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14. ABSTRACT

The MURI center for Multidimensional Surface-Enhanced Sensing and Spectroscopy seeks to develop fundamentally new approaches to detect chemical and biological agents with unprecedented sensitivity and to provide chemical characterization of functional nanoscale materials for applications in photonics and electronics. A great deal of substantive progress has been made in all areas of this MURI project. The MURI PIs have authored or co-authored one hundred fifty three (153) peer-reviewed publications. In addition, the MURI Faculty gave approximately four hundred eighty (~480) presentations at meetings, conferences, and seminars were given. Peer recognition was high with the MURI Faculty receiving many prestigious awards. The highlights of the MURI project period were the election of Louis Brus and George Schatz to the U.S. National Academy of Sciences.

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MURI Center for Multidimensional Surface-Enhanced Sensing and Spectroscopy

Final Technical Report for July 1, 2002 – June 30, 2007

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2. Objectives

2a. Strategic Objectives

The primary science and technology objective of MURI F49620-02-01 was to design, develop, and implement new, ultrasensitive, multidimensional, surface-enhanced spectroscopic approaches for: a) the detection of chemical and biological agents and b) the chemical characterization of functional nanoscale materials for applications in photonics and electronics. In other words, our intent was to extract the maximum amount of chemical information from the minimum amount of sample in the shortest possible data acquisition time. The scientific achievements of this MURI, exemplified by its substantial list of publications, have indeed advanced the state-of-the-art in this field. The knowledge so generated will become the foundation for developing new sensing and spectroscopy platforms that will greatly advance the DOD technology base.

2b. Program Abstract

The MURI center for Multidimensional Surface-Enhanced Sensing and Spectroscopy seeks to develop fundamentally new approaches to detect chemical and biological agents with unprecedented sensitivity and to provide chemical characterization of functional nanoscale materials for applications in photonics and electronics. A great deal of substantive progress has been made in all areas of this MURI project. The MURI PIs have authored or co-authored one hundred fifty three (153) peer-reviewed publications. In addition, the MURI Faculty gave approximately four hundred eighty (~480) presentations at meetings, conferences, and seminars were given. Peer recognition was high with the MURI Faculty receiving many prestigious awards. The highlights of the MURI project period were the election of Louis **Brus** and George **Schatz** to the U.S. National Academy of Sciences.

3. Status of Effort

This section begins with the required 200 word MURI Status of Effort Summary Statement. It is followed by Status of Effort Statements for each MURI faculty member.

3a. MURI Status of Effort Summary (200 Word Summary)

MURI research activities have substantively advanced knowledge in the general area of molecular plasmonics which encompasses surface-enhanced sensing and surface-enhanced Raman spectroscopy (SERS). We have developed: a nanoscale electrical and optical sensing methodologies possessing a sensitivity of 1-10 molecules; new understanding of the basic science of excited metallic electrons, their interaction with adsorbed molecules and the plasmon states in Ag and Au nanoparticles; new insights into the enhancement mechanisms associated with single molecule SERS using 2D correlation analysis and isotopically labeled analytes; new instrumental approaches to confocal Raman microscopy, tip-enhanced Raman microscopy, and spatially correlated plasmon spectroscopy and AFM; a multidimensional frequency domain approach to calculate pulse propagation and detect distortions of multidimensional spectra that is applicable to both bulk and interfacial experiments; improved techniques in spectral interferometry used for 2D spectroscopy and a new method for measuring coherent infrared pulses by up-conversion of spectral interferograms into the visible; stable and biocompatible nanoparticles for biological tagging and detection using SERS; new understanding of the electromagnetic enhancement properties of nanohole arrays; new first principles theoretical

methods for understanding SERS; and developed new approaches for the fabrication of nanoparticle arrays and the characterization of their linear and nonlinear optical properties.

3b. MURI Faculty Individual Status of Effort Statements

Paul W. Bohn

The objectives of MURI research in the **Bohn** group over the 5-year period were: (1) implement an externally-controlled gap-closure strategy for preparing atom-scale gaps in a microfluidic electrochemical cell; (2) improve the reliability and robustness of junction formation; (3) demonstrate low mass sensitivity in a robust and regenerable platform; and (4) exploit porous GaN (PGaN) structures for chemical sensing. The present status, accomplishments, and new findings related to this effort follow. Additional discussion of Brus group Status of Effort is integrated with accomplishments and new findings in section 4.

Louis E. Brus

The objectives of MURI research in the Brus group over the 5-year period were: (1) to understand the basic science of excited metallic electrons, and their interaction with adsorbed molecules, in plasmon states of Ag and Au particles and (2) to understand the near field effect associated with plasmon states that allows Raman detection of single molecules under specific circumstances. Additional discussion of Brus group Status of Effort is integrated with accomplishments and new findings in section 4.

Alan Campion

The objectives of our research were: 1) to develop improved Raman microscopic and Raman near-field (NSOM) techniques for chemical imaging on the sub-micron and sub-100 nm length scales; 2) to understand the mechanism of surface-enhanced Raman scattering (SERS) and single molecule SERS and 3) to apply these methods and this understanding to detect and characterize chemical and biological agents at the ultratrace level and to characterize electronic and photonic materials on the sub-100 nm length scale.

We have acquired and installed a state-of-the-art four color Raman microscope and we have developed techniques for characterizing electronic materials that allow us to look selectively at various layers in multilayer films of interest comprising strained Si, strained Si on oxide and Si_xGe_{1-x}. In particular we have demonstrated surface depth selectivity to 4 nm, enabling the analysis of the topmost layer of interest in strained Si technology. We have also demonstrated the ability to measure strain in structures in which one dimension is as small as 10 nm. In our SERS work we continue to try to understand the role of co-adsorbed water in creating or stabilizing new metal/molecular charge transfer states that we believe play an important role in the so-called "chemical" mechanism of SERS.

David M. Jonas

The originally proposed objectives of our research were to: 1) understand several factors (i.e., pulse propagation and kinetic coupling) that control the signal intensity and observables of 2D FT optical spectroscopy in bulk samples; 2) discover new methods of background suppression and detection of vibrational transitions; and 3) develop for the first time methods to dramatically amplify the signal intensities of multidimensional infrared and Raman spectroscopy through electromagnetic enhancement at well-controlled nanofabricated surfaces. After MURI

year one, we added objective 4) developing 2D correlation analysis for single molecule and single nanoparticle spectra, which represented an unanticipated outcome of the collaboration between **Jonas** and **Rowlen**.

Work on (1) is essentially complete: we systematically developed, starting from Maxwell's equations, a multidimensional frequency domain approach to calculating pulse propagation and detection distortions of multidimensional spectra that is applicable to both bulk and interfacial experiments. We quantified the distortions of standard 2D spectra under typically attainable low signal conditions and discovered a new representation of 2D spectra with similar distortions under maximum signal conditions. We also found a way to determine vibrational symmetry in fully time-domain Raman experiments. Work on (2) led to improved accuracy (20 attosecond time delays) in spectral interferometry used for 2D spectroscopy and a new method for measuring coherent infrared pulses by up-conversion of spectral interferograms into the visible. The new method has multiplex and cost advantages over infrared detector arrays, and has comparable if not better sensitivity. In work on (3), our signals never exhibited a lowest order power dependence, there are indications from other MURI work that the nonlinear enhancement is shifted from the linear enhancement, and there are indications from other MURI work that molecules are trapped in SERS active sites by weak cw fields, which would not occur in a pulsed experiment. Work on (4) resulted in the discovery that SERS active sites have some molecular specificity, which we have subsequently attempted to characterize.

Shuming Nie

Nie developed stable and biocompatible SERS nanoparticles for biological tagging and detection. In particular, a new class of pegylated SERS nanotags was prepared and is now ready for use. They have been tested for various biological samples.

Kathy L. Rowlen

Rowlen achieved significant progress over the course of the MURI grant. We have discovered complexities of the surface adsorbate relationship that influence both the blinking phenomena and SERS. We anticipate that these discoveries will play a critical role in the implementation of SERS as an ultra-low detection limit sensing technology. A highly successful collaboration with both Prof. Jonas on two-dimensional correlation spectroscopy has yielded insight into the complex interrelated optical effects observed in single molecule SERS (SMSERS). In collaboration with **Schatz**, the electric field distributions in nanoaperture arrays were modeled and proved to be crucial in advancing our understanding the surface-enhancing capabilities of nanoaperture arrays. This collaboration also allowed us to use theory to guide experiment and to provide a necessary foundation for the computational models being applied to real-world nanosensing systems. Our most recent advances have involved the incorporation of SERS active nanomaterials into organic semiconductors for enhanced photoconversion. Preliminary findings indicate these nanomaterials do enhance light absorption in organic semiconductors.

George C. Schatz

Schatz was involved in the following projects that were designed to provide theory and modeling support for the experimental program:

1. *Studies of the electrodynamics of molecules adsorbed on anisotropic nanoparticles and nanoholes to determine what structures lead to the largest SERS enhancements and to the*

largest extinction sensitivities. Included was a comparison of particles and holes having the same structure, and studies of the influence of local dielectric environment. The studies also included both isolated particles and small clusters, and we performed extensive studies of electromagnetic hot spots. This work demonstrated the quantitative predictive value of classical electromagnetic theory in studies of SERS. We also demonstrated that the excited states of molecules near metal particles are largely unperturbed by the particles, unless molecule-molecule interactions are strong.

2. *Studies of metal nanoparticle array structures, to study SERS enhancement factors.* Early in the funding period we discovered that arrays of relatively large (100 nm) silver and gold particles that are separated by the wavelength of light (multiplied by the local index of refraction) have strong photonic resonances that can couple to plasmon resonance excitation in the particles to produce narrow extinction lineshapes and intense SERS. This work was greatly extended during the project to establish the sensitivity of these results to array structure, and we eventually discovered that the combined photonic/plasmonic resonances can be used to "steer" light.

3. *Electronic structure methods to enable the calculation of frequency dependent polarizabilities and polarizability derivatives to model extinction and SERS from first principles.* The bulk of our work involved using time dependent density functional theory methods that we were able to apply to small clusters such as Ag_{20} and Au_{20} interacting with small molecules like pyridine. These studies demonstrated that SERS can be understood using electronic structure theory, with electromagnetic effects being the dominant contributor to the enhancement.

These projects are designed to provide important input to the design of SERS experiments as well as interpretation to on-going extinction/Raman measurements by many of the group members. Several papers were written in collaboration with **Van Duyne**, and we also did joint projects with **Spears** and **Rowlen**. In addition to these projects, we developed a collaboration with **Stephen Gray** at Argonne National Laboratory to develop finite difference time-domain (FDTD) software for time-dependent electrodynamics studies of nanoparticle systems, including studies of nanoscale holes.

Kenneth G. Spears

Spears was involved with the systematic fabrication of nanoparticle arrays and characterization of their properties has uncovered a number of new insights into nanoparticle interactions that will make new designs possible for a variety of applications.

Richard P. Van Duyne

The objectives of MURI research in the **Van Duyne** group over the 5-year period were: (1) linear and nonlinear plasmonics of nanoparticle arrays fabricated either by nanosphere lithography (NSL) or electron beam lithography (EBL); (2) the fundamentals of surface-enhanced Raman spectroscopy (SERS) with a emphasis on single molecule SERS (SMSERS) and the role played by coupled molecular and plasmon resonances; (3) tip-enhanced Raman spectroscopy (TERS); (4) spatially correlated plasmon spectroscopy with atomic force microscopy (AFM); and (5) surface-enhanced sensing. Additional discussion of the Van Duyne group Status of Effort is integrated with accomplishments and new findings in section 4.

4. Accomplishments/New Findings

Paul W. Bohn

Implement an externally-controlled gap-closure strategy for preparing atom-scale gaps in a microfluidic electrochemical cell. We developed an externally-controlled gap-closure strategy for preparing atom-scale gaps in a microfluidic electrochemical cell and successfully halted the gap closure at a resistance value corresponding to the conductance quantum, $G_0^{-1} = h/2e^2$. The strategy exploits a combination of lithography, microfluidics, and electrochemistry to prepare atom-scale junction electrodes that can be used as the active nanosensing elements in a conductance-based sensor. Control over junction conductance, G, is largely due to the active termination step, in which current through the gap is monitored continuously, and the directional electrodeposition is terminated when a current corresponding to the desired number of conductance quanta, $G_0 = 2e^2/h$, is reached. To regenerate the device, the atom-scale junction is broken with a potential sweep, the microfluidic channel rinsed, and the junction can be reformed with a subsequent comparator-terminated directional electrodeposition. The circuit designed to achieve active termination of growth of the atom-scale junction is shown in **Figure 1**.

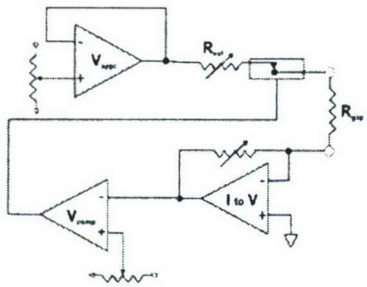


Figure 1. Comparator-based mechanical relay triggers directional electrodeposition to stop when current reaches a preset threshold.

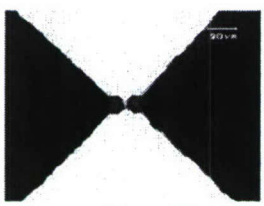


Figure 2. Optical micrograph of a closed atom-scale junction. Scale bar is 20 μm.

Improve the reliability and robustness of junction formation. Perhaps the most crucial aspect of our strategy from the standpoint of practical sensing applications is the robustness and the capacity to make repeated measurements. Our original approach utilized a two-step thickening/growth process, in which the original photolithographically prepared microelectrodes were first propagated by omnidirectional electrodeposition on both electrodes, then directional (vectorial) electrodeposition was used to complete the atom-scale junction. An optical micrograph of a junction prepared in this manner is shown in **Figure 2**. We sought to improve the reliability and robustness of junction formation, primarily through the development of electron-beam lithographically defined starting structures on Si <100>, rather than glass (**Figure 3**). Processing on a silicon <100> wafer also improved electron beam processing time, because the wafer was easily broke into nine 25 mm square samples after writing the e-beam nanotips and aligning the contact pads (Cr mask). A commercially-

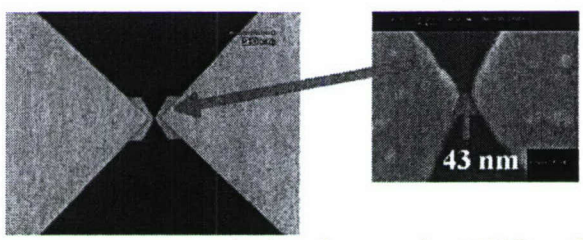


Figure 3. Optical micrograph (40X) of electrodes with nanotips (left), and high resolution SEM image of nanotips (right). Electron beam lithography was used to form the nanotips with a spacing of ~40 nm.

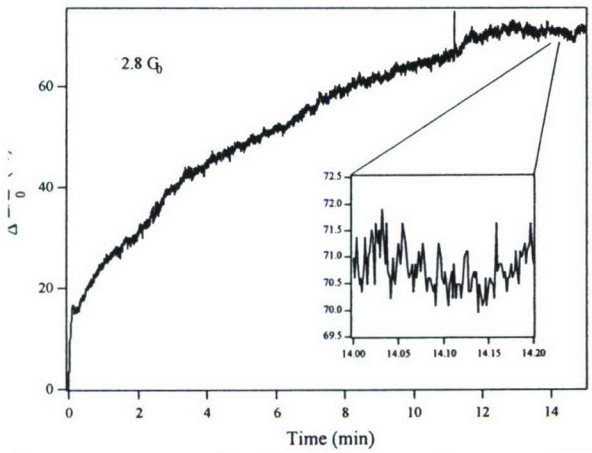


Figure 4. Normalized impedance change, $\Delta Z/Z_o$ (%), at 5 kHz in an atom-scale junction (2.8 G_0) after adding 10 mM HDT/EtOH. The inset shows an expanded portion of the saturation region of the curve, which can be used to assess the noise associated with the electrical measurement from all sources.

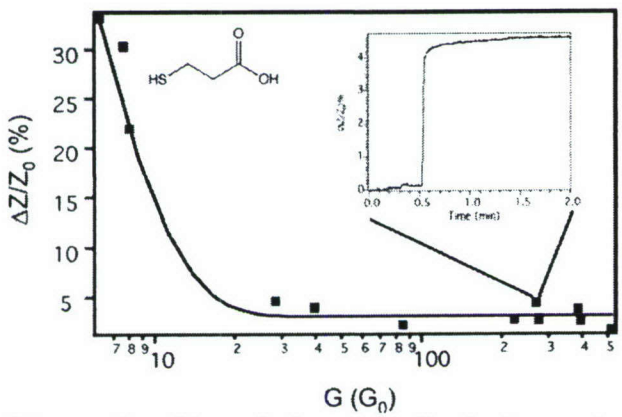


Figure 5. Plot of the normalized change in impedance ($\Delta Z/Z_0$) from introducing MPA/H_2O to atom-scale Au junctions of various sizes, as characterized by the intrinsic conductance in units of G_0. (*Inset*) Assembly curve for one specific junction of ~280 G_0.

produced laser-drawn Cr mask with nine electrodes was designed and purchased. The e-beam lithography nano-scale starting gaps enabled three major improvements in junction formation: (1) atom-scale junctions can be formed much quicker than with photolithographically-produced μm-scale starting gaps (~1 min vs ~30 min); (2) the silicon substrate eliminated charging during SEM imaging, improving the resolution (< 5 nm) of SEM images used to estimate the junction length for calculating the junction thickness; and (3) the success rate for producing high sensitivity ($G < 5G_0$, *vide infra*) atom-scale junctions rose from a few percent, with photolithographically-formed starting structures, to >80%, thereby greatly facilitating progress on building chemical sensor structures.

Demonstrate low mass sensitivity

sensing measurement is made by measuring to the atom-scale junction. **Figure 4** shows introducing 10 mM HDT to a 2.8 G_0 atom- impedance change of 71% ± 1%) and the ifferent than observed for the same adsorbate onolayer coverage of HDT produces *ca.* 2% from 1 mM solution. Clearly the fractional the atom-scale junction. The same low-noise ients are also observed here. The noise in the **nset**) represents the sum of all noise sources. ve rise to a signal equivalent to this 1% noise on the estimated (hemicylindrical) junction pproximate HDT coverage of 4 x 10^{14} cm^{-2}, molecules. In a subsequent experiment the ge were decreased for greater precision, and nding to a population fluctuation of a single

The relevance of this approach to nanosensor technology is clear. The most important characteristics of the device described here are: (1) the ability to regenerate the sensing structure once used, and (2) its extreme sensitivity. By utilizing a self-limiting fabrication strategy and by incorporating all of the critical fabrication steps within a microfluidic channel, it is possible to sequentially prepare an atom-scale junction with precisely defined conductance properties, test an analyte-containing solution, then break the connection, regenerate the atom-scale junction and perform another measurement cycle. The other salient feature is its extreme mass sensitivity. By exploiting the inherent low-noise properties of the I-V measurement at an atom-scale gold

junction, it is possible to assay very small numbers of analyte molecules, a necessary capability for use in mass limited chemical analysis. The capabilities of these structures for measurements of small numbers of adsorption/desorption events makes a powerful case for pushing the limits of sensitivity to electrical measurements of single molecule events. Finally we note that the self-limiting control strategy employed is equally well-suited to the formation of atom-scale gaps, which could then be derivatized suitably to yield wires in which the conductance is ultimately determined by molecular properties.

We also explored the relationship between the junction characteristics and sensitivity. Large area thin films of Au display normalized conductance changes of the order 2-3% upon the formation of a full monolayer of Lewis base, *e.g.* HDT. The experiments summarized in **Figure 5** illustrate that similar sensitivities are obtained for nanowire junctions in the regime $G > 20\ G_0$. However, junctions with initial conductivities in the range $G < 20\ G_0$ display enhanced sensitivity to the adsorption of mercaptopropionic acid (MPA). These experiments yield two important conclusions: (1) they define the target range of atom-scale junctions which can exhibit significantly enhanced sensitivity relative to thin film sensors, and (2) they illustrate that the sensitivity obtained for measurements of MPA adsorption are comparable to those obtained with HDT.

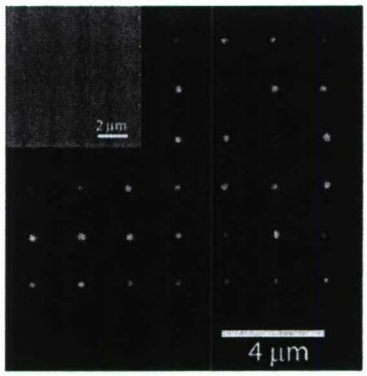


Figure 6. Multiphoton luminescence image of the etched PSi pattern produced from the FIB-Pt pattern shown in the SEM image in the *inset*.

Exploit porous GaN (PGaN) structures for chemical sensing. Our efforts to produce nanoscale pixel arrays of porous optoelectronic materials focused on the development of light scattering, photoconductivity and photoluminescence responses from these structures. A unique metal-assisted electroless etching approach was developed for the preparation of porous Si (PSi) and GaN (PGaN), which is contactless and is capable of spatially directing the etching of these materials, *viz.* **Figure 6**. To further enhance the utility of these structures for nanoscale chemical sensing we developed a metallization strategy for PGaN via electroless deposition of Au and Pt in the nanopores. The high surface activity of Au towards PGaN biases Au deposition on PGaN toward cluster formation, but Pt was obtained either as Pt clusters or thin film coatings by careful selection of the deposition conditions. These deposition strategies were exploited to produce high surface-area surface enhanced Raman spectroscopy (SERS) substrates. The SERS signal strength across the metal coated PGaN substrates was uniform and was not plagued by "hot" or "cold" spots on the surface, a common problem with other SERS surfaces. Ag films deposited by electroless deposition exhibited the highest overall SERS response, with an enhancement factor relative to normal Raman spectroscopy of 10^8. A portion of the increase in EF relative to typical SERS-active substrates could be assigned to the large surface area characteristic of the PGaN-Ag structures, but some of the enhancement was intrinsic and likely related to the specific morphology of the metal-nanopore composite structure.

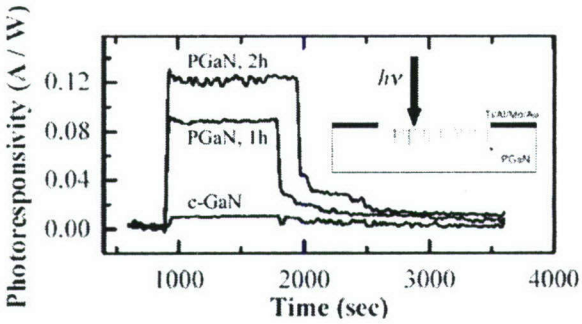


Figure 7. Buildup, steady state and decay transients of the photoresponse for crystalline (unetched) GaN, PGaN after 1 h etching, and PGaN after 2 h etching. (*Inset*) Geometry of the samples used for both dark and photoconductivity measurements.

The ultraviolet photoconductivity of PGaN-based conducting structures was also investigated. The photoresponse of PGaN prepared from highly doped GaN ($n > 10^{18}$ cm^{-3}), *viz.* **Figure 7**, shows enhanced (15x) magnitude and faster decay of persistent photoconductivity relative to bulk crystalline (CGaN), suggesting advantages for nanostructured PGaN in photodetector applications. A space charge model for changes in photoconductivity was used to explain these observations. Heightened defect density in the etched material plays an important role in the enhanced photoconductivity in PGaN. Flux-dependent optical quenching (OQ) behavior, linked to the presence of metastable states, was also observed in PGaN as in CGaN.

The most recent efforts of the **Bohn** Group have focused on improving the controllability of the electrochemical deposition (ECD) process by protecting most of exposed area of Au film with an oxide. After formation of electromigration-generated nanogaps in a narrow (100 nm – 1 μm) Au bridge a 3-μm slot on top of the bridge is subsequently opened by conventional photolithography. This approach has two advantages. In the fabrication stage the atom-scale junction is easier to grow, because much less Au is consumed. Then, in the measurement stage, the results are limited to adsorption only in the immediate vicinity of the atom-scale junction by the lithographic masking step. A typical example of such a structure is shown in **Figure 8**. Directional ECD was accomplished using cysteine as a deposition additive and an exposed slot only 2-3 μm wide on top of the nanogap. Even though the exposed area is small, the two exposed Au areas constitute a nearly ideal anode/cathode pair. Since the gap formed by electromigration is in the order of nm, the ECD process can be accomplished in a single step in a solution of 2mM $HAuCl_4$ in 50mM $HClO_4$ containing 0.1 mM cysteine as the additive. Step-wise conductance changes are always discernable when the junction forms. We are now ready to test these structures for the improved sensitivity for which they were designed.

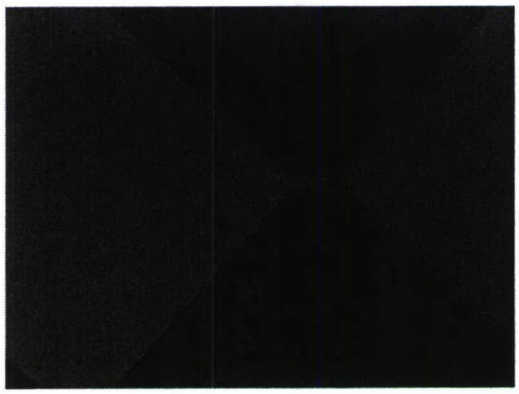


Figure 8. Photomicrograph showing the photolithographically defined slot covering the area of the nanogap opened in the Au bridge.

Louis E. Brus

Single Molecule Surface Enhanced Raman Spectroscopy. We systematically investigated the basic science of electromagnetic field enhancement that occurs at the junctions of large ca. 40 nm diameter Ag nanocrystals. In a small region of space at the junction, the field enhancements are so high that single molecule Raman spectroscopy is possible, if the molecule

is also electronically resonant with the laser. We extended this work to other consequences of field enhancement. We did calculations on optical forces between particles due to the instantaneous, un-dephased electronic polarization -- this polarization also creates the near field electromagnetic enhancement.

This work has used thermally prepared Ag colloidal particles from reduction using citrate; the test molecule, the dye R6G, was present by accident at the junction. The particles have a fairly wide size distribution, and are partially aggregated by the addition of salt. We studied the correlation between near field Raman enhancement and far-field Rayleigh scattering enhancement. We have also looked carefully at the blinking and spectral fluctuation of the emission spectrum, with an apparatus that simultaneously records the S and P Raman spectra after grazing incidence irradiation. These studies show that the fluctuation occurs in the cross section magnitude, and not in the orientational tensor properties of the Raman scattering. A systematic study of the angle of incidence dependence of the Raman depolarization ratio implies a simple uniaxial (non rotating and non degenerate Stokes dipole) Raman scattering. This is expected if one molecule is present at one junction in the compact aggregate of Ag nanocrystals.

