# NEW HCI CHEMICAL LASERS: CHLORINE REACTIONS WITH GROUP IV, V, AND VI HYDRIDES

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The reactions of chlorine with hydrides of elements in groups IV, V, and VI have been investigated with respect to their potential as sources for HCl chemical lasers. For these systems, chain reactions involving Cl<sub>2</sub> should contribute in some measure to the production of chlorine atoms. New HCl lasers based on the reactions of chlorine atoms with H<sub>2</sub>S, H<sub>2</sub>Se, and  $PF_3H_2$  were observed.

### 1. Introduction

The  $H_2-Cl_2$  chain is perhaps the most studied of all reactions used to pump HCl chemical lasers [1]. This system suffers from a serious drawback in that the chain propagation step (Cl +  $H_2 \rightarrow$  HCl + H) produces vibrationally cold HCl. In addition, this step is much slower than the pumping reaction (H +  $Cl_2$  $\rightarrow$  HCl<sup>†</sup> + Cl), and consequently does not sustain a concentration of hydrogen atoms necessary for the chain to make a significant contribution to the laser efficiency (i.e., relative to the initiation energy). In this report, we present preliminary results of our investigations of a "conjugate" chain mechanism involving chlorine atoms rather than hydrogen atoms as an intermediate:

 $Cl + RH \to HCl^{\uparrow} + R, \tag{1}$ 

 $R + Cl_2 \rightarrow RCl + Cl. \tag{2}$ 

These Cl + RH systems offer better opportunities for matching the rates of reactions (1) and (2) above, hence yielding longer chain length (in the time frame of the laser experiments) and minimizing the concentrations of Cl and R radical intermediates (efficient deactivators of HCl<sup> $\dagger$ </sup>).

In the absence of absolute rate data, candidate species RH were chosen such that both reactions (1) and (2) are substantially exothermic. Specifically, experiments were performed for reactions of chlorine atoms with  $H_2S$ ,  $H_2Se$ ,  $PF_3H_2$ , and three silicon hydrides. In each case, chlorine atoms were created by flash photolysis of  $Cl_2$ . We report the laser emissions observed and their spectral content.

#### 2. Experimental details

Experiments were performed with a typical flash photolysis chemical laser apparatus [2]. A concentric laser tube—flashlamp assembly was employed, with the laser tube made of pyrex (this limited photolysis mainly to the Cl<sub>2</sub>). The ends of the tube were cut at a few degrees off Brewster's angle and sealed with either sapphire or CaF<sub>2</sub> windows. Two flashbanks were used. The first was capable of discharging a maximum of 800 joules. Typical flashes from this bank had a risetime of 4  $\mu$ s with a half-peak duration of 10  $\mu$ s. Flashes from the second bank, which could discharge up to 2800 joules, exhibited a risetime of 10  $\mu$ s and a half-peak duration of 13  $\mu$ s.

Reagent gases were continuously flowed through the laser tubes to  $LN_2$ -cooled traps and a 3 cfm pump In most cases, a stream of  $Cl_2$  was mixed with a strear of RH (heavily diluted in helium or argon) just prior to entering the laser tube. Diluents were mixed with the RH approximately two meters upstream. Flowrates were monitored with Matheson rotameter flowmeters, and the total pressure in the laser tube was monitored with a stainless steel Heise gauge.

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In most cases, the optical cavity was formed by two 1.75 m radius of curvature gold-coated mirrors (Oriel Corp.) placed 1.65 meters apart (i.e., in confocal configuration). Laser emission was coupled out of the cavity by reflection from the off-Brewster windows. The emission was focused onto room temperature InSb photoconductive detectors (Mullard, Inc.), whose response was displayed on a Tektronix 7603 oscilloscope. The scope was triggered by the pick-up from a photodiode (UDT PIN-5) which monitored the flash. The spectral composition of laser emissions observed was analyzed with a McKee-Pederson 0.5 m monochromator.

