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POTENTIAL LASER ACTION IN A FLAME
(Final Report)

The Ohio State University

ElectroScience Laboratory

Department of Electrical Engineering
Columbus, Ohio 43212

FINAL REPORT 2745-3

August 1970

Contract No. DAHC04 69 C 0033

Sponsored by
Advanced Research Projects Agency
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United States Army Research Office - Durham
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NOTICES

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2745-3	"Potential Laser Action in a Flame," Final Report,

POTENTIAL LASER ACTION IN A FLAME

INTRODUCTION

About two years ago instead of the usual CO_2, He and N_2 mixture used in the CO_2 laser, we applied mixtures of air and different hydrocarbons, such as acetone, toluene, dimethyl ether, etc. When the ratio of the mixture and the flow rates were correctly adjusted, we noticed strong laser action on both the P and R branches of the CO_2 (001) -- (100) vibrational transitions, as well as on many different vibrational-rotational levels of the CO molecule[1]. This experiment was done on a one meter long water-cooled laser with internal mirrors. The power was coupled out through a one millimeter hole drilled in the center of one of the mirrors. The internal diameter of the discharge tube was one inch.

We can to some extent analyze the physics and the chemistry taking place within this discharge laser. In all likelihood, the hydrocarbon was decomposed under discharge conditions and oxidized, producing both CO and CO_2 and also releasing into the discharge the heat of combustion. If we look at Fig. 1 we notice that the electric discharge was to supply an amount of power proportional to the heat of activation ΔE and subsequently the hybrocarbon upon oxidation releases an amount of energy ΔH, the heat of combustion. The net amount of heat $\Delta H'$ dissipated to produce the CO and CO_2 molecules is

$$\Delta H' = \Delta E + \Delta H.$$

In burning a substance such as acetone ($CH_3 - CO - CH_3$) one produces one water molecule for each CO_2 molecule which is produced. Moreover, as we will discuss later, the production of the CO_2 and CO does not occur instantaneously, but the mixture of air and hydrocarbons must flow together for some distance within the discharge tube until full combustion is accomplished and the CO_2 molecule is produced. Fast flow rates will not produce the CO_2 molecule within the laser cavity.

If we now assume that the excitation of the CO_2 in the hydrocarbon-air mixture laser is only due to the transfer of energy from the vibrationally-excited metastable state of nitrogen molecules in the discharge, then this laser is operating under unfavorable conditions. Namely excess heat of combustion is released in the discharge and has to be removed through water cooling, and excessive water vapor is present, which would tend to de-excite the upper CO_2 laser level. Methane, for example, produces two water molecules for every CO_2 molecule.

The question asked was whether or not any excitation of the CO_2 molecule was achieved through the chemical reaction. In other words, since the laser was operating under non-ideal conditions, we inquired as to the possibility of some of the heat of reaction going into vibrational excitation of the CO_2 levels. To obtain the answer, we had to devise a few experiments. These experiments are chronologically and briefly presented in the following pages. This work has shown promise of producing laser action, and it is therefore proposed that this grant be carried on for an additional twelve month period.

