

# A Multiwatt All Gas-Phase Iodine Laser (AGIL)

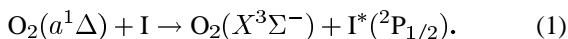
Gerald C. Manke, II, Chris B. Cooper, Shiv C. Dass, Timothy J. Madden, and Gordon D. Hager

**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  $\text{NCl}(a^1\Delta)$  for a series parametric studies of the  $\text{I}^*(^2\text{P}_{1/2}) - \text{I}(^2\text{P}_{3/2})$  small-signal gain and extracted power dependence on reactant flow rates and reaction time. The highest measured gain was  $2.5 \times 10^{-4} \text{ cm}^{-1}$  and the highest power observed was 15 W.

**Index Terms**—All gas iodine laser (AGIL), chemical lasers, chemical oxygen iodine laser (COIL).

## I. INTRODUCTION

SINCE the invention of the chemical oxygen iodine laser (COIL) in the mid-1970s [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  $\text{I}^*(^2\text{P}_{1/2})$  via

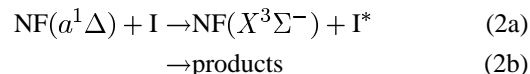


In principle, all molecules with the  $(p\pi^*)^2(p\sigma^*)^0$  electronic configuration will have the same electronic states as  $\text{O}_2$ , i.e.,  $(X^3\Sigma^-)$ ,  $(a^1\Delta)$ , and  $(b^1\Sigma^+)$ . Because of the selection rules for electronic transitions, the singlet delta state is metastable. The singlet nitrenes in particular (i.e.,  $\text{NF}$  and  $\text{NCl}$ ) have been investigated as possible replacements or alternatives to  $\text{O}_2(a^1\Delta)$  because they share the requisite  $(p\pi^*)^2(p\sigma^*)^0$  electronic configuration [2]. These metastable molecules have radiative lifetimes in the 2–5 s range [3]–[5] and have the potential to be useful energy carriers in energy transfer chemical laser applications.

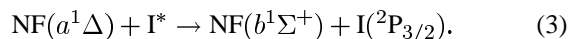
Unfortunately, metastability is not the only figure of merit for chemical laser devices based on an energy transfer process. The ability to transfer energy to a suitable laser species (such as iodine atoms) depends on the detailed kinetics and dynamics of the interaction between the energy donor and acceptor, which are determined by the details of the complex multidimensional potential energy surfaces that govern the interaction [2].

To date, only  $\text{NF}(a^1\Delta)$  and  $\text{NCl}(a^1\Delta)$  have 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 [6], [7]. Indeed, there have been several demonstrations of efficient energy transfer from  $\text{NF}(a^1\Delta)$  to  $\text{Bi}$  [8], [9],  $\text{BiF}$  [10]–[12],

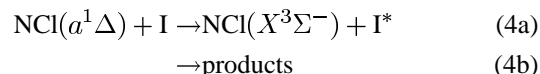
and  $\text{BH}$  [13]–[15]. Unfortunately, these systems were not suitable for generating high-energy chemical lasers [2]. Attempts to generate an  $\text{NF}(a^1\Delta)/\text{I}$  energy transfer laser have also failed [16]. The reason for this failure is that despite the fast reaction of  $\text{NF}(a^1\Delta)$  with atomic iodine ( $k_2 = 1.8 \pm 0.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [17]



an inversion is prevented by a poor branching fraction for (2a) ( $\sim 10\%$ – $20\%$ ) and fast quenching of  $\text{I}^*$  by  $\text{NF}(a^1\Delta)$  ( $k_3 = 5.7 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) [17], [18]

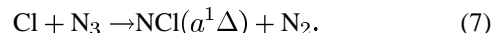
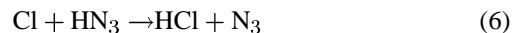


On the other hand,  $\text{NCl}(a^1\Delta)$  not only has a fast reaction with atomic iodine ( $k_4 = 1.5 \pm 0.7 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) [19], [20]



but the branching fraction for the  $\text{I}^*(^2\text{P}_{3/2})$  formation is large ( $\Gamma \geq 0.7$ ) [20] and the energy-pooling reaction between  $\text{NCl}(a^1\Delta)$  and  $\text{I}^*(^2\text{P}_{1/2})$  does not appear to be important. Hence,  $\text{NCl}(a^1\Delta)$  should be an efficient energy carrier suitable for a scalable energy transfer chemical iodine laser.

Indeed, a subsonic continuous-wave chemical  $\text{I}^*(^2\text{P}_{1/2})$  laser pumped by  $\text{NCl}(a^1\Delta)$  was reported by Henshaw and co-workers in 2000 [21]. In their experiment, the energy carrier  $\text{NCl}(a^1\Delta)$  was produced from  $\text{F}$  atoms and hydrogen azide by a three-step process [20], [22]–[24]



The authors named their discovery the all gas-phase iodine laser (AGIL). Their demonstration was motivated and enabled by the small-signal gain measurements of Herbelin, *et al.* [25], Bower *et al.* [26], and the transient lasing demonstration of Ray and Coombe [27]. Other milestones in the history of AGIL are discussed in detail elsewhere [2].

Since the initial subwatt laser demonstration [21], there has been considerable effort expended to scale this device to multiwatt powers. This paper summarizes the results of these experiments.

