Investigations on the CS_2–O_2 Chemical Laser

F. G. SADIE *, P. A. BÜGER, and O. G. MALAN

National Physical Research Laboratory, C.S.I.R., P.O. Box 395, Pretoria, South Africa

(Z. Naturforsch. **27 a**, 1260—1263 [1972]; received 26 June 1972)

The reactions producing vibrationally excited CO in the continuous wave CS_2-O_2 chemical laser are considered. Fundamental and overtone transitions were observed in the systems CS_2+O_2, CS_2+N_2O, O_2+CS and it is concluded that the two reactions $O+CS \rightarrow CO+S$ and $O_2+CS \rightarrow CO+SO$ are the reactions in which vibrationally excited CO are produced. The second reaction appears to be responsible for overtone laser action at low buffer gas partial pressures and low discharge currents.

Introduction

Continuous wave (CW) laser action resulting from the oxidation of carbon disulphide has been reported [1–6]. These systems were observed to lase in the CO-fundamental band between 5.2 μm and 5.6 μm. In the system [7] used for the present study the CO-overtone band around 2.5 μm was observed in addition to the fundamental band, and fifteen vibrational transitions from $2-0$ up to $16-14$ could be resolved (Figure 1).

It is generally believed that the reactions

$$O + CS_2 \rightarrow CS + SO \qquad (1)$$

and

$$O + CS \rightarrow CO + S + 75 \text{ kcal/mole} \qquad (2)$$

are responsible for laser action in the $CS_2 - O_2$ chemical laser. The energy produced by reaction (2) is sufficient to populate vibrational levels of CO up to and including $v = 14$. However, in our previous investigation [7] and also in the study reported by GREGG and THOMAS [8] on their pulsed system, lasing transitions from the 16-th vibrational level were observed. A further process responsible for populating the CO vibrational levels $v = 14$, 15 and 16 must thus also have been operative. SUART, ARNOLD and KIMBELL [9] suggested the reaction

$$O_2 + CS \rightarrow CO + SO + 87 \text{ kcal/mole}. \qquad (3)$$

Later results [10] indicated that reaction (3) is more important than reaction (2).

The use of a diluent gas, helium, is known to decrease the rate of recombination of oxygen atoms; it further inhibits deactivating collisions of vibrationally excited CO with the resonator walls by

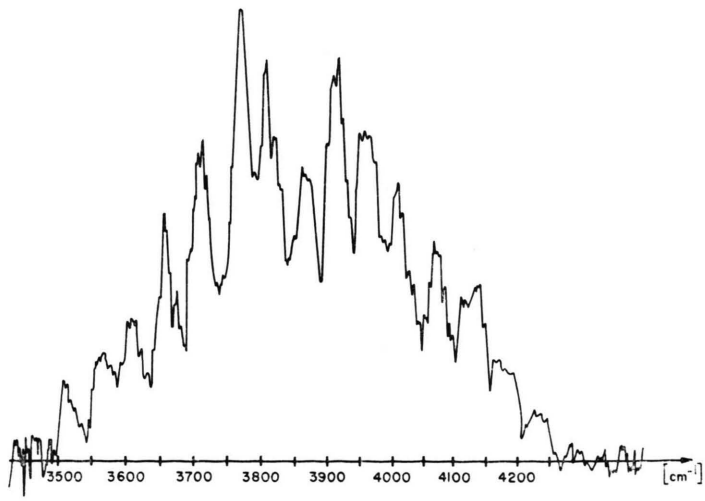

Fig. 1. Overtone transitions.

Reprint requests to Prof. Dr. P. A. BÜGER, National Physical-Research-Laboratory, C.S.I.R., P.O. Box 395, *Pretoria*, South Africa.

* On leave from the University of the Western Cape, Private Bag, Bellville, South Africa.

lowering the rate of diffusion of the lasing gas to the walls [11]. The diluent further provides for greater thermal conduction, thereby lowering the translational temperature of the lasing gas. A more favourable TREANOR distribution [12] is obtained and laser gain is enhanced.

Experimental

The laser system is shown schematically in Fig. 2 and has been described previously [7]. The following aspects were investigated:

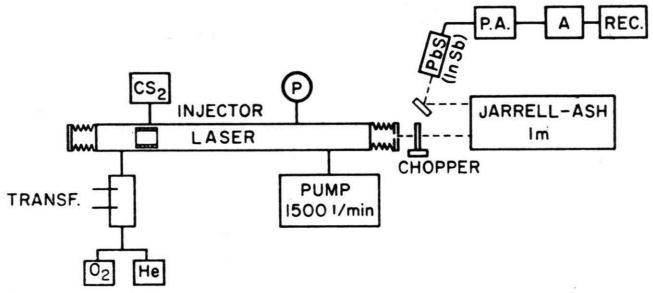

Fig. 2. Diagram of laser system.

