

CHEMICAL LASERS

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A LITTLE OVER A DECADE HAS ELAPSED since the demonstration of the first laser by Maiman. The intervening time period has seen many developments in laser technology. Lasers whose spectral outputs span the ultraviolet to far infrared have been built with a variety of optically-active mediums—gases, liquids, crystalline solids, and semiconductors. Power outputs have advanced from a few microwatts cw produced by the first He-Ne laser to over 60,000 watts cw produced by the CO₂ gas dynamic laser. Energy pulses exceeding 1000 joules have been extracted from modern glass lasers in contrast to the millijoule pulses delivered by Maiman's first ruby laser. Novel techniques for pulse shortening (Q-switching and mode locking) have been used to generate transient peak powers of 10¹³ watts. Many new interesting physical phenomena are observed at these intense electrical fields.

Laser scientists have been particularly motivated to develop high-power lasers with an eye toward efficiency and size. After all, no one gets too concerned about the 100 watts used to power a 0.1 watt output He-Ne laser. But at the tens of kilowatts laser output level, this inefficiency cannot be ignored.

Extremely high powers have been obtained from large solid-state lasers, particularly glass, containing trivalent neodymium ions. However, the high-power densities obtained in these systems

are reaching a limit set by the durability of the glass. The optical pumping process is inherently inefficient and yields conversion efficiencies of input electrical energy to useful output radiant energy of a few percent at best; a large part of the waste energy appears as heat. These difficulties can be circumvented in a gas laser where the waste energy which appears as heat can be convectively removed. Further, there are several gas laser molecules with radiative transitions between low order vibrational levels; this allows the radiated photon energy to be an appreciable part of the energy required to pump the system to the upper laser level. Such a lasing system is potentially capable of operating simultaneously at a high efficiency and high power.

Carbon Dioxide Laser Mechanisms

The most promising of the molecular gas lasers are those that use carbon dioxide as the optically-active molecule.^{1, 2} Since the CO₂ lasing mechanism forms an essential step in our chemical laser systems, it is worthwhile to review the physics of this particular molecular laser.

Carbon dioxide is a simple polyatomic molecule

¹ C. K. N. Patel, "Continuous-Wave Laser Action on Vibrational-Rotational Transitions of CO₂," *Phys. Rev.* **136**, Nov. 30, 1964, A1187-A1193.

² C. K. N. Patel, "Selective Excitation through Vibrational Energy Transfer and Optical Laser Action in N₂-CO₂," *Phys. Rev. Letters* **13**, Nov. 23, 1964, 617-619.

Molecular gas lasers are the most promising sources of high-efficiency, high-energy coherent radiation. The chemical laser, which can produce radiation with little or no external excitation energy, has begun to emerge as an important class of laser systems.

and the details of its molecular structure are well established. Polyatomic molecules are classified according to the relation between moments of inertia about the principal axes of symmetry of the molecule when considered as a rigid rotating body. If the three moments of inertia are different, the molecule is called an asymmetric top; if two of the principal moments are equal, it is a symmetric top. One of the special cases of the symmetric top is the so-called linear molecule in which the atoms lie along a straight line giving rise to two equal moments and a third of approximate zero order. Carbon dioxide is a linear molecule, with the oxygen atoms arranged symmetrically about the carbon atom as shown in Fig. 1.

The relative motions of the atom in the molecule are characterized by rotation and vibration about its center of mass. Both of these motions are quantized. The vibrations of a polyatomic molecule can be described in terms of the normal vibrations of a simple harmonic oscillator. The linear CO₂ molecule has symmetric stretching (ν_1), bending (ν_2), and asymmetric stretching (ν_3) modes as illustrated in Fig. 1. The vibrational modes have a set of allowed energies which are represented in the energy level diagram of Fig. 2. The allowed rotational energies are closely spaced compared to the vibrational energies and can be described by superimposing a fine structure of rotational levels on each vibrational level.

Radiative transitions between these vibrational-rotational levels give rise to a band spectrum.

The strongest CO₂ laser line arises from the vibrational-rotational transition from the $\nu_3 = 1$ level (001) to the $\nu_1 = 1$ level (100). The radiation emitted is approximately a wavelength of 10.6 μm in the infrared portion of the spectrum. In this wavelength range, the atmosphere has negligible attenuation; this is an important factor in both the construction of CO₂ lasers and their possible applications.

When thermal equilibrium exists, the population of the upper and lower laser levels are governed by the Boltzmann factor so that

$$\frac{N(001)}{N(100)} = \frac{g(001)}{g(100)} e^{-\Delta E/kT}$$

where $N(\nu_1, \nu_2, \nu_3)$ is the population of a particular level, $g(\nu_1, \nu_2, \nu_3)$ is a statistical weighting factor, ΔE is the energy difference between the energy states, k is the Boltzmann constant, and T is the system temperature. Obviously, at equilibrium $N(001) < N(100)$.