We tentatively assign the fluctuations in the spectrum intensity to desorption and adsorption kinetics in the junction. If this is true, then it implies that the coupling between the molecular vibrations and the huge oscillating AC transition dipole in the Ag nanocrystals occurs by electron exchange, and not by canonical near field scattering. In this connection we tentatively assign the underlying Stokes shifted continuum to electronic Raman scattering from the metallic Ag electrons. Normally this is absent in crystalline Ag, but it is known to occur in the presence of defects. We believe the adsorbed dye molecule acts as a scattering defect for the optically excited AC polarization electrons. We have shown, using numerical solutions to Maxwell's equations inside the nanocrystals, that these electrons concentrate at the junction in a form of coherent capacitive coupling.

Spontaneous Electrochemical growth of Field Enhancing Ag Nanocrystals in water. Nanocrystal physical properties, including the Fermi energy and redox potential, differ from those in the bulk material in theory. We found that significant morphological reformations of thermally evaporated silver nanoparticles on conducting surfaces in aqueous solutions. We found that the reformation is caused by an electrochemical Oswald ripening mechanism. In this mechanism, small particles are scavenged by larger ones due to the shifted equilibrium potential and work function of small particles (less than100nm). Silver metal thin films were thermally deposited under vacuum onto polished fused quartz slides, indium tin oxide (ITO) coated quartz slides, and freshly cleaved highly oriented pyrolytic graphite forming arrays of nanoparticles. The films were exposed by placing a drop of solution on the substrate in ambient conditions. Films exposed to a potential were placed in a two electrode system with a clean piece of ITO as the counter electrode. The samples were imaged using a high resolution SEM and elemental analysis was carried out using EDX. It was found that silver thin films in the sub 200nm range reshape in aqueous solution to form pure silver faceted structures up to 2um in size on conducting substrates. Films exposed to solution while held under a reducing potential were found not to react thus suggesting an electrochemical mechanism. This new process can be used to grow desired structures.

Plasmon Laser Irradiation Thermal and "hot electron" Photochemistry. We studied optically induced Cu^{2+} reduction onto gold nanoparticles, under electrochemical potential control

on a transparent ITO electrode. The photocurrent is a nonlinear function of laser intensity and increases sharply with cathodic voltage in the underpotential deposition region. We explore both single electron excitation and thermal heating mechanisms. Our present data are understood as due to laser heating, causing a temperature rise of just a few Kelvin. Simulations of the Butler-Volmer equation within our underpotential deposition conditions show that such a modest temperature rise can increase the reduction current by one or two orders of magnitude.

As the MURI program began in 2002 we reported that low intensity optical plasmon irradiation, in aqueous Ag colloids, photocatalyzes adsorbed Ag^+ reduction, leading to particle growth. The irradiation wavelength controls the particle shape. As shown by Mirkin, plasmon excitation can also photocatalyze small Ag colloid reformulation into large truncated prisms, and even fusion of such prisms into yet larger prisms. The mechanisms of these processes are not well understood. The Ag electrochemical potential, unknown in these colloidal experiments, should be a critical parameter. In 2007 we made progress in understanding these experiments. The photo-catalyzed reduction of aqueous silver ions, by citrate adsorbed on silver nanocrystals, was studied on Formvar/carbon TEM grids and in photoelectrochemical cells. The reaction was characterized by transmission electron microscopy (TEM) monitoring of individual particles throughout the growth process. The photo-initiated growth on the silver particles is uniform and is not dependent upon the laser polarization. The photo-charging is initiated by Ag plasmon electronic excitation which causes the "hot hole" oxidation of surface bound citrate ions. The potential of silver particle working electrodes was shown to shift negatively under irradiation in solutions of citrate. Adding silver ions to this system quenches the charging of the particle working electrode through charge-transfer to the silver ions. In aqueous citrate solution, the particles discharge by reducing hydrogen. The electrochemical kinetics is quantitatively modeled using the Butler-Volmer equation. The capacitance of the particle electrode is experimentally determined to be $\sim 2.22 \times 10^{-4}$ C/V. We conclude that high quantum yield surface photochemistry and photo-charging is possible for well formed nanocrystals.

Alan Campion

Measuring Composition and Strain in Si and Si_xGe_{1-x} Thin Films and Structures. We have developed a comprehensive protocol for analyzing composition and strain in semiconductor thin films and structures nondestructively using Raman microscopy. We routinely achieve a precision of one part in 10^4 in the strain and better than 10% in the composition in Si_xGe_{1-x} alloys. Our measurements do not require ancillary techniques for calibration, obviating the need for destructive ultrahigh vacuum techniques like secondary ion mass spectrometry, for example. Theoretical lateral spatial resolution using 325 nm excitation is better than 200 nm. The outermost layer of a multilayer film stack can be probed selectively and nondestructively with a sampled depth of 4 nm. We have also demonstrated the ability to probe composition and strain as a function of depth, using beveled samples, with a depth resolution of 4 nm. Finally, we have demonstrated the ability to measure strain in structures with one lateral dimension as small as 10 nm, which is a remarkable result considering that the spatial resolution of our probe is at best only about 200 nm. As long as the area of the strained region is at least 5-10% of the area probed by the focused laser beam, the position of the strain-shifted Raman band, which appears as a shoulder on the relaxed Si peak, can be measured quite precisely and the strain determined accurately. It is clearly not necessary to spatial resolve the distribution of strain in a sample to be able to detect and quantify it.

The techniques that we have developed during the MURI period have been used to support a number of collaborative projects directed towards achieving an understanding of the issues involved in the processing of strained Si and SiGe alloys to make devices with feature sizes relevant to the 65 to 45 nm ITRS nodes. These issues include, for example, the factors that govern the persistence or relaxation of strain as wafers undergo typical manufacturing steps like ion implantation and annealing. We have shown that the strain persists in patterned regions in extremely thin films (4 nm) of strained Si on insulator with lateral dimensions on the order of 500 nm or so. We have investigated the strain state in these materials after they are subjected to typical ion implantation and annealing cycles and find that strain relaxation becomes increasingly important as the perimeter/area ratio of the feature size increases for small features. This observation supports the widely held view that relaxation propagates from the edges of structures inward. We have also looked at model systems for inducing local strain in Si lines bordered by Si_xGe_{1-x} lines of various compositions and dimensions. Throughout our investigations our focus has been on developing the measurement capabilities and applying it to systems of particular interest to our industrial and consortium collaborators. We anticipate additional publications from this work once these collaborators review the results for intellectual property and proprietary issues.

Development of Raman Near Field Optical Microscopy (NSOM). During the period of this MURI we have constructed and tested three different Raman NSOMs. Our goal was to design an instrument that would reliably and reproducibly obtain Raman spectra from a wide variety of samples with sub-100 nm spatial resolution. We started with a NIST design and discovered, after much effort, and even with the gracious advice of its designer, that the instrument was simply not stable enough mechanically for routine use. The first generation system used a near-field-illumination/far-field-collection geometry. Three piezoelectric transducers supported the sample holder in a slip/stick arrangement; tilting the piezos moves the sample up or down for coarse *z* positioning. A second set of piezos (transmitting and listening) was used for fine positioning; the resonance frequency and phase of the signal changed as the tip experienced the shear force of interaction with the surface. The chief problem with this design was the system of optical rails and platforms that held the various components together; accessing any component of the system required complete disassembly and reassembly, making it impractical to further the development of that design.

With the issues outlined above in mind we designed a second-generation Raman NSOM in which each layer of the microscope was mounted on or within an aluminum ring. These rings were kinematically aligned so that each layer could be removed, worked on and replaced without disturbing the optical alignment of the rest of the system. The ellipsoidal mirror/microscope objective combination used for collecting forward or backscattering, which was part of the original NIST design, was retained. A key feature of the second generation NSOM was that the *z* motion was separated from the motions in *x* and *y*, greatly facilitating alignment and both coarse and fine *z* focus. Linear actuators controlled the z position. We demonstrated the ability to detect Raman scattering from diamond in the forward scattering geometry with excellent signal-to-noise ratios and established from the retraction curve that we were in the near field limit. After a considerable amount of effort, however, we concluded that this geometry was not optimal for backscattering, which is the required geometry for opaque materials like silicon so we constructed a third generation instrument, which is now under test.

The third generation system employs the near-field-illumination/near-field-collection geometry in which the backscattered Raman radiation is collected by the NSOM tip and sent back through the fiber to the spectrometer. The sample is scanned in the x,y plane by a single quadrant-poled piezo and z axis control is provided by a dual element positioning system comprising a piezo rigidly mounted to a linear actuator. We are currently investigating two different feedback mechanisms simultaneously: 1) optical feedback, in which the laser light scattered from the tip/surface region is attenuated as the tip approaches the surface and 2) miniature tuning forks whose resonance frequency and phase change as the tip engages the surface. We are optimistic that this new design will open up the possibility for more routine Raman NSOM measurements than have been previously possible.

SERS Mechanism(s). We continue to try to understand the role of electronic excitations in the so-called chemical enhancement mechanism of SERS. We have focused on the role of co-adsorbed water in developing the new electronic excitations thought to be responsible for the enhancement observed for certain anhydrides adsorbed on Cu(111) single crystal surfaces in ultrahigh vacuum, for which the electromagnetic enhancement is negligible. It has been necessary to modify our ultrahigh vacuum surface Raman spectrometer so that we can dry these anhydrides completely and then prepare a series of complexes with known water/anhydride ratios. The results of these experiments will be compared with high-level quantum chemistry calculations underway that take advantage of the capabilities of the Teragrid.

David M. Jonas

Multidimensional Spectroscopy. In optical analogs of 2D magnetic resonance, an absorbing sample is required to generate a nonlinear signal, but the excitation pulses and signal are then necessarily distorted by propagation. Thus, quantitative interpretation of 2D optical spectroscopy requires a treatment of propagation effects, and we published a new multidimensional frequency domain solution of this problem in 2004 (letter) and 2005 (full paper). In 2005/2006, we used our theory to treat propagation and non-collinear detection distortions on peak shapes in bulk 2D spectra. Sample absorption and non-collinear detection distortions are significant at the 10% level for typical small signal experimental conditions. We have also discovered a transformation of 2D spectra that reduces propagation distortions to below 10% for the sample absorption that generates maximum signal. This transformation, described in a 2007 publication, requires knowledge of only the standard 2D spectrum and the absorption spectrum of the sample, enabling experiments in strongly absorbing samples or at buried interfaces. This left non-collinear detection distortions as the primary source of error in 2D experiments: ways of reducing this distortion are important because it affects interfacial signals, especially when sample scattering (encountered in SERS substrates) necessitates increased crossing angles. In 2006/2007, we extended our studies of propagation and detection distortions of peakshapes in 2D spectroscopy to 2D spectra with cross-peaks. We found that 2D spectra with well-separated peaks can be corrected for propagation effects in the same way as 2D peakshapes and discovered that detection distortions could be corrected on a peak by peak basis. In this manner, it is possible to obtain 2D spectra at peak optical densities of around one, where signal is maximized, with distortions of less than 10%. A manuscript describing this work is nearing completion.

A related investigation of the relationship between real and imaginary parts of 2D spectra revealed that the time domain data underlying 2D spectra are not strictly causal when a non-collinear beam geometry is used, and that there are two sources of departures from causality. The first is a distortion from interference detection which is closely related to the crossing-angle smearing encountered in time domain measurements of pulse duration. This first departure from causality disappears for plane waves and a point detector. The second arises from propagation of non-collinear plane waves and is related to a smearing effect encountered in spatially encoded single-shot pulse duration measurements: it disappears for an infinitely thin sample. These distortions can cause a breakdown of the Kramers-Kronig relations between real and imaginary 2D spectra. Apart from these distortions, the real and imaginary parts of 2D spectra obey Kramers-Kronig relations that are analogous to those in linear optics and 2D magnetic resonance.

We found an all time-domain approach to determining the symmetry of Raman active vibrations through the pump-probe polarization anisotropy. This approach is fundamentally based on the same microscopic factors as the frequency domain Raman depolarization ratio and should be useful in time domain SERS experiments. A manuscript describing this work has been completed. This polarization method, which also provides information on excited state electronic dynamics, has been very useful in NSF supported studies of electronic motion at conical intersections.

We built a stabilized interferometer and used it for the first tests of the accuracy of spectral interferometry, the method used for measuring optical fields in 2D spectroscopy. Our early measurements indicated 20 attosecond accuracy for time delays, but revealed systematic errors in the constant phase shift. In 2007, re-investigation of the phase-shift errors led us to realize that the resolution function of standard spectrograph designs (e.g. Czerny-Turner) is both asymmetric (due exclusively to the spherical aberration known as coma) and appreciably wavelength dependent (also largely due to coma - the ideal grating resolution is negligible). The wavelength dependence is large enough to account for the observed systematic phase shifts. We have developed an algorithm to correct for both asymmetry and wavelength variation of the resolution function simultaneously. The algorithm is working on simulated data and we are currently testing whether the new correction for wavelength dependence of the resolution function finally removes the systematic phase shift errors which have plagued experimental data. Some preliminary data give 10 attosecond accuracy for time delays.

In collaboration with Manuel Joffre and Kevin Kubarych at Ecole Polytechnique (France), Nadia Belabas and Amy Moore demonstrated a novel way to characterize ultrashort mid-infrared pulses through upconversion with the stretched pulses obtained from the uncompressed output of a chirped-pulse amplifier. The power spectrum thus translated into the visible region can be readily measured using a standard silicon CCD camera-based spectrometer. The spectral phase is characterized using a variant of zero-added-phase spectral phase interferometry for direct electric field reconstruction. This is a general method that provides a multiplex advantage over conventional HgCdTe array-based methods in the infrared. This multiplex advantage arises not only from the available detectors, but has a fundamental origin in the smaller diffraction limit in the visible. Preliminary indications are that sensitivity is competitive with, and with sufficient up-conversion pulse energy, may surpass that of infrared detector arrays for detection of femtosecond pulses.

Single Molecule Surface Enhanced Raman Spectroscopy. We applied a 2D correlation analysis to single molecule and single nanoparticle spectra during the first year of MURI support. This led the Rowlen group to rebuild their apparatus to obtain clean single molecule spectra of R6G suitable for 2D correlation analysis. The signatures of spectral diffusion identified in the preliminary work were less pronounced in the single molecule data. We found that slices through a 2D covariance map are useful for identifying the continuum involved in SERS enhancement. A principal result is that two different continua are involved: The first, centered at ~1600 cm^{-1}, enhances the single molecule SERS spectrum of R6G; A second, centered at ~3000 cm^{-1}, enhances the sharp lines in the SERS spectrum of the native colloid (four occur near ~1600 cm^{-1} even in the absence of R6G, due to contaminant molecules on the surface of the nano-particles). The covariance slices clearly showed that all of the sharp R6G Raman peaks are correlated to the same continuum, even if the Raman peaks lie in the far wings of the continuum (for example, the 623 cm^{-1} line). The same is true for the SERS Raman peaks from the native colloid. The 3000 cm^{-1} does not enhance R6G Raman spectra and can be identified with a non-enhancing continuum reported by **Brus** in single molecule SERS from R6G. Conversely, the 2D correlation map shows the ~1600 cm^{-1} continuum does not enhance the SERS spectra of the native colloid. Our interpretation is that these continua arise from two different SERS active sites, that R6G is enhanced exclusively by sites with a ~1600 cm^{-1} continuum, and that the contaminant is enhanced exlusively by the site with a ~3000 cm^{-1} continuum. These results may also help explain the apparent discrepancy between the single molecule studies and the earlier picosecond Raman gain studies of Heritage and co-workers, who found that no more than 25% of the continuum near the cyanide SERS peaks could arise from Raman processes. We suggest that the cyanide SERS peaks are enhanced by a continuum which has low amplitude in the vicinity of the cyanide peaks, so that the continuum adjacent to the peaks may be dominated by luminescence even if a Raman process in the metal is responsible for the enhancement. A communication describing this work was published in J. Am. Chem. Soc. and highlighted as an "Editor's Choice" in Science magazine. This work is clearly leading to an important advance in fundamental understanding of the SERS process needed for systematic exploitation of the SERS effect in sensing applications of importance to DOD. In particular, it strongly suggests that SERS active sites must be specifically engineered to enhance the Raman spectrum of a given target molecule. This might explain the difficulties encountered in fabricating controlled substrates for single molecule SERS. Further, this selective enhancement of particular molecules by certain SERS active sites might even be used to actively discriminate against a background of contaminants.

In collaboration with **Van Duyne**, we found spectral splittings in 2D time-dependent correlation spectra of SERS signals from single colloidal nanoparticle clusters with hundreds of adsorbed molecules per nanoparticle. The simultaneous splitting of most lines into two lines of equal intensity is evidence that the SERS process is dominated by only one or two molecules despite the presence of hundreds. This supports the hypothesis, advanced soon after the discover of single molecule SERS, that measured bulk SERS enhancements result from much larger single molecule enhancements for a subset of molecules on the surface.

The above results indicated a need to understand the unexpected molecular specificity of single molecule SERS active sites on 'dirty' surfaces such as those resulting from colloidal preparations. While investigating the oxygen induced photo-blinking of thin silver films, we have discovered that argon purging is superior to nitrogen purging for maximizing the total resonant radiation, but that both gases enhance the sharp Raman lines on top of the continuum by

about the same amount. The origin of this difference probably arises from an interaction between nitrogen and the sites that contribute to the continuum, currently hypothesized to contain small silver clusters, on the surface.

Shuming Nie

A new class of biocompatible and nontoxic nanoparticles for in-vivo tumor targeting and detection has been developed by using pegylated gold nanoparticles and surface-enhanced Raman scattering (SERS). A major discovery is that various Raman reporters (small molecules used for spectroscopic encoding) are not displaced, but are stabilized by thiol-modified polyethylene glycols (PEG). These pegylated SERS nanoparticles are over 200 times brighter than semiconductor quantum dots with light emission in the same near-infrared window. When conjugated to tumor targeting ligands such as single chain variable fragment (ScFv) antibodies, the conjugated nanoparticles are able to target tumor biomarkers such as the epidermal growth factor receptor (EGFR) on human cancer cells and in xenograft tumor models with high specificity and affinity. The pegylated gold nanoparticles are dual-modality probes for optical and electron microscopic imaging, and also plasmonic light-absorbing materials for photothermal cancer imaging and therapy.

Kathy L. Rowlen

Substantial accomplishments have been made over the last five years. Our accomplishments have been partitioned according to three themes: a) photodynamics of Stokes-shifted light from SERS active systems, b) fabrication and characterization of designed SERS active nanomaterials, and c) advanced solar conversion materials incorporating SERS active nanoparticles.

Photodynamics of Stokes-shifted light from SERS active systems. Initial studies reported on the temporal fluctuations in the Raman spectrum from molecules adsorbed to noble metal colloids (i.e., "blinking"). Typically, blinking has been viewed as a single molecule signature. We demonstrated that silver colloids exhibit blinking that is independent of the nature of the adsorbate. Blinking was observed on silver colloids in the presence and *absence* of a SERS probe (e.g., R6G, BPE), sodium chloride, poly-L-lysine, an alkanethiol layer, and a liquid overlayer (e.g., water, ethanol). These observations suggest that the mechanism that gives rise to blinking is insensitive to the nature of the adsorbate and is likely to be a property of the nanoparticle. Consistent with this idea, blinking was observed from vapor deposited silver films and silver powders with no added molecular probe. In addition, two distinct broad luminescence-like (continuum) features also exhibited blinking and spectral diffusion, with no apparent adsorbate dependence.

As an alternative to colloids, the utility of vapor deposited thin metal films (TMFs) for mechanistic studies of SERS was evaluated. TMF morphology can be fully characterized and these substrates are also less variable in chemistry and morphology than colloids. Like colloidal particles, TMFs can exhibit single molecule detection via Raman scattering and display blinking behavior. Image analysis of the surface optical response on a native thin silver film during excitation revealed a dynamic system that blinked and photobleached with time. A mechanism involving silver clusters as an emitting species has been developed and discussed in the context of the integrated frequency-shifted intensity as a function of time. In addition, the role of oxygen has been thoroughly investigated with respect to its participation in production of an emitting species. The blinking phenomenon was eliminated in the absence of atmospheric oxygen and the intensity of light emitted from the surface was significantly enhanced when oxygen was removed. A complete mechanism that adequately described the kinetics behavior of the system has been developed.

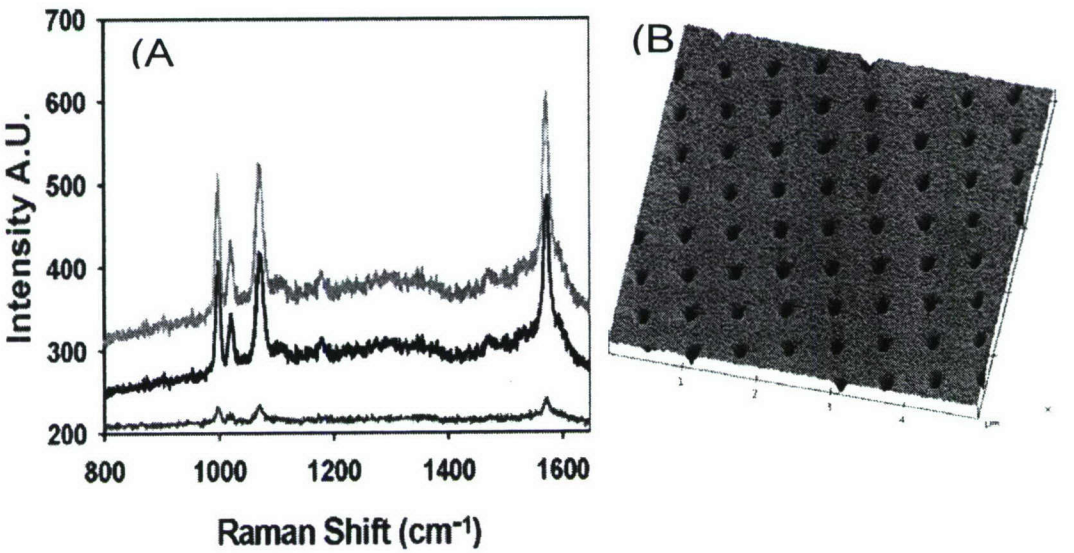


Figure 9. (A) The Raman spectrum of benzenethiol obtained from nanoaperture array SERS sensors. The spectrum shown in red was obtained from an unpatterned portion of the film; the spectrum shown in black was obtained from a nanoaperture array with 450 nm lattice spacing. The spectrum shown in green was corrected for the reduced geometric area on the array. (B) AFM micrograph of a typical nanoaperture array fabricated using electron beam lithography and thermal vapor deposition.

We collaborated with Prof. Jonas on the two-dimensional correlation analysis of photodynamics observed in SMSERS. Single molecule spectra of Rhodamine 6G were collected in our lab at one second time intervals for several minutes. These experiments were repeated numerous times to provide an extensive collection of data with widely distributed spectral characteristics to be analyzed by Jonas. A detailed presentation of the 2D correlation analysis software and findings is provided by Prof. Jonas.

Fabrication and characterization of designed SERS active nanomaterials. We had early success in making silver nanodots using a modified AFM technique. This method was replaced by an electron beam lithography technique which offered higher throughput and the ability to use arbitrary substrates. A new procedure to fabricate nanoaperture arrays on glass substrates provided the opportunity to interrogate the enhanced transmission properties of the arrays as well as the SERS response. In order to measure the transmission characteristics of the arrays, our micro-Raman spectroscopy experiment was modified to also allow for optical transmission measurements to be made from areas as small as ~9 μm^2. This capability allowed us to compare the SERS response from nanoaperture arrays with the transmission characteristics of the arrays. Interestingly, the transmission spectrum of nanoaperture arrays revealed a distributed transmission spectrum originating from individual nanoapertures.

When the nanoaperture arrays were evaluated for molecular sensing capabilities, see **Figure 9,** it was found that the arrays enhanced the Raman signal over that of the the neighboring unpatterned rough silver film by orders of magnitude. A quantitative analysis of the Raman enhancement factors originating from the nanoaperture arrays agreed exceptionally well with the theoretical calculations by the Schatz group.

In order to quantify the enhancement factors on nanoaperture arrays it was necessary to develop a method of analyte deposition that could evenly coat a microscopic SERS sensor (~100 μm^2). Out of this requirement a method of vapor phase analyte deposition was developed whereby a slow stream of ultrahigh purity nitrogen gas was passed over a dilute ethanolic solution of benzenethiol. The vapor phase analyte deposition method was found to deposit [illegible] (~1 um^2). When this method [illegible] on used for large area SERS [illegible] ıethods differed by less than [illegible] ition method demonstrating

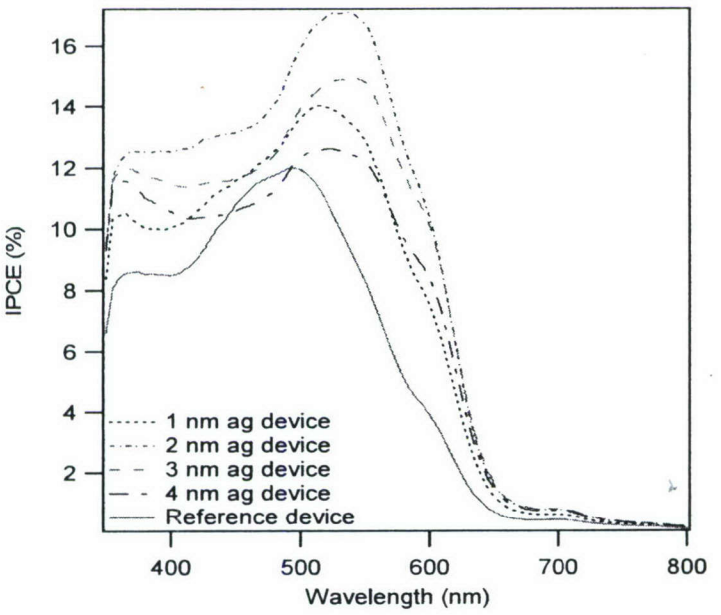


Figure 10. Incident photon-to-current conversion efficiencies of organic semiconductor films as a function of wavelength. Vapor deposited silver thin films of varying thicknesses were incorporated into a semiconducting polymer diode device. The silver films were vapor deposited onto the support substrate and the organic layers were spun cast on top. The wavelength dependent current measurements indicate that the presence of the silver particle films increase the photo-sensitivity of the organic layers above that of the reference.

ive substrates. A central [illegible] of nanoscale materials for [illegible] ıis objective by performing [illegible] ɔmaterials in contact with [illegible] ted the influence thin metal [illegible] rs. These basic studies have [illegible] conversion and solid state

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incorporated into the absorbing layer of the diode instead of being only in contact with the surface. Colloids within the absorbing layer may create even larger absorbance enhancements than those observed with thin silver films. Through extensive fundamental studies of how surface plasmon active nanomaterials influence organic semiconductors we are laying the groundwork for next generation opto-electronic chemical and biological sensors that may utilize both the specificity of SERS and the surface plasmon enhancements of the aforementioned nanoparticles.

