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Contributions of IBM to Laser Science—1960 to the Present

IBM's role in the discovery of new lasers and in the development of their scientific potential is described. A brief survey is presented of laser-related projects conducted within IBM's Research Division laboratories at Yorktown Heights, NY, San Jose, CA, and Zurich, Switzerland.

Introduction

IBM has played a significant role in the discovery of new types of lasers and in the development of their scientific potential, beginning shortly after the publication in December 1958 of the famous paper by A. L. Schawlow (Bell Telephone Laboratories) and C. H. Townes (Columbia University) [1], which suggested that stimulated emission devices operating in the infrared and visible portion of the electromagnetic spectrum could be realized [2]. Research emphasizing lasers and their scientific uses has continued at IBM, with active groups at Yorktown, San Jose, and Zurich. Tables 1 and 2 indicate some of IBM's achievements in the field of lasers and quantum electronics during the past nineteen years. Table 1 lists the various lasers and other forms of coherent light generators invented at IBM; included are certain accessory devices which can greatly influence the character of the output beams delivered. Table 2 lists various scientific contributions of IBM featuring the use of lasers.

Table 1 Lasers and other forms of coherent light generators invented at IBM.

1960	First four-level lasers (second and third lasers on record)
1962	GaAs injection laser, discovered independently and simultaneously at IBM and General Electric Corp.
1964	Saturable dye Q-switch
1966	Laser-pumped dye laser Stimulated electronic Raman scattering, discovered independently and simultaneously at IBM and by Rokni and Yatsiv in Israel
1967	Flashlamp-pumped dye laser
1968	Nitrogen-laser-pumped dye laser, demonstrated independently at IBM and at Avco Everett
1969	Vacuum ultraviolet (H_2) laser, discharge excited, discovered independently at IBM and the Naval Research Laboratory
1972	Use of relativistic e-beams for ultraviolet and vacuum ultraviolet gas laser pumping, discovered independently at IBM and by Clerc and Schmidt in France
1973–1974	Tunable infrared and vacuum ultraviolet sources using four-wave mixing in atomic vapors
1976	Frequency switching technique for dye lasers
1976–1977	16-μm source using four-wave mixing in para-hydrogen

First, IBM's role in the discovery of new lasers is presented, with emphasis on historical sequences leading to the development of each device. The second part of this paper focuses on achievements by IBM scientists using lasers. Here selected topics are presented, approximately in chronological order.

Types of lasers discovered at IBM

- *Four-level lasers*

At the time of publication of the Schawlow-Townes article, the development of what is now generally called the field of quantum electronics was well underway. The ammonia beam maser, the first device to produce microwaves by stimulated emission, had been realized several

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years earlier [3]. Shortly thereafter, the solid state microwave maser was proposed [4] and almost immediately realized [5]. Indeed, when the first Conference on Quantum Electronics was held in September 1959 at High View, New York, a sophisticated understanding of masers and other devices such as atomic frequency standards and parametric amplifiers had already been reached [6]. During the conference (with the Schawlow-Townes paper having appeared several months earlier) there was speculation about the form a practical source of coherent infrared or optical radiation would take. At about this time, various laboratories, both in industry and the academic world, began to take interest in stimulated emission devices. At IBM Research, a small group under the direction of W. V. Smith had been studying a relaxational mechanism important in the operation of microwave masers and had presented their results at the High View conference. Even before attending the conference, Smith felt that his group should seriously begin considering possible material systems that might lead to the realization of infrared or optical masers. Stimulated by the conference, members of the group began to think along these lines.

The most valuable and stimulating aspect of the Schawlow-Townes article was the derivation of a simple, explicit formula applicable to a general system, showing the minimum rate at which atoms must be supplied to an excited state for coherent generation of light to occur. The formula showed that this rate (actually a measure of the necessary pump power) was inversely proportional to the longest time that fluorescence from the excited state could be contained between the two cavity end mirrors in the parallel-plate geometry proposed by Schawlow and Townes. As there existed some uncertainty concerning maximum reflectivities achievable with metallic or multiple dielectric surfaces, I decided to investigate the possibility of using optical cavities based on total internal reflection. A solid state cavity structure in the form of a rectangular block with accurately cut and highly polished edges was conceived. It was thought that the coherently generated light could circulate in a low-loss manner in the cavity, with the light rays internally reflecting at an angle of about 45°. This, of course, imposed the requirement that the index of refraction n_r of the medium exceed $2^{1/2}$. Additionally, as was pointed out by Smith, if n_r were quite close to $2^{1/2}$, the number of high-Q cavity modes coupled to the fluorescent bandwidth would be dramatically lowered, with the expected result that the generated light would have improved coherence properties.

I soon noted that fluorite ($n_r \approx 1.43$) was an optical-quality host material with seemingly eminent suitability for this scheme. The literature was searched for studies of narrow-line fluorescence of ions incorporated in this lattice, to determine whether there existed in CaF_2 luminescent centers favorable for obtaining stimulated emission. For example, it was strongly felt that a suitable ionic candidate should display luminescence primarily concentrated in a transition terminating on a thermally unoccupied state. It was also felt that there should be broad, strong absorption bands that could be utilized to populate the fluorescing state efficiently with broad band incoherent light. These two requirements generally define a four-level optical pumping scheme.

The literature revealed two promising four-level ionic systems in CaF_2: trivalent uranium [7] and divalent samarium [8]. The striking spectral data presented in these studies convinced me and my colleague M. J. Stevenson to have uranium- and samarium-doped fluorite crystals grown by outside vendors [9]. By the middle of May 1960,

Table 2 Some scientific achievements at IBM using lasers.