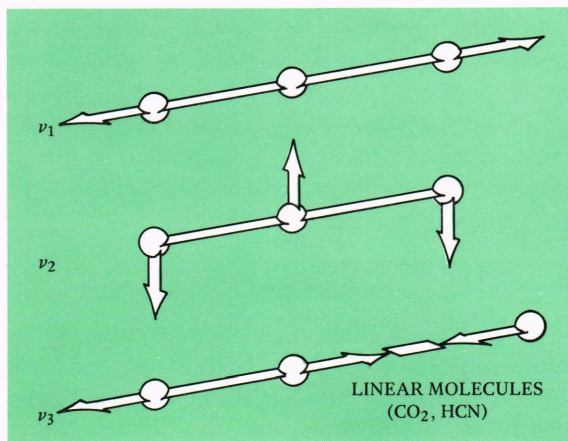


Fig. 1—Normal vibrations of linear laser molecules.

When radiation interacts with this molecular system, photons at the resonant frequency ($\nu_3 - \nu_1$) can induce radiative transitions to occur between these two energy levels. A photon can be absorbed by a molecule in the lower energy state thereby “lifting” the molecule to the upper energy level; or it can induce a molecule in the upper energy level to emit a second photon and fall to the lower energy level. The second process is called “stimulated emission” and this emitted photon is coherent, i.e., in phase with the stimu-

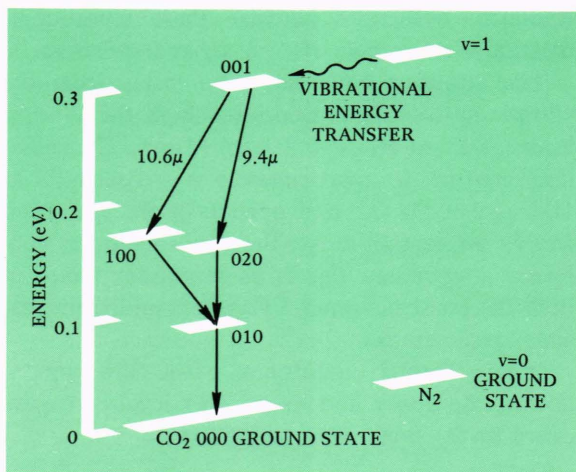


Fig. 2—Energy level diagram of CO₂ laser.

lating radiation. The absorption and stimulated emission processes have equal probability as shown by Einstein. It follows therefore that a beam of resonant radiation will increase in intensity or be amplified only if $N(001) > N(100)$, that is the population ratio must be inverted—a laser amplifying medium is not in equilibrium.

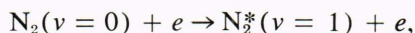
In order to achieve laser action, external excitation of some kind is necessary to promote the inverted nonequilibrium population. This process is called “pumping.” Three useful techniques have been employed to achieve inversion in CO₂ lasers: electrical gas discharge, rapid adiabatic expansion, and chemical reaction.

Electrical Discharge CO₂ Lasers

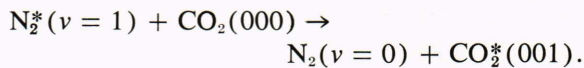
In conventional electrical discharge lasers, the upper laser level is excited by inelastic collisions with free electrons accelerated by the externally-applied electric field



where the asterisk indicates that the CO₂ molecule is now excited to a higher energy state. However, since the other vibrational levels (for example, the lower laser level) can be similarly excited, this process is not particularly efficient. To circumvent this problem, nitrogen is added to the CO₂. In such a mixture, the N₂ is vibrationally-excited by electron impact

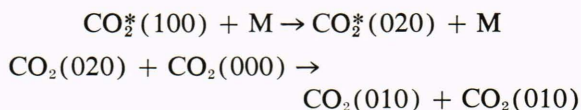


and, in turn, can preferentially excite the CO₂ upper laser level,



This latter process is very rapid and efficient because of the close match (resonance) between the two vibrational levels as illustrated in Fig. 2. With a judicious choice of gas density and electric field strength, one can funnel nearly 80% of the electrical discharge power into the CO₂ upper laser level. This feature, coupled with the nearly 40% quantum efficiency (i.e., the fraction of the upper laser level energy that is radiated—see Fig. 2), provides a maximum electrical-to-laser efficiency of about 30%—one to two orders of magnitude greater than in most other lasers.

