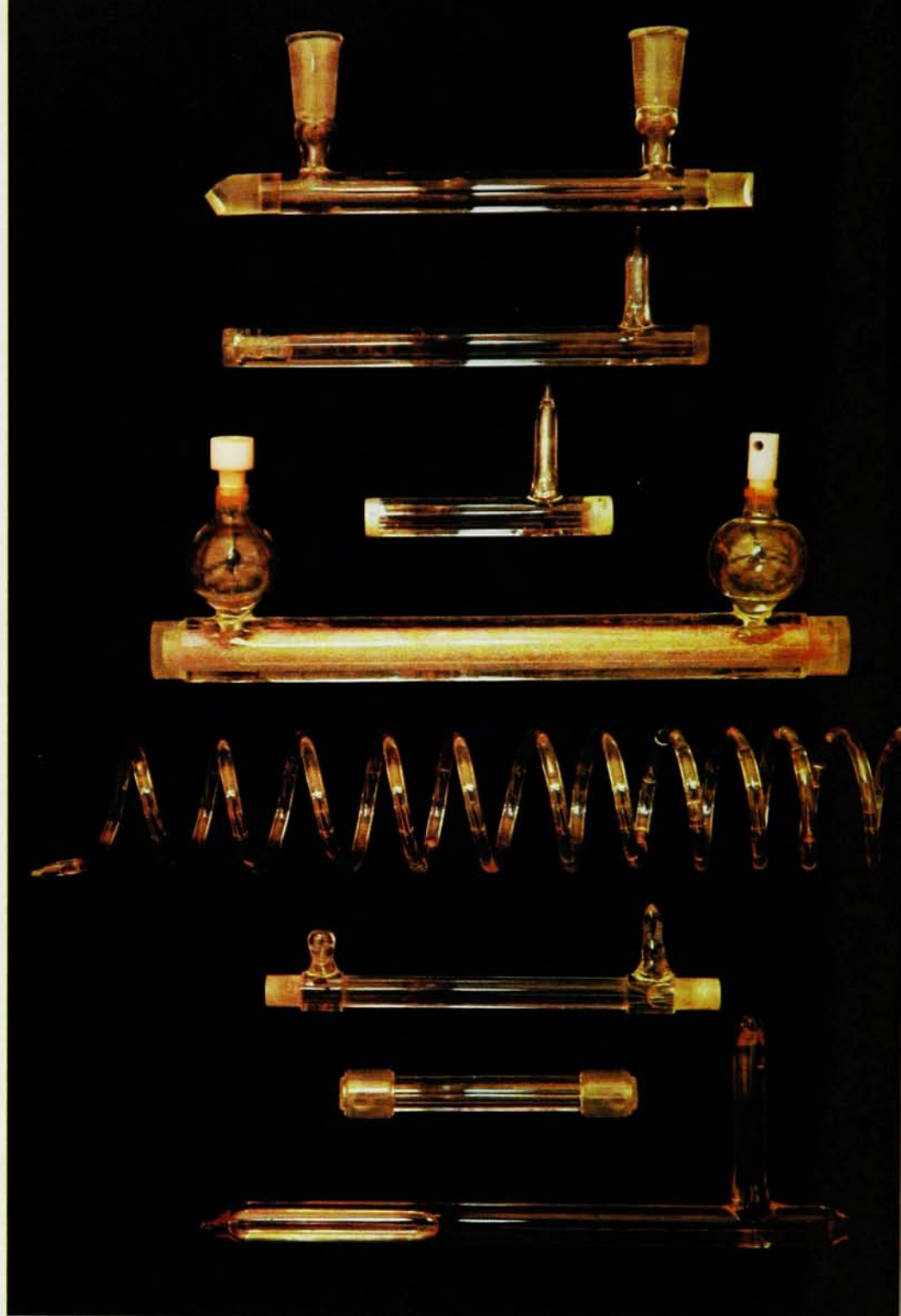


LASER-ACTIVE liquid (left) is relatively easy and cheap to prepare in large quantities. "Cells" (right) can have a variety of shapes because the gain of liquid lasers is so high. Luminescence of trivalent samarium in selenium oxychloride (bottom) is enhanced relative to its luminescence in water because radiationless relaxations are reduced in solvents containing heavy atoms.



COLOR PHOTOS BY FRED WEISS



Laser Action in Liquids

Reduction of radiationless relaxation has led to new liquid lasers that are at least equivalent in performance to pulsed crystal and glass lasers.

by Adam Heller

LIQUID-LASER RESEARCH, as many other fields in science, has oscillated between periods of activity and semi-slumber. In the period immediately following the first papers suggesting the possibility of light amplification by stimulated emission,¹ the search for liquid-laser materials was at least as active as the search for solids or gases. However, unlike research on solids and gases, research on liquids did not produce active materials. This initial failure led most of the industrial and academic laboratories to discontinue work on liquids and to concentrate on gaseous and solid-state systems, in which tremendous progress has been made over the last eight years.

