surfacebound product species. Combined with contact angle measurements carried out before and after ozonolysis, our kinetic and spectroscopic studies suggest a reaction pathway involving vibrationally hot Criegee intermediates that strongly compete with pathways that involve thermalized surface species, a chemical insight which may help reduce uncertainties associated with aerosols when included in global climate change models. We also study the impact of stereochemistry on heterogeneous oxidation reaction rates. We studied quartz functionalized with R- and S- diastereomers which orient their vinylic C=C double bonds towards or away from the gas phase. At low ozone levels, the more accessible S-diastereomer exhibited 2xs higher reaction rates with ozone than the R-diastereomer. Spectroscopic signatures of the methylene moieties before and after ozonolysis also suggest that the R-diastereomer reorients more significantly upon reaction with ozone than the S-diastereomer. These studies may provide insight into the reactions that led to chiral selectivity of biogenic terpenes and other biological materials in the troposphere.

Index of Newsletter Sponsors

Adsorption and Dehydrogenation of Ortho-Carboraneon the Pt(111) Surface

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Chicago,Illinois 60607

The surface chemistry of 1,2-closo-dicarbadodecaborane (ortho-carborane), $C_2B_{10}H_{12}$, on Pt(111), was studied with reflection absorption infrared spectroscopy (RAIRS), temperature programmed desorption, and X-ray photoelectron spectroscopy (XPS). This molecule has a cage-like structure in which boron and carbon atoms occupy the vertices of a slightly distorted icosahedron with 2 C-H and 10 B-H radially directed bonds. At submonolayer coverages at 85 K, the RAIRS spectrum of carborane displays strong B-H stretching vibrations near 2600 cm-1, and a weak C-H stretch at 3090 cm^{-1} that are close in value to those of the isolated molecule. This indicates molecular adsorption at low temperature. At 85 K and low coverages, the B-H stretch peaks of carborane are unusually narrow with full widths at half maxima as low as 4.4 cm-1. Comparison of calculated spectra for various assumed orientations reveals that the molecule is oriented with its permanent dipole moment and the C-C bond parallel to the surface. The molecule is stable on the surface up to 250 K, where it is transformed into a new intermediate with a strongly red-shifted B-H stretch vibration at 2507 cm-1. This intermediate is stable up to 400 K, above which no B-H stretch vibrations are observed. Hydrogen is released in stages as the carborane monolayer is heated from 85 to 800 K, indicating the formation of partially hydrogenated surface intermediates. From XPS measurements of the B 1s peak area as a function of annealing temperature, the boron coverage steadily decreases as the boron cage structure is disrupted and boron atoms diffuse into the bulk of the crystal.

SFG Studies of the Hybridization of Oligonucleotide-Functionalized Fused Silica at the Aqueous/Solid Interface

Stephanie Walter
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We use the surface-specific nonlinear optical spectroscopies second harmonic generation and broadband sum frequency generation (SFG) to track the hybridization of oligonucleotide-functionalized fused silica at the aqueous/solid interface. The chiral properties of DNA single and double strands are used as the molecular origin for the signal response reporting on the hybridization event. The experiments are carried out on attomoles of material, in real time, and without the use of external labels. We believe that the label-free, molecularly specific nature of these measurements will assist in biodiagnostic applications and enhance the fundamental characterization of surfaces modified with biopolymers.

Synthesis and Characterization of Isolated VOx species on q-Al_2O_3

Staci L. Wegener, Hack-Sung Kim, Tobin J. Marks, Peter C. Stair
Department of Chemistry, Institute for Catalysis in Environmental Processes,
Northwestern University, Evanston, IL 60208

In recent years, supported vanadium oxides have been proposed as catalysts for the oxidative dehydrogenation (ODH) of alkane feedstocks. The nature of the surface vanadia species plays a significant role in the reactivity patterns of the catalyst, however, it is unclear which types of V-O bonds and environments are selective for selective oxidation. In this work, we attempt to isolate well-defined VO surface bonds. A series of organometallic vanadium cluster compounds: $VO(Mes)_3$, $[(Mes)_3V]_2(\mu\text{-O})$, and $[(\eta\text{-}C_5Me_5)V]_4(\mu\text{-O})_6$ have been synthesized and grafted onto $\theta–Al_2O_3$ surfaces. X-ray absorption spectroscopy suggests surface VO_x species in a distorted tetrahedral environment. Edge energies of the supported powder catalysts, determined by DRS UV-Visible spectroscopy, decrease as the vanadium cluster size of the organometallic precursor increases. This signifies an increased number of V-O-V type bonds present in the samples prepared with the $[(\eta\text{-}C_5Me_5)V]_4(\mu\text{-O})_6$ precursor than with the $VO(Mes)_3$ precursor. Further evidence of cluster size dependence on catalyst precursor was observed with a shift in the V=O band frequency in the UV-Raman spectra. Continued characterization of the supported catalysts by solid state ^{51}V NMR spectroscopy, EPR spectroscopy, and temperature programmed reduction are currently underway. Catalytic testing for cyclohexane ODH and benzene hydroxylation reactions are ongoing.

Peptide Structure Stabilization: A Study Of Aromatic-aromatic Interaction And pH Effect On A b-hairpin Stability

Ling Wu, Takahiro Takekiyo[2], Dan McElheny1 and Timothy A. Keiderling
University of Illinois at Chicago, Chicago, IL, [2]National Defense Academy,
Hashirimizu, Yokosuka, Kanagawa, Japan.