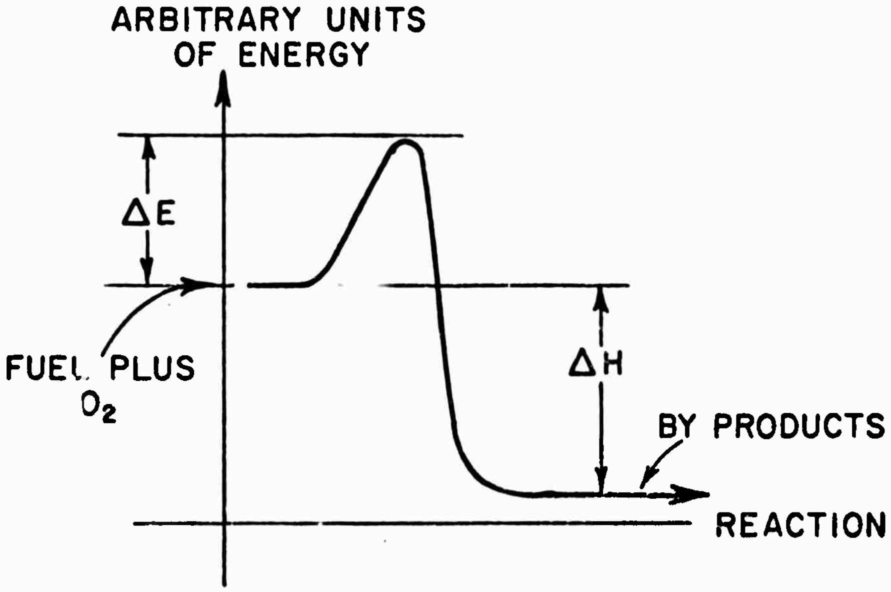


Fig. 1. ΔE is the activation energy. ΔH is the heat of combustion.

TECHNICAL APPROACH

In order to minimize the excitation caused by the electric discharge a geometry such as shown in Fig. 2 was desired, but actually that of Fig. 3, was constructed as a compromise. These geometries were thought to give us the advantage of having the by-products removed from the discharge as soon as they were produced so that if the by-products were not excited through chemical means, they would not linger in the discharge tube and be excited by the excited metastable state of nitrogen. In that geometry the discharge was transversely situated with respect to the laser axis and the gas was removed after a short travel within the laser tube. However, it was seen that the short length of the discharge was not sufficient to produce the necessary chemical reaction: that is to say, no CO_2 molecule was produced. Different geometries and catalysts, such as platinum, etc., were introduced to facilitate and expedite the chemical reaction of the hydrocarbon and oxygen but with little improvement. However, longer discharge lengths and slower flow rate did produce the CO_2 molecules.

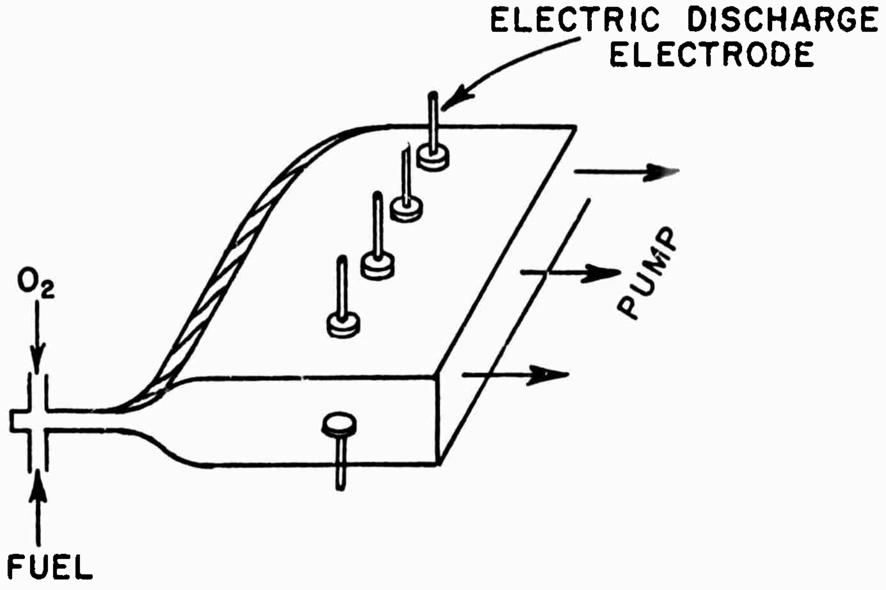


Fig. 2. The discharge is transverse to the direction of the flow. The discharge is only to help the chemical reaction.