Cl<sub>2</sub> (Matheson U.H.P., > 99.5%), He (Airco, 99.9995%), Ar (Matheson, 99.998%), H<sub>2</sub>S (Matheson C.P., 99.5%), H<sub>2</sub>Se (Matheson, > 98%), and SiH<sub>4</sub> (Matheson, diluted 1:10 in U.H.P. Ar) were used without further purification. SiH<sub>2</sub>Cl<sub>2</sub> (Matheson) and SiHCl<sub>3</sub>(PCR, Inc.) were purified by freeze-pumpthaw cycles followed by trap to trap distillation.  $PF_3H_2$  was prepared at the Rocketdyne division of Rockwell International.

## 3. Results and discussion

For each reaction, experiments were performed under a variety of conditions. Sample mixtures, total pressures, and flash energies were varied. Laser emissions observed exhibited characteristics typical of pulsed HX chemical lasers, e.g., microsecond threshold times and spiking temporal behavior. When no emission was observed, cavity and detector alignment were verified by observation of laser emission from known HCl lasing systems. When lasing occurred, conditions were adjusted to obtain optimum output (shortest time to threshold, maximum intensity and duration) before spectral analysis of the pulse.

# 3.1. $Cl + H_2S$ , $H_2Se$

The reaction between chlorine and  $H_2S$  would not seem to be a very likely candidate for an HCl laser. The pumping reaction has an exothermicity of only 13 kcal/mole:

 $Cl + H_2S \rightarrow HCl + HS$ ,  $\Delta H \approx -13 \text{ kcal/mole.}$  (3)

A subsequent hydrogen abstraction from HS is also

possible. Chain behavior seems unlikely since the reaction to form chlorine atoms (HS +  $Cl_2 \rightarrow HSCl + Cl$ ) is exothermic by only two kcal/mole. Perhaps the most serious drawback, however, is the expected efficient deactivation of HCl (v = 1) by parent H<sub>2</sub>S (from its similarity to H<sub>2</sub>O, and because of HCl-H<sub>2</sub>S near-resonant vibrations) [3].

None the less, intense HCl laser emission was observed from this system. Optimum output was obtained from mixtures of  $H_2S:Cl_2:He = 1:10:40$  at 40 torr total pressure, flashed at 1400 joules. The laser pulses were very intense but short,  $\approx 4 \mu s$  in duration. The laser apparently had high gain, reaching threshold well before the peak of the flash. In fact, laser emission was observed readily when one of the gold coated cavity reflectors was replaced by a sapphire flat, the equivalent of inserting a 94% loss in the cavity. The emission was very sensitive to the  $H_2S$  pressure, and was completely quenched at three torr and above. This sensitivity and the short pulse length indicate that parent deactivation of HCl<sup>†</sup> is in fact the dominant limitation on the system.

All the laser emission was found to be due to HCl  $v = 1 \rightarrow v = 0$  transitions. Lines observed included P<sub>1</sub>(6) through  $P_1(13)$ , with  $P_1(7)$  having highest gain (i.e., shortest time to threshold). Highest gain shifted to  $P_1(6)$  when the pressure was increased to 170 torr by addition of helium. This effect is opposite to that expected from pressure broadening of the emission lines, in that broadening would favor gain in higher Jtransitions [4, 5]. It is possible that the laser medium was not equilibrated to room temperature (the pyrex tube, which absorbs a good part of the flash energy, became noticeably warmer on successive flashes). If we ignore this effect and presume  $P_1(7)$  to be the highest gain transition at room temperature, relative gain calculations [7] indicate that the ratio of populations lies in the range  $0.55 \le N_1/N_0 \le 0.70$ . Subsequent measurements of the relaxation rate of HCl (v = 1) by  $H_2S$  have shown that, if the average  $HC1^{7}$  has a lifetime of 2  $\mu$ s before laser threshold,  $\approx 25\%$  of the v = I population will be relaxed to v = 0 before threshold is reached [3]. This leads us to conclude that the initial population ratio  $N_1/N_0 > 1.0$ . Moreover, it would seem that the  $Cl + H_2S$  reaction must be very rapid in order to account for the high gain of this laser.