The maintenance of a population inversion in CO₂ depends not only on a source of energy to excite the upper laser level, but also on relaxation processes to depopulate the lower level. In CO₂ this is effectively accomplished in resonant collisional processes



which provides an avenue to remove molecules from the (100) energy level. In the above reaction M is any colliding partner. Rapid depopulation of the (010) level by collisions with other gas molecules is essential for sustained efficient, high-power laser operation, i.e., $\text{CO}_2(010) + \text{M} \rightarrow \text{CO}_2(000) + \text{M}$. A variety of gases including H₂, H₂O, He, and CO are effective in relaxing the (010) level. Many of these gas additives also rapidly depopulate the upper laser level (001) and so cannot be used. Helium with a somewhat smaller rate constant is generally used for this purpose since it does not seriously affect the upper level. Energy finally deposited in the ground state appears as heat. Within a given vibrational band, all of the rotational levels are very rapidly brought to thermal equilibrium because of extremely fast rotational relaxation rates.

The above discussions have ignored three deleterious effects that affect the overall laser efficiency. First, the upper laser level is also relaxed by collisions with all other molecules, representing a loss in potential laser radiation. Second, as the gas temperature increases, relaxation processes are markedly accelerated. And, finally, this thermalization process increases the chance of re-populat-

ing the lower laser level by inverse collisions of the type discussed above.

The typical electrical discharge CO₂ laser is a relatively simple system as shown in Fig. 3. A glass laser tube, surrounded by a water jacket, of about one meter length is sealed at the ends by infrared transmitting windows such as NaCl. The windows are set at the Brewster angle to minimize reflection losses. In the usual cw laser, electrodes of molybdenum, nickel, or stainless steel are used to establish a discharge of about 5 kV and 20 mA. The conversion efficiency of input electrical power to output radiation can approach 20% with an output power of 80 W/m discharge length at optimum output coupling. The optical cavity is generally defined by two large radius of curvature mirrors with at least one of these being a partially transmitting mirror to couple power from the cavity. The transmitting mirror for 10.6 μm radiation is usually a germanium substrate coated with thin dielectric layers constructed to give the desired amount of transmission. The amount of power generated by an electrical laser depends on the total gas pressure, the partial pressures of the various constituents, gas flow rate, discharge current, and wall temperature. A typical gas mixture would be CO₂:N₂:He::1:1:6 of a total pressure of approximately 20 Torr (760 Torr = 1 atm) in a flowing system.

The amount of power obtained from an electrically-excited CO₂ laser depends on the number of excited molecules in the system, and hence, on the pressure. Since the relaxation times are increased with gas pressure and temperature, a continuously operating electrical discharge laser is limited to operation at relatively low pressure. A pulsed electrical system is capable of operating at high pressures with the 10.6 μm radiation pulse length being determined by the vibrational re-

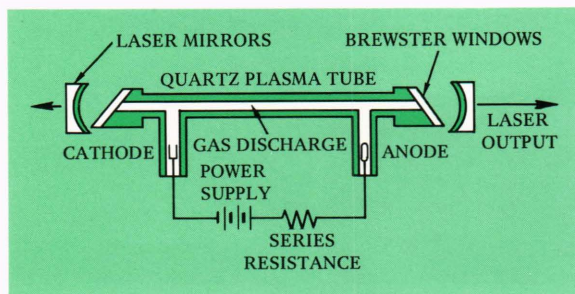


Fig. 3—Typical electrical discharge gas laser system.

laxation times with an inverse dependence on pressure. However, at high gas pressures, the voltages required to cause breakdown between electrodes spaced at opposite ends of the usual laser tube are quite high. A recently developed laser obtains breakdown at atmospheric pressure by use of extended electrodes with the field transverse to the optical axis.³ This so-called Transverse Excited Atmospheric (TEA) laser requires relatively modest excitation voltages although the exciting pulse must be of short time duration to prevent the diffuse glow discharge from evolving into an intense arc. The original TEA laser consisted of a series of pin cathodes opposite to a simple bar anode as illustrated in Fig. 4. More recent developments with these lasers have centered around electrode systems capable of establishing a more uniform large volume discharge. Typical output pulses from these TEA lasers are of 50 to 100 nanoseconds duration with peak powers on the order of ten megawatts.

