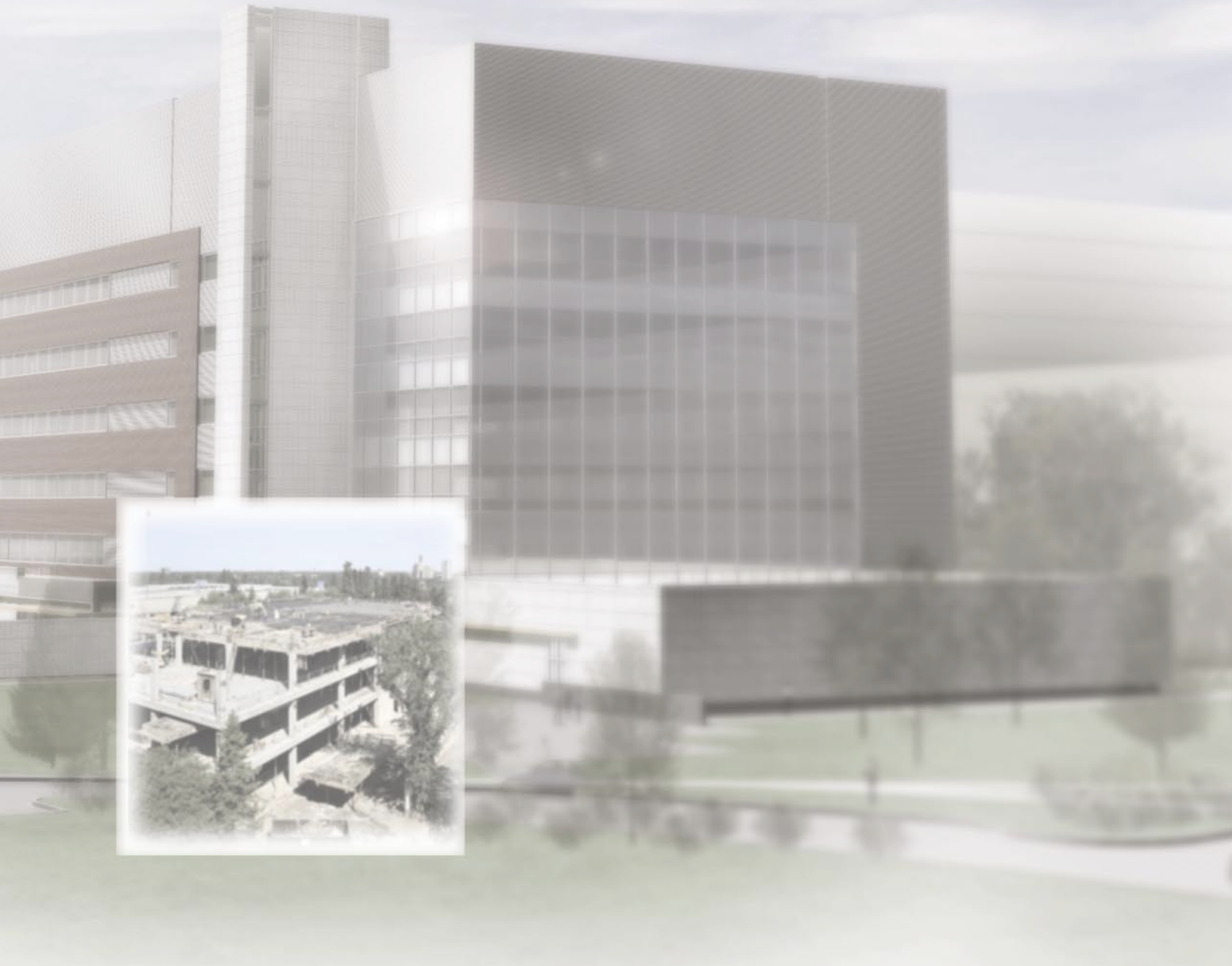
NANOSCALE INFORMATION AND COMMUNICATION TECHNOLOGIES



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The Molecular Scale Devices Group addresses key issues facing future molecular device technologies. Our involvement in the study of molecules as devices began approximately 15 years ago. Some of our early work helped define the concepts and methods that opened up a new field.