## II. EXPERIMENTAL METHODS

A new subsonic flow device for the generation of  $\text{NCl}(a^1\Delta)$  was constructed following the completion of the work that cul-

Manuscript received October 31, 2002; revised April 1, 2003. This work was supported by the Air Force Office of Scientific Research (AFOSR).

G. C. Manke, II, T. J. Madden, and G. D. Hager are with the Air Force Research Laboratory, Directed Energy Directorate, Kirtland AFB, NM 87117 USA.

C. B. Cooper and S. C. Dass are with Boeing-Rocketdyne, Kirtland AFB, NM 87117 USA.

Digital Object Identifier 10.1109/JQE.2003.814381

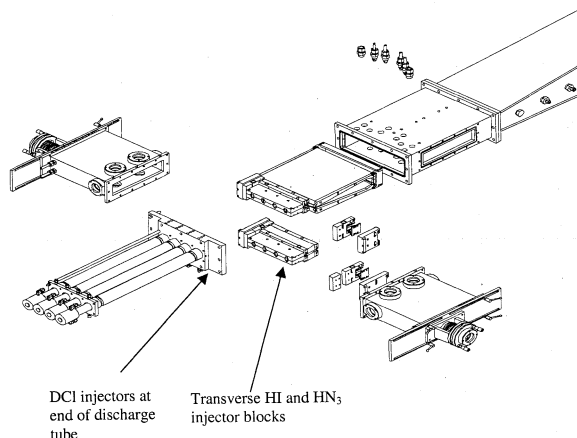


Fig. 1. Construction schematic for AGIL 2. Major components include the four discharge tubes with radial He and DCI injectors attached to the ends, HI and  $\text{HN}_3$  injector blocks, flow reactor with adjustable ramps, He injectors for containment of the flow, and laser mirror tunnels and mounts.

minated in the demonstration of a 180-mW AGIL device. The new reactor (AGIL 2) is very similar in design to the old device (AGIL 1) [21], [25], [28] 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 Fig. 1. The flow-channel height in the injector block section and the separation between the HI and  $\text{HN}_3$  injectors are adjustable. To accommodate heat release, area relief is provided by an adjustable ramp. The experiments described here reproduce the AGIL 1 device geometry.

The four discharge tubes are powered by a power supply and cooled by chilled water. Fluorine atoms are generated when either pure  $\text{NF}_3$  or a mixture of 20%  $\text{F}_2$  in He are diluted with  $6 \text{ mmol s}^{-1}$  of He and passed through the discharges. The power supply was powerful enough to dissociate  $1 \text{ mmol s}^{-1}$  of  $\text{F}_2$  or  $1.5 \text{ mmol s}^{-1}$  of  $\text{NF}_3$  such that approximately  $2 \text{ mmol s}^{-1}$  of F atoms were generated. Higher flow rates of  $\text{F}_2$  (20% in He) led to incomplete dissociation, while higher flow rates of  $\text{NF}_3$  extinguished the discharge.  $\text{NF}_3$  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 ClF—strong quenchers of  $\text{I}^*(^2\text{P}_{1/2})$  and  $\text{NCl}(a^1\Delta)$ . The new power supply was routinely operated at maximum current per tube which allowed higher  $\text{F}_2$  and  $\text{NF}_3$  flow rates and yielded larger F atom flows than previously generated in AGIL 1 [28].

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  $40 \text{ mmol s}^{-1}$ ). Hydrogen iodide was highly diluted to approximately 0.5% by adding  $\sim 90 \text{ mmol s}^{-1}$  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  $\text{HN}_3$  and HI were injected from the top and bottom walls into the flow downstream of the DCI injector. The HI and  $\text{HN}_3$  injector blocks consisted of two rows of holes each.

TABLE I  
TYPICAL EXPERIMENTAL CONDITIONS

Species	Flow Rates ( $\text{mmol s}^{-1}$ )		
	AGIL 1 (Herbelin)[25]	AGIL 1 (Henshaw)[21]	AGIL 2 (this work)
He	150 (600)	130 - 150 (520 - 600)	480 - 1000
$\text{NF}_3$	NA	1 - 1.5 (4 - 6)	4 - 20
$\text{F}_2$	0.66 (2.64)	NA	2 - 8
DCI	2.0 (8.0)	2.0 - 2.5 (8 - 10)	16 - 25
HI	0.032 (0.12)	0.04 - 0.07 (0.16 - 0.28)	0.12 - 0.60
$\text{HN}_3$	3.32 (13.3)	3 - 4.5 (12 - 18)	10 - 70
Pressure (Torr)	16	15 - 16	20 - 30

The discharge efficiency was characterized according to the titration methods described previously by Manke and co-workers [28]. Initially, gas-phase titrations were performed by measuring the yield of I atoms with a tunable diode laser (New Focus, Model 6248) that probes the  $1.315\text{-}\mu\text{m I}(^2\text{P}_{3/2}) - \text{I}^*(^2\text{P}_{1/2})$ , F(3,4) spin-orbit transition. As the difficulty of maintaining high flows of HI increased and the cost of HI became prohibitive, the titration technique was altered by adding HCl as the titrant and monitoring the relative concentration of  $\text{HF}(v=0)$  via absorption on nearby  $\text{HF}(2-0)$  ro-vibrational transitions. To expedite data collection, the diode laser output was split into three beams that probed three streamwise positions along the reactor. Small-signal gain measurements were performed as previously described by Herbelin *et al.* [25].

