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□ Research Report

Intracavity Laser Absorption Spectroscopy

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Introduction

Absorption spectroscopy is one of the oldest scientific methods for studying atomic and molecular structure. It is also one of the most powerful research tools for providing information about the world around us. One important application is ultrasensitive trace gas analysis, which is used in many areas from environmental monitoring to high technology applications.

Absorption spectroscopy is based on the Lambert-Beer law. Many methods of sensitive detection of absorption exist. This article will review several of these and focus on a new one, Intracavity Laser Absorption Spectroscopy (ICLAS).

The physical limit to the minimum detectable concentration for a given absorption path length is determined by the shot noise of the detected photons. There are two ways to increase the sensitivity of an absorption measurement: increasing the absorption path length, or decreasing the noise. The first method, which can be used with both classical and laser sources, employs a mirror system which produces multiple passes of light in a limited cell volume (multi-pass cell, or MPC). One of the best known MPC's was introduced by White in 1942, and an improved version[1] is still widely used today. Many other more or less sophisticated MPC designs have been introduced since then.[2] This approach

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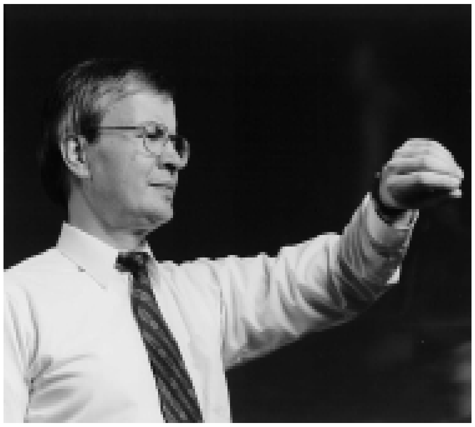

Theodor Hänsch makes a time measurement.

Theodore Hänsch Selected as Eighth Lord Lecturer

Theodore Hänsch, a professor of physics at the University of Munich and Director of the Max Planck Institut für Quantenoptik in Garching, has been selected as the eighth Richard C. Lord Lecturer, and will speak on "Precision Spectroscopy of the Hydrogen Atom" in the Spectroscopy Laboratory's Modern Optics and Spectroscopy seminar on May 4th. Professor Hänsch's research has advanced our fundamental understanding of the hydorgen atom, and has also led to the development of novel technologies for acurate frequency measurements and atomic clocks.

Hänsch was born in Heidelberg, Germany on October 30, 1941. Working with Dr. Peter Toschek and Professor Christoph Schmelzer at the University of Heidelberg, he received his doctoral degree in 1969. In 1970, he came to the United States to pursue laser research with Professor Arthur L. Schawlow at Stanford University as a NATO Postdoctoral Fellow. He joined the Stanford Physics faculty as an Associate Professor in 1972, and he became a full professor in 1975. He returned to his native Germany in 1986 to assume his present positions. He is also a Consulting Professor at Stanford University, and a part-time Professor at the University of Florence.

Dr. Hänsch's research has opened new frontiers in fundamental atomic physics with the help of advanced laser techniques. After designing the first highly monochromatic, widely tunable dye laser in 1970, he

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Research Report

Endoscopic Detection of Dysplasia in Patients with Barrett's Esophagus Using Light Scattering Spectroscopy

Michael Wallalace, Lev Perelman, James Crawford, Maryann Fitzmaurice,
Michael Seiler, Kamran Badizadegan, Steven Shields, Irving Itzkan,
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Note: Over the past year Spectroscopy Laboratory researchers have been working on an important new spectroscopic method for detecting invisible precancer. This is particularly important because with early detection, most such diseases can be easily treated. In addition, there is much interesting science. The following report summarizes our first clinical results. --MSF

Introduction

Surveillance to detect dysplasia in Barrett's esophagus (BE) is prone to sampling error and has not reduced the mortality from esophageal adenocarcinoma. We have developed an *in situ* method to identify dysplasia based on the use of light scattering spectroscopy (LSS) to detect nuclear enlargement and crowding. White light is delivered and collected during endoscopy via optical fibers and analyzed to measure the size and population density of nuclei in the mucosal layer.

Methods

Consecutive patients with known BE or suspected adenocarcinoma arising in BE underwent endoscopy and systematic biopsy. Prior to biopsy, each tissue site was sampled by LSS via an optical fiber probe. The probe delivered white light to the tissue and the diffusely reflected light was spectrally analyzed. From this reflectance spectrum, we extracted the component due to elastic scattering, which provides information about the size and population density of mucosal nuclei, a measure of nuclear crowding. Based on initial data, we assigned a diagnosis of dysplasia if greater than 30% of the nuclei were enlarged (>10 microns). The spectral diagnosis was compared to the histologic diagnosis, determined independently by four pathologists, who were blinded to the experimental results and each other's findings.