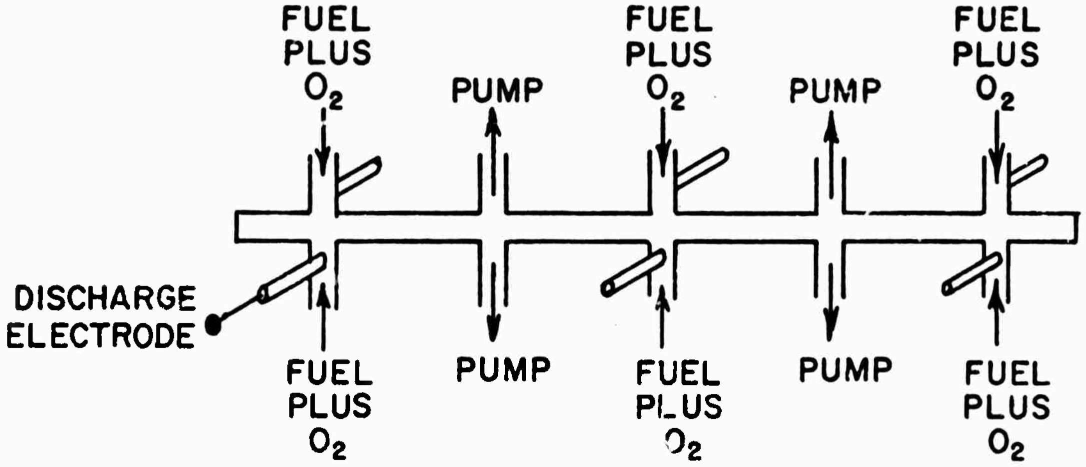


Fig. 3. A modified form of Fig. 2 which was actually built and tested.

To increase the reaction rate and have the reaction contained over a shorter length of travel, we were forced to consider other possibilities; that is to say, to have the reaction expedited through high temperatures rather than the electric discharge. For this reason, we heated the reaction chamber, Fig. 4, and later decided to have the reaction take place within a flame. Considerable effort was expended in the art of sustaining a stable flame in a pressure of less than 5 Torr. The mixture of air and the hydrocarbon gas was passed through a ceramic disc to attain a completely homogeneous mixture of oxygen and hydrocarbon and then the flame was sustained on top of the ceramic disc. The oxygen and the hydrocarbon fuel were passed through orifices of less than half a millimeter in diameter to regulate the flow and make the system independent of pressure fluctuations. Mixtures of methane as well as acetylene with oxygen were burned at pressures of as low as one Torr in a bell jar.

Finally six burners were constructed and were housed in an aluminum tube as shown in Fig. 5. However with this arrangement, because of the metallic natures of the burners we were not able to have a discharge as envisioned in Fig. 2. For most of our experiments, no more than four of the burners could be burned simultaneously, since the running of the two at the ends caused the one inch thick plexiglass plates to warm up excessively. Preliminary crude gain measurements using a CO_2 source have shown attenuation within the flame and some gain just outside the flame thickness when using O_2-C_2H_2 mixtures.

THE CHEMISTRY AND THE THERMODYNAMICS OF THE FLAME STRUCTURE

The geometry shown in Fig. 5 provides a flat flame 2" wide and three feet long when all six burners can be lit. If we look at the cross section of the flame (Fig. 6) we have a luminous zone just above the burners having a thickness of L centimeters where L is empirically given by the relation[2]

$$L = \frac{2.5}{pv}$$

with p being the pressure in millimeters of mercury and v the flame velocity in cm/sec. Now in such a flame about 55% of the total chemical energy is released within the luminous zone and the remaining 45% is released in an extended region in front of the flame. If we take methane gas as our fuel, the overall reaction that takes place within the luminous zone is,

$$2CH_4 + 3O_2 \rightarrow 2\,CO + 4\,H_2O$$

where most of the CO is produced. However, in the nonluminous zone of the flame the overall production of the CO_2 is achieved, and in here the overall reaction is of the form