Since the small-signal gain for AGIL is optimized when the density of  $\text{NCl}(a^1\Delta)$  is the highest, a series of experiments were performed to determine the optimum conditions for  $\text{NCl}(a^1\Delta)$  production. This was accomplished by measuring the  $\text{NCl}(a^1\Delta)$  emission intensity as a function of  $\text{HN}_3$  and DCI flow rates for constant  $\text{NF}_3$ . The  $\text{NCl}(a^1\Delta)$  emission spectrum was collected with a near-infrared (NIR) Optical Multichannel Analyzer (Roper Scientific, OMA V) attached to a 0.3-m monochromator (Acton Research Corporation). The OMA V consists of a 256-pixel array of InGaAs detectors and a well-resolved  $\text{NCl}(a^1\Delta)$  spectrum with high signal to noise ratio can be collected in less than 1 s.

Table I compares the typical experimental conditions used in this study to those from AGIL 1. The flow rate values in parentheses in the first and second columns are Herbelin's [25] and Henshaw's [21] values multiplied by four. Since the AGIL 2 device is essentially four times larger than AGIL 1, these were the initial target values for our study. All gas flows were controlled in the same manner as for the previous AGIL 1 studies [21], [25], [28].

### III. EXPERIMENTAL RESULTS

#### A. F Atom Titrations

The initial experiments performed with the AGIL 2 device were gas-phase F + HI titrations [28], where the density of

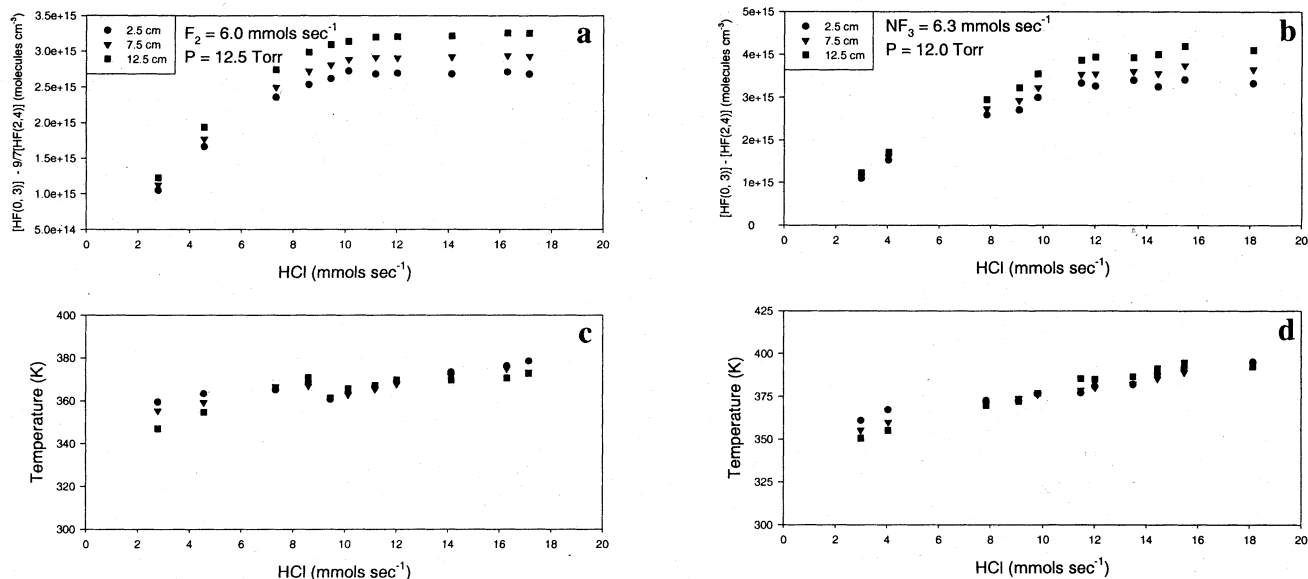


Fig. 2. F + HCl titrations. The upper plot in each panel shows the measured population difference ( $[HF(0,3)] - 9/7[HF(2,4)]$ ) as a function of added HCl, see text for details. The lower plot in each panel shows the variation in temperature with added HCl. In all cases, the various symbols indicate different downstream positions:  $\bullet$  = 2.5 cm,  $\blacktriangledown$  = 7.5 cm, and  $\blacksquare$  = 12.5 cm downstream from the HI/ $HN_3$  injector blocks.

$I(^2P_{3/2})$  was measured via absorption spectrometry and then related to the density of F atoms produced by the dc discharges via titration plots. Several complications were encountered with this method, all of which could be related to the difficulty of generating and maintaining known, large flows of HI [29]. Gaseous HI is commercially available, but the purity of the bottle contents degrades with time according to the well-known  $2HI \leftrightarrow H_2 + I_2$  equilibrium. More seriously, for large flows of HI, liquid and solid particulates may be entrained in the flow that can clog and degrade the performance of the flow-control system. Expansion and cooling of the HI gas after passing through a sonic orifice may lead to condensation along the tubing.

