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Chemical Applications of Raman Spectroscopy

In recent years, Raman spectroscopy has become increasingly popular for chemical analysis. When Raman spectroscopy first emerged as a method for vibrational analysis complimentary to infrared absorption, applications were limited by a lack of intense narrowband light sources and a general lack of sensitivity in the technique. Numerous advances in instrumentation, technique, and basic scientific understanding of the Raman scattering process have greatly improved its sensitivity and the ease at which the technique can be applied. There are now a plethora of intense laser light sources available spanning from the UV to the infrared. The rapid development of cheap and highly sensitive CCD (charged coupled device) detectors has had a major impact. These detectors allow spectra to be routinely obtained in a parallel detection manner, recording a wide spectral range simultaneously rather than sequentially. The marriage of optical microscopes to Raman instruments, including confocal optical imaging, has allowed Raman spectra to be recorded with submicrometer spatial resolution. Near field optical techniques have pushed the spatial limits to near 100 nm. Resonance and surface enhancements can yield phenomenal sensitivity increases. Sensitivity enhancements of over 10^{15} have been demonstrated on select systems.

Over the past few years, it has been my goal to develop the Raman Spectroscopy Lab in the Department of Chemistry into a world class facility. We have just replaced an aging Raman spectrometer with new more versatile instrument that has a wider operational range, improved resolution and sensitivity. The optics and detector on this instrument are capable of working over the spectral range of 200-1000 nm. We currently have three laser sources available which allow excitations from 457.9 to >800 nm, and are seeking funds to purchase two additional lasers that will extend that range from 197-1000 nm. Extension into the UV is an important addition. The UV excitation range has some very distinct advantages. First, the intensity of the Raman scattering goes like the 4th power of the frequency ($I \sim \nu^4$). Simply changing from 514 nm to 257 nm excitation yields a $2^4=16$ -fold increase in intensity. Second, fluorescence is frequently an insidious interference in Raman spectroscopy. Fluorescence typically concentrates from the lowest excited state of the molecule. With visible excitation, fluorescent molecules often emit in the same region as Raman scattering and the intense fluorescence masks the Raman signal. With UV excitation, the fluorescence most often occurs at longer wavelengths than the vibrational Raman region and a spectrum free from fluorescent interference can be obtained. UV excitation also allows one to take advantage of electronic resonance enhancements to the Raman scattering. Resonance enhancements can provide a high degree of selectivity to the Raman technique. An important application in the UV is protein analysis. Different excitation wavelengths allow one to target resonant enhancement of different chemical groups in amino acids. One then has a residue specific spectroscopic probe to apply for the study of protein interactions. UV resonance Raman has also become an important technique for the study of catalysts. In the near-IR region, resonance enhancements of electronic transitions involving van Hove singularities, allows one to resolved single walled carbon nanotubes of differing diameters. This is currently the most elegant and powerful method for size selected analysis of carbon nanotubes.

I collaborate with scientists around the world to provide Raman analysis on samples of interest. Applications include single-walled carbon nanotubes, SERS (surface enhanced Raman spectroscopy) and two color induced fluorescence thermometry for physical and chemical characterization of an electrospray, spectroscopic analysis of isomers of chemically modified buckyball (C_{60}), polarization analysis of stress induced alignment in elastic polymers, and analysis of chemical substitution effects in ZnO nanocrystals. Students specializing in physical or analytical chemistry are welcome to participate in these and other developing projects at the MS or PhD level. Training would include both theory and practice of Raman analysis, including ab-initio computation of vibrational frequencies as a guide to spectral assignment. Projects in the near future will include extension to UV excitation and wide range temperature control of samples for more complete crystal phase analysis.

Optical and Chemical Properties of Nanomaterials

Surface Enhanced Raman Spectroscopy (SERS) has played an important role in the rising interest in nanomaterials. Shortly after the SERS effect was demonstrated by van Duyne and coworkers using a roughened silver surface, solution based nanoparticles of silver were shown to also exhibit the SERS effect. Synthesis of silver nanoparticle SERS solutions can be achieved using amazingly simple chemistry. The particles can be made using a variety of reducing agents to reduce Ag^+ (typically from silver nitrate) to neutral silver, which grows into silver nanoparticles in solution. The size distribution produced can be controlled by reaction conditions and the optical properties of the particles are directly related to size. SERS solutions have been shown capable of producing Raman enhancements of $>10^{15}$. The enhancements are linked to the particle's optical absorption (surface Plasmons).

In recent years, further control of nanoparticle synthesis has been achieved by the addition of capping agents (often glycols or thiols) to the synthesis. These have allowed not only greater control of particle size distributions, but also regulate crystal growth morphology to yield well faceted nanocrystals. Growth conditions have been further used to control the relative growth rate in different crystallographic directions and produce crystal geometries that include octahedral, cubo-octahedra, cubes and rods. Differences in the physical and chemical properties of nanoparticles as a function of particle size and shape are an active area of research. These nanoparticles have applications in medicine, catalysis, device fabrication, energy production and use, and pollution control. The absorption of light by nanoparticles and conversion to heat is the basis for a cancer treatment known as photothermal therapy.

In collaboration with Dr. Robert Shaw, Analytical Spectroscopy and Microfabrication group of the Chemical Sciences Division, ORNL, we are currently studying the optical properties of octahedral gold nanocrystals using atomic force microscopy, near field optical microscopy and fluorescence. Nonlinear optical properties of these materials are also being explored using ultrafast lasers.

While some progress has been made in wet synthesis and characterization of nanoparticles of elements beyond silver and gold, there is considerable room for future research. An area of personal interest is synthesis and properties of nanocrystals of Nickel. Nickel is well known for its catalytic activity, especially with hydrogen. These properties may be significantly enhanced

in nanocrystals of this material, making it a candidate for hydrogen storage and catalysis. The enhanced catalytic activity of nanoparticles of common metals makes them potential replacement materials for the rare metal catalysts used in automotive catalytic converters. We expect to draw on our extensive prior experience in studies of the surface chemical properties of single crystal nickel in this project.

Select Publications

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11. "The Morphology of Diamond Grown by Hot Filament Chemical Vapor Deposition", Prabhjot Mehta Menon, C.S. Feigerle, L. Heatherly, Jr., and R.E. Clausing, *Diamond and Related Materials* **7**, 1201-6 (1998).
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