In the same period a widely accepted opinion spread over the scientific community to the effect that the achievement of liquid lasers is unlikely because the scattering losses introduced by the change of index of refraction in liquids upon heating by exciting flashes of light are greater than those in solids by one or even two orders of magnitude. However, as we all know, the laws of nature do not always follow our opinions, and in 1963 Alex Lempicki and Harold Samelson² reported the first liquid laser using a red-emitting organic chelate of trivalent europium as active material, dissolved in an organic solvent. (A chelate is a compound of closed structure

formed by a metal ion and two negatively charged or uncharged groups of the same molecule.) Although some felt that the material of this first liquid laser, which was highly viscous at the operating temperature of 77°K, was actually a glass rather than a liquid, subsequent work showed that laser action is not restricted to low temperatures or to viscous liquids.

Operation of this chelate laser revived interest in liquids, and research on rare-earth chelates flourished. The period of the chelates probably reached its peak in 1964 with the suggestion of using acetonitrile as solvent,³ the subsequent spectroscopic studies on chelates⁴ and the achievement of room-temperature laser action.⁵ Despite achievement of room-temperature operation, the chelate laser never approached in performance the better gaseous or solid-state laser materials. The thresholds remained close to the upper limits of light fluxes available from flashlamps, and the outputs of power and energy were disappointingly low. An analysis of the inferior performance showed that intense absorption by the chelates limits the penetration depth of pumping radiation to a few microns. Since the active volume, and therefore the total number of ions participating in stimulated emission, is small, the laser was doomed to be inefficient.⁶ After

this inherent limitation of the chelates was realized, liquid-laser research came to a near standstill. Among the few optimists who remained in the field of chelate lasers, Erhard Schimitchek succeeded in improving the active chelates and, more importantly, showed that circulation of the liquid does not interfere with the laser's performance.⁷ Recently laser action in solutions of a chelate of a second rare-earth ion, terbium, which emits in the green, has been reported in the literature.⁸

In 1966 Peter Sorokin and Jack Lankard had reported a nonchelate organic liquid laser.⁹ They proved a point that people working in this field had suspected¹⁰ but had not previously demonstrated, namely, that it is possible to attain stimulated emission in organic molecules excited to and emitting from singlet states. One major difficulty in making organic singlet lasers is that excited molecules

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tend to cross over to metastable long-lived triplet states that not only act as sinks for excited molecules (by removing them from the cycle of excitation and emission) but may also have transitions in which the fluorescent emission is reabsorbed. Since the cross-over is generally quite rapid, one must have pumping sources of high intensity and sufficiently short rise time to achieve laser action. To meet pumping requirements Q-spoiled ruby lasers were used for excitation.^{2,9,11-13} The initial active materials were solutions of cyanine dyes. More recently, in a series of independent experiments using the second harmonic of a giant pulsed ruby at 347.2 nanometers as a pumping source, laser action has been obtained throughout the whole 400-700-nm range of the visible spectrum in aqueous and alcohol solutions of well-known fluorescent dyes.¹⁴⁻¹⁶ Advancing still one step further, Sorokin has also succeeded in using a special flashlamp¹⁷ that has extremely high intensity and sufficiently fast rise time to pump fluorescent dye solutions and to obtain laser action in several of these.¹⁶

Although these successes with the chelate and singlet lasers showed that it is possible to attain laser action in liquids, the apparent inferiority of liquids as primary laser materials remained an unsolved problem; there did not appear to be any limiting factor inherent in the nature of the liquid state. The argument of excessive change of the index of refraction with temperature was unacceptable because several liquids were known in which the changes are smaller than in solids. For example, the index of refraction of water shows little change with temperature at 4°C; in addition, water has good optical properties and a high heat capacity. Neither could the broadening of spectral lines in liquids (relative to crystalline solids) account for the inferior performance of liquids: A similar broadening in glasses has permitted us to achieve laser action in a number of materials.¹⁸ Since no obvious explanation was at hand, we initiated studies to find the causes of the poor performance of liquids. These studies, as will now be related, did indeed lead to an understanding of the causes and to the design of a new liquid laser that is at

least equivalent in its performance to pulsed crystal or glass lasers.

Radiationless relaxation

The first important clue to the poor performance of liquids appeared when we discovered that the quantum yield of luminescence of trivalent neodymium, the best performing ion in solids, was as low as 10^{-5} in aqueous solutions.¹⁹ This yield implied quenching rates of 10^8 sec^{-1} . Obviously such fast rates of depletion of the luminescent level excluded the possibility of building up a sufficient population to permit stimulated emission in water. It became evident that the key to producing better liquid lasers was in the study of radiationless relaxation processes. The study we undertook rewarded us not only with new liquid lasers but also with an understanding of the processes in which light is converted into heat or chemical energy. However exciting lasers might appear to be today, the latter reward is the more important because conversion of light into heat and chemical energy influences our daily lives profoundly. Understanding of these processes will lead to developments more important than lasers.

