

Senior Scientist Mentor Program

<u>Institution</u>	<u>Awardee</u>	<u>Department</u>	<u>Area of Interest</u>
2007			
Clemson University	John W. Huffman	Chemistry	The research is a continuation of our program that has developed a number of indole based cannabinoid receptor ligands. The compounds are synthesized from commercially available indoles, an acid chloride and an alkyl halide using established synthetic procedures. Pharmacology is carried out by our collaborators at the Virginia Commonwealth University.
Cornell University	Jerrold Meinwald	Chemistry & Chemical Biology	There are ~ 40,000 described spider species, and it is thought that they all produce venoms capable of paralyzing their prey. Although many venoms have been studied chemically, it was only during our Cornell research that a neuroactive sulfated nucleoside derivative was characterized and synthesized. Direct NMR-analysis of spider venoms now reveals that sulfated nucleosides, previously undetected, occur frequently. We will use NMR techniques to characterize new venom constituents, and synthesize the most important compounds for biological study.
Duquesne University	Omar Steward	Chemistry & Biochemistry	The resources from this grant will enable undergraduate students to study in the area of structural inorganic chemistry under my direction. The research project is designed to introduce undergraduate students to the challenge of tailoring the synthesis and determining the structures of coordination polymers. Extensive use of X-ray diffraction techniques are required to investigate the use of ligand steric effects to control the polymer geometry and the arrangement of metal centers in bimetallic coordination polymers.
Lafayette College	Joseph A. Sherma	Chemistry	The Senior Scientist Mentor and his students will use high performance thin-layer chromatography (HPTLC) techniques to determine the differences in the amounts of various compound classes in the feces and urine of mice experimentally infected with the intestinal trematode <i>Echinostoma caproni</i> . The HPTLC method, which could be easily adapted for use with humans, would be simpler and faster than the cumbersome technique of fecal examination presently used to detect trematode eggs in host stool.

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New York University	David Schuster	Chemistry	For the past ten years, the Schuster lab has studied the synthesis and photophysics of [60]fullerene-porphyrin hybrid materials which function as artificial photosynthetic reaction centers. Upon exposure to light in the visible region, these materials undergo extremely rapid intramolecular energy and electron transfer processes to produce very long lived charge separated states. New examples of such materials with unusual molecular architectures are envisaged, building on work carried out with the participation of undergraduate research students. The photophysical studies on very short time scales are done in collaboration with scientists at other institution. A second set of studies involved fullerene derivatives which act as nontoxic inhibitors of HIV protease, again building on prior studies with strong undergraduate participation.
Oberlin College	Norman Craig	Department of Chemistry and Biochemistry	A combined spectroscopic-quantum chemical method is used to determine equilibrium structures accurate to 0.001 Å for small molecules. The high accuracy of these structures reveals for the first time subtle structural consequences of electronic effect. A recent example is the demonstration that pi-electron delocalization in butadiene is evident in lengthened "double" bonds and a shortened "single" bond. New systems proposed for study are cis- and trans-hexatriene, the three isomers of 1,4-difluorobutadiene, 1,1-difluorocyclopropane, and 1,1-difluoroethylene. In the hexatrienes we expect to find bigger structural effects of pi-electron delocalization than in butadiene. The other systems will show the impact of fluorine substitution on structures.
San Jose State University	Juana Acrivos	Chemistry	The structural chemistry involved in the insulator to metal phase transitions in low dimensional solids is investigated by spectroscopic and computational methods. Presence of transverse periodic lattice distortions in YBa ₂ Cu ₃ O _{7-d} , YBCO along the a-b plane diagonal and the effect of X-ray flux on the phases in YBCO 50nm films gives evidence for excitations leading to activated state complex: X-Ray photons(hν)+YBCO =>Xfi and YBCO(metal) <=>Xfi<=>YBCO(insulator), promising to explain the details of the phase transition to superconductivity.
University of Pittsburgh	Theodore Cohen	Chemistry	The project involves undergraduate participation in exploiting recently discovered techniques of greatly generalizing cyclizations by intramolecular carbometallations of unactivated or weakly activated alkenes. Key features are the ability to convert readily available alkyl or allyl phenyl sulfides or sulfones into alkyllithiums or allylzincs and the highly diastereoselective reduction of esters by DIBAL. Biologically important natural products are being synthesized. The senior mentor will be heavily involved, on a daily basis, with the undergraduate researchers.