1964	Studies of laser-oscillator noise
1963–67	Two-photon excitation in organic crystals and liquids
1964–73	Stimulated Brillouin and Rayleigh scattering in liquids and self-trapped filaments
1966–67	Measurement of thermal relaxation times of thin films and the Fermi velocity in gallium
1967–75	Measurement of picosecond pulse widths and ultrafast relaxation times
1969–78	Nonlinear optical spectroscopy: infrared nonlinear spectroscopy of molecular gases, solid state nonlinear spectroscopy, autoionization spectroscopy via sum frequency generation, multiphoton ionization spectroscopy
1968–77	Coherent optical transients and nonlinear pulse propagation in resonant systems; adiabatic following, observation of nonadiabatic coherent optical transients
1972–75	Optically written memory schemes
1973	Laser-induced thermoelectric voltages in thin films
1973–76	Forced Rayleigh scattering
1974–78	Infrared absorption spectroscopy of highly transparent media
1970–78	Conventional laser spectroscopy
1974–78	Laser-induced fluorescence detection of reactive scattering
1976–78	Photochemical hole burning
1977	Generation of thermoelastic waves
1978	Laser-induced isomerization; optical detection of nmr; metastable ion spectroscopy; time-resolved infrared spectral photography; laser-enhanced electroplating and electroetching

optimal sample boules had been selected for careful fabrication and polishing in the favored total internal reflection geometry.

The finished rectangular doped CaF_2 cavities received a few months later were never to be tested as coherent light generators, for in June 1960 T. H. Maiman [10, 11] of Hughes Aircraft Co. electrified the scientific world with the announcement that he had demonstrated stimulated emission in the visible region of the electromagnetic spectrum with a ruby crystal fabricated in the form of a plane-parallel resonator, the same geometry originally proposed by Schawlow and Townes. Maiman's successful experiment also greatly influenced the direction of future experimental work in this area by showing that pulsed xenon flashlamps, commonly used for flash photography, were effective optical pumping sources with intensities high enough to obviate the requirement for very high end mirror reflectivities. The active ion species (Cr^{3+}) in Maiman's device could only be utilized in a three-level pumping scheme, *i.e.*, one requiring an actual population inversion between excited and ground states. This raises the required threshold pumping power by several orders of magnitude over four-level systems having comparable fluorescent linewidths and quantum efficiencies.

Stimulated by Maiman's results, we quickly had $CaF_2:U^{3+}$ and $CaF_2:Sm^{2+}$ samples still in hand fabricated into rods with plane-parallel silvered ends, purchased a xenon flashlamp apparatus, and within a few months' time successfully demonstrated stimulated emission with both materials [12, 13]. The materials $CaF_2:U^{3+}$ and $CaF_2:Sm^{2+}$ thus became the second and third lasers [14] on record. When cooled to cryogenic temperatures, both systems operated in a striking manner as true four-level lasers. Threshold pumping energies were reduced from that required for ruby by two to three orders of magnitude. Our demonstration of this important feature stimulated subsequent intensive research efforts in several laboratories to find a suitable rare earth ion for four-level laser operation at room temperature. More than a year later, such an ion (Nd^{3+}) was found [15, 16]. Because it operates in a four-level manner at room temperature, Nd^{3+} has since been the most widely used ion in solid state optically pumped lasers, which now have a wide variety of industrial and scientific uses and are commercially available throughout the world.

• *Injection laser*

The discoveries of the two four-level lasers just described and of the continuously operating gas discharge laser [17] achieved at Bell Telephone Laboratories shortly thereafter made it clear that stimulated optical emission was not merely a lucky accident allowed by nature for ruby; it might well be sought in a wide variety of systems, perhaps through a number of excitation mechanisms. The possibility of a laser using the radiation emitted by a forward-biased p-n junction had been invoked in a number of fairly early proposals [18]; however, none of these proposals were made with enough knowledge about the relevant materials parameters. In fact, at the second Quantum Electronics Conference (May 1961, Berkeley, California) the key paper related to injection lasers [19] was still limited to semiconductors with indirect transitions (*i.e.*, Ge or Si) rather than III-V compounds.

Serious interest in the possibility of achieving an injection laser took root at IBM in the spring of 1961. Informal conversations took place during the summer of 1961 with representatives of the U.S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey, who became interested in IBM's speculations along these lines. They later issued a request for proposal, announcing their willingness to support injection laser work. On January 4, 1962, the IBM Research Center at Yorktown submitted to Fort Monmouth a proposal for a research and development program to find an electron injection laser. The proposal, put together by R. W. Keyes, resulted in a subsequent contract award. This proposal described a 12-month program of research designed to culminate in the delivery of an experimental injection laser device. This history differs from that at General Electric Corp., which R. N. Hall has summarized by stating [20]: "I recall having been asked on several occasions before the summer of 1962 whether I thought a semiconductor laser might be possible. My response was negative."

Early soul searching at IBM in 1961 sought a promising specific direction. Germanium was regarded by Aigran in Paris (who had repeatedly made injection laser proposals) as the most likely candidate. It was known that Si and Ge had at low temperatures particularly sharp lines associated with exciton recombination. Other suitable candidates were the II-VI compounds, such as ZnS, ZnSe, and CdSe. While efficient recombination in these materials could be easily achieved, the formation of p-n junctions in these materials seemed difficult. Near the end of 1961, R. Landauer, the principal advocate of the injection laser at IBM, encouraged a number of scientists in his group at Yorktown to address these questions. One result was a calculation by G. J. Lasher, included in the proposal to Fort Monmouth, which showed that free-carrier absorption in germanium or silicon would far outweigh the stimulated emission gain. A similar conclusion was independently reached at about the same time by W. P. Dumke [21], who was in another group. Dumke also noted that these difficulties were much less serious in direct bandgap semiconductors such as GaAs. For these

materials, the intensity of induced emission from an inverted population (electron-hole recombination) usually exceeds induced absorption of electrons into higher levels in the conduction band (free-electron absorption). These considerations clearly pointed to GaAs as a likely injection laser material.

Gallium arsenide had been studied in IBM Research for some years, originally as a candidate for bipolar transistors. Later IBM successes in GaAs were to include J. B. Gunn's discovery of oscillations under high fields [22, 23] and the successful development in Zurich of the highest-frequency transistors, in the form of GaAs Schottky barrier transistors. Further emphasis was placed on GaAs when S. Mayburg of General Telephone and Electronics Laboratories, Inc., in a lecture at the IBM Research Center and in a postdeadline paper [24] at the March 1962 APS meeting, emphasized his belief that he had obtained 100% luminescence efficiency in incoherent GaAs diodes. Although Mayburg's evidence was indirect and did not include actual radiative output measurements, in early 1962 several other laboratories [18], supplying these actual measurements, reported phenomenally high electroluminescent efficiencies in some forward-biased GaAs p-n diodes.