An experiment was also performed for the similar reaction of chlorine with  $H_2$ Se. For this system the

possible reactions are

 $Cl + H_2Se \rightarrow HCl + HSe, \quad \Delta H \approx -30 \text{ kcal/mole, (4)}$ 

HSe + Cl<sub>2</sub> 
$$\rightarrow$$
 HSeCl + Cl,  $\Delta H \approx -11$  kcal/mole. (5)

Again, subsequent reactions involving HSe and ClSeH are possible.  $H_2Se$  is a more likely candidate for producing an HCl chemical laser since reactions (4) and (5) above are thermodynamically more favorable than their  $H_2S$  counterparts, and because  $H_2Se$  should be a much less efficient deactivator of HCl [3].

Only a single experiment was done in this case, since there was a spontaneous reaction between  $H_2Se$ and  $Cl_2$ . Presumably the reaction was the chain described above, initiated by the finite concentration of Cl atoms present in the  $Cl_2$  at room temperature. None the less, laser emission was observed from a mixture of  $H_2Se$ :  $Cl_2$ : He = 1:10:40 at 50 torr total pressure. The emission consisted of a short spike, again well before the peak of the flash. After the flash, the tube and Brewster windows were completely coated with yellow deposits of  $SeCl_4$ , apparently the endproduct of the chain. It is likely that these deposits (which formed on the windows even without flashing) were responsible for quenching the laser.

3.2.  $Cl + PF_3H_2$ 

A pentacoordinated phosphorus compound was chosen because trivalent species (e.g.,  $PH_3$ ) are known to react spontaneously with halogens with the emission of visible light [6,7].  $PF_3H_2$ , a gas at room temperature which is stable to above 100°C, seemed ideal for our purposes. The pertinent reactions are:

 $Cl + PF_3H_2 \rightarrow HCl + PF_3H$ ,  $\Delta H \approx -25$  kcal/mole, (6)

 $PF_3H + Cl_2 \rightarrow PF_3HCl + Cl, \quad \Delta H \approx -18 \text{ kcal/mole.} (7)$ 

Subsequent reactions involving  $PF_3H$  and  $PF_3$  may also contribute:

 $Cl + PF_3H \rightarrow PF_3 + HCl, \quad \Delta H \approx -25 \text{ kcal/mole}, (8)$ 

 $PF_3 \div Cl_2 \rightarrow PF_3Cl \div Cl, \quad \Delta H \approx -18 \text{ kcal/mole}, (9)$ 

 $PF_3Cl + Cl \rightarrow PF_3Cl_2$ ,  $\Delta H \approx -76 \text{ kcal/mole.}$  (10)

The reactions of  $PF_3$  with  $F_2$  and F [analogous to (9) and (10)] are known to be very rapid [8]. The pump-

ing step, reaction (6), should have sufficient energy to produce HCl in vibrational states up to v = 2 and possibly v = 3.

Laser emission from excited HCl produced in these reactions was observed readily under a variety of conditions. For 45 torr samples of  $PF_3H_2:Cl_2:He$ = 3:10:30 flashed at 1400 joules, the laser pulse was  $\approx 10 \ \mu s$  in duration. Increasing the total pressure resulted ' longer pulses (12 to 13  $\mu s$ ). Optimum pulse char. steristics were obtained by drastically reducing the flash energy. Pulses 25  $\mu s$  in duration (with reduced intensity) were obtained by flashing 135 torr mixtures of H<sub>2</sub>Se:Cl<sub>2</sub>:He = 3:18:110 at 300 joules. With these conditions, HCl transitions observed included P<sub>1</sub>(7) through P<sub>1</sub>(12), and P<sub>2</sub>(7).

