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PURELY CHEMICAL HCℓ LASER BASED UPON THE REACTION OF Cℓ ATOMS WITH HBr

by

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RESUME

On a étudié l'émission stimulée de $HC\ell$ excité vibrationellement dans un laser à écoulement transversal. Ce laser était axé sur la réaction $C\ell + HBr \rightarrow HC\ell^{\dagger} + Br$. Les atomes de chlore ont été produits *in situ* par la réaction chimique de NO avec $C\ell O_2$. La puissance de sortie maximale a atteint 0.34 W, ce qui représente approximativement le tiers de la puissance observée lorsque HI était utilisé au lieu de HBr. On croit que l'efficacité chimique du laser utilisant $C\ell + HBr$ est inférieure à celle du laser employant la réaction $C\ell + HI$ parce qu'une portion de l'énergie vibrationnelle de $HC\ell$ est transférée au HBr; en outre, l'énergie de réaction dans le système $C\ell + HBr$ est plus faible. (NC)

ABSTRACT

Laser emission from vibrationally excited $HC\ell$ has been achieved in a transverse flow system whose pumping energy relied upon the reaction $C\ell + HBr \rightarrow HC\ell^{\dagger} + Br$. For these experiments the chlorine atoms were produced *in situ* from the chemical reaction of NO with $C\ell O_2$. The observed maximum output power of 0.34 W was approximately one third the output power if hydrogen iodide was substituted for HBr. Loss of $HC\ell$ vibrational quanta through collisions with HBr is believed to be a severe limitation on $C\ell + HBr$ system and probably accounts for the reduced $HC\ell$ laser efficiency of $C\ell + HBr$ compared with $C\ell + HI$ along with the reduced exothermicity of the pumping reaction. (U)

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1.0 INTRODUCTION

Infrared lasers operating in the 3-5 μm wavelength region are of special interest because of the generally high transmission of the atmosphere at these wavelengths. One example is the hydrogen chloride laser operating on vibration-rotation transitions at (3.6 - 4.0) μm. The use of elementary chemical reactions has proved to be an efficient means of producing vibrationally excited HCℓ. The particular reaction which has received the most attention is the very fast reaction of atomic chlorine with hydrogen iodide $k_1 = 1.64 \times 10^{-10}\ cm^3 s^{-1}$ (Ref. 1):

$$C\ell + HI \rightarrow HC\ell^{\dagger} + I \quad \Delta H = -32\ kcal/mole \qquad (1)$$

Another source of vibrationally excited HCℓ is the reaction of atomic chlorine with hydrogen bromide

$$C\ell + HBr \rightarrow HC\ell^{\dagger} + Br \quad \Delta H = -15.5\ kcal/mole \qquad (2)$$

Because the exothermicity of this reaction step is only about one half that of the Cℓ + HI reaction, only the vibrational levels v=2, v=1 and v=0 are substantially populated. The total rate coefficient for the process is $7.4 \times 10^{-12}\ cm^3 s^{-1}$ (Ref. 1), i.e. reaction occurs for one in every 30 gas kinetic collisions.

The successful operation of a Cℓ + HBr pumped chemical laser was demonstrated by Airey (Ref. 2) who flash-photolyzed mixtures of $C\ell_2$ and HBr. The laser operated on HCℓ lines emanating from the v=1 → v=0 band only, and it was concluded that the specific reaction rate forming HCℓ (v=1) was at least as large as that forming HCℓ (v=0). Another conclusion of this work was that the most important process resulting in HCℓ (v=1) deactivation was vibration-vibration (V-V) relaxation of $HC\ell^{\dagger}$ by HBr:

$$HC\ell_{v=1} + HBr_{v=0} \rightarrow HC\ell_{v=0} + HBr_{v=1} \qquad (3)$$

That the rate coefficient for process (3) was indeed large was subsequently demonstrated by Chen (Ref. 3) and by Bott and Cohen (Ref. 4). These workers measured rate constants of 1.11×10^{-12} cm^3 s^{-1} and [illegible] 96×10^{-12} cm^3 s^{-1} respectively.

Recently, the chemistry associated with the $NO/C\ell O_2$ system has been exploited to produce laser emission at 10.6 μm and 3.8 μm (Refs. 5, 6). For these systems, Cℓ atoms were produced chemically and the Cℓ + HI reaction produced vibrationally excited HCℓ which lased directly at 3.8 μm or the energy was transferred to CO_2 which lased at 10.6 μm.