THE SPECTROGRAPH

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GEORGE R. HARRISON SPECTROSCOPY LABORATORY

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The Spectroscopy Laboratory houses two laser research resource facilities. The MIT Laser Research Facility, supported by the National Science Foundation, 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. More information can be found on our web site //http:web.mit.edu/spectroscopy. Write or call for further information or to receive our mailings, (617) 253-4881.

Results

Histologic samples from 847 sites were obtained from 49 patients. Initial histologic results were determined by one pathologist. All indefinite or dysplastic sites and a random sample of non-dysplastic sites were then selected for review by all four pathologists. According to the average diagnosis of the four pathologists, 4 sites contained high grade dysplasia (HGD), 8 contained low grade dysplasia (LGD), 12 were indefinite for dysplasia (IND), and 52 were non-dysplastic Barrett's (NDB). As the histologic grade of dysplasia increased, LSS reliably detected a progressively increasing population of enlarged nuclei.

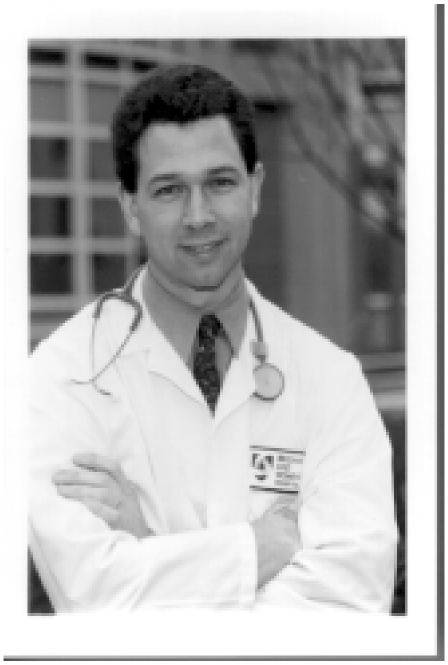
Figure 1 plots the surface density and percentage of enlarged nuclei, as measured by LSS for each of the 76 samples in the study set. The average histological diagnosis for each sample is also indicated. As can be seen, non-dysplatic samples tend to cluser at low values of nuclear enlargement and surface density, whereas the samples diagnosed as high grade dysplasia exhibit the largest values of both. The sensitivity and specificity of the prospective method of LSS for detecting low grade or high grade dysplasia in this study were 90% and 90%, respectively.

Figure 1. Percentage of enlarged nuclei and nuclear surface density, as determined by LSS, for each of the 76 biopsy sites. The average histological diagnoses are indicated: NDB-circles; IND-squares; LGD- filled triangles: HGD-filled diamonds. The filled symbols denote samples diagnosed as dysplasia. The dashed line indicates the dysplasia/non dysplasia threshold.

Conclusion

This study demonstrates the potential of LSS as a minimally-invasive means of detecting low grade and high grade dysplasia in patients with Barrett's Esophagus based on detection of enlarged nuclei. Such information may provide a new method for endoscopic localization of dysplasia in other disorders which exhibit epithelial dysplasia, as well.

☐ Personalities



MICHAEL WALLACE

Michael B. Wallace was born in Durham, North Carolina in 1965. Although a third generation physician and researcher, his early career interests were far from medicine and science. Determined to diverge from his genealogy, Mike showed an early interest in the arts. Although the squealing sound of his first trumpet lessons suggested he was unlikely to ever find fortune in performance, he eventually set off on an early career in the management of arts.

At Oberlin college, Mike was immersed in music and art history, but then began to find seedlings of interest in the sciences and medical arts. By his second year, he "caught the bug" of science and his path changed course. At Oberlin, he first expressed an interest in cancer research, studying a bacterium which caused tumor growths in plants. In summers he returned to Durham to learn about medicine, working as a research assistant in the Department of cardiology at Duke University, and later at Stanford University.

Mike deferred admission to Duke University Medical School for one year to teach and travel in Africa. Working with the World Teach organization at Harvard University, he took a few crash courses in Swahili and moved to a small village in western Kenya where he planned to teach English. Upon arrival, he discovered that what the school really needed was a physics and chemistry teacher. Mike gave it a try and soon developed a strong interest in physics (although chemistry remained less than his favorite subject). His first task was to start a new library at the school. After a few fund raising events through his former high school in Durham, Mike purchased a new library of physics and chemistry textbooks for the high school of 400 students, and set out teaching. Although the highlight of the year was seeing the love of science develop in his students, Mike was also able to visit the top of Mount Kenya, the Masai Mara game park, and the mountain gorillas of Zaire and Rwanda.