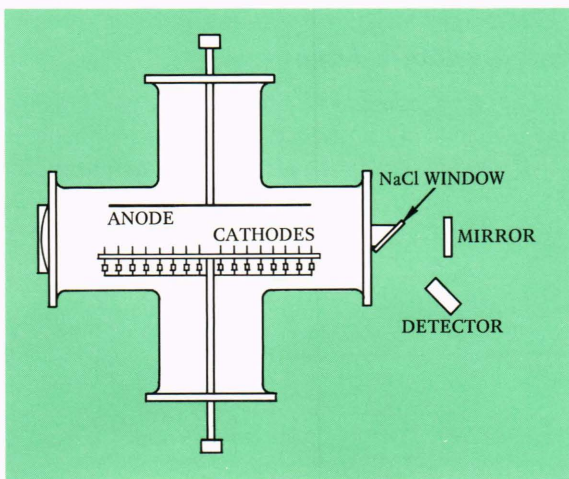


Fig. 4—TEA CO₂ laser.

The common limitation on the electrically pumped CO₂ lasers is the amount of input energy that is eventually converted to heat tending to increase relaxation rates and the population of the lower laser level. In the typical laser configuration of a long, thin cylinder as shown in Fig. 3, the thermal energy is removed from the system by diffusion to the walls. This process severely limits the average power that can be dissipated. However, by using high speed gas flow to obtain cool-

³ A. J. Beaulieu, "Transversely Excited Atmospheric Pressure CO₂ Lasers," *Appl. Phys. Letters* 16, June 15, 1970, 504-505.

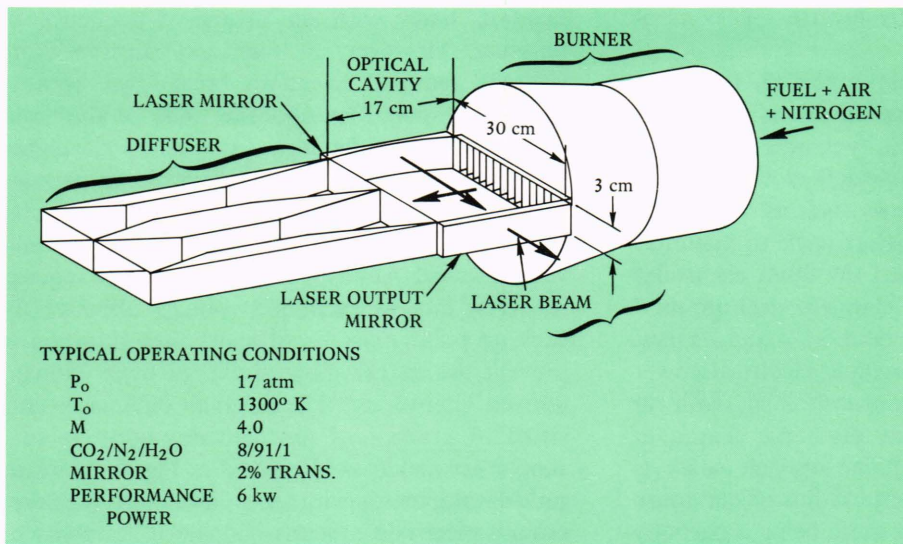


Fig. 5—Gas dynamic laser.

ing, the average power can be increased several orders of magnitude. Fast flow CO_2 lasers capable of producing tens of kilowatts from a relatively small system have been reported.

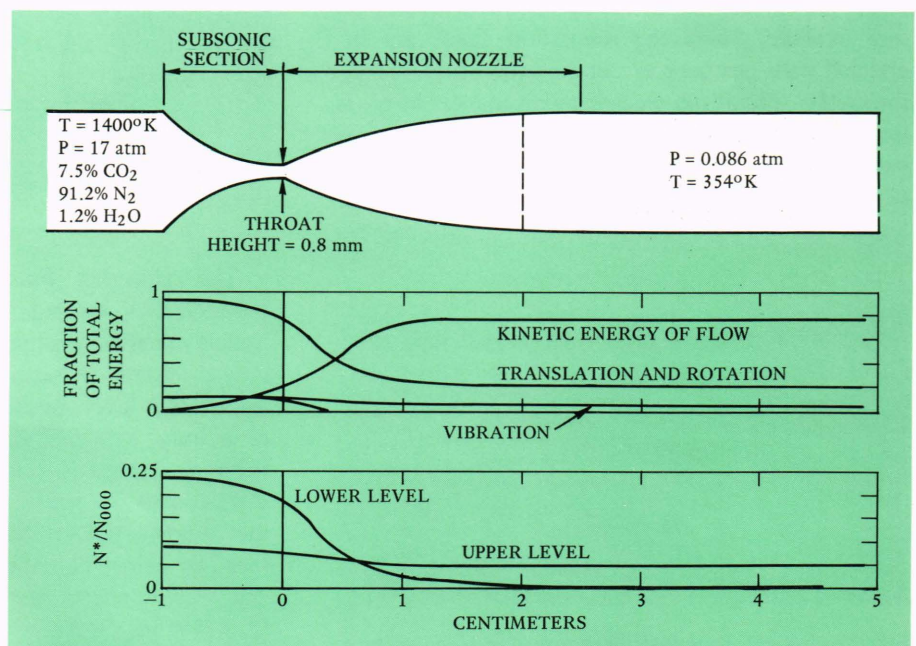
Gas Dynamic Lasers

The ultimate use of gas flow is in the gas dynamic laser where flow is used to create an inversion in what was previously a gas in thermal equilibrium.⁴

⁴ E. T. Gerry, "Gasdynamic Lasers," *IEEE Spectrum* 7, Nov. 1970, 51-58.