The mechanism for the reaction of NO with $C\ell O_2$ has been discussed previously (Ref. 7); and therefore only a brief summary will be included here. The three reactions involved in the branched chain mechanism leading to the conversion of $C\ell O_2$ to Cℓ atoms or CℓO radicals are shown below. The first of these reactions is slow while the latter two reactions are fast (Ref. 8). The net effect for equi-molar addition of NO and $C\ell O_2$ is to produce NO_2 and CℓO (conversion of $C\ell O_2$ to CℓO radicals). If twice as much NO is added as $C\ell O_2$, the complete conversion of $C\ell O_2$ to Cℓ atoms occurs yielding NO_2 and atomic chlorine, Cℓ.

$$NO + C\ell_2 \rightarrow NO_2 + C\ell O \qquad (4)$$

$$NO + C\ell O \rightarrow NO_2 + C\ell \qquad (5)$$

$$C\ell + C\ell O_2 \rightarrow 2C\ell O \qquad (6)$$

The flexibility of the $NO/C\ell O_2$ system in connection with laser experiments was recently demonstrated (Ref. 7). The HCℓ laser was successfully operated in three distinct kinetic regimes which were defined as chemical (or kinetic) MODES I, II and III depending upon whether the reactant $C\ell O_2$ was converted to atomic Cℓ (MODE I) to CℓO radicals (MODE II) or was unaltered (MODE III) before the laser pumping reaction was allowed to occur.

Continuous wave operation of a chemical HCℓ laser in which hydrogen bromide is a principal reactant does not appear to have been reported in the literature. This report describes experiments with a CW purely chemical HCℓ laser employing transverse flow. The laser pumping reaction for this system was $C\ell + HBr \rightarrow HC\ell^{\dagger} + Br$. It also presents kinetic modelling results in which the rates of relevant processes in the $C\ell + HBr$ system are integrated numerically. The experimental results for the $C\ell + HBr$ chemical laser are compared with those of the $C\ell + HI$ chemical laser. Some of the experimental findings for the $C\ell + HBr$ system are also examined in the light of kinetic modelling calculations.

This work, which represents a continuation of purely chemical laser studies based upon the $NO/C\ell O_2$ reaction system, was performed at DREV in mid 1975 under PCN 34B01 (formerly PCN 07C01, Project 97-01-39) "Research on Chemically Excited Lasers".

2.0 EXPERIMENTAL

Although the $C\ell O_2$ generator and transverse flow laser have been described previously (Refs. 6, 7), a schematic diagram of the apparatus is shown in Fig. 1 for convenience. For the experiments described here, three injector rows were employed. These allowed the sequential addition of NO#1, HBr and then NO#2 to the mainstream which contained dilute $C\ell O_2/He$ mixtures. The symbol NO#1 refers to the upstream location for the addition of NO and NO#2 refers to the downstream location for NO injection.

The optical cavity consisted of two externally mounted mirrors, a 'total' reflector of the 'protected metal' type having a 4-m radius-of-curvature (RC) and a partially reflecting flat. The flat decoupling mirror was a 4% transmitting multilayer dielectric mirror on a CaF_2 substrate. The reaction vessel was sealed by two CaF_2 flats placed at Brewster's angle.

The experimental conditions which were common to most experiments are:

Helium (in $NaC\ell O_2$ column) = 17,360 SCCM
Helium (auxiliary) = 26,000 SCCM
$C\ell_2$ (in $NaC\ell O_2$ column) = 595 SCCM
NO#1 < 1000 SCCM (variable)
NO#2 < 6500 SCCM (variable)
HBr < 5000 SCCM (variable)

Total Pressure 2-3 torr
Average Linear Velocity ∿ 210 ms^{-1}

The above velocity was determined from the above flow rates knowing the pressure and the flow channel area.

To handle $C\ell O_2$ safely certain precautions were routinely followed (Refs. 5, 6, 9).

2.1 Kinetic Model-Numerical Procedure

As in the HCℓ laser in which HI was used as a reactant (Ref. 7), a computer simulation of the relevant processes has been carried out for the Cℓ + HBr system. A list of the individual processes which were considered along with their rate coefficients is given in the Appendix. The computer program DOLPHIN was used to compute the time evolution of the various reacting species. This program, which is a general program for treating rate processes, will be described in detail elsewhere (Ref. 10).

Since most of the available rate data apply to ∿300°K, no attempt in the program was made to vary the temperature. A simple one-dimensional model was assumed. The rate equations were integrated in the time domain and the results compared to experiment by assuming a constant linear flow velocity.

