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ARPA-NRL Laser Program

Semiannual Technical Report to Advanced Research Projects Agency

July 1, 1971 - December 30, 1971

ARPA Order No. 2062

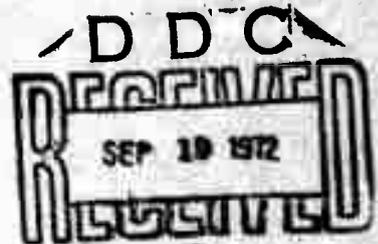
*Laser Physics Branch
Optical Sciences Division*

August 1972

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Details of illustrations in this document may be better studied on microfiche

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ABSTRACT

The ARPA-NRL high energy laser program is concerned with the development of laser technology in four program areas: Chemical Lasers, Electric Discharge Lasers; High Power Glass Lasers and New Laser Techniques. This report summarizes the progress made in those areas during the first half of FY 72.

PROBLEM STATUS

This is a semi-annual technical report; work is continuing.

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CHEMICAL LASER PROGRAM

DF-CO₂ Supersonic Transfer Chemical Laser

A preliminary theoretical study of a proposed supersonic DF-CO₂ chemical laser capable of operation with full atmospheric exhaust pressure recovery has been completed. The device concept is illustrated in Fig. 1. Approximately one-half of the CO₂ required for operation is chemically formed from the combustion of CO with O₂ in the presence of a helium diluent. Premixed F₂ and He (1:9) and a mixture of the remainder of the CO₂ and additional He diluent are injected and mixed with the primary flow at a location downstream of the CO/O₂ combustion zone. Stagnation conditions for the mixed flows are about 1400°K and 15 atm. Partial thermal dissociation of the F₂ occurs before the combined flow is accelerated through an array of supersonic nozzles. Immediately upstream of the nozzle throats the requisite D₂ flow is injected by means of multiple arrays of small sonic orifices. Mixing and chemical reaction do not occur to an appreciable extent until the flow has expanded to a Mach number of about 4 as it enters the optical cavity. The cavity consists of a constant-area flow channel situated between rectangular mirrors. The cavity is terminated at the downstream end by the converging entrance section of a supersonic diffuser designed to bring the exhaust gases to ambient pressure in the divergent subsonic section of the diffuser.

Because the flow conditions for this device are quite similar to those found in existing gasdynamic lasers, it was judged to be feasible to make modifications to an existing gasdynamic laser, the AVCO Mark III, to permit supersonic transfer-chemical laser (TCL) operation. Calculations of expected laser performance for the modified device have been performed to provide a rational basis for experimental design. Dr. George Emanuel of the Aerospace Corporation has provided generous assistance with this task. The Resale I laser program was modified to include the latest data for energy transfer and deactivation in the DF-CO₂ system obtained under that portion of the present ARPA contract at Cornell University.

A favorable operating condition has been found for the approximate exhaust compositions indicated in Fig. 1. Figures 2-4 indicate several features of the anticipated performance from the present device. Figure 2 shows the calculated variations in integrated power output and intracavity radiation flux with a cavity output coupling of 15%. The 45 kwatt total power output figure represents an order of magnitude increase in output over the values obtained from this device when operated as a GDL with the same mass flow.

Figures 3 and 4 indicate the expected variations in pressure, temperature, and Mach number within the cavity. The laser output ceases at a distance of 9 cm downstream from the exit plane of the supersonic nozzle array where the gas temperature has climbed to 680°K. The laser is quenched at this point because the thermal population of the lower level has reached a value high enough to prevent the further maintenance of population inversion. A calculation for a divergent channel with an isothermal reaction zone was performed to investigate the possibility of improved performance when thermal cut-off of the laser is avoided. No improvement in laser performance was calculated for this case; the reason being that laser output is quite effectively quenched by the significant collisional deactivation of the $\text{CO}_2(00^01)$ level by ground state DF when the reaction is about 60% complete. Since the thermal cut-off for the constant area channel occurred at about the same stage of reaction, it is believed that only a small advantage would be realized for a divergent channel at a cost of considerable complexity in design.

Figure 3 indicates a pressure rise in the laser test section caused by chemical reaction of such a magnitude as to violate the one-dimensional gasdynamic assumptions made in the computations. It is expected that this Rayleigh heating effect will cause shock formation and boundary layer separation within the test section; poor optical quality is an expected result.

Until a supersonic TCL capable of ambient exhaust pressure recovery has been successfully operated, the projected performance figures based on the computer calculations just discussed should be regarded with reservation. Nevertheless, if devices can be built to perform to theoretical estimates, one can envision the production of large amounts of cw 10.6 micron laser power in a considerably more efficient manner than has been demonstrated with present GDL technology.

The Mark III H gasdynamic laser is currently en route to NRL. After modification it will be operated as a DF- CO_2 supersonic transfer laser to check out the concepts and calculations described above.

CO Laser Research

Flame Lasers

During the period July - December a higher power $\text{CS}_2\text{-O}_2$ flame laser project was completed and a superior laser-probe technique was developed. With the use of an additive, N_2O , a 12" long $\text{CS}_2\text{-O}_2$ flame burning at a pressure of ~ 25 torr gave an output of 0.6 W on CO P-branch transitions. The effect of other additives was studied. The results indicated that the high excess of oxygen could not be replaced substantially by a mixture of stoichiometric oxygen and inert gas. Excluding certain gas dynamic lasers, the flame laser is one of two purely chemical lasers. However, since its chemical efficiency is low,

$\approx 0.1\%$, the project was terminated after submission of a report to Chemical Physics Letters, a copy of which is incorporated later into this report.

Since other more exothermic flames, such as $C_2H_2-O_2$, may be the basis of better flame lasers, a sensitive probe technique was developed to measure optical gain in CO produces in these flames. The development of the technique, the laser-oscillation-range technique, required an extremely-stable single-line single-mode CO laser. After some experimentation, an air-bag-suspended steel beam was used to hold the mirror mounts. It was also found that the gaseous laser mixture and electrical discharge power must be carefully adjusted to stabilize the discharge. After stabilization optimization, optical gain (or loss) as small as about 0.01% could be detected. This is at least a three order of magnitude improvement over the direct gain-probe technique. With the high sensitivity of this technique and due to certain realizations about the inter-relation of gain and stimulated emission processes, it was decided that, for the first time, relative Einstein A_{v+1}^v coefficients could be experimentally determined for CO. [An explanation of the derivation of the coefficients from the optical gain measurements on a number of vibration-rotation transitions in adjacent bands will be reported in the Journal of Quantum Electronics and in the Journal of Chemical Physics.] These coefficients are important to an understanding of all CO lasers. Their measurements are now underway and will be continued into the next reporting period. Following that, experiments with the $C_2H_2-O_2$ flame will be initiated.

N_2 -CO Transfer Laser

In an effort to obtain laser oscillation on the low lying fundamental bands of CO, a low temperature N_2 -CO energy transfer device was built. The basic idea was to mix vibrationally hot N_2 with ambient CO to achieve an even higher characteristic temperature in CO as a result of its lower vibrational frequency. Low temperature was used to maximize the increase in the characteristic vibrational temperature, as well as to promote partial inversion at the relatively low inversion ratios anticipated.

A fast-longitudinal-flow apparatus was used for the experiment. A mixture of He and N_2 passed through an electrical discharge in a sidearm and was then allowed to mix with cold CO before entering into the main tube. The entire apparatus was cooled to 77°K at the wall. The average temperature at the middle of the tube was 150°K; the average linear flow rate was 80 msec⁻¹. The laser cavity consisted of a totally reflective mirror and a 1/2 mm hole coupling mirror.

At low CO to N_2 ratios, cw laser oscillation on bands as low as $v = 2 \rightarrow v = 1$ was obtained. As the CO/ N_2 ratio was increased, the higher vibrational transitions in the output spectrum increased at the expense of the lower transitions. Unexpectedly, bands as high as $v = 35 \rightarrow v = 34$ were observed in the laser output. The result attests

to the very slow V-T relaxation rate for CO even in those high vibrational levels.

The spectrum of the present laser ranges from 4.8 μ to 8.0 μ . This is believed to be the widest in the literature. It is quite possible that, with some effort, laser oscillation at even longer wavelengths can be achieved in this type of laser.

A paper describing these experiments is included later in this report.

HF/DF - CO Transfer Studies

A series of experiments have been performed to determine whether vibrationally excited HF (or DF) will transfer sufficient energy to CO to induce lasing or to enhance the output of a CO TEA laser. These experiments were unsuccessful, but it has been observed that the addition of small amounts of SF₆ improve the performance of a CO TEA laser. With SF₆, the laser energy was increased by a factor of 3, the wavelength range was extended to higher and lower transitions and the laser could be operated at higher pressures of CO.

These experiments, which are continuing, appear to suggest an improved electron energy coupling to CO but the role of SF₆ is as yet unknown.

SHORT PULSE CO₂ MOLECULAR LASERS

The NRL short pulse molecular laser program under ARPA support was initiated during the first half of FY 72. Although the delay in receiving the ARPA funding delayed the initiation of some experiments which required large expenditures, progress has been made in establishing research facilities and initiating a broad range of experiments aimed at the generation and understanding of short pulse phenomena at 10.6 microns.

Two complete TEA laser facilities have been established, one for saturable absorber studies and one for active mode-locking and pulse-gating experiments when the electro-optic components can be acquired after receipt of ARPA funds. Preliminary experiments on saturation in liquid and gaseous absorbers at CO₂ wavelengths have been done. A small scale double-discharge volumetric TEA device was built and tested to evaluate its suitability as an intermediate stage amplifier device when suitably scaled. In the area of electron beam machines, a small scale cold cathode e-beam ionizer-sustainer device was constructed and operated to investigate this alternative to the hot cathode gun as a large volume short pulse amplifier.

