Linear and Nonlinear Laser Spectroscopy

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Spectroscopy has been a fundamental part of optics ever since Newton first showed that white light could be dispersed into its constituent colors and later when Young showed that light was wavelike and provided a grating with which to measure its wavelength. The role of The Optical Society (OSA) in spectroscopy during the pre-laser era is described in an essay entitled "Spectroscopy from 1916 to 1940" in an earlier part of this book. The first experimental demonstration of a laser, a ruby laser, was made by Theodore Maiman in 1960, and soon after, in 1964, a Nobel Prize was awarded for prior theory on the topic to Charles Townes, Nikolay Basov, and Alexander Prokhorov. Additionally, parametric nonlinear optics was discovered by Peter Franken in 1961. The combination of lasers and nonlinear optics made possible incredible advances in spectroscopy leading to linear and nonlinear laser spectroscopy. Developments in this field were so numerous that this short account can only hope to capture the principal events of an important chapter in optics and OSA history.

Almost immediately upon the invention of the laser, scientists recognized that the two most obvious features of laser light, its high intensity and its spectral purity, were far beyond anything that had been available before. In less than a year following Maiman's ruby laser, Franken took advantage of its high intensity to demonstrate optical second harmonic generation and open up the field of nonlinear optics. This would lead to numerous nonlinear spectroscopies mentioned below. Different designs also permitted wide-ranging variations in the type of output obtainable from lasers. Very pure single-frequency light was created with continuous-wave lasers and very broad, supercontinuum sources were created with ultrashort pulse lasers. The availability of lasers with large or small bandwidths and short or long pulse durations enabled the development of dozens of new and powerful approaches to precision optical measurements.

The Debut of Laser Spectroscopy

In 1960 the extraordinarily high intensity and short pulse duration available from the first ruby lasers ushered in a whole new era of experimentation in optical spectroscopy. The shift to laser methodology was rapid. Consider that G. Dieke and H. Crosswhite published a landmark paper in 1963 on the spectroscopy of doubly and triply ionized rare earths. For emission experiments they used pulsed discharges with currents in excess of kiloamperes together with photographic emulsions. For absorption measurements they employed high-pressure mercury and xenon lamps. Yet Dieke's student, S. Porto, who had labored to record infrared spectra of molecular hydrogen with the same apparatus only a few years earlier, was at that very moment pioneering the use of lasers in revolutionary spectroscopic techniques at Bell Labs in Murray Hill. There, Porto and his colleagues made the first observations of scattering from F-centers and spin waves, and introduced resonant Raman laser spectroscopy for the study of solids. Porto was a Fellow of OSA, and when he returned to Campinas, Brazil, in 1974 he was also elected a Fellow of the Brazilian Academy of Science. The seeds of a quiet revolution in optics had been sown as far away as Brazil. This can be considered a key starting point in the internationalization of OSA as it heralded widespread scientific exchange between the United States and many other countries.

Time-domain laser spectroscopy offered optical measurement capabilities on time scales that were six orders of magnitude faster than stroboscopes. Pump–probe experiments with picosecond pulses could time-resolve the fastest luminescent processes and follow the pathways of rapid chemical reactions. Dynamic grating spectroscopies soon lent sophistication to the dynamical processes that could be read out from the interference patterns formed by intersecting beams in various systems. Processes that produced no luminescence at all, such as energy transport among excited states in molecular crystals (coherent exciton migration), began to be investigated using transient grating approaches.

The realization that all systems possessed finite third-order susceptibilities and could easily be phase-matched to yield intense signals led to widespread popularity of coherent four-wave-mixing spectroscopy. Degenerate four-wave mixing in a counterpropagating pump geometry came into vogue. Another approach was coherent anti-Stokes Raman (CARS) spectroscopy devised by P. Maker and R. Terhune. This and other "coherent spectroscopies" not only achieved high resolution but gave signal waves that conveniently emerged from the sample as beams. As a consequence they are still used today to study molecular dynamics in chemistry.

Monochromaticity, wavelength control, and frequency stabilization improved steadily throughout the late 1960s. Barger and Hall reported a versatile frequency-offset locking technique in 1969 that permitted the frequency of one laser to be tuned relative to that of a second laser locked to a saturated absorption feature of methane that was a candidate for an absolute frequency reference. Their experiment demonstrated tunable control over the frequency of light to a precision of ~1 kHz for periods as long as an hour. For the first time this hinted at the possibility of frequency references and clocks based on optical schemes rather than radio frequency sources.