EXECUTIVE SUMMARY

Our first year in Alberta has been a period of rapid team and facilities growth. We were a mature group before leaving NRC in Ottawa – we are a yet more substantial group now. We are based in both the National Institute for Nanotechnology and the department of Physics, both on the University of Alberta campus. Six people moved from Ottawa to Edmonton. We have since hired or engaged a number of other people, to create a vital team, currently numbering 16 people.

Lab equipment valued at several million dollars was also moved. The re-establishment of that equipment and the building of new labs has been a substantial undertaking. We now have several working instruments. More new equipment is to come on-line in the coming year.

Our central tools, the scanning tunneling microscope and advanced quantum mechanical computations, together with in-group expertise in organic synthesis, condensed matter physics, surface chemical physics and instrument engineering, prepare us to compete effectively with other leading efforts in the world.

One indication of our standing in the area is given by citation statistics; three of our early papers have collectively been cited 800 times; a more recent article, proposing hybrid silicon-organic molecular structures as a foundation for molecular devices has received over 100 citations.

Wolkow, Dilabio and Pitters are increasingly well integrated in the larger campus community. Some activities include: serving on the executive committee of the WestGrid computer system, aiding in the search for a new NINT Director, giving numerous lay-accessible lectures, sharing in teaching a nanotechnology course, together with the Health Law Institute helping to form an awareness of nanoscience-ethics issues, and judging contributions to a science essay-writing contest for primary school students from across Alberta.

Our scientific work came near to a halt during our move. We are now regaining momentum. 13 new papers have been published and 14 invited lectures have been delivered in the last year. The group has a fine spirit and vigour. All team members appear to be aware of our special opportunity.

RESEARCH PROGRAM OVERVIEW

As laid-out in our original proposal, our program covers a range of activity: ultra high vacuum surface analysis (primarily with scanning tunneling microscopy), extensive quantum mechanical modeling (in-house and via external collaborations) and some chemical synthesis. Increasingly, we lithographically prepare samples that allow macro (electrical) characterization of nano-scale structured samples. We push ahead by designing new instruments – an activity that leads us to collaborate with engineers, and will in future link us to medicine. In this section, a program of interconnected activities is briefly described.

Self-Directed Growth

A substantial advance has been made in automatically growing well-defined molecular structures on a surface. We showed for the first time that arduous atom-by-atom crafting techniques are not the only way to build well-defined structures on the smallest scale. Many extensions of our process are underway including new mechanisms for attaching molecules, new functionality in the attached molecules and several theory advances (barriers controlling kinetics, physical forces and their role in growth and on configurations).

Robert Wolkow

In addition to seeing our molecular lines as, potentially, the commensurately small wires needed for connecting functional nano-entities, or as functional elements within detector assemblies, we have exciting indications that our line growth procedure provides a miniature lab, beautifully suited to direct and detailed examination of molecule-molecule electronic coupling.

Connections to Nanostructures

In order to use nanostructures we must find means to address them. Most reports to date have suffered from having ill-defined connections. Connections must be defined in absolute position and in terms of internal structure. Our molecule-silicon studies have solved the most complex silicon interface problems approached to date and as a result we are well positioned to continue leading in this area.

Other Directed Growth

A variety of schemes (distinct from the self-directed growth work described above) for efficient, controlled growth of nanostructures are being explored. Directed growth is a centrally important issue in nanoscience and directed growth will be key to nano/molecular technologies.

Exploratory Devices

Simple proto-devices are being fabricated to test and develop ideas. These projects are broadly collaborative and interdisciplinary. Molecular sensing applications will be both a lucrative end, and a stepping-stone to more complex devices such as molecular computers.

Theory

Theory and computation are integrally important in all we do – these activities do not stand alone. Ongoing efforts involve determinations of adsorbate geometries, spectra and STM images. Methods are being developed to describe ubiquitous dispersion interactions. Calculations of reaction barriers are progressing, leading to new predicative capabilities. Modeling of transport (conduction) characteristics of our hybrid organic silicon structures with several external collaborators is underway.