George C. Schatz

Electrodynamics of metal nanoparticles, small clusters of nanoparticles and nanoholes. We have performed extensive electrodynamics studies of silver and gold nanoparticles having a variety of sizes and shapes, of dimers and other clusters of these particles, and of holes in metal films. For the isolated metal particles and clusters, our primary goal was to determine which particle shapes, sizes and arrangements lead to the largest local electromagnetic field enhancement. This enhancement is relevant to single molecule SERS studies being done by **Brus, Nie, Rowlen and Van Duyne**, since it determines the maximum contribution that electromagnetic effects can give to this effect. Although electromagnetic effects are well known to be important for ordinary SERS, their importance for single molecule SERS is still uncertain. The present work established upper bounds to the possible enhancement from this mechanism.

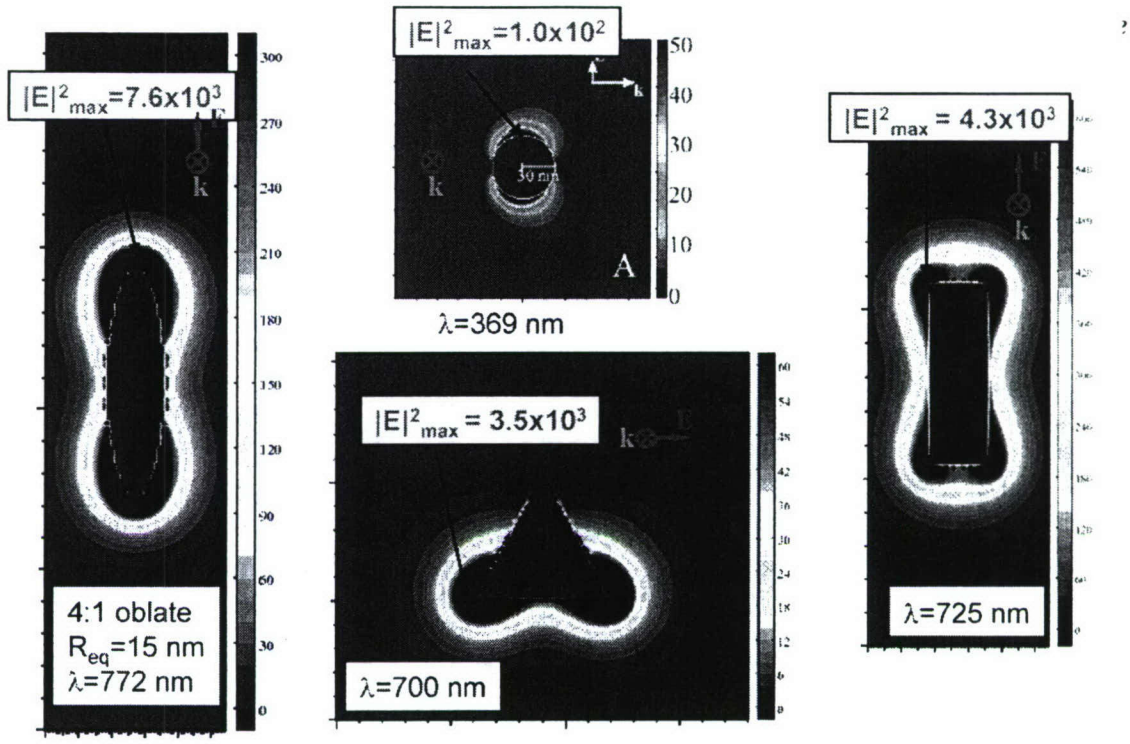


Figure 11. Contours of $|E|^2$ for a silver sphere, spheroid, triangular prism and rod. Location and magnitude of maximum E-field is indicated.

Figure 11 presents a compendium of maximum E-field results for silver spheres, spheroids, triangular prisms, and rods. What we find is that spheres have much lower E-fields, but the other particles are all very much comparable, with $|E|^2$ being less than 10^4. Since this is much less than is needed to explain single molecule SERS (which needs $|E|^2$ of 10^6 or greater if all of the enhancement comes from electromagnetic effects), we conclude that in the absence of nonelectromagnetic effects, single particles may not be sufficient to produce single molecule SERS. **Figure 12** shows results for dimers of triangular prisms. This shows that $|E|^2$ is an order of magnitude higher than for single particles, and furthermore the value of $|E|^2$ is close to 10^5. This is close to what is required to produce single molecule SERS. Thus it seems likely that dimers will be adequate for this effect to work. This result is in agreement with conclusions from **Brus**'s work.

Many of our projects in this area involved collaborations with experimental groups on specific particle/hole shapes and structures. For example, we performed a detailed study of silver nanocubes on a glass substrate (**Figure 13**) where we found a "split plasmon" extinction spectrum that arises from the asymmetric dielectric environment that the metal particle experiences, with the bluer peak being associated with the part of the cube that is exposed to

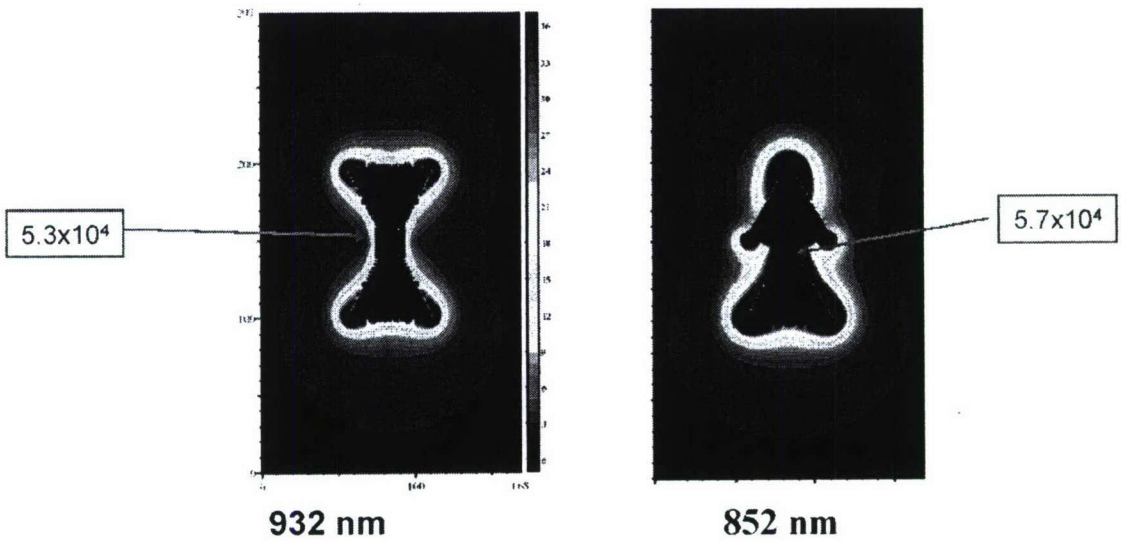


Figure 12. Contours of $|E|^2$ as in Figure 1, but for a dimer of triangular prisms in head to head or head to tail configuration.

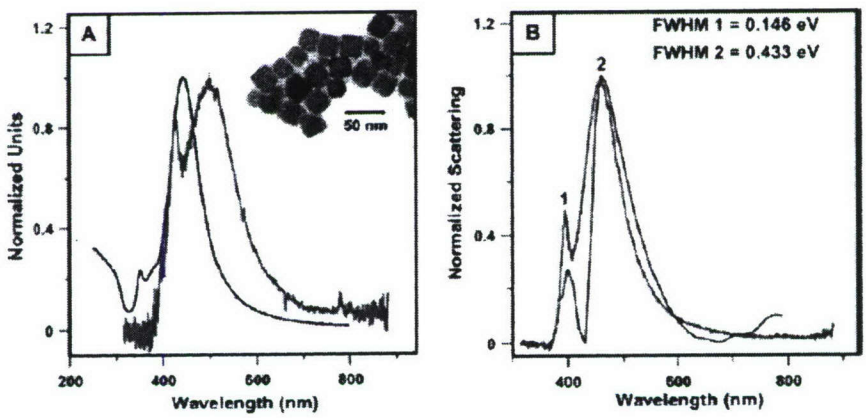


Figure 13. Comparison of the LSPR spectra of (A) nanocube ensemble extinction (black) and single nanocube dark-field scattering (red) in water and (B) single nanocube (red) and FDTD calculations (blue) in nitrogen.

solvent, and the redder peak reflecting the high local index associated with the part of the cube that is exposed to glass. We have also studied particles that are coated with aluminum oxide layers, showing that the extinction spectra have a predictable variation with layer thickness. And yet another project involved studying the scattering spectra of nanohole arrays that are made using a variant of nanosphere lithography. This hole array structure leads to very sharp plasmon lineshapes due to coherent interactions between the induced polarization near each hole. The sharp resonances lead to better refractive index sensing capabilities than for the nanosphere lithography structures we have studied. Our studies of nanoholes in collaboration with **Rowlen** demonstrated that SERS enhancement factors associated with the holes act on top of the enhancements that arise from plasmon excitation in the films around the holes to generate an overall enhancement factor that can be comparable to that for the best particle-based structures.

A significant collaboration between **Schatz** and **Van Duyne** involved studies of the excited states of resonant molecules that are adsorbed onto metal nanoparticles. There had been much uncertainty about the nature of these states as interaction with the surface could lead to important wavelength and width changes. A monolayer of dye molecules interacting with a 100 nm nanoparticles does not produce enough extinction to be distinguishable from extinction by the particle, but it does produce a measureable wavelength shift. If this shift is determined for many different nanoparticle sizes and shapes, it is possible to determine shift as a function of plasmon wavelength. We found empirically that this shift exhibits an inflection at the position of the molecular excited state, and with a width similar to the molecular state, thus demonstrating that the excited state of the molecule is largely unperturbed by the surface. **Figure 14** shows comparisons between theory and experiment for a magnesium porphyrazine that arose from this analysis, showing that the inflection in wavelength is due to the excited state of the molecule.

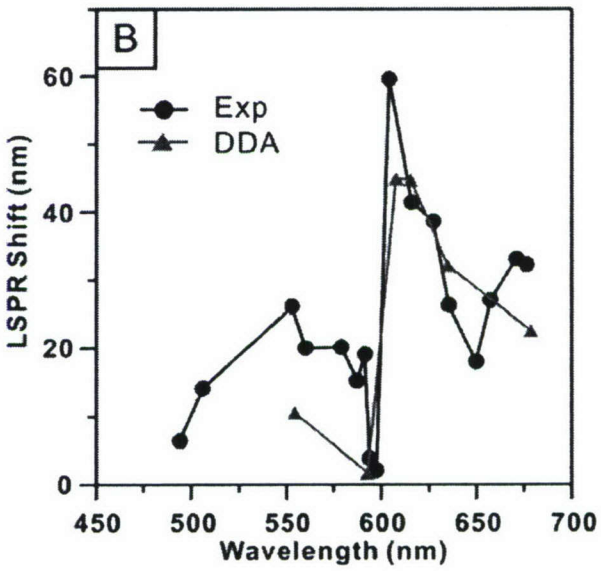


Figure 14. Wavelength shift spectrum for magnesium porphyazine on silver nanosphere lithography nanoparticles. The data interpretation uses a Kramers-Kronig analysis to extract the molecule dielectric constant, and then the discrete dipole approximation (DDA) to calculate the extinction and the wavelength shift.

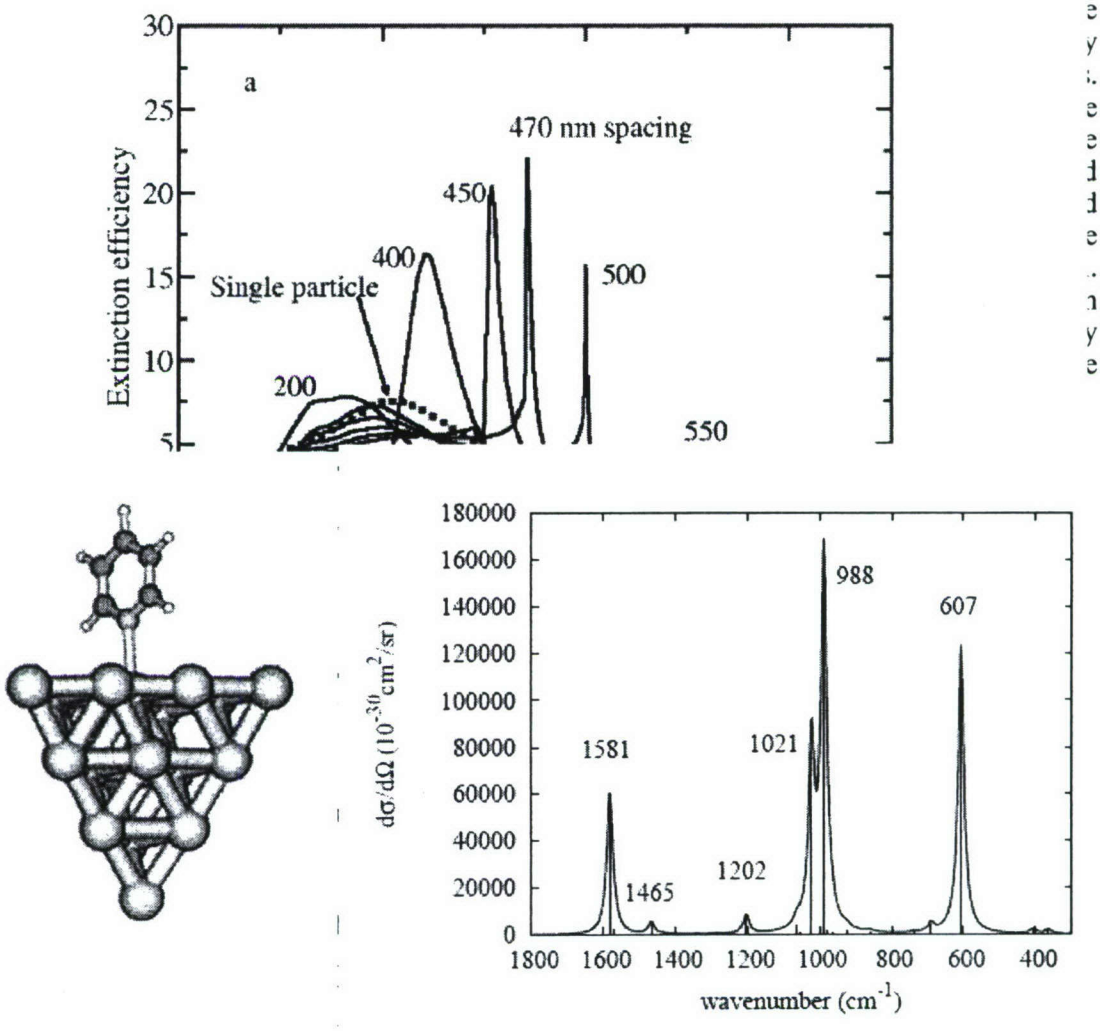


Figure 16. Structure of Ag_{20}-pyridine cluster used for SERS intensity calculation.

Figure 17. SER spectrum associated with Ag_{20}-pyridine cluster from **Figure 12**.

ORD and CD.

In addition, we have pushed this method to the determination of SERS spectra of pyridine on a twenty atom silver cluster (structure in **Figure 16** and spectra in **Figure 17**). Comparison of these results with the spectra of isolated pyridine indicates an enhancement factor of over 10^5, which is lower than for silver particles >10 nm dimensions, but still large enough to show that the primary enhancement process for SERS, i.e., electromagnetic enhancement, is operative for small (1 nm) particles. In another study, we examined the junction between two Ag_{20} clusters, and we found strong chemical enhancements for pyrazine bridging a junction, but a suppressed electromagnetic enhancement. The results show that both electromagnetic and chemical effects play an important role SERS.

Kenneth G. Spears

The initial phase of the work developed an improved femtosecond laser system capable of providing tunable pulses from the mid-infrared to the visible at 1 kHz repetition rate. An optical system was fabricated that was capable of nanometer scanning of x-y coordinates and sample rotation to provide studies of nanoparticle arrays by polarized white light spectroscopy and tunable laser excitation.

Nanoparticle arrays fabricated by nanosphere lithography were studied by femtosecond nonlinear spectroscopy. Studies of Second Harmonic Generation (SHG) with femtosecond lasers tunable from 1.2-1.5 nm demonstrated that the in-plane plasmon resonance of particles (truncated tetrahedrons with a base bisector of 125 nm) near 750 nm was not contributing to SHG due to symmetry cancellation in the array. Typical results are shown in **Figure 18**. However, an out-of-plane particle resonance hidden in the linear extinction spectrum was contributing with SHG near 650 nm (see publication).

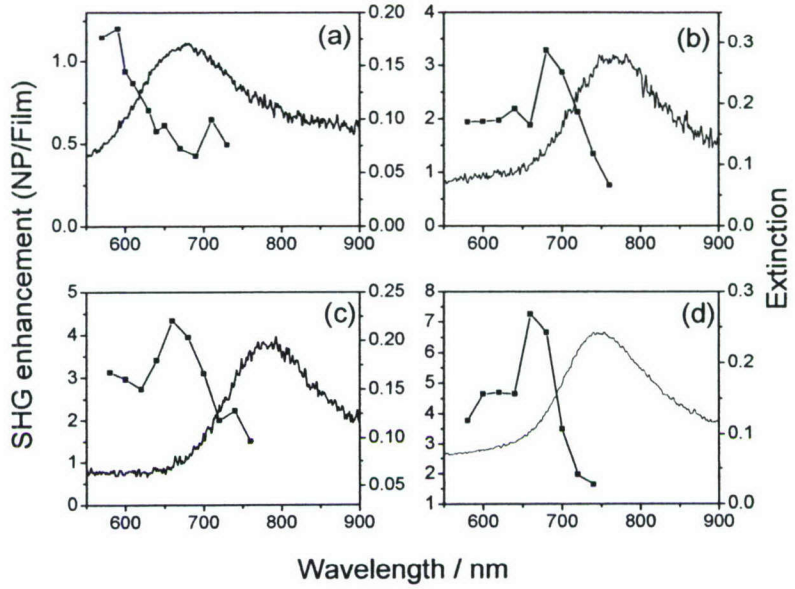


Figure 18. SHG profiles (squares are SHG output) measured for (a), (b) p-in:p-out at 45 degrees incidence (c), (d) p-in:p-out at 10 degrees incidence. All profiles are on different samples, the extinction spectrum showing the in-plane plasmon resonance is a continuous curve.

In order to study the resonance effects of in-plane resonances we required samples with deliberately created asymmetric nanoparticles, and therefore undertook to fabricate an extensive series of arrays by e-beam lithography. These arrays were studied by linear spectroscopy methods and the results provide many new insights into how nanoparticle interactions affect the optical properties of arrays. The work was conducted by students who were working jointly with **Van Duyne** and **Spears**, with most laser and optical studies conducted in the **Spears** laboratory and e-beam fabrication at two other sites.

The plasmon resonance was measured for two-dimensional arrays of L-shaped Ag nanoparticles fabricated by electron beam lithography. A variety of particle sizes were studied with nominal total edge lengths of ~150 nm, 63 nm arm widths and 30 nm height. The single nanoparticle localized surface plasmon resonance (LSPR) of the L particles had two polarized components, which independently coupled in the arrays to create plasmon resonances for the array. The arrays had peak resonance locations and bandwidths that were dependent on grid spacing and particle number in the grid. The array plasmon resonance had a minimum bandwidth of 700-800 cm^{-1} at a grid spacing ~75 nm smaller than the grid having the largest red shift of the plasmon resonance. This bandwidth is about half of the single nanoparticle resonance bandwidth. **Figure 19** summarized some of this data. For arrays with small numbers of nanoparticles, the resonant wavelength and bandwidth had large deviations from the semi-infinite arrays, but approached those results as the number of nanoparticles increased to 25 particles on an edge, which defines the range of effective dipole coupling for a 400 nm grid spacing. This observation is consistent with optical changes observed by scanning across a 300x300 μm^2 pad. A solvent effect on these arrays demonstrated a red shift with similar bandwidth effects, and some small grating induced features due to waveguide effects. These

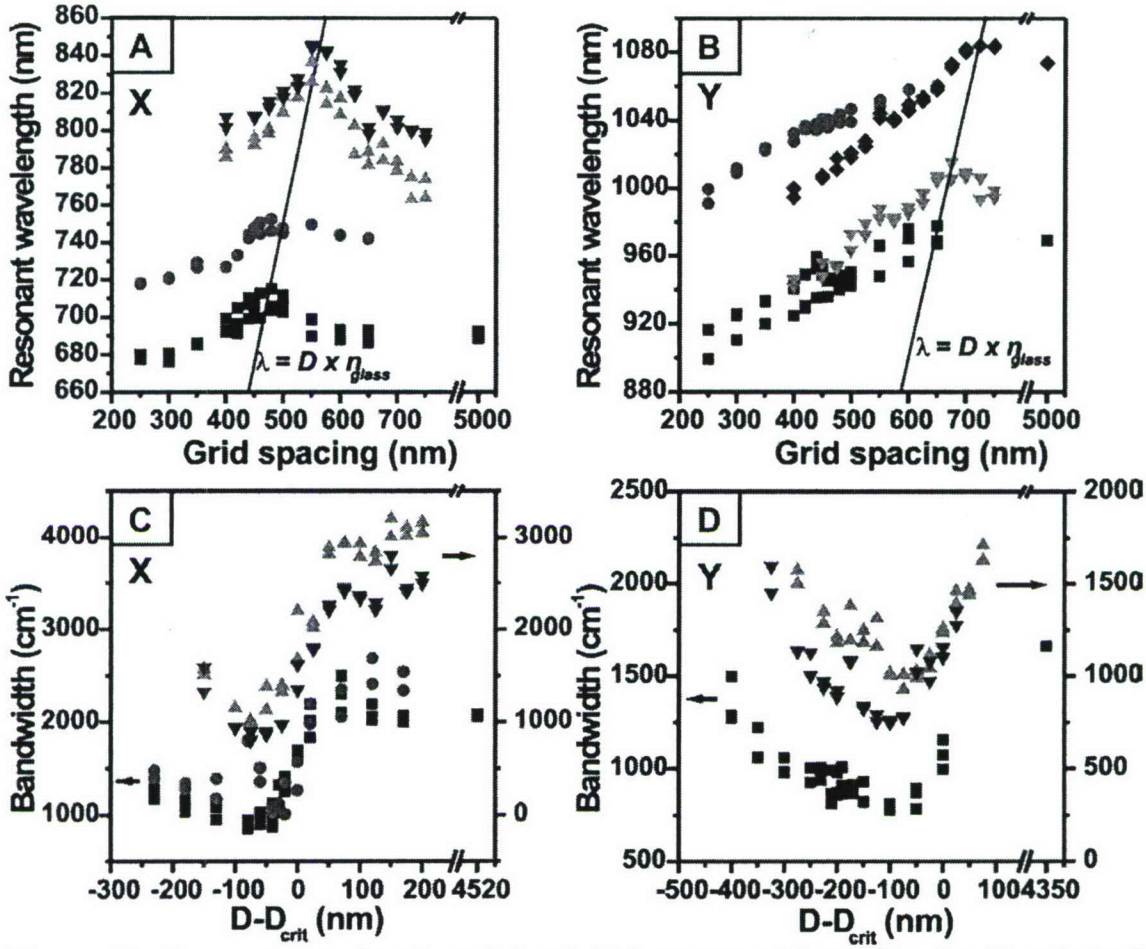


Figure 19. Resonant wavelength and bandwidth versus grid spacing for X polarized extinction (A and C) and Y polarized extinction (B and D) for 2D nanoparticle arrays of L and V orientation. L arrays with 82 and 92 nm arm length are plotted with black squares and red circles respectively, and V arrays with 83 and 103 nm arm length are plotted with green triangles and blue inverted respectively. Duplicate and triplicate (82 nm L, black) arrays are shown for different array pads prepared on the same chip. The line $\lambda = D$ x n_{glass} is shown with a black solid line in (A) and (B). The bandwidth is plotted versus $(D - D_{crit})$, where D is the actual grid spacing and D_{crit} is the critical grid spacing where the resonant wavelength shows maximum red shift. Plots for L arrays follow the left axis and the plots for V arrays follow the right axis.

results clearly show the key design elements required to use 2D arrays in chemical and biological sensing. Studies of SHG require samples to be fabricated without an indium-tin-oxide (ITO) conducting layer.

The optical response of L-shaped silver nanoparticles has three resonances with respect to the incident polarization relative to the particle axes. From theoretical modeling collaborations with Professor T. Seideman of Northwestern and Dr. M. Sukharev the physical origin of the resonances were traced to different plasmon phenomena. In particular, a high energy band with unusual properties was interpreted in terms of volume plasmon oscillations arising from the asymmetry of a nanoparticle.

Additional measurements and theory were done to characterize the birefringence or polarization rotation of single nanoparticles and arrays of nanoparticles. We measured the

depolarization as a function of wavelength, which was interpreted in terms of the phase shift or birefringence. Light interaction with two different transitions at two wavelengths allows a single nanoparticle to have this birefringence behavior for an optical element only 30 nm thick. Such optical properties can have applications in a wide variety of nanoparticle systems, and these measurements are the first to clearly demonstrate such effects and model them with phenomenological and single particle computational models.

Additional studies of the effects of short range and long range coupling on small arrays (4 particles) to large arrays of cylindrical nanoparticles with gaps of 1, 2 and 8 particles have shown a dependence of resonance shift and bandwidth on whether the gaps are small or large (with only long range coupling between the particles). This study suggests that gaps of 1 or 2 particles are insufficient to damp either type of interaction, and theory will be required to fully understand these observations. The optimal design of small sensing arrays requires more experimental and theoretical models, although these results map out a range of experimental phenomena.

The study of arrays for chemical or biological sensing requires stability of the nanoparticles to environmental effects and optical power, especially for nonlinear optical effects. In prior work of Van Duyne, the method of atomic layer deposition of Al_2O_3 showed thermal stability and we have extended this to femtosecond laser pulses. The deformation of the nanoparticles was monitored by extinction measurements. It is demonstrated that the 1.0 nm Al_2O_3 layers fabricated by ALD provide 10 times enhanced stability of the silver nanoparticles against femtosecond laser exposure compared to bare nanoparticles. This enhanced stability is explained by the increased surface melting temperature which results from the decreased mean-square displacement of the atoms located on the nanoparticle surface by Al_2O_3 layers. This study demonstrates that the Al_2O_3 coated nanoparticles can serve as a stable platform for surface-enhanced laser spectroscopy, including nonlinear spectroscopy.

Richard P. Van Duyne

Linear and Nonlinear Plasmonics of Nanoparticle Arrays. Three projects representing significant advances have been completed: (a) using single nanoparticles as LSPR nanosensors; (b) understanding the effect of electromagnetic coupling in 2D arrays of nanoparticles with no center of symmetry (viz., L-shaped); and (3) exploring the plasmonic properties of copper.

