

## Environmental Chemistry • Monday Oral Sessions

1. **Naturally Occurring Organohalogen Compounds.** Gordon W. Gribble, Dartmouth College, Department of Chemistry, Hanover, NH 03755

More than 3700 organohalogen compounds, mainly containing chlorine and/or bromine, are either produced by living organisms or are formed during natural abiogenic processes such as volcanoes, forest fires, and geothermal processes. The ocean is the greatest single source of natural organohalogens, and myriad sponges, corals, seaweeds, tunicates, nudibranchs, bacteria, and other marine organisms produce such compounds. Terrestrial plants, fungi, lichen, bacteria, and insects are also significant producers of organohalogen compounds. Nearly all types of organic compounds are represented, including alkanes, aromatic hydrocarbons, phenols, pyrroles, indoles, fatty acids, terpenes, peptides, steroids, alkaloids, acetogenins, furans, and dioxins. Some of the halogenated byproducts of the mammalian immune system, which uses chlorine and bromine to fight infection, have been identified. Dioxins, chlorophenols, chloromethane, and chloroform are now recognized to have several natural sources. The first examples of natural bioaccumulative compounds have been discovered in seabirds and a related polychlorinated bipyrrole, "Q1", has been found in Eskimo women who consume whale blubber. These compounds apparently have a marine origin and enter the food chain in the same manner as DDT. Clearly, nature employs halogen as a basic building block to construct essential molecules for survival of the particular organism. The notion that these thousands of unique organohalogens are isolation artifacts or are the result of anthropogenic activities can now be dismissed. This presentation will discuss recent developments as to the origin and abundance of these natural halogenated chemicals.

### Environmental Chemistry Symposia Oral Session

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2. **Analysis of Herbicide Residues in Ground and Surface Water Using Portable High Performance Immunoaffinity Chromatography.** Mary Anne Nelson, Arther Gates, Maud Dhoutaut, and David S. Hage, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0304.

Biointeraction analysis is a growing area in analytical chemistry, including areas such as clinical analysis, drug discovery and environmental analysis. The advent of techniques including BIAcore and IAS has piqued interest in applications of antibody-antigen interactions to immunoanalysis and immunoaffinity chromatography. The interaction of antibody-antigen is governed by second order association and first order dissociation kinetics. To understand these interactions, kinetic studies using immunoaffinity chromatography were performed. Adsorption kinetics were studied under adsorption-limited conditions as determined by frontal analysis, with values in the range of  $1.8 - 8.4 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  for the binding of 2,4-dichlorophenoxyacetic acid to monoclonal antibodies (E2/G2 clone line). Dissociation rate constants were studied under low pH conditions with rate constants of  $180 - 840 \text{ sec}^{-1}$  for the binding of 2,4-dichlorophenoxyacetic acid and analogs 2,4-dichlorophenoxyacetic methyl ester and 2,4,5-trichlorophenoxyacetic acid. Another aspect of biointeraction analysis includes the cross-reactivity of the antibody with compounds that share structural similarity with the antigen. Studies comparing the cross-reactivity of the antibodies with the association and dissociation constants were performed showing the dependence of the cross-reactivity on the dissociation rate constant. These rate constants and cross-reactivity parameters are used to optimize a portable high-performance immunoaffinity chromatographic (HPIAC) system with on-site capabilities for monitoring point and non-point source pollution in ground and surface waters.

### Environmental Chemistry Symposia Oral Session

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3. **Evaluation of a Dual-system Purge-and-trap Interface – the Duet.** Glynda A. Smith; Mark Krigbaum; Don Harrington, Tekmar-Dohrmann, 4736 Socialville-Foster Road, Mason, OH 45040.

Sample throughput is an increasing concern in analytical laboratories. Newer columns and gas chromatographs are available that offer great reductions in analysis times without sacrificing chromatographic resolution. Such capability puts pressure on GC sampling devices such as static headspace analyzers and purge & trap concentrators to also reduce cycle times. In purge & trap applications, a sample is purged for a specified period of time. USEPA drinking water methods specify a purge time of 11 minutes. The trap is usually baked for 10 minutes, and, if an autosampler is attached, rinse cycles are employed to prevent carryover between samples. A new sample cannot be loaded into the concentrator

until all of these steps are finished. In the dual-system arrangement described in this paper, sample preparation time is reduced by synchronizing the actions between two systems in such a way that one concentrator loads a new sample immediately after the other concentrator begins its desorption step. As a result, there is no delay in waiting for the bake and rinse cycles to be completed before a new sample can be prepared for analysis. The system set up will be described along with the calibration and reproducibility data that was obtained.

#### **Environmental Chemistry Symposia Oral Session**

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#### **4. Environmental Monitoring Using Membrane Introduction Combined with Proton-transfer-reaction Mass Spectrometry**

**(PTR-MS).** Michael L. Alexander, Pacific NW National Laboratory, K8-93, PO Box 999, Richland, WA 99352; Tom Jobson, Pacific NW National Laboratory, K8-93, PO Box 999, Richland, WA 99352; Elena Boscaini, Institut für Ionenphysik, Technikerstrasse 25, Innsbruck, Austria; and Tilmann Märk, Institut für Ionenphysik, Technikerstrasse 25, Innsbruck, Austria.

A mass spectrometer for on-line measurements of trace environmental components with concentrations as low as a few pptv has been developed on the basis of proton transfer reactions. Applications have included monitoring volatile organic compound (VOC) emissions from fruit, coffee and meat as well as real-time monitoring of VOC compounds from an aircraft. Membrane introduction is used to expand the capabilities of the PTR-MS method.

Proton-Transfer-Mass Spectrometry (PTR-MS) uses  $H_3O^+$  as a Chemical Ionization (C.I.) agent in an ion flow-drift tube reactor to provide real-time monitoring of trace environmental components. The PTR-MS does not require calibration because concentrations can be calculated from the ion signal and well-known rate constants. We present results of several environmental monitoring applications using a membrane interface to enhance the inherent sensitivity and selectivity of the PTR-MS instrument, and to extend its application to direct monitoring of liquid samples. We present new applications of the PTR-MS using a silicon membrane to enhance sensitivity and selectivity. The transmission of several classes of organic compounds through the membrane is monitored as a function of time. This response is found to depend on both the functional group and the backbone of the organic molecule. We demonstrate how the difference in transmission rates through the membrane can be used to eliminate certain isobaric interferences in the PTR-MS such as acetone and propanal. This enhancement is demonstrated in monitoring VOC's in the ambient air and in human breath. Measurements of trace components in liquid samples are demonstrated using the membrane as a direct interface and compared with headspace measurements. Various applications are discussed.

#### **Environmental Chemistry Symposia Oral Session**

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#### **5. Evaluation of the High Dilution Capabilities of a Multi-matrix Vial Autosampler.** Glynda A. Smith; Mark Krigbaum; Don Harrington, Tekmar-Dohrmann, 4736 Socialville-Foster Road, Mason, OH 45040.

Today's analytical laboratories are faced with increasing demands for greater efficiency and productivity. Automated sampling systems provide the greatest flexibility for labs that require a high turnover in sample analyses. The SOLATek 72 multi-matrix vial autosampler automates the purge-and-trap analysis of water, wastewater, and soil samples in accordance with current USEPA methods for the analysis of volatile organic compounds (VOC's). One of the unique features of the SOLATek 72 is the ability to program automatic dilutions for water samples as low as 1:250. As a result, high concentration samples can be diluted and analyzed with no manual intervention. In this paper, the dilution capabilities of the SOLATek 72 are examined. Specifically, the data will show that calibration curves can be automatically generated from a single high concentration VOC standard. The results will further show that the calculated %RSD's for the calibrations of the 524.2 compound list fall within the acceptable parameters specified in the USEPA drinking water method. As a result, performing dilutions with the SOLATek 72 allows maximal automation opportunities in busy analytical laboratories.

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#### **6. A National Reconnaissance for Pharmaceuticals and Other Emerging Contaminants in Streams of the United States.**

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To provide the first nationwide investigation of the occurrence of pharmaceuticals, hormones and other organic wastewater contaminants (OWCs) in streams of the United States, the U.S. Geological Survey's Toxic Substances Hydrology Program conducted a reconnaissance study of 142 streams in 32 states during 1999 and 2000. Sampling sites were biased toward streams susceptible to contamination (i.e. downstream

of intense urbanization and livestock production). Samples were analyzed for 95 OWCs (during the 1999 sampling not all target compounds were analyzed at all streams sampled). Almost 90% of the streams sampled had a detection of one or more of these compounds. The compounds detected represent a wide range of residential, industrial, and agricultural origins and uses with 77 of the 95 OWCs being found. Detergent metabolites, plasticizers, and fecal sterols contributed almost 80% of the total measured concentration (sum concentration of detected compounds in any given sample) for this study. The detection of multiple OWCs was common, with a median of 14 compounds detected per stream sample (maximum of 31 compounds). Little is known about the potential interactive effects (synergistic or antagonistic toxicity) that may occur from complex mixtures of these compounds in the environment. The results of this study are not only intended to determine the extent to which OWCs are present in potentially susceptible streams, but to also provide a focal point for the development and testing of new laboratory methods for measuring OWCs in environmental samples at trace levels, an interpretive context for future assessments of OWCs, and a means for establishing research priorities and future monitoring strategies.

#### **Environmental Chemistry Symposia Oral Session**

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7. **Emerging Contaminants In Drinking Water: Analytical Results Vs Reporting Results.** Maria W. Tikkanen, Kennedy/Jenks Consultants, 3336 Bradshaw Road, Suite 140, Sacramento, CA 95827, and Cheryl Ross, Central Basin Municipal Water District, West Basin Municipal Water District, 17140 S. Avalon Blvd. Suite 210, Carson, CA 90746

Emerging contaminants, all those elements or chemicals that have recently been “detected” in a drinking water source merit a discussion of analytical and reporting practices.

These emerging contaminants may be on any number of drinking water regulatory “investigative” lists. For example, federal and state drinking water regulations such as the Unregulated Contaminant Monitoring Regulation, the Contaminant Candidate List, the California Public Health Goal Listing, continue to generate increased analytical demands often with questionable results. How the results from these monitoring activities are reported can generate conflicting messages.

This presentation will detail some of the analytical and reporting problems that perchlorate, N-nitrosodimethylamine (NDMA), chromium (VI), and methyl-tert butyl ether (MTBE) have generated in the state of California.

#### **Environmental Chemistry Symposia Oral Session**

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8. **Improvements in ICP-MS Sample Introduction Design for Routine Analysis of Environmental Samples.** Steve Shuttleworth, Rob Henry, Thermo Elemental, 27 Forge Parkway, Franklin, MA 02038

ICP-MS is currently being used for the analysis of a wide range of environmental samples from pristine waters, drinking waters, wastewaters, soils and toxic waste. The matrix concentrations may change from sample to sample, which puts extra demands on the sample introduction systems and mass spectrometer tuning characteristics. Significant advances in productivity have recently been made by reduction of interferences, improvements in signal to background and greater automation. Data from rigorous testing of a more robust sample introduction system and numerous performance checking samples will be presented.

#### **Environmental Chemistry Symposia Oral Session**

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9. **Continuous Monitoring Of The Distribution Systems – What Can Be Learned.** Terry Engelhardt and John Parsons, Hach Company, 5600 Lindbergh Drive, Loveland, CO 80539

Recent terrorist threats have moved distribution system monitoring to a higher priority for many water utilities. While the motivation may be to detect intentional introduction of harmful contaminants, the real benefit is likely to be a better day-to-day understanding of the fate of water quality in the distribution system. In many utilities the occasional grab sample for coliform analysis and occasional measurement of pH or chlorine residual is the limit of distribution system monitoring. If a contaminant is intentionally introduced, it is unlikely its presence would even be recognized until people become ill. It is important to begin an aggressive continuous on-line monitoring program to establish baseline information. Such a program will provide a basis for detecting abnormal events. Gaining an understanding of the causes for the variation will lead to a process where one can proactively ‘operate’ the distribution system to maintain water quality. Examples of what other systems have discovered will be presented.

#### **Environmental Chemistry Symposia Oral Session**

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11. **Uniform Field Cavities for Use in EPR Spectroscopy.** James S. Hyde, Richard R. Mett and James R. Anderson, Biophysics Research Institute, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, WI 53226

Uniform-field resonators were introduced in Ref. 1, considering both rectangular TE<sub>102</sub> and cylindrical TE<sub>011</sub> modes using finite-element high frequency structure simulator (HFSS) software. These structures consist of three sections. The central section has a cross-section that is set to the cutoff condition for propagation in the direction corresponding to index *l* for the rectangular mode or index *n* for the cylindrical mode. The two end sections are made electrically larger in the structures of Ref. 1 by filling them with dielectric and making them ¼ of a wavelength long. The resonance frequency is independent of the length of the center section and the field is uniform in that section. Uniformity of EPR response from all portions of a line sample is obviously desirable. Reference 2 extends the concepts of Uniform Field resonators to include aqueous sample flat-cell geometries. References 3 and 4, under review as this is being written, describe two other ways to construct the end sections: by making them physically larger even though there is a resulting discontinuity in cross-section dimensions, and by making them electrically larger using re-entrant cavity techniques. The latter consist of metal rods inserted into the electric field regions in rectangular geometries, or so-called toroidal capacitors lying in the circular region of maximum electric field in the cylindrical resonators. In addition, microwave coupling structures and sample access “stacks” have been optimized using HFSS. The stability of the modes to the dielectric properties of the sample has been analyzed. Several practical designs have been constructed suitable for use with 100 kHz field modulation, and EPR experiments have been carried out.

- [1] R.R. Mett, W. Froncisz, and J.S. Hyde, Axially uniform resonant cavity modes for potential use in electron paramagnetic resonance spectroscopy. *Rev. Sci. Instrum.*, **72**, 4188-4200 (2001).
- [2] J.S. Hyde, and R.R. Mett, Aqueous Sample Considerations In Uniform Field Resonators For Electron Paramagnetic Resonance Spectroscopy. *Curr. Top. Biophys.*, in press (2002).
- [3] J.R. Anderson, R.R. Mett, J.S. Hyde, Cavities With Axially Uniform Fields For Use In Electron Paramagnetic Resonance. II. Free Space Generalization, *Rev. Sci. Instrum.*, submitted 2002.
- [4] J.S. Hyde, R.R. Mett, J.R. Anderson, Cavities With Axially Uniform Fields for Use in Electron Paramagnetic Resonance. III. Re-entrant Geometries

### EPR Symposia Oral Session

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12. **Transient Rafts and Transient Partitioning of Raft-related Molecules Into Rafts Detected by Pulse EPR and Single Molecule Nanotracking.** Akihiro Kusumi, Kusumi Membrane Organizer Project, ERATO, Department of Biological Science, Nagoya University, Nagoya 464-8602, Japan. Witold K. Subczynski, National Biomedical ESR Center, Biophysics Research Institute, The Medical College of Wisconsin, Milwaukee, WI 53226.

To investigate raft dynamics in the membrane, we have developed (1) pulse EPR spin labeling methods based on the collision rate between the nitroxide spin labels and molecular oxygen and (2) a high-speed single molecule nanotracking using optical microscopy. These methods are sensitive to in/out's of the probe molecules from the rafts. The main points we would like to emphasize in this presentation are the following. (1) The lifetime of some rafts or the residency time of some raft-constituent molecules in the rafts may be on the order of 10 – 100 μs in the steady state without extracellular stimulus. (2) When the cells are stimulated, some rafts are stabilized and/or they grow in size by coalescing, which may be due to crosslinking or assembly of GPI-anchored or transmembrane receptor molecules by lectins, ligands, or antibodies. (3) In the binary mixture of cholesterol and an unsaturated phospholipid, such as L- $\alpha$ -dioleoylphosphatidylcholine (DOPC), cholesterol is segregated out from the bulk DOPC phase, forming cholesterol-enriched domains or clustered-cholesterol domains. However, such domain is small, likely to consist of only several cholesterol molecules, and is short-lived, on the order of 1-100 ns. We speculate that these cholesterol-enriched domains may be stabilized by the presence of saturated alkyl chains of sphingomyelin or glycosphingolipids, and that the major drive for formation of rafts may not be the affinity of cholesterol and saturated alkyl chains but segregation of cholesterol out of the liquid-crystalline unsaturated bulk-phase membrane.

### EPR Symposia Oral Session

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13. **Recent Low Frequency EPR Studies of Cu(II) in Proteins.** William E. Antholine, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226-0509

Detection of the Cu<sub>A</sub> site in both nitrous oxide reductase and cytochrome *c* oxidase lead to the realization that the Cu<sub>A</sub> site is a mixed valence [Cu<sub>A</sub>(1.5+)...Cu<sub>A</sub>(1.5+)] site (1). Recently, multifrequency EPR spectra for the Cu<sub>A</sub> site in W.T. and Met263Leu mutant in CcO in *Rhodobacter*



*sphaeroides* confirmed from analysis of the high field lines that the Cu<sub>A</sub> site in W.T. and mutant is a mixed valence dinuclear copper site. In the mutant A<sub>II</sub> increases from 30 G and a seven line pattern to a range of values with nonequivalent couplings centered about 65 G and 57 G (2). In a separate study, the equatorial His120 in azurin engineered to form the Cu<sub>A</sub> site was changed to Asn or Gly to understand the role of His in the mixed valence site (3). CW multifrequency EPR gives a four line pattern in the g<sub>II</sub> region, consistent with a trapped valence structure following mutation, but other spectroscopic methods predict a mixed valence structure. This dilemma is still not fully understood.

Recently, well resolved S-band (low frequency), but not X-band, EPR spectra for fragments of the N-terminal domain of prion protein were used to identify the type 2 square pyramidal binding site by synthesizing several fragments in which one amino acid had <sup>15</sup>N while the others had <sup>14</sup>N atoms (4). Another study utilized uptake of <sup>15</sup>N from the growth medium to obtain better resolved spectra from the EPR detectable type 2 cupric site in *M. album* BG8 cells with high a concentration of pMMO (5). pMMO, particulate methane monooxygenase, is a membrane bound enzyme that converts methane to methanol. These new examples show how low frequency EPR is a very useful technique for current studies on EPR detectable copper sites.

- [1] Kroneck et al., FEBS Lett., 268, 274-276, 1990
- [2] Zhen et al., Biochemistry, 41(7), 2288-97, 2002
- [3] Lukoyanov et al., Biophys. J., 82, 2758-66, 2002
- [4] Burns et al., Biochemistry, 41, 3991-4001, 2002
- [5] Lemos et al., Biophys. J., 79, 1085-94, 2000

#### EPR Symposia Oral Session

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#### 14. Role of Carbonate Anion Radical in Bicarbonate-dependent Peroxidase Activity of Cu, Zn-superoxide Dismutase—implications in Protein Aggregation in ALS. Balaraman Kalyanaraman, Joy Joseph, and Hao Zhang; Biophysics Research Institute and Free Radical Research Center, Medical College of Wisconsin, Milwaukee, WI 53226 USA

The first evidence for increased peroxidase activity of familial amyotrophic lateral sclerosis (FALS) SOD1 mutants came from the use of ESR-spin trapping. By monitoring the oxidation of spin trap 5,5'-dimethyl-1-pyrroline (DMPO) to its hydroxyl adduct (DMPO-OH), the investigators concluded that FALS SOD1 mutants exhibit an increased peroxidase activity. Recently, we reported that the bicarbonate anion is required for the peroxidase activity of SOD1 and FALS SOD1 mutants (1,2). We proposed that the carbonate anion radical (CO<sub>3</sub><sup>•-</sup>) formed from oxidation of bicarbonate anion at the active site of SOD1 by the Cu,Zn SOD-bound hydroxyl radical is responsible for oxidation and hydroxylation of DMPO and other nitron traps. This model has provided a new perspective on the peroxidative mechanism of SOD1 and explains in part the published discrepancies on the nature and structure of oxidants generated from FALS SOD1 mutant/H<sub>2</sub>O<sub>2</sub> interaction. We further validated the above mechanism using an independent approach in which an inorganic cobalt carbonate complex that generated CO<sub>3</sub><sup>•-</sup>. These and other radical scavenging reactions of carbonate anion radical in the context of SOD1 aggregation will be discussed.

1. Zhang H, et al., J. Biol. Chem., 2000, 275, 14038-14045.
2. Zhang H, et al., J. Biol. Chem., 2002, 277, 1013-1020.

#### EPR Symposia Oral Session

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#### 15. A New Spin on Protein Dynamics. Wayne L. Hubbell and Linda Columbus, Jules Stein Eye Institute and Department of Chemistry and Biochemistry, University of California, Los Angeles CA 90095

The dynamic nature of a protein is essential for function, and experimental techniques for mapping dynamics are needed for exploring structure/function relationships. The technique of site-directed spin labeling (SDSL) may make important contributions in this arena. The dynamics of the nitroxide side chains used in SDSL have contributions from both internal modes within the side chain and fluctuations of the backbone on the nanosecond time scale. The internal modes are modulated by interactions of the side chain, and this effect has been used to monitor conformational changes in structure in real time. On the other hand, the sequence dependence of side chain dynamics apparently reveals backbone fluctuations in the protein at equilibrium. To explore this idea, SDSL data have been compared with order parameters for the N-H bonds in a protein backbone determined from NMR <sup>15</sup>N relaxation data. In the leucine zipper DNA-binding protein GCN4, both NMR and SDSL data show a striking gradient in motion along the helices. This suggests that the motion detected by the two techniques has the same physical origin: *fluctuation of the dihedral angles* in the helical backbone. In contrast, a comparison of SDSL-detected helical motions in Annexin and Colicin suggests differences attributable to *rigid body fluctuations of the helices* rather than fluctuations in dihedral angles. The dynamic sequences detected by SDSL can be correlated with protein structure and function.

#### EPR Symposia Oral Session

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16. **Saturation Transfer EPR: Applications to Membrane Protein Dynamics.** Albert H. Beth and Eric J. Hustedt, Department of Molecular Physiology and Biophysics, Vanderbilt University, Nashville, TN 37232-0165

Saturation transfer EPR (ST-EPR), a technique developed by Hyde and Dalton in the early 1970's, has proven to be exquisitely sensitive to the  $\mu\text{sec}$  to msec rotational dynamics of intrinsic membrane proteins in cell membranes. Recent progress in developing fast computational methods for simulating ST-EPR spectra for the uniaxial rotational diffusion (URD) model has enabled determination of diffusion coefficients, probe orientation, and constraints to URD by non-linear least-squares fitting of experimental ST-EPR data obtained from intrinsic membrane proteins. These computational tools have been employed to establish the sensitivity of ST-EPR to each of these parameters at a wide range of microwave and Zeeman-field modulation frequencies and to extract these parameters from two different membrane proteins (the anion exchange protein in human erythrocytes and the EGF-receptor in A-431 cells) in their native membranes. Supported by: NIH R37 HL34737.

#### **EPR Symposia Oral Session**

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17. **Molecular Dynamics in Spin-labeled Muscle.** David D. Thomas, Department of Biochemistry, University of Minnesota, Minneapolis, MN 55455.

The power of nitroxide EPR spectroscopy has been crucial to elucidating the molecular mechanism by which force and movement are generated in muscle. Spin label EPR has a unique combination of capabilities — high orientational resolution that remains even in the presence of partial disorder and dynamics, sensitivity to rotational dynamics from picoseconds to milliseconds for a single probe, sensitivity to very small samples, insensitivity to light scattering, small probes that can be directed to unique labeling sites — have all been ideal for the complex macromolecular system of muscle. The EPR concepts and technologies developed by Hyde and coworkers have played central roles in making these investigations possible. The result is a picture of a molecular machine that employs transitions among dynamically disordered states to achieve the efficiency and flexibility needed for biological strength and movement.

#### **EPR Symposia Oral Session**

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18. **Post-processing Strategies for EPR Spin-trapping Data.** Agnes Kezler, Neil Hogg, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226-0509

Modern EPR machines and modern computers allow rapid collection, digitization and storage of data. In addition, data storage capacity is unlikely to be an issue in spin-trapping EPR. On the principal that it is better to save all the raw data, this abstract proposes that signal averaging before data storage is an anachronistic technique in EPR –spin trapping. This is because spin-adduct spectra are almost always changing as a function of time due to formation and decay of radical species.

In order to get the maximum amount of spectral and kinetic information from a single reaction, we have used the strategy of scanning the reaction system as rapidly as possible for as long as required, and storing the raw data as 3-dimensional data set (time x field x intensity). The application of post-processing strategies to this data set (singular value decomposition, least squares multiple linear regression) can then be used to reduce noise and to extract kinetic and spectral data. In addition, principal component analysis can aid accurate simulation of complex multicomponent spectra.

We have assessed these techniques using DMPO and DEPMPO spin traps and by examining the kinetics of formation and decay of superoxide, hydroxyl and glutathionyl spin adducts. Our data indicate that full kinetic and spectral data can be accurately determined for sub-micromolar concentrations of spin-adduct using a 100 G scan range and a time resolution of 3s.

#### **EPR Symposia Oral Session**

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19. **EPR Spectroscopy of Function in Vivo: Origins, Achievements and Future Possibilities.** Harold M. Swartz, EPR Center for Viable Systems, Dartmouth Medical School, Hanover, NH 03755

The capability of following function *in vivo* is an important and growing application of EPR spectroscopy. These capabilities are different but often complimentary to EPR imaging, which is especially useful for studies of morphology, but also can be very effective for functional measurements. While the earliest *in vivo* spectroscopic studies were done by Piette (1) and colleagues, Jim Hyde and colleagues at the ESR Center in Milwaukee were pioneers in the area that today seems most promising when they followed dynamic changes in oxygen in mice (2). Subsequently, *in vivo* spectroscopy has been taken up and expanded at several sites, especially via formal EPR Centers at the U. of Illinois, Dartmouth, Ohio State University, the U. of Chicago, Johns Hopkins, the NCI, and several sites in Japan. The most widespread application continues to be oximetry, but studies of other functions also are very promising. These include measurements of free radicals *in vivo*, pharmacokinetics, and following biophysical parameters. The ESR Center at Milwaukee continues to have an important role in *in vivo* studies of

free radicals. The presentation will summarize the latest developments in *in vivo* EPR, including the start of direct clinical studies. An assessment of the future potential of *in vivo* EPR will be made. Not surprisingly, formal EPR centers are likely to continue to be at the forefront of these developments. Supported by NCRP and NIH RR11602.

[1] Piette et al., Phys. Med. Biol., 1975, 20, 602.

[2] Subczynski et al, Magn. Reson. Med., 1986, 3, 747.

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20. **Calibration of Oxygen Sensitivity of Narrow Line Width Spin Labels.** Colin Mailer, Benjamin B. Williams, Howard J. Halpern, Dept. of Radiation and Cellular Oncology, University of Chicago, Chicago, IL 60637, Lu Yong, Richard Quine, Sandra S. Eaton, Gareth R. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver CO 82080, all from the Center for EPR Imaging *In Vivo* Physiology

EPR spectral-spatial imaging of oxygen requires precise ( $\pm 0.1$   $\mu$ Tesla) and accurate (also  $\pm 0.1$   $\mu$ Tesla) extraction of 0.5 – 10  $\mu$ T Lorentzian line widths from trityl radical (Nycomed Innovations, Malmo, SW) EPR lines inhomogeneously broadened by unresolved hyperfine couplings of 10 – 20  $\mu$ Tesla. A crucial aspect of the calibration is the determination of the intercept of the linewidth vs oxygen concentration linear relationship. The Lorentzian line width is obtained using spectral fitting. A broad minimum in chisquare is obtained for various assumptions about the individual hydrogen hyperfine splittings. This gives various intercepts of the line width vs oxygen concentration relationship.

Resolving this requires time domain measurements of the trityl  $T_{1s}$  and  $T_{2s}$ . Further broadening is introduced by power saturation and Zeeman field modulation, especially when one is seeking to maximize signal-to-noise ratio and minimize data collection time. The work to be presented describes the strategies we use to overcome these difficulties.

Supported by NIH grant RR12257

#### EPR Symposia Oral Session

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## EPR • Tuesday Oral Sessions

21. **High Frequency (140 and 180 GHz) Pulsed EPR and ENDOR Spectroscopy for the Investigation of the Active Site in Proteins.** M. Bennati<sup>a</sup>, O. Brüggemann<sup>a</sup>, T. Prisner<sup>a</sup>, G. Bar<sup>b</sup>, J. Stubbe<sup>b</sup> and R.G. Griffin<sup>b</sup>, <sup>a</sup>Dept. of Physical Chemistry, J. Goethe University of Frankfurt, Frankfurt, 60439 Germany, <sup>b</sup>Center for Magnetic Resonance and Dept. of Chemistry, MIT, Cambridge MA, 02139 USA

High frequency EPR has been shown to considerably improve the capability of EPR spectroscopy in terms of spectral resolution and sensitivity. The use of pulsed methods additionally allows to manipulate the spin system and disentangle complex spectra of overlapping signals.

Particularly, pulsed ENDOR spectroscopy becomes very attractive at high fields ( $B \geq 3$  Tesla) since the Larmor frequencies of common low-gamma nuclei are well resolved and, in the most cases, hyperfine spectra simplify to 'first order'.

In this contribution we present different examples of pulsed EPR and ENDOR at 140 and 180 GHz, aimed at elucidating the active site of proteins and enzymes, in particular of ribonucleotide reductase class I, which contains a stable tyrosyl radical-diiron cofactor and undergoes a radicalic enzymatic reaction, and of protein-G nucleotide complexes with a sixfold coordinated  $Mn^{2+}$  in the active site.

#### EPR Symposia Oral Session

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22. **ESR in Studies of Membranes and Proteins at ACERT.** P.P. Borbat, A.J. Costa-Filho, K.A. Earle, J.K. Moscicki, J.H. Freed, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853

Modern ESR techniques for studying the dynamic structure of proteins and membranes using nitroxide spin labels include the following: multiple quantum coherence FT-ESR to measure distances in biomolecules, multi-frequency ESR based on high frequency ESR, 2D-ESR to study the dynamic structure of bio-membranes and proteins, and FT-ESR imaging to study diffusion in biosystems. These techniques are being applied to a variety of bio-systems at the new National Biomedical Center for Advanced ESR Technology (ACERT). An overview of the capabilities of these techniques will be presented. The multi-frequency 2D-FT-ESR capability (9, 17, and 95 GHz) is based on intense microwave  $B_1$  fields requiring  $\pi/2$  pulse widths of only 3-5ns with large resonator bandwidths (200-500 MHz), short dead times (25-35ns),

with rapid data acquisition yielding high sensitivity of ca. 200pmoles. The double-quantum coherence ESR also requires intense  $B_1$  fields which leads to high sensitivity. FT-ESR Imaging requires rapid pulsed field gradients (e.g. 100G/cm with 40 ns rise and fall times). Very high frequencies (170, and 250 GHz) require quasi-optical ESR bridges and Fabry-Perot resonators, and this technology has been extended to 95 GHz. They provide high sensitivity, (e.g.  $10^8$  spins/G at 250 GHz). The application and power of these technologies at ACERT will be illustrated by examples of: protein structure determination using bilabeled proteins, unraveling the complex dynamics of proteins, the dynamic structure of membranes in liquid-crystalline vs. liquid-ordered phases, and the dynamic structure of boundary lipids that coat membrane peptides. Supported by NIH/NCRR.

#### **EPR Symposia Oral Session**

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#### **23. The P85 Coiled-coil: Protein Structure Determination Using SDSL-EPR, CD and Molecular Homology Modeling and Dynamics.**

Elijah Aronoff-Spencer,\* Zheng Fu,† Jonathan M. Backer‡ and Gary J. Gerfen\*, Department of Physiology and Biophysics\* and Department of Molecular Pharmacology,‡ Albert Einstein College of Medicine of Yeshiva University, 1300 Morris Park Avenue, Bronx, NY 10461.

The Phosphoinositide 3'-kinases (PI3'-K) constitute a family of lipid kinases that are modulated through interactions with receptor tyrosine kinases and G-protein coupled receptors. The regulatory p85 subunit of PI3'-K forms inhibitory heterodimers with the catalytically active p110 subunit. When PI3'-K is bound to phosphorylated receptors through at least one of two serial SH2 domains found in p85, the p85/p110 heterodimer is disinhibited through a presently unknown mechanism. Positioned between the two SH2 domains is the inter-SH2 (iSH2) domain which has been proposed to form a long coiled-coil and to be responsible for binding p110.<sup>1</sup> To test these hypotheses we employed site directed spin labeling (SDSL) EPR studies in conjunction with molecular homology modeling and dynamics to determine the structure of the iSH2 domain of an active truncated p85 molecule containing the n-terminal SH2 and iSH2 domains. A large set of single and double cysteine-containing mutants were engineered for SDSL EPR measurements. Single mutants supplied information on the local mobility of the nitroxide, including mapping of solvent exposed and interfacial helical sites, and double mutants allowed direct measurement of inter-spin distances. These data were then compared with a homology model of the iSH2 domain based primarily on coordinates from the coiled-coil domain of Colicin E3 (pdb: 1JCH).<sup>2</sup> The model, which was refined using MD and energy minimization, was found to be consistent with the SDSL-EPR data. Initial circular dichroism experiments indicate that roughly 50% of the protein is helical, also consistent with predictions based on our model. Finally, we studied the effect of phosphopeptide binding on p85 structure. No evidence was found for a phosphopeptide induced change in global or local conformation in the iSH2 domain, indicating that disinhibition must occur through direct association of other domains of p85 with p110.

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#### **24. Lipoxygenases Take New Spins. B.J. Gaffney, F. Wu and L.J. Katsir, Florida State University, Department of Biological Science, Tallahassee, FL 32306-4370**

Polyunsaturated fatty acids are rapidly converted to cell signaling molecules in multi-step syntheses involving a lipoxygenase or prostaglandin synthase step followed by further conversions employing other, frequently heme, enzymes. These multi-step syntheses are thought to be regulated by localization of the enzymes in subcellular compartments and by protein-protein associations. Two newer lipoxygenases expand our understanding of the modes of action of these enzymes. One new mode of regulation is represented by a fusion protein identified in the coral *Plexaura homomalla*, in which an N-terminal catalase-like domain is fused to a lipoxygenase domain. The N-terminal domain of this protein has allene oxide synthase (AOS) activity, but not catalase activity. We have found that stoichiometric addition of peracetic acid leads to a protein radical in the AOS domain. This radical is shown to be tyrosyl by EPR of AOS substituted with deuterated tyrosines. The radical site has been examined by mutagenesis, saturation and line-shape simulations. The AOS radical has a shorter relaxation time, and a larger  $\beta$ -proton splitting ( $A_{x,y,z}$  45, 35, 35 MHz), than the tyrosine radical in catalase compound II. A second new mode of lipoxygenase action is represented by manganese lipoxygenase, which is the first example of an exported lipoxygenase. High frequency EPR has been particularly helpful in characterizing the metal site in this enzyme because the value of  $D$  is in the range of  $0.10 \text{ cm}^{-1}$ . The EPR assignment argues for some nitrogen ligation to  $\text{Mn}^{2+}$ , and this is now confirmed in the sequence completed by E. Oliw and C. Su (Eur. J. Biochem in press).

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25. **Information on the Determinants of Activity in Aminopeptidases from EPR Spectroscopy of the Hyperactive Copper-substituted Aminopeptidase from *Aeromonas proteolytica*.** Brian Bennett, William E. Antholine, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226-0509; Ventris M. D'souza, Guanjing Chen, Leila Ustynyuk, Richard C. Holz, Dept. of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300.

The prototypical aminopeptidase (AAP) from *Aeromonas proteolytica* has strong active site homology to human aminopeptidases involved in tumorigenesis, tumor growth, HIV infectivity, ageing and cataract formation. Intermediates in the catalytic cycle have been characterized largely on the basis of EPR spectroscopy of the active cobalt-substituted AAP and crystallography of the native di-zinc enzyme (1-5). However, an outstanding question in metallohydrolase chemistry is: to what extent do geometry and Lewis acidity influence the reactivity of both the hydrolytic and non-hydrolytic metal ions? We have addressed this question through EPR and kinetic studies of copper-mono- and disubstituted hyperactive forms of AAP. We have shown that geometry is the principal determinant of reactivity of the hydrolytic metal ion. We have rationalized the tenfold hyperactivity of copper-disubstituted AAP *versus* the hundredfold hyperactivity of the heterodimetallic [CuZn(AAP)] by the observation that the non-hydrolytic copper ion in [CuCu(AAP)] binds in a site 1.5 Å distant from the usual position of the non-hydrolytic metal ion. Thus, the non-hydrolytic copper ion is not correctly sited to stabilize the transition state.

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26. **Structure of the Substrate Binding Pocket in the Multidrug Transporter EmrE.** Hanane A. Koteiche and Hassane S. Mchaourab, Vanderbilt University, Department of Physiology and Biophysics, Nashville, TN 37232.

EmrE is a 12kDa multidrug transporter from *Escherichia coli*. It confers resistance to a variety of positively charged toxic compounds, such as ethidium bromide, methyl viologen and tetraphenylphosphonium, by actively removing them from the cell interior in exchange for protons. Previous studies on the structure of EmrE have proposed a model for its secondary structure that includes four helical transmembrane segments separated by loops and turns. Functional studies have implicated the residue Glu 14, the only charged residue embedded in the membrane, as part of the substrate binding site. Studies have shown that EmrE functions as an oligomer, however there are conflicting reports about the size of the oligomeric unit which vary from 2 to 4 subunits. We are using site directed spin-labeling and Electron Paramagnetic Resonance Spectroscopy (EPR) to determine the secondary, tertiary and quaternary structure of EmrE. Sequential cysteine mutants were constructed throughout the sequence, then reacted with a sulfhydryl specific paramagnetic spin label (MTSSL) and analyzed by Electron Paramagnetic Resonance (EPR) spectroscopy. For each mutant, the local environment of the spin label was characterized by determining its mobility and its accessibility to collisions with molecular oxygen and a paramagnetic reagent exclusively soluble in the aqueous phase. Subunit interactions were studied by distance measurements between residues located on different subunits. The results obtained from these studies were combined with molecular modeling to determine the geometry of the substrate binding pocket.

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27. **In Vivo Lipid-derived Free Radical Formation by NADPH Oxidase in Acute Lung Injury Induced by Lipopolysaccharide – a Model for ARDS.** Ronald P. Mason, Maria B. Kadiiska, NIEHS/NIH, Research Triangle Park, NC 27709; Andrew J. Ghio, EPA, Research Triangle Park, NC 27709; Jean Corbett, Yang C. Fann, NIEHS/NIH, Research Triangle Park, NC 27709; Steven M. Holland, NIAID/NIH, Bethesda, MD 20892; Ronald G. Thurman, Department of Pharmacology, UNC, Chapel Hill, NC 27599-7365; Keizo Sato, NIEHS/NIH, Research Triangle Park, NC 27709

Intratracheal instillation of lipopolysaccharide (LPS) activates alveolar macrophages and infiltration of neutrophils causing lung injury / acute respiratory distress syndrome. Free radicals are a special focus as the final causative molecules in the pathogenesis of lung injury caused by LPS. While *in vitro* investigation has demonstrated radical generation after exposure of cells to LPS, *in vivo* evidence is lacking. Therefore, using electron spin resonance (ESR) and the spin trap  $\alpha$ -(4-pyridyl-1-oxide)-*N*-tert-butyl nitron (POBN), we investigated *in vivo* free radical production by rats treated with intratracheal instillation of LPS. ESR spectroscopy of lipid extract from lungs exposed to LPS for six h gave a spectrum consistent with that of a POBN/carbon-centered radical adduct ( $a^N = 14.94 \pm 0.07$  G and  $a^{H\beta} = 2.42 \pm 0.06$  G) tentatively assigned as a product of lipid peroxidation. To further investigate the mechanism of LPS-initiated free radical generation, rats were pretreated with the phagocytic toxicant  $GdCl_3$ , which significantly decreased the production of radical adducts with a corresponding decrease in neutrophil infiltration as indicated by histopathological studies. NADPH oxidase knockout mice totally blocked this phagocyte-mediated ESR detectable radical production in this model of acute lung injury. In conclusion, rats treated with intratracheal instillation of LPS generate lipid-derived free

radicals via the activation of NADPH oxidase.

### EPR Symposia Oral Session

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## EPR • Tuesday Poster Sessions

### 28. Study of Electron Paramagnetic Resonance and Optical Absorption Spectra of VO<sup>2+</sup> Ions in Bi<sub>2</sub>O<sub>3</sub>: Li<sub>2</sub>O: B<sub>2</sub>O<sub>3</sub> Glasses.

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Electron paramagnetic resonance and optical absorption spectra of the glasses  $x \text{ Bi}_2\text{O}_3 : (0.30 - x) \text{ Li}_2\text{O} : 0.7 \text{ B}_2\text{O}_3$  ( $0.00 \leq x \leq 0.15$ ) containing 2.0 mol. % of V<sub>2</sub>O<sub>5</sub> have been studied. Spin Hamiltonian parameters (SHP) of VO<sup>2+</sup> ions, dipolar hyperfine parameter, P and Fermi contact interaction parameter, K and molecular orbital coefficients ( $\alpha^2$  and  $\gamma^2$ ) have been calculated. The values of the SHP indicate that the V<sup>4+</sup> ions are present in the glasses as VO<sup>2+</sup> ions in octahedral coordination with a tetragonal compression and belong to C<sub>4v</sub> symmetry. The tetragonal distortion of V<sup>4+</sup>O<sub>6</sub> complex is minimum at  $x = 0.06$  and at the same composition the contraction of the 3d<sub>xy</sub> orbit of the unpaired electron in the vanadyl ion is maximum. The theoretical values of optical basicity ( $\Lambda_{\text{th}}$ ) of the glasses have also been evaluated. The optical absorption spectra exhibit two bands characteristic of VO<sup>2+</sup> ions in tetragonal symmetry. The two bands have been assigned to the  $b_2 \rightarrow e_{11}^*$  and  $b_2 \rightarrow b_1^*$  transitions.

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### EPR Symposia Poster Session

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### 29. Slotted EPR Structures for Field Modulation Transparency. James R. Anderson, Richard R. Mett and James S. Hyde, Biophysics Research Institute, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, WI 53226.

Slotted structures can be used in cavities and loop gaps to provide high frequency (100 kHz) field modulation transparency to the sample. It is essential in such structures to maintain the integrity of the microwave current paths in order that microwave leakage be minimal and the Q adequate. A detailed study of the uniformity and attenuation of the modulation entering the cavity for various slot geometries (width, thickness and spacing) has been carried out using conventional magnetic measurement techniques. The sizes were scaled up for convenience of measurement and fabrication by maintaining a constant wavelength with respect to the slot size for a specific modulation frequency. Effects of different modulation frequencies on a 100 kHz optimized structure have been characterized as well. Particular attention was paid to modulation amplitude near the sidewalls for applications using flat cells and samples that are near the sidewalls. A comparison of the measurements to finite element simulations using Ansoft (Pittsburgh, PA) High Frequency Structure Simulator (HFSS) was also made. Microwave leakage through the slots, as well as field modulation penetration were considered. Analysis of the effect of different wall thicknesses and slot spacings on microwave leakage and modulation transparency is included.

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### 30. Sodium Nitrite, Methemoglobin and Nitrosylhemoglobin: An EPR Study. Steve I. Baskin<sup>1</sup>, Gary A. Rockwood<sup>2</sup>, Anita V. Moran<sup>2</sup>, K.R. Armstrong<sup>3</sup>, M.T. Huiku<sup>4</sup>, David W. Kahler<sup>2</sup>, Damon L. Burman<sup>3</sup>, Silvia L. Mioc<sup>4,5</sup> and Carmen M. Arroyo, J Lukey<sup>2</sup>, Pharmacology<sup>1</sup> and Drug Assessment<sup>2</sup> and Comparative Medicine<sup>3</sup> Divisions, US Army Medical Research Institute of Chemical Defense, Aberdeen Proving Grounds, MDMD; <sup>3</sup>ORISE<sup>3</sup>, Oak Ridge Institute For Science and Education, Oak Ridge, TN; Datex-Ohmeda, Inc.<sup>4</sup>, Kuortaneenkatu<sup>2</sup>, Helsinki, Finland; Datex-Ohmeda, Inc.<sup>4,5</sup>, 1315 1315 West Century Drive, Louisville, CO.

Cyanide (CN) is a rapidly acting military/terrorist threat agent. Our laboratory has evaluated several pharmaceutical pre-treatments designed to protect the warfighter against CN poisoning. One promising pre-treatment strategy involves the application of a methemoglobin (MHB)-forming

drug prior to anticipated CN exposure. A logistical concern is field-compatible Mhb detection capability. We describe a comparative Mhb study using standard, invasive oximetry, and a novel prototype non-invasive multi-wavelength pulse oximeter being developed by Datex-Ohmeda. This non-invasive monitor can detect Mhb, oxyhemoglobin, carboxyhemoglobin and reduced hemoglobin, although only Mhb data is reported here. Five male rhesus monkeys were evaluated for hematological effects of the Mhb former sodium nitrite ( $\text{NaNO}_2$ ). Intravenous infusions of  $\text{NaNO}_2$  were administered every 20 min until ~15% Mhb was produced. Arterial blood samples were taken at 2 and 18 min after each infusion, and analyzed using the OSM-3 Hemoximeter. Subjects were also continuously monitored using the prototype pulse oximeter. Two non-invasive probes were placed on the right and left middle fingers of each animal subject. Data were recorded continuously and post-processed. Mhb levels estimated by the non-invasive Mhb monitor strongly correlated with those levels determined invasively ( $r = 0.9722$ ). Due to the continuous operation of the non-invasive device, the transient behavior of Mhb formation was observed for the first time. Across time, a scallop-shaped curve, corresponding to the repeated dosing of  $\text{NaNO}_2$  was observed. This study suggests that a non-invasive device could provide rapid and reliable clinical analyses of Mhb levels in personnel who could be exposed to CN.

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### 31. **Electron Spin Echo Envelope Modulation of High Spin Systems in Weak Crystal Field.** Andrei V. Astashkin, Arnold M. Raitisimring, Department of Chemistry, University of Arizona, Tucson, AZ 85721-0041.

While investigating MRI contrast agents containing  $\text{Gd}^{3+}$  ( $S = 7/2$ ) by electron spin echo envelope modulation (ESEEM), we noticed an abnormally small intensity of the proton sum combination line in primary and four-pulse ESEEM spectra. The same phenomenon was observed in the ESEEM spectra of  $\text{Mn}^{2+}(\text{H}_2\text{O})_6$  ( $S = 5/2$ ). In the X-band EPR experiments, both the  $\text{Gd}^{3+}$  and  $\text{Mn}^{2+}$  complexes that we studied were characterized by a weak crystal field. Trial ESEEM simulations based on related published works [1-3] have shown that the current theory does not satisfactorily explain the low intensity of the sum combination line observed in these experiments. We, therefore, developed a more comprehensive ESEEM theory for high-spin ions that properly accounts for the effects of the weak crystal field, and predicts that the intensity, shape and width of the sum combination line, even for  $|1/2\rangle \leftrightarrow |-1/2\rangle$  electron spin transitions, are significantly affected by the crystal field parameters. These theoretical predictions were applied to successfully interpret the results of the ESEEM experiments with  $\text{Mn}^{2+}$  complexes. The HYSCORE spectra of such systems are also discussed. This work was supported by NSF BIR-9224431 and DBI-0139459.

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#### EPR Symposia Poster Session

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### 32. **Direct Evidence That the Antioxidant Flavonoid Baicalein Scavenges Superoxide.** Eugene Barth,<sup>1</sup> Gerald Rosen,<sup>2</sup> Zuo-Hui Shao,<sup>3</sup> Terry Vanden Hoek,<sup>3,4</sup> Yimin Qin,<sup>3,4</sup> Lance Becker,<sup>3,4</sup> Paul T. Schumacker,<sup>3,4</sup> and Howard Halpern,<sup>1</sup> <sup>1</sup>Department of Radiation and Cellular Oncology, and Center for Low Frequency EPR Imaging for *In Vivo* Physiology, University of Chicago, Chicago, Illinois 60637; <sup>2</sup>Department of Pharmaceutical Sciences, University of Maryland School of Pharmacy, and Medical Biotechnology Center, University of Maryland, Baltimore, Maryland 21210; <sup>3</sup>Section of Emergency Medicine and, <sup>4</sup>Emergency Resuscitation Center, University of Chicago, Chicago, Illinois 60637

Investigators pursuing *In Vivo* studies of the role of reactive oxygen species (ROS) in cellular response to oxidant stress employ intracellular probes that fluoresce in a characteristic manner upon oxidation by ROS. Investigators value such fluorescent probes for their relative ease of detection and sensitivity to endogenous levels of reactive oxygen species. However, fluorophores such as 2',7'-dichlorofluorescein (DCFH) and dihydroethidium (DHE) are oxidized by multiple reactive oxygen species, so they lack the specificity required to implicate a particular oxidant. In the present study, we use electron paramagnetic resonance spectroscopy with the spin trap 5-methoxycarbonyl-5-methyl-1-pyrroline-N-oxide (MMPO) to provide evidence that the flavonoid baicalein scavenges superoxide. The spin trap MMPO reacts with the superoxide anion to create an adduct (MMPO-OOH) with a unique EPR spectrum. We generated superoxide *In Vitro* using a xanthine/xanthine oxidase system. In the absence of baicalein, the MMPO-OOH levels increased for the first 15 min, then decreased toward zero as the rate of superoxide generation declined and the MMPO-OOH adduct decayed spontaneously. Addition of SOD abolished the increase in MMPO-OOH, confirming that the EPR spectrum reflected the spin trapping of superoxide. Addition of baicalein produced a concentration-dependent attenuation of the EPR spectrum of MMPO-OOH, suggesting that baicalein scavenged superoxide. This EPR study provides evidence of a specific mechanism for the *In Vivo* observations that baicalein attenuates oxidant stress in cultured chick cardiomyocytes subject to hypoxia, simulated ischemia, and reperfusion.

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- 33. Consequences of Nitric Oxide Generation in Epileptic-seizure Rodent Models: in Vivo EPR Studies.** Kenshi Kaneko and Kazuo Miyasaka, Department of Radiology, Hokkaido University School of Medicine, Sapporo, Hokkaido 060-8638, Japan; Kouichi Itoh, Department of Molecular Biodynamics, The Tokyo Metropolitan Institute of Medical Science, Tokyo Metropolitan Organization for Medical Research, Bunkyo-ku, Tokyo 113-8613, Japan; Lawrence J. Berliner, Laboratory of In vivo Electron Spin Resonance Spectroscopy, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208-2436, USA; Hirota Fujii, School of Health Sciences, Sapporo Medical University, Sapporo, Hokkaido 060-8556, Japan

The role of nitric oxide (NO) in epileptogenesis was studied in pentylenetetrazole (PTZ)-treated animals using in vivo and ex vivo EPR spectroscopy (1,2). NO generation was measured directly in the brain of a PTZ-induced mouse in vivo in an L-band EPR spectrometer. An elevation in NO production in the brain was observed during convulsions, and more NO was generated in tonic vs. clonic seizure. NO content in several brain tissues (such as cerebral cortex, cerebellum, olfactory bulb, hippocampus, and hypothalamus) of PTZ-doped rats were analyzed quantitatively ex vivo by X-band EPR. In order to test the involvement of NO on seizure development, pharmacological analyses were performed using the NO synthase (NOS) inhibitors, N  $\gamma$ -nitro-L-arginine (L-NNA), N  $\gamma$ -monomethyl-L-arginine (L-NMMA), and 3-Bromo-7-nitroindazole (3Br-7NI). All of these inhibitors suppressed the convulsion from tonic to clonic convulsion in rats doped with up to 80 mg/kg PTZ. 3Br-7NI completely inhibited NO production, but L-NNA and L-NMMA showed only 70% inhibition of NO production in PTZ-doped rats. In order to examine the contributions of NO in convulsions, rats were treated with anticonvulsants, phenytoin and diazepam, before PTZ treatment. Both drugs completely suppressed tonic convulsion in PTZ-doped rats at doses up to 80 mg/kg, but NO levels similar to that detected in clonic convulsion. To our knowledge, this is the first direct EPR observation confirming NO production in convulsive living animals. These results support the notion that NO does not directly induce clonic convulsion but is generated as a consequence of onset of the seizure.

[1] Fujii H, Berliner LJ. *Magn. Reson. Med.* 1999, **42**, 599-602.

[2] Fujii H, Koscielniak J, Berliner LJ. *Magn. Reson. Med.* 1997, **38**, 565-568.

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- 34. Structure Determination of Proteins by Double-quantum Coherence ESR.** Petr P. Borbat and Jack H. Freed, Baker Laboratory of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301; Hassane Mchaourab, Department of Molecular Physiology and Biophysics, Vanderbilt University School of Medicine, Nashville, TN 37232

Protein Structure determination by spectroscopic approaches relies primarily on the measurement of distances on the scale of the macromolecule. In general, the number of these constraints and their softness determine the uniqueness and resolution of the resulting structure. In reporter group techniques, the range and quality of the distances are even more critical to throughput and resolution. We report the use of a novel pulsed ESR technique for distance measurement, based on the detection of double quantum (DQC), which yields high quality dipolar spectra, to significantly extend the range of measurable distances in proteins using nitroxide spin-labels.<sup>1</sup> Eight T4 lysozyme (T4L) mutants, double labeled with methanethiosulfonate spin label (MTSSL), have been studied using DQC-ESR at 9 and 17 GHz at temperatures of 77K and 200K. The distances span the range from 20 Å to nearly 50 Å. The high quality of the dipolar spectra also allows the determination of the distance distributions, the width of which can be used to set upper and lower bounds in future computational strategy. It is also demonstrated that the shape of these distributions can reveal the presence of multiple conformations of the spin label, an issue of critical relevance to the structural interpretation of the distances. The distances and distributions found in this study are readily rationalized in terms of the known crystal structure, the characteristic conformers of the nitroxide side-chains, and molecular modeling. This technique offers a useful and convenient way of determining the tertiary structure of large proteins with just a small number of constraints. Supported by grants from NIH and NSF.

[1] P.P. Borbat, H.S. Mchaourab, J.H. Freed, *J. Am. Chem. Soc.* (in press, 2002)

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- 35.  $T_{1e}$  in Two  $Gd^{3+}$  Chelates: LODEPR Measurements and Models for Electron Spin Relaxation.** A. Borel<sup>1</sup>, L. Helm<sup>1</sup>, A.E. Merbach<sup>1</sup>, B.M. Odintsov<sup>2</sup>, R.L. Belford<sup>2</sup>, and R.B. Clarkson<sup>2</sup>, <sup>1</sup>Institut de Chimie Minérale et Analytique, Université de Lausanne, Lausanne Switzerland, <sup>2</sup>Illinois EPR Research Center, University of Illinois, Urbana, IL USA

In a previous paper [1], we reported the first LODEPR measurements of fast  $T_{1e}$  values in aqueous solutions of two  $Gd^{3+}$  chelates, and we included predicted values for these relaxation times, based on zero field splitting (ZFS) parameters derived from multi-frequency EPR data on the two systems. The model used in that analysis was derived from the original work of Hudson and Lewis, and did not explicitly consider the static and dynamic parts of the ZFS. A more comprehensive model for relaxation in these  $S=7/2$  systems recently has been published. Here, we re-examine the multi-frequency data in light of this new model, re-calculate the ZFS parameters, and calculate new predictions for  $T_{1e}$ , which much more closely agree with experimental values. Both the importance of the new model and the validity of the LODEPR values are strengthened.