An internal IBM laboratory report by Lasher, dated August 28, 1962, appeared in published form [25] only after the announcement of the observation of stimulated emission. Lasher tried to consolidate for the first time all available information in order to calculate the actual threshold current needed for laser action in GaAs. He showed that stimulated emission should occur at reasonable currents and without the need for extremely complex structures.

The observation of stimulated emission in GaAs was reported on November 1, 1962 in simultaneous publications from IBM [26] and GE [27]. At IBM, M. Nathan, who took on the informal leadership and coordination of the injection laser work during 1962, made the first actual observation of stimulated emission. Dumke and Lasher provided the theoretical groundwork. A number of device makers, including R. Dill, R. F. Rutz, and J. Marinace, supported the injection laser work; Dill was the one most intimately involved with this aspect. G. Burns was Nathan's collaborator in a series of spectroscopic experiments on GaAs. In large part, the success of the IBM effort was due to Landauer's early conviction that an injection laser could be realized and to his managerial efforts to translate this conviction into reality.

The comparable history at General Electric Corp. has already been recorded [20]. A third injection laser paper [28], from Lincoln Laboratory, reporting similar achievements, was received by *Applied Physics Letters* on November 5, 1962, immediately after the appearance of the IBM and General Electric publications and their associated press releases.

The January 1963 issue of the *IBM Journal of Research and Development*, containing seven injection laser papers, testifies to the excitement produced at IBM and elsewhere by the injection laser discovery. While IBM had been correct and perceptive in recognizing the injection laser possibility, it was also overly optimistic about the speed and ease with which this device would find applications. The applications promise is being fulfilled only now, after the passage of seventeen years and considerable effort.

• *Saturable dye Q-switch*

Despite its very high pumping energy threshold, the pulsed ruby laser continued to be used extensively by scientists for many years for several reasons. Ruby itself is a durable refractory material, and the laser conveniently operates at room temperature. Although high pumping energies are required and the laser is basically inefficient, the means of excitation are relatively simple, provided one is content with "once-in-a-while" pulse repetition rates. Large energy storage capabilities are also inherent in this system because of its long radiative lifetime.

In 1964 we asked J. J. Luzzi to prepare some organic molecules known as metal phthalocyanines, which were chosen for their high optical absorption cross sections at the ruby laser frequency. Our intent was to try to realize a simple self-opening Q-switch that would transform the unruly train of random ruby laser pulses into a single short pulse with orders of magnitude more intensity than the individual random pulses of the train. Q-switching had been accomplished earlier with the use of electrically switched Kerr cell shutters by F. J. McClung and R. W. Hellwarth [29] of Hughes Aircraft Co. The general idea that a bleachable absorber might work in this application evolved from a conversation between myself and my colleague W. A. Hardy.

The organic dye Q-switch experiment worked beautifully from the start; so-called "giant pulses" of ruby laser light were produced simply by including in the laser cavity a dye cell containing solutions of the phthalocyanine compounds [30]. The success of this bleachable-absorber technique stimulated efforts in other laboratories to find corresponding dyes for Q-switching other kinds of lasers, such as those based on Nd^{3+}. Among the most successful of these efforts was one by K. H. Drexhage and U. T. Mueller-Westerhoff [31], in which a new

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family of ultrastable nickel chelate molecules with excellent Q-switching properties was synthesized for the first time.

It was subsequently discovered that with the use of certain dyes as bleachable absorbers, the pulses of coherent light generated were orders of magnitude shorter, with peak intensities correspondingly higher than previously generated pulses [32, 33]. This operation became known as mode-locking. Bleachable dye absorbers today are used both for the generation and shaping of nanosecond pulses of laser light, and for the production of trains of picosecond pulses through mode-locking.

• *Dye laser*

We were to benefit further from having on hand generous amounts of the remarkably stable phthalocyanine compounds prepared for the bleachable dye absorber experiment just described. Their singular spectra led to suggestions for other experiments in which the dyes could be utilized. One idea was to try to produce stimulated (resonance) Raman scattering from concentrated solutions of the dyes, with the required primary beam being provided by a Q-switched ruby laser. Another thought was to attempt to obtain stimulated emission from the dyes, using a ruby laser as a fast flashlamp. Because the most soluble of the phthalocyanines, chloro-aluminum phthalocyanine, had its maximum absorption peak shifted somewhat from the ruby laser frequency, we initially opted to try the first experiment. When the spectrum of the light emitted from the ruby-laser-irradiated cell was examined, it was apparent that we had instead succeeded with the *second* experiment: we had observed stimulated emission from the dye [34]. This led to an intensive investigative effort by our group at Yorktown. The effect was soon seen to be quite general, occurring for many dyes, with outputs covering the whole visible and near ir spectral range [35]. Interest in this subject spread rapidly, and important results started flowing from other laboratories, most notably that of F. P. Schäfer in Marburg, Germany. Our group was the first to show that the dyes could also be made to lase efficiently when pumped with incoherent light from flashlamps [36, 37]. Later important contributions of IBM to the development of dye lasers include the successful effort of J. R. Lankard and R. J. von Gutfeld in pumping dye lasers with a nitrogen laser [38], resulting in a convenient high-repetition-rate source that opened the door to many spectroscopic experiments, and the relatively recent frequency-switching technique developed by R. G. Brewer and A. Z. Genack [39]. The latter invention has made possible a new class of elegant optical experiments; these are discussed in the second part of this paper.

Dye lasers today are in wide scientific use, partly because the active dye media can be handled conveniently, but more so because these lasers provide beams of light with sharply defined frequencies that can be *continuously tuned* throughout the visible, near infrared, and near ultraviolet. This feature permits the selective excitation of various atomic and molecular energy levels, thus forming the basis for a true revolution in spectroscopy that has evolved. Selective excitation by dye lasers has many practical applications. For example, dye lasers play an essential role in one of the two main technologies currently being developed for uranium isotope separation.