The relatively high J of these transitions and the improved performance of the laser at higher pressures suggest again that the reaction medium was not equilibrated to ambient temperature. It is also possible that  $N_1/N_0 \ll 1.0$ , but this seems unlikely in view of the good output observed with very low flash energies.

# 3.3. Cl + silicon hydrides

Flash photolysis laser experiments were performed with mixtures of  $Cl_2$  and silicon hydrides ( $R_3SiH$ ) in the hope of observing HCl laser emission from the following chain system:

 $Cl + R_3SiH \rightarrow HCl + R_3Si, \quad \Delta H \leq -16 \text{ kcal/mole}, (11)$ 

$$R_3Si + Cl_2 \rightarrow R_3SiCl + Cl, \quad \Delta H \approx -33 \text{ kcal/mole.} (12)$$

 $\Delta H$  for reaction (3) was assigned using the limit on the dissociation energy of H<sub>3</sub>Si-H suggested by Chang and Setser [9]. Lasing seems possible on the basis of these exothermicities and a recent estimate (by Setser and co-workers [10]) that approximately 60% of the energy liberated in the similar F + SiH<sub>4</sub> reaction enters HF vibration. No HCl<sup>†</sup> laser emission was observed, however, from the reaction of chlorine with any of the three silicon compounds tested.

SiH<sub>4</sub> reacted spontaneously with Cl<sub>2</sub> prior to initiation by the flash, with the emission of green light and the evolution of heat. It is likely that this reaction is due to chain processes like (11) and (12) above, initiated (as with H<sub>2</sub>Se) by the small concentration of chlorine atoms present in the Cl<sub>2</sub>. For the analogous reaction between F<sub>2</sub> and SiH<sub>4</sub>, it has been postulated that F atoms strip off successive hydrogens from the silane, followed by a reaction of free silicon with  $F_2$ . The blue emission seen in this case has been identified as due to SiF\* [10]. Emission from the SiCl diatomic  $(A \rightarrow X \text{ band})$  would in fact be green [11], but the Si + Cl<sub>2</sub> reaction does not have sufficient exothermicity to pump the A state. SiCl\* (or RSiCl\*) may be formed by some recombination process, however. HCl laser emission would of course not be observed from our apparatus if prereaction occurs to any great extent.

The spontaneous reaction should be slower for reactions of SiH<sub>2</sub>Cl<sub>2</sub> and SiHCl<sub>3</sub> with Cl<sub>2</sub>(Cl). Green emission was seen only in experiments in which very high partial pressures ( $\geq 10 \text{ torr}$ ) of SiH<sub>2</sub>Cl<sub>2</sub> were used, suggesting some SiH<sub>4</sub> impurity. No visible emission was seen in experiments with SiHCl<sub>3</sub>. None the less, HCl laser emission was not observed from the Cl + SiH<sub>2</sub>Cl<sub>2</sub> or SiHCl<sub>3</sub> reactions, leading us to believe that prereaction still occurred. Although we can draw no conclusions regarding energy disposal in these systems, it is apparent that reactions like (11) and (12) are quite rapid, and the chain effective enough to build up an appreciable concentration of HCl from the small initial concentration of chlorine atoms present before the flash.

### 4. Summary

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New HCl chemical lasers have been observed from the reactions of chlorine atoms with  $PF_3H_2$ ,  $H_2S$ , and  $H_2Se$ . Chain reactions are possible not only for the  $PF_3H_2-Cl_2$  and  $H_2Se-Cl_2$  systems, but also for the  $R_3SiH-Cl_2$  systems, from which no laser emission was observed (presumably due to prereaction). Both the  $H_2S$  and  $H_2Se$  systems exhibit high gain, though the  $Cl + H_2S$  laser is severely limited by collisional deactivation of HCl by  $H_2S$ . Further study of these systems would appear to require a fast flow, rapid mixing apparatus.

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