Strangely, the conversion processes had hardly been studied until 1960. In that year Clyde Hutchinson and Billy Magnum reported a decreased rate of radiationless relaxation from a metastable state of naphthalene upon replacement of the molecules' hydrogen atoms by deuterium.²⁰ The effect has been correctly explained as resulting from the lower vibrational energies of deuterated bonds (relative to hydrogenated bonds), the higher energy vibrations being better acceptors for electronic energy of the excited molecule. Since the experiment of Hutchinson and Magnum on naphthalene, the very general nature of their observation has been demonstrated for benzene,²¹ rare-earth ions,^{21,22} transition-metal-ion chromium,²⁴ and for the actinide uranyl ion.²⁵ In all these experiments the substitution of hydrogen by deuterium slowed down the rates of radiationless relaxations, thus increasing the luminescent lifetimes and the quantum yields of luminescence.

In retrospect, the strong dependence of the rate of radiationless relaxation on the energy of acceptor vibra-

tions appears to be hardly unexpected because perturbation theory tells us that the more closely we match energy a donor can donate with energy an acceptor can accept, the faster the rate of energy transfer becomes. By increasing the energy of vibrations we necessarily improve the overlap between vibrational energy (or its overtones) and larger electronic transitions of electronically excited species. With this simple idea of overlap requirement, we can predict that, for systems of similar radiative lifetimes, quantum yields are high when the energies of electronic transitions between excited and ground levels are much higher than the energies of the highest vibrations in the system, and that quantum yields are low when the two approach each other.

This general tendency is easily observed when we survey the vast number of organic liquid luminescent systems in most of which the highest energy vibrations (due to the stretching of C-H, O-H and N-H bonds) are similar. High-quantum-yield systems generally have short lifetimes and emit in the ultraviolet to blue region. Very few are long lived and luminesce in the red or infrared. Similarly, in inorganic compounds high quantum yields of luminescence are observed either in systems with large gaps between the metastable level and the upper level of the ground multiplet or in systems free of high-energy vibrations. Thus aqueous Gd^{3+} with a $32\,000\text{-cm}^{-1}$ separation is hardly quenched by OH vibration of 3600 cm^{-1} , while Nd^{3+} , in which the separation is only 5300 cm^{-1} , has a quantum yield of about 10^{-5} in water.¹⁹

After it was evident that radiationless relaxations occur by transfer of electronic energy to high-energy vibrations, we sought to determine the mechanism of the transfer. Electronic energy could be transferred to vibrations of several modes of several molecules, to several modes of a single molecule, or to one mode of a single molecule. The first two possibilities conform with selection rules for a harmonic oscillator since they allow each vibrational mode to undergo only transitions from one quantum state to the next higher one. Energy transfer to several vibrational modes, however, requires breaking the quantum of en-