• *Stimulated electronic Raman scattering (SERS)*

In 1966, our colleague N. S. Shiren predicted that a certain resonant three-photon scattering process could be made to undergo coherent stimulated scattering if the primary beam intensity were sufficiently high. Although stimulated versions of other types of scattering, *e.g.*, rotational and vibrational Raman, Brillouin, Rayleigh, etc., had already been discovered and intensively studied, Shiren's idea was sufficiently novel and compelling to interest our group in attempting to find a material system with which the effect could be realized. The most promising candidate appeared to be potassium vapor, since its energy level separations were nearly resonant with the frequencies of strong light beams that could readily be provided at the time. (The continuous narrow band tunability [40] of dye lasers had not yet been discovered.) A potassium vapor cell was prepared and the experiment was tried. An intense, directional stimulated scattering beam was indeed observed; however, careful examination of the spectrograph plates containing the spectrum of the beam revealed that what we actually had observed was stimulated electronic Raman scattering involving well-known states in potassium [41]. Although it was clearly not the effect we were looking for, it was the first time that a purely electronic stimulated scattering had been observed. Thus, as in the case of the discovery of the dye laser, the disappointment at failing to observe an expected effect was more than offset by the excitement of discovering a new effect. The SERS effect was independently observed by M. Rokni and S. Yatsiv in Israel at about the same time [42], and the original effect predicted by Shiren was subsequently observed in rubidium vapor by still another group [43].

The SERS process has reappeared from time to time to play important roles in subsequent IBM discoveries and inventions in quantum electronics. In 1972 it was observed [44] that SERS in metal vapors could be excited by a train of pulses from a mode-locked laser. With existing technology, the generation of intense tunable picosecond pulses from mode-locked dye lasers becomes possible. As a result, it is likely that the development of means for generating tunable infrared picosecond pulses by SERS

will soon follow, resulting in a useful tool for scientific investigations in chemistry and biology.

By using tunable dye lasers for generating primary beams, it was shown in 1973 that the SERS process provides a means for generating tunable infrared narrow band ≈5-nanosecond pulses of coherent light [45, 46]. This tunable ir coherent light was produced in two regimes: directly as the secondary beam generated by the SERS process, and as a result of four-wave mixing based on SERS. The latter regime is characterized by a much wider range of frequency generation than the former, but the intensities of the output beams are rather weak.

Finally, broad band SERS is used as the basis for a new technique of time-resolved ir spectral photography [47]; a detailed discussion of this technique is presented in a paper by D. S. Bethune *et al.* in this issue [48].

• *Vacuum ultraviolet lasers*

In 1968, R. T. Hodgson, at W. V. Smith's suggestion, began intensive efforts toward the realization of short-wavelength lasers, instead of concentrating on longer-wavelength (ir) gas laser research in vogue at that time. Realizing that the power needed for short-wavelength lasers increases at least as fast as the fourth power of the frequency, he designed a very fast, powerful Blumlein gas discharge in molecular hydrogen gas to provide the required excitation. Hodgson's efforts were successful and led to the discovery [49] in 1969 of hydrogen laser action at 160 nm. This was the first laser to operate in the vacuum ultraviolet region.

Hodgson and R. W. Dreyfus later pioneered in the use of relativistic electron beams (REBs) for the excitation of various laser gases. By early 1971, REB generators with gigawatt (10^9 W) pump capabilities had become commercially available. Hodgson and Dreyfus soon began considering them as potential pump sources for both proven and as yet unrealized laser systems. They devised a system for guiding the e-beam with a longitudinal magnetic field and were at once successful in exciting the 337.1-nm band of molecular nitrogen [50] (a well-known gas laser system). Unknown to them at the time, M. Clerc and M. Schmidt in France had also successfully pumped an N_2 laser with an REB [51]. With their effective pumping apparatus Hodgson and Dreyfus not only produced strong lasing on the 160-nm hydrogen bands [52], but also discovered that lasing within the H_2-Werner bands from 116.1 to 124 nm could be made to occur [53]. Achievement of lasing on the H_2-Werner band system using a Blumlein discharge was also reported by R. A. Waynant of the Naval Research Laboratory at exactly the same time [54]. Finally, longitudinal pumping was used with cooled para-hydrogen to produce lasing at 109.8 nm [55a], a short-wavelength laser record that remains today, although higher frequencies of coherent light have been produced by generation of laser beam harmonics [55b].

Hodgson and Dreyfus, with S. C. Wallace, then turned their attention to e-beam pumping of the high-pressure xenon laser, achieved earlier with use of a very large e-beam machine [56]. They succeeded in pumping this laser with their much smaller, laboratory-sized e-beam device [57] and demonstrated tuning of the Xe laser for the first time [58]. By this time there was already widespread interest in the use of REBs for laser pumping; this interest remains high. For example, it was with the use of REB pumps that a very important class of new uv lasers, the rare gas halides, were subsequently demonstrated [59–61] for the first time.

At present, the study of short-wavelength sources continues with attention focused on systems with large gas pressure differentials between the e-beam cathode and the light-emitting gas volume [62]. The object is to eliminate e-beam transmitting windows with their limiting effects on minimum electron energy and maximum current density.

• *Sources based on four-wave mixing*

In 1974 a successful experiment was conducted in which tunable coherent vacuum uv radiation was generated using four-wave sum mixing in Sr vapor [63]. The input beams for this experiment were provided by two independently tunable nitrogen-laser-pumped dye lasers. One of the lasers, at frequency ν_1, was specifically tuned to a two-photon resonance of the Sr atoms, thereby greatly enhancing the nonlinear susceptibility. The other laser, at frequency ν_2, could be tuned throughout its entire range. What emerged from the Sr cell was a tunable output beam with frequency $2\nu_1 + \nu_2$. With the use of a few dyes, the entire range from 150 to 200 nm could be spanned [64]. This provided for the first time a source of coherent light that could be conveniently tuned in this spectral region. Several spectroscopic investigations with this type of source are currently in progress in various laboratories.