[1] "Direct Measurement of Fast Electron Spin-Lattice Relaxation: Method and Application to Nitroxide Radical Solutions and  $Gd^{3+}$  Contrast Agents, V. A. Atsarkin, V. V. Demidov, G. A. Vasneva, B. M. Odintsov, R. L. Belford, and R. B. Clarkson, *J. Phys. Chem.*



**EPR Symposia Poster Session**

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- 36. Transient-EPR of Fullerene C<sub>60</sub> Bisadducts: a Comparison Between X-band and High-field Data.** Marco Bortolus; Johan Van Tol, Florida State University, National High Magnetic Field Laboratory, Center for Interdisciplinary Magnetic Resonance, Tallahassee, FL 32310; Anna Lisa Maniero, Università degli Studi di Padova, Dipartimento di Chimica Fisica A. Miolati, Padova, Italy.

A series of Fullerene C<sub>60</sub> bisadducts with bis(ethoxycarbonyl)methylene has been studied at very high frequency by time-resolved EPR spectroscopy. Available data at X-band show that the EPR spectra of the photo-excited triplet states are remarkably distinct for different bisadducts<sup>1</sup>; at higher frequency (up to 240GHz) the resolution between the various adducts is further improved. EPR spectroscopy can thus identify the individual compounds and distinguish the various components in mixtures. The simulation of the high-frequency spectra conveys all of the information available at X-band, that is the Zero-Field Splitting principal values and the population of the zero-field triplet sublevels accounting for spin polarization; additionally the g anisotropy is well resolved. The fit of high-frequency data provides the g tensor principal values and establishes the relative orientation of the Zero-Field Splitting tensor with respect to the g tensor; this information allows for the study of the effect of the substituent position on the symmetry relationship between g- and zero-field splitting tensors.

[1] Pasimeni et al., J. Am. Chem. Soc. 1997, 119, 12896-12901.

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- 37. Multiquantum EPR of Arrestin K267C-MT SL at 35 GHz.** Theodore G. Camenisch<sup>1</sup>, Candice Klug<sup>1</sup>, Joseph Ratke<sup>1</sup>, Wayne Hubbell<sup>2</sup>, James S. Hyde<sup>1</sup>, <sup>1</sup>Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226; <sup>2</sup>Jules Stein Eye Institute, UCLA, Los Angeles, CA 90095-7008.

Three and five quantum absorption and dispersion multiquantum (MQ) spectra of spin-labeled arrestin have been obtained at Q-band (35 GHz). Spectra were obtained at room temperature on non-degassed samples as a function of microwave power. The separation of irradiating microwave frequencies,  $\Delta f$ , was 10 kHz. A newly-designed multiquantum Q-band EPR bridge was utilized, operating in a superheterodyne detection mode. The sample volume was 30 nl using a 3 loop—2 gap resonator. Most spectra were obtained at 300 $\mu$ M concentration in single, two-minute scans with 0.2 s time constant. The signal-to-noise ratio (SNR) was of the order of 100:1 under optimum conditions. Some spectra were obtained at 30  $\mu$ M, corresponding to one picomole of protein. Enhanced sensitivity to T<sub>1</sub> and T<sub>2</sub> was evident in the spectra. Linewidths varied considerably across the spectra, and the pure absorption displays were beneficial relative to field modulation methods for spectral characterization. The presence of two conformations with different relaxation times is evident, particularly in dispersion MQ, which is expected to exhibit enhanced sensitivity to T<sub>2</sub> relative to absorption. Qualitatively, one might characterize the MQ dispersion display as like a true derivative of the absorption with sensitivity to inflections in the pure absorption that are difficult to detect using finite difference or field modulation methods. Feasibility is established for site directed spin labeling (SDSL) studies of protein structure and dynamics using this new modality.

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- 38. 35 GHz Multiquantum Bridge.** Theodore G. Camenisch, Robert A. Strangeway, Joseph J. Ratke, James S. Hyde, Biophysics Research Institute, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, WI 53226.

A 35 GHz microwave bridge is described for use in EPR spectroscopy. The bridge can be used for multi-quantum (MQ) and conventional field modulation experiments. Planned modifications of the receiver will allow electron-electron double resonance (ELDOR) capability. The bridge has three translational arms capable of irradiating the sample with any combination of microwave frequencies within the bandwidth of the sample resonator. The receiver allows detection of an EPR signal in one of the following modes: homodyne, using an analog lock-in; superheterodyne at 1 GHz intermediate frequency (IF) using analog lock-in detection after down conversion; and time-locked digital detection of the IF using subsampling or oversampling techniques. Significant improvements in baseline signals of MQ spectra have been achieved through the use of an automatic frequency control (AFC) system locking to the sample resonator using the  $dF/2$  component present in the signal. Spectra of 10<sup>-4</sup> M TEMPO in aqueous solution demonstrating the performance of the bridge are shown, using a three-loop, two-gap loop gap resonator having an effective sample volume of 30 nl. Digitally detected data showing 3, 5, 7, 9, and 11 quantum spectra for both absorption and dispersion were obtained in one field sweep, decoding multiple channels from one IF signal path using an analog-to-digital converter (A/D).

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39. **Utilizing Magnetically Aligned Phospholipid Bilayers to Study Spin-labeled Integral Membrane Proteins in X-band Spin-labeled EPR Spectroscopy: Developing New and Expanding Current Techniques.** Thomas B. Cardon, Gary A. Lorigan, Miami University, Department of Chemistry and Biochemistry, Oxford, OH 45056

Our lab is developing new techniques for studying the orientation, structure, and function of integral membrane proteins in a model membrane system utilizing spin-labeled EPR spectroscopy. We have recently optimized the magnetic alignment of a model membrane system called bilayered micelles or bicelles in low magnetic field strengths used in X-band EPR studies. The magnetic alignment process of bicelle disks is sensitive to experimental conditions (i.e., phase(s), viscosity, magnetic field strength, presence of lanthanide ions, etc.) The orientation of the normal to the bilayer can be induced to be either parallel or perpendicular to the static magnetic field by adding, respectively, either  $Tm^{3+}$  or  $Dy^{3+}$ . The orientation of the bicelle disks was determined by incorporating spin-labeled probes into the bicelle disks (i.e.,  $3\beta$ - $5\alpha$ -cholestane or 5-doxyl stearic acid) and analyzing the orientation-dependent hyperfine splittings from the spin-labeled EPR spectra. Similarly, the orientation of spin-labeled integral membrane peptides (with respect to the bilayer normal) incorporated into these magnetically aligned bicelle disks could be determined by measuring the resultant anisotropic hyperfine splitting from the spin-labeled EPR spectra. This new technique can be coupled to existing spin-labeled EPR spectroscopic techniques to determine secondary structure, depth within the membrane, interactions with other peptide domains, changes in conformation, with possible enhancements in the resolution and extraction of structural information from spin-labeled EPR spectra. In the present study, we will discuss the optimization of the magnetic bicelle alignment process in the X-band EPR spectrometer and the factors that affect the thermodynamics and kinetics of the alignment process. Also, we will discuss recent results on studies of spin-labeled model integral membrane peptides.

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40. **Electron Spin Resonance Evidence for Isomorphous Substitution of Titanium Into Titanosilicate TiMCM-48 Mesoporous Materials.** Zhixiang Chang and Larry Kevan, Department of Chemistry, University of Houston, Houston, Texas 77204-5003

Hydrothermal synthesis of TiMCM-48 with varying Si/Ti ratios has been achieved. Comparative electron spin resonance (ESR) studies between synthesized TiMCM-48 and ion-exchanged Ti-AiMCM-48 show significant differences with respect to location and adsorbate interactions. Gamma-irradiation at 77 K of TiMCM-48 after a thermal activation treatment produces a strong ESR signal due to V centers and an axial signal with  $g_{||} = 1.976$  and  $g_{\perp} = 1.903$  for isolated trivalent titanium in framework tetrahedral sites. An axial ESR signal with reversed  $g$  values of  $g_{||} = 1.900 < g_{\perp} = 1.977$  typical of Ti(III) with distorted octahedral symmetry is observed after  $\gamma$ -irradiation at 77 K of ion-exchanged Ti-AiMCM-48. Both TiMCM-48 and Ti-AiMCM-48 also differ in their behavior towards various adsorbates. The Ti(III) species observed in TiMCM-48 and Ti-AiMCM-48 after adsorption of  $D_2O$ ,  $CO$ ,  $NH_3$  and  $CH_3OD$  change their ESR characteristics indicating significant interaction with adsorbates. The ESR characteristics of the Ti(III) species in TiMCM-48 after adsorption of these adsorbates are different from those of Ti(III) in Ti-AiMCM-48. The contrasting characteristics of Ti(III) in TiMCM-48 and Ti-AiMCM-48 suggest that the titanium ion is in a framework site in TiMCM-48.

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41. **A Reaction of Molecular Oxygen Dissolved in Water Occurring at a Carbon Char/water Interface.** R.B. Clarkson, P.J. Ceroke, and B.M. Odintsov, Department of Veterinary Clinical Medicine and the Illinois EPR Research Center, University of Illinois, Urbana, IL 61801.

In the course of developing new carbon chars for EPR oximetry, we have observed that at the surface of some freshly prepared chars, there is a reaction between oxygen dissolved in water and chars suspended in the water. We have studied this reaction by magnetic resonance methods (EPR, NMR), as well as by means of a Clark oxygen electrode and XPS, in work designed to characterize the chemical process that consumes dissolved oxygen. We will report on the rates of oxygen consumption on different chars that have been characterized by SAXS and XPS, and show the correlation between EPR line width changes and dissolved oxygen concentrations as measured by the Clark oxygen electrode.

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42. **High Frequency Electron Spin Resonance of Thin Film Manganites.** C.N. Colesniuc<sup>a</sup>, J. van Tol<sup>a</sup>, S. Zvyagin<sup>a</sup>, L.C. Brunel<sup>a</sup>, N. Mateeva<sup>b</sup>, K.H. Dahmen<sup>b</sup>, <sup>a</sup> Center For Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, Tallahassee, FL 32310, <sup>b</sup> Department of Chemistry and MARTECH, Florida State University, Tallahassee, FL 32306

The manganites of general formula  $RE_{1-x}AE_xMnO_3$  (RE = rare earth and AE = alkaline earth) have an uncommon behavior in which structural, transport and magnetic properties are very closely related. In order to further investigate the basic physical properties and also to identify potential applications of these materials we performed continuous wave (CW) and transient electron spin resonance (ESR) in thin films of

La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> and La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> on a broad range of temperatures, identifying the evolution of the spectra with the metal to insulator transitions. The ESR spectra of La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> in perpendicular geometry consist of several lines in the ferromagnetic state shifting to lower fields as the temperature is increased and also transforming into one broad line in the paramagnetic phase. The multiple peak structure is possibly determined by the magnetic inhomogeneities in the sample. The broad lines observed in the parallel geometry indicate the presence of an in-plane anisotropy. The spectra of La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> look very similar and exhibit the same temperature dependence. We also obtained the transient ESR spectra for these samples. The change in the ESR signal upon excitation with a laser pulse in the visible region of the spectrum shows different response times at different positions in the ESR spectrum, which may be associated with a differentiation in the rate of restoration of the ferromagnetic order in the sample.

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#### 43. **Electron Paramagnetic Resonance Spectral Investigations of Magnetically Aligned Lipid Bilayer Utilizing Two Different Types of Spin Probe.** Paresh C. Dave, Nisreen A. Nusair and Gary A. Lorigan\*, Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056.

Electron Paramagnetic resonance (EPR) spectroscopy of lipid soluble spin labels is widely used to study model biological membranes. Phospholipid bicelles are disk-shaped bilayered micelles formed by mixing appropriate ratios of a long-chain phospholipid with a short-chain phospholipid in an aqueous medium. In our present study, fatty acid spin label, n-Doxyl stearic acid (n-DSA) and phospholipid spin labels, 1-Palmitoyl-2-steroyl-(n-doxyl)-sn-glycero-3-phosphocholine (n-PSPC), labeled at different positions on their doxyl group (n= 5, 7, 12 and 16), were used to probe the structural characteristics and molecular motions of lipid bicelles. Addition of lanthanide ions changes the overall magnetic susceptibility anisotropy of the bicelles such that the bicelles flip with their normal either parallel or perpendicular to the magnetic field. The present study reveals that in the case of n-DSA and n-PSPC spin label, the bilayer normal is aligned parallel and perpendicular to the magnetic field in the presence of lanthanide ions having positive magnetic susceptibilities anisotropy (Tm<sup>3+</sup>) and negative susceptibilities anisotropy (Dy<sup>3+</sup>), respectively. A previous study indicates that the changes in the amount of cholesterol in lipid bilayers, orientated on glass plates, changes the degree of extension of fatty acid chains and amplitude of motion of the chains as a whole. The results obtained from two different spin probes incorporated in magnetically oriented lipid bilayers. The results obtained from the variation of cholesterol concentration in lipid bicelles will also be discussed.

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#### 44. **Overhauser Enhanced MRI Studies of Spin Probe Perfusion and Oxygenation of a Murine Tumor as a Function of Tumor Size and Core Temperature.** Sean English, Koen Reijnders, Sankaran Subramanian, John Cook, Anastasia Sowers, James B. Mitchell, and Murali C. Krishna, Radiation Biology Branch, Center for Cancer Research, NCI, NIH, Bethesda, MD 20892

Abnormal values of tissue  $pO_2$  are linked to many pathophysiological conditions (e.g., ischemic conditions, reperfusion injury, and oxygen toxicity). Approximately one third of human tumors evaluated for oxygen status have shown significant oxygen deficiency, and such deficiency increases the tumor's resistance to cancer treatment modalities such as radiation and chemotherapy. Additionally, hypoxic microenvironments in tumors are known to promote malignant progression, such as angiogenesis, elimination of p53 tumor suppressor activity, genetic instability, and metastases. A priori determination of tumor hypoxia could lead to the development of diagnostic and prognostic markers for malignant proliferation, discovery of novel therapeutic targets, and the development of new constructs for gene therapy applications in human cancer.

Overhauser enhanced Magnetic Resonance Imaging (OMRI) is a non-invasive method for *in vivo* imaging, which utilizes the principle of dynamic nuclear polarization and affords the measurement of tumor oxygenation using a low-field magnetic resonance scanner and a paramagnetic contrast agent. Anatomically based spin probe maps co-registered with calculated  $pO_2$  maps of tumors can be obtained by combining the morphological resolution of proton-based MRI, and the superior  $pO_2$  sensitivity of EPR. Furthermore, OMRI affords the opportunity to perform non-invasive and repeated  $pO_2$  measurements of the same animal with useful spatial (~1 mm) and temporal (2 min) resolution, making OMRI a powerful imaging modality for small animal, tumor physiology research. OMRI experiments have been performed on mice bearing a squamous cell carcinoma (SCC, ~1cm<sup>3</sup>) by intravenous administration of the contrast agent, Oxo63, is a highly derivatised tri-aryl-methyl (TAM) radical, at non-toxic doses in the range of 2–7 mmol/kg, either as a bolus or via continuous infusion. Spatially resolved  $pO_2$  images from OMRI experiments of tumor-bearing mice exhibited heterogeneous oxygenation profiles and revealed regions of hypoxia in tumors (<10 mm Hg). In addition, OMRI  $pO_2$  measurements agreed with those obtained by independent polarographic measurements using an Eppendorf  $pO_2$  electrode. For this poster, experiments considering the degree of spin probe perfusion and oxygen status of SCC tumors as a function of size will be presented. The effects of core and tumor temperatures as well as the mode of spin probe administration (bolus vs. continuous infusion) on the tumor oxygen status will be discussed.

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45. **EPR and DFT Studies of the One-electron Reduction Product of the -P=C=C-P- System.** Michel Geoffroy, Mostafa Chentit, Helena Sidorenkova, Sylvie Choua, University of Geneva, Department of Physical Chemistry, 1211 Geneva, Switzerland; Yves Ellinger, Université de Nice-Sophia Antipolis et Observatoire de la Côte d'Azur, 06108 Nice, France.

ArP=C=C=PAr (Ar = 2,4,6 tri *tert* butyl phenyl) was electrochemically reduced *in situ* in the EPR cavity at room temperature. The resulting EPR spectrum, similar to the spectrum obtained after reaction of this compound at the surface of a potassium mirror, exhibited hyperfine coupling (165 MHz) with two  $^{31}\text{P}$  nuclei. Additional splittings of 6 MHz were detected with the  $^{13}\text{C}$ -enriched compound. The spectrum was sensitive to temperature variations; at 110 K the frozen solution spectra could be measured, they indicated that the phosphorus coupling tensors have axial symmetry with a maximum dipolar coupling constant equal to 280 MHz. DFT calculations were carried out on two models: 1) the radical anion (HP=C=C=PH) $^-$  and 2) the diphosphabutadiene radical anion (HP=CH-CH=PH) $^-$ . Geometry optimizations showed that the structures of these two species are different: (HP=C=C=PH) $^-$  is quasi-linear whereas (HP=CH-CH=PH) $^-$  has a planar arrangement governed by the geometry of the  $\text{sp}^2$  carbons. The calculated  $^{31}\text{P}$  and  $^{13}\text{C}$  coupling constants are similar for these two radical anions and both species are consistent with the experimental spectrum. Therefore, they could not lead to a decisive identification of the reduction product of ArP=C=C=PAr. However, the quasi reversibility of the electrochemical reduction, together with the absence of proton couplings on the EPR spectrum are in favor of the formation of the (ArP=C=C=PAr) $^-$  radical anion. Supported by the Swiss National Science Foundation.

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46. **Xsophe, a Computer Simulation Software Suite (V 1.1) and its Application to the Analysis of EPR Spectra from the Molybdoenzyme Dimethylsulfide Dehydrogenase.** Graeme R. Hanson,<sup>a</sup> Christopher Noble,<sup>a</sup> Kevin. E. Gates,<sup>b</sup> Kevin Burrage,<sup>b</sup> <sup>a</sup>Centre for Magnetic Resonance and <sup>a</sup>Department of Mathematics, The University of Queensland, St. Lucia, Queensland, Australia, 4072.

The XSophe computer simulation software suite consisting of a daemon, the XSophe interface and the computational program Sophe is a state of the art package for the simulation of electron paramagnetic resonance spectra. The XSophe software suite has been used to simulate multifrequency EPR spectra (200 MHz to 6 00 GHz) from isolated spin systems ( $S \gg \frac{1}{2}$ ) and coupled centres ( $S_i, S_j \gg \frac{1}{2}, i, j=1, \dots, N$ ). Enhancements to the XSophe computer simulation (v 1.1) will be presented, including: (i) a generalised treatment of distributions of orientational parameters, termed the mosaic misorientation linewidth model and a faster more efficient algorithm for the calculation of resonant field positions and transition probabilities, (ii) inclusion of energy level diagrams, transition surfaces and transition roadmaps, (iii) a rewrite of the Sophe daemons to substantially improve security and a number of bug fixes. The installation routines have been improved enabling the user the choice of Linux distribution (Mandrake, RedHat or SuSe). For complex systems the parallelisation enables the simulation of these systems on a parallel computer and the optimisation algorithms in the suite provide the experimentalist with the possibility of finding the spin Hamiltonian parameters in a systematic manner rather than a trial-and-error process. The application of the XSophe software to the analysis of CW- and pulsed-EPR spectra of the [Fe-S] clusters and the Mo(V) active site in dimethylsulfide dehydrogenase will be also presented. The results from these studies provides important new insights into the structural characterization of these redo centres.

*Griffin, M.; Muss, A.; Noble, C.; Wang, D.; Eldership, C.; Gates, K.E.; Burrage, K.; Hanson, G.R. "XSophe, a Computer Simulation Software Suite for the Analysis of Electron Paramagnetic Resonance Spectra", 1999, Mol. Physic. Rep., 26, 60-84.*

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48. **Corrin Nitrogens and Remote Dimethylbenzimidazole Nitrogen Interactions in Cob(II)alamin Studied with HYSORE at X- and Q-band.** Jeffrey Harmer<sup>1</sup>, Sabine Van Doorslaer<sup>2</sup>, Igor Gromov<sup>1</sup> and Arthur Schweiger<sup>1</sup>. <sup>1</sup>Physical Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland; <sup>2</sup>Spectroscopy in Biophysics and Catalysis (SIBAC Laboratory), University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium.

A continuous wave and pulse electron paramagnetic resonance study of the base-on form of cob(II)alamin diluted in hydroxocob(III)alamin powder is presented <sup>1</sup>. HYSORE spectroscopy at X- and Q-band was used to study the weakly coupled corrin nitrogens and the remote nitrogen of the axial dimethylbenzimidazole ligand. The accuracy of the parameters is greatly enhanced by using two mw frequencies since this overcomes many ambiguities from the analysis of data employing a single mw frequency. At Q-band the spectral interpretation is greatly simplified since the number of combination peaks is significantly decreased. At X-band the combination peaks between different corrin nitrogens and between a corrin nitrogen and the remote nitrogen make spectral interpretation very demanding and often ambiguous. Many combination peaks are observed at X-band because the hyperfine interactions are close to the exact cancellation regime, which causes strong mixing. Simulations of the spectra measured at different field positions enabled the following parameters to be determined; for the corrin nitrogens the hyperfine principal values are  $A_1=-4.5$  MHz,  $A_2=-3.4$  MHz and  $A_3=(-2.2$  to  $-2.5)$  MHz with Euler angles  $[\alpha, \beta, \gamma]=[n90, 25, 0]^\circ$  and the nuclear quadrupole parameters are  $e^2qQ/h=1.75$  MHz and  $\eta=0.95$  with Euler angles  $[\alpha, \beta, \gamma]=[90+n90, 90, 12.5]^\circ$  where  $n=0, 1, 2, 3$ . The remote nitrogen of the dimethylbenzimidazole ligand has  $A_1=1.75$  MHz,  $A_2=1.75$  MHz and  $A_3=2.10$  MHz with Euler angles  $[\alpha, \beta, \gamma]=[-45, -10, 0]^\circ$  and  $e^2qQ/h=-3.3$  MHz and  $\eta=0.1$  with Euler angles  $[\alpha, \beta, \gamma]=[45, 90, 67]^\circ$ .

1. Harmer, J.; Van Doorslaer, S; Gromov, I.; Schweiger, A.; Chem. Phys. Lett. 2002 (in press).



### EPR Symposia Poster Session

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49. **New Models and Methods for the Analysis of Dipolar Coupling Between Spin Labels.** Eric J. Hustedt, Vanderbilt University, Department of Molecular Physiology and Biophysics, Nashville, TN 37209.

Models are being developed which will account for orientational disorder in the simulation of the CW-EPR spectra of dipolar coupled nitroxides. These models require the averaging over Euler angles which determine orientation of nitroxide 2, the interelectron vector, and the magnetic field, all relative to nitroxide 1. Difficulties encountered in simulations averaged over all three sets of Euler angles have motivated an examination of different methods for performing these calculations in a computationally efficient and numerically robust manner. Currently, the best method appears to be averaging over a discrete set of points which form a spiral pattern on the surface of a sphere. This approach has been used to analyze data from several 4K peptides doubly labeled with pyrroline and pyrrolidine based methanethiosulfonate spin labels. The same peptides have been doubly labeled with MTSSL and with the saturated version of MTSSL using either a racemic mixture of the two possible stereoisomers or with the individual racemates. Since these labels used differ only in the presence or lack of two hydrogen atoms and in the stereochemistry at the chiral center of the saturated version of MTSSL, they provide an excellent basis for determining how the geometry and flexibility of the nitroxide label will determine the resulting spectra of the dipolar coupled nitroxides. These spectra have been analyzed to determine how the subtle changes in the linkage effect the interspin orientation and distance distributions determined from analysis of the EPR spectra. Supported by NIH GM60538.

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50. **Radical Anions in Silica Zeolites.** Andrew S. Ichimura, Department of Chemistry and Biochemistry, San Francisco State University, San Francisco, CA 94132

Alkali metal doped pure silica zeolites (M@SZ; M=Na-Cs) are a novel class of solid state reducing agents that have high reducing power combined with the robust and size-shape selective lattice of the molecular sieve. Preliminary experiments show that M@SZ effectively reduce electron acceptors, such as p-benzoquinone, to the corresponding radical anion. EPR measurements clearly demonstrate the presence of the p-benzoquinone radical anion, a result that is supported by reflectance UV-vis-NIR spectroscopy. The reducing agent was prepared by adding Cs metal to the silica zeolite, ITQ-4, from the gas phase. ITQ-4 has one-dimensional channels 7 Å in diameter that run parallel to the c-axis. Electron acceptors absorbed by Cs@ITQ-4 from the gas phase are subsequently reduced to the anionic products. The initial substrates in this work are simple aldehydes and ketones because the reduction products and behavior under homogeneous conditions are well known. EPR and optical spectra of the radical anions in silica zeolites will be compared to solution spectra. In addition, the effects of metal concentration and metal to substrate ratio on the product outcome will be presented. The reduced products, ion-pairs, are indefinitely stable in the silica lattice at room temperature under an inert atmosphere or vacuum. M@SZ present the opportunity to study the reactive intermediates and final products that result from solid state reduction in zeolite molecular sieves and may ultimately lead to novel synthetic methodologies. The fundamental physical properties of the metal doped silica will also be reviewed.

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51. **EPR Spectroscopy Studies on the Structural Transition of Nitrosyl Hemoglobin in the Arterial-venous Cycle of DEANO-treated Rats.** Adrian R. Jaszewski, Yang C. Fann, Yeong R. Chen, Jean Corbett, and Ronald P. Mason, NIEHS, Research Triangle Park, NC 27709

Hemoglobin exists in two alternative quaternary structures: low-affinity tense state (T) and high-affinity relaxed state (R). The three-line hyperfine structure observed in the EPR spectrum of  $\alpha$ -NO hemoglobin in the T state is associated with pentacoordinate heme. In the R state of HbNO hexacoordinate heme shows no three-line hyperfine structure. In the present in vivo studies a dynamic cycle is observed in which  $\alpha$ -nitrosylated hemoglobin is in the R state in arterial blood of rats treated with 25  $\mu$ M of 2-(N,N-diethylamino)-diazene-2-oxide (DEANO) and converts to the T state during arterial-venous transit. A detailed analysis shows that different EPR spectra recorded for  $\alpha$ -nitrosyl hemoglobin in arterial and venous blood at 77K originate only from a different ratio between 5- and 6-coordinated heme without any change in the concentration of HbNO. In venous blood the five- $\leftrightarrow$ six-coordination equilibrium of the  $\alpha$ -nitrosyl heme is shifted in favor of the 5-coordinate state (55% venous versus 20% arterial).

### EPR Symposia Poster Session

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52. **A Simple and Efficient Method for Measuring the Spin Concentration of Anthracite Coals and Soots.** Yi Jin Jiang, Mark S. Solum, and Ronald J. Pugmire, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA.

The measurement of the unpaired electron spin concentrations of anthracite coals and soots were carried out on a Bruker EMX ESR spectrometer utilizing a microwave cavity 4103 TM operating at 9.75 GHz. A series of standard samples of BDPA (Aldrich catalogue 15256-0) were used for the calibration of spin concentration measurements. Since the ESR signal is proportional to the Q value of the cavity all experiments were performed at a constant cavity Q value (the operational Q value of the cavity is about 12500). Approximate sample volume and position were maintained inside the cavity. Samples exhibiting high conductivity that decreased the Q value of the cavity were diluted in silica gel (Aldrich catalogue 28859-4) to restore the original cavity Q value. All the samples studied were treated under vacuum at 100 mTorr for 48 hours in order to exclude the effects of oxygen on the ESR spectra. The experiments were carried out at room temperature. This experimental procedure was used to estimate the amount of graphite-like structure in a wide range of anthracite coals and soot samples. The results obtained will be presented and discussed.

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53. **Paradoxical Effects of Metalloporphyrins on Doxorubicin-induced Apoptosis: Scavenging of Reactive Oxygen Species Versus Induction of Antiapoptotic Proteins.** Joy Joseph, Eugene Konorev, Srigriridhar Kotamraju, Hongtao Zhao, Shasi Kalivendi, and B. Kalyanaraman, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226

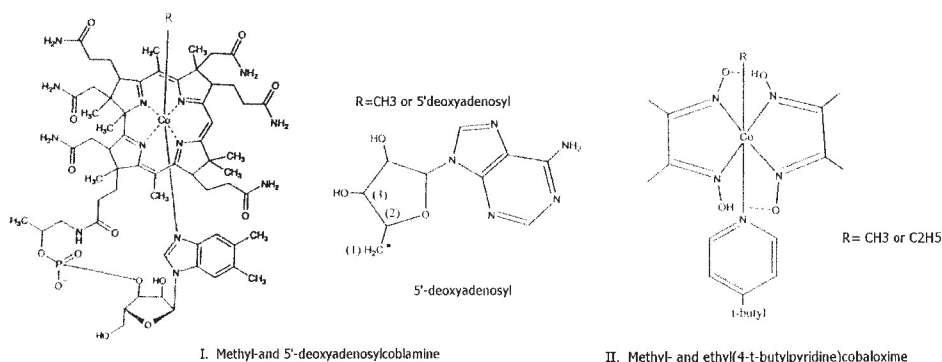
The cytoprotective effects of redox-active metalloporphyrins (e.g., FeTBAP and MnTBAP) were generally attributed to their ability to scavenge reactive oxygen and nitrogen species. In this study, we evaluated the pro- and antiapoptotic potentials of different metalloporphyrins containing iron, cobalt, zinc, and manganese in adult rat cardiomyocytes exposed to doxorubicin (DOX), an anticancer drug that forms superoxide and hydrogen peroxide via redox-cycling of DOX semiquinone in the presence of molecular oxygen. We used electron spin resonance-spin trapping and cytochrome *c* reduction to assess the scavenging of superoxide anion by metalloporphyrins. Superoxide anion was effectively scavenged by FeTBAP and MnTBAP but not by CoTBAP and ZnTBAP. FeTBAP efficiently scavenged H<sub>2</sub>O<sub>2</sub>. Both CoTBAP and FeTBAP inhibited DOX-induced cardiomyocyte apoptosis. These findings implicate that mechanisms other than oxy-radical scavenging may account for their antiapoptotic property. In addition, CoTBAP and FeTBAP induced heme oxygenase-1 more potently than did MnTBAP and ZnTBAP. We propose that metalloporphyrins can inhibit apoptosis either by inducing antiapoptotic protein signaling or by scavenging reactive oxygen species.

#### EPR Symposia Poster Session

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54. **FT-EPR Study of Alkyl Radicals Photogenerated from Cobalamines and Cobaloximes.** Alejandro P. Bussandri, Cecilia W. Kiarie, Debora M. Martino, Hans van Willigen, Chemistry Department, University of Massachusetts at Boston, 100 Morrissey Blvd, Boston, MA 02125

Fourier Transform Electron Paramagnetic Resonance (FT-EPR) has been used to study free radicals generated by photo-induced homolytic cleavage of the Co-C bond in methyl and adenosyl cobalamines and methyl and ethyl cobaloximes. Spectra of the methyl and adenosyl radicals generated by photo excitation of cobalamines in aqueous solutions show Chemically Induced Dynamic Electron Polarization (CIDEP) produced in precursor radical pairs. This effect can be accounted for in terms of bond cleavage via the cobalamine singlet excited state. The spectrum of CH<sub>3</sub><sup>•</sup> produced by photo-excitation of methyl-cobalamine is wavelength dependent. This confirms earlier observations that bond cleavage can occur via two reaction channels involving distinct transient intermediates. CIDEP patterns in the FT-EPR spectra of methyl and ethyl radicals generated by the photo-excitation of cobaloximes show a striking dependence on solvent (toluene, ethanol, pyridine, water) and, in aqueous solution, on pH. The effect is attributed tentatively to shifts in energy levels of the cobalt complexes induced by changes in axial coordination. Consequently, the spin polarization pattern may be dominated by a contribution from a singlet excited state reaction channel in some solvents, and by a triplet excited state channel in others.



### EPR Symposia Poster Session

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55. **Pulsed ENDOR and ELDOR at 94 GHz.** A. Kamlowski, A. Tavernier, D. Loehr, A. Wolff, P. Höfer, and D. Schmalbein, EPR Division, Bruker BioSpin GmbH, Silberstreifen, 76287 Rheinstetten, Germany

With the increasing availability of high-frequency CW- and FT-EPR instrumentation, research demands were directed to extending the high-field advantages to double resonance techniques. With several new developments in hardware and software we have extended the application range of the E680 in this direction.

These developments include a new W-band probehead with optimized performance for both EPR and ENDOR as well as a new FT-EPR Intermediate Frequency (IF) microwave bridge with two fully remote controlled microwave sources. The former development was based on our TeraFlex W-band probehead which was extended to Pulsed ENDOR operation. In addition, the tuning and matching mechanics have been modified for improved low-temperature operation. Key features of this probehead and Pulsed ENDOR experiments will be presented. Moreover, to the best of our knowledge the first W-band ELDOR experiments will be presented.

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56. **Identification of Paramagnetic Defects at the Hafnium Oxide/Silicon Interface.** Andrew Y. Kang, and Patrick M. Lenahan, The Pennsylvania State University, 212 Earth and Engineering Science Building, University Park, PA 16802; John F. Conley, Jr., Sharp Labs of America, 5700 NW Pacific Rim Blvd., Camas, WA, 98607

Moore's Law has been maintained for the last thirty years by aggressively downscaling metal-oxide-semiconductor (MOS) devices. However, further scaling is limited by a fundamental physical limit of the SiO<sub>2</sub>/Si system. At present thickness of 1.5nm, further scaling is virtually impossible because silicon conduction electrons tunnel through the ultra-thin gate insulating dielectric, leading to immense heat generation. A replacement dielectric material with a dielectric constant larger than that of SiO<sub>2</sub> must be found if Moore's Law is to be maintained beyond 2005. A higher dielectric constant material enables the use of a physically thicker insulating layer in MOS devices. In this study we employ electron spin resonance (ESR) to identify trapping centers in the most promising replacement: HfO<sub>2</sub>/Si. HfO<sub>2</sub> is a so-called "high-k" material with a dielectric constant significantly higher than SiO<sub>2</sub>. We report ESR results on paramagnetic defects at the HfO<sub>2</sub>/Si interface that will almost certainly limit the performance of devices based upon this system. Work performed at Penn State was supported by NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

### EPR Symposia Poster Session

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57. **In Vivo ESR Measurement of the Mouse Administered Triarylmethyl Radical.** Shunsuke Kazama, School of Pharmaceutical Sciences, Hisashi Yoshioka, Institute for Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka, Japan; Hisayuki Tanizawa, Life Science Department, Hiroshima Jogakuin University, 4-13-1 Ushita-Higashi, Japan; Mihoko Kumakura, Tomohiro Ito and Tateaki Ogata, Department of Chemistry and Chemical Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Japan.

Over the last several years, we have been studying in vivo ESR of the radical distribution in the mouse using polysaccharide spin probe TEMPO-DX, which is a large molecule (40-100 kDa) with low toxicity, and works as a long-life spin tracer in vivo. However, the TEMPO moiety is reduced in the liver and kidneys, thereby leading to the slow disappearance of the ESR signal.

Another long-life spin probe is the water-soluble and chemically stable triarylmethyl radical (TAM), developed by Nycomed Co. (Sweden).<sup>1</sup> This spin probe is very stable against reducing agents. It is not reduced by ascorbic acid in vitro. The ESR spectrum of an aqueous solution of TAM shows a singlet with a width of 0.02 mT. TAM is eliminated rapidly in the kidneys by excretion since it is a small molecule (M.W. of 1.3 kDa). Even if TAM is rapidly eliminated from the mouse body, we could expect highly resolved images of organs from the very sharp ESR spectrum.

In this report, we demonstrate the distribution and elimination of TAM by measuring the time dependence of the ESR signal in mouse with normal/nephritic kidney. The radical disappearance was measured as 1 min half-life at the liver surface at the beginning after the administration, however, 20-30% of the initial dose still remained 8 min after the initial rapid elimination. The remaining TAM disappeared slowly. The ESR-CT image of the mouse with nephritic kidney containing the distributed TAM is compared with that of normal mouse.

[1] Patent [International Application published under PCT (1997), International Publication Number: WO 97/09633 ]

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58. **Multifrequency EPR Study of Fe-MCM-41 Molecular Sieves with Incorporated Carotenoids.** T. A. Konovalova, L. D. Kispert, University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487; J. van Tol, L.-C. Brunel, Florida State University, NHMFL, Tallahassee, FL 32310

Multifrequency EPR spectroscopy was applied to study Fe(III)-MCM-41 mesoporous molecular sieves with incorporated carotenoids. Comparison of the X-band and 94-287 GHz EPR spectra indicates that Fe<sup>3+</sup> ions in Fe(III)-MCM-41 exist in their high-spin state ( $S = 5/2$ ). The X-band  $g = 4.3$  with a shoulder at  $g = 9.0$ , which is characteristic of high-spin Fe(III), is not observed at 94 GHz and higher frequencies because the condition  $g\beta B_0 \ll D$  is no longer valid at high frequencies. The  $g = 2.0$  signal broadened at 9 GHz was well resolved at 94 – 193 GHz. The signal with  $g = 2.1$  is attributed to extraframework Fe(III) cations on the outer surface of the pore. The peak with  $g = 2.4$  could be assigned to aggregated Fe(III). Assignment of other paramagnetic species detected at higher frequencies is discussed. Incorporation of carotenoids into Fe-MCM-41 results in carotenoid radical cation formation. 9-94 GHz EPR measurements demonstrated that extraframework Fe(III) are mostly responsible for carotenoid oxidation in molecular sieves. ENDOR measurements revealed the orientation of 7'-apo-7',7'-dicyano- $\beta$ -carotene and canthaxanthin inside Fe-MCM-41.

*Supported by DOE Grant DE-FG02-86ER13465.*

#### **EPR Symposia Poster Session**

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59. **Quantitative Analyses of Mn<sup>2+</sup> Cations Dispersed in Adsorbents, Catalysts and Clays by Electron Paramagnetic Resonance Spectroscopy.** Krystyna Dyrek, Krzysztof Kruczała, Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland; Joanna Babińska, University of Mining and Metallurgy, Faculty of Geology, Geophysics and Environmental Protection, Mickiewicz Avenue 30, 30-059 Krakow, Poland; Ewa Bidzińska, Regional Laboratory of Physico-Chemical Analyses and Structural Research, Ingardena 3, 30-060 Kraków, Poland.

Electron paramagnetic resonance is a suitable method for investigation of manganese cations dispersed in various matrices. EPR spectroscopy provides information about the interaction of paramagnetic centers with neighboring ions, symmetry of the complexes, the type of chemical bonding etc. Moreover, quantitative EPR measurements are important and have become more common. The most preferred way to determine the spin concentration is based on comparing the area under the EPR spectrum of investigated sample with that of the standard of known spin concentration:  $N_x = N_{st} * I_x / I_{st}$ . A series of EPR standards were developed in our laboratory (K. Dyrek, A. Madej, E. Mazur, A. Rokosz, *Colloids Surfaces* 45 (1990) 135; K. Dyrek, A. Rokosz, A. Madej, *Appl. Magn. Reson.* 6 (1994) 309.). In this study, quantitative determination of the amount of Mn in investigated systems was performed using MnO-MgO standards calcined at 400 °C in air. Spin concentrations were measured for: (1) catalysts containing Mn and Co oxides dispersed on: the surface of proton free mesoporous silica (SBA15, ref.) a material of enhanced stability, (2) clays containing adsorbed Mn compounds, used as adsorbents, and (3) montmorillonites pillared by hydroxy complexes of Al<sup>3+</sup> and doped with Mn<sup>2+</sup>. This study shows that the spin concentrations determined by EPR are smaller than that obtained by chemical analyses. The results indicate presence of antiferromagnetic Mn-Mn interactions and/or manganese cations in oxidation state other than 2+.

#### **EPR Symposia Poster Session**

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## **EPR • Wednesday Oral Sessions**

60. **Free Radical Production from Peroxynitrite: EPR Studies in Test Tubes and Cells.** Ohara Augusto, Instituto de Química, Universidade de São Paulo, CxP. 26077, 05513-970 São Paulo, Brazil

Peroxynitrite (PN), which is formed by the fast reaction between nitric oxide and superoxide anion, has been receiving increasing attention as a mediator of human diseases and as a toxin against microorganisms. An initial controversy about the possibility of free radical production from peroxynitrite has been resolved and presently these species are considered to participate in the biological effects of the oxidant. Fast-flow EPR and EPR spin trapping studies by our group have contributed to characterize which of the peroxynitrite-derived radicals are likely to be relevant in biological environments. In most of them, the carbonate radical anion and nitrogen dioxide should play major roles due to the presence of high levels of the bicarbonate/carbon dioxide pair. At acid pHs, however, the hydroxyl radical may also become important. In test tubes, we also demonstrated that these peroxynitrite-derived radicals oxidize low and high molecular weight biomolecules to produce their corresponding radicals such as thiyl, sulfinyl, disulfide radical anion, protein-thiyl and protein-tyrosyl. Next, we examined whether peroxynitrite produces free radicals in cells. It was possible to demonstrate intracellular radical production upon peroxynitrite addition to a macrophage cell line



(J774) and to human erythrocytes. The glutathionyl radical was produced in both cell types. In macrophages, protein-tyrosyl radicals were also detected and, in erythrocytes, both hemoglobin-tyrosyl and hemoglobin-thiyl were demonstrated. Finally, we have been examining the relevance of peroxynitrite-derived radicals *in vivo* by using a murine model of a protozoan infection. These studies indicated that peroxynitrite-derived radicals are important in macrophage microbicidal mechanisms. Overall, our studies suggest that nitrogen dioxide and carbonate radical anion are likely to become increasingly recognized as important biological mediators.

#### **EPR Symposia Oral Session**

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- 61. High-resolution High Field EPR to Study Self-assembly of Phospholipids in Nanoscale Confinement.** [Alex I. Smirnov](#) and Matthew S. Lewis, <sup>1</sup>Chemistry Department, North Carolina State University, Raleigh, NC 27606-8204; Oleg G. Poluektov, Chemistry Division, Argonne National Laboratory, Argonne, IL 60431.

Spin-labeling High Field (95 GHz) EPR was used to monitor self-assembly of phospholipids in nanopores formed in Anodic Aluminum Oxide (AAO) films. AAO membranes are of special interest because they possess an aligned through-film porous structure that is suitable for designing vectorial transport assemblies. The pores in AAO films are macroscopically homogeneous and hexagonally packed. By utilizing a series of membrane EPR probes we have observed that under certain conditions the phospholipids form cylindrical assemblies inside the AAO pores. The use of high field (HF) EPR at 95 GHz enhances the information on structural organization of phospholipids obtained by spin-labeling methods. At magnetic fields of 3.4 T (95 GHz, W-band) and above, the rhombic Zeeman term provides new data on dynamics of nitroxide spin labels and full angular resolution that are inaccessible by means of traditional EPR. By using just 0.5x2.0x0.06 mm<sup>3</sup> fragments of AAO membranes containing phospholipids doped with nitroxide membrane probes at 1 mol% level, we were able to achieve a good signal-to-noise ratio spectra at both room and cryogenic temperatures. This makes HF EPR an exceptional tool to study the self-assembly of phospholipids and the effects of nanoscale confinement. Additional information on cylindrical phospholipid assemblies was obtained using oxygen accessibility method. Supported by North Carolina Biotechnology Center 2001-ARG-0033 (Raleigh). Work at ANL was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract W-31-109-Eng-38.

#### **EPR Symposia Oral Session**

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- 62. Time Domain EPR Imaging Studies of Septic-shock Induced Changes in Tissue Oxygen Status in Mice.** [Koen Reijnders](#)<sup>1</sup>,<sup>2</sup>, Gooitzen M. van Dam<sup>2</sup>, Sean English<sup>1</sup>, Nallathanmy Devasahayam<sup>1</sup>, Sankaran Subramanian<sup>1</sup>, James B. Mitchell<sup>1</sup>, Murali C. Krishna<sup>1</sup>, <sup>1</sup>Radiation Biology Branch, National Cancer Institute, Bethesda, MD 20892, <sup>2</sup>Department of Surgery, University Hospital, Groningen, The Netherlands

Shock and sepsis claim thousands of lives each year, despite over two decades of efforts to develop clinically effective agents for their treatment as well as diagnostic tools for a timely diagnosis. Sepsis is said to be severe when it is associated with organ dysfunction, caused by hypo perfusion or hypotension, which leads to hypoxia and cell dysfunction and (if prolonged) cell death. Currently there is no reliable diagnostic tool to identify septic patients in an early stage of the disease rather than monitoring cardiac output, peripheral vascular resistance, blood pressure, urine output, oxygen tension and daily hematological, immunologic and blood chemistry tests. Time-Domain EPR Imaging is a convenient tool to provide spatially resolved quantitative oxygen maps in live animals in a non-invasive manner. Recently Fourier imaging methods have been implemented in Time-domain EPR in the Radio frequency range (~ 300 MHz) using the Single-Point (constant-time) mode of data acquisition. In this presentation, Time-Domain EPR imaging studies of phantom objects containing narrow-lined paramagnetic spin probes (trityl radicals) and mice infused with the spin probes will be presented using the Single-Point Imaging (SPI) methods. Details related to the spatial and temporal resolution will be discussed. Results comparing the EPR images obtained with SPI vs. Filtered Back-projection (FBP) modalities of image data acquisition will be presented. Strategies to obtain spatially resolved spectral information such as the line widths will be discussed and results with phantoms presented to validate the oxymetric imaging capabilities with SPI. Oxygen maps from tumor bearing mice while breathing air and carbogen will be presented. Preliminary results on the changes in oxygen status in organs such as kidneys and liver in mice subject to lipopolysaccharide (LPS) -induced endotoxemia will be presented.

#### **EPR Symposia Oral Session**

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63. **Quantitative, Calibrated Oxygen Images of Tumors in Living Mice with EPR Imaging.** Martyna Elas<sup>1,3</sup>, Colin Mailer<sup>1</sup>, Benjamin B. Williams<sup>1</sup>, Adrian Parasca<sup>1</sup>, Eugene D. Barth<sup>1</sup>, Charles A. Pelizzari<sup>1</sup>, V. S. Subramanian<sup>1</sup>, Kazuhiro Ichikawa<sup>1,4</sup>, George A. Rinard<sup>2</sup>, Richard W. Quine<sup>2</sup>, Gareth R. Eaton<sup>2</sup>, Sandra S. Eaton<sup>2</sup>, Howard J. Halpern<sup>1</sup>, <sup>1</sup> University of Chicago, Chicago IL, <sup>2</sup> University of Denver, Denver CO <sup>3</sup> on leave from the Jagiellonian University, Cracow, Poland, <sup>4</sup> on leave from Kyushu University, Kyushu, Japan, from the Center for EPR Imaging *In Vivo* Physiology

Using 250 MHz EPR with continuous wave spectral/projection acquisition and stepped fixed gradients high spatial resolution (better than 1 mm)<sup>3</sup> spectral-spatial EPR images (spectroscopic images) have been obtained. The spin probe substrates were various trityl spin probes obtained from Nycomed Innovations, Malmo, SW. These spin probes sampled the extracellular fluid compartment and reported oxygen concentrations through the width of the trityl spectral line. The spectral resolution of 0.17 microtesla was obtained in the animals. This was verified with images of homogeneous solutions of substrate with concentrations similar to those in the animal obtained under conditions similar to those obtained from the animal tumor. The bridge was stabilized using coupling and frequency control to minimize spectral distortion. Full modeling of Zeeman modulation effects on lineshape enabled the use of high modulation fields which improved the signal to noise in the image without poisoning the spin packet linewidth information. Using inhomogeneous phantoms we verify both the spatial and the spectral resolution statements. Of interest is the fact that these hard edged phantoms probably underestimate resolution *in vivo*. Line distortion has been measured with the inhomogeneous phantoms. We have implemented relatively rapid scanning techniques to increase the number of projections in the same 10<sup>3</sup> s time required animal images. Since we can obtain projections with different numbers of otherwise identically obtained scans, signal to noise can be controlled and more time spent on the high gradient scans with less signal than the low gradient scans. We have found that a spectral spatial image requires no more than twice the acquisition time of a purely spectral image. With order of magnitude smaller hypoxic line widths, oxygen broadening of trityls is similar to that of nitroxides. This gives higher oxygen sensitivity. The trityl insensitivity to other fluid conditions allows a water calibration to yield oxygen partial pressure in living tissues. We will present progress in the synthesis of trityls. We show calibrated quantitative oxygen maps obtained in mouse tumors with the above stated resolution. Again we will compare these with BOLD subtraction MRI of the same tumors.

#### EPR Symposia Oral Session

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64. **Degradation of Heterophasic Propylene-ethylene Copolymers (HPEC) by ESR, ESR Imaging and FTIR.** K. Kruczala, B. Varghese, J. Bokria and S. Schlick, Department of Chemistry, University of Detroit Mercy, Detroit, Michigan 48219.

We present a study of the thermal degradation of two heterophasic propylene-ethylene copolymer (HPEC) samples containing 12 and 25 % wt ethylene (E), respectively, as an ethylene-propylene rubber (EPR) component. The polymers contained a hindered amine stabilizer (HAS). The formation of nitroxide radicals from HAS during heat treatment provided the contrast in the ESR imaging experiments. Additional details were obtained by spin probe ESR and FTIR. ESR spectra at 300 K of the thermally treated polymers indicated the presence of radicals in two environments differing in their dynamics: The fast component was assigned to nitroxides located in the rubber domains; and the slow component to nitroxides in amorphous regions where the local mobility is restricted due to the proximity to crystalline domains. The results from the spin probe study confirmed the conclusion that nitroxides located in amorphous domains are sensitive to the degree of crystallinity. The radical distribution was deduced from 1D ESRI and the variation of the ESR line shapes along the sample depth was determined from 2D spectral-spatial ESRI. The spatial variation of the chemical processes during aging was inferred from the imaging experiments.

*Supported by NSF-Polymers Program*

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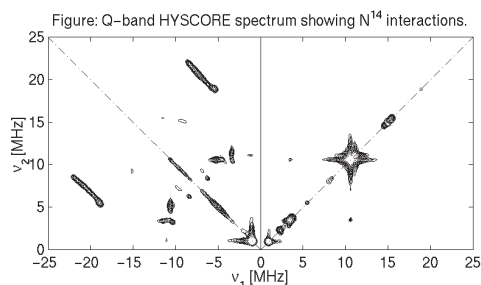
#### EPR Symposia Oral Session

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65. **Advantages of Multi-frequency ESEEM. Applications to Transition Metal Complexes at X-band and Q-band.** Jeffrey Harmer, Igor Gromov, and Arthur Schweiger. Physical Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland.

Electron spin echo envelope modulation (ESEEM) spectroscopy (e.g three-pulse ESEEM, HYSCORE) are powerful methods aimed at obtaining information on the hyperfine and nuclear quadrupole couplings in solids <sup>1</sup>. To date most applications of these techniques have been carried out at X-band, where the required conditions to obtain favorable echo-modulation depths are fulfilled. At higher frequencies (W-band, 95 GHz) the echo-modulation depth parameter *k* is usually very small and in most samples no information can be obtained. Q-band (35 GHz) however has many positive aspects; *k* is still in a useful range, the nuclear Zeeman interaction is increased by approximately a factor of 4 as compared to X-band which spreads the spectrum, cavities supporting large samples are possible (2.9 mm), and high microwave (mw) power is available <sup>2</sup>. As demonstrated in this contribution by a number of examples, there are often deep echo-modulations at Q-band and the information obtained is of great assistance in determining the magnetic interactions of nuclei. Significant sensitivity improvements can also be achieved by using matched

mw pulses to optimize the generation and transfer of coherence<sup>3</sup>. In many samples there is sufficient echo-modulation depth at both X- and Q-band to enable multi-frequency ESEEM spectroscopy to be carried out. In this contribution we present several examples where X- and Q-band ESEEM spectroscopy enable greater precision of the magnetic parameters to be determined, and an example where only at Q-band could interactions be detected from a nitrogen directly coordinated to a Ni complex (see Figure).



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### EPR Symposia Oral Session

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### 66. High Resolution Room Temperature EPR Spectra of S-state Ions in Liquids: What We Can Learn About Ion Environment.

Tatyana I. Smirnova and Alex I. Smirnov. Department of Chemistry, North Carolina State University, Raleigh, NC, 27695

Development of High Field (HF) EPR makes S-state ions Mn<sup>2+</sup> and Gd<sup>3+</sup> particularly attractive as spin probes because of exceptionally long relaxation times and high spectral resolution at the fields above 2 T. With an increase in magnetic field the EPR spectra of these ions become first-order, significantly narrower, and Lorentzian in shape. Moreover, the EPR of these ions could be observed in liquid aqueous solutions at concentrations down to 0.01 mM, thus, making many new biophysical experiments possible. Here we show that liquid solution spectra of either Gd<sup>3+</sup> or Mn<sup>2+</sup> arising from complexes residing in different environments (e.g., membrane and aqueous phases) could be resolved and independently analyzed. The high spectral resolution is also essential for double label experiments utilizing nitroxide-Gd<sup>3+</sup> ion pairs allowing simultaneous and independent analysis of both lines for interspin distances and local polarity effects. We will show that solution EPR experiments at high field allow to track changes in Mn(II)-protein coordination upon unfolding of protein. More recently, we directly observed magnetic interactions between Mn(II) ions and molecular oxygen in aqueous solutions from Mn(II) EPR line width broadening. We speculate that the magnitude of this oxygen effect is related to transient molecular surrounding of the ion. Those methods were further applied to study site-specific infections of paramagnetic metals with the bioenvironment. Support was provided by NSF 0075042 to T.S. W-band EPR resources were supported by NIH R01 01811.

### EPR Symposia Oral Session

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### 67. Absolute Rate Constants and Arrhenius Parameters for Ketyl-ketone Hydrogen Transfer Using Kinetic ESR: Investigations on the Question of a Concerted Proton-electron Transfer Transition State.

Wendy J. Shaw, Donald M. Camaioni, Tom Autrey, Bart Beinze, James A. Franz, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352.

Absolute rates and Arrhenius parameters for the novel radical-molecule hydrogen transfer from ketyl radical to ketones have been measured. Kinetic parameters were obtained for the reduction of benzaldehyde and 2-butanone with 2-hydroxy-2-propyl radical (HPR) using kinetic electron spin resonance spectroscopy (KESR). The Arrhenius expression for the transfer of hydrogen atom from HPR to benzaldehyde is  $\log(k/M^{-1}s^{-1}) = (7.65 \pm 0.24) - (3.31 \pm 0.65)/\theta$ ,  $\theta = 2.303RT$  kcal/mol, errors are  $2\sigma$ . The room temperature rate for this reaction was found to be  $1.43 \times 10^5 M^{-1}s^{-1}$ . The Arrhenius expression for hydrogen atom transfer from HPR to 2-butanone is  $\log(k/M^{-1}s^{-1}) = (6.13 \pm 0.85) - (5.38 \pm 1.2)/\theta$ , with a room temperature rate of  $1.90 \times 10^2 M^{-1}s^{-1}$ . Using *ab initio* calculations, we found that cyclic (*syn*) transition structures are stabilized relative to the corresponding acyclic *anti* structures by 5-11 kcal/mol. The trends observed experimentally are consistent with theoretical calculations, in agreement with a cyclic transition state involving concerted proton-electron transfer.

### EPR Symposia Oral Session

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68. **Heterogeneous Functionalization of PAMAM Starburst Dendrimers Investigated by Spin-labeling.** Eric Walter, Robert Usselman, Alex Boulet, Mary Cloninger, David Singel, Montana State University, Chemistry Department, Bozeman, MT, 59717

Surface functionalization of dendrimers with receptor ligands is an area of great interest, as dendrimers provide a platform for multi-ligand amplification of binding interactions. Although the synthesis of numerous heterogeneously surface-functionalized dendrimers has been reported, little information is available regarding the distribution of the functional groups on dendrimer surface – information of crucial importance for understanding binding interactions. This information can be obtained through EPR studies of nitroxide spin-labeled dendrimers. EPR spectra of nitroxide labeled PAMAM dendrimers of generation 0-6, entailing up to 256 label sites on the macromolecule, have been obtained, and the systematic variation of the dipolar broadening exhibited in the spectra as a function of the degree of loading examined. Dipolar broadening is quantified by deconvolution and reconvolution techniques. In our analysis, proper attention is given to the well-known “3/2 effect”. Our results, through computational modeling, enable us to measure the dendrimer size and reactive topology; it further gives insight into cooperative effects associated with the labeling of the dendrimer.

