George R. Harrison Spectroscopy Laboratory

The George Russell Harrison Spectroscopy Laboratory conducts research in modern optics and spectroscopy to further fundamental knowledge of atoms and molecules and to explore advanced engineering and biomedical applications. Professor Michael S. Feld is director; Professor Robert W. Field and Dr. Ramachandra R. Dasari are associate directors. As an interdepartmental laboratory, the Spectroscopy Laboratory encourages participation and collaboration among researchers in various disciplines of science and engineering. Core investigators include Professors Mongi G. Bawendi, Robert W. Field, Keith A. Nelson, Andrei Tokmakoff, and Jeffery I. Steinfeld of the MIT Chemistry Department; Professors Feld and Alexander van Oudenaarden of the Physics Department; Professors William H. Green of the Chemical Engineering Department, Mildred Dresselhaus and Jing Kong of the Department of Electrical Engineering and Computer Science, and Dr. Dasari.

The laboratory operates two laser resource facilities. The MIT Laser Biomedical Research Center, a biomedical technology resource of the National Institutes of Health, develops basic scientific understanding and technology for advanced biomedical applications of lasers, light, and spectroscopy; core, collaborative, and outside research are conducted. The MIT Laser Research Facility provides resources for core research programs in the physical sciences for nine faculty members from the MIT departments of Chemistry, Physics, Chemical Engineering, and Electrical Engineering and Computer Science.

Research Highlights

Professor Field and Dr. Hans Bechtel developed a millimeter wave spectrometer capable of measuring the nascent vibrational-level populations of molecules generated in nonequilibrium sources. An initial test of this apparatus on acrylonitrile and methyl azide photolysis products showed that the HCN and HNC photofragments were the result of unwanted multiphoton vacuum ultraviolet (VUV) photolysis. Dr. Bechtel and collaborators used PHOFEX spectroscopy to record the near-VUV spectrum of the HCN A-X band system. By monitoring the CN photofragment light-induced fluorescence as the VUV excitation laser is scanned, it was possible to observe strongly predissociated vibrational levels of the HCN A-state. Professor Bryan Lynch (a visitor on sabbatical from the University of Evansville) and Dr. Bechtel also used CN PHOFEX to detect the A-X band system of isocyanogen. This is the first electronic transition ever observed for the isocyanogen molecule. Dr. Wilton Virgo and collaborators used two-photon optical pumping to produce metastable Xe atoms and to efficiently transfer the electronic excitation to N_2, which demonstrates the power of this new source of metastable molecules. Working with Dr. Christian Jungen (Laboratoire Aime Cotton, Orsay, France), they obtained a complete multichannel quantum defect theory model of all spectra and all dynamical processes in the CaF molecule by fitting all spectroscopic data to a quantum defect matrix (including E and R derivatives). CaF is now the diatomic molecule with the most completely characterized electronic spectrum.

Professor Bawendi and Dr. August Dorn studied the effect of near-field microwave radiation on nanocrystal photophysics. In addition, they investigated optoelectronic properties of nanocrystals in field effect transistor geometries and light-emitting device (LED) structures with an emphasis on processes at the single quantum dot (QD) level. The work on photoluminescence from multiexciton states continued, with many experiments on single nanocrystals such as multiexciton spectral resolution and correlation with fluorescence intermittency. Streak camera equipment was used to study the enhanced carrier multiplication in nanocrystals, a recent development that could have a great impact on solar cell technology. Drs. Preston Snee and Andrew Greytak, together with Professor Daniel Nocera of the MIT Chemistry Department, continued to develop novel fluorescent chemical sensors based on energy transfer, with a focus on the development of nanocrystalline fluorescence resonance energy transfer probes suitable for pH imaging in biological microenvironments, including live cells and tissues. MIT Professors Bawendi, Michael Rubner of Materials Science and Engineering, Klavs Jensen of Chemical Engineering, Marc Kastner and Raymond Ashoori of Physics, and Vladimir Bulovic of Electrical Engineering and Computer Science continued their studies of close-packed QD films, with orders-of-magnitude increases in photocurrent gain. This has inspired new projects and photodetector designs for the visible and near-infrared. Dr. Xavier Brokmann investigated approaches to fabricate linear assemblies of nanoparticles and developed a method to surpass the exposure-time limitation of conventional spectroscopy to explore fast optical processes on single nano-objects. Dr. Jean-Michel Caruge is developing all-inorganic QD-LEDs that contain high-band-gap semiconductor oxides as electron and hole-injecting layers. The goal is to increase the stability and lifetime of QD-LEDs and lay the foundation for the fabrication of electrically pumped nanocrystal lasers, a significant improvement over the first generation of optically pumped nanocrystal lasers.

Professor Tokmakoff and his colleagues use multidimensional infrared spectroscopy to observe molecular dynamics in complex condensed phase systems. Recent work has concentrated on investigating the mechanism of hydrogen bond rearrangements in water by using ultrafast infrared spectroscopy. Past experiments suggested that these rearrangements occur in concerted rearrangements involving multiple molecules, and ongoing experiments aim to test this hypothesis. Additionally, the mechanism by which hydrogen bond rearrangements guide the transfer of protons through water is being investigated. In an important technical achievement, the ability to perform single-shot two-dimensional optical and infrared spectroscopy has been demonstrated.