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California Institute of Technology	John D. Roberts	Chemistry and Chemical Engineering	Support is sought for continuation of research involving a summer program of ten weeks involving 4-7 undergraduates on conformational analysis by NMR of 1,2-substituted ethanes and 1,3-disubstituted propanes. The program involves undergraduate students from the United States and abroad. Each student is assigned an individual compound for study, chosen to give previously unknown and unpredictable results. Throughout the years of our study in this arena, new and surprising results are very often encountered.
James Madison University	Benjamin A. DeGraff	Chemistry	The project involves the design, synthesis, characterization, and evaluation of luminescent transition metal complexes which can serve as molecular reporters. The luminescent behavior of suitable complexes is altered by interaction with the microenvironment and "reported" by changes in luminescent intensity, color distribution, and/or lifetime. These materials find applications as diverse as monitoring the blood oxygen level in cardiac care patients to tracking the pH of the water in fish farms. The students involved receive training in synthesis, establishing molecular structure by several types of spectroscopy, and evaluation of reporter suitability using a variety of modern techniques.
Michigan State University	James L. Dye	Chemistry	Alkali metals added to silica gel or other nanoporous oxides form "sequestered alkali metals" that are as reducing as the parent metals or alloys, but much safer and easier to handle. Undergraduates would work with the Senior Scientist to prepare and study these materials. Techniques would include glovebox and vacuum line use, NMR analysis, DSC and computer graphics. Other possible methods include magnetic susceptibility, solid state NMR and EPR, electron microscopy, conductivity, XPS and XRD.
Morehouse College	James King	Chemistry	The reaction rates of hydrogen fluoride (HF) with the dominant ions of the ionosphere O^+ , O_2^+ and NO^+ will be measured using an Ion Cyclotron Resonance (ICR) Spectrometer (on loan from the Jet Propulsion Laboratory (JPL)). Students in the program will learn laboratory chemical kinetics and spectroscopy with the expectation that such experience will encourage them to select a career in one of these fields. Along with active participation in the experiments, students will be required to lead weekly seminars on kinetics and spectroscopy.

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Oregon State University	Joseph W. Nibler	Chemistry	This project will involve student participation in the synthesis and spectroscopic analysis of several unusual molecules. These are the quasi-linear molecule C ₃ O ₂ , the reactive molecule SO ₃ , and the "pinwheel" molecule B(OH) ₃ . Students will obtain laboratory experience with gas phase vibrational-rotational spectroscopy at state-of-the-art resolution (0.0015 cm ⁻¹). The molecules to be studied have sufficiently high symmetry that detailed theoretical analysis will be feasible, leading to accurate molecular parameters such as bond lengths and vibrational frequencies.
Purdue University	Jurgen M. Honig	Chemistry	Proposed to investigate consequences of building into current thermodynamic theory of phase transitions the effects of assigning two components of a binary mixture two different interaction energies. Also, x-ray investigations are planned to study vanadium sesquioxide.
Rice University	Robert Curl	Chemistry	Exploratory research aimed at developing a method for simultaneously determining many genetic anomalies, primarily SNPs, without amplification of the genetic material through whole-chip imaging. The chip is to be covered with thousands of primer features with each feature containing ~100000 primers complementary to the region just before a SNP location. Terminating bases labeled with four different dyes and polymerase add a single labeled base to the primer. Four lasers of different wavelengths matching the dyes read the whole chip's fluorescence at once.
Stanford University	James Collman	Chemistry	Using self-assembled monolayers (SAMs) and covalently attached functional-synthetic models of the active site in cytochrome c oxidase (CcO) the catalytic reduction of dioxygen will be studied under conditions of rate-limiting electron transfer. These conditions are involved in the steady-state turnover of CcO during respiration. The selectivity and turnover number will be evaluated as a function of the rate of electron transfer.
The University of Chicago	Stuart A. Rice	Chemistry/PSD	Support is requested for experimental studies of confined quasi-one-dimensional (q-1D) and quasi-two-dimensional (q-2D) colloid suspensions. The research proposed will examine several structural and dynamic properties of q-2D and q-1D systems, and the nature of the changes in those properties as the degree of confinement of the system changes, thereby testing some of the many predictions that, as a generic class of materials, two-dimensional and one-dimensional matter have unusual properties.

