George R. Harrison Spectroscopy Laboratory

The George Russell Harrison Spectroscopy Laboratory conducts research in modern optics and spectroscopy for the purpose of furthering fundamental knowledge of atoms and molecules and pursuing advanced engineering and biomedical applications. Professor Michael S. Feld is director; Professor Jeffrey I. Steinfeld 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. Professors Moungi G. Bawendi, Robert W. Field, Stephen J. Lippard, Keith A. Nelson, Steinfeld and Andrei Tokmakoff of the MIT Chemistry Department, professors Feld and Alexander Van Oudenaarden of the Physics Department, Professor William H. Green of the Chemical Engineering Department, and Dr. Dasari are core investigators.

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; core, collaborative, and outside research are conducted. The National Science Foundation–supported MIT Laser Research Facility provides resources for core research programs in the physical sciences for nine MIT Chemistry, Physics, and Chemical Engineering faculty.

Research Highlights

Professor Field and collaborators have used cavity ringdown spectroscopy to measure the absorption strength of the UV electronic spectrum of acetylene. They have also begun a study of isomerization in the HNC<->HCN system. A novel feature of the approach is that millimeter wave spectroscopy is used to monitor the molecules exiting the discharge/pyrolysis jet source so that conditions in the source can be optimized. This is more generally applicable and more sensitive than using ultraviolet laser fluorescence excitation or photoionization spectroscopy. Professor Field, Dr. Adya Mishra, and associates have developed a suite of complementary spectroscopies (surface electron ejection by laser-excited metastables and UV-laser induced fluorescence) and statistical pattern recognition schemes by which the detailed mechanism of intersystem crossing in small polyatomic molecules can be characterized. The strong anharmonic and Coriolis mixing among the triplet states is the “ergodic limit,” and it is very surprising that the spectra is so regular in this statistical limit. Professor Field, Dr. Daniel Byun, Professor Anthony Merer (University of British Columbia), Dr. Christian Jungen (Laboratoire Aime Cotton, Orsay, France), and associates have completely characterized the Rydberg states of CaF. A global representation of the electronic structure and dynamics is given by the quantum defect matrix, which is parametrically dependent on internuclear distance.

Professor Steinfeld and his student have extended the studies of IntraCavity Laser Absorption Spectroscopy to carry out time-resolved measurements on transient, weakly absorbing species such as atmospheric free radicals. The rate of the recombination reaction H + NO + M --> HNO + M in a discharge flow system has been measured.

Professor Bawendi and Dr. Jean-Michel Caruge continue research that has uncovered transient photoluminescence from multiple-exciton excited states of quantum dots (QDs) on subnanosecond timescales. This is the first known observation of emission from these 2- and 3-exciton states. Using single QD spectroscopy, Bawendi's group demonstrated that the excited state lifetime of single QDs varies as a function of time. They also showed the novel relationship between the fluorescence intermittency in single QDs and the luminescence behavior of ensemble QD samples. Professors Bawendi, Michael Rubner, Klavs Jensen, Marc Kastner, Raymond Ashoori, and Vladimir Bulovic have demonstrated orders-of-magnitude gains in photocurrent of close-packed QD films. The increased photocurrent has revealed a previously unseen bimolecular recombination process. Highly efficient electroluminescence from hybrid organic-QD LEDs was demonstrated as well. The work highlighted the numerous advantages that these hybrid organic-QD LEDs have over current LEDs, and the work has also suggested a novel mechanism for device function.

Professor Tokmakoff and his colleagues are investigating the hydrogen bond dynamics of liquid water using femtosecond infrared spectroscopy. Recently they have used two-dimensional infrared experiments of the OH stretching vibration to watch the femtosecond configurational fluctuations in hydrogen bonding between neighboring molecules and subsequent hydrogen bond breaking and forming. The experiments are interpreted using models that draw on molecular dynamics simulations.

Professor Nelson and his colleagues have determined the relationship between heat transport properties of low-temperature glasses and the high-wavevector acoustic phonons that mediate thermal diffusion, by relating two separate classes of experiments with computer modeling. Direct measurement of the acoustic properties of complex materials has been refined, and new processes have been uncovered. Finally, Professor Nelson and NSF postdoctoral fellow Dr. Rebecca Slayton have established an outreach laboratory aimed at high school students to make photoacoustic measurements on thin films used in microelectronics manufacturing. They will learn about modern optics and spectroscopy and advanced materials.