Toward Spin-Offs and Economic Impact

In the past, though our work has been suggestive of practical functions, we have been unable to see a path to application. With the extraordinary team now assembled, we see a number of substantial opportunities emerging. These range from small market licensing of novel instruments, to a basis for a wide range of powerful, widely accessible new detectors – and more. Currently, we are trying to capatilize on an idea related to ultra-fine electron beam resists for nano-lithography applications.

RESEARCH PROJECTS

Self-Directed Growth

We can now widely alter the nature of the molecules assembled. For example, our paper "Ring-Opening Radical Clock Reactions for Hybrid Organic-Silicon Surface Nanostructures: A New Self-Directed Growth Mechanism and Kinetic Insights," describes a new chemical process for self-directed growth of molecular nanostructures. This method indicates new avenues of direction (shape) control over growth, while also providing a rare glimpse into kinetics of a nanoscale assembly process.

Our study, "Reversible Passivation of Silicon Dangling Bonds with the Stable Radical TEMPO," shows a remarkable new capability to individually tailor the growth of molecular nanostructures. The molecule TEMPO is used as a molecular "cork" that can at will be placed to block reaction at any particular site. This cork can also be controllably removed to continue growth when desired. No similar single-molecule level control over nanostructure growth has been demonstrated before.

Our most recent work, "The Role Of Physical Interactions In Self-Directed Organic Nanostructure Growth On Silicon", uncovers the important role of physical interactions – that all atoms and molecules share – on our nanostructure growth processes. Because of this new understanding, the door is open to growth of a far greater range of materials than was previously possible.

Connections to Nanostructures

We continue to lead the world in defining the exact nature of molecule silicon nature interactions. Our paper, "A Self-Directed Growth Process for Creating Covalently Bonded Molecular Assemblies on the H-Si(100)-3×1 Surface," shows a new self-directed growth mechanism that causes molecular structures to grow in a direction that is 90o (across, rather than parallel to dimer rows on Si(100)) to what we observed previously. This new capability moves us a step closer to creating a "molecular etch-a-sketch" that will allow structures of arbitrary shape to be easily made.

Our "Connected STM" project is moving ahead after a long dwell. Hiring of design engineer Mark Salamons and the contributions during her sabbatical visit of Professor Qiao Sun (Faculty of Engineering, Calgary) have made a great difference.

Robert Wolkow and some research team members at the 2004 Banff Informatics Summit

Undergraduate student Tony Tadic is pushing ahead our plans to make an optical interferometer that can routinely measure displacements at the level of 1 Angstrom. He will use that machine to characterize new scanner ideas we have developed. Again, Professor Sun plays a significant role in advancing this work by performing finite element analyses. The new techniques and instruments resulting will move our efforts forward, and might lead to commercially viable devices.

Exploratory Devices

We have worked very hard (postdoc Adam Dickie in particular) in the last year to create a proto device. We have succeeded in making our first hybrid silicon-organic molecular device. We have learned how to gain electrical measurements that reveal microscopic changes on a silicon surface. In essence this is a pressure sensor. It is not very useful at this point but proves some key points. Many improvements are planned and being attempted.

Theory

Theory, primarily performed by Dr Gino DiLabio, has been a part of virtually all of our projects. Gino continues to steadily refine his craft, as shown by the impressive list of publications led by him.

Our numerous collaborators – W.Hofer/Liverpool, H.Guo/McGill, G.Kirczenow/SF, A.Rochefort/Montreal – bring to the effort a broad theory and modeling strength. A number of works are well advanced. We are quite sure we have seen the first direct evidence of intermolecular coupling and electronic tuning. This has implications on organic electronic design strategies. This work will be published in the near future.

Toward Spin-Offs and Economic Impact

Progress has been made in planning studies related to new electron-resist materials and nano-scale lithographic procedures. An instrument that will be crucial to these studies is a new combined electron energy loss spectrometer and scanning tunneling microscope. Over the past year that system has been designed, a proposal has been written, funds have been secured and the custom-made instrument has been ordered. Full operation of the instrument is expected in October 2004.

OBJECTIVES FOR NEXT YEAR

Self-Directed Growth

Again, self-directed growth phenomena will be central to our studies. We aim to bring more control to the process, both directional and compositional.

Our studies of molecular assemblies on silicon will also be used as little laboratories for exploring the nature of intermolecular and molecule-substrate coupling. We will unveil the essence of those interactions and thereby open the door to new device concepts that are inherent to the properties of matter at the nanoscale.