For these reasons, as well as the increasingly prohibitive cost of purchasing large quantities of high purity HI, an alternative titration method was sought and developed. Instead of flowing HI and measuring the yield of atomic I, HCl was added to the flow of F atoms and [HF] was monitored via absorption on a HF(2–0) overtone ro-vibrational transition. Because the F+HCl reaction generates a multitude of HF ro-vibrational states including significant HF( $v=2$ ), the measured absorption signal is proportional to the population difference between HF(0, $J$ ) and HF(2, $J'$ ) and the measured signal does not directly give  $[F]_0$ . Rather, the yield of F atoms is given by the titration endpoint. As HCl is added to the flow, the absorption signal increases until all of the F atoms are consumed and the initial F atom flow rate is given by the HCl flow necessary to reach the maximum observed signal. Large flow rates of high-purity HCl are easily (and inexpensively) generated because there are no condensation or particulate entrainment issues.

A series of F atom titrations using HCl as the titrant are shown in Fig. 2. The results from these experiments complement the results from the F + HI titrations, and aid in their interpretation [29]. While this method is not as direct or as precise as measuring [I], it is well suited to our application since we do not need a very precise endpoint and are loath to install a compli-

cated system to deliver large flows of pure and particulate-free HI in a reliable manner.

For  $F_2$  and  $NF_3 = 6 \text{ mmol s}^{-1}$  [Fig. 2(a) and (b)], the titration endpoints occur at approximately 11–12 mmol  $\text{s}^{-1}$  of HCl, which in the case of  $NF_3$  corresponds to approximately two atoms per molecule. In the case of  $F_2$ , this represents 90%–100% dissociation. The population difference signal increases as the flow progresses downstream, consistent with relaxation of vibrationally excited HF. For  $F_2$ , the translational temperature is  $360 \pm 20 \text{ K}$ , while for  $NF_3$ , the linewidth analyses give  $T = 375 \pm 15 \text{ K}$ . These data are in agreement with the thermocouple data; the  $NF_3$  discharge is slightly hotter than the  $F_2$  discharge. It should be noted that there is considerable uncertainty (at least  $\pm 20\%$ ) about the titration endpoint because there is not a sharp break between the linear growth and plateau regions of the titration plots and the data is indirectly related to the initial [F]. However, it is clear that a large fraction of molecular  $F_2$  is dissociated and that both  $F_2$  and  $NF_3$  can be used to produce large F atom fluences.

### B. Optimization of $NCl(a^1\Delta)$

The energy carrier  $NCl(a^1\Delta)$  is produced from F atoms and hydrogen azide by a three-step process described above [reactions (5)–(7)] [20], [22], [23]. According to this mechanism, two F atoms, two DCI molecules, and 1  $HN_3$  molecule are required to produce a single  $NCl(a^1\Delta)$ . The stoichiometry can be tested by monitoring the density of  $NCl(a^1\Delta)$  via its spontaneous emission signal as a function of added DCI and  $HN_3$ .

The conditions for Fig. 3 were  $NF_3 = 6 \text{ mmol s}^{-1}$ ,  $HN_3 = 12 \text{ mmol s}^{-1}$ , and pressure  $\sim 12 \text{ Torr}$ . A fiber-optic bundle, placed 12.5-cm downstream of the end of the HI/ $HN_3$  injection block was used to collect the emission. Two series of experiments were performed, separated in time by approximately 30 days. For purposes of comparison, the spectral areas are