Professor William Green used lasers to measure the rate of addition of oxygen to stabilized free radicals in several solvents. These measurements combined with his theoretical calculations resolved a long-standing controversy in the literature about why these reactions are 100 times faster in solution than in the gas phase.

Professor Daniel G. Nocera and his associates study the basic mechanisms of energy conversion in biology and chemistry. Nocera and his group described the first molecule to produce hydrogen photocatalytically from homogeneous solutions of hydrohalic acid. During the past year, they worked out the details of the catalytic cycle. Their research in energy conversion was featured the past year on the nationally broadcast television programs *ABC Nightline* and *NOVA*. They are currently working on increasing the efficiency of the hydrogen-producing photocycle and are developing other molecules to effect the production of hydrogen from water.

Professor Lippard and associates use resonance Raman spectroscopy to study intermediates that form upon oxidation of small molecule model complexes for the hydroxylase component of methane monooxygenase. This nonheme diiron (II) enzyme activates O_2 for the conversion of methane to methanol. Identification of oxygenated intermediates is especially amenable to study by rR methods. A current goal is to characterize the putative peroxo complex that forms upon reaction of $[Fe_2($◎-$O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(2\text{-}Etpy)_2]$ with O_2 at –30 ^{o}C.

Professor van Oudenaarden and his colleagues explore applications of microscopy to cell biology. Professor van Oudenaarden and Dr. Samadani focus on chemotaxis by studying the model organism, *Dictyostelium discodeum,* a social amoeba that can read spatial and temporal cues in the environment. The main focus of these experiments is to obtain quantitative data to test existing models and design better models of eukaryotic chemotaxis. Professor van Oudenaarden and colleagues have been studying a genetic system in the cyanobacterium *Synechococcus* resulting in a robust circadian rhythm in individual cells. Their focus centers on stochastic noise and the mechanisms by which *Synechococcus* resist this noise and thus maintain the appropriate circadian phase, even in the absence of external cues. This work involves monitoring rhythms in individual cells and their descendants using novel optical fluorescence microscopy techniques.

Professor Feld, Dr. Christopher Fang-Yen, and Professor H. Sebastian Seung (Howard Hughes Medical Institute and MIT Department of Brain and Cognitive Sciences) have developed a novel low-coherence interferometer and made the first noncontact optical measurements of the nanometer-scale motions associated with the action potential in a nerve bundle.

Professor Feld and doctors Dasari, Joseph Gardecki, Kamran Badizadegan (Massachusetts General Hospital, Boston), Christopher Fang-Yen, Gabriel Popescu, Martin Hunter, James Tunnell, and Thomas Scecina have conducted basic and applied spectroscopic and optical studies in biology and medicine. A combination of techniques including fluorescence, reflectance, Raman scattering, elastic light scattering, and low-coherence interferometry are employed for histological and biochemical analysis of tissues, diagnosis and imaging of disease, and cell biology applications. Clinical studies employing reflectance and laser-induced fluorescence spectroscopy were conducted by Dr. Tunnell and associates with researchers from the Cleveland University Hospitals, Brigham and Women's Hospital, and Boston Medical Center using a FastEEM apparatus capable of giving real-time diagnosis. Successful diagnosis of dysplasia in Barrett's esophagus, the oral cavity, and the uterine cervix has been demonstrated. Drs. Popescu and Fang-Yen and their associates have developed novel interferometers for quantitative phase measurement of light transmitted through and reflected from living cells and tissues. The Fourier quantitative phase microscope is capable of measuring the light phase shift through transparent biological samples with 0.1 nanometer path-length sensitivity and is being used for noninvasive monitoring of cell structure, growth, and transport. Dr. Hunter and colleagues have used light-scattering spectroscopy (LSS) to characterize the subcellular particle size distribution in epithelia of normal and precancerous rat esophagi, extending the diagnostic capability of LSS down to the range of 10s of nanometers. Progress has been made in correlating LSS spectra with fractal properties of biological tissue. Thomas Scecina and colleagues have improved a device that uses near-infrared Raman spectroscopy noninvasively to measure concentrations of blood analytes.

Michael S. Feld
Director
Professor of Physics

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