



George R. Harrison Spectroscopy Laboratory Massachusetts Institute of Technology

Good Vibrations!

Professor Mounji Bawendi, an MIT chemistry professor and Spectroscopy Laboratory core researcher, has been selected as one of eight winners of the 2007 Ernest Orlando Lawrence Award of the Department of Energy, Secretary of Energy Samuel W. Bodman has announced.

The award honors scientists and engineers at mid-career for exceptional contributions in research and development that support its mission to advance the national, economic and energy security of the United States. Bawendi is cited for “chemical synthesis and char-

Bawendi, continues on page 2



Professor Mounji Bawendi

Also in this issue

- ⊙ **Research Report:**
Chirality Distribution of Carbon Nanotube Materials
- ⊙ **Research Report:**
A New Hybrid Multivariate Calibration Method
- ⊙ **Spring Seminar:**
Modern Optics and Spectroscopy
- ⊙ **Workshop**
Lester Wolfe Workshop : Optical Methods in Breast Cancer
- ⊙ **Spectral Lines:**
Pop Spectrum

MIT Institute Professor and Spectroscopy Laboratory core researcher **Mildred Dresselhaus** is the North American winner of a 2007 L'Oréal-UNESCO Award for Women in Science.

She and four other recipients, each representing a different continent, were named at a February 22 ceremony at UNESCO House

Dresselhaus, continues on page 3

The Executive Committee of the MIT Corporation has announced that **William H. Green**, a professor in MIT's Chemical Engineering Dept and a core Spectroscopy Laboratory researcher, has been promoted to full professor. Green is known for his work in formulating accurate chemical kinetic models using state-of-the art quantum chemistry techniques to quantitatively predict the time evolution of chemical mixtures, and for methods for constructing and solving the associated large reaction schemes. These models relate to combustion, pyrolysis and other complicated, technologically important, reactive chemical processes. The results are used to test and predict experimental data he obtains using laser techniques to probe free radicals in the gas phase. Green is well known as an excellent teacher, and has made significant contributions to the revitalizing the Chemical Engineering curriculum, including a new course “Introduction to Chemical Engineering”. He was a member of MIT's Energy Research Council, and plays a leadership role in several industry-sponsored energy research projects at MIT.



Professor William H. Green, Jr.

Graham Fleming to Give Lord Lecture April 24



Graham Fleming

Professor Graham R. Fleming of UC Berkeley will deliver the 2007 Richard C. Lord lecture on April 24, on “Two dimensional ultrafast electronic spectroscopy”.

Fleming was born in Barrow, England in 1949. He received his Bachelor of Science degree in 1971 from the University of Bristol and his Ph.D. in chemistry in 1974 from London University. He conducted postdoctoral research at the California Institute of Technology, the University of Melbourne, and the Royal Institute, UK. In 1979 Dr. Fleming joined the faculty at the University of Chicago where he became the Arthur Holly Compton Distinguished Service Professor in 1987. In 1997 he accepted a position at the University of California-Berkeley where he is currently the Melvin Calvin Distinguished Professor of Chemistry.

Fleming is one of the world's foremost authorities on ultrafast processes and continues to make revolutionary discoveries in biophysics. Currently, his group is studying dynamical processes in a range of complex systems, such as liquids, solutions and proteins, with the goal of understanding the primary steps of photosynthesis. This may lead to a breakthrough in artificial

Lord, continues on page 3

Bawendi, continued from page 1

acterization of functional semiconducting nanocrystals, also known as quantum dots.”

Bawendi, a materials chemist, developed a synthesis of semiconductor nanocrystals that was the first to enable precise control of their size and precise determination of their properties. Using the Bawendi synthesis, nanocrystals are now routinely made to order. One of the world’s leaders in nanotechnology, his research focuses on the synthesis, electronic properties and optical properties of semiconductor nanocrystals (quantum dots) for applications as diverse as biology, optoelectronics and nanoelectronics.

Moungi G. Bawendi was born in 1961 in Paris, France. He received his A.B. in Chemistry from Harvard University in 1982, his A.M. in Chemical Physics from Harvard in 1983, and his Ph.D. in Chemistry from The University of Chicago in 1988. He was a Postdoctoral Member of the Technical Staff at AT&T Bell Laboratories from 1988-1990. In 1990, he began teaching at MIT.

The Lawrence Award was established in 1959 in honor of Ernest O. Lawrence, a UC Berkeley physicist and Nobel Laureate who invented the cyclotron and after whom two major DOE laboratories at UC Berkeley and in Livermore, California are named.

THE SPECTROGRAPH

Published by the George R. Harrison Spectroscopy Laboratory at the Massachusetts Institute of Technology, Cambridge, MA 02139-4307. Comments, suggestions, and inquiries can be directed to the editor.

Editors: Geoff O’Donoghue & Mei-Hui Liu

GEORGE R. HARRISON SPECTROSCOPY LABORATORY

Director: Michael S. Feld

Assoc. Director for Scientific Coordination:
Robert W. Field

Associate Director:

Ramachandra R. Dasari

The Spectroscopy Laboratory houses two laser research resource facilities. The MIT Laser Research Facility provides shared facilities for core researchers to carry out basic laser research in the physical sciences. The MIT Laser Biomedical Research Center, a National Institutes of Health Biomedical Research Technology Center, is a resource center for laser biomedical studies. The LBRC supports core and collaborative research in technological research and development. In addition, it provides advanced laser instrumentation, along with technical and scientific support, free of charge to university, industrial, and medical researchers for publishable research projects. Call or write for further information or to receive our mailings.

(617) 253-4881

<http://web.mit.edu/spectroscopy>

Personality Ramachandra Dasari



Ramachandra Dasari, Associate Director of the Spectroscopy Laboratory, is the glue that binds the Laboratory together. Confidant to Spectroscopy Laboratory graduate students and professors, expert negotiator, project organizer and troubleshooter, Ramachandra is always there when he is needed. And when it comes to equipment purchases, Ramachandra always knows how to get those special discounts. Sometimes the equipment manufacturers even pay him for the privilege of placing their equipment in Spectroscopy Laboratory laboratories—at least it seems that way!

Ramachandra was born in a village of 50 houses or less in the Krishna District of Andhra Pradesh, probably in 1933. His exact birth date is not recorded. His parents owned a small farm. Neither his father nor his mother had any schooling, although his mother could read and write. His grandfather, a deeply religious man who lived in a neighboring village, had the strong belief that his family must start to become educated. Overcoming enormous difficulties, he built an elementary school in his village and selected Ramachandra as one of the students. Ramachandra moved to his grandfather’s village where his grandfather raised him. Ramachandra did well and was sent on to high school, although this required walking a few miles each day without slippers.

Ramachandra’s early education was in Telugu, his mother tongue, and thus his English was weak until he entered college. His undergraduate studies were at Andhra University, 15 miles from his village. He received his Masters degree in 1956 from Benaras Hindu University and his Ph.D. degree in 1960 from Aligarh Muslim Uni-

versity, both national universities. Ramachandra’s graduate research was on the electronic spectroscopy of simple molecules. After graduation, in 1962, he joined the Physics Department of the Indian Institute of Technology, Kanpur (IIT), a new university established in collaboration with nine US universities, led by MIT. He was one of the first new faculty and one of the few faculty members with an all Indian education, more than 90% of the new faculty coming from the nine US universities.

Ramachandra’s connection to MIT dates back to 1966, when he came for two years as a fellow under the US AID program with an allowance of \$8 per day. For two years he worked in the research group of Professor Ali Javan, who had just arrived at MIT from Bell Laboratories after having invented the helium-neon laser. During this period Ramachandra gained valuable experience in fabricating lasers and conducting research based on the new laser spectroscopy. With this background, he returned to IIT and established one of the largest laser laboratories in India, and trained a large number of Ph.D. students

“...Ramachandra did well and was sent on to high school, although this required walking a few miles each day without slippers...”

in laser research. Graduate students were trained to fabricate then-novel and (then considered by some) esoteric lasers such as molecular nitrogen and argon ion, in addition to helium-neon. Few if any

lasers could be purchased at that time, and there were no company reps. And besides, laser equipment, even if it did exist, would be beyond the tiny budget of a fledgling Indian university. So, as Ramachandra explains, building lasers became the way of life of his laboratory, and this provided excellent training for the graduate students.

Ramachandra’s laboratory was also noted for developing interactions with R&D laboratories throughout India. And using the home built lasers and classical sources, Ramachandra continued his studies in molecular spectroscopy, which led to the first observation of the electronic spectra of the NSe molecule. He was promoted to full professor at IIT in 1973. As a member of the Physics Panel of the University Grants Commission, he introduced new initiatives for improving undergraduate education and organized workshops for training teachers.

Ramachandra left IIT in 1978, and spent a year as a visiting Senior Research Officer at the National Research Council

of Canada, Ottawa, and another year as a visiting scientist at the Department of Physics, University of British Columbia before coming to MIT in 1980 as a Visiting Professor of Physics. He has been a Principal Research Scientist in the Spectroscopy Laboratory since 1981. He was appointed Assistant Director of the Spectroscopy Laboratory in 1984 and promoted to Associate Director in 1992.

Ramachandra has played a major role in the Spectroscopy Laboratory over the past 27 years. He oversees project coordination and facility development of the NIH-supported Laser Biomedical Research Center, and coordinates research programs of the physical science-based MIT Laser Research Facility.

Ramachandra's research has covered a wide range. His early studies include classical high-resolution spectroscopy of simple molecules, atomic and molecular collisions, vibrational-rotational relaxation, laser frequency measurements in the far infrared, and laser spectroscopy of rare-earth ions in single crystals. He then progressed to study Dicke narrowing in infrared transitions, multiphoton ionization, laser-nuclear studies, molecular collisions and dynamics, cavity-QED, the single atom laser, and surface-enhanced Raman scattering. More recently, his research emphasis has switched to laser-biomedical studies, where he has pursued spectral diagnosis of atherosclerosis and early-stage cancer in various organs of the body using light scattering, reflectance, fluorescence, and Raman spectroscopy. His most recent research is in the field of low coherence interferometry for detecting nanometer motions in red blood cells and nerves. He has given numerous lectures at universities in the US, Canada and India. His research publications, which number well over 200, have appeared in most of the major physics and chemistry journals. Under his guidance, twelve MIT students have received Ph.D. degrees, and several others Masters degrees.