The plasmonic properties of single silver triangular nanoprisms are investigated using dark-field optical microscopy and spectroscopy. Two distinct localized surface plasmon resonances (LSPR) are observed. These are assigned as in-plane dipolar and quadrupolar plasmon excitations using electrodynamic modeling based on the Discrete Dipole Approximation (DDA). The dipole resonance is found to be very intense and its peak wavelength is extremely sensitive to the height, edge length, and tip sharpness of the triangular nanoprism. In contrast, the intensity of the quadrupole resonance is much weaker relative to the dipole resonance in the single particle spectra than in the ensemble averaged spectrum. Several parameters relevant to the chemical sensing properties of these nanoprisms have been measured. The dependence of the dipole plasmon resonance on the refractive index of the external medium is found to be as high as 205 nm RIU^{-1} and the plasmon linewidth as narrow as ~ 0.17 eV. These data lead to a sensing figure of merit (FOM), the slope of refractive index sensitivity in eV RIU^{-1}/linewidth (eV), as high as 3.3. In addition, the LSPR shift response to alkanethiol chain length

was found to be linear with a slope of 4.4 nm per CH_2 unit. This is the highest short range refractive index sensitivity yet measured for a nanoparticle.

The plasmon resonance was measured for two-dimensional arrays of L-shaped Ag nanoparticles fabricated by electron beam lithography. A variety of particle sizes were studied with nominal total edge lengths of ~150 nm, 63 nm arm widths and 30 nm height. The single nanoparticle localized surface plasmon resonance (LSPR) of the L particles had two polarized components, which independently coupled in the arrays to create plasmon resonances for the array. The arrays had peak resonance locations and bandwiths that were dependent on grid spacing and particle number in the grid. The array plasmon resonance had a minimum bandwidth of 700-800 cm^{-1} at a grid spacing ~75 nm smaller than the grid having the largest red shift of the plasmon resonance. This bandwidth is about half of the single nanoparticle resonance bandwidth. For arrays with small numbers of nanoparticles, the resonant wavelength and bandwidth had large deviations from the semi-infinite arrays, but approached those results as the number of nanoparticles increased to 25 particles on an edge, which defines the range of effective dipole coupling for a 400 nm grid spacing. This observation is consistent with optical changes observed by scanning across a 300x300 μm^2 pad. A solvent effect on these arrays demonstrated a red shift with similar bandwidth effects, and some small grating induced features due to waveguide effects.

The localized surface plasmon resonance (LSPR) of oxide-free Cu nanoparticles fabricated by nanosphere lithography is examined by UV-vis extinction spectroscopy and electrodynamics theory. The LSPR of the Cu nanoparticles is significantly affected by the presence of copper oxides and the removal of the oxide species yields a dramatic difference in the observed LSPR. From a comparison of the LSPR of Cu, Ag, and Au nanoparticles of similar geometry, we conclude that Cu displays an intense and narrow LSPR peak that is comparable to Ag and Au.

Fundamentals of Surface-Enhanced Raman Spectroscopy. Four topics were explored in detail: (1) plasmon and wavelength scanned surface enhanced Raman excitation spectroscopy; (2) surface-enhanced hyper-Raman spectroscopy; (3) single molecule surface enhanced Raman spectroscopy; and (4) the role of coupled molecular and plasmon resonances in single molecule surface enhanced Raman spectroscopy.

1. Plasmon and wavelength scanned surface enhanced Raman excitation spectroscopy

Although it has been well-known that the LSPR of a metallic substrate should be close to the excitation wavelength used for SERS, a systematic study of the relationship between the two had never been completed. Two approaches were used to measure the SERS enhancement factor as a function of either the LSPR wavelength or the laser excitation wavelength (wavelength scanned surface enhanced Raman excitation spectroscopy). In the case of plasmon scanned SER excitation spectroscopy, the enhancement factor was measured as a function of the LSPR spectral position at constant laser excitation wavelength. **Figure 20(a)** shows the Raman enhancement factor of the 1081 cm^{-1} peak from benzenethiol adsorbed to NSL-fabricated arrays with different LSPR wavelengths. The figure illustrates that the maximum enhancement occurs when the plasmon resonance is to the red of the fixed excitation wavelength (λ_{exc} = 632.8 nm) and to the blue of the Stokes-shifted Raman band (shifted 1081 cm^{-1} from λ_{exc}). Additional experiments of this type demonstrated that the largest SERS enhancement factor is observed

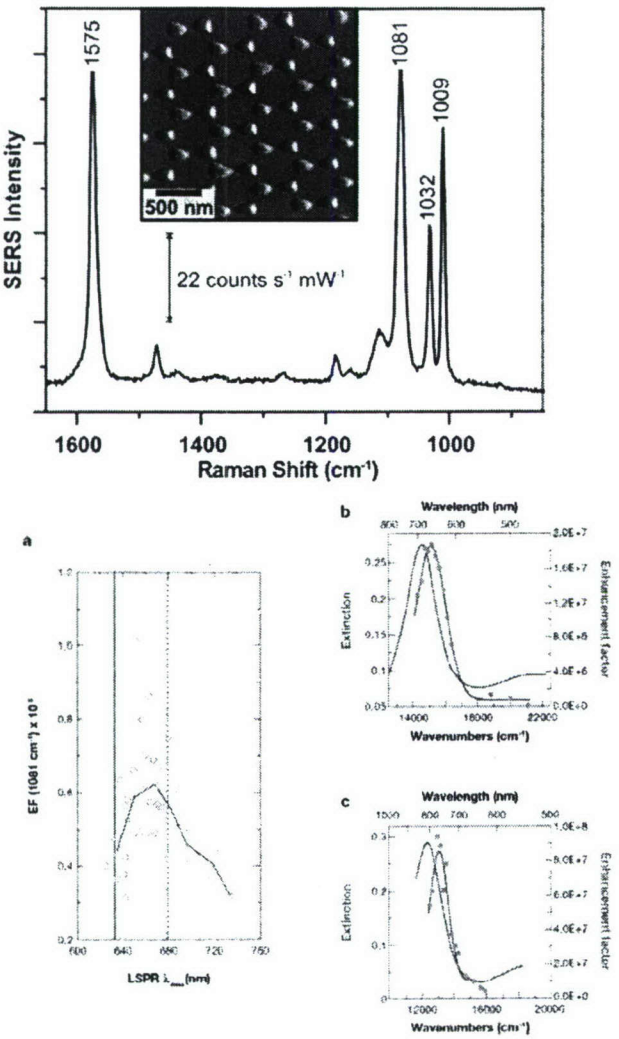


Figure 20. SERS of benzenethiol adsorbed on NSL-derived Ag nanoparticles (top panel). Excitation spectroscopy of benzenethiol adsorbed on NSL-derived Ag nanoparticles (bottom panel). (a) Plasmon-sampled surface enhanced Raman excitation spectrum of the 1081 cm^{-1} peak of benzenethiol (dashed line) excited at 632.8 nm (solid line). The enhancement factor is highest when the plasmon wavelength is between the Raman excitation and emission energies. (b) Wavelength scanned surface-enhanced Raman excitation spectra of the 1081 cm^{-1} peak of benzenethiol, LSPR λ_{max} = 690 nm, profile fit maximum at 662 nm. (c) Wavelength scanned surface-enhanced Raman excitation spectra of the 1575 cm^{-1} peak of benzenethiol, LSPR λ_{max} = 810 nm, profile fit maximum at 765 nm.

when the LSPR falls within a 120 nm window that includes both the excitation wavelength and the Raman shifted wavelength.

An alternative and more general approach is to use a single NSL-fabricated nanoparticle array sample with a constant LSPR wavelength and scan the excitation wavelength using a tunable laser system. **Figure 20 (b)** shows data from such an experiment in which the enhancement factor of the same 1081 cm^{-1} peak from benzenethiol is monitored as the excitation wavelength was varied between 475-800 nm. The excitation spectrum shows the highest SERS enhancement factor is observed when the excitation wavelength is to the blue of the LSPR wavelength, consistent with the plasmon-scanned results above (note that the axes on this plot are in units of increasing wavenumber and thus decreasing wavelength). Based on Gaussian fits to the spectra, the shift between the maximum energy of the excitation profile and the LSPR spectrum is 613 cm^{-1}, placing it at roughly the midpoint of the shift between the excitation and the Stokes Raman scattering energies (i.e. 1081 cm^{-1}). This relationship is also demonstrated with the 1575 cm^{-1} peak of benzenethiol shown in **Figure 20 (c)**. Again, the shift between the excitation wavelength producing the maximum enhancement and the peak in the extinction spectrum is 726 cm^{-1}, or roughly half of the shift between the excitation and Raman shifted scatter. By repeating this measurement on different vibrational bands, a distinct trend emerges: for higher energy Raman transitions, the shift between the excitation profile and the LSPR spectrum also moves to higher energy. This is because the LSPR should be located at some intermediate energy between the excitation and Raman EM fields in order to provide the maximum enhancement of the two. As the Raman

transition moves to higher energy, the gap between the excitation and Raman energies widens, and the LSPR maximum must shift to remain roughly midway between the two. In this case, the LSPR is static, so the effect is reversed: the excitation profile will shift to higher energy. This is in agreement with the EM enhancement mechanism and is an important outcome of these wavelength-scanned SERS experiments. Moreover, these experiments illustrate the importance of optimizing the plasmon and excitation wavelengths to achieve maximum SERS enhancements; as **Figure 20 (c)** shows, enhancements of nearly 10^8 can be produced when experimental conditions are properly optimized. Although ensemble averaged SERS enhancement factors of 10^8 are the highest we have measured to date, there is good reason to believe that future experiments will reveal substantially higher values for systems involving highly crystalline single nanoparticles and specific, finite nanoparticle assemblies.

2. Surface-enhanced hyper-Raman spectroscopy

Electrochemical surface-enhanced hyper-Raman scattering (SEHRS) and surface-enhanced Raman scattering (SERS) of centrosymmetric molecules on Ag film over nanosphere (AgFON) electrodes were measured. The SEHR spectra of *trans*-1,2-bis(4-pyridyl)ethylene (BPE) at different potentials (vs. Ag/AgCl) were presented for the first time, and a reversible potential tuning of the SEHR spectra of BPE was demonstrated. The SEHRS and SERS techniques were used to determine to what extent either site symmetry reduction or field gradient effects dictate the origin of the observed vibrational spectra. It was found that the SEHR and SER spectra for the molecules studied were distinctly different at all frequency regions at a fixed voltage, suggesting that centrosymmetry is largely retained upon adsorption to the AgFON surface and that field gradient effects are negligible. This work also showed that the SEHR spectra clearly depend on potential, while the SER spectra are essentially independent of potential. It is determined that the combination of changes in ΔG_{ads} and the presence of coadsorbed counterions are responsible for altering the local symmetry of the adsorbate, and only SEHRS has the sensitivity to detect these changes in the surface environment. Thus, SEHRS is a uniquely useful spectroscopic tool that is much more sensitive to the local adsorption environment than is SERS.

3. Single molecule surface enhanced Raman spectroscopy

The existence of single molecule surface-enhanced Raman spectroscopy (SMSERS) was placed on a vastly more solid footing by employing a frequency-domain approach rather than the usual methods involving spectral blinking/wandering or a statistical analysis of intensity fluctuations. This was demonstrated using two isotopologues of Rhodamine 6G that offer unique vibrational signatures but identical absorption spectra, surface affinities, and surface diffusion rates. When an average of one molecule was adsorbed per silver nanoparticle in a dry nitrogen environment, only one isotopologue was observed (**Figure 21**). Additionally, the distribution of vibrational frequencies hidden under the ensemble average is revealed by examining the single molecule spectra. Correlation with transmission electron microscopy reveals that SMSERS active aggregates are composed of multiple randomly size and shape nanoparticles. At higher coverage and in a humid environment, adsorbate interchange was detected. Using 2D cross-correlation, vibrational modes from different isotopologues was anti-correlated indicating that the dynamic behavior was from multiple molecules competing for a single hot spot of molecular dimensions. This allows hot-spot diffusion to be directly observed without analyzing the peak intensity fluctuations.

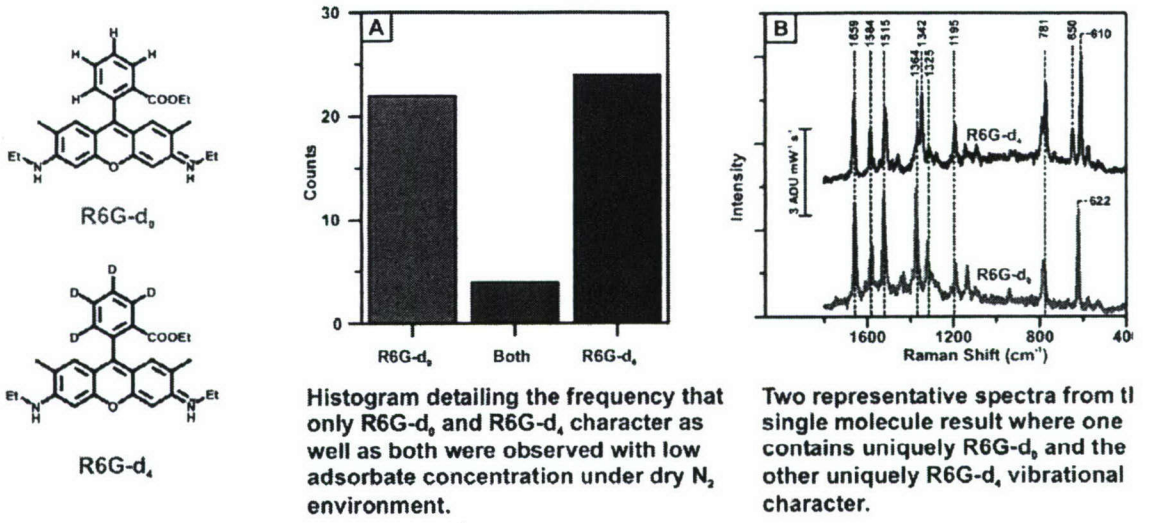


Figure 21. Single molecule surface-enhanced Raman scattering from two isotopologues (left panel) of Rhodamine 6G, R6G-d_0 and R6G-d_4 , adsorbed on silver nanoparticles. (A) Histogram detailing the frequency with which (1) only R6G-d_0, (2) only R6G-d_4 and (3) both R6G-d_0 and R6G-d_4 vibrational modes were observed with low adsorbate concentration under dry N_2 environment. (B) Two representative spectra from the single molecule results where one contains uniquely R6G-d_0 (red line) and the other uniquely R6G-d_4 (blue line) vibrational character. (λ_{ex} = 532 nm, t_{aq} = 10s, P_{ex} = 2.4 W/cm^2, grazing incidence)

4. *Coupled molecular and plasmon resonances*

This project started in 2004 with preliminary experimental data from **Van Duyne** showing that strong coupling between the plasmon resonance of the nanoparticle and the molecular electronic resonances of magnesium porphyrazine produced very large shifts in the LSPR extinction wavelength. The major outcome of our study of the magnesium porphyrazine system was that the magnitude of the LSPR peak shift and line shape change induced by a resonant molecule varies with wavelength. In most instances, the oscillatory dependence of the peak shift on wavelength tracks with the wavelength dependence of the real part of the refractive index, as determined by a Kramers-Kronig transformation of the molecular resonance absorption spectrum. A quantitative assessment of this shift based on discrete dipole approximation calculations by **Schatz** shows that the Kramers-Kronig index must be scaled by a factor of ~ 5 in order to match experiment.

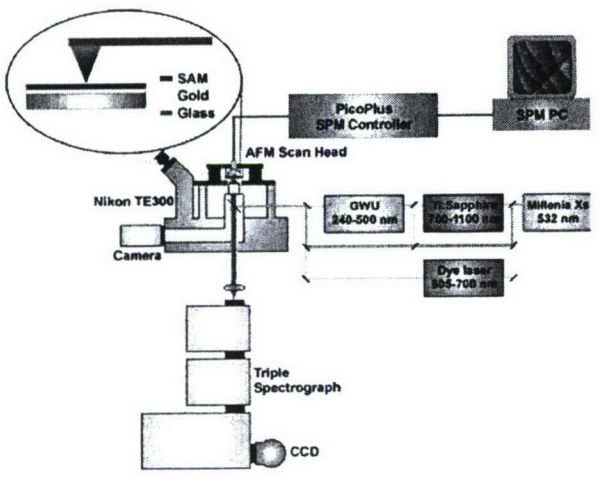


Figure 22. Schematic of the experimental setup for transmission mode TERS. The novel features of this apparatus include a broadly tunable Ti:Sapphire laser system for tip excitation and a triple spectrograph for high-resolution Raman detection and efficient rejection of scattered light from the AFM deflection laser.

Two additional adsorbate systems, cytochrome P450 and Rhodamine 6G, have now been characterized in addition to magnesium porphyrazine by LSPR shift spectroscopy. The study of cytochrome P450 lead to the development of an optical nanosensor designed to study low molecular weight substrate molecule interaction with

cytochrome P450 proteins. Sensing a low molecular weight binder using a refractive index based method such as propagating surface plasmon resonance spectroscopy is extremely difficult. Resonant LSPR spectroscopy transforms this hard problem into one that is vastly easier. The Rhodamine 6G study revealed the formation of J-type (head-to-tail dipole moments) and H-type dimers (parallel dipole moments) near monolayer coverage. At low coverages, only the Rhodamine monomer was observed. Furthermore, **Van Duyne and Schatz** demonstrated that there was no shift or broadening of the $S_0 - S_1$ transition of R6G when it adsorbed to Ag surfaces. These results are consistent with our developing understanding that the enhancement factor of 10^{14} widely reported in single molecule SERS is the product of a purely electromagnetic contribution of 10^{10} and the adsorbate localized resonance Raman enhancement of 10^4 for R6G. No chemical contribution involving metal to adsorbate charge transfer transitions is required to understand our results. These two new pieces of information are extremely important in understanding the surface chemistry of the R6G/Ag system which has become the most widely studied adsorbate/surface system in the burgeoning field of single-molecule surface enhanced Raman spectroscopy.

Tip-enhanced Raman spectroscopy (TERS)

One of the original goals of this MURI was to "extract the maximum amount of chemical information from the minimum amount of sample in the shortest possible data acquisition time." One approach to achieve this goal was to develop tip-enhanced Raman spectroscopy. This goal was achieved.

In this work, we have explored the utility of TERS in the field of nanotribology -- the study of friction, wear, and pressure at the nanoscale. We conducted a study of the force dependence of TER spectra from self-assembled monolayers (SAMs). From the tribology perspective, the SAM is viewed as a model lubricant. The role of lubricants in determining mechanical properties is critical for modern technologies including hard disk drives, microelectromechanical systems (MEMS), and many others.

Figure 22 shows a schematic diagram of the TERS apparatus used for the results reported here. The laser excitation light is delivered using the inverted microscope objective, and the Raman scattered light is collected through the same objective. The AFM scan head is mounted directly on the inverted microscope, and contact mode feedback is used to bring the tip into contact with the sample. The Raman scattered light is collected through a triple spectrograph in order to block the incident laser and the AFM laser. The SAM samples were formed on a thin (8nm) layer of Au deposited on a glass cover slip.

In **Figure 23** representative TER spectra are shown for benzenethiol adsorbed on an 8 nm Au island film that is very weakly SERS active at λ_{ex} = 532 nm. In Fig. 7 (A), the AFM tip, coated with 40 nm Ag, is

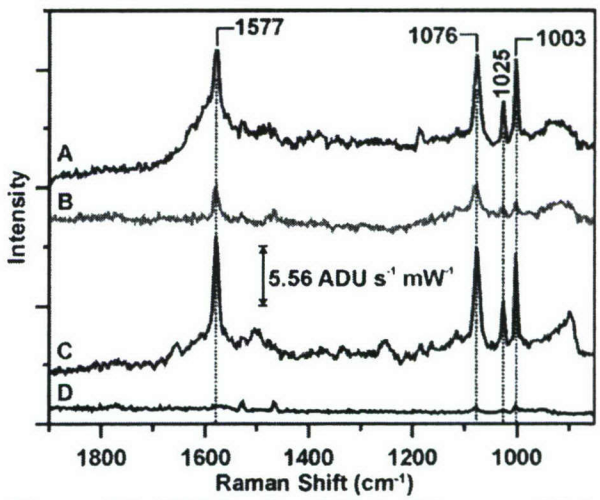


Figure 23. TERS of a SAM of benzenethiol adsorbed to an 8 nm Au film on glass. AFM tip is coated with 40 nm Ag. λ_{ex} = 532 nm. (A) AFM tip engaged in contact mode. (B) AFM tip withdrawn by 100μm. (C) AFM tip re-engaged in contact mode. (D) Laser focused solely on the AFM tip after the sample has been removed.

engaged and makes contact with the sample yielding a high signal to noise ratio TER spectrum. In Fig. 7 (B), the tip is withdrawn from the sample by 100 μm, with the laser spot still focused on the sample. Fig. 7 (C) shows the same high signal to noise ratio TER spectrum when the AFM tip is re-engaged in contact mode. Finally, Fig. 7 (D) shows a spectrum with the laser focused on the AFM tip after the sample has been removed. This spectrum was acquired after several engage-disengage cycles and serves to show that benzenethiol molecules do not transfer from the Au film to the AFM tip. Thus, the majority of the signal originates from molecules that are not themselves adsorbed to the tip. Taking the difference in surface areas between the laser spot, ~ 1 μm^2, and the contact area of the AFM tip, ~ 300 nm^2, into account, the average enhancement factor for each of the Raman modes is estimated to be $>10^4$. These high signal-to-noise spectra unambiguously demonstrate significant enhancement brought on by the presence of the Ag-coated AFM tip.

Figure 24 presents a data set that shows the effect of tip force on the TER spectra. An AFM tip, coated with 15 nm of Ag, was brought into contact with a SAM of benzenethiol, again on an 8 nm Au island film on glass. The tip was scanned over the monolayer at a constant speed, and the force was increased from a starting value of 19 nN to a final tip force of 391 nN. Throughout this force range, the TERS spectra acquired are of high signal to noise ratio. The TER intensities show a weak dependence of force. Over the range 0 – 50 nN, the TER intensity decreases by 10-15% of its low force value. This is followed by the 50 – 400 nN range where the TER intensity is approximately force independent. It is also observed that there are no significant changes in vibrational frequency over the entire 0 – 400 nN range. Clearly much more work is needed to further investigate the force dependence of TERS. At present our working hypothesis is that the decrease in TER intensity in the 0 – 50 nN range is due to reversible orientation changes of the benzenethiol molecules in the vicinity of the tip.

Spatially correlated plasmon spectroscopy and either atomic force microscopy (AFM)

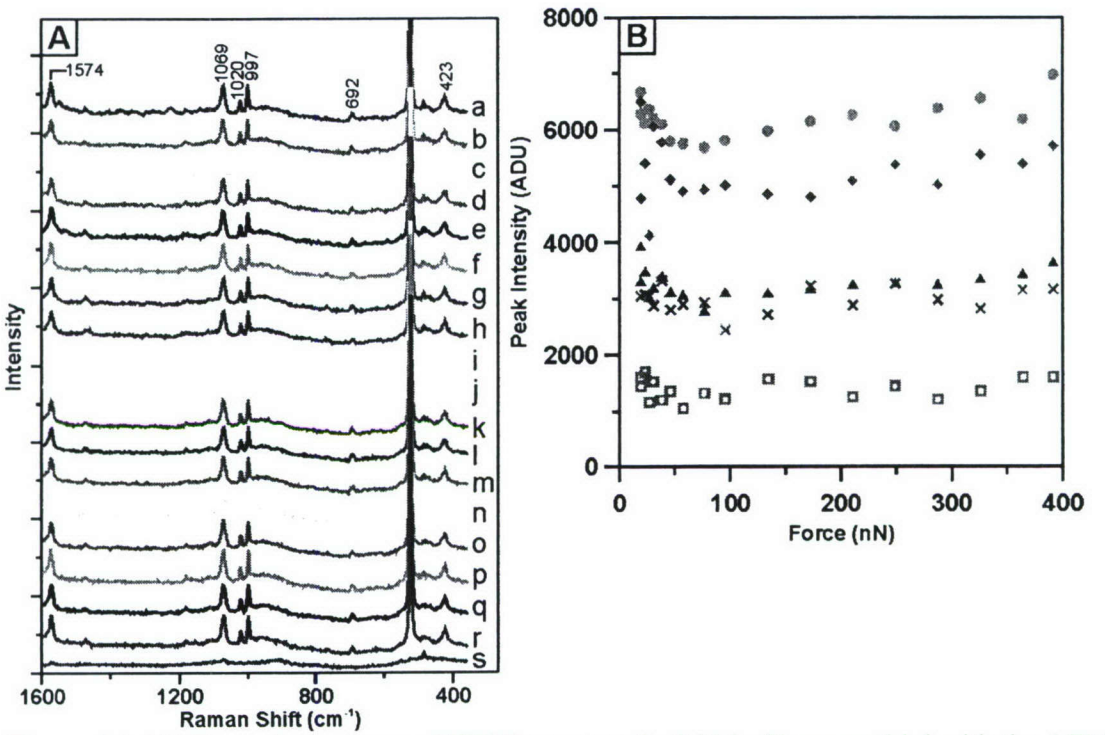


Figure 24. (A) Force dependence of TERS spectra of a SAM of benzenethiol with the AFM tip scanning in contact mode at a constant speed (2.0 lines/s) and varying force. The very intense peak at 520 cm^{-1} comes from the Si AFM tip. (a) tip in contact, not scanning, (b) tip scanning, force = 19 nN, (c) 23 nN, (d) 27 nN, (e) 31 nN, (f) 38 nN, (g) 46 nN, (h) 58 nN, (i) 77 nN, (j) 96 nN, (k) 134 nN, (l) 173 nN, (m) 211 nN, (n) 249 nN, (o) 288 nN, (p) 326 nN, (q) 364 nN, (r) 391 nN, (s) tip withdrawn 100 μm. (B) Graph of the peak intensity of each of the benzenethiol Raman modes as a function of tip force. • denotes the 1069 cm^{-1} peak, denotes the 997 cm^{-1} peak, ♦ denotes the 1574 cm^{-1} peak, ▲ denotes the 423 cm^{-1} peak, **x** denotes the 1020 cm^{-1} peak, and □ denotes the 692 cm^{-1} peak. The intensity of each of the peaks remains relatively constant over this force range.

