

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 was director until his death on April 10, 2010; the current acting director is professor Robert J. Silbey. 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. A special relationship has developed with the Department of Chemistry, which now administers personnel and fiscal matters. Core investigators in 2009–2010 included professors Field and Mongi G. Bawendi, Keith A. Nelson, and Andrei Tokmakoff of the Chemistry Department; professor William H. Green of the Chemical Engineering Department; professors Mildred Dresselhaus and Jing Kong of the Department of Electrical Engineering and Computer Science; professors Peter T.C. So and Kimberley Hamad-Schifferli of the Department of Mechanical Engineering and the Department of Biological Engineering; and Dr. Dasari; and, until his death, Professor Feld of the Department of Physics. The laboratory operates the MIT Laser Biomedical Research Center, a biomedical technology resource of the National Institutes of Health, the goal of which is to develop basic scientific understanding of and technology for advanced biomedical applications of lasers, light, and spectroscopy; core, collaborative, and outside research is conducted at the center. The MIT Laser Research Facility provides resources for core research programs in the physical sciences for core faculty members.

A memorial service for Michael Feld was held on June 16 in the MIT Chapel. Colleagues and friends of Michael reflected on his life, his professional achievements, and his personal impact, including the more than half-century he spent at MIT and his 34 years as director of the spectroscopy laboratory. The speakers reminded the assembly of nearly 200 people about Professor Feld's contributions to physics and laser spectroscopy, his later focus on using spectroscopy in biomedicine, his gift for collaboration, and his commitment to equality and diversity, including his support for African American students. The service concluded with a performance by the laboratory's singing group, the Spectratones, which had been started by Professor Feld.

Research Highlights

Professor Field, Dr. Kirill Kuyanov, and graduate students have recorded Rydberg-Rydberg Chirped Pulse Millimeter-Wave (CPmmW) spectra in a pulsed supersonic jet by direct detection of mm-wave free induction decay signals rather than by indirect detection of ions, electrons, or UV photons. Dr. Kuyanov has designed and nearly finished construction of a pulsed, slit-jet apparatus that is expected to increase the sensitivity of the laboratory's CPmmW spectrometer by a factor of 104. Investigations continue of the acetylene S1 state, including all vibrational levels up to the top of the trans-cis isomerization barrier (with professor Anthony Merer); of a diabatic model for the trans- and cis-bent conformers (with professor John Stanton); and of the doorway-mediated mechanism of intersystem crossing (with professor Wilton Virgo).

Professor Bawendi and Dr. August Dorn further studied nanowire growth between two electrodes controlled by an applied voltage, coating them with J-aggregates and demonstrating an enhanced absorption of photoconductive/photovoltaic response. Professor Bawendi and his students developed a novel spectroscopic method to measure the average line width of single chromophores (dyes or quantum dots) in solution by combining fluorescence correlation spectroscopy and photon correlation Fourier spectroscopy. Dr. Andrew Greytak, with professors Bawendi and Daniel Nocera, worked with Dr. Euan Kay and students in both laboratories to develop novel quantum dot probes of pH and oxygen concentration *in vivo*, collaborating with the Jain group at MIT. Professors Bawendi, Vladimir Bulovic, and Marc Kastner continued their studies of close-packed quantum dot (QD) films in light-emitting and photodetecting devices, demonstrating novel AC-driven QD light-emitting devices and QD-based photovoltaic devices with high open circuit voltages.

Professor Nelson and his group completed study of complex structural relaxation in supercooled liquids by examining longitudinal and shear acoustic behavior as a function of frequency and sample temperature down to the glass transition. They also measured heat transport in supercooled liquids, in partially disordered crystals, and in high-quality single crystals which showed nondiffusive energy flow because of the long mean free paths of acoustic phonons that move coherently across macroscopic distances. The optical generation and measurement of acoustic waves and thermal transport are replicated in the spectroscopy laboratory's outreach laboratory for high-school students, who conduct experiments on thin films and learn about advanced materials and modern optics.