$$2\,CO + O_2 \rightarrow 2CO_2 \quad .$$

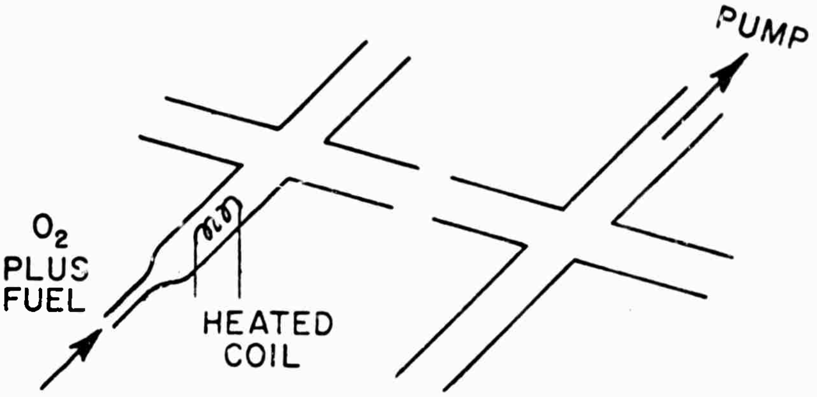


Fig. 4. In this figure some red hot heated coils were placed to facilitate the chemical reaction.

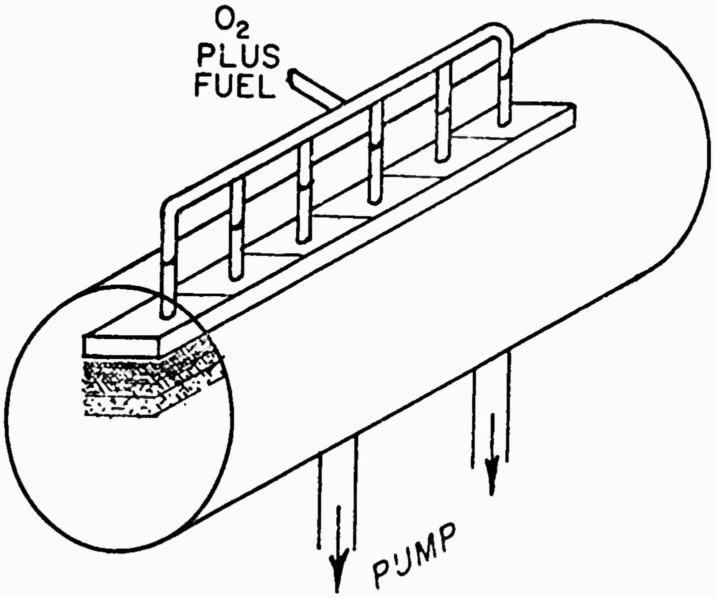


Fig. 5. Six burners are placed side by side to give a length of 36" by 2" wide.

However, kinetic and rate equations cannot be derived from the above two overall equations. The mechanisms are not simple but in general one has at least a number of reactions which contain the short-lived radicals. Briefly, the reactions are first[2].

$$CH_4 + OH \leftrightarrow CH_3 + H_2O$$

$$CH_4 + H \leftrightarrow CH_3 + H_2$$

$$CH_4 + O \leftrightarrow CH_3 + OH$$

where CH_4 is being attacked. Then we have

$$CH_3 + O_2 \leftrightarrow H_2\,CO + OH,$$

$$H_2\,CO + OH \leftrightarrow HCO + H_2O$$

And finally the steps which produce the CO, i.e.,

$$HCO + OH \leftrightarrow CO + H_2O$$

$$CH_3 + O \leftrightarrow CO$$

For the nonluminous zone where most of the CO_2 gas is generated, the most probable reaction is

$$OH + CO \leftrightarrow CO_2 + H$$

since spin consideration makes direct oxidation of the CO gas with oxygen improbable and the reaction rate is very small.

Composition of the Flame: Again let us consider only the CH_4-O_2 flame which has been extensively studied. Figure 7 gives the mole fraction concentration of the final products of interest, such as CO, CO_2, H_2O, O_2 and CH_4 as a function of its distance from the burner. One notices that as CO_2 and H_2O increase after the luminous zone, the CO and CH_4 concentration decreases, also twice as much H_2O is produced as CO_2. In this particular flame much more oxygen is used then methane.

Temperature Distribution: The temperature across the flame rises very sharply to a few thousand degrees centigrade and then gradually drops down to about the temperature of the surrounding water-cooled aluminum tube. Figure 8 shows the approximate temperature distribution about the flame and the surroundings, for our geometry. One notices that the temperature drops from a value of a few thousand degrees within the luminous zone of the flame to about 20 degrees at the edge, the temperature of the surrounding aluminum tube.