A second approach to the goal of extracting the maximum amount of chemical information from the minimum amount of sample is correlated plasmon spectroscopy and AFM. Van Duyne has developed a novel approach to this problem. **Figure 25A** shows a schematic of the approach used for a real time correlated optical and atomic force microscope. This approach also allows an AFM tip to be brought into contact with the sample, with no overwhelming background due to scattering from the AFM cantilever as in **Figure 25B**. This is due to the short decay length of the evanescent field generated through the use of TIR. **Figure 25C** is a wide field LSPR image of single silver nanoprisms with an AFM tip engaged on the sample. Since the tip and the nanoparticle can be co-localized, the resulting spectrum can be assigned to its corresponding AFM image without the need for pattern matching. Using through-the-objective total internal reflection (TIR) for high-angle white light illumination of individual nanoparticles, scattering spectra can be collected as in **Figure 25D**. A Comparison of normalized scattering spectra taken using the standard dark field (DF) transmission geometry and the TIR approach demonstrates that valid LSPR spectra are being obtained by this novel TIR approach. Moreover, by properly treating the glass substrate, the particles can be actively manipulated by the tip.

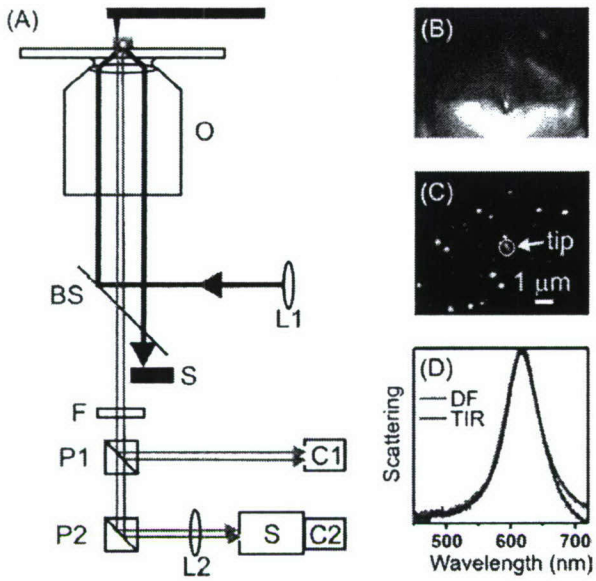


Figure X7 Van Duyne. (A) Schematic of the white light through-the-objective TIR experiment. Full details can be found in the text. (B-C) Single nanoparticle scattering image when an AFM tip is in contact with the sample using (B) a dark field scattering objective and (C) the TIR approach. (B) is dominated by scattering from the AFM cantilever, while the AFM tip appears only as a diffraction limited spot in (C). (D) Comparison of normalized scattering spectra taken using the standard dark field (DF) transmission geometry and the TIR approach.

reported.

Optical feedback of this process allows the motion of the particles due to pushing by the tip to be followed at video rates. In particular, plasmonic coupling between two particles as they are pushed close together by the tip can be followed in real time. Using a closed-loop AFM scanner, plasmonic structures can be assembled and spectroscopically interrogated without the need for complicated lithographic techniques.

Surface-Enhanced Sensing

There were several significant advances in surface-enhanced sensing. It was shown that an ultrathin layer of Al_2O_3 deposited on silver by atomic layer deposition (ALD) yielded a nanostructured surface with SERS enhancement factors ~ 10^7 that were stable over a one-year period. Our efforts to demonstrate an effective SERS-based sensor for metabolic analytes advanced by showing that in vivo SERS was possible and that sequential detection of glucose and lactate was possible. Finally, progress toward a thermally stable, nanoparticle-based SERS active surface for application to heterogeneous catalysis was

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Christine Aikens (postdoc)
Greg Cvetanovich (undergrad)
Lasse Jensen, Postdoctoral Research Associate
Prof. George C. Schatz, MURI Faculty

Kenneth G. Spears
Andrew Moran, Postdoctoral Research Associate
Erin McLellan-Hicks, Graduate Student (joint with Van Duyne)
Jiha Sung, Graduate Student (joint with Van Duyne)
Maxim Sukharev, Postdoctoral Research Associate (6 weeks 2007)
Prof. Kenneth G. Spears, MURI Faculty

Richard P. Van Duyne
Christy L. Haynes, Graduate Student
Adam D. McFarland, Graduate Student
Jon Dieringer, Graduate Student
Erin McLellan-Hicks, Graduate Student (joint with Spears)
Leif Sherry (joint student with Schatz)
Jiha Sung, Graduate Student (joint with Spears)
Kevin Biggs, Graduate Student (03/01/05 – 06/15/05)
Prof. Richard P. Van Duyne, MURI Faculty

6. Publications (Note: MURI PI Authors in Boldface)

1. "Two-Dimensional Femtosecond Spectroscopy," D. M. Jonas, Annu. Rev. Phys. Chem. 54, 425-463 (2003).
2. "Optical Analogs of 2D NMR," D. M. Jonas, Science 300, 1515-1517 (2003)
3. "Role of Cyclic Sets of Transition Dipoles in the Pump-Probe Polarization Anisotropy: Application to Square Symmetric Molecules and Chromophore Pairs," W. Qian and D. M. Jonas, J. Chem. Phys., 119, 1611-1622 (2003).
4. "Spectroscopic tags based on dye-embedded nanoparticles and surface-enhanced Raman scattering," W. E. Doering and S. M. **Nie**, *Anal. Chem.*, 75, 6171-6176 (2003).
5. "The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape and Dielectric Environment," L. Kelly, E. Coronado, L. Zhao, G. C. **Schatz**, J. Phys. Chem. B, 107, 668-77 (2003).
6. "The extinction spectra of silver nanoparticle arrays: influence of array structure on plasmon resonance wavelength and widths," LinLin Zhao, K. Lance Kelly and George C. **Schatz**, J. Phys. Chem. B, 107, 7343-7350 (2003)
7. "Extinction spectra of silver nanoparticle arrays," Shengli Zou, Linlin Zhao, George C. **Schatz**, SPIE Proceedings, 5221(Plasmonics: Metallic Nanostructures and Their Optical Properties), 174-181 (2003).
8. "Nanoparticle Optics: The Importance of Radiative Dipole Coupling in Two-Dimensional Nanoparticle Arrays," C. L. Haynes, A. D. McFarland, L. Zhao, R. P. **Van Duyne**, G. C. **Schatz**, L. Gunnarsson, J. Prikulis, B. Kasemo, M. Käll, *J. Phys. Chem. B*, 107, 7337-7342 (2003).
9. "Toward a Glucose Biosensor Based on Surface-Enhanced Raman Scattering," K. E. Shafer-Peltier, C. L. Haynes, M. R. Glucksberg, and R. P. **Van Duyne**, J. Am. Chem. Soc.,125, 588-593 (2003).
10. "Plasmon-Sampled Surface-Enhanced Raman Excitation Spectroscopy," C. L. Haynes, R. P. **Van Duyne**, *J. Phys. Chem. B*, 107, 7426-7433 (2003).
11. "Dichroic Optical Properties of Extended Nanostructures Fabricated Using Angle-Resolved Nanosphere Lithography," C. L. Haynes, R. P. **Van Duyne**, *Nano Lett.*, 3, 939-943 (2003).
12. "Nanosensors Enable Portable Detectors for Environmental and Medical Applications," A. J. Haes, R. P. **Van Duyne**, Laser Focus World, 39, No. 5, 153-156 (2003).
13. "Single Silver Nanoparticles as Real-Time Optical Sensors with Zeptomole Sensitivity," A. D. McFarland, R. P. **Van Duyne**, *Nano Lett.*, 3, 1057-1062 (2003).
14. "An electrochemical surface-enhanced Raman spectroscopy approach to anthrax detection", X. Zhang, C. R. Yonzon, R. P. **Van Duyne**, Proceedings of SPIE-The International Society for Optical Engineering, 5221, 82-91 (2003).
15. "Localized surface plasmon resonance immunoassay and verification using surface-enhanced Raman spectroscopy", C. R. Yonzon, X. Zhang, R. P. **Van Duyne**, Proceedings of SPIE-The International Society for Optical Engineering, 5224, 78-85 (2003).
16. "Nanoparticle optics: sensing with nanoparticle arrays and single nanoparticles", A. J. Haes, A. D. McFarland, R. P. **Van Duyne**, Proceedings of SPIE-The International Society for Optical Engineering, 5223, 197-207 (2003).

17. "Nanoscale optical biosensors based on localized surface plasmon resonance spectroscopy", A. J. Haes, R. P. **Van Duyne**, Proceedings of SPIE-The International Society for Optical Engineering, 5221, 47-58 (2003).
18. "Effect of Acidic and Basic Surface Dipoles on the Depletion Layer of Indium Tin Oxide as Measured by In-Plane Conductance," A.L. Swint and P.W. **Bohn**, Appl. Phys. Lett. 84, 61-63 (2004).
19. "Effect of the Interfacial Chemical Environment on In-Plane Electronic Conduction of Indium Tin Oxide: Role of Surface Charge, Dipole Magnitude and Carrier Injection," A.L. Swint and P.W. **Bohn**, Langmuir, 20, 4076-4084 (2004).
20. "Fourier-algorithm for four-wave mixing signals from optically dense systems with memory," N. Belabas and D. M **Jonas**, Opt. Lett. 29, 1811-1813 (2004).
21. "Flashy silver nanoparticles," Andersen, PC; Jacobson, ML; **Rowlen**, KL., J. Phys. Chem. B, 108, 2148-2153 (2004).
22. "Harnessing Surface Plasmons," Jacobson, M. L., Reilly, T., **Rowlen**, K. L., SPIE Proceedings, 5513, 86-100 (2004).
23. "Investigation of the Blinking Phenomenon in SERS," Jacobson, M. L., **Rowlen**, K. L., SPIE Proceedings, 5513, 107-15 (2004).
24. "Enhancement on Nanoaperture Arrays," Reilly, T., **Rowlen**, K. L., SPIE Proceedings 5513, 250-257 (2004).
25. "Electromagnetic Fields Around Silver Nanoparticles and Dimers", E. Hao and G. C. **Schatz**, J. Chem. Phys. 120, 357-66 (2004).
26. "The Optical Properties of Metal Nanoshells", Encai Hao, Shuyou Li, Ryan C. Bailey, Shengli Zou, George C. **Schatz**, and Joseph T. Hupp, J. Phys. Chem. B, 108, 1224-1229 (2004)
27. "Synthesis and Optical Properties of "Branched" Gold Nanocrystals," E. Hao, R. C. Bailey, G. C. **Schatz**, J. T. Hupp and S. Li, Nano Letters, 4, 327-330 (2004).
28. "Synthesis and Optical Properties of Anisotropic Metal Nanoparticles," Encai Hao, George C. **Schatz**, Joseph T. Hupp, Journal of Fluorescence, 14, 331-41 (2004).
29. "Silver nanoparticle array structures that produce remarkably narrow plasmon lineshapes," Shengli Zou, Nicolas Janel, and George C. **Schatz**, J. Chem. Phys. 120, 10871-10875 (2004).
30. "Synthesis and Optical Properties of Anisotropic Metal Nanoparticles," Encai Hao, George C. **Schatz**, Joseph T. Hupp, Journal of Fluorescence, **14**, 331-41 (2004).
31. "Electronic structure studies of surface enhanced Raman scattering," L. Zhao and G. C. **Schatz**, Proc. SPIE 5512, 10-19, Plasmonics: Metallic nanostructures and Their Optical Properties II, N. J. Halas, T. R. Huser, Eds. (2004).
32. "Generating narrow plasmon resonances from silver nanoparticle arrays: influence of array pattern and particle spacing," Shengli Zou, George C. **Schatz**, Proc. SPIE 5513, 22-29, Physical Chemistry of Interfaces and Nanomaterials III, G. V. Hartland, X. –Y. Zhu, Eds. (2004).
33. "Narrow plasmonic/photonic extinction and scattering lineshapes for one and two dimensional silver nanoparticle arrays," Shengli Zou and George C. **Schatz**, J. Chem. Phys., 121, 12606-12612(2004).
34. "Optical properties of one-dimensional metal nanostructures." Encai Hao, Shengli Zou, George C. **Schatz**, Materials Research Society Symposium Proceedings 818, 53-58 (2004).

35. "Using Solution-Phase Nanoparticles, Surface-Confined Nanoparticle Arrays and Single Nanoparticles as Biological Sensing Platforms", A. J. Haes, D. A. Stuart, S. **Nie**, R. P. **Van Duyne**, Journal of Fluorescence, 14, 355-367 (2004).
36. "Nanosphere Lithography: Fabrication of Large Area Ag Nanoparticle Arrays by Convective Self-Assembly and their Characterization by Scanning UV-vis Extinction Spectroscopy", A. D. Ormonde, E. C. McLellan, J. Castillo, and R. P. **Van Duyne**, Langmuir, 20, 6927-6931 (2004).
37. "Sub-100 nm Triangular Nanopores Fabricated with the Reactive Ion Etching Variant of Nanosphere Lithography and Angle-Resolved Nanosphere Lithography", A. V. Whitney, B. D. Myers, and R. P. **Van Duyne**, Nano Lett., 4, 1507-1511 (2004).
38. "Probing the long range distance dependence of noble metal nanoparticles", A. J. Haes and R. P. **Van Duyne**, Mat. Res. Soc. Symp. Proc., 789, 409-414 (2004).
39. "A Nanoscale Optical Biosensor: The Short Range Distance Dependence of the Localized Surface Plasmon Resonance of Silver and Gold Nanoparticles", A. J. Haes, S. Zou, G. C. **Schatz**, R. P. **Van Duyne**, J. Phys. Chem. B, 108, 6961-6968 (2004).
40. "A Nanoscale Optical Biosensor: The Long Range Distance Dependence of the Localized Surface Plasmon Resonance of Noble Metal Nanoparticles", A. J. Haes, S. Zou, G. C. **Schatz**, R. P. **Van Duyne**, J. Phys. Chem. B, 108, 109-116 (2004).
41. "A Glucose Biosensor Based on Surface-Enhanced Raman Scattering: Improved Partition Layer, Temporal Stability, Reversibility, and Resistance to Serum Protein Interference", C. L. Haynes, C. R. Yonzon, X. Zhang, J. T. Walsh, R. P. **Van Duyne**, Anal. Chem., 76, 78-85 (2004).
42. "Preliminary studies and potential applications of localized surface plasmon resonance spectroscopy in medical diagnostics", A. J. Haes and R. P. **Van Duyne**, Expert Rev. Mol. Diagn., 4, 527-537 (2004).
43. "Comparative Study of a Localized and Propagating Surface Plasmon Resonance Sensors: Concanavalin A Binding to a Monosaccharide Functionalized Self-Assembled Monolayer", C. R. Yonzon, E. Jeoung, S. Zou, G. C. **Schatz**, M. Mrksich, and R. P. **Van Duyne**, J. Am. Chem. Soc., 126, 12669-12676 (2004).
44. "A Unified View of Propagating and Localized Surface Plasmon Resonance Biosensors," A. J. Haes, and R. P. **Van Duyne**, Analytical and Bioanalytical Chemistry 379, 920-930 (2004).
45. "Molecular Plasmonics," R. P. **Van Duyne**, Science, 306, 985-986 (2004).
46. "Surface-Enhanced Raman Spectroscopy with a Laser Pointer Light Source and Miniature Spectrometer," M. A. Young, D. A. Stuart, A. D. McFarland, O. Lyandres, M. R. Glucksberg, and R. P. **Van Duyne**, Can. J. Chem., 82, 1435-1441 (2004).
47. "Refractive index sensitive, plasmon resonant scattering, and surface-enhanced Raman scattering nanoparticles and arrays as biological sensing platforms," D. A. Stuart, A. J. Haes, A. D. McFarland, S. **Nie**, and R. P. **Van Duyne**, Proceedings of SPIE-The International Society for Optical Engineering, 5327, 60-73 (2004).
48. "Porous GaN as a template to produce surface enhanced Raman scattering (SERS)-active surfaces," Williamson, T.L.; Guo, X.; Zukoski, A.; Sood, A.; Díaz, D.J.; **Bohn**, P.W., J. Phys. Chem. B, 109, 20186-20191 (2005).
49. "Interfacial Scattering at Electrochemically Fabricated Atom-Scale Junctions between Thin Gold Film Electrodes in a Microfluidic Channel," P.J. Castle and P.W. **Bohn**, Analyt. Chem., 77, 243-249 (2005).

50. "Electrochemical Ostwald Ripening of Colloidal Ag particles on Conductive Substrates," P. L. Redmond, A. J. Hallock, and L. E. **Brus**, Nano Letters 5, 131 (2005)
51. "Optical Forces between Metallic Particles," A. J. Hallock, P. L. Redmond, L. E. **Brus**, Proc. Nat. Acad. Sci. 102, 1280 (2005)
52. "Three-dimensional view of signal propagation in femtosecond four-wave mixing with application to the boxcars geometry," N. Belabas and D. M. **Jonas**, J. Opt. Soc. Am. B 22, 655-674 (2005)
53. "Propagation and detection distortions of four-wave mixing signals: application to 2D spectroscopy," N. Belabas and D. M. **Jonas** in Ultrafast Phenomena XIV, edited by T. Kobayashi, T. Okada, T. Kobayashi, K. Nelson, S. De Silvestri (Springer, New York, 2005) pp.572-574
54. "Mid-Infrared Electric Field Characterization Using a Visible Charge-Coupled-Device-Based Spectrometer," K. J. Kubarych, M. Joffre, A. Moore, N. Belabas, and D. M. Jonas, Opt. Lett. 30, 1228-1230 (2005)
55. "Real-Time Detection of Virus Particles and Viral Protein Expression with Dual-Color Nanoparticle Probes," A. Agrawal, R. Tripp, and S. M. **Nie**, *Journal of Virology*, 79, 8625-8628 (2005).
56. "2D correlation analysis of the continuum in single molecule surface enhanced Raman spectroscopy," Moore, AA; Jacobson, ML; Belabas, N; **Rowlen**, KL; **Jonas**, DM., J. Am. Chem. Soc., 127, 7292-7293 (2005). "Editors' Choice" in Science 308 p.927 (2005)
57. "Photodynamics on thin silver films," Jacobson, ML; **Rowlen**, KL. Chem. Phys. Lett., 401, 52-57 (2005).
58. "Confined plasmons in nanofabricated single silver particle pairs – experimental observations of strong interparticle interactions," Linda Gunnarsson, Tomas Rindzevicius, Juris Prikulis, Bengt Kasemo, Mikael Kall, Shengli Zou and George C. **Schatz**, J. Phys. Chem. B, 109, 1079-1087, (2005).
59. "Silver nanoparticle array structures that produce giant enhancements in electromagnetic fields," Shengli Zou and George C. **Schatz**, Chem. Phys. Lett, 403, 62-67 (2005).
60. Reply to "Silver nanoparticle array structures that produce remarkable narrow plasmon lineshapes" [J. Chem. Phys. 130, 10871 (2004)], Shengli Zou and George C. **Schatz**, J. Chem. Phys., 122, 097102/1-097102/2 (2005).
61. "Finite lifetime effects on the polarizability within time-dependent density functional theory," L. Jensen, J. Autschbach and G. C. **Schatz**, J. Chem. Phys. 122, 224115 (2005).
62. "Theory and method for calculating resonance Raman scattering from resonance polarizability derivatives," L. Jensen, L. Zhao, J. Autschbach and G. C. **Schatz**, J. Chem. Phys., 123, 174110/1-174110/11 (2005).
63. "Second Harmonic Excitation Spectroscopy of Silver Nanoparticle Arrays", A. M. Moran, J. Sung, E. M. Hicks, R. P. **Van Duyne**, K. G. **Spears**, J. Phys. Chem. B., 109, 4501-4506 (2005).
64. "Nanopatterning with Lithography," C. L. Haynes, A. D. McFarland, R. P. **Van Duyne**, and H. A. Godwin, J. Chem. Edu. 82, 768A-768B (2005).
65. "Biological Applications of Localized Surface Plasmon Resonance Phenomenae," D. A. Stuart, A. J. Haes, C. R. Yonzon, E. M. Hicks, and R. P. **Van Duyne**, IEE Proc.-Nanobiotechnol., 152, 13-32 (2005).
66. "Detection of a Biomarker for Alzheimer's disease from Synthetic and Clinical Samples using a Nanoscale Optical Biosensor," A. J. Haes, L. Chang, W. L. Klein, and R. P. **Van Duyne**, J. Am. Chem. Soc., 127, 2264-2271 (2005).

67. "Rapid Detection of an Anthrax Biomarker by Surface-Enhanced Raman Spectroscopy," X. Zhang, M. A. Young, O. Lyandres, and R. P. **Van Duyne**, J. Am. Chem. Soc., 127, 4484-4489 (2005).
68. "Surface-enhanced Raman sensors: early history and the development of sensors for quantitative biowarfare agent and glucose detection," C. L. Haynes, C. R. Yonzon, X. Zhang, and R. P. **Van Duyne**, J. Raman Spectrosc., 36, 471-484 (2005).
69. "Glucose Sensing Using Near Infrared Surface-Enhanced Raman Spectroscopy: Gold Surfaces, 10-Day Stability, and Improved Accuracy," D. A. Stuart, C. R. Yonzon, X. Zhang, O. Lyandres, N. Shah, M. R. Glucksberg, J. Y. Walsh, and R. P. **Van Duyne**, Anal. Chem., 77, 4013-4019 (2005).
70. "Plasmonic Materials for Surface-Enhanced Sensing and Spectroscopy," A. J. Haes, C. L. Haynes, A. D. McFarland, S. Zou, G. C. **Schatz**, and R. P. **Van Duyne**, MRS Bulletin, 30, 368-375 (2005).
71. "Wavelength-Scanned Surface-Enhanced Raman Excitation Spectroscopy," A. D. McFarland, M. A. Young, J. A. Dieringer, and R. P. **Van Duyne**, J. Phys. Chem. B., 109, 11279-11285 (2005).
72. "Solution-Phase, Triangular Ag Nanotriangles Fabricated by Nanosphere Lithography," A. J. Haes, J. Zhao, S. Zou,, C. S. Own, L. D. Marks, G. C. **Schatz**, and R. P. **Van Duyne**, J. Phys. Chem. B., 109, 11158-11162 (2005).
73. "Controlling Plasmon Line-shapes through Diffractive Coupling in Linear Arrays of Cylindrical Nanoparticles Fabricated by Electron Beam Lithography," E. M. Hicks, S. Zou, L. Gunnarsson, T. Rindzevicius , M. Käll, B. Kasemo, G. C. **Schatz**, K. G. **Spears**, and R. P. **Van Duyne**, Nano Lett., 5, 1065-1070 (2005).
74. "Nanoscale plasmonics begins to unravel Alzheimer's disease", A. J. Haes, W. P. Hall, and R. P. **Van Duyne**, Laser Focus World, 41, No.6, 105-109 (2005).
75. "Electrochemical Tuning of Silver Nanoparticles Fabricated by Nanosphere Lithography," X. Zhang, E. M. Hicks, J. Zhao, G. C. **Schatz**, and R. P. **Van Duyne**, Nano Lett., 5, 1503-1507 (2005).
76. "Real-Time Glucose Sensing by Surface-Enhanced Raman Spectroscopy in Bovine Plasma Facilitated by a Mixed Decanethiol/Mercaptohexanol Partition Layer", O. Lyandres, N. C. Shah, C. R. Yonzon, J. T. Walsh Jr., M. R. Glucksberg, and R. P. **Van Duyne**, Anal. Chem., 77, 6134-6139, (2005).
77. "Optimized Silver Film over Nanosphere Surfaces for the Biowarfare Agent Detection Based on Surface-Enhanced Raman Spectroscopy" X. Zhang, R. P. **Van Duyne**, *Materials Research Society Symposium Proceeding*, 876E, R8.54 (2005)
78. "Towards advanced chemical and biological nanosensors - An overview," D. A. Stuart, C. R. Yonzon, X. Zhang, A. D. McFarland, C. L. Haynes, and R. P. **Van Duyne**, Talanta, 67, 438-448 (2005).
79. "Surface-Enhanced Raman Spectroscopy", C. L. Haynes, A. D. McFarland, and R. P. **Van Duyne**, Anal. Chem., 77, 338A-346A (2005).
80. "The Localized Surface Plasmon Resonance Nanosensor: A High Resolution Distance Dependence Study Using Atomic Layer Deposition", A. V. Whitney, J. W. Elam, S. Zou, A. V. Zinovev, P. C. Stair, G. C. **Schatz**, R. P. **Van Duyne**, J. Phys. Chem. B., 109, 20522-20528 (2005).
81. "Localized Surface Plasmon Resonance Spectroscopy of Single Silver Nanocubes,"

L. J. Sherry, S-H. Chang, B. J. Wiley Y. Xia, G. C. **Schatz**, and R. P. **Van Duyne**, Nano Lett., 5, 2034-2038 (2005).