Four-wave mixing was recently used at IBM for the generation of intense beams at ≈16 μm [65, 66]. Infrared beams tuned precisely to a classified wavelength near 16 μm are critically needed in a Los Alamos laboratory uranium isotope separation scheme involving uranium containing molecules (UF_6) [67]. It is currently felt that a version [68] of the source demonstrated in Refs. [65] and [66] could play an important role in the Los Alamos scheme.

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Scientific achievements at IBM using lasers

As the development of new types of lasers proceeded, IBM scientists began using them to support other research. A brief representative survey is now given of some of the ways IBM scientists have used lasers in their studies. This account is neither exhaustive nor detailed; it is meant only to give an idea of the diversity of laser research and applications within the IBM Research Division over the past 19 years. The topics are presented approximately in chronological order. Many of these subjects are treated in detail in accompanying papers in this issue.

• *Studies of laser-oscillator noise*

Because of inevitable spontaneous emission, there is always random noise accompanying the coherent emission of a laser oscillator; this gives rise to low-frequency fluctuations in excess of the inevitable shot noise in the output of any photodetector on which the light is incident. On the other hand, the nonlinear characteristic of a laser oscillator tends to stabilize its amplitude. If the measured mean-squared fluctuation of this detector current is compared with the mean-squared fluctuations calculated to be present from an "equivalent" random-noise optical source of the same power and bandwidth as the laser, the former is predicted to be many orders of magnitude smaller than the latter. This was confirmed in measurements of the relative mean-squared fluctuations in a single-mode laser near threshold made in 1964 by J. A. Armstrong and A. W. Smith [69, 70]. The ratio showed a sharp decrease as the laser oscillated more and more strongly, illustrating the quieting behavior expected from any good oscillator.

• *Two-photon excitation in organic crystals and liquids*

Two-photon excitation experiments became quite feasible after the discovery of the laser. The earliest studies were performed on CaF_2:Eu^{2+} crystals [71] and in Cs vapor [72]. IBM scientists were the first to observe the effect in organic molecules [73]; W. L. Peticolas *et al.* used a Q-switched ruby laser to observe two-photon excitation of organic crystals such as anthracene, pyrene, benzpyrene, etc. This was confirmed by S. Singh and B. P. Stoicheff [74] of the National Research Council and by J. L. Hall (Joint Institute for Laboratory Astrophysics), D. A. Jennings, and R. M. McClintock (NBS) [75]. The question of whether the observed effect was due to triplet-triplet exciton annihilation was raised by R. G. Kepler *et al.* of E. I. du Pont de Nemours and Co. [76], but measurements in dilute solutions [77] and polarization measurements [78] showed that while both processes can occur, two-photon absorption via an intermediate virtual state had indeed been observed by Peticolas *et al.* The mechanism was shown to involve the $\vec{p} \cdot \vec{A}$ term of the Hamiltonian and not the A^2 term. Laser excitation of biphenyl and related compounds gave rise to multiphoton processes which in turn led to molecular dissociation [79, 80]. The main themes of these early experiments are still strongly evident in many current laser-related studies of chemistry.

• *Stimulated Brillouin and Rayleigh scattering in liquids and self-trapped filaments*

Soon after R. Y. Chiao, Townes, and Stoicheff [81] observed stimulated Brillouin scattering in quartz and sapphire at MIT, R. G. Brewer and K. E. Rieckhoff at IBM observed the same effect in water and benzene [82]. Here an amplification of the Brillouin process was observed, as was cavitation into filaments. In collaborative work with Townes, the spatial beats in self-trapped light filaments were observed [83]. The shift in beat patterns with filament diameter led to a determination of the high electric fields due to the light. An electric field strength as high as 3.7×10^7 V/cm was determined for the filaments formed in CS_2. Self-trapping experiments performed with picosecond laser pulses showed that electronic distortion contributed to self-trapping in $\approx$2-μm-diameter filaments [84]. In this time scale, the orientational Kerr effect postulated to be responsible for self-trapping had insufficient time to contribute to filament formation.

Further work on the formation of self-trapped filaments in nonlinear index liquids was done by E. Courtens. Detailed calculations of steady state focusing were performed and compared to experimental results [85, 86]. The stabilizing effect of the medium relaxation time was demonstrated in decisive computer calculations [87]. Further, a novel experimental approach was developed to study the influence of longitudinal E-field components in self-focusing beams by comparing the evolution of TE_{01} and TM_{01} beams, which differ in that component [88, 89]. These studies required the development of suitable laser sources: single-mode ruby lasers with TE_{00}, TE_{01}, and TM_{01} modes [90].

Another interesting nonlinear effect that has been studied [91] at IBM is stimulated thermal or Rayleigh scattering. Here, the intensity of light propagating in absorbing media is limited because of a periodic heat pattern that causes diffraction and reflection with extremely small frequency shifts.

• *Measurement of thermal relaxation times in thin films and the Fermi velocity of gallium*

In 1966 Q-switched ruby and GaAs lasers were used by R. J. von Gutfeld *et al.* to thermally excite thin films on various substrates in order to measure thermal relaxation times both in the liquid helium range and as a function of

temperature [92, 93]. In 1967, a ruby-laser-pumped dye laser was used to generate light that could be converted into short heat pulses for direct measurement of the Fermi velocity in single-crystal Ga [94].

• *Measurement of picosecond pulse widths and ultrafast relaxation times*

The usefulness of nonlinear optical methods for measurements that go beyond the state of the art was particularly well illustrated by J. A. Armstrong's technique for measuring picosecond laser pulses [95], whereby pulses from a mode-locked neodymium glass laser as short as 4 ps were measured, with a resolution at least one tenth of this. This is about 50 times shorter than the shortest event that can be measured by direct optical detection. The technique utilizes generation of second harmonic light from 1.06-μm Nd laser pulses incident on the surface of an oriented GaAs crystal. The orientation was chosen so that second harmonic light would be generated in reflection only if the crystal were simultaneously irradiated with orthogonally polarized 1.06-μm light beams, one of which could be delayed in time with respect to the other by mechanical translation of an optical element. The beams were then recombined on the surface of the GaAs crystal, and produced a second harmonic response only when they were made time coincident.