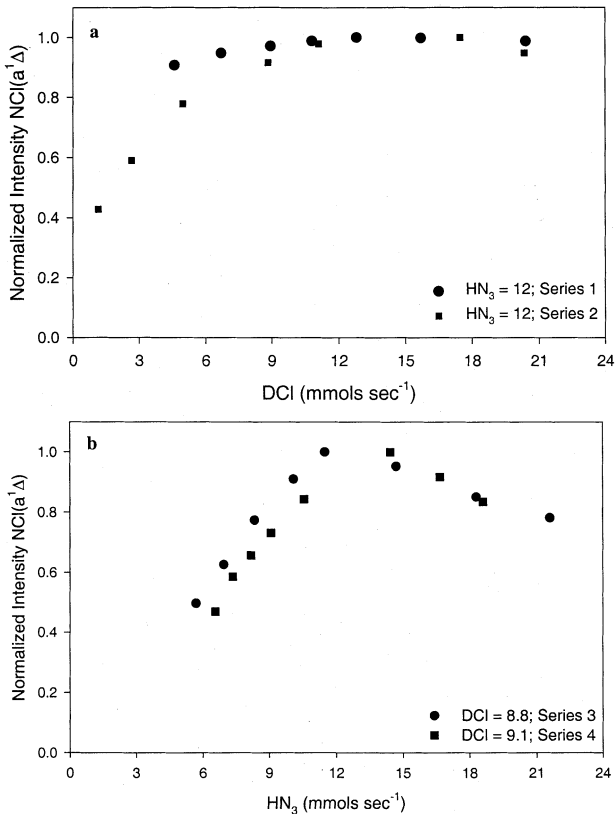


Fig. 3. Optimization of  $\text{NCl}(a^1\Delta)$  emission intensity. (a)  $\text{NCl}(a^1\Delta)$  versus DCI. The  $\text{NF}_3$  flow rate used for these was  $6 \text{ mmol s}^{-1}$ . The emission intensity of  $\text{NCl}(a^1\Delta)$  is optimized at  $\text{DCI} = 12 \text{ mmol s}^{-1}$ , consistent with the expectation that  $\text{NCl}(a^1\Delta)$  production is optimal when  $[\text{DCI}] = [\text{F}] = 2[\text{NF}_3]$ , and all of the F atoms have been consumed. (b)  $\text{NCl}(a^1\Delta)$  versus  $\text{HN}_3$ . The  $\text{NF}_3$  flow rate used for these experiments was  $6 \text{ mmol s}^{-1}$ . The emission intensity of  $\text{NCl}(a^1\Delta)$  is optimized at  $\text{HN}_3 = 12 \text{ mmol s}^{-1}$ . According to the stoichiometry of the F/DCI/ $\text{HN}_3$  chemical mechanism for the formation of  $\text{NCl}(a^1\Delta)$ , the density of  $\text{NCl}(a^1\Delta)$  should be optimized at  $[\text{HN}_3] = 0.5[\text{F}] = [\text{NF}_3]$  rather than the twofold excess of  $\text{HN}_3$  shown here.

normalized to the maximum observed intensity for that experimental series. The two data series are qualitatively the same and the intensity of  $\text{NCl}(a^1\Delta)$  reaches a plateau at approximately  $12 \text{ mmol s}^{-1}$  of DCI. Inasmuch that one would expect the  $\text{NCl}(a^1\Delta)$  to optimize at the stoichiometric limit of  $[\text{DCI}] = [\text{F}]$ , this supports the F atom titration results which indicate that  $[\text{F}] \sim 2[\text{NF}_3]$ . Furthermore, the intensity of  $\text{NCl}(a^1\Delta)$  did not decrease significantly when a nearly twofold excess of DCI was added. The presence of excess DCI does not appear to strongly quench  $\text{NCl}(a^1\Delta)$ .

In the lower panel of Fig. 3, the flow rates for  $\text{NF}_3$  and DCI were held constant ( $6$  and  $9 \text{ mmol s}^{-1}$ , respectively) while  $\text{HN}_3$  was varied from  $6$  to  $24 \text{ mmol s}^{-1}$ . For both series of experiments, the maximum yield of  $\text{NCl}(a^1\Delta)$  was achieved when  $\text{HN}_3 \sim 12 \text{ mmol s}^{-1}$ . The Cl/ $\text{HN}_3$  stoichiometry suggests that the optimum condition for  $\text{NCl}(a^1\Delta)$  production is  $\text{HN}_3/\text{Cl} = 0.5$ , and our result  $\text{HN}_3/\text{Cl} \sim 1$  is a factor of two too large. This is not a surprising result considering that Herbelin [25] and Henshaw [21] reported a similar trend for AGIL 1. Their optimum  $\text{HN}_3 : \text{Cl}$  ratios for gain/lasing power were  $2.5$  and  $1.9$ , respectively.

### C. Optimization of $I^*(^2P_{1/2}) - I(^2P_{3/2})$ Small-Signal Gain

Sample results from one series of gain optimization experiments are shown in Fig. 4. In the upper panel, the  $\text{F}_2$ , DCI, and HI flow rates were fixed at  $6$ ,  $15$ , and  $0.25 \text{ mmol s}^{-1}$ , respectively. At  $x = 2.5$  and  $7.5 \text{ cm}$ , positive gain is observed for a wide range of  $\text{HN}_3$  flow rates. For  $x = 12.5 \text{ cm}$ , a small absorption signal is observed in all cases. While the dependence of the gain on  $\text{HN}_3$  looks similar to the  $\text{NCl}(a^1\Delta)$  optimization plot in Fig. 3, the small-signal gain data reaches an optimum at  $\text{HN}_3 \sim 25 \text{ mmol s}^{-1}$ , approximately a factor of two higher than was required to reach the optimum  $\text{NCl}(a^1\Delta)$  intensity. The peak gain for  $x = 2.5 \text{ cm}$  and  $\text{HN}_3 = 20 - 60 \text{ mmol s}^{-1}$  is  $2.2 \times 10^{-4} \text{ cm}^{-1}$ . The dependence of the small-signal gain on the DCI flow rate is shown in the center panel of Fig. 4. For  $\text{DCI} \geq 12 \text{ mmol s}^{-1}$ , the gain is essentially constant at  $2.0 \pm 0.2 \times 10^{-4} \text{ cm}^{-1}$ . This result supports the previous observation that DCI is not a strong quencher of  $\text{NCl}(a^1\Delta)$  or  $I^*(^2P_{1/2})$  and the F atom titration results which give  $\text{F} = 12 \text{ mmol s}^{-1}$  when  $\text{F}_2 = 6 \text{ mmol s}^{-1}$  is discharged. Finally, in the lower panel, the small-signal gain dependence on the HI flow rate is shown. For  $x = 2.5 \text{ cm}$ , the gain is a relatively weak function of HI. For  $x = 7.5$  and  $12.5 \text{ cm}$ , however, the gain decreases dramatically for  $\text{HI} \geq 0.3 \text{ mmol s}^{-1}$ .