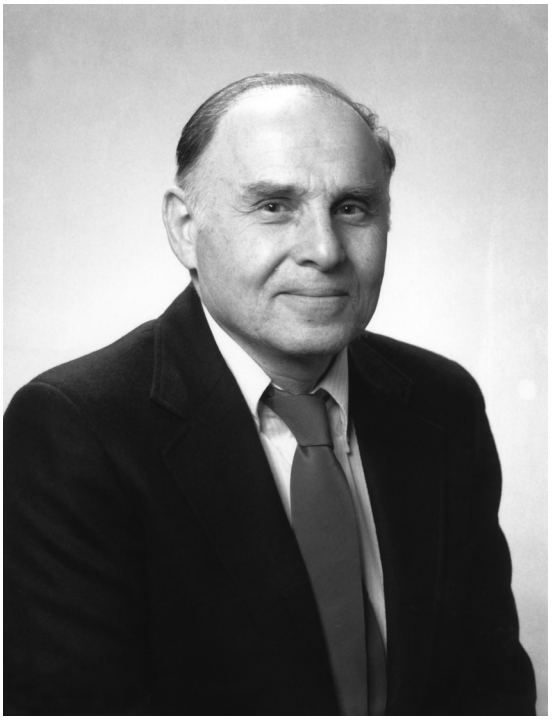
Optical modulation spectroscopies yielded still other measurement tools. When more than one transition of an atom was excited by a coherent optical pulse, excited-state fine or hyperfine structure produced modulation effects in the emission known as "quantum beats." At Columbia, D. Grischkowsky and S. Hartmann extracted frequency-domain splittings from time-domain photon echo signals in rare-earth-doped solids by simply Fourier transforming their data. This resolved the excited-state hyperfine structure with sub-megahertz precision and provided a beautiful example of the reciprocity between time- and frequency-domain measurements. In atomic spectroscopy the method of quantum beats also proved to be effective in resolving extremely fine splittings of energy levels in atomic vapors.

Gradual improvements in laser frequency control and methods of locking lasers together had the effect of encouraging researchers to think that the use of more than one laser in an experiment might eventually become possible, or even routine. The idea still seemed futuristic in 1972, so it came as quite a shock when the speed of light was redefined that year in a remarkable experiment by K. Evenson and his colleagues, who determined the speed of light to ten significant figures with an entire room full of frequency-locked lasers.

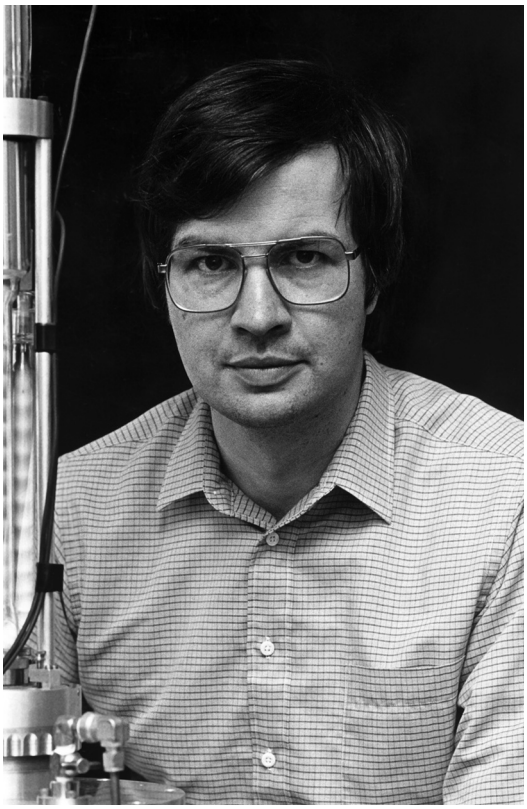
Following this, H. Dehmelt trapped ions in free space at the University of Washington, a feat for which he and W. Paul would share the 1989 Nobel Prize in Physics. A. Ashkin (see Fig. 1) at Bell Labs, and P. Toschek and H. Walther in Germany were thinking of ways to trap and cool individual neutral atoms. W. E. Moerner reported that single, isolated centers could be interrogated spectroscopically even in the complex environment of solids. The field of spectroscopy was poised to take on the challenges of laser cooling, Bose–Einstein condensation (BEC), single-molecule spectroscopy, and the control of trapped atoms for quantum information science.

