

MINISTERE DE LA DEFENSE NATIONALE CANADA

and an arrive and a state of a state of the state of the

Martin King

DEPARTMENT OF NATIONAL DEFENCE CANADA

NON CLASSIFIE

DREV-R-1459/" TLE: 3634B-001

CEDV R-4059/76 DOSSIER: 3634B-001 UNCLASSIFIED



HEL

AN EFFICIENT, PURELY CHEMICAL HC& LASER

by K.D./Foster, R.D./Suart and D.R./Snelling

(D) N. 176 (13

DISTRIBUTION TATI MENT A

CENTRE DE RECHERCHES POUR LA DEFENSE

DEFENCE RESEARCH ESTABLISHMENT

VALCARTIER

Tel: (418) 844-4271

Québec, Canada

November/novembre 1976

NON CLASSIFIE

404 145 KB

RESUME

On a obtenu une émission laser purement chimique à 3.6-4.0 um en utilisant le HC2 dans un appareil à écoulement transversal. La réaction bien connue $Cl + HI + HC2^{\dagger} + I$ a été utilisée pour le pompage. Le chlore atomique a été produit chimiquement par l'interaction de NO et ClO_2 . Le système laser a donné une puissance maximale de 4 W, ce qui correspond à une efficacité de 9% basée sur la fraction d'énergie de la réaction de pompage transformée en énergie de vibration. Le rendement laser multiligne fut observé sur 8 bandes P provenant des bandes de vibration v=3 + 2, v=2 + 1 et v=1 + 0. En outre, le laser fonctionna efficacement lorsque le CL de la réaction de pompage était produit '*in situ*', une caractéristique qui peut être importante dans la recherche de plus grandes puissances. (NC)

ABSTRACT

Purely chem _al laser emission at 3.6 to 4 µm from HCl has been achieved in a transverse flow device. The pumping reaction was the well known Cl + HI + HCl + I reaction. Atomic chlorine was produced chemically from the reaction of NO with ClOT. The maximum power obtained from this system was 4 W, which corresponded to a chemical efficiency of 9% based upon the fraction of pumping reaction energy that goes into vibration. Multiline laser output was observed for eight P-branch lines emanating from the v=3 + 2, v=2 + 1 and v=1 + 0 vibrational bands. The laser also operated successfully under conditions where the Cl for the pumping reaction was produced in situ, a feature which may be important in scaling to higher powers. (U)

λ

UNCLASSIFIED ii

TASLE OF CONTENTS

1

	RESUME/ABSTRACT	i
1.0	INTRODUCTION	1
2.0	EXPERIMENTAL	5
	2.1 ClO ₂ Generator	5
	2.2 Transverse Flow HCl Laser	7
3.0	RESULTS AND DISCUSSION	9
	3.1 Preliminary Modeling of Pre-Pumping Chemistry	9
	3.2 Power and Efficiency Measurements	11
	3.3 Spectral Output Characteristics	12
	3.4 Scaling Considerations	14
	3.4.1 The Effect of NO ₂	15
	3.4.2 Split NO Addition	16
4.0	CONCLUSIONS	18
5.0	REFERENCES	19

 $\frac{1}{2}$

TABLE I

FIGURES 1 to 3

1.0 INTRODUCTION

The advantages of directly converting the energy stored in chemical bonds into laser radiation has been recognized for some time. Such purely chemical lasers could be portable and could operate in environments where electrical power is unavailable. However, since atomic species are usually required to initiate chemical laser action, many chemical lasers need electrical energy to initiate the reaction. This electrical energy can be used directly, in the form of transverse or longitudinal electrical discharges, or indirectly by using flash lamps to photolytically initiate laser chemistry.

However, atomic species have been produced thermally by burning suitable gas mixtures in high-temperature plenums (Refs. 1,2). This method has proved to be suitable for dissociating fluorine, which is a weakly bound molecule (bond energy = 35 kcal/mol). For chlorine, however, the bond energy is much larger (57 kcal/mol), and prohibitively high temperatures are required to produce significant amounts of chlorine atoms. Because this method of atom production is accomplished at high pressures and temperatures, an environment not suited to lasing action, the hot gas must be cooled before it is introduced into the laser. This is commonly accomplished by rapid supersonic expansion of the high-pressure, high-temperature plenum gases. This ravid expansion, which reduces both the temperature and the pressure of the gas, is accomplished so rapidly that the atomic species do not have time to decay (recombine). This type of laser can be regarded as purely chemical since no electrical excitation is required, but it is perhaps better classified as a thermally assisted chemica, laser.

In some purely chemical lasers it has proved possible to chemically produce atomic species at more modest temperatures and pressures where direct utilization of the atoms is possible. Three such systems discovered previously are described below:

(1) HF, DF, HF-CO₂ and DF-CO₂ lasers (Ref. 3)

Laser action was achieved by producing F atoms from the reaction $F_2 + NO \Rightarrow NOF + F$ followed by the reaction of these atoms with either H_2 or D_2 . The product HF^{\dagger} or DF^{\dagger} could be made to undergo laser action directly (at 2.8 µm and 3.8 µm, respectively) or the energy could be transferred to CO_2 with subsequent lasing of the excited CO_2 at 10.6 µm.