Aromatic side chains in proteins are often involved in aromatic pairs, most of which form interacting networks of three or more aromatic side chains. (Petsko et al, Science, 1985, 229, 23-28) Analysis of neighboring aromatic groups can lead to improved understanding of protein folding mechanisms and stability. We have used the β-hairpin forming peptide Trpzip2 (Cochran et al, PNAS, 2001, 98, 5578-5583) as a template to study the effect of aromatic-aromatic interaction on peptide stability. Optical spectra (ECD, FTIR) and NMR of the original TZ2 peptide and its Tyr and Val-substituted mutants were measured to characterize their conformation and thermal stability. Compared to the strongly interacting Trp-Trp edge-to-face geometry, Tyr-Tyr shows much weaker aromatic-aromatic interaction. These aromatic-aromatic interactions were also compared to simple hydrophobic interaction by substituting Val for two interacting Trp residues in this peptide. Aromatic interaction showed a stronger effect than hydrophobic interaction for stabilization of this peptide. The thermal unfolding process of three Val mutants was studied under both neutral and acidic conditions by IR and ECD. We see more random coil content at acidic pH than those at neutral pH from analysis of the IR amide I' band, which reflects peptide secondary structure, and the transition temperatures obtained using both IR and CD are lower at acidic pH than at neutral pH, which suggests that this peptide is less stable at acidic pH.

Go to www2.uic.edu/~aalakhan/ to view the abstracts online.

Directions and Parking

Proceed to parking lot 5 located at 1135 South Morgan Street. Parking tokens will be handed out at the event. On street parking is also available. The poster session will be held in the SES (Science and Engineering South) building. This event is located in the Student Learning Center, which is accessible by going through the west entrance when approaching the SES building through the underpass walkway. Turn right immediately upon entering the building. Call 847-530-1348 or go to www.uic.edu/index.html/maps_directions.shtml for directions.
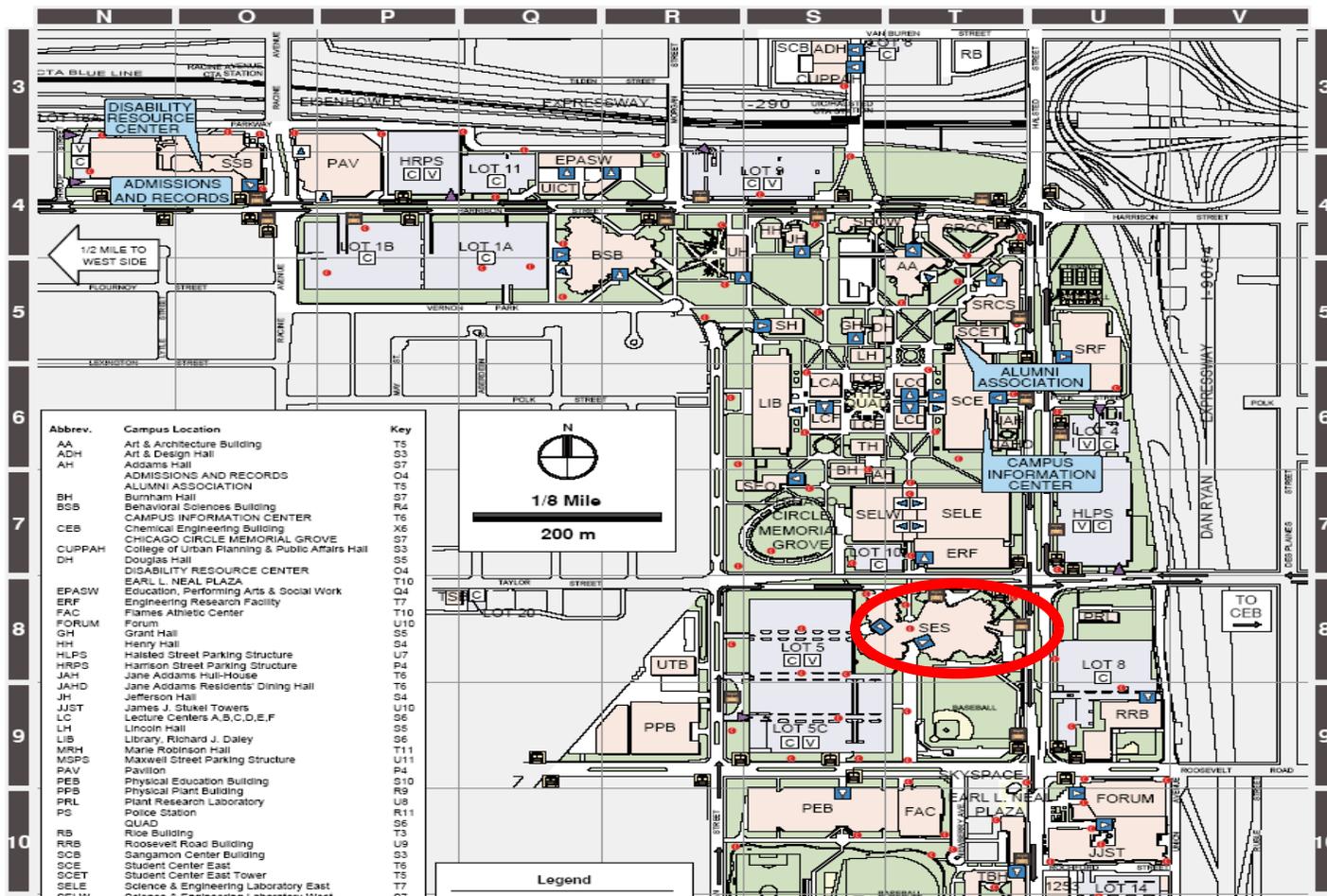
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