Connections to Nanostructures and Exploratory Devices

Work in this key area will continue. Silicon on insulator (SOI) will be employed to create structures that are more sensitive to surface chemical modifications.

- Un-patterned SOI will be probed in our existing ultra high vacuum multiprobe station. We expect to demonstrate greatly improved sensitivity in our measurements.
- Patterned SOI will be employed also. Preliminary experiments will be required to prove high surface quality can be attained after lithographic processing. (Many procedures that are adequate for standard silicon device manufacture, create surfaces too contaminated for our purposes.) Once we overcome those hurdles, we will make transport measurements that test the sensitivity limits of our detection schemes.
- We will endeavor to move our proto-molecular detectors to a wet environment. This will pose many challenges. We likely will need new strategies to protect against attack by water and oxygen, among other species.
- A new generation of ultra high vacuum probe device will be made. This device will employ much finer (100x closer spaced) probes, thereby improving the surface sensitivity of our measurements.

In past experiments in our probe station, we uncovered a surprising mode of chemical to electrical transduction. We will design and perform further experiments

to elucidate that effect. This effect is quite interesting as it allows even weakly (physically) bound species to be detected. This accidental development may turn out to be superior to our planned approach.

Our instrument design and building effort will continue.

- The combined electron energy loss and scanning tunneling microscopy system will be tested and fully operational by October 2004;
- Our home made multiprobe instrument that we call the "connected STM" will be quite far along by next year's end;
- We may purchase or begin to build a low temperature (4K) scanning tunneling microscope next year;
- Our existing ultra high vacuum atomic force microscope has recently been shown capable of gaining atomic resolution images of Si(100) (to our knowledge, these are the first such images). We hope to push this further to gain acute sensitivity to electrical charges. The identification and manipulation of fixed charges is key to developing molecular computation schemes.

Theory

Our theoretical methods will continue to advance. We foresee having the ability to describe the behavior of single dopant atoms in nanoscale pieces of silicon. This work will then lead to a predictive capability and the capacity to design new types of dopant species. We are hoping to create surface bound dopants – not conventional substitutional dopants. The great attraction of our approach is that doping could be achieved without thermal activation, which partially destroys the spatial definition of a doped region.

Transport theory of our hybrid molecular silicon systems, primarily done by George Kirczenow of Simon Fraser University will mature, allowing us to understand and predict new properties. Our expectation is that truly conducting molecular structures can be designed and built.

We are yet missing one key theoretical capability. It is necessary to compliment our rigorous atom-scale treatments with a description of bands, fields and carriers in the bulk. That device-level description is well established, but not yet in our group. We seek a suitable collaborator.

Other Directed Growth

New schemes for directing nanostructure growth are being planned. We aim to develop quite a general field-driven process. Theory work has already begun. New lithographic strategies that will be required for experimental testing and are in the planning phase.

RESEARCH TEAM MEMBERS AND CONTRIBUTIONS

Research Team Members

TEAM LEADER	ROLE
Dr Robert Wolkow	Professor in Physics at University of Alberta, also adjunct Professor of Chemistry, and Principal Research Officer and Molecular Scale Devices group leader at National Institute for Nanotechnology (NINT), NRC.

STAFF SCIENTISTS	ROLE
Dr Jason Pitters	Research officer at NINT, NRC Responsible for all of our complex ultra high vacuum scanning tunneling microscopy and related laboratories
Dr Gino DiLabio	Research officer at NINT, NRC Responsible for all of our quantum mechanical computational work

SUPPORT AND TECHNICAL STAFF	ROLE
Doug Moffatt	Staff technician
Martin Cloutier	Senior technician
Mark Salomons	Instrument Design Engineer

OTHER TEAM MEMBERS	ROLE
Dr Qiao Sun	Visiting Professor, University of Calgary
Professor Dr Joachim N. Burghartz	Future Visiting Professor, Scientific Director DIMES, Delft University of Technology
Dr Judy Xu	Group Administrator