Upon return to the U.S., Mike completed his basic medical training at Duke, and then received the Stanley Sarnoff scholarship to spend a year doing basic research with Drs. Don Ganem and Harold Varmus at the University of California, San Francisco. There he studied basic molecular biologic and genetic regulation techniques. In San Francisco, he met his future wife, Claudia, whom he married one year later in her home town of Oyten, Germany.

Upon completing this work and his final clinical year of medical school, Mike headed for Boston to begin three years of internal medicine postdoctoral training at the Brigham and Women's Hospital. Although, he had always thought he would return to San Francisco, the academic buzz of Boston had taken hold, and he signed up for three more years at the BWH to complete a gastroenterology fellowship. It was there that he met Dr. Jacques Van Dam, and took interest in spectroscopic methods to diagnose precancerous conditions in the gastrointestinal tract.

During his clinical year, Mike saw a large number of patients at the BWH and associated Veterans Hospitals with a condition called Barrett's esophagus. Patients with Barrett's have a 30-100 fold increase in their risk of developing cancer of the esophagus, and thus undergo yearly surveillance with a flexible endoscope to detect pre-cancerous or early cancerous changes at a time when these are still amenable to therapy. Although thousands of patients undergo this procedure yearly, there are many limitations to the current methods. One of the most important is that early cancers are often not visible to the naked or endoscopic eye, and thus physicians must take many "random" biopsies throughout the esophagus in order to find a cancer. Even with these methods, many cancers are missed. It has been estimated that up to 50% of patients with cancer can be missed by "random" biopsy, because only a small portion of the esophagus can be sampled. This problem prompted Mike to apply spectroscopic methods to detect pre-cancerous changes in Barrett's.

Mike began work with Professor Feld and the G.R. Harrison Spectroscopy Laboratory in September of 1996. Using the multi-excitation EEM spectroscopy system developed there, he began to perform spectroscopic evaluation of a large series of patients undergoing endoscopy for Barrett's. He teamed up with Dr. Steven Shields, the director of endoscopy at the West Roxbury and Brockton VA Medical Center, and Dr. Van Dam at BWH, and in the subsequent two years they studied over 70 patients with Barrett's esophagus. Although the study was originally designed to look primarily at laser-induced fluorescence spectroscopy, attention soon turned to using reflectance. A collaboration developed with a new graduate student, Vadim Backman, and staff scientist Lev Perelman. Using methods described by Gustav Mie almost 100 years previously, they developed a method to measure the size of the nuclei in the cells lining the esophagus.

A principal feature of dysplasia is that the nuclei become increasing large and crowded as tissue transforms from normal, to pre-cancerous, to cancerous. Using reflectance spectra to measure this increase, the team showed that reflectance spectroscopy could be used to detect dysplasia in patients with Barrett's.

In August of 1998, Mike completed his gastroenterology training and M.P.H. and took a faculty position at the Medical University of South Carolina where he continues research on the early identification of esophageal and other malignancies of the gastrointestinal tract. ☐

T. Hänsch...continued from page 1

pioneered many of the now commonly used methods of Doppler-free laser spectroscopy,motivated by precision spectroscopy of the simple hydrogen atom, which can provide precise values of fundamental constants and which permits unique confrontations between experiment and quantum electrodynamic theory. Recently, Dr. Hänsch has developed new methods for measuring the frequency of light which allow further dramatic advances. In 1974, jointly with Arthur Schawlow, Hänsch made the first proposal for laser cooling of atomic gases. In 1992, he and his Munich team were the first to realize 2- and 3- dimensional atomic lattices bound by light. In 1998, his group realized the first continuous source of coherent matter waves, an atom laser with a cw output coupler.

Hänsch was named California Scientist of the Year in 1973, and he held an Alfred P. Sloan Fellowship from 1973 to 1975. His prizes include an Alexander von Humboldt Senior Scientist Award (1977), the Otto Klung Prize of the Free University of Berlin (1980), the Cyrus B. Cornstock Prize of the National Academy of Science (1983), the Herbert P. Broida Prize of the American Physical Society (1983), the William F. Meggers Award of the Optical Society of America (1985), the Michelson Medal of the Franklin Institut (1986), the Italgas Prize for Research and Innovation (1987), the Gottfied Wilhelm Beibniz Prize of the German Physical Society (1988), the King Faisal International Prize for Science (1989), the Einstein Medal for Laser Science (1995), the Arthur L. Schawlow Prize for Laser Science (1996), and the Philip Morris Prize (1998). Hänsch is a Fellow of the American Physical Society and of the Optical Society of America. He is also a Fellow of the American Academy of Arts and Sciences, and a member of the Bavarian Academy of Sciences.