82. "Plasmonic Properties of Film Over Nanowell Surface Fabricated by Nanosphere Lithography," E. M. Hicks, X. Zhang, S. Zou, O. Lyandres, K. G. **Spears**, G. C. **Schatz**, and R. P. **Van Duyne**, J. Phys. Chem. B., 109, 22351-22358 (2005).
83. "Investigating narrow plasmons in nanoparticle arrays fabricated using Electron Beam Lithography," E. M. Hicks, L. Gunnarsson, T. Rindzevicius, S. Zou, B. Kasemo, M. Käll, G. C. **Schatz**, K. G. **Spears**, and R. P. **Van Duyne**, Mat. Res. Soc. Symp. Proc., 872, 317-322 (2005)
84. "Surfactant-Induced Modulation of Light Emission in Porous Silicon Produced by Metal-Assisted Electroless Etching," Chattopadhyay, S.; **Bohn**, P.W., Analyt. Chem., 78, 6058-6064 (2006).
85. "Enhanced ultraviolet photoconductivity in porous GaN prepared by metal-assisted electroless etching," Guo, X.; Williamson, T.L.; **Bohn**, P.W., Solid State Comm., 140, 159-162 (2006).
86. "Electroless Deposition of Au and Pt for Metallization of the Intrapore Space in Porous GaN," Díaz, D.J.; Williamson, T.L; Guo, X.; Sood, A.; **Bohn**, P.W., Thin Solid Films, 514, 120-126 (2006).
87. "Photo-induced Thermal Copper Reduction onto Gold Nanocrystals Under Potentiostatic Control," A. J. Hallock, P. L. Redmond, L. E. **Brus**, J. Phys. Chem. B *110*, 25158 (2006)
88. "Pure Ge epitaxial growth on thin strained SiGe graded layers on bulk Si substrate for high channel mobility MOSFET," S. Dey, S. Joshi, D. Garcia-Gutierrez, M.Chaumont, M. Jose-Yacaman, A.**Campion** and S.K. Banerjee, J. Electron. Mater., 35, 1607 -1612 (2006)
89. "Counting Single Native Biomolecules and Intact Viruses with Color Coded Nanoparticles," A. Agrawal, C. Zhang, T. Byassee, and S. M. **Nie**, *Anal. Chem.*, 78, 1061-1070 (2006).
90. "Reexamining the origins of spectral blinking in single-molecule and single-nanoparticle SERS," S. R. Emory, M. Y. Han, and S. M. **Nie**, *Faraday Discussions* 132, 249-259 (2006).
91. "The role of O_2 in SERS-active thin metal film photodynamics," Jacobson, ML; **Rowlen**, KL., J. Phys. Chem. B, 110, 19491-19496 (2006).
92. "Time-dependent density functional calculations of optical rotatory dispersion including resonance wavelengths as a potentially useful tool for determing absolute configurations of chiral molecules," Jochen Autschbach, Lasse Jensen, George C. **Schatz**, Y. C. Electra Tse and Mykhaylo Krykunov, J. Phys. Chem. A 110, 2461-73 (2006)
93. "Pyridine-Ag_{20} Cluster: A model system for studying surface enhanced Raman scattering," L. Zhao, L. Jensen and G. C. **Schatz**, J. Am. Chem. Soc. 128, 2911-19 (2006)
94. "Coupled plasmon/photonic resonance effects in SERS," Shengli Zou and George C. **Schatz**, in Surface Enhanced Raman Scattering: Physics and Applications, Ed. K. Kneipp, M. Moskovits and H. Kneipp, Springer Topics in Applied Physics, 103, 67-86, 2006
95. "Electromagnetic mechanism of SERS," George C. **Schatz**, Matthew Young and Richard P. **Van Duyne**, in Surface Enhanced Raman Scattering: Physics and Applications, Ed. K. Kneipp, M. Moskovits and H. Kneipp, Springer Topics in Applied Physics, 103, 19-46, 2006

96. "Resonance Raman scattering of Rhodamine 6G as calculated using time-dependent density functional theory," Lasse Jensen and George C. **Schatz**, J. Phys. Chem. A, 110, 5973-77 (2006).
97. "Theoretical studies of plasmon resonances in one-dimensional nanoparticle chains: narrow lineshapes with tunable widths," Shengli Zou and George C. **Schatz**, Nanotechnology, 17, 2813-20 (2006).
98. "Surface-enhanced Raman scattering of pyrazine at the junction between two Ag_{20} nanoclusters," Linlin Zhao, Lasse Jensen and George C. **Schatz**, Nano Letters, **6**, 1229-1234 (2006).
99. "Metal nanoparticle array waveguides: Proposed structures for subwavelength devices," S. Zou and G. C. **Schatz**, Phys. Rev. B, 74, 125111/1-/15 (2006).
100. "Surface-Enhanced Raman Spectroscopy of Half-Mustard Agent," D. A. Stuart, K. B. Biggs, and R. P. **Van Duyne**, The Analyst, 131, 568-572 (2006).
101. "Surface-enhanced Raman spectroscopy: new materials, concepts, characterization tools, and applications," J. A. Dieringer, O. Lyandres, A. D. McFarland, N. C. Shah, D. A. Stuart, A. V. Whitney, C. R. Yonzon, M. A. Young, J. Yuen, X. Zhang, and R. P. **Van Duyne**, Faraday Discussion 132, 9-26 (2006).
102. "Nanosphere Lithography Fabricated Plasmonic Materials and Their Applications," X. Zhang, C. Yonzon, and R. P. **Van Duyne**, J. Mat. Res., 21, 1083-1092 (2006)
103. "Glucose Sensing with Surface-Enhanced Raman Spectroscopy," C. R. Yonzon, O. Lyandres, N. C. Shah, J. A. Dieringer, and R. P. **Van Duyne**, In Topics in Applied Physics; Vol. 103: Surface Enhanced Raman Scattering – Physics and Applications; Kneipp, K., Moskovits M., Kneipp, H. Eds.; Springer; New York, 2006; pp. 367-379.
104. "Advances in Contemporary Nanosphere Lithographic Techniques," X. Zhang, A. V. Whitney, J. Zhao, E. M. Hicks, and R. P. **Van Duyne**, Journal of Nanoscience and Nanotechnology, 6, 1920-1934, (2006)
105. "Localized Surface Plasmon Resonance Spectroscopy near Molecular Resonances," A. J. Haes, S. Zou, J. Zhao, G. C. **Schatz**, and R. P. **Van Duyne**, J. Am. Chem. Soc., 128, 10905-10914, (2006)
106. "Localized Surface Plasmon Resonance Spectroscopy of Single Silver Triangular Nanoprisms," L. J. Sherry, R. Jin, C. A. Mirkin, G. C. **Schatz**, and R. P. **Van Duyne**, Nano Lett., 6, 2060-2065, (2006)
107. "Alkanethiol Mediated Release of Surface Bond Nanoparticles Fabricated by Nanosphere Lithography," J. Zhao, A. J. Haes, X. Zhang, S. Zou, E. M. Hicks, G. C. **Schatz**, and R. P. **Van Duyne**, Mat. Res. Soc. Symp. Proc., 900E, 0900-O13-08.1--0900-O13-08.6 (2006)
108. "Localized Surface Plasmon Resonance Biosensors," J. Zhao, X. Zhang, C. Yonzon, A. J. Haes, R. P. **Van Duyne**, Nanomedicine, 1, 219-228 (2006)
109. "Resonance Localized Surface Plasmon Spectroscopy: Low Molecular Weight Substrate Binding to Cytochrome P450," J. Zhao, A. Das, X. Zhang, G. C. **Schatz**, S. G. Sligar, and R. P. **Van Duyne**, J. Am. Chem. Soc., 128, 11004-11005, (2006).
110. "Ultrastable Substrates for Surface-Enhanced Raman Spectroscopy Fabricated by Atomic Layer Deposition: Improved Anthrax Biomarker Detection," X. Zhang, J. Zhao, A. Whitney, J. Elam, and R. P. **Van Duyne**, J. Am. Chem. Soc., 128, 10304-10309 (2006)
111. "Sensitive and Selective Chem/Bio Sensing Based on Surface-Enhanced Raman Spectroscopy (SERS)," X. Zhang, N. C. Shah, and R. P. **Van Duyne**, Vibrational Spectroscopy, 42, 2–8, (2006).

112. "Localized surface plasmon and molecular resonance: fundamental study and application," J. Zhao, X. Zhang, A. J. Haes, S. Zou, G. C. **Schatz** and R. P. **Van Duyne**, Proceedings of SPIE-The International Society for Optical Engineering, 6323, 1B-1 – 1B13 (2006).
113. "Surface-Enhanced Hyper-Raman Scattering (SEHRS) on Ag Film Over Nanosphere (FON) Electrodes: Surface Symmetry of Centrosymmetric Adsorbates," J. C. Hulteen, M. A. Young, and R. P. **Van Duyne**, Langmuir, 22, 10354-10364 (2006).
114. "*In Vivo* Glucose Measurement by Surface-Enhanced Raman Spectroscopy," D. A. Stuart, J. M. Yuen, N. C. Shah, O. Lyandres, C. R. Yonzon, M. R. Glucksberg, J. T. Walsh, and R. P. **Van Duyne**, Anal. Chem., 78, 7211-7215 (2006).
115. "Photo-Voltage and Photo-Catalyzed Growth in Citrate Stabilized Colloidal Silver Nanocrystals," P. L. Redmond, X. Wu and L. **Brus**, J. Phys. Chem. C, 111, 8942 (2007).
116. "Ultra-thin Si1-xGex dislocation blocking layers for Ge /strained Si CMOS devices" S. Joshi, S. Dey, M. Chaumont, A. **Campion** and S. K.Banerjee, J. Electron. Mater. 36, 641- 647 (2007).
117. "Propagation, beam geometry, and detection distortions of peak shapes in two-dimensional Fourier transform spectra," M. K. Yetzbacher, N. Belabas, K. A. Kitney, and D. M. **Jonas**, J. Chem. Phys. 126, 044511 (2007) (19 pages)
118. "Dispersion Relations in Two-Dimensional Spectroscopy," K. A. Kitney, M. K. Yetzbacher, A. A. Ferro, and D. M. **Jonas**, Springer Series in Chemical Physics 88, 395-397 (2007)
119. "Propagation, beam geometry, and detection distortions of peak shapes in two-dimensional Fourier transform spectroscopy," M. K. Yetzbacher, K. A. Kitney, N. Belabas, and D. M. **Jonas**, Springer Series in Chemical Physics 88, 338-340 (2007)
120. "Etching Colloidal Gold Nanocrystals with Hyper-branched and Multivalent Polymers: A New Route to Fluorescent and Water-Soluble Atomic Clusters," H. Duan and S. M. **Nie**, J. Am. Chem. Soc. 129, 2412-2413 (2007).
121. "Vapor Deposition Method for Sensitivity Studies on Engineered Surface-Enhanced Raman Scattering-Active Substrates," Reilly, T. H., III; Corbman, J. D.; **Rowlen**, K. L., Anal. Chem. 79, 5078-5081 (2007).
122. "Quantitative evaluation of plasmon enhanced Raman scattering from nanoaperture arrays," Reilly, T.H. III; Chang, SH; Corbman, JD; **Schatz**, GC; **Rowlen**, KL., J. Phys. Chem. C, 111, 1689-1694 (2007).
123. "Size-dependence of the enhanced Raman scattering of pyridine adsorbed on Ag_n (n=2-8,20) clusters," Lasse Jensen, Linlin Zhao, George C. **Schatz**, J. Phys. Chem. C 111, 4756-4764 (2007).
124. "Quantitative evaluation of plasmon enhanced Raman scattering from nanoaperture arrays," Thomas Reilly III, Shih-Hui Chang, Jordan D. Corbman, George C. **Schatz**, Kathy L. **Rowlen**, J. Phys. Chem. C, 111, 1689-94 (2007).
125. "Nanoparticle Spectroscopy: Dipole Coupling in 2D Arrays of L-shaped Silver Nanoparticles," J. Sung, E. M. Hicks, R. P. **Van Duyne** and K. G. **Spears**, J. Phys. Chem. C., 111, 10368-10376 (2007).
126. "Localized Surface Plasmon Spectroscopy and Sensing," K. A. Willets and R. P. **Van Duyne**, Ann. Rev. Phys. Chem., 58, 267-297 (2007).
127. "Plasmonic Materials for Surface-Enhanced and Tip-Enhanced Raman Spectroscopy,"

M. A. Young, J. A. Dieringer, and R. P. **Van Duyne**, In Advances in Nano-Optics and Nano-Photonics; Vol. 2: Tip Enhancement; Kawata S., Shalaev, V.M. Eds.; Elsevier; Amsterdam, 2007; pp.1-39.

128. "Surface-Enhanced Nanosensors," C. R. Yonzon, X. Zhang, J. Zhao, and R. P. **Van Duyne**, Spectroscopy, 22, 42-56 (2007).
129. "Nanoscale Localized Surface Plasmon Resonance Biosensors," K. A. Willets, W. P. Hall, L. J. Sherry, X. Zhang, J. Zhao, and R. P. **Van Duyne**, In Nanobiotechnology: Concepts, Methods and Perspectives; Mirkin C. A., Niemeyer C. M. Eds,; Wiley-VCH; New York, 2007; pp. 159-173.
130. "Plasmonic Properties of Anchored Nanoparticles Fabricated by Reactive Ion Etching and Nanosphere Lithography," E. M. Hicks, O. Lyandres, M. R. Glucksberg, and R. P. **Van Duyne**, J. Phys. Chem. C, 111, 4116 - 4124 (2007).
131. "Interaction of Plasmon and Molecular Resonances for Rhodamine 6G Adsorbed on Silver Nanoparticles," J. Zhao, J. Sung, S. Zou, L. Jensen, G. C. **Schatz**, and R. P. **Van Duyne**, J. Am. Chem. Soc., 129, 7647-7656 (2007).
132. "Plasmonic Properties of Copper Nanoparticles Fabricated by Nanosphere Lithography," G. H. Chan, J. Zhao, E. M. Hicks, G. C. **Schatz**, and R. P. **Van Duyne**, Nano Letters, 7, 1947-1952 (2007).
133. "Lactate and Sequential Lactate-Glucose Sensing Using Surface-Enhanced Raman Spectroscopy", N. C. Shah, O. Lyandres, J. T. Walsh Jr., M. R. Glucksberg, and R. P. **Van Duyne**, Anal. Chem., 79, 6927-6932 (2007).
134. "Surface-Enhanced Raman Sensing: Glucose and Anthrax," N. C. Shah, O. Lyandres, C. Yonzon, X. Zhang, and R. P. **Van Duyne**, In ACS Symposium Series Vol.963, 107-122 (2007).
135. "Preparation and Properties of Porous GaN Fabricated by Metal-Assisted Electroless Etching," Williamson, T.L.; Díaz, D.J.; **Bohn**, P.W., Porous Silicon Carbide and Gallium Nitride, in press (2007).
136. ""Hot Electron" Photo-Charging and Electrochemical Discharge Kinetics of Silver Nanocrystals," P. L. Redmond and L. E. **Brus**, J. Phys. Chem C, accepted (2007).
137. "Watching Electrons Move through a Conical Intersection" D. A. Farrow, W. Qian, E. R. Smith, A. A. Ferro, and D. M. **Jonas**, J. Chem. Phys. (submitted, revised) (2007).
138. "In-Vivo Tumor Targeting and Spectroscopic Detection with Surface-Enhanced Raman Nanoparticle Tags," X.-M. Qian, Xiang-Hong Peng, Dominic Ansari,Qiqin Yin-Goen,Dong M. Shin, Lily Yang, Andrew N. Young, and S. M. **Nie**, submitted to Nature Biotechnology, under in-depth review, (2007).
139. "Colocalization of color-coded nanoparticle probes at nanometer precisions: a new method for single molecule detection and biomolecular conformation studies," A. Agrawal, M. D. Wang, and S. M. **Nie**, submitted to Proc. Natl. Acad. Sci. USA, under in-depth review, (2007).
140. "Annealing effects on surface-plasmon-enhanced bulk heterojunction, organic photovoltaics," Morfa, A.J., Reilly, T.H., **Rowlen**, K.L., van de Lagemaat, J., SPIE Proceedings on Solar Energy + Applications, accepted (2007)
141. "Plasmon Enhanced Solar Energy Conversion in Organic Bulk Heterojunction Photovoltaics," Morfa, A.J., Reilly, T.H., **Rowlen**, K.L., van de Lagemaat, J., Advanced Materials, submitted (2007)

142. "Classical electromagnetic theory analysis and density functional theory study of local field gradient effects in SERS," Christine M. Aikens and George C. **Schatz**, ACS Books Symp. Series (2007) in press.
143. "Resonance vibrational Raman optical activity: a time-dependent density functional theory approach," L. Jensen, J. Autschbach, M. Krykunov and G. C. **Schatz**, J. Chem. Phys., in press (2007).
144. "Optical properties of metal nanoparticles without a center of inversion symmetry: observation of volume plasmons," M. Sukharev, J. Sung, K. G. **Spears**, and T. Seideman, Phys. Rev. B, submitted September (2007)
145. "Nanoparticle Spectroscopy: Plasmon Coupling in Finite Sized 2D Arrays of Cylindrical Silver Nanoparticles," J. Sung, E. M. Hicks, K. G. **Spears** and R. P. **Van Duyne**, J. Phys. Chem. C, submitted September 12 (2007)
146. "Nanoparticle Spectroscopy: Birefringence in 2D Arrays of L-shaped Silver Nanoparticles," J. Sung, M. Sukharev, E. M. Hicks, R. P. **Van Duyne**, T. Seideman, and K. G. **Spears**, J. Phys. Chem. C, accepted (2007)
147. "Surface-Enhanced Raman Sensors for Metabolic Analytes," O. Lyandres, M. R. Glucksberg, J. T. Walsh, N. C. Shah, C. R. Yonzon, X. Zhang and R. P. Van Duyne, In Modern Concepts of Biomedical Vibrational Spectroscopy; Kneipp, J., Lasch, P., Eds., John Wiley & Sons, Inc, New York, 2008; pp.221-241
148. "Towards A Thermally Robust Operando Surface-Enhanced Raman Spectroscopy (SERS) Substrate," A.V. Whitney, J. W. Elam, P. C. Stair, and R. P. **Van Duyne**, J. Phys. Chem. C., 111, 16827-16832 (2007)
149. "Molecular Plasmonics: Chromophore-Plasmon Coupling and Single Particle Nanosensors," J. Zhao, L. J. Sherry, G. C. **Schatz** and R. P. **Van Duyne**, IEEE Journal of Selected Topics Quantum Electronics, submitted July 1, 2007.
150. "Surface-Enhanced Raman Spectroscopy for Glucose Analysis," N. C. Shah, J. M. Yuen, M. R. Glucksberg, J. T. Walsh, and R. P. **Van Duyne**, In *In Vivo* Analytical Chemistry of Glucose, Stenken, J., Cunningham, D., Eds., John Wiley & Sons, Inc.; submitted August 22, 2007.
151. "Stability of Silver Nanoparticles Fabricated by Nanosphere Lithography and Atomic Layer Deposition to Femtosecond Laser Excitation," J. Sung, K. Kosuda, J. W. Elam, K. G. **Spears**, and R. P. **Van Duyne**, J. Phys. Chem. C, under revision (2008)
152. "A Frequency Domain Existence Proof of Single-Molecule Surface Enhanced Raman Spectroscopy," J. A. Dieringer, R. B. Lettan, K. A. Scheidt, and R. P. Van Duyne, J. Am. Chem. Soc., 129, 16249-16256 (2007).
153. "Surface-Enhanced Raman Spectroscopy," P. Stiles, J. Dieringer, N. C. Shah, and R. P. **Van Duyne**, Ann. Rev. Anal. Chem., 1, in press (2008).

7. Interactions/Transitions

7a. Participation/presentations at meetings, conferences, seminars, etc. (482)

All MURI Faculty spoke at the MURI kickoff meeting held at Northwestern University on Friday, February 07, 2003. Paul Bohn organized a symposium entitled, "Enhanced Chemical and Biochemical Sensing at Engineered Nanostructures," for the February 2004 Pittsburgh Conference. All of the speakers (Van Duyne, Nie, Rowlen, Campion, Bohn) were members of the MURI. Similarly, all MURI Faculty spoke at the mid-term MURI Center Review held November 4-5, 2004 at WPAFB Dayton, OH. These meetings introduced the MURI Team's

capabilities and projects to a wide variety of interested DoD, industrial, and other academic researchers. Students and postdocs from all MURI groups were also present and gave posters.

The MURI Faculty have given ~480 invited lectures during the past five years. These are enumerated below:

Paul W. Bohn

1. "Engineered Surfaces for the Active Control of Cell Motility - Electrochemically Generated Chemical Potential Gradients," Fall 2002 National Meeting of the American Chemical Society, Boston, MA, August 18-22, 2002.
2. "Active Control of Surface Transport with Electrochemically Generated Surface Chemical Potential Gradients," 2002 Federation of Analytical Chemistry and Spectroscopy Societies, Providence, RI, October 13-17, 2002.
3. "Spatiotemporal Control of Surface Properties with Electrochemical Gradients: Self-Aligning Materials to Cellular Motility," Eastern Analytical Symposium, Somerset, NJ, November 18-21, 2002.
4. "Active Control of Surfaces with Electrochemically Generated Composition Gradients," Spring 2003 National Meeting of the American Chemical Society, New Orleans, LA, March 23-28, 2003.
5. "Electronic and Optical Sensing at Atom-Scale Metal Junctions," 2004 PittCon, Chicago, IL, March 7-12, 2004.
6. "Sensing Molecular Adsorption through Interfacial Scattering at Conducting Films and Atom-Scale Junctions," 2004 Spring National ACS Meeting, Anaheim, CA, March 28-April 2, 2004.
7. "Spatiotemporal Control of Transport with Anisotropic In-Plane Electrochemical Potential Gradients, Department of Chemistry, University of Chicago, Chicago, IL, May 14, 2004.
8. "Spatiotemporal Control of Transport with Anisotropic In-Plane Electrochemical Potential Gradients," 205th National Meeting of the Electrochemical Society, San Antonio, TX, May 9-13, 2004.
9. "Growth of Self-Limiting Atom-Scale Metal Junctions for Electronic and Optical Sensing of Lewis Base Adsorbates," AFOSR Meeting on Optical Nanosensing, Dayton, OH, November 4-5, 2004.
10. "Electronic and Optical Sensing at Atom-Scale Metal Junctions," Nanoscale Science and Technology at the Bio-Nano Interface: A US-Asia Forum, Hong Kong, November 22-24, 2004.
11. "Growth of Self-Limiting Atom-Scale Metal Junctions for Electronic and Optical Sensing of Lewis Base Adsorbates," 2005 Spring National ACS Meeting, San Diego, CA, March 13-18, 2005.
12. "In-Plane Electrochemical Potential Gradients Produce Interfacial Free Energy Gradients and Active Spatiotemporal Control of Molecular Recognition, International Society of Electrochemistry Meeting, Singapore, April 15-19, 2006.
13. "In-Plane Electrochemical Potential Gradients for Active Spatiotemporal Control of Molecular Composition and Physical Properties, 2006 Spring National ACS Meeting, Atlanta, GA, March 26-30, 2006.
14. "Novel Conductance Effects in Chemistry: Atom-Scale Junctions and Electrochemical Gradients," Department of Chemistry, U.S. Air Force Academy, Colorado Springs, CO, February 22, 2006.

15. "Frequency Domain Probes of Single Molecule Adsorption and Desorption Events at Atom-Scale Junctions," PittCon 2007, Chicago, IL, February 25-March 1, 2007.

Louis E. Brus

Louis Brus has given about 12 invited presentations each year during the MURI, describing this and other nanoscience research.

Alan Campion

1. "On the Chemical Enhancement Mechanism in Surface-Enhanced Raman Scattering" University of Dusseldorf, April 2002.
2. "On the Chemical Enhancement Mechanism in Surface-Enhanced Raman Scattering" University of Liverpool, April 2002.
3. "On the Chemical Enhancement Mechanism in Surface-Enhanced Raman Scattering" University Pierre and Marie Curie, Paris, May 2002
4. "At the Frontier of Raman Spectroscopy: SERS, Single Molecules and Chemical Enhancement," IGERT Symposium, Strasbourg, June 14, 2002
5. "On the Chemical Enhancement Mechanism in Surface-Enhanced Raman Scattering" University of Bordeaux, July 2002
6. "Applications of Raman Microscopy and Raman NSOM: Focusing on Strain" Advanced Materials Research Center Symposium, February 12, 2004, Austin
7. "Raman Microscopy and Raman NSOM: Chemical Imaging on the Submicron Length Scale," Pittcon 2004, March 10, 2004, Chicago.
8. "Raman Microscopy and Raman NSOM: Chemical Imaging on the Submicron Length Scale," ACS Nobel Laureate Signature Award Symposium, March 15, 2004, San Diego.
9. "Raman Spectroscopy and Near Field Raman Microscopy as Characterization Tools for Semiconductor Materials and Nanostructures", Texas Instruments, Dallas, January 6, 2005
10. "Raman Microscopy and Raman Mear Field Optical Microscopy Characterization of Strained Silicon" SRC Device Sciences CMOS Process and Device Technology Review, May 5, 2005, New Haven
11. "Carrier confinement in almost pure Ge channels grown on Si substrates by rapidly graded Si1-xGex growth", S. Joshi, S. Dey, K. Jones, M.Chaumont, A. Campion, D. Kelly, J Donnelly and S.K. Banerjee, Electronic Materials Conference, July 2005.
12. "Raman Microscopy and Raman Near Field Optical Microscopy Characterization of Strained Silicon" Texas Instruments, Dallas, August 1, 2005
13. "Raman Spectroscopy and Near Field Raman Microscopy as Characterization Tools for Semiconductor Materials and Nanostructures", Texas Instruments, Dallas, August 8, 2005
14. "Ge channel MOSFETs fabricated using thin Ge on strained SiGe epitaxial layers using bulk Si substrates, HfO2 gate dielectric and TaN metal gate electrode" Sachin Joshi, S. Dey, D. Garcia-Gutierrez, M.Chaumont, M. Yacaman, A.Campion, D Kelly, J. Donnelly and S.K. Banerjee, Semiconductor Research Corporation, Techcon, October 2005
15. "Carrier confinement in almost pure Ge channels grown on Si substrates by rapidly graded $Si_{1-x}Ge_x$ growth", Sachin Joshi, S. Dey, K. Jones, M. Chaumont, A. Campion, D. Q. Kelly, J. Donnelly and S.K. Banerjee, Electronic Materials Conference, Santa Barbara, 2005
16. "Raman Spectroscopy and Near Field Raman Microscopy as Characterization Tools for Semiconductor Materials and Nanostructures", Texas Instruments, Dallas, January 10, 2006
17. "Raman Microscopy and Raman Near Field Optical Microscopy Characterization of

Strained Silicon" SRC Device Sciences CMOS Process and Device Technology Review, May 4, 2006, Austin
18. "Ultra-thin $Si_{1-x}Ge_x$ dislocation blocking layers for Ge /strained Si CMOS devices" Sachin Joshi, Sagnik Dey, Michelle Chaumont, Alan Campion and Sanjay K.Banerjee, International Symposium on Advanced Gate Stack Technology, September 2006
19. "Raman Spectroscopy and Near Field Raman Microscopy as Characterization Tools for Semiconductor Materials and Nanostructures", Texas Instruments, Dallas, January 10, 2007

David M. Jonas
1 "Femtosecond Two Dimensional Fourier Transform Spectroscopy" Symposium on Two-dimensional Laser Spectroscopy, Laser Science XVIII, October 2, 2002 (INVITED)
2. "Vibrational Dynamics in 2D Electronic Spectra" Symposium on Vibrational Spectroscopy, Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Providence, RI, October 14, 2002 (INVITED)
3. "Coherent Multiple Dipole Excitation and Reorientation in 2D spectroscopy" Coblentz Award Symposium, Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Providence, RI, October 14, 2002 (INVITED)
4. "Role of Vibrations in Two-Dimensional Electronic Spectroscopy" International Symposium on 2D Vibrational Spectroscopy, Seoul, South Korea, October 22, 2002 (INVITED)
5. "2D electronic spectroscopy: What can we learn from optical analogs of 2D NMR?" Physical Chemistry Seminar, Northwestern University, Evanston, IL, November 15, 2002
6. "2D electronic spectroscopy: What can we learn from optical analogs of 2D NMR?", Ecole Polytechnique, FRANCE, Nov. 18, 2002
7. "Electronic Wavefunction Reorientation Revealed by Femtosecond 2D Spectra" Symposium on Frontiers of Ultrafast Dynamics in Complex Systems, American Physical Society March Meeting, March 5, 2003 (INVITED)
8. "Two-Dimensional IR-Visible Measurements of □(2) ", Quantum Electronics and Laser Science Conference, June 3, 2003 (INVITED talk given by Dr. Nadia Belabas)
9. "Two-Dimensional Femtosecond Spectroscopy: Optical Analogs of 2D NMR", Analytical and Physical Chemistry Seminar, Department of Chemistry, University of Delaware, Newark, DE, April 30, 2003
10. "Femtosecond and 2D Fourier Transform Experiments on Jahn-Teller Dynamics" Physical Chemistry Seminar, University of Wisconsin, Madison, WI, Nov. 4, 2003
11. "Femtosecond Two-Dimensional Fourier Transform Spectroscopy: Maximizing Time and Frequency Resolution to Reveal Dynamics in Disordered Materials" Time and Frequency Division Seminar, NIST, Boulder, CO, Dec. 2, 2003
12. Interviewed by Jonathan Hamilton about the Shortest Time Interval Measured on "Morning Edition", broadcast on National Public Radio at 6:00 am EST, February 26, 2004 http://www.npr.org/features/feature.php?wfId=1702094
13. "Femtosecond and 2D Fourier Transform Experiments on Jahn-Teller Dynamics" Symposium on Mixed Quantum, Classical and Semiclassical Dynamics, 227th ACS National Meeting, Anaheim, CA, March 31, 2004 (INVITED)
14. "3D view of signal generation and propagation in femtosecond four-wave mixing" Symposium on Emerging Ultrafast Spectroscopies: from Physics to Biology, 227th ACS National Meeting, Anaheim, CA, March 28, 2004 (talk given by Dr. Nadia Belabas)