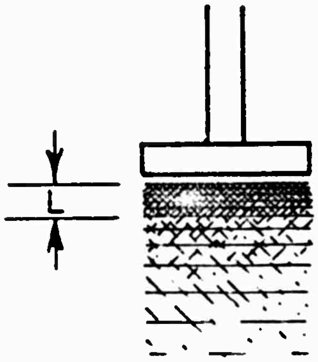


Fig. 6. The thickness of the luminous zone is $L = 2.5/Pv$. The non-luminous zone extends to several times this thickness.

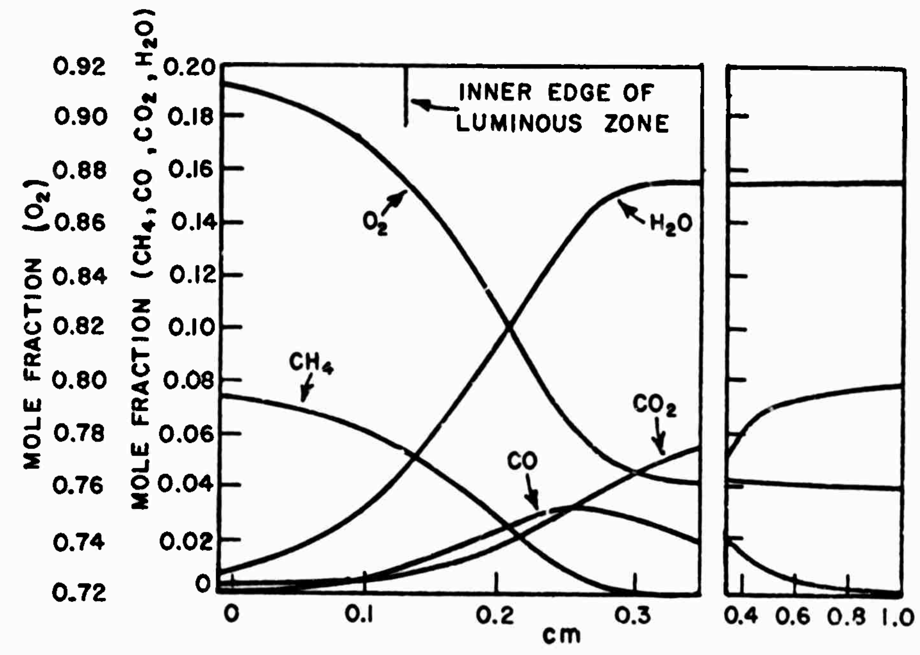


Fig. 7. Concentration profiles in 0.1-atm methane-oxygen flame.