Chelate
singlet states

Chelate
triplet states

Eu^{3+}
levels

Nonradiative processes

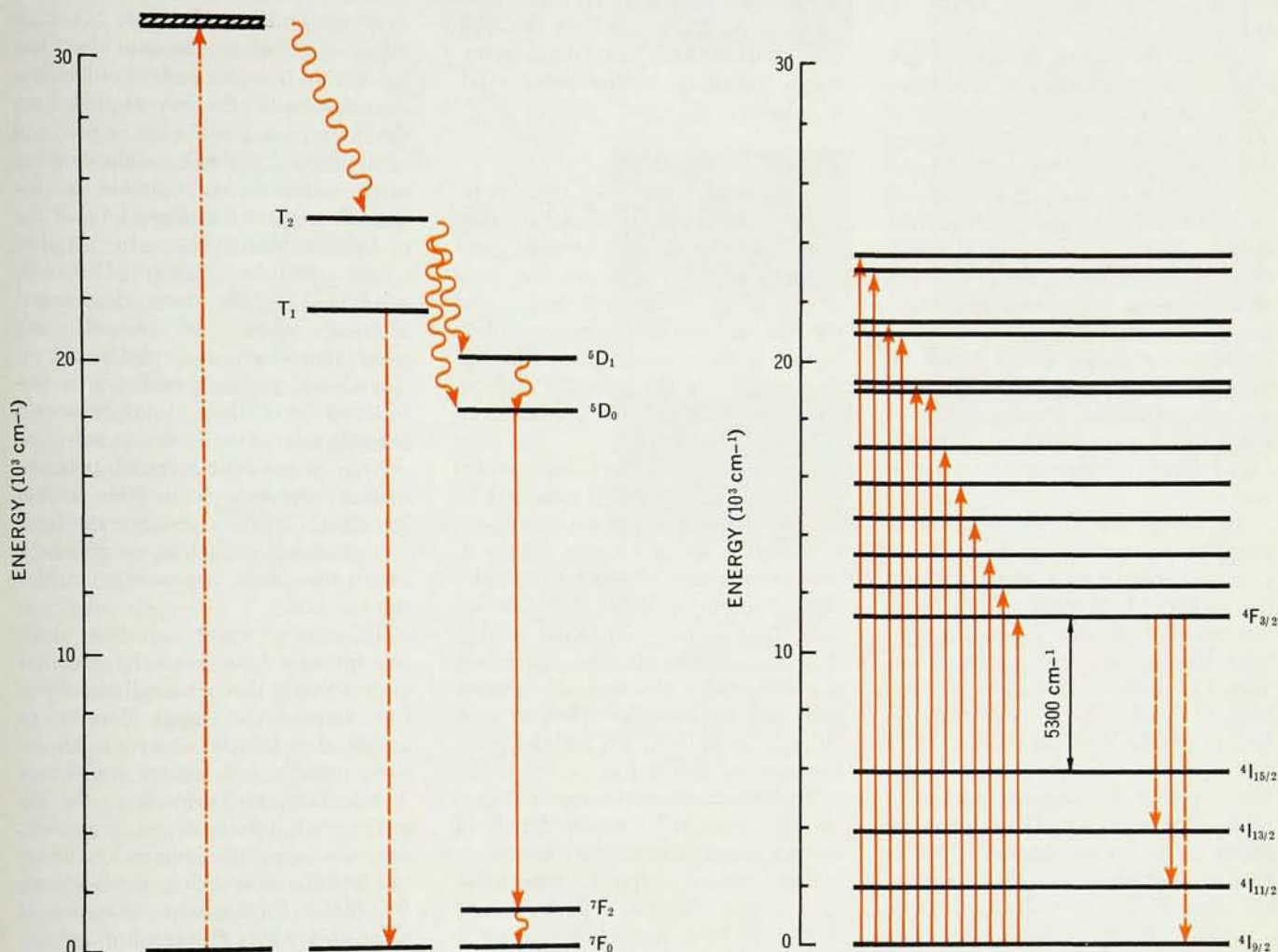
Phosphorescence

Fluorescence

Absorption

ENERGY-LEVEL SCHEMES for the europium chelate (left) and ionic neodymium (right) liquid lasers. Optical pumping processes in the two lasers are different. In the first laser, the chelate molecule is excited to a singlet state and relaxes to be the lowest triplet state. The europium ion is then excited by intramolecular energy transfer from the triplet state. Neodymium is directly pumped to higher levels by ion excitation, followed by radiationless relaxation to the $^4F_{3/2}$ metastable level.

—FIG. 1



ergy of the donor into several smaller quanta, which is equivalent to assuming a series of virtual states in the donor, each donating its energy to a different vibrational mode. The third possibility, energy transfer to one vibrational mode of a molecule, merely requires anharmonicity in the accepting vibration; this mechanism could permit transitions to other than neighboring levels and therefore acceptance of greater energies.

To find the transfer mechanism, we determined the dependence of radiationless-relaxation rates of a group of

ions on the hydrogen concentration of their heavy-water solutions. These solutions are unique since they have only chemically identical but vibrationally different OH and OD bonds. We found that the rates increase in a rigorously linear way with the concentration of OH bonds present, establishing that individual OH bonds act as energy acceptors. No cooperative effect between various OH groups was found: All the electronic energy of each excited ion was transferred to vi-

brations of one OH bond of one water molecule. The OH bonds undergo jumps of as much as five vibrational levels, thus "heating" the bond to vibrational temperatures that could be reached under equilibrium conditions only above $20\,000^\circ\text{K}$.²⁶

The fact that radiationless relaxations depend on the anharmonicity of vibrations explains the decrease in quantum yields of luminescence at increased temperatures: Potential wells are closest to harmonic at their deepest portions and become more and

more anharmonic at higher energies. The higher the temperature, the more vibrationally excited molecules there are. The more vibrationally excited molecules there are, the larger the population of molecules with more anharmonic vibrations and the faster the rates of energy transfer to vibrations that accept large packets of energy, that is, which undergo jumps of $\Delta\nu > 1$.

Most of the liquids one encounters in the laboratory contain hydrogen and therefore have stretching vibrations of considerably higher energy than the highest vibrational energies in many common hydrogen-free inorganic crystals and glasses. This fact explains why, in spite of great initial effort on liquid lasers, the first round of the race for high-power and high-energy lasers was won by solids. The liquids were doubly handicapped by their vibrational energies that not only induced radiationless relaxations but also made them opaque in the near-infrared region, where many laser-active ions emit.