On February 28, 2005, the Center for Laser Technology/Laser Technology Program at IIT created a distinguished annual symposium to honor Ramachandra. (February 28 is National Science day in India, as well as C.V. Raman's birthday.) Each symposium is centered on a presentation from a distinguished scientist from India or abroad. The inaugural symposium was a day-long program of talks from professors and senior scientists who were former IIT

graduates, and a poster session from current IIT students. Ramachandra spoke on "Spectroscopy for diagnosis of disease." Michael Feld was the inaugural lecturer.

Ramachandra has been happily married for 56 years to Suhasini Dasari, who works at the MIT Medical Department. Following typical Indian tradition they married young, in 1951, when he was 18 and she was 15. Many believe that much of Ramachandra's wisdom actually emanates from Suhasini. They have two children, a son, Satish, who is a physician in Indiana, and a daughter, Lakshmi, an M.S. in computer sciences who teaches high school mathematics in Seattle, and two grandchildren, Siddharth and Vivek.

Ramachandra will be semi-retiring at the end of the summer. But he will continue to oversee the Spectroscopy Laboratory's fiscal and strategic activities. So we won't be saying *adieu*, only *au revoir*.

Dresselhaus, continued from page 1



Professor Mildred Dresselhaus received a 2007 L'Oréal-UNESCO Award for Women in Science for her research on carbon nanotubes, images of which she points to on a monitor. Photo courtesy / L'Oréal ©Micheline Pelletier/Gamma in Paris where Sir Lindsay Owen-Jones, chairman of L'Oréal, and Koïchiro Matsuura, director-general of UNESCO, presented each laureate with her \$100,000 award.

Dresselhaus was selected for "conceptualizing the creation of carbon nanotubes," according to L'Oréal and UNESCO (United Nations Educational, Scientific and Cultural Organization). Due to their small size, high strength and electrical conductivity, carbon nanotubes are ideal for new materials used in objects such as lightweight bicycles and flat-panel screens.

A native of Bronx, N.Y., Dresselhaus has conducted scientific research for more than four decades. An MIT Professor of Physics and Electrical Engineering, she received her Ph.D. from the University of Chicago. She began her MIT career at Lincoln Laboratory studying superconductivity; she later switched to magneto-optics, carrying out a series of experiments that led to a fundamental understanding of the electronic structure of semi-metals, especially graphite.

Lord, continued from page 1

photosynthesis that can provide efficient and sustainable energy for mass consumption. A second research goal is to develop complex pulse sequences in order to manipulate and modify molecular dynamics.

Throughout his career, Dr. Fleming has been an active and successful scientific researcher, having co-authored over 345 publications. In addition to his cutting-edge research, Dr. Fleming has proved to be a capable leader. He served as Chair of the Chemistry Department for three years at the University of Chicago, during which he oversaw the creation of the Institute for Biophysical Dynamics. After moving to UC Berkeley, he initiated and directed the Physical Biosciences Division at Lawrence Berkeley National Laboratory and also became co-director of the California Institute for Quantitative Biomedical Research (QB3). In 2005 Dr. Fleming was appointed as Deputy Director at Lawrence Berkeley National Laboratory. Dr. Fleming has received numerous awards for his contributions, including his election as a fellow of both the Royal Society of London and the American Academy of Arts and Sciences.

Dr. Fleming has received numerous awards for his contributions. He is a Fellow of the Royal Society and a Fellow of the American Academy of Arts and Sciences. He is recipient of Marlow, Tilden and Centenary Medals from the Royal Society of Chemistry, the Nobel Laureate Signature Award for Graduate Education Chemistry, the Peter Debye Award and the Harrison Howe Award of the American Chemical Society. He has also received Sloan, Dreyfus, and Guggenheim Fellowships, as well as the Coblentz Award and the Inter-American Photochemical Society Award.

Now in its 15th year, the Lord lecture commemorates the achievements of Richard C. Lord, a pioneer in infrared and biochemical spectroscopy and director of the Spectroscopy Laboratory for 30 years. Each year's lecturer is selected by a committee of chemists, physicists and engineers at MIT who are active in various fields of spectroscopy.



Dresselhaus was the first tenured woman professor at MIT's School of Engineering and one of the first women to receive a Fulbright Fellowship. She has received numerous awards, including the U.S. National Medal of Science and 19 honorary doctorates worldwide.

Now in its ninth year, the L'Oréal-UNESCO Award for Women in Science is the only one of its kind to honor eminent women scientists at the international level.

A New Hybrid Multivariate Calibration Method

Kate L. Bechtel, Wei-Chuan Shih, Michael S. Feld

G. R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Multivariate calibration is a powerful chemometric technique for extracting analyte concentrations in complex chemical systems that exhibit linear response. Multivariate techniques are particularly well suited to analysis of spectral data because information about all of the analytes can be collected simultaneously at many wavelengths. The goal of multivariate calibration is to obtain a spectrum of regression coefficients, \mathbf{b} , such that an analyte's concentration, c , can be accurately predicted by taking the scalar product of \mathbf{b} with a prospective experimental spectrum, \mathbf{s} :

$$c = \mathbf{s}^T \mathbf{b}. \quad (1)$$

(Lowercase boldface type denotes a column vector, uppercase boldface type a matrix; and the superscript T denotes transpose.) In the absence of noise and other component correlations, the regression vector, \mathbf{b} , is unique and is equivalent to the spectrum of the analyte of interest. Under realistic experimental conditions, however, \mathbf{b} is more complicated and only an approximation to the ideal \mathbf{b} can be found. The "accuracy" of \mathbf{b} is judged by its ability to correctly predict concentrations via the standard error of prediction (SEP) with independent data.

There are two categories of multivariate techniques: explicit and implicit. Explicit techniques are those in which the pure component spectra are known or can be extracted from existing information. The most common of these techniques is ordinary least squares (OLS), in which a spectrum is fit with a matrix of pure component spectra, the fit coefficients being directly related to the concentrations. Mathematically, this is equivalent to deriving regression vectors for all components simultaneously, \mathbf{B} , directly from the pure component spectral matrix, \mathbf{P} :

$$\mathbf{B}^T = (\mathbf{P}^T \mathbf{P})^{-1} \mathbf{P}^T \quad (2)$$

and then applying Eq. (1).

One obvious limitation of explicit cali-

bration methods is the requirement of complete knowledge of the model components. In many cases, such as in biological spectroscopy, this is not feasible. Therefore, implicit calibration methods may be used. Implicit calibration methods require only a set of calibration spectra, \mathbf{S}_c , associated with several known concentrations of the analyte of interest that are expressed as a column vector, \mathbf{c} . The forward problem for implicit calibration is similar to Eq.(1):

$$\mathbf{c} = \mathbf{S}_c^T \mathbf{b}, \quad (3)$$

with the objective to use the set of calibration data $[\mathbf{S}_c, \mathbf{c}]$ to obtain an accurate \mathbf{b} by inverting Eq.(3).

There are two primary difficulties in directly inverting Eq.(3). First, the system is usually underdetermined, i.e., there are more variables (e.g., wavelengths) than

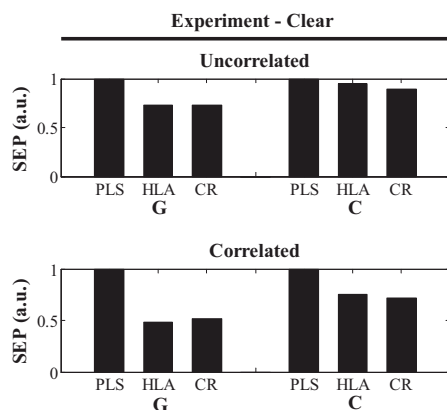


Figure 1: SEP values normalized to PLS results for glucose (G) and creatinine (C) in clear sample experiments without (Uncorrelated) and with (Correlated) analyte correlations

equations (e.g., number of calibration samples). Thus, direct inversion does not generally yield a unique solution. Second, even if a pseudo-inverse exists and results in a unique solution, such a solution tends to be unstable because all measurements contain noise and error. That is, small variations in \mathbf{c} or \mathbf{S} can lead to large variations in \mathbf{b} . Therefore, data reduction methods are usually applied to arrive at an equivalent data set that can be easily inverted.

Principal component regression (PCR) [1] and partial least squares (PLS) [2] are two frequently used implicit calibration methods. PCR decomposes the matrix of calibration spectra into orthogonal principle components which best capture the variance in the data. These new variables eliminate redundant information and by using a subset of these principle components, filter noise from the original data. With

this compacted and simplified form of the data, Eq.(3) may be inverted to arrive at \mathbf{b} . PLS is similar to PCR with the exception that the matrix decomposition for PLS is performed on the covariance matrix of the spectra and the reference concentrations, while for PCR only spectra are used. PLS and PCR have similar performance if noise in the spectral data and errors in the reference concentration measurements are negligible. Otherwise, PLS generally provides slightly better analysis than PCR [3].

Although these are powerful methods, they are not without their limitations. As pointed out in the literature [4], spurious effects such as instrument drift and co-variations among components can be incorrectly interpreted as arising from the analyte of interest. Thus, when the calculated \mathbf{b} is applied to a future spectrum in which one or all of those correlations are not present, an erroneous result may be obtained. It may be possible to improve calibration and limit spurious correlations by incorporating additional information about the system or analytes.