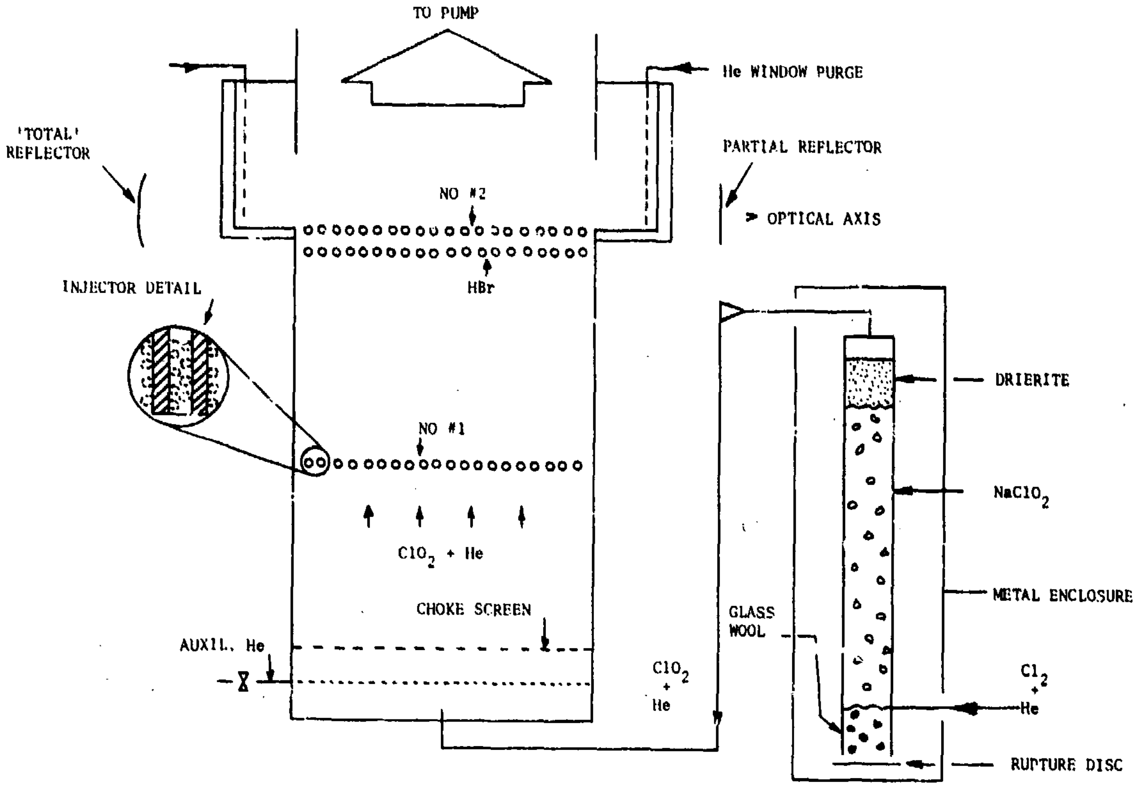

FIGURE 1 - Diagram of $C\ell O_2$ generator and $HC\ell$ transverse flow chemical laser

3.0 RESULTS AND DISCUSSION

All experiments were carried out with the injector sequence NO#1 - HBr - NO#2, already used with HI in place of HBr (Ref. 7). With this type of arrangement it was possible to delay the formation of atomic chlorine until the flowing gases reached the optical region, i.e. the initial injection of NO converted some or all of the $C\ell O_2$ to $C\ell O$ (MODE II).

When HI was replaced with HBr, $HC\ell$ laser oscillation was again observed. The first experiments were conducted with a flow of NO at the downstream location, NO#2, of 3000 SCCM and a flow of 1800 SCCM of HBr. The maximum laser output power was 0.34 W and was observed with the laser axis located 1.5 cm downstream of the NO#2 injector and with a flow of 500 SCCM of NO through the upstream injector NO#1. This experiment therefore demonstrates the successful operation of the Cℓ + HBr chemical laser in the kinetic MODE II, a kinetic regime which was described previously (Ref. 7). At the termination of this experiment the reactant was changed to HI. With 1000 SCCM of NO through NO#1, 3000 SCCM of NO through NO#2 and 1000 SCCM of HI, the HCℓ laser output power was 1 W. For these experimental conditions then, the Cℓ + HBr system gave a total HCℓ laser power about one third that obtained with the Cℓ + HI system. It should be kept in mind, however, that the laser output for the Cℓ + HI system is spread over the v=3-2, v=2-1 and v=1-0 vibrational bands, whereas the Cℓ + HBr system yields v=1 → v=0 laser transitions only (Ref. 2).

The HBr flow required to obtain maximum HCℓ laser power was found to far exceed the corresponding HI flow when HI was used as a reactant. This was probably due to the fact that the rate coefficient for the Cℓ + HBr reaction is some 22 times slower than that for the Cℓ + HI reaction. A high concentration of HBr is therefore required to increase the HCℓ pumping rate in the Cℓ + HBr system.

At sufficiently high flows of NO#2 (= 6400 SCCM), it was possible to operate the laser with no NO passing through the upstream injector. None of the $C\ell O_2$ was therefore pre-converted to CℓO. The dependence of the HCℓ laser power on the HBr flow in such a kinetic regime, which has been referred to previously as Chemical MODE III, is shown in Fig. 2. The optical axis was located 2 cm downstream of the NO#2 injector. It will be noted that an HBr flow of $\geq$ 4000 SCCM was required to obtain the maximum power of 0.31 W.

At an HBr flow of 4500 SCCM in the previous experiment, a flow of NO was added at injector NO#1, which converted the laser from MODE III to MODE II operation. The laser power increased by 10%. The Cℓ + HI system behaved differently. Whereas the laser power in MODE III for HCℓ was about 70% that of MODE II for the Cℓ + HI system, it was about the same for MODES II and III for the Cℓ + HBr system.