The gas dynamic laser which is shown schematically in Fig. 5 starts with a hot gas mixture in thermal equilibrium. The gas is then permitted to expand rapidly through a supersonic nozzle. The CO_2 gas dynamic system uses a gas mixture composed primarily of nitrogen, carbon dioxide, and a small amount of water. When this mixture is expanded through the nozzle, the gas temperature and pressure are reduced very rapidly. This rapid expansion reduces the translational energy of the molecules downstream from the nozzle as illustrated in Fig. 6. The fast relaxation rate of the

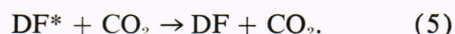
Fig. 6—Gas dynamic laser.



lower laser level in the presence of the H₂O causes the population of this level to drop in an equally short time or equivalently in a short distance past the nozzle. The upper laser level, however, relaxes relatively slowly and so remains at a population almost equal to that before expansion. These rate processes cause an inversion of the laser levels in the region indicated in Fig. 6. As shown in Fig. 5, an optical cavity established perpendicular to the direction of gas flow yields a high volume CO₂ gas laser capable of producing at least 60 kW in steady state operation.

Chemical Systems

All of the lasers described above require significant amounts of energy, usually in the form of electrical power, to excite or heat the laser medium. A system that has evoked great interest in recent years is the chemical laser where population inversion arises from direct conversion of the energy released by chemical reactions into vibrational excitation of a laser molecule. The most promising of these chemical systems are the DF-CO₂ laser and the HF laser.⁵ The DF-CO₂ laser is based on the chemical reactions



Here F₂ and NO are mixed (Eq. 1) to release a controlled number of F atoms to initiate the sub-

⁵ T. A. Cool, T. J. Falk, and R. F. Stephens, "DF-CO₂ and HF-CO₂ Continuous-Wave Chemical Lasers," *Appl. Phys. Letters* 15, Nov. 15, 1969, 318-320.

Fig. 8—CW fluid-mixing chemical laser.

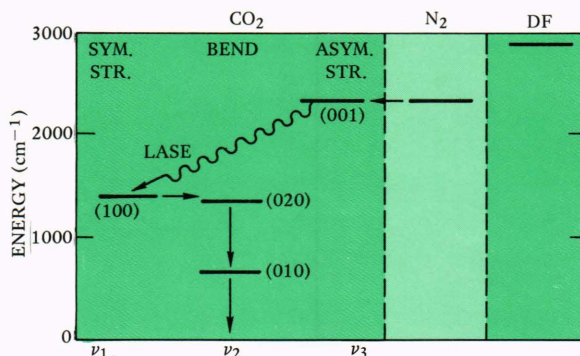
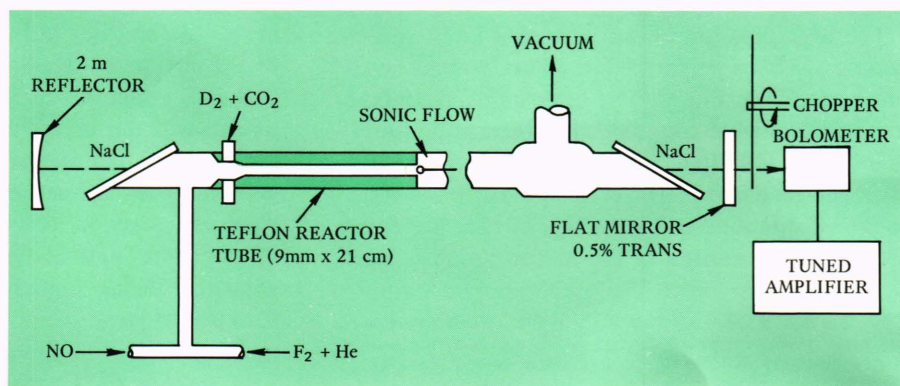


Fig. 7—Vibrational energy level diagram.