1. Dependence of laser action on buffer gas partial pressure. – The partial pressures of oxygen and CS_2 were kept constant and p_{He} was varied in the range between 0 and 5 Torr.

2. Dependence of laser action on discharge current. – Oxygen or N_2O partial pressures were kept constant and the discharge current was varied between 0 and 70 mA at two different helium partial pressures.

3. Use of N_2O instead of O_2 as a source of oxygen atoms.

4. The reaction between molecular oxygen and carbon monosulphide. – A dilute mixture of CS_2 with helium ($p_{CS_2} = 0.1$ Torr, $p_{He} = 4.2$ Torr) was passed through the electrical discharge at a pump rate of 1500 l/min. Molecular oxygen was allowed into the laser cavity through the injector at a partial pressure of 0.95 Torr.

Results

1. Figure 3 shows the influence of the diluent on both the fundamental and overtone bands. It is evident that the fundamental band has zero output in the absence of helium while the overtone still exhibits a distinct output under these conditions. At lower discharge currents the fundamental band shows a parallel behaviour but that of the overtone is obviously changed. Addition of helium increases the overtone output as expected but according to a step-like function which is shifted to higher partial pressures of helium as the discharge current is lowered. When helium is replaced by argon as a diluent, the maximum output in both bands falls considerably (Figure 3).

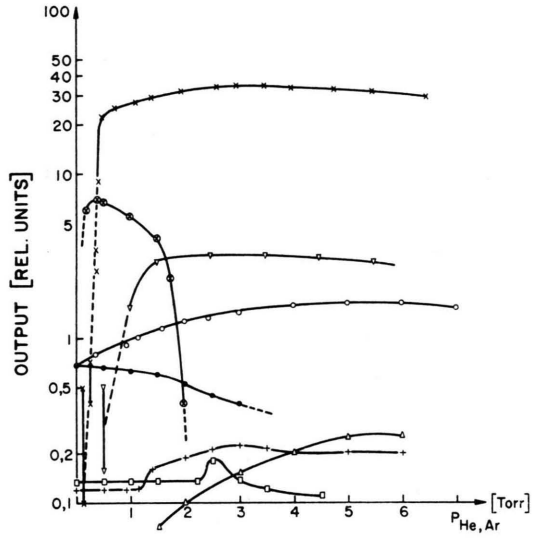

Fig. 3. Variation of output with buffer gas partial pressure at varying discharge currents.

×	fundamental	$-CS_2-O_2-He$	at 70 mA,
(x)		CS_2-O_2-Ar	at 70 mA,
▽		CS_2-N_2O-He	at 70 mA,
△	Overtone	$-CS_2-N_2O-He$	at 70 mA,
○	Overtone	CS_2-O_2-He	at 70 mA,
+		CS_2-O_2-He	at 12 mA,
□		CS_2-O_2-He	at 8 mA,
●		CS_2-O_2-Ar	at 70 mA.

2. Oxygen atoms required for reactions (1) and (2) are generated by passing oxygen (or an oxygen-helium mixture) through a discharge produced with a variable transformer, the maximum discharge current being 70 mA.

The fundamental band starts to lase at a discharge current of approximately 20 mA, being unstable initially and then increasing rapidly with increasing current (Figure 4). The overtone band behaves quite differently. Laser action can be detected at the moment of breakthrough, i. e. already at fractions of 1 mA. The output goes through a maximum at approximately 6 mA before increasing slowly with increasing current.

The discharge current-voltage characteristic of the discharge is also shown in Figure 4. The decrease in voltage at 6 mA (characteristic for passing only oxygen) is rather well pronounced and indicates a change in the composition of the plasma.