(2) The $CS_2/O_2/N_2O$ Free-Burning-Flame Laser (Ref. 4)

Laser power at 5.0 to 5.5 µm due to CO^{\dagger} may be extracted from this system. The requisite 0 atoms and CS radicals for the laser pumping reaction 0 + CS $\rightarrow CO^{\dagger}$ \rightarrow S are produced by the flame. The region of positive gain lies immediately upstream of the flame front in lean CS₂/O₂/N₂O flames.

(3) The N_2O Chemical-Flame Laser

This system relies upon the catalytic effect of atomic sodium as a chain carrier in the reaction sequence:

Na + N₂ O + NaO + N₂ NaO + CO + CO₂⁺ + Na

The atomic sodium was provided by passing helium over sodium azide (NaN_3) which was fed in with a 'hopper'. Although the excited CO_2 did not lase directly, laser action was observed from N_2O (Ref. 5). This presumably resulted from energy transfer from the CO_2 molecule to the N_2O .

The chemical lasers which are most likely to have military applications are HCL and DF since these lasers exhibit multiline output in a wavelength region (3.5 to 4.0 μ m) that is readily transmitted through the atmosphere. The DF laser has so far attracted the most interest since atomic fluorine is readily formed thermally as described above. Although CL atoms are difficult to produce thermally, the reaction of CL atoms with HI is suitable for converting chemical energy into laser energy.

$$C\ell + III \rightarrow HC\ell^{\dagger} + I$$
 (1)

This reaction, which produces vibrationally excited HC^{ℓ} , proceeds at almost every bimolecular collision. More than 70% of the energy released in this reaction appears in the newly formed $HC\ell$ bond, and the energy is so distributed between the various vibrational states of HCl that a population inversion is attained on the first three fundamental vibrational transitions (Ref. 6).

HCl chemical lasers have been built using the Cl + HI reaction to provide the pumping mechanisms. Atomic chlorine was produced by electrical discharges in Cl_2 using a transverse flow-configuration (i.e., flow transverse to the optical axis (Ref. 7, 8)). In these experiments powers of less than 100 mW were obtained, but recently Linevsky and Carabetta (Ref. 9) substantially improved the performance of this laser, achieving output powers of 5 V.

The achievement of an efficient purely chemical HCl laser employing transverse flow and operating at 3.8 µm is reported herein. The pumping reaction for the present system is the well known Cl + HI reaction. Atomic chlorine is provided by the reaction of chlorine dioxide (ClO₂) with nitric oxide (NO). This reaction was used to achieve laser action in a longitudinal HCl/CO₂ transfer laser (Refs. 10, 11). The reaction steps leading to the formation of atomic Cl are the following:

> NO + $ClO_2 \rightarrow NO_2$ + ClO (2) $k_1 = 3.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$



The rate coefficients for these processes have been measured by Clyne (Ref. 12).

La santuk a

The above sequence constitutes a branched chain mechanism whereby NO is converted to NO_2 , and ClO_2 is converted to ClO (if the initial NO concentration is equal to that of ClO_2) or Cl atoms (if the initial NO concentration is twice that of ClO_2). The chain-branching step is reaction (4). As long as starting material (ClO_2) is present, reaction (4) keeps the ambient Cl concentration low and stores the chlorine in the form of ClO. Reaction (4) decreases in importance as the ClO_2 concentration diminishes. Provided enough NO remains, this accumulated ClO is then converted to Cl via reaction (3). Because of the chain-branching step in this reaction sequence, the overall reaction may be rapid even though the initial reaction (2) is quite slow.

This paper represents a continuation of work on purely chemical lasers based upon the NO/CLO₂ reaction chemistry. The work described herein was conducted in mid-1975 under PCN 34B01 (formerly PCN 07C01, Project No. 97-01-39) "Research on Chemically Excited Lasers".

2.0 EXPERIMENTAL

2.1 CLO, Generator

The ClO_2 generator used has already been described (Ref. 13); hence only a brief summary will be included here. A schematic diagram of the apparatus is shown in Fig. 1. The conversion of molecular chlorine to chlorine dioxide was accomplished by passing Cl_2 through a column which was packed with NaClO₂ (Ref. 14). The following heterogeneous reaction then occurred:

$$Cl_2 + 2NaClO_2 + 2NaCl + 2ClO_2$$
(5)

Complete conversion yielded a flow rate of ClO_2 that was twice that of the input Cl_2 .

The column was constructed of Corning 'Double-Tough' pyrex tubing and tees. Teflon gaskets were employed in all Double-Tough connections. Two columns were in fact fabricated. The first column, 3-in diameter tubing, was packed with 17 lb of $NaClO_2$ whereas the second column, 4-in diameter, was packed with 25 lb of $NaClO_2$. Each column was also equipped at the downstream end with a 2-lb charge of Drierite. This removed water vapor from the effluent gas. Water has an adverse effect on laser performance. With the exception of the spectroscopy experiments, in which both columns were employed, all other experiments were done using the 3-in column only.