Saturable Absorbers

The need for saturable absorbers in a short-pulse amplifier system are two-fold; one to serve as interstage isolators to prevent parasitic oscillations from depleting the inversion in a high gain multi-stage amplifier system and second as a mode-locking medium to circumvent the materials-damage limits of available IR materials and coatings. The broad absorption bands and wide variety of liquids which absorb at 10.6μ make them attractive as saturable absorber candidates and experiments during this reporting period have concentrated primarily in this area.

The facility used for these investigations is shown in Fig. 5. A wavelength controlled TEA laser emitting 200 millijoule, 200 nano-second pulses in a fundamental TEM_{00q} mode is used to irradiate a liquid sample. Power density at the sample is controlled both by a polarizer-stack attenuator and translation of the sample along the focal axis of the Ge lens. Transmitted radiation is collected by an integrating sphere to average out any spatial variations in the beam and sampled by a Ge:Cu photoconductor.

A variety of liquids with absorption bands at CO₂ wavelengths were diluted in the cell with carbon disulfide as the solvent. Liquids investigated include: Dimethyl sulfide (CH₃)₂ SO, m-Difluorobenzene C₆H₄F₂, Acetyl Bromide CH₃COBr, Trichloroethylene CHCl:CCl₂, 2-Propanal CH₃CHOH CH₃, and 1-2 dichloroethane. None of the samples tested to date showed evidence of saturation up to a power density of 50 MW/cm² where other effects such as window damage and gas bubble formation in the liquid were encountered.

While liquid absorbers will continue to be tested, measurements are beginning on gases and mixtures of gases. While liquids tend to have high saturation parameters because of very rapid relaxation, the relaxation time in gases can be controlled over a wide range by controlling the pressure. The large number of lasing lines in CO₂ indicate that no one gas can possibly cover all the CO₂ even when broadened at high pressures. A series of measurements are now being performed to measure the absorption and saturation characteristics of gaseous mixtures as a function of the CO₂ laser wavelength.

Mode Locking

A complete TEA laser system is operating and is awaiting arrival of Ge acoustic cells and gallium arsenide electro-optic Pockels cells for mode-locking and pulse-gating experiments.

In addition to this conventional method of generating short pulses, it has been recognized at NRL that double-Raman-shifting of Nd³⁺:YAG and Nd³⁺:YA₂O₃ laser lines in a high pressure H₂ cell would

shift the wavelength into the lasing bands of CO_2 . Table I gives some of the possible coincidences. This possibility offers a very elegant solution to the generation of short pulses at 10.6μ by circumventing the primitive optical shutter technology at 10μ and by using an already developed, highly reliable short-pulse solid state laser system. Experiments to Raman shift Nd^{3+} :YAG pulses are now being assembled using the short-pulse driver of the large glass-laser system.

Double Discharge TEA Amplifier

An 0.3 liter double discharge TEA device utilizing glass rods as trigger electrodes was built and tested. Uniform discharges over the entire volume was achieved for CO_2 concentrations as high as 10% and energy density deposition of 150 joules per liter with gains in excess of 2% per centimeter. Repeatability of discharge uniformity and electrical characteristics was very good. Based on these results, a one meter long double-discharge amplifier with a variable gap spacing of 5 cm and 7 cm is presently being designed to operate as a 3.5 liter or a 5 liter amplifier. Energy storage, for short pulse extraction, of 15 joules in the 5 liter configuration is expected.

e-Beam Amplifier

The possibility of replacing the hot-cathode electron gun by a plasma cold-cathode gun as the ionizer element in a short pulse e-beam amplifier is very attractive both from the standpoint of device simplicity and cost. The inherent short pumping times ($\sim 1 \mu\text{sec}$) due to the higher current densities ($1 - 10 \text{ amps/cm}^2$) of the cold cathode gun makes them ideal for the energy storage role required for short pulse amplification.

A cold cathode electron gun, Fig. 6, consisting of a single razor blade driven by a 300 kV Marx bank was constructed to illuminate a cylindrical sustainer-discharge volume with a circular cross-section of 75 cm^2 . Uniform discharges in CO_2 lasing mixtures have been achieved over the entire volume. Gain measurements are being made on the sustainer discharge simultaneously with electrical measurements on the gun to determine energy-storage pumping-time characteristics of a sustainer driven at high e-beam current densities. These measurements will be augmented by a collaborative effort between NRL, Maxwell Laboratory and the Institute of Fluid Mechanics at Marseille, to perform laser measurements on a $10 \text{ cm} \times 100 \text{ cm}$ high current density ($1 - 10 \text{ amps/cm}^2$) electron gun-sustainer device being built by Maxwell Labs.

Although the cold cathode e-gun concept offers great promise, the e-beam uniformity and therefore sustainer medium uniformity of this device has yet to be established. To complement the cold cathode investigations, a RFQ is being prepared for a $10 \text{ cm} \times 100 \text{ cm}$ hot cathode e-gun in anticipation of ARPA funding.

HIGH POWER GLASS LASER PROGRAM

At the beginning of the reporting period the major constructional aspects of the disc laser amplifier were completed. Figure 7 shows the capacitor bank and Fig. 8 shows the disc laser head itself with the top reflector and the lamps on top removed.

Testing of the amplifier with input pulses of high enough intensity to achieve the design output intensity has not been possible in this reporting period for a number of reasons. The outputs that were achieved were 750 joules in 30 nsec with a 350 joule input pulse and 180 joules in a 200 picosecond pulse with a 60 joule input pulse.

Operating the VD640 laser system with subnanosecond pulses presented a larger number of problems than anticipated. These problems fell into a number of categories.

(1) Parasitic Oscillation: even with 30 nsec pulses the VD640 was only marginally stable against parasitics and extreme care with blackening and roughening all metal surfaces near the beam was necessary to keep the amplifiers from oscillating. For subnanosecond pulses, higher gain was required because of the lower input signal and an additional Pockel's cell shutter had to be designed and inserted between the first and second amplifiers to suppress oscillation.

(2) Electronic Difficulties: It was necessary to rebuild the triggering circuits and recable the capacitor banks to achieve a reasonable degree of reliability.

(3) Laser Heads: Several types of difficulties made themselves evident when the system was operated which were not a problem with the older VD320 system. The French have changed the lamp construction and now spot weld the electrodes to the tungsten rod using a sheet metal collar. This method of construction leads to failure at random times 0 - 2000 shots and essentially defies pre-testing.

Because of the low damage threshold of the continuous flow process MG915, the French supplied Schott LG-56 laser rods. This is not a good choice since LG-56 appears to have two problems when used in the VD640:

(a) the laser glass ion exchanges with the potassium chromate in the coolant leading to yellow precipitate on (and into) the surface of the rods which blocks the pump light;

(b) radial cracks (originating at the surface) develop in the larger rods over a few hundred of shots and ultimately lead to breakage and/or obscuration of the rod aperture.

These difficulties were not ones that were related specifically to subnanosecond pulses but ones which would have caused equal problems in operation with thirty-nanosecond pulses. With subnanosecond pulses, there is a basic problem which limits a VD640 with LG56 or MG915 to ~60 joules in a 250 psec pulse. With short pulses, one wishes to run all amplifiers under conditions where the self focusing length is equally long compared to the rod length. For the VD640 this would imply a fourfold gain in energy/stage. Because of the low gain coefficient of LG56, this is difficult to achieve in the last two stages and the intermediate amplifiers must be run at higher than optimal levels to achieve outputs greater than 50-60 joules.

The Owens-Illinois ED-2 would seem to be a much better choice for short-pulse operation because of the higher gain coefficient. This glass will give the necessary gain in the final stages to allow the primary stages to be run more conservatively. It also appears that shorter (and cheaper) rods could be used in the first three stages.

The following testing sequences have been run with the NRL disc amplifier during the reporting period:

(1) gain measurements with 30 nsec pulses up to ~ 50% pump energy on the disc using the VD640 at up to 350 joules input energy. An output of 750 joules was obtained at 350 joules input and the gain appeared to be what was predicted by the computer program.

(2) Gain measurements with subnanosecond pulses up to 60 joules input. An input of 180 joules was obtained at ~50% pump energy. Above this level, the amplifier train was not stable.

(3) During both sequences, the level of operation was limited by oscillation of the French amplifier train. To circumvent this problem a Chromatix Nd:YAG laser was used for a set of gain measurements with ~100 nsec q-switched pulses to examine the gain of the system as a function of pump energy. The gain was found to follow the predictions of the calculations up to ~50% of the pump energy and reached a hard limit above that point. A sequence of experiments was performed which determined that the problem was parasitic oscillation of the discs on a disc by disc basis. This showed that the black anodized copper bands used around the discs were not sufficient to prevent oscillation at the design levels.

Two approaches are being followed to find a workable solution to this problem. Owens-Illinois is synthesizing black edge coatings for the discs and the ZAP code is being modified to treat superfluorescence and parasitic oscillation problems.

