A MULTIWATT ALL GAS-PHASE IODINE LASER (AGIL)

Gerald C. Manke IIa*, Chris B. Cooperb, Shiv C. Dassb, Timothy J. Maddena, and Gordon D. Hagera

a Air Force Research Laboratory, Directed Energy Directorate, Kirtland AFB, NM 87117
b Boeing-Rocketdyne, Kirtland AFB, NM 87117

ABSTRACT

The demonstration and characterization of a multiwatt All Gas-phase Iodine Laser (AGIL) are described. A 20-cm subsonic reactor was used to produce NCl(a1∆) for a series parametric studies of the I*(2P1/2) - I(2P3/2) small signal gain and extracted power dependence on reactant flow rates and reaction time. A reduction in the flow channel height led to improved performance. The highest measured gain was $4.2 \times 10^{-4}$ cm$^{-1}$ and the highest power observed was 31 W.

INTRODUCTION

Since the invention of the COIL laser in the mid-1970's[1], there has been interest in energy carrier molecules that react via energy transfer with ground state iodine atoms to generate an inversion on the electronic spin-orbit transition. Singlet delta oxygen, for example, efficiently generates I*(2P1/2) via

$$O_2(a^1\Delta) + I \rightarrow O_2(X^3\Sigma^-) + I^*(2P_{1/2})$$

[1]

To date, NF(a1∆) and NCl(a1∆) have also been found to have the properties necessary to serve as energy carriers. Namely, both have long radiative lifetimes and are relatively inert to chemical reaction and physical quenching[2, 3]. Kinetic measurements have shown that NCl(a1∆) has a fast reaction with atomic iodine ($k_2 = 1.5 \pm 0.7 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$)[4, 5],

$$NCl(a^1\Delta) + I \rightarrow NCl(X^3\Sigma^-) + I^*$$

[2a]

$$\rightarrow \text{products}$$

[2b]

a large branching fraction for I*(2P3/2) formation ($\Gamma \geq 0.7$)[5], and a small rate constant for the energy pooling reaction between NCl(a1∆) and I*(2P1/2). Hence, NCl(a1∆) has been demonstrated to be an efficient energy carrier suitable for a scalable energy transfer chemical iodine laser.

A subsonic, continuous wave, chemical I*(2P1/2) laser pumped by NCl(a1∆) was reported by Henshaw and co-workers in 2000[6]. In their experiment, the energy carrier NCl(a1∆) was produced from F atoms and hydrogen azide by a three step process[5, 7-9]:

$$F + DCl \rightarrow DF + Cl$$

[3]

$$Cl + HN_3 \rightarrow HCl + N_3$$

[4]

$$Cl + N_3 \rightarrow NCl(a^1\Delta) + N_2.$$  

[5]

The authors named their discovery the All Gas-phase Iodine Laser, or AGIL. Their demonstration was motivated and enabled by the small signal gain measurements of Herbelin, et. al.[10], Bower et. al.[11], and the transient lasing demonstration of Ray and Coombe[12]. Other milestones in the history of AGIL are discussed in detail elsewhere[13].

Since the initial, sub-watt laser demonstration[6] there has been considerable effort expended to scale this device to multi-watt powers. Power levels as high as 15 W were reported in 2003[14]. These experiments used a 2 cm high cavity. To assess the role of mixing, the AGIL device was modified with a 1 cm channel height reactor. This report summarizes the results of those experiments.

EXPERIMENTAL METHODS

A new subsonic flow device for the generation of NCl(a1∆) was constructed following the completion of the work that culminated in the demonstration of a 180mW AGIL device. The new reactor (AGIL 2)[14] is very similar in design to the old device (AGIL 1)[6, 10, 15] in terms of materials, geometry, and injector locations. The most significant changes are the optical path length was increased to 20 cm(as opposed to 5 cm), F atoms are produced by four discharge tubes (as opposed to one), and the purge flows along the sides of the reactor were improved to provide better containment of the reactive flow. A construction schematic of AGIL 2 is shown in Figure 1. The flow channel height in the injector block section and the separation between the HI and HN3 injectors are adjustable. To accommodate heat release, area relief is provided by an adjustable ramp.
The four discharge tubes are powered by a power supply and cooled by chilled water. Fluorine atoms are generated when either pure NF₃ or a mixture of 20% F₂ in He are diluted with 6 mmol sec⁻¹ of He and passed through the discharges. The power supply was powerful enough to dissociate 1 mmol sec⁻¹ of F₂ or 1.5 mmol sec⁻¹ of NF₃ such that approximately 2 mmol sec⁻¹ of F atoms were generated. Higher flow rates of F₂ (20% in He) led to incomplete dissociation, while higher flow rates of NF₃ extinguished the discharge. NF₃ is the preferred F atom source because it does not produce any molecular fluorine which would react with Cl and I to generate IF and CIF - strong quenchers of I*(2P₁/₂) and NCl(a¹Δ). The new power supply was routinely operated at maximum current per tube which allowed higher F₂ and NF₃ flow rates and yielded larger F atom flows than previously generated in AGIL 1[15].