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The University of Chicago	R. Stephen Berry	Chemistry	Atomic valence electrons correlate so strongly that, in alkaline earth atoms, their properties are better described by a molecule-like, rotor-vibrator model than by the traditional independent-particle orbital model. This project has two goals: quantifying the validity of various models from the variances, from accurate calculations, of quantities that are precise constants of motion in specific simple models, and determining the extent and nature of valence shell correlation in atoms with three and four valence electrons.
The University of Wisconsin-Madison	Julius Adler	Biochemistry	Undergraduates will contribute to Julius Adler's further research on the biochemistry of the <i>Drosophila</i> brain. How vision and smell are integrated is the primary subject. This will be studied by biochemical methods, along with molecular genetics. The outcome will provide new information about the mechanism of an animal's response to stimuli.
University of Arizona	Michael A. Wells	Biochemistry & Molecular Biophysics	We will investigate the use of stable isotopes and mass spectrometry to study carbohydrate metabolic rates in mosquitoes. Trehalose containing ¹³ C in specific carbons will be prepared biologically. These molecules will be used to determine the fragmentation patterns of trehalose in order to find the most useful ions to characterize metabolism. Then mosquitoes will be fed [2- ¹³ C] - glucose and the labeling pattern in trehalose will be used to measure the rate of the pentose phosphate pathway.
University of Washington, Seattle	Bruce A. Finlayson	Chemical Engineering	Undergraduates will perform research in computational fluid dynamics on problems of interest in microfluidics, problems with graduate students in bioengineering, and problems jointly with industrial firms. The computer program FEMLAB (now Comsol Multiphysics) will be used to solve two- and three-dimensional flow and diffusion problems. This computer program has allowed undergraduates to be creative and solve problems much more difficult than those in their textbooks. Students who perform these projects gain a deeper understanding of transport processes and confidence as problem-solving engineers, but they also receive cross cutting experiences in important professional skills like teamwork and communication. The Senior Scientist Mentor Program would continue the success in which students bring enthusiasm and energy to problems they don't know 'can't be solved'.
Wake Forest University	George Holzwarth	Physics	The maximum force generated by 1 kinesin motor protein molecule in vitro is 7 pN. There is indirect evidence that in cells, several kinesin motors need to cooperate to move a single vesicle, because the drag force that must be overcome is 5-40 pN. We will measure velocity-force curves for 2, 3, or 4 kinesin motors pulling a single load in vitro against a carefully measured viscous or magnetic force.

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Cornell University	Harold A. Scheraga	Chemistry and Chemical Biology	We will determine the intramolecular interactions that dictate the regeneration of RNase A from the reduced form. Mutants of RNase A will be used to investigate the interaction between residues in the native state, and to develop a general model to explain the oxidative folding of multi-disulfide-containing proteins. Furthermore, in vivo protein folding will be addressed by investigating the mechanism by which the oxidoreductase protein disulfide isomerase catalyzes the formation of native disulfide bonds in the protein.
Oberlin College	Norman C. Craig	Chemistry	A combined spectroscopic-quantum chemical method is used to obtain equilibrium structures for interesting small molecules, such as butadiene, the three isomers of 1,4-difluorobutadiene, and the two isomers of hexatriene. Ground state rotational constants for a variety of isotopomers are obtained from microwave spectroscopy for polar molecules or from the rotational structure in high-resolution infrared spectra for nonpolar molecules. The ground state rotational constants are "corrected" to vibration-free equilibrium rotational constants with vibration-rotation constants computed with high-level quantum chemical methods. Equilibrium structures are then fit to the equilibrium rotational constants. These combined spectroscopic-QC equilibrium structures reveal fine adjustments in bond lengths and bond angles, which should correlate with electronic effects such as partial pi-electron delocalization and the effects of fluorine substitution. Equilibrium structures may be used to evaluate structures computed by QC methods alone.
Purdue University	Ronald P. Andres	Chemical Engineering	The aims of this project are to: 1) attach folic acid to novel magnetic nanoparticles synthesized for the first time at Purdue University, 2) measure the uptake of these particles by cancer cells via folate receptor-mediated endocytosis, 3) determine the optimum conditions for MRI imaging of cancer cells that have been exposed to folate conjugated magnetic nanoparticles, and 4) determine the time-dependent viability of cancer cells treated with resonant microwave radiation after exposure to folate conjugated magnetic nanoparticles.
The University of Texas at Austin	James E. Boggs	Chemistry and Biochemistry	Support will be used to enable two undergraduate students per year to join an active research program and become involved in computational chemistry directed either toward predicting the thermochemistry of free radical intermediates in atmospheric and combustion chemistry or toward understanding the role of vibronic interactions in determining the chemistry of transition metal compounds. Students will be directed from simple systems into the complexities at the forefront of modern theoretical research.