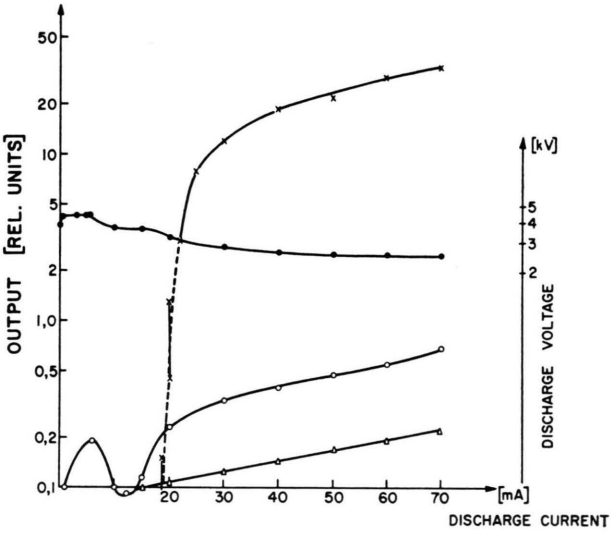

Fig. 4. Dependence of output on discharge current.
× fundamental $p_{O_2} : p_{He} = 2.3 : 3$,
○ Overtone $p_{O_2} : p_{He} = 2.3 : 0$,
△ Overtone $p_{N_2O} : p_{He} = 0.6 : 0$,
● Current-voltage characteristic.

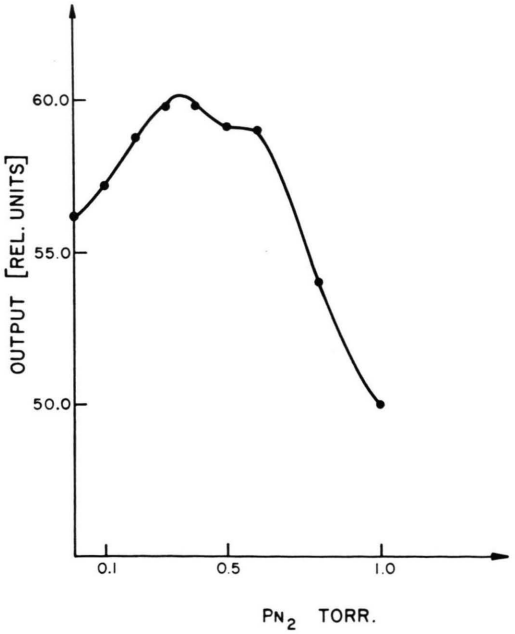

Fig. 5. Effect of "Cold" N_2 on laser output.

3. Using N_2O instead of O_2 as a source of oxygen atoms we found laser action both in the fundamental and overtone bands (Figure 4). The most striking observations are firstly that the overtone now only starts lasing at aproximately 12 mA while the fundamental band, apart from having a smaller output, does not change its behaviour. Secondly, no laser action was observed in either of the two bands in the absence of helium.

Since N_2 is produced in the dissociation of N_2O, the effect was investigated of N_2 added through the injector to the laser with oxygen passing through the discharge (Figure 5).

4. Laser action in both the CO-overtone and fundamental bands were observed when reacting molecular oxygen with carbon monosulphide. The total output was now about 30% of the output when the laser was operated in its normal way.

Discussion

The following observations are pertinent:

(a) Laser action in the overtone band can be obtained in the absence of a diluent gas such as helium.

(b) At low discharge currents (<20 mA) laser action results only from overtone transitions.

(c) Using N_2O instead of O_2 as a source of oxygen atoms, there is, apart from the intensity of the output, no striking difference between the behaviour of fundamental and overtone bands as regards the effect of diluent gas and discharge currents.

(d) Laser action in both fundamental and overtone bands is observed when reacting molecular oxygen with carbon monosulphide.

The dissociation energy of N_2O (into N_2 and O) is 0.4 eV whereas that of oxygen is 5.1 eV. At low discharge currents, therefore, N_2O will be completely dissociated, while the plasma, when passing O_2 through the discharge, consists mainly of oxygen molecules, O_2^+, O, O^+ and excited species. There is thus a strong possiblity that our observations can be attributed to a reaction involving molecular oxygen.

ARNOLD and KIMBELL [13] did not observe laser action using N_2O instead of O_2 as source of oxygen atoms. In the present investigations lasing in both fundamental and overtone bands were observed under these conditions. The lower output now obtained can most probably be attributed to an inadequate

supply of oxygen atoms (the maximum p_{N_2O} was 0.6 Torr above which lasing ceases) and not the result of a quenching effect of N_2 produced in this dissociation since addition of up to 0.4 Torr of "cold" N_2 enhances laser output under normal operating conditions (i. e. oxygen through the discharge). This is to be expected since near-resonant V – V energy transfer between CO and N_2 is possible [14].