Helium and deuterium chloride are added through radial injectors at the end of each discharge tube to convert the flow of F atoms into Cl atoms (The He flow rate was fixed at approximately 40 mmol sec⁻¹). Hydrogen iodide was highly diluted to approximately 0.5% or less by adding ~90 mmol sec⁻¹ or more of He prior to its injection into the reactor. Hydrogen azide was synthesized and stored in six 150 L tanks as a 10% mixture in He. Both HN₃ and HI were injected from the top and bottom walls into the flow downstream of the DCl injector. The HI and HN₃ injector blocks consisted of 2 rows of holes each. All gas flows were controlled in the same manner as for the previous AGIL 1 studies[6, 10, 15]. Small signal gain measurements were performed as previously described by Herbelin, et. al[10].

For the laser demonstrations, all of the high reflector optics were 2 inches in diameter and had a 5 meter radius of curvature. A variety of output coupler mirrors were used, see below. The alignment of the resonator was performed with an auto-collimating alignment telescope.

**EXPERIMENTAL RESULTS**

I*(2P₁/₂) - I(2P₃/₂) small signal gain measurements

Sample results from one series of gain optimization experiments with the 2 cm high channel are shown in Figure 2. In the upper panel, the F₂, DCl, and HI flow rates were fixed at 6, 15 and 0.25 mmol sec⁻¹, respectively. At x = 2.5 and 7.5 cm, positive gain is observed for a wide range of HN₃ flow rates. For x = 12.5 cm, a small absorption signal is observed in all cases. The peak gain for x = 2.5 cm and HN₃ = 20 - 60 mmol sec⁻¹ is 2.2 x 10⁻⁴ cm⁻¹. The dependence of the small signal gain on the DCl flow rate is shown in the center panel of Figure 2. For DCl ≥ 12 mmol sec⁻¹, the gain is essentially constant at 2.0 ± 0.2 x 10⁻⁴ cm⁻¹. This result supports the hypothesis that DCl is not a strong quencher of NCl(a¹Δ) or I*(2P₁/₂)[16]. Finally, in the lower panel, the small signal gain dependence on the HI flow rate is shown. For x = 2.5 cm, the gain is a relatively weak function of HI. For x = 7.5 and 12.5 cm, however, the gain decreases dramatically for HI ≥ 0.3 mmol sec⁻¹.

In an attempt to partially assess the role of mixing, the small signal gain measurements were repeated in a 1 cm high channel, see Figure 3. When examining the data in Figure 3, it is important to note that there are two competing phenomena. First, because the channel height was reduced without a concomitant reduction in the total flow of all gases and/or increase in the reactor pressure, there is a substantial increase to the bulk gas flow velocity. Hence, if |NCl(a¹Δ)| is at its highest at short ∆t, higher small signal gain should be observed for the 1 cm channel when compared with the 2 cm high flow channel at equivalent conditions. In Figures 3a and 3b, the small signal gain is plotted as a function of the HN₃ and HI flow rates for constant DCl, NF₃, and pressure. In nearly all cases, the measured gain with the 1 cm channel height is higher than for the 2 cm high reactor. The improvement is particularly evident in Figure 3a where the highest gain in the 2 cm channel was 2.4 x 10⁻⁴ cm⁻¹ and the peak gain at the same conditions for the 1 cm high channel was 4.2 x 10⁻⁴ cm⁻¹.