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University of Pittsburgh	Theodore Cohen	Chemistry	The project will involve undergraduate participation in the exploitation of recently discovered techniques of greatly generalizing cyclizations by intramolecular carbometallations of unactivated or weakly activated alkenes or of carbonyl groups. A key feature is the ability to convert readily available allyl phenyl sulfides or sulfones to allylmetals. Biologically important natural products will be synthesized. The senior mentor will be heavily involved, on a daily basis, with the undergraduate researcher.
University of Rochester	Esther M. Conwell	Chemistry	A basic question still undecided is whether the wavefunction of an exciton or excess electron or hole on the base stack of DNA is localized on a single base or delocalized over a number of bases. The argument vs. delocalization is that the bases are weakly coupled and subject to strong thermal vibrations. To aid in resolving this question we propose further calculations of the delocalized wavefunctions and comparison with experiment.
University of Vermont	A. Paul Krapcho	Chemistry	Telomerase is an enzyme which is able to restore telomeres and has been found in over 90% of tumor cell lines. Telomerase in tumors promotes the uncontrolled growth and immortality of these cells. Telomers are rich in guanine(G) and fold back on themselves to form G-tetrads. We wish to design and synthesize molecules that will stabilize the G-quadruplex and inhibit the function of telomerase.

2004

California Institute of Technology	John D. Roberts	Chemistry and Chemical Engineering	Even after some 20 years of investigations, involving some 86 undergraduate summer students, on hydrogen bonding, electrostatic, polar "gauche" effects, we are still finding very unexpected perturbations of conformational equilibria of 1,2-disubstituted ethanes and 1,2,3-trisubstituted propanes. The results are most interesting in non-polar solvents and we now have multiple examples where two negative substituents prefer to be close together, rather than assuming positions as far apart as possible. Naturally, we wish to continue this research.
Harvard University	William Klemperer	Chemistry and Chemical Biology	The determination of intermolecular interactions is made quantitative by the spectroscopic measurement of the structure of molecular complexes. We study hydrogen bonding by laser induced fluorescence of the $v=3$ and 4 levels of hydrogen fluoride in complexes previously characterized at the $v=1$ level complexes. The research provides the vibrational dependence of interaction energy and predissociation lifetime. This may be analyzed in terms of the dependence of hydrogen bonding upon the H-F internuclear distance.

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Harvard University	Dudley R. Herschbach	Chemistry and Chemical Biology	Undergraduates may chose to pursue either of two projects, both striving to develop and exemplify new research tools that will have broad application: (1) Experimental means to generate beams of ultracold molecules and manipulate their trajectories, in order to study collision dynamics of "nanomatter waves" having deBroglie wavelengths of 1 to 100 nm; or (2) A computer model for enzyme catalysis of DNA replication, including response to tension applied to the DNA template strand.
Lafayette College	Joseph A. Sherma	Chemistry	Neutral lipids and phospholipids will be analyzed in <i>Helix pomatia</i> , the edible terrestrial snail used for escargot, and the medically important leech <i>Hirudo medicinalis</i> . The data obtained will be of value in assessing the nutritive value of <i>H. pomatia</i> and in better understanding the chemical composition of the active anticoagulant (hirudin) present in the saliva of the leech. Sample preparation and quantitative high performance thin layer chromatography (HPTLC) methods we have previously developed for identification and quantification of lipids in <i>Biomphalaria glabrata</i> and <i>Helisoma trivolvis</i> snails will be modified and validated in order to carry out analyses of these invertebrates. As time permits after completing the lipid studies, the following additional research will be carried out on these samples: (1) HPTLC methods will be developed and used to qualitatively and quantitatively characterize the fat-soluble chloroplast pigments, amino acids, and carbohydrates, and (2) inductively coupled plasma-atomic emission spectrometry and atomic absorption spectrometry methods will be developed and used for analysis of metals. Six students will
San Jose State University	Juana V. Acrivos	Chemistry	Research on the solid state properties and the possible applications of layer materials, especially organic conductors, superconducting cuprates and nano-films of the latter are to be carried out by two undergraduates working at San José State University and traveling to synchrotron sources to measure their X-Ray diffraction and absorption spectra with the PI. The work will involve molecular orbital computations to understand the effects discovered under the support of the 2002 grant.
University of Wisconsin-Madison	Julius Adler	Biochemistry	Undergraduates will contribute to Julius Adler's research on the roles of calcium ions, sodium ions, and potassium ions in the chemotaxis of <i>Escherichia coli</i> bacteria. This will be studied by biochemical methods, and molecular genetics will also be used. The outcome will provide new information about the mechanism of bacterial chemotaxis. In addition, undergraduates will contribute to Adler's research on the biochemistry of the <i>Drosophila</i> brain.