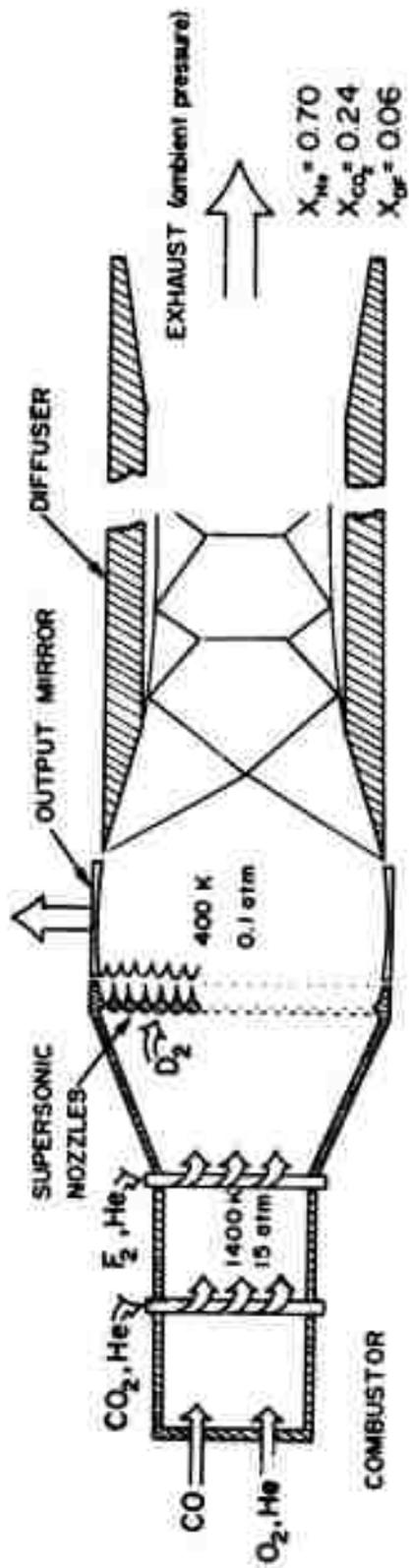


Fig. 1 - Schematic diagram of supersonic transfer chemical laser

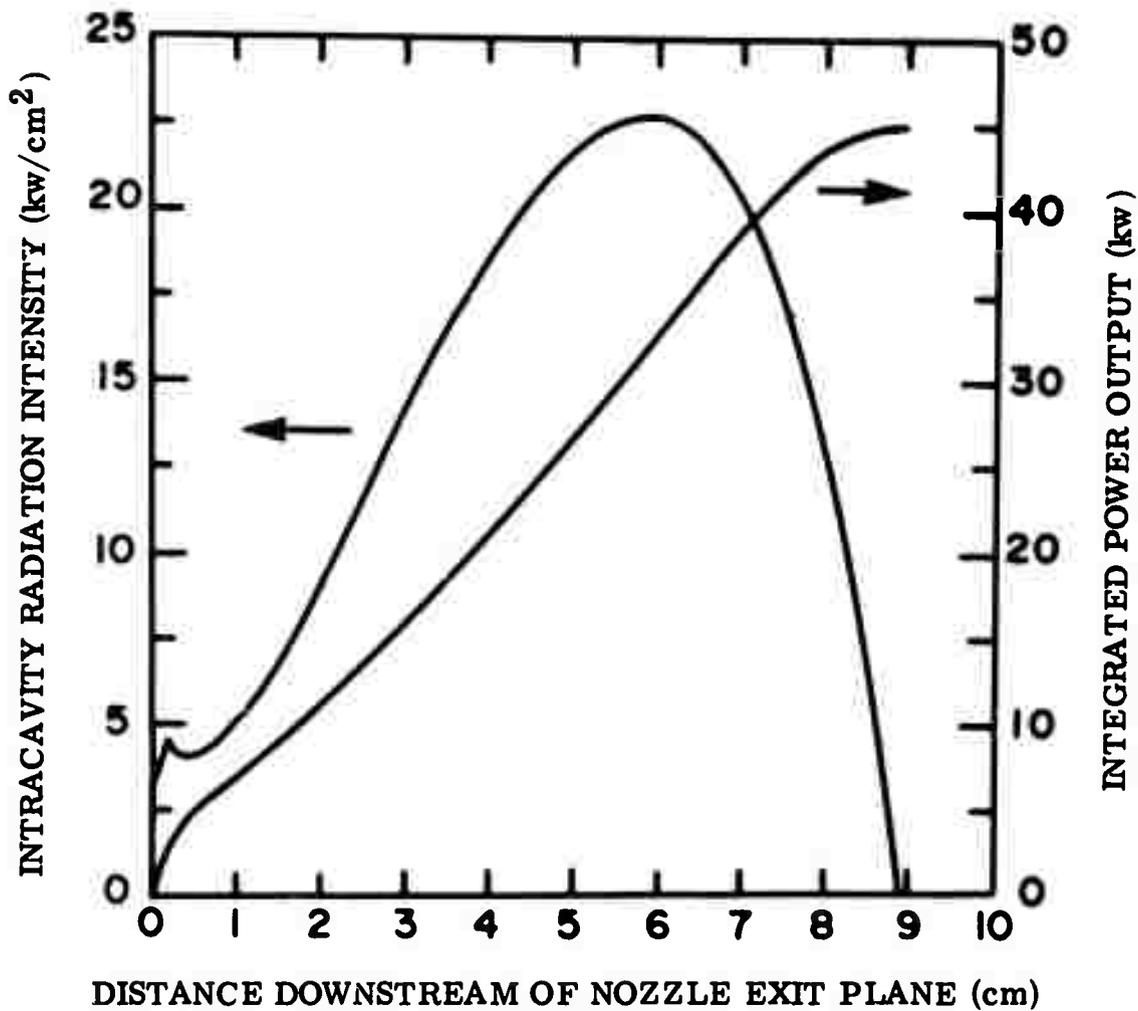


Fig. 2 - Intracavity radiation intensity and integrated power output as a function of cavity length

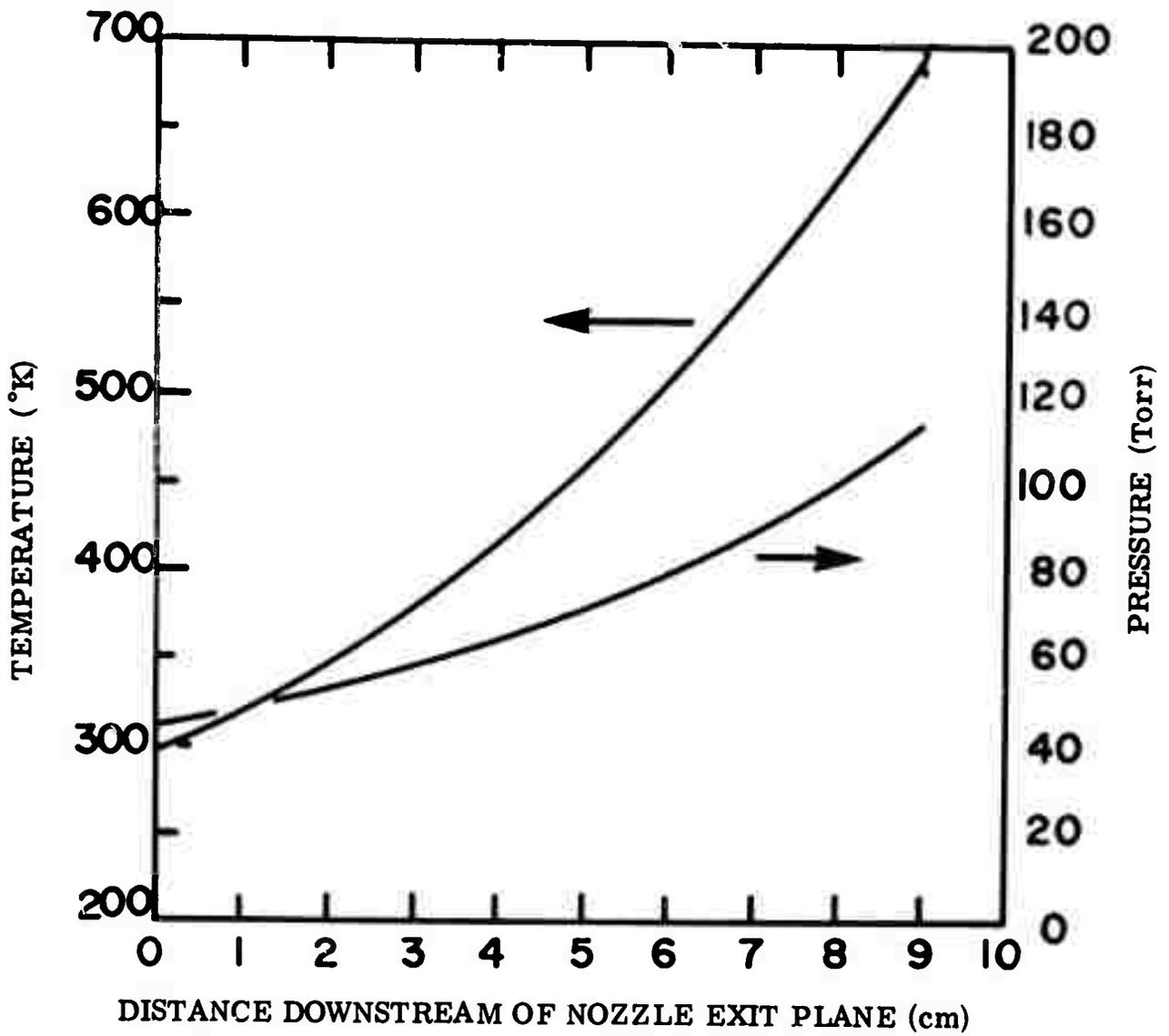


Fig. 3 - Cavity temperature and pressure as a function of distance from the nozzle exit plane