In both Figures 2 and 3, the HN₃ flow required to reach an optimum gain is much higher than one would expect according to the reaction stoichiometry (i.e. HN₃ : Cl should be 1 : 2). In the past, we have attributed non-stoichiometric HN₃ : Cl ratios to poor mixing. Visual inspections of the flow did not reveal any obvious mixing problems for either HN₃ or HI. We attempted to test the homogeneity of HN₃ and HI in the flow by measuring the variation of I atom absorption and small signal gain along the vertical axis of the 2 cm high reactor. The results are shown in the upper and lower panels of Figure 4. For both plots, the experimental conditions were F₂ = 8, HI = 0.4, and DCl = 18 mmol sec⁻¹. In the lower panel, HN₃ = 28 mmol sec⁻¹ was added. In the upper panel, the measured [I(2P₃/₂)] is peaked in the center for x = 2.5 cm and decreases slightly as the diode probe laser position was shifted away from the centerline of the reactor. The x = 5 and 10 cm data are fairly constant across the entire range. Clearly, the injected HI has penetrated into the center of the flow, even at x = 2.5 cm. The profile change between x = 2.5 cm and x = 5 cm, however, suggests that the HI may not be uniformly distributed across the vertical axis at its injection point, and that some time must elapse before diffusion or another mixing mechanism can establish a homogenous medium. The lower panel data shows that the
vertical profile of the small signal gain is essentially the same as the \([I(2P_{3/2})]\) data. The addition of 28 mmol s\(^{-1}\) of HN\(_3\) (and the accompanying 250 mmol s\(^{-1}\) of He) does not appear to affect the degree of penetration or mixing rate of the HI.

Computational fluid dynamics calculations\cite{17} are consistent with the observations that mixing plays a critical role in AGIL performance. The calculations further indicate that the amount of He dilution to the HI flow stream can be used to enhance the degree of HI penetration and possibly improve the mixing. Relevant experiments to test this hypothesis were performed for both the 1 cm and 2 cm channel heights. The results are shown in Figures 5a and 5b. The data for the 1 cm high channel shows a distinct change in the dependence of the measured small signal gain on the He dilution ratio relative to the 2 cm channel height data. The small signal gain decreases for He > 120 mmol s\(^{-1}\) in the 1 cm channel, compared to He > 250 mmol s\(^{-1}\) for the 2 cm channel. These results suggest that for the reduced channel height, less additional He is necessary to give full penetration of the HI into the main flow. Clearly, both reaction time and mixing play an important role in the magnitude of the small signal gain in the current AGIL configuration.

Table 1 summarizes the optimum gain measured for \(F_2 = 6 - 8\) and \(NF_3 = 4 - 12\) mmol s\(^{-1}\) for both the 2 cm and 1 cm channel heights. It is important to note that the results for \(NF_3 = 10\) and 12 mmol s\(^{-1}\) were not optimized for the HI flow rate. The gain scales more or less monotonically with increasing F atom flow rate when \(NF_3\) is the discharge source of the F atoms. Interestingly, the gain does not appear to scale well when \(F_2\) is discharged even though nearly 100% of the \(F_2\) is dissociated. The highest gain measured in this study was \(4.2 \times 10^{-4}\) cm\(^{-1}\). These results are nearly a factor of 2 larger than AGIL 1\cite{6} which gave a maximum gain of \(2.7 \times 10^{-4}\) cm\(^{-1}\). However, for AGIL 2 the positive gain does not persist along the length of the reactor.

**Power Extraction**

Because changing the channel height involves a disassembly of the reactor and power extraction efficiency is critically dependent upon the resonator alignment, it is difficult to accurately and reproducibly compare the extractable power for the 1 cm and 2 cm channel heights. This is particularly true when the power extraction experiments are separated by an extended period of time. Nonetheless, Figure 6 compares the measured powers for similar experimental conditions but with different flow channel heights. The power for the 1 cm channel is in excess of 30 W, while the 2 cm channel height gives < 15 W. Table 2 compares the measured power for fixed conditions and a variety of mirror reflectivities. In both cases the center of the resonator was 4 cm downstream of the end of the injection blocks. Because the mirrors were 2” in diameter, the resonator included the high gain region measured above at \(x = 2.75\) cm downstream of the injection blocks. Considering the extended period of time between the two experimental series (~ 4 months) the results are very consistent in the region where \(1-R_1R_2 < 0.002\). As one would expect, the 1 cm channel height experiments give higher powers for \(R_1R_2 > 0.998\) and extrapolate to a higher threshold gain according to equation (8) in Manke, et. al\cite{14}.

**DISCUSSION AND CONCLUSIONS**

The performance of a 1 cm high subsonic AGIL device has been examined. Enhanced mixing and increased flow velocity lead to significantly improved small signal gain and extracted power. To date, the highest observed small signal gain for AGIL 2 is \(4.2 \times 10^{-4}\) cm\(^{-1}\), a factor of ~2 greater than the highest gain measured in AGIL 1. The highest observed power was 31 W, a factor of 2 greater than the results of the 2 cm high reactor.