To overcome these undesirable properties, we searched for solvents that do not have light atoms and the consequent high-energy vibrations. The number of these solvents is considerable. However, since the solvent must also have a high dielectric constant to dissolve ionic compounds, selenium oxychloride was chosen. This solvent has a sufficiently high dielectric constant to dissolve rare-earth salts at the concentrations required in lasers. The highest energy of vibration of this solvent is only 955 cm^{-1} ,

a small value compared with the 5300-cm^{-1} minimum possible energy loss in the deexcitation of trivalent neodymium. Because of poor overlap between vibrational and electronic transitions, radiationless relaxation is not significant, and the ion luminesces in this solvent more intensely than it does not only in neodymium-doped laser glasses but also in many laser crystals. As a result the solutions also show desirable laser characteristics that compare favorably with those of the better solid-state lasers.

The new liquid lasers

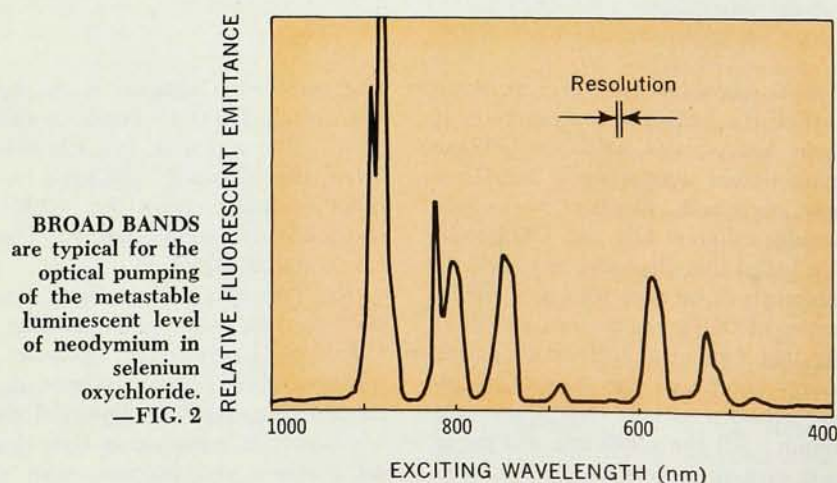
Two types of liquid-laser systems resulted from our study of radiationless relaxation. Both use trivalent neodymium as the active ion but vary greatly in their chemical design. In the first we have an inorganic solution in which ionic neodymium salts are dissolved.²⁷ In the second a molecular complex of neodymium is dissolved in an organic solvent.²⁸

Inorganic liquid lasers contain neodymium, selenium oxychloride and either tin tetrachloride or antimony pentachloride. As previously discussed, we use selenium oxychloride because of the need for a solvent that does not have high-energy vibrational modes, that is, is made of relatively heavy atoms. Although several solvents meet this requirement, selenium oxychloride in addition has a high dielectric constant and is transparent in the 400–3000-nm spectral range that covers excitation and emission bands of several potential laser-active ions.

The second solvent component

added, either tin tetrachloride or antimony pentachloride, makes the liquid a powerful acid in which the solubility of rare-earth ions is greatly increased. Increased acidity, however, is only part of the function of the added chlorides; they also prevent extensive self-quenching in trivalent neodymium solutions. Such self-quenching has been shown to occur when the neodymium ions are sufficiently close to each other. (The mechanism for this quenching consists of simultaneous deexcitation of the ion excited from the metastable level to the upper level of the ground multiplet, and excitation of the second ion, initially in the ground state, to the upper level of the ground multiplet.²⁹) In liquids, where diffusion takes place, self-quenching is far more detrimental than in solids. To prevent such quenching, chemical conditions are required under which each ion is surrounded by a shell of selenium-oxychloride solvent molecules (a solvation shell). When fully solvated, two ions cannot approach each other within less than 1.5 nm, a distance too large to permit self-quenching or polymerization that leads to precipitation of a solid.

To ensure intact solvation shells one must exclude from the chemical system anions that are small and therefore have high charge density, or anions that coordinate rare-earth cations strongly and replace a molecule of selenium oxychloride from the solvation shell. Such anions, if present, attract a second neodymium ion, bringing it within quenching distance from the first. Furthermore, presence of these anions may also result in precipitation by polymerization. With large noncoordinating anions like $\text{SnCl}_6^{=}$ or SbCl_6^- (anions formed from the addition of tin tetrachloride or antimony pentachloride to selenium-oxychloride solutions) solvation shells remain intact and self-quenching is practically eliminated. Such large anions, which ensure intact solvation shells, diminish not only the probability of self-quenching but also the probability of energy transfer between various dissolved rare-earth ions. When energy transfer is desired, presence of small coordinating anions, such as the chloride anion, is beneficial; the anion replaces a solvent molecule from the solvation shell