In view of the potentially explosive nature of CLO₂, certain precautions were taken:

- (a) Installing a rupture disc, held in place with teflon putty, in the column;
- (b) Installing the column in a metal enclosure;

- (c) Blackening the surface of the CLO₂ column and associated tubing to reduce the possibility of photo-initiated chain reactions;
- (d) Maintaining the partial pressure of CLO₂ below
 30 torr. Diluent helium was added such that the total column pressure was slightly more than
 1 atmosphere;
- (e) Maintaining a constant flow of NO sufficient to react with the ClO_2 , thus avoiding condensation of ClO_2 in the cold trap.





2.2 Transverse Flow HCL Laser

The transverse flow laser apparatus used was very similar to that employed for the CS_2/O_2 system by Foster and Kimbell (Ref. 15), except for some modifications. These modifications included: lengthening of the flow channel in the flow direction by adding a duplicate housing in series; mounting HI injectors in a teflon rather than an aluminum block; installing a liquid-nitrogen cooled trap in the exhaust line.

The modified transverse-flow laser (Fig. 1) consists of a rectangular 1.5-cm by 14-cm flow channel having two injector rows separated by 12 cm. Each row consisted of twenty injector 'needles' containing eight 0.3-mm-diameter holes. Situated upstream of both injector rows was a teflon choke screen, which served to make the flow of ClO_2 /He uniform across the full channel width. This screen was simply a teflon gasket through which about 80 holes were drilled over the 1.5-cm by 14-cm cross section.

Molar flow rates of the individual gases were measured with either Matheson or Hastings-Raydist mass flowmeters. These latter are directly calibrated in standard cm³/min (SCCM) where the reference temperature is 295° K and the pressure is 1 atm. The Hastings-Raydist flow meters were particularly convenient since they could be operated accurately over a wide pressure range. Back pressure in the individual flow lines was monitored with Leybold-Heraeus gauges (0 to 1500 torr precision manometers) for helium and with corrosion resistant gauges (Helicoid) for the more corrosive gases. The pressure in the main flow channel containing the laser region was measured with a 'quartzspiral' type of gauge (Texas Instruments Model 145).

In a typical experiment, a flow of some 11 mmol s⁻¹ of He was established through the ClO_2 generator. The pressure in the column, set at 970 torr, was controlled by a teflon metering value at the exit of the column. A flow of approximately 0.22 mmol s⁻¹ of Cl_2 was then

UNCLASSIFIED 8

added. After about 30 s the characteristic yellow-green color of ClO_2 was visible at the exit of the column. Subsequently, an additional 25 mmol s⁻¹ of He was injected just upstream of the choke screen. The addition of He with the ClO_2 above ensured safe operation of the column. The second downstream addition of helium allowed an independent control over the optimum dilution for maximum laser output power. Typical pressures immediately upstream of the choke screen were 50 to 100 torr. In the low-pressure region (2.5 torr) 1.2 mmol s⁻¹ of NO were added through the upstream injector row and 0.94 mmol s⁻¹ of HI was added through the downstream injector row. An additional flow of 4 mmol s⁻¹ of helium was added through each window support to prevent deposition on the window surface and to eliminate the build-up of ground state HC¹. The average linear velocity of the gas was 160 m s⁻¹ in the laser region.

The optical cavity consisted of a 'total' reflector of the 'protected metal' type having a radius of curvature of 10 m, and a partially reflecting (96% R) multilayer dielectric mirror on a CaF_2 flat. The distance between the optical axis and the HI injector row could be varied but was typically kept at 0.5 to 1 cm. For most experiments the mirrors were externally mounted. However, certain total power measurements were performed in which the CaF_2 windows were eliminated and the mirrors were mounted internally.

Total continuous-wave (CW) power measurements for the HCL chemical laser were conducted with a Coherent Radiation power meter.

The spectral content of the multiline laser output was chopped at 670 Hz and analyzed with a 0.3 m MacPherson Model 218 monochromator which employed a $150-\ell/mm$ grating, blazed for 3 µm. Detection was accomplished with a cooled photovoltaic InSb detector, and the signal was processed with a Princeton Applied Research (HR8) Lock-In amplifier. The approximate small signal gain of the most intense lines was measured by a variable loss technique. This technique has been used elsewhere (Ref. 7); it has also been used in connection with the longitudinal HC^2/CO_2 laser (Ref. 11). The laser power was measured as a function of the angular orientation of two CaF_2 flats introduced as intra-cavity loss elements.

3.0 RESULTS AND DISCUSSION

3.1 Preliminary Modeling of Pre-Pumping Chemistry

The rate equations corresponding to the NO/CRO_2 reactions (2), (3), and (4) were integrated numerically to follow the time evolution of CRO radicals and atomic CR. The technique used is described more fully in another publication (Ref.16) and was employed in an earlier publication (Ref. 11).

Some of the results of these calculations appear in Fig. 2 and show the corresponding times for 90% completion of the conversion of ClO_2 to ClO (for equal initial NO and ClO_2 concentrations) and for conversion of ClO_2 to Cl atoms (for an initial NO concentration twice that of ClO_2). In this simple kinetic scheme, all Cl atom or ClOradical loss processes have been neglected.