In another pioneering experiment utilizing picosecond pulses [96], J. W. Shelton and Armstrong measured the relaxation time of a bleachable absorber dye used to mode-lock a Nd glass laser by observing the transmission of the dye inside the mode-locked laser as a function of the delay between the saturating laser pulse and a delayed probing pulse derived from the same laser.

In subsequent years the mode-locking technique of producing picosecond light pulses was used by K. B. Eisenthal *et al.* to study a variety of processes of interest to chemists. These studies were conducted in liquid solutions (where most chemistry occurs) and included orientational relaxation of molecules [97, 98], energy transfer [99], and photoionization and charge transfer processes [100–102].

• *Gas analysis in films by laser-induced flash evaporation*

One of the first experiments to use lasers in surface analyses (now a standard procedure) was performed by H. F. Winters [103, 104]. A ruby laser beam, directed through a window in an ultrahigh-vacuum chamber onto a film, was used to evaporate the surface of the film, and the liberated gases were quantitatively analyzed by mass spectrometry.

• *Nonlinear optical spectroscopy*

Pioneering experiments in the fields of nonlinear optical spectroscopy and coherent transients have been heavily represented in the work done in quantum electronics by various groups at IBM Research.

Infrared nonlinear spectroscopy of molecular gases A series of elegant experiments in molecular spectroscopy was begun in 1969 by R. G. Brewer, who with his colleagues [105] devised various nonlinear techniques utilizing what are called Lamb dip resonances to perform ultrahigh-resolution measurements on molecular gases such as NH_2D, CH_4, and CH_3F. Normally, if one is not limited by instrumental resolution, the lineshapes of infrared and optical transitions in gases are determined by the Doppler effect. This inhomogeneous broadening can obscure structure in the spectrum resulting from molecular rotation, isotope shifts, hyperfine splitting, or the Zeeman and Stark effects. However, if the gaseous sample is placed in the standing wave field of a highly monochromatic laser beam and the frequency of the latter is tuned through one of the transitions of the molecule, a sharp nonlinear resonance (Lamb dip) occurs at the peak of the line, with a width typically one thousand times less than the inhomogeneous linewidth. This nonlinear effect lies at the base of the various techniques that Brewer and his colleagues used to obtain their results. These techniques also involved Stark and Zeeman tuning of the molecular lines, double resonance, etc. Among the results obtained were precision determinations of the electric dipole moments of both ground and excited vibrational states of CH_3F [106] and molecular rotational magnetic moments and relaxation rates in both ground and excited vibrational states of CH_4 [107, 108].

Solid state nonlinear spectroscopy One of the earliest solid state nonlinear spectroscopy experiments was carried out by J. J. Wynne [109], who measured the resonant enhancement of the nonlinear susceptibility $\chi^{(2)}$ in InSb as a function of CO_2 laser frequency. This resonant enhancement was observed as the second harmonic frequency was tuned through the bandgap. He later used tunable dye lasers to study the third-order nonlinear susceptibility $\chi^{(3)}$ in $LiNbO_3$ [110]. This susceptibility showed resonant enhancement when the difference between two dye laser frequencies was tuned near the polariton frequencies of the crystal. This marked the first time that resonances had been observed in $\chi^{(3)}$ in solids. Results similar to Wynne's were obtained at about the same time by a Harvard University group [111]. These experiments were the first applications to solids of a nonlinear technique later known as CARS (coherent anti-Stokes Raman spectroscopy).

Autoionization spectroscopy via sum frequency generation In the course of work on four-wave mixing in Sr

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vapor for vacuum ultraviolet generation [64], the output at the sum mixing frequency was found to display giant resonances corresponding to autoionization states of the Sr atom. A theory [112, 113] accounting for the shape of these resonances can be used in conjunction with experimentally determined lineshapes to give values of important atomic parameters that characterize autoionizing electronic states.

Multiphoton ionization spectroscopy Even more useful for obtaining basic data about atomic states is multiphoton ionization spectroscopy. Resonantly enhanced ionization is produced in atomic vapors when dye lasers tuned to one-, two-, or three-photon transitions irradiate the vapors. The power of this method for locating new states was demonstrated by Esherick *et al.* in 1975 in an experiment involving Ca [114]. A vast amount of data about new states (both bound and autoionizing) in Ca, Sr, and Ba [115] was subsequently collected and analyzed within a theoretical framework known as multichannel quantum defect theory (MQDT). This subject is treated in a paper by Wynne and Armstrong appearing in this issue [116].

• *Coherent optical transients and nonlinear pulse propagation in resonant systems*

Coherent optical transient techniques are pulsed resonant techniques whose analogues, for the most part, were discovered in nmr and epr spectroscopy in the late 1940s and early 1950s. The extension of these techniques into the optical domain could not have occurred without the development of lasers.

Early IBM work In the late 1960s scientists in quantum electronics were intrigued by nonlinear propagation phenomena in two-level systems. E. Courtens predicted that a giant Faraday effect accompanied by no energy loss would occur for 2π pulses in the self-induced transparency regime [117]. Similarly, the steady state propagation of π pulses in lossy and dispersive amplifiers was treated in theoretical studies [118, 119].

In an earlier paper, R. Joenk and R. Landauer solved the problem of pulse propagation in a medium with an intensity-dependent refractive index but no dispersion [120]. They noted the possibility of observing self-steepening of optical pulses and the formation of shocks. However, six more years were required for the first direct observation of self-steepening of optical pulses caused by a nonlinear electric susceptibility [121], which occurred in a resonant two-level system in the adiabatic following approximation (*vide infra*).