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Washington State University	Roger D. Willett	Chemistry	The synthesis, crystal growth and characterization of novel low dimensional magnetic systems will be pursued. Emphasis will predominantly be placed on chain systems with competing ferromagnetic and antiferromagnetic interactions. Techniques employed will include single crystal diffraction, spectroscopic techniques and magnetic studies.
Williams College	J. Hodge Markgraf	Chemistry	A new synthetic route to sampangine alkaloids is proposed that affords these tetracyclic structures in three steps from 2,7-naphthyridine via formation and rearrangement of Reissert compounds, followed by radical aryl-aryl coupling. The incorporation of a variety of ring-D components is readily accommodated. This pathway avoids the regioselective ambiguities associated with the cycloaddition step in all previous methods.

2003

Florida State University	Gregory R. Choppin	Chemistry and Biochemistry	It is proposed to synthesize a complexing ligand consisting of an acridine yellow G backbone with a taci (1,3,5-triamino-2,4,6-trihydroxycyclohexane) group on each of the two outer phenyl rings. This basket-shaped ligand would complex with trivalent lanthanides. Potentiometry, calorimetry, nuclear magnetic resonance and laser-induced fluorescence would be used to study the complexes. Undergraduate students would conduct the research with consultation and oversight by the PI and senior research associates in the group.
Fordham College	Mary G. Hamilton	Natural Sciences	Marine invertebrates offer a convenient source of interesting proteins in the hemolymph for investigation by "classic" biochemical techniques. Since many are very large multisubunit assemblies, they can also be "seen" by electron microscopy. We continue to study: ferritin and a non-respiratory protein of unknown function in chitons; carbonic anhydrase and esterase(s) in oysters; acetylcholinesterase in gastropods. We also have begun to study the heat shock proteins in organ cultures of oyster tissues.
Michigan State University	James L. Dye	Chemistry	Alkali metals added to all-silica zeolites form "inorganic electrides" in which complete or partial ionization of the alkali metal atoms occurs to form extended arrays of spin-paired electrons. Undergraduates would work with the Senior Scientist and a postdoc to form and study these adducts. Techniques would include zeolite synthesis, glovebox and vacuum line use, wet and instrumental analysis, DSC and computer graphics. Some or all of the following instrumental methods would also be used: magnetic susceptibility, solid state NMR, EPR and ENDOR, reflectance spectroscopy, electron microscopy, conductivity, XPS and X-ray diffraction.

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Oberlin College	Norman C. Craig	Chemistry	High-resolution (0.002 cm ⁻¹) infrared spectroscopy is used to determine complete structures of nonpolar molecules. Of current interest are the structural adjustments in going from butadiene to the three isomers of 1,4-difluorobutadiene, among which, surprisingly, the cis,cis isomer has the lowest energy. In addition to finding substitution structures (rs), more fundamental equilibrium structures (re), comparable to those from quantum chemical calculations, will be explored. The re structures will come from combining experimental ground state rotational constants with anharmonic vibration-rotation interaction constants obtained from ab initio calculations.
Occidental College	Katsumi Niki	Chemistry	Cytochrome c is a redox-active protein that functions as an electron carrier in several critical cellular processes. Of particular physiological interest is the interaction between cytochrome c and the mitochondrial enzyme cytochrome c oxidase. We propose to model this interaction using surface electrochemical techniques at functionalized self-assembled monolayers. Through site-directed mutagenesis, we can precisely control the nature of the protein/monolayer interface, allowing us to delineate the subtle structural factors that control ET within this complex.
Portland State University	Gary L. Gard	Chemistry	Three specific research projects for undergraduate chemistry students have been proposed. These include: (a) new solid state salts containing fluorinated ligands and their evaluation as precursors for new electronic systems; (b) new fluorinated polymers with terminal fluorinated bulky groups; (c) new SF ₅ (CF ₂) _n -aromatic derivatives. These projects involve synthesis and characterization of new compounds along with a systematic evaluation of their chemical, physical, electronic and structural properties.
University of Arizona	Robert B. Bates	Chemistry	(A) Syntheses of prodrug analogues of the potent natural anticancer agent dolastatin 11 for testing as anticancer drugs. (B) Structure determinations of new natural products, especially bioactive ones, by nuclear magnetic resonance and mass spectrometry. These natural products are provided by research groups doing isolation work.
University of Pittsburgh	Theodore Cohen	Chemistry	The project will involve undergraduate participation in the exploitation of recently discovered techniques of greatly generalizing cyclizations by intramolecular carbolithiations, carbозincations, and other carbometallations of unactivated or weakly activated alkenes. A key feature is the ability of oxyanionic groups that are allylic or homoallylic to the alkene to greatly accelerate the cyclization and to control the stereochemistry. The senior mentor will be heavily involved, almost on a daily basis, with the undergraduate researcher.