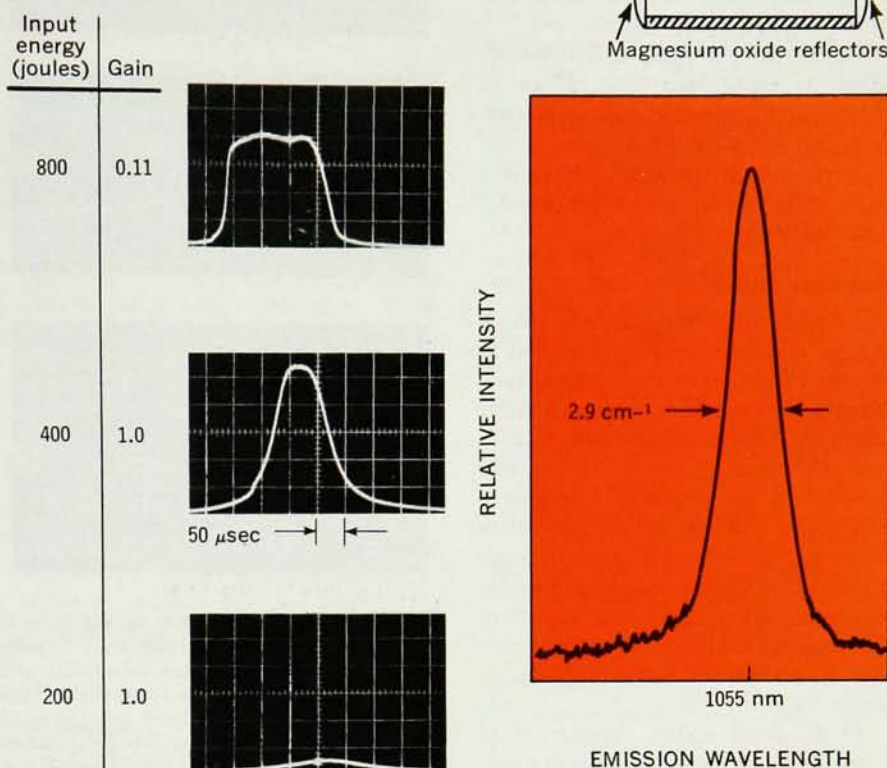
and attracts other cations within the radius of interaction for energy transfer. The distance between two rare-earth ions bridged by a chloride ion is now less than 0.5 nm.

Design of the second type of liquid laser, also based on prevention of radiationless relaxations, did not follow the total elimination of high-energy vibrations from the system, but relied on exclusion of any such vibration from the immediate proximity of the laser-active neodymium ion, and on the decrease in the rate of radiationless relaxation with the distance between the ion and the nearest bond of high-energy stretching vibration. The active ion was incorporated into a molecular complex in which it was shielded to prevent self-quenching. The solvent was so chosen that if solvation of the ion took place, high-energy vibrations of the solvent molecule would be as far as possible from the active ion. The specific compound in the laser experiment was formed by the addition of phenanthroline to neodymium pentafluoropropionate, and the solvent was deuterated dimethylsulfoxide. Although the laser-active molecule has eight high-energy carbon-hydrogen stretching vibrations ($\sim 3000\text{ cm}^{-1}$), none of these is in the immediate proximity of the rare-earth ion.

Quantum yield of neodymium luminescence is higher in the first discussed inorganic (selenium oxychloride) system from which high-energy vibrations are completely excluded. Thus inorganic liquids have superior performance although room-temperature laser action is also obtained in organic liquids. Consequently, the following discussion will be limited to the characteristics of these.

Performance

The gain of inorganic liquid lasers is high. An estimate of the cross section for stimulated emission is $5 \times 10^{-20}\text{ cm}^2$ per ion. This cross section is not much higher than that in glasses,³⁰ yet it implies higher gains. In glasses and certain crystals ions can occupy different sites, absorbing and emitting at different wavelengths. When the solid is excited, energy is distributed between different groups of ions. Each group lases independently unless the laser is operating at extremely high power levels. For reasons explained



EMISSION from the ionic neodymium liquid laser collapses from a spontaneous line width of 180 cm^{-1} to 2.9 cm^{-1} when stimulated emission takes place. A confocal cell, with MgO scattering-reflector coatings and roughened walls, assures that the laser's emission line width will not be determined by narrower preferred cavity modes. (Wall roughening prevents modes propagating by total internal reflection at the liquid-quartz interface.) The emission collapse to one line indicates that neodymium ions in the liquid occupy sites indistinguishable from each other. The liquid here does not show relaxation oscillation ("spiking").

—FIG. 3

in the next section, ions in a liquid are indistinguishable from each other, and, unlike ions in solids, they all contribute to the same pool of excited population. Since the concentration range over which we observe laser action extends from 10^{19} to 5×10^{20} ions/ cm^3 , initial gains at hypothetical total inversion are between 1 and 40 dB/cm. In a similar hypothetical solid with, for example, 10 different equally populated sites the gain at total inversion would be between only 0.1 and 4 dB/cm.

