Major Research Instrumentation Enriches Educational Experiences

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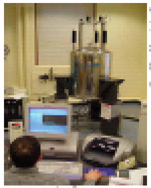
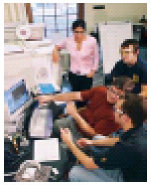
Overview

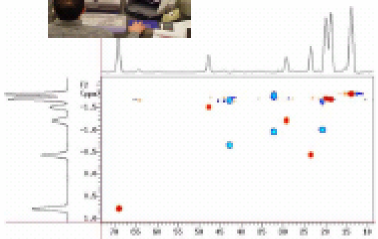
In 2002, Washington and Jefferson College was awarded $386,000 from the National Science Foundation's Major Reseach Instrumentation Program for the acquistion of a 400 MHz NMR spectrometer (CHE-0216075). The spectrometer has served in many facets of instruction and research at the College. Some of the highlights of the Varian Inova spectrometer include a widebore 9.4 T Oxford magnet, two fullband RF channels, pulsed field gradient system, a complete solid-state module, autoswitchable gradient liquid-state probe and two magic-angle-spinning solid-state probes. These modern spectrometer features have expanded our research capability, enhanced chemical instruction and provided student training with technology.



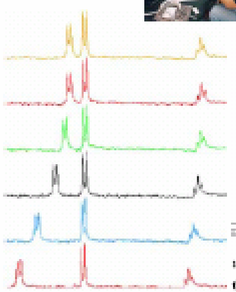


Education Through Hands-On Experiences

At W&J we pride ourselves on giving the student hands-on experiences with modern chemical instrumentation. Chemistry majors are expected to setup and run the spectrometer as well as interpret the NMR data. The spectrometer has been incorporated into all W&J chemistry laboratory courses with the exception of first year general chemistry. Advanced student experimentation has included gradient pulse sequences, 2D NMR and solid-state NMR. Students who have an interest with chemical instrumentation have the opportunity to help maintain the NMR spectrometer. The student NMR manager runs calibration tests, aids with cryogen filling, and sets the spectrometer to either liquid or solid-state configuration.



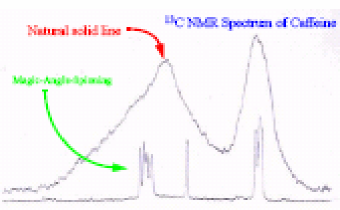
The $^{1}H/^{13}C$ gradient Heteronuclear Single-Quantum Coherence spectrum of Menthol (above) provides correlation between proton and carbon signals, as well as spectral editing information via the sign of the signal. The addition of gradients to pulse sequences reduces the time requirement of 2D NMR.

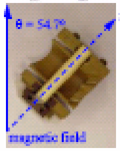


The spectral array shows the sensitivity of the ^{31}P chemical shift of ATP to pH. The autoswitchable probe enables ^{31}P acquistion without instrument modification.

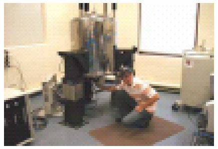
Special Solid-State Capabilities Encourage Collaborations

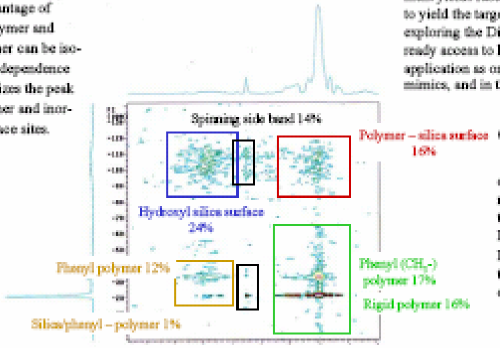
The ability to study polymer materials by solid-state NMR has resulted in off-campus collaborations. Most notably, one associated with the Enhanced Surveillance Project at Los Alamos National Laboratories focuses on the degradation of soft materials used in weapons. Here, $^{1}H/^{29}Si$ cross-polarization methods are explored to probe the polymer-filler interface in siloxane elastomers. By taking advantage of chemical shift differences of the polymer and filler, the components of the elastomer can be isolated in a 2D spectrum. The spatial dependence of the polarization mechanism localizes the peak correlation. Thus, peaks with polymer and inorganic shifts must correspond to surface sites.