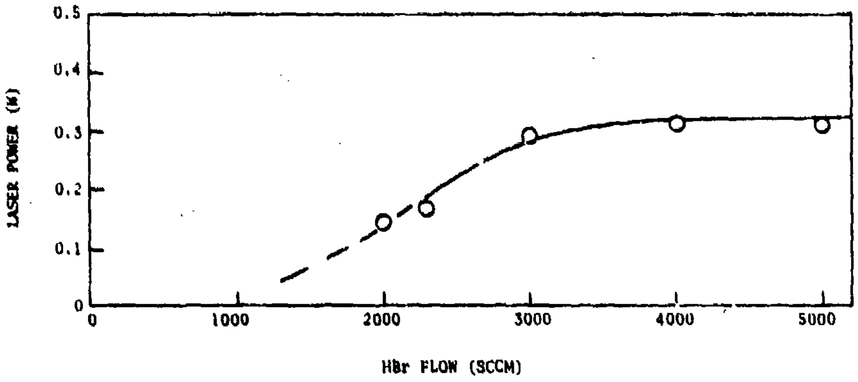

FIGURE 2 - Dependence of laser power on initial HBr flow for chemical MODE III

3.1 Modelling Results

Computer simulations were carried out with input conditions corresponding to the above experiment. Specifically, the conditions corresponded to

He (total diluent)	46,320	SCCM
$C\ell_2$	595	SCCM
HBr	4500	SCCM
NO#1	0 or 330	SCCM
NO#2	6400	SCCM

Total Pressure 3.2 torr

The time evolution of the species $C\ell O_2$, $C\ell$ and $HC\ell$ was plotted along with the total amount of vibrationally excited $HC\ell$ and also the amount of vibrationally excited HBr. The relative rates of excitation of $HC\ell_{v=1}$ and $HC\ell_{v=2}$ has been measured by Polanyi et al (see Appendix, note G and Ref. A-16). The amount of excitation in $HC\ell_{v>0}$ was estimated by assuming the rate of formation of $HC\ell_{v=0}$ in reaction (2) was 1/10 of that in v=1. This assumption is somewhat arbitrary but is consistent with evidence indicating that the rate into $HC\ell_{v=1}$ is greater than that into $HC\ell_{v=0}$ (Ref. 2). The conclusion is unaffected by the choice of the precise value of the ratio of the rates. The first plot, Fig. 3, corresponds to a NO#1 flow of 330 SCCM (MODE II operation) which is sufficient to convert 33% of the $C\ell O_2$ to $C\ell O$ radicals. Figure 4, on the other hand, corresponds to zero NO#1 flow (MODE III operation) which means that no $C\ell O$ radicals are initially present at NO#2.

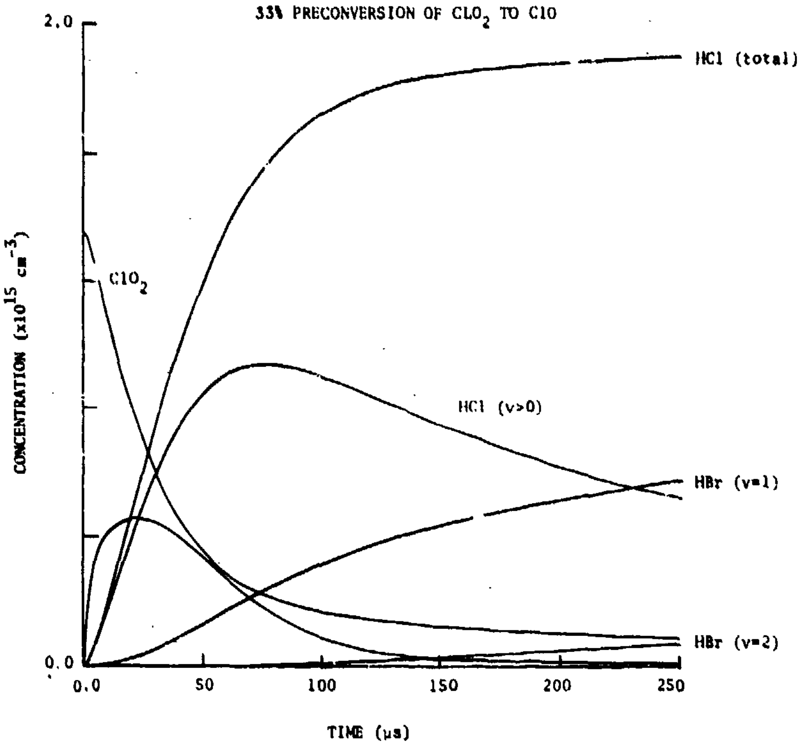

FIGURE 3 - Time evolution of $HC\ell$ for 33% conversion of $C\ell O_2$ to $C\ell O$ (MODE II)