Figure 2 clearly shows that there is a linear relationship between the faitial $C\ell_0$ concentration and the time required for 90% completion of the reaction. The results were used to estimate reaction times for various laser conditions. For example, the average linear flow velocity was 160 m/s. For this velocity, the time between the injection of NO and the subsequent injection of HI was 750 µs. The estimated concentration of $C\ell_0$ (assuming a $C\ell_0$ flow rate twice that of $C\ell_2$, i.e., complete conversion of $C\ell_2$ to $C\ell_0$ in the sodium chlorite UNCLASSIFIED 10

columns) was 10^{15} cm⁻³. For this concentration of $C\&O_2$ and an NO concentration of twice this value, the estimated time for 90% conversion of $C\&O_2$ to CL atoms was 470 µs (see Fig. 2). Thus, sufficient time was provided in the present apparatus to accomplish this conversion before the injection of HI.



Figure 2 - Time for 90% Completion of the NO + ClO_2 Reaction to form ClO radicals (for $[NO]_1 = [ClO_2]_1$) and to form atomic Cl(for $[NO]_1 = 2 [ClO_2]_1$) as a function of initial ClO_2 concentration

3.2 Power and Efficiency Measurements

The purely chemical HCL laser described herein gave a maximum CW multiline power of 4 W. This occurred when the mirrors were mounted internally. The flow conditions corresponding to the forementioned power were:

He:	10.8 mmol	s ⁻¹		
C٤ ₂ :	0.22 mmol	s ⁻¹		
He:	25 mmol	s ⁻¹	(auxiliary)	
NO:	1.2 mmo1	s ⁻¹		
HI:	0.94 mmol	s ⁻¹		
He:	8.9 mmo1	s ⁻¹	(total window p	urge

Total cavity pressure: 2.43 torr

From these conditions, it is possible to compute an overall chemical efficiency. On the basis of the total exothermicity of the pumping reaction:

$$C\ell + HI \rightarrow HC\ell + I + 32.8 \text{ kcal/mol}$$
(1)

the total energy input is 137.2 J/mmol. The limiting flow rate of CL will be twice the CL₂ flow rate, i.e., 0.44 mmol s⁻¹. The chemical power input $P_{in} = 137.2 F_{C2}$, where F_{C2} is the flow rate of atomic CL in mmol s⁻¹. The chemical laser efficiency is then:

 $n = \frac{\text{Laser Power Out}}{\text{Chemical Power In}} = \frac{4}{137.2 \text{ x } F_{C2}}$

= 6.6%

In the literature, the chemical efficiency is sometimes computed on the basis of the fraction of the pumping reaction exothermicity that goes into the vibration of the lasing molecule. For the Cl + HIreaction, about 70% of the reaction exothermicity appears in HCl vibration (Ref. 6). By this definition, then, the efficiency of the present chemical HCl laser would be 9.4%. To our knowledge, this represents the most efficient purely chemical laser performance so far reported.

The dependence of the laser power near the HI injectors on the HI flow rate can, in fact, be used to 'titrate' for atomic CL, as shown in Fig. 3. The laser power increases monotonically with HI flow until the atomic CL has been exhausted. The power then remains relatively independent of the HI flow rate. It will be noted that the 'end-point' of the titration corresponds to an HI flow rate that is slightly greater than twice the CL_2 input flow. This may be attributable to incomplete mixing near the HI injectors. The conversion of CL_2 to CLO_2 and the subsequent reaction with NO to produce CL appear to be quantitative. That the portion of the curve above 0.6 mmol s⁻¹ of HI flow does not decline sharply indicates that the depletion of HCL^{\ddagger} by energy transfer processes with HI is not important.

3.3 Spectral Output Characteristics

The laser output spectra were taken with the optical axis 1 cm from the HI injectors. Eight P-branch lines were found to lase. The relative contributions of the various lines and their identity are shown in Table I. These results may be directly compared with the spectra obtained in the electrically assisted HCL laser of Linevsky and Carabetta (Ref. 9). These authors observed nine P-branch lines emanating from HCL³⁵ and four weak lines from HCL³⁷. No HCL³⁷ lines were observed in the present system, an indication that the gain in this chemical HCt laser was lower than that in its electrically assisted counterpart. Some 60% of the total power originates from $v = 2 \rightarrow 1$ transitions while the $P_{2-1}(6)$ line is responsible for about 30% of the total power.

An estimation of the highest small signal gains which prevail in the present system was made using the Fresnel loss technique. This involved measuring the effect of the cavity loss, incroduced by two CaF_2 flats of varying orientation, on the total laser power. The small signal gain coefficients of the most intense lines were found to exceed 1.1%/crn by this method.