Professor Tokmakoff's group investigated hydrogen bond rearrangements in liquid water, the dynamics of proton transfer in aqueous solution, and protein-protein binding. Femtosecond two-dimensional infrared (2D IR) spectroscopy using polarized light was used to reveal the correlated changes in hydrogen bond strength and molecular reorientation during concerted hydrogen bond switching events. These methods were also used to characterize the time-scale and mechanism of proton transfer to aqueous hydroxide ion. Two-dimensional IR spectroscopy of the protein amide I vibrations of insulin was used to monitor insulin dimer formation as a function of temperature and concentration by the folding of a beta-sheet at the dimer interface.

Willam Green, the newly appointed Hoyt C. Hottel professor of chemical engineering, measured the kinetics of the vinyl radical reactions with several different alkenes using one of the laboratory's advanced laser systems. In contrast to expectations, the rates of addition to terminal alkenes decrease as the exothermicity increases. This important and strange behavior was explained with help of quantum chemistry.

Professors Dresselhaus and Kong used resonant Raman spectroscopy to characterize nanocarbon materials including single- and double-walled carbon nanotubes (SWNTs and DWNTs) and graphene. During this past year, the Kong-Dresselhaus group continued to work on studies of phonon softening in metallic SWNTs; a very interesting, new electronic Raman phenomenon was observed in metallic SWNTs as well. For the studies on single DWNTs, the wall-to-wall stress induced in (6,5) semiconducting

nanotubes by encapsulation in metallic outer tubes of different diameters was characterized. Another project involved study of defects in SWNTs and how defects affect the Raman resonant profile.

Professor Hamad-Schifferli and Dr. Joshua Alper studied triggered release from gold nanorods by laser excitation with ultrafast laser pulses. Gold nanorods can be melted by laser excitation in resonance with their surface plasmon resonance. The rate of release was found to vary with laser power and concentration of the surface-coating molecule; certain concentrations could favor either release or binding. Photothermal dissipation from gold nanorods was measured for nanorods coated with different chemistries and found to vary depending on how well the coatings excluded water from the nanorod surface. These results have significant implications for biological applications of nanorods.

Professor Feld and his group conducted basic and clinical spectroscopy biomedical studies. With Drs. Zahid Yaqoob, Dan Fu, and Wonshik Choi (now of Korea University), Feld continued to develop refractive index tomography and, in collaboration with Dr. Kenneth Anderson (Dana Farber Cancer Institute), applied it to study myeloma cells. With Drs. Fu and Yaqoob, Feld developed a new technique to observe cell membrane motion; they studied cell electromotility and improved the contrast of existing quantitative phase microscopy by using biomolecule's dispersion property. In collaboration with Dr. Marc Kirschner (Harvard Medical School), the group initiated a study to measure cell growth using cell dry mass as the growth marker. With professor Subra Suresh, Feld studied cell membrane fluctuations in human red blood cells to assess the role of ATP on red blood cell shape and membrane fluctuations. With Drs. Timothy Hillman, Yaqoob, and Choi, Feld designed and implemented a new optical instrument based on digital phase conjugation to counter the effects of multiple light scattering in highly turbid media. Feld and Dr. Dasari studied fluorescence and photobleaching suppression, dynamic concentration correction between blood and interstitial fluid glucose, and the support vector regression models to improve Raman spectroscopy-based blood glucose monitoring. With Dr. Jeon Woong Kang, Feld developed a multimodal microscopy system to study malaria in collaboration with professor Jaquin Niles and Dr. Tom Jeys (Lincoln Laboratory). With Dr. Narahara Dingari, Feld worked on creating a novel hand-held clinical Raman spectrometer for real time disease diagnostics. Feld and Dr. Maryann Fitzmaurice (University Hospitals, Cleveland) continued clinical studies to diagnose breast cancer. With Drs. Kang and Jessie Weber, Feld worked on the development of a wide-field tissue scanner for ex vivo margin assessment of breast tissue. Feld and Drs. Weber and Fitzmaurice researched solid phantoms to determine depth sensitivity of side-viewing probes and calibration of tissue scanners. With Drs. Fu and Elizabeth Stier (Boston Medical Center), Feld continued clinical studies to diagnose precancer in the uterine cervix.

Robert J. Silbey
Acting Director
Class of 1942 Professor of Chemistry

Additional information about the Spectroscopy Laboratory can be found at <http://web.mit.edu/spectroscopy/>.