High resolution in solid-state NMR can be achieved by magic-angle-spinning and strong rf pulse decoupling. Thus, solid-state NMR requires unique probes and kilowatt amplifiers.





Faculty Guided Student Research

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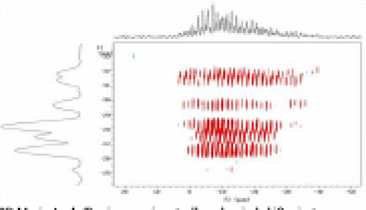
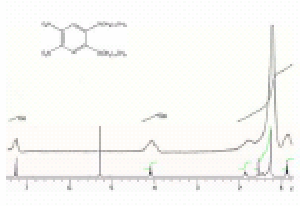
The department's faculty rely heavily on NMR for their research, which spans a wide breadth of topics. The fundamental interest of Dr. Robbie Iuliucci is the elucidation of molecular structure by chemical-shift measurements. The power to resolve molecular structure by the chemical shift has long been known, but now, due largely to the recent success of computational techniques, the chemical shift can be represented in terms of geometric parameters. Only solid-state NMR allows the measurement of the chemical-shift tensor.



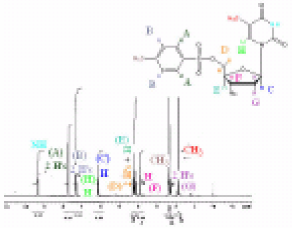
2D Magic-Angle-Turning experiments allow chemical-shift anisotropy measurements in complex systems by separating the side-band pattern of chemical sites by their isotropic value.

The department's synthetic chemists and their students routinely use NMR for product characterization. Dr. Steven Malinak is currently pursuing the design and synthesis of potential metallomesogens. The goal is to combine the unique properties of liquid crystals (fluidity, ease of processibility, one- or two-dimensional order) with those of transition metal complexes (color, paramagnetism, electron-rich environments).



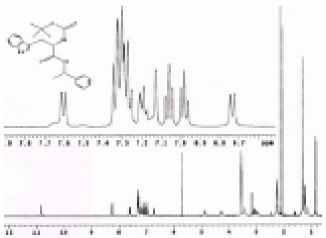
A comparison of the ^{1}H NMR spectra of 1,2-bis(decoxy)-4,5-dinitrobenzene, taken on 60 MHz (top) and 400 MHz (bottom) spectrometers.

The focus of organic synthesis by Dr. Mark Harris is on new DNA analogs with an amide linkage. Such nucleic acid analogs would follow Watson-Crick rules for complementary binding, but, because of structural changes, potentially have improved cell permeability and/or nuclease resistance. Additionally, Dr. Harris' student isolate and characterize products from kudzu.



^{1}H spectrum of an AZT-5'-tosylate, the first intermediate in the synthesis of a DNA analog containing a novel linkage.

Dr. Michael Leonard mentors students conducting research on two different projects. One group of students is investigating the synthesis of bioactive heterocycles through novel methodology. The strategy involves initial Pictet-Spengler reaction between an amino acid or amino acid derivative and ninhydrin. Subsequent rearrangement yields fused polycyclic structures, which are susceptible to oxidative ring cleavage to yield the target heterocycles. Another team of students in Dr. Leonard's lab is exploring the Diels-Alder chemistry of coumalate esters. These cycloadditions provide ready access to highly functionalized bicyclic scaffolds. These scaffolds have potential application as organic chiral shift reagents, as keystones for the preparation of beta-turn mimics, and in the preparation of polysubstituted aromatic compounds.



^{1}H NMR spectroscopy allowed identification of this Boc-protected tryptamide, an intermediate in the synthesis of a complex bioactive heterocycle.

Community Outreach

Project SEED is a unique program administered by the American Chemical Society. It is designed to place high school juniors and seniors from economically disadvantaged backgrounds in research laboratories for an 8-10 week period during the summer. SEED students have an opportunity to perform hands-on research under the supervision of a faculty mentor. Tamara Scherer, Washington High School class of 2005, has had the opportunity to acquire NMR spectra while doing research with Prof. Leonard under the aegis of the SEED program. Tamara has used the spectrometer to characterize the products of Diels-Alder reactions. This is one of the many facets of her summer research project conducted at W&J.