Figure 3 - Dependence of Laser Power (W) on HI Input Flow Rate (mmol s⁻¹)

TABLE I

HCl ³⁵ Line	Approx % Total Power
P ₁₋₀ (5)	6.5
P ₁₋₀ (6)	8.1
P_{1-0} (7)	0.8
P ₂₋₁ (5)	4.9
P ₂₋₁ (6)	29.3
P ₂₋₁ (7)	26.0
P_{-} (6)	9.7
$P_{}(7)$	14 6
3-2 (7)	14.0

LASER OUTPUT SPECTRUM

3.4 Scaling Considerations

and the state of the second second second

In a subsonic laser such as that described here, the power cannot be increased indefinitely by increasing the $C(0)_2$ concentration since $HC(t)^{\dagger}$ self-deactivation eventually limits the power extraction because collisions between excited HCL molecules lead to vibrationalvibrational (v-v) energy transfer and to a consequent decay of the initially inverted population. As the $C(0)_2$ (and hence $HC(t)^{\dagger}$ concentration) is increased a point will be reached where this process occurs in a time that is comparable to the flow time between the HI injection needles and the laser axis. At this point power loss will occur because of the reduced gain of the HCL vibration-rotation transitions. To reduce this flow time, it would be advantageous to accomplish the HI injection and lasing in a supersonic flow regime. In such a device the Cl atom production could be accomplished in a high-pressure plenum; the consequent flow of Cl atoms could be expanded to obtain a low-pressure supersonic flow in which HI injection and lasing occurs. In the supersonic flow, much higher HCl^{\dagger} concentration can be tolerated (provided mixing is sufficiently fast) before power degradation occurs.

3.4.1 The Effect of NO_2

Certain questions immediately arise if the scaling possibilities of a purely chemical HCL laser are considered. The fact that scaling to supersonic velocities requires a high pressure plenum suggests that recombination of atomic chlorine may be a limiting factor in such a laser.

A review of the relevant kinetic rate data indicates that in this laser the predominant loss process for Cl atoms will be the NO_2 catalyzed recombination of atomic chlorine.

A chemical laser based on the chemical formation of atomic C& by the reaction of NO with ClO_2 has, out of necessity, ambient flows of NO₂ which are approximately twice the C& atom flows. In order to ascertain if this NO₂ has an undesired effect on the HCC laser operation of the present subsonic device, an additional flow of NO₂ was added immediately upstream of the HI injector row. This was accomplished by inserting a third injector row between the NO and the HI injectors. The laser output power was virtually independent of the additional NO₂ input for NO₂ concentrations ranging from 1.0 to 1.3 times the NO₂ level. This indicates that, at least for the conditions of these experiments, the ambient NO₂ does not severely limit the performance of the laser.

Although NO₂ did not greatly affect the laser performance under the present conditions, it is possible that the operation at high pressures would be limited by this NO₂ catalyzed recombination of Cl atoms as noted previously:

$$C\ell + NO_2 + M \rightarrow C\ell NO_2 + M$$
 (6)
 $k = 7.2 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ (Ref. 17)

followed by $ClNO_2 + Cl \rightarrow Cl_2 + NO_2$. If the second process is sufficiently rapid, then the apparent third-order rate constant for Cl atom loss would be $k_{ipp} \sim 14.4 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$. The rate constant for the reaction $ClO + ClO + M \rightarrow \text{products has been estimated to be}$ only 6.6 x $10^{-32} \text{ cm}^6 \text{ s}^{-1}$ (Ref. 18).

3.4.2 Split NO Addition

From the above considerations it is evident that in a highpressure regime CRO radicals decay much more slowly than CL atoms: this suggests that the CL atoms could then be released in a two step process with two separate additions of NO:

Step	1	NO	+	Ceo2	•	NO_2	+	Clo		(2)
------	---	----	---	------	---	--------	---	-----	--	-----

 $NO + CRO + NO_2 + CR$ (3)

$$C\ell + C\ell O_2 \rightarrow 2C\ell O_2 \qquad (4)$$

In the first step, a flow of NO equal to that of ClO_2 is established. Atomic chlorine produced in the second reaction is rapidly consumed in the branching step (4) until all the ClO_2 and NO is consumed. This first reaction sequence (Step 1) therefore converts all the ClO_2 to ClO radicals.

Step 2 NO + $ClO \rightarrow NO_2 + Cl$ (3)

$$C\ell + HI + HC\ell^{\dagger} + I.$$
 (1)

in the second s

The requisite Cl atoms for the laser pumping reaction are then formed *in situ* in Step 2 by the second addition of NO. This NO can be added with the HI or just upstream of the HI injection. The rate of HCl^{\dagger} formation, therefore, is determined by the rate of the NO + ClO reaction.

It should be emphasized that chain reactions are involved in Step 1 but not in Step 2. If appreciable concentrations of HI are present during the branched chain reaction then Ci atoms can react with HI rather than ClO_2 , thus interfering with the chain branching reaction. However, in Step 2 there is no ClO_2 present and the Ci release reaction is a simple molecular reaction which is not affected by the HI.