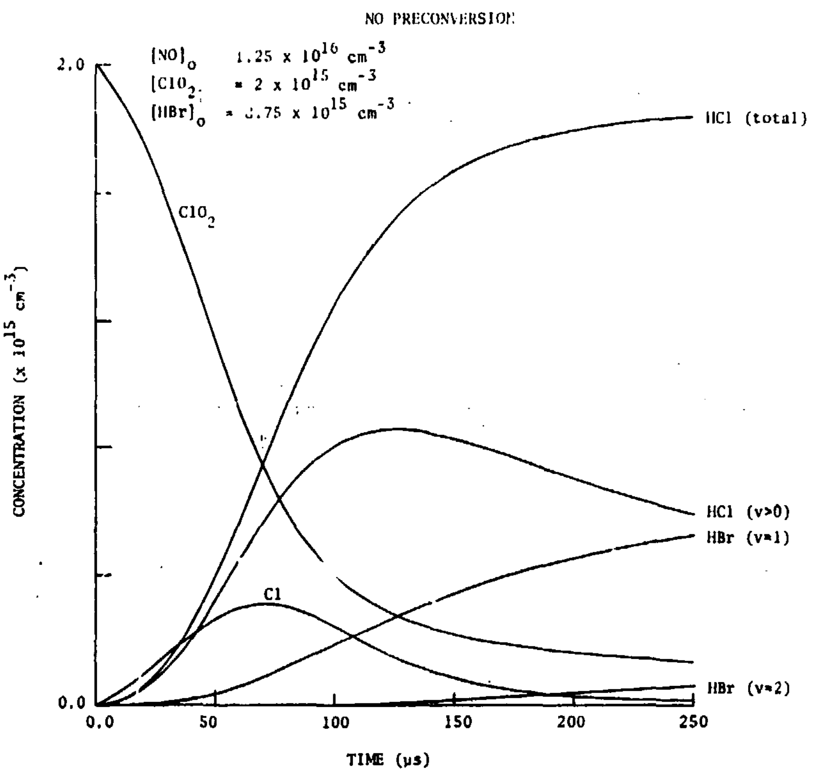

FIGURE 4 - Time evolution of HCℓ in Chemical MODE III

The difference between the total HCℓ produced and the HCℓ (v>0) in these plots points out a severe limitation of Cℓ + HBr as a laser system. Since the pumping reaction for Cℓ + HBr is slow compared to that of the Cℓ + HI system, an excess of HBr is required to increase the pumping rate. The ultimate attainable output power, however, becomes more and more limited with increasing HBr because of the vibrational relaxation of HCℓ by collisions with HBr (Refs. 3, 4). The build-up of HBr (v=1,2) and accompanying fall-off of HCℓ (v>0) will be noted in both Figs. 3 and 4.

The results of Figs. 3 and 4 were combined in Fig. 5 to compare the simulation with experimental results. The data in Fig. 2 were obtained with the laser axis about 2 cm downstream of the NO#2 injector, which corresponded to ~100 μs of flow time from the NO#2 injector. It will be recalled that for this experiment the addition of NO through the upstream injector needles did not greatly affect the output power. This result seems to be in accord with the modelling results of Fig. 5 which show that at 125 μs the total excited HCℓ concentration is fairly insensitive to the extent of pre-conversion of $C\ell O_2$ to CℓO radicals. According to Fig. 5, the concentration of excited $HC\ell^\dagger$ is determined primarily by $HC\ell^\dagger \rightarrow HBr$ relaxation for reaction times greater than 100 μs.

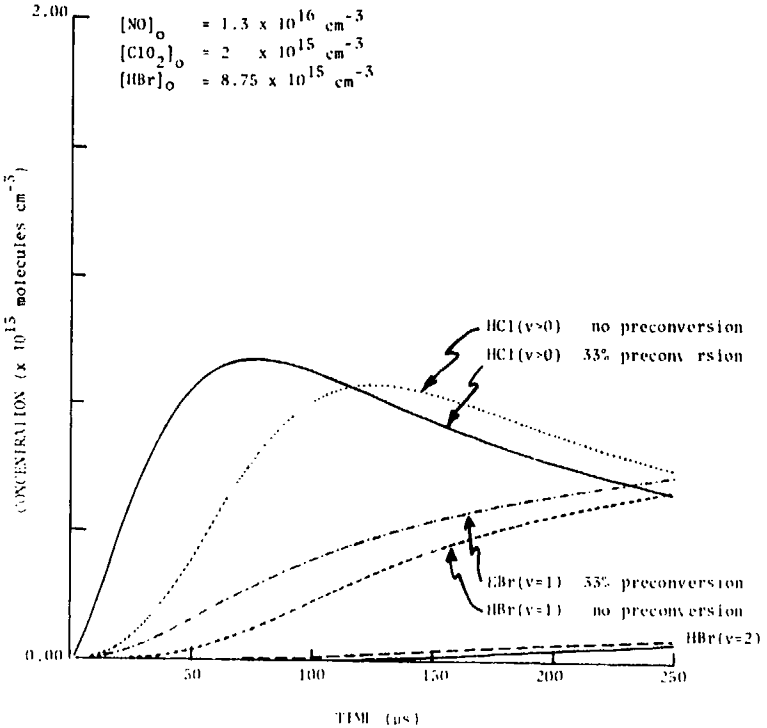

FIGURE 5 - Composite of Figures 3 and 4

4.0 SUMMARY AND CONCLUSIONS

Continuous wave purely chemical laser emission in a transverse flow system has been demonstrated in HCℓ in which the pumping reaction was $C\ell + HBr \rightarrow HC\ell_{v=0,1,2} + Br$. These experiments were performed using the $NO/C\ell O_2$ chemical system in a regime where the atomic Cℓ for laser pumping was formed in the optical region.