POSTDOCTORAL FELLOWS
Dr Adam Dickie
Dr Mohamed Rezeq
Dr Paul Piva

PHD STUDENTS	
Janik Zakovsky	University of Montreal

MSC STUDENTS
Owen Clarkin

COLLABORATIONS

NAME/INSTITUTION	NATURE OF COLLABORATION
Dr Werner Hofer	
Liverpool	An expert in solid state density functional calculations. We have been working together for five years. Werner is working with us on the project described above, involving postdoc Paul Piva.
Professor Alain Rochefort	
Département de génie physique, École Polytechnique de Montréal and Centre de Recherche en Calcul Appliqué (CERCA)	A theorist with expertise molecular interactions related to electrical transport. He also is working on the Piva project.
Dr Yuh-Lin Wang	
Academia Sinica in Taiwan	An expert in focused ion beam instruments, nanostructures and scanned probe microscopy. We have worked for three years on a project that aims to connect small numbers of molecules to macroscopic electrodes, allowing direct electrical characterization of hybrid silicon-molecular structures.
Dr ChiiDong Chen	
Academia Sinica in Taiwan	An expert in low temperature characterization of solid state semiconductor structures and shares in the above project aimed at hybrid silicon-organic devices.
George Kirczenow	
Renowned mesoscopic physics and transport theorist of Simon Fraser physics	Recently joined the effort to describe electrical transport through our hybrid molecular-silicon proto-devices. We have preliminary results that unveil the processes at work as electrons traverse our structures.

INTELLECTUAL PROPERTY

Our first patent application has been prepared, but not yet filed. It describes a unique way to grow molecular nanostructures.

FUNDING

Robert Wolkow receives major funding from NRC ($1.1M) to work with the National Institute of Nanotechnology. He also received a number of awards from NSERC, CFI and the university worth approximately $500K to assist with the startup of his research program. He is also an ongoing participant with CIAR and a close associate of the National Institute for Nanotechnology ($120M).

OUTREACH

We have created a section here for outreach activities, as we believe the job entails more than scientific leadership. It also falls to make our work accessible to the public, and to help transmit the excitement and possibilities of our work to young students. Toward this end, we have given a number of public or non-expert lectures this year. Jason Pitters has spoken to keen young science students at local high schools. Gino DiLabio is particularly good at nurturing junior University students and finding projects that are both within their reach and valuable to our group.

The Chair has just returned from Halifax to give a keynote lecture at an undergraduate chemistry conference. The Discovery Channel and Jay Ingram, host of the excellent program "Daily Planet," will soon be in Edmonton to film a segment in our lab.

The Chair has made a determined effort this past year to help engage NINT in discussions related to science ethics. This is in part a defensive action, but it is more than that. We must be sure that our scientists proceed with an awareness of potential dangers of emerging technologies and with awareness that the public has a right to know what we do.

It is also important to spread the truth about nanoscience. There exists a substantial, perhaps unprecedented, current of misinformation concerning nanotechnology. The Chair has just completed a paper, and have given some public talks, entitled "The Ruse and the Reality of Nanotechnology". The plan is to lay out clearly what we can do today, what we expect to some day do, but also what we expect never to be able to do, thereby promoting informed discussion.

NINT has made available funds to pay the salary of a researcher and a student in UofA's Health Law Institue. Our lead contact there is Tim Caulfield. The person we routinely interact with is Lori Sheremeta. One further tangible effort has led to the creation of a fellowship that will support a visiting social scientist, specializing in science ethics issues, who wishes to spend a sabbatical period in Edmonton and in association with NINT. We will have an arm's length arrangement for selecting the fellowship holders. Any serious scholar, pro or con Nano, is welcome. By rubbings shoulders, both nanoscience researchers and the social scientist will benefit. By establishing this position, we show that our doors are open and that we wish to engage society.

PUBLICATIONS

"A Self-Directed Growth Process for Creating Covalently Bonded Molecular Assemblies on the H-Si(100)-3×1 Surface." X. Tong, G. A. DiLabio and R. A. Wolkow, *Nano Letters*, 2004, 4,979-983.

"Ring-Opening Radical Clock Reactions for Hybrid Organic-Silicon Surface Nanostructures: A New Self-Directed Growth Mechanism and Kinetic Insights." X. Tong, G. A. DiLabio, O. J. Clarkin and R. A. Wolkow, *Nano Letters*, 2004, 4, 357-360.