The Richard C. Lord Lecture is an annual event sponsored by the MIT Department of Chemistry and The G.R. Harrison Spectroscopy Laboratory to honor a scientist who has made important contributions to the field of spectroscopy. Professor Lord was a distinguished spectroscopist and chemist, who directed the Spectroscopy Laboratory from 1946 to 1976.

Intracavity Laser Absorption Spectroscopy...continued from page 1

has obvious limitations and disadvantages. Very long absorption paths require both large cell volumes (up to several cubic meters) and a large number of reflections. Since the cell mirrors have losses, multiple reflections reduce the source intensity. This is equivalent to increasing the relative noise and, after a certain number of reflections, further increasing the number of reflections is of no value. Further, the large volume occupied by the multiple light beams makes this method inapplicable to compact sources, such as a supersonic jet. Fragile, high quality mirrors would be damaged by corrosive gases, discharges and chemical reactions. Using an internal cell inside the multiple pass mirror system results in aberrations, and also has very limited application. As a result, the largest MPC has an absorption length of a few kilometers, and most commonly, lengths are limited to a few hundred meters.

The second method, which is more frequently used with tunable laser sources, is to reduce the excess noise of the source with various types of double-beam balancing schemes. The most impressive realization of this method - electronic noise cancellation, introduced by Hobbs[3] -indeed permits the excess noise and spurious signal to be decreased by 50 dB or more, and so to reach the shot noise limit. Unfortunately, this method, as well as frequency modulation spectroscopy,[4] have limited application. A shot-noise limited source in the visible or near IR of only 1 mW optical power would permit detection of a fractional absorption as small as 10^{-8} in one second. But scattered light from the beamsplitter, cell windows, or any surface in the beam path reaching either of the two photodetectors will interfere with the main beam, producing fringes. Suppression of these interferance fringes to a fractional value of 10^{-8} would require spurious light suppression to an unrealistic value of 10^{-16}, so these methods are limited to fractional absorptions of 10^{-5}-10^{-6}. Similar problems also exist with MPCs.

In the early 1970's several groups recognized that lasers with a large emission bandwidth are very sensitive to intracavity narrowband losses (narrow absorption lines of the gas either filling the cavity or contained in a small intracavity absorption cell). This observation led to the development of ICLAS.

Physical principles

In the very first paper on intracavity laser absorption, very fine structure was observed in the emission spectrum of a Nd:Glass laser. This was attributed to very weak absorption lines of atmospheric water, and understood to arises from mode competition. In a CW laser, the total gain is automatically kept equal to the intracavity losses, due to gain saturation. For narrow absorption lines this loss cannot be compensated by gain, which has a much larger homogeneous spectral line width. As a result, the laser intensity will decrease and narrow absorption lines will show up on the broad laser emission spectrum envelope. ICLAS can thus be understood as a very long path multiple pass cell in which the mirror losses are compensated by the laser gain medium. The authors have also shown that the minimum detectable absorption is determined by spontaneous emission of the laser gain medium, and can be as low as 10^{-10} cm^{-1}.

Since this very encouraging result, there were many attempts to use ICLAS for quantitative absorption spectroscopy. Very soon several problems were recognized. First, the maximum enhancement by intracavity absorption was found to be several orders of magnitude lower than could be expected from the prediction of reference 6. Moreover, in the first attempts to use ICLAS, the reproducibility of the relative intensities of the absorption lines were found to be poor, and sometimes the lineshapes were distorted. In addition, weak light scattering from the intracavity elements resulted in irregular fringes, which limited the minimum detectable absorption to values far above predicted limits. These difficulties led to the generally held opinion that ICLAS is a non-quantitative method, complicated to understand and difficult to apply. As a result, most of the efforts to understand ICLAS and develop it into a reliable and easy-to-use laboratory method were concentrated in the former Soviet Union, until the "rediscovery" of ICLAS by the international spectroscopy

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Oncology and Spectroscopy

Tuesday, April 27, 1999, 4:30-7:00 PM

The Structural and Chemomechanical Nature of the Cancer Cell
Donal S. Coffey, Johns Hopkins University School of Medicine

Imaging Gene Experssion in Cancer Therapy
Ralph Weissleder, Massachusetts General Hospital and Harvard Medical School

Using Reflectance and Fluorescence Spectroscopy to Monitor Tumor Response to Therapy
Thomas H. Foster, Uniersity of Rochester

Two-Photon Deep Tissue Microscopy
Peter T. C. So, MIT Mechanical Engineering

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Schepens Eye Research Institute
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Refreshments at 4:00 P.M.