Adiabatic following In 1970 D. Grischkowsky introduced the adiabatic following (AF) approximation by experimentally demonstrating its importance to the understanding of the interaction between atomic vapors and near-resonant light [122]. The AF picture applies when the effective field changes adiabatically [123] and when the frequency of the light is close enough to an atomic transition for the atoms to be considered as two-level systems. Here, in terms of a vector model analogous to the one used to describe precessing spins in magnetic resonance, the state vector (pseudomoment) describing the atomic system remains aligned along the effective field. The AF model provides an important simplification that bridges the gap between the region where linear dispersion theory is applicable and the region where the full Maxwell-Bloch equations must be solved. The AF approximation provides an immediate solution to the point response problem in that the near-resonant atomic response is expressed as a nonlinear electric susceptibility, which allows comparisons with other nonlinear systems and convenient numerical integration of the wave equations. This resonantly enhanced AF nonlinearity can be enormously large compared to other mechanisms and has been demonstrated to cause the effects of self-focusing [122] and defocusing [124], self-phase-modulation, and self-steepening [121]. These nonlinear effects had no analogues in magnetic resonance. Recently, the AF model has been extended to the case of two-photon resonance. It provides a simple picture for two-photon resonantly enhanced susceptibilities [125].

An example of an adiabatic coherent effect observed earlier in nmr and widely used in magnetic resonance to achieve population inversion of spin systems is adiabatic rapid passage (ARP). In 1974, M. M. T. Loy reported the first unambiguous observation of population inversion using optical ARP [126]. The experiment involved a CO_2 laser beam and a close-lying transition of NH_3 that was adiabatically swept across the fixed CO_2 laser frequency by the Stark effect. (Stark switching was a technique previously used by R. G. Brewer and R. L. Shoemaker [127, 128] in observing *nonadiabatic* transient coherent effects; see later discussion.) In Loy's experiment, the pressure dependence of the relaxation time T_1 was also determined, making possible the first estimate of the collision-induced rotational lifetime of NH_3 in an excited band.

A two-photon analogue of ARP has recently been demonstrated by Loy [129]. Population inversion of a two-photon transition in NH_3 was demonstrated by observation of stimulated two-photon gain and emission, and the two-photon population relaxation time T_1 was measured. As for one-photon ARP [126], Stark switching with an external electric field was used. This was the first time a clear observation of this phenomenon had been made.

Nonadiabatic coherent optical transients Brewer and his colleagues were the first to observe optical analogues of a number of coherent transient effects known from nmr, including optical nutation [127] and free-induction decay [130]. Both these effects and photon echoes [127] were observed in molecular gases by Stark switching the molecules in and out of resonance with a frequency-stabilized laser. Recent development of the technique of "laser frequency switching" [39, 131], applicable primarily to dye lasers, removed the need for Stark switching and allowed the laser light to be quickly tuned in and out of resonance. The first optical free-induction decay in a solid was observed with the use of this technique [132].

The first observation of two-photon free-induction decay and two-photon optical nutation was reported by Loy [133]. The experimental result, on a two-photon transition in NH_3 with all relevant parameters known, was in quantitative agreement with the predictions of two-photon vector models [124, 134]. In a further experiment [135] in which the two-photon optical nutation effect was achieved with the use of Stark switching, the collision-induced dephasing time in a two-photon transition in NH_3 was measured. A paper by Loy on two-photon coherent transients appears in this issue [136].

• *Optically written memory schemes*
A Rhodamine 6G nitrogen-laser-pumped dye laser was used by von Gutfeld and P. Chaudhari in conjunction with exploratory work on high-speed optical memories [137]. The concept and embodiment of "reverse mode writing" based on their results was patented [138]. This technique permits information to be written in nanoseconds, rather than microseconds, as in the case of the original Ovshinsky memory [139].

Another type of optical nonlinearity, the laser-induced phase transition in the surface of SmS, was investigated by D. W. Pohl *et al.* with a view towards its potential use in optical storage [140, 141]. This material, changing from metallic to semiconducting upon intense irradiation by a laser beam, provides optical storage with excellent legibility [142].

• *Laser-induced thermoelectric voltages in thin films*
A Rhodamine 6G nitrogen-laser-pumped dye laser was used by von Gutfeld in the discovery of a transverse voltage found to exist in certain metallic thin films [143]. The effect, attributed to a thermoelectric voltage resulting from anisotropy of the film during deposition, has been incorporated into a light detector [144].

• *Forced Rayleigh scattering (FRS)*
Around 1972, D. W. Pohl became interested in the possibility of investigating second sound in solids with a light scattering technique. This phenomenon, predicted long ago [145], had just been observed at Cornell University [146]. Pohl, with his background in stimulated Rayleigh scattering, devised a new scattering scheme based on the excitation of thermal gratings by absorbed laser beams. This technique became known as *forced Rayleigh scattering* (FRS) [147]. About the same time FRS was developed independently by Eichler *et al.* [148] at the Berlin Technical University. After several years of work Pohl *et al.* detected second sound in solids with this technique [149]. Forced Rayleigh scattering has since proven to be a powerful diagnostic tool in studies with topics ranging from low-temperature anomalies in glasses to ambipolar diffusion in semiconductors. A review article on FRS in this issue describes the technique and its applications [150].

• *Infrared absorption spectroscopy of highly transparent media*
Attempts to develop highly transparent windows for high-power infrared lasers soon provided evidence of thermal runaway and lensing in window materials such as the alkali halides. The basic effect responsible was rapidly identified as multiphoton absorption; however, the details were not well understood. Systematic investigations by D. Pohl *et al.* of the temperature and frequency dependencies of the absorption helped to clarify the mechanism [151–153].

The development of a novel all-glass liquid-nitrogen-cooled CO laser by Pohl *et al.* [154a], in combination with opto-caloric techniques, allowed gas impurity detection in the sub-ppm range. In addition to its use as an excitation source in conventional opto-acoustic spectroscopy [154b], this laser was used in a newly developed method [155] called "forced Schlieren spectroscopy," which is based on deflection of a laser beam by an absorbed pump beam that heats the sample gas [156]. The Schlieren method provides high sensitivity and good spatial resolution, and avoids disturbing window effects.