**EPR Symposia Oral Session**

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## EPR • Wednesday Poster Sessions

69. **Quantum Computing with Solid State Magnetic Resonance.** Patrick M. Lenahan, The Pennsylvania State University, University Park, PA 16802.

Recent publications suggest that “quantum” computing may have enormous advantages over the “classical” computers of the present day. The most promising quantum computing ideas involve either electron or nuclear spin. Although many proposals have been made, no practical quantum computer yet exists. Arguably, the greatest challenge in the construction of a spin-based quantum computer is developing a method to measure the response of very small numbers of spins in small devices through some reasonably straightforward electronic measurement of a current or voltage. This poster presentation will discuss an approach based upon spin dependent recombination, electron nuclear double resonance, and recent advances in very high field EPR.

**EPR Symposia Poster Session**

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70. **W-band EPR Spectroscopy of Fe-nitrosyl Human Hemoglobin.** Benjamin P. Luchsinger, Eric Walter, David J. Singel, Montana State University, Department of Chemistry & Biochemistry, Bozeman, MT 59717.

An investigation of the EPR spectra of  $[\text{Fe}(\text{II})\text{NO}]_4$  human hemoglobin at 94.9 GHz is reported. EPR spectra obtained over the temperature range 7K to 230K exhibit both axial and rhombic spectral components similar to those previously reported.<sup>1-3</sup> For certain spectral features, the W-band spectra show a notable increase in resolution over both X- and Q-band spectra. Detailed spectral simulation and target factor analysis is utilized in the study of the temperature dependence of the spectra. Our results unambiguously indicate the presents of at least three, resolved species at low temperature, and clarify the interplay between motion and chemical dynamics in this complex system.

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**EPR Symposia Poster Session**

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**71. A Radiation Chemical Study of DMPO Spin Adduct Stability. Environmental Effects on Spin Adduct Termination.**

Keith P. Madden, Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556-0579, U.S.A.; Hitoshi Taniguchi, Department of Veterinary Radiology, Faculty of Agriculture, Yamaguchi University, Yamaguchi 753-8515, Japan

Recent quantitative experiments (Madden and Taniguchi, *Free Radical Biol. Med.* 2001, **30**,1374) have shown that the apparent yield of spin adducts produced by the scavenging of radiolytically-produced radicals by DMPO can be greatly altered by rapid reactions with other spin adducts. The polar nature of DMPO and DMPO spin adducts suggests that changes in solvent polarity and pH will alter spin adduct decay kinetics as well. Here we present preliminary results on the influence of solvent environment on the decay kinetics of DMPO-OH spin adduct radicals in aqueous solution.

**EPR Symposia Poster Session**

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**72. What Is the Source of the Gamma-splitting in the EPR Spectrum of 2,2-dimethyl-5-hydroperoxy-1-pyrroldinyloxyl (DMPO-OOH)?**

Colin Mailer, University of Chicago, Dept. of Radiation and Cellular Oncology, 5841 South Maryland Ave., Chicago, IL 60637; Saba Mattar, Dept. of Chemistry, University of New Brunswick, Fredericton, New Brunswick, 3B 6E2 Canada, Gerald M. Rosen, University of Maryland, Dept. of Pharmaceutical Sciences, Baltimore, MD 21201; Howard J. Halpern, University of Chicago, Dept. of Radiation and Cellular Oncology, Chicago, IL 60637 from the Center for EPR Imaging In Vivo Physiology

Spin trapping consists of using a nitron or nitroso compound to “trap” an unstable free radical as a long-lived aminoxyl that can be characterized by EPR spectroscopy. The spin-trapped adduct exhibits hyperfine splitting constants that are dependent on the spin trap and the free radical. Such is the case with 2,2-dimethyl-5-hydroxy-1-pyrroldinyloxy (DMPO-OH) and 2,2-dimethyl-5-hydroperoxy-1-pyrroldinyloxy (DMPO-OOH) whose hyperfine splitting constants,  $A_N = 14.91$  G,  $A_H = 14.69$  G and  $A_N = 14.11$  G,  $A_{\beta H} = 11.28$  G and  $A_{\gamma H} = 1.22$  G, respectively, have been used to demonstrate the generation of HO• and O2•-. However, to date, the source of the  $A_{\gamma H}$  hyperfine splitting in DMPO-OOH is not known. We consider three possible explanations to account for the unique EPR spectrum of DMPO-OOH. The first is that the  $\gamma$ -splitting arises from the hydrogen atoms at either carbon 3 or carbon 4 of DMPO-OOH. The second is that the  $\gamma$ -splitting originates from the hydrogen atom of the hydroperoxide of DMPO-OOH. The third is that DMPO-OOH exists in two conformations, each of which gives a six-line EPR spectrum and a g shift of 1.22 G between conformers. Further experimental and theoretical chemical approaches were used to investigate which of these hypotheses may explain the asymmetric EPR spectrum of DMPO-OOH. The results of these studies will be discussed.

*Supported by NIH grant RR12257*

**EPR Symposia Poster Session**

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**73. Multi-frequency CW and Pulsed X-band EPR Study on Mn(II)- Nucleotide Model Complexes.** Anna Lisa Maniero; Marina Brustolon; Luca Pinato; Alfonso Zoleo, Università di Padova, Dipartimento di Chimica Fisica, Padova, Italy; Louis-Claude Brunel, Florida State University, National High Magnetic Field Laboratory, Tallahassee, FL 32310.

The nucleotide ATP plays the fundamental role of chemical energy source in living cells. From ATP, energy is released through the hydrolysis reaction:  $ATP + H_2O \rightarrow ADP + Pi$ , which is coupled to many important endoergonic biochemical reactions. The synthesis of ATP from ADP and phosphate (Pi), i.e. the reversal reaction of the previous one, is catalyzed by a class of enzymes called ATPsynthases. It is commonly accepted that the effective substrates in the reaction are complexes MgATP and MgADP, though other divalent ions like  $Mn^{2+}$ ,  $VO^{2+}$  can replace the  $Mg^{2+}$ . Moreover, no reaction occurs in absence of any divalent metal in solution, which strongly supports the role of the divalent ion in the mechanism. Since Mn(II) replaces well Mg(II) in many different enzymes (not only in the ATPsynthases) and occurs naturally in other important ones (Superoxidismutase, Catalase), it is very useful to investigate by EPR and related techniques Mn-nucleotides complexes at least for two reasons: generically, as model compounds of Mg-nucleotides complexes and specifically from the point of view of the EPR, as model systems in the study of the ligand-manganese interactions and their effects on the spectral parameters (ZFS, hyperfine and superhyperfine couplings). In our study, we have included also the MnAMPPNP complex: this complex is widely used as a non-hydrolyzable complex analogous to MnATP. In the poster we will present the results on Mn(II) complexes with ATP, ADT, and AMPPNP, obtained by cw multifrequency EPR and X-band ESEEM techniques, and the experimental data will be discussed in relation to the complexes structure. The multifrequency approach, together with the use of pulsed techniques, has shown to be essential for obtaining detailed structural information.

**EPR Symposia Poster Session**

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74. **Accurate Computations of the Methyl Isotropic Hyperfine Coupling Constants in the 2-methyl-1,4-benzosemiquinone Radical Intermediate.** Saba M. Mattar, Alyson D. Stephens and Abdul H. Emwas, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada. E3B 6E2.

The accuracy of the Unrestricted-Becke-1-parameter Lee-Yang-Parr (UBLYP) hybrid density functional as a method of calculating the isotropic hydrogen hyperfine coupling constants,  $a^{iso}(^1H)$ , of a rapidly rotating methyl functional group in a semiquinone radical is investigated for the first time. The 2-methyl-1,4-benzosemiquinone anion is chosen as the simplest case. Its geometry is optimized as the torsion angle between the semiquinone ring plane and the methyl hydrogen atoms is varied in  $5^\circ$  intervals. From these extensive computations, the rotationally averaged coupling constants,  $\langle a^{iso}(^1H) \rangle_{Rot.}$ , are calculated and found to be in excellent agreement with experiment.

Supported by the Natural Sciences and Engineering Research Council of Canada

#### EPR Symposia Poster Session

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75. **Design of Cavities with Large Sample Access Stacks for Use in EPR Spectroscopy.** Richard R. Mett, James S. Hyde, and James R. Anderson, Medical College of Wisconsin, Biophysics Research Institute, 8701 Watertown Plank Road, P.O. Box 26509, Milwaukee, WI 53226.

A modal frequency finite element method<sup>1</sup> of solving Maxwell's equations now available through Ansoft (Pittsburgh, PA) High Frequency Structure Simulator (HFSS) has proven to be very useful in the design of EPR cavity resonator structures. Using this method, it is possible to design a specialized resonator,<sup>2,3</sup> including stacks and coupling structures, in less than a day, starting from analytically targeted dimensions and using appropriate impedance boundary conditions. This paper focuses on the design of sample access stacks and accounts for the presence of dewars, sample holders, and samples. The main conclusion of this work is that it is possible to have much larger sample access ports than have been used in the past. For example, in cylindrical geometries, the diameter of the sample access port can be up to 85% of the diameter of the cavity itself. This is because significant coupling to a  $TE_{11}$  mode propagating out of the sample access port requires far more asymmetry than is generally possible. In addition, we find that a larger port may produce *less*  $TE_{11}$  mode coupling than a smaller one. We find that it is possible to maintain high  $Q$  by ensuring evanescence of the  $TE_{01}$  mode in the stack and by making the sample access tube long (longer than usual). Thin-walled quartz also allows larger sample access. The design of a  $Q$ -band  $TE_{011}$  cavity, including experimental measurements and observations, is presented. Our findings have significant consequences for  $Q$ -band and  $W$ -band EPR cavity resonator design.

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#### EPR Symposia Poster Session

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76. **Q-band Loop-gap Resonator for Aqueous Samples.** James S. Hyde, Richard R. Mett, James R. Anderson, Theodore G. Camenisch, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226

W. Froncisz et al. (1) described an asymmetric two-loop—one gap Q-band (35 GHz) resonator designed to accommodate aqueous samples. That design consisted of a large loop, 2.5 mm in diameter, to which the incoming microwave power from a waveguide was coupled through a slotted iris, and a small loop, 0.45 mm in diameter, in which the sample was placed. The gap was 0.13 mm. This structure has proven useful in a number of studies, but there is a problem: the electric field in the small loop *goes to zero at the wall opposite the gap*. Aqueous samples should not be centered in the small hole, but pushed against the wall opposite the gap. Nevertheless, the samples are separated from the wall by the thickness of the sample tube and all portions of the sample experience dielectric loss. To address this problem, a symmetric three-loop—two-gap resonator has been constructed. It follows some of the design aspects given in Ref. 1 as well as the three-loop—two-gap resonators described in Refs. 2, 3. However, in the structures of Ref. 2 and 3, the outer loops were small and the inner loop was large; in the new Q-band resonator, it is the reverse. The outer loops are 2.06 mm in diameter and the inner (sample) loop is 0.65 mm. The electric field goes to zero in the center of the small loop, reducing dielectric loss from aqueous samples. The structure was constructed in aluminum and is presently not suitable for high frequency field modulation. The gap, 0.13 mm, was cut by EDM (electrical discharge machine) methods. The resonator has been used extensively for multi-quantum, MQ, experiments at Q-band. A strategy for modification of the structure to accommodate field modulation has been developed and initial tests establish feasibility.

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77. **EPR Linewidth Study of the Mn<sup>2+</sup> Ion in MnSO<sub>4</sub>·H<sub>2</sub>O in Single-crystal and Powder States at X-, Q-, W-, and Infra-red Bands: Origin of Narrowing at Very High Frequencies.** Sushil K. Misra, Physics Department, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Quebec H3G 1M8, Canada; Keith A. Earle, Jack H. Freed, Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301, U.S.A.

We have measured EPR linewidth of the Mn<sup>2+</sup> ion in MnSO<sub>4</sub>·H<sub>2</sub>O, both in powder and single-crystal states, at X (~9.6 GHz), Q (~35.7 GHz), W (95 GHz), and infra-red (249.9 GHz) bands in order to study the effect of frequency on the linewidth. The data indicate that in both the powder and single-crystal states there is observed only one unsplit EPR line, centered at g = 2, at X, Q, and W bands. On the other hand, at 249.9 GHz there is observed splitting of this line. This is obviously due to narrowing of EPR lines with increasing frequency. This narrowing is analyzed in terms of overlapping effects of (i) 10/3-narrowing with increasing frequency as discussed by Anderson (A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Metal ions*, Oxford, 1970); (ii) reduction in the divergence of the effective g-tensor values of the central ½ ↔ -½ transition with increasing frequency; and (iii) g-strain broadening with increasing frequency. EPR spectra at various frequencies will be presented. Theoretical mechanisms behind the three mechanisms will be discussed. It is concluded that there is enhanced resolution of EPR spectra at very high frequencies, greater than 200 GHz.

#### **EPR Symposia Poster Session**

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78. **Analysis of EPR Signal Enhancement by a Quartz Cavity Insert.** Yu. E. Nesmelov, Jack T. Surek, D.D. Thomas, University of Minnesota, Department of Biochemistry, Minneapolis, MN 55455

A hollow cylindrical quartz insert was used to enhance the EPR signal in a standard X-band TE<sub>011</sub> cavity through the redistribution of microwave fields. This was analyzed theoretically and experimentally. The microwave field distribution in a cavity with an insert was modeled by radial mode matching, which was used to determine resonant frequency and filling factor for a point sample in a cavity with an insert, for various insert geometries. Experimental measurements, using the insert, were made of resonant frequency, quality factor, intensity of microwave magnetic field at the sample, and distribution of signal intensity of a point sample along the cavity's axis of symmetry of a cavity. The insert was shown to redistribute microwave fields in a cavity and increase its filling factor. On the other hand, the resonant frequency of a cavity with an insert decreases with an increase in insert wall thickness as a result of exciting higher frequency modes in the cavity. These act to decrease filling factor. The dependence of filling factor on insert geometry is discussed, with the aim of maximizing filling factor and sensitivity.

*The support of University of Minnesota Supercomputing Institute is acknowledged.*

#### **EPR Symposia Poster Session**

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79. **Strategies for the Efficient Computer Simulation of Pulsed Electron Paramagnetic Resonance Spectra.** Christopher J. Noble, Graeme R. Hanson, Centre for Magnetic Resonance, University of Queensland, St Lucia, Queensland, 4072, Australia; Kevin E. Gates, Department of Mathematics, University of Queensland, St Lucia, Queensland, 4072, Australia.

A general program for the computer simulation of cw electron paramagnetic resonance spectra has previously been developed.<sup>1</sup> This simulation package is currently being extended to include the simulation of pulsed EPR spectra. A number of different strategies have been necessary to both accurately and efficiently simulate different pulsed EPR experiments and different spin systems. For spin systems that have little anisotropy transformation to the rotating frame is effective in removing the time dependent component of the Hamiltonian allowing efficient simulation of time domain EPR spectra. With spin systems with S > 1/2 and large zero field parameters this is no longer valid and an implementation of Floquet theory is necessary. The calculation time for many simulations can be greatly reduced by using 'frequency domain' methods.<sup>2</sup> The 'frequency domain' method also allows interpolation and extrapolation methods that are utilized to increase the speed of the cw EPR simulations to be used for the simulation of pulsed EPR spectra. Many of the spin systems currently being investigated with pulsed EPR techniques, particularly in biological samples, involve a distribution or 'strain' in one or more of the spin Hamiltonian parameters. Efficient methods for the integration over these distributions have also been developed for use in the pulsed EPR simulations.

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80. **Spin Labels As Probes of Solvent Polarity and Hydrogen Bonding - Using 95-GHz EPR Spectroscopy and DFT Calculations as An "Environmental Ruler".** Rikard Owenius<sup>1</sup>, Maria Engström<sup>2</sup>, Mikael Lindgren<sup>1</sup>, and Martina Huber<sup>3</sup>. IFM-Departments of <sup>1</sup>Chemical Physics and <sup>2</sup>Computational Physics, Linköping University, SE-581 83 Linköping, Sweden; <sup>3</sup>Huygens Laboratory, MAT Group, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands.

The isotropic and anisotropic hyperfine coupling constants and  $g$ -values of the nitroxide spin label (1-oxyl-2,2,5,5-tetramethylpyrroline-3-methyl)methanethiosulfonate (MTSSL) were determined from 9-GHz and 95-GHz electron paramagnetic resonance (EPR) measurements in various solvents with a large distribution in polarity and proticity. The parameters  $A_{iso}$ ,  $g_{iso}$ ,  $A_{zz}$ , and  $g_{xx}$  of MTSSL were found to be sensitive to changes in solvent properties, where  $A$ -values increased and  $g$ -values decreased due to increased solvent polarity or proticity. A linear correlation was found for the isotropic ( $g_{iso}$ ,  $A_{iso}$ ) and anisotropic ( $g_{xx}$ ,  $A_{zz}$ ) parameters, respectively. Furthermore, density functional theory (DFT) calculations of the same parameters were performed for a model spin label with the possibility to vary the dielectric constant ( $\epsilon$ ) of the medium and the number of hydrogen bonds formed with the nitroxide oxygen. From a qualitative analysis of experimental and calculated results it was possible to specify the causes of the parameter shifts in more detail. In the "apolar region" ( $\epsilon < 25$ ), the sensitivity of  $A_{iso}$  and  $A_{zz}$  to  $\epsilon$  is large. However, in the "polar region" ( $\epsilon > 25$ ), the sensitivity to  $\epsilon$  is small, and the shifts in  $A_{iso}$  and  $A_{zz}$  are mainly determined by the proticity of the solvent. Methanol was found to form ~one and water ~two hydrogen bonds to the nitroxide on average. The DFT method determined the shifts in  $g_{iso}$  and  $g_{xx}$  due to hydrogen bonding more accurately compared with the restricted open-shell Hartree-Fock method. The anisotropic spin label-solvent data can be used in the interpretation of rigid-limit data from spin-labeled proteins to gain further insight in local environmental properties.

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81. **Hydroxyl Radical Spin Trapping with 5-carboxy-5-methyl-1-pyrroline-N-oxide and its Methyl and t-butyl Esters: Dose Response and Stability in the Face of Thiol.** Adrian Parasca, Eugene D. Barth, Kazuhiro Ichikawa, Howard J. Halpern, Dept. Radiation and Cellular Oncology, University of Chicago, Chicago, IL 60637 and Gerald M. Rosen, Dept. Pharmaceutical Sciences, University of Maryland School of Pharmacy, Baltimore, MD 21201 all from the Center for EPR Imaging *In Vivo* Physiology

The hydroxyl radical spin trapping characteristics of several closely related DMPO analogs, 5-Carboxy-5-methyl-1-pyrroline *N*-oxide [1], its methyl [2] and t-butyl [3] esters were studied. HO• was generated in 40 mM spin trap solutions in PBS (pH 7) by applying  $\gamma$  radiation at doses of 46, 50, 150, and 184Gy. Spectra were recorded at X-Band. Following irradiation, the peak-to-peak (ptp) heights were plotted versus time. Each decay curve was fitted with a first order biexponential—one with a short half-life, ranging 3-3.72min and one with a longer half-life, 16.6-21.3min. We then extrapolated to the time point marking the end of irradiation, and recorded the ptp height values. We plotted the extrapolated ptp heights versus radiation dose and generated dose response curves for each of the analogs. [1] showed a roll-off in ptp height at 150Gy, while [2] and [3] began to plateau at 184Gy. We further tested hydroxyl adduct stability in a reductive environment such as it might face in cytoplasm or extracellular fluid. Reduced glutathione (GSH) was added at 5mM concentration to the spin trap solutions after the end of 184 Gy irradiation and shortly before the spectral acquisition. Following the same fitting method described above, we calculated and compared the half-lives of each adduct in the presence of GSH with the half-lives without GSH. We found that GSH did not affect the half-lives of [2] and [3] adducts, but it did decrease the slow component half-life of [1] adduct from 16.6 $\pm$ 1.1min without GSH to 11.0 $\pm$ 0.56min with GSH.

Supported by NIH grant RR 12257. EPR Symposia

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82. **Spin States of  $C_{120}O^n$  Anions ( $n = 3, 4$ ) and Other Complexes Using Electron Spin Transient Nutation Spectroscopy.** S.C. Drew\*, J.F. Boas and J.R. Pilbrow, School of Physics and Materials Engineering, Box 27, Monash University, Australia; Peter D.W. Boyd, Department of Chemistry, The University of Auckland, Private Bag, Auckland, NZ; Dayong Sun and Christopher A. Reed, Department of Chemistry, University of California, Riverside 92521.

Transient nutation methods using pulse sequences have long been applied in EPR spectroscopy to measure small  $g$ -factors for highly anisotropic paramagnetic ions and to determine spin multiplicities for single and multiple species. Transient nutation spectroscopy has been applied to different states of the dimeric fullerene  $C_{120}O$  and to  $Re(abt)_3$  complexes. These experiments reveal that there are only low multiplicity states for  $C_{120}O^{3-4-}$  fullerides, thus resolving ambiguities arising from the interpretation of previous CW EPR spectra in the literature. Analogous experiments carried out on polycrystalline powders and frozen solutions of the  $Re(abt)_3$  complex have proven more difficult to interpret and have not at this stage led to definite spin assignments.

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83. **A Digital Boxcar Averager Optimized for Electron Spin Echo Data Collection.** Richard W. Quine, Department of Engineering, University of Denver, Denver, CO 80208, James R. Harbridge and Gareth R. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208, and Malin Persson, IFM-Chemistry, Linköping University, Sweden.

A digital boxcar averager, optimized for data collection in ESE experiments, was designed, developed and tested at the University of Denver. By numeric accumulation of large numbers of electron spin echo intensities into a microprocessor memory, the dynamic range of the instrument is greatly expanded over that of a conventional analog boxcar. An analog boxcar is limited by the accumulation of charge on a capacitor, which saturates at the power supply rails. The digital boxcar has no such dynamic range limitation and can therefore accumulate large numbers of samples per point. This results in greater data collection efficiency when measured as the S/N achieved per unit time. Application of the digital boxcar to double electron-electron resonance (DEER) experiments (for measurement of spin separation distances in proteins) resulted in speed-up factors of 3x to 4x over the time previously required using an analog boxcar.

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84. **Pulsed EPR Studies of the Exchangeable Proton at the Molybdenum Center of Dimethyl Sulfoxide Reductase.** Arnold M. Raitsimring, Andrei V. Astashkin, Changjian Feng, John H. Enemark, Department of Chemistry, University of Arizona, Tucson, AZ 85721-0041; Kimberly E. Johnson, K. V. Rajagopalan, Department of Biochemistry, Duke University Medical Center, Durham, NC 27710

Electron spin echo envelope modulation (ESEEM) spectroscopy has been used to determine the hyperfine and quadrupole interactions of the exchangeable deuteron (proton) at the Mo(V) site of DMSO reductase. The data obtained have been translated into structure-related parameters. It was found that *isotropic hfi* constant of the proton is not unique, but is distributed within a range of 26 - 36 MHz. From this *hfi* distribution, using theoretical results for a model system [1], a 30°-wide distribution of the OH bond orientations due to a rotation around the Mo-O bond was estimated. The angle between the axes of the *nqi* and anisotropic *hfi* tensors was found to be anomalously small in comparison with that expected from the Mo-O-D bond geometry. This peculiarity was explained by a contribution of spin density on the hydroxyl oxygen [2] to the anisotropic *hfi* of the hydroxyl deuteron (proton). The orientation of the Mo-OH fragment with respect to the g-frame was determined from the experimental orientations of the *nqi* and *hfi* tensor axes and a theoretical evaluation of the anisotropic *hfi* axis direction. Supported by NSF BIR-9224431, and DBI-0139459.

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85. **Continuous Wave and Time Domain Studies of Spin Labeled Human Group IIa Secreted Phospholipase A<sub>2</sub>.** Robert D. Nielsen, Stephane Canaan, Farideh Ghomashchi, Michael H. Gelb, Bruce H. Robinson, University of Washington, Department of Chemistry, Seattle, Wa. 98195

Human Group IIa secreted Phospholipase A<sub>2</sub> (hGIIa-PLA<sub>2</sub>) is representative of a family of enzymes which hydrolyze the sn-2 position of glycerophospholipids, liberating fatty acids. This protein has numerous surface exposed basic residues (implicated in its unique anti-bacterial activity) that give much of the surface a positive charge. Spin labeled, site-directed mutants of hIIa-PLA<sub>2</sub> were prepared, in which only surface residues were labeled. Previously, we had used continuous wave Electron Paramagnetic Resonance (EPR) with spin-relaxants to investigate the binding of other proteins to membrane surfaces (*Science* 279, 20 March 1998, p1926). The continuous wave method is here augmented through the use of the Time Domain EPR techniques of saturation recover (SR) and pulsed ELDOR. Time Domain EPR measures the spin-lattice relaxation rates directly, and provides an alternative method for quantifying exposure of spin-labeled sites to relaxants (e.g. oxygen). The effects of water-soluble relaxants on the spin-lattice relaxation rates were studied as a function of ionic strength, and charge of spin relaxant. The relaxation rates were compared to the estimates from CW techniques, and agreed well with the predictions of electrostatic theory. The high protein surface charge on hGIIa-PLA<sub>2</sub> (pI = 9.39) was thereby measured at several spin labeled sites using both CW and TD techniques. hIIa-PLA<sub>2</sub> was bound to large unilamellar vesicles (LUV) of 1,2-dimyristoyl-sn-glycero-3-phosphomethanol (DTPM), and mixed micelles of 10% DTPM in TritonX-100. Time Domain and Continuous Wave EPR were used to measure Crox (Chromium (III) tris-Oxalate), NiEDDA (Nickel Ethylene diaminediacetic acid), and oxygen exposure for a set of spin labels, which decorate the surface of the hIIa-PLA<sub>2</sub> protein. Certain residues were found to be in the interfacial region because the Time Domain EPR data showed a reduced exposure to Crox and NiEDDA. From this data, the position of hGIIa-PLA<sub>2</sub> on the membrane was determined.

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86. **Density Functional Theory Calculations of EPR Parameters of Vanadium and Copper Model Complexes.** [Alexander Saladino](#), Sarah C. Larsen, Department of Chemistry, University of Iowa, Iowa City, IA 52242

Density functional theory methods for calculating EPR parameters, such as electronic  $g$ -tensors and electron nuclear hyperfine interaction ( $A$ ) tensors, were applied to vanadium (IV) and copper(II) complexes.  $g$ -tensors were calculated using the Amsterdam Density Functional (ADF) program.  $A$ -tensors were calculated using ADF and Gaussian98 (G98) programs, respectively. The accuracy of ADF and G98 calculations of  $A$ -tensors for vanadyl model complexes was compared. The best agreement with experimental  $A$ -values was obtained with Gaussian98 using hybrid functionals, such as BHPW91. The isotropic  $A$ -values ( $A_{\text{iso}}$ ) calculated with Gaussian98 (BHPW91) deviated by about 10% from the experimental  $A_{\text{iso}}$ -values. The  $A_{\text{iso}}$ -values calculated with ADF and generalized gradient correction (GGA) functionals, such as BP86, deviated by approximately 35% compared to the experimental  $A_{\text{iso}}$ -values. However, the deviations of the calculated  $A$ -values from the experimental values are systematic for related complexes (ie.  $\text{VO}^{+2}$  complexes with similar structures) so that general trends in EPR parameters can be reproduced even if the results are not quantitative. The orientation dependence of the metal and ligand hyperfine coupling constants for vanadyl imidazole complexes was also calculated. Recent results show that empirical trends in EPR parameters of copper complexes can be reproduced by the calculations.

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87. **Heterogeneous Structure of Gd(3+)-doped Glasses: HF EPR Line Shapes and Inter-ion Distances.** [Alex I. Smirnov](#), Chemistry, Department, North Carolina State University, Box 8204, Raleigh, NC 27606-8204; S. Sen, Glass Research Division, Corning Inc., Corning, New York 14831.

Rare earth doped glasses have found numerous applications in optical devices such as amplifiers and lasers. One of the problems in developing these new materials is the low solubility of rare-earth ions in glasses with high  $\text{SiO}_2$  or  $\text{GeO}_2$ . Here we report the results of a High Field EPR study to characterize the clustering of  $\text{Gd}^{3+}$  ions in a modified silicate glass and an unmodified  $\text{GeO}_2$  glass as a function of Gd concentration. We have chosen  $\text{Gd}^{3+}$  as a model rare-earth ion for studying clustering since it is an  $S$ -state ion and therefore its EPR spectrum is expected to undergo significant narrowing and simplifications at high magnetic field. Least squares line shape analyses based on convolution equation show that in the case of the silicate glass the line broadening is well described by a single Lorentzian function with a width proportional to the average  $\text{Gd}^{3+}$  concentration. HF EPR indicates an onset of clustering of  $\text{Gd}^{3+}$  ions in the modified silicate glass at  $>1\text{wt}\%$   $\text{Gd}_2\text{O}_3$  doping levels. In the case of the unmodified  $\text{GeO}_2$  glass the  $\text{Gd}^{3+}$  line shapes show clear presence of a narrow and a broad EPR component corresponding to isolated and clustered  $\text{Gd}^{3+}$  centers, respectively, even at a doping level of 0.12 wt% of  $\text{Gd}_2\text{O}_3$ . This result indicates significantly low solubility of rare earth ions in an unmodified glass network and is consistent with the observation of phase separation in Gd-doped  $\text{GeO}_2$  glasses at a doping level of  $\sim 1\text{wt}\%$   $\text{Gd}_2\text{O}_3$ . Details of these structural aspects of clustering will be discussed.

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88. **Pulse EPR Detection of Liquid-ordered Phase Domains in Saturated and Unsaturated Phosphatidylcholine Membranes: Effect of Sphingomyelin.** [Witold K. Subczynski](#)<sup>1</sup>, James S. Hyde<sup>1</sup>, and Akihiro Kusumi<sup>2</sup>; <sup>1</sup>Medical College of Wisconsin, Milwaukee, WI 53226, USA; <sup>2</sup>Nagoya University, Nagoya, Japan

Molecular organization and dynamics in dimyristoylphosphatidylcholine (DMPC)/cholesterol (CHOL) and 1-palmitoyl-2-oleoylphosphatidylcholine (POPC)/CHOL/sphingomyelin (SM) membranes have been investigated by measuring transport (diffusion-concentration product) of molecular oxygen at various locations in these membranes. Oxygen transport was evaluated by monitoring the bimolecular collision of molecular oxygen with phospholipid analogue spin labels (n-PC) and cholesterol analogue spin labels (androstande (ASL) and cholestane (CSL)). The collision rate was estimated from the spin-lattice relaxation times ( $T_1$ ) measured at various oxygen partial pressures by analyzing the short-pulse saturation recovery EPR signals. In DMPC/CHOL gel-phase membranes, two collision rates were observed. The one with slower oxygen transport is attributed to solid-phase domains (s) and the other to liquid-ordered phase domains ( $l_o$ ). In the liquid-crystalline phase, two collision rates were also observed, one is close to  $l_o$  in the gel phase, while the other is about the same as in the liquid-crystalline phase of pure DMPC. We attribute these domains to  $l_o$  and to liquid-disordered ( $l_d$ ) phase domains. In the *cis*-unsaturated POPC bilayer in the presence of CHOL or CHOL and SM, the lipid environment is homogenous on a microsecond time scale ( $T_1$ ), probably because the exchange rate of lipids between  $l_o$  and  $l_d$  domains is greater than the  $T_1$  relaxation rate in the presence of oxygen ( $3 \times 10^6 \text{ s}^{-1}$ ). The oxygen collision rate in these membranes is smaller by a factor of 1.0–1.7, depending on temperature and spin label. We demonstrated here that the discrimination by oxygen transport (DOT) detection method (Ashikawa et al., *Biochemistry* 33, 4947-4952(1994)), which is sensitive to the lipid component of the raft domain, and can be successfully applied to studies of lipid rafts.

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**89. Does the Polarity of Carotenoids Influence Their Effects on Membrane Properties and Antioxidant Activity?**

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It is supposed that the differing abilities of lutein, cryptoxanthin, and  $\beta$ -carotene (dipolar, monopolar, and nonpolar carotenoid, respectively) to protect membranes against oxidation is caused not only by the different orientations of these molecules in the membrane (Woodal et al., *Biochim. Biophys. Acta* 1336, 575-586(1997)), but also by their different effects on membrane properties. It has been shown with the use of stearic acid spin labels that these carotenoids increase the order and decrease the motion of alkyl chains in fluid-phase phosphatidylcholine (PC) membranes. Additionally, the main-phase transition of PC membranes monitored by the abrupt change of spin label motion is broadened and shifted to the lower temperature when carotenoids are present in the membrane. The strongest effect is observed for lutein, weaker for cryptoxanthin, and practically no effect is observed for  $\beta$ -carotene. The effect of carotenoids decreases as the membrane thickness increases. These results suggest that the anchoring of the carotenoid molecule at the membrane surface by the polar hydroxyl group (or groups) is significant in enhancing its effect on membrane properties.

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**90. Fixed-frequency Operation of a Low Frequency Continuous Wave EPR Imaging Spectrometer.** V.S.Subramanian, Colin Mailer, Kazuhiro Ichikawa, Eugene D. Barth, Benjamin B. Williams, Howard J. Halpern, Department of Radiation Oncology, University of Chicago Medical Center, 5841 South Maryland Avenue, MC1105, Chicago, IL 60637 and the Center for EPR Imaging In Vivo Physiology

In continuous wave (CW) electron paramagnetic resonance imaging (EPRI) as applied to the measurement of free radicals *in vivo*, the time dependent resonator frequency drift caused by the changes in the resonator parameters is traditionally handled by the automatic frequency control (AFC) of the radio frequency (RF) source. However, fixing the oscillator frequency and tuning the resonator frequency by an automatic tuning control (ATC) circuitry has the added advantage over the conventional AFC operation, particularly at high RF power where the source phase noise impairs the signal to noise ratio (SNR) of the EPR signal. We developed a compact inductive-loop mutually coupled to a loop-gap resonator (LGR) for automatic tuning of its frequency. The effective inductance of the inductive-loop itself is controlled by a varactor that is located far from the loop by the addition of a quarter-wavelength coaxial cable. The quarter wave coaxial cable transforms the variable capacitance of the varactor to a variable inductance. Distance reduces the influence of the modulation and the RF fields on the varactor diode. The varactor reverse bias voltage is automatically controlled by a negative feedback voltage derived from the quadrature component of the reflected signal from the EPR bridge. This provides automatic resonator tune function. This fixes the source frequency of our 250 MHz CW imaging spectrometer, eliminates the shift in the position of the acquired EPR spectra and eliminates unwanted RF phase-shifts, enabling high power operation. The performance is experimentally verified.

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**91. Spin Relaxation Times of Conduction Electrons in Si/SiGe Quantum Wells.** A.M. Tyryshkin, S.A. Lyon, Department of Electrical Engineering, Princeton University, Princeton, NJ 08544; W. Jantsch, F. Schäffler, Institut für Halbleiterphysik, Johannes Kepler Universität Linz, A-4040 Linz, Austria.

Silicon is a good candidate for spintronics and quantum computing applications, because its weak spin-orbit interaction gives long electron spin lifetimes. We will report pulse EPR measurements of the spin relaxation times of 2-dimensional (2D) electrons in a strained, 200Å thick, one-side modulation-doped Si quantum well grown on a relaxed SiGe buffer. The X-band EPR experiments were conducted with the 2D layer oriented perpendicular to the external magnetic field at temperature 4K. Persistent photoconductivity was used to control the electron density in the well. After illumination at 4K the EPR spectrum showed a narrow (~150mG) Lorentzian resonance centered at  $g \approx 2$  and a total of about  $10^{11}$  spins in the sample. Inversion-recovery ( $\pi$ -T- $\pi/2$ -FID) and 2-pulse echo ( $\pi/2$ - $\tau$ - $\pi$ - $\tau$ -echo) experiments were used to measure  $T_1$  and  $T_2$ , respectively. The relaxation decays are not purely exponential indicating a distribution of relaxation times. As illuminated, we find the dominant  $T_1 = 0.6\mu\text{sec}$  and  $T_2 = 0.9\mu\text{sec}$ . Relaxation slows after short annealing to 30-40K, with  $T_1 = 2.3\mu\text{sec}$  and  $T_2 = 3.0\mu\text{sec}$ . While similar in magnitude, in all cases we find that  $T_2 > T_1$  (though  $T_2 < 2T_1$ , as is required by their definitions). Such behavior has been seen previously in only a few systems, and requires that the relaxation processes be very anisotropic. The relaxation can be viewed, abstractly, as caused by rapid fluctuating fields. If fluctuating fields are anisotropic, i.e. in-plane  $H_{x,y}$  are greater than  $H_z$ , this can explain the observed  $T_2 > T_1$  of the conduction electrons in 2D layer. These results are consistent with the suggestion that an in-plane Bychkov-Rashba field (caused by rapid in-plane motion of the conduction electrons,  $\tau_c = 10$  psec) dominates the spin relaxation. Supported in part by Los Alamos National Laboratory and the Army Research Office.

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92. **Mechanisms of Electron Spin Relaxation of Phosphorus Donors in Silicon.** A.M. Tyryshkin, S.A. Lyon, Department of Electrical Engineering, Princeton University, Princeton, NJ 08544; A.V. Astashkin, A.M. Raitsimring, Department of Chemistry, University of Arizona, Tucson, AZ 85721.

The spins of electrons bound to donors in Si have been identified as promising candidates for quantum computing qubits, because of their long spin relaxation times, both  $T_1$  and  $T_2$ . We report a detailed pulse-EPR study, at 9.6 and 16.4 GHz, of the electron spin relaxation times of Si:P ( $< 10^{16}/\text{cm}^3$ ). The EPR spectra consist of two lines split by 42G from the hyperfine interaction with the  $^{31}\text{P}$  nuclear spin. Individual linewidths of 2.5G in natural silicon (4.7%  $^{29}\text{Si}$ ) and 70mG in isotopically purified  $^{28}\text{Si}$  ( $< 30$  ppm  $^{29}\text{Si}$ ) were found. Inversion-recovery and 2-pulse echo experiments were used to measure  $T_1$  and  $T_2$ , respectively. The longitudinal relaxation was essentially exponential, with  $T_1$  falling rapidly with temperature, from 1sec at 6K to 1 $\mu\text{sec}$  at 20K. This dependence is ascribable to an Orbach-relaxation process involving a low-lying excited state at  $\Delta E = 127$  K. In contrast, the  $T_2$  relaxation was clearly non-exponential in both  $^{29}\text{Si}$  and  $^{28}\text{Si}$  samples, being best described by  $\exp(-\tau/T_2 - \tau^3/T_S^3)$  with  $T_S$  about 1.5 times smaller in natural Si. In both samples,  $T_S$  was nearly temperature-independent which is consistent with electron and nuclear (in natural Si) spin diffusion. The  $T_2$  term (linear in  $\tau$ ) was temperature-independent ( $T_2 = 600\mu\text{sec}$ ) below 8K but decreases above this temperature to coincide with  $T_1$  above about 15K. Echo experiments with variable turning angle of the 2<sup>nd</sup> microwave pulse show that instantaneous diffusion dominates below 8K. The  $T_2$  increases for smaller turning angles and extrapolates to  $T_1$  ( $T_2 = T_1 = 10\text{msec}$  at 8K). Thus, we demonstrated that the intrinsic  $T_2$  relaxation times of donor electron spins is possibly limited only by  $T_1$  relaxation processes and is up to many minutes at 1.6 K. This finding makes these spins even more attractive for quantum computing applications. Supported in part by Los Alamos National Laboratory and the Army Research Office.

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93. **Dual-mode EPR of  $\text{Mn}^{2+}/\text{Mn}^{3+}$ : the First Photooxidized Intermediate During Assembly of the Photosynthetic Water Oxidizing Complex.** A.M. Tyryshkin, R.K. Watt<sup>1</sup>, S.V. Baranov, G.C. Dismukes, Princeton University, Chemistry Department, Princeton, NJ 08544; <sup>1</sup>Current address: Chemistry Department, The University of New Mexico, Albuquerque, NM 87131.

The assembly of the  $\text{O}_2$ -evolving  $\text{Mn}_4\text{Ca}_1\text{O}_x\text{Cl}_{1-2}$  cluster within the apo-protein of PSII occurs spontaneously during illumination starting from the free inorganic cofactors in solution. The very first steps involve binding of  $\text{Mn}^{2+}$  and its oxidation to  $\text{Mn}^{3+}$  via PSII photochemistry. Dual-mode EPR was used to follow the conversion of  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and how it interacts with its ligand environment and with  $\text{Ca}^{2+}$ . The  $\text{Mn}^{3+}$ -apo-PSII center has a spin  $S=2$  ground state and exhibits a transition between the  $M_S = \pm 2$  sublevels that gives rise to an EPR signal centered at  $g_Z \sim 8$  with resolved  $^{55}\text{Mn}$  hyperfine structure ( $A_Z$ ). The  $g_Z$  and  $A_Z$  values and the signal intensity were found to depend on three parameters in a systematic way: the solution pH, the binding of bicarbonate and the binding of  $\text{Ca}^{2+}$ . A self-consistent molecular interpretation of these changes was possible using ligand field theory. The pH dependence reveals an equilibrium,  $\text{Mn}^{3+}(\text{OH}_2) \leftrightarrow \text{Mn}^{3+}(\text{OH}^-)$ , with the deprotonated species being EPR-detectable. Raising the pH shifts the equilibrium to  $\text{Mn}^{3+}(\text{OH}^-)$ .  $\text{Ca}^{2+}$  binding at its effector site alters  $A_Z$  and  $g_Z$  of the  $\text{Mn}^{3+}$  and in addition shifts the equilibrium in favor of  $\text{Mn}^{3+}(\text{OH}^-)$ . These changes indicate that  $\text{Ca}^{2+}$  interacts with  $\text{Mn}^{3+}$ , possibly via a bridging hydroxo ligand. Binding of bicarbonate greatly stimulates the assembly kinetics and leads to appreciably different values for  $A_Z$ ,  $g_Z$  and a 3.5-fold greater signal intensity. This is consistent with formation of a lower-symmetry intermediate, proposed to be  $\text{Mn}^{3+}(\text{OH}^-)_{1-2}(\text{HCO}_3^-)_{1-0}$ . ESEEM and ENDOR experiments are under run in this laboratory to further test this conclusion. Supported by NIH-GM39932.

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94. **Comparison of Saturation Recovery and Pulsed EPR Measurements of Interspin Distances in Spin Labeled Myoglobin Mutants.** Dmitriy Ulyanov, Bruce Bowler, Sandra S. Eaton, and Gareth R. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208.

Thirteen variants of sperm whale myoglobin were prepared by site directed mutagenesis with cysteine at desired locations. Apo-protein was expressed, spin-labeled with MTSL, and reconstituted with heme. Samples containing high spin or low spin iron were prepared by addition of  $\text{F}^-$  or  $\text{CN}^-$ . Spin labels placed at these mutation sites provided a range of distances and orientations with respect to the magnetic axes of spin. The interspin distances were determined in two ways. (i) The effect of the rapidly relaxing iron on the relaxation rate of the nitroxyl spin label was measured by saturation recovery (SR). Data were analyzed using a modified version of the Bloembergen equation (ii) The effect of the iron on the temperature dependence of the 2-pulse spin echo intensity for the nitroxyl was measured. The minimum echo intensity correlated well with the distance obtained by SR. The effects of the high-spin Fe(III) on nitroxyl echo intensity are detectable at longer distances than the effects on SR curves. The SR data indicate that more than one conformation of the spin label is present for some mutants. The distances obtained by SR were compared to those calculated using the Insight II software, starting from X-ray crystal structures of wild-type protein.

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95. **Site-directed Spin Labeling of Cowpea Chlorotic Mottle Virus to Characterize Chemico-physico Properties of a Protein Cage.** Robert J. Usselman, Eric D. Walter, Trevor Douglas, and David J. Singel, Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59715; Mark J. Young, Department of Plant Science, Montana State University, Bozeman, Montana 59715.

EPR spectroscopy with site-directed spin labeling has emerged as a powerful tool for the study of the structure and dynamics of biological macromolecules. In typical applications single labels or a pair of labels are placed at selected locations within a protein. In this work we explore the feasibility and utility of spin-label studies involving “lots and lots” of spins. The protein coat of the CCMV (cowpea chlorotic mottle virus) provides a template for exploring chemico-physico properties of large assembly of interacting spins. CCMV is composed of 180 chemically identical sub-unit proteins; each sub-unit has a molar mass of 19.8 kD and 190 amino acids. The assembled virus protein cage exhibits a Ca<sup>2+</sup> and pH dependent structural transition that involves a swelling of a close packed, icosohedral structure - in which the cage has an outer diameter of ~29 nm and a thickness of ~ 25 Å - to an open structure that admits sixty pores ~20 Å wide, and has an overall diameter of ~31 nm. The cooperativity of this transition is poorly understood, and the possible existence of intermediate structures has not been addressed. This study aims to characterize the structure, dynamics, and kinetics of CCMV through the use of methanethiosulfonate spin label (MTSSL) and EPR spectroscopy, with the specific goal of using the dipolar interaction among many spin labels to probe the cooperativity of this structural transition.

#### **EPR Symposia Poster Session**

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96. **Phosphorus Doped Silicon As a Candidate for Quantum Computing. The Relaxation Mechanisms Revisited.** Johan van Tol; Marco Bortolus; Louis-Claude Brunel, Florida State University, National High Magnetic Field Laboratory, Center for Interdisciplinary Magnetic Resonance, Tallahassee, FL 32310.

Different authors suggested the use of Si-based technology for the realization of Quantum Computers [1,2]. Mostly Phosphorus doped devices are proposed, in which electron nuclear interactions are involved. Little has been done regarding the properties of Si:P since the pioneering works of Feher [3,4] in the fifties, and the proposals concerning a Si-based approach rely on exchange interaction and relaxation mechanisms that need further study. In particular the relaxation times in Si:P are dependent on dopant concentration, strain, temperature, magnetic field, and the presence of <sup>29</sup>Si nuclear spins. We decided to systematically study the relaxation and dynamic nuclear polarization mechanisms in the relevant Si:P samples by pulsed EMR and pulsed ENDOR and TRIPLE at X-band and CW EPR/ENDOR at 220 GHz. We focused on samples with [P] in the 10<sup>14</sup>-10<sup>16</sup> P atoms/cm<sup>3</sup>, and made with natural Si, with 4.7% <sup>29</sup>Si. The results are discussed in relation to the possible use of phosphor-doped silicon in quantum computing.

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97. **Determination of the Binding of S-Adenosylmethionine to the Catalytically Active [4Fe-4S]<sup>+</sup> Cluster of Pyruvate Formate-lyase Activating Enzyme by 35 GHz ENDOR.** Charles J. Walsby, Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston, IL 60208-3113; Danilo Ortillo, Wei Hong, William E. Broderick, Jennifer Cheek, Joan B. Broderick, Michigan State University, East Lansing, Michigan 48824-1322

Pyruvate formate-lyase activating enzyme (PFL-AE) is a representative member of an emerging family of enzymes that utilize S-adenosylmethionine (AdoMet) to initiate radical catalysis. We have used 35 GHz EPR and ENDOR to demonstrate that the iron-sulfur cluster participates directly in the formation of a 5'-deoxyadenosyl radical. The EPR spectrum of the [4Fe-4S]<sup>+</sup> cluster of PFL-AE (S = 1/2) is affected dramatically by the presence of AdoMet, changing it from rhombic (g = 2.02, 2.94, 1.88) to nearly axial (g = 2.01, 1.88, 1.87). <sup>2</sup>H and <sup>13</sup>C Mims ENDOR experiments of [4Fe-4S]<sup>+</sup>-PFL-AE in the presence of AdoMet labeled at the methyl position have shown substantial <sup>2</sup>H couplings (~ 1 MHz) as well as hyperfine-split signals from <sup>13</sup>C indicating that the AdoMet lies close to the cluster. Further, Davies ENDOR experiments with <sup>17</sup>O and <sup>15</sup>N labels on the methionine end of AdoMet have demonstrated bidentate coordination to the unique iron site of the cluster. We have performed 2D field-frequency analyses on the spectra from all four labeled nuclei and have determined the distance from the cluster to the <sup>2</sup>H and <sup>13</sup>C labeled atoms of the methyl group and simulated the ENDOR from the coordinated nuclei. Both EPR and ENDOR have been obtained for the interaction of AdoMet with the [4Fe-4S]<sup>2+</sup> state of PFL-AE, which was visualized through cryoreduction of the frozen [4Fe-4S]<sup>2+</sup>/PFL-AE complex to form the reduced state in the structure of the oxidized state. All spectra were essentially identical to those of the of the [4Fe-4S]<sup>+</sup> which had been reduced at room temperature showing that the cofactor binds in the same geometry to both the 1+ and 2+ states. Supported byt NIH HL 13531 (B.M.H) and NIH GM54608 (J. B.B.).

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98. **Passages.** David J. Singel, Eric D. Walter, Sean J. McIlwain, Dwight A. Schwartz, Department of Chemistry and Biochemistry, Montana State University Bozeman, MT 59717

Although conventionally regarded as “unwanted”, rapid passage effects are commonly and easily encountered in CW high-frequency EPR spectroscopy [1,2]. An exploration of these effects - featuring experimental studies of simple, “test-bed” systems in combination with detailed numerical simulations - will be reported. The simulations involve direct integration of Bloch equations augmented with sinusoidal external field modulation. Results obtained by numerical integration will be contrasted with results obtained by approximate analytical treatments presented in prior studies [3]. The dependence of EPR signal amplitudes, line width, and line on experimental variables – specifically, incident microwave power, and field modulation frequency will be described. Results will be discussed with the primary aim of identifying experimental strategies: to maximize signal amplitude (~100-fold), while maintaining readily interpretable line shapes; and to selectively minimize amplitudes, for spectral-editing applications. We also aim to define the range of experimental conditions over which salient spectral properties are alternatively highly sensitized to, or robust against, variation of conditions and of relaxation properties.

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99. **Broad-band ENDOR Coil Matching Circuit for Liquid Helium Temperature K-band EPR/ENDOR Resonance Cavity.** Tomasz Wasowicz, William H. Nelson, Georgia State University Department of Physics and Astronomy, 29 Peachtree Center Ave, Ste. 400, Atlanta, GA 30303

In ENDOR systems the high level of RF power can cause substantial baseline effects when the overall transmission line system containing the RF coil includes significant lengths with impedance mismatch. This effect is especially disturbing in cases requiring sweep of the RF over a wide frequency range. A frequency-independent impedance matching circuit as described previously<sup>1,2</sup> was implemented for a low temperature (4 K) K-band ENDOR cavity – part of a home-built K-band EPR/ENDOR spectrometer. The two-turn RF coil is connected in series with 50 ohm load in one branch, parallel to cryogenic non-magnetic trimmer (1.5-55.0 pF from Voltronics) connected in series to another 50 ohm load. In this arrangement, all lengths of transmission line are connected to 50 ohm impedances since the RF coil and the capacitor are immediately adjacent to each other at the cavity in the liquid He cooled cryostat. Both 50 ohm resistors are mounted on a water cooled plate placed outside of the cryostat. The circuit provides flat ENDOR baseline response in RF frequency range from few up to about 110 MHz.

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100. **A Liquid-solution EPR Study of 2,2-diphenyl-1-(monosulfodinitro)-hydrazyl Salts.** D.F. Howarth, M.D. Lafond and J.A. Weil, Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, SK S7N 5C9, Canada.

The electron paramagnetic resonance (EPR) spectroscopic characterization of several stable paramagnetic salts of sulfonated versions of the well-known free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) is presented herein. Liquid-solution room-temperature EPR spectra of the previously unknown 2,2-diphenyl-1-(2,6-dinitro-4-sulfofenyl)hydrazyl (i.e., the *para* version of the) salt with the 2,2-diphenylhydrazinium ion (DPH<sup>+</sup>) in a variety of solvents, including water, were obtained. In addition, we have gathered EPR spectra for the analogous potassium (K<sup>+</sup>) salts of both the *ortho*- and *para*-sulfonated (–1) anions in solvents not previously studied. The EPR parameters obtained demonstrate that, except for a few exceptions, the unpaired-electron probability density at the hydrazinic nitrogen nuclei is relatively unaffected by the hydrogen-bonding and the polarizability capabilities of the organic solvents studied. However a significant shift of the unpaired-electron density does occur when these sulfonated hydrazyl salts are dissolved in water. Possible reasons for the observed effects are discussed.

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101. **A Regularized Inverse-filtering Technique for Suppressing Noise and Blurring in Spatial EPR Imaging.** Benjamin B. Williams, Kazuhiro Ichikawa, Chien-Min Kao, Howard J. Halpern, Xiaochuan Pan, University of Chicago, Departments of Radiation Oncology and Radiology, Chicago, IL 60637 and the Center for EPR Imaging In Vivo Physiology

Electron paramagnetic resonance imaging has been used to map in vivo spatial distributions of endogenous and introduced free radicals. Because of the appreciable spectral linewidths of the radicals and the finite magnitude of the gradients, it is necessary to perform deblurring and noise suppression to achieve images with high spatial resolution. Recently, a regularized inverse-filtering technique for suppressing noise and blurring was described and evaluated for use with 3D single photon emission computed tomography.<sup>1</sup> This filtering technique uses an *a priori* random image field (RIF) to specify the expected region of support and degree of smoothness in the image. Here, we generalize this technique for application to spatial EPR imaging, including a realistic noise model and experimentally measured blurring function. A set of experimental spectra for a 2D spatial image was acquired. Images were reconstructed from the original spectra and again after the implementation of a previously described deconvolution technique<sup>2</sup> or the generalized RIF technique. This was repeated after addition of Gaussian distributed random noise. The resulting images and profiles through the signal regions were qualitatively compared. Without the addition of noise, where the RIF technique reduces to the deconvolution technique, spatial resolution is markedly improved. With added noise, application of the deconvolution technique resulted in an image with suppressed noise, but compromised spatial resolution. The RIF filtering technique suppressed image noise with less degradation of the spatial resolution. These results demonstrate the ability of the generalized RIF filtering technique to reduce image blurring and to suppress noise while maintaining spatial resolution in spatial EPR images. Supported by NIH RR-12257.

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102. **Extraction of Linewidth Information from Spatial-spectral EPR Images Using Spectral Fitting.** Benjamin Williams, Kang-Hyun Ahn, Colin Mailer, Howard Halpern, University of Chicago, Department of Radiation Oncology, Chicago, IL 60637 and the Center for EPR Imaging in Vivo Physiology

In vivo oxymetric imaging may be accomplished through measurement of the localized EPR linewidths of an injected spin probe solution. The spin probe solution is injected intravascularly and distributes throughout the fluid compartment of the subject, though not uniformly. Local oxygen concentration may be calculated from the estimated linewidths through an empirical linear calibration. In order to make a diagnostic decision based on the estimated oxygen concentration values it is necessary to consider the reliability of the linewidth measurements. Linewidth estimates in some pixels may be unreliable due to significant corruption by image artifacts or due to their proximity to the edges of the object. Many studies have made use of thresholding based on spectral intensity to distinguish those pixels with reliable linewidth estimates from those with dubious values. Though this method has been used with some success, it has some serious drawbacks. At low concentrations, the linewidth and spectral intensity are independent, though low intensity spectra will be more susceptible to image noise and artifacts. Also, thresholding is a binary decision criterion and does not account for continuously distributed errors. Additional information provided by spectral fitting may be used to better distinguish those pixels with meaningful linewidth estimates in an objective and statistically significant manner. Pixels may be excluded based on the estimated spectral centers, linewidths, RF phase and known physical or physiologic conditions. For instance, spectra with offset centers or unreasonably large linewidths may be excluded. The errors in the estimated linewidths may be used to weight the statistical significance of the linewidth estimate in each pixel. Spectra with linewidth errors inconsistent with that based on random noise may contain image artifacts contaminating the linewidth measurement. Information from spectral fitting was used in the analysis of images of objects with inhomogeneous linewidths and intensities.