Similar plots were generated for a variety of  $\text{F}_2$  and  $\text{NF}_3$  flow rates. Table II summarizes the optimum gain measured for  $\text{F}_2 = 6-8$  and  $\text{NF}_3 = 4-12 \text{ mmol s}^{-1}$ . It is important to note that the results for  $\text{NF}_3 = 10$  and  $12 \text{ mmol s}^{-1}$  were not optimized for the HI flow rate. The gain scales more or less monotonically with increasing F atom flow rate when  $\text{NF}_3$  is the discharge source of the F atoms. Interestingly, the gain does not appear to scale well when  $\text{F}_2$  is discharged even though nearly 100% of the  $\text{F}_2$  is dissociated. The highest gain measured in this study was  $2.5 \times 10^{-4} \text{ cm}^{-1}$ . These results compare favorably with AGIL 1 [21] which gave a maximum gain of  $2.7 \times 10^{-4} \text{ cm}^{-1}$ . Our peak gain is essentially the same for comparable conditions. However, in contrast to the AGIL 1 results, positive gain does not persist along the length of the reactor.

In the past, we have attributed nonstoichiometric  $\text{HN}_3 : \text{Cl}$  ratios to poor mixing. Visual inspections of the flow did not reveal any obvious mixing problems for either  $\text{HN}_3$  or HI. We attempted to test the homogeneity of  $\text{HN}_3$  and HI in the flow by measuring the variation of I atom absorption and small-signal gain along the vertical axis of the reactor. The results are shown in the upper and lower panels of Fig. 5. For both plots, the experimental conditions were  $\text{F}_2 = 8$ ,  $\text{HI} = 0.4$ , and  $\text{DCI} = 18 \text{ mmol s}^{-1}$ . In the lower panel,  $\text{HN}_3 = 28 \text{ mmol s}^{-1}$  was added. In the upper panel, the measured ( $I(^2P_{3/2})$ ) is peaked in the center for  $x = 2.5 \text{ cm}$  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  $x = 2.5 \text{ cm}$ . The profile change between  $x = 2.5 \text{ cm}$  and  $x = 5 \text{ cm}$ , 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