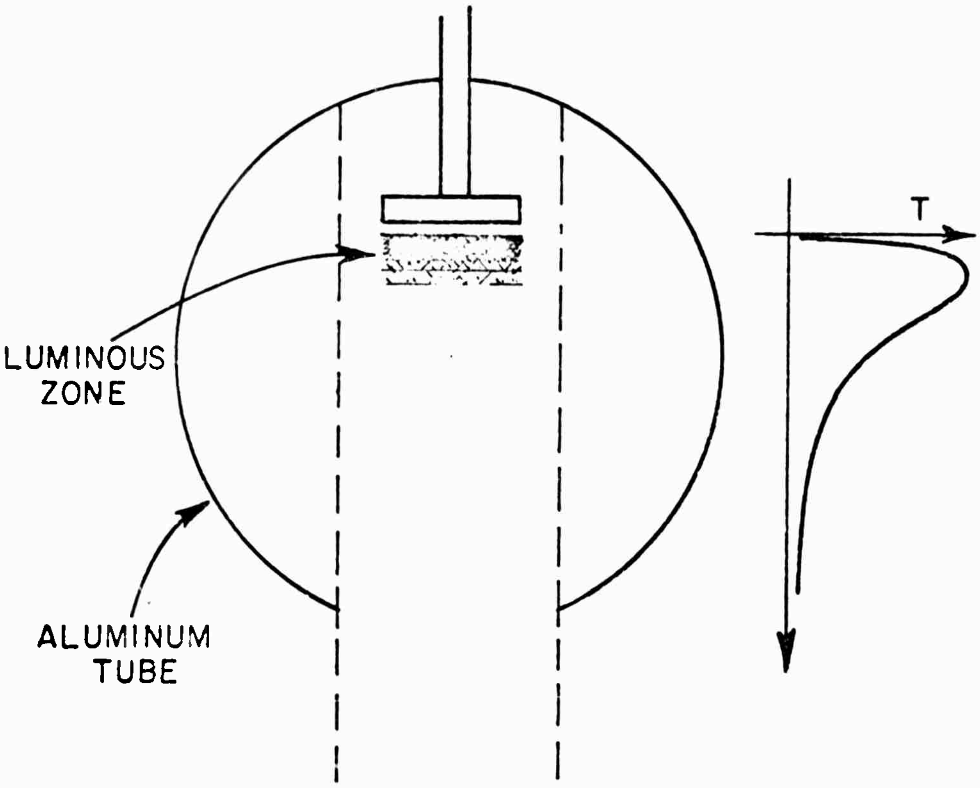


Fig. 8. The temperature profile across the flame.

Density and Pressure: The pressure across the flame is more or less constant. The gas density ρ can be found from the equation of state, namely,

$$\rho = \frac{P\overline{M}}{RT} = \frac{P}{T} \quad \frac{\overline{M}}{R}$$

where P is the pressure, $\overline{M}$ is the average molecular mass of the gas constituents, T is the temperature in degrees Kelvin and R is the molar gas constant. The gas pressure is somewhere between one to five Torr. This depends upon the number of the pumps being used and their capacity. The low pressure of gas reduces the collision frequency, thus allowing a vibrationally excited level to have a longer relaxation time. The change of geometry as shown in Fig. 9 could change the pressure profile and hence the density.