The maximum total HCℓ laser output power observed was 0.34 W. This represents about one third the output power observed if HI was used as a reactant under similar conditions. The lower HCℓ laser efficiency when HBr was used, rather than HI, probably reflects the lower pumping reaction exothermicity as well as the adverse effects of a slower pumping rate for Cℓ + HBr and the resultant more rapid $HC\ell^{\dagger}$ relaxation because of the presence of excess HBr.

The experimental observation that for certain conditions the laser output power was insensitive to the extent of pre-conversion of $C\ell O_2$ into CℓO radicals was consistent with the kinetic model, which indicated that the effects of pre-conversion should be most dramatic early in the reaction sequence. As the reaction proceeds, however, the level of vibrationally excited HCℓ is determined largely by the HBr concentration. The initial presence or absence of CℓO radicals by pre-conversion is therefore less important at these later reaction times and the efficiency in MODE III is almost equal to that in MODE II.

For applications in which the HCℓ laser efficiency is a prime consideration, the $C\ell + HBr \rightarrow HC\ell^{\dagger} + Br$ system would be inferior to the $C\ell + HI \rightarrow HC\ell^{\dagger} + I$ system.

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APPENDIX "A"

A generalized computer model describing the chemical processes taking place in the laser has been developed. The mechanics of the computer simulation are described in detail in DOLPHIN, a general program for the treatment of chemical rate equations. The time evolution of the reaction ensemble was simulated using a Runge-Kutta numerical integration routine.

This Appendix consists of a listing of the processes considered in a computer simulation of reacting mixtures typically used in the laser experiments. Table A-I contains those reactions used to produce chlorine atoms and Table A-II, those used to generate vibrational excitation during the reaction of chlorine atoms with HBr and some of the subsequent V-V exchange reactions of HCℓ thus formed. Table A-III considers further deactivation reactions of HCℓ for which reliable rate data are available. (No rate data is available for the deactivation of HCℓ by NO_2, O_2 or NOCℓ, all of which are present in appreciable concentrations at various times in the evolution of the reacting mixture.) Table A-IV consists of additional reactions of bromine atoms.

References are given to the literature in support of the rate constant assignments when available. Additional explanations are given in the lettered footnotes. Rate constants are given in cm^3 $molecule^{-1}s^{-1}$.

The tables are presented directly by a line printer with the notation E-11 = 10^{-11}.

NOTES

(A) Rate constants calculated for 300°K; M=He

(B) The overall rate constant for the reaction

$$2C\ell O \xrightarrow{k_f} \text{products}$$

is given in Ref. A-3 as $(1.3 \pm 0.1) \times 10^{12} \exp(-1150 \pm 50/T)$. Clyne et al (Ref. A-10) indicate that at 298°K reaction 4 accounts for 4% of the total reaction. The ratio of reaction 5 to reaction 6 is not accurately known. Watson (Ref. A-11) indicates that $k_5 / k_6 \sim 1$ at low pressures (1-3 torr) while Clyne et al (Ref. A-10) state that reaction 5 is a major reaction channel in the second order decay of CℓO. For the present calculations $k_4 = k_6 = 0$ and $k_5 = k_f$.

(C) A value of the rate constant, k_7, was calculated from the relationships

$$\mathrm{C\ell OO} + \mathrm{M} \underset{k_8}{\overset{k_7}{\rightleftarrows}} \mathrm{C\ell} + \mathrm{O_2} + \mathrm{M}$$

$$k_7 = \frac{k\mathrm{equil}}{k_8} = \frac{e^{-\Delta H/RT} \, e^{\Delta S/R}}{k_8} \; ,$$

where $k_8 = 5.6 \times 10^{-34}$, and the required thermodynamic data from Ref. A-12.

(D) A value of the rate constant, k_{10}, was obtained from the ratio $k_g/k_{10} = 15$ of Ref. A-13 and the value of $k_g = 1.56 \times 10^{-10}$ of Ref. A-5.

(E) Basco et Dogra (Ref. A-14) in a study of CℓO recombination over a pressure range similar total to that of Johnston et al (Ref. A-5) found no dependence of the overall rate constant on M. For the present calculations $k_{11} = 0$.

(F) The value of the rate constant k_{16} is assumed equal to k_{13}.