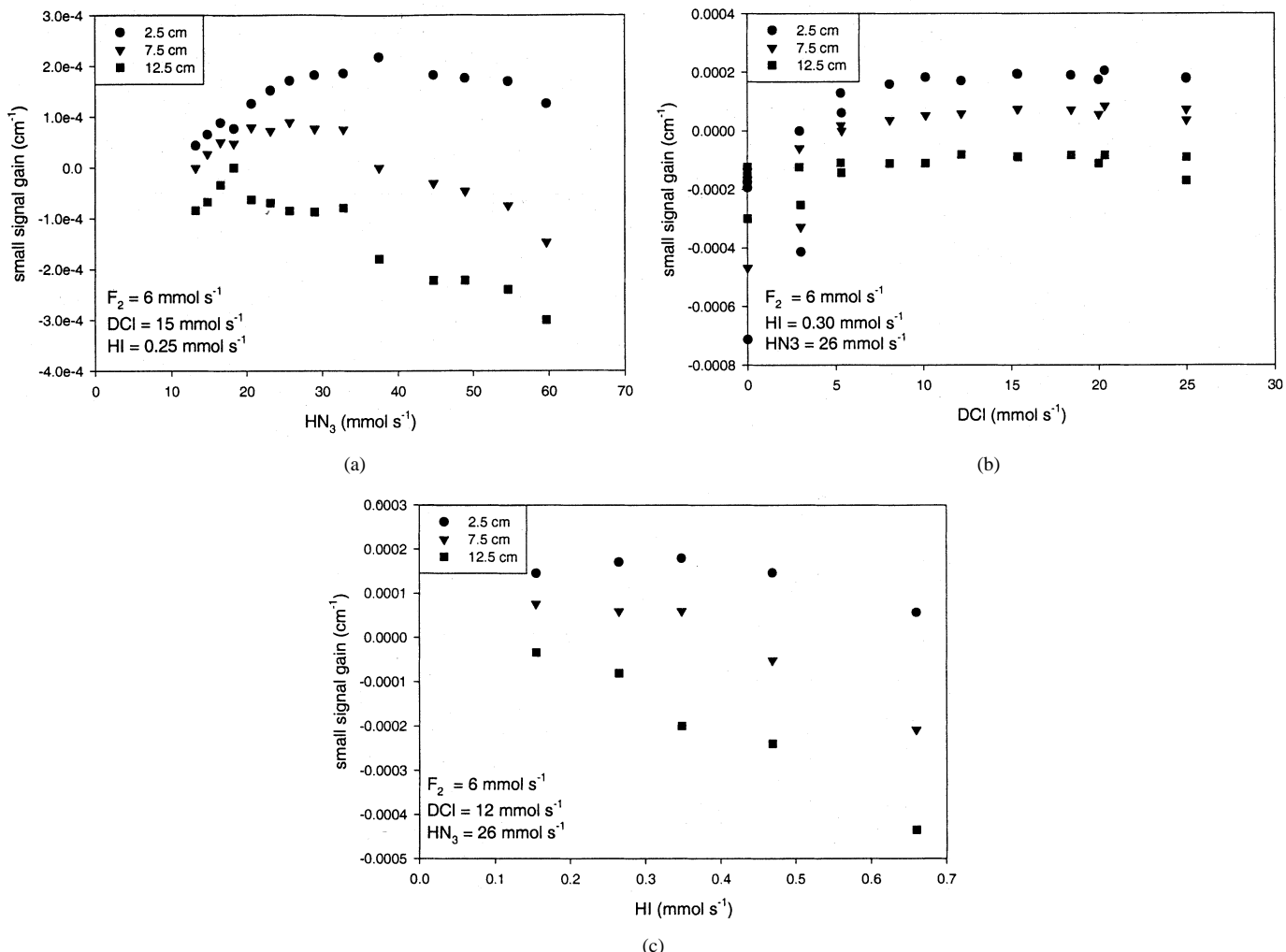


Fig. 4. Optimization of small-signal gain for  $F_2 = 6 \text{ mmol s}^{-1}$ . (a) Small-signal gain versus  $\text{HN}_3$ . The  $F_2$ , HI, and DCI flow rates are as indicated in the figure. The highest small-signal gain ( $2.2 \times 10^{-4} \text{ cm}^{-1}$ ) is observed for  $\text{HN}_3 = 38 \text{ mmol s}^{-1}$  and 2.5-cm downstream of the  $\text{HN}_3$  injection block. The gain decreases significantly as the flow progresses downstream while smaller variations are observed for increasing or decreasing  $\text{HN}_3$  flow rates. (b) Small-signal gain versus DCI. The  $F_2$ , HI, and  $\text{HN}_3$  flow rates are as indicated in the figure. The highest small-signal gain ( $2.0 \times 10^{-4} \text{ cm}^{-1}$ ) is observed for  $\text{DCI} = 20 \text{ mmol s}^{-1}$  and 2.5-cm downstream of the  $\text{HN}_3$  injection block. The gain is relatively constant for  $\text{DCI} = 12 - 25 \text{ mmol s}^{-1}$  but decreases for  $\text{DCI} < 12 \text{ mmol s}^{-1}$ . As noted above, the gain decreases significantly as the flow progresses downstream. (c) Small-signal gain versus HI. The  $F_2$ , DCI, and  $\text{HN}_3$  flow rates are as indicated in the figure. The highest small-signal gain ( $1.8 \times 10^{-4} \text{ cm}^{-1}$ ) is observed for  $\text{HI} = 0.35 \text{ mmol s}^{-1}$  and 2.5-cm downstream of the  $\text{HN}_3$  injection block. The gain decreases significantly as the flow progresses downstream.

TABLE II  
SMALL-SIGNAL GAIN SUMMARY

F atom source	Flow rate (mmol s <sup>-1</sup> )	F atom flow rate (mmol s <sup>-1</sup> )	Maximum gain (10 <sup>-4</sup> cm <sup>-1</sup> )
NF <sub>3</sub>	4	8	1.04
NF <sub>3</sub>	6	12	1.80
NF <sub>3</sub>	8	16	2.50
NF <sub>3</sub>	10	-- <sup>a</sup>	1.81 <sup>b</sup>
NF <sub>3</sub>	12	-- <sup>a</sup>	2.04 <sup>b</sup>
F <sub>2</sub>	6	10 – 11	2.18
F <sub>2</sub>	8	14 – 15	2.05

<sup>a</sup> Titration not performed for this condition.

<sup>b</sup> Gain not optimized for HI flow rate.

the small-signal gain is essentially the same as the ( $I^2 P_{3/2}$ ) data. The addition of 28 mmol s<sup>-1</sup> of  $\text{HN}_3$  (and the accompanying 250 mmol s<sup>-1</sup> of He) does not appear to affect the degree of penetration or mixing rate of the HI. In fact, the small-signal

gain data are consistent with a uniform  $\text{NCl}(a^1\Delta)$  density, and efficient mixing of  $\text{HN}_3$ . We have previously [29] suggested that poor mixing is the dominant factor that limits AGIL performance based on computational fluid dynamics results. Unfortunately, the present results are not conclusive and further tests of the role of mixing will be conducted in the near future.

#### D. AGIL Power Extraction

Power-extraction experiments for AGIL 2 gave significantly higher powers than AGIL 1. The results are summarized in Table III and Fig. 6. As was the case for AGIL 1, the power-extraction demonstrations required extremely high quality mirrors; the high reflector (HF) and output coupler mirror reflectivities (as measured by cavity ringdown spectroscopy) were 0.9999 and 0.998, respectively. All high reflector optics had a 2-in diameter and a 5-m radius of curvature. The alignment of the resonator was initially accomplished by superimposing a He:Ne laser beam through the centerline of the flow