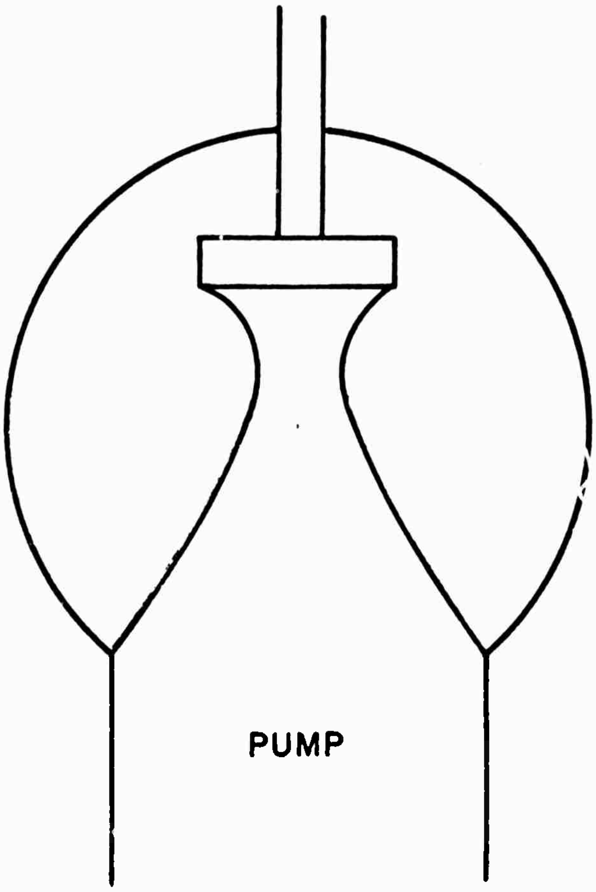
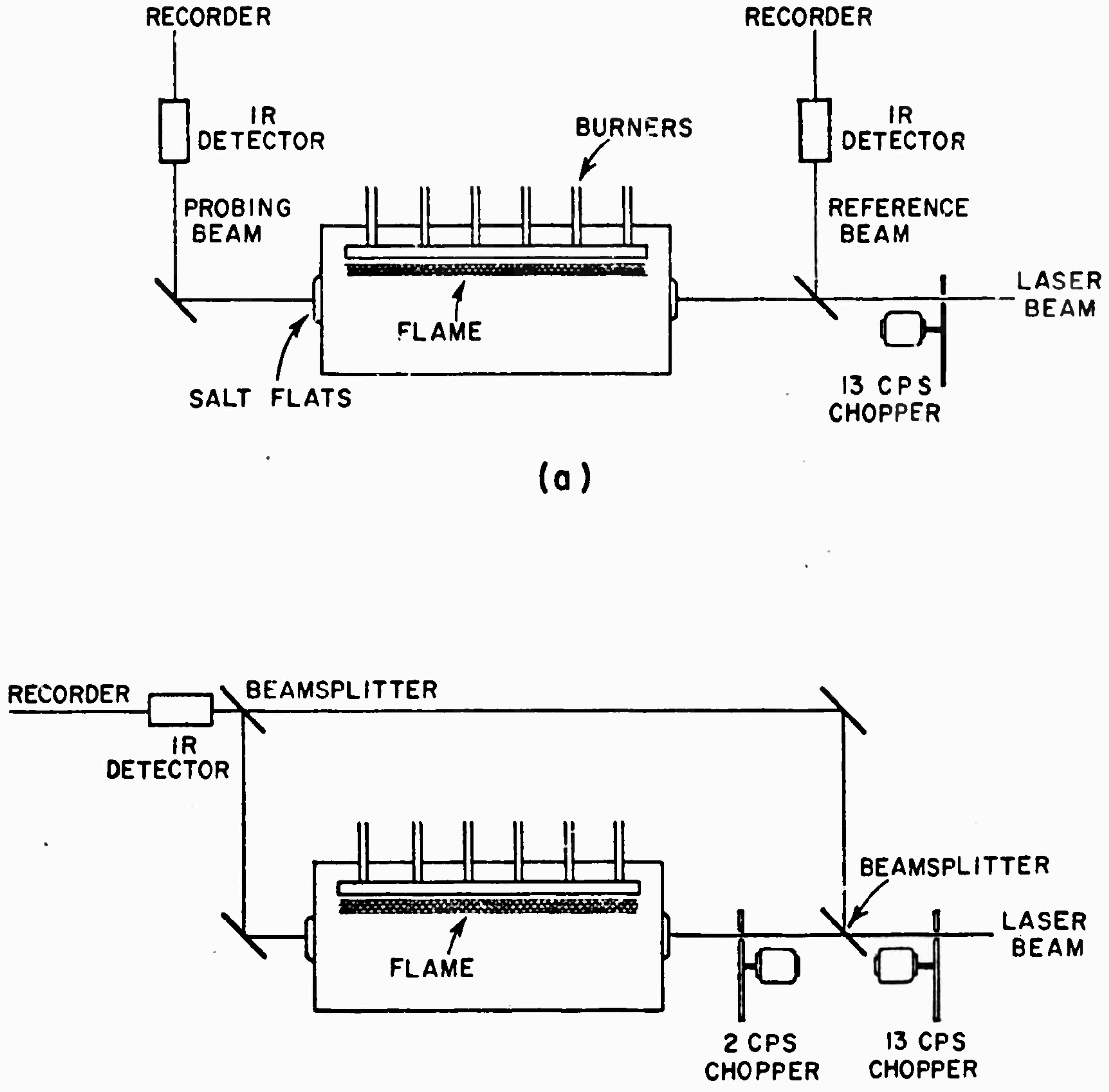


Fig. 9. Modified version of Fig. 5.

MEASUREMENT PROCEDURE

With a stable flame established, apparatus was set up to measure the gain of some of the rotational-vibrational transitions of the (001) → (100) CO_2 levels. Flame size of 24 inches was limited by end window heating and by available vacuum pump capacity of 25 c.f.m. A quick check was made to see if laser action could be obtained by fortuitous choice of parameters. No laser action was observed under conditions tested.

The configuration of Fig. 10a was therefore set up. This particular technique has the inherent limitation of allowing gain measurements only for available laser wavelengths, i.e., in this case only for the 10.6μ CO_2 laser lines. Possible inversion of other levels such as CO* would be missed. The method is however capable of measuring gains lower than necessary for laser threshold; even decreases in measured losses could be of significance.