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Seminar on

MODERN OPTICS AND SPECTROSCOPY

Spring SEMESTER, 1999

February 9	**Patrick Thaddeus**, Harvard University Radio Spectroscopy of Large Organic Molecules in Space
February 16	**Robert Whetten**, Georgia Institute of Technology Gold Clusters Nanocrystals in the Strong Quantum-Size-Effect Regime
February 23	**Raymond Ashoori**, MIT Charge Accumulation Imaging of the Quantum Hall Liquid
March 2	**Mildred Dresselhaus**, MIT Raman Spectroscopy as a Probe of the Remarkable Properties of Carbon Nanotubes
March 16	**Daniel Heinzen**, University of Texas at Austin Magnetic Resonance with a New Twist: Quantum Control of an Atomic Spin
April 13	**Hideo Mabuchi**, California Institute of Technology Proving you are at the SQL
April 20	**Daniel Kleppner**, MIT How Physics Got Precise
April 27	**Evan Williams**, University of California, Berkeley Gas-Phase Analogues of Solution-Phase Interactions: Evidence for Zwitterions, Salt-Bridges and Watson-Crick Base Pairing in Vacuo
May 4	**Eighth Annual Richard C. Lord Lecture** **Theodor W. Hänsch**, University of Munich Precision Spectroscopy of the Hydrogen Atom
May 11	**Kurt Gibble**, Yale University Juggling Atomic Fountains
May 18	**Marta Dark**, MIT Laser Diagnosis of Knee Joints: Thermomechanical and Cavitation Effects

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TUESDAYS, 12:00-1:00, Marlar Lounge (37-252), Ronald E. McNair Building

For map see <http://amo.mit.edu/mos.html>

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Intracavity Laser Absorption Spectroscopy...continued from page 1

The key point for understanding ICLAS is that the transient evolution of the multimode laser spectrum from the onset of laser generation has to be considered in order to obtain very precise quantitative information from the absorption spectra. Most early ICLAS research employed pulsed lasers with poorly controlled transient evolution. In 1975 Antonov et. al. suggested modulating the pump laser radiation by means of steady-state CW lasers, and a mechanical chopper, thus fixing the number of intracavity round trips. Further extention of this technique was introduced by Stoeckel et. al,[5] who used acuosto-optic modulators (AOM's) to interrupt the pump beam, and thus start the spectral evolution, and to select a short slice of the ICLAS laser output with a fixed delay time, and send it to the spectrograph. ICLAS in this form, which can be called time-resolved ICLAS, provides the most precise way to measure absorption spectra quantitatively. No additional calibration is needed, and therefore ICLAS is an absolute absorption method.

The experimental setup for time resolved ICLAS shown in Fig.1 is the most common. The cavity of the ICLAS laser (a dye laser in this example) is formed by three mirrors. The radiation of the pump laser is interrupted by an acousto-optic modulator, AOM1, and the ICLAS laser output beam is deflected by AOM2 into the spectrograph and detected by means of a linear diode array. The laser cavity is designed so that an absorption cell, such as a supersonic jet, a chemical reactor, or a discharge cell, with Brewster windows can be inserted into the cavity. In Fig. 2 a time-dependent spectrum of a Ti:sapphire laser obtained with this setup is presented. One can see the Gaussian envelope of the spectral narrowing in time, and weak atmospheric water absorption lines growing linearly in time. The equivalent absorption pathlength at generation times $t_g = 200$ micro seconds is 60 km.

In some types of lasers, for generation times longer than a few hundred micro seconds mode competetion can induce exchange of photons between the modes, and the absorption line intensities can then stop growing. This happens with dye lasers pumped well above threshold.[6] Even in this case, exact quantitative results are still possible, when the operating parameters of the laser are properly controlled. For very long generation times, when spontaneous emission dominates the spectral evolution and the spectrum becomes stationary, the absorption line intensities are no longer represented by the modified Lambert-Beer law, and will depend on the laser intensity. This is why early ICLAS experiments with CW lasers showed nonlinear behavior. This domain is not suitable for quantitative measurements.

Figure 1. Experimental Setup for time-resolved ICLAS.

Figure 2. Time-dependent ICLAS spectra of water.

Noise and sensitivity

In order to determine the minimum absorption coefficient for which a weak absorption line can be distinguished from noise, the equivalent absorption path length and the noise level in the ICLAS spectrum must be specified. The maximum absorption length is given by the time t_{sp} for which the intracavity absorption becomes nonlinear due to spontaneous emission. This time depends on the number of photons in the laser mode, and thus on the gain medium and laser cavity parameters. For a very wide class of lasers this time is of the order of one second.