sequent reactions. There are several chain propagation reactions (Eqs. 2 to 4) that produce DF* in an excited vibrational state. Approximately 128 kcal/mole are liberated in the strongly exothermic reactions described in Eqs. 2 and 3. As illustrated in Fig. 7, there is a reasonable match between the upper CO₂ laser level and the excited DF molecule. A fast rate constant for energy transfer between these states allows much of the energy to be transferred to the CO₂ (001) state (Eq. 5) from which lasing occurs. The actual realization of this chemical pumping of the CO₂ laser at 10.6 μm was achieved in the apparatus depicted in Fig. 8. Gases are admitted to a Pyrex laser tube sealed with NaCl flats at the Brewster angle between external mirrors. Initial dissociation of the F₂ was accomplished by reaction with NO in a sidearm tube from which the gases flow into the main tube where they were mixed with D₂ and CO₂. The gas then passes through a constricted Teflon tube where the high pumping rates produce a sonic gas flow. Most of the laser action in this rapidly reacting mixture occurs in this region. The output CO₂ laser power at 10.6 μm in this system is at

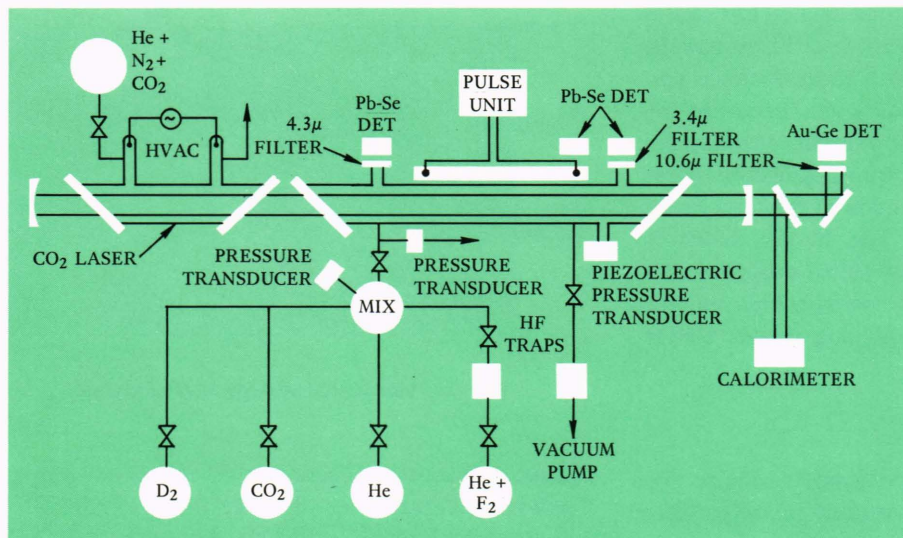


Fig. 9—Schematic of pulsed chemical laser.

most several watts, although by use of a high flow speed, large volume system with the flow transverse to the optical axis, power levels of several hundred watts have been achieved. The radiation in this laser is purely the result of selective chemical excitation of the laser molecule, and no external excitation is required.

High-Pressure Pulsed Chemical Lasers

The continuous flow cw chemical laser is limited in the range of operating pressure by mixing. A logical improvement of this system is a high-pressure laser operating in a pulsed mode.⁶ Such a laser has the potential of being an efficient compact system capable of producing very large pulse energies. The chemical reactions for this system are identical to the reaction (Eqs. 2 to 5) for the continuous flow system. The initial F atom concentration required to initiate the reactions is obtained by dissociating a relatively small amount of F₂ using an intense light pulse.

The high-pressure pulsed chemical laser experiments have been performed in an apparatus shown schematically in Fig. 9. The laser gases are mixed in a stainless steel chamber, and then a measured quantity is admitted to the laser reaction tube when the reaction is triggered by flash photolysis. Premixed quantities of D₂, CO₂, and He are combined with F₂ diluted in He in the stainless steel

chamber through calibrated orifices. The mixing chamber is held at an internal temperature of approximately -60°C by solid CO₂ to improve the stability of the mixture. It is possible to hold this refrigerated mixture in the tank for periods of several hours without any loss in the energy of reaction. The stability observed in these experiments is a considerable improvement over other work which does not make use of low temperature mixing and diluents such as He. The construction of this system is restricted to the use of such materials as quartz, stainless steel, Teflon, and aluminum because of the tendency of F₂ to react with most common plastics and ferrous metals. Within the optical cavity defined by the two mirrors is both the quartz reactor tube and a normal electrical discharge CO₂ laser used for alignment, testing, and gain measurements.

