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. Core investigators include professors Moungi G. Bawendi, Robert W. Field, Keith A. Nelson, 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; professors 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 made the first laboratory measurements of the nuclear quadrupole hyperfine structure of HNC and its isotopomers with a millimeter wave jet spectrometer. In agreement with ab initio calculations, this structure was shown to depend dramatically on the extent of the bending vibration and thus serves to indicate progress along the HCN-HNC isomerization coordinate. In collaboration with Professor Anthony Merer (University of British Columbia and Academia Sinica) and Dr. Nami Yamakita (Japan Women's University), Dr. Bechtel and Dr. Adam Steeves identified more than 40 new low-lying vibrational levels of the $A\ ^1A_u$ state of C_2H_2 from high-sensitivity infrared-ultraviolet double resonance and laser-induced fluorescence spectroscopy. Among these are the pure bending polyads consisting of the low-lying bending vibrations, n_4 (torsion) and n_6 (in-plane bend), which are strongly coupled by Coriolis interactions and a Darling-Dennison resonance. The analysis of the $A\ ^1A_u$ state of C_2H_2 has facilitated a collaboration with Dr. Wilton Virgo and colleagues who are attempting to unravel singlet-triplet interactions using surface electron ejection of laser-excited metastables (SEELEM). Dr. Virgo and collaborators recorded Au:SEELEM spectra by selective excitation of near-isoenergetic, mixed S_1 vibrational levels of acetylene in order to understand the basis for T_3-mediated intersystem crossing. Dr. Virgo and collaborators also used two-photon, two-color optical pumping to produce a pulsed atomic beam of metastable Hg atoms. Collisional excitation transfer from metastable Hg ($^3P_2$) to acetylene (T_3) was demonstrated using SEELEM detection.

Professor Bawendi, with Professor Vladimir Bulovic of the MIT Department of Electrical Engineering and Computer Science and Dr. August Dorn, studied incorporation of single nanocrystals in layered organic electro-optic devices using the single molecule apparatus in Professor Bawendi's laboratory. Professor Bawendi studied the possibility of enhanced carrier multiplication in nanocrystals, but concluded that this effect is not as universal or efficient as was 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 FRET probes suitable for pH imaging in biological microenvironments, including live cells and tissues. Professors Bawendi, Bulovic, and Marc Kastner of the MIT Physics Department continued their studies of close-packed quantum dot films in light-emitting and photodetecting devices. Dr. Xavier Brokmann developed a new method for acquiring fast dynamic information in the spectrum of single chromophores, combining photon correlation spectroscopy and Fourier transform spectroscopy.

Professor Tokmakoff and his colleagues used ultrafast two-dimensional infrared spectroscopy to observe molecular dynamics in complex condensed phase systems. Recent femtosecond experiments and simulation have been used to propose and test a mechanism of hydrogen bond rearrangements in water. Experiments are also probing the mechanism of hydrogen bond rearrangements in aqueous base solutions that drive proton transfer from water to hydroxide. The group is performing experiments to understand the role of hydrogen bonding to proton-coupled electron transfer between molecular heterodimers. A number of technical advances for performing multimode two-dimensional vibrational spectroscopy have been developed and are being applied to understand water penetration into protein secondary structures.

Professor Nelson used optical methods to generate and measure longitudinal and shear acoustic phonons covering nearly every wavelength and frequency range in amorphous condensed matter. Structural correlation lengths in glasses were assessed at the shortest acoustic wavelengths, while complex structural relaxation dynamics were assessed with the full range of acoustic frequencies. Thermal transport properties of nanofluids were also optically investigated to determine the influence of the suspended nanoparticles on thermal conductivity. An outreach laboratory in which photoacoustic measurements of the same class are 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. The program introduced students to modern optics and spectroscopy and advanced materials.

Professor Green measured directly many reactions of unsaturated free radicals using the Laboratory's unique laser flash kinetics facility. By combining these measurements with quantum chemical calculations, he unraveled some of the complex kinetics leading to soot formation in combustion. Manuscripts reporting these results were published in the *Journal of Physical Chemistry*. Professor Green was promoted to professor of Chemical Engineering.