The noise in the envelope of the broadband ICLAS spectrum is due to the quantum nature of light. It results from random spontaneous emission of the photons into the cavity modes during the initial stage of laser generation. As soon as a mode is excited by such a "seed" photon, it starts to build up exponentially in time until saturation of the total intensity is reached. In this process the spectrum becomes very jagged and does not have a smooth envelope.

This indicates that the noise of any particular mode is as large as the intensity of this mode, and that this noise will mask absorption lines if only one spectrum is detected. Thus, in order to record a low noise spectrum, many laser pulses should be averaged. If N laser pulses are averaged in time, then the noise expressed in terms of the absorption coefficient δk_{min} will be , with m the the number of photons in the mode. As a numerical example, consider a laser with a cavity length of 100 cm. Let its spectrum be recorded with a spectral resolution of 0.01 cm^{-1}, so that m=2 at the generation time of 1 ms, resulting in an equivalent path length of L_{eq} = $3x10^7$ cm. With a one second averaging time, δk_{min} = $8x10^{-10}$ cm^{-1}. With averaging, δk_{min} will be proportional to , because the increase in L_{eq} will be compensated by the decrease in the number of averaged laser pulses.

This quantum noise or seed noise sets the fundamental limit for ICLAS sensitivity. In practice, various sources of excess noise usually limit the actual sensitivity to much smaller values. In ICLAS, one of the most important sources of this excess noise is the presence of fringes due to selective scattering of the standing-wave intensity distribution of the laser modes by small optical defects of the intracavity elements. If a ring travelling wave cavity is used instead of a linear cavity, this scattering becomes non-selective, and the fundamental sensitivity limit due to quantum noise can be reached.

Time resolution

The time resolution in ICLAS is, in principle, determined by the required generation time, so there is a trade off between sensitivity and resolution. For periodic processes, such as laser-initiated chemical reactions, it is possible to sample the transient absorption spectra of the reaction products by ICLAS. By changing the delay between the laser pulse that initiates the reaction and the ICLAS laser pulse, the time dependent concentration of the products can be extracted. The time resolution depends on the sensitivity required, and can vary from a few microseconds to a few milliseconds.

In time-resolved studies, the need to average many laser pulses in order to obtain good signal-to-noise (S/N) ratio may become a serious limitation. Indeed, as seen from the example in the previous section, it is necessary to average about 1000 individual pulses in order to obtain a S/N ratio of about 1%. It is possible, however, to get good S/N ratio from a single pulse ICLAS spectrum using a recently developed ICLAS technique called correlated double sampling. After the initial intensity buildup in the single laser pulse, which results in a very noisy distribution, the laser will "remember" this distribution until the end of the spectral evolution. If we now record two spectra of the same generation pulse at the values of the generation times, t_{g1} and t_{g2} and take the ratio of the two spectra, we find that this ratio spectrum is free of noise. It contains only a smooth Gaussian envelope and the absorption term, which depends only on the time difference $\Delta t=t_{g1}-t_{g2.}$ The elimination of the noise comes from the fact that the two spectra are strongly correlated. Spontaneous emission slowly destroys this correlation, thus increasing the noise in the ratio spectrum. The noise in the ratio spectrum is proportional to . At $t_g=\tau_{sp}$ the spectra will lose this correlation, and the ratio will become 100% noisy. This means that if τ_{sp}= 1 sec and Δt=400 microseconds, we can expect about 1% noise in the ratio spectrum. This very attractive theoretical prediction was verified recently,[7] and very good agreement with the theoretical predictions was found. With a ring Ti:sapphire laser, the noise in a single pulse ratio spectrum corresponding to an absorption of $2x10^{-9}cm^{-1}$ was obtained at Δt=400 microseconds. If we take into account that 1000 spectral elements were recorded in this single spectrum, the detectivity in this experiment is $4x10^{-14}$ $cm^{-1}/$. To our knowledge, this is the highest value reported for absorption measurements. With this technique, it is now possible to study single-event transient weak absorption spectra.

Spectral range

The spectral range of ICLAS depends on two factors: the availability of a broadband laser gain medium and the availability of linear detector arrays in this range. Argon ion laser-pumped dye lasers can cover the range from about 380 to 1000 nm, while solid state lasers can cover from 0.7 to 2.6 µm. Both classes of lasers have been widely used for ICLAS.