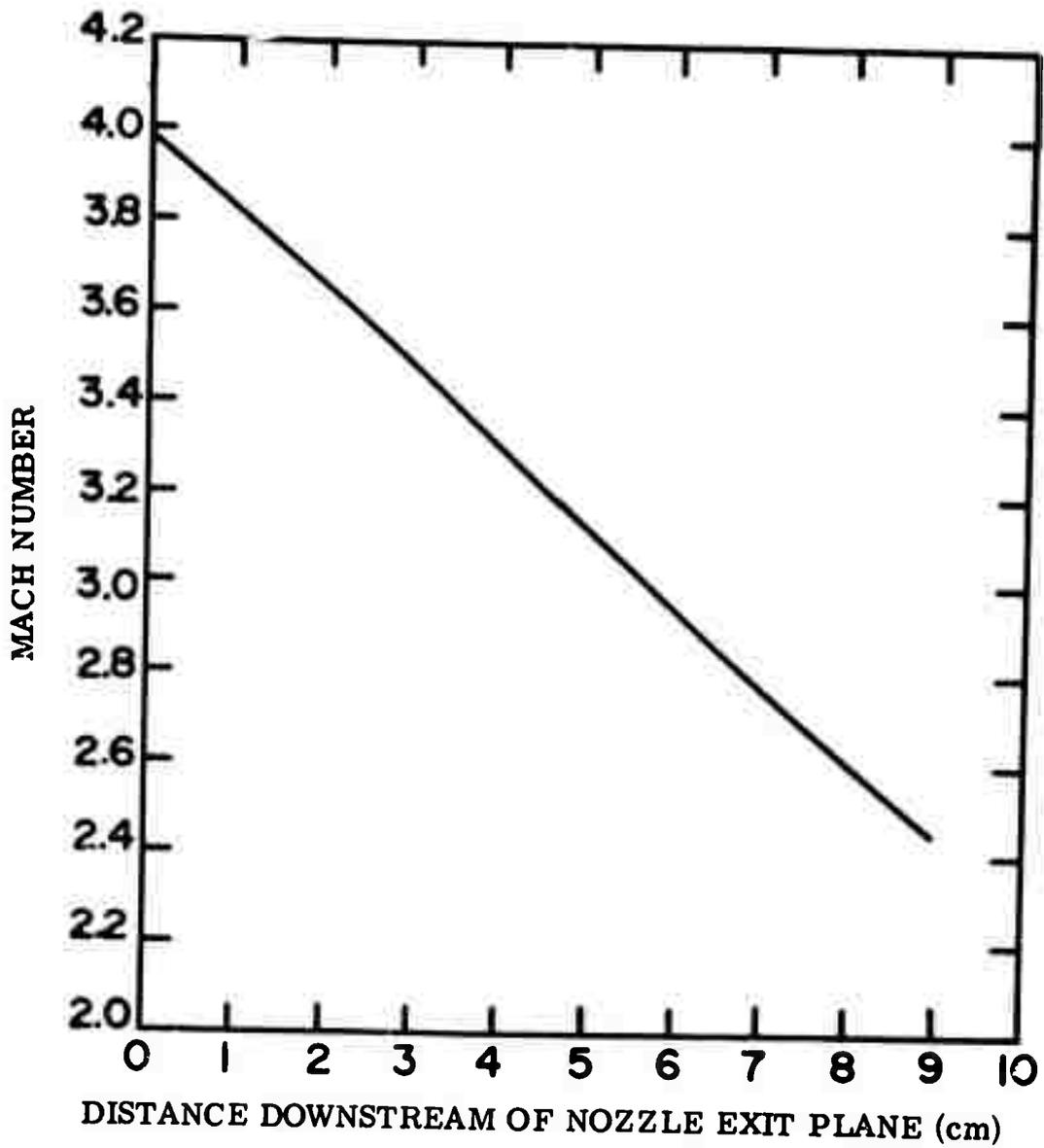


Fig. 4 - Flow Mach number as a function of distance from the nozzle exit plane

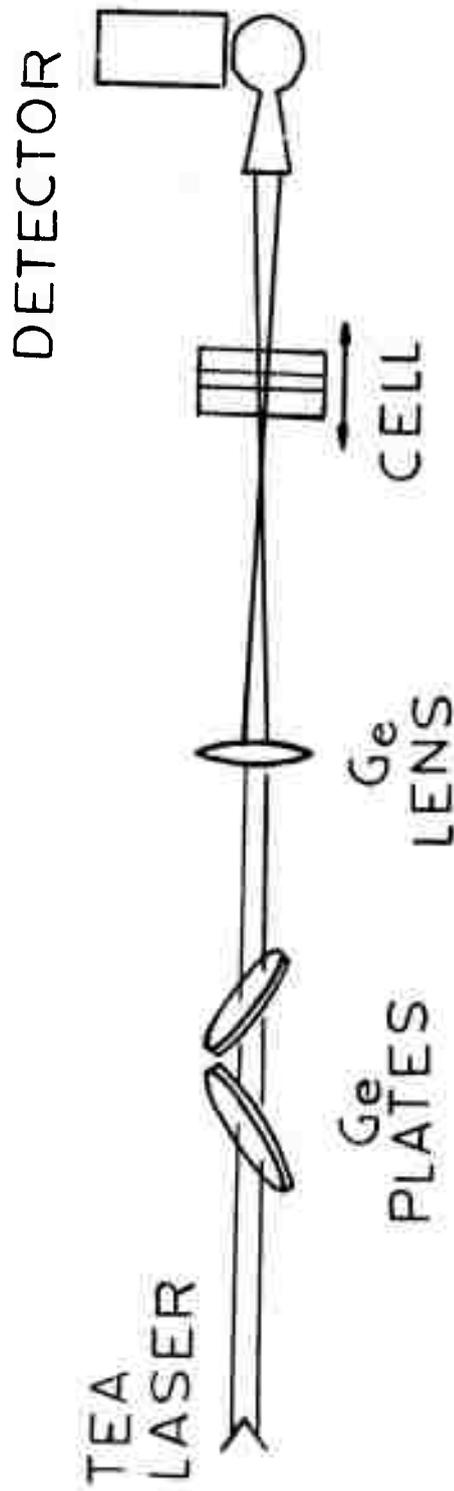


Fig. 5 - Schematic diagram of experimental arrangement to test liquid saturable absorbers

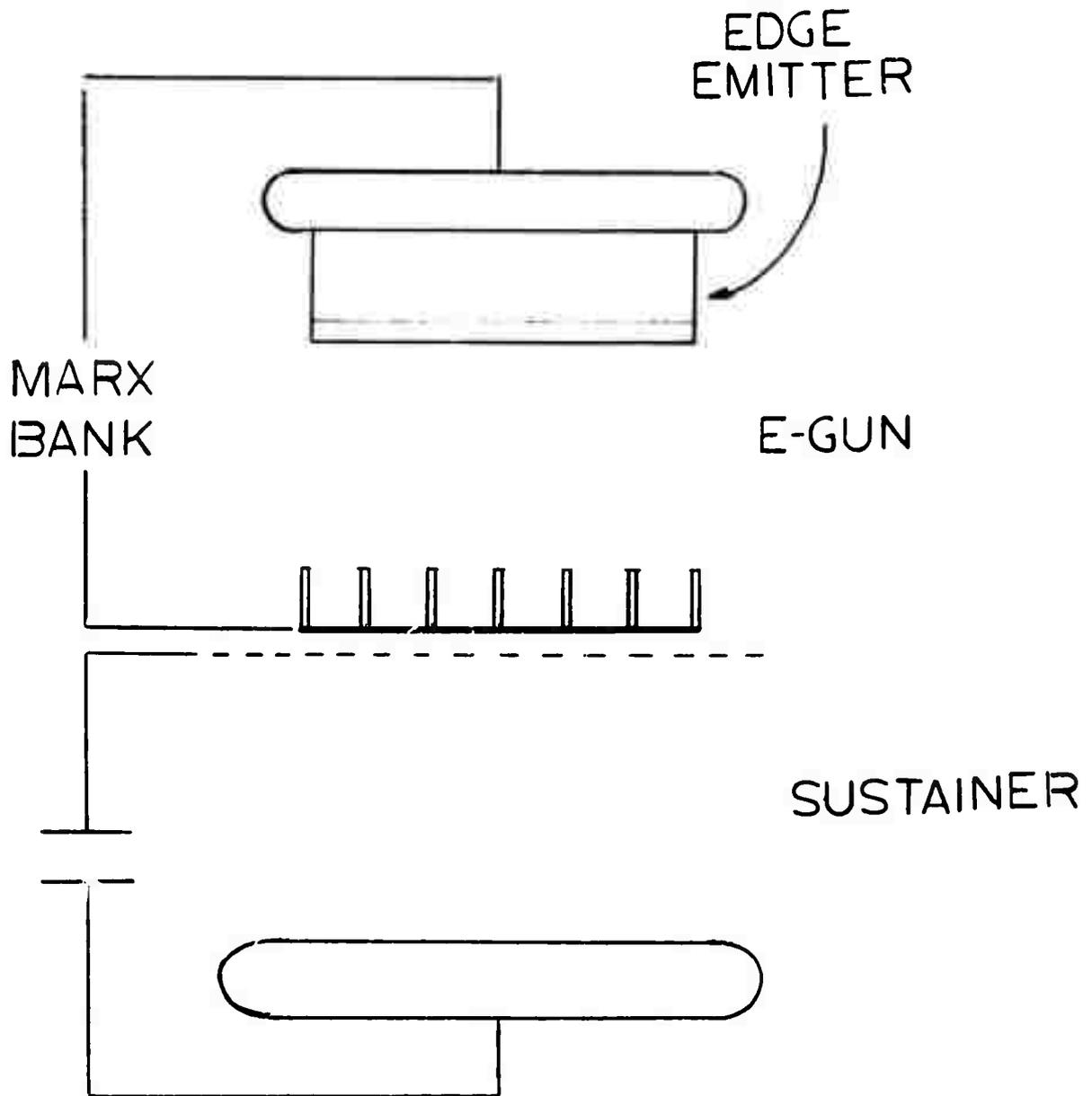
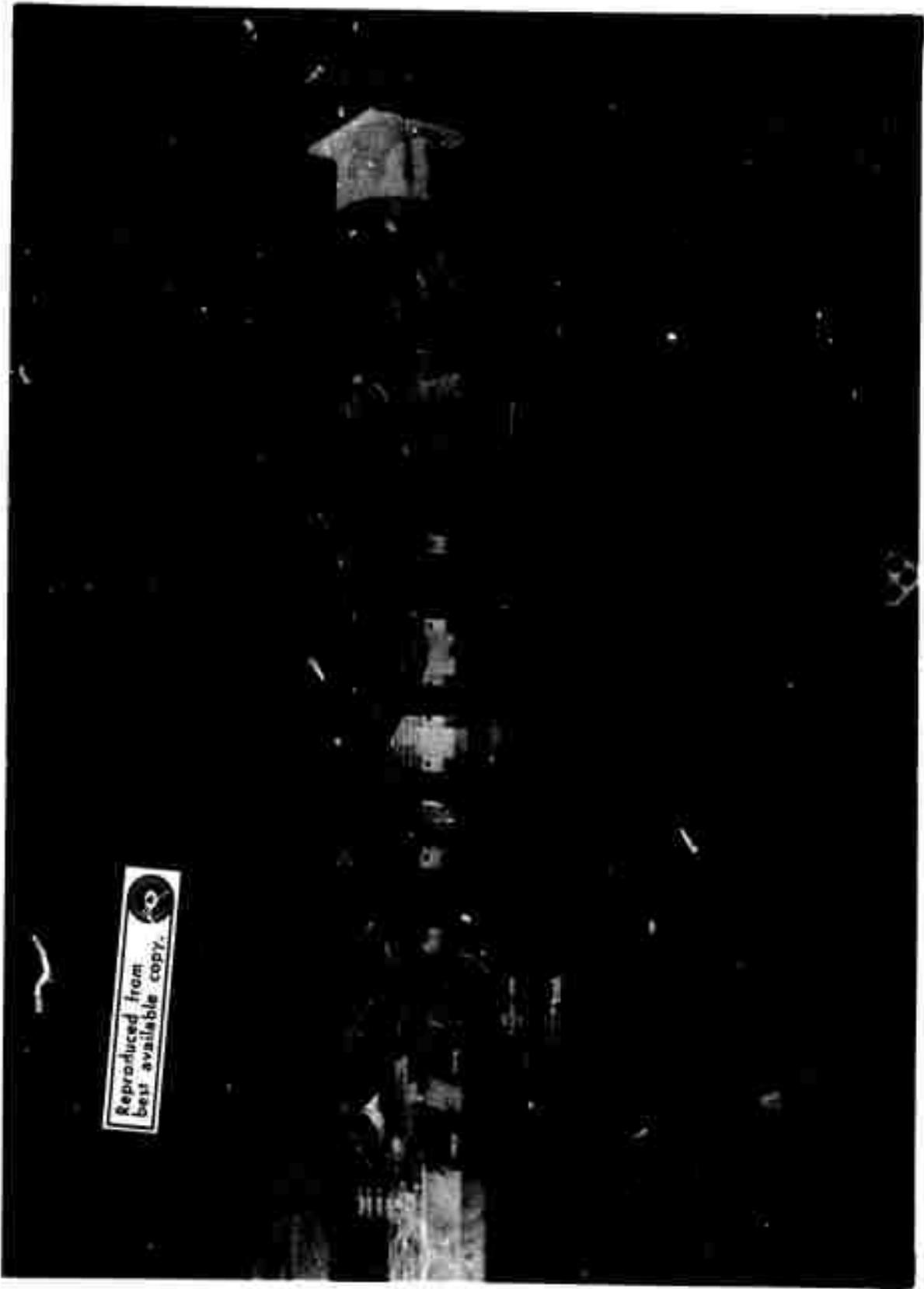