Professors Dresselhaus and Kong used resonance Raman spectroscopy to characterize single-walled and double-walled carbon nanotubes and graphene nanomaterials. By monitoring the Raman G band spectra while tuning the Fermi energy of the metallic nanotubes, important information on electron-phonon coupling in metallic nanotubes was obtained. In other experiments, quantum confinement effects were observed with short (~50 nm) DNA-wrapped nanotubes. Particular emphasis was given to studying differences in behavior between metallic and semiconducting nanotubes. Raman spectra of double-walled nanotubes under doping also revealed many interesting phenomena depending on the various possible inner shell and outer shell metallic versus semiconducting configurations. In their study of Raman spectra in monolayer and bilayer graphene, they used the lineshape of the graphene G′ band Raman spectra to determine the number of layers in a piece of graphene.

Professor van Oudenaarden and his colleagues explored stochastic gene expression in out-of-equilibrium systems. Recent advances in measuring gene expression at the single-cell level have highlighted the stochastic nature of mRNA and protein synthesis. Stochastic gene expression provides a source of variability in the abundance of cellular components, even among isogenic cells exposed to an identical environment. This might play important biological roles ranging from controlling microbial diversity to robust developmental patterning. Recent experimental and modeling studies elucidate the molecular sources of this variability. However, these studies predominantly apply to steady-state systems and therefore do not address a large class of out-of-equilibrium phenomena, including oscillatory gene expression dynamics. A general experimental protocol for analyzing and predicting stochastic gene expression in systems that never reach steady state was developed. This framework was used to analyze stochastic expression of genes driven by the *Synechococcus elongatus* circadian clock.

Professor Feld and doctors Ramachandra Dasari, Kate Bechtel, Wonshik Choi, Christopher Fang-Yen, Martin Hunter, Gabriel Popescu, and Chung-Chieh Yu of MIT; Kamran Badizadegan of Massachusetts General Hospital; Maryann Fitzmaurice of University Hospitals, Cleveland; and Gregory Grillone and Elizabeth Stier of Boston Medical Center conducted basic and applied spectroscopic and optical studies in biology and medicine. The overall goal is to develop instruments and methodologies to advance medical diagnosis and cell biology. Interferometric methods were used to create quantitative phase images (QPI) of live cells without contact. Dr. Popescu and associates developed QPI techniques capable of measuring the optical phase shifts through transparent biological samples with 0.1-nm path length sensitivity and kilohertz frame rates; mechanical properties of red blood cell membranes were measured as well as the first refractive index measurements of live cells and tissue sections. Dr. Choi and colleagues developed a novel method for obtaining three-dimensional refractive index tomograms of living cells based on QPI images projected from various angles. Dr. Fang-Yen and associates and Professor H. Sebastian Seung of the MIT Department of Brain and Cognitive Science used a novel full-field imaging interferometer to measure membrane-potential–dependent motions of single cells and neurons. Dr. Bechtel and colleagues continued studies of noninvasive concentration measurements of blood analytes (no needle stick) using near-infrared Raman spectroscopy. A new method of multivariate spectral analysis—constrained regularization—was developed as well as a technique called intrinsic Raman spectroscopy, which uses diffuse reflectance to correct for spectral and intensity distortions in the measured Raman spectra due to tissue scattering and absorption. Doctors Badizadegan, Grillone, Stier, Fitzmaurice, and colleagues conducted clinical studies using optical probe techniques to diagnose precancer in the breast, Barrett's esophagus, the oral cavity, and the uterine cervix. These studies use fluorescence, reflectance, and elastic light-scattering spectroscopies in combination (trimodal spectroscopy, or TMS). Raman spectroscopy was also used, both alone and in combination with TMS (multimodal spectroscopy). Real-time instruments were developed for these studies. Dr. Yu and colleagues extended TMS contact probe technology to the imaging mode in a noncontact geometry to facilitate a wide area study of cervix and oral cavity tissues. The TMS imaging system provides a 20 by 20 matrix of 1-mm^2 tissue sites, each providing biochemical and morphological information, which are combined to give disease classification. Dr. Hunter and colleagues used light-scattering spectroscopy to characterize nuclear morphology, subcellular particle size, and fractal properties of rat esophageal tissue.

Michael S. Feld
Director

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