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 explore 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. Core investigators include professors Moungi G. Bawendi, Robert W. Field, Keith A. Nelson, Andrei Tokmakoff, and Jeffrey 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; 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 faculty from the MIT departments of Chemistry, Physics, Chemical Engineering, and Electrical Engineering and Computer Science.

Research Highlights

Professor Field and collaborators developed a millimeter wave spectrometer capable of measuring the nascent vibrational level–dependent populations of molecules generated in nonequilibrium sources. The first application has been to CS v = 0-10 produced by UV photolysis of CS_2. Dr. Hans Bechtel demonstrated a new form of polarization spectroscopy, mmOPS, in which the angular anisotropy written into a molecular sample by a UV laser is detected by modifying the polarization of the mm-wave beam. Optical saturation of the two-photon excitation transition, the first step toward developing a metastable atom excitation-transfer jet source of molecules in long-lived electronically excited states, was demonstrated for Xe and Hg atoms. Dr. Severine Boye-Peronne applied a new form of double resonance spectroscopy to the singlet and triplet Rydberg states of acetylene, a two-color scheme in which the detected fluorescence is from an electronically excited photofragment molecule rather than the strongly predissociated parent Rydberg state. Working with Professor Richard Zare (Stanford) and Dr. Christian Jungen (Laboratoire Aimé Cotton, Orsay, France), a suite of indirect processes in Rydberg states mediated by a repulsive valence state was observed in NO and CaF and explained. For indirect autoionization, the signature of each intersecting repulsive state was identified in the fragment ions.

Professor Steinfeld and his group studied the chemical properties of reactive free radicals in the atmosphere. It was demonstrated that intracavity laser absorption spectroscopy can detect free radical species in a discharge flow tube. The reaction rate of atomic hydrogen and NO to form HNO was measured in a helium carrier gas. These studies suggest that intracavity spectroscopy will be a useful probe of kinetics on free radicals and other reactive species.

Professor Bawendi and Dr. August Dorn studied the effect of near-field microwave radiation on nanocrystal photophysics. The work on transient photoluminescence from multiexciton states continued, with many experiments at the single-nanocrystal level. Ordered single-photon emission in a radiative quantum cascade of multiexciton states was shown. New streak camera equipment was used to study the underlying nature of Auger relaxation of multiexciton states. Dr. Preston Snee and Professor Daniel Nocera of the MIT Chemistry Department continued to develop novel laser-based chemical sensors, as well as FRET–based pH–sensitive nanocrystalline fluorophores for use in living cells. The novel relationship between the fluorescence intermittency in single-quantum dots (QDs) and the luminescence behavior of ensemble QD samples was also pursued. 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. Doctors Dirk Weiss and Xavier Brokmann used gold nanocrystals to study single-electron transport. Dr. Jean-Michel Caruge initiated new projects to develop all-inorganic nanocrystal-based LEDs that can handle higher currents. The goal is to develop electrically injected lasers, which would constitute a significant advance over optically pumped lasers.

Professor Tokmakoff and his colleagues use multidimensional infrared spectroscopy to observe molecular dynamics in complex condensed-phase systems. Recent work investigating the hydrogen bond dynamics of water has provided the first direct observations of the ultrafast motions of individual water molecules as they fluctuate about their hydrogen-bonded neighbors and the subsequent rearrangement of the hydrogen-bonded network. Critical to this effort is the reduction of cost and complexity of multidimensional infrared spectroscopy. To this end, Professor Tokmakoff and Dr. Matthew DeCamp have recently developed an upconversion spectrometer that utilizes sum frequency generation to detect infrared signals using previously unavailable silicon detector technology.

Professor Nelson studied the relationship between heat transport properties of low-temperature glasses and 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 was refined and new processes uncovered. Finally, Professor Nelson and Dr. Rebecca Slayton established an outreach laboratory for photoacoustic measurements on thin films used in microelectronics manufacturing. The students are introduced to modern optics and spectroscopy and advanced materials.