Fig. 6 - Schematic diagram of cold-cathode electron gun



Fig. 7 - Capacitor bank assembly for disc laser amplifier



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Fig. 8 - Disc laser head

TABLE I
 Coincidence between double-Raman-shifted glass-laser pulses in H₂ and CO₂ absorption lines.

Nd ³⁺ :YAG (cm ⁻¹) (micron)		Nd ³⁺ :YAlO ₃ (cm ⁻¹) (micron)		Laser Line Shifted by 2Q ₀ ; (1)=8310.44 cm ⁻¹ (cm ⁻¹)	Nearest CO ₂ Line (cm ⁻¹)
9268	1.0787	9262	1.0793	951.6	951.2 P(12) 001-100
		9277	1.0777	957.6	957.8 P(4) 001-100
		9321	1.0726	966.6	966.3 R(6) 001-100
9356	1.0685			1010.6	1010.0 P(56) 001-020
9385	1.0652	9385	1.0652	1045.6	1045.0 P(22) 001-020
9391	1.0645			1074.6	1074.6 R(14) 001-020
				1080.6	1081.0 R(24) 001-020

APPENDIX ACHARACTERISTICS OF A CW CO LASER
RESULTING FROM A CS₂-O₂ ADDITIVE FLAME*

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The use of a ribbon burner resulted in a 100 fold laser power enhancement from a CS₂-O₂ free burning flame. The effect of He, SF₆, N₂O, CO, CO₂, N₂, SO₂, and NO₂ on laser power was examined. The highest power, 0.6 W, was achieved from a mixture of CS₂, O₂, and N₂O at flow rates of 3.9, 110, and 7.6 millimoles/sec, respectively.

A flame laser is an example of a purely chemical laser. On the basis of a simple model its existence was predicted in 1965 by Bleekrode and Nieuwpoort [1]. As a result of a study of the chemiluminescence from a CS₂, O₂, N₂ flame, Foster and Kimbell [2] reported that this system appeared to be a likely candidate for the achievement of laser oscillation in a free burning flame. Subsequently laser oscillation was observed by Pilloff et al. in a free burning CS₂-O₂ flame [3]. This flame laser system may be compared to the only other purely chemical laser system [4], NO-F₂-D₂-CO₂. From a mechanistic viewpoint, the primary difference between these two systems is that a fraction of the chain carriers and thermal energy must be transported toward the burner in the flame. This condition does not apply to the NO-F₂-D₂-CO₂ system.

In ref. [3] the CS₂-O₂ flame laser was not characterized in detail because operating conditions were close to laser threshold. In this paper we wish to report operating characteristics based on a more compact burner.

The burner used was a Bethlehem Apparatus Co., Inc. Model PM2-12" gas-oxygen ribbon burner in which gases are surface mixed rather than premixed. The average center to center distance between a gas injector hole and an oxygen injector hole was \approx 1.3 mm. The dimensions of the injector area were 30.5 cm by 0.79 cm. An eighty mesh stainless steel screen was placed over the top of the burner and attached to the sides of the burner. The distance between the screen and the injector area was about 3mm. The burner was mounted on a translation stage which was inside a 4 ft diameter x 9 ft long vacuum chamber connected to a 300 CFM mechanical pump. For safety reasons the pump was operated at full

* This work was supported by the Advanced Research Projects Agency, ARPA Order No. 660.

ballast. Also, about 50 CFM of compressed air was injected into the pump on its atmospheric side.

The vacuum chamber was fitted with NaCl Brewster angle windows. For most of the experiments, the optical cavity consisted of a 4 m radius of curvature maximal reflectivity dielectric mirror and a gold coated flat with a 1 mm diameter coupling hole. Laser output was measured with an Eppley thermopile up to 200 mW and with a Coherent Radiation powermeter for higher power levels.

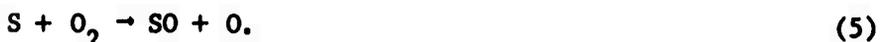
It is interesting to consider the general properties of the burner and the flame. Fig. 1 shows a photograph of the flame. Combustion appears to take place primarily in a jet of gas above the burner. Some combustion occurs at the sides of the burner due to the use of the screen, which forms a hemicylindrical surface over the burner. In the absence of this screen, a stable flame could not be achieved. Its effects are to partially premix the fuel and the oxygen, to introduce turbulence, and, of course, to spread out the flame.



Fig. 1. A one second exposure photograph of the $\text{CS}_2\text{-O}_2$ flame with $(\text{CS}_2) = 1.8$ and $(\text{O}_2) = 57$ millimoles/sec. The circle behind the flame resulted from the lucite Brewster cup. Pressure ≈ 15 torr.

If we assume that all of the gas passing through the screen flows through a cross-sectional area of 30 cm^2 , the gas velocity in the X direction on fig. 1 is typically $\approx 30 \text{ m/sec}$. This compares with $\approx 1.5 \text{ m/sec}$ reported previously on a different burner [3]. (Please note that there is a typographical error in [3] and that 1.5 m/sec is the correct value.) From the equation [5] $S_u = U \sin \alpha$, where S_u is the burning velocity normal to the flame front, U is the cold gas velocity, and α is the angle between the flame front and the X direction, S_u is $\approx 2 \text{ m/sec}$. The angle α was determined from fig. 1 with the assumption that the angle across the visible cone equalled the angle across the flame front. Although the present calculation of S_u gives only an approximate value of S_u , clearly the S_u of the $\text{CS}_2\text{-O}_2$ flame is high compared to other fuel - O_2 flames.

The processes occurring in the flame which are reported here may be different from the other flame studies since wall reactions other than on the burner are unimportant in the present apparatus. A possible mechanism for the flame propagation involves the reactions.



The results of Homann et al. [6] and Sarkisyan et al. [7] on the flame reactions indicate that the actual mechanism is more complex. For example, Homann et al. [6] have identified the intermediate species: O , S , CS , SO , COS , S_2O , S_2O_2 , and $\text{S}_2\text{-S}_8$. A mass spectrometric analysis of the stable end products from the $\text{CS}_2\text{-O}_2$ flame revealed the following species and relative concentrations: CS_2 , < 0.1 ; O_2 , 60; SO_2 , 4; CO , 1; and CO_2 , 1. The significance of the CO_2 formation to laser oscillation depends on whether the reaction to laser oscillation depends on whether the reaction yielding CO_2 occurs in the propagation zone or in the termination zone of the flame. Additional information on reactions (1)-(5) and other reactions which may occur in flame can be found in ref. [8-10] and references cited therein.