Helium reduces the rate of recombination of oxygen atoms formed in the discharge. Without helium the recombination rate is relatively high, oxygen molecules are formed and reaction (3) is enhanced. When helium is replaced by argon as a diluent gas, the maximum total output of both bands falls considerably (Figure 3). This behaviour of the laser output could possibly be explained by a more efficient vibration to translation (V – T) deactivation of excited CO by argon than by helium.

Various reaction mechanisms have been proposed to account for laser action in the CS_2-O_2 chemical laser [8–10, 13, 15]. However, considering rate constants and exothermicities, only the reactions

$$O + CS \rightarrow CO + S \qquad (2)$$

and

$$O_2 + CS \rightarrow CO + SO \qquad (3)$$

appear to be important. Reaction (3) is sufficiently exothermic to populate levels up to $v = 16$. It is therefore highly likely that reaction (3) is responsible for laser action in the overtone band, especially at low discharge currents and low partial pressures of helium. The observation [7] that at low partial pressures of helium transitions from levels higher than $v = 13$ are pronounced can be explained by this assumption. Furthermore, comparison of the resolved overtone spectrum obtained when (a) reacting molecular oxygen with carbon monosulphide, with that obtained under (b) normal operating conditions (i. e. O_2 through discharge, CS_2 through injector) shows a marked shift in the intensity distribution. It appears that population of low ($v \leqq 6$) and high ($v > 14$) vibrational levels is favoured by condition (a) [16].

Conclusion

The reaction

$$O + CS \rightarrow CO + S$$

appears to be responsible for laser action, in the $CS_2 - O_2$ chemical laser, resulting from the intense fundamental band. The much less intense overtone band is, however, also controlled by the reaction

$$O_2 + CS \rightarrow CO + SO\,.$$

For extreme cases, i. e. no diluent gas and low dissociation rate (low discharge current), the latter reaction appears to be mainly responsible for laser action, resulting now only from overtone transitions. This conclusion is further supported by the fact that this reaction does produce vibrationally excited CO.

Acknowledgements

We would like to thank Dr. A. STRASHEIM, Director of the National Physical Research Laboratory, for permission to publish this work. F. G. S. wishes to express his gratitude towards Dr. STRASHEIM for permission to spend his sabbatical leave at this Institute and also to Dr. G. J. RITTER, Head of the Optics and Spectroscopy Division, for encouragement and interest taken in this work.

[1] C. J. WITTIG, J. C. HASSLER, and P. D. COLEMAN, Appl. Phys. Lett. **16**, 117 [1970].
[2] C. J. WITTIG, J. C. HASSLER, and P. D. COLEMAN, Nature **226**, 845 [1970].
[3] R. D. SUART, G. H. KIMBELL, and S. J. ARNOLD, Chem. Phys. Lett. **5**, 519 [1970].
[4] W. Q. JEFFERS and C. E. WISWALL, Appl. Phys. Lett. **17**, 67 [1970].
[5] T. V. JACOBSEN and G. H. KIMBELL, J. Appl. Phys. **41**, 5210 [1970].
[6] C. J. WITTIG, J. C. HASSLER, and P. D. COLEMAN, J. Chem. Phys. **55**, 5523 [1971].
[7] F. G. SADIE, P. A. BÜGER, and O. G. MALAN, J. Appl. Phys. **43**, 2906 [1972].
[8] D. W. GREGG and S. J. THOMAS, J. Appl. Phys. **39**, 4399 [1968].
[9] R. D. SUART, S. J. ARNOLD, and G. H. KIMBELL, Chem. Phys. Lett. **7**, 337 [1970].
[10] S. ROSENWAKS and S. YATSIV, Chem. Phys. Lett. **9**, 266 [1971].
[11] J. T. YARDLEY, J. Chem. Phys. Lett. **52**, 3983 [1970]; Appl. Optics **10**, 1760 [1971].
[12] C. E. TREANOR, J. W. RICH, and R. G. REHM, J. Chem. Phys. **48**, 1798 [1968]. – J. D. TEARE, R. L. TAYLOR, and C. W. VON ROSENBERG, Nature **225**, 240 [1970].
[13] S. J. ARNOLD and G. H. KIMBELL, Appl. Phys. Lett. **15**, 351 [1969].
[14] F. LEGAY, N. LEGAY-SOMMAIRE, and G. TAÏEB, Can. J. Phys. **48**, 1949 [1970].
[15] G. HANCOCK and I. W. M. SMITH, Appl. Optics **10**, 1827 [1971].
[16] F. G. SADIE, P. A. BÜGER, and O. G. MALAN, J. Appl. Phys. Nov. [1972].