*Supported by NIH RR-12257.*

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- 103. EPR Studies of Vanadia Gels.** James Woodworth, Sarah C. Larsen, Department of Chemistry, University of Iowa, Iowa City, IA 52242; Craig Fontenont, Jerzy Wiench, Marek Pruski, Glenn Schrader, Department of Chemical Engineering and Ames Laboratory-USDOE, Iowa State University, Ames, Iowa 50011

Sol-gel synthesis is a promising method for the preparation of metal oxides and mixed metal oxides with physical properties that lead to high catalytic activity for selective oxidation reactions. In this study, peroxovanadates are being used as reactive precursors in the sol-gel synthesis of binary and ternary catalysts. The resulting materials were characterized using solid state NMR, x-ray diffraction, and thermal gravimetric analysis. The  $V^{4+}$  species in vanadium and vanadium/molybdenum gels were characterized using EPR spectroscopy. Quantitative and structural information about the  $V^{4+}$  species present during the sol-gel synthesis was obtained from the EPR spectra. The EPR results were correlated with the  $^{51}V$  NMR results.

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- 104. EPR Study of  $Cr^{3+}$  Ion in a  $PbWO_4$  Single Crystal.** T.H. Yeom, I.G. Kim, and S.H. Lee, Chongju University, Department of Physics, Chongju 360-764, Korea; S.H. Choh, Korea University, Department of Physics, Seoul 136-701, Korea; T.H. Kim and J.H. Ro, Pusan National University, Department of Physics, Pusan 609-735, Korea

The lead tungstate ( $PbWO_4$ ) single crystal has been intensively studied in recent years due to its potential application as a scintillation material for calorimetric detectors in high-energy accelerations.<sup>1,2</sup> Since  $PbWO_4$  has the structural sensitivity and its luminescence is remarkably affected by doping ions in the crystal, the doping of various ions into  $PbWO_4$  has become a conventional way to find the approach to improve its luminescence,<sup>3</sup> emission, transmittance and scintillation characteristics. Lead tungstate single crystals doped with  $Cr_2O_3$  were grown by the Czochralski method in Ar atmosphere. The electron paramagnetic resonance of the  $Cr^{3+}$  ion in a  $PbWO_4$  single crystal has been investigated using an X-band spectrometer. The spectroscopic splitting tensor and zero-field splitting parameters are determined with the effective spin Hamiltonian. The local site symmetry of the  $Cr^{3+}$  ion in  $PbWO_4$  crystal is studied. Energy levels of the ground state for  $Cr^{3+}$  embedded in the crystal are calculated. The substitutional sites of  $Cr^{3+}$  ion are also discussed.

Supported by grant No. (R05-2002-000-00006-0) from the Basic Research Program of the Korea Science & Engineering Foundation.

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- 105. The Effects of Conjugated Linoleic Acid on Oxidative Damage in Membranes.** Jun-Jie Yin, Magdi M. Mossoba, Yuoh Ku, Martin P. Yurawecz. Center for Food Safety and Applied Nutrition, FDA, MD 20740 and John K.G. Kramer, Southern Crop Protection, Food Research Center, Ontario, Canada

The effect of CLA on the relation between structure and function of membranes is described in this work. Electron spin resonance (ESR) spin-label oximetry was used to evaluate if oxygen transport and oxygen depletion was affected by incorporation of conjugated linoleic acid (CLA) instead of linoleic acid (LA) into membrane phospholipids. Specifically, 1-stearoyl-2-(9*cis*,11*trans*-octadecadienoyl)-phosphatidylcholine ( $C_9T_{11}$  CLA) and 1-stearoyl-2-(10*trans*,12*cis*-octadecadienoyl)-phosphatidylcholine ( $T_{10}C_{12}$  CLA) was incorporated into soy plant phosphatidylcholine (Soy PC) and egg yolk PC (EYPC) bilayers. Moreover, the use of spin labels attached to different carbons along the fatty acid chain makes it possible to carry out structural and oximetric determinations with the same test sample. Specifically, the incorporation of 5 mol% CLA increased the oxygen diffusion-concentration product in soy PC or EYPC liposomes at 37°C, slightly decreased the ordering of the hydrocarbon chains at the C10 and C12 positions (in the region of the conjugated double bonds). In our model system, free radical generation was initiated by incubation of the liposomes, induction by AAPH, AMVN or by ultraviolet (UV) irradiation of  $H_2O_2$ . The effects on the oxygen consumption rate of 5 mol% CLA in soy PC was significantly larger compared to the 5 mol% LA in soy PC; the response patterns with soy PC and EYPC were similar. The perturbation of membrane structure and the increase of the relative oxygen diffusion-concentration products provided a potential mechanism by which CLA incorporated into membrane lipids could affect oxidative stress.

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106. **The Application of Microprocessors to EPR Instrumentation.** Richard W. Quine, University of Denver, Department of Engineering, Denver, CO 80208

The first microprocessor, dubbed the “4004”, was invented and first marketed by the Intel Corporation in 1971. While ultimately leading to the ubiquitous Personal Computer, microprocessors also generally revolutionized the way circuit design is done. In particular the use of imbedded microprocessors in scientific instrumentation has led to much more accurate and reliable control of complex processes and has made most systems much more user friendly than would have otherwise been the case. Some instances of the uses of microprocessors in EPR instrumentation will be reviewed, including a specialized timing unit for Saturation Recovery spectroscopy, a Programmable Timing Unit for the control of complex pulses sequences in ESE spectroscopy, a control system for a VHF spectrometer and, finally, the microprocessor implementation of a boxcar averager.

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107. **Frequency Dependence of EPR Signal Intensities.** George A. Rinard, Department of Engineering, University of Denver, Denver, CO 80208

Comparisons were made for three different samples in two pairs of loop gap resonators. Each pair was geometrically scaled by a factor of 6. One pair of resonators was scaled from 250 MHz to 1.5 GHz, and the other pair was scaled from 1.5 GHz to 9 GHz. All terms in the comparison were measured directly, and their uncertainties estimated. When both the resonator size and the sample size are scaled with the inverse of RF/microwave frequency,  $\omega$ , the EPR signal at constant  $B_1$  scales as  $\omega^{-1/4}$ . The theory predicts that the signal at the lower frequency will be larger than the signal at the higher frequency by the ratio 1.57. For 250 MHz to 1.5 GHz, the experimental ratio was 1.52 and for the 1.5 GHz to 9 GHz comparison the ratio was 1.14. Experimental EPR signal intensities at 250 MHz, 1.5 GHz, and 9.1 GHz agree within experimental error with predictions from first principles.<sup>[1]</sup>

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108. **Broadband FT-ESR at 95 GHz.** Keith Earle, Wulf Hofbauer, Curt Dunnam and Jack Freed, Baker Laboratory of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853

We report the development of a pulsed 95GHz spectrometer using a high-powered coherent source and a quasiopitcal bridge developed at Cornell University for the study of dynamical processes in simple and complex fluids. The source is an extended interaction klystron EIK (CPI Canada) with nominal power output of 1kW and a bandwidth of 511MHz. We operate the EIK as an amplifier EIKA with modulator and control software developed by us. The EIKA is driven by a commercial transmit/receive unit (ELVA-1) with a nominal maximum output of 80mW, full quadrature phase-cycling capability, receiver protection circuitry, minimum pulse width of 2.5ns and minimum pulse separation of 10ns. We operate the quasiopitcal bridge, designed and built at Cornell University, in the induction mode to maximize the isolation of the receiver from pulse feed-through in the transmit arm. In initial experiments, we have achieved  $\pi/2$  pulses of 4ns, that allow full irradiation of motionally narrowed nitroxide spectra at 95GHz. The timing system is sufficiently flexible to allow us to perform simple FID and echo experiments, as well as more sophisticated two- (SECSY and COSY) and three- pulse sequences (2D-ELDOR) with full phase cycling. We illustrate the capabilities of this unique instrument with a variety of examples in solid and liquid systems. We thank Peter Borbat for useful discussions and assistance with the hardware and software to facilitate the multi-pulse and phase-cycling experiments reported here. We also thank Józef Moscicki for his assistance in the early stages of this work. Supported by NIH RR16292 and NSF CHE-0098022.

### EPR Symposia Oral Session

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- 109. Multi Technique EPR Study of the Photo-excited Triplet State of Substituted Thiophenes with Two and Four Oligomeric Units.** Antonio Barbon; Anna Lisa Maniero; Marina Brustolon, Università degli Studi di Padova, Dipartimento di Chimica Fisica A. Miolati, Padova, Italy; [Marco Bortolus](#); Johan Van Tol; Louis-Claude Brunel, Florida State University, National High Magnetic Field Laboratory, Center for Interdisciplinary Magnetic Resonance, Tallahassee, FL 32310.

The combination of Time-Resolved EPR methodologies, Transient High-Frequency EPR (up to 240GHz), and X-band Pulsed EPR, conveys a full wealth of information about the excited triplet state of a system, both on an electronic level and on a molecular level. Substituted Thiophenes are good examples of such systems. The simulation of the cw spectra, both at X-band and at high field, gave us the Zero-Field Splitting tensor principal values, the g tensor principal values, the relative orientation of the two tensors, and the population of the triplet sublevels. Pulsed X-band experiments characterized the relaxation properties of the magnetization and the properties of the residual motion in rigid matrices; the effect of different solid matrix environments on the dynamic properties has also been highlighted.

**EPR Symposia Oral Session**

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- 110. Electric Field Effects on Nitroxide Spin-labels Observed by High Frequency EPR.** [David E. Budil](#), Rajesh Satyamurti, Kevin McCabe, and Andrea Gullà, Department of Chemistry, Northeastern University, Boston MA 02115

It has been demonstrated that both the nuclear hyperfine interaction and the electronic g-tensor of nitroxide spin labels are sensitive to local electric fields. The g-factor resolution achievable by high frequency EPR (HFEP) renders the  $g_x$  principal value sensitive to electric field magnitudes of at least  $10^6 \text{ V cm}^{-1}$ . Such magnitudes are comparable to the local fields expected near charged groups on the surface of a protein. We present some preliminary calculations of local electric field distributions at the label site of selected spin-labeled proteins that predict that both the center and the width of the HFEP  $g_x$  peak of a nitroxide on the protein surface should change significantly with pH. At surface label sites, the average field sensed by the nitroxide exhibits a sigmoidal pH dependence that reflects the titration of nearby ionizable groups. The results also suggest that the broadening near  $g_x$  that is typically observed in HFEP is more than simply nuisance "g-strain"; the underlying distribution of  $g_x$  values may contain useful information about the distribution of charged groups on the protein surface. The electric field sensitivity of  $g_x$  also suggests that experimentally attainable applied electric fields should produce a linear electric field effect (LEFE) in nitroxides, analogous to the effect that is observable in transition metal ions by conventional EPR. Possible approaches to studying the LEFE in spin-labeled proteins are discussed.

**EPR Symposia Oral Session**

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- 111. Identification and Characterization of a Remarkably Stable Flavin Radical in the  $\text{Na}^+$ -pumping NADH:quinone Oxidoreductase: High-frequency EPR and ENDOR Studies.** [Mark J. Nilges](#), Illinois EPR Research Center, University of Illinois at Urbana-Champaign, 506 S. Mathews St. Urbana, IL 61801; Blanca Barquera, Joel E. Morgan, and Robert B. Gennis, Department of Biochemistry, University of Illinois at Urbana-Champaign, 600 South Mathews St. Urbana, IL 61801, USA; Dmitriy Lukoyanov and Charles P. Scholes, Department of Chemistry and Center for Biological Macromolecules, University at Albany, State University of New York, Albany, NY 12222

$\text{Na}^+$ -NQR is the entry point for electrons into the respiratory chain of *Vibrio cholerae*. It oxidizes NADH, reduces ubiquinone and uses the free energy of this redox reaction to translocate sodium. The enzyme is a membrane complex of six subunits that accommodates a 2Fe-2S center and several flavins. The enzyme also contains an unusual radical, present in both oxidized and reduced enzyme. We present high-frequency EPR and ENDOR data clearly showing that this radical is a flavin-semiquinone. By combining results of ENDOR and multifrequency cw EPR, we have made an essentially complete determination of the g-matrix and all major nitrogen- and proton-hyperfine matrices. From careful analysis of the W-band data, the full g-matrix of a flavin radical has been determined for the first time and the g-matrix has significant rhombic character, which decreases significantly upon deprotonation. The out-of-plane component of the g-matrix and that of the nitrogen hyperfine matrices are found to be non-coincident as a result of puckering of the pyrazine ring. We show that in the oxidized enzyme, the flavin radical is in its neutral form, while in the reduced enzyme its anionic form. The data are consistent with the explanation that the neutral and anionic radicals both arise from the same flavin moiety. The role of the flavin radical and its deprotonation upon reduction of the enzyme will be discussed as it relates to translocation of  $\text{Na}^+$  by the enzyme.

**EPR Symposia Oral Session**

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112. **Cu<sup>2+</sup> – Framework Al: HYSCORE, High Field ENDOR and DFT.** Patrick Carl, Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel; D.E.W. Vaughan, Material Research Laboratory, Penn State University, State College, PA; D. Goldfarb, Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel

In transition metal ion (TMI) exchanged zeolite catalysts, the framework charge distribution (Si:Al ratio) of the zeolite has been shown to be important in the distribution and the local structure of the TMI center as indicated by changes in catalytic activity. In this work we investigate the specific dependence of the Cu<sup>2+</sup>-framework Al interaction in a series of copper(II) exchanged zeolite X and Y catalysts with Si:Al in the range 1-12 in hydrated and dehydrated states. The interactions of the Cu<sup>2+</sup> with framework Al was followed using the two-dimensional hyperfine sub level correlation (HYSCORE) experiment which reveals a surprisingly large <sup>27</sup>Al hyperfine coupling in hydrated zeolites with Si/Al ≤ 5. Moreover, HYSCORE measurements reveal a decrease in the observed <sup>27</sup>Al hyperfine coupling as the Si:Al ratio decreased. A combination of simulations of the experimental data and the use of DFT calculations on model six-ring structures was used to interpret the experimental spectra. HYSCORE simulations indicate that peak positions and intensities can be used to determine the number of interacting Al. DFT calculations indicate the decrease in <sup>27</sup>Al hyperfine coupling with decreasing Si:Al ratio can result from an increase in the number of Al in the six-ring. Analysis of the HYSCORE spectra indicate the Cu<sup>2+</sup> associates with only one <sup>27</sup>Al at Si:Al ratios as low as 2.5. At lower Si:Al, a second peak appears in the HYSCORE spectra which can be attributed to weakly coupled <sup>27</sup>Al. The presence of water or hydroxyl ligands was followed by W-band <sup>1</sup>H ENDOR. Orientation selective ENDOR experiments indicate the presence of multiple water ligands around the Cu<sup>2+</sup> with <sup>1</sup>H at a distance between 2.7-2.8 Å in the hydrated state.

#### **EPR Symposia Oral Session**

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## **FTIR • Wednesday Oral Sessions**

113. **Wheat Straw Composites: The Effect of Temperature on the Infrared Spectra.** S. Amanuel, V.M. Malhotra, Southern Illinois University at Carbondale, Department of Physics, Carbondale, Illinois 62901-4401.

Wheat straw, an abundant but renewable and environmentally friendly resource, has a remarkable composite structure, which can be exploited to form nano-bio-composites, especially for the automotive and structural industries. However, before this can be accomplished, we need to understand how the straw's composite structure is affected under thermal perturbations. In pursuit of this, we undertook in-situ high temperature diffuse reflectance-infrared (INHTDR-IR) spectroscopic measurements at 300 K < T < 850 K on micronized straw to gauge how the chemical and physical structures of it were altered. Additional supportive evidence was obtained from differential scanning calorimetry (DSC) and scanning electron microscopic (SEM) measurements. Our INHTDR-IR results suggest that there are four distinct structural phases of straw in the temperature range of 300 K – 850 K, and these phases can have a profound effect on the formulation and the performance of the composites. Based on these results, structural composites were formulated from straw at 423 K, 433 K, 443 K, 453 K, and 463 K. The dynamic mechanical analyzer (DMA) and three-point flexural bending mechanical tests suggest that strength of the material increases as the formation temperature is increased. Infrared results on the formed composites suggest that hydroxyl groups play a crucial role in the curing of the natural polymers in straw.

#### **FTIR Symposia Oral Session**

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114. **Infrared – Spectral Searching for the Best.** Ty Abshear, Bio-Rad Laboratories Inc., Informatics Division, 3316 Spring Garden Street, Philadelphia, Pa. 19104; Michael Boruta, Bio-Rad Laboratories Inc., Informatics Division, 3316 Spring Garden Street, Philadelphia, Pa. 19104

Until recently, the ability to access large amounts of high-quality, full spectrum infrared data was only available to a small number of well-funded laboratories. Until recently this restricted the number of people who had access to even moderate amounts of spectra data. With some recent changes in the pricing structure of how data can be accessed, large data sets are now available to almost anyone who has an infrared spectrometer. These changes along with the impact of these changes on the selection of spectral search strategies will be reviewed. The fundamentals of spectral search strategies will be explored including examples that produce poor results and ways to improve these results. In addition this paper will look at strategies that can be employed to take advantage of the vast amount of data that is currently available.

#### **FTIR Symposia Oral Session**

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115. **FTIR Microscopy: Determining Composition and Manufacturer of Over the Counter Medications.** Shannon M. Richard, Shimadzu Scientific Instruments, 7102 Riverwood Drive, Columbia, MD 21046

FTIR spectroscopy has long been a standard method in the pharmaceutical industry. It has been used for years in the research and development of new drugs as well as a quality control method. In today's market place there are a variety of over the counter medications. While each of the medications is unique in its own rights, it is sometimes hard to determine what these medications are by their outward appearance. FTIR microscopy allows the ability to measure cross sections of various over the counter medications. The coatings as well as the interior components of each particular tablet or capsule can be directly determined from each cross section. With this information, in combination with a spectral database containing a variety of known samples, an unknown medication or drug can be quickly and easily identified.

**FTIR Symposia Oral Session**

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116. TBA

117. TBA

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## General Posters • Monday, Tuesday & Wednesday Sessions

118. **A Fully Integrated Data Management Environment for Raman Spectroscopy.** Mark Hollenbach, and Eric Melanson, Bio-Rad Laboratories, Informatics Division, 3316 Spring Garden Street, Philadelphia, PA 19104-2596 USA

An informatics solution is presented that provides organic, inorganic, polymer and analytical chemists with a reliable source of Raman data that they can use as a reference in the first, fully integrated data management environment for Raman spectroscopy. Software modules are described to manage various analytical tasks, including methods to build and search databases of Raman spectra, and cross-reference Raman data with other analytical techniques. In addition, the system supports the import and interpretation of Raman spectral data and correlates spectra and structure with functional groups and includes tools to draw and annotate chemical structures. Spectral data can be processed to optimize search results, and searching can be done on names, structure, substructure, and properties in addition to multiple spectral search algorithms. Either commercial or user-created databases can be managed and searched; user databases can include a unique weblink capability that expands and extends the informatics environment and its utility. Through the use of a single interface in an integrated Raman informatics environment, switching between multiple programs is seamless and the training issues are eliminated. Data from multiple analytical techniques--including <sup>1</sup>H and <sup>13</sup>C NMR, IR, NIR, Raman, MS, GC, and UV--can also be accessed, searched, processed or analyzed as well as presented in reports or web publications.

**General Poster Session**

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119. **Enzyme-based Sensor Arrays for Simultaneous Detection of Multiple Analytes in Solution.** David J. Javier, Anuradha Kochhar-Prasad, Theo Curey, Mary A. Salazar, Jason B. Shear, University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX 78712

Measurement of multiple components in complex solutions presents significant analytical challenges. To circumvent issues that can limit the utility of separation procedures (e.g., inadequate resolution, poor specificity and extended analysis times), we are developing an integrated enzyme-based sensor array that can efficiently and simultaneously analyze multiple analytes, including mono- and disaccharides, alcohols, glycerol, and other small biological solutes. In our approach, enzymes are immobilized on porous agarose beads, which then are localized to addressable sites on a microfabricated silicon chip. Detection is accomplished by coupling enzyme-catalyzed consumption of analytes to fluorometric and colorimetric reporting schemes. Our current research focuses on extending the dynamic range of analysis by using multiple sensors for each analyte in which the amount and ratio of multiple enzymes required for a sensing scheme are varied. Alternatively, a particular enzyme isolated from different biological sources can maintain significantly different kinetic parameters, a fact that opens the possibility to devise enzyme-based sensing strategies that can be tuned for different concentration regimes. An important consideration in creating versatile arrays capable of analyzing the widest range of analytes is the potential need for creating localized microenvironments at different sensing sites.



Initially, we are exploring immobilization of pH-altering macromolecules at select sensor sites as a means to create localized pH environments.

#### General Poster Session

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- 120. The Analytical Digital Sciences Library (ASDL).** C.K. Larive and T. Kuwana, University of Kansas, Department of Chemistry, Lawrence, KS, 66045; S.J. Chalk, University of North Florida, Department of Natural Sciences, 4567 St. Johns Bluff Road S., Jacksonville FL 32224; R.C. Dorey, University of Central Arkansas, Department of Chemistry, Conway, AR 72035; G.R. Long, Indiana University of Pennsylvania, Department of Chemistry, Indiana, PA 15705-1085; F. Settle, Washington & Lee University, Department of Chemistry, Lexington, VA 24450

The Analytical Sciences Digital Library (ASDL), a NSF funded National Digital Sciences Library project will be described. The ASDL is an electronic library that collects, catalogs and links peer reviewed web-based discovery materials pertinent to innovations in curricular development and supporting resources in the Analytical Sciences. Illustrations of the types of materials included in the collection will be presented such as innovations in teaching and learning pedagogy, resource materials for analytical sciences course and laboratory instruction, supplementary materials on analytical instrumentation and methods and a discussion forum to promote interactive discussions about teaching and learning in the analytical sciences.

#### General Poster Session

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- 121. Traceability of Measurements in Spectrometry.** Jerry D. Messman, Stranaska LLC, P.O. Box 270334, Fort Collins, CO 80527-0334 USA.

Molecular absorption spectrophotometry is an important measurement technique in many industrial sectors. For a spectrophotometer to be compliant with laboratory measurement quality assurance and regulatory requirements, it shall be calibrated at regular intervals by personnel having the necessary education, training, and experience. The laboratory may assign this important calibration responsibility to one of its own analysts, or it may outsource the calibrations to the corporate instrumentation unit, instrument manufacturer, or an independent third-party calibration company. Certified reference material (CRM) standards are integral to the calibration process, and the CRMs must be traceable to national and international standards for the calibration to be in compliance. Unchallenged "self-declaration" claims of traceability represent the historical norm for spectrophotometric CRMs, but now they are coming under close scrutiny as quality inspectors and regulatory auditors become more knowledgeable about the specific requirements comprising the international definition of traceability. The need for proof of measurement traceability is applicable to spectrophotometric standards from non-accredited CRM suppliers as well as from accredited laboratories that do not have a scope for spectrophotometric certification and recertification measurements on the relevant CRM. This paper will address how the international definition of traceability applies to spectrometry companies or organizational units in the private sector that provide certification and recertification of secondary wavelength, photometric and stray radiant energy (stray light) standards. The presentation will focus on science-based issues impacting the validity of claims of traceability such as rigor of calibration procedures, relevancy of transfer standards, benchmark timelines, measurement uncertainty analysis and budget, and Certificate contents.

#### General Poster Session

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- 122. Continuous Real-time Monitoring of Elemental and Oxidized Mercury in Waste Incinerator Stack Emissions.** Brian Radford and Don Almond, Genesis Laboratory Systems, 1005 North 12<sup>th</sup> Street #214, Grand Junction, CO 81501.

Mercury emissions from incinerator waste combustion pose a serious environmental concern requiring thorough compliance monitoring. Unfortunately, most installed stack gas monitors used to verify incinerator compliance with existing emission regulations fail to provide thorough mercury monitoring capabilities. Common monitors neither operate in real-time nor detect both elemental and oxidized mercury species. Batch monitors require chemical process and/or amalgamation delays before a mercury concentration reading may occur. Small, but highly concentrated mercury peaks are routinely averaged over the batch period (often exceeding 15 minutes) sometimes falsely representing an unacceptable over-limit peak concentration as a much lower time-averaged concentration. Elemental-only mercury monitors fail to report concentration readings for oxidized mercury compounds that are often present in stack gas emissions. Genesis Laboratory Systems has developed a continuous emission mercury monitor (CEMM) capable of monitoring incinerator stack gas emissions in real-time. Without process or amalgamation delays, this new monitor can produce updated mercury concentration readings every second. Elemental mercury in the incinerator stack gas is monitored by direct atomic absorption spectroscopy (AAS). Oxidized mercury compounds are first converted catalytically to ground state mercury and then analyzed by AAS in a separate path. In addition to the speciated path results, results for both paths are combined to provide total gaseous mercury concentration. Genesis Laboratory Systems is a participant in the 2002 Oakridge National Laboratory Environmental Technology Verification

Program sponsored by the EPA. The ETV program is a pilot-scale verification of commercial continuous emission mercury monitors. The paper will present the results of Genesis Laboratory Systems' mercury stack monitor in the ETV program.

#### **General Poster Session**

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- 123. Minimizing Your Instrument Background for Total Organic Carbon (TOC) Analysis.** Brian Wallace, Mike Purcell, and Ken O'Neal. Tekmar-Dohrmann, 4736 Socialville-Fosters RD, Mason, OH 45040.

Consideration of detection limits is important for low-level TOC measurements, particularly of pharmaceutical and drinking waters. An instrument detection limit not only establishes the minimal amount of TOC in a sample that is quantifiable, but it is also an indirect indicator of the ease at which TOC in samples can be measured with good accuracy and precision. Detection limits are determined by the ratio of sample response to background for a given TOC instrument. Instrument background, often referred to as the instrument blank, can be broken down into elements that are common to all TOC instrumentation and elements that are specific to a particular oxidation technology. General background elements include: the rinse water used to clean sample pathways, the TOC derived from the surface encountered in the sample pathway either from the material itself (often Teflon based) or through permeation of that material by CO<sub>2</sub> in the atmosphere, and any TOC contribution from the acid that is used in the removal of inorganic carbon interferences. The design of this experiment is to present a description of common challenges experienced with the instrument blank for TOC analysis using the most commonly used oxidation techniques of UV/persulfate and High Temperature Combustion (HTC). Minimization of contamination from sampling containers, reagents, rinse water and carrier gases will be discussed using both techniques.

#### **General Poster Session**

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- 124. Total Organic Carbon Analysis As a Precursor to Disinfection Byproducts.** Brian Wallace, Mike Purcell, and Ken O'Neal. Tekmar-Dohrmann, 4736 Socialville-Fosters RD, Mason OH 45040.

Conflicting views have challenged the opinion that both UV/ Persulfate and catalytic combustion methods are both acceptable oxidation technologies for the TOC analysis of natural organic matter (NOM) of potable water. In recent years, an increasing number of regulations and methodologies are utilizing Total Organic Carbon (TOC) analysis for monitoring microbial contamination and/or disinfectant byproduct (DBP) precursors. This paper highlights some analytical differences and similarities between the two widely used TOC oxidation techniques: persulfate and high temperature combustion (HTC). Previous papers have come to different and sometimes contradictory conclusions on this subject. However, these studies either compared instruments with significantly different flow paths or TOC systems from different eras. Unlike previous studies, this paper compares two modern TOC analyzers with nearly identical flow paths for sample recovery, detection limits, and analysis of particulates. On average, both persulfate and HTC oxidation yielded good recoveries for hard to oxidize compounds and real world potable water samples. In general, persulfate yielded more precise results because of its lower background response relative to sample response. Whereas, HTC gave slightly higher results, roughly 2% to 3% on average, for surface water samples.

#### **General Poster Session**

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## **ICP-MS • Wednesday Oral Sessions**

- 126. Artificial Neural Networks and Origin of Orange Juices Analyzed for Rare Earths by ICP-MS.** Seif Nikdel, and Murat Azik; Florida Department of Citrus, CREC, 700 Experiment Station Road, Lake Alfred, FL 33850

Fresh or pure pasteurized juice should contain only the constituents of the natural fruit juice prepared from the fruit itself. It has been recognized that the trace mineral composition of a fruit is indicative of the trace mineral composition of the soil in which the fruit plant grows. Three kinds of analytical methods devoted to the authentication or geographical origin of fruit juices, roughly speaking, they are chemical markers, elemental markers, and isotopic markers. As far as stable isotope ratio methodology is concerned, work involving mass spectrometric determination of hydrogen and oxygen isotope ratios were able to distinguish between pure juice and juice reconstituted from concentrates and tap water. The distinction between sugars from cane or corn and orange or apple is done by carbon isotope analysis. Just as every person has a unique

fingerprint, the naturally occurring isotope ratios for any given element are unique and can be used for identification. This feature of ICP-MS is particularly useful for ascertaining the origin of any orange juice from any citrus growing region. Authentic orange juice samples were collected from Florida, Brazil and Mexico during one season for each growing region. A microwave closed vessel digestion method developed to extract the rare earth elements for analysis by ICP-MS (VG PQ ExCell). In this presentation the comparison of the diluted orange juice concentrate with tap water and deionized water for rare earth elements from Florida, Brazil and Mexico will be shown. Also, the power of an artificial neural networks applied to the rare earth will be demonstrated for geographical origin determination of Florida, Brazil and Mexico orange juices.

#### **ICP-MS Symposia Oral Session**

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#### **127. ICP-MS Using Collision Cell Technology with Kinetic Energy Discrimination Expands the Applications of Quadrupole-Based ICP-MS Technology.** Steve Shuttleworth, Thermo Elemental, 27 Forge Parkway, Franklin, MA 02038.

Polyatomic interferences limit low level detection capability for many elements in normal quadrupole-based ICP-MS. Since collision and reaction cells were introduced in 1999 various gases have been used in an attempt to reduce or eliminate these polyatomic interferences. It has been found that not all interfering species can be efficiently removed using a single collision gas. "Low-reactivity" gases such as hydrogen and helium give excellent performance for the removal of simple argide species and can be used as a mixture or in combination to give a good compromise for many species. Unfortunately, their efficiency of removal of some species, such as Ar<sup>+</sup>, ArO<sup>+</sup> and ClO<sup>+</sup> is poor. Ammonia is very effective at removing these species, however it must be used with caution as its reactive nature can cause problems by creating new interferences. It has been shown that either mass or energy discrimination can be used successfully to provide effective reduction of new, unwanted polyatomic species. In our experience, excellent interference attenuation can be achieved under conditions used to produce very effective energy discrimination. A range of applications will illustrate the use of a range of collision gases and energy discrimination with collision cell technology.

#### **ICP-MS Symposia Oral Session**

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#### **128. Infrared Laser Ablation ICP-MS Analysis of Ceramic Materials.** Steven W. Govorchin, CoorsTek, 600 Ninth Street, P.O. Box 4025, Golden, CO 80401-0025

Ceramic materials are especially resistant to dissolution and are therefore difficult to analyze for elemental composition using standard sample preparation techniques. In principle, a laser ablation sampling accessory for the ICP-MS can overcome some of the problems associated with sample preparation. But in practice, the application of the technique to the analysis of ceramics does not guarantee that a quantitative analysis can be achieved. Various factors such as non-availability of standards and inhomogeneous distribution of elements can limit the accuracy of the analysis. A strategy to optimize the utility of the infrared laser ablation sampling technique is discussed.

#### **ICP-MS Symposia Oral Session**

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#### **129. New Applications of UV Laser Ablation ICP-MS.** Steve Shuttleworth, Thermo Elemental, 27 Forge Parkway, Franklin, MA 02038.

The higher coupling efficiency of UV Lasers (266nm & 213nm) allows direct analysis of virtually all solid materials. Improvements in the laser sampling cell design, laser optics, energy density at the sample surface and spatial resolution make the analysis of microscopic samples a routine application. In addition, advances in quadrupole ICP-MS technology allow low ng/g detection limits directly in the solid material. Analytical methodologies for analysis of synthetic, mineral and biogenic materials using quadrupole ICP-MS will be presented to illustrate the current state of the art of LA-ICP-MS.

#### **ICP-MS Symposia Oral Session**

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130. **Sector ICP-MS: Your Best Friend for Plutonium Fingerprinting.** Michael E. Ketterer, Wendy Hartsock, and Kevin M. Hafer, Department of Chemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698

The use of ICP-MS to determine Pu at environmental levels is receiving more attention, as ICP-MS is competitive with traditional alpha spectrometry. Compared to other MS techniques such as accelerator MS and thermal ionization MS, ICP-MS is more pragmatic as a routine, high-volume analytical technique. The use of high-sensitivity quadrupole ICP-MS or magnetic sector ICP-MS in plutonium analysis opens up several new and exciting areas of environmental geochemistry: A) soil/sediment chronology; B) soil erosion and transport studies; and C) “fingerprinting” sources of Pu in the environment. This paper will focus upon the use of sector ICP-MS and its use in Pu isotopic measurements. The isotope ratios  $^{240}\text{Pu}/^{239}\text{Pu}$ ,  $^{241}\text{Pu}/^{239}\text{Pu}$ , and  $^{242}\text{Pu}/^{239}\text{Pu}$  can all be used to distinguish Pu sources in the environment. Several appropriate case study examples will be discussed.

#### ICP-MS Symposia Oral Session

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131. **Ammonia Residue Analysis by High Resolution Inductively Coupled Plasma Mass Spectroscopy.** Greg W. Johnson, Jude O. Proctor and Virginia H. Houlding, Matheson Tri-Gas, 1861 Lefthand Circle, Longmont, CO 80501.

Matheson Tri-Gas is recognized as the world’s leading manufacturer and supplier of specialty and high-purity gases and gas delivery systems. As part of an on-going program of purifier filter performance characterization, a set of  $\text{NH}_3$  residue samples were generated by R&D. Samples were collected as liquid ammonia [i.e.  $\text{NH}_{3(l)}$ ] in 375 mL PTFE teflon sample tubes. Samples were gradually warmed above  $-33^\circ\text{C}$  and the  $\text{NH}_{3(g)}$  vented. The sample tubes were then submitted to the analytical lab for total metals analysis. The residues were dissolved in either 1%(v/v) HCl or 1%(v/v)  $\text{HNO}_3$ , and internal standard added. The Axiom high resolution ICP-MS (HR-ICP-MS) was used to monitor seventy-two isotopes of the elements for analytical purposes. Fifty-nine isotopes were observed under low resolution ( $R = m/\Delta m = 400$ ) while fourteen were monitored under higher resolution settings ( $R = 3200$ ,  $R = 6040$ , or  $R = 10440$ ). Quality of analytical data was monitored by running controls, measuring background equivalent concentrations, and determining detection limits from repetitive measurements on the samples and/or zero concentration reference. Accuracies were generally better than  $\pm 20\%$  with detection limits in the 0.1 to 100 ng range. With sample weights of 100 g  $\text{NH}_{3(l)}$  or more, detection limits were observed to lie within 1 to 1000 parts per trillion on an  $\text{NH}_3$  weight basis. It was concluded that the Axiom HR-ICP-MS is an excellent choice of instrumentation for the determination of elemental concentrations in ammonia residue samples.

#### ICP-MS Symposia Oral Session

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132. **Determination of  $^{236}\text{U}$  by Sector ICP-MS: a Unique Tracer of Anthropogenic U in the Environment.** Michael E. Ketterer, Carolyn L. Link, Cari Royden, and Kevin M. Hafer, Department of Chemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698

$^{236}\text{U}$  ( $T_{1/2} = 23.4$  Ma) is formed as a result of thermal neutron capture by  $^{235}\text{U}$ . These processes are operative in artificial reactors as well as in Nature. The production of  $^{236}\text{U}$  in reactors is undesirable, and limits the recycling of irradiated U in new fuels. In naturally occurring U ores, where a high neutron flux is present from spontaneous fission of  $^{238}\text{U}$ ,  $^{236}\text{U}$  is found at relatively high levels. Several groups have used accelerator mass spectrometry (AMS) to show that  $^{236}\text{U}/^{238}\text{U}$  atom ratios are on the order of  $10^{-10}$  in U ores.  $^{236}\text{U}/^{238}\text{U}$  atom ratios in the natural Earth’s crust, unaffected by nuclear fallout, are expected to be on the order of  $10^{-14}$ . However, reactor-irradiated U exhibits high  $^{236}\text{U}/^{238}\text{U}$  atom ratios approaching  $10^{-2}$ . As a result, the presence of very small quantities of reactor-irradiated U will significantly enhance the “background”  $^{236}\text{U}/^{238}\text{U}$  atom ratio. The  $^{236}\text{U}/^{238}\text{U}$  signature could therefore be followed over considerable distances despite dilution by large amounts of naturally occurring U. We have used sector ICP-MS under medium resolving power conditions ( $R=3400$ ) to measure  $^{236}\text{U}$  in the environment. The fundamental limitations of this measurement are the formation of  $^{235}\text{U}^1\text{H}^+$  and the background originating from the  $^{238}\text{U}^+$  peak tail. These limitations constrain the use of ICP-MS to samples containing  $^{236}\text{U}/^{238}\text{U}$  atom ratios of  $\geq 10^{-7}$ . Applications of sector ICP-MS and the determination of  $^{236}\text{U}$  in several specific case studies will be presented.

#### ICP-MS Symposia Oral Session

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133. **Combined High Resolution, Collision Cell, and Enhanced Extraction Multiple Collection ICP-MS with the Micromass IsoProbe.** Mike Colucci, Micromass, Inc., 100 Cummings Center, Suite 407N, Beverly, MA 01915; Ed Young, Dept. of Earth and Space Sciences, UCLA; Sarah Goldsmith, Zenon Palacz, Simon Meffan-Main, Micromass UK Ltd., Floats Road, Wythenshawe, Manchester, UK.

Collision cells have become widely established as an effective method for removing Argon and Argon molecular species from the mass spectra of elements such as Fe, Ca, Cr, Se. The Micromass IsoProbe is the only multicollector magnetic sector instrument equipped with a collision cell, and it can measure isotope ratios of these elements to high precision at high RF power and low resolution. In some situations, non-argide isobars can interfere with the isotopes of interest. The challenge is to resolve these species without degrading the precision of the measurement. Conventional methods are to increase mass resolution by reducing the source and collector slit widths. This results in poor peak shape with compromised analytical precision. An alternative approach is to reduce the width of the source slit but retaining the collector slit widths. The ion beam width is substantially reduced and isobars can be resolved away from the peak flat of the element of interest. This approach still allows full isotope multicollection capability which is essential for high precision.

We present results of measurements of Silicon isotopes using this approach. The Silicon isotopes are interfered with by NN, m/z 28, NNH m/z 29, and NO m/z 30, but these isobars can be resolved with a resolution of 3000 with peak coincidence achieved through fine scale collector positioning adjustment.

We also present some preliminary results on  $^{32}\text{S}/^{34}\text{S}$  using the collision cell to suppress the  $\text{O}_2$  (m/z 32) and  $(\text{OH})_2$  species. In addition, the combination of Ar as the collision cell gas and enhanced extraction techniques strongly suppress the  $^{16}\text{O}$ ,  $^{16}\text{OH}$ , and  $\text{H}_2\text{O}$  peaks, which leads to the possibility of measuring O isotopes by MC-ICP-MS. Enhanced extraction techniques suppress both analyte background and signal imparted from the plasma and interface region, such as oxygen isotopes (m/z 16,17,18), while effectively increasing signal to noise.

#### ICP-MS Symposia Oral Session

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## Luminescence • Monday Oral Sessions

134. **Spectral Deconvolution of Fluorescence Spectra from Plant Extracts.** Timothy L. Danielson and Gary D. Rayson, Box 30001 MSC 3C, New Mexico State University, Las Cruces, NM 88003; D.M. Anderson, R. Estell, E.L. Fredrickson and K.M. Havstad, Box 30001 MSC JER, United States Department of Agriculture, Agriculture Research Service – Jornada Experimental Range, Las Cruces, NM 88003

Fluorescence emission spectra have been observed to yield information pertaining to the identification of plant species. One approach to acquiring these characteristic spectra has been to record the spectral signature resulting from an extract of the plant. Often these spectra have been overwhelmed by the fluorescence from chlorophyll species. In an effort to acquire spectral information from less ubiquitous molecular species, plant samples have been extracted using phosphate buffered saline solutions. This has resulted in the acquisition of emission spectra from 370 to 620 nm in the absence of the red chlorophyll fluorescence. The combination of fluorescent and absorbing molecular species extracted from each sample of plant material provides an identifying spectral signature. Variation in solution pH has also been found to provide yet another dimension to the total fluorescence response surface. The results of a study of six plants common to the northern Chihuahuan desert will be presented. The implications of these findings on the development of a fluorescence-based technique for the identification of plants from pre- and post-digestive samples will also be discussed.

#### Luminescence Symposia Oral Session

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135. **Investigation of Lanthanide and Actinide Metal Ion Passive Binding to *Datura innoxia* Cell Walls.** Debbie D. Martinez and Gary D. Rayson, Department of Chemistry and Biochemistry, New Mexico State University, Box 30001, MSC 3C, NM 88003

A part of the legacy of the cold war era consists of many square miles of land contaminated with significant amounts of lanthanide and actinide metals. Current technologies for the remediation of these areas have included the physical removal of the topmost several feet of ground for relocation. An alternate technology that is currently being studied involves the application of plants that are able to accumulate these metals from the soil and transport them into their shoots. A significant contribution of the mechanisms of intra-plant transport of metals involves the passive binding of these metal ions to chemical functionalities located on the cell walls of the different plant tissues. A number of studies have shown that fungi and bacteria are able to absorb heavy-metal ions. In this study we are interested in the metal sorption of higher plant species. One of the viable biomasses, which have been investigated in our laboratory, is derived from anther cells cultured from the plant *D. innoxia*. *D. innoxia* has shown the ability of accumulating many heavy metals with adequate capacities and the feasibility to be cultured with high biomass production. In an effort to understand these processes, the binding of a lanthanide metal ion ( $\text{Eu}^{3+}$ ) and an actinide metal ion ( $\text{UO}_2^{2+}$ )

has been investigated. Metal uptake by nonliving biomaterials occurs through sorption processes that are connected to the cell walls. These studies have included the elucidation of affinity spectra from binding isotherms and the application of luminescence spectroscopy. The results of these investigations and their impact of the application of *Datura innoxia* for phytoremediation (the use of plants to remove contaminants from polluted environments) will be discussed.

#### **Luminescence Symposia Oral Session**

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- 136. Elimination of Fluorescence and Scattering Backgrounds in Luminescence Lifetime Measurements Using Gated Phase Fluorimetry.** Heather M. Rowe, Sing Po Chan, J.N. Demas, University of Virginia, Department of Chemistry, McCormick Road, P.O. Box 400319, Charlottesville, VA22904-4319; B. A. DeGraff, James Madison University, Department of Chemistry, Harrisonburg, Virginia 22807

A new gated form of phase fluorimetry for measuring lifetimes will be presented. The technique uses a square wave excitation and gates the detector on only during the off-period of the excitation. Using a long-lived sample, this eliminates or reduces errors from scattered light and short-lived fluorescences. Using a square wave modulated excitation source with a 50% duty cycle, traditional data treatment can be used after, at most, a simple  $\pi/2$  phase adjustment. A combination of theory and experimental results demonstrates the validity of this new gated method and its utility for background elimination or reduction. The results are precise, accurate, eliminate scattering errors, and greatly reduce errors due to short-lived fluorescence impurities. Using an offset time prior to gating the detector on can mitigate error from fluorescence bleed-through into the detection period or a slow excitation source turn off.

#### **Luminescence Symposia Oral Session**

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- 137. Metal Ion Sensors Based on a Luminescent Ruthenium(II) Complex: the Role of Polymer Support in Sensing Properties.** Heather M. Rowe, Wenying Xu, J.N. Demas, University of Virginia, Department of Chemistry, McCormick Road, P.O. Box 400319, Charlottesville, VA22904-4319; B.A. DeGraff, James Madison University, Department of Chemistry, Harrisonburg, Virginia 22807

Oxygen and copper(II) ion quenching studies were conducted on a model sensor system to elucidate the significant, yet not fully characterized, role of polymer supports in sensor performance. The system consisted of  $[\text{Ru}(\text{Ph}_2\text{phen})_2(4\text{-cyclamCH}_2(4'\text{-Me})\text{bpy})]\text{Cl}_2$  ( $\text{Ph}_2\text{phen}$  = 4,7-diphenyl-1,10-phenanthroline,  $\text{bpy}$  = 2,2'-bipyridine,  $\text{cyclam}$  = 1,4,8,11-tetraazacyclotetradecane) as the sensor molecule, copper(II) ions as the quenching analyte, and two polymer supports. One polymer used was a cyclic siloxane crosslinked with a hydrophilic polyethylene oxide; the other was a ternary polymer with polyethylene oxide, polydimethylsiloxane, and 2-hydroxyethylmethacrylate. Both polymers contain a hydrophobic binding region for the sensor molecule and a hydrated hydrophilic region for transport of the ions to the sensor. Luminescence intensity and lifetime measurements show the polymer supports to be equally effective at shielding the sensor molecule from oxygen quenching but not copper(II) ion quenching. Unlike oxygen, the copper(II) ions quench the sensor molecule in solution and in the polymer supports through a combination of static and dynamic quenching. The unquenched excited state lifetimes, bimolecular rate constants, and equilibrium constants are presented, and their differences are interpreted to provide information about the local environment of the sensor molecule immobilized in the polymer supports.

#### **Luminescence Symposia Oral Session**

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- 138. Design and Applications of Highly Luminescent Metal Complexes.** J.N. Demas, Wenying Xu, Z. Fuller, W.D. Bare, Department of Chemistry, A. Periasamy, Keck Center for Cellular Imaging, University of Virginia, Charlottesville, VA 22904; B.A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807. Kristi Kneas and R.D. Bowman, Department of Chemistry, Maryville College, Maryville, TN 37804.

Inorganic complexes show great promise as molecular probes and luminescence-based sensors. The majority of work uses Ru(II), Re(I), and Os(II) complexes with  $\alpha$ -diimine ligands (e.g., 2,2'-bipyridine, 1,10-phenanthroline, and analogues). The rational design of practical systems requires an intimate understanding of the interactions between the probe or sensor molecule and the polymer-based support or the target. Advances in understanding the interactions of metal complexes and polymeric supports will be discussed using examples from oxygen and pH sensors. Conventional, two photon, and confocal fluorescence microscopy will be shown to be a powerful tool in sorting out the system complexities. In addition, photochemical results demonstrate the unique role the polymer can play in the photostability of the sensor molecules.

#### **Luminescence Symposia Oral Session**

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**139. Solid-Matrix Phosphorescence Lifetimes of Tetrols I-1 and Benzo[a]pyrene-DNA Adducts as a Function of the Amount of Heavy-Atom Salt.** Barry W. Smith and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071.

It is well known that polycyclic aromatic hydrocarbons (PAHs) are potential mutagenic and/or carcinogenic compounds. When they are metabolized in living cells, products from PAHs such as benzo[a]pyrene (B[a]P) are formed. The B[a]P then can be metabolically activated to benzo[a]pyrene-trans-7,8-dihydrodiol-9,10-epoxide (BPDE). This in turn can bind to DNA to form BPDE-DNA adducts and by hydrolysis produce tetrols (tetrol I-1). Thus, both the BPDE-DNA adducts and tetrol I-1 are important in cancer research. Solid-matrix phosphorescence (SMP) lifetime data were obtained for tetrol I-1 and two samples of BPDE-DNA adducts as a function of amount of heavy-atom salt, TINO<sub>3</sub>. All of the decay curves obtained for tetrol I-1 and BPDE-DNA adducts were found to be biexponential. Detailed analysis of the decay curves showed that there was no specific pattern for several log plots of the SMP lifetime data for tetrol I-1 with different amounts of heavy-atom salt. However, for the BPDE-DNA adducts the long-decaying component showed parallel lines for log plots of the SMP lifetime as a function of the amount of TINO<sub>3</sub>. This result indicated very selective interaction of TINO<sub>3</sub> with the BPDE-DNA adducts. Most likely the external form of the BPDE-DNA adducts were responsible for this. Generally, the SMP lifetime data showed that at least two forms of the BPDE-DNA adducts were present. At this time, attempts are being made to determine the relative amounts of the external forms and the quasi-intercalated forms of the adducts.

**Luminescence Symposia Oral Session**

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**140. A Fundamental Study of the Partitioning of Polycyclic Aromatic Hydrocarbon Metabolites in Three Phases Using Liquid-Liquid-Liquid Microextraction and Fluorescence Spectrometry.** Matthew Marlow, and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, P.O. Box 3838, Laramie, WY 82071-3838.

A novel fluorescence method was developed to investigate the partitioning of polycyclic aromatic hydrocarbon metabolites in the three phases of a liquid-liquid-liquid microextraction (LLLME) technique. The LLLME technique is a relatively new process for the extraction and preconcentration of analytes from aqueous solution and has significant potential for applications involving capillary electrophoresis. The analyte of interest partitions from the aqueous donor phase through the pores of a porous hollow fiber impregnated with an organic solvent and into an aqueous acceptor phase within the fiber. In this work, several fluorescent metabolites, with different numbers of aromatic rings, were investigated to determine enrichment factors, equilibrium constants, extraction efficiency, and recovery factors using fluorescence spectrometry. Depending on the number of rings, enrichment factors from 10 to 40 could be achieved. From mass balance calculations, it was determined that several of the compounds partitioned into the organic layer or were adsorbed to the external fiber surface which diminished the extraction efficiency. The adsorption phenomenon did not permit the calculation of reliable equilibrium constants. However, the enrichment factors were high for several of the compounds investigated.

**Luminescence Symposia Oral Session**

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**141. Solid-Matrix Phosphorescence of Heterocyclic Aromatic Amines in Glucose Glasses as a Function of Temperature.**

Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071; Shaun D. Mendonsa, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

Solid-matrix phosphorescence (SMP) intensities and lifetimes were obtained for 2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP) and 2-amino-9H-pyrido[2,3-b]indole (A $\alpha$ C) as a function of room temperature to 93 K. Two glucose glasses were used. They were prepared with crystalline glucose and a glucose melt, both with and without the heavy-atom salt, NaI. The intensity-to-lifetime ratios showed that the triplet state formation efficiency of PhIP changed as a function of temperature for glasses prepared without NaI. For glasses prepared with NaI, the triplet state formation efficiency of PhIP remained essentially constant with temperature. The phosphorescence intensity for A $\alpha$ C was almost the same at room temperature and at 93 K in glasses prepared with 10% NaI. Thus, this heavy-atom salt/glucose system achieved the maximum phosphorescence signal at room temperature. Using the phosphorescence lifetime data as a function of temperature, activation energies for the phosphors in the glasses were calculated. The phosphorescence lifetime data fit to a biexponential equation and two activation energies were obtained. The activation energies were related to low-frequency vibrational modes and  $\beta$ -relaxation processes in the glucose glasses.

**Luminescence Symposia Oral Session**

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- 142. Luminescence Properties of CdS Nanoparticles.** Barbara A. Harruff, Universal Technology Corporation, 1270 North Fairfield Road, Dayton OH 45432-2600; Christopher E. Bunker, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

Nanomaterials are receiving significant scientific interest because of the great potential they possess to alter many technological areas (e.g., sensors, catalysts, light-weight structures, pharmaceuticals). Our interest lies in developing fuel-quality diagnostics — sensors capable of determining the properties and deficiencies of aviation fuels. Once determined, additives designed to improve the performance of the fuel can be added as required, reducing costs of operation and maintenance and enhancing the versatility of the fuel. We have begun our efforts to develop nanomaterial-based sensors by investigating CdS — a well known and well-understood material that is highly luminescent and can serve as a baseline for our photophysical investigations. During the course of our studies, we have found that the luminescence yield of the CdS nanoparticles prepared in AOT reverse micelles can be enhanced by an order of magnitude through photoirradiation. The results of these investigations are presented here.

**Luminescence Symposia Oral Session**

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- 143. Luminescence Properties of Core-Shell CdS-Ag Nanoparticles.** Steven W. Buckner, James R. Gord, and Christopher E. Bunker, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103; Barbara A. Harruff, Universal Technology Corporation, 1270 North Fairfield Road, Dayton OH 45432-2600

Growing interest in the fabrication and characterization of nanomaterials as well as a desire to develop field-quality fuel diagnostics based on such materials has motivated our recent investigations of various nanoparticles and their associated luminescence properties. Core-shell type CdS-Ag nanoparticles have been synthesized over a range of sizes by using the reverse-micelle method. The resulting nanoparticles have been characterized spectroscopically through measurements of absorption and fluorescence emission spectra, quantum yields, and fluorescence lifetimes. These properties have been evaluated as a function of silver concentration and particle size. The results obtained are discussed in terms of the known photophysical properties of CdS.

**Luminescence Symposia Oral Session**

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- 144. Spectral Characterization of Unique Carbon-Nanotube-Based Dendromer Molecules.** Daniel A. Zweifel and Ya-Ping Sun, Clemson University, Department of Chemistry, Clemson SC 29634; James R. Gord and Christopher E. Bunker, Air Force Research Laboratory, Propulsion Directorate, WPAFB OH 45433-7103

Novel materials with potential as electro-optical devices, donor-acceptor complexes, and fuel-additive modifiers have been prepared by researchers at Clemson University. At the 43<sup>rd</sup> Rocky Mountain Conference on Analytical Chemistry, we reported absorption spectra, fluorescence emission and excitation spectra, quantum yields, and lifetimes obtained for a C<sub>60</sub>-based unimolecular micelle, a pyrene-functionalized nanotube structure, and suspended single-wall and multi-wall nanotubes. This work has been extended and enhanced through spectroscopic characterization of new carbon-nanotube-based dendromer molecules synthesized by the Clemson research team. These results are presented within the context of potential applications of these unique materials.

**Luminescence Symposia Oral Session**

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- 145. Cu<sup>2+</sup> Measurements with Long-Period-Grating Fiber-Optic Sensors in Support of Smart Nozzle Development.** Justyna Widera, Christopher E. Bunker, and James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103; Sean D. Puckett and Gilbert E. Pacey, Department of Chemistry and Biochemistry, Miami University, Oxford OH 45056

The Air Force Research Laboratory has been actively involved in investigating technologies with potential as fuel-quality diagnostics (Smart Nozzle Program). The long-term goal of this program is to develop a state-of-the-art diagnostics package attached to a single-point refueling nozzle designed to assess key fuel properties as the fuel is dispensed. The short-term goal is to explore and develop novel technologies capable of providing in-the-field, real-time fuel analysis. Long-period-grating (LPG) based fiber-optic sensors show great potential in this regard. Sensorgrams have been obtained for aqueous solutions of Cu<sup>2+</sup> using a novel long-period-grating fiber-optic sensor. Data from the sensorgrams are evaluated with respect to repeated exposure, Cu<sup>2+</sup> concentration, and time-dependent response. The results of the experiments indicate the need for sensor conditioning prior to quantitative use, a non-linear response in the spectral shift of the sensor with Cu<sup>2+</sup> concentration, and a strong dependence of response time on Cu<sup>2+</sup> concentration.