The temporal behavior of the laser radiation at $10.6\ \mu\text{m}$ is measured with a fast gold-doped germanium photoconductive detector, while measurements of the laser pulse energy are made using a disc calorimeter. Radiation from the excited DF and CO₂ molecules at $3.4\ \mu\text{m}$ and $4.3\ \mu\text{m}$, respectively, was observed using PbSe photodetectors with narrow band interference filters. The pressure generated in the laser reactor tube by the triggered chemical reaction reaches peak values of about 75 psi; the nature of these pressure pulses is measured using a high speed piezoelectric pressure transducer.

A xenon flashlamp excited by an electrical pulse with energy of several hundred joules and the

⁶ T. O. Poehler, M. Shandor, and R. E. Walker, *Third Conference on Chemical and Molecular Lasers*, St. Louis, Mo., 1972; also "High-Pressure Pulsed CO₂ Chemical Transfer Laser," *Appl. Phys. Letters* **20**, June 15, 1972, 497-499.

laser reactor tube are mounted at the foci of an elliptical reflecting cavity. The light flash from the lamp used to trigger the reaction is approximately 20 μs in duration. The 10.6 μm emission from a $\text{D}_2:\text{F}_2:\text{CO}_2:\text{He}::1:1:6:19$ mixture with a total pressure of 200 Torr is shown in Fig. 10. The laser oscillation begins during the flashlamp pulse, reaches a peak value when the flashlamp output has fallen to virtually zero, and continues for some period thereafter. The time delay before emission begins, the time of peak output, and the output pulse duration are functions of the light intensity, fill pressure, and ratio of the constituents. Also shown in the figure are the large pressure pulses in the reaction tube as measured by the piezoelectric transducer. The time delay associated with the observation of the initial pressure pulse is the propagation time of the pressure wave to the transducer located in a sidearm approximately 10 cm from the center of the reactor. The amplitude and temporal behavior of these pressure pulses are also strongly dependent on the operating parameters.

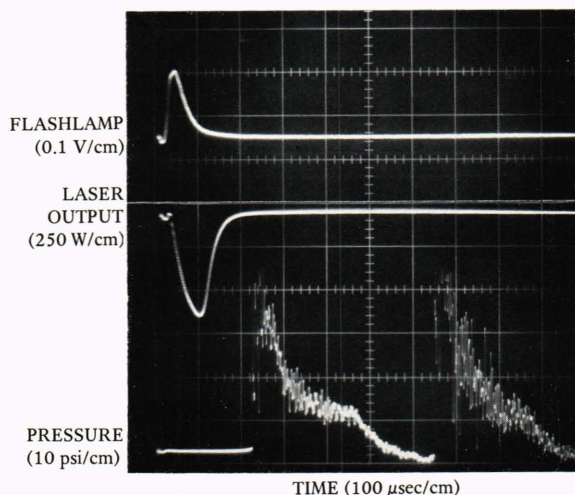


Fig. 10—Pressure and power output from a high-pressure pulsed chemical laser.

A series of measurements of the characteristics of laser emission as a function of gas composition, pressure, and pumping energy have been used to characterize the laser. The laser energy for a typical mixture ($\text{D}_2:\text{F}_2:\text{CO}_2:\text{He}::1:1:6:19$) was found to be a smoothly increasing function of fill pressure over a pressure range from 10 to 760 Torr as shown in Fig. 11. The duration of the laser pulses varies from more than 1 ms at 10

Torr to less than 50 μs at atmospheric pressure. The time delay to reach maximum output power also decreases sharply with increasing fill pressure. The laser output characteristics depend on the flashlamp energy in a fashion quite analogous to the pressure.

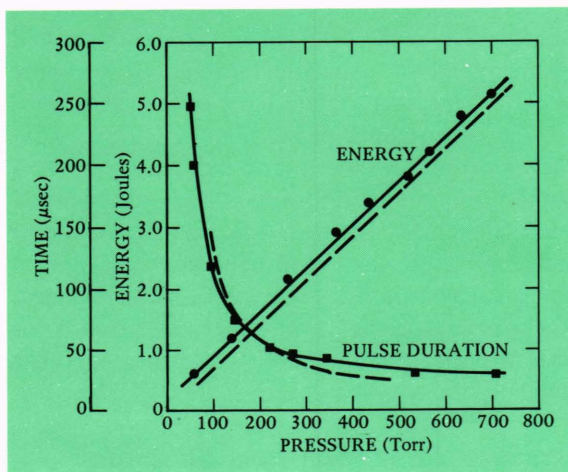


Fig. 11—Laser energy and pulse duration as a function of pressure.

At a fixed fill pressure, the output energy increases as a function of pump energy over a range from 100 to 500 joules with some saturation above 500 joules. The output pulse duration and time delay to reach maximum output vary inversely with pump energy over the entire range of the experiment; this behavior is expected from chemical kinetic considerations. The laser output power, efficiency, and pulse duration are also influenced by the D_2 to F_2 ratio with a 1:1 ratio apparently yielding the strongest reaction. The ratio of CO_2 to the reactive components is another factor of importance with measurements to date showing a $\text{CO}_2:\text{D}_2:\text{F}_2$ ratio of 6:1:1 to be optimum.