Professor William Green received the American Chemical Society’s R. A. Glenn Award for his work on free radical kinetics. In collaboration with Professor Paul Barton, he demonstrated the first algorithm that is guaranteed to find the best least-squares fit to models involving systems of differential equations. This allowed him to prove that a published chemical kinetic model was inconsistent with laser-transient absorption data measured in the Spectroscopy Laboratory.

Professor Nocera and his associates studied the basic mechanisms of energy conversion in biology and chemistry. They developed a series of light-activated redox cofactors that can be attached to the R1 subunit of the enzyme ribonucleotide reductase. Excitation initiates a cascade of proton-coupled electron transfer (PCET) reactions, leading ultimately to turnover at the active site and allowing for the kinetic resolution of intermediary steps. Additionally, ultrafast visible spectroscopies were applied to single PCET reactions in fixed-geometry model systems to reveal unprecedented mechanistic insight into the coupling between electron transfer and proton motion. Finally, in collaboration with Professor Bawendi, the Nocera group developed a new class of biological sensors featuring CdSe nanocrystals conjugated to energy-accepting organic dye molecules. A ratiometric sensor for biological pH was developed and will be employed to measure the pH of cancer tumors.

Professors Dresselhaus and Kong studied the optical and transport properties of novel carbon materials using resonance Raman spectroscopy with tunable laser excitation. A detailed resonance Raman spectroscopic study gave valuable structural information that can be used for developing novel synthetic routes for making high-purity carbon nanotubes that can be used for large-scale nanotube-based circuits. Optical studies, in combination with transport measurements, gave insight into the excitonic structure of semiconducting nanotubes.

Professor van Oudenaarden and his colleagues explored the initial chemotactic response in single *Dictyostelium* cells by monitoring the localization dynamics of key signaling proteins in response to repeated spatiotemporal pulses of chemoattractants. They found that the response of a single cell is reproducible from pulse to pulse. In contrast, a large variability in the chemotactic response from cell to cell was observed, even when different cells were exposed to the same pulse. Although on average, a population of cells accurately detects the direction of the pulse, a significant cell-to-cell variability was observed in the direction, magnitude, and amplification of the response. These experiments underscore the importance of the development of stochastic chemotaxis models.

Professor Feld, doctors Kate Bechtel, Ramachandra Dasari, Christopher Fang-Yen, Joseph Gardecki, Martin Hunter, Gabriel Popescu, Thomas Scecina, James Tunnell, and Chung-Chieh Yu and doctors 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 disease detection in medicine and the understanding of cellular biology. Fluorescence, reflectance, Raman scattering, elastic light scattering, and low-coherence interferometry were employed for analysis of tissues, diagnosis and imaging of disease, and cell biology applications. Clinical studies employing diffuse reflectance, fluorescence, and light-scattering spectroscopy were conducted. Real-time diagnosis of cancer and precancer was pursued in the breast, Barrett's esophagus, the oral cavity, and the uterine cervix. Dr. Yu and colleagues made important progress in adapting this point-probe technology to wide-area screening of dysplasia. Dr. Gardecki conducted clinical studies for detection of breast cancer and characterization of atherosclerotic plaques using Raman spectroscopy. Development of optical-fiber Raman probes enabled these successful clinical trials and demonstrated the potential of Raman spectroscopy as a real-time clinical tool. Dr. Bechtel and her colleagues made improvements to instrumentation and methodologies that use near-infrared Raman spectroscopy to noninvasively measure concentrations of blood analytes. Professor Feld, Dr. Fang-Yen, and Professor H. Sebastian Seung (Department of Brain and Cognitive Sciences) developed a low-coherence interferometer for high-resolution phase imaging of action potentials in neurons. Dr. Popescu and associates developed Fourier and Hilbert quantitative-phase microscopy techniques 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 shear elasticity moduli of live red blood cells was measured in a noncontact manner. Dr. Hunter and colleagues employed light-scattering spectroscopy to characterize the subcellular particle size distribution and fractal properties of the epithelia of normal and precancerous rat esophagi.

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