In the flame, laser power as a function of burner-optical axis distance and as a function of the flow rates of CS_2 , O_2 , and additive gases was measured. Fig. 2 shows a plot of normalized output intensity versus the CS_2 flow rate. On this plot, a constant chemical efficiency would be a straight line parallel to the (CS_2) axis. At each point (O_2) was adjusted for maximum power. Table 1 gives some specific data for the output dependence on (CS_2) from 1.6 - 2.3 millimoles/sec. Within

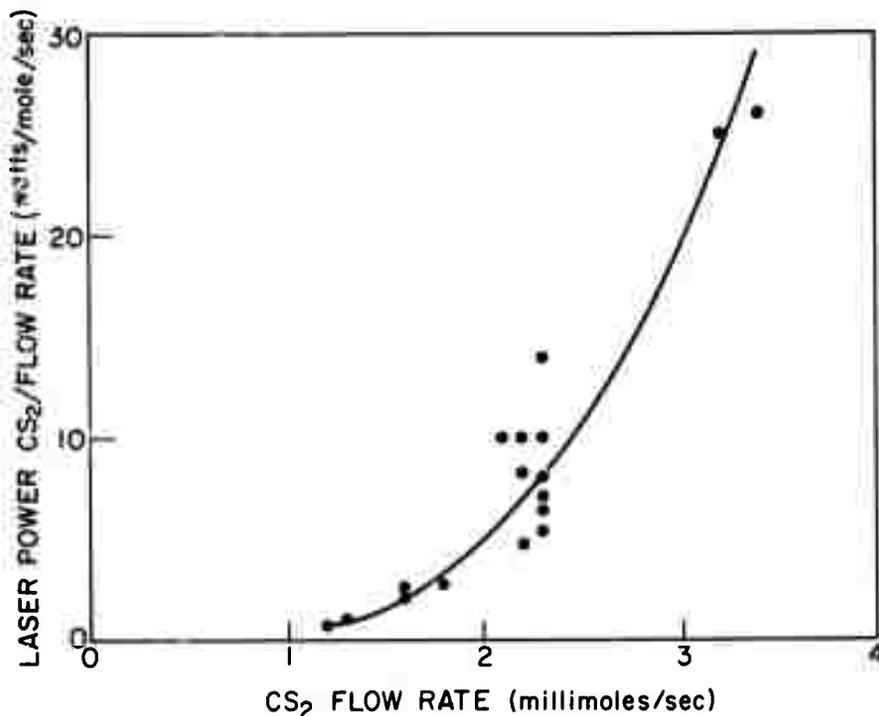


Fig. 2. Normalized laser power versus (CS₂). Burner to optical path distance on the X axis is 1.1 cm.

the limits of experimental error, the (O₂)/(CS₂) ratio was a constant, with a value of 34 ± 4 . The effect of a three fold increase in (CS₂) under these conditions is to increase the chemical efficiency about thirty fold.

The intensities plotted on fig. 2 were obtained at $x = 1.1$ cm and $Y = 0$ cm (the origin being at the center of the burner top). By translation in the X direction, it was found that peak performance occurred at 1.1 cm. Power generally dropped by a factor of two for $X = 0.6$ cm and 2.0 cm. This laser power dependence on X was essentially pressure independent. These results were obtained by moving a vertical translation stage onto which the burner was mounted. With the use of a reference position it was verified that the power at any point did not change more than $\pm 10\%$ during the course of a scan. In the Y direction a single experiment was carried out to estimate diffraction losses. At $X = 1.1$ cm and (CS₂) = 2.1 millimoles/sec, laser intensity was measured for $Y = 0$. The angular orientation devices were then moved 0.3 cm off center ($Y = 0.3$ cm) and the cavity was realigned. The laser intensity was about 30% lower.

One feature of the flame laser is the requirement of a large excess of O₂ in order to optimize the laser power. If this excess is reduced, the laser power falls sharply. For example, in a particular experiment with (CS₂) = 1.6 millimoles/sec, a change of (O₂) from 64 millimoles/sec to 57 millimoles/sec lowered the power from an optimal 19 mW to 11 mW.

TABLE 1
EFFECT OF ADDITIVES ON THE FLAME AT 1.1 CM DOWNSTREAM FROM THE BURNER
TOTAL PRESSURE IN VACUUM CHAMBER 10 - 20 TORR

FLOW RATE millimoles/sec		ADDITIVE	POWER mW	FRACTION OF INITIAL POWER	
CS ₂	O ₂			PRESENT	REF. 11
2.3	82		12		
2.3	82	63 He	7	0.5	
2.3	65		10		
2.3	54	3.3 SF ₆	19	1.9	
2.3	86		15		
2.3	72	6.5 N ₂ O	130*	8.6	1.5
2.3	74		25		
2.3	65	14 CO	210	8.4	10
2.2	82		18		
2.2	58	18 C.	86*	4.8	<1
2.1	97		20		
2.1	85	9.2 N ₂	24	1.2	<1
1.6	68		4		
1.6	65	1.4 SO ₂	9	2	
2.2	79		23		
2.2	70	5.0 NO ₂	0	0	

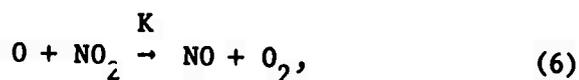
* Use of a narrow band pass filter which transmitted 5.2 - 5.4 μ radiation showed that only CO was responsible for laser transitions.

There are a number of possible reasons for the excess oxygen requirement. One is that the flame temperature is reduced. If this were the only effect, addition of an inert diluent such as He could replace much of the oxygen. Table 1 tabulates the effect of He and other additives. In these experiments the laser power was first measured at the optimum (CS₂)/(O₂) ratio. The additive was next added to the oxygen. In our system this also reduced the (O₂). Once the power was maximized with the additive, oxygen and additive were alternately adjusted until a peak power was reached. The additive was then shut off and (O₂) was readjusted and the laser power remeasured. These experiments were all carried out at X = 1.1 cm, since it was found that the additive did not shift position for the peak power. The effect of He on the flame was detrimental to the laser power. At higher flow rates, ≈ 80 millimoles/sec the flame was blown off the burner. The He additive experiment suggests that an important role of the excess oxygen is to affect the rates of the chemical reactions propagating the flame by increasing the O₂ concentration. To check this interpretation SF₆ was added to the flame and a 90% laser power increase resulted at (SF₆) = 3.3 millimoles/sec. At (SF₆) = 3.6 and (O₂) ± 50 millimoles/sec, the laser power dropped back to the original intensity. This further indicates that the excess oxygen cannot be replaced substantially by an inert additive which functions only as a heat sink.

Table 1 compares the effect of added N_2O , CO , CO_2 and N_2 on the flame to the effect of these additives on the discharge sustained CS_2-O_2 [11]. The comparison shows that the addition of CO is similar in both types of lasers - an addition of CO such that $(O_2)/(CO) \approx 4$ gives an 8-10 fold power increase. The addition of N_2O and CO_2 was more beneficial to the flame than to the discharge sustained laser. This may be due to a higher temperature leading to faster V-V rates. In both systems nitrogen does little to enhance laser power.

The effect of SO_2 on the flame was examined to determine if an increase in SO_2 concentration downstream from the burner was responsible for the termination of laser oscillation. Because of the low vapor pressure of the liquid SO_2 in the lecture bottle, it was necessary to add the SO_2 to a lower pressure flame than in the other experiments. Under these conditions a maximum of 1.0 millimoles/sec of SO_2 could be added to the flame. This yielded a 100% power increase. (Unlike the other additive experiments the (SO_2) which gave peak performance could not be determined.) The effect of SO_2 may be to cause V-V transfer from CO to the $SO_2(200)$ overtone at 2305 cm^{-1} . The SO_2 result and our interpretation contrasts to the report [7] that SO_2 inhibits the combustion of CS_2 by removal of O atoms and SO radicals.

Recently a series of flash photolysis experiments were carried out on a mixture of CS_2 , O_2 , and NO_2 [12]. The effect of a small amount of NO_2 to a CS_2-O_2 mixture was found to reduce laser intensity. In the flame the addition of NO_2 , as given in table 1, extinguished the flame. The occurrence of the reaction



with $K = 1 \times 10^{13} \exp(-580/RT)$ [10], is probably responsible.

From the use of two different hole coupling mirrors, the small signal gain coefficient was estimated. The total cavity loss with the 1 mm-hole mirror was estimated to be 7%, and the 2 mm-hole mirror 13%. In the CS_2-O_2 flame there was no laser oscillation with the 2 mm-hole mirror and a stable output with the 1 mm-hole mirror. Therefore, the round trip optical gain for the flame with no additives should be in the neighborhood of 10%. The corresponding linear gain coefficient would then be about 0.2/m. This value is to be compared to 0.1-0.5/m for a conventional discharge laser running on CO , air and He with liquid nitrogen cooling [13].

Finally an experiment was performed to achieve high power. The combustion of 3.9 millimoles/sec CS_2 in 110 millimoles/sec O_2 and 7.6-millimoles/sec N_2O gave 0.6 W laser intensity. This may be compared to the highest powers obtained from the discharge sustained CS_2-O_2 systems by normalizing power by the CS_2 flow rate. On this basis, the flame

power is only a factor of 2 lower than that reported in ref. [14] and a factor of 6 lower than that reported in ref. [11].

The authors wish to thank Dr. F. Saalfeld for performing the mass spectrometric analysis of the stable flame products.

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APPENDIX B
ENERGY EXCHANGE PROCESSES
IN A LOW TEMPERATURE N₂-CO TRANSFER LASER*

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ABSTRACT

A liquid-nitrogen-cooled, active-N₂-pumped CO laser has produced cw oscillation from $v = 2 \rightarrow v = 1$ (4.8 μm) to $v = 35 \rightarrow v = 34$ (8.0 μm). An analysis of the output spectrum gives the V-T relaxation rate of CO ($v \approx 30$) by He at 150°K as $2 \times 10^3 \text{ sec}^{-1} \text{ torr}^{-1}$.