Recent progress in external cavity surface emitting, multiple quantum well lasers looks very promising for ICLAS. Such lasers have very low threshold powers, typically smaller than 100 mW, thus permitting diode pumping, and they can emit from 800 nm to about 2.3 µm. A single structure can be tunable in the range of a few tenths of a nanometer. The first ICLAS system based on this structure, operating at 1.05 µm, has recently been built . With it, a sensitivity of 10^{-10} cm^{-1} has been achieved.

To detect an ICLAS spectra throughout the entire visible range, and in the near IR up to 1.1 micron, silicon linear diode arrays can be used. This technology is very well developed, and now many types of such detectors are available. Another approach for detection of IR ICLAS spectra is to use a Fourier transform (FT) spectrometer. Recently, an experiment demonstrating the power of this new approach has been conducting using a Ti:sapphire laser and a Bruker IFS 120HR FT spectrometer. The entire Ti:sapphire laser bandwidth at a generation time of 80 msec was recorded in a single 2 hour experiment. At 337 nm laser excitation, all of the lines of the $\nu_1+\nu_2+2\nu_3$ and $\nu_2+3\nu_3$ bands of atmospheric water in the range of 12450-12700 cm^{-1} listed in the HITRAN database were observed, with a minimum detectable absorption of 2.8 x 10^{-9} cm^{-1}. In addition to the ability to record spectra at any wavelength available to ICLAS, FT-ICLAS has the additional advantage that the spectra are already frequency calibrated. The uncertainty of the frequency determination in this FT-ICLAS experiment was 0.005 cm^{-1}. FT-ICLAS offers a further advantage in its ability to record in the same FT scan the spectra at different time delays, with a time resolution limited only by the photodetector.

□

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☐ History of Spectroscopy: III

Ramachandra Dasari and Michael Feld

The authors are with the G.R. Harrison Spectroscopy Laboratory at MIT

Adapted from the article, “Spectroscopy”, Colliers Encyclopedia, by the same authors

This three part article has reviewed the remarkable history of the field of spectroscopy over the past 300 years. The subject of the the initial part was classical spectroscopy, and Part II discussed the role of spectroscopy in the development of quantum mechanics. Part III discusses the era of modern spectroscopy.

Part III. The Era of Modern Spectroscopy

The era of modern spectroscopy began with the invention of the laser, which provides intense, collimated monochromatic radiation throughout optical spectral range. Historically, the laser was an extension of the maser, a microwave oscillator developed by N.G. Basov and A.M. Prokhorov in the USSR and C.H. Townes in the US (1954). In a brilliant intellectual breakthrough, in 1958 Townes and A.L. Schawlow proposed extending the maser principle into the optical regime. They pointed out that an interferometer of the type developed by Fabry and Perot in 1900 would also function as an optical resonator. When atoms or molecules in a state of inversion (more atoms in the upper level of the atomic transition than in the lower one) are placed within the resonator, the emission should dramatically increase in intensity and decrease in linewidth. They called their device an *optical maser*, but the term laser (for light amplification using stimulated emission of radiation) soon caught on instead. The first working prototypes were built soon after. The ruby laser, a pulsed solid state laser emitting red light at a wavelength of 694 nm, was developed by T.H. Maiman in 1960 , and the He-Ne laser, a continuous-wave gas laser emitting infrared light at 1.15 mm, was developed shortly afterwards by A. Javan. There rapidly followed a host of new laser sources: CO_2 (λ=9-10 μm), Nd:YAG (λ=1.06 μm), argon and krypton ion lasers, which produce multiple visible wavelengths, and many others. The dye laser, developed by P.P. Sorokin, F.P. Schäfer, B.B. Snavely and others in 1966, is of particular significance because it provides monochromatic radiation which can be broadly tuned over the visible spectral range.

Laser light, with its high intensity, narrow spectral linewidth and phase coherence, immediately stimulated new interest in atomic and molecular spectroscopy. Because the first lasers were fixed in frequency, the earliest work was done on the laser medium itself, and on spectral lines which happened to coincide with the frequency of a laser source. Transitions under study were sometimes Stark or Zeeman-tuned into resonance. Tunable lasers, the dye laser in particular, greatly extended the scope of possible measurements.

Laser light opened the field of ultrahigh resolution spectroscopy. Saturation spectroscopy, developed by Javan, Schawlow, W.E. Lamb, Jr. and others, provided sub-Doppler resolution of spectral lines of atomic and molecular vapors. Ordinarily, such lines are limited in resolution by thermal atomic motion (“Doppler broadening”). Intense, monochromatic laser light can selectively saturate an optical transition, producing extremely narrow *Doppler-free* resonances. Techniques for producing two-photon Doppler-free resonances were devised (V.P. Chebotayev). Atomic beams were also used to to eliminate Doppler broadening and produce narrow spectral lines. Figure 1 illustrates the advances made over conventional spectroscopy measurements.