The MIT Spectroscopy Laboratory has a history of developing hybrid methods, which combine elements of both explicit and implicit calibration by including prior information. The first such method, hybrid linear analysis (HLA) was developed by Berger, et al. [5]. In HLA, the separately measured pure component spectrum of the analyte of interest, \mathbf{p} , is used together with the reference concentrations, \mathbf{c} , to subtract the spectral component attributed to the analyte of interest, $\mathbf{c}\mathbf{p}^T$, from the set of calibration spectra, \mathbf{S} . Principle components are derived using the modified spectra and these principle components are then subtracted from \mathbf{p} to form \mathbf{b} . In this manner, only the portions of \mathbf{p} that are orthogonal to the other components in the system are retained. As a result, HLA is insensitive to spurious correlations in a well-defined system. However, because HLA relies on the subtraction of the analyte spectrum from the calibration data, it is highly sensitive to the accuracy of the analyte spectral shape and intensity. For complex turbid samples in which absorption and scattering are likely to alter the analyte spectral features in unknown ways, we find that the performance of HLA is impaired.

Motivated by advancing transcutaneous in vivo blood analysis, we have developed a new calibration method, constrained regularization (CR), recently

published in Analytical Chemistry [6], which is more robust against inaccuracies in the previously measured pure analyte spectra. In the following, we show that with CR the prediction error is lower than methods without prior information, such as PLS, and is less affected by analyte co-variations. We further show that CR is more robust than our previously developed hybrid method, HLA, when there are inaccuracies in the applied constraint, as often occurs in complex or turbid samples such as biological tissue.

Multivariate calibration can be considered as the minimization of a least-squares quadratic cost function, Φ :

$$\Phi = \|\mathbf{S}_c^T \mathbf{b} - \mathbf{c}\|^2, \quad (4)$$

with $\|\mathbf{x}\|$ the Euclidean norm (i.e., magnitude) of \mathbf{x} [7]. CR is based on a technique known as regularization [8] in which instabilities associated with the inversion process are removed by damping the effect of smaller principle components with the aid of a regularization parameter, Λ :

$$\Phi(\Lambda) = \|\mathbf{S}_c^T \mathbf{b} - \mathbf{c}\|^2 + \Lambda \|\mathbf{b}\|^2. \quad (5)$$

Thus, \mathbf{b} is limited to a finite value based on a proper choice for the value of Λ . In CR, an additional piece of information is included in the cost function. Rather than simply limit the norm of \mathbf{b} itself, the cost function is minimized based on the difference between \mathbf{b} and a spectral constraint, \mathbf{b}_0 :

$$\Phi(\Lambda, \mathbf{b}_0) = \|\mathbf{S}_c^T \mathbf{b} - \mathbf{c}\|^2 + \Lambda \|\mathbf{b} - \mathbf{b}_0\|^2. \quad (6)$$

The insight for CR is that a well-chosen \mathbf{b}_0 , namely, the spectrum of the analyte of interest or the elements of which that are orthogonal to other system components, can constrain \mathbf{b} to a more accurate solution. In other words, this constraint can help the minimization algorithm arrive at the ‘‘correct’’ local minimum when performing a calibration in which other analytes may partially correlate with the analyte of interest.

We have studied the effectiveness of CR using numerical simulations and experimental Raman spectra. In the interest of space, only the experimental results are presented here. In all studies, glucose and creatinine were chosen as analytes of interest, while urea was always present as an additional active Raman spectral interference. Because the goal of these studies is not to champion detection limits, results are normalized to PLS results, an objective baseline.

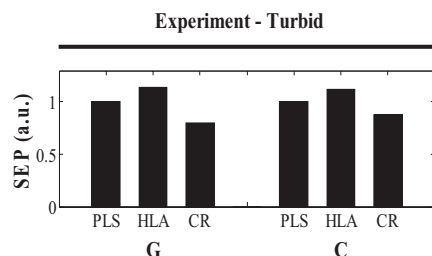


Figure 2: SEP values normalized to PLS results for glucose (G) and creatinine (C) in the turbid sample experiment

The results from the first experiment, in which analyte concentrations were uncorrelated, are summarized in Fig. 1 (Uncorrelated). OLS results are not listed because the three-constituent model does not account for all experimental variations, e.g. low amounts of fluorescence from the quartz cuvette; therefore, OLS no longer provides the best achievable performance. It is observed that substantial improvement over PLS is observed using the hybrid methods. CR and HLA generate similar SEP values, suggesting that these two methods have comparable performance under highly controlled experimental conditions with clear samples and without analyte correlations.

The second experiment, in which correlations between analytes were introduced, demonstrates that CR is less susceptible than PLS to spurious correlations among co-varying analytes. We modified the calibration data set such that the concentration of glucose correlated to creatinine with $R^2 \sim 0.5$. The prospective set remained uncorrelated. The results are displayed in Fig. 1 (Correlated). Again, CR and HLA are observed to have similar performance. In principle, HLA should be less affected by analyte correlations than CR, however, possible explanations include imperfect experimental conditions and the higher sensitivity of HLA to inaccurate constraints.

The third experiment was performed with turbid (scattering and absorbing) samples, created by addition of intralipid and India ink. The results are summarized in Fig. 2. Substantial improvement over both PLS and HLA is observed using CR. As expected, the performance of HLA is significantly impaired as a result of the turbidity-induced distortions in the analyte spectra. The distortions render the pure component spectrum an inaccurate representation of the analyte spectrum as exists in the turbid medium.

In CR, however, the pure component

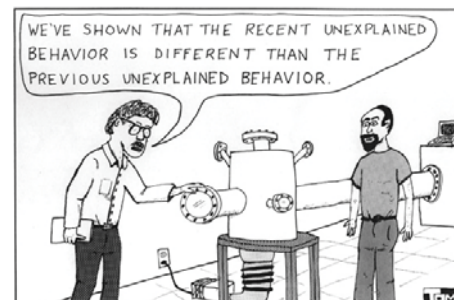
spectrum used as the spectral constraint only guides the inversion process, allowing the minimization algorithm to arrive at the optimal solution, thereby reducing its dependency on the accuracy of the spectrum.

These results demonstrate that there is a tradeoff between maximizing prior information utilization and robustness concerning the accuracy of such information. Multivariate calibration methods range from explicit methods with maximum use of prior information (e.g. OLS, least robust when accurate model is not obtainable), hybrid methods with an inflexible constraint (e.g. HLA), hybrid methods with a flexible constraint (e.g. CR), and implicit methods with no prior information (e.g. PLS, most robust, but is prone to be misled by spurious correlations). We believe that CR achieves the optimal balance between these ideals in practical situations.



References

1. Gunst, R.F. & Mason R.L. Regression analysis and its application : a data-oriented approach. M. Dekker (1980).
2. Wold, S., Martin H. & Wold H. Lecture Notes in Mathematics. Springer-Verlag (1983).
3. Thomas, E.V. & Haaland, D.M. Analytical Chemistry 62, 1091-1099 (1990).
4. Arnold, M.A., Burmeister J.J. & Small G.W. Analytical Chemistry 70, 1773-1781 (1998).
5. Berger, A.J., Koo T.W., Itzkan I. & Feld, M.S. Analytical Chemistry 70, 623-627 (1998).
6. Shih, W.-C., Bechtel K.L. & Feld M.S. Analytical Chemistry 79, 234-239 (2007).
7. Bertero, M. & Boccacci P. Introduction to inverse problems in imaging. Institute of Physics Pub (1998).
8. Tikhonov, A.N. & Arsenin V.I.F.A.F. Solutions of ill-posed problems. Winston (1977).



Cartoon courtesy Tom Swanson's Science Cartoons (<http://home.netcom.com/~swansont/science.html>).

Research Report

Characterizing the Chirality Distribution of Single-Walled Carbon Nanotube Materials with Tunable Raman Spectroscopy

H. B. Son^{1,4}, A. Reina^{2,4}, M. S. Dresselhaus^{1,4}, and J. Kong¹

¹ Department of Electrical Engineering and Computer Science

² Department of Material Science and Engineering

³ Department of Physics

⁴ G.R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139-4037

Single-walled carbon nanotubes (SWNT) are fascinating one-dimensional materials with remarkable properties and many promising applications [1]. They can be considered as tiny cylinders rolled up from a single layer of graphite and their structure can be indexed by two integers (n,m) which, are called the chirality of SWNTs. A very unique feature of SWNTs is that their properties depend sensitively on their chiralities; for example, a SWNT is metallic if n-m equals 3 times an integer, or semiconducting otherwise [2]. The bandgap of a semiconducting nanotube is inversely proportional to its diameter. This unique characteristic gives rise to many different applications; on the other hand, it poses a significant challenge for the production of SWNT material. With current synthetic methods, there is always a mixture of SWNTs with a variety of chiralities obtained, whereas for many applications it is highly desirable to have SWNTs with only one type of structure. In order to have better control of the synthesis process, more understanding of how each synthetic parameter can be used to tune or control the chirality distribution of the SWNT material is needed. Therefore a good method of characterizing the chirality distribution of a synthesized material is the first step to enable such an investigation.

Here we present our methodology of characterizing the chirality distribution of SWNT materials with tunable Raman Spectroscopy. Figure 1 explains the basic procedure. Figure 1(a) is a schematic diagram of the sample used in our method. The gray area is part of the substrate and the yellow squares are markers for posi-

tion recognition. The dimensions of the markers are 0.5~1 μm and the distance between them is ~20 μm . The black lines indicate nanotubes which can be either directly grown on the substrate or dispersed from solutions of a bulk material. The samples are then put onto an automatic scanning stage of a home-built confocal Raman microscope. Figure 1(b) is the Kataura-plot calculated by the extended-tight binding method [3], where the optical transition energies E_{ii} for different (n,m) structural indices are plotted against the Raman radial breathing mode (RBM) frequency. The blue points correspond to semiconducting SWNTs and red ones correspond to metallic SWNTs. These calculations match the experimental data of

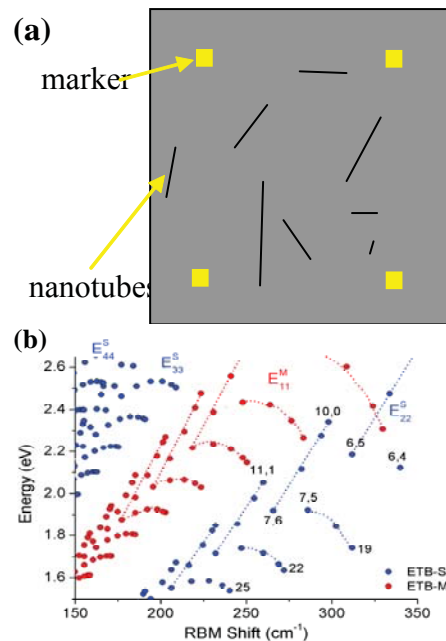


Figure 1: Method for obtaining a chirality distribution of a SWNT material. (a) Schematic diagram of the sample used in these experiments. (b) Kataura plot calculated by the extended-tight binding method [3].