Laser oscillation has been achieved by mixing electrically excited N₂ with CO in a fast-flow, liquid-nitrogen-cooled apparatus. The observed spectrum of laser transitions, ranging from $v = 2 - v = 1$ to $v = 35 \rightarrow v = 34$, extends significantly the number of bands obtainable in similar devices operated at room temperature.^(1,2) The characteristics of this laser can be adequately explained on the basis of the existing theories on V-V exchange probabilities^(3,4) and vibrational distribution functions.^(5,6) An analysis of the dependence of the output spectral content on CO partial pressure shows that as much as 2% of all the CO molecules can be present in each vibrational level up to $v = 25$. Thus, mixing active N₂ with CO at low temperatures seems to be an excellent way of preparing large concentrations of CO in very high vibrational levels.

The apparatus for the experiment is of all glass construction and is shown schematically in Fig. 1. Both the main tube and the side arm have 2.22 cm I.D. The linear flow speed under typical operating conditions is 65 m sec⁻¹ at the position marked O and 92 m sec⁻¹ at Q. The mixture of pre-cooled He and N₂ is passed through a 20 cm D.C. glow discharge maintained at 50 mA, and CO is injected into the stream at O. A 50 cm interaction region is provided for the build-up of CO vibrational level populations. The main tube is 1 m long and has NaCl Brewster angle windows. All three cooling jackets are filled with liquid nitrogen. A totally reflecting 4 m radius of curvature mirror is used with either a 1/2 mm hole coupling or a 1 mm hole coupling output mirror. The output is modulated by a chopper wheel and sent through a 1 m monochromator into a gold doped germanium detector.

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The experimental results from a typical run with the 1 mm hole output mirror are shown in Figs. 2 and 3. The partial pressures of He and N₂ used were 3.5 torr and 2.5 torr respectively. The presence of He was essential to the laser's performance, probably because it reduced the role of wall deactivation of vibrationally excited molecules and improved the thermal conductivity of the medium. The temperature in the tube was measured with a thermocouple to be 173°K at P and 118°K at Q. The interpretation of the results is somewhat hindered by the axial variations due to the longitudinal flow of the system. Nevertheless, we have found it possible to estimate the V-T relaxation rate by He for certain high-lying CO vibrational levels.

The general features of the output spectrum and power dependence on CO partial pressure can be understood as follows. At the lowest CO partial pressure there are not enough molecules in $v = 2$ and $v > 12$ for the gain to exceed threshold for the related transitions. At slightly elevated pressures, the higher vibrational bands as well as $v = 2 \rightarrow v = 1$ begin to oscillate. In this regime the power output increases almost linearly with CO partial pressure, indicating that the small amount of CO initially is not deactivating N₂ noticeably. Above $P_{CO} \approx 10$ m torr CO deactivation through radiative decay and V-T relaxation begins to drain the energy stored in N₂, causing the $2 \rightarrow 1$ band to disappear and the power output to increase less than linearly with CO partial pressure. The peak in power output is reached when the rate of deactivation of the mixture is so great that a portion of the CO distribution becomes absorbing before arriving at Q. As we increase the CO pressure further, the highest oscillating bands begin to disappear. Since the high vibrational levels are populated mainly by near resonant collisions of levels immediately below them, the highest levels cannot be built up if the distribution is significantly relaxed in a time comparable to that needed for it to be fully developed.

To examine a few of the points more quantitatively, we shall consider the high wavelength cutoff in some detail. The numerical computations of ref. (6) have shown that the vibrational levels follow the Treanor distribution out to its minimum. Then, if near resonant collisions dominate, the level population would remain nearly constant until V-T relaxation becomes important, at which point the population drops off sharply. Assuming that such a distribution (to be referred to as the modified Treanor distribution) is appropriate for the present experiment, we can write for the level $v + 1$ where the drop-off begins the following steady state rate equation: (7)

$$0 = \frac{d N_{v+1}}{dt} = Z N_v \left(\frac{1}{2} P_{v,v-1}^{v,v+1} N_v + P_{v-1,v-2}^{v,v+1} N_{v-1} + P_{v-2,v-3}^{v,v+1} N_{v-2} + \dots \right) - R N_{v+1}. \quad (1)$$

Here R is the V-T relaxation rate for N_{v+1} , Z is the CO-CO gas kinetic collision frequency per unit concentration, and the P 's are V-V exchange probabilities. For the high v levels under consideration, an application of the Sharma-Brau theory^(4,8) shows that the first two or three probabilities in eq. (1) are roughly unity; then they diminish very rapidly. It is therefore possible to calculate the V-T relaxation rate given the concentrations of the levels. But the distribution can be determined from the lowest lasing band, provided that there is not much axial variation along the flow, and that the levels above the Treanor minimum are pumped primarily by near resonant CO-CO collisions. These conditions are met, as will be shown later, for $P_{CO} \approx 10$ m torr. The lowest lasing band at $P_{CO} = 10$ m torr is $v = 3 \rightarrow v = 2$, implying that $N_3/N_2 \approx 0.8$ at the point where the distribution is fully developed. Using the modified Treanor distribution, then, one calculates a pressure of 0.2 m torr for CO molecules in $v = 25$. The sharp drop-off occurs a few levels higher up where $N_v/N_{v+1} > 2$. Using $ZN_v = 1.7 \times 10^3 \text{ sec}^{-1}$, $N_v/N_{v+1} = 2$, and the first three terms only in the parenthesis in eq. (1), one readily estimates a V-T relaxation rate of $R = 8 \times 10^3 \text{ sec}^{-1}$ for CO ($v \approx 30$) at an average temperature of 150°K . As a point of reference, the radiative lifetime for CO ($v \approx 30$) is about 300 sec^{-1} .

It is now necessary to show that for a CO partial pressure of 10 m torr the higher vibrational levels are pumped by CO-CO near resonant collisions only. For this purpose, we need to reconstruct the N_2 distribution. This can be done by noting that the CO ($v \rightarrow v - 1$) transition is in resonance with the $N_2(v + 6 \rightarrow v + 5)$ transition. We then deduce a characteristic N_2 vibrational temperature of $\theta_1^* = 1500^\circ\text{K}$. It follows that $N_2(v)$ has a pressure of less than 0.2 m torr for $v \geq 8$. To estimate the relative importance of the various kinds of collisions, we have calculated the V-V exchange probabilities due to long range forces from the Sharma-Brau theory.⁽⁸⁾ They are $P(\text{CO}^v \rightarrow v+1, N_2^{v'} \rightarrow v'-1) = 3 \times 10^{-4} v'(v+1)$ and $P(\text{CO}^v \rightarrow v+1, \text{CO}^{v'} \rightarrow v'-1) = 1 \times 10^{-2} v'(v+1)$ for $T = 150^\circ\text{K}$, provided the probabilities are less than unity. They level off to a constant value of one for sufficiently high v and v' . The short range contribution to the exchange probabilities can be found in ref. (3). From the magnitude of the various exchange probabilities and the N_2 and CO distributions it is readily seen that the high CO vibrational levels are indeed primarily populated by CO-CO near resonant collisions.

The experimental data compiled by Millikan and White⁽⁹⁾ show that at 300°K the deactivation of CO ($v=1$) by He is about three orders of magnitude faster than that by CO. Because of the similarity between N_2 and CO, one can assume that the deactivation of CO ($v \approx 30$) in the present experiment is primarily by He. Then our experimental result gives the V-T relaxation rate of CO ($v \approx 30$) by He at 150°K as $2 \times 10^3 \text{ sec}^{-1} \text{ torr}^{-1}$. Miller and Millikan⁽¹⁰⁾ have recently measured a V-T relaxation rate of CO ($v = 1$) by He at 150°K of $0.1 \text{ sec}^{-1} \text{ torr}^{-1}$.

In a separate experiment, under similar gas flow conditions but with the 1/2 mm hole coupling mirror, vibrational bands as high as $v = 35 \rightarrow v = 34$ have been observed to oscillate. We have seen that He is needed to cool the gas mixture, but it is also responsible for the deactivation of CO vibrational levels. Therefore, if some means could be found to reduce the temperature of the medium without deactivating either the N₂ or the CO, much higher vibrational bands can be expected to oscillate. The prospect of being able to study in detail CO vibrational levels very near the dissociation limit is an exciting one.