### Luminescence Symposia Oral Session

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- 146. Fuel Diagnostics Based on Fast Gas Chromatography and Principal Component Analysis.** Sophie M. Rozenzhak and Christopher E. Bunker, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

The U. S. Air Force is currently working to develop in-the-field diagnostic systems for evaluating fuel quality. The ultimate goal is a “Smart Nozzle” integrating various technologies to provide online analysis and additive injection during the aircraft-refueling process. Toward this end, chromatographic data have been collected for a series of aviation, missile, and automotive fuels and analyzed using the factorial analysis method principal component analysis (PCA). Results from PCA are used to demonstrate pattern-recognition capabilities. In support of rapid field-level fuel diagnostics, chromatographic data acquired with run times of seven minutes or less have also been analyzed using PCA.

### Luminescence Symposia Oral Session

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- 147. Laser-Induced Incandescence (LII) for Soot Measurements in Combusting Flows.** James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103; Michael S. Brown and Terrence R. Meyer, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638

In concert with an Air Force program designed to study the effects of additives on particulate production, laser-induced incandescence (LII) measurements have been performed in a JP-8-fueled, single swirl-cup combustor with a central nozzle. Single-shot LII images of the soot exhibit localized high concentrations with varying spatial and temporal behavior. High-speed luminescence images reveal a similarly complex soot structure driven by local fluid and chemical behavior. Averages of the single-shot images permit parametric studies of the impacts of laser fluence, camera gate and delay settings, and global equivalence ratio on the LII signal. Examples of single-shot LII signals and the results of these parametric studies are presented in the context of the fuel-additive study.

### Luminescence Symposia Oral Session

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- 149. Qualitative Studies of Unsteady Combustion Processes Through High-Speed Imaging of Flame Luminosity.** Joseph Miller and James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103; Terrence R. Meyer, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638

Improved fuel-air mixing and subsequent flame propagation are essential for enhanced combustor performance. Highly intermittent, three-dimensional combustors are difficult to study with single-frame, laser-based imaging. In the current work, the use of high-speed digital imaging of flame luminosity as a real-time diagnostic for such processes is evaluated. The technique is demonstrated in three configurations—a single swirl-cup combustor, a trapped-vortex combustor, and a pulsed-detonation engine. Imaging rates up to 63,000 frames-per-second and exposure times as low as 10  $\mu$ s surpass the capabilities of conventional high-speed photography and provide new insights into phenomena such as soot formation, flame morphology at elevated pressures, and deflagration-to-detonation transition. In addition to these real-time combustor-diagnostics applications, the use of high-speed digital imaging for coherent-structure velocimetry (CSV) is presented. CSV enables time-resolved studies of flame structure/fluid dynamics interactions in unsteady, turbulent reacting flowfields.

### Luminescence Symposia Oral Session

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- 150. Molecular Emission as a Monitor of Combustion Chemistry.** Heidi Meicenheimer, Universal Technology Corporation, 1270 North Fairfield Road, Dayton OH 45432-2600; Michael S. Brown, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638; James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

Active control of the fuel/air ratio is an important goal of advanced combustor development. Local fuel/air ratios in combustors reflect the complex dynamics of fuel atomization and fuel/air mixing. These processes directly impact the operating efficiency of combustors. Active control requires some type of monitoring along with real-time signal processing. Molecular emission in a combustor’s reaction zone offers promise as a monitor suitable for active control. Changes in local fuel/air ratios are manifested in changes in the local combustion chemistry as evidenced by changes in the local concentration of key radical species. To this end, we have collected molecular emission spectra in three combustion environments to assess the use of such spectra for determination of the local fuel/air ratio. In particular, molecular emission from the

combustion intermediates OH, CH and C<sub>2</sub> has been collected in a time-averaged mode. In addition, OH emission has been collected in a time-resolved manner at fixed wavelengths. Measurements have been performed in two model combustors—one burning hydrogen and one burning aviation fuel—and a laminar laboratory burner. The emission data collected in the model combustors has been correlated with the operating conditions of the combustors. The data collected in the laboratory are being used to gain understanding of the correlation studies at a more fundamental chemistry level. Examples of data from all these studies will be presented along with modeling results of the gas-fueled combustor.

#### **Luminescence Symposia Oral Session**

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- 151. Simultaneous Single-Shot Measurements of Temperature and Three Species Concentrations by Triple-Pump Coherent Anti-Stokes Raman Scattering (CARS) in Dynamically Reacting Flows.** Sukesh Roy and Michael S. Brown, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638; Viswanathan N. Velur and Robert P. Lucht, Department of Mechanical Engineering, Texas A&M University, College Station TX 77843; James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

The demonstration of a triple-pump CARS system for simultaneous measurements of temperature and species concentrations with high spatial and temporal resolution is presented. The triple-pump CARS approach employs four laser beams generating CARS signals near two distinct wavelengths. Temperature and relative concentrations of the target species (with respect to N<sub>2</sub>) are extracted by fitting the measured CARS spectra in each wavelength region. For the proof-of-concept measurements, CARS signals from N<sub>2</sub>/O<sub>2</sub> and N<sub>2</sub>/H<sub>2</sub> pairings were collected. Single-shot and time-averaged measurements were performed in an atmospheric-pressure H<sub>2</sub>/air diffusion flame. Simultaneous single-shot data acquisition may enhance significantly the precision/accuracy of the temperature measurements due to the correlation afforded by the presence of N<sub>2</sub> features in each of the two spectral windows. Moreover, this technique offers the possibility of monitoring local temperature and concentrations of three target species using a single hardware platform. The implications of the demonstrated measurements for applications in test rigs at Wright-Patterson AFB will be discussed.

#### **Luminescence Symposia Oral Session**

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- 152. Effects of Unsteady Strain Rate on OH and CH LIF in Counterflow Diffusion Flames.** Terrence R. Meyer and Viswanath R. Katta, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638 USA; James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103 USA; Alix Lemaire, Katharina Zähringer, and J. Carlos Rolon, Laboratoire E.M2.C, École Centrale Paris and CNRS, 92295 Châtenay-Malabry Cedex, France

Vortex-induced flame wrinkling and extinction represent fundamental turbulent flame phenomena that must be understood for the development of accurate numerical models. In the current work, repeatable flame wrinkling and extinction are produced using a counterflow diffusion flame and a piston-actuated vortex. Planar laser-induced fluorescence (PLIF) measurements of OH and CH are used to mark the flame front, and particle-image velocimetry (PIV) is used to obtain the unsteady strain rate during the vortex-flame interaction. Phase-correlated OH/PIV and CH/PIV data show that flame extinction occurs within one millisecond after the vortex begins to wrinkle the flame. Velocity measurements show that a five-fold increase in the fuel-side peak strain rate occurs during this extinction process. To help assess the viability of using OH and CH LIF as markers for flame extinction, a numerical simulation of the unsteady Navier-Stokes equations with full chemistry is performed. Data from the simulation are in good qualitative agreement with the experimentally observed flame structure and can be used to assess the relative quenching rates during vortex-flame interactions using the output of the numerical code. In addition, the time rate of extinction as measured by various observables (*e.g.*, OH/CH PLIF, temperature) can then be evaluated.

#### **Luminescence Symposia Oral Session**

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- 153. Application Overview of a Linear Ion Trap (QTRAP) in the Identification of Metabolites.** Yves LeBlanc, Applied Biosystems/MDS Sciex, MDS SCIEX Instruments, 71 Four Valley Drive, Concord ON, Canada, L4K 4V8.

Identification of metabolites in biological matrices requires MS instrumentation to offer a high degree of specificity and sensitivity. Hence, analysis of samples is frequently performed on multiple systems in order to identify and further confirm the presence of these metabolites. By combining the specificity of quadrupole scans, such as precursor and neutral loss with the full scan MSMS sensitivity of a linear ion trap, into a single system (QTRAP) the user can now automate the metabolite identification process with software tools such as Information Dependent Acquisition and Metabolite ID. An overview of strategies and application data will be presented.

**MS, GC/MS, LC/MS Symposia Oral Session**

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- 154. A Novel Approach to Large Volume Liquid Injections in Gas Chromatography.** Dan DiFeo, Jr., SGE Incorporated, 2007 Kramer Lane, Austin, TX USA 78758; Stuart Allan and Peter Dawes, SGE International, 7 Argent Place, Ringwood 3134, Australia

For many years capillary gas chromatography has been the standard technique for the analysis of volatile and semi-volatile liquid samples. Its greatest limitation has always been the very small sample volumes that must be injected to avoid overloading the injection port or capillary column. There have been many accessories developed to combat this deficiency, such as Programmed Temperature Vaporizing (PTV) injectors, that can dispose of more than one hundred microliters of solvent prior to the sample being introduced to the capillary column. Such systems require a completely new injection port to be fitted to the instrument and rely on a large boiling point difference between the solvent and the analytes of interest.

SGE has developed a novel way of injecting large volumes of liquid into a gas chromatograph without having to install a new injector or without overloading the existing one. Over one hundred microliters of solvent can be injected into a standard injection port, transferred to a capillary column, separated from the analytes of interest and disposed of. The result is a concentrated form of the sample that is deposited directly onto the capillary column. This new technology resulted from a breakthrough in multidimensional chromatography that allows a high-pressure high-flow pre-separation column to be used in conjunction with a low-pressure low-flow standard capillary column. The system is much easier to install than a standard multidimensional system and uses the standard injector hardware of the gas chromatograph.

**MS, GC/MS, LC/MS Symposia Poster Session**

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Tel: (512) 837-7190, Fax: (512) 836-9159, ddifeo@sge.com

- 155. Benefits of a High Temperature Wax Phase.** Dan DiFeo, Jr., SGE Incorporated, 2007 Kramer Lane, Austin, TX USA 78758; Angus Hibberd and Gerard Sharp, SGE International, 7 Argent Place, Ringwood 3134, Australia

This paper describes the benefits of high temperature wax columns over conventional wax columns. The added thermal stability along with a high degree of inertness is the result of a unique bonding process. The polyethylene glycol phase is essentially embedded into a sol gel matrix. The sol gel is a synthetic glass, which is bonded to the fused silica. This gives the wax phase added thermal stability, inertness and robustness. Data will be presented that shows comparisons of bleed levels and applications of the high temperature wax columns compared with a standard wax column. The columns will be subjected to high temperature analyses of mixtures not normally analyzed on conventional wax columns due to their low maximum temperature.

The increased thermal stability of the SolGel/Wax column gives greater flexibility to perform a wide range of analyses normally not able to be achieved on conventional wax phases. Along with an increased thermal stability, the unique bonding of the phase gives an increased inertness to a wide range of compounds such as alcohols, acids and amines. This inertness will be demonstrated with a series of chromatograms comparing high temperature and conventional wax columns.

**MS, GC/MS, LC/MS Symposia Poster Session**

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Tel: (512) 837-7190, Fax: (512) 836-9159, ddifeo@sge.com

- 156. The Benefits and Disadvantages of Using Small Inner Diameter Capillary Columns.** Dan DiFeo, Jr., SGE Incorporated, 2007 Kramer Lane, Austin, TX USA 78758; Angus Hibberd and Gerard Sharp, SGE International, 7 Argent Place, Ringwood 3134, Australia

This paper describes the advantages and disadvantages of small bore capillary columns. It is well known that capillary columns of 0.10 and 0.15mm inner diameter can produce faster chromatography than conventional capillary column diameters of 0.25 and 0.32mm ID. These smaller diameter columns have been available for several years but have not been adopted by the general chromatography community. The columns are more difficult to use but with greater understanding, the benefits can be realized.

Application data will be presented which shows the benefits and disadvantages of each of the diameters of 0.10, 0.15 and 0.25mm inner diameter. On the one hand, very small-bore capillary columns will yield faster chromatography but at a cost. The sources of the limitations are the sample introduction and detection parts of the chromatographic system. Lower flow rates of small bore columns will more easily show deficiencies in GC injector design, and smaller peak widths will test sampling rates in mass spectrometers. Nonetheless, the benefits of small-bore columns are waiting to be gained.

**MS, GC/MS, LC/MS Symposia Poster Session**

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- 157. A Comparison between Micro and Capillary HPLC Column Designs.** Dan DiFeo, Jr., SGE Incorporated, 2007 Kramer Lane, Austin, TX USA 78758; James Mazaraki, Peter Dawes and Gerard Sharp, SGE International, 7 Argent Place, Ringwood 3134, Australia

Micro and capillary HPLC have become more popular since several major instrument manufacturers introduced systems that easily accommodate the low flow and low dead volume requirements of these techniques. When coupled with MS and MS/MS detection micro and capillary HPLC becomes an extremely powerful analytical tool for the characterization of small samples. For this reason micro/capillary HPLC is especially useful for the analysis of proteins and peptides.

Micro and capillary HPLC columns are readily available from several niche and mainstream manufacturers. The durability and robustness of these columns is inherently dependent on the column design. Researchers tend to prefer capillary tubing to use as column tubing, though many column manufacturers prefer the use of glass lined tubing for packing micro/capillary columns. This paper will compare the features of these two common micro/capillary column tubing materials with PEEKsil, a PEEK sheathed fused silica tubing.

Data will be presented to illustrate the influence of the column materials on micro/capillary column design and performance. The fragility of fused silica makes it easy to remove voids by cutting the column down. Glass lined columns are extremely robust making them far more user friendly. PEEKsil is far more robust than fused silica and is available in bores of 50 microns or less.

**MS, GC/MS, LC/MS Symposia Poster Session**

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- 158. Improved Separation of Semi-Volatiles.** Dan DiFeo, Jr., SGE Incorporated, 2007 Kramer Lane, Austin, TX USA 78758; Angus Hibberd and Gerard Sharp, SGE International, 7 Argent Place, Ringwood 3134, Australia; Mark Ferry, ECS/MDL, 196 Riva Avenue, Milltown, NJ USA 08850

Semi-volatile contaminants in water are some of the most targeted compounds for analysis in environmental laboratories today. This class of contaminants constitutes a wide range of compounds with differing physical properties and as such, is extremely difficult to analyze in a cost effective turnaround time. Low-bleed or mass-spectrum grade columns are required with the US environmental protection agency recommending that the analysis be carried out on a 5% phenyl column.

This paper will show the use of a 5% phenyl column and a 100% polydimethylsiloxane column to give improved separation of 71 components of the US EPA 8270 mix in a reduced analysis time. The 100% methyl column used for this analysis is a sol gel derived column with high temperature properties. This is especially beneficial for the late eluting semi-volatiles, because the lower bleed levels leads to better signal-to-noise ratios and the higher temperature gives better peak shape and faster retention times. Both phases also show excellent inertness. Chromatograms will highlight some difficult-to-analyze compounds to demonstrate this.

The high temperature limits of both of these columns is also handy for 'burning' any contaminants from the column after analysis of dirty samples. Thus, although the upper maximum recommended temperature of the method is 320°C, these columns can be used to temperatures in the 370-380°C range to remove column contamination. This ultimately can be incorporated in the GC method and results in less instrument downtime.

**MS, GC/MS, LC/MS Symposia Poster Session**

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- 159. Analysis of Pharmaceutical Solvents Using a New Low-bleed Capillary Column.** Dan DiFeo, Jr., SGE Incorporated, 2007 Kramer Lane, Austin, TX USA 78758; Angus Hibberd and Gerard Sharp, SGE International, 7 Argent Place, Ringwood 3134, Australia

Analysis of pharmaceutical solvents has become an important issue in the development of new drug design. Most of these solvents are low molecular weight, volatile compounds that can be difficult to remove from the final target drug. As such, analyses to determine the levels of these solvents are usually performed on specifically designed volatile columns. These columns are usually thick-filmed and have low thermal stability. The low thermal stability of these custom-designed volatile columns usually results in higher bleed levels in the later part of the chromatogram. Conversely, the high thermal stability and increased level of inertness of a high-temperature volatile column results in lower bleed levels at elevated temperatures while still retaining excellent partitioning properties for pharmaceutical solvents as well as drinking water, wastewater and groundwater volatile mixes.

This paper will present data showing the analysis of pharmaceutical solvents using USP methods along with standard US EPA 502.2 and 624 mixes and difficult-to-separate alcohols. Bleed chromatogram comparisons of the high temperature volatile column with standard volatile columns will also be presented.

The increased thermal stability of this new phase gives the flexibility of a wider variety of analyses to be performed at higher temperatures unable to be achieved on a standard volatile column. In addition, a more thermally stable phase will allow baking out of the column at higher temperatures, otherwise not possible with conventional phases. This allows for rapid analysis of volatile components in a semi-volatile matrix.

**MS, GC/MS, LC/MS Symposia Poster Session**

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- 160. Sample Focusing Techniques in Gas Chromatography.** Dan DiFeo, Jr., SGE Incorporated, 2007 Kramer Lane, Austin, TX USA 78758; Stuart Allan and Peter Dawes, SGE International, 7 Argent Place, Ringwood 3134, Australia

Peak focusing is the term used to describe the narrowing of the width of a peak. As a technique, it is extremely useful for improving the signal-to-noise ratio and increasing the detection limit of an analysis. There are many advantages of focusing a peak rather than injecting more sample when attempting to improve the method detection limit. In most cases, there is already enough sample on the column to achieve up to 1000 times better sensitivity, and injecting any more sample would almost certainly cause problems. Sample focusing uses the existing amount of sample that is on the column and decreases its bandwidth to make it more concentrated. This increases the peak height significantly, therefore improving the detection limit.

There are many different ways to focus peaks in gas chromatography. This presentation will outline the pros and cons of each and how to execute them efficiently.

**MS, GC/MS, LC/MS Symposia Poster Session**

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- 161. Ultra-Sensitive Assay for Analytes/Metabolites with Different Optimization Behaviors.** Yves LeBlanc, Applied Biosystems/MDS Sciex, MDS SCIEX Instruments, 71 Four Valley Drive, Concord ON, Canada, L4K 4V8.

Optimum sensitivity for analytes and their metabolites is frequently encountered under different instrument conditions. When ion optics are considered, most instruments can rapidly alternate between optimum lens conditions to provide the lowest detection limits possible. When source conditions are found to be different, compromise conditions need to be used due to hardware limitations in establishing and equilibrating temperatures. With the integrated ceramic heaters technology of the API 4000, optimum source temperatures can be used for each analyte even when minimal chromatographic separation is achieved. This poster will outline the performances characteristics of the API 4000 for the detection of nucleosides.

**MS, GC/MS, LC/MS Symposia Poster Session**

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- 162. Development of an HPLC/MS/MS Method for the Quantitative Analysis of Pyridostigmine, a Pretreatment Compound for Chemical Warfare Agents, in Guinea Pig and Mouse Plasma.** Shane Needham and Binying Ye, Alturas Analytics, Inc. 1282 Alturas Drive Moscow, Idaho

In collaboration with the US military we have developed an HPLC/MS/MS method for the analysis of Pyridostigmine Bromide (PB) from guinea pig plasma. PB is a pretreatment drug used to protect against chemical warfare nerve agents. By itself PB is not protective against chemical warfare nerve agent poisoning. However, when used as a pretreatment, PB might enhance the antidote effects of the standard atropine/oxime treatments used by the U.S. military for nerve agent poisoning.

Since the guinea pig and mouse PK experiments required the use of less than 30  $\mu$ L of plasma with quantitation limits near 500 pg/mL a highly

sensitive analytical method was needed such as HPLC/MS/MS. Previous methods employed HPLC/MS [1], however, the method required 50  $\mu$ L of plasma with a limit of quantitation of 700 pg/mL. In addition, the use of single ion monitoring subjected the assay to interferences. Here we report on the development of a novel HPLC/MS/MS assay for the determination of PB in guinea pig and mouse plasma. To accelerate sample analysis, all sample preparation was done in 96 well plates. PB and internal standard (PB-D6) were isolated from 25  $\mu$ L of plasma by precipitation. After centrifugation and evaporation, the sample was reconstituted and injected onto the HPLC system. A PRP 1 (50 x 2.1 mm, 5  $\mu$ m) HPLC column was used in tandem with a Sciex API3000. Multiple reaction monitoring was used to detect PB and PB-D6. The assay had a range from 500 pg/mL to 100 ng/mL with accuracies better than 15%. The run time for the assay was less than 1.5 minutes per sample. This presentation illustrates a rapid, selective and sensitive method for the determination of PB in guinea pig and mouse plasma.

#### **MS, GC/MS, LC/MS Symposia Oral Session**

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#### **163. Mass Directed Purification: a Look at Two Ends of Continuum: Active Ingredients in Green Tea and Isolation of Drug Impurities at Trace Levels.** John MacKay, Waters Corporation

#### **164. An Overview of Recent Developments for Mass Spectrometry in the Field of Proteomics.** Jeffrey W. Finch, Life Sciences R&D Laboratory, Waters Corporation, 34 Maple Street, Milford, MA 01757

In the field of proteomics, scientists are faced with increasing challenges in characterizing proteins in an attempt to understand function at the cellular level. Such understanding is critical in diagnosis and prevention of disease. In response, analytical methodology has expanded rapidly with emerging new technologies in sample preparation, liquid chromatography, and mass spectrometry. The purpose of this presentation will be to highlight some recent developments in the Waters Life Sciences and Micromass LTD. R&D laboratories in providing enabling tools to meet unique challenges in life sciences research. Some of these new tools include advances in sample preparation techniques. One example is a new chemical reagent, RapiGest™ SF, which improves solubility of hydrophobic proteins, and is capable of accelerating digestion, without generating interfering background ion signals in MALDI and ESI LC/MS. In addition, results with a new MALDI sample target plate, which integrates both sample concentration and desalting, will be presented. New tools for HPLC separations for protein analysis and identification will be also be featured, including an ESI-TOF LC/MS system for multi-dimensional analysis of whole proteins. For nano-scale LC/MS/MS analysis of complex protein digests, a fully automated multidimensional capillary LC system has been developed, which utilizes a novel format of trapping/desalting and strong-cation exchange (SCX) columns coupled to a 75  $\mu$ m id capillary analytical column. Considerations and recent advances for improving the performance of nanoLC columns coupled with nanoelectrospray MS will be discussed. Results from a new interface which allows off-line collection of capillary LC separations to MALDI target plates, via spots or continuous sample tracks, will be also be presented.

#### **MS, GC/MS, LC/MS Symposia Oral Session**

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#### **165. Migrating from LC/UV to LC/MS: Why Would I Add to My High Priced LC Today Anyhow? Is it Even Possible to Transfer My Current Methods?** John MacKay, Waters Corporation

#### **166. 21 CFR Part 11 Compliance Software for Total Organic Carbon (TOC) Instrumentation.** Brian Wallace, Mike Purcell and Ken O'Neal, Tekmar-Dohrmann, 4736 Socialville-Fosters RD, Mason, OH 45040.

21 CFR part 11 requires that laboratory analytical equipment have traceable, secure electronic records and signatures within an instrument's software. Mandatory system logins enforces electronic records and signature compliance for a TOC analyzer. Examples will be given of time-stamped audit trails and the data revision controls. The software manages access and user profiles to ensure data integrity. Current user information can be viewed in real time. Examples of how administrators can quickly identify potential security breaches- before they occur -with the error notification e-mail feature will be discussed. This paper will provide information on software compliance with 21 CFR Part 11. Also, this paper will provide features of a Total Organic Carbon (TOC) analyzer's software revision for electronic signatures and records.

#### **MS, GC/MS, LC/MS Symposia Oral Session**

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**167. Cleaning Validation by Total Organic Carbon Analysis: Implementing a New Technology to Improve the Process.**

Brian Wallace, Mike Purcell and Ken O'Neal, Tekmar-Dohrmann, 4736 Socialville-Fosters RD, Mason, OH 45040.

Current trends in pharmaceutical manufacturing have seen increasing demand for rapid sample analysis time along with low detection limits for cleaning validation samples. Total Organic Carbon (TOC) analysis provides a quick, accurate screening alternative for critiquing cleaning validation samples.

Some qualities that make TOC a viable part of a cleaning validation includes: high sensitivity, high recovery of samples, non-specific measurement, high throughput, ease of use (little method development), minimal interferences and cost effectiveness. In addition, general implementation guidelines for performing cleaning validation using TOC will be discussed. Analytical precision and analyte recovery for cleaning agents (detergents) and other possible contaminants that may be found in clean in place (CIP) solutions will be investigated for TOC. Typical laboratory testing includes the development and implementation of analytical methods that test for residues of previously manufactured products, cleaning detergents, chemicals, solvents, byproducts, degradants, and microbial contaminants (from wet environments after the cleaning validation). Almost any residual compound can be detected if three non-specific analytical (screening) tests are applied to a cleaning validation: TOC (for organics characteristics– carbon), pH (for acid/base characteristics) and conductivity (for ionic characteristics). TOC analysis demonstrated equivalent or better correlation to cleaning validation compounds in comparison to traditional analytical methods. In 1993, the FDA established guidelines on cleaning validation for the removal of both the product being manufactured and the cleaning agents used in the cleaning process. There are a variety of analytical techniques that can be used to comply with these guidelines. TOC analysis can be an effective tool for achieving fast, accurate and economical results for one's cleaning validation process. With a minimal amount of up front planning, standard operating procedures can be established simply and quickly. By taking a proactive approach to one's cleaning validation program, one can guarantee effective performance while minimizing downtime.

**MS, GC/MS, LC/MS Symposia Oral Session**

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**168. Fundamentals of Dissolution.** Barbara Hubert, United States Pharmacopeia, 12601 Twinbrook Parkway, Rockville, MD 20852-1790.

This synopsis of the USP Fundamentals of Dissolution Short Course presents the application of dissolution from the USP perspective, and will address the concept and scope of dissolution testing. The history of dissolution and details of USP Chapter <711> will also be discussed. The USP one-day Fundamentals of Dissolution Short Course is being offered at the Rocky Mountain Conference on Wednesday, July 31, 2002.

**MS, GC/MS, LC/MS Symposia Oral Session**

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## Nanotechnology • Monday Oral Sessions

**169. Preparation of Metal and Metal-Sulfide Nanoparticles by Reactive Spray Processing Using Carbon Dioxide Solutions.**

Harry W. Rollins, Idaho National Engineering and Environmental Laboratory, Chemistry Department, PO Box 1625, Idaho Falls, ID 83415-2208.

We have developed a reactive supercritical fluid spray processing method using carbon dioxide solutions of metal salts for the size-controlled preparation of nano-scale metal and metal-sulfide particles. The method has advantages over other nanoparticle preparation methods including the Rapid Expansion of Supercritical Solutions (RESS), the Supercritical Anti-Solvent process (SAS), and supercritical fluid micro-emulsions. In this method, carbon dioxide solutions of the metal salt are prepared using organo-phosphorous reagents. The carbon dioxide solution is then heated to supercritical temperatures and rapidly expanded through a nozzle into a liquid solution containing a second reactant. Reaction of the metal salt with the reactant in the solution results in the formation of the desired product. Silver and silver sulfide nanoparticles have been prepared using this method and characterized by UV-Vis absorption spectroscopy, X-ray diffraction, and transmission electron microscopy. The effects of processing conditions on material properties will be presented.

**Nanotechnology Symposia Oral Session**

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**170. Optimizing the Growth and Properties of Al<sub>2</sub>O<sub>3</sub>/W Nanolaminates Fabricated Using Atomic Layer Deposition Techniques.** Z.A. Sechrist, F.H. Fabreguette and S.M. George, Depts. of Chemistry and Chemical Engineering, University of Colorado, Boulder, CO 80309

Nanolaminates are expected to have unique thermal, mechanical, electrical and optical properties. Atomic layer deposition (ALD) methods have been used to grow Al<sub>2</sub>O<sub>3</sub>/W nanolaminates. Al<sub>2</sub>O<sub>3</sub> ALD is based on the binary reaction:  $2\text{Al}(\text{CH}_3)_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{CH}_4$ . W ALD is based on the binary reaction:  $\text{WF}_6 + \text{Si}_2\text{H}_6 \rightarrow \text{W} + 2\text{SiF}_3\text{H} + 2\text{H}_2$ . To optimize Al<sub>2</sub>O<sub>3</sub>/W nanolaminate growth, W ALD has been examined using in situ quartz crystal microbalance (QCM) investigations. The QCM measurements reveal extremely linear W growth versus the number of binary reaction cycles. The W deposition rates are dependent on substrate temperature and Si<sub>2</sub>H<sub>6</sub> exposures. The W ALD deposition rates vary from ~4 Å per AB cycle at 177 °C and ~10<sup>5</sup> L Si<sub>2</sub>H<sub>6</sub> exposures to ~7 Å per AB cycle at 325 °C and ~10<sup>7</sup> Si<sub>2</sub>H<sub>6</sub> exposures. QCM studies of Al<sub>2</sub>O<sub>3</sub>/W nanolaminate growth reveal that the nucleation of W ALD on Al<sub>2</sub>O<sub>3</sub> surfaces is a critical variable. Atomic force microscope studies indicate that the shortest W ALD nucleation times yield the lowest surface roughnesses for the Al<sub>2</sub>O<sub>3</sub>/W nanolaminates. Using minimum surface roughness as the goal, the reaction variables for Al<sub>2</sub>O<sub>3</sub>/W nanolaminate growth were further optimized using a Hadamard matrix approach. This optimization indicates that the surface roughness is: increased by WF<sub>6</sub> exposure time; decreased by Si<sub>2</sub>H<sub>6</sub> exposure time; decreased if Si<sub>2</sub>H<sub>6</sub> is the last reactant during W ALD; and decreased if Al(CH<sub>3</sub>)<sub>3</sub> is the starting reaction during Al<sub>2</sub>O<sub>3</sub> ALD. In addition, the surface roughness is decreased if the Al<sub>2</sub>O<sub>3</sub> is deposited first on the Si(100) substrate. A variety of Al<sub>2</sub>O<sub>3</sub>/W nanolaminates have then been grown using the conditions for minimal surface roughness. The structural analysis of these nanolaminates using transmission electron microscopy yields very well-defined superlattice structures. X-ray reflectivity measurements confirm very conformal W and Al<sub>2</sub>O<sub>3</sub> deposition with low interfacial roughness.

**Nanotechnology Symposia Oral Session**

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**171. Liquid Chromatographic Analysis of Nanosize Metal and Semi-Conductor Colloids.** J.P. Wilcoxon, Nanostructures and Advanced Materials Chemistry Dept. 1152, Sandia National Labs, Albuquerque, N.M. 87185-1421

We report liquid chromatography (HPLC) studies of the cluster size distributions, surface chemistry, and optical properties of nanosize colloids such as Au, Ag, Pt, MoS<sub>2</sub> and Si dispersed in organic solvents. Size-exclusion chromatography (SEC) measurements are calibrated by comparison with dynamic light scattering (DLS), and transmission electron microscopy (TEM). Synthesis of the colloids by solution epitaxial growth on extremely small (d < 2 nm) seed nanocrystals stabilized by surfactants provides several discrete generations of increasing size for study. The same technique allows the formation of core/shell colloids. SEC is used for feedback to improve the synthesis process. Our on-line characterization of the clusters includes a photodiode array (PDA) which provides the complete colloid absorbance spectra as a function of elution time (i.e. size). A scanning on-line fluorescence spectrometer is used to obtain the size-dependent photoluminescence (PL) of the colloids. A significant advantage of on-line optical characterization over conventional spectroscopy is that the spectra obtained are free of other chemical contaminants produced in the synthesis, and only a single size cluster contributes to the spectra. Among the interesting findings are:

- Evidence for discrete “magic” stability sizes in a variety of metal colloids.
- Observations of visible PL from chemically etched nanoparticles of Au
- Observations of the size-dependent PL from nanoparticles of Si and Ge
- Determination of the size-dependent plasmon resonance shift of Ag and Au.
- Effect of the MoS<sub>2</sub> band-gap on the photo-catalytic oxidation of organic molecules.

*This work was supported by the Division of Materials Science and Engineering, Office of Science, US Department of Energy under contract DE-AC04-AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.*

**Nanotechnology Symposia Oral Session**

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**172. Nucleation and Growth Chemistry of Tungsten Atomic Layer Deposition on Oxide Surfaces.** R.K. Grubbs; J.W. Elam; N. Steinmetz; and S.M. George, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309-0215

The nucleation and growth chemistry during tungsten (W) atomic layer deposition (ALD) on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> surfaces were studied using Auger electron spectroscopy (AES) and quadrupole mass spectrometry. W ALD was performed using sequential exposures of WF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub>. Differences in the nucleation process were observed for the two oxide substrates. The nucleation of W on SiO<sub>2</sub> required 8-9 WF<sub>6</sub>/Si<sub>2</sub>H<sub>6</sub> ALD reaction cycles while fewer cycles were needed for the nucleation of W on Al<sub>2</sub>O<sub>3</sub>. These results indicate that the identity of the underlying substrate has an affect on W nucleation using ALD. Additionally, the growth chemistry of W ALD was studied using quadrupole mass spectrometry. The gas-phase reaction products from each sequential half reaction were identified. The reaction products and Auger results were correlated to provide the stoichiometry of the surface reactions during the growth of W using atomic layer deposition.

**Nanotechnology Symposia Oral Session**

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173. **Mesoporous Silica Nanosphere-Based Fluorescence Sensor and Controlled Release Delivery System.** Victor S.Y. Lin, Cheng-Yu Lai, Daniela R. Radu, Brian G. Trewyn, Iowa State University, Department of Chemistry, Ames, Iowa 50011-3111.

We have recently synthesized a series of multi-functionalized mesoporous silica nanosphere (MSN) materials via an interfacial electrostatic interaction directed co-condensation reaction. The high surface areas and structurally ordered nano-scale pores of these molecular sieve materials allow guest molecules, such as drugs or neurotransmitters, to be adsorbed inside the porous framework. The functional groups of the inner pore surface of these MSN materials provides an excellent nanoenvironment for developing synthetic “enzyme or antibody active sites” for highly selective molecular recognition centers. Utilizing these derivatized mesoporous silica nanospheres, various fluorescence sensory systems with multi-functional group selectivity have been designed and fabricated to detect neurochemicals that are involved in interneuronal communication during neural stem cell differentiation in vitro. The incorporated functional groups on the pore surfaces of these MSN materials could also serve as linkers to covalently capture surface derivatized metal or semiconductor nanoparticles. The immobilized nanoparticles function as caps of the nanoporous channels and physically block the entrapped guest molecules from leaching out of the MSN materials. We demonstrated that the release of entrapped guest substrates could be regulated by removing the nanoparticle caps from the MSN materials. The results indicated that these nanoparticle-MSN composite materials are suitable for various controlled-release delivery applications.

**Nanotechnology Symposia Oral Session**

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174. **Creation of Sub-Micron Structures Through a ‘Bottom-Up’ Approach of Alternate Adsorption of Charged Polymeric Nanoparticles and Ultraviolet Irradiation.** Andrew D. Pris, Iowa State University, Department of Chemistry, 54 Spedding Hall, Ames, IA 50011; Marc D. Porter, Iowa State University, Department of Chemistry, 42 Spedding Hall, Ames, IA 50011

The drive to create increasingly small fluidic manipulation and handling devices is paramount to a variety of niches, including the separation, combinatorial, and pharmaceutical sciences. This presentation discusses the construction and characterization of three-dimensional sub-micron structures created through a novel ‘bottom-up’ fabrication technique that combines layer-by-layer deposition of charged polymeric nanoparticles and patterned photo-decomposition. The reproducible vertical and lateral size of the structure as a function of the number of nanoparticle layers is studied and confirmed with atomic force microscopy. Utilizing a variety of techniques, liquids have been confined in a structure created that possess volumes of ~10 fL. Several potential application schemes of this novel platform, including substrate patterning in micron domains as well as several catalytic and biological assays, will be discussed.

**Nanotechnology Symposia Oral Session**

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## NMR • Monday Oral Sessions

175. **Spun Silk and Spinning Bicelles: Studies by Solid-State NMR.** Beat H. Meier, Jacco van Beek, Giorgia Zandomenighi, Phil Williamson, Matthias Ernst and Marco Tomaselli, Physical Chemistry, ETH Zurich, ETH-Hönggerberg, 8093 Zurich, Switzerland

(i) NMR experiments for the structural characterization of spider dragline silk and related silks will be presented. It will be demonstrated, that the secondary and higher structure of the silk protein is not only dependent on the primary structure of the protein but also on the spinning process. Principles for the extraction of parameter distributions from experimental spectra will be discussed. (ii) The application of variable-angle spinning to bicellar systems (in solution) will be discussed. Bicellar nematic liquid-crystalline phases can be oriented with the director (the normal to the bilayer plane) at an arbitrary angle  $\theta$  to the applied magnetic field by sample rotation around one axis (variable-angle spinning) or around two axes (switched-angle spinning). Because the macroscopic order is lost for spinning around the magic angle, we apply switched-angle spinning experiments to measure the spectra as a function of the spinning angle. This allows one to tune the relative importance of dipolar and J interaction. Spectra of membrane-bound peptides will be presented.

**NMR Symposia Oral Session**

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- 176. The Use of Bicelles to Investigate the Interaction Between Methionine-Enkephalin and Membranes: a  $^{31}\text{P}$ ,  $^2\text{H}$  and  $^1\text{H}$  NMR Study.** Michèle Auger, Isabelle Marcotte and Marise Ouellet, Université Laval, Department of Chemistry, Quebec, Canada G1K 7P4; Stéphane Gagné, Université Laval, Department of Biochemistry and Microbiology, Quebec, Canada G1K 7P4; Érick J. Dufourc, Institut Européen de Chimie et Biologie, 33607, Talence, France

Methionine-enkephalin (Tyr-Gly-Gly-Phe-Met) (Menk) is a small endogenous peptide with a biological action similar to that of morphine. The conformation of this peptide in interaction with lipid membranes is of great interest since it is related to its biological activity. The interaction of the neuropeptide methionine-enkephalin with bicelles was studied by solid-state NMR. Bicelles, usually composed of long (DMPC) and short chain (DHPC) phospholipids, were modified to determine the effect of the lipid head group on the association with Menk. 10 mol% DMPC was replaced by the anionic lipid DMPG (Bic/PG). The  $^{31}\text{P}$  NMR results reveal changes in the lipid dynamics when Menk is interacting with the different bicellar systems. The  $^2\text{H}$  NMR results reveal a disordering effect of Menk on the lipids in the non-modified bicelles. Study of changes in the choline head group conformation by  $^2\text{H}$  NMR shows an increased order of the lipid head groups in non-modified bicelles (Bic) and the opposite effect in Bic/PG. Our results suggest that Menk would be located in the lipid head group/acyl chain interface of non-modified bicelles while it would associate with the Bic/PG surface. Finally, the conformation of Menk in isotropic bicelles in the absence and presence of DMPG was determined by high-resolution  $^1\text{H}$  NMR spectroscopy.

#### **NMR Symposia Oral Session**

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- 177. Probing Secondary Structure in Uniformly  $^{13}\text{C}$ ,  $^{15}\text{N}$  Labeled Peptides and Proteins by Solid State NMR: Three-Dimensional Dipolar Chemical Shift Spectroscopy.** Vladimir Ladizhansky, Massachusetts Institute of Technology, Francis Bitter Magnet Laboratory and Department of Chemistry, Cambridge, MA 02139; Christopher P. Jaroniec, Massachusetts Institute of Technology, Francis Bitter Magnet Laboratory and Department of Chemistry, Cambridge, MA 02139; Hartmut Oschkinat, Forschungsinstitut für Molekulare Pharmakologie, Robert-Rössle-Strasse 10, 13125 Berlin (Germany); Robert G. Griffin, Massachusetts Institute of Technology, Francis Bitter Magnet Laboratory and Department of Chemistry, Cambridge, MA 02139

A variety of solid state MAS NMR experimental methods have been developed which facilitate measurement of torsion angles in peptides and proteins. Applications of these techniques to uniformly labeled samples are particularly interesting since they allow simultaneous determination of multiple torsion angle constraints. However, spectra of uniformly labeled compounds usually suffer from lack of resolution. Hence, the existing torsion angle measurement techniques should be combined with chemical shift correlation methods in order to achieve a necessary spectral resolution. We explore different possibilities to combine 2D chemical shift correlation methods with the existing torsion angle experiments. In particular, we will focus our attention on the measurement of  $\psi$  torsion angle. The experiments are demonstrated in [ $^{13}\text{C}$ ,  $^{15}\text{N}$ ] labeled 62 residue  $\alpha$ -spectrin SH-3 domain.

#### **NMR Symposia Oral Session**

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- 178. Direct Detection of Sodium Ions in Biological Structures by Solid-State  $^{23}\text{Na}$  NMR Spectroscopy.** Gang Wu, Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Recent discoveries in X-ray crystallography have provided strong evidence to challenge the traditional view about the roles of alkali metal cations such as  $\text{Na}^+$  ions in biological structures. However, direct detection of  $\text{Na}^+$  ions bound to biological macromolecules is a difficult task even with state-of-the-art X-ray crystallographic techniques. This is because  $\text{Na}^+$  ions have virtually identical X-ray scattering power as water molecules, making it very difficult to distinguish these two species on electron density maps. We propose to use solid-state  $^{23}\text{Na}$  NMR as a complementary technique for detecting  $\text{Na}^+$  ions in biological structures. Results on solid-state  $^{23}\text{Na}$  NMR of DNAs and proteins will be presented. Potentials of performing solid-state  $^{23}\text{Na}$  NMR at very high magnetic fields will also be discussed.

#### **NMR Symposia Oral Session**

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- 179. Solid State  $^{17}\text{O}$  NMR of Organic Materials - Characterisation of Hydrogen Bonding.** R. Dupree, A.P. Howes, K.J. Pike and M.E. Smith, Department of Physics, University of Warwick, Coventry, CV4 7AL, U.K.; D.H.G. Crout and R. Jenkins, Department of Chemistry, University of Warwick, Coventry, CV4 7AL; A. Kukol, Department of Biological Sciences, V. Lemaitre and A. Watts Department of Biochemistry, University of Oxford, South Parks Road, Oxford, OX1 3QU; A. Samoson, National Institute for Chemical Physics and Biophysics, Estonian Academy of Sciences, Akadeemia Tee 23, Tallinn, EE12618, Estonia

$^{17}\text{O}$  NMR is reported from a range of organic materials including strongly hydrogen bonded carboxylic acids, and amino acids and salts. A range

of techniques including static MAS, 3Q and DOR are employed to distinguish the different sites and determine the NMR interactions ( $\chi_Q$ ,  $\eta$  and  $\delta_{iso}$ ) at each site. High resolution spectra can be obtained with DOR linewidths in some cases being  $\sim 0.2$  ppm allowing clear resolution of all the oxygen sites. The quadrupolar coupling constant can be greater than 9 MHz, amongst the largest yet observed for  $^{17}\text{O}$  from a solid. Fast (up to 42 kHz)  $^1\text{H}$  MAS NMR spectra are also reported to examine the sensitivity of the  $^1\text{H}$  chemical shift to the hydrogen bond strength. The NMR parameters are compared to other measures of the hydrogen bond strength. Calculations within the Gaussian programme have been used to investigate the sensitivity of the NMR interaction parameters to the location of the proton in the hydrogen bond. The EPSRC and the Royal Society are thanked for their support of this research.

#### **NMR Symposia Oral Session**

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#### **180. Deuterium NMR, Temperature, and Hydrogen Bonding in 2,4 Diketones.** Xingang Zhao, Carter Silvermail, John Belot and Gerard S. Harbison, University of Nebraska at Lincoln

Deuterium quadrupole coupling constants (QCCs) are a sensitive probe of the hydrogen bond strength in O-D...O and similar systems, tending to increase as the hydrogen bond strength decreases. In such systems, we can define a strong hydrogen bond as having an O-O distance of less than 2.60 Å. At about this distance, in linear hydrogen bonds (and about 2.45 Å in 120° bent hydrogen bonds) the potential energy along the hydrogen bond coordinate goes from a shallow single-well minimum to a low barrier double-well. It is not easy to distinguish between these two alternatives from their QCCs alone.

2,4-diketones are known to enolize at one of the carbonyl oxygens and form an internal O-H...O hydrogen bond, which can readily be exchanged with deuterium. 3-cyano-2,4-pentanedione and 4-cyano-2,2,6,6-tetramethyl-3,5-heptanedione were studied by variable temperature solid state deuterium NMR. While the compounds differ in O-O distance by only 0.07 Å, their temperature coefficients are different in sign; the QCC of the shorter hydrogen bond increases with temperature, while that of the longer hydrogen bond decreases. We can reproduce these effects quantitatively by solving a three-dimensional vibrational Hamiltonian constructed using high-level *ab-initio* calculations of the potential. This unusual behavior could be a characteristic probe of hydrogen bonds in macromolecules.

#### **NMR Symposia Oral Session**

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#### **181. Examples of NMR Investigation of Secondary Transitions and Motional Cooperativity in Solid Polymers.** Françoise Lauprêtre, Laboratoire de Recherche sur les Polymères, 2 à 8 rue Henri Dunant, 94320 Thiais, France

In solid polymers, the secondary relaxations arise from local motions involving a small number of main-chain or side-chain atoms. Therefore, the identification of the mobile units by using a selective technique such as high-resolution solid-state  $^{13}\text{C}$  NMR is a necessary step to determine the origin of the transitions. Besides, a comprehensive description of the local motions that are responsible for the secondary transitions also requires the determination of the geometry of the motions, the size of the moving units or the length of cooperativity. In order to obtain such information, we have used an approach based on i) the study of materials as a function of progressive changes introduced in their chemical structure and ii) the comparison of results obtained from NMR and other techniques. Examples will deal with the secondary transitions of neat and antiplasticized polyethylene terephthalate, epoxy resins and methylmethacrylate-imide copolymers.

#### **NMR Symposia Oral Session**

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#### **182. Dynamics of Poly(vinyl acetate)- $\text{d}_3$ in Bulk and on Silica.** Frank D. Blum, University of Missouri-Rolla, Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65409-0010; Robert O'Connor, Washington University, St. Louis, MO, Department of Chemistry, Campus Box 1134, One Brookings Drive, St. Louis, MO 63130-4899.

We have used deuterium NMR line shapes and two-dimensional exchange NMR to probe the dynamics of poly(vinyl acetate)- $\text{d}_3$  in bulk and adsorbed on silica at very low amounts. In bulk, the dynamics of the polymer are complex, but spatially homogeneous. On silica, the polymer dynamics are heterogeneous near the glass transition with a motional gradient occurring perpendicular to the surface. 2D exchange NMR has also been used to confirm and quantify the dynamics of the polymer both in bulk and on silica. We also discuss the implications of this motional gradient on some of the physical properties of thin film systems.

#### **NMR Symposia Oral Session**

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- 183. Segmental Dynamics and Penetrant Diffusion in a Permeable Polymer Blend.** Haihui Cao, Guoxing Lin, Jinghui Zhang, Marcus Giotto, Paul T. Inglefield, [Alan A. Jones](#), Clark University, Carlson School of Chemistry and Biochemistry, Worcester MA 01610

Deuterium spin-lattice relaxation times and deuterium quadrupolar line shapes are used to characterize the chain dynamics of  $d_4$  poly(ethylene oxide) (PEO) in a blend with poly(methyl methacrylate) (PMMA). At low concentrations of PEO (10 to 30 wt %), segmental dynamics of this component is in the range of nanoseconds well below the thermal glass transition although there is a broad distribution of correlation times. At the same temperature, diffusion of diethyl ether was measured using the pulse field gradient diffusion experiment. Diffusion constants typical of rubbery polymers were observed and the diffusion constant was dependent on the time over which diffusion occurs in a three pulse diffusion experiment. This is indicative of tortuous diffusion. To account for this, rapid diffusion is proposed to take place in PEO rich domains which are bounded by PMMA rich domains. The latter act as barriers to penetrant diffusion. A simulation model for this situation will be presented.

**NMR Symposia Oral Session**

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- 184. Dopant Distribution in a Conducting Polymer by Dipolar Recoupling Methods.** [Matthew Espe](#), Tanya Young and Jennifer Rapp, Department of Chemistry, University of Akron, Akron, OH 44325-3601.

The conductivity of polyaniline (PANI) can range over 3-4 orders of magnitude depending on the acid used for doping the polymer. In addition, the conductivity of PANI is higher than expected at doping levels well below the maximum. As the materials are completely, or nearly completely amorphous, little structural information is currently available for these systems, inhibiting the correlation of conductivity and dopant. We have been investigating the structure -electronic and geometric- of the polymer/acid complex by solid-state NMR where the polymer is doped with phosphoric or phosphonic acids. The  $^{31}\text{P}$  chemical shift of the acid indicates that at lower doping levels the acid preferentially occupies sites in the polymer matrix that are more disordered in the solid-state. Structural differences between the *ordered* and *disordered* regions of the doped polymer have been characterized by  $^{31}\text{P}$ - $^{15}\text{N}$  REDOR when  $^{15}\text{N}$ -PANI is used. The distribution of the acid in the polymer, at various doping levels, has been monitored by measuring the  $^{31}\text{P}$ - $^{31}\text{P}$  dipolar couplings with the homonuclear dipolar recoupling technique of DRAMA. The data show that the acid molecules are clustered in the polymer and not uniformly distributed, and this clustering accounts for the unexpectedly high conductivities.

**NMR Symposia Oral Session**

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- 185. Molecular Adsorption in Single-Walled Carbon Nanotubes.** [Alfred Kleinhammes](#), Xiaojing Yang, and Yue Wu, University of North Carolina, Department of Physics and Astronomy, Chapel Hill, NC 27599-3255

Single-walled carbon nanotubes (SWNTs) possess interesting properties for both electron transport and molecular transport. The tubular structure and the nanometer-sized diameter make adsorption of various gas molecules inside SWNTs very efficient. The unique electronic structure of SWNTs allows the control of adsorption inside SWNTs via external parameters. This makes SWNTs attractive for understanding molecular and ionic transport inside nano-channels, an issue of importance in biological systems. We will discuss adsorption properties of a variety of gases inside SWNTs. Relaxation mechanisms and diffusion processes in the confined one-dimensional geometry of SWNTs will be discussed.

**NMR Symposia Oral Session**

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## NMR • Tuesday Oral Sessions

- 186. SIMPSON and SIMMOL: a Flexible Vehicle for Numerical Simulations in Biomolecular Solid-State NMR.** [Thomas Vosegaard](#), Robert Schultz, Jimmy T. Rasmussen, Mads Bak, and Niels Chr. Nielsen, Laboratory for Biomolecular NMR Spectroscopy, University of Aarhus, Denmark.

Numerical simulations play an increasingly important role in solid-state NMR for development of new pulse sequences as well as for interpretation of experimental spectra. For biological solid-state NMR this evolution goes hand in hand with the increasing complexity of the spin systems typically encountered when going from sparse to uniform isotope labeling. The SIMPSON "computer spectrometer" was recently introduced (Bak et al., JMR 147, 296, 2000) and proved capable of simulating multi-dimensional, multi-pulse experiments on spin systems



counting multiple spins. More recently, SIMMOL (Bak et al., JMR 154, 28, 2002) has been introduced to help setting up and visualizing these complex spin systems in polypeptide structures. Here we present examples on how the flexibility of the Tcl-interfaced SIMPSON/SIMMOL programs may be used to speed up numerical simulations, perform spectrum simulations on large proteins, and provide insight into complex pulse sequences. This includes a detailed analysis of the prospects of solid-state NMR on large uniformly labelled membrane proteins in oriented bilayer samples (Vosegaard and Nielsen, JBN 22, 225, 2002) and interpretation of experimental spectra in terms of structural constraints.

#### NMR Symposia Oral Session

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- 187. New Structural Probes in High-Resolution Solid-State NMR.** Anne Lesage, Steven Brown, Sabine Hediger and Lyndon Emsley, Laboratoire de Stereochimie et des Interactions Moleculaires, UMR-5532 ENS-Lyon/CNRS, Laboratoire de Recherche Conventione du CEA (23 V), Ecole Normale Superieure de Lyon, 46 Allee d'Italie, 69364 Lyon, France.

Scalar couplings are potentially very rich probes of structure in solids. However, until recently their use in solid-state NMR has been rather limited, since they are usually about two orders of magnitude smaller than the dominant dipolar interactions. In the first part of this talk we will discuss recent results involving scalar couplings in three areas of solid-state NMR. First we present an analysis of carbon-13 lineshapes in solid-state magic-angle-spinning experiments on carbon-13 enriched compounds. It has recently been noticed by several groups that the lineshapes observed in carbon-13 spectra often do not present the simple multiplet structures expected from the J couplings. We provide an explanation for these lineshapes in terms of a *coherent cross correlation mechanism*. Second, we show that *J couplings across hydrogen bonds can be observed and measured* in the solid-state using nitrogen-15 CPMAS INADEQUATE experiments. To our knowledge, these experiments constitute the first-ever direct detection of a solid-state hydrogen bond, i.e., we do not infer the presence of a bond from either the position of the proton (X-ray) or from the proton chemical shift, but rather directly from the presence of an interaction that requires a bond. Third, we show that *carbon-proton scalar couplings can also be measured*. We show examples for catalytically active organometallic complexes on silica surfaces. In these cases, the one-bond C-H J couplings vary substantially from one conformer to another, and we relate this variation to structural changes in the complex, thereby providing a direct measurement of *agosticity in a surface species*.

These last experiments, involving heteronuclear C-H correlation, rely for their success on good proton-proton homonuclear decoupling. Moreover, due to its high sensitivity, the proton constitutes an attractive probe nucleus for the study of powdered organic molecules by solid-state NMR. However in solids the dominant homonuclear proton-proton dipolar interactions lead to broad proton resonances that usually obscure resolution of the spectrum. In the second part of the talk, a new family of proton-proton homonuclear decoupling sequences based on continuous phase modulation and dubbed DUMBO will be discussed. Several examples are provided where the DUMBO decoupling scheme is incorporated into either homonuclear proton-proton experiments or heteronuclear proton-carbon experiments. The performance of the DUMBO sequence is analysed experimentally for various  $B_1$  decoupling fields, various spinning speeds (*up to 30 kHz*) and various  $B_0$  fields (up to 750 MHz).

#### NMR Symposia Oral Session

Steven Brown, Laboratoire de Stereochimie et des Interactions Moleculaires, UMR-5532 ENS-Lyon, France.

- 188. Dipolar Couplings in Solids: Measurement and Assignment Using Novel Techniques.** Robert H. Havlin, Jamie D. Walls, Wyndham B. Blanton, Alexander Pines Materials Sciences Division, Lawrence Berkeley National Labs, Berkeley, CA, 94720; Department of Chemistry, University of California Berkeley, Berkeley, CA, 94720,

We have developed an experiment that measures dipolar couplings in a solid sample by removing the anisotropic part of the dipolar spectrum. The experiment eliminates the angular dependence of dipolar coupling using the familiar equality  $\sin^2 \theta + \cos^2 \theta = 1$  through the addition of evolution pathways generated at one angle. We present results showing the application of this experiment to homonuclear dipolar coupling in solids to provide isotropic spectra. Additionally we are working towards the exciting prospects of extending these techniques to heteronuclear dipolar couplings. The technique developed should allow for the analysis of dipolar couplings in more complex systems in the solid state.

#### NMR Symposia Oral Session

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- 189. ISTMAS and New Developments for High-Resolution NMR of Half-Integer Spin Nuclei.** Christian Fernandez, Cláudia Morais, Laboratoire de Catalyse et Spectrochimie, CNRS-6506, ISMRA/Université de Caen, 14050 Caen, France; Jean-Paul Amoureux, Julien Trebosc, LCPS, CNRS-8012, Université de Lille-1, 59655 Villeneuve d'Ascq, France; João Rocha, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

Until recently, getting high-resolution NMR spectra of quadrupolar nuclei has been quite challenging. In the late 80's, DOR and DAS were first proposed in order to cancel the second-order quadrupolar interaction that is one of the major contributions to broadening of the central transition

(CT) in conventional MAS experiments. Both methods, however, strongly suffer from technical limitations. Frydman et al (1) demonstrated that CT line narrowing may be obtained by using the MQMAS experiment that correlates in a 2D spectra single-quantum and multiple-quantum (MQ) transitions. However, in spite of considerable efforts for optimization of the MQMAS pulse sequence, it remains non quantitative and suffers from low sensitivity. Very recently, Gan (2) proposed a new 2D method, called STMAS, that generates isotropic spectra by correlating the CT and STs (satellite transitions). This method is more efficient than MQMAS, because the required transfers occur only between observable single-quantum coherences. In this communication, we suggest a reverse experiment called I-STMAS (Inverse STMAS). Similarly to STMAS, this method correlates CT and STs coherences but in a reverse manner, i.e., that the CT evolves during the t1 period while STs are detected during t2. We will show that this method is actually a complementary experiment with respect to STMAS and MQMAS with some interesting new properties. Moreover, we will discuss some features that allow designing new sequence for heteronuclear correlation. Finally, some examples of application of I-STMAS and STMAS to various systems will be given.