SDS-wrapped SWNTs very well [4]. The $2n+m = \text{constant}$ families are denoted by the dotted lines and the $2n+m$ family [5] numbers are also indicated. As the optical transition energy and the RBM signal of a SWNT are obtained simultaneously in the resonant Raman process, the nanotubes's chirality (n,m) can therefore be identified from the Kataura Plot [4]. However, since the optical transition energy spans a wide range (from <1.5eV to >2.6eV), in order to access most of the nanotubes with the resonant Raman process, the Raman spectrometer needs to be tunable over a similarly large range (1.5eV~2.6eV corresponds to 470nm ~ 840nm laser excitation

energy). We have overcome this challenge with our home-built Raman spectrometer.

In a typical measurement, the sample, depicted in Fig 1(a), is placed on an automatic scanning stage and the laser spot is scanned over a 40 μm by 20 μm area with a 0.5 μm X 1 μm step size, and 1701 Raman spectra are taken for the area being mapped. The laser excitation is then tuned to a different wavelength and the same area is mapped. For SWNTs that are resonant at a particular laser energy, their Raman spectra will then appear. If the nanotube is long enough, the Raman signal along the nanotube can also be imaged in a spatial mapping. This mapping method allows us to follow and identify each nanotube, regarding its spatial position. The tuning of the excitation energy allows the recognition of a SWNT going in and out of resonance. Therefore a resonance profile of each SWNT can be obtained and the optical transition energy can be more accurately determined [6]. With automatic scanning and data collection, hundreds to thousands of nanotube resonant Raman spectra can be obtained, and this will allow us to perform the statistical analysis of the chirality distribution.

Figure 2 shows a typical result obtained with our tunable Raman spectrometer. In Fig 2(a) the substrate is Si with 300 nm thermally grown SiO₂, and trenches (which run horizontally in Fig 2(a)) of width 1.5, 3, 6 μm are etched into the SiO₂. SWNTs are grown on the substrates lying across the trenches aligned in the vertical direction [7]. Fig 2(a) demonstrates the mapping result of Raman signals of a particular SWNT lying across the trenches. Three panels are shown: the left one is the G band Raman signal of the nanotube at 1600 cm⁻¹, the middle one is the RBM signal of this particular nanotube at 173 cm⁻¹, and the right is the Si signal at 520 cm⁻¹. It can be seen that at the trench region, the Si signals are relatively lower, which is due to the fact that the auto-focusing is on the substrate surface. This allows us more capability for position recognition making use of surface irregularities. From the left and middle panels, one can see that the same nanotube has a different peak intensity for the RBM and G-band signals depending on whether the tube is suspended or in contact with the substrate. It has been proposed that the substrate interactions alter the optical transition energy and Raman frequencies [4]; this

is called the “environmental effect”. For different substrates and environments (for example, solutions), the effects are different, which complicates the chirality assignment, a topic still under investigation.

Figure 2(b) demonstrates the example of the resonant profile of a metallic nanotube, which is identified as a (10,4) nanotube in the Kataura plot (it is circled in Fig 1(b)). Due to the trigonal warping effect [8], the optical transition energy for non-armchair metallic nanotubes splits, as can be seen in the Kataura plot. When the RBM signal (240 cm^{-1}) intensity versus the excitation energy is plotted, an interesting two-peak resonance can be seen in the resonant profile, confirming the theoretical prediction. The red dots are experimental data and the black curve shows the calculated resonance profiles for the RBM intensity for both transitions obtained from time-dependent third-order perturbation theory [9]. The blue diamonds indicate the predicted resonant energy. From our results we concluded that there is a downshift of ~ 70 meV for the resonant energy between the experimental data and theoretical prediction, which is due to the environmental effect mentioned above.

With the spatial mapping and energy profile capabilities confirmed for our Raman spectrometer, we investigated two SWNT samples grown with the same catalyst and same chemical vapor deposition (CVD) conditions except for the growth temperature. The catalyst is Al_2O_3 supported Fe/Mo nanoparticles [10] directly spun onto Si/ SiO_2 substrates and the CVD conditions at the growth temperature are methane with a flow rate of 1000 standard cubic centimeter per minute (sccm) mixed with hydrogen of 500 sccm. The growth temperatures for the two samples are 650°C and 900°C , respectively. In Figure 3 the data of the samples are shown. The calculated Kataura plots are also displayed for reference. Figure 3(a) corresponds to the data obtained with the sample grown at 650°C (green dots), and Fig 3(b) displays the data of the sample grown at 900°C (yellow dots). The blue shaded areas indicate the regions where we have laser excitation energies available. The size of the dots is proportional to the logarithm of the intensities of the Raman signal. Currently we are limited by the available laser sources, and thus are not able to perform the chirality distribution for these two samples. However, these preliminary results demonstrate the

effectiveness of the basic principle. In addition, we can see that there is a fairly large environmental effect: the experimental data points appear at lower excitation energy and at a slightly higher RBM frequency compared with the calculated ones. Since these calculated results fit the SDS-wrapped nanotubes in water solutions fairly well, it is reasonable for the nanotube lying on Si to have a different environmental shift. However, this complicates the chirality assignment and renders the (n,m) identification not definitive when two (n,m) points are very close to each other. Further in-depth investigations of the environmental effect will be carried out in order to achieve clear chirality as-

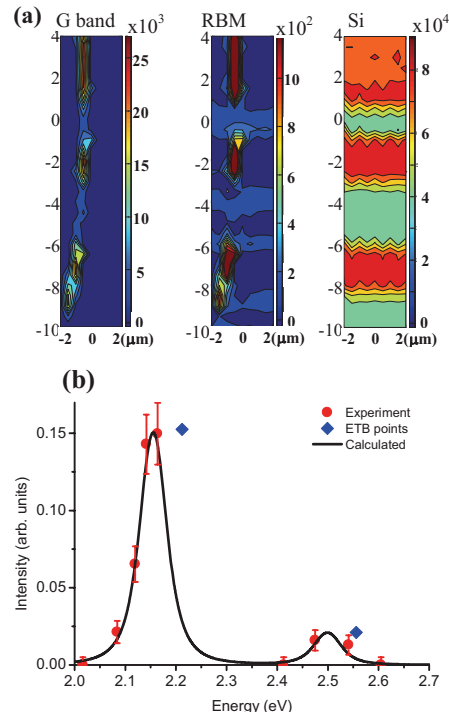


Figure 2: Typical results obtained with the tunable Raman spectrometer. (a) Spatial mapping capability allows the registering of each nanotube with regard to its position. The laser excitation wavelength is 579 nm in this example. (b) Resonant energy profile of a metallic nanotube.

signments in the future. Nevertheless, it can be seen from Fig. 3 that once the rest of the laser excitation energies are available, it will be straightforward to obtain a diameter distribution and metallic/semiconducting ratio characterization easily.

With these preliminary results, we performed a rough estimate of metallic to semiconducting nanotube ratio. For the 900°C sample, we have observed 256 RBM signals within the current excitation ranges for $160 \text{ cm}^{-1} \leq \omega_{\text{RBM}} \leq 340 \text{ cm}^{-1}$ (we exclude $\omega_{\text{RBM}} < 160 \text{ cm}^{-1}$ because

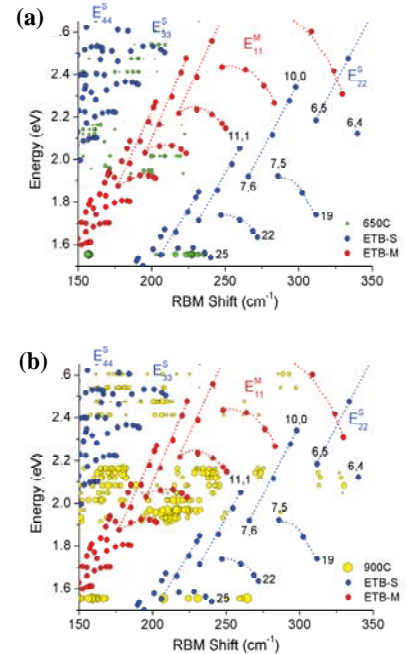


Figure 3: Preliminary results for the comparison of two samples grown at two different temperatures (the rest of the growth conditions are all the same). (a) Growth carried out at 650°C . Green dots are the data points. (b) Growth at 900°C . Yellow dots are the data points.

at blue excitation energies, small ω_{RBM} are difficult to observe). Among these, 130 correspond to metallic SWNTs, 126 correspond to semiconducting ones. The same SWNT can be observed at different excitation energies if the laser energies are close enough to be within the nanotube’s resonance window. We include this factor into our consideration by using a $\pm 0.1\text{eV}$ resonance window and a 50 meV environmental downshift (these parameters work well for our experimental data points) and found that it is expected to observe 177 RBM signals corresponding to metallic nanotubes and 166 RBM signals corresponding to semiconducting nanotubes. This means if there is no preference in the chirality distribution, there should be a roughly 1:1 ratio of metallic to semiconducting nanotubes in these laser excitation regions. Our results give 130:126, which falls within this energy range. For the 650°C sample, we observed 29 RBM signals corresponding to metallic SWNTs and 53 for semiconducting nanotubes in the region $160 \text{ cm}^{-1} \leq \omega_{\text{RBM}} \leq 340 \text{ cm}^{-1}$. The number of data points at the current stage is not enough for making a statistically meaningful estimate for this sample.