• *Conventional laser spectroscopy*
Inelastic scatterings of light by vibrational modes in a medium are generally known as Raman and Brillouin scatterings. In scattering experiments a source of intense monochromatic radiation is usually used to excite the medium. These requirements are easily fulfilled by a laser. Since the advent of the laser, light scattering has become a standard technique for studying a wide variety of materials ranging from solids to gases and from semiconductors to macromolecules.

For many years G. Burns and his coworkers have used Raman spectroscopy to study solids, particularly ferroelectric materials. For example, the paraelectric-to-ferro-

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electric transition in the ferroelectric $PbTiO_3$ was studied by Raman scattering [157]. In another study, it was shown how useful information about the optical modes of vibration can be extracted even from polycrystalline powders [158].

The invention of the tunable dye laser has introduced a new dimension to light-scattering spectroscopy. One can now study the variation of scattering efficiencies with excitation wavelengths. These new kinds of light-scattering spectroscopies are known as resonant Raman and resonant Brillouin spectroscopies. P. Yu and his coworkers have used these techniques to study interactions in semiconductors between electrons and photons, as well as between electrons and lattice vibrations and defects [159–164].

Classical Fabry-Perot and photocorrelation spectroscopy with the help of laser sources is being applied to solid state problems by E. Courtens *et al.* to investigate materials with internal motion (such as liquid and plastic crystals) and to gain a deeper understanding of various phase transitions. The shape of nematic clusters in the isotropic phase of liquid crystals was determined for the first time [165], and the coupling in plastic crystals between shear waves and molecular reorientation was dramatically exhibited [166]. Earlier, plastic crystals were shown to have a remarkable Kerr effect [167]. Coupled with computer data handling, Fabry-Perot spectroscopy has become a highly accurate tool; *e.g.*, the first spectra of solids with statistically perfect fitting were recently produced using this technique [168].

In 1974, von Gutfeld *et al.* studied the fluorescence spectra of acidified dyes [169] as a function of concentration, using a streak camera to provide time resolution. In this work, evidence was provided for the presence of an excited transient dimeric species.

Lasers have also been used extensively for surface spectroscopy; *e.g.*, J. Swalen and his coworkers have measured optical spectra of molecules at surfaces with high sensitivity by new techniques using guided optical and surface waves. Both polarization and spatial information on absorbing molecules have been determined by specific experimental arrangements and by computer analyses of complex wave equations derived from Maxwell's equations. Using these techniques, they obtained new information about molecular monolayers on surfaces [170].

• *Laser-induced fluorescence detection of reactive scattering*

The most detailed information about a chemical reaction is best obtained in the laboratory when the reaction is studied as a single collisional event. Experimentally this is achieved by the use of crossed molecular beams in an ultrahigh vacuum. Under these conditions, the number of reaction products produced is very small, typically $<10^8$ molecules/cm^3-s, and cannot be detected directly. Laser-induced fluorescence (LIF) can detect molecules at concentrations <10/cm^3-s and has now made the reactive scattering experiment possible [171]. A paper by A. Luntz in this issue [172] discusses the study of chemical reactions via crossed molecular beam LIF techniques.

• *Photochemical hole burning*

The laser techniques of fluorescence line narrowing and photochemical hole burning (PHB), also referred to as site-selective photochemistry, are revolutionizing the study of the spectroscopy of molecules in the condensed phase. A new storage phenomenon based on PHB has been proposed and this technique has been used to obtain the narrowest homogeneous linewidth ever measured for an excited state of a molecule. The PHB phenomenon has also been shown to occur for two-photon photochemistry [173–175]. Two papers on this subject appear in this issue [176, 177].

• *Generation of thermoelastic waves*

Thermoelastic waves were generated in thin constrained films in the MHz range using a nitrogen-laser-pumped Rhodamine 6G laser. The feasibility of using such waves for the nondestructive evaluation of materials has been demonstrated. In addition, a study was made of ways in which the amplitude could be increased and the optical-to-elastic energy conversion efficiency could be enhanced [178, 179].

• *Laser-induced isomerization*

In 1978, D. S. Bethune *et al.* demonstrated that application of single pulses of CO_2 laser radiation could entirely convert a vapor of methyl isocyanide into its isomer, methyl cyanide [180]. The result was interpreted in terms of a laser-induced thermal explosion. Time-resolved spectra of this reaction are included in an accompanying paper in this issue [48].

• *Optical detection of pulsed nmr*

Advances in the technology of frequency stabilization of dye lasers have now provided tunable light sources whose linewidth is capable of distinguishing different nuclear magnetic resonance energy levels. This feature of the laser has allowed R. M. Shelby *et al.* to perform pulsed nmr experiments (transient nutation, spin echoes, and free-induction decay) using optical detection [181], which is inherently more sensitive than radio-frequency methods, thus extending the very powerful nmr techniques to very dilute spin systems.

• *Metastable ion spectroscopy*

B. Fan, A. Lurio, and D. Grischkowsky have used the relatively new technique of ion beam spectroscopy to make the most accurate measurements to date of the hyperfine structure of the $2\ ^3S$ and $2\ ^3P$ states of the lithium ion [182]. Their measurements agree well with theory and resolve a troubling discrepancy between previous experimental work and theoretical predictions. They used the technique of Doppler tuning the ion beam to make their measurements. The metastable ions were produced via charge exchange processes with an ion beam accelerator.

• *Time-resolved infrared spectral photography*

A new technique for photographic or multichannel photoelectric recording of broad band infrared absorption spectra with 5-ns time resolution was invented in 1978 by D. S. Bethune, J. R. Lankard, and P. P. Sorokin [47], and a paper on this subject appears in this issue [48].

• *Laser-enhanced electroplating and electroetching*

R. J. von Gutfeld *et al.* recently reported experiments on electroplating and electroetching in which a focused laser beam was used to provide large enhancement factors in the local rate of deposition or removal of material [183, 184]. Electrodeposition rates as high as $\approx 10^3$ and electroetching rates as high as $\approx 10^4$ above background rates were measured. Patterns were generated by using a cw or pulsed laser in conjunction with a scanning mirror to produce regions of plating or etching without the use of masks. The results were explained in terms of the electrochemical boundary layer and convective mass transport produced by thermal gradients.

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