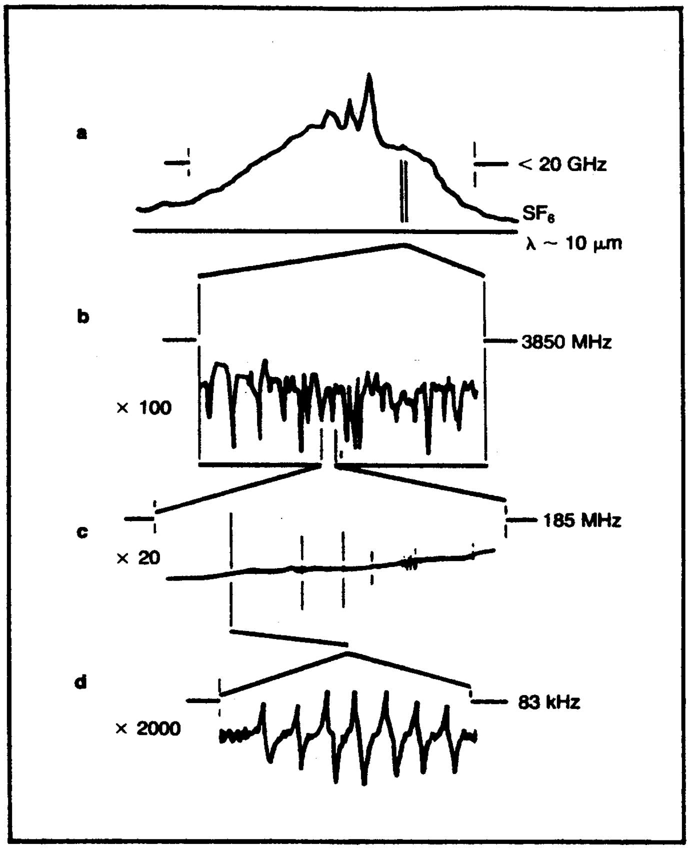

Figure 1. Advances in spectral resolution, illustrated in the SF_6 vapor spectrum near 10 μm. a) Low resolution spectrum from a conventional spectrometer; b) high resolution from the best conventional spectrometer; c) ultrahigh resolution spectrum taken with a laser using saturation spectroscopy; d) single spectral line from (c), split into multiple components by an external electric field (Stark spectrum). Figure courtesy of Prof. J.I. Steinfeld.

These narrow resonances allowed the centers of spectral lines to be defined with improved accuracy. Small splittings could be resolved, enabling structural parameters to be measured. By studying the shapes of these narrow lines, collisional processes could be studied. Further, by locking the laser frequency to a narrow spectral line, its wavelength (or frequency) could be accurately defined, making possible laser wavelength and frequency standards, and eventually laser atomic clocks (J. Hall, K. Evenson).

Laser light also opened the possibility of conducting spectroscopy in the time domain. Coherent transient processes such as free induction decay and photon echoes, which had been observed earlier at radio frequencies, now began to be studied in the optical domain (S.G. Hartmann). In addition, the interaction of laser light with optically thick samples, in which coherent radiation can significantly modify the response of the sample, was studied for the first time. Effects observed included self-induced transparency (E. Hahn), in which a normally opaque sample becomes transparent to an intense light pulse, and Dicke superradiance (M.S. Feld), in which atoms are made to undergo emission proportional to the square of the number of radiators.

Intense laser light has opened the field of nonlinear optics, the formalism of which was developed by N. Bloembergen. Frequency mixing processes such as second harmonic generation (P. Franken) were discovered and exploited to generate coherent light at new wavelengths deep in the ultraviolet and far in the infrared. Other nonlinear optical effects studied include the stimulated Raman effect (R. Hellworth), four wave mixing and other stimulated processes induced by the high intensities of laser light (large number of photons per mode). Multiphoton absorption in atoms was used to ionize and detect trace quantities, and multiphoton absorption in molecules was used to produce large quantities of highly excited state species (V.S. Letokhov).

New results in laser spectroscopy continue to advance the field. The development of atom traps by H. Dehmelt and W. Paul, combined with laser slowing of atomic beams due to photon recoil, called laser cooling, has led to techniques for highly localized confinement of isolated atoms, as well as dense collections of atoms (S.Chu) and, recently, Bose-Ensten condensation (C. Weimann, E. Cornell and W. Ketterle). These species, arrested in space, can then be studied free of the usual external perturbations, providing spectroscopic data of extremely high resolution for fundamental studies and applications.

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