Acknowledgements We thank the Intel Higher Education Program for support. *Carbon Nanotubes, continues on page 15*

Seminar on
**MODERN OPTICS AND
SPECTROSCOPY**
Spring 2007

- February 27 Dana Dlott, University of Illinois
Ultrafast vibrational spectroscopy with high time and space resolution
- March 6 Mounqi Bawendi, MIT
Nanocrystal quantum dot science and technology: The importance of spectroscopy
- March 13 Daniel Murnick, Rutgers University
Counting carbon 14 atoms for health improvement
- March 27 Mriganka Sur, MIT
Imaging cells, synapses, and molecules in the live brain
- April 3 Xi-Cheng Zhang, Rensselaer Polytechnic Institute
Recent development of THz wave technology for sensing and imaging applications
- April 10 Andrei Tokmakoff, MIT
The fluctuations and switching of hydrogen bonds in water
- April 17 János Hebling, MIT
Generation and application of high field THz pulses
- | |
|---|
| <p>April 24 <i>16th Annual Richard C. Lord Lecture:</i>
Graham Fleming, University of California Berkeley
Two-dimensional ultrafast electronic spectroscopy</p> |
|---|
- May 1 Rebecca Richards-Kortum, Rice University
Point-of-care optical diagnostics to improve global health
- May 8 Adam Steeves, MIT
Acetylene: What happens when a well-behaved molecule gets bent out of shape?

Tuesdays, 12:00 - 1:00 p.m., Grier Room (34-401)

Refreshments served following the seminar

Sponsored by the George R. Harrison Spectroscopy Laboratory, Department of Electrical Engineering and Computer Science and School of Science, MIT.



GEORGE R. HARRISON SPECTROSCOPY LABORATORY
MICHAEL S. FELD, DIRECTOR
77 MASSACHUSETTS AVENUE, ROOM 6-014
CAMBRIDGE, MASSACHUSETTS 02139-4307

TELEPHONE: (617) 253-7700
FAX: (617) 253-4513
URL: <http://web.mit.edu/spectroscopy/>

Lester Wolfe Workshop in Laser Biomedicine

Optical Methods in Breast Cancer

Tuesday, April 17, 2007, 4:00-6:00 pm

Richard B. Simches Research Center, Room 3110

185 Cambridge St. Boston

(Located in Charles River Plaza next to Whole Foods Market and CVS)

Increasing incidence rates of breast cancer amongst US women and the importance of early detection in predicting outcome has led to searches for better screening methods. Mammography, although useful, has been called a double-edged sword due to the occurrence of many false positives. This workshop will cover some applications of optics to the problem of breast cancer detection and diagnosis and monitoring response to therapy.

Introduction and clinical overview

Barbara L. Smith, Massachusetts General Hospital

Shedding light on breast cancer: Advances in spectroscopic diagnosis

Maryann Fitzmaurice, Case Western Reserve University

Diffuse optical tomography for breast cancer detection and characterization

Arjun Yodh, University of Pennsylvania

Intra-operative optical biopsy of breast cancer

Stephen Boppart, University of Illinois at Urbana-Champaign

Refreshments served at 3:30 pm

Sponsored by G.R. Harrison Spectroscopy Laboratory, MIT
MGH Wellman Center for Photomedicine
Harvard-MIT Division of Health Sciences and Technology
and Center for the Integration of Medicine and Innovative Technology

PLEASE POST

Spectroscopy Laboratory Published Articles, 2006

Reprints of articles can be obtained by downloading from the Spectroscopy Laboratory and/or core faculty websites, and/or upon e-mail request (zqueen@mit.edu).

- Angheloiu, G. O., Arendt, J. T., Muller, M. G., Haka, A. S., Georgakoudi, I., Motz, J. T., Scepanovic, O. R., Kuban, B. D., Myles, J., Miller, F., Podrez, E. A., Fitzmaurice, M., Kramer, J. R. and Feld, M. S., "Intrinsic fluorescence and diffuse reflectance spectroscopy identify superficial foam cells in coronary plaques prone to erosion," *Arterioscler Thromb Vasc Biol* **26** (7), 1594-1600 (2006)
- Anikeeva, P. O., Madigan, C. F., Coe-Sullivan, S. A., Steckel, J. S., Bawendi, M. G. and Bulovic, V., "Photoluminescence of CdSe/ZnS core/shell quantum dots enhanced by energy transfer from a phosphorescent donor," *Chemical Physics Letters* **424** (1-3), 120-125 (2006)
- Barros, E. B., Souza Filho, A. G., Son, H., Mendes Filho, B. J., Jorio, A., Dresselhaus, G. and Dresselhaus, M. S., "Double resonance Raman spectroscopy of graphitic foams," *Phys. Rev. B* (2006)
- Bechtel, H. A., Steeves, A. H. and Field, R. W., "Laboratory measurements of the hyperfine structure of (HNC)-N-14-C-12 and (DNC)-N-14-C-12," *Astrophysical Journal* **649** (1), L53-L56 (2006)
- Brokmann, X., Bawendi, M. G., Coolen, L. and Hermier, J-P, "Photon-correlation Fourier spectroscopy". *Optics Express*, 14:6333-6341 (2006)
- Caruge, J. M., Halpert, J. E., Bulovic, V. and Bawendi, M. G., "NiO as an inorganic hole-transporting layer in quantum-dot light-emitting devices," *Nano Letters* **6** (12), 2991-2994 (2006)
- Cavalleri, A., Wall, S., Simpson, C., Statz, E., Ward, D. W., Nelson, K. A., Rini, M. and Schoenlein, R. W., "Tracking the motion of charges in a terahertz light field by femtosecond X-ray diffraction," *Nature* **442** (7103), 664-666 (2006)
- Chan, Y. T., Snee, P. T., Caruge, J. M., Yen, B. K., Nair, G. P., Nocera, D. G. and Bawendi, M. G., "A solvent-stable nanocrystal-silica composite laser," *Journal of the American Chemical Society* **128** (10), 3146-3147 (2006)
- Choi, W., Lee, J. H., An, K., Fang-Yen, C., Dasari, R. R. and Feld, M. S., "Observation of sub-poisson photon statistics in the cavity-QED microlaser," *Phys Rev Lett* **96** (9), 093603 (2006)
- Chung, I., Witkoskie, J. B., Cao, J. S. and Bawendi, M. G., "Description of the fluorescence intensity time trace of collections of CdSe nanocrystal quantum dots based on single quantum dot fluorescence blinking statistics," *Physical Review E* **73** (1), 011106 (2006)
- DeCamp, M. F. and Tokmakoff, A., "Single-shot two-dimensional spectrometer," *Optics Letters* **31** (1), 113-115 (2006)
- Dresselhaus, M. S., Villalpando-Paez, F., Samsonidze, G. G., Chou, S. G., Dresselhaus, G., Jiang, J., Saito, R., Souza Filho, A. G., Jorio, A., Endo, M. and Kim, Y-A, "Raman Scattering from One-Dimensional Carbon Systems," *Physica E* j.physe.2006.07.048, (in press) (2006)*
- Endo, M., Kim, Y. A., Hayashi, T., Muramatsu, H., Terrones, M., Saito, R., Villalpando-Paez, F., Chou, S. G. and Dresselhaus, M. S., "Nanotube coalescence-inducing mode: A novel vibrational mode in carbon systems," *Small* **2** (8-9), 1031-1036 (2006)
- Esswein, A. J., Veige, A. S. and Nocera, D. G., "Photocycle for hydrogen production from homogeneous solution," *Abstracts of Papers of the American Chemical Society* 231 (2006)
- Fang-Yen, C., "Quantum trajectory studies of many-atom and finite transit-time effects in a cavity QED microlaser or micromaser," *Optics Communications* **262** (2), 224-228 (2006)
- Fang-Yen, C., Yu, C. C., Ha, S., Choi, W., An, K., Dasari, R. R. and Feld, M. S., "Observation of multiple thresholds in the many-atom cavity QED microlaser," *Physical Review A* **73** (4), 4 (2006)
- Green, W. H., "Predictive Kinetics: A New Approach for the 21st Century," *Advances in Chemical Engineering* (in press) (2006)
- Haka, A. S., Volynskaya, Z., Gardecki, J. A., Nazemi, J., Lyons, J., Hicks, D., Fitzmaurice, M., Dasari, R. R., Crowe, J. P. and Feld, M. S., "In vivo margin assessment during partial mastectomy breast surgery using raman spectroscopy," *Cancer Res* **66** (6), 3317-3322 (2006)
- Halpert, J. E., Porter, V. J., Zimmer, J. P. and Bawendi, M. G., "Synthesis of CdSe/CdTe nanobarells," *Journal of the American Chemical Society* **128** (39), 12590-12591 (2006)
- Hodgkiss, J. M., Damrauer, N. H., Presse, S., Rosenthal, J. and Nocera, D. G., "Electron transfer driven by proton fluctuations in a hydrogen-bonded donor-acceptor assembly," *Journal of Physical Chemistry B* **110** (38), 18853-18858 (2006)
- Hodgkiss, J. M., Rosenthal, J. and Nocera, D. G., "The Relation Between Hydrogen Atom Transfer and Proton-Coupled Electron Transfer in Model Systems," In *Handbook of Hydrogen Transfer. Physical and Chemical Aspects of Hydrogen Transfer*, Vol. 1: J.T. Hynes, R.L. Schowen, H.H. Limbach, Eds.; Wiley VCH: Weinheim, Germany (2006)
- Hunter, M., Backman, V., Popescu, G., Kalashnikov, M., Boone, C. W., Wax, A., Gopal, V., Badizadegan, K., Stoner, G. D. and Feld, M. S., "Tissue self-affinity and polarized light scattering in the born approximation: a new model for precancer detection," *Phys Rev Lett* **97** (13), 138102 (2006)
- Kojima, M., Tada, S., Umenmoto, S., Ishii, Y., Mizusaki, H., Muramatsu, H., Shimamoto, D., Kim, Y.A., Hayashi, T., Endo, M., Terrones, M. and Dresselhaus, M. S., "In-situ Raman study on electrochemical Li insertion into multiwalled carbon nanotubes," *Carbon* (2006)
- Liu, S. Y. and Nocera, D. G., "A simple and versatile method for alkene epoxidation using aqueous hydrogen peroxide and manganese salophen catalysts," *Tetrahedron Letters* **47** (12), 1923-1926 (2006)
- Liu, S. Y., Soper, J. D., Yang, J. Y., Rybak-Akimova, E. V. and Nocera, D. G., "Mechanistic studies of hangman salo-