As a result of higher gain in liquids, stimulated emission has been obtained not only in optical-quality cells with reflectors but also without reflectors in a collection of odd vessels that includes test tubes, bulbs, as well as straight and spiral glass tubes.

Thresholds in these "cells" are in the range 8–50 joules (for flashes from standard flashlamps of 20- μsec rise time and 200- μsec pulse duration).

Although we attribute low thresholds in these "lasers" to spiraling modes propagating by total internal reflection from (higher index) liquid-(lower index) glass or quartz interfaces, laser action can also be obtained in axial modes in cells without reflectors (except for Fresnel reflection from the windows) below 300 joules.³¹ With proper reflectors the threshold for oscillations in axial modes in 10-cm cells falls to 2 joules. When magnesium-oxide scattering reflectors are used,³² the emission narrows from 180 cm^{-1} to 2.85 cm^{-1} and a single burst of stimulated emission is obtained. Also, if precautions are taken

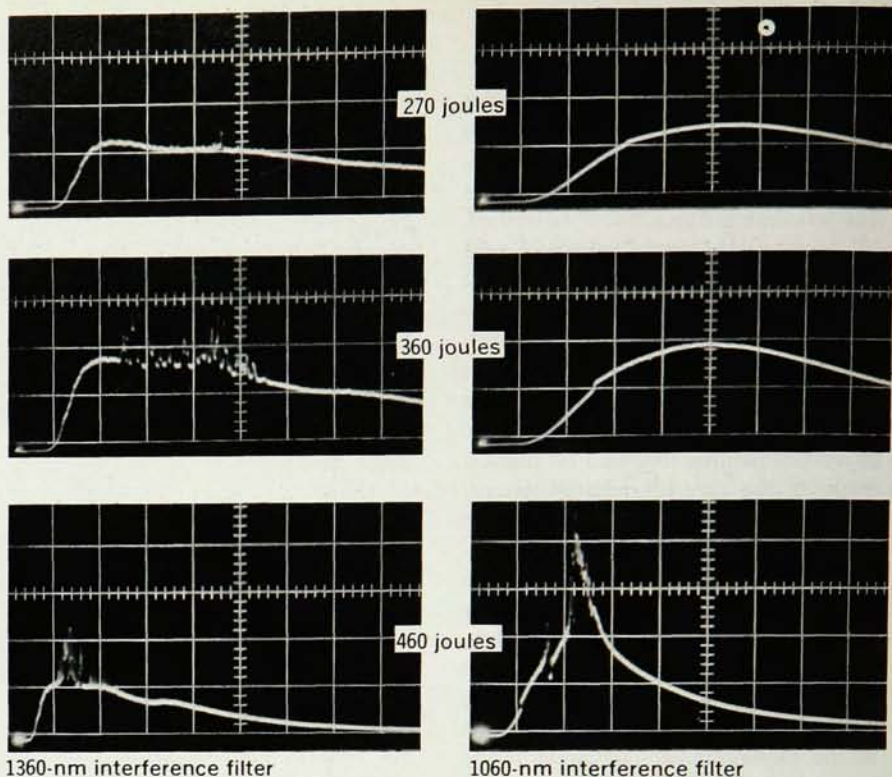
to prevent spiraling modes and Fresnel reflection, the excited liquid emits an intense burst of monochromatic light without spiking.³¹

Energy output and conversion efficiencies are higher than those in crystals and similar to those in glasses. Peak powers obtained are above 10^7 W (without Q-switching), exceeding peak powers of all other non-Q-switched lasers.

Motion in liquids

The features that make liquids unique as laser materials are due to motion in liquids. Because of this motion, fast, diffusion-controlled, energy-transfer reactions between different species may take place. Such reactions can be used to "cross pump" laser-active ions with added sensitizers, thus increasing the effective optical pumping bands. However energy transfer from laser-active species to impurities that do not luminesce, or luminescence that is useless for laser purposes, is also enhanced.