Reversible Passivation of Silicon Dangling Bonds with the Stable Radical TEMPO, Pitters, J. L.; Piva, P. G.; Tong, X.; Wolkow, R. A. *Nano Lett.*;3, 1431-1435 (2003).

The Role Of Physical Interactions In Self-Directed Organic Nanostructure Growth On Silicon, Gino DiLabio, Paul Piva, Peter Kruse and Robert A. Wolkow, in press, *Phys. Rev. Lett.*

The Ruse and the Reality of Nanotechnology, in press, University of *Alberta Health Law Review*.

"6-Amino-3-Pyridinols: Towards Diffusion-Controlled Chain-Breaking Antioxidants" M. Wijtmans, D. A. Pratt, L. Valgimigli, G. A. DiLabio, G. F.Pedulli, and N. Porter, *Angewandte Chemie International Edition* 2003, 42,4370-4373.

"The Effect of Ring Nitrogen Atoms on the Homolytic Reactivity of Phenolic Compounds: Understanding the Radical-Scavenging Ability of 5-Pyrimidinols" L. Valgimigli, G. Brigati, G. F. Pedulli, G. A. DiLabio, M. Mastragostino, C. Arbizzani, and D. A. Pratt, *Chemistry - A European Journal* 2003, 9, 4997-5010.

"Overlooked Difference Between Hydrogen Bonds of Equal Strength Formed Between Catechol and an Oxygen or Nitrogen Base. Experiments and DFT Calculations." M. C. Foti, G. A. DiLabio, and K. U. Ingold, *Journal of the American Chemical Society* 2003, 125, 14642-14647.

"Density Functional Theory based Model Calculations for Accurate Bond Dissociation Enthalpies. 3. A Single Approach for X-H, X-X, and X-Y (X, Y = C, N, O, S, Halogen) Bonds." E. R. Johnson, O. J. Clarkin, and G. A. DiLabio *Journal of Physical Chemistry* A 2003, 107, 9953-9963

"Solvolysis of para-Substituted Cumyl Chlorides. Brown and Okamoto's Electrophilic Substituent Constants Revisited Using Continuum Solvent Models" G. A. DiLabio and K. U. Ingold, *Journal of the American Chemical Society* 2004, 69, 1620-1624.

"Bond Strengths of Toluenes, Anilines and Phenols: To Hammett or Not" D. A. Pratt, G. A. DiLabio, P. Mulder, and K. U. Ingold, *Accounts of Chemical Research* 2004, 37, 334-340.

"Kinetic Studies on Stilbazulenyl-bis-nitrone (STAZN), a Nonphenolic Chain-Breaking Antioxidant in Solution, Micelles, and Lipid Membranes." S.C. Mojumdar, D. A. Becker, G. A. DiLabio, J. J. Ley, L. R. C. Barclay and K. U. Ingold, *Journal of Organic Chemistry*, 2004, 69, 2929-2936.

"Quantum Capping Potentials with Point Charges: A Simple QM/MM Approach for the Calcualtion of Large Molecule NMR Shielding Tensors." S. Moon, P. A. Christiansen and G. A. DiLabio, *Journal of Chemical Physics*, 2004, 120, 9080-9086.

SPECIAL/INVITED PRESENTATIONS

Talk to Edmonton Rotary club, Mar 2004

Distinguished Lecture series, Department of Chem. Eng. and Applied Chem., University of Toronto, March 2004.

Sigma Xi lecture, Edmonton Alberta

Physics Seminar, Simon Fraser University, Jan 2004

International Conference on Materials for Advanced Technologies, Singapore, Dec 2003.

Condensed Matter Physics Seminar at the University of Rochester, New York, Dec 2003

Health Law Institute, University of Alberta, ethical implications of nanotechnology, Nov. 2003

Edmonton Council for Advanced Technology lecture, Nov, 2003

International Conference on Atomically Controlled Surfaces, Nara, Japan, Nov. 2003

Nanotechnology Seminar at Purdue, Oct 2003

CIAR Nanoelectronics Molecular Electronics student school, July, 2003.

Molecules and Nanoscience, Montpellier, April 2003

Invited lecture, APS March meeting, Austin Texas, 2003