RECORDER
IR DETECTOR
PROBING BEAM
BURNERS
FLAME
SALT FLATS
RECORDER
IR DETECTOR
REFERENCE BEAM
LASER BEAM
13 CPS CHOPPER
RECORDER
BEAMSPLITTER
IR DETECTOR
FLAME
BEAMSPLITTER
LASER BEAM
2 CPS CHOPPER
13 CPS CHOPPER

(a)

(b)

Fig. 10.

The output of a CO_2 laser was divided by a beam splitter into a reference and a probing beam and two thermopile detectors were positioned as shown in Fig. 10a. A flame was started and the output of the two detectors recorded for about five minutes. The flame was then extinguished and the two outputs would again be measured. The flame assembly would then be displaced so that a new section of the flame would be measured and the process would be repeated.

In order to decrease drift problems with the thermopiles, measurements were also made with the system of Fig. 10b, where only one detector is used. For one half the period of the 2 cps chopper both beams illuminate the detector, while for the other half cycle only the reference beam is incident on the detector. Measurements made with and without a flame will lead to the gain figure.

Experimental runs were made with methane, acetylene, and cyanogen under different combustion conditions and for different flame regions. No definite gain conditions would be established for any case tested. Although extremely discouraging, this lack of positive results should not be taken as evidence that no population inversion or gain exists in the flame. Definite stability problems existed in both the measuring system and the probing laser which should be improved if more measurements are to be made.

CONCLUSIONS AND RECOMMENDATIONS

A considerable amount of time and expense has been invested in the development and operation of a continuous sheet of flame, i.e., a region where chemical reaction and excitation takes place. This region is two inches wide and is several feet in length and operates at very low pressures where collisional de-excitation decreases greatly. The by-products of the flame are then expanded and pumped out. The flame itself is a few centimeters in thickness and the pressure across it remains constant. However the pressure decreases as one approaches the vacuum pump input region. The potentialities of chemical excitation in this form has not yet been fully investigated. We have a confined region in the form of a long strip where intense chemical reactions take place at very low pressures, i.e., about 1/200th of atmospheric pressure. Out of the heat of combustion released, it is highly probable that some of the energy will be exciting some of the vibrational levels of the by-products.

Shimoda[3] in his calculations of a thermally pumped laser had shown the possibility of CO_2 (001) vibrational level inversion if the CO_2 molecules are placed in between two plates, one held at 1400°K and the other at 280°K. Moreover Bronfin, et al.[4] have experimentally shown that the expansion of heated CO_2 gas through an expansion nozzle to pressures of few millimeters of mercury and its subsequent cooling could cause actual CO_2 laser action. The geometry of Fig. 9 has more or less some of the above two features inherent in its operation. To compare with Shimoda's calculations we have a region of intense temperature of a few thousand degrees Kelvin with surrounding plates of about 300^{o}K. Secondly the flame, that is to say the heating of CO_2, takes place over a range of a few centimeters in thickness at a constant low pressure and then is expanded to still lower pressures.

Stable low pressure flames were successfully maintained. Gain measurements were made with a CO_2 laser, with no overall positive gain measured under flame conditions attempted.

It is recommended that measurements be made with a more sensitive and stable system, using improved durable optics and a stable laser source. The laser used should be capable of single line operation, and both CO_2 and CO lasing transitions should be tested.

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13. ABSTRACT

A continuous sheet of flame, i.e., a region where chemical reaction and excitation takes place was developed. This region is two inches wide and is several feet in length and operates at very low pressures where collisional de-excitation decreases greatly. The by-products of the flame are then expanded and pumped out. The flame itself is a few centimeters in thickness and the pressure across it remains constant. However the pressure decreases as one approaches the vacuum pump input region. The potentialities of chemical excitation in this form has not yet been fully investigated. However, a region in the form of a long strip where intense chemical reactions take place at very low pressures, i.e., about 1/200th of atomospheric pressure has been confined. Out of the heat of combustion released, it is highly probable that some of the energy will be exciting some of the vibrational levels of the by-products. ( )

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