[1] Frydman, L.; Harwood, J. S. J. Am. Chem. Soc. 1995, 117, 5367.

[2] Gan, Z. J. Am. Chem. Soc. 2000, 122, 3242.

### NMR Symposia Oral Session

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- 190. New Strategy for Structural Analyses by Solid-State NMR.** JP. Amoureux,<sup>1</sup> J. Trebosc,<sup>1</sup> M. Pruski,<sup>2</sup> J. Wiench,<sup>2</sup> S. Ganapathy,<sup>3</sup> C. Huguenard,<sup>4</sup> F. Taulelle,<sup>4</sup> D. Massiot<sup>5</sup> <sup>1</sup>Université de Lille (LCPS-CNRS 8012); <sup>2</sup>Ames Laboratory, Iowa, USA; <sup>3</sup>NCL, Pune, India <sup>4</sup>Université de Strasbourg (FRE-CNRS 2423), France; <sup>5</sup>CRMHT, Orléans, CNRS 4212, France

We will present several new or improved methods for structural analysis of solids by NMR spectroscopy. First, a new, unified representation will be shown for the three high-resolution MAS-based methods that are now available for half-integer quadrupolar nuclei: MQMAS, STMAS and I-STMAS. Second, an extension of the FS-REDOR experiment will be demonstrated, which allows for selective determination of internuclear distances between spin-1/2 and quadrupolar nuclei under isotropic resolution. Third, a new type of REDOR experiment (FS-J-REDOR) will be shown which, in addition to the internuclear distances, provides a direct measure of the J couplings and the geometric arrangement of the nuclear spins. The FS-J-REDOR can be applied to quadrupolar nuclei under isotropic resolution, as well. Finally, we will show the two-dimensional correlation spectra between <sup>1</sup>H and <sup>15</sup>N, in natural abundance, observed in catalysts.

### NMR Symposia Oral Session

JP. Amoureux, Université de Lille (LCPS-CNRS 8012)

- 191. Theoretical and Experimental Developments of the Chemical Shift Tensor and its Use for Structure Determination.** Raiker Witter, Wolfam Prieß, Stephanie Hesse, Ulrich Sternberg PAF / IOQ / HF, F.-S.-Universität Jena, Max Wien Platz 1, 07743 Jena, Germany

First, an effective method for calculating coordinate dependent chemical shift tensors will be represented<sup>[1,2,3]</sup>. Starting from the bond polarization theory<sup>[1]</sup> energetically derived chemical shift pseudo forces are added<sup>[4]</sup>. They are used in the COSMOS<sup>[4,5,6,7,8]</sup> NMR force field for structure determination. To the molecular force field, NOE restrictions and energetically derived chemical shift pseudo forces are introduced. With <sup>13</sup>C chemical shift pseudo forces the proton positions of the x-ray crystal structure of d-mannitol are refined<sup>[4]</sup>.

The 3D structure of a pseudopeptide zinc complex, which was designed and synthesized similar to the catalytic center of the carbonic anhydrase<sup>[9]</sup>, was determined. 18 NOE distance restraints and 17 <sup>13</sup>C chemical shifts were applied for molecular dynamics, simulated annealing and geometry optimizations. To confirm the COSMOS-NMR results, the three best structures were optimized by density functional theory calculations. A complex with tetrahedral coordinated zinc has been found to be most favorable. Additionally, a complex with threefold coordinated zinc was found. It can be supposed that this structure can function as a transition state in the catalytic reaction (CO<sub>2</sub> + H<sub>2</sub>O HCO<sub>3</sub><sup>-</sup> + H<sup>+</sup>)<sup>[10]</sup> of the carbonic anhydrase.

Second, a new powder pattern recoupling experiment is introduced. The idea of Tycko<sup>[11]</sup> is generalized and improved. Real pulse lengths are taken into account. The method is applicable to spinning speeds up to 30kHz and ultra high fields. The powder patterns are scaled and this scaling factor can be chosen to fit the spectra into the spectral window. No suppression of sidebands is necessary, so that this method is more efficient than the SUPER<sup>[12]</sup> sequence for chemical shift anisotropies higher than ~7kHz. Spectra shearing can be avoided easily. The theoretical background and experimental verifications on model substances will be given. The chemical shift anisotropies of silk<sup>[13]</sup>, cellulose<sup>[14]</sup> and bradykinin are obtained. Structural discussions will be given.

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#### NMR Symposia Oral Session

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192. **Polymer-Inorganic Composite Electrolytes for Lithium Ion Batteries.** C.-G. Joo, L. Bronstein, R. Karlinsey, and J. W. Zwanziger, Department of Chemistry, Indiana University, Bloomington, IN 47405

We are developing a class of lithium ion electrolytes based on polyethylene oxide and an organic-inorganic composite, itself consisting of an aluminosilicate/polyether silane material. These materials show good mechanical and thermal properties, and good electrochemical properties when combined with lithium salts. We report here on their intermediate range structure as characterized largely by NMR methods, including spin diffusion to determine the sizes and origins of mobile domains, multiple quantum spin counting to assess ion aggregation, and relaxation measurements to characterize the dynamics. These measurements are supplemented with impedance spectroscopy, Raman spectroscopy, transmission electron microscopy, and thermal analysis.

#### NMR Symposia Oral Session

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193. **Recent Insights into Silica-Water Surface Chemistry by  $^{23}\text{Na}$ ,  $^{133}\text{Cs}$ , and  $^{29}\text{Si}$  MAS NMR Spectroscopy.** Robert S. Maxwell, Susan A. Carroll, William Bourcier, Chemistry and Materials Science Directorate and Earth and Environmental Sciences Directorate, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94551

The dissolution of crystalline and amorphous  $\text{SiO}_2$  polymorphs plays a critical role in a variety of environmental processes, including soil formation and weathering, disposal of radioactive waste, and thermally enhanced oil recovery. Traditional kinetic studies have concentrated on batch dissolution studies and comparison to various surface complexation models. Direct spectroscopic evidence for proposed reaction species, however, has been rare. We have combined traditional batch and flow-through dissolution experiments and surface complexation modeling with multinuclear NMR spectroscopy to re-evaluate amorphous silica reactivity as a function of solution pH and reaction affinity in NaCl and CsCl solutions.  $^{23}\text{Na}$  and  $^{133}\text{Cs}$  MAS and wide-line NMR have been used to measure cation speciation while  $^{29}\text{Si}$   $\{^1\text{H}\}$  CPMAS experiments have been used to measure silica surface speciation. All of our NMR data suggest that changes in surface speciation are driven by solution pH and to a lesser extent alkali concentrations, and not by reaction time or saturation state. The  $^{29}\text{Si}$  cross-polarization NMR results show that silanol surface complexes decrease with increasing pH. The  $^{23}\text{Na}$  and  $^{133}\text{Cs}$  NMR results show that the alkali cations form outersphere surface complexes and that the concentration of these complexes increase with increasing pH, opposite to that of the silanol complexes ( $>\text{SiOH}$ ). We have described the silica-water surface chemistry in the context of the triple layer model and equilibrium constants derived from solution analyses alone do not fit our experimental data. Our NMR data, as a result, has provided new insights into dissolution kinetics. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

#### NMR Symposia Oral Session

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194. **It's Not Only About Detection Limits: the Role of NMR in Environmental Analyses.** Cynthia K. Larive, Laurie A. Cardoza, William H. Otto, Christine Hellriegel and Ceyda Uyguner, University of Kansas, Department of Chemistry, Lawrence, KS 66045

Although a significant focus of many environmental studies is trace analysis at low concentrations (typically ppm to ppb), qualitative analysis of compounds present in the environment, either naturally or as contaminants, is also important. NMR is well recognized as the premiere analytical method for problems related to structure elucidation. Recent results from our research will be presented illustrating the power of NMR for structure elucidation of complex natural samples such as humic substances. We are also engaged in a study of the environmental fate of a class of antibiotics known as the fluoroquinolones, synthetic antibiotics with broad-spectrum antibacterial activity. Although these compounds are present in the environment in low concentration they have the potential to disturb the natural balance of microbial communities and have

been suggested to induce antibiotic resistance in non-pathogenic organisms. Little is known about the attenuation and fate of these antibiotics in the environment. LC-NMR along with LC-MS-MS is being used for the qualitative analysis of transformation products of fluoroquinolone antibiotics formed in “quasi-natural” water conditions.

#### **NMR Symposia Oral Session**

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- 195. Solid-State NMR Characterization of Pyrene Sorption to Cuticular Materials.** Joseph R. Sachleben, Department of Chemistry, Otterbein College, Westerville, OH 43081; Benny Chefetz, Department of Agricultural, Food and Environmental Quality Sciences, Hebrew University of Jerusalem, Rehovot 76100, Israel; Ashish Deshmukh, Patrick G. Hatcher, Department of Chemistry, The Ohio State University, Columbus, OH 43210

Cuticular materials such as cutin and cutan can make up significant portions of some soils. Characterizing the sorption of pollutants to these soil components is a critical step in understanding the physical processes occurring in real soils. We probed the interaction between pyrene and tomato fruit cutin and *Agave americana* cutan with one- and two-dimensional solid-state nuclear magnetic resonance (1D and 2D NMR) spectroscopy. We found that the  $^{13}\text{C}$  longitudinal relaxation time ( $T_1$ ) of pyrene decreases significantly from that of crystalline pyrene upon sorption to both cutin and cutan, indicating that the pyrene is mobile upon sorption. Magic angle spinning experiments at low spinning frequencies (2-4kHz) demonstrates that this motion can be either isotropic or anisotropic depending upon the cuticular material and the length of time after sorption the NMR experiment is acquired. This result indicates the pyrene can access different regions of the cuticular materials with time possibly explaining aging effects in sorption/desorption experiments. 2D Heteronuclear correlation experiments elucidate the interactions between the soil organic matter and the pollutant. These experiments are allowing the development of models of sorption of hydrophobic pollutants to cuticular materials.

#### **NMR Symposia Oral Session**

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- 196. The Identification and Quantification of Reaction Sites at Surfaces of Glasses Using Solid-State NMR.** Karl T. Mueller, Roderick A. Fry, and Natia Tsomaia, Penn State University, Department of Chemistry and Materials Research Institute, University Park, PA 16802.

The characterization of reactive glass surface and subsurface environments is of primary importance in understanding the chemistry of the interface between a glass and its surrounding environment. In one set of studies, glasses in the family  $\text{Na}_2\text{O} - x\text{Al}_2\text{O}_3 - (3-x)\text{SiO}_2$ , as well as variable Na-containing glasses which have mineral analogues, have been exposed to acidic solutions under ambient conditions. Solid-state NMR spectroscopy reveals the identity of aluminate and silicate environments in the leached surface layers of these glasses as well as a sample of albite crystal subjected to the same aqueous leaching. While  $^{29}\text{Si}$  and  $^{27}\text{Al}$  magic-angle spinning (MAS) NMR experiments report on the bulk structures of the samples, cross-polarization from hydrogen atoms that are present only in the surface layers provides structural information from the regions of the sample transformed during treatment. In a second set of studies to be reported here, we focus on fiberglass materials, where the surface hydroxyl concentration plays the most important role in determining the interfacial properties. Probing these fiberglass surfaces is inherently difficult due to their low surface area and complex morphology, and it is well known that in most cases NMR spectroscopy is too insensitive of a technique to quantitatively probe low surface area samples. Therefore, to enhance the sensitivity and increase the dynamic range of NMR for detecting and quantifying surface hydroxyl groups on fiberglass, fiber surfaces may be modified with chemical agents containing highly NMR-sensitive nuclei. Using this chemical modification, we have been able to provide a novel use of single-resonance NMR for the detection and quantification of reactive hydroxyl groups on fiberglass surfaces.

#### **NMR Symposia Oral Session**

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## NMR • Wednesday Oral Sessions

197. **Through the Electrons, Darkly.** Jeffrey A. Reimer, Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462

My research colleagues have been able to exploit hyperfine couplings between electrons and nuclei to direct the systematic design of engineering materials. Along the way we have learned some interesting things, such as the “covalency” of chemical bonds...and, most recently, a strategy for preparing hyperpolarized nuclei.

### NMR Symposia Oral Session

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198. **Density Functional Theory Calculations of EPR Parameters of Transition Metal Complexes.** Sarah C. Larsen, Department of Chemistry, University of Iowa, Iowa City, IA 52242

Density functional theory methods for calculating EPR parameters, such as electronic g-tensors and electron nuclear hyperfine interaction (A) tensors, were applied to transition metal complexes. g-tensors were calculated using the Amsterdam Density Functional (ADF) program. A-tensors were calculated using ADF and Gaussian98 programs, respectively. Several examples of the application of these methods to transition metal complexes will be presented. In the first example, DFT calculations of the EPR parameters of vanadyl complexes were able to successfully reproduce experimental trends in g and A with ligand identity. The computational results were used to interpret the EPR data for vanadyl-exchanged zeolites. In the second example, the orientation dependence of proton hyperfine coupling constants for water molecules in a vanadyl pentaquo complex was calculated using DFT methods. The computational results compared favorably with single crystal ENDOR data. In the third example, the orientation dependence of the metal and ligand hyperfine coupling constants for vanadyl imidazole complexes was calculated. In the fourth and final example, the EPR parameters were calculated for a series of copper complexes. This selection of computational results demonstrates the potential of DFT methods for enhancing the interpretation of EPR data of transition metal complexes.

### NMR Symposia Oral Session

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199. **1- and 2-Dimensional “Relaxation” Experiments for Elucidation of Structures from Micron to Millimeter.** Yi-Qiao Song, Schlumberger-Doll Research, Old quarry road, Ridgefield, CT 06877

Why does an hourglass work? How does water flow in aquifers and crude oil in rocks? What causes concrete to fail? The answer to these diverse questions lies in the structures of the constituents, such as the grain packing, pore sizes, pore shape, and connectivity. The central technique in our study is based on molecular diffusion and the internal field inhomogeneity due to susceptibility contrast. The stimulated echo sequence is used to first create a magnetization modulation and then to monitor its Decay due to Diffusion in the Internal Field (DDIF). This method allowed a detailed characterization of pore sizes in a variety of porous materials. We have combined this method with mercury intrusion to identify details of pore structure, such as pore bodies and throats, connectivity and pore shape. The pore connectivity information is shown to be essential to understand fluid drainage in rocks. DDIF has also been applied to biological tissues. Central to the analysis of DDIF and other relaxation experiments is numerical Laplace inversion. We have developed 1-D, and recently a fast 2D Laplace inversion algorithm to be used on desktop PCs. The 2D algorithm enables 2D relaxation and diffusion experiments in a fashion analogous to 2D Fourier spectroscopy.

*Collaborations: D. F. Allen, W. Kenyon, S. Ryu, P. N. Sen, L. Venkataramanan, M. D. Hurlimann, Schlumberger-Doll Research; Quan Chen, Chinese Academy of Sciences & CNPC; N. V. Lisitza, W. S. Warren, Princeton University; L. J. Zielinski, Harvard University.*

### NMR Symposia Oral Session

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200. **Thin Film and Interfacial Characterization by Solid State  $^{19}\text{F}$  NMR.** Karen K. Gleason, Department of Chemical Engineering, MIT, Cambridge, MA 02139

The low sensitivity of NMR relative to other characterization techniques has limited its application to the study of thin films and interfaces. However, the 100% isotopic abundance, the high gyromagnetic ratio, and the large chemical shift range of the  $^{19}\text{F}$  nucleus allow for NMR detection using a relatively small number of spins. Indeed,  $^{19}\text{F}$  solid-state NMR is sufficiently sensitive to determine the bonding configurations on fluorinated diamond surfaces and for two-dimensional wide-line separation (WISE) spectroscopy on thin film samples. Under fast magic angle spinning,  $^{19}\text{F}$  NMR becomes a rapid and straightforward method for quantitatively determining the molecular architecture of thin films and interfaces. For fluorocarbon films deposited by chemical vapor deposition,  $^{19}\text{F}$  NMR has provided details on crosslinking, branching, and chain termination unavailable by any other method. This understanding has enabled the CVD method to be tailored for the production of films with high thermal stability at enhanced growth rates. Additionally, the mechanistic understanding has led to CVD synthesis of unique fluorocarbon-

silicon copolymers, having structures that can be verified by  $^{19}\text{F}$  NMR.

#### **NMR Symposia Oral Session**

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- 201. Magnetic Resonance Imaging Microscopy—Pushing Sensitivity and Resolution Limits.** Luisa Ciobanu, Charles H. Pennington, Department of Physics; Ohio State University, 174 W. 18th Avenue; Columbus, OH 43210.

We report advances in sensitivity and resolution of MRI microscopy and resulting new applications. Using strong ( $>10$  Tesla/meter) gradient fields, tiny ( $\sim 100\mu\text{m}$ ) micro-receiver coils, and suitably designed pulse sequences we achieve proton MRI resolutions of  $\sim 3\mu\text{m}$  in all three spatial dimensions, with somewhat wide field-of-view ( $\sim 100\mu\text{m}$ ). We report multiple applications of the technique, including advances in imaging of biological cells. *Supported by NSF/DBI9987079.*

#### **NMR Symposia Oral Session**

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- 202. New Methods for Enhancing Sensitivity in Solid-State NMR and their Application to Glasses.** P.J. Grandinetti, H.T. Kwak, S. Prasad, and T. Clark, The Ohio State University, Department of Chemistry, 100 West 18th Ave, Columbus, OH 43210

We will describe new methods for enhancing the NMR sensitivity of the central transition of quadrupolar nuclei using an improved RAPT (Rotor Assisted Population Transfer) preparation that employs off-resonance Gaussian pulses. We will also show how Gaussian-RAPT can be used to measure quadrupolar coupling constants as well as perform selective suppression or excitation of solid state NMR resonances of quadrupolar nuclei based on their coupling constants. RAPT can be combined with any solid-state NMR experiment that draws its polarization from the central transition. Gaussian-RAPT has been applied in an O-17 MAS-detected DAS experiment on silica glass. These results, and their implications for the Si-O-Si bond angle distribution and structure of silica glass will also be discussed.

#### **NMR Symposia Oral Session**

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- 203. Materials Characterization and NMR Spectroscopy — Dynamics, Disorder and Pores.** Dmitriy Soldatov, Steven Lang, Andrei Nossov, Igor Moudrakovski, Gary Enright, Chris Ratcliffe, John Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada

In the study of solids, it is well known that NMR spectroscopy can provide the all-important information on local order. For non-crystalline materials, this has become a leading technique for structural characterization, and for crystalline materials, it provides an important adjunct to diffraction methods which are sensitive mainly to long-range order. Supramolecular chemistry, crystal engineering and templated assembly have emerged as important techniques for the design and construction of novel frameworks with designed functionality. Porosity has been one of the main design elements in crystal engineering and also for self-assembled mesoporous materials such as MCM's. Soft, transformable frameworks have the potential for behaving as "smart" materials, that is, they can respond to external stimuli by changing function. Many such soft frameworks have proved to be difficult to characterize because of disorder that often also is dynamic. In this presentation we will examine several instances where the application of simple  $^{13}\text{C}$  and  $^2\text{H}$  NMR techniques have provided critical insight in constructing better structural models, sometimes with surprising implications. By the same token we provide some examples where structural information was needed to distinguish among various dynamic models derived by NMR methods, or to correct proposed models. A second problem is that of characterizing pore space and surfaces on a molecular level. Sufficient data has now been obtained on  $^{129}\text{Xe}$  chemical shifts to provide a "universal" calibration curve for pores in mesoporous solids. In this way, spectroscopy with hyperpolarized Xe provides a rapid means of assessing porous materials. For "smart" materials, transformations between dense and open forms can be followed *in situ*.

[1] Problem solving in the characterization of materials

[2] calixarenes

a. figure - structure toluene

b. NMR -  $^{13}\text{C}$  phase change

c.  $^2\text{H}$  - local symmetry

d. structure redone - Cu vs Mo

[3] acetone - NMR - proposed structure vs actual structure

[4] pentane - NMR and structure

[5] Dianin's compound - local vs long-range order

#### **NMR Symposia Oral Session**

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- 204. Through-Bond and Through Space Characterisation of Crystalline Phosphates.** F. Fayon, and D. Massiot, CRMHT - CNRS, 45071 Orléans cedex 2, France; I. King and R.K. Harris, Department of Chemistry, University of Durham, Durham, UK DH1 3LE

ZrP<sub>2</sub>O<sub>7</sub> and SnP<sub>2</sub>O<sub>7</sub> are members of the AM<sub>2</sub>O<sub>7</sub> class of compounds. These are of interest as a number of members of the family show isotropic negative thermal expansion at high temperature in their simple cubic form. The exact room temperature structure of both of these compounds have not been determined. They are both metrically cubic 3x3x3 superstructures at room temperature making structure solution from x-ray powder diffraction data extremely complex. Symmetry reduction from the high temperature simple cubic structure (space group Pa-3) suggests one of twelve possible space groups. These different space groups contain from 11 to 216 crystallographically unique P sites. <sup>31</sup>P MAS and <sup>31</sup>P-<sup>31</sup>P homonuclear through-space (POSTC7) and through-bond correlation (INADEQUATE) NMR techniques has been used to probe these materials in an attempt to find the correct space group and three dimensional structure for each. A correct understanding of the room temperature structures is an essential prerequisite in understanding the unusual thermal expansion properties of these materials.

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#### **NMR Symposia Oral Session**

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- 205. The Degree and Nature of Radiation Damage in Zircon Observed by <sup>29</sup>Si Nuclear Magnetic Resonance.** Ian Farnan, University of Cambridge, Department of Earth Sciences, Downing Street, Cambridge, CB2 3EQ, UK.

Ceramic mineral analogues are being proposed as host phases for high level radioactive wastes, especially for actinides such as plutonium. Characterisation of the behaviour of these crystalline wastefoms under internal  $\alpha$ -decay and in particular their resistance to amorphisation is essential for the determination of the most suitable host phase. Zircon (ZrSiO<sub>4</sub>) occurs naturally in the earth with significant concentrations of uranium and thorium. Isotopes of these elements decay by an  $\alpha$ -process and zircons can be found in nature with different degrees of amorphisation (metamictisation) depending on the radiation dose they have received. Here a quantitative analysis of <sup>29</sup>Si NMR spectra of radiation damaged, natural zircons has allowed the total number of permanently displaced atoms per  $\alpha$ -recoil event to be determined. This is ~3800 atoms for low radiation doses and decreases to ~2000 atoms for 10 x 10<sup>18</sup>  $\alpha$ -events/g. These values are much greater than previously assumed based on density measurements. The local structure in crystalline and amorphous regions also depends explicitly on radiation dose in disagreement with simplistic crystalline/amorphous models. There is a continuous evolution of the local structure of the crystalline phase, as determined by <sup>29</sup>Si NMR chemical shifts, up to a  $\alpha$ -dose of 3.5 x 10<sup>18</sup>  $\alpha$ -decays/g and the amorphous phase up to 6 x 10<sup>18</sup>  $\alpha$ -decays/g. The changes in chemical shifts are difficult to interpret in terms of structural change with normal empirical rules for amorphous silicates. Periodic, ab initio DFT calculations of chemical shifts allow us to investigate the effect of the presence of an amorphous phase on the crystalline structure (pressure). We predict the correct shift for the high pressure scheelite form of ZrSiO<sub>4</sub>. Chemical shifts calculated directly from the output of ab initio MD to simulate the amorphous phase are in good agreement with measured spectra.

#### **NMR Symposia Oral Session**

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- 206. Dynamic Effects on Solid State NMR Lineshapes of Non-Integer Quadrupolar Nuclei.** Yong Ba, Meghan Lobsinger, Igor L. Moudrakovski, Victor V. Tersikh, Chris I. Ratcliffe, John A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6.

Solid state NMR lineshapes are widely used to study dynamics. Changes in the line width and shape as a function of increasing temperature reflect the effects of rapid modulation of the interaction tensors, and there are very many examples involving dipolar coupling tensors, e.g. of <sup>1</sup>H, <sup>19</sup>F, integer quadrupolar tensors, especially <sup>2</sup>H, and chemical shift tensors, <sup>13</sup>C, <sup>15</sup>N, <sup>19</sup>F etc. However reports of cases involving dynamic averaging of the lineshapes of non-integer nuclei with 2<sup>nd</sup> order quadrupolar interactions are quite rare. Here we will present work on several different cases involving a number of quadrupolar nuclei. Specifically: <sup>17</sup>O NMR of ice and THF structure II clathrate hydrate, <sup>131</sup>Xe NMR of xenon structure I clathrate hydrate, and <sup>23</sup>Na, <sup>87</sup>Rb and <sup>17</sup>O NMR of hydrated and dehydrated zeolites. In several cases motional averaging leads to apparently isotropic lines which retain a second order shift, and it is of interest to address the question of what happens to this line as the dynamics become rapid enough to average the satellite transition lineshapes.

#### **NMR Symposia Oral Session**

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207. **Spin Relaxation in Isolated and Coupled Spin Systems: Theory and Applications.** Klaus Müller, Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

A general theoretical description for spin relaxation in isolated and coupled spin systems is presented. The approach is valid for both  $I = 1/2$  and quadrupolar nuclei and is employed for the description of both NMR lineshape effects and spin-spin relaxation studies. For the description of spin-spin relaxation various types of internal and overall motions (jump or diffusion processes) are considered. Model simulations are presented that demonstrate the influence of the magnetic interaction parameters (chemical shift interaction, quadrupolar interaction and dipole-dipole interaction), finite pulse effects and the underlying motional models on the NMR lineshapes and relaxation data. In the case of quadrupolar nuclei with non-integer spins both central and satellite transitions are taken into account.

Several applications are presented from studies of motionally disordered solids, such as guest-host systems and molecular crystals. These investigations are based on variable temperature  $^2\text{H}$  ( $I = 1$ ) and  $^{11}\text{B}$  ( $I = 3/2$ ) NMR experiments.

#### NMR Symposia Oral Session

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## NMR • Thursday Oral Sessions

208. **MAT in Mice: High Resolution NMR in Biological Samples Using Ultra-Slow Magic Angle Spinning.** Robert A. Wind, Jian Zhi Hu, and Donald N. Rommereim, Pacific Northwest National Laboratory, P. O. Box 999, MS K8-98, Richland, WA 99352

Recently it was shown that methods such as phase-altered spinning sidebands (PASS) and phase-corrected magic angle turning (PHORMAT), employing slow and ultra-slow magic angle turning (MAT), can be used successfully in biological samples to suppress or eliminate the line broadening arising from magnetic susceptibility gradients, using spinning speeds as low as 40 Hz (1) and even 1 Hz (2). As a result high-resolution and spinning sideband-free  $^1\text{H}$  NMR spectra are obtained. Until this work, such high-resolution spectra were only obtained by standard Magic Angle Spinning experiments, where typical spinning speeds of several kHz are employed to eliminate magnetic susceptibility broadening. Tissue and cell damage associated with the large centrifugal forces at high spinning rates is avoided with the new development. The new development promises to enhance significantly the NMR capabilities to study live intact cells, tissues, and live small animals in a non-invasive way, and perhaps even for examining patients in the hospital for improved diagnosis and therapy evaluation (in the latter case by rotating the magnetic field rather than the patient). Results from both PASS and PHORMAT will be shown on excised rat/mouse organs. Finally, the potentials of these different MAT techniques as well as future developments and improvements of the methods will be discussed.

[1] Wind RA, Hu JZ, Rommereim DN, *Magn. Reson. Med.* 2001; 46:213-218.

[2] Hu JZ, Rommereim DN, and Wind RA, *Magn. Reson. Med.* (in press)

#### NMR Symposia Oral Session

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209. **Ultrasensitive Detection of NMR by Magnetic Resonance Force Microscopy.** John A. Marohn, Cornell University, Department of Chemistry and Chemical Biology, Ithaca, NY 14853-1301; Sean Garner and Erik Muller, Cornell University, Department of Physics, Ithaca, NY 14853-1301; Neil Jenkins, Lauren DeFlores, Tina Ng, William Silveira, and Jim Kempf, Cornell University, Department of Chemistry and Chemical Biology, Ithaca, NY 14853-1301.

Recently invented strategies for detecting magnetic resonance mechanically have generated considerable interest, as they do offer a generally applicable route to achieving the sensitivity required for nanoscale NMR. We are employing magnetic resonance force microscopy (MRFM) to answer fundamental and applied questions in organic electronic devices, and will detail our associated efforts at significantly expanding the capabilities of MRFM, required to put the microscope to use to study nanoscale phenomena in working devices. We have recently force detected ESR at low temperature and NMR at room temperature and high magnetic field using a homebuilt force microscope. We have invented and tested a novel route to Fourier Transform (FT) image encoding that will increase MRFM imaging resolution by at least an order of magnitude, from the current micron scale down to the nanoscale. Using our recently developed scaling laws and numerical signal-to-noise simulations, we will show that MRFM can detect NMR from a single small-area monolayer. We will describe force microscopes under development that are optimized to detect monolayer NMR and perform FT-MRFM imaging at variable temperature. In order to improve sensitivity, we have fabricated silicon cantilevers, only 340 nm thick, exhibiting force sensitivity as good as a few tens of attoNewtons per root Hertz at low temperature - orders of magnitude more sensitive than the best commercially available cantilevers. We will describe efforts underway to append single nanoscale magnets to the tips of these cantilevers and characterize the magnets by our highly accurate variant of cantilever magnetometry. We will report on recently-tested improvements in experimental protocol that allow application of such cantilevers in a scanned-probe MRFM



operating at high magnetic field and cryogenic temperatures. Supported by Cornell University, the National Science Foundation (DMR-0134956, EEC-0117770, and ECS-9731293), and the Army Research Office.

#### **NMR Symposia Oral Session**

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- 210. High Pressure  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR Microimaging Studies of Gas Hydrate Formation.** Igor L. Moudrakovski, Christopher I. Ratcliffe, John A. Ripmeester, Steacie Institute for Molecular Sciences, NRC, Ottawa, Ontario, K1A 0R6, Canada; Yu-Taek Seo, Department of Chemical Engineering, Korea Advanced Institute for Science and Technology, Daejeon 305-701, South Korea

The products of gas-solid interactions between  $\text{CO}_2$  or  $\text{CH}_4$  and the surfaces of ice and various clathrate hydrates have been examined with  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR microimaging (MRM). Using a homebuilt high-pressure cell of relatively simple design the hydrate formation experiments can be carried out over a period of several days at pressures as high as 320 bars. A great advantage of MRM is the ability to combine spatial resolution with spectroscopic information. With this technique it has been relatively straightforward to monitor the conversion of the ice into hydrates and to follow any unusual behavior under the conditions of hydrate formation. Depending on the experimental conditions, the conversion of ice into hydrate proceeds quite inhomogeneously, where some of the ice particles convert significantly faster than the rest. A combination of  $^{13}\text{C}$  NMR and MRM allows us to identify the hydrate structural type and monitor the kinetics of the hydrate growth. In certain cases we have been able to identify and monitor substitution of one hydrate guest species by another and to follow the formation of mixed clathrate hydrates with two different guests.

#### **NMR Symposia Oral Session**

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- 211. NMR Studies of Single Crystal Surfaces - Techniques and Results.** Heinz J. Jaensch, Philipps-University, Department of Physics, 35032 Marburg, Germany.

Single crystal surfaces of metals or semiconductors are investigated to study properties like: adsorption, desorption, local geometric structure of adsorbates and substrates, diffusion, metallicity, just to name a few. NMR could contribute in many ways to the questions studied. This is in general not possible, since crystals typically used have a size of 1 cm diameter, which provides about  $10^{15}$  surface sites, by far not enough for solid state NMR. Especially if less than a monolayer should be investigated. Outer surfaces of solids do provide the chance to prepare and/or detect an NMR sample away from the surface. All NMR studies described here use hyperpolarized adsorbates ( $^6\text{Li}$ ,  $^7\text{Li}$ ,  $^8\text{Li}$ ,  $^{129}\text{Xe}$ ), which are prepared in an atomic beam (the Lithium isotopes) or in a gas (xenon). For  $^6,7\text{Li}$  Stern-Gerlach magnets and adiabatic rf-transitions are used to achieve nuclear polarization ( $P_z$ ) of 0.3 to 0.6. The NMR measurements of  $^6,7\text{Li}$  involve laser spectroscopy or beam foil spectroscopy of the desorbing atomic/ionic species.  $^8\text{Li}$  is radioactive with a half-life of 0.8s and decays by  $\beta$ -electron emission. A faint beam of  $^8\text{Li}$  is produced from a nuclear reaction and thermalization of the fast reaction products. Laser optical pumping is used to achieve  $P_z$  of about 0.8. The parity violation of the  $\beta$ -decay is the means to detect the nuclear polarization.  $^{129}\text{Xe}$  is optically pumped in a Rubidium spin exchange cell and then transferred to an ultra high vacuum system where it adsorbs on the crystal surface studied. The detection is by induction in this case. Results are shown on the diffusion measurements of  $\text{Li}/\text{Ru}(001)$ ,<sup>1</sup> the question of metallicity of  $\text{Si}(111)7\times 7$ ,<sup>2</sup> the quadrupolar interaction of  $\text{Li}$  on  $\text{Ru}^3$  and  $\text{Si}$  and the proof of principle of the detection of monolayer quantities of  $^{129}\text{Xe}$  on a single crystal surface.<sup>4</sup>

[1] H.D. Ebinger, et al., Surf. Sci., 1998, 412/413, 586.

[2] D. Fick, et al., Phys. Rev. B, 1999, 60, 8783.

[3] H. Arnolds, D. Fick, H. Unterhalt, A. Voss, and H.J. Jaensch, Sol. St. NMR, 1998, 11, 87.

[4] U. Ruth, T. Hof, J. Schmidt, D. Fick, and H.J. Jaensch, Appl. Phys. B, 1999, 68, 93.

#### **NMR Symposia Oral Session**

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- 212. Optical Polarization of Nuclear Spins in Bulk GaAs.** Anant K. Paravastu, Sophia E. Hayes, Birgit Schwickert, and Jeffrey A. Reimer, University of California, Berkeley, Department of Chemical Engineering, Berkeley, CA 94720; Long N. Dinh and Mehdi Balooch, Lawrence Livermore National Laboratory Livermore, CA 94551

We present the photon energy, laser irradiation time, and sample temperature dependence of laser-enhanced NMR spectra of bulk GaAs at 9.4 T. Significant optical enhancements are observed at a range of photon energies, starting below the band gap and persisting through 100 meV above the band gap and at anomalously high sample temperatures. We propose a mechanism for NMR enhancements that originates with cross relaxation between nuclear spins and spin-polarized excitons. This mechanism accounts for discrepancies between the present data and previous models that rely on nuclear spin diffusion from fixed dilute sources of magnetization. Potential for NMR signal enhancements in other classes

of materials will be discussed in the context of these new experimental results.

#### **NMR Symposia Oral Session**

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- 213. Using Hyperpolarized  $^3\text{He}$  to Detect Surface Ferromagnetism.** R.E. Jacob and B. Saam, University of Utah, Department of Physics, 115 South 1401 East #201, Salt Lake City, UT 84112-0830.

Hyperpolarized (HP) noble gases ( $^3\text{He}$  and  $^{129}\text{Xe}$ ) are of great interest as novel NMR materials (having polarizations 4 to 5 orders of magnitude above the thermal-equilibrium value) and in various applications such as MRI of the lung (J.C. Leawoods, *et al.*, Concepts Magn. Reson. **13**, 277, 2001). They are produced by optical means, either by spin-exchange (T.G. Walker and W. Happer, Rev. Mod. Phys. **69**, 1997) or metastability exchange (F. D. Colegrove, *et al.*, Phys. Rev. **132**, 2561, 1963) optical pumping. The limiting factor in the production of HP gases is very often  $T_1$  due to collisions with the wall of the (typically glass) container (cell). For  $^3\text{He}$ , we recently showed that the glass walls themselves can become magnetized in the presence of large magnetic fields (R.E. Jacob, *et al.*, Phys. Rev. Lett. **87**, 143004, 2001). The net magnetic moments of multi-domained ferromagnetic inclusions in the glass can be changed by exposure to fields of various size, strength, and frequency. The changes are reflected in the wall relaxation rate, which, for example, increases dramatically when a cell is exposed to fields above a few hundred Gauss, where the site domains become aligned. The change in wall rate is completely reversed by “degaussing” the cell, *i.e.*, exposing it to a slowly decreasing oscillating field. Assuming the sites are metallic iron impurities, a simple model for the relaxation implies that they may number as few as hundreds per  $\text{cm}^2$ . Indeed, we have been unable thus far to confirm the presence of this ferromagnetism by other standard means, including SQUID and ESR. The exquisite sensitivity of  $T_1$  to the changing magnetic moments suggests the use of  $^3\text{He}$  as an inert probe of trace surface magnetism or of critical phenomena in thin ferromagnetic films.

#### **NMR Symposia Oral Session**

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## **NMR • Monday & Tuesday Poster Sessions** (A = even numbers/ B = odd numbers)

- 214. Investigation of Structure in Diamond Thin Films Using  $^{13}\text{C}$  MAS, 2D Exchange MAS NMR Spectroscopy and Ab Initio Chemical Shift Calculations.** Todd M. Alam, Brian R. Cherry, and Tom A. Friedmann, Sandia National Laboratories, Albuquerque, NM 87185-0888

The local and medium range order (MRO) in amorphous diamond thin films have been investigated using solid-state  $^{13}\text{C}$  magic-angle spinning (MAS) NMR spectroscopy. The evolution of the relative concentration of the disordered graphite- and diamond-like carbon environments in these films as a function of high temperature annealing time were directly monitored by MAS NMR. At high temperature the concentration of the graphite-like  $\text{sp}^2$  carbons increases with annealing, as was expected. In contrast, low temperature annealing produced a narrowing of the observed  $^{13}\text{C}$  MAS NMR line width, without changes in the relative concentrations of the carbon species. This decreasing line width has been correlated to a change in the residual internal pressure or stress, allowing quantification of the extent of stress relief with annealing by NMR. *Ab initio* calculations of the  $^{13}\text{C}$  chemical shift tensor were also performed on primitive model cells obtained from MD simulations. These results confirm the distribution of NMR chemical shifts observed is due to amorphization of the carbon structure. In addition, the *ab initio* calculations allowed the variation of the  $^{13}\text{C}$  chemical shift for the amorphous carbon as a function of volume/pressure to be addressed. The low temperature annealing results are discussed in light of these recent calculations. The MRO in the diamond thin films was also investigated using two-dimensional (2D)  $^{13}\text{C}$  MAS radio-frequency dipolar recoupling (RFDR) exchange experiments. The reintroduction of the dipolar interaction between carbons in these 2D RFDR experiments allows the spatial proximity of the different carbon environments to be measured. The connectivity results of these  $^{13}\text{C}$  exchange experiments will be compared to various models describing carbon amorphous thin-films. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

#### **NMR Symposia Poster Session**

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- 215. Optical Pumping Processes in Mixtures with High Noble Gas Partial Pressures.** Anala Satyanarayana, Muhammad G. Mortuza, Galina E. Pavlovskaya, Todd J. Dieken, and Thomas Meersmann; Department of Chemistry, Colorado State University, Fort Collins CO 80523

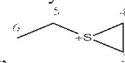
Rubidium-vapor optical-pumping for the production of hyper-polarized (HP)  $^{129}\text{Xe}$  appears to be little affected by radiation trapping if gas mixtures with unusually high xenon partial pressure ( $> 400$  kPa) are chosen. Comparison of the rubidium infrared  $\text{D}_2$  emission lineshape with the spin-polarization obtained from  $^{129}\text{Xe}$ -NMR demonstrates that radiation quenching is of no substantial benefit for the pumping process at elevated pressures. High-density xenon will be of importance for future continuous flow optical-pumping applications with particular relevance for various material science applications.

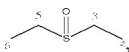
#### NMR Symposia Poster Session

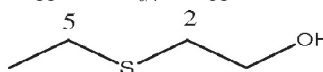
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- 216. Application of EPR and NMR to the analysis of phosphovanadomolybdate polyoxometalate,  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ , reacting with chloroethyl sulfides (H-MG and HD).** Carmen M. Arroyo, James M. Sankovich<sup>1</sup>, David W. Kahler, Damon L. Burman, Ernest H. Braue and Brennie E. Hackley, Jr.<sup>2</sup>. Drug Assessment Division and <sup>2</sup>Scientific Advisor U.S. Army Medical Research Institute of Chemical Defense, 3100 Ricketts Point Road, Edgewood Area, Aberdeen Proving Ground, MD 21010-5400; <sup>1</sup>USAMRD, MCMR-UWB-L, Brooks AFB, TX 78235-5138

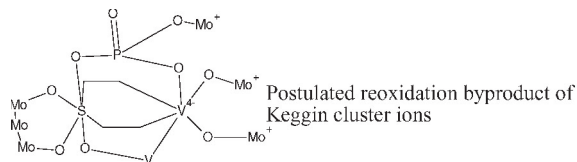
The mechanism of aerobic oxidation of chloroethyl sulfides, 2-chloroethyl sulfide (half-sulfur mustard, H-MG) and bis-2-chloroethyl sulfide (sulfur mustard, HD), was investigated using a phosphovanadomolybdate polyoxometalate,  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ , as a catalyst under mild, liquid-phase conditions [reaction conditions:  $3 \mu\text{mol}$   $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  and  $30 \mu\text{mol}$  of the halogenated alkylsulfides in one mL of deuterated water ( $\text{D}_2\text{O}$ ) at  $25^\circ\text{C}$ ]. Polyoxometalates (POMs) are  $d^0$  [e.g., V (V) and Mo (VI)] transition metal oxide cluster compounds, which easily undergo redox cycling. POMs have been used to catalyze the oxidative breakdown of halogenated organic compounds and are good candidates to inactivate chemical warfare agents such as HD. Electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) spectra, together with kinetic experiments, support a Mars-van Krevelen-type mechanism in which the rate-determining step is the oxygen-transfer reaction between the polyoxometalate and the intermediate ethylene sulfonium cation. Chloroethyl sulfides, which have an electron-rich center, are very reactive in aqueous solutions, and all their intermediates were characterized by multinuclear ( $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{51}\text{V}$  and  $^1\text{H}$ ) NMR spectroscopy. Again, kinetic experiments support the notion of an oxygen transfer rate-determining step between the ethylene sulfonium cation,



and the polyoxometalate, with the formation of sulfoxide, , this intermediate was detected  $\sim 12$  min after the reaction began with  $^{13}\text{C}$ -NMR peaks at  $\text{C}_{5/3}$  42.25 ppm and  $\text{C}_{6/4}$  8.34 ppm.

The 2-(ethylthio) ethanol, , appeared  $\sim 30$  min after the reaction started showing  $^{13}\text{C}$ -NMR peaks at  $\text{C}_3$  60.52 ppm,  $\text{C}_2$  34.89 ppm,  $\text{C}_5$  25.27 ppm, and  $\text{C}_6$  8.34 ppm.

Fifteen hours later, after the reaction proceeded, a Keggin structure cluster ion was detected, with  $^{13}\text{C}$ -NMR peaks at  $\text{C}_{9/15}$  33.04 ppm and  $\text{C}_{8/16}$  25.44 ppm, presumably resulting from the reoxidation by air of the chloroethyl sulfide under study:



Extensive oxidation of HD results in the formation of the sulfone-HD. Schemes summarizing the proposed reaction mechanisms will be presented.

#### NMR Symposia Poster Session

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- 217. NMR Characterization of Steamed Dehydrated HBeta Zeolite.** V. Montouillout, S. G. Aiello, C. Fernandez, Laboratoire de Catalyse et Spectrochimie, CNRS-UMR6506 University of Caen Basse-Normandie, 6 bd du Maréchal Juin 14050 Caen (France), and F. Fayon, CRMHT - CNRS 1D Av. Recherche Scientifique 45071 Orleans cedex 2 (France)

As the catalytic active sites in zeolites are related to framework or extraframework aluminum, the characterization of both aluminum and proton environment would provide important information to understand the solid acidity of these materials. Various solid state NMR techniques, applied to proton and aluminum, have been used to characterize the acid sites in dehydrated steamed Hbeta zeolite. Two samples, steamed following industrial process at  $500$  and  $700^\circ\text{C}$ , were studied. The effect of dehydration treatment was also investigated. The different hydroxyl groups (silanols, Brönsted sites and H-EFAL) were determined from  $^1\text{H}$  MAS spectrum.  $^1\text{H}$ - $\{^{27}\text{Al}\}$  TRAPDOR experiments provide the assignment

of the peaks due to hydroxyl groups connected to alumina species and allow the indirect characterization of aluminum sites. We estimate the quadrupole coupling constants of aluminum connected to proton from analyses of TRAPDOR profiles. Eventually, these parameters were used to simulate the  $^{27}\text{Al}$  Hahn-Echo and QPASS spectra to determine the number of aluminum sites and their chemical shift.

#### **NMR Symposia Poster Session**

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- 218. Quadrupolar Nuclei: from NMR to NQR without Perturbation Theory.** Alex D. Bain, Department of Chemistry, McMaster University, 1280 Main St. West, Hamilton, Ontario, Canada.

In NMR of nuclei with spin  $> 1/2$ , the quadrupole interaction is often treated using perturbation theory. Similarly, the effect of weak magnetic fields on pure quadrupole resonance (NQR) is calculated with perturbation theory. However, by re-defining the “rotating” frame of reference, it is quite simple to do the calculation exactly. The method depends on making maximum use of the angular momentum properties of the system. This paper presents some experiments and the related theory from the middle ground between quadrupole-perturbed NMR and Zeeman-perturbed NQR. In particular, phase effects are important, since the NMR signal appears out of phase with the rf, but the NQR signal appears in-phase. The consequences for realistic systems are discussed.

#### **NMR Symposia Poster Session**

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- 219. STMAS-REDOR and STMAS-HETCOR NMR Experiments for the Study of Half-Integer Quadrupolar Nuclei in Inorganic Materials.** Cláudia M. Morais, Christian Fernandez, LCS, Univ. de Caen, 14050 France; Joao Rocha, Dept. of Chem., Univ. Aveiro, 3810-193, Portugal; Jean-Paul Amoureux, Univ. Lille-1, Villeneuve d'Ascq, 59655 France; Clarisse Huguenard, RMN et Chimie du Solide, Univ. L. Pasteur, 67070 France

The development of high-resolution methods for half-integer quadrupolar spins has inspired subsequent progress in measurements of interactions between these nuclei and their spin- $1/2$  neighbours. Most of these methods utilise indirect excitation via cross polarization (CP) for spectral editing of the DOR and MQMAS spectra or for DAS and MQMAS-based heteronuclear correlation (HETCOR) experiments. In 1998 Fernandez et. al. presented an alternative method of studying internuclear connectivities between half-integer quadrupolar and spin- $1/2$  nuclei under high resolution conditions and without the quantitative uncertainties that are associated with the complex dynamics of CP. This technique, referred to as MQ-REDOR, combines MQMAS with (quadrupolar spin)-observe (spin  $1/2$ )- dephase rotational echo double resonance (REDOR). In 2000 Gan introduced a 2D new experiment, called satellite-transition magic-angle-spinning (STMAS), that as DOR, DAS and MQMAS allows high resolution spectra of half-integer quadrupolar nuclei to be obtained. The experiment correlates satellite and central transitions in a way that removes the second order quadrupolar broadening along the indirect dimension leading to isotropic NMR spectra. In this work we combine the REDOR and the HETCOR methods with the STMAS experiment in order to obtain two new methods that allow studying internuclear connectivities between half-integer quadrupolar and spin- $1/2$  nuclei under high resolution. These two methods are similar to the MQREDOR and MQHETCOR experiments, respectively, but they are more efficient. They have been applied to several inorganic materials.

#### **NMR Symposia Poster Session**

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- 220. An NMR Investigation of Lanthanum and Zirconium Substitution into Lead Titanate Ceramics.** Allan Baldwin; Ray Dupree, Department of Physics, University of Warwick, Coventry, CV4 7AL

Lanthanum modified lead titanate, where the lanthanum substitutes onto the ‘A’ site of the  $\text{ABO}_3$  perovskite crystal structure, has been reported to possess the highest electrical permittivity of any material yet discovered. The reason for this is not fully understood. Zirconium modified lead titanate, where the zirconium ions substitute into the ‘B’ sites has large piezo and pyro-electric constants.  $^{47,49}\text{Ti}$ ,  $^{17}\text{O}$ ,  $^{139}\text{La}$  and  $^{207}\text{Pb}$  NMR have been used to probe the changes that occur to the atomic level structure of lead titanate (PT) as it is gradually modified by the incorporation of increasing amounts of lanthanum (PLT) or zirconium (PZT). The static  $^{49,47}\text{Ti}$  spectral lines of PZT and PT have a very similar axial lineshape, but a large difference is observed in the PLT spectra, where the electric field gradient (EFG) is considerably reduced and the asymmetry parameter is increased. This indicates that the lanthanum is acting to significantly reduce the tetragonal distortion of the titanium coordination octahedra. The  $^{207}\text{Pb}$  MAS-NMR data shows that the ‘A’ site is far more disordered in PLT than for a similar level of zirconium substitution in PZT. The  $^{139}\text{La}$  NMR is found to be sensitive to the processing temperature. Two different lanthanum environments can be observed for powders processed at  $850^\circ\text{C}$ , one with a large axial EFG and one with a small non-axial EFG lineshape. For powders sintered at  $1200^\circ\text{C}$  the axial line is removed leaving a single line that can be narrowed by MAS. Little difference in the oxygen environment between PT and PLT can be observed from the  $^{17}\text{O}$  NMR data. However,  $^{17}\text{O}$  NMR is found to be very sensitive to changes made at the B site, allowing



PZT to be studied as the zirconium composition is increased.

#### **NMR Symposia Poster Session**

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#### **221. Residual Quadrupolar Couplings in NMR Spectra of Cations in Fully Hydrated Zeolites.** Victor Terskikh, Meghan Lobsinger, Igor Moudrakovski, Christopher Ratcliffe and John Ripmeester, Steacie Institute for Molecular Sciences, NRC, Ottawa, K1A 0R6, Canada

The NMR of charge balancing cations in zeolites such as  $^{23}\text{Na}$ ,  $^{6,7}\text{Li}$  and some others has been studied extensively over the past 30 years. The prime goal of these studies was the location of the cations in zeolite lattice, and the majority of work has been performed on dehydrated materials. Very few studies have dealt with the hydrated zeolites, and it has been generally assumed that the isotropic lines which are usually observed indicate that the quadrupole interactions of cations in fully hydrated zeolites are completely averaged by fast exchange processes. From variable field measurements of chemical shifts in hydrated zeolites of different structural types (X, Y, A and Mordenite) we have found significant second order shifts corresponding to quadrupolar coupling constants of up to 1.2 MHz for  $^{23}\text{Na}$  and 3.6 MHz for  $^{87}\text{Rb}$ . These quadrupolar interactions, however, do not appear in the line shapes, which in most cases remain featureless. In order to explore the observed phenomena further we have performed variable temperature  $^{23}\text{Na}$ ,  $^1\text{H}$ ,  $^2\text{H}$  and  $^{17}\text{O}$  NMR of cations and water and have also carried out the  $T_1$  and  $T_2$  relaxation studies for  $^{23}\text{Na}$  and  $^1\text{H}$ . The effects of diffusion of the sorbed water and cations on the quadrupolar interactions will be discussed.

#### **NMR Symposia Poster Session**

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#### **222. Double-Quantum Filtered MAS NMR at and around the $n = 0$ Rotational-Resonance Condition.** Matthias Bechmann and Angelika Sebald, Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany

Rotational-resonance (RR) MAS NMR has long been known to yield structurally informative experimental data, including spin systems at or near the so-called  $n = 0$  RR condition. Additional application of double-quantum filtration (DQF) greatly expands the range of circumstances where RR experiments can be applied successfully. We present experimental and numerical RR-DQF studies employing a straightforward COSY-like pulse sequence<sup>1</sup> which performs well in the presence of large chemical shielding anisotropies.<sup>2,3</sup> In particular, we consider the properties of isolated  $^{31}\text{P}$  spin pairs in pyro-phosphate units  $\text{P}_2\text{O}_7$ , or in the  $\text{PtP}_2$  moiety of platinum(II) phosphine complexes at and near the  $n = 0$  RR condition. Another type of spin-system properties near the  $n = 0$  RR condition will be represented by the  $^1\text{H}$  spins attached to the C=C fragment in solid maleic acid at various degrees of isotopic deuterium dilution.

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#### **NMR Symposia Poster Session**

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#### **223. Characterization of Acid Sites in Zeolites using Perdeuterated Trimethylphosphine Oxide.** Karl T. Mueller, Murthy D. Karra, Nancy M. Washton, and David E.W. Vaughan, Penn State University, Department of Chemistry and Materials Research Institute, University Park, PA 16802; Kevin J. Sutovich, Grace Davison Catalysts, Columbia, MD, 21044.

Characterization of active sites in solid-acid catalyst systems is enhanced by performing a suite of  $^{31}\text{P}$  magic-angle spinning (MAS) NMR experiments on samples treated with a fully deuterated form of trimethylphosphine oxide (TMPO- $d_9$ ). Zeolites are excellent catalysts for a wide host of chemical reactions and have been the object of extensive study and research. Bronsted acid sites in zeolites are thought to be essential for the catalytic activity and NMR studies with fully deuterated TMPO (TMPO- $d_9$ ) allow simultaneous probing of  $^1\text{H}$  species specifically associated with the zeolite host, rather than introduced in the sample in methyl groups that are part of non-deuterated TMPO. Methods such as one-pulse  $^{31}\text{P}$  MAS NMR,  $^1\text{H}/^{31}\text{P}/^{27}\text{Al}$  TRAPDOR NMR, and  $^{31}\text{P}/^1\text{H}$  REDOR NMR are demonstrated. We present initial results of studies performed on zeolite Y samples, which have a faujasite structure. Zeolite Y is used extensively as a fluid cracking catalyst in petroleum refining and provides an excellent demonstration of the enhanced information obtained in these experiments. Newer results also indicate that TMPO- $d_9$  provides excellent resolution in the zeolite ZSM-5, with resolution of multiple Bronsted sites. This is consistent with recent reports, where three cation positions for cesium have been identified by crystallographic methods.