Publications, continues on page 12

Publications, continued from page 11
phen-mediated activation of O-O bonds,”
Inorganic Chemistry **45** (19), 7572-7574
(2006)

Loparo, J. J., Roberts, S. T. and Tokmakoff, A., “Multidimensional infrared spectroscopy of water. I. Vibrational dynamics in two-dimensional IR line shapes,” Journal of Chemical Physics **125** (19), (2006)

Loparo, J. J., Roberts, S. T. and Tokmakoff, A., “Multidimensional infrared spectroscopy of water. II. Hydrogen bond switching dynamics,” Journal of Chemical Physics **125** (19), (2006)

Lu, J., Kopley, T., Dutton, D., Liu, J., Qian, C., Son, H., Dresselhaus, M. S. and Kong, J., “Generating suspended single-walled carbon nanotubes across a large surface area via patterning self-assembled catalyst-containing block copolymer thin films,” J. Phys. Chem. B **110** 10585—10589 (2006)

Lue, N., Popescu, G., Ikeda, T., Dasari, R. R., Badizadegan, K. and Feld, M. S., “Live cell refractometry using microfluidic devices,” Opt Lett **31** (18), 2759-2761 (2006)

Matan, K., Grohol, D., Nocera, D. G., Yildirim, T., Harris, A. B., Lee, S. H., Nagler, S. E. and Lee, Y. S., “Spin waves in the frustrated kagome lattice antiferromagnet $KFe_3(OH)(6)(SO_4)(2)$,” Physical Review Letters **96** (24), (2006)

McKee, T. D., Grandi, P., Mok, W., Alexandrakis, G., Insin, N., Zimmer, J. P., Bawendi, M. G., Boucher, Y., Breakefield, X. O. and Jain, R. K., “Degradation of fibrillar collagen in a human melanoma xenograft improves the efficacy of an oncolytic herpes simplex virus vector,” Cancer Research **66** (5), 2509-2513 (2006)

Mettetal, J. T., Muzzey, D., Pedraza, J. M., Ozbudak, E. M. and van Oudenaarden, A., “Predicting stochastic gene expression dynamics in single cells,” Proceedings of the National Academy of Sciences of the United States of America **103** (19), 7304-7309 (2006)

Motz, J. T., Fitzmaurice, M., Miller, A., Gandhi, S. J., Haka, A. S., Galindo, L. H., Dasari, R. R., Kramer, J. R. and Feld, M. S., “In vivo Raman spectral pathology

of human atherosclerosis and vulnerable plaque,” J Biomed Opt **11** (2), 021003 (2006)

Muzzey, D. and van Oudenaarden, A., “When it comes to decisions, myeloid progenitors crave positive feedback,” Cell **126** (4), 650-652 (2006)

Oluwole, O. O., Bhattacharjee, B., Tolsma, J. E., Barton, P. I. and Green, W. H., “Rigorous valid ranges for optimally reduced kinetic models,” Combustion and Flame **146** (1-2), 348-365 (2006)

Park, Y. K., Popescu, G., Badizadegan, K., Dasari, R. R. and Feld, M. S., “Diffraction phase and fluorescence microscopy,” Optics Express **14** (18), 8263-8268 (2006)

Pedraza, J. M. and van Oudenaarden, A. “Noise in gene regulatory networks”, book chapter in ‘Complex Systems Science in BioMedicine’ (Kluwer Academic, New York, 2006)

Ploeger, J. M., Bielenberg, P. A., Dinario-Blanchard, J. L., Lachance, R. P., Taylor, J. D., Green, W. H. and Tester, J. W., “Modeling oxidation and hydrolysis reactions in supercritical water-free radical elementary reaction networks and their applications,” Combustion Science and Technology **178** (1-3), 363-398 (2006)

Ploeger, J. M., Green, W. H. and Tester, J. W., “Co-oxidation of methylphosphonic acid and ethanol in supercritical water - II: Elementary reaction rate model,” Journal of Supercritical Fluids **39** (2), 239-245 (2006)

Popescu, G., Badizadegan, K., Dasari, R. R. and Feld, M. S., “Observation of dynamic subdomains in red blood cells,” J Biomed Opt **11** (4), 040503 (2006)

Popescu, G., Ikeda, T., Dasari, R. R. and Feld, M. S., “Diffraction phase microscopy for quantifying cell structure and dynamics,” Opt Lett **31** (6), 775-777 (2006)

Popescu, G., Ikeda, T., Goda, K., Best-Popescu, C. A., Laposata, M., Manley, S., Dasari, R. R., Badizadegan, K. and Feld, M. S., “Optical measurement of cell membrane tension,” Phys Rev Lett **97** (21), 218101 (2006)

Porter, V. J., Mentzel, T., Charpentier,

S., Kastner, M. A. and Bawendi, M. G., “Temperature-, gate-, and photoinduced conductance of close-packed CdTe nanocrystal films,” Physical Review B **73** (15), (2006)

Poulin, P. R. and Nelson, K. A., “Irreversible organic crystalline chemistry monitored in real time,” Science **313** (5794), 1756-1760 (2006)

Reece, S. Y., Hodgkiss, J. M., Stubbe, J. and Nocera, D. G., “Proton-coupled electron transfer: the mechanistic underpinning for radical transport and catalysis in biology,” Philosophical Transactions of the Royal Society B-Biological Sciences **361** (1472), 1351-1364 (2006)

Reece, S. Y., Seyedsayamdost, M. R., Stubbe, J. and Nocera, D. G., “Electron transfer reactions of fluorotyrosyl radicals,” Journal of the American Chemical Society **128** (42), 13654-13655 (2006)

Rosenthal, J., Hodgkiss, J. M., Young, E. R. and Nocera, D. G., “Spectroscopic determination of proton position in the proton-coupled electron transfer pathways of donor-acceptor supramolecule assemblies,” Journal of the American Chemical Society **128** (32), 10474-10483 (2006)

Rosenthal, J., Luckett, T. D., Hodgkiss, J. M. and Nocera, D. G., “Photocatalytic oxidation of hydrocarbons by a bis-iron(III)-mu-oxo Pacman porphyrin using O₂ and visible light,” Journal of the American Chemical Society **128** (20), 6546-6547 (2006)

Samadani, A., Mettetal, J. and van Oudenaarden, A., “Cellular asymmetry and individuality in directional sensing,” Proceedings of the National Academy of Sciences of the United States of America **103** (31), 11549-11554 (2006)

Scepanovic, O. R., Fitzmaurice, M., Gardecki, J. A., Angheloiu, G. O., Awasthi, S., Motz, J. T., Kramer, J. R., Dasari, R. R. and Feld, M. S., “Detection of morphological markers of vulnerable atherosclerotic plaque using multimodal spectroscopy,” J Biomed Opt **11** (2), 021007 (2006)

Seyedsayamdost, M. R., Reece, S. Y., Nocera, D. G. and Stubbe, J., “Mono-, di-, tri-, and tetra-substituted fluorotyrosines: New probes for enzymes that use