Nonlinear Optics and Nonlinear Spectroscopy

A year after the (future OSA president) Peter Franken announced the experimental discovery of nonlinear optics at the University of Michigan in 1961, M. Bass observed sum frequency generation and then optical rectification. OSA meetings buzzed with the anticipation of additional possible discoveries of nonlinear phenomena. A general analysis of nonlinear interactions was published in September of 1962 by J. A. Armstrong and his colleagues. It indicated that an enormous number of nonlinear effects were possible at high laser intensities, and reports of experiments by other groups began to pour in. Nonlinear optics provided spectroscopists with



▲ **Fig. 1.** Arthur Ashkin. (AIP Emilio Segre Visual Archives, Physics Today Collection.)



▲ **Fig. 2.** Theodor Hänsch. (© OSA. Photo courtesy of Dr. W. John Tomlinson, Princeton, New Jersey.)

tools to reach otherwise inaccessible wavelengths, inaccessible spectral resolution, and unimagined short pulse durations.

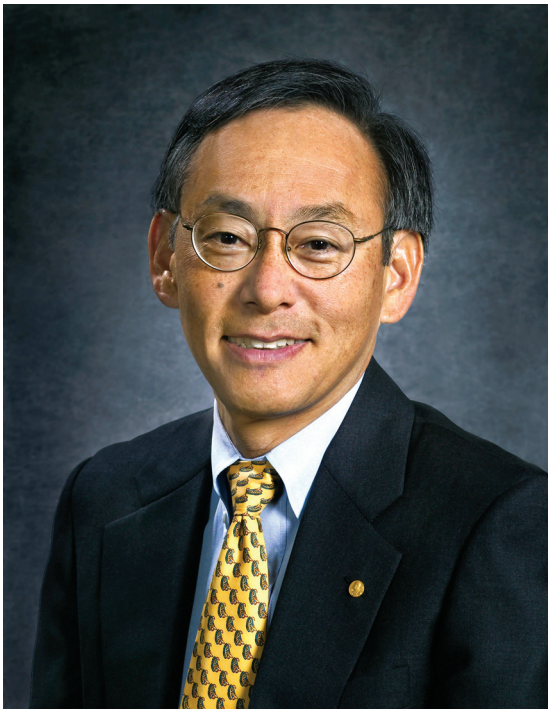
The push for better resolution took a leap forward with the introduction of "Doppler-free" laser spectroscopy. C. Borde, T. W. Hänsch, A. L. Schawlow, V. Chebotayev, and V. Letokhov moved forward quickly to investigate its implications in Paris, Stanford, and Novosibirsk. It was widely recognized that spectral broadening due to motion of the atoms in a gas could be eliminated using a variety of methods: saturation spectroscopy, or 2-photon absorption, or by trapping atoms. The anticipated improvement in resolution from $\sim 10^4$ to $\sim 10^{11}$ using relatively simple experimental techniques was substantial enough that optical Lamb shift measurements could provide stringent tests of quantum electrodynamics. By 1975, research at Stanford based on 2-photon Doppler-free spectroscopy of hydrogen yielded a determination of the 1S Lamb shift for the first time. A concerted effort began to improve measurements of the Rydberg constant. At the time, the Rydberg constant was one of the most poorly determined fundamental quantities. In the decades that followed, its precision would improve a millionfold.

In 1977 the next tool for precision spectroscopy was introduced when the Ramsey fringe method was adapted for high resolution optical spectroscopy in Russia and in the U.S. This succeeded in extending the separated field technique from microwave to optical frequencies, for which Norman Ramsey received the 1989 Nobel Prize.

T. Hänsch (see Fig. 2) and A. Schawlow proposed a technique to stop atoms in order to improve spectroscopic resolution using laser radiation tuned below resonance. Their 1975 paper galvanized the spectroscopic community focused on precise frequency measurements. That same year laser spectroscopy on trapped barium ions was proposed, and by 1980 collaboration between Dehmelt and Toschek had succeeded in trapping a single Ba^+ ion in a quadrapole trap, cooling it to 10 mK with light, and observing its resonance fluorescence. Doppler-free spectroscopy of single Ba and Mg ions was on the horizon, and "optical clock" transitions became a topic of discussion. In 1982 H. Metcalf cooled a beam of neutral sodium atoms with a Zeeman "slower," and the next year D. Pritchard suggested a magnetic geometry to trap atoms. In 1985 S. Chu (see Fig. 3) reported an all-optical trap dubbed "optical molasses" and jointly with the MIT group announced an efficient magneto-optic trap in 1987

that could rapidly cool a variety of atoms to milli-Kelvin temperatures. Then in 1988 P. Lett of W. Phillips's group at NIST demonstrated cooling below the Doppler limit in alkali vapors. J. Dalibard and C. Cohen-Tannoudji (see Fig. 4) at ENS explained Lett's mechanism in a widely read 1989 publication in the *Journal of The Optical Society of America B*. Halfway around the world, researchers in Japan were in close pursuit, applying these advances to laser cooling of noble gases.