#### **NMR Symposia Poster Session**

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- 224. Obtaining Quantitative Information from Quadrupolar Nuclei in Solid Catalyst Systems.** Larry W. Beck; Kathryn Hughes; Mark V. Wilson; Brett S. Duersch, The University of Michigan, Department of Chemistry, Ann Arbor, MI 48109-1055

NMR spectroscopy has become a well-established characterization method for the study of solid heterogeneous catalysts. For example, the catalytically active sites  $^{27}\text{Al}$  and  $^{11}\text{B}$  MAS NMR of acidic zeolite catalysts provides direct information about the coordination number and heterogeneity of the catalytic sites. However, strictly quantitative information relating signal strength to the number of metal sites in the solid samples has proven much more elusive. For quadrupolar nuclei the strength of the observable signal depends on the acquisition parameters, including: field strength, pulse length, frequency offset, and MAS rate. However, under explicit conditions quantitative NMR signal can be directly related to the analytical concentration by quantum mechanical scaling factors. In the materials studied the Al, and B-content of active catalysts were determined, which provided a direct measure of intrinsic acid strength for these materials. Two new NMR methods were developed as a result of the explicit exploration of the strength of the quadrupolar coherence (signal) and the acquisition parameters. The first sequence uses a four-pulse excitation train, which provides a 50- 100% increase in signal strength. The signal gain arises from the excitation of two different coherence pathways with the composite pulse train. A second method employs a two-pulse train consisting of one non-selective (hard)  $\pi/2$ -pulse and a selective (soft)  $\pi/2$ -pulse to measuring the magnitude of the quadrupolar interaction (splitting frequency,  $\nu_Q$ ). The quadrupolar interaction is determined in a series of experiments where the offset frequency of the selective (soft) pulse is varied. Differences in the coherence strengths excited by the hard and soft pulses as a function frequency offset closely resemble the expected first-order quadrupolar line width. The quantitative information provided from these methods has provided new insight into the nature of catalytic active sites in zeolites but should be broadly applicable to other quadrupolar systems with moderate quadrupolar interactions.

#### **NMR Symposia Poster Session**

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- 225. Uniform-Sign Cross-Peak Double-Quantum-Filtered Correlation Spectroscopy in Solids.** Leonard J. Mueller and Douglas W. Elliott, Department of Chemistry, University of California, Riverside, CA 92521

Establishing through-bond and through-space connectivity is essential to the role of nuclear magnetic resonance in answering questions of molecular structure and dynamics. In NMR, it is the scalar or J coupling interaction that signifies covalent through-bond contact, while the dipolar coupling provides through-space distance constraints. While an array of experiments for determining through-space connectivity in disordered solids has been developed, relatively few correlation experiments in solids make use of scalar couplings. Scalar coupling-driven correlation in solids is essential for two reasons. First, as in liquid state NMR, delineating through-bond and through-space connectivity is a critical step for establishing structure. Second, unlike dipolar interactions, which can average to zero under molecular motion even in the solid state, scalar couplings are relatively insensitive to global molecular dynamics and can provide for correlation and spectral assignment in situations where dipolar-driven experiments fail. We introduce a novel solid state correlation method, which is a variant of the popular double-quantum-filtered correlation spectroscopy (2QF COSY) experiment in liquids. This experiment maintains the many advantages of the 2QF COSY experiment, but is also robust for solids by providing in-phase diagonal and cross-peaks. We call this variant the uniform-sign cross-peak (UC) 2QF COSY. Despite two relatively long ( $1/2J$ ) refocusing periods, we find good efficiency in a number of organic and inorganic solids. Several applications from our laboratory will be presented including through-bond connectivities in the protonated Fullerene cations  $\text{HC}_{60}^+$  and  $\text{HC}_{70}^+$ . In  $\text{HC}_{60}^+$  and  $\text{HC}_{70}^+$ , anisotropic molecular motion renders  $^{13}\text{C}$ - $^{13}\text{C}$  dipolar driven correlation ineffective and  $^1\text{H}$ - $^{13}\text{C}$  cross-polarization experiments lead to inaccurate structural conclusions. The scalar coupling driven UC 2QF COSY, however, provides reliable experimental characterization of the direct bond between the  $\text{sp}^2$  cationic site and the protonated  $\text{sp}^3$  hybridized site in  $\text{HC}_{60}^+$ .

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- 226. Solid-State NMR of Melamine Phosphates.** Andreas Brinkmann, Solid State NMR, University of Nijmegen, 6525 ED Nijmegen, The Netherlands; Adriana Campeanu, Solid State NMR, University of Nijmegen, 6525 ED Nijmegen, The Netherlands; Adri A.K. Klaassen, Solid State NMR, University of Nijmegen, 6525 ED Nijmegen, The Netherlands; Victor M. Litvinov, DSM Research B.V., Campus Geleen, Center for Technology & Analysis (CT&A), Competence Center Molecular Identification & Quantification, P.O.Box 18, 6160 MD Geleen, The Netherlands; Ad Braam, DSM Research B.V., Campus Geleen, Center for Technology & Analysis (CT&A), Competence Center Molecular Identification & Quantification, P.O.Box 18, 6160 MD Geleen, The Netherlands; Arno P. M. Kentgens, Solid State NMR, University of Nijmegen, 6525 ED Nijmegen, The Netherlands

An important application of melamine phosphates is in the development of environmentally friendly flame retardant polymeric materials. We used proton spectroscopy under magic-angle-spinning conditions to gain insight into the proton proximities and molecular structure of melamine phosphates. Experimental results are presented and discussed. The results were obtained by applying homonuclear decoupling sequences to record high-resolution proton and heteronuclear correlation spectra of types  $^1\text{H}$ - $^{13}\text{C}$ ,  $^1\text{H}$ - $^{15}\text{N}$  and  $^1\text{H}$ - $^{31}\text{P}$ . Our goal is to determine the proton positions and hydrogen bonds in the melamine phosphates, which may be of significance for the function of these compounds as flame retardants.

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- 227. Molecular Motions and Disorder in Inclusion Compounds as Evaluated by Solid State NMR Spectroscopy.** Thomas Handel, Jorge Garibay and Klaus Müller, Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Inclusion compounds are ideal systems to study small organic molecules under confined spatial conditions. In this contribution we report on solid state NMR studies of various inclusion compounds, that are formed by a host component (urea, thiourea or cyclophosphazene) in the presence of suitable guest compounds (linear and branched alkanes, benzene) and which are characterized by a pronounced dynamic disorder of the guest species as well as distinct order-disorder transitions.

During the present variable temperature  $^2\text{H}$  NMR studies (between about 25 K and 370 K) particular emphasis is given to lineshape effects, orientation-dependent spin-spin and spin-lattice relaxation data which allow a discrimination and assignment of the underlying molecular processes of the guest species as well as their ordering characteristics within the host channels. The analysis of the experimental NMR data is done on the basis of appropriate simulation programs which account for different guest motions in such systems.

It is shown that - despite the large spatial constraints imposed by the rigid host matrix - the guest species in general are highly mobile and exhibit various motional processes. Depending on the particular system, (local) conformational as well as (overall) rotational motions and molecular fluctuations can be registered, which in some cases might prevail even below 30 K. The comparative studies reveal the particular influence of both the actual guest structure and the host lattice on the molecular behavior of the guest species in such inclusion compounds.

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- 228. Combined Solid-State  $^{17}\text{O}$  NMR and Ab initio Computational Studies of Hexagonal and Vitreous  $\text{P}_4\text{O}_{10}$ .** Brian R. Cherry and Todd M. Alam, Department of Organic Materials, Sandia National Laboratories, Albuquerque, NM 87185-1411; Zhehong Gan, National High Magnetic Field Laboratory, Tallahassee, FL 32310; Carol Click and Richard K. Brow, Ceramic Engineering Department, University of Missouri-Rolla, Rolla, MO 65409-0330.

We report the solid-state  $^{17}\text{O}$  NMR studies of h- $\text{P}_4\text{O}_{10}$  (hexagonal) and vitreous  $\text{P}_4\text{O}_{10}$ . For h- $\text{P}_4\text{O}_{10}$ ,  $^{17}\text{O}$  magic angle spinning (MAS) NMR spectra were collected at a variety of field strengths: 9.4T, 14.1T, 16.9T, and 19.6T. Three distinct  $^{17}\text{O}$  sites were resolved in the MQMAS spectra, with quadrupolar coupling constants (QCC) ranging from 3 to 8 MHz. In addition, MQMAS NMR at 9.4T and satellite transition (ST)MAS NMR at 19.6T was utilized to improve the  $^{17}\text{O}$  resolution and sensitivity of the oxygen environments with the larger QCCs. In addition, ab initio calculations of the  $^{17}\text{O}$  chemical shift and electric field gradient (EFG) tensor for hexagonal  $\text{P}_4\text{O}_{10}$  were obtained using the Gaussian 98 program. The effects of variations in the bridging P-O-P bond angle on the  $^{17}\text{O}$  chemical shift, QCC, and asymmetry parameter ( $\eta$ ) of the oxygen EFG tensor in the  $\text{H}_4\text{P}_2\text{O}_7$  cluster are presented. These results are discussed and compared to the experimental  $^{17}\text{O}$  NMR values obtained for the both the crystalline and vitreous  $\text{P}_4\text{O}_{10}$ . Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

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- 229. Quantitation of Crystalline and Amorphous Forms of Neotame Using  $^{13}\text{C}$  CPMAS NMR Spectroscopy.** Thomas J. Offerdahl<sup>1</sup>, Jonathon S. Salsbury<sup>1</sup>, Zedong Dong<sup>2</sup>, David J.W. Grant<sup>2</sup>, Eric J. Munson<sup>1</sup>, <sup>1</sup>Department of Pharmaceutical Chemistry, University of Kansas, Lawrence, KS 66047, and <sup>2</sup>Department of Pharmaceutics, University of Minnesota, Minneapolis, MN 55455.

The ability to effectively deliver solid pharmaceuticals is directly related to the form of the drug in the solid state. Although most drugs are formulated in the crystalline state, amorphous forms are often generated during the formulation process. Moreover, many of these drugs exhibit polymorphism, or the ability to exist in two or more crystalline phases that differ in the arrangement or conformation of the molecules in the crystal lattice. The ability of solid-state  $^{13}\text{C}$  NMR spectroscopy with cross polarization (CP) and magic-angle spinning (MAS) to quantify the amounts of multiple crystalline and amorphous forms present in formulations of the artificial sweetener neotame will be described. In a mixture of two polymorphic forms of anhydrous neotame, we have identified the presence of one polymorph at levels below 0.25%. We have also been able to quantify the amount of each polymorph to within 2%. More accurate quantitation could be possible if pure crystalline forms were used. In mixtures of amorphous and crystalline forms of neotame, the amorphous content could be determined to at least 10%. The effects of differences in relaxation parameters and cross polarization efficiencies on characterizing mixtures of different polymorphs will be addressed.

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- 230. Development of New Solid State NMR Techniques for Studying Anisotropic Motion of Half-Integer Quadrupole Nuclei.** Jorgen Holm Kristensen and Ian Farnan, University of Cambridge, Department of Earth Sciences, Downing Street, Cambridge, CB2 3EQ, UK

Advanced solid state NMR techniques are presented for studying motional disorder of half-integer quadrupole nuclei. The results include a theoretical formalism for simulating effects of anisotropic motion and relaxation on central transition NMR spectra. This formalism is based on density operator algebra and involves the stochastic Liouville-von Neumann equation. In this approach the nuclear spin interactions are represented by the Hamiltonian while the motion is described by a stochastic operator. The nuclear spin interactions fluctuate randomly in the presence of motion. These fluctuations stimulate the relaxation of the system and are represented by a relaxation operator. The system may be solved recursively to obtain the density operator at any time and for all motional regimes. The formalism has been applied to simulate central transition  $^{17}\text{O}$  NMR spectra of selected model systems. The simulations have shown the usefulness of central transition spin echo and inversion-recovery NMR experiments for investigating motion in solids. As an example we have applied central transition spin echo and inversion-recovery  $^{17}\text{O}$  NMR spectroscopy to polycrystalline cristobalite ( $\text{SiO}_2$ ) at temperatures both below and above the  $\alpha$ - $\beta$  phase transition. The simulations show that the oxygen motion is slow in  $\alpha$ -cristobalite. The slow motion has no significant effects on the fully relaxed lineshapes but may be monitored by studying the partially relaxed spectra. The  $\alpha$ - $\beta$  phase transition is characterized by structural and motional changes involving a slight increase in the Si-O-Si bond angle and a substantial increase in the mobility of the oxygen atoms. The increase in the Si-O-Si angle is supported by the results of  $^{17}\text{O}$  and  $^{29}\text{Si}$  NMR spectroscopy. The oxygen motion is orders of magnitude faster in  $\beta$ -cristobalite resulting in much faster relaxation and characteristic lineshapes.

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- 231. Mapping Vortex Development During Entry Flow of a Shear Thinning Fluid.** Galina E. Pavlovskaya, Chemistry Department, Colorado State University, Fort Collins CO 80523; Susan J. Muller, Jeffrey A Reimer, Department of Chemical Engineering, University of California, Berkeley CA 94528.

Magnetic Resonance Imaging (MRI) Velocimetry methods were used for spatial mapping of fluid velocity and diffusion of a shear thinning fluid (0.5% Xanthan gum in water) as flow develops towards an abrupt contraction. Radial diffusion and velocity profiles derived from diffusion and velocity images were measured for a few values of  $\Delta$  times in order to see the effect of temporal averaging on either type of profiles. Radial diffusion profiles were dependent on  $\Delta$  time. Furthermore, the dependence of radial diffusion profiles on  $\Delta$  can be used to spatially map vortex formation as flow develops towards the contraction plane.

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- 232. Advances in ENMR of Solid-State Electrolytes.** Rex E. Gerald II, Jairo Sanchez, Robert J. Klingler, and Jerome W. Rathke, Argonne National Laboratory, Chemical Technology Division, 9700 S. Cass Ave., Argonne, IL 60439-4873

The ideal polymer electrolyte has the following properties: high ionic conductivity over a wide temperature range, very low electronic conductivity (electrical insulator), exclusive transport of electroactive ions, wide electrochemical redox window, and excellent rheology (to maintain electrode contact in batteries of any size and shape). We continue to investigate several solid-state ion conductors (PEO-salt and PEO-composite) that we have synthesized in our laboratory. We employ novel electrochemical-NMR (ENMR) detectors to record, in situ, the quantity of charge that is passed through the cell, the voltage response of the cell, and the NMR spectrum (Li-7 and F-19) of the electrode and electrolyte components at different points along the first discharge/charge cycle and subsequent cycles. The goals of our efforts include comparison and quantification of: cation transport numbers, ionic mobilities, and electrode adhesion for binary and composite electrolytes. This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.

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- 233. New Approaches to High Resolution Double Resonance Experiments Between Spin-1/2 and Quadrupolar Nuclei.** J. W. Wiench,<sup>1</sup> J. Trebosc,<sup>2</sup> J.-P. Amoureux<sup>2</sup> and M. Pruski,<sup>1</sup> <sup>1</sup>Ames Laboratory and Iowa State University, Ames, IA, 50011; <sup>2</sup>Université de Lille (LCPS-CNRS 8012).

High resolution NMR methods for the half-integer quadrupolar nuclei in solids (MQMAS, STMAS and I-STMAS) can be most effectively used for structural determination when combined with various double resonance schemes. We report an I-STMAS experiment with cross polarization (CP-I-STMAS) and TEDOR, and new approaches to the TEDOR-MQMAS and CP-MQMAS methods. The efficiency, quantitative accuracy and experimental conditions for successful polarization transfer with CP and TEDOR will be discussed. New schemes for heteronuclear correlation



experiments will be proposed.

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- 234. Advanced High-Resolution Solid-State NMR Studies of Imidazole-Based Proton Conductors.** Gillian R. Goward, McMaster University, Hamilton ON, L8S 4M1 Canada; I. Schnell, D. Sebastiani, and H.W. Spiess, Max-Planck Institute for Polymer Research, Postfach 3148, D-55021, Mainz, Germany

Here we demonstrate the success of several advanced solid-state NMR techniques in characterising both structure and dynamics in imidazole-based proton-conducting materials. These methods include homonuclear  $^1\text{H}$  DQ NMR,<sup>[1]</sup> and  $^{15}\text{N}$ - $^1\text{H}$  CP-TEDOR,<sup>[2]</sup> and are implemented under fast MAS (30kHz). The latter method makes use of inverse detection with the support of gradients or  $^1\text{H}$  dephasing pulses, and has been successfully implemented to measure  $^{15}\text{N}$ - $^1\text{H}$  couplings in natural abundance. Both methods can be implemented in rotor-encoding variants, such that the relevant dipolar couplings can be extracted from rotor-encoded sideband patterns acquired in the indirect dimension. Quantitative evaluation of these patterns provides accurate dipolar coupling constants, which are particularly useful for characterising hydrogen-bond distances or motional averaging. Materials of interest include ethylene-oxide-tethered imidazoles (Imi-nEO),<sup>[3]</sup> polyvinazene,<sup>[4]</sup> and 4,5-dicarboxyimidazole.<sup>[5]</sup> Relative proton mobilities are accessed by comparing single pulse  $^1\text{H}$  MAS spectra and double quantum filtered  $^1\text{H}$  MAS spectra. Similar temperature dependent behaviours were observed for the Imi-nEO oligomers and for polyvinazene. We propose a model for proton transport in the Imi-nEO family, based on chemical shift trends, chemical exchange analysis, and structural insights provided by quantum chemical calculations of the  $^1\text{H}$  NMR spectra.<sup>[6]</sup>

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- 235. Experimental Distinction Between Velocity, Velocity Distribution and Diffusion in PFG NMR.** Antje Gottwald, Ulrich Scheler, Institute for Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

Pulsed field gradient NMR can be applied for the investigation of directed flow as well as diffusive motion. The first gradient pulse provides labeling according to the spatial position of the spins, which would be refocused without any displacement by the second pulse. Incoherent motion results in a incoherent superposition of phases and thus a signal attenuation which yields the diffusion coefficient at given experimental parameters. In contrast coherent motion results in a coherent phase modulation at constant signal amplitude. In most experiments a superposition of both is present. Thus flow and diffusion can be distinguished by data processing<sup>[1]</sup>. Incoherent contributions from diffusion and an inherent velocity distribution are indistinguishable by this approach. Therefore an experimental separation of diffusion and velocity distribution is proposed here, where the driving force of the motion is incremented in the two-dimensional experiment at constant magnetic field gradients. Thus contributions from relaxation and diffusion are constant throughout the experiment, amplitude modulation results from the distribution of the velocity of the directed motion only. This approach has been applied to motion resulting from electrical [us] and mechanical forces [ag]. A generalized coordinate representation is proposed to facilitate the comparison between flow and diffusion experiments, where all known variables are combined in a new Fourier conjugate of displacement  $q'$ .

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- 236. Ab initio Studies of Pseudorotation and the Chemical Shift of Tetrahydrofurans.** Chunlei Guo, Gerard S. Harbison, University of Nebraska at Lincoln, Lincoln, NE 68588

To understand the chemical shifts, J couplings and other NMR measurables for the 5 membered puckered sugar ring of DNA and RNA requires a combination of liquid- and solid-state NMR and ab initio quantum chemical calculations. We have carried out such calculations for tetrahydrofuran and substituted tetrahydrofurans at the MP2/6-311++G(2d,p) level. In agreement with microwave spectroscopic results, we find the pseudorotation potential to be very flat, with significant thermal population of all pseudorotation angles at room temperature. Quantum chemistry disagrees with the interpretation of the microwave spectrum in the positions of the potential minima, although the experimental and theoretical pucker amplitudes match closely. In contrast with the flatness of the potential surface, there is significant variation in the NMR chemical shift with pseudorotation angle, suggesting that a significant part of the experimentally-observed conformation dependence of RNA and DNA sugar chemical shifts can be explained from the pucker alone and without considering interactions with exocyclic substituents.

#### **NMR Symposia Poster Session**

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- 237. Solid-State NMR of Half-Integer Quadrupolar Nuclei in Alkali and Alkali Earth Metal Metallocenes.** Robert W. Schurko\*, Ivan Hung and Mathew J. Willans. Department of Chemistry and Biochemistry, University of Windsor; Windsor, Ontario, Canada N9B 3P4

A variety of monomeric and polymeric metallocenes are investigated from the perspective of the central quadrupolar metal nucleus and cyclopentadienyl rings via solid-state NMR methods. The structure and dynamics of polymeric sodium metallocenes are probed using variable-temperature spin-echo  $^{23}\text{Na}$ ,  $^{13}\text{C}$  CPMAS and  $^1\text{H}$  MAS NMR experiments in combination with ab initio calculations. Metallocenes containing unresponsive half-integer quadrupolar nuclei (i.e., low natural abundance and/or low magnetogyric ratio) are also investigated using the quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) spin echo pulse sequence.<sup>1</sup> Polymeric potassium metallocenes are examined by  $^{39}\text{K}$  static QCPMG NMR combined with wideline methods, rotor-synchronized  $^{39}\text{K}$  QCPMG MAS NMR experiments and  $^{13}\text{C}$  CPMAS NMR. Monomeric magnesium metallocenes are studied using  $^{25}\text{Mg}$  and  $^{13}\text{C}$  NMR experiments analogous to those above. Anisotropic quadrupolar and chemical shielding interactions are shown to be extremely sensitive to substitution of the cyclopentadienyl rings and molecular geometry, making multi-nuclear solid-state NMR an excellent tool for the study of these materials.

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#### **NMR Symposia Poster Session**

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- 238.  $^1\text{H}$ -Decoupled  $^{29}\text{Si}$  and  $^{19}\text{F}$  MAS NMR Spectra of Isolated  $^{29}\text{Si}(^{19}\text{F})_2$  and  $^{29}\text{Si}(^{19}\text{F})_3$  Spin Systems: Experiments and Simulations.** Xavier Helluy, Angelika Sebald; Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany

The large gyromagnetic ratio of the isotope  $^{19}\text{F}$  renders the spectral lineshapes of straightforward  $^{29}\text{Si}$  MAS NMR spectra of solid organosilicon compounds  $\text{R}_2\text{SiF}_2$  and  $\text{RSiF}_3$  highly informative. Over wide ranges of Larmor and MAS frequencies the magnitudes and orientations of the various interaction tensors in these  $^{29}\text{Si}(^{19}\text{F})_2$  and  $^{29}\text{Si}(^{19}\text{F})_3$  spin systems remain encoded in the often complicated  $^{29}\text{Si}$  spectral lineshapes. Relatively slow spinning conditions play an important role. The experimental data can conveniently and efficiently be analysed in a quantitative manner by means of numerically exact lineshape simulations. In this way some/most of the (many) spin-system parameters characterising the  $^{29}\text{Si}(^{19}\text{F})_2$  and  $^{29}\text{Si}(^{19}\text{F})_3$  moieties can be extracted from experimental  $^1\text{H}$ -decoupled  $^{19}\text{F}$  and  $^{29}\text{Si}$  MAS NMR spectra. For our compound  $\text{RSiF}_3$  we find that rapid reorientation of the  $\text{SiF}_3$  group around the R-Si bond direction must be taken into account in order to satisfactorily simulate the experimental  $^{29}\text{Si}$  MAS spectra. Molecular solid-state dynamic properties do not need to be taken into account in the analysis of  $^{19}\text{F}$  and  $^{29}\text{Si}$  MAS spectra of our compound  $\text{R}_2\text{SiF}_2$ . Here the two  $^{19}\text{F}$  spins in the molecule represent a so-called near  $n = 0$  rotational-resonance condition, which renders the  $^{29}\text{Si}$  MAS NMR lineshapes particularly sensitive to all anisotropic interaction parameters within the  $^{29}\text{Si}(^{19}\text{F})_2$  spin system.

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- 239. Calculations of  $^{129}\text{Xe}$  Chemical Shifts in Cryptophane Cages.** Cynthia J. Jameson and Devin N. Sears, University of Illinois at Chicago, Department of Chemistry M/C-111, Chicago, Illinois 60607-7061

The exquisite sensitivity of the xenon chemical shift to its environment has motivated the development of Xe included in functionalized cages as biosensors for proteins in solution [M.M. Spence, S.M. Rubin, I.E. Dimitrov, E.J. Ruiz, D.E. Wemmer, A. Pines, S.Q. Yao, F. Tian, P.G. Schultz, Proc. Nat. Acad. Sci., 98, 10654 (2001)]. Prediction of caged Xe shifts for this purpose require a quantitative understanding of the sensitivity of the isotropic Xe chemical shift in various cryptophane cages, in particular the observed dependence on cage size, isotopic substitution, and temperature. To investigate these effects, we use half the cryptophane-A cage, a cyclooveratrylene bowl, as a model system within which the

shielding of a Xe atom is calculated at various positions, using ab initio and density functional methods. The resulting values, expressed as an analytical function of Xe position, are used in Monte Carlo canonical averaging of a Xe atom within cryptophane cages to investigate the dependence of the Xe chemical shifts on cage size (A versus E), isotopic substitution, and temperature.

#### NMR Symposia Poster Session

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#### 240. Solid State $^{91}\text{Zr}$ NMR Study of Organometallic and Inorganic Zirconium Compounds. Ivan Hung and R.W. Schurko\*, Department of Chemistry and Biochemistry, University of Windsor; Windsor, Ontario, Canada N9B 3P4

Zirconium-91 NMR is uncommon, especially in the solid-state, due to its low sensitivity (0.087 times as receptive as  $^{13}\text{C}$ ), which arises from the low magnetogyric ratio and low natural abundance of  $^{91}\text{Zr}$  and the fact that  $^{91}\text{Zr}$  is a half-integer quadrupolar nucleus ( $\gamma = -2.4975 \times 10^7 \text{ rad s}^{-1} \text{ T}^{-1}$ , n.a. = 11.23%,  $Q = -0.21 \times 10^{-28} \text{ m}^2$ , spin = 5/2). Notably, in the solid state, where the NMR signal is broadened by large second-order quadrupolar interactions, studies have only been conducted on zirconium salts, oxides and metals, using very time-consuming spin-echo techniques.<sup>1-3</sup> We report the application of the Carr-Purcell Meiboom-Gill train of echoes for quadrupolar nuclei (QCPMG)<sup>4</sup> combined with wideline NMR techniques and magic angle spinning to study inorganic and organometallic zirconium-containing compounds, including  $\text{Zr}(\text{acac})_4$  and a series of catalytic precursors,  $\text{Cp}_2\text{ZrXY}$  (Cp =  $\text{C}_5\text{H}_5$ ; X, Y = Cl, Br,  $\text{CH}_3$ , H). Efficient acquisition of such spectra make  $^{91}\text{Zr}$  NMR plausible for studying the electronic structure of a wide array of zirconium compounds. The viability of using these solid state NMR methods to study  $^{91}\text{Zr}$  and other low- $\gamma$  nuclei is discussed.

[1] Hartmann, P.; Scheler, G. Z. Naturforsch. A 1995, 50, 90.

[2] Bastow, T.J.; Smith, M.E.; Stuart, S.N. Chem. Phys. Lett. 1992, 191, 125.

[3] Bastow, T.J.; Hobday, M.E.; Smith, M.E.; Whitfield, H.J. Solid State Nucl. Magn. Reson. 1994, 3, 49.

[4] Larsen F.H.; Jakobsen H.J.; Ellis P.D.; Nielsen N.C. J. Magn Reson. 1998, 131, 144.

#### NMR Symposia Poster Session

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#### 241. Applications of $^{17}\text{O}$ MAS NMR to characterising the structure of silicate-based sol-gel materials. P. Gunawidjaja and M.E. Smith, Department of Physics, University of Warwick, Coventry, CV4 7AL, U.K.; M.A. Holland, G. Mountjoy, R.J. Newport and D.M. Pickup, School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NR, U.K.

Silica-based sol-gel materials are of widespread scientific and technological interest. The addition of a secondary oxides such as titania, zirconia, hafnia and tantalum can be used to tailor the properties of the material for specialised optical and catalytic applications as examples. Solid state NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$ ) can follow the structural changes of these sol-gel materials as the subsequent heat treatment is varied for the structure which remains largely amorphous.  $^{17}\text{O}$  has proved to be an extremely powerful probe of the distribution of the metals in the structure through the resolution of different metal fragments. The effects of different heat treatment schemes and annealing atmospheres on the  $^{17}\text{O}$  signal intensity and the apparent oxygen distribution are discussed. This  $^{17}\text{O}$  data should be used with caution if it is going to be used quantitatively. NMR data is used to compare the effects of the different metals on the structure of the silicate matrix in a binary mixture. The work on binary systems is extended to the ternary  $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$  to compare the effects of different, competing metals on the silicate structure.

#### NMR Symposia Poster Session

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#### 242. NMR Studies of Guest-Mediated Zeolite Crystallization. Son-Jong Hwang, California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, CA 91125; Stacey I. Zones, Chevron Research and Technology Company, P.O. Box 1627, Richmond, CA 94802

Our main research interests are focused on the understanding of the mechanistic difference in the crystallization process for a system that results in the synthesis of SSZ-42 (IFR) and beta zeolite (BEA\*) when boron and aluminum were used, respectively, in the presence of the same structure directing agent (N-Benzyl DABCO). In this progress report, we will present multinuclear MAS, CP MAS, MQ-MAS and REDOR NMR results that were obtained from powder samples recovered during the crystallization processes. NMR studies provide the valuable information on the structural changes of the host framework, the guest organics, and the incorporated trivalent metal ions during the formation of crystalline zeolite phase. NMR quantitation of  $^{11}\text{B}$  and  $^{27}\text{Al}$  elements shows that Al ions are highly incorporated in the stage of gel formation while B ions slowly get fixed into the solid phase from the liquid phase of the reaction mixture as the nucleation of SSZ-42 proceeds. The earlier incorporation of metal ion is found to be a responsible factor for forming the intercrossing three dimensional pore structures (beta) although the difference in behavior of Al and B needs to be further investigated. In addition, two distinctive tetrahedral boron sites were observed in the crystalline product and the characterization was made using a number of NMR methods. Site selectivity of Al in the framework was not

observed for the crystalline beta zeolite. The role of guest organics and the counter charge ion ( $\text{Na}^+$ ) was also investigated by  $^{13}\text{C}$  and  $^{23}\text{Na}$  NMR methods.

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- 243. Study of the Formation and Molecular Structure of Zeolites and Molecular Sieves by Liquid State  $^{29}\text{Si}$  NMR and Solid State  $^{29}\text{Si}$  and  $^{23}\text{Na}$  NMR.** Christopher M. Snively, Hugh W. Hillhouse, and Kendall T. Thomson, School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-1283.

NMR in both the liquid and solid state is capable of providing detailed molecular and structural information of microporous materials. We are interested in two specific areas - the early stages of formation of these materials and the dependence of molecular structural parameters on external stimuli. Understanding the formation of these materials is important in order to be able to tailor the synthesis to produce the desired end properties. We have employed  $^{29}\text{Si}$  NMR liquid state NMR to track the distribution of silicon species in the precursor solution as a function of pH. ETS-4, a microporous molecular sieve, shows great potential for gas separation due to the tunability of its pore size as a function of temperature. ETS-4 is a disordered material, faulted in two directions, and as a result the commonly used technique of x-ray diffraction is unable to determine the local environment of the extraframework cations. We have employed  $^{23}\text{Na}$  MAS and MQMAS to elucidate the distribution of cation sites within the molecular framework. These studies, along with  $^{29}\text{Si}$  MAS NMR has also been used to study the structure and understand the unique framework contraction in this system.

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- 244. The Calculation of NMR Chemical Shifts and Quadrupolar Coupling Parameters for Xe in Clathrate Hydrates Using Canonical Monte Carlo Averaging.** Dirk Stueber and Cynthia J. Jameson, Department of Chemistry M/C111, University of Illinois at Chicago, 845 W. Taylor, Chicago, Illinois 60607-7061

The Xe chemical shielding and quadrupolar coupling interactions are very sensitive to void size and shape in clathrate hydrates. The water molecules in these systems are linked together by hydrogen bonds in polyhedral cage-like structures in a three-dimensional network. Each cage in this host lattice can accommodate one Xe guest atom. The theoretical calculations of the NMR tensors of the Xe atom in this environment is a very demanding task due to the inherent proton disorder and the effect of the hydrogen bonding network. In the present study, we investigate the influence on the Xe NMR tensors coming from atoms in the network beyond the water molecules that constitute the cage in which the Xe is trapped. The inherent proton disorder in clathrate hydrate structure can be simulated by randomly assigning each hydrogen atom to one of the two distinct positions along the O-O line, subject to the ice rules. We study the ability of the Embedded Ion Method (EIM) to mimic the electrostatic part of hydrogen bonding effects on the Xe response properties elicited by a hydrogen-bonded solvent. In this approach, a self-consistent point charge array simulates the Ewald potential in a defined region where the NMR properties are calculated. We obtain both, the direct long range effects on the electric field gradient and the shielding tensors at the Xe, and the indirect influence on the Xe tensors via the effects of the extended network on the electronic structure of the cage  $(\text{H}_2\text{O})_n$ . Monte Carlo methods are employed in the simulation of the proton disorder and in the averaging of the Xe NMR tensors.

#### **NMR Symposia Poster Session**

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- 245. Multinuclear NMR and EPR of Alkali Metals Confined in Porous Matrices.** V.V. Terskikh, I.L. Moudrakovski, C.I. Ratcliffe, and J.A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada, C.J. Reinhold, P.A. Anderson, and P.P. Edwards, School of Chemistry, The University of Birmingham

Nanoporous frameworks can be used as templates for the preparation of extremely thin semiconductor and metal wires of nanometer dimensions. Such nanowires possess unique electronic properties, which are fundamentally different from those of the corresponding bulk materials (quantum size effect, QSE). Nowadays, the QSE is not only of academic interest, but also is practically important. We use multinuclear NMR spectroscopy to study alkali metals (in this work Na and Cs) deposited via the gas phase into controlled pore glasses (CPGs) and zeolites. In porous glasses the alkali metals form 3D filamentary structures. The diameter of the filaments is governed by the pore size of the CPG used (4-60 nm). The NMR Knight shift spectra of such species are strongly size and temperature dependent. In cage zeolites alkali atoms exist mainly as individual clusters of different structure (often coupled through spin exchange), while in channel zeolites short or extended 1D chains of alkali atoms may be present. In Cs-loaded ZSM-5 zeolite the  $\text{Cs}_2^+$  dimer has been discovered with EPR spectroscopy.



### NMR Symposia Poster Session

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- 246. The First Observation of Heteronuclear Two-Bond J-Coupling in the Solid State: Crystal Structure and Solid State NMR Spectroscopy of  $\text{Rb}_4(\text{NbO})_2(\text{Si}_8\text{O}_{21})$ .** Hsien-Ming Kao<sup>a</sup> and Kwang-Hwa Lii<sup>a,b</sup> <sup>a</sup>Department of Chemistry, National Central University, Chungli, Taiwan 320, <sup>b</sup>Institute of Chemistry, Academia Sinica, Nankang, Taipei 115.

High-temperature, high-pressure hydrothermal synthesis of the title compound and its <sup>93</sup>Nb and <sup>29</sup>Si MAS NMR spectra are reported. The <sup>29</sup>Si MAS NMR spectrum shows four signals corresponding to the four distinct Si sites in the structure. Three signals show multiplet patterns which arise from <sup>93</sup>Nb(sp<sup>in</sup>-9/2)-<sup>29</sup>Si J-coupling. This is the first example of two-bond J-coupling between a quadrupolar nucleus and a spin-1/2 nucleus in the solid state. A combination of <sup>93</sup>Nb and <sup>29</sup>Si solid-state NMR and X-ray diffraction data has provided a correlation between NMR interaction parameters and local structure. This opens a new opportunity to examine the relationship between <sup>2</sup>J-coupling and structural parameters in the solid state.

### NMR Symposia Poster Session

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- 247. High Temperature MAS NMR for Molecular Structure Characterization of Insoluble Polymers and Functionalized Silica Nanoparticle Surfaces.** Khalid Thakur, 3M Corporate Analytical Technology Center, 3M Center, Bldg 201-BS-08, St. Paul, MN 55144.

Molecular structure characterization by NMR often requires relatively narrow, resolved, and quantitative resonances. Proton MAS NMR spectra of rigid materials are too broad to be useful and CP-MAS NMR spectra are usually non-quantitative. Causes for broad resonances include: (1) "Inhomogeneous" broadening; (2) "Homogeneous" broadening; and (3) frozen variations in bond angles and lengths. Magic Angle Spinning (MAS) averages inhomogeneous broadening that is related to scalar orientation dependencies e.g. CSA. Homogeneous broadenings that are related to spin diffusion and relative orientation of nuclei spin vectors in the static magnetic field are difficult to reduce by typical MAS speeds. However, high temperature in combination with MAS can be effective in reducing homogenous broadening and increasing movement of the molecules. In the absence of anisotropic bulk magnetic susceptibility broadening, high temperature proton MAS NMR of polymers can have resolution comparable to that in solution. For silica nanoparticles, high temperature enables separation of adsorbed versus covalently bound species. Here, the observed line widths of component resonances are proportional to their binding strength to the surface.

### NMR Symposia Poster Session

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- 248. Solid-State NMR of the Polycarbonate/tri-p-tolylamine Blend.** Brian Kesling, Terry Gullion, West Virginia University, Morgantown, WV, 26506

The miscible blend of polycarbonate and the organic photoconductor tri-p-tolylamine (TTA) serves as a model for organic photoconducting systems used in xerography. We have been interested in the structural aspects of such blends. In particular, when small molecules such as TTA are blended with polymers, do the dopant molecules exhibit any structural organization within the blend or are they just randomly scattered throughout the polymer matrix? Solid-state NMR experiments (including <sup>13</sup>C-<sup>15</sup>N REDOR and <sup>13</sup>C-<sup>2</sup>H REDOR) have been performed on this amorphous system and evidence for the formation of chains of TTA within the polycarbonate matrix has been found. The experimental results will be presented and a structural model of the blend will be proposed based on CH- $\pi$  hydrogen bonding between TTA molecules.

### NMR Symposia Poster Session

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249. **A Study of the Ca<sup>2+</sup>-ATPase Regulator Protein Phospholamban Using Solid-State NMR Spectroscopy.** Elvis K. Tiburu, Paresh C. Dave, Thomas B. Cardon, Gary A. Lorigan, Miami University, Department of Chemistry and Biochemistry, Oxford, Ohio 45056; Baowei Chen, Diana J. Bigelow, University of Kansas, Department of Biochemistry, Lawrence, Kansas 66045.

The cycle of muscle contraction/relaxation is controlled by the release/reuptake of Ca<sup>2+</sup> from the sarcoplasmic reticulum (SR). The reuptake of Ca<sup>2+</sup> is accomplished by Ca<sup>2+</sup>-ATPase, which is a calcium ATP-dependent pump. In cardiac and smooth muscles this pump is regulated by phospholamban (PLB). PLB is a 52 amino acid transmembrane protein that interacts with the pump and lowers its affinity for Ca<sup>2+</sup>. Two basic models have been proposed for the structure and mechanism of PLB. Both models have the N-terminal domain IA (residues 1-16) and the transmembrane domain II (residues 33-52) in  $\alpha$ -helical conformations. Another model has described the remaining domain IB (residues 17-32) as  $\alpha$ -helical and continuous (no separation between the transmembrane and cytosolic segments); whereas, another model has described this domain as a relatively unstructured loop. The discrepancies in the orientation and dynamics of PLB are being investigated in our lab using solid-state NMR techniques. The PLB peptide (24-52) was synthesized using a peptide synthesizer and purified using reverse-phase high performance liquid chromatography (HPLC). The orientation and dynamics of PLB in lipid bilayers is being evaluated by one-dimensional solid-state <sup>15</sup>N and <sup>2</sup>H NMR spectroscopy. Also, the uniformly <sup>15</sup>N labeled full length PLB protein was also overexpressed, purified by affinity chromatography and incorporated into mechanically oriented phospholipid bilayers composed of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC).

#### **NMR Symposia Poster Session**

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250. **CH<sub>4</sub> + C<sub>3</sub>H<sub>8</sub> sII Hydrate Growth Rate Measurements via <sup>13</sup>C NMR.** Ramesh A. Kini, Steven F. Dec, and E.D. Sloan, Jr., Center for Hydrate Research, Colorado School of Mines, Golden CO 80401

Gas hydrates, the inclusion compounds of natural gas and water, form in oil and gas producing pipelines usually at high pressures and low temperatures. Without proper precautions, hydrates can eventually block pipelines resulting in heavy production losses. Hydrate growth rate measurements are crucial in understanding pipeline plugging. Natural gas hydrates that form in oil and gas producing pipelines are usually Structure II (sII). Until spectroscopic techniques became available for these systems, most researchers derived hydrate growth rates from the rates of gas or liquid hydrocarbon consumption accompanying hydrate formation. In this work, we use <sup>13</sup>C NMR spectroscopy to directly measure the growth rates of methane + propane sII hydrates. The CH<sub>4</sub> + C<sub>3</sub>H<sub>8</sub> hydrate NMR spectra were collected as a function of time in a custom-built non-spinning probe. Hydrate and gas peak intensities change with time to follow the rate of hydrate formation and gas consumption, respectively. Hydrate formation from ice particles initially occurs from a reaction between ice and gas until a hydrate layer completely covers the ice particle surface. Further, the hydrate growth is controlled by the diffusion of gas to the particle core through the hydrate film. The CH<sub>4</sub> + C<sub>3</sub>H<sub>8</sub> hydrate surface reaction growth data suggest that the large cages form twice as fast as small cages, although there are twice as many small cages as large cages in a sII unit cell. Propane preferentially goes into the hydrate denuding the vapor of propane as hydrates form. Hydrate growth rates were measured as a function of ice particle surface-to-volume ratio and pressure. The time to form a complete hydrate layer on the particle surface depends on the particle size. The faster growth of large cages was explained based on cluster formation hypothesis. A simple surface reaction model, which relates growth rate to pressure and particle size, was developed.

#### **NMR Symposia Poster Session**

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251. **Molecular Dynamics of Main- and Side-chain Aliphatic Rings in Modified Poly(carbonate)s and Poly(ester carbonate)s by <sup>13</sup>C NMR.** Thomas Weldeghiorghis and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis MO 63130

Magic-angle spinning dipolar-echo <sup>13</sup>C NMR experiments have been performed at 15.1 MHz on modified poly(carbonate)s and poly(ester carbonate)s based on 1,1'-bis(4-hydroxyphenyl)-cyclohexane (Z-PC), 1,1'-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (TMC-PC) and 1,1'-spiro[bis(3,3-dimethyl-6-hydroxyindane)] (SBI-PC). The goal of these experiments is to study the mobility of the main and side-chain cyclohexylene rings and fused five membered rings and to correlate with impact resistance and yielding of the polymers. The results showed that main-chain cyclohexylene rings in ZPC-based polymers are less mobile than their counterparts in TMC-based polymers. Surprisingly, bulky fused side-chains in SBI-based polymers have more wiggling than side-chain cyclohexylene rings. Nevertheless, phenyl-ring  $\pi$ -flips in the polymers are not significantly enhanced or suppressed by the main-chain cyclohexylene rings. The main-chain cyclohexylene ring motions are not correlated with yield stress.

#### **NMR Symposia Poster Session**

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**252. Predictive Testing, Quality Control and Failure Analysis of Rubber Compounds by MR Crosslink Density Measurements.** W. Kuhn and M. Sauzade, IIC Innovative Imaging Corp. KG, Blieskastel, Germany

The chemical and physical properties of cured rubber compounds are mainly determined by the concentration and chemical structure of the crosslinks, the nature and modifications of the hydrocarbon backbone, and the amount and type of filler and its physical bonds to the network structure. The most important single factor in determining the physical properties of a rubber is the degree of crosslinking. During the past 10 years, magnetic resonance techniques were progressively used to investigate the network structure and degree of crosslinking of natural rubber, but also rubber compounds such as EPDM, EVA, SBR, PB and others. This paper demonstrates the use of a low-cost and compact NMR system with dedicated features for automatic quality control and quality assurance in rubber testing, optimization of curing parameters, and failure analysis on rubber compounds such as car tires, car window sealings, rubber springs etc. Quick and accurate information on curing performance, chemical and total crosslink density (XLD), and entanglements of the hydrocarbon chain of the uncured compound can be obtained within a few minutes. A large number of differently cured and filled rubber compounds have been investigated using MR-XLD in comparison to swelling and Mooney Rivlin measurements. It could be shown, that the MR-XLD technique - as used here and based on an easy to use low-cost system - seems to be the ideal method for quality control of rubber compounds and in elastomer production. Simultaneous XLD measurements during the vulcanization process may provide a new insight into rubber curing and may contribute to the optimization of rubber processing parameters.

**NMR Symposia Poster Session**

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**253. NMR Studies of New Albany Shale to Characterize Maturity, Organic Matter Types and Hydrogen Exchangeability.**

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A suite of New Albany Shale (Devonian and Mississippian) samples from the Illinois Basin containing different types and amounts of organic matter has been analyzed using  $^{13}\text{C}$  CP-MAS NMR, FTIR, carbon and hydrogen isotopic ratios, as well as organic hydrogen isotopic exchangeability ( $H_{\text{ex}}$ ). Thermal maturity was assessed via vitrinite reflectance,  $R_o$ , ranging in values from 0.29 to 1.4%. The  $^{13}\text{C}$  CP-MAS NMR data show an increase in aromatic versus aliphatic sites, which correlates well with vitrinite reflectance. Furthermore, additional peaks in the NMR spectra of the more mature samples allow insight into thermal maturation. Values of  $\delta\text{D}$  of isotopically non-exchangeable organic hydrogen range from  $-125\text{‰}$  ( $R_o=0.29$ ) to  $-67\text{‰}$  ( $R_o=1.27$ ) and exhibit a linear trend towards enrichment in deuterium with increasing maturity. This trend may indicate thermally mediated interchange between  $^2\text{H}$ -depleted organic hydrogen and relatively  $^2\text{H}$ -enriched formation water hydrogen. The abundance of exchangeable organic hydrogen decreases from 7.3% to 2.4% with  $R_o$  increasing up to 0.6%, followed by a reverse trend of increasing  $H_{\text{ex}}$  up to 6.6% at higher  $R_o$  with increasing aromaticity. We monitor the exchange of hydrogen with deuterium in the  $^{13}\text{C}$ -CP MAS and  $^2\text{H}$  NMR spectra.

**NMR Symposia Poster Session**

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**254. Theoretical Prediction of  $^{51}\text{V}$  Quadrupolar Parameters in Vanadates.** Andy Y.H. Lo and Robert W. Schurko\*, Department of Chemistry and Biochemistry, University of Windsor; Windsor, Ontario, Canada N9B 3P4

The vanadates are inorganic materials which are of great industrial importance in heterogeneous catalysis. Vanadium-51 solid-state NMR has been one of the most important methods for their structural characterization.<sup>1,2,3</sup> It is therefore of great interest to be able to predict the local structure about vanadium atoms by applying theoretical calculations of the  $^{51}\text{V}$  quadrupolar coupling constant,  $C_Q$ , and the quadrupolar asymmetry parameter,  $\eta_Q$ . Here we report a theoretical study of  $^{51}\text{V}$  electric field gradient (EFG) tensors in vanadates. The Gaussian 98 software package is applied, using both Hartree-Fock methods and hybrid density functional theory, and a variety of basis sets on the  $^{51}\text{V}$  atom and the lighter atoms. The smallest molecular units which can be used to correctly calculate the  $^{51}\text{V}$  quadrupolar parameters are determined. B3LYP/14s8p5d (4F)/6-311+G\*\* calculations are the most suitable for calculating  $C_Q$  and  $\eta_Q$  for vanadates possessing  $\text{V}_2\text{O}_7$  clusters. B3LYP/14s8p5d (4F)/6-311++G\*\* calculations combined with proton termination on corner-sharing vanadium atoms are suitable for  $\text{VO}_4$  clusters, while B3LYP/14s8p5d (6D)/6-311+G\*\* calculations are acceptable for other types of clusters. The origins of vanadium-51 EFG tensors in vanadates are discussed, by considering the symmetry of the vanadium-oxygen clusters, EFG tensor orientations and charges within the cluster and surrounding lattice.

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**NMR Symposia Poster Session**

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**255. Extracting Useful Chemical Information Via Quadrupolar NMR of Systems with Small to Moderate Quadrupolar Interactions.**  
Mark V. Wilson; Larry W. Beck, The University of Michigan, Department of Chemistry, Ann Arbor, MI 48109-1055

The acidity of Bronsted acidic catalytic sites in the pores of zeolite frameworks depends on the immediate chemical environment surrounding the catalytic metal site. New information about the local structure of acid sites in zeolite catalysts will be presented from NMR investigations of the quadrupolar parameters of these metal centers. Techniques like MQ-MAS, Quadrupolar Nutation and TRAPDOR have enabled the NMR investigation of quadrupolar nuclei with large (several MHz) quadrupolar splitting interactions. The TRAPDOR pulse sequence has been used where information about the quadrupolar nuclei can be obtained indirectly through a dipolar coupled  $I=1/2$  nucleus (like  $^1\text{H}$ ). This enables the investigation of quadrupoles that were previously "NMR invisible" due to very large quadrupolar interactions. However,  $^{11}\text{B}$  in current zeolite samples has quadrupolar interactions that are sufficiently small to make such techniques ineffective. Data will be presented for a new method of determining the magnitude of moderate to small quadrupolar splitting even in the presence of other inhomogeneous line broadening, such as CSA or strong dipolar coupling. This method exploits a combination of non-selective and selective excitation pulses, where the latter is scanned across the entire first-order quadrupolar linewidth. This method is capable of measuring small to moderate quadrupolar splittings over a very large range, from several kHz to MHz. New insights about the local structure and possible acidic function of these materials are possible by examining the magnitude of the quadrupolar splitting and asymmetry under different simulated reaction conditions.

**NMR Symposia Poster Session**

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**256. Structural Characterization of Selective Ligand Binding in the SH2 Domains of Grb7 and Grb14.** Monika Ivancic, Peter J. Brescia; Paul J. Scharf; Barbara A. Lyons, University of Vermont, Department of Biochemistry, College of Medicine, Burlington, VT 05405-0068

The Grb7 family of proteins, consisting of Grb7, Grb10 and Grb14, is known to mediate the coupling of multiple cell surface receptors to downstream signaling pathways in the regulation of many cellular functions. The molecular architecture of this family of proteins is highly conserved, and includes a C-terminal SH2 domain. It has been demonstrated that the SH2 domain is responsible for the protein's adapter functionality, linking the membrane-bound receptor phosphate tyrosine kinase with downstream signaling proteins. One of the binding partners of the Grb7 protein is the erbB2 receptor; both genes map closely to each other and are found coamplified in a subset of breast cancers. Our laboratory is utilizing structural methods to elucidate the molecular details of erbB2-Grb7 binding, by investigating the interaction between Grb7 SH2 and a 10 amino acid peptide "pY1139" mimicking the binding site on the erbB2 receptor. Sequence specific resonance assignments and a solution structure of Grb7 SH2 in complex with pY1139 have been completed. Along with the Grb7 SH2 domain, our laboratory is investigating the interaction between the Grb14 SH2 domain and the pY766 undecapeptide representing the FGFR receptor tyrosine kinase. Resonance assignments of the free Grb14 SH2 domain have been accomplished and progress is being made towards the three dimensional structure. The detailed molecular structure of both Grb7 and Grb14 SH2 domains will shed light on differences in their ability to bind different receptor tyrosine kinases. For example, Grb7 binds to the erbB2 receptor while Grb14 does not. In addition to structure determinations, we are investigating the dynamic properties of these SH2 domains. Longitudinal ( $T_1$ ) and transverse ( $T_2$ ) relaxation experiments as well as  $^{15}\text{N}$  NOE experiments are being utilized to gain information on the behavior of the Grb7 SH2 domain in solution, both free and in complex with the pY1139 peptide.

**NMR Symposia Poster Session**

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**257. Dipolar Distance Measurements with Lee-Goldburg Off-Resonance Cross-Polarization Applied to Host-Guest Systems.**  
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Though it is relatively straightforward to probe the interactions of covalently bonded nuclei in a fixed crystalline lattice, information on the non-covalent interaction between two molecules in the solid state is more difficult. This knowledge is of great interest in many modern chemical problems, such as host-guest interactions. NMR is a useful tool for probing the structure, position, and motion of a guest molecule inside a host. The heteronuclear dipolar coupling between nuclei of the guest molecule and the host can provide distance information, while the heteronuclear dipolar coupling between nuclei of a guest molecule can provide information on the motion of that molecule inside its host. Recently, HETCOR and variable contact time CP experiments have been combined with off-resonance Lee-Goldburg decoupling to probe the relationships between specific A-X spin pairs in the solid state. So far, these techniques have been applied only to well-defined, rigid crystalline solids. We have explored the robustness and applicability of the variable contact time CP technique to systems of interest, including guest-host systems and molecules with greater mobility. Our results indicate that these techniques are relatively insensitive to small deviations of the Lee-Goldburg field from the magic angle, but extremely sensitive to the CP matching condition at high spinning speeds. Scaled dipolar coupling values measured with this technique vary with  $\omega_A - \omega_B$  with the scaling factors known only for the  $\omega_A - \omega_B = \omega_r$  and  $\omega_A - \omega_B = 2\omega_r$  conditions. We will present our findings as well as a novel method for determining the optimized Lee-Goldburg off-resonance field strength.



### NMR Symposia Poster Session

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#### 258. Double Resonance Decoupling for Resolution Enhancement of $^{31}\text{P}$ Solid-State MAS and $^{27}\text{Al}$ – $^{31}\text{P}$ MQHETCOR NMR.

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Solid-state NMR double-resonance (or  $^1\text{H}$  triple-resonance) experiments often involve a half-integer quadrupolar ( $I > 1/2$ ) nucleus that has the main disadvantage of exhibiting second-order anisotropic broadening. A break-through in the study of these nuclei by solid-state NMR spectroscopy was the introduction in 1995 of the two-dimensional multiple-quantum magic-angle spinning (MQMAS) technique. By correlating triple- (or higher) quantum with observable single-quantum coherences Frydman et al. demonstrated that it is possible to remove the second-order quadrupolar interaction leading to high-resolution spectra. Taking advantage of the highly resolved dimension of the experiment, several double resonance schemes have been proposed to obtain a better insight into the connectivity of solids. However, the effect of decoupling applied on a half-integer quadrupolar nucleus while acquiring the spin  $1/2$  free induction decay has not yet been reported. In this communication, we investigate the effect of  $^{27}\text{Al}$  decoupling applied during the acquisition of  $^{31}\text{P}$  spectra of several microporous aluminophosphates. In combination with  $^1\text{H}$  high-power decoupling,  $^{27}\text{Al}$  decoupling yields  $^{31}\text{P}$  spectra with optimal sensitivity and resolution. The importance of double-resonance decoupling is further demonstrated by incorporating this technique in the MQHETCOR sequence. Unambiguous assignment of all the  $\text{AlPO}_4$ -14 NMR resonances is achieved by combining multiple-quantum evolution in the  $^{27}\text{Al}$  dimension and double-resonance decoupling in the  $^{31}\text{P}$  acquisition domain.

### NMR Symposia Poster Session

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#### 259. 3D Structure Elucidation with the COSMOS-NMR Force Field. Raiker Witter, Wolfram Prieß, Ulrich Sternberg, PAF / IOQ / HF, F.-S.-Universität Jena, Max Wien Platz 1, 07743 Jena, Germany

The COSMOS<sup>[1,2]</sup> NMR force field is used for structure determination. To the molecular force field, NOE restrictions and energetically derived chemical shift pseudo forces are introduced. These  $^{13}\text{C}$  chemical shift pseudo forces<sup>[3]</sup> can be used for all carbon atoms bonded to C, N, O as well as H. The bond polarization theory<sup>[4]</sup> is used to calculate coordinate dependent atomic charges<sup>[5,6]</sup>, chemical shifts<sup>[7,8]</sup> and their derivatives<sup>[3]</sup>. The 3D structure of a pseudopeptide zinc complex, which was designed and synthesized similar to the catalytic center of the carbonic anhydrase<sup>[9]</sup>, was determined. 18 NOE distance restraints and 17  $^{13}\text{C}$  chemical shifts were applied for molecular dynamics, simulated annealing and geometry optimizations. To confirm the COSMOS-NMR results, the three best structures were optimized by density functional theory calculations. A complex with tetrahedral coordinated zinc has been found to be most favorable. Additionally a complex with threefold coordinated zinc was found. It can be supposed that this structure can function as a transition state in the catalytic reaction ( $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+$ )<sup>[10]</sup> of the carbonic anhydrase.