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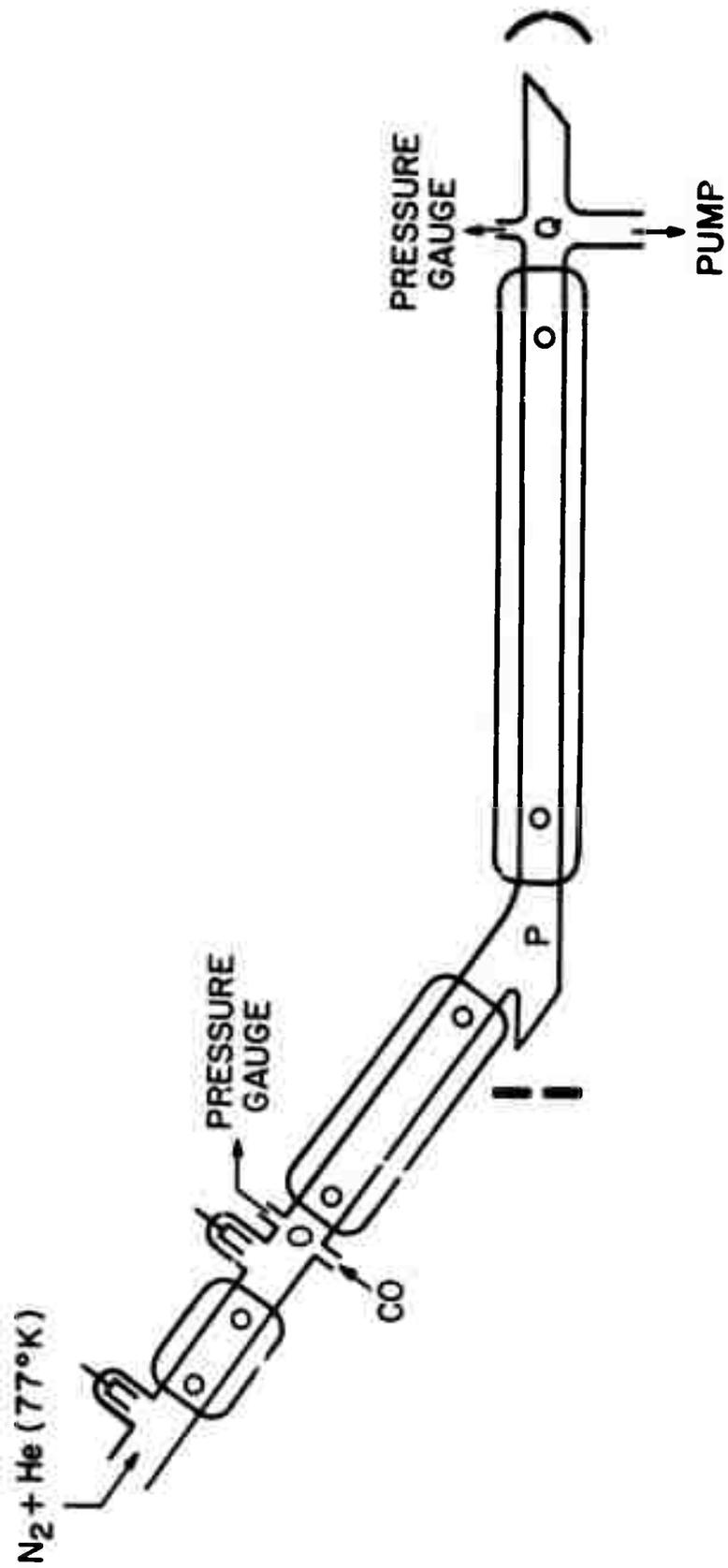


Fig. 1 - Schematic of experimental apparatus

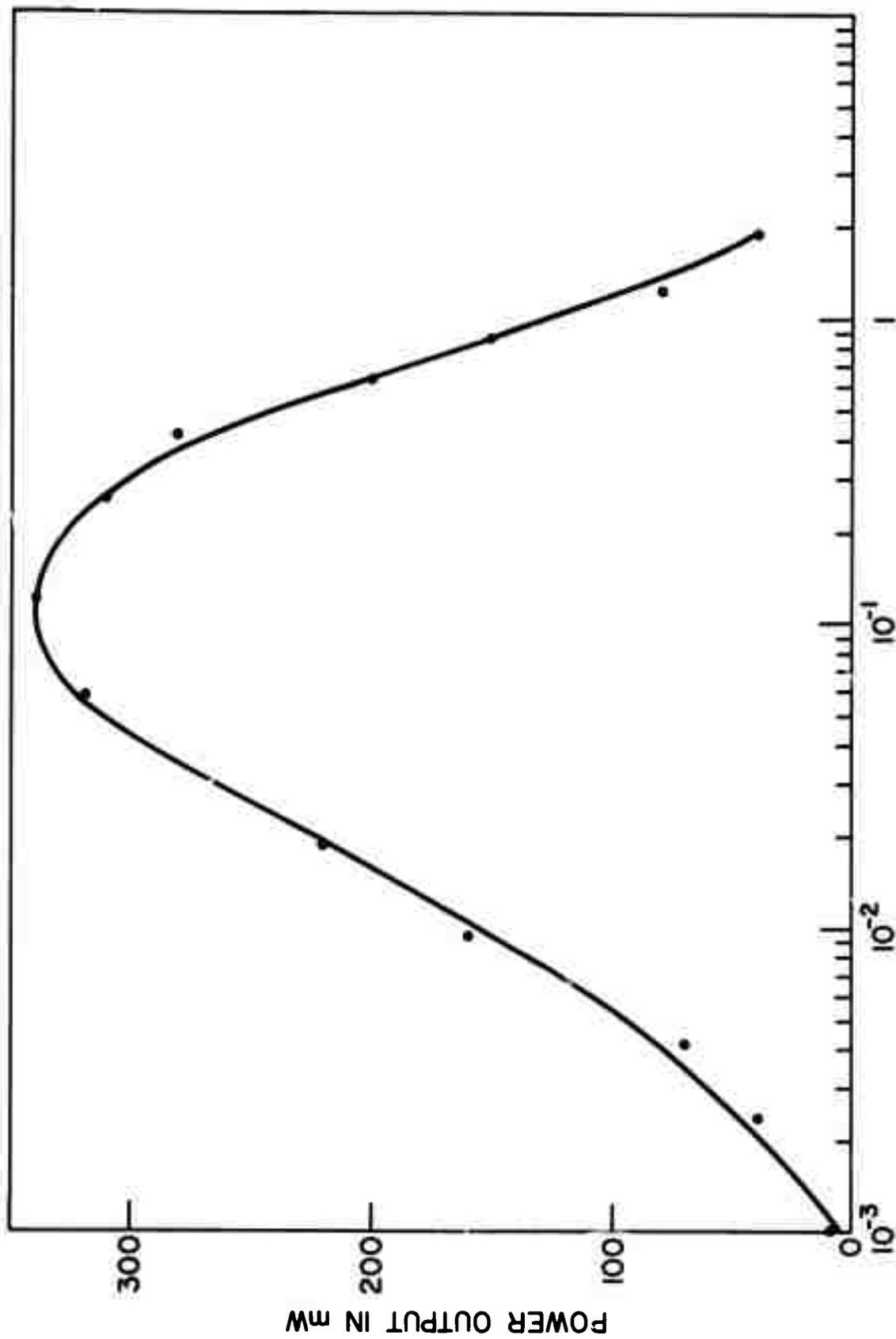


Fig. 2 - Laser output power dependence on CO partial pressure

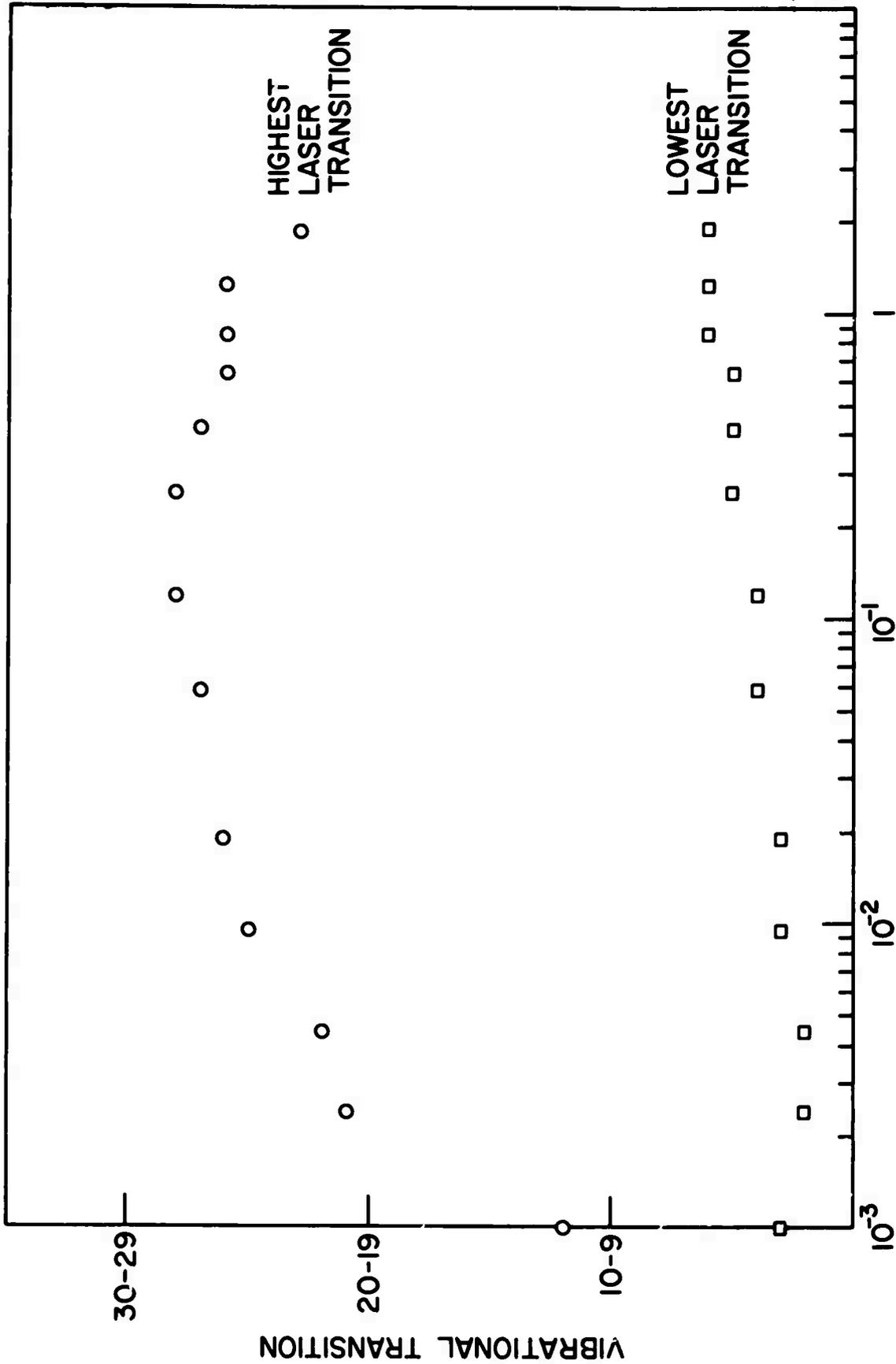


Fig. 3 - Range of laser transitions as a function of CO partial pressure. For each band, several P branch transitions around P (10) were observed.