Although the ambient pressures in the present device were too low for the potential advantage of this 'Split NO Addition' technique to be fully exploited, evidence was found that the in sime formation of atomic Cl is possible. In these experiments employing internal mirrors, 950 SCCM of NO was added through the upstream injector row, an amount which was insufficient for conversion of the CO_{2} to atomic chlorine. An additional 850 SCCM of NO was admitted through the downstream injector row by mixing NO and 1000 SCCM of HI before injection into the main flow channes. Laser action was indeed found and the output power was about 2 W. This may be compared to a laser power of 2.6 W which was observed in the same experiment when all the NO was directed through the upstream injector row. It should be noted that although a maximum laser power of J W was observed, typical power levels were about 2 to 2.5 W. The experiment giving 4 W output power was performed with a reduced cavity loss since the mirrors were mounted internally.

UNCLASSIFIED 18

4.0 CONCLUSIONS

Multiline laser output powers of up to 4 W have been achieved in a purely chemical HCL laser based upon the reaction of NO with ClO_2 and subsequent pumping by CL + HI. The chemical efficiency of the present device, corresponding to the forementioned maximum power and based on the fraction of the reaction exothermicity going in to HCL vibration, was about 9%.

The laser output consisted of eight P-branch lines of HCl^{35} emunating from the 3+2, 2+1, 1+0, vibrational bands with the 2+1 band providing about 60% of the output power.

The ambient flow of NO_2 , an unavoidable product of the Cl forming reaction and therefore present in the lasing region, does not appear to adversely affect the laser performance under the present experimental conditions.

Laser power of some 2 W has been observed under conditions where the requisite atomic chlorine was formed in site with HI by a 'Split NO Addition' technique. This involved the initial conversion of Clo_2 to ClO relials by an upstream injection of NO, with an additional downstream injection of NO along with HI. This possibility of 'storing' atomic Cl in the form of a ClO radical may have important consequences in the scaling of the chemical HCl laser to higher powers.

UNCLASSIFIED 19

5.0 REFERENCES

- Spencer, D.J., Jacobs, T.A., Mirels, H. and Gross, R.W.F. "Continuous Wave Chemical Laser", Int. J. Chem. Kinetics <u>1</u>, 493-494 (1969).
- Schulman, E.R., Burwell, W.G. and Meinzer, R.A. "Design and Operation of Medium Power CW HF/DF Chemical Lasers", AIAA Paper No. 74-546, AIAA 7th Fluid & Plasma Dynamics Conference, Palo Alto, California June 17-19, 1974.
- Shirley, J.A., Sileo, R.N., Stephens, R.R. and Cool, T.A. "Purely Chemical Laser Operation in the HF, DF, HF-CO₂ and DF-CO₂ Systems", AIAA Paper No. 71-2/, AIAA 9th Aerospace Sciences Meeting, 25-27 Jan 1971, New York, N.Y.
- Searles, S.K. and Djeu, N. "Characteristics of a CW CO Laser Resulting From a CS₂-O₂ Additive Flame", Chem. Phys. Lett. <u>12</u>, 53-56 (1971).
- 5. Bernard, D.J., Benson, R.C. and Walker, R.E. "N₂O Pure Chemical CW Flame Laser", Appl. Phys. Lett. <u>23</u>, 82-84 (1973).
- 6. Maylotte, D.H., Polanyi, J.C. and Woodall, K.B. "Energy Distribution Among Reaction Products. IV.

 $X + HY(X \equiv C\ell, Br; Y \equiv Br, I), C\ell + DI.$

J. Chem. Phys 57, 1547-1560 (1972).

- 7. Glaze, J.A., Finzi, J. and Krupke, W.F. "A Transverse Flow CW HCl Chemical Laser", Appl. Phys. Lett. 18, 173-175 (1971).
- 8. Naegeli, D.W. and Ultee, C.J. "A CW HC& Chemical Laser" Chem. Phys. Lett. 6, 121-122 (1970).
- Linevsky, M.J. and Carabetta, R.A., results presented at the 14th Conference on Chemical and Molecular Laser, St. Louis, Mo. October 1974, Paper MB-7.
- Suart, R.D., Snelling, D.R., Foster, K.D. and Arnold, S.J. "Purely Chemical Laser Based on Chlorine Atom Reactions: Hybrid CO₂ Laser", DREV R-4015/76, UNCLASSIFIED.
- 11. Suart, R.D., Snelling, D.R. and Arnold, S.J., "Purely Chemical Laser Based on Chlorine Atom Reactions: ClO₂-NO Reaction as Chlorine Atom Source", DREV R-4014/76, UNCLASSIFIED.

12. Bemand, P.P., Clyne, M.A.A. and Watson, R.T., "Reactions of Chlorine Oxide Radicals: Part 4 - Rate Constant for the Reactions Cl + OCLO, O + OCLO, H + OCLO, NO + OCLO and O + CLO, J.C.S., Faraday Trans. J. <u>69</u>, 1356-1374 (1973), and,

Clyne, M.A.A. and Watson, R.T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry. Part 2. Rapid Bimolecular Reactions Involving the CLO $X^2 \Pi$ Radical", J.C.S. Faraday Trans. I. 70, 2250-2259 (1974).