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### NMR Symposia Poster Session

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- 260. An Analytic Solution to REDOR Lineshapes for  $IS_N$  Spin Clusters.** Leonard J. Mueller and Douglas Elliott, Department of Chemistry, University of California, Riverside, CA 92521

The analysis of REDOR data for isolated IS spin pairs is both quite advanced and straightforward. By contrast, the analysis of data for REDOR experiments performed on  $IS_N$  spin clusters, which contain multiple dipolar couplings, is significantly more difficult. The application of REDOR experiments to spin clusters, however, has received considerable attention. Disentangling structural information from the REDOR data in spin clusters often requires numerically intensive simulations. Here we present a novel framework for understanding the multispin REDOR experiment and present an analytic solution to the time-domain signal with respect to powder averaging. Significantly, we find that the REDOR dipolar dephasing curve for an  $IS_N$  spin cluster can be separated into the sum of N individual generalized dephasing curves each of which depends on parameters that can be obtained directly from the N individual dipolar couplings and the relative orientation of the N dipolar tensors. The formalism we describe for analyzing these spin systems is analogous to the work of Grant and Zilm in static and slow MAS solid-state NMR experiments, where they find that evolution under multiple tensor interactions can be decomposed into a sum of signals for evolution of single transitions, each of which has a generalized tensor interaction which can be determined from the tensor properties of the system. This decomposition is easily generalized to many different recoupled tensor interactions under fast MAS, providing insight into multi-spin effects. From the practical standpoint, even when analytic expressions for the powder-averaged components are not known, this decomposition greatly increases computational speed, which scales linearly with the number of interactions. Accuracy is also improved in many experiments by allowing for a fast method of including long-range dipolar couplings.

#### **NMR Symposia Poster Session**

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- 261. Powder Pattern Recoupling and Scaling.** Raiker Witter, PAF / IOQ / HF, F.-S.-Universität Jena, Max Wien Platz 1, 07743 Jena, Germany

A new powder pattern recoupling experiments is introduced. The idea of Tycko/1/ is generalized and improved. Real pulse lengths are taken into account. The method is applicable to spinning speeds higher than 30kHz and ultra high fields. The powder patterns are scaled and this scaling factor can be chosen to fit the spectra into the spectral window. No suppression of sidebands is necessary, so that this method is more efficient than the SUPER/2/ sequence for chemical shift anisotropies higher than ~7kHz. Spectra shearing can be avoided easily. The theoretical background and experimental verifications on model substances will be given.

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#### **NMR Symposia Poster Session**

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- 262. Internuclear Distances from Lee-Goldburg Cross Polarization Between  $^{19}F$ ,  $^1H$  and  $^{13}C$**  Ulrich Scheler, Institute for Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

Heteronuclear atomic distances provide valuable information for structural refinement which can be used to describe the three-dimensional structures, sidechain packing or chain arrangement in polymers. Such heteronuclear distances can be determined in an elegant way from the frequency of dipolar oscillations in the magnetization build up during cross polarization. For a spin pair the magnetization shows oscillations of a frequency determined by the dipolar coupling strength and thus the internuclear distances. Under application of Lee- Goldburg crosspolarization the homonuclear coupling is suppressed and the time evolution of the signal governed by the heteronuclear coupling, exhibiting the dipolar oscillations like in spin pairs. For a spin pair, the coupling can be determined from a Fourier transform of the oscillation. For more complex spin systems a comparison with simulations based on SIMPSON, taking the spin multiplicity, and relative orientations of dipolar and CSA tensors into account, is required. In partially fluorinated organic compounds and polymers a complex picture is obtained from a combination of  $^1H$ - $^{19}F$ ,  $^1H$ - $^{13}C$  and  $^{19}F$ - $^{13}C$  internuclear distances which are compared with molecular simulations based on COSY. Applications involve a benzoic acid derivative and semi- fluorinated polymers like PVDF.

#### **NMR Symposia Poster Session**

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- 263. Biomedical Technology Resource for Solid-State NMR of Proteins.** C. H. Wu, C. V. Grant, S. J. Opella, Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093 USA

The on-going development of instrumentation and methods at the Resource for Solid-State NMR of Proteins at the University of California, San Diego will be described. The Resource is dedicated to the advancement of solid-state NMR spectroscopy for the study of proteins that defy analysis by the traditional techniques of structural biology, solution NMR spectroscopy and X-ray crystallography. The development of instrumentation is focused on the implementation of high magnetic fields, low temperature operation, and on the development of double and triple resonance probes capable of handling the high power irradiations used for solid-state NMR experiments. The Resource has magnets with standard (52 mm), mid (64 mm), and wide (89 mm) bore and probes have been constructed for application of these bore sizes over the frequency range of 400 MHz to 900 MHz. In addition to established static and MAS NMR techniques, much of the focus is on the development of pulse sequences derived from the PISEMA experiment optimized for flat coil probes operating at high frequencies, appropriate for aligned samples of membrane proteins in lipid bilayers. The application of this technology to selected examples of membrane proteins will be presented. The Biomedical Technology Resource for Solid-state NMR of Proteins is supported by grant P41RR09789 from the National Center for Research Resources, National Institutes of Health.

#### **NMR Symposia Poster Session**

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- 264.  $^{129}\text{Xe}$  Lineshapes in a Molecular Solid.** Cynthia J. Jameson and Devin N. Sears, University of Illinois at Chicago, Department of Chemistry M/C-111, Chicago, Illinois 60607-7061

The NMR lineshapes of Xe in the inclusion compound of tris(o-phenylenedioxy)cyclotriphosphazene (TPP) have recently been measured over a range of loadings [P. Sozzani, A. Comotti, R. Simonutti, T. Meersmann, J.W. Logan, and A. Pines, *Angew. Chem. Int. Ed.*, 39, 2695-2698 (2000)]. Anisotropic lineshapes observed for Xe atoms in nanochannels, such as those in TPP, originate from the distribution of the orientations of the nanochannels in the sample, coupled with the anisotropy of the average shielding tensor of the Xe within the channels. We construct a model fragment for the TPP channels from three benzo[1,3,2]dioxaphosphole molecules following the crystallographic positions. This fragment closely mimics the electron density of the TPP channel. The Xe shielding tensors are calculated within the channel fragment using ab initio and density functional methods. The resulting tensor, expressed as a function of Xe position, are used in a Monte Carlo grand canonical ensemble average to generate the lineshapes.

#### **NMR Symposia Poster Session**

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- 266. Determination of the  $^{13}\text{C}$  Chemical Shift Anisotropy of Silk, Cellulose and Bradykinin.** Raiker Witter, Stephanie Hesse, Ulrich Sternberg, PAF / IOQ / HF, F.-S.-Universität Jena, Max Wien Platz 1, 07743 Jena, Germany

With a new powder pattern recoupling experiment the chemical shift anisotropies of silk/1/, cellulose/2/ and bradykinin are obtained. Structural discussions will be given.

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#### **NMR Symposia Poster Session**

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## Separations • Wednesday Oral & Poster Sessions

- 267. Enantioselectivity of Teicoplanin Aglycon with Modified Amine Group.** Max Q. Zhong, Iowa State University, Department of Chemistry, Gilman Hall, Ames, IA 50011

The amine group on the aglycon basket of teicoplanin is believed to be one of the most important sites for interaction between the chiral selective teicoplanin and the analytes with negative charges. It is a logical step to convert this positively-charged amine group to some negatively-charged group so that novel chiral recognition ability of teicoplanin aglycon upon positively-charged analytes is expected. One way to modify this amine group is a diazotization reaction and substitution by a neutral hydroxyl group. In present study, this amine group endures a sulfonation reaction and becomes a negatively-charged sodium sulfonate group. The enantioselectivity of this modified teicoplanin is being studied.

### Separations Symposia Poster Session

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- 268. High Efficiency CE Identification and Characterization of Microorganisms: Mechanism and Use.** D.W. Armstrong, Department of Chemistry, Iowa State University, Gilman Hall, Ames, Iowa 50011-3111

It has been recognized for decades that charged colloids and particulate matter will transport in direct current electric fields. However, routine, high efficiency separation and analysis of colloidal or larger particles by electrophoresis has not been as successful as it has for small molecules and macromolecules. Selective, high efficiency separations of intact microbes (e.g., bacteria, viruses, etc.) may, in some cases, allow them to be identified and quantified in much the same way that molecules are done today. Two different capillary electrokinetic approaches can be utilized. The first approach used a dissolved polymer based CE separation that may be affected by the size and shape considerations. Another approach uses capillary isoelectric focusing (CIEF). Remarkably high peak efficiencies ( $10^6$  -  $10^9$  theoretical plates per meter) in capillary electrophoresis (CE) can be achieved in the separation of microorganisms. No deliberate stacking is used in these applications. Seemingly, the investigated living organisms behave differently than molecules under an applied electric field. For molecules, these extremely high efficiencies are very unusual, and have not been reported thus far. Using a 488nm argon-ion laser coupled to a charge-coupled device camera (CCD), it was possible to monitor the migration behavior of stained microorganisms of a length of a 10cm capillary. In some cases, 60 - 70% of the monitored detection window could be filled with analyte without significant loss in peak efficiency. The effect of pH, polymer concentration, buffer concentration, etc. on the ultra-high efficiency and reproducibility of the separation was investigated.

### Separations Symposia Oral Session

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- 269. Capillary Electrophoretic Separation of Isolated Organelles.** Edgar A. Arriaga, Department of Chemistry, University of Minnesota, Minneapolis, MN, U.S.A., 55455

Much of our present knowledge about the role of organelles in metabolism, abnormal and normal cell function, and molecular processes such as apoptosis, has been acquired using isolated organelles. These studies reveal an average response that does not take into account the heterogeneous nature of organelles. It is envisioned that by further separating organelles into "sub-populations," we may be able to refine the existing description of their biological role and function. In this presentation, we describe the use of capillary electrophoresis with laser-induced fluorescence detection (CE-LIF) to perform individual measurements on isolated mitochondria, nuclei, and lysosomes. These measurements describe their heterogeneity in terms of fluorescence and electrophoretic related properties. Using 10-nonyl acridine orange to selectively label cardiolipin in mitochondria isolated from NS-1 cells, we monitor the amount of this phospholipid per organelle. In addition, we describe the heterogeneous nature of the electrophoretic mobility of individual mitochondria under varying conditions of pH, ionic strength, and osmolarity. We further use CE-LIF to compare the electrophoretic mobility distributions of organelles isolated from several rat tissues, including soleus muscle, brain, and liver.

### Separations Symposia Oral Session

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- 270. Two Decades of Chiral Analysis: What Challenges Lie Ahead.** Timothy J. Ward, Millsaps College, Department of Chemistry, Jackson, MS 39210

The field of chiral analysis has enjoyed phenomenal success while undergoing many changes over the past decade. From the beginning of the early 1980s, the field of chiral separations has emerged from being an academic curiosity to being the primary influence in the U.S. Food and Drug Administration (FDA) issuing guidelines for the development of stereoisomeric drugs in the early 1990s. The availability of such a large collection of powerful separation techniques has resulted in greater scrutiny of the stereochemical properties of compounds in foods, agrochemicals, and fragrances to name a few. While there have always been several chiral phases or columns that have dominated the field at any given time, these preferred phases have evolved substantially over time. In addition new and more effective chiral phases, such as the macrocyclic antibiotics, have had an immediate and substantial impact on the field of separations. Probably the greatest evolution in separations from the 1980s to the 1990s has been the explosion in the number of chiral applications which now utilize capillary electrophoresis. This lecture will examine the evolution in the field of separations from the 1980s to the 1990s with respect to individual classes of chiral selectors as well as the development of new separation techniques.

**Separations Symposia Oral Session**

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- 271. Advances in Chiral Resolution of Amino Acids by LC and LC/MS.** Thomas E. Beesley, Advanced Separation Technologies Inc., 37 Leslie Court, P.O. Box 297, Whippany, NJ 07981

Proteomics and the analysis of amino acids for human health coupled with the utility of amino acids in biotechnology and other pharmaceuticals has made the chiral analysis of amino acids imperative. There is a long history in chiral separation of amino acids from the development of the first LC methods for separating various alpha, primary amines by the chiral crown ether design of Cram, to the work of Davankov and ligand exchange chromatography. The application of macrocyclic glycopeptides since 1995 however, has opened the doors to an array of applications for all forms of amino acids including primary, secondary as well as beta and gamma amino acids. This technique has also allowed for the resolution of a wide variety of N-blocked amino acids. This presentation will cover the history of chiral stationary phase development in this area and focus primarily on developments with macrocyclic glycopeptides. Very large increases in selectivity have been obtained with the aglycone forms of at least one macrocyclic in particular, teicoplanin. Comparison of amino acid separations on different versions of these various CSP's will be presented and the utility of some for preparative application will be outlined. The use of these novel stationary phases has not only expanded the applications possible in this area but has tied the technology to a wide variety of methodologies like SFC and LC/MS.

**Separations Symposia Oral Session**

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- 272. Chromatographic Immunoassays and Ultrafast Affinity Extraction: a New Group of Techniques for the Selective Analysis of Biological and Environmental Samples.** D.S. Hage, University of Nebraska, Department of Chemistry, Lincoln, NE 68588-0304

The combined use of immunoassays and HPLC systems has given rise to a new group of analytical methods known as chromatographic immunoassays. These methods combine the selectivity and low detection limits of immunoanalytical methods with the precision, speed and ease-of-use of HPLC. A key advantage of these methods is their ability to look at specific analytes in complex samples with little or no sample preparation and with results often being generated in only a few minutes. These methods can be combined with a variety of detection methods and can be employed in a number of different formats, including competitive binding assays, immunometric assays and multidimensional separation systems. Some recent work has explored the ability of chromatographic immunoassays to operate under extremely short time conditions while also allowing the detection of trace compounds in biological or environmental samples. Various examples of such work will be presented. One application concerns the use of HPLC-based immunoextraction for the capture and analysis of herbicides and their metabolites in water samples. This involves the use of a multidimensional affinity/reversed-phase system for the selective extraction and isolation of multiple agents within the same class of compounds. A second application that will be discussed is the use of affinity microcolumns for the extraction of drug and hormone samples in the millisecond-time domain. When combined with an immunometric assay and fluorescence or chemiluminescence detection, the result is a method that can quickly determine the free concentration of a drug or hormone in serum or plasma samples. The analytical performance of these techniques will be described, as well as their potential advantages in the analysis of clinical, pharmaceutical and environmental samples.

**Separations Symposia Oral Session**

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- 273. Capillary Electrophoresis and Single-Cell Gene Expression.** Sheri J. Lillard, University of California, Riverside, Department of Chemistry, Riverside, CA 92521; Jennifer L. Zabzdyr, University of California, Riverside, Department of Chemistry, Riverside, CA 92521; Sandra Villa, University of California, Riverside, Department of Chemistry, Riverside, CA 92521; Amisha Shah, University of California, Riverside, Department of Chemistry, Riverside, CA 92521.

Capillary electrophoresis (CE) is highly suited for profiling the chemistry of individual cells. Advantages include manipulation of ultra-low sample volumes (e.g., 1 cell ~ pL), efficient separation of important biomolecules, and sensitive detection of finite levels of material. Our method utilizes reverse-transcriptase polymerase chain reaction (RT-PCR) to monitor the expression of  $\beta$ -actin and other genes in individual mammalian cells. Virtually no sample preparation is required other than simple cell lysis and thermal cycling of the reaction mixture. CE analysis of the DNA products is performed using an entangled polymer solution (HPMC and PVP) and ethidium bromide fluorescence, yielding excellent separation efficiency and detection sensitivity. Different instrumentation strategies will be presented, which compare improvements in S/N and quantitative capabilities. These improvements make it possible to detect low-abundance genes at the single-cell level, and to apply these results to relevant biological situations.

#### **Separations Symposia Oral Session**

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- 274. High-Throughput Screening Based on Multiplexed CE and Absorption Detection.** Edward S. Yeung, Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, IA 50011

Capillary electrophoresis (CE) is now a mature technique for analytical separations. In its various modes, impressive performance has been demonstrated for ionic as well as for neutral compounds. The Human Genome Project provided the impetus for developing multiple capillary systems. However, capillary arrays are not just for DNA analysis. Every CE protocol can be similarly multiplexed to achieve higher throughput and reduced reagent consumption without sacrificing its good resolving power and full automation. To extend the applicability to non-fluorescing compounds, we constructed a simultaneous multiplexed absorption detector for 96 capillaries. Entire sample trays in the 96-well microtiter plate format can be analyzed in one operation. This high-throughput capability gives CE a unique advantage over column liquid chromatography in most applications. Examples from DNA analysis, enzyme assay, peptide mapping and combinatorial synthesis will be presented.

#### **Separations Symposia Oral Session**

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- 275. Uses of Ionic Liquids in Analytical Chemistry.** Alain Berthod, Laboratoire des Sciences Analytiques, CPE, Bat. 308-D, Universite de Lyon 1, 3, rue Victor Grignard, 69622 Villeurbanne cedex

Ionic liquids are salts with low melting points. When the melting point is below room temperature, the salts are called room temperature ionic liquids (RTILs). The first RTIL was ethyl ammonium nitrate with a melting point of 12°C; it was developed as early as 1914 [1]. In the eighties, the research group of Seddon started to use RTILs as nonaqueous polar solvents for electrochemical and spectroscopic studies of transition metal complexes [2-4]. Typically, RTIL consists of nitrogen or phosphorous containing organic cations and large organic or inorganic anions [1]. They stay liquid over 200 to 300°C temperature variation with practically no vapor pressure [5]. RTILs are extensively investigated as alternative "green" solvents [4]. They can replace volatile organic solvents in several chemical reactions [1, 6]. They have a wide window of electrochemical stability, good electrical conductivity, high ionic mobility and excellent chemical and thermal stabilities [6].

Increasingly, uses for RTILs are being found in chemical analysis. They were used in GC as stationary phase. Their solvent properties are not fully known. They are polar solvents whose miscibility with water is highly dependent on their structure. The physico-chemical properties of different ionic liquids are described. The effect of the nature of the cation and the anion on the melting point and other properties is given. The partition coefficients of a large selection of solutes were measured between 1-butyl-3-methyl imidazolium hexafluorophosphate (BMIM-PF<sub>6</sub>) and water and between BMIM-PF<sub>6</sub> and heptane. The results allowed to compare the BMIM-PF<sub>6</sub> solvent properties with the corresponding properties of water, octanol and heptane.

The very low vapor pressure of RTILs makes them possible candidates for matrixes in MALDI experiments. The MALDI matrix should absorb the light energy, transfer it to the analyte and ionize (adding a proton) the analyses. [ref.] The capabilities of several ionic liquids as MALDI matrixes were tested with proteins and small oligonucleotides.

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#### **Separations Symposia Oral Session**

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## Separations • Thursday Oral & Poster Sessions

- 276. Enantioselectivity of Teicoplanin Aglycon with Modified Amine Group.** Max Q. Zhong, Iowa State University, Department of Chemistry, Gilman Hall, Ames, IA 50011

The amine group on the aglycon basket of teicoplanin is believed to be one of the most important sites for interaction between the chiral selective teicoplanin and the analytes with negative charges. It is a logical step to convert this positively-charged amine group to some negatively-charged group so that novel chiral recognition ability of teicoplanin aglycon upon positively-charged analytes is expected. One way to modify this amine group is a diazotization reaction and substitution by a neutral hydroxyl group. In present study, this amine group endures a sulfonation reaction and becomes a negatively-charged sodium sulfonate group. The enantioselectivity of this modified teicoplanin is being studied.

### Separations Symposia Poster Session

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- 277. Use of Native and Derivatized Cyclodextrin Chiral Stationary Phases for the Enantioseparation of Sulfoxides and Substituted Furocoumarins by High Performance Liquid Chromatography.** Clifford R. Mitchell, Iowa State University Department of Chemistry, Gilman Hall, Ames, IA 50011; Douglas D. Schumacher, Iowa State University Department of Chemistry, Gilman Hall, Ames, IA 50011;

The enantioselectivity of native and derivatized cyclodextrin stationary phases for chiral sulfoxides and substituted chiral furocoumarins was evaluated using high performance liquid chromatography (HPLC). Many enantiomers could be baseline resolved using derivatized cyclodextrin stationary phases in the reverse phase mode. The most important factors influencing enantioselectivity are steric effects and the ability of the analyte to hydrogen bond. The dimethyl- $\beta$ -cyclodextrin and acetyl- $\beta$ -cyclodextrin exhibit the broadest enantioselectivity for the chiral sulfoxides while the hydroxypropyl- $\beta$ -cyclodextrin exhibits the broadest enantioselectivity for the substituted furocoumarins. Native cyclodextrins demonstrated far less utility in separating this class of compounds.

### Separations Symposia Oral Session

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- 278. Super/Subcritical Fluid Chromatography Chiral Separations with Macrocyclic Glycopeptide Stationary Phases.** Ying Liu, Iowa State University, Department of Chemistry, Gilman Hall, Ames, IA 50011, USA

The chiral recognition capabilities of three macrocyclic glycopeptide chiral selectors, namely teicoplanin (Chirobiotic T), its aglycone (Chirobiotic TAG) and ristocetin (Chirobiotic R), were evaluated with supercritical and subcritical fluid mobile phases. A set of 111 chiral compounds including heterocycles, analgesics (nonsteroidal anti-inflammatory compounds),  $\beta$ -blockers, sulfoxides, *N*-blocked amino-acids and native amino-acids was separated on the three chiral stationary phases (CSP). All separations were done with an outlet pressure regulated at 100 bar, 31°C and at 4.0 mL/min. Various amounts of methanol ranging from 7 to 67% v/v were added to the carbon dioxide along with small amounts (0.1 to 0.5 % v/v) of triethylamine and/or trifluoroacetic acid. The Chirobiotic TAG CSP was the most effective closely followed by the Chirobiotic T column. Both columns were able to separate, partially or fully, 92% of the enantiomers of the compound set. The ristocetin chiral selector could partially or baseline resolve only 60% of the enantiomers tested. All separations were done in less than 15 min and 70% were done in less than 4 min. The speed of the separations is the main advantage of the use of SFC compared to normal phase HPLC. Also, the smaller volume of waste mobile phase produced is advantageous for preparative separations and solvent disposal. Currently it appears that this is the only SFC-based method that can be used to separate enantiomers of underivatized amino acids.

### Separations Symposia Oral Session

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- 279. Separation of Chiral Sulfoxides and Biologically Active Coumarine Derivatives by Liquid Chromatography Using Macrocyclic Glycopeptide Chiral Stationary Phases.** Tom Ling Xiao, Department of Chemistry, Iowa State University, Gilman Hall, Ames, IA 50011, USA

A set of over 60 chiral sulfoxides and coumarine derivatives compounds were separated using five different macrocyclic glycopeptide chiral stationary phases (CSPs), namely ristocetin A, teicoplanin, teicoplanin aglycone (TAG), vancomycin and vancomycin aglycone (VAG) in normal phase mode, reversed phase mode, and polar organic modes. Altogether the macrocyclic glycopeptide CSPs were able to separate the two classes of over 50 sulfoxide enantiomers, tosylated derivatives and coumarine derivatives. The macrocyclic glycopeptides once again proved to be exceptionally selective for both classes of compounds. Indeed, when coupled with circular dichroism, and exciton coupling CD together with coupled oscillators

calculation, the absolute configuration of the chiral sulfoxides and coumarine derivatives was determined. The teicoplanin and TAG CSPs were the most effective CSPs able to resolve most number of racemates among these two series chiral compounds. The normal-phase mode was the most effective followed by the reversed-phase mode with methanol–water mobile phases for both of the different series analyses. Few of these compounds could be separated in the polar organic mode with 100% methanol mobile phases. Acetonitrile was also not a good solvent for the resolution of enantiomers of both classes of chiral compounds, neither in the reversed-phase nor in the polar organic mode. The structure of the chiral molecules was compared to the enantioselectivity factors obtained with the teicoplanin and TAG CSP. It is shown that the polarity, volume and shape of the sulfoxide and neutral coumarine substituents influence the solute enantioselectivity factor significantly. Changing the oxidation state of the sulfur atom from sulfoxides to sulfinate esters is detrimental to the compound's enantioselectivity. The enantiomeric retention order on the teicoplanin and TAG CSPs was very consistent: the (*S*)-(1)-sulfoxide and coumarine enantiomer was always the less retained enantiomer. In contrast, the (*R*)-(2)-enantiomer was less retained by the ristocetin A, vancomycin and vancomycin aglycone columns, showing the complementarity of these CSPs. The macrocyclic glycopeptide CSPs provided broad selectivity and effective separations of chiral sulfoxides and neutral coumarine derivatives.

#### **Separations Symposia Oral Session**

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#### **280. Development of Chiral LC-MS Methods Using Mass Spectrometry Compatible Mobile Phases.** Meera J. Desai, Department of Chemistry, Iowa State University, Gilman Hall, Ames, IA 50011

High performance liquid chromatography coupled to atmospheric pressure ionization mass spectrometry (API-MS) is becoming a popular method for analysis of pharmaceuticals primarily due to sensitivity, speed, and specificity. Chirality has long been an important criterion for drug discovery and analysis. Most LC methods developed for separation of enantiomers utilize mobile phases that are incompatible with MS. Frequently, changing the mobile phase slightly can cause significant reduction or loss of enantioselectivity. Therefore, the development of chiral LC-MS methods using mass spectrometry compatible mobile phases is desirable. Macrocyclic antibiotics have proven to be viable, multi-modal chiral selectors for HPLC. Using these chiral stationary phases, a variety of compounds of pharmaceutical interest were analyzed using LC-API-MS in polar organic and reverse phase modes. Baseline resolution of enantiomers was achieved with relatively short retention times and high efficiencies. Mobile phase systems applied in this method include 100% methanol with additives such as ammonium trifluoroacetate, ammonium formate, and ammonium acetate. In addition, methanol with aqueous solutions containing additives such as those previously mentioned was also employed. The sensitivity and robustness of LC-MS make it an important tool in determination and characterization of enantiomers.

#### **Separations Symposia Oral Session**

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#### **281. Biointeraction Analysis by Affinity Chromatography: Kinetic and Optimization Studies of Antibody Columns.**

Mary Anne Nelson, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0304; Matthew Egger, Iowa State University, Ames, Iowa, 50011; David S.Hage, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0304

Biointeraction analysis is a growing area in analytical chemistry, including areas such as clinical analysis, drug discovery and environmental analysis. The advent of techniques including BIAcore and IAS has piqued interest in applications of antibody-antigen interactions to immunoanalysis and immunoaffinity chromatography. The interaction of antibody-antigen is governed by second order association and first order dissociation kinetics. To understand these interactions, kinetic studies using immunoaffinity chromatography were performed. Adsorption kinetics were studied under adsorption-limited conditions as determined by frontal analysis, with values in the range of  $1.8 - 8.4 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  for the binding of 2,4-dichlorophenoxyacetic acid to monoclonal antibodies (E2/G2 clone line). Dissociation rate constants were studied under low pH conditions with rate constants of  $180 - 840 \text{ sec}^{-1}$  for the binding of 2,4-dichlorophenoxyacetic acid and analogs 2,4-dichlorophenoxyacetic methyl ester and 2,4,5-trichlorophenoxyacetic acid. Another aspect of biointeraction analysis includes the cross-reactivity of the antibody with compounds that share structural similarity with the antigen. Studies comparing the cross-reactivity of the antibodies with the association and dissociation constants were performed showing the dependence of the cross-reactivity on the dissociation rate constant. These rate constants and cross-reactivity parameters are used to optimize a portable high-performance immunoaffinity chromatographic (HPIAC) system with on-site capabilities for monitoring point and non-point source pollution in ground and surface waters.

#### **Separations Symposia Oral Session**

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- 282. The Analysis of Microbes Using Capillary Electrophoresis.** M.A. Rodriguez, Iowa State University, Department of Chemistry, Gilman Hall, Ames, IA 50011

Capillary Electrophoresis (CE) has become an exceptional analytical tool for a variety of purposes, including the separation and analysis of biomolecules, pharmaceuticals, and chiral molecules. The aqueous nature of CE is a feature that adds to its attractiveness for use in studying biological materials, in fact, the run buffers used can be made to very closely resemble the environment in the human body (Salt concentration, pH). The study of intact bacterial cells by CE has been shown to be feasible because of this. However, much is still unknown about the behavior of bacteria when subjected to CE conditions and exactly how much valuable information can be obtained from such analysis. The experiments presented here aim to reveal as much as possible about the behavior of the bacteria under these conditions, to find out what conditions are the most favorable for such analysis, and to show that not only has valuable information already been obtained, such as evaluating how microbes interact with molecules, but that much more information may still be ahead, such as utilizing this technique to perhaps identify and separate viable bacteria. This area is very exciting and holds much promise to become a vital tool in the analysis of bacteria and other microbes.

**Separations Symposia Oral Session**

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- 283. Applications of Ionic Liquids in Gas Chromatographic Separations.** Jared L. Anderson and Jie Ding, Iowa State University, Department of Chemistry, Gilman Hall, Ames, IA 50011; Jie Ding, Iowa State University, Department of Chemistry, Gilman Hall, Ames, IA 50011

Room temperature ionic liquids (RTILs) have recently received a lot of attention due to their use as novel solvent systems for organic synthesis. They possess good thermal stability with no effective vapor pressure making them ideal “green” solvents. We have applied ionic liquids to studies in mass spectrometry, liquid-liquid extraction, and gas chromatography. The application of ionic liquids in gas chromatography has yielded unique stationary phases and provided the ability to characterize the ionic liquid based on its interaction with varying classes of molecules in the gas phase. This presentation will discuss the gas chromatographic use of RTILs and illustrate their unique separation capabilities.

**Separations Symposia Oral Session**

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- 284. Coupling Size Exclusion Chromatography with Double Focusing ICP-MS to Monitor Microbial Uptake and Removal of Uranium from Aqueous Solutions.** Bo Zhang, Iowa State University, Department of Chemistry, Gilman Hall, Ames, IA 50011

Waste uranium solutions generated from uranium mining and processing has long been an environmental threat. Microbial removal of soluble uranium and other heavy metals is a possible remediation approach. Many bacteria strains were suggested for this task, but it is always difficult to find an easy and effective way to monitor the removal process without digesting microbes, which is tedious and error-prone. In this presentation, we report a special size exclusion chromatography (SEC) column directly connected to a double focusing, inductively coupled plasma mass spectrometer (DF-ICP-MS) to evaluate uranium in bacteria. The homemade column separated microbes both from large molecules and small molecules. The column effluent containing successively the microbes, larger molecules and small molecules plus ions were directly fed into an ICP-MS through a nebulizer. It is shown that whole cells can be atomized directly and uranium, magnesium and calcium can be monitored simultaneously. *Bacillus Subtilis* and *Shewanella Putrefaciens* were examined in this work. Uranium spiked fermentation processes for both strains were compared to their blank controls. It is clearly shown that both strains were able to uptake uranium from their environments. However, the growth / maturation rates of the bacteria were affected by the uranium in solution. The overall uptake of uranium is much more substantive than surface adsorption of uranium from solution (which occurs in a matter of minutes). When the cells die, a significant proportion of the uranium is released back into solution.

**Separations Symposia Oral Session**

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- 285. Enantiomeric Separation of Coumarine Derivatives by CE.** Matthew Egger, Iowa State University, Department of Chemistry, Gilman Hall, Ames, IA 50011

Coumarine and coumarine derivatives have been isolated as natural products and shown to have a wide array of pharmaceutical properties including activity against Alzheimer's disease, breast cancer, and arthritis. The current methods for the synthesis of coumarines typically produce a racemate; however methods of asymmetric synthesis are currently under development. In order to speed up the synthetic process, quick methods for the recognition of the stereoisomers of natural products as well as the identification of their synthetic counterparts are needed. To date, no enantioseparation has been reported on this potentially important class of compounds. Capillary electrophoresis (CE) is a powerful separation tool that requires only minute amounts of sample for fast analysis. Since coumarine derivatives are neutral compounds, they need to be associated with a charged chiral selector in order to observe a possible separation of their enantiomers. Cyclodextrins are the most

useful chiral selectors in CE. They were associated with micelles of anionic surfactant in order to enantioseparate the coumarine isomers. The optimum selectivity was observed when using substituted cyclodextrins and macrocyclic glycopeptides as the chiral selector.

#### **Separations Symposia Oral Session**

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#### **286. Separation of R-Phycoerythrin Digests and Subunits Using Capillary Zone Electrophoresis and High Performance Liquid Chromatography.** Dragan Isailovic, Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, IA 50011, USA

Investigation and usage of different fluorescent proteins have revolutionized research in biochemistry. R-phycoerythrin (R-PE) is a highly fluorescent ~240kDa protein that was used widely as an excellent fluorescent probe. Novel fluorescent probes with spectroscopic and chemical characteristics similar or improved comparing to R-PE could enhance research capabilities of bioanalytical methods. In order to determine the spectroscopic properties of its fragments, R-PE was digested by pepsin and trypsin. The polypeptides obtained were separated using capillary zone electrophoresis (CZE) with ultraviolet-visible (UV/VIS) absorption and laser-induced fluorescence detection (LIF). Also, they were separated and detected by high performance liquid chromatography (HPLC) with UV/VIS and spectrofluorometric detection. Using urea and trifluoroacetic acid (TFA) as on-column denaturing reagents,  $\alpha$ ,  $\beta$ , and  $\gamma$  subunits of RPE were separated by CZE, and separated and collected by HPLC. Determined spectroscopic properties of both polypeptide fragments and subunits are characteristic for presence of phycoerythrobilin (PEB) and phycourobilin (PUB) chromophores in them. Molecular weights of digest peptides and subunits, as well as the amino acid sequences of the most fluorescent peptides were determined using HPLC combined with electrospray ionization mass spectrometry (ESI-MS). Since R-PE digests and subunits were efficiently excited with the argon-ion laser and show high fluorescence, good photochemical stability and biocompatibility, they have good potential for use as fluorescent probes.

#### **Separations Symposia Oral Session**

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#### **287. Thermodynamic Insights Into Retention Processes at Carbon-Based Stationary Phases.** Lisa M. Ponton, Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Carbon-based materials are used extensively as substrates in electroanalytical chemistry and as stationary phases in liquid chromatography. In spite of widespread use, fundamental details related to adsorption on these materials remain poorly understood. Electrochemical descriptions of adsorption focus primarily on the role of edge plane sites (i.e., multiple adsorption sites), whereas chromatographic descriptions view interactions with the basal plane (i.e., a single adsorption site) to be the basis of adsorption. This presentation examines issues related to adsorption on carbon materials within the context of retention data obtained using electrochemically-modulated liquid chromatography (EMLC). EMLC is a separation strategy that couples electrochemistry and liquid chromatography, exploiting the ability to manipulate analyte retention through changes in the potential applied to conductive stationary phases like glassy carbon and porous graphitic carbon. To examine the merits of the two descriptions of adsorption, we examined the retention dependence of a series of model compounds (i.e., monosubstituted benzene sulfonates) as a function of the column temperature and applied potential. The results of these experiments will be examined by the van't Hoff analysis to delineate the enthalpic and entropic contributions to the overall retention mechanism.

#### **Separations Symposia Oral Session**

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#### **288. Thermal Field-Flow Fractionation for Particle Surface Composition Analysis.** Paul M. Shiundu, University of Nairobi, Department of Chemistry, P.O. Box 30197 Nairobi, Kenya; Kim R. Williams, Colorado School of Mines, Department of Chemistry and Geochemistry, Golden, CO 80401

Field-flow fractionation (FFF) is a family of analytical-scale separation techniques applicable to the separation and characterization of macromolecules, colloids, and particles.<sup>1</sup> Sample components are retained in FFF as a result of their interaction with an externally applied field, which differentially forces components into flow streamlines of decreasing velocity toward one wall. In the FFF technique known as thermal FFF (ThFFF), the external field is a temperature gradient, which interacts with sample components forcing the material to the cold wall by the process of thermal diffusion. For nearly four decades since its inception, ThFFF has been applied almost exclusively to synthetic polymer analysis. Recently, however, ThFFF has been used for the fractionation and analysis of particulate matter.<sup>2-4</sup> The retention and separation of particles in ThFFF are affected by several factors such as particle size, chemical composition of particle and suspending medium and electrolyte concentration; many of which present unique opportunities for the technique for particle characterization. Of particular interest is the strong dependence of retention of colloidal particles on the chemical composition of the particles or the particle surfaces. These results are observed among similar or between dissimilar particles suspended in either aqueous or nonaqueous carrier liquids. In this presentation, we report and

discuss the potential for performing both bulk and surface compositional analysis of particles using ThFFF. Possibilities of this technique complementing both sedimentation and flow FFF techniques for analysis of complex particulate materials will be highlighted.

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#### Separations Symposia Oral Session

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## Spectroscopy & Microscopy • Tuesday Oral Sessions

- 289. Dynamic Two-Beam Fluorescence Cross-Correlation Spectroscopy: New Methods for Studying Intra- and Intermolecular Dynamics in Biomolecular Systems.** Alan Van Orden, Lori L. Carillo, Keir Fogarty, Department of Chemistry, Colorado State University, Fort Collins, CO 80523 USA.

Two-beam fluorescence cross-correlation spectroscopy (FCCS) is a far-field single molecule optical microscopy technique for measuring the transit times of individual molecules as they flow in a uniform fashion between two spatially separate laser beam foci positioned along the axis of flow.<sup>1,2</sup> This method has been used to characterize the flow parameters of individual molecules in a microfluidics device<sup>1</sup> and to resolve the bound and unbound fractions of a DNA-protein complex continuously flowing through a capillary electrophoresis column, based on their characteristic electrophoretic flow velocities.<sup>2</sup> We describe a two-beam FCCS-based technique that can measure the rate parameters for individual molecules undergoing conformational fluctuations on a time scale similar to the transit time between the two laser beam foci. These fluctuations are monitored by introducing pairs of fluorescent dye molecules that interact via fluorescence resonance energy transfer, such that alterations in the molecular conformation will vary the energy transfer efficiency. By altering the flow velocity and/or the distance between the laser beam foci, it is possible to access a broad range of time scales corresponding to the kinetics characteristic of various biomolecular systems. The application of this method to the solution-phase conformational dynamics of individual DNA hairpin molecules will be discussed.

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#### Spectroscopy and Microscopy Symposia Oral Session

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- 290. Spectroscopy and Applications of Two-Photon Activated Photoacid Generators.** Kevin L. Braun, Stephen M. Kuebler, Wenhui Zhou, J. Kevin Cammack, Seth R. Marder, and Joseph W. Perry, Department of Chemistry, The University of Arizona, Tucson, AZ 85721; Tianyue Yu, Christopher K. Ober, Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853.

New two-photon-activatable photoacid generators based on *bis*[(diarylamino)styryl]benzene and *bis*[(diarylamino)stilbene] cores with covalently attached sulfonium groups have been synthesized. The electronic absorption and emission characteristics and photoactivated acid generation properties were studied under one and two-photon excitation<sup>1,2</sup>. These molecules have both a large two-photon cross section ( $690 \times 10^{-50} \text{ cm}^4 \text{ sec photon}^{-1}$ ) and a high quantum yield for the photochemical generation of acid ( $\Phi_{\text{H}^+} \sim 0.5$ ) depending on the location of the sulfonium group. These efficient two-photon photoacid generators permit two-photon microfabrication<sup>3,4</sup> to be extended to acid-activated chemical systems, such as polymerizable epoxides and chemically amplified resist materials. Applications of this technology include the development of microfluidic devices, which has been demonstrated through the fabrication of a three-dimensional microchannel structure in a positive-tone chemically amplified resist. Under near infrared excitation, the threshold for initiating the polymerization of epoxides with such compounds has been shown to be between one and two orders of magnitude lower than with conventional UV-active photoacid generators.

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- 291. Application of Fluorescence Analysis in the Formulation Development and Performance Reliability of Photovoltaic Module Encapsulants.** F.J. Pern, National Center for Photovoltaics (NCPV), National Renewable Energy Laboratory (NREL), 1617 Cole Blvd., Golden, CO 80401

This paper will review fluorescence analysis applied in our work that has extended over a period of nearly 10 years. In the fabrication of solar photovoltaic modules, ethylene-vinyl acetate (EVA) copolymers have been widely used as the lamination encapsulants. Other than providing the needed mechanical support, optical coupling, and electrical insulation for the solar cell strings, long-term weathering performance reliability of the encapsulant is critically required. Previous commercial EVA formulations (fast-cure 15295 and slow-cure A9918) have shown to discolor if no UV-filtering glass superstrates were used to protect them. The EVA yellow-browning is attributed partly to the photodecomposition by-products of the UV absorber (UVA), Cyasorb UV 531<sup>®</sup>, and partly to the lengthening conjugation mixtures transformed from the initial short  $\alpha,\beta$ -unsaturated carbonyl groups that were generated at the curing stage at  $\sim 150^{\circ}\text{C}$  (for cross-linking) in a vacuum laminator. These UV-excitable carbonyl chromophores are responsible for the UV-induced degradation and discoloration of the EVA in the absence of UVA. In the development of NREL-EVA formulations, while removing UV absorber from the formulations, fluorescence analysis was employed to examine with high sensitivity the curing-generated chromophore concentration as the formulations were varied with different UV light stabilizers and antioxidants. The results show that some antioxidants are better than others in reducing the formation and concentration of chromophores by curing. Fluorescence analysis was also more powerful than UV-vis spectroscopy in detecting and monitoring the evolution and growth of discoloring chromophores. Superior photothermal stability under accelerated exposures ( $\sim 7$  UV suns) has been achieved for the NREL-developed and patented EVA formulations, which always exhibit low initial chromophore concentrations upon curing. (*This work was conducted at NCPV, NREL under U.S. Department of Energy Contract No. DE-AC36-99-G010337.*)

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- 292. Application of Spectroscopic and Thermal Analyses in the Formulation and Processing Developments of New Photovoltaic Module Encapsulants.** F.J. Pern and Z. Mei,\* National Center for Photovoltaics (NCPV), National Renewable Energy Laboratory (NREL), 1617 Cole Blvd., Golden, CO 80401

As described in another paper, superior photothermal stability has been achieved for NREL-developed and patented EVA (ethylene-vinyl acetate) copolymer encapsulant formulations. However, the NREL and commercial EVA formulations are designed primarily for vacuum lamination processing at  $\sim 150^{\circ}\text{C}$  for photovoltaic module encapsulation. It is very desirable to have encapsulant materials and/or formulations that can be fast-processed in the ambient at lower temperatures. We have developed some preliminary formulations that use EVA and non-EVA base resins. Various spectroscopic analyses, including Fourier Transform infrared (FTIR), fluorescence analysis, and UV-vis-NIR transmittance, and thermal analyses, including thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and TGA-FTIR, were employed to characterize the thermal reaction and optical properties of the new formulations. The thermal reaction primarily deals with the cross-linking of the base resin, which is needed to provide sufficient mechanical strength to support the solar cell strings and initiated by free-radical chain reactions using a curing peroxide. The results show that (1) decomposition rate of curing peroxides is affected by the composition/structure of the organic peroxides, (2) release of  $\text{CO}_2$  from decomposition of the peroxide, Luperox TBEC<sup>®</sup>, took place more significantly above  $130^{\circ}\text{C}$ , and (3) the sluggish cross-linking reaction peak in DSC shifts sharply by  $\sim 20^{\circ}\text{C}$ - $30^{\circ}\text{C}$  to lower temperatures in the presence of molecular cross-linkers added to the formulations. These findings have allowed us to cure conveniently in the ambient with a shorter time at  $\leq 130^{\circ}\text{C}$  in contrast to the typical processing at  $\sim 150^{\circ}\text{C}$  in vacuum. The new, albeit preliminary, EVA and non-EVA formulations have demonstrated outstanding photothermal stability.

*This work was supported by the Director's Discretionary Research and Development Program at NREL under U.S. Department of Energy Contract No. DE-AC36-99-G010337.*

*\* Presently with Magellan Laboratories, Cary, NC.*

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- 293. Initiating the Conformational Transitions of Single DNAs with Optical Trapping.** Daniel T. Chiu, Department of Chemistry, University of Washington, Seattle, WA 98195 USA.

We describe our efforts to manipulate single DNA molecules ranging from few thousand base pairs to tens of thousand base pairs directly in solution using optical trapping. The direct trapping of such DNA molecules is made possible by compacting the DNA into a globular state using a number of chemical and biological condensing agents. Once confined in the trapping laser beam, the globular DNA is “locked” into its conformation by its interactions with the trapping laser even after the surrounding medium is replaced and the condensing agent removed. The unfolding of this trapped globular DNA can be precisely initiated and its dynamics followed by controlling the laser trap.

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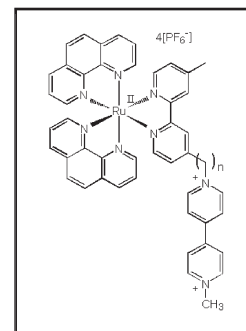
- 294. Charge Transfer Interactions in Donor-Chromophore-Acceptor Triads.** John M. Weber, C. Mike Elliott, Colorado State University, Department of Chemistry, Fort Collins, CO, 80523-1872.

Donor-chromophore-acceptor (D-C-A) triads containing a ruthenium complex of polypyridyl ligands as the chromophore, a diquaternary 2,2'-bipyridinium “diquat” acceptor and a phenothiazine donor were found to form a charge-separated state (CSS) with a quantum efficiency of 86% in solution.<sup>1</sup> To rationalize such high efficiencies, we proposed that a charge transfer interaction involving the donor and the polypyridyl ligands contributes to CSS formation. To test this hypothesis, the related C-A complex (see below) was synthesized in order to carry out bimolecular quenching studies with phenothiazine in solution. Transient absorbance studies were conducted to determine the initial amount of CSS formed as a function of donor concentration in solution. The results from these bimolecular experiments indicate that more CSS is initially formed than can be rationalized from simple diffusional encounters between the oxidized chromophore and donor.<sup>2-3</sup> Moreover, purely diffusion-controlled processes should be dramatically affected by increases in solution viscosity. In fact, when the viscosity of a dichloromethane solution is increased by a factor of ca. 40, the amount of CSS initially formed does not change. Our conclusion from these studies is that a charge transfer type interaction must be occurring between the donor and ligands in order to form the CSS with such high efficiency.

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- 295. Molecular organic semiconductors at the Au(111) interface.** C.B. France, P.G. Schroeder, B.A. Parkinson, Colorado State University, Department of Chemistry, Fort Collins, CO 80523

Thorough understanding of the interface between organic semiconductors and metal contacts is important because of charge transfer events that take place in new devices based on organic semiconductors. Transistors<sup>1</sup> and photovoltaic devices<sup>2</sup> have been fabricated using pentacene as the organic semiconductor. In the interest of understanding the structural and electronic environments of these interfaces we have investigated thin films of pentacene and *p*-sexiphenyl on the Au(111) surface in ultrahigh vacuum using multiple characterization techniques. The energetics of these heterojunctions have been measured using photoemission spectroscopy. Large interfacial dipole barriers exist at the interface of both systems. Temperature programmed desorption has been used to investigate the binding environment of the organic semiconductors on the metal substrate. Two different binding environments have been uncovered for both molecular semiconductors on the Au(111) substrate. Scanning tunneling microscopy has been used to investigate the coverage dependant structures that are formed by thin films of semiconductor molecules on the Au(111) surface. Pentacene was found to generate many overlayer structures at differing film thickness. Structures found on low coverage, monolayer and multilayer films will be discussed.

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- 296. DNA Alignment, Patterning, Nanofabrication and Characterization on Surfaces.** Adam T. Woolley, S. Darbi Hughes, Christopher F. Monson, Allison R. Nelson and Huijun Xin, Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602-5700

We are developing methods for surface patterning, manipulation, and characterization of nucleic acid molecules for use in nanofabrication and DNA analysis. Specifically, we have been working to study, understand and optimize conditions for controlled alignment of DNA molecules on Si, mica and other substrates. This work builds upon our earlier results in devising methods for reproducible alignment of well-extended single-stranded and double-stranded DNA fragments on surfaces.<sup>1</sup> We have now carried out a thorough study of the deposition and alignment of both single-stranded and double-stranded nucleic acids on surfaces to optimize our techniques. We are also performing single-molecule experiments to understand the underlying biophysical mechanisms that lead to directional alignment of DNA on surfaces under different conditions. Furthermore, aligned surface-deposited nucleic acid molecules are being utilized as templates for construction of nanowires. One approach involves photochemical and electrochemical reduction of ions associated with surface bound DNA to build up conductive nanostructures. Techniques for DNA-templated positioning of carbon nanotube nanowires on surfaces are also being pursued. These results show great promise for DNA-based fabrication of materials with nanometer dimensions, and also demonstrate the versatility of atomic force and optical fluorescence microscopy techniques for DNA characterization. Supported by startup funds from Brigham Young University and the Petroleum Research Fund of the American Chemical Society.

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- 297. Two-Photon Ion Sensors.** Stephanie J.K. Pond, Wim Wenseleers, Mariacristina Rumi, Osamu Tsutsumi, Marcus Halik, Seth R. Marder, Joseph W. Perry, University of Arizona, Department of Chemistry, Tucson AZ 85721 USA; Ahmed A. Heikal, Shaohui Huang, Watt W. Webb, Cornell University, School of Applied and Engineering Physics, Ithaca, NY 14853 USA.

Molecules with large two-photon absorption (TPA) cross-sections,  $\delta$ , are in great demand for a variety of applications, including two-photon excited fluorescence microscopy, optical limiting, and three-dimensional microfabrication. In these applications, the ability of two-photon absorption to access excited states with photons of half the nominal excitation energy provides improved depth penetration in scattering media, and the dependence of the two-photon absorption probability on the square of the excitation intensity allows for excitation of chromophores with a high degree of spatial selectivity in three dimensions. It has been demonstrated that intramolecular charge transfer (ICT) can be correlated to enhanced values of  $\delta$  in conjugated linear quadrupolar molecules symmetrically substituted with donors, D and/or acceptors, A (D- $\pi$ -D, D-A-D, and A-D-A molecules)(1,2). We have investigated molecular systems in which a chemical moiety with the ability to bind metal ions is incorporated as one of the donor groups in a D-A-D molecule. If the TPA properties are modified by the presence of ions, these systems can be used as TPA ion sensors. For example, when a mono-aza-15-crown-5 macrocycle is bound to a TPA chromophore, the two-photon induced fluorescence signal  $\eta\delta$  ( $\eta$  is the fluorescence quantum yield) decreases by a factor of 6 (810 nm) in upon addition of  $Mg^{+2}$  in acetonitrile. As  $\eta$  exhibits only small changes on ion binding, the contrast in  $\eta\delta$  is chiefly due to changes in  $\delta$ , presumably due to decreased ICT from the nitrogen lone pair which is involved in ion binding. In molecules incorporating the BAPTA ligand (1,2-bis(*o*-aminophenoxy)ethane-*N,N,N',N'*-tetraacetic acid), a 5-fold enhancement of  $\eta\delta$  is observed upon calcium binding in water at 720 nm. Changes in the TPA spectrum upon binding of  $Ca^{+2}$  in micellar systems are also observed.

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- 298. The Mast Cell Function Associated Antigen and its Interactions with the High Affinity Receptor for IgE.** Guy M. Hagen, B. George Barisas, Colorado State University, Department of Chemistry, Fort Collins, CO, 80523; Jinming Song, Deborah A. Roess, Colorado State University, Department of Biomedical Sciences, Fort Collins, CO, 80523.

Rat mucosal-type mast cells of the RBL 2H3 line express a glycoprotein termed the MAFA cell Function-associated Antigen (MAFA). When MAFA is clustered by its specific monoclonal antibody G63, secretion normally triggered by aggregating these cells' Type I Fc $\epsilon$ RI receptor (Fc $\epsilon$ RI) is substantially inhibited. The nature of MAFA-Fc $\epsilon$ RI interactions giving rise to this inhibition remains unclear. Rotational diffusion of a membrane protein is a sensitive probe of its involvement in intermolecular interactions. We have therefore studied by time-resolved phosphorescence anisotropy the rotational behavior of both MAFA and Fc $\epsilon$ RI as ligated by various reagents involved in Fc $\epsilon$ RI-induced degranulation and MAFA-mediated inhibition thereof. From 4°C to 37°C the rotational correlation times (mean  $\pm$  SD) of Fc $\epsilon$ RI-bound, erythrosin-conjugated IgE resemble those observed for MAFA-bound erythrosin-conjugated G63 Fab, 82.17  $\mu$ s and 79.31  $\mu$ s at 4°C, respectively. Clustering the Fc $\epsilon$ RI-IgE complex by antigen or by anti-IgE increases the phosphorescence anisotropy of G63 Fab and slows its rotational relaxation. Lateral diffusion of G63 Fab is also slowed by antigen clustering of the receptor. Taken together, these results indicate that

unperturbed MAFA associates with clustered FcεRI. They are also *consistent* with its interaction with the isolated receptor.

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- 299. Effect of Showerhead Configuration on Coherent Raman Spectroscopic Monitored Pulsed Radio Frequency Plasma Enhanced Chemical Vapor Deposited Silicon Nitride.** BarJean Phillips, Rene G. Rodriguez, Lisa D. Lau, and Shane D. Steidley, Idaho State University, Department of Chemistry, Pocatello, ID 83209-8023

The effect of showerhead design, number of holes and geometry, in a parallel plate reactor was studied by measuring the concentration of silane reactant by coherent anti-Stokes Raman scattering (CARS) spectroscopy as a function of radio frequency (rf) pulse width and peak power during pulsed power plasma enhanced chemical vapor deposition (PECVD) of silicon nitride thin films. Film deposition rate, stress, SiH/NH ratio, and thickness and index of refraction homogeneity were correlated with the silane depletion rate for each of the three head geometries: radial, square, and asymmetrical. The asymmetrical head caused plasma quality problems which effected the films qualities. The square pattern showed good mixing qualities, but produced a film with high compressive stress. The radial head provided the films with the most homogenous refractive index and film thickness for the most plasma conditions. But, with a 10 ms pulse width, the radial head plasma acted as a continuous plasma for depletion and stress data. The showerhead geometry affects the plasma behavior, like stability and intensity, and reactant gas velocities, which in turn affects the nitride film thickness, nitride composition, and stress.

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- 300. Characterization of the Structure and Function of Individual Antibodies at the Solid/Liquid Interface.** Jonathon Gerding, Alan Van Orden, Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA.

Single molecule fluorescence spectroscopy and atomic force microscopy (AFM) are complimentary techniques for studying individual biological molecules on surfaces. For example, single molecule spectroscopy can be used to monitor the on/off binding of fluorescently labeled ligands to an individual immobilized receptor molecule positioned in the confocal detection region of a far-field optical microscope. Such measurements provide the single molecule association/ dissociation rate constants, and hence, the binding affinity of the individual receptor. AFM provides molecular scale structural information, such as the molecular height and orientation relative to the surface, for the immobilized receptor. By combining these methods, we can characterize the relationship between structure and activity of individual receptor molecules that have been immobilized on solid supports and thereby resolve the heterogeneity that often exists in these systems. These studies will lead to a better understanding of the surface-induced conformational changes that hinder the performance of analytical devices based on immobilized biological molecules. We describe a novel approach to spatially correlated single molecule fluorescence spectroscopy and AFM<sup>1</sup> and its application to the study of individual immobilized antibodies. The experimental procedure involves 1) positioning an individual antibody immobilized on a mica coverslip within the confocal detection region, 2) introducing fluorescently labeled antigens in the solution above the support, 3) monitoring the fluorescence intensity time trace to observe individual on- and off- binding events and determine the reaction rate constants, 4) recording an AFM image of the immobilized antibody to determine its molecular height and orientation, and (5) simultaneously imaging the excitation laser light being scattered from the apex of the AFM probe tip. The latter measurement enables unambiguous identification and structural characterization of the individual molecule residing within the confocal detection region. The model system currently being evaluated is tetramethylrhodamine labeled biotin as the model antigen and anti-biotin monoclonal antibody as the model receptor.

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