**ACKNOWLEDGMENTS**

The authors wish to acknowledge helpful discussions with Profs. M. C. Heaven (Emory University) and R. D. Coombe (Denver University) regarding AGIL chemistry. Financial support from the AFOSR (Michael R. Berman, program manager) is gratefully acknowledged.
Table 1: Small signal gain summary

| F atom source | Flow rate (mmol s\(^{-1}\)) | F atom flow rate (mmol s\(^{-1}\)) | Maximum gain 2 cm channel \((10^{-4} \text{ cm}^{-1})\) | Maximum gain 1 cm channel \((10^{-4} \text{ cm}^{-1})\) |
|---------------|-------------------------------|----------------------------------|---------------------------------|---------------------------------|
| NF\(_3\)      | 4                            | 8                               | 1.04                            | 2.23\(^b\)                     |
| NF\(_3\)      | 6                            | 12                              | 1.80                            | 2.84\(^b\)                     |
| NF\(_3\)      | 8                            | 16                              | 2.50                            | 4.17                            |
| NF\(_3\)      | 10                           | --\(^a\)                        | 1.81\(^b\)                      | 3.78                            |
| NF\(_3\)      | 12                           | --\(^a\)                        | 2.04\(^b\)                      | 2.09\(^b\)                     |
| F\(_2\)       | 6                            | 10 – 11                         | 2.18                            | --                              |
| F\(_2\)       | 8                            | 14 – 15                         | 2.05                            | --                              |

\(^a\) Titration not performed for this condition

\(^b\) Gain not optimized for HI flow rate.

Table 2: AGIL 2 Power Extraction Summary\(^a\)

| Output Coupler Reflectivity | Power (W) 2 cm channel | Power (W) 1 cm channel |
|-----------------------------|-------------------------|------------------------|
| 0.9952\(^c\)               | --                      | 9.09                   |
| 0.9958\(^c\)               | 6.6                     | 11.0, 10.8             |
| 0.9963\(^b\)               | --                      | 15.8                   |
| 0.9973\(^b\)               | 10.0                    | 10.6, 10.4             |
| 0.9980\(^b\)               | 14.1                    | --                     |
| 0.9980\(^b\)               | --                      | 13.0                   |
| 0.9985\(^c\)               | --                      | 10.3, 10.0             |
| 0.9995\(^c\)               | --                      | 4.1, 3.9               |
| 0.9997\(^b\)               | 0.7                     | 0.8                    |

\(^a\) NF\(_3\) = 8, DCl = 25, HN\(_3\) = 26, and HI = 0.5 mmol s\(^{-1}\)

\(^b\) flat mirror

\(^c\) concave with 2 meter radius of curvature

Figure 1. Construction schematic for AGIL 2. Major components include the 4 discharge tubes with radial He and DCl injectors attached to the ends, HI and HN\(_3\) injector blocks, flow reactor with adjustable ramps, He injectors for containment of the flow, and laser mirror tunnels and mounts.
Figure 2. Optimization of small signal gain vs. HN₃, DCl and HI for constant $F_2 = 6$ mmol s⁻¹. See text for details.
Figure 3. Gain dependence for 1 and 2 cm channel heights. For both panels, the various symbols indicated different downstream positions: ● = 2.5 cm, ▼ = 7.5 cm, and ■ = 12.5 cm downstream from the HI / HN3 injector blocks. The solid symbols indicate data from the 2 cm high channel while the open symbols indicate data from the 1 cm high channel.

a. Small signal gain vs. HN3. The NF₃, DCl, and HI flow rates were 8, 25, and 0.25 mmol s⁻¹, respectively.
b. Small signal gain vs. HI. The NF₃, HN3, and DCl flow rates were 8, 25, and 25 mmol s⁻¹, respectively.
Figure 4. Vertical profile of small signal gain and [I]_{tot}.

a. Vertical profile of [I(2P_{3/2})]. The experimental conditions were F_2 = 8, HI = 0.4, and DCl = 18 mmol s\(^{-1}\). The density of I(2P_{3/2}) atoms in the absence of HN_3 is shown.