- tyrosyl radicals in catalysis,” *Journal of the American Chemical Society* **128** (5), 1569-1579 (2006)
- Seyedsayamdost, M. R., Yee, C. S., Reece, S. Y., Nocera, D. G. and Stubbe, J., “pH rate profiles of F_nY356-R2s (n=2, 3, 4) in *Escherichia coli* ribonucleotide reductase: Evidence that Y-356 is a redox-active amino acid along the radical propagation pathway,” *Journal of the American Chemical Society* **128** (5), 1562-1568 (2006)
- Sheng, W. C., Kim, S., Lee, J., Kim, S. W., Jensen, K. and Bawendi, M. G., “In-situ encapsulation of quantum dots into polymer microspheres,” *Langmuir* **22** (8), 3782-3790 (2006)
- Singer, A. B., Taylor, J. W., Barton, P. I. and Green, W. H., “Global dynamic optimization for parameter estimation in chemical kinetics,” *Journal of Physical Chemistry A* **110** (3), 971-976 (2006)
- Snee, P. T., Somers, R. C., Nair, G., Zimmer, J. P., Bawendi, M. G. and Nocera, D. G., “A ratiometric CdSe/ZnS nanocrystal pH sensor,” *Journal of the American Chemical Society* **128** (41), 13320-13321 (2006)
- Son, H. B., Reina, A., Samsonidze, G. G., Saito, R., Jorio, A., Dresselhaus, M. S. and Kong, J., “Raman characterization of electronic transition energies of metallic single-wall carbon nanotubes,” *Physical Review B* **74** (7), (2006)
- Son, H. B., Reina, A., Dresselhaus, M. S. and Kong, J., “Characterizing the chirality distribution of single-walled carbon nanotube materials with tunable Raman spectroscopy,” *Physica Status Solidi B-Basic Solid State Physics* **243** (13), 3161-3165 (2006)
- Souza, A. G., Endo, M., Muramatsu, H., Hayashi, T., Kim, Y. A., Barros, E. B., Akuzawa, N., Samsonidze, G. G., Saito, R. and Dresselhaus, M. S., “Resonance Raman scattering studies in Br₂-adsorbed double-wall carbon nanotubes,” *Physical Review B* **73** (23), 235413 (2006)
- Steckel, J. S., Snee, P. T., Coe-Sullivan, S. A., Zimmer, J. P., Halpert, J. E., Anikeeva, P. O., Kim, L.-A., Bulovic, V. and Bawendi, M. G., “Color-Saturated Green-Emitting QD-LEDs,” *Angewandte Chemie International Edition*, **45** 5796-5799 (2006)
- Steckel, J. S., Yen, B. K. H., Oertel, D. C. and Bawendi, M. G., “On the mechanism of lead chalcogenide nanocrystal formation,” *Journal of the American Chemical Society* **128** (40), 13032-13033 (2006)
- Tharp, W. G., Yadav, R., Irimia, D., Upadhyaya, A., Samadani, A., Hurtado, O., Liu, S. Y., Munisamy, S., Brainard, D. M., Mahon, M. J., Nourshargh, S., van Oudenaarden, A., Toner, M. G. and Poznansky, M. C., “Neutrophil chemorepulsion in defined interleukin-8 gradients in vitro and in vivo,” *Journal of Leukocyte Biology* **79** (3), 539-554 (2006)
- Tracy, J. B. and Bawendi, M. G., “Defects in CoO in oxidized cobalt nanoparticles dominate exchange biasing and exhibit anomalous magnetic properties,” *Physical Review B* **74** (18), (2006)
- Tsang, J. and van Oudenaarden, A., “Exciting fluctuations: monitoring competence induction dynamics at the single-cell level,” *Molecular Systems Biology* (2006)
- Van Geem, K. M., Reyniers, M. F., Marin, G. B., Song, J., Green, W. H. and Matheu, D. M., “Automatic reaction network generation using RMG for steam cracking of n-hexane,” *Aiche Journal* **52** (2), 718-730 (2006)
- Vaughan, J. C., Feurer, T., Stone, K. W. and Nelson, K. A., “Analysis of replica pulses in femtosecond pulse shaping with pixelated devices,” *Optics Express* **14** (3), 1314-1328 (2006)
- Villalpando-Paez, F., Zamudio, A., Elias, A. L., Son, H., Barros, E. B., Chou, S. G., Kim, Y. A., Muramatsu, H., Hayashi, T., Kong, J., Terrones, H., Dresselhaus, G., Endo, M., Terrones, M. and Dresselhaus, M. S., “Synthesis and characterization of long strands of nitrogen-doped single-walled carbon nanotubes,” *Chemical Physics Letters* **424** (4-6), 345-352 (2006)
- Weiss, D. N., Brokmann, X., Calvet, L. E., Kastner, M. A. and Bawendi, M. G., “Multi-island single-electron devices from self-assembled colloidal nanocrystal chains,” *Applied Physics Letters* **88** (14), 143507 (2006)
- Wong, B. M., Steeves, A. H. and Field, R. W., “Electronic signatures of large amplitude motions: Dipole moments of vibrationally excited local-bend and local-stretch states of S-0 acetylene,” *Journal of Physical Chemistry B* **110** (38), 18912-18920 (2006)
- Wong, B. M., Thom, R. L. and Field, R. W., “Accurate inertias for large-amplitude motions: Improvements on prevailing approximations,” *Journal of Physical Chemistry A* **110** (23), 7406-7413 (2006)
- Wong, H. W., Cesa, M. C., Golab, J. T., Brazdil, J. F. and Green, W. H., “Kinetic modeling to estimate fundamental yield bounds for selective propylene oxidation over bifunctional catalysts,” *Applied Catalysis a-General* **303** (2), 177-191 (2006)
- Yang, J. Y., Bachmann, J. and Nocera, D. G., “Hangman salen platforms containing two xanthene scaffolds,” *Journal of Organic Chemistry* **71** (23), 8706-8714 (2006)
- Yu, C. C., Lau, C., Tunnell, J. W., Hunter, M., Kalashnikov, M., Fang-Yen, C., Fulghum, S. F., Badizadegan, K., Dasari, R. R. and Feld, M. S., “Assessing epithelial cell nuclear morphology by using azimuthal light scattering spectroscopy,” *Opt Lett* **31** (21), 3119-3121 (2006)
- Yu, J., Sumathi, R. and Green, W. H., “Accurate and efficient method for predicting thermochemistry of Furans and ortho-arynes: Expansion of the bond-centered group additivity method,” *Journal of Physical Chemistry A* **110** (21), 6971-6977 (2006)
- Zalc, J. M., Green, W. H. and Iglesia, E., “NO_x-mediated homogeneous pathways for the synthesis of formaldehyde from CH₄-O₂ mixtures,” *Industrial & Engineering Chemistry Research* **45** (8), 2677-2688 (2006)
- Zimmer, J. P., Kim, S. W., Ohnishi, S., Tanaka, E., Frangioni, J. V. and Bawendi, M. G., “Size series of small indium arsenide-zinc selenide core-shell nanocrystals and their application to in vivo imaging,” *Journal Of The American Chemical Society* **128** (8), 2526-2527 (2006) 

Spectral Lines

Pop Spectrum

by Stephen R. Wilk
Textron Defense Systems
Cambridge, MA



Stephen R. Wilk

Red, yellow, green, red, blue, blue, blue
Red, purple, green, yellow, orange, red, red
Red, yellow, green, red, blue, blue, blue
Red, purple, green, yellow, orange, red, red

Blend them all and what do you get?

Cerise, chartreuse, and aqua,

Mauve, beige, and ultramarine, and every color
in between,

Hazo ka li ka no cha lum bum

Color has its harmony, and just like I have
said,

Red, yellow, green, red, blue, blue, blue,

Red, purple, green, yellow, orange, red, red

-The Spectrum Song (Ludwig von Drake)

One of the questions that must greet anyone working at the George Harrison Spectroscopy Laboratory – or any laboratory doing spectroscopy – is one addressed by spouses, children, relatives, and friends not in the sciences: “What do you do in there all day?” And so all of the professors, students, and technicians have to try and explain in layman’s terms just what spectroscopy is, and why they do it. Not everyone has the advantage of a friend or relative working at a spectroscopy laboratory, however. What do they think is going on? What is the pop culture perception of the spectrum and spectroscopy?

I’m not going to consider the rainbow, or interference bands in soap bubbles and oil films. How is the practice and art of splitting light into its constituent colors and interpreting their intensities perceived by the general public?

Pretty vaguely, for the most part. Spectroscopy is one of those tools seen in forensic science television series such as CSI, one of a battery of tests used in

analyzing unknown substances. But the instruments are known, if at all, by their casings, in the current laboratory equipment style, and to the general public it doesn’t matter whether the instrument is a Fourier Transform Infrared Spectrometer or an Atomic Absorption Spectrometer or a Mass Spectrometer. It’s a magical device that spits out correct and infallible answers in no time at all and without that troubling ambiguity. (I know I would’ve loved to have had one of those when I found a very regular absorption structure in one of my superoxide-doped laser crystals that was turning the normally clear crystals brown. It took me weeks to track down the source of that alien absorption. I finally tumbled to the fact that it was due to ozonide only by analogy with the similar unexpected absorbing species S3- seen in sulfur-doped crystals. I sure could’ve used a computer-assisted analysis routine with a built-in reference library.)

Usually one only hears the results, but in the film *Outland* you actually see a spectrum with peaks. This the doctor immediately interprets as a particular drug on sight, without having to consult any references. But I’ll let that slide in the interests of compact and concise story-telling. At least you saw an analytical mind at work there. Even in most science fiction, ironically, you generally don’t see the mechanics of analysis – you get instant results.

There’s very little of the physical nature of light or the spectrum in most pop literature. There are a very few exceptions, but they’re from the end of the nineteenth and the beginning of the twentieth centuries. In 1894 Ambrose Bierce published the short story *The Damned Thing*, about an invisible creature that attacks people. The creature is invisible because, as Bierce’s narrator tells us,

“At each end of the solar spectrum the chemist can detect the presence of what are known as ‘actinic’ rays. They represent colours – integral colours in the composition of light – which we are unable to discern. The human eye is an imperfect instrument; its range is but a few octaves of the real ‘chromatic scale’. I am not mad; there are colours that we cannot see.

And, God help me! The Damned Thing is of such a colour!”

It’s an explanation that makes sense, as long as you don’t think about it too much.

Edgar Rice Burroughs’ novel, *A Princess of Mars*, is science fantasy, rather than science fiction, a work having the

trappings of science fiction but not aspiring to anything resembling scientific accuracy or technical rigor. So we shouldn’t blame him for his errors in science, but rather credit him for knowing what he does and using it as a plausible-sounding rationale for his background.

In Burroughs’ universe, there are at least two rays beyond the visible spectrum of seven colors, and these “eighth” and “ninth” rays have wonderful properties. The ninth ray is used to manufacture oxygen in the Martian atmosphere factory.

This ray is separated from the other rays of the sun by means of finely adjusted instruments placed upon the roof of the huge building, three-quarters of which is used for reservoirs in which the ninth ray is stored.

The eighth ray is also remarkable: This ray, like the ninth ray, is unknown on Earth, but the Martians have discovered that it is an inherent property of all light no matter from what source it emanates. They have learned that it is the solar eighth ray which propels the light of the sun to the various planets, and that it is the individual eighth ray of each planet which “reflects,” or propels the light thus obtained out into space once more.

Burroughs doesn’t say where these rays lie relative to the visible spectrum (indeed, he suggests that they are themselves visible, just unknown to terrestrial vision and science). One naturally suspects they are infrared, but the atmosphere-making properties suggest the high energy photons of the ultraviolet. If one were feeling generous, one could argue that UV rays could provide both photochemical effects and some form of laser propulsion, but that’s more thought than Burroughs probably put into it.