In 1995 these activities, originally motivated to improve spectroscopic resolution, culminated in the creation of a new form of matter. E. Cornell and C. Wieman observed BEC of Rb atoms at JILA in Colorado. By this time A. Schawlow and N. Bloembergen had shared the 1981 Nobel Prize for advances in spectroscopy. Chu, Cohen-Tannoudji, and Phillips were due to share this honor in 1997 for laser cooling. For producing and studying properties of BECs, Wieman, Cornell, and Ketterle would receive the Prize in 2001. J. Hall (see Fig. 5) and T. Hänsch would earn the Nobel prize in 2005 for the development of frequency "combs" that enabled tests of the variation of the gravitational constant and frequency references with uncertainties at the level of a few parts in 10^{15}.



▲ **Fig. 3.** Steven Chu. (Courtesy of U.S. Department of Energy.)

▲ **Fig. 4.** Claude Cohen-Tannoudji. (Photograph by Studio Claude Despoisse, Paris, courtesy AIP Emilio Segre Visual Archives, Physics Today Collection.)

Laser Spectroscopy: An Enabling Science

The transition from spectroscopic research in the period 1960–2000 to its many applications had a long gestation period. D. Auston disclosed a method of generating single cycles of terahertz radiation in the 1980s. However, applications such as imaging through plastics and ceramics with terahertz waves would not become routine until the beginning of the twenty-first century. Similarly, as early as 1980, T. Heinz and Y. R. Shen found that second harmonic generation was allowed on the surfaces of centro-symmetric media but forbidden in their interior. IBM exploited this interaction to inspect silicon wafers for electronic circuits, but decades passed before species-specific structural and dynamic studies became popular with chemists. By the 1990s, experiments in the research groups of S. Harris and B. P. Stoicheff had established that opaque materials could be rendered transparent through quantum interference. This had immediate impact on spectroscopy and the generation of short wavelength

▲ **Fig. 5.** John Hall. (Courtesy of AIP Emilio Segre Visual Archives, Physics Today Collection.)

radiation via nonlinear mixing. Yet once again a 20-year interval would pass before Rohlsberger was to achieve electromagnetically induced transparency at x-ray wavelengths, thereby hinting at the prospect of nuclear quantum optics.

There are other striking examples of how technological outgrowths of the last 50 years of spectroscopy continue to enable new science topics. The sub-Doppler laser cooling techniques of 1986 became tools for the fledgling field of quantum information. Only recently have they been applied to demonstrate 14-qubit entanglement with Ca^+ ions. Despite the frenzied activity in laser cooling and trapping that accompanied the race to achieve BEC, a quarter of a century also passed between the invention of "optical tweezers" by Ashkin for trapping particles and single cells and the studies of single biomolecules by S. Chu and others.

The Future

Over its 100-year lifespan, The Optical Society has been led by many accomplished scientists, many of whom were spectroscopists. It is partly for this reason that the society has been able to maintain a prominent role throughout an explosive period of scientific history that relied on precise spectral tests of new theories. Spectroscopists contributed to but also benefited from and were nurtured by the emphasis on fundamental science and the open, relaxed style of the Society, where many disciplines intersect. The vibrancy of OSA has rested on personal relationships fostered by the Society across ideological boundaries. OSA has followed a tradition of internationalization that began long before globalization made it necessary. Past president Art Schawlow understood how important international connections were for spectroscopy and science in general. He knew that when it came time for visitors from China, New Zealand, Canada, and Ireland to return home, they would inevitably take home part of his magic recipe for having fun with great science. They had learned that "You don't need to know everything to do good research. You just have to know one thing that isn't known," and of course you also had to be a spectroscopist! By sharing this attitude, Art was a great ambassador for the field of spectroscopy and for OSA itself. The rich history of both, and his encouraging message, accumulated in the hearts of his students and visitors. Current and future OSA members will sustain the unique strengths of the Society that account for its remarkable spectroscopic legacy and its future contributions.

Acknowledgement

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