b. Vertical profile of small signal gain. The experimental conditions were F_2 = 8, HI = 0.4, DCl = 18, and HN_3 = 28 mmol s\(^{-1}\).
Figure 5: Gain dependence on HI diluent. According to computational fluid dynamics calculations, increasing the amount of diluent He for the HI flow can enhance the degree of HI penetration. The upper panel is data taken from the 2 cm high hardware while the lower panel is data taken from the 1 cm hardware. The differences for the two reactor heights suggest that mixing is an important factor in the measured gain in this device.
Figure 6: AGIL power dependence on HN₃ for 2 cm and 1 cm reactor heights. Note that the output coupler reflectivity is different for the two different reactor heights.
REFERENCES

[1] W. E. McDermott, N. R. Pchelkin, D. J. Benard, and R. R. Bousek, "An Electronic Transition Chemical Laser," Appl. Phys. Lett., vol. 32, pp. 469-470, 1978.
[2] K. B. Hewett, G. C. Manke II, D. W. Setser, and G. Brewood, "Quenching Rate Constants of NCl(a1Δ) at Room Temperature," J. Phys. Chem., vol. 104, pp. 539 - 551, 2000.
[3] K. Y. Du and D. W. Setser, "Quenching Rate Constants of NF(a1Δ) At Room-Temperature," J. Phys. Chem., vol. 94, pp. 2425-2435, 1990.
[4] A. J. Ray and R. D. Coombe, "Energy-Transfer From NCl(a1Δ) to Iodine Atoms," J. Phys. Chem., vol. 97, pp. 3475-3479, 1993.
[5] T. L. Henshaw, S. D. Herrera, and L. A. V. Schlie, "Temperature-Dependence of the NCl(a1Δ)+I(2P3/2) Reaction From 300 to 482 K," J. Phys. Chem. A, vol. 102, pp. 6239-6246, 1998.
[6] T. L. Henshaw, G. C. Manke II, T. J. Madden, M. R. Berman, and G. D. Hager, "A new energy transfer chemical laser at 1.315 μm," Chem. Phys. Lett., vol. 325, pp. 537 - 544, 2000.
[7] G. C. Manke II and D. W. Setser, "Kinetics of NCl(a1Δ and b1Σ+) Generation: The Cl + N3 Rate Constant, the NCl(a1Δ) Product Branching Fraction , and Quenching of NCl(a1Δ) by F and Cl Atoms," J. Phys. Chem. A, vol. 102, pp. 7257-7266, 1998.
[8] G. C. Manke II and D. W. Setser, "Measuring Gas-Phase Chlorine Atom Concentrations : Rate Constants For Cl+HN3 , CF3I , and C2F5I ," J. Phys. Chem. A, vol. 102, pp. 153-159, 1998.
[9] G. C. Manke II, T. L. Henshaw, T. J. Madden, and G. D. Hager, "Temperature dependence of the Cl + HN3 reaction from 300 to 480 K," Chem. Phys. Lett., vol. 310, pp. 111-120, 1999.
[10] J. M. Herbelin, T. L. Henshaw, B. D. Rafferty, B. T. Anderson, R. F. Tate, T. J. Madden, G. C. Manke, and G. D. Hager, "The measurement of gain on the 1.315 μm transition of atomic iodine in a subsonic flow of chemically generated NCl(a1Δ)," Chem. Phys. Lett., vol. 299, pp. 583-588, 1999.
[11] R. D. Bower and T. T. Yang, "I(2P3/2) Produced By the Energy-Transfer From NCl(a1Δ) to I(2P3/2)," J. Opt. Soc. Am. B, vol. 8, pp. 1583-1587, 1991.
[12] A. J. Ray and R. D. Coombe, "An I* Laser-Pumped By NCl(a1Δ)," J. Phys. Chem., vol. 99, pp. 7849-7852, 1995.
[13] M. C. Heaven, "Chemical Dynamics in Chemical Laser Media," in Chemical Dynamics in Extreme Environments, Advanced Series in Physical Chemistry, R. A. Dressler, Ed.: World Scientific, 2001.
[14] G. C. Manke II, C. B. Cooper, S. C. Dass, T. J. Madden, and G. D. Hager, "A Multi-Watt All Gas-phase Iodine Laser (AGIL)," IEEE J. Quant. Elect., vol. 39(8), pp. 995 - 1002, 2003.
[15] G. C. Manke II, T. L. Henshaw, T. J. Madden, J. M. Herbelin, B. D. Rafferty, and G. D. Hager, "Characterizing fluorine and chlorine atom flow rates using iodine atom spectrometry," AIAA Journal, vol. 39, pp. 447 - 454, 2001.
[16] M. C. Heaven, "to be published," 2003.
[17] T. J. Madden, "unpublished results," 2002.