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 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 been developed with the MIT Department of Chemistry which now administers personnel and fiscal matters. Core investigators include professors Field and Mongi G. Bawendi, Keith A. Nelson, and Andrei Tokmakoff of the MIT Chemistry Department; professors Feld and Alexander van Oudenaarden of the Physics Department; professors William H. Green of the Chemical Engineering Department; professors Mildred Dresselhaus and Jing Kong of the Department of Electrical Engineering and Computer Science; and Dr. Dasari.

The laboratory operates a resource facility, 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 and technology for advanced biomedical applications of lasers, light, and spectroscopy; core, collaborative, and outside research is conducted. The MIT Laser Research Facility provides resources for core research programs in the physical sciences for eight faculty members from the MIT departments of Chemistry, Physics, Chemical Engineering, and Electrical Engineering and Computer Science.

On February 27, a celebration was held to commemorate the opening of the new Spectroscopy Laboratory physical plant. This new plant provides offices, common space, and much-needed modern laboratories. There are dedicated areas for biological and chemical preparations. In total, the renovation includes 14 new spectroscopy laboratories designed for a wide range of research, including tomographic phase mapping of human cancer cells, Raman spectroscopy of carbon nanotubes, and two-dimensional infrared spectroscopy of peptides. There is also an outreach laboratory to host programs for high school students to enable them to participate in independent research using state-of-the-art equipment.

Research Highlights

Professor Field and Dr. Wilton L. Virgo have investigated both intermolecular and intramolecular dynamics of molecules in long-lived, highly reactive triplet states. In collisional energy transfer experiments with Xe* and N_2, a "momentum punch" was observed in which a fraction of the exoergic energy is converted into an observable amount of kinetic energy of the product metastable N_2^*. In a new class of experiments on triplet acetylene, the spectroscopic patterns of distant doorway-mediated intersystem crossing were investigated. Using Au:SEELEM (surface electron ejection of laser-excited metastables) spectroscopy, it was found that the mechanism of doorway-mediated coupling by an energetically distant T_3 level skews the pattern of the local $T_{1,2}$ states appearing in the SEELEM spectrum, resulting in a "center-of-gravity" shift between the light-induced fluorescence and SEELEM spectra. Stimulated emission pumping experiments led to the first observation of the large-amplitude local-bending states of acetylene. These states, which lie along the minimum energy isomerization path, are crucial to understanding the bond-breaking isomerization process, because their energies contain information such as the isomerization barrier height and width. Professors Field and Anthony Merer, University of British Columbia and Academica Sinica, made two key advances from the study of high-sensitivity infrared-ultraviolet double-resonance and laser-induced fluorescence spectra of the S_1 acetylene state. An accurate value for the fundamental frequency of the symmetric C-H stretching mode was obtained, and a glimpse of the optically dark *cis* isomer was provided. In addition, a reduced dimension discrete variable representation calculation on S_1 acetylene confirmed the existence of strong anharmonic resonances between the *cis* and *trans* bending modes of the S_1 *trans* configuration and tentative spectroscopic assignments of the previously unobserved S_1 *cis* configuration.

Professor Bawendi and Dr. August Dorn studied the growth of semiconductor nanowires seeded by boron nanocrystals to bridge two electrodes. Professor Bawendi studied the possibility of enhanced carrier multiplication in PbSe nanocrystals using a photoluminescence up-conversion apparatus developed by his students and concluded again that this effect is not as universal or efficient as previously stated in the literature. Dr. Andrew Greytak, with professors Bawendi and 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. Professors Bawendi, Vladimir Bulovic, and Marc Kastner of the MIT Physics Department continued their studies of close-packed quantum dot films in light-emitting and photodetecting devices. Professor Bawendi and his students continued developing a method to measure fast (<1 μsec) dynamics at the single molecule scale, with the goal of applying this technique to biological systems.

Professor Tokmakoff used ultrafast infrared spectroscopy to observe molecular dynamics in complex condensed phase systems. In the past year, the Tokmakoff group moved an ultrafast system into the newly renovated Spectroscopy Laboratory. Multimode two-dimensional vibrational spectroscopy was used in conjunction with hydrogen–deuterium exchange measurements, along with simulations, to understand water penetration into protein secondary structures. Femtosecond experiments were performed to understand the equilibrium vibrational dynamics of asymmetric hydrogen-bonded interfaces, which are critical structural motifs in biological systems. Current studies involving photoinitiation are investigating how proton transfer in these systems depends on changes in electronic structure across the hydrogen bonding interface.