- Suart, R.D., Snelling, D.R., Foster, K.D. and Lambert, R., "Purely Chemical Laser Based on Chlorine Atom Reactions: ClO₂ Generator", DREV R-4005/76, UNCLASSIFIED.
- Woodward, E.W., Petroe, G.A. and Vincent, G.P., "A New Process for Producing Chlorine Dioxide for Industrial Use", Trans. Am. Inst. of Chem. Engineers <u>40</u>, 271 (1945).
- 15. Foster, K.D. and Kimbell, G.H., "Characteristics of CS₂/O₂ Chemical Laser with Flow Transverse to the Optical Axis", 14th Symposium (International) on Combustion Aug 20-25 (1972), pp 203-210.
- Arnold, S.J., Snelling, D.R. Foster, K.D. and Suart, R.D., "Computer Simulation of the Chemistry of HCl Chemical Laser Systems", (to be published), UNCLASSIFIED.

L'Andrew and the set of the set o

「「「「「「「「」」」」

- Clyne, M.A.A. and White, I.F., (unpublished data) see page 2882 of Clyne, M.A.A. and Cruse, H.W., Trans. Faraday Soc. <u>67</u>, 2869-2885 (1971).
- Johnston, H.S., Morris, E.D. and Van den Bogaerde, J., "Molecular Modulation Kinetic Spectrometry. Cl00 and Cl02 Radicals in the Photolysis of Chlorine in Oxygen", J. Am. Chem. Soc. <u>91</u>, 77:2-7727 (1969).

DREV REPORT 4059/76 (UNCLASSIFIED)

Bureuu - Recherche et Développement, Ministère de la Défense nationale, Canada. CRDV, C.P. 880, Courcelette, Qué. GOA IRO.

"An Efficient, Purely Chemical HC: Laser" by K.D. Foster, R.D. Suart and D.R. Snelling On a obtemu une émission laser purement chimique à 3.6-4.0 µm en utilisant le ifC: dans un appareil à écoulement transversal. La réaction bien comme Cz + HI ifC: dans un appareil à écoulement transversal. La réaction bien comme Cz + HI ifC: $^{+}$ - i a été utilisée pour le pompage. Le chlore atomique a été produit chimiquement par l'interaction de NO et C?O₂. Le système laser a donné une puissance maximale de 4 h, ce qui correspond à une efficacité de 9% basée sur la fraction d'énergue de la réaction de pompage transformée en énergie de vibration. Le rendement laser multilique fut observé sur 8 bandes P provenant des bandes de vibration v=5 $^{+}$ 2, v=2 + 1 et v=1 + 0. En outre, le laser fonctionna efficacement lorsque le C: de la réaction de pompage était produit 'én n'fu', une caractéristique qui peut être importante dans la recherche de plus grandes puissances. (NC)

DREV REPORT 4059/76 (UNCLASSIFIED)

Bureau - Recherche et Développement, Ministère de la Défense nationale, Canada. CRDV, C.P. 880, Courcelette, Qué. GOA IRO.

"An Efficient, Purely Chemical HC2 Laser" by K.D. Foster, R.D. Suart and D.R. Sneiling On a obtenu une émission laser purement chimique à 3.6-4.0 µm en utilisant le HCI dans un appareil à écouiement transversal. La réaction bien connue CX + HI - HCI⁺ + I a été utilisée pour le pompage. Le chlore atomique a été produit chimiquement par l'interaction de NO et CiO₂. Le système laser a donné une puissance maximale de 4 K, ce qui correspond à une efficacité de 9% basée sur la fraction d'énergie de la réaction de pompage transformée en énergie de vibration. Le rendement laser multiligne fut observé sur 8 bandes P provenant des bandes de vibration v=3 + 2, v=2 + 1 et v=1 + 0. En outre, le laser fonctionna efficacement lorsque le Ci de la réaction de pompage était produit 'in *situ*', une caractéristique qui peut être importante dans la recherche de plus grandes puissances. (NC)

DREV REPORT 4059/76 (UNCLASS IF 1807

1

·· · · · · · · ·

site of the second s

Solution and a lite shart of the

Bureau - Recherche et Développement, Ministère de la Défense mutionale, Canada. CRDV, C.P. 880, Coarcelette, Qué. 604 MC.

"An Efficient, Purely Chemical HC/ Laser" by K.D. Foster, R.D. Swart and D.R. Snelling On a obtenu une émission laser purement chimique à ?.6-4.0 µm en utilisant le IIC dans un appareit à écoulement transversal. La réaction bien connu. (? + HI - HC^{\dagger} + I a été utilisée pour le pompage. Le chlore atomique a été produit chimiquement par l'interaction de NO et ClO₂. Le système laser a donné une puissance maximale de 4 W, ce qui correspond à une efficacité de 9% basée sur la fraction d'énergie de la réaction de pompage transformée en énergie de vibration. Le rendement laser multiligne fut observé sur 8 bandes P provinant des bandes de vibration v=5 · 2, v=2 · 1 et v=1 · 0. En outre, le liter fonctionna efficacient lorsque le Ci de la réaction de pompage était produit 'én *sizit*', une caractéristiqué lorsque le Ci de la réaction de pompage était produit 'én *sizit*', une caractéristiqué lorsque le Ci de la réaction de pompage était produit 'én *sizit*', une caractéristiqué lorsque le Ci de la réaction de pompage était produit 'én *sizit*', une caractéristiqué lorsque le toit baser lans la recherche de plus grandes puissances. (%C)

DREV_REPORT_4059/76 (INCLASSIFIED)

Bureau - Recherche et Développement, Ministère de la Réfense nationale, Canada. CRDV, C.P. 880, Courcelette, Qué. GOA IRO.