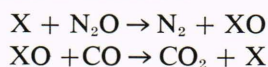
At a laser pressure of one atmosphere, the radiated energy at 10.6 μm is approximately 5 joules. The chemical efficiency, which is the ratio of the radiated energy to the available chemical energy of reaction, is approximately 3.25% based on the energy available in the gas in the total cavity volume. Since the actual diameter of the laser beam is approximately 7.5 mm compared to the 24.5 mm diameter of the resonator, the active volume is about one-tenth of the total cavity volume. Since there is little energy transfer by diffusion in

the short times involved in the laser pulse, a true measure of the chemical efficiency is the ratio of emitted energy to the chemical energy in the active volume. According to this definition, the chemical efficiency of the CO₂ transfer chemical system is approximately 30%. The peak gain coefficient of this laser system used as an amplifier is approximately 3 m⁻¹ with a time dependence quite similar to the behavior of the pulses emitted by the oscillator. Analytical studies of a kinetic model of this laser system have been used to predict the performance of the laser in terms of gain coefficient, power output, and pulse duration as a function of the various operating parameters.⁷ Good agreement between the experimental and analytical results has been achieved, providing a model capable of assessing the feasibility of new experiments together with analyzing results of these experiments and those performed in other similar systems.

Another Approach to a Chemical Laser

The pulsed chemical transfer laser program has been most successful. The original concept that the chemical pumping and vibrational relaxation kinetics are equally affected by operating pressure has been verified by operating the laser at pressures up to one atmosphere, with no apparent loss in chemical-to-laser efficiency. Theoretical studies show that the operating pressure can probably be increased to nearly ten atmospheres before three-body reactions begin to starve the chemical kinetics of essential free-radical chain carriers.

With all this success, the D₂-F₂-CO₂ chemical transfer laser retains its one major drawback—the reactants and products are toxic and corrosive and difficult to handle outside a laboratory environment. In recognition of this problem, APL has undertaken to study other chemical reactions that offer potential as chemical lasers yet have reasonable handling qualities. One such approach has been a pure chemical CO₂ laser based on the catalyzed combustion of CO with N₂O. The chemical kinetic chain of interest is



where X is a catalyst element from the first col-

umn of the periodic table, i.e., X = H, Li, Na, K, or Cs. Of these catalysts, Na appears most attractive from the kinetics standpoint and experiments to date have concentrated on its use. This chemical kinetic scheme offers several obvious advantages for a chemical laser:

1. Relatively safe fuel and oxidizer and combustion products (CO-N₂O mixtures are inert in the absence of the catalyst).
2. Desirable products for a CO₂ laser.
3. High exothermicity (87 kcal/mole).

Actually, when a sodium catalyst is used, about 70% of the heat of reaction occurs in the CO₂-producing-step. This energy is equivalent to nine CO₂ upper laser level vibrational quanta and could potentially directly excite the CO₂ product molecule since excess chemical energy tends to accumulate in the newly-formed bond. However, there is no assurance that the upper laser level vibrational mode will be preferentially excited if this process occurs. One of the striking features of the Na-catalyzed CO-N₂O combustion is the strong visible Na D-line chemiluminescence that occurs with it; this chemiluminescence is a visible indicator of disequilibrium.

These chemical laser experiments are being conducted in a low-pressure fast-flow reactor similar to that used by Cool for the D₂-F₂-CO₂ cw transfer laser. In this coaxial flow configuration, however, the chemical laser gain is expected to be too low for self-sustained laser oscillation and the experiments have been generally restricted to laser gain measurements. To date no positive indication of gain has been recorded.

Conclusion

It appears that chemical lasers will be an important source of radiant energy capable of operating with high efficiency. The strong chain reaction occurring in the pulsed chemical CO₂ transfer laser is able to produce high power pulses of considerable energy. Provided that more efficient means of producing the original F atom concentration can be found, the system could be scaled to much larger sizes without requiring large external power sources. The applicability of the chemical laser would obviously be enhanced if safer and less expensive fuels could be discovered. A mode-locked pulsed chemical system capable of generating high-energy pulses in the nanosecond range might prove to be important in plasma fusion studies.

⁷T. O. Poehler, J. C. Pirkle, R. E. Walker, "A High-Pressure Pulsed CO₂ Chemical Transfer Laser," *IEEE J. Quantum Elec.* 8, Nov. 1972.