Professor Nelson used optical methods to generate and measure longitudinal and shear acoustic waves covering nearly every frequency and wavelength range that can be supported in condensed matter. The acoustic properties of glass-forming liquids were measured at various sample temperatures to assess complex structural relaxation dynamics including the onset of shear wave propagation, a signature of the onset of solid-like behavior as a viscous liquid is cooled. The results allowed direct testing of recent theoretical models of the liquid–glass transition, which continues to elude fundamental understanding. In addition, the Spectroscopy Laboratory's new outreach laboratory provided opportunities for high school students to make photoacoustic measurements on thin films and learn about advanced materials and modern optics.

Professor Green directly measured several reactions of unsaturated free radicals using the Laboratory's unique laser flash kinetics facility. These results were presented at the 32nd International Symposium on Combustion.

Professors Dresselhaus and Kong used resonant Raman spectroscopy to characterize nanocarbon materials including single- and double-walled carbon nanotubes and graphene. These experiments made use of a high-throughput tunable confocal micro-Raman system that enabled resonant excitation of electronic transitions in these materials over a large energy range. The diameter and chiral angle distributions of single-walled nanotube samples grown by chemical vapor deposition (CVD) was determined by counting radial breathing mode frequencies of large ensembles of isolated single-walled nanotubes. Raman characterization of the number of layers and the defect concentration of graphene samples was valuable in developing CVD growth methods for large area graphene films. Progress was made toward understanding the interaction between the layers of double-walled nanotubes by resonantly exciting both walls of several spatially isolated double-walled nanotubes with different inner and outer wall configurations. In other experiments, Raman spectroscopy of electrochemically doped isolated single-walled nanotubes revealed a variety of charge-induced changes in nanotubes that are evident only at the single nanotube level.

Professors Feld and Drs. Dasari, Wonshik Choi, Gajendra Singh, Zahid Yaqoob, and Chung-Chieh Yu of MIT; Kamran Badizadegan of MIT and Massachusetts General Hospital; and Drs. Maryann Fitzmaurice of University Hospitals, Cleveland, Gregory Grillone and Elizabeth Stier of Boston Medical Center, and Arnold Miller of MetroWest Hospital conducted basic and clinical spectroscopic biomedical studies. Dr. Choi and Professor Feld continued to develop refractive index tomography, a novel interferometric technique that produces three-dimensional images of refractive index in live biological cells. The image acquisition rate was enhanced to 30 Hz, and a three-dimensional reconstruction algorithm was developed and applied to account for diffraction. Dr. Choi and professors Feld and Subra Suresh of MIT's Department of Materials Science and Engineering studied the mechanical properties of red blood cells infected by the malaria parasite and demonstrated that disease status can be determined from mechanical properties and that hemoglobin concentration decreases as disease progresses. Dr. Choi and professors Feld and George Benedek of the MIT Physics Department studied the structure of newly discovered cholesterol helices on the 10-nm scale. Dr. Yaqoob and professors Feld and H. Sebastian Seung of the MIT Department of Brain and Cognitive Science imaged cellular electromotility, the subnanometer motions of live cells induced by oscillatory electrical stimulation, for the first time. Dr. Singh and Professor Feld developed two new techniques for noninvasive blood analyte detection using near-infrared Raman spectroscopy: (1) turbidity-corrected Raman spectroscopy for improving concentration accuracy by removing the effects of scattering and absorption, and (2) extension of shifted-excitation Raman difference spectroscopy to remove background fluorescence and photobleaching from Raman spectra. Drs. Badizadegan, Miller, and Fitzmaurice and Professor Feld conducted clinical studies using multimodal spectroscopy—the combination of Raman, fluorescence, and reflectance spectroscopy—to identify vulnerable plaques in the artery and to diagnose cancer lesions in the breast. Drs. Badizadegan, Grillone, and Stier and Professor Feld conducted clinical studies to diagnose precancer in the oral cavity and the uterine cervix. These studies use quantitative spectroscopy (QS), the combination of fluorescence and reflectance spectroscopy. The two studies showed that QS can differentiate both disease state and anatomy. Dr. Yu and Professor Feld extended QS to the imaging mode in a noncontact geometry. This system combines biochemical and morphological information to produce images of dysplasia in the clinical setting of colposcopy. Finally, Drs. Choi and Yu and Professor Feld characterized subcellular morphology with both intensity- and field-based light-scattering spectroscopy.

Michael S. Feld
Director

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