Professor Nelson used optical methods to generate and measure acoustic phonons covering nearly every wavelength and frequency range in amorphous condensed matter. Stuctural correlation lengths in glasses can be assessed at the shortest acoustic wavelengths, while complex structural relaxation dynamics can be assessed with the full range of acoustic frequencies. Multilayer polymer/inorganic phononic band-gap structures also were examined. Separately, an outreach laboratory in which the same class of photoacoustic measurements can be conducted on thin films used in microelectronics manufacturing is now fully operational. Small groups of high school students came to the laboratory, made measurements, analyzed their results, and presented them to their classes and in local science fairs. This program introduces students to modern optics and spectroscopy and advanced materials.

Professor Green constructed a state-of-the-art laser flash photolysis apparatus for measuring chemical kinetics, the first apparatus to become operational in the newly renovated Spectroscopy Laboratory space in the ground floor of Building 6. He used this new apparatus to directly measure the rates of several reactions of the vinyl radical (C_2H_3), a key intermediate in combustion.

Professors Dresselhaus and Kong are using resonance Raman spectroscopy with tunable laser excitation to study carbon nanotube graphite-related materials. By scanning the excitation energies, a structural distribution analysis can be performed on a synthesized nanotube material, and this has provided valuable information in controlling the synthesis of single-walled carbon nanotubes. Defect-induced Raman modes in graphite have also been used to investigate the evolution of defect structures induced by ion irradiation.

Professor van Oudenaarden and his colleagues explored cellular individuality and asymmetry in single *Dictyostelium* cells. It is generally assumed that single cells in an isogenic population, when exposed to an identical environment, exhibit the same behavior. However, it is becoming increasingly clear that, even in a genetically identical population, cellular behavior can vary significantly from cell to cell. This variability was explored in the gradient-sensing response of *Dictyostelium* cells when exposed to repeated spatiotemporal pulses of chemoattractant. The experiments show the response of a single cell to be highly reproducible from pulse to pulse. In contrast, a large variability in the response direction and magnitude is observed from cell to cell, even when different cells are exposed to the same pulse.

Professor Feld, Drs. Kate Bechtel, Wonshik Choi, Christopher Fang-Yen, Joseph Gardecki, Martin Hunter, Gabriel Popescu, Chung-Chieh Yu, and Dasari as well as Drs. Kamran Badizadegan of Massachusetts General Hospital and Maryann Fitzmaurice of University Hospitals, Cleveland, conducted basic and applied spectroscopic and optical studies in biology and medicine. The overall goal is the development of instrumentation and methodologies to advance medical diagnosis and cell biology. Fluorescence, reflectance, Raman scattering, elastic light scattering, and low-coherence interferometry were all used for analysis of tissues, diagnosis and imaging of disease, and cell biology applications. Clinical studies with optical fiber contact probes using diffuse reflectance, fluorescence, and light-scattering spectroscopy (LSS), a combination known as trimodal spectroscopy (TMS), as well as Raman spectroscopy, were also conducted. Real-time diagnosis of cancer and precancer was pursued in the breast, Barrett's esophagus, the oral cavity, and the uterine cervix. In vivo Raman spectroscopy, made possible by the development of optical fiber Raman probes, was also conducted and demonstrated the potential of Raman spectroscopy as a real-time clinical tool for studying breast cancer and atherosclerosis. Dr. Bechtel and her colleagues continued their studies of noninvasive concentration measurements of blood analytes using near-infrared Raman spectroscopy. They developed constrained regularization, a method of multivariate analysis that enables external information to be incorporated in the spectral analysis process. They also used diffuse reflectance, in concert with Raman, to characterize the optical sampling volume and hence provide robustness in their measurements. Dr. Yu and colleagues developed a novel technique, phi-LSS, which employs azimuthial asymmetry of the light-scattering process to measure the size distribution of small and large subcellular structures. Important progress was also made in extending TMS contact probe technology to the imaging mode in a noncontact geometry to facilitate a wide area study of cervix and oral cavity tissues. Dr. Hunter and colleagues used LSS to characterize the nuclear morphology, subcellular particle size distribution, and fractal properties of human epithelial cell monolayers. Dr. Fang-Yen and associates and Professor H. Sebastian Seung of the Department of Brain and Cognitive Sciences used a novel full-field imaging interferometer to measure voltage-dependent motions in single cells and spontaneous contractions in cardiac myocytes. Dr. Popescu and associates developed Fourier, Hilbert, and diffraction-phase microscopy, capable of measuring the light-phase shift through transparent biological samples with 0.1-nanometer path-length sensitivity, with scan rates on the order of milliseconds. The tension in live red blood cell membranes was measured in a noncontact manner. Dr. Choi and colleagues are developing a new type of microscope capable of obtaining three-dimensional refractive index tomograms, which is based on the quantitative phase images projected from various angular illuminations.

Michael S. Feld
Director
Professor of Physics

Additional information about the George R. Harrison Spectroscopy Laboratory can be found at http://web.mit.edu/spectroscopy/.