(G) The value of the overall rate constant

$$\mathrm{C\ell} + \mathrm{HBr}\ (v=0) \rightarrow \mathrm{HC\ell}\ (v=n) + \mathrm{Br} \qquad n=0,1,2$$

is 7.4×10^{-12} (Ref. A-15). Polanyi et al (Ref. A-16) give the relative rate of formation into v=1 and v=2 to be 1.0:0.4. It is assumed that the rate of formation into v=0 is 1/10 of that into v=1.

(H) The values of the rate constants for

$$\mathrm{C\ell + HBr(v{=}n) \rightarrow HC\ell(v{=}m) + Br} \qquad n=1,2 \quad m=0,1,2$$

are assumed to be the same as that of G.

(I) The average value of the rate constants given in Refs. A-17 and A-19 was used.

(J) No reliable values of the rate constants for reactions 28-31 are given in the literature. A detailed discussion of the V-V transfer processes occurring for $HC\ell$ is given in Ref. A-20.

(K) The average value of the rate constants given in Refs. A-21 - A-24 was used.

(L) No reliable values of the rate constants for reactions 34-39 are given in the literature. Estimates of the rate constants for reactions 34-37 can be made from the value of the rate constant for reaction 32 using the method described in Ref.A-25 for estimating V-V transfer probabilities for $HC\ell\,(v=n) + NO(v=0) \rightleftarrows HC\ell(v=n-1) + NO(v=1)$.

(M) The average value of the rate constants given in Refs. A-26 - A-27 was used.

(N) The values of the rate constants for reactions 43-47 were obtained from the ratios given in Ref. A-29 and the value of $k_{42} = 8.8 \times 10^{-12}$ given in Ref. A-28.

(O) $k\,[HC\ell(v=n)] = nk\,[HC\ell(v=1)]$.

(P) The average value of the rate constant given in Refs. A-31 - A-33 was used.

(Q) Leone et al (Ref. A-34) have measured the total rate of removal of $HCl(v=2)$ by Br atoms

$$HCl(v=2) + Br \xrightarrow{k_T} \text{products}$$

and obtained a value of the rate constant, $k_T = (1.8 \pm 0.33) \times 10^{-12}$ at $294^{o}K$. They believe that reaction 64 is predominent. For the present calculation, $k_{63} = 1/10\ k_T$ and $k_{64} = 9/10\ k_T$. The value of the rate constant for the total rate of removal of $HCl(v=3)$ by Br atoms is assumed to equal that for removal of $HCl(v=2)$ with $k_{65} = 1/10\ k_T$ and $k_{66} = 9/10\ k_T$.

(R) The average value of the rate constants given in Refs. A-32-A-53 was used.

(S) Clyne et al (Ref. A-37) state that the heteroatom recombination

$$Cl + Br + M \rightarrow BrCl + M$$

is noticeably faster than the homoatom recombination

$$Br + Br + M \rightarrow Br_2 + M$$

Consequently the value of the rate constant for reaction 73 was multiplied by 1.5 to give an approximate value for the rate constant for reaction 74.

TABLE A-I

	REACTION	RATE CONSTANT	REFRENCE
1	CL + OCLO → CLO + CLO	5.9 E-11	1
2	NO + OCLO → CLO + NO2	3.4 E-13	1
3	NO + CLO → CL + NO2	1.7 E-11	2
4	CLO + CLO → CL + OCLO		
5	CLO + CLO → CLOO + CL	2.8 E-14	3B
6	CLO + CLO → CL2 + O2		
7	CLOO + M → CL + O2 + M	1.34E-14	C
8	CL + O2 + M → CLOO + M	5.6 E-34	4
9	CL + CLOO → CL2 + O2	1.56E-10	5
10	CL + CLOO → CLO + CLO	1.04E-11	D
11	CLO + CLO + M → CL2 + O2 + M	6.6 E-32	5E
12	CL + CL + M → CL2 + M	6.39E-33	6
13	NOCL + CL → NO + CL2	3.0 E-11	7
14	NO + CL + M → NOCL + M	9.3 E-32	8
15	NO2 + CL + M → NO2CL + M	7.2 E-31	9
16	NO2CL + CL → NO2 + CL2	3.0 E-11	F