15. "Measurement of conical intersection dynamics by impulsive femtosecond polarization spectroscopy", International Conference on Ultrafast Phenomena, Niigata, Japan, July 28, 2004
16. "Femtosecond 1D and 2D FT experiments on vibrational and electronic motions at a conical intersection" 2nd International Symposium on 2D Vibrational Spectroscopy, Madison, WI, to be given August 15-17, 2004 (INVITED)
17. "Femtosecond 1D and 2D Fourier transform spectroscopy of vibrational and electronic motions" symposium on Coherent Two-Dimensional Vibrational Spectroscopy, 31st Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Portland OR, October 5, 2004 (INVITED)
18. "Femtosecond 1-D and 2-D Fourier transform spectroscopy of vibrational and electronic motions" Laser Science XX, Rochester, NY, October 11, 2004 (INVITED)
19. "Watching electrons move through a conical intersection", General Chemistry Seminar, Cornell University, Ithaca, NY, February 24, 2005
20. "Watching electrons move through a conical intersection", Telluride Summer Workshop on "Nonlinear ultrafast spectroscopy in fluids", Telluride, CO, to be given June 26 - July 1, 2005 (INVITED).
21. "Propagation distortions and dispersion relations in 2D FT spectroscopy" Third International Conference on Coherent Multidimensional Spectroscopy, Rigi Kulm, SWITZERLAND, May 28, 2006 (INVITED)
22. "Infrared to visible translation for straightforward measurement of mid-infrared pulses" Third International Conference on Coherent Multidimensional Spectroscopy, Rigi Kulm, SWITZERLAND, May 28, 2006 (INVITED) (presented by Manuel Joffre)
23. "Absorptive Propagation Effects in Femtosecond Four-Wave-Mixing" XVth International Conference on Ulltrafast Phenomena, July 31, 2006 (oral presentation by Michael Yetzbacher)
24. "Dispersion Relations in Two-Dimensional Spectroscopy" XVth International Conference on Ulltrafast Phenomena, August 3, 2006 (poster presentation by Katherine Kitney)
25. "Watching electronic motion through a conical intersection" symposium on Frontiers in Molecular Dynamics: Experiment and Theory, American Chemical Society National Meeting, San Francisco, California, September 10, 2006 (INVITED)

26. "Two-dimensional spectroscopy and fast electronic processes" workshop on New Scientific Opportunities with VUV and Soft X-Ray Free Electron Lasers, Synchrotron Radiation Center, University of Wisconsin, Madison, October 18, 2006 (INVITED)
27. "Watching electronic move through a conical intersection" 54th Annual Western Spectroscopy Association Conference, Pacific Grove, California, February 1, 2007 (talk given by E. Ryan Smith)
28. "Watching the electronic motions driven by a conical intersection" Session on Non-adiabatic Molecular Dynamics and Control at Conical Intersections, American Physical Society March Meeting, Denver, Colorado, March 7, 2007 (INVITED)

Shuming Nie

During the last 5 years, Dr. Nie has delivered more than 150 invited lectures at meetings, conferences, and universities. Listed below are only keynote and plenary lectures from 2003 to 2007:

1. **Keynote Lecture**: "Biomedical Nanotechnology," International Symposium on Single-Molecule Bioanalysis and Nano-biodevices, National Institute of Advanced Industrial Science and Technology (IAST), Takamatsu, Japan, March 11-12, 2003.
2. **Plenary Lecture**: The First International Congress on Bio-Nanointerface (ICBN), Tokyo, 2003.
3. **Keynote Speaker**: "Nanotechnology for Personalized Medicine," NanoMedicine Summit 2004, the Cleveland Clinic Foundation, Cleveland, Ohio, 2004.
Plenary Lecture: Belgian Society for Analytical cytology, November 2005, Brussels.
4. **Keynote Speaker**: "Bioconjugated Nanoparticles for Probing Single Molecules and Single Cells," 2005 International Nano Biomedical Technology Symposium, Taiwan, December 15, 2005.
5. **Keynote Speaker**: "Biomedical Nanotechnology for Molecular Imaging, Profiling, and Drug Targeting," 2005 Annual Symposium of Biomedical Engineering Society, Taiwan, December 17, 2005.
6. **Alberta Heritage Foundation Lecturer**, "Biomedical Nanotechnology: Adventures at the Interface of Chemistry, Engineering, and Medicine," March 2006, University of Calgary, Calgary, Canada.
7. **Nan-Qiang Lecture**: "Biomedical Engineering and Nanotechnology for Personalized Medicine," Xiamen University, China, May 7, 2006.
8. **Plenary Lecture**: "Nanotechnology for Molecular and Cellular Imaging," The Society of Molecular Imaging Annual Meeting, Hawaii, September 2, 2006.
9. **Plenary Lecture**: "Biomedical Nanotechnology for Personalized and Predictive Oncology," The International Conference on Bio-Nano-Informatics Fusion and International Forum on Biochip Technology," Beijing, China, October 9-12, 2006.
10. **Foster Colloquium Speaker**: "Interdisciplinary Research at the Interface of Chemistry, Engineering, and Medicine," Department of Chemistry, SUNY-Buffalo, Buffalo, NY, October 20, 2006.
11. **Keynote Speaker**: "Quantum Dots and Targeted Nanoparticles for In-vivo Tumor Imaging," Yonsei University Cancer Center Symposium, Seoul, Korea, November 17, 2006.
12. **Keynote Speaker**: "Bioengineering and Nanotechnology for Personalized Medicine," Ajou University, Suwon, Korea, November 20, 2006.
13. **Keynote Speaker**: "Nanotechnology for Personalized Medicine," University of Texas – Dallas Symposium on Nanomedicine, Dallas, TX, December 11, 2006.
14. **The 2007 Schwann Lecture**, "Biomedical Nanotechnology for Molecular Imaging and Targeted Therapy," the Department of Bioengineering and the Institute of Medicine, University of Pennsylvania, Philadelphia, April 9, 2007.
15. **Distinguished Speaker:** The University of Illinois Center for Nanoscale Science and Technology Seminar Series, "Nanotechnology and Bioengineering for Personalized Medicine," University of Illinois, Urbana-Champaign, April 18, 2007.

Kathy L. Rowlen

1. "Single Molecule SERS," MURI Meeting at Northwestern University, Evanston, IL February 7, 2003
2. "Catching the Flu: Diagnostic for Emerging Strains of Influenza A," Department of Chemistry, Iowa State University, Ames IA October 30, 2003.

3. "Rapid Analysis of Viral Pathogens," Department of Chemistry, Grand Valley State University, Allendale, MI October 3, 2003.
4. "Harnessing Surface Plasmons," 49th Annual SPIE Meeting, Denver CO August 5, 2004.
5. "Diagnostic Microarrays," American Society for Clinical Laboratory Science Spring Meeting,Denver CO May 5, 2004.
6. "On-Chip Signal Amplification for BioChips, " PittCon, Chicago, Il March 2004
7. "Electromagnetic Enhancement at Ag Nano-Spheres, Dots and Apertures," PittCon, Chicago, Il March 2004.
8. "Rapid Virus Enumeration," PittCon, Chicago, Il March 2004.
9. "Surface Plasmon Optics for Nanostructured Sensors and Multidimensional Spectroscopy" AFOSR MURI Program Review, November 6, 2004
10. "Photodynamics on Thin Silver Films" ACS Nobel Signature Award Symposium, National ACS Meeting, San Diego CA March 16, 2005.
11. "Potential of Nanoaperture Arrays in Photonics and Spectroscopy" Novel Directions in Photonics: Nanophotonics and Biophotonics, National ACS Meeting, San Diego CA March 13, 2005.
12. "FluChip Project" Centers for Disease Control and Prevention, Atlanta GA, March 2006
13. "Microarrays as High Throughput Screening Tools" NSF Workshop on Analytical Instrumentation, Tucson AZ, April 21, 2006
14. Participant: NIAID Blue Ribbon Panel on Influenza Research, Washington, D.C. September 2006 (FluChip research highlighted in keynote summary by Anthony Fauci, Director NIAID)
15. "FluChip" Technologies for Enhanced Global Surveillance of Influenza Viruses" Department of Chemistry, University of California, Riverside, April 5, 2007

George C. Schatz

1. Schatz spoke about MURI-related research at the Workshop in Information and Communication at the National Academy of Sciences, October 31, 2002 as part of the Chemical Sciences in the 21st Century Initiative of the NAS.
2. Schatz presented a talk on nanoparticle optical properties at Montana State University, December 6, 2002 in a talk entitled "Theoretical Studies of Nanoparticles and DNA".
3. Schatz presented a workshop on his nanoparticle optical studies at Illinois Benedictine University, September 10, 2002 entitled "Nanoparticle Optical Properties and DNA Sensing"
4. Schatz presented a talk on nanoparticle optical properties at Michigan State University, February 20, 2003, in a talk entitled "Theoretical Studies of Nanoparticles and DNA".
5. Schatz presented a talk on nanoparticle optical properties at the Morrison Inaugural Lecture, "Theory and Nanoparticles", Northwestern University, February 26, 2003.
6. Schatz presented a talk to the Northwestern Chemistry Department Industrial Affiliates, May 8, 2003 entitled "Nanoparticle Optical Properties and DNA Sensing"
7. Schatz presented an invited talk at the Gordon Conference on Electronic Spectroscopy and Dynamics, July 6-9, 2003 at Bates College, Maine entitled "Optical Properties of Metal Nanoparticles and Nanoparticle Arrays".
8. Schatz presented a tutorial on Nanoparticle Optical Properties at the Summer Nanoschool at Argonne National Laboratory, August 6, 2003.
9. Schatz presented a seminar on Nanoparticle Optical Properties at a workshop at Argonne National Laboratory on Electromagnetic Scattering theory methods, Aug. 22, 2003.
10. Nanoparticle Optical Properties and DNA Detection: Theoretical Studies, University of Pisa, Sept. 11, 2004.
11. "Nanoparticle Optics and DNA Melting", Center for Nanomaterials, Argonne National Laboratory, Oct. 3, 2003.
12. "Nanoparticles and Nanoconfined DNA: New Challenges for Theory", Stanford University, Dec. 1, 2003
13. "Nanoparticles and Nanoconfined DNA: New Challenges for Theory", University of Colorado, Feb. 6, 2004
14. "Nanoparticles and Nanoconfined DNA: New Challenges for Theory", Pusan University, Korea, Feb. 19, 2004
15. "Metal Nanoparticle Optical Properties and DNA Structures and Thermodynamics", Dupont, March 8, 2004
16. Particles 2004 meeting, Orlando Fl March 7-9, 2004, Optical Properties of Anisotropic Particles (invited)

17-18. ACS National Meeting, Anaheim CA March 28-31, 2004, "Anisotropic Metal Nanoparticles", "Optical Properties of Arrays of Nanoparticles"

19. "Nanoparticles and Biomolecule Detection: New Challenges for Theory", Queen's University, Dec. 3, 2004
20. "DNA Melting and Optical Sensors", Jan. 18, 2005, Integrated DNA Technologies, Skokie IL
21. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory", University of Buffalo, Jan. 21, 2005
22. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory", University of Michigan, Feb. 24, 2005

23. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory", University of Chicago, March 8, 2005.
24-25. ACS National Meeting, San Diego, CA March 12-17, 2005, "Biological sensing with silver nanoparticles and nanoparticle arrays: theoretical studies," "The Pople years at Northwestern: a dynamicist learns electronic structure theory"
26. "New Uses for Electronic Structure and Molecular Dynamics Calculations" (BIMAT and NSF) Foundations of Nanoscience, Snowbird, Utah, April 24-28, 2005, Session organizer, Track on DNA/Nanoparticle aggregates
27. "Theoretical studies of nanoparticle and nanohole arrays," SPP2 Conference, Graz Austria May 22-25, 2005.
28-30. "Empirical Potential Modeling of Proteins;Computational Chemistry; Modeling Bioadhesian" (three invited talks); NSF Summer Institute on Nano Mechanics and Materials, Northwestern University, June 6-10 (2005)
31. "Reactive Collision Dynamics; Metal Nanoparticle Optical Properties" (invited) IAMS Retreat, Taipei, Taiwan, June 16-17, 2005
32. American Conference on Theoretical Chemistry, UCLA, July 18-21, 2005; Session Chair on Biophysics Theory
33. "Electronic structure studies and mixed QM/ED studies of SERS" (invited); DARPA Workshop on SERS, San Francisco, CA, July 29, 2005
34. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory", (W. Albert Noyes, Jr. Lecture), University of Texas, Sept. 8, 2005-10-10
35. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory", (C. A. Coulson Lecture), University of Georgia, Athens, GA, Sept. 27, 2005.
36. "Theory and SERS" (Van Duyne Festschrift), Northwestern University, Evanston IL Oct. 15, 2005.
37. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory", Caltech, November 15, 2005.
38. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory", Emory University, November 28, 2005.
39. "DNA-linked Nanoparticle Aggregates", Condensed Matter Physics, Ohio State University, January 23, 2006
40. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory", Department of Chemistry, University of Maryland, February 15, 2006
41. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory," Department of Chemistry, University of Pennsylvania, February 16, 2006
42. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory," Harvard/MIT Physical Chemistry Colloquium, March 2, 2006
43. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory," Pennsylvania State University, March 24, 2006
44. "Modeling the optical and structural properties of nanoparticle arrays and DNA-linked nanoparticle aggregates," NSF Workshop on Emerging Opportunities of Nanoscience to Energy Conversion and Storage, Washingon, DC Nov. 21-22, 2005.
45. "Theoretical Studies of Plasmon-based Optical Sensors (Invited)," Pacifichem (ACS Meeting), Honolulu, Dec. 15-18, 2005

46. "Optical Properties of Silver and Gold Clusters and Particles: Bridging Quantum Chemistry and Electrodynamics (Invited)," Pacifichem (ACS Meeting), Honolulu, Dec. 15-18, 2005
47. "Narrow melting transitions in DNA-linked aggregates (Invited talk)," Foundations of Nanoscience, Snowbird, Utah, April 24-27, 2006
48. "Plasmonic effects in nanoparticles and nanoholes (Invited)," APS Users Meeting, Nanophotonics Workshop, May 2, 2006
49. "Theoretical Studies of SERS," AFOSR Contractors Meeting, June 5-7, 2006, Arlington VA
50. "Modeling the optical and structural properties of nanoparticle arrays and DNA-linked nanoparticle aggregates (Invited)," Nanonet-6 Workshop, Portsmouth, England, July 28, 2006
51. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory," Jackson State University, Sept. 1, 2006
52. "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory," Kilpatrick Lecture, Illinois Institute of Technology, Sept. 15, 2006
53-54. "The strength of carbon nanotubes, and nanoscale diamond and graphite", "Medical diagnostics with gold and silver nanoparticles," University of Missouri (Thomas Lectures), Nov. 30, Dec. 1, 2006
55. "Nanoparticle optical properties and biomolecule detection: New challenges for theory", Marquette University, Jan. 19, 2007
56. "Nanoparticle optical properties and biomolecule detection: New challenges for theory", Columbia University, Jan. 24, 2007
57. "Surface-Enhanced Raman Sensors: Theory and Experiment," JSTO PST Basic Science Review, Lorton, VA, February 7-8, 2007.
58. "Nanoparticle optical properties and biomolecule detection: New challenges for theory", Cherry Emerson Lecture, Georgia Tech, Feb. 13, 2007
59. "Plasmon-based biomolecule sensing: theory and experiment (invited)," Trends in Nanoscience 2007, Irsee, Germany, Feb. 24-28 (2007).
60. "Electronic structure studies of metal cluster optical properties (invited)," W. A. Lester Birthday Celebration Symposium, Berkeley, March 28-30 (2007)
61. "Metal nanoparticle optical properties and biomolecule sensing: New challenges for theory," Workshop Honoring George C. Schatz, April 27, 2007, University Pierre et Marie Curie, Paris, organized by Marie-Paule Pileni.
62. "Nanparticle optical properties," Lectures at Pierre and Marie Curie University, April 25-May 8, 2007
63. "Hole arrays and extraordinary transmission," Lectures at Pierre and Marie Curie University, April 25-May 8, 2007
64. "Self assembly modeling," Lectures at Pierre and Marie Curie University, April 25-May 8, 2007
65. "Fracture of nanomaterials," Lectures at Pierre and Marie Curie University, April 25-May 8, 2007
66. "DNA and DNA aggregates," Lectures at Pierre and Marie Curie University, April 25-May 8, 2007
67. "Plasmonic properties of silver and gold clusters (invited)," International Symposium on Atomic and Molecular Clusters (TAMC5), Richmond, VA May 13-17, 2007

68. "Optical properties of metal nanoparticles (invited)," Plasmonics Meeting, Strasbourg, France, May 28-31, 2007

Kenneth G. Spears

1. AFOSR review meeting of MURI research, Nov 4-5, 2004
2. "Nonlinear Spectroscopy of Silver Nanoparticles: SHG and Other Resonances," Wayne State University, February 23, 2005.
3. "Nonlinear Spectroscopy of Silver Nanoparticles: SHG and Other Resonances," University of Akron, March 9, 2005.
4. AFOSR program review meeting, May 2005
5. AFOSR program review conference, Washington DC, June 2006. Poster Paper.
6. "Nonlinear Spectroscopy of Silver Nanoparticles: SHG and Other Resonances," Bowling Green State University, April 25, 2007

Richard P. Van Duyne

1. "Nanosphere Lithography: A Versatile Platform for the Study of Size Dependent Nanoparticle Optical Properties", SPIE 47th Annual Meeting, Seattle, WA, July 7-11, 2002.
2. "Nanosphere Lithography: Nanoparticle Optics, Biosensors, and Surface-Enhanced Spectroscopy", Department of Chemistry, The University of Illinois, Urbana-Champaign, IL, September 20, 2002.
3. "Nanosphere Lithography: Nanoparticle Optics, Biosensors, and Surface-Enhanced Spectroscopy", FACSS 2002, Providence, RI, October 17, 2002.
4. "Localized Surface Plasmon Resonance Spectroscopy", Department of Chemistry, Indiana University, Bloomington, IN November 7, 2002.
5. "Nanoscale Optical Biosensors", Invited Speaker at Lester Wolfe Workshop in Laser Biomedicine, Massachusetts Institute of Technology, Cambridge, MA, December 3, 2002.
6. "Surface Methods for Optical Biosensing", Invited Speaker at World Technology Evaluation Center (WTEC) Biosensing Workshop, National Institutes of Health, Baltimore, MD, December 4, 2002.
7. "Silver Nanoparticles: Size Dependent Optical Properties, Biosensors, and Surface-Enhanced Spectroscopy", Frontiers in Chemistry Lecture, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, February 20, 2003.
8. "Nanoparticle Optics for Chemical/Biological Sensing and Surface-Enhanced Spectroscopy", PITTCON 2003, Orlando, FL, March 11, 2003.
9. "Nanoscale Optical Biosensors", Northwestern University, Air Products & Chemicals, Center for Nanofabrication and Molecular Self-Assembly, Evanston, IL, March 17, 2003.
10. "Surface-Enhanced Raman Spectroscopy: A Funny Thing Happened to me on the Way to Southampton," Symposium on That'll Never Work: Analytical Chemists Doing the Perceived Impossible, 225th ACS National Meeting, New Orleans, LA, March 23, 2003.
11. "Nanoparticle Optics: Surface-Enhanced Spectroscopy", Symposium in Memory of Mike Weaver, 225th ACS National Meeting, New Orleans, LA, March 23, 2003.
12. "Nanoparticle Optics: Single Silver Nanoparticles as Chemical Sensors", 225th ACS National Meeting, New Orleans, LA, March 24, 2003.
13. "Nanoscale Optical Biosensors Based On Localized Surface Plasmon Resonance Spectroscopy", 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003.

14. "Nanoscale Optical Biosensors", Northwestern University, Abbott Laboratories, Center for Nanofabrication and Molecular Self-Assembly, April 29, 2003.
15. "Toward a Glucose Biosensor Based on Surface-Enhanced Raman Spectroscopy", Institute for Bioengineering and Nanoscience in Advanced Medicine Symposium, Northwestern University, Galter Pavilion, Chicago, IL, May 02, 2003.
16. "Silver Nanoparticles: Size Dependent Optical Properties, Biosensors, and Surface-Enhanced Spectroscopy", Department of Chemistry, Northwestern University, 2003 Industrial Associates Meeting on Electrons, Photons, Chemistry, and Materials, May 09, 2003.
17. "Multidimensional Surface-Enhanced Sensing and Spectroscopy", AFOSR Molecular Dynamics and Theoretical Chemistry Contractors Meeting, San Diego, CA, May 19, 2003.
18. "Nanoscale Optical Biosensors Based on Localized Surface Plasmon Resonance Spectroscopy," Great Lakes Regional ACS Meeting, Chicago, IL, May 2003.
19. "Nanoscale Optical Biosensors", Center for Nanofabrication & Molecular Self-Assembly, NSEC NSF Site Visit, June 4-5, 2003.
20. "Nanoscale Optical Biosensors", Northwestern University, Medtronics, Evanston Northwestern Hospital/Northwestern University Sensors Group, Evanston, IL, July 18, 2003.
21. "Localized Surface Plasmon Resonance Immunoassay and Verification Using Surface-Enhanced Raman Spectroscopy", SPIE Annual Meeting, San Diego, CA, August 3-8, 2003.
22. "Nanoparticle Optics: Sensing with Nanoparticle Arrays and Single Nanoparticles", SPIE Annual Meeting, San Diego, CA, August 3-8, 2003.
23. "Nanoscale Optical Biosensors Based on Localized Surface Plasmon Resonance Spectroscopy", SPIE Annual Meeting, San Diego, CA, August 3-8, 2003.
24. "An Electrochemical Surface-Enhanced Raman Spectroscopy Approach to Anthrax Detection", SPIE Annual Meeting, San Diego, CA, August 3-8, 2003.
25. "Optical Nanoarrays SRG & Nanopatterning SRG", NU-NSEC Annual Review Meeting, Center for Nanofabrication & Molecular Self-Assembly, Northwestern University, Evanston, IL, August 21, 2003.
26. "Noble Metal Quantum Dots: Fabrication, Structure, and Size-Dependent Optical Properties", 2nd Annual Workshop on the Evolution and Self-Assembly of Quantum Dots, Northwestern University, August 27, 2003.
27. "Nanoporus Membranes Fabricated by Nanosphere Lithography and Reactive Ion Etching", Poster Session, Annual Scientific Meeting of Molecular Modeling as a Mainstream Research Tool in Catalysis, Northwestern University, September 16, 2003.
28. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy", Inorganic and Electrochemistry Seminar, California Institute of Technology, Pasadena, CA, September 30, 2003.
29. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy", Seminar, Department of Chemistry, University of California-Berkeley, Berkeley, CA, October 2, 2003.
30. "Nanoparticle Optics for Chemical and Biological Sensing", FACSS Meeting, Ft. Lauderdale, FL, October 19-23, 2003.
31. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy", Seminar, Materials Science, University of Tennessee, Knoxville, TN, October 23, 2003.
32. "Noble Metal Nanoparticles: Fabrication, Structure, and Size-Dependent Optical Properties", The University of Wisconsin-Madison, Madison, WI, Materials Science Seminar, Materials Science Department, November 06, 2003.

33. "Nanoparticle Optics", Seminar, Materials Science Program and Materials Science Center, Miami University Nanotechnology Symposium, Oxford, OH, November 13-14, 2003.
34. "Probing the Long Range Distance Dependence of Noble Metal Nanoparticles," Materials Research Society Meeting, Boston, MA, December 2003.
35. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy", Department of Applied Physics, Chalmers University, Göteborg, Sweden, December 15, 2003.
36. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy", Workshop France-USA, Molecular Scale Electronics, Paris, France, December 19, 2003
37. "Localized Surface Plasmon Resonance Nanosensors", Nanobiotech 2004, Kohala Coast, Hawaii, January 09, 2004.
38. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy", Nanophotonics Workshop, Stanford Photonics Research Center, Stanford University, Stanford, CA, January 24, 2004.
39. "Refractive index sensitive, plasmon resonant scattering, and surface enhanced Raman scattering nanoparticles and arrays as biological sensing platforms," SPIE Photonics West (BiOS 2004), Symposium on Plasmonics In Biology And Medicine, San Jose, CA, January 26, 2004.
40. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy", CPCC Seminar, Northwestern University, February 09, 2004.
41. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy," 7th Symposium on Molecular Reaction Dynamics in Condensed Matter, Laguna Beach, CA, March 3-6, 2004.
42. "Opportunities for Analytical Chemistry in Nanoscale Science and Technology," Pittcon 2004, Chicago, IL, March 10, 2004.
43. "Localized Surface Plasmon Resonance Nanosensors," Pittcon 2004, Chicago, IL, March 10, 2004.
44. "Nanoparticle Optics for Surface-Enhanced Sensing," Pittcon 2004, Chicago, IL, March 12, 2004.
45. "Nanoparticle Optics: From Surface-Enhanced Raman Scattering, to Localized Surface Plasmon Resonance Spectroscopy, to Single Nanoparticle Sensors," 2004 Earle K. Plyler Prize Address, Annual American Physical Society March Meeting, Montreal, Quebec, Canada, March 23, 2004.
46. "Nanoparticle Optics for Surface-Enhanced Sensing and Raman Spectroscopy," 227th American Chemical Society National Meeting, Anaheim, CA, March 29, 2004.
47. "Optimization of Nanoparticle Biosensors Based On Localized Surface Plasmon Resonance Spectroscopy," 227th American Chemical Society National Meeting, Anaheim, CA, March 31, 2004.
48. "A Glucose Biosensor based on Surface-Enhanced Raman Spectroscopy," 227th American Chemical Society National Meeting, Anaheim, CA, April 01, 2004.
49. "Analysis of Biological Targets using Localized Surface Plasmon Resonance Spectroscopy", Department of Chemistry, Northwestern University, 2004 Industrial Associates Meeting, Chemistry of Life Processes and Nanobiotechnology, Amanda J. Haes, April 20, 2004.
50. "Nanoparticle Optics for Surface-Enhanced Sensing and Raman Spectroscopy," Chicago Section, American Chemical Society, Chicago, IL, April 23, 2004.
51. "Nanoparticles: Applications in Clinical Diagnostics," Distinguished Speakers Forum, Abbott Laboratories, Diagnostics Division, Abbott Park, IL, May 11, 2004.

52. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy," Surface Analysis 04/PNWAVS Conference, Pacific Northwest National Laboratory, Richland, WA, June 16, 2004.
53. "Nanoscale Optical Biosensors," Gordon Research Conference on Bioanalytical Sensors, Queen's College, Oxford, UK, July 06, 2004.
54. "Surface-Enhanced Raman Spectroscopy (SERS): Where Have We Been and Where are We Going?" Gordon Research Conference on Vibrational Spectroscopy, Roger Williams University, Bristol, RI, July 15, 2004.
55. "Surface-Enhanced Raman Scattering: Detection of Glucose in Physiological Conditions", Presented by Chanda Ranjit Yonzon, ICORS2004, International Conference on Raman Spectroscopy, Brisbane, Australia, August 08-13, 2004.
56. "Metal Nanoparticle Interfaces as Studied by Surface-Enhanced Spectroscopy and Scanning Probe Microscopy," Gordon Research Conference on Chemistry at Interfaces, Kimball Union Academy, Meriden, NH, August 15, 2004.
57. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy," North Carolina State University, Raleigh, NC, August 27, 2004.
58. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy," University of North Carolina, Chapel Hill, NC, August 30, 2004.
59. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy," University of Michigan, Ann Arbor, MI, September 16, 2004.
60. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy," Materials Science & Engineering Department, University of Illinois, Urbana-Champaign, IL, September 27, 2004.
61. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy," Chemistry Department Colloquium, University of Chicago, Chicago, IL, October 25, 2004.
62. "Molecular Plasmonics for Surface-Enhanced Spectroscopy and Biosensing," Graz-Mainz Joint Seminar on Plasmonics, Max Planck Institut für Polymerforschung, Universität Mainz, Germany, November 19, 2004.
63. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy," Inter-Pacific Workshop on Nanoscience and Nanotechnology, City University of Hong Kong, November 23, 2004.
64. "Molecular Plasmonics for Biosensing and Surface-Enhanced Spectroscopy," Nanoplex Technologies, Inc., Menlo Park, CA, January 11, 2005.
65. "Molecular Plasmonics for Surface-Enhanced Spectroscopy and Biosensing," National Institute of Science and Technology, Gaitherburg, MD, January 28, 2005.
66. "Molecular Plasmonics for Surface-Enhanced Spectroscopy and Biosensing," Analytical Division Seminar, Purdue University, West Lafayette, IN, February 15, 2005.
67. "Spectroscopic Detection of Glucose with Novel Surface Enhanced Raman Substrates," Pittcon 2005, Orlando, FL, March 2, 2005.
68. "Nanoscale Optical Biosensors," Pittcon 2005, Orlando, FL, March 2, 2005.
69. "From the Fundamentals of Nanoparticle Optics to the Development of Practical Chemical and Biological Sensors based on Surface-Enhanced Raman Scattering," 2005 Nobel Laureate Signature Award for Graduate Education, American Chemical Society National Meeting, San Diego, CA, March 15, 2005.
70. "Molecular Plasmonics for Surface-Enhanced Spectroscopy and Biosensing," Chemistry Department Seminar, Clemson University, Clemson, SC, April 14, 2005.

71. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy," Chemistry Department Colloquium, The Pennsylvania State University, University Park, PA, April 21, 2005.
72. "Nanoparticle Optics for Surface-Enhanced Sensing and Spectroscopy," Nanotechnology Seminar, University of Washington, Seattle, WA, April 26, 2005.
73. "Molecular Plasmonics for Surface-Enhanced Spectroscopy and Biosensing," Atlanta Area Chemical Physics Seminar, Emory University/Georgia Institute of Technology, Atlanta, GA May 02-03, 2005.
74. "Molecular Plasmonics: Origins, Fundamentals, and Sensor Applications," Molecular Plasmonics International Symposium, Institute for Physical High Technology, Jena (Germany), May 19-21, 2005.
75. "New Materials and Characterization Methods for Molecular Plasmonics," Surface Plasmon Photonics 2, SPP2, Auditorium, University of Graz, Universitätsplatz 3, 1st floor, Graz (Austria), May 22-26, 2005.
76. "Tip-Enhanced Raman Spectroscopy for Applications in Nanotribology and High Spatial Resolution Chemical Analysis," Graduate Research Seminar and Gordon Research Conference on Analytical Chemistry, Roscoff, France, Matthew Young, June 10-17, 2005.
77. "Chem/Bio Sensors Using Surface-Enhanced Raman Scattering," DARPA Workshop on SERS, San Francisco, CA, July 29, 2005.
78. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," Plenary Lecture, Third International Conference on Advanced Vibrational Spectroscopy, Lake Lawn Conference Center, Delavan, WI, August 14, 2005.
79. "Molecular Plasmonics for Biosensing," Abbott Laboratories, Diagnostics Division, Abbott Park, IL, August 23, 2005.
80. "Molecular plasmonics for ultrasensitive biosensing," 230th American Chemical Society National Meeting, Washington, DC, August 28, 2005.
81. "Nanostructures for SERS," 230th American Chemical Society National Meeting, Washington, DC, August 28, 2005.
82. "First steps toward understanding Alzheimer's Disease using localized surface plasmon resonance spectroscopy," 230th American Chemical Society National Meeting, Washington, DC, August 31, 2005, Lecture delivered by Dr. Amanda J. Haes.
83. "An innovative Surface-Enhanced Raman Spectroscopy (SERS) method for the Identification of Traditional Red Lakes and Dyestuffs," 3rd International Conference on the Application Raman Spectroscopy in Art and Archaeology, Paris, France, Alyson Whitney, August 31 – September 03, 2005.
84. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," The Introductory Lecture, Faraday Discussion 132: Surface Enhanced Raman Spectroscopy, Imperial College London, London, United Kingdom, September 19-21, 2005.
85. "From Dinner at the Carolina Inn to Molecular Plasmonics," Pete Kissinger Symposium on Advances in Bioanalytical Chemistry and the Changing Climate for Academic Engagement with Commercial Entities, Department of Chemistry, Purdue University, West Lafayette, IN, October 6-7, 2005.
86. "Silver island films as substrates for surface-enhanced Raman spectroscopy (SERS): a methodological study of their applications to artists' red dyestuffs," SPIE Optics East Conference in Boston, MA, October 23-26, 2005, Lecture delivered by Ms. Alyson V. Whitney.

87. "Nanoparticle/Solution Interfaces Studied by Surface-Enhanced Raman Spectroscopy," 2005 Welch Foundation Conference on Chemical Research, Houston, Texas, October 24-25, 2005.
88. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," Seminar, Department of Chemistry, University of Cincinnati, Cincinnati, OH, December 2, 2005.
89. "Molecular Plasmonics for Biosensing: New Concepts, Materials, and Methods," Nanobiotech 2005, Lahaina, Hawaii, December 11-15, 2005.
90. "Biomedical Applications of Molecular Plasmonics," Pacifichem 2005, Ballroom Salon G (Renaissance Ilikai), Honolulu, Hawaii, 9:20-9:50 AM, December 15, 2005.
91. "New Directions in Nanoparticle Optics," Pacifichem 2005, Waianae (Sheraton Waikiki), Honolulu, Hawaii, 12:35-1:05 PM, December 15, 2005.
92. "Surface Enhanced Raman Spectroscopy: New Materials, Concepts, Characterization Tools, and Applications," Society for Applied Spectroscopy, Chicago Section, Arlington Heights, IL Tuesday, January 10, 2006.
93. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," Chemistry Division Colloquium, Naval Research Laboratory, Washington, DC, January 19, 2006.
94. "Nanoparticle Optics: New Materials, Concepts, and Characterization Methods," Invited Talk, American Physical Society Meeting, Baltimore, MD, Monday March 13, 2006.
95. "Surface-Enhanced Raman Sensors for Quantitative Biowarfare Agent Detection," Pittcon 2006, Orlando, FL, Tuesday March 14, 2006.
96. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," Modern Optics and Spectroscopy Seminar, G.R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, MA, March 21, 2006.
97. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," Inorganic Chemistry Seminar, Department of Chemistry, University of Pennsylvania, Philadelphia, PA, April 4, 2006.
98. "Nanoparticle Optics: New Materials, Concepts, and Applications," 2006 Optical Science and Technology Center Symposium, Department of Chemistry, University of Iowa, Iowa City, IA, April 10, 2006.
99. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," 2006 Guy Fleming Lipscomb Lecture, Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC, April 21, 2006.
100. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," Colloquium, Department of Chemistry, Texas A&M University, College Station, TX, May 2, 2006.
101. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," Colloquium, Laboratory for Nanophotonics, Rice University, Houston, TX, May 10, 2006.
102. "Surface Enhanced Raman Sensors for Metabolic Analytes," Gordon Research Conference on Lasers In Medicine & Biology, Holderness School, Plymouth, NH, July 2-7 2006.
103. "Size and Shape Effects on Plasmon Resonances" Gordon Research Conference on Plasmonics, Keene State College, Keene, NH, July 23-28, 2006, Lecture delivered by Dr. Amanda J. Haes.
104. "Molecular Plasmonics for Surface Enhanced Sensing and Raman Spectroscopy," Plenary Lecture, International Conference on Raman Spectroscopy (ICORS) 2006, Yokohama, Japan, August 20-25, 2006.
105. "SERS 2006: New Concepts, Materials, and Characterization Methods," Keynote Lecture, The International Symposium of Surface Enhanced Raman Scattering and Spectroscopy

(SERSS-2006), Kwansei Gakuin University Convention Center, Nishinomiya, Hyogo, Japan, August 28-30, 2006.
106. "Regular and random nanoparticle arrays for LSPR and SERS," 232nd American Chemical Society National Meeting, San Francisco, CA, September 10-14, 2006, Lecture delivered by Dr. Katherine A. Willets.
107. "Operando surface-enhanced Raman spectroscopy (SERS)," 232nd American Chemical Society National Meeting, San Francisco, CA, September 10-14, 2006, Lecture delivered by Ms. Alyson V. Whitney.
108. "Nanoparticle/Solution and Electrode/Solution Interfaces Studied by Surface-Enhanced Raman Spectroscopy," 2007 Electrochemistry Gordon Research Conference, Ventura, CA, January 14 - 19, 2007.
109. "Molecular Plasmonics for Surface Enhanced Sensing and Raman Spectroscopy," Seminar, Department of Chemistry, Stanford University, Stanford, CA, January 29, 2007.
110. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," 1st International Max Planck Research School, "Complex Surfaces in Materials Science (IMPRS-CS)," Ringberg Castle, Germany, February 5-9 2007.
111. "Localized Surface Plasmon Resonance Spectroscopy," Pittcon 2007, Chicago, IL, Tuesday February 27, 2007.
112. "Surface Enhanced Raman Sensors," Pittcon 2007, Chicago, IL, Tuesday February 27, 2007.
113. "Plasmonics and Diffractive Coupling in 1D and 2D Arrays of Nanoparticles Produced by Electron Beam Lithography," Pittcon 2007, Chicago, IL, Thursday March 01, 2007.
114. "Towards Understanding the Relationship Between a Single Nanoparticle's Structure and its Localized Surface Plasmon Resonance," Midwest MRSEC 2007 Symposium, April 14, 2007, Lecture delivered by Dr. Katherine A. Willets.
115. "Molecular Plasmonics for Surface Enhanced Sensing and Raman Spectroscopy," Seminar, Department of Chemistry, Tufts University, Boston, MA, April 17, 2007.
116. "Molecular Plasmonics for Surface Enhanced Sensing and Spectroscopy," Seminar, Department of Chemistry & Biochemistry, University of Maryland, College Park, MD, April 27, 2007.
117. "Coupled Molecular and Plasmon Resonances," AFOSR Molecular Dynamics and Theoretical Chemistry Contractors Meeting, Irvine, CA, May 20-22, 2007.
118. "Molecular Plasmonics for Surface Enhanced Sensing and Raman Spectroscopy," Harteck Lecture, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY, June 06, 2007.
119. "Localized surface plasmon resonance spectroscopy and sensing" 234th American Chemical Society National Meeting, Boston, MA, Sunday, 19 August 2007, 2:00 PM to 2:30 PM
120. "Coupled Molecular and Plasmon Resonances," SPIE, Plasmonics: Metallic Nanostructures And Their Optical Properties V (OP213) San Diego, CA, August 26, 2007. (Presented by Jing Zhao)
121. "Surface Enhanced Raman Spectroscopy: New Insights From Coupled Molecular and Plasmon Resonances," Plenary Lecture, Colloquium Spectroscopicum Internationale XXXV, Xiamen, China, September 23-27, 2007.

7b. Consultative and advisory functions

Paul W. Bohn
Editor for the Americas, *The Analyst*, Royal Society of Chemistry, 2007 - present
DoD Workshop, Nanotechnology for Chemical and Biological Defense-2030, 2007
Editorial Board, *Biomicrofluidics*, American Institute of Physics, 2006 – present
Center for BioModular MultiScale Systems, Scientific Advisory Board, 2005-present
Purdue University, Department of Chemistry, External Advisory Panel, 2005
The Ohio State University, Department of Chemistry, External Advisory Panel, 2005
DOE E.O. Lawrence Award Panel, 2002

Louis E. Brus
Chemical Sciences Panel, DOE Basic Energy Sciences
Advisory Board, Nanosys Corporation
External Advisory Board, NSF Funded RPI Nanocenter

Shuming Nie
Founding SAB Member – Nanoplex Technologies, Mountain View, CA
Editorial Board Member – "Journal of Single Molecules", Jena, Germany
Editorial Board Member – "Small – A New Journal for Nanoscience and Nanotechnology"
Editorial Board of "Current Pharmaceutical Biotechnology"
Editorial Advisory Board – "Nanotech Briefs".
Nanotechnology Advisory Committee, nGimat, Atlanta, GA.
Member of Honorary Editorial Board, International Journal of Nanomedicine
Editorial Board – Science in China, Part B – Chemistry

George C. Schatz
Schatz collaborated with James Prober of Dupont on SERS theory. He has visited Dupont 3 times during 2004.
External Advisory Board, Center for Nanomaterials, Argonne National Laboratory 2007-present
External Advisory Board, National Center for Design of Biomimetic Nanoconductors, University of Illinois, 2007-present
Editor-in-Chief, Journal of Physical Chemistry

Richard P. Van Duyne
Founding SAB Member, Nanoplex Technologies, Mountain View, CA
Founding SAB Member, Ohmx, Evanston, IL
Nanotechnology Special Emphasis Panels, NIH: July 2003
Fakultetsopponent, Department of Applied Physics, Chalmers University of Technology Göteborg, Sweden, December 2003
Nanotechnology Special Emphasis Panels, NIH: July 2005
Essential Science Task Force, Museum of Science and Industry, Chicago, 2004-2005
Science Storms Advisory Panel, Museum of Science and Industry, Chicago, 2006-2007
Member, Editorial Board, Annual Reviews of Physical Chemistry (2007-11)
Member, Editorial Board, Accounts of Chemical Research (2007-9)

7c. Transitions

Paul W. Bohn

Paul Bohn collaborated with Dr. Donald Cropek of the US Army Construction Engineering Research Laboratory (Champaign, IL) on a project which seeks to integrate the microfluidically-enabled chemical sensing expertise in the Bohn laboratory with DNAzyme-based approaches to molecular recognition for the remote sensing of heavy metals, in particular Pb(II). In FY07 they will extend their collaboration to the development of a human toxicology chip which combines elements of nanoscale electrical sensing developed during the MURI project to the characterization of transepithelial electrical resistance changes upon exposure of cell arrays to cytotoxic agents.

Paul Bohn collaborated with Dr. (Maj.) Patrick Castle as he establishes an independent undergraduate research program in the Department of Chemistry at the US Air Force Academy (Colorado Springs, CO)

Paul Bohn collaborated with Prof. Henry White of the University of Utah (Salt Lake City, UT) to construct nanoscale electrodes to test theories of enhanced charge transport on the nanoscale.

Louis E. Brus

Brus collaborated with Prof. Heinz of Columbia Physics on electromagnetic theory, and with Research Scientist Michael Steigerwald of Columbia Chemistry on Ag nanocrystal synthesis and passivation.

Alan Campion

The Campion group had extensive industrial collaborations with a number of individuals in the following organizations: International SEMATECH, IMEC, Advanced MicroDevices, Cerium Laboratories, Texas Instruments, SOITECH, MEMC, Amberwave, and Freescale (formerly Motorola).

David M. Jonas

Jonas jointly supervised graduate student Jordan Corbman (with Kathy Rowlen).

Shuming Nie

Nie collaborated with Applies Biosystems (ABI) and Beckman-Coulter Corp to develop Raman-activated flow cytometry and cell sorting (RACS), which could be used for blood and cell diagnostics in the battle field. Nie also invited to attended a DARPA workshop on the development of SERS nanoparticles for bioagent detection and other military applications.

Kathy L. Rowlen

Rowlen jointly supervised graduate student Jordan Corbman (with David Jonas).

George C. Schatz

Schatz collaborated with Dr. Stephen Gray, Argonne National Laboratory, in the development of electromagnetic theory light scattering methods and software.

Schatz collaborated with Professors Mikael Käll and Bengt Kasemo, Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden

Kenneth G. Spears

The Spears Group worked at the MC2 process lab at Chalmers University of Technology for access to their facilities. The authors would also like to acknowledge the Käll group for their help and guidance while performing the work at MC2.

The Spears Group worked at the Michigan Nanofabrication Facility (MNF) which is part of the National Nanotechnology Infrastructure Network (NNIN).

Spears collaborated with Professors George Schatz, Tamar Seideman and Dr. Maxim Sukharev of Northwestern. All have contributed theoretical models of nanoparticle optical properties.

Richard P. Van Duyne

Van Duyne collaborated with Dr. Nick Fell at the Army Research Laboratories (Adelphi) on the detection of anthrax by surface-enhanced Raman spectroscopy. SERS active surfaces fabricated by nanosphere lithography at Northwestern were delivered to ARL. Dr. Fell and his postdoctoral associate visited Northwestern. This work led to 2 JACS papers on anthrax detection.

Van Duyne collaborated with Dr. Jeffrey W. Elam, Materials Science Division, Argonne National Laboratory (ANL) on atomic layer deposition (ALD) to fabricate ultrathin (0-2 nm) dielectric layers to protect and passivated Ag nanoparticles for sensor and spectroscopy application. Professor Peter C. Stair (joint Northwestern University and Chemistry Division, Argonne National Laboratory) was also involved with this collaboration. This is an ongoing interaction involving one of Van Duyne's students doing ALD and LSPR experiments at ANL ~ two days per week. This work led to several publications.

Van Duyne collaborated with Professors Mikael Käll and Bengt Kasemo, Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden. This work led to several publications.

8. New discoveries, inventions, or patent disclosures

Paul W. Bohn

1. "Method of Forming Nanoscale Features Using Soft Lithography," P. W. **Bohn**, A. Shim, F. Hua and J.A. Rogers, patent pending
2. "Multilayer Microfluidic-Nanofluidic Device," P. W. **Bohn,** J.V. Sweedler, B.A. Flachsbart, and M.A. Shannon, patent pending.
3. "Hybrid Microfluidic and Nanofluidic System," P. W. **Bohn,** J.V. Sweedler, T.-C. Kuo, and M.A. Shannon, U.S. Patent No. 7,220,345 (2007).
4. "Metal-Assisted Chemical Etch Porous Silicon Formation Method," P. W. **Bohn,** X. Li and J.V. Sweedler, U.S. Patent No. 6,790,785 (2004).
5. "Metal-Assisted Chemical Etch to Produce Porous Group III-V Materials," P. W. **Bohn,** X. Li, J.V. Sweedler and I. Adesida, U.S. Patent No. 6,762,134 (2004).

David M. Jonas

We have quantified the propagation and detection distortions found in standard 2D spectra under typically attainable low signal conditions. We have found a new representation of

2D spectra that reduces distortions to the same level under conditions which optimize the signal strength.

We discovered that the active sites for single molecule SERS on colloidal silver nanoparticles exhibit molecular specificity. This suggests that SERS active sites must be specifically engineered to enhance the Raman spectrum of a given target molecule. Further, this selective enhancement of particular molecules by certain SERS active sites might even be used to actively discriminate against a background of contaminants.

Shuming Nie

1. X. Gao and S. **Nie**, "Block Copolymers for Surface Encapsulation, Modification, and Functionalization of Nanoparticles," Emory Invention No. 04019, 2004.
2. William Doering and S. **Nie**, "Spectroscopic Tags Using Dye-Embedded Nanoparticles and Surface-Enhanced Raman Scattering," Emory Invention No. 03075, 2003
3. X. Gao and S. **Nie**, "Dual Modality Optical and Magnetic Nanoparticle Probes," Emory Invention Disclosure, 2004
4. X. M. Qian, D. O. Ansari, and S. **Nie**, "Pegylated and biocompatible SERS nanoparticle tags," Emory Invention Disclosure, 2007

Richard P. Van Duyne

1. Invention Disclosure, NU22078, "A Nanoscale Optical Biosensor for Immunoassay," Inventors: A. J. Haes, A. D. McFarland, R. P. **Van Duyne**
2. "Surface-enhanced Raman nanobiosensor," R. P. Van Duyne, M. R. Glucksberg, K. Shafer-Peltier, C. L. Haynes, and J. Walsh, In U.S. Pat. Appl. Publ.; (Northwestern University, USA). US, 2004; pp 33 pp.
3. Invention Disclosure, NU 25080, 8/29/2005, "Localized Surface Plasmon Resonance Spectroscopy of Single Silver Nanocubes," Inventors: L. Sherry, G. C. **Schatz**, and R.P. **Van Duyne**
4. Invention Disclosure, 8/29/2005, "The Localized Surface Plasmon Resonance Nanosensor: A High Resolution Distance Dependence Study Using Atomic Layer Deposition," Inventors: A. Whitney, P. Stair, G. **Schatz**, and R. P. **Van Duyne**.
5. Invention Disclosure, NU 25119, 12/06/2005, "Nanoscale Plasmonic Hydrogen Sensor," Inventors: D. Stuart and R.P. **Van Duyne**
6. "Portable device for detection of microorganisms," R. P. Van Duyne, X. Zhang, M.Young, O. Lyandres, Olga. In *U.S. Pat. Appl. Publ.*; (Northwestern University, USA). US 2006; 16pp.
7. Invention Disclosure, NU 26091, 6/21/2006, "Resonance Surface Plasmon Spectroscopy," Inventors: R. P. **Van Duyne**, A. Haes, S. Zou, J. Zhao, G. **Schatz**
8. Invention Disclosure, NU 26096, 6/21/2006, "Resonance Surface Plasmon Spectroscopy: Low Molecular Weight Substrate Binding To P450," Inventors: R. P. **Van Duyne**, G. **Schatz**, J. Zhao, Z. Zhang
9. Invention Disclosure, NU 2611, 7/31/2006, "Localized Surface Plasmon Resonance Spectroscopy of Single Silver triangular Nanoprisms," Inventors: R. P. Van Duyne, G. Schatz, L. Sherry, R. Jin

10. Patent Filed, #601856, 601, 1/02/2007, "Localized Surface Plasmon Resonance Nanosensors and Uses Thereof," Inventors: R. P. **Van Duyne**, G. **Schatz**, P. Stair, S. Zou, A. Whitney

9. Honors/Awards

Paul W. Bohn
2007 CERL Research Team Award
2005 Bomem-Michelson Award (Coblentz Society)
2004 Spectroscopy Society of Pittsburgh Award

Louis E. Brus
2006 R. W. Wood Prize (Optical Society of America)
2005 Chemistry of Materials Prize (ACS)
2004 Elected to the U. S. National Academy of Sciences

Shuming Nie
2007 Heinrich-Emanuel-Merck Award for Analytical Chemistry, Merck
2007 Elected Fellow, American Institute of Medical and Biological Engineering
2007 Schwann Lecture, University of Pennsylvania, Philadelphia
2006 Cheung Kong Distinguished Professorship, The Chinese Ministry of Education
2006 Plenary Lecture, International Conference on Bio-Nano-Informatics Fusion, Beijing
2006 Plenary Lecture, Society of Molecular Imaging Annual Meeting, Hawaii
2006 Nan-Qiang Lecture, Xiamen University, China
2006 Alberta Heritage Foundation Lecturer, University of Calgary, Canada
2005 The Rank Prize (The Rank Prize Funds, London, UK), for the Realization of Quantum Dot Nanocrystals as Biological Labels.
2005 Plenary Lecture, Belgian Society for Analytical cytology, Brussels
2003 Plenary Lecture, The First International Congress on Bio-Nanointerface (ICBN), Tokyo

Kathy L. Rowlen
2006 Inventor of the Year (CU)
2005 Council on Research and Creative Work Faculty Fellowship (CU)
2004 Council on Research and Creative Work Faculty Fellowship (CU)
2003 Distinguished Alumna, Grand Valley State University

George C. Schatz
2007 Bourke Lecturer and Medal of the Faraday Division of the Royal Society of Chemistry
2007 Professeur invite classe exceptionnelle – University Pierre et Marie Curie, Paris
2007 Cherry Emerson Lecture, Georgia Tech
2006 Thomas Lecture, University of Missouri
2006 Kilpatrick Lecture, Illinois Institute of Technology
2005 C. A. Coulson Lecture, University of Georgia
2005 W. Albert Noyes Lecture, University of Texas
2005 Elected to the US National Academy of Science.
2004 Editor-in-Chief, Journal of Physical Chemistry

2002 Elected to the American Academy of Arts and Sciences
2002 Morrison Professor of Chemistry, Northwestern University

Richard P. Van Duyne
2007 National Science Foundation Creativity Extension Award
2007 Plenary Lecture, Colloquium Spectroscopicum Internationale XXXV
2007 Harteck Lecture, Rensselaer Polytechnic Institute
2006 L'Oreal Art and Science of Color Prize
2006 Keynote Lecture, The International Symposium on SERS
2006 Plenary Lecture, International Conference on Raman Spectroscopy (ICORS)
2006 Lipscomb Lecture, University of South Carolina
2005 Nobel Laureate Signature Award for Graduate Education (ACS)
2005 Welch Foundation Lecturer
2005 The Introductory Lecture, Faraday Discussion 132
2005 Plenary Lecture, 3rd International Conference on Vibrational Spectroscopy
2004 The Earle K. Plyler Prize for Molecular Spectroscopy (APS)
2004 Elected to American Academy of Arts and Sciences
2003 Frontiers in Chemistry Lecture, Case Western Reserve University

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