"An Efficient, Purely Chemical HC. Laser" by K.D. Foster, R.D. Suart and D.R. Snelling On a obtenu une émission laser purement chimique à 3.6-4.0 \pm m en utilisant le HC: dans un appureit à écoulement transversal. La réaction bien connue C: HH \pm HC.[†] + I a été utilisée pour le pompage. Le chlore atomique a été produit chimiquement par l'interaction de NO et C:O₂. Le système laser a donné une puissance maximale de 4 W, ce qui correspond à une efficacité de 9% basée sur la fraction d'énergie de la réaction de pompage transformée en énergie de vibration. Le rendement laser multiligne fut observé sur 8 bandes P provenant des bandes de vibration v=5 \pm 2, v=2 \pm I et v=1 \pm 0. En outre, le laser fonctionna efficacement lorsque le Ci de la réaction de pompage était produit 'in *rilixi*', une caractéristique qui peut être importante dans la recherche de plus grandes puissances. (NC)

DREV REPORT 4059/76 (UNCLASSIFIED) Research and Revelopment Branch, Department of National Defence, Canada. DREV, P.O. Box 880, Courcelette, Que. GOA IRO. "An Efficient, Purely Chemical HCL Laser" by K.D. Foster, R.D. Suart and D.R. Snelling Purely chemical laser emission at 3:6 to 4 µm from HCL has been achieved in a transverse flow device. The pumping reaction was the well known Ci + HI + HCL ² + 1 reaction. Atomic chlorine was produced chemically from the reaction of NO with CO ₂ . The maximum power obtained from this system was 4 W, which corresponded to a chemical efficiency of 95 based upon the fraction of pumping reaction energy that goes into vibration. Multiline laser output was observed for eight P-branch lines emanating from the v=3 + 2, v=2 + 1 and v=1 + 0 vibrational bands. The laser also operated succersfully under conditions where the C2 for the pumping reaction was produced for eight powers. (U)	DREW REPORT JUS9/76 (UNCLASSIFIED) Rescarch and Development Branch, Department of National Defence, Canada. DREW, P.O. Box 820, Courcelette, Que. GOA 180. "An Efficient, Furely Chemical HGT Laser" by K.D. loster, R.D. Suart and D.R. Snelling Furely chemical laser emission at 5.6 to 4 µm from HGs has been achieved in a transverse flow device. The pumping reaction was the well known C. + HI + HGt ⁷ + 1 reaction. Atomic chlorine was produced chemically from the reaction of NO with C202. The maximum power obtained from this system was 4 W, which corresponded to a chemical efficiency of 9% based upon the fraction of pumping reaction energy that goes into vibration. Multiline laser output was observed for eight P-branch lines emanating from the v=3 + 2, v=2 + 1 and v=1 + 0 vibrational bands. The laser also operated successfully under conditions where the C4 for the pumping reaction was produced A. v ^{1/2} , a feature which may be important in scaling to higher powers. (II)	
DREW REPORT 4059/76 (UNCLASSIFIED) Research and Development Branch, Department of National Defence, Canada. The Efficient, Purely Chemical HCG Laser" by K.D. Foster, R.D. Suart and D.R. Snelling Purely chemical laser emission at 3.6 to 4 µm from HCi has been achieved in reaction. Atomic chlorine was produced chemically from the reaction of NO with C602. The maximum power obtained from this system was 4 W, which corresponded to a chemical efficiency of 9% hased upon the fraction of pumping reaction energy that goes into vibration. Multiline laser output was observed for eight P-branch lines emanating from the v=3 + 2, v=2 + 1 and v=1 + 0 vibration-1 bands. The laser also operated successfully under conditions where the Ci for the pumping reaction was produced (a v ²⁺¹), a feature which may be important in scaling to higher powers. (0)	DREV REPORT 4059/76 (UXCLASSIFIED) Research and Development Branch. Department of National Defence, Canada. DREV, P.O. Box 880, Courcelette, Que. GOA 1RO. "An Efficient, Purely Chemical HC: Laser" by K.D. Foster, R.D. Suart and D.R. Snelling Purely chemical laser emission at 3.6 to 4 µm from HC: has been achieved in reaction. Atomic chlorine was produced chemically from the reaction of NO with CKO ₂ . The maximum power obtained from this system was 4 W, which corresponded to a chemical erficiency of 9°, based upon the fraction of pumping reaction energy that goes into v:bration. Multiline liser output was observed for eight P-branch lines emanating from the v=5 + 2, v=2 + 1 and v=1 + 0 vibrational bands. The laser also operated successfully under conditions where the CX for the pumping reaction was produced i. Jifu, a feature which may be important in scaling to higher powers. (U)	

<u>نې</u> د د