TABLE A-II

	REACTION	RATE CONSTANT	REFERENCE
17	CL + HBR(V=0) → HCL(V=0) + BR	4.93E-13	G
18	CL + HBR(V=0) → HCL(V=1) + BR	4.93E-12	G
19	CL + HBR(V=0) → HCL(V=2) + BR	1.97E-12	G
20	CL + HBR(V=1) → HCL(V=0) + BR		[illegible]
21	CL + HBR(V=1) → HCL(V=1) + BR		
22	CL + HBR(V=1) → HCL(V=2) + BR		H
23	CL + HBR(V=2) → HCL(V=0) + BR		H
24	CL + HBR(V=2) → HCL(V=1) + BR		H
25	CL + HBR(V=2) → HCL(V=2) + BR		H
26	HCL(V=1) + HCL(V=1) → HCL(V=2) + HCL(V=0)	4.69E-12	(17-19)I
27	HCL(V=2) + HCL(V=0) → HCL(V=1) + HCL(V=1)	[illegible].85E-12	(17-19)I
28	HCL(V=2) + HCL(V=2) → HCL(V=3) + HCL(V=1)		J
29	HCL(V=3) + HCL(V=1) → HCL(V=2) + HCL(V=2)		J
30	HCL(V=2) + HCL(V=1) → HCL(V=3) + HCL(V=0)		J
31	HCL(V=3) + HCL(V=0) → HCL(V=2) + HCL(V=1)		J
32	HCL(V=1) + HBR(V=0) → HCL(V=0) + HBR(V=1)	1.09E-12	(21-24)K
33	HCL(V=0) + HBR(V=1) → HCL(V=1) + HBR(V=0)	2.26E-13	(21-24)K
34	HCL(V=2) + HBR(V=0) → HCL(V=1) + HBR(V=1)		L
35	HCL(V=1) + HBR(V=1) → HCL(V=2) + HBR(V=0)		L
36	HCL(V=3) + HBR(V=0) → HCL(V=2) + HBR(V=1)		L
37	HCL(V=2) + HBR(V=1) → HCL(V=3) + HBR(V=0)		L
38	HCL(V=1) + HBR(V=1) → HCL(V=0) + HBR(V=2)		L
39	HCL(V=0) + HBR(V=2) → HCL(V=1) + HBR(V=1)		L
40	HCL(V=2) + HBR(V=1) → HCL(V=1) + HBR(V=2)		L
41	HCL(V=1) + HBR(V=2) → HCL(V=2) + HBR(V=1)		L
42	HBR(V=1) + HBR(V=1) → HBR(V=2) + HBR(V=0)	6.76E-12	(26-27)M
43	HBR(V=2) + HBR(V=0) → HBR(V=1) + HBR(V=1)	4.38E-12	(26-27)M

TABLE A-III

	REACTION	RATE CONSTANT	REFERENCE
44	HCL(V=1) + CL → HCL(V=0) + CL	8.8 E-12	28
45	HCL(V=2) + CL → HCL(V=1) + CL	1.05E-11	N
46	HCL(V=2) + CL → HCL(V=0) + CL	4.11E-12	N
47	HCL(V=3) + CL → HCL(V=2) + CL	1.13E-11	N
48	HCL(V=3) + CL → HCL(V=1) + CL	5.86E-12	N
49	HCL(V=3) + CL → HCL(V=0) + CL	2.54E-12	N
50	HCL(V=1) + NO → HCL(V=0) + NO	9.69E-14	30
51	HCL(V=2) + NO → HCL(V=1) + NO		O
52	HCL(V=3) + NO → HCL(V=2) + NO		O
53	HCL(V=1) + HCL(V=0) → HCL(V=0) + HCL(V=0)	2.93E-14	(31-33)P
54	HCL(V=2) + HCL(V=0) → HCL(V=1) + HCL(V=0)		O
55	HCL(V=3) + HCL(V=0) → HCL(V=2) + HCL(V=0)		O
56	HCL(V=1) + CL2 → HCL(V=0) + CL2	1.00E-14	21
57	HCL(V=2) + CL2 → HCL(V=1) + CL2		O
58	HCL(V=3) + CL2 → HCL(V=2) + CL2		O
59	HCL(V=1) + BR2 → HCL(V=0) + BR2	3.26E-14	34
60	HCL(V=2) + BR2 → HCL(V=1) + BR2		O
61	HCL(V=3) + BR2 → HCL(V=2) + BR2		O
62	HCL(V=1) + BR → HCL(V=0) + BR	2.8E-13	34
63	HCL(V=2) + BR → HCL(V=1) + BR		Q
64	HCL(V=2) + BR → HBR(V=0) + CL		Q
65	HCL(V=3) + BR → HCL(V=2) + BR		Q
66	HCL(V=3) + BR → HBR(V=0) + CL		Q
67	HBR(V=1) + HBR(V=0) → HBR(V=0) + HBR(V=0)	1.72E-14	(32-33)R
68	HBR(V=2) + HBR(V=0) → HBR(V=1) + HBR(V=0)		O
69	HBR(V=1) + BR → HBR(V=0) + BR	6.3 E-12	35
70	HBR(V=2) + BR → HBR(V=1) + BR	1.93E-11	35
71	HBR(V=2) + BR → HBR(V=0) + BR	1.05E-11	35

TABLE A-IV

	REACTION	RATE CONSTANT	REFERENCE
72	BR + NOCL → BRCL + NO	1.0 E-11	7
73	CL + BRCL → CL2 + BR	1.45E-11	36
74	CL + BR2 → BRCL + BR	1.2 E-10	36
75	BR + B[illegible] + M → BR2 + M	3.[illegible]5E-33	6
76	BR + CL + M → BRCL + M	4.5 E-33	S
77	BR + OCLO → BRCL + O2	5.17E-14	37

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