Probably the most extravagant use of the spectrum in pop literature is in H. P. Lovecraft’s 1927 story, *The Colour out of Space*. Lovecraft was an extremely creative and influential author, whose works are still in print and avidly read. In *The Colour out of Space* he managed to make a color the Monster in his story. It all begins with the fall of a strange meteorite at the Gardner farm in the fictional town of Arkham, Massachusetts. Professors from nearby Miskatonic University examine it and take samples, which subject to a battery of tests. Lovecraft was an amateur astronomer, and his descriptions of these tests are pretty accurate.

“...and when upon heating before the

spectroscope it displayed shining bands unlike any known colours of the normal spectrum there was much breathless talk of new elements, bizarre optical properties, and other things which puzzled men of science are wont to say when faced by the unknown.....They had uncovered what seemed to be the side of a large coloured globule embedded in the substance. The colour, which resembled some of the bands in the meteor's strange spectrum, was almost impossible to describe; and it was only by analogy that they called it colour at all."

Eventually, the meteorite dissolves and the evil color seems to invest all things growing on the farm, poisoning them. In fact, Lovecraft's description of the failing health of the crops, animals, and people living on the farm strongly suggests to the modern mind contamination by some chemical substance:

"Specimens could be analyzed....under the spectroscope both samples gave off an unknown spectrum, in which many of the baffling bands were precisely like those which the strange meteor had yielded in the previous year."

But in Lovecraft's universe it was the color itself that caused the blight, and which had a sort of life of its own. "It was just a colour out of space – a frightful messenger from unformed realms of infinity beyond all Nature as we know it..."

Many years later, Lovecraft's story was turned into a feature film starring Boris Karloff, but the aspect of a monstrous color was completely dropped. The title was changed to the more lurid and salable *Die, Monster, Die*. The meteorite produces its effects by a physical contamination, probably radioactive in nature. There is no spectral analysis in the film, but at the end Karloff's character does glow with a weird greenish light. (When pressed to actually show a weird or unusual color, the default is invariably greenish.) A 1987 adaptation of the story bore the title, *The Curse*, and was even less memorable.

It might seem odd that appearances of spectroscopy and odd colors in popular literature are confined to the first quarter or so of the twentieth century, and virtually ignored or taken for granted since, but it's actually pretty typical. When a new technology or phenomenon appears, it becomes the item of interest in popular stories. When television first became common, there were pulp magazine stories of evil televisions (I kid you not). Af-

ter the first atomic tests, radiation became the source of B-movie monsters and other wonders. (Spiderman originally resulted from a student bitten by a radioactive spider). As new effects and technologies come into the limelight, they take over this role. (In the recent movies, Spiderman was the result of a student being bitten by a genetically engineered spider. Radiation is passé.) Spectroscopy was already an old and established discipline by the time Bierce wrote, but the fledgling field of science fiction and science fantasy literature hadn't yet had a chance to embrace it. Over the next few years Bierce, Burroughs, Lovecraft, and a few others used the still unfamiliar discipline to give an air of verisimilitude to their fantasies. But now the technology is old and established. There was a flurry of interest in lasers when they were new, but it focused on the potential destructive power of these coherent beams. Laser spectroscopy was too esoteric to grab the public interest, and couldn't really compete with real-life "Death Beams".

Reference

1.) Music and Lyrics by Richard M. and Robert B. Sherman for the Sept. 24, 1961 inaugural episode of Disney's *The Wonderful World of Color*. Performed by Paul Frees as Ludwig von Drake.

Carbon Nanotubes, continued from page 7
 port on computer resources. Alfonso Reina acknowledges MARCO interconnect focus center for financial support.



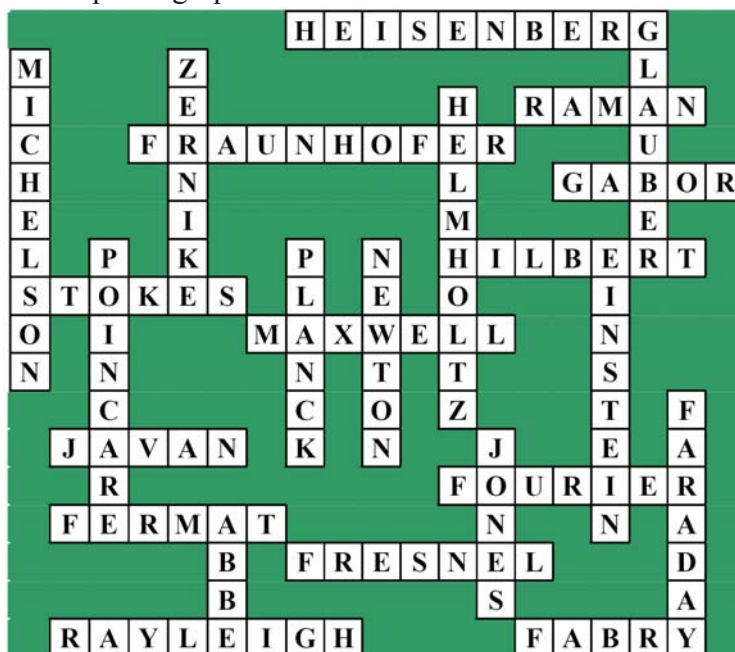
References

1. M. S. Dresselhaus, G. Dresselhaus, and Ph. Avouris, Springer (2001)
2. C. L. Kane and E. J. Mele, *Phys. Rev. Lett.* **78**, 1932 (1997).
3. G. G. Samsonidze, R. Saito, N. Kobayashi, et.al, *Appl. Phys. Lett.* **85**, 5703 (2004).
4. C. Fantini, A. Jorio, M. Souza, et. al, *Phys. Rev. Lett.* **93**, 147406 (2004).
5. S. M. Bachilo, M. S. Strano, C. Kittrell, et.al, *Science* **298**, 2361(2002).
6. A. Jorio, R. Saito, J. H. Hafner, et. al, *Phys. Rev. Lett.* **86**, 1118 (2001).
7. Y. Y. Zhang, J. Zhang, H. B. Son, J. Kong, and Z. F. Liu, *JACS* **127**, 17156 (2005).
8. R.Saito,G.Dresselhaus,andM.S.Dresselhaus, *Phys. Rev. B* **61**,2981 (2000).
9. H.B. Son, A. R. Cecco, G. G. Samsonidze, et. al, manuscript submitted to *Phys. Rev. B*.
10. J. Kong, H. T. Soh, A. M. Cassell, C. F. Quate, and H. J. Dai, *Nature* **395**, 878 (1998).

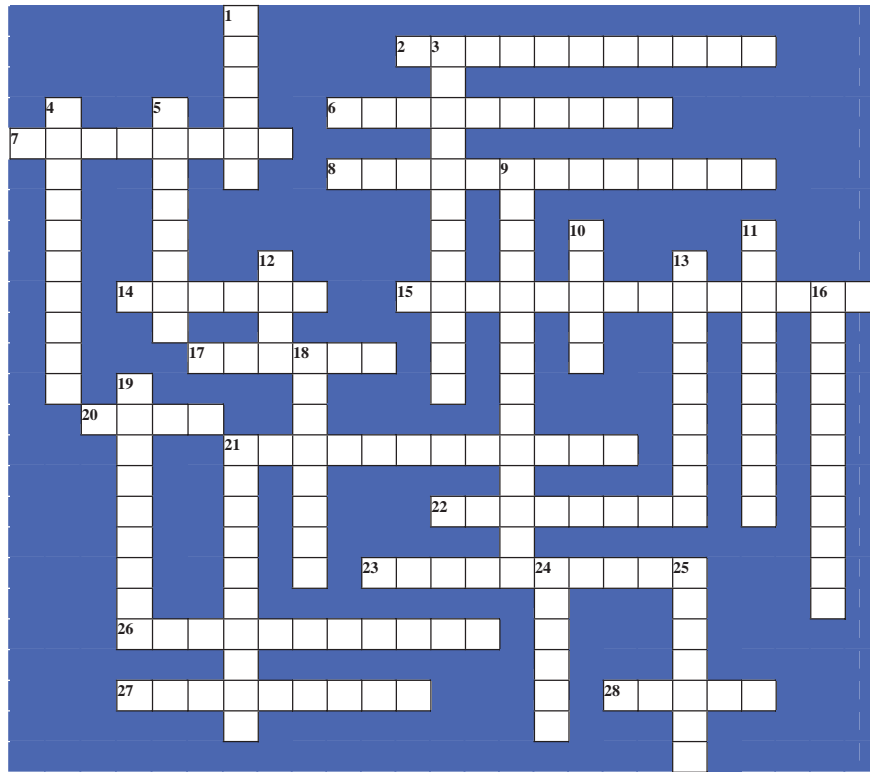
Answers to last issue's crossword

The winner of the Fall 2006 Spectrograph crossword challenge was Scott Mohr, Visiting Fellow, MIT Engineering Systems Division.

The winner of this issue's challenge will be published in the Fall 2007 issue of *The Spectrograph*.



Optics Lab Essentials



Across

- 2. holographic grating type
- 6. multi-wavelength wave plate
- 7. stand-alone post
- 8. laser table screw
- 14. plano-plano
- 15. grey-black filter
- 17. the bane of screw-hunters everywhere
- 20. a degree of freedom
- 21. optic that gets you 2 for 1
- 22. safer than your eye
- 23. colorblind lens
- 26. 1-axis lens
- 27. most common lens
- 28. famously depicted on Pink Floyd album

Down

- 1. optic mount with orthogonal rotation
- 3. shiny filter
- 4. grating type commonly used in lasers
- 5. no spherical aberration
- 9. optic mount screw
- 10. holds base to table
- 11. colored glass filter
- 12. connects to optic mount
- 13. true half-wave plate
- 16. motion along an axis
- 18. motion around an axis
- 19. optic mount with independent axis control
- 21. essential yellow- or orange-handled tool
- 24. reflective optic

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
G. R. HARRISON SPECTROSCOPY LABORATORY
CAMBRIDGE, MA 02139-4307

Nonprofit Organization
US Postage
PAID
Cambridge, MA
Permit No. 54016