As discussed earlier, three types of quenching are encountered: quenching by molecules with high-energy vibrations, self-quenching and quenching by impurities. The lowest acceptor or quencher concentrations at which either energy transfer or quenching phenomena become effective can be as much as three orders of magnitude lower than concentrations for similar energy-transfer reactions in solids, in which energy-carrying species and energy-acceptor species are unable to diffuse. Since quenching reactions can be efficient at very low quencher concentrations that in practice are difficult to exclude, any liquid-laser design must provide not only for reducing quenching by high-energy vibrations but also for reducing self-quenching and quenching by impurities. Our solution to this problem is generation of an envelope of protective molecules around the laser-active ion, using solvent molecules in the inorganic laser, and coordinating anions as well as uncharged molecules in the organic neodymium laser. An alternative solution would be to reduce the rate of possible quenching reactions between the species by increasing the viscosity. This approach, however, leads ultimately to glasses. It is of course not



1360-nm interference filter

SIMULTANEOUS LASER ACTION in the $F_{3/2} \rightarrow I_{11/2}$ (1056 nm) and in the $F_{3/2} \rightarrow I_{13/2}$ (1330 nm) transitions of ionic neodymium can be achieved by using mirrors selectively reflecting light at 1330 nm. Since both of these transitions have their origins in the same metastable level, stimulated emission at 1330 nm (upward spiking) also causes stimulated depopulation of the metastable level, shown in the figure by downward spiking for the 1056-nm emission. Beyond a certain threshold laser action takes place at both wavelengths and both upward and downward oscillations are observed.

—FIG. 4

necessary to provide protection to laser-active species with radiative lifetimes shorter than the quenching time. Thus the earlier-mentioned singlet lasers, whose lifetimes are in the nanosecond range, need no protection whatsoever.^{9,11-16}

Another effect that results from increased motion in liquids is that laser-active cations experience a rapidly changing environment and thus a rapidly changing crystal field. This effect can be a disadvantage with ions for which desirable laser properties are obtained only in a site of a particular symmetry (for example, trivalent chromium, which requires the unique trigonal site offered by aluminum oxide in ruby). However in other ions, such as rare earths, the rapidly changing environment actually improves laser characteristics. Because of the changing environment both emission bands and absorption bands broaden. While the broadening of the emission band increases thresholds for laser action, the broad-

ening of absorption bands lowers these. The broadening also increases the conversion efficiency of the laser. In solutions containing neodymium both emission and absorption bands broaden to cover wavelength ranges similar to those in laser glasses. Consequently their conversion efficiency also matches that of the better laser glasses.

Although optical pumping characteristics of liquid lasers are as desirable as those of glasses, their stimulated-emission characteristics show advantages exhibited only by crystals with a single site. The reason is that in glasses and in certain crystals neodymium ions occupy a large number of different sites, each of which is defined by a different chemical environment and thus by a different radiative lifetime and emission spectrum. Evidence comes from the fact that fluorescent decay in glasses is not exponential. When the rate of optical pumping in glasses is increased, laser action takes place over an increasingly

broad spectral range, and the width of the output band often exceeds 100 cm^{-1} . Also, in certain single crystals, laser action can take place in more than one spectral line. Liquids are different in this respect. Ions change their environment with each vibration of a solvating solvent molecule or at rates of 10^{12} – 10^{13} sec^{-1} . These rates are fast not only relative to ion decay rate, which is in the range 10^3 – 10^4 sec^{-1} , but also relative to the time it takes photons to sweep through a cell that is a few centimeters long. By the time the beam is reflected, the population of ions emitting at the peak of the fluorescence band, which has been depleted by stimulated emission, is reestablished and the photon beam at the initial frequency is further reinforced. Thus it becomes impossible to differentiate between ions experiencing different instantaneous environments by emission experiments: All ions have the same apparent lifetime, making decay rigorously exponential, and all ions continue to emit in one or in a few closely spaced and narrow spectral lines (defined by cavity modes) however vigorously the liquid solution is pumped optically. The other important result of site uniformity in liquids—the single pool of excited ions that leads to unusually high gains—has already been discussed.

We would like to emphasize that, unless the broader emission bands are compensated for by broader effective pumping bands, the advantages of the nonuniform site caused by motion in liquids cannot be realized. In chelate lasers, for example, pumping bands originate in broad and intense singlet-singlet transitions of the organic part of complex molecules, which are hardly affected by the state of aggregation or by the local site symmetry that the molecule as a whole experiences. In passing from the solid to the liquid state in chelate systems, effective pumping bands remain unchanged, while emission bands broaden. Because of this broadening, a good part of the effort in liquid-chelate-laser research has been devoted to generating conditions under which the central rare-earth ion experiences a fixed quasi-crystalline field and emits only in a few narrow emission lines. The quasi-crystalline

environment is not required or desired in the neodymium-doped liquid lasers: Broadening of pumping bands by nonuniformity of instantaneous sites in liquids is now an advantage.

Liquid lasers have obvious inherent advantages over solid-state lasers: They cannot be permanently damaged even at extremely high power levels of about 10^{10} W that have been generated by, but permanently damage, laser glasses in mode-locked operation.³³ They can be circulated and cooled in heat exchangers. Their average power output is not dependent on heat dissipation by thermal conductivity. Finally the cost of their preparation is a small fraction of the cost of solid materials.

Liquids are now joining solids and gases as laser materials of equal importance. Development of liquid-laser technology, which will lead to the realization of their inherent advantages over gases and solids, has just started.

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