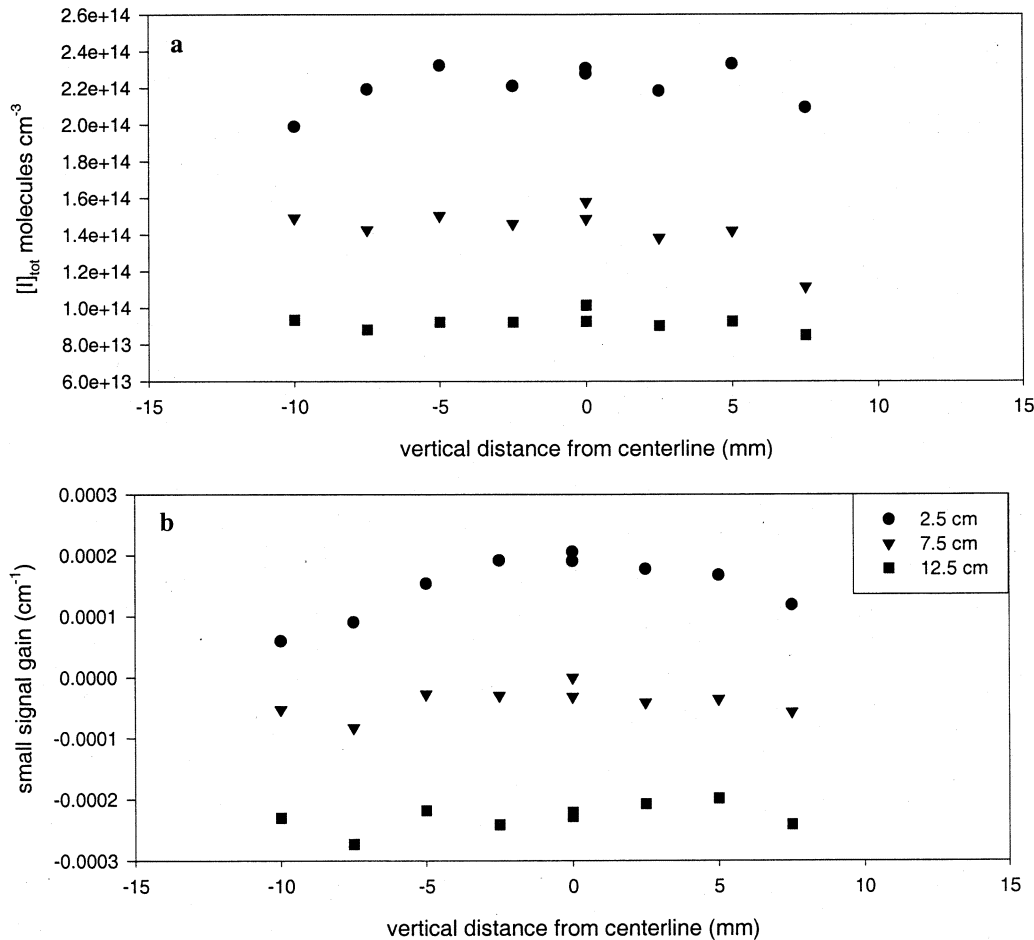


Fig. 5. Vertical profile of small-signal gain and  $[I]_{\text{tot}}$ . (a) Vertical profile of  $[I(^2P_{3/2})]$ . The experimental conditions were  $F_2 = 8$ ,  $HI = 0.4$ , and  $DCI = 18 \text{ mmol s}^{-1}$ . The density of  $I(^2P_{3/2})$  atoms in the absence of  $HN_3$  is shown. The observed profile is slightly peaked. There is a noticeable variation in I atom density along the vertical axis in the absence of  $HN_3$ , suggesting that while HI is fully penetrated into the center of the flow, the I atom density is not homogenous across the entire flow profile. (b) Vertical profile of small-signal gain. The experimental conditions were  $F_2 = 8$ ,  $HI = 0.4$ ,  $DCI = 18$ , and  $HN_3 = 28 \text{ mmol s}^{-1}$ . In a pattern similar to the  $(I(^2P_{3/2}))$  profile in the upper panel, the small-signal gain is peaked in the center and decreases slightly as the diode probe laser position was shifted. The lack of difference between the upper and lower panels suggests that the injected  $HN_3$  is fully penetrated into the flow and is well mixed.

TABLE III  
AGIL 2 POWER-EXTRACTION SUMMARY

Position	Output Coupler Reflectivity	Power (W)
4.0 <sup>a</sup>	0.9997 <sup>c</sup>	0.5
	0.998 <sup>c</sup>	14.3
	0.998 <sup>b</sup>	11.6
	0.9973 <sup>c</sup>	9.7
	0.9958 <sup>d</sup>	6.9

<sup>a</sup>  $NF_3 = 8$ ,  $DCI = 25$ ,  $HN_3 = 26$ , and  $HI = 0.5 \text{ mmol s}^{-1}$ .

<sup>b</sup> Concave with 5-m radius of curvature.

<sup>c</sup> Flat mirror.

<sup>d</sup> Concave with 2-m radius of curvature.

reactor and then adjusting the resonator mirrors such that the reflected beams from the resonator mirrors were collinear with the reactor centerline. It was subsequently learned that much more reliable and reproducible alignments could be achieved with an auto-collimating alignment telescope.

Fig. 6 shows the relationship between out-coupled power versus HI flow rate for two different downstream positions,

$x = 1.5$  and  $4.0$  cm. For the sake of convenience, the  $HN_3$  and  $DCI$  flow rates were fixed at the previously determined optimum values,  $26$  and  $25 \text{ mmol s}^{-1}$ , respectively. In the upper panel, series A and B were measured using a resonator aligned with the He:Ne laser. Series C and D were measured after alignment with the alignment telescope. Clearly, the latter method gave higher powers, most likely due to an improved alignment. Interestingly, the extracted power was higher at  $x = 1.5$  cm for  $NF_3$  as the discharge source of F atoms. At the next downstream position,  $NF_3$  and  $F_2$  give comparable power values. We attribute this difference to the fact that the  $F_2$  discharge gives slightly lower temperatures than  $NF_3$ . Since the rate determining step for  $NCl(a^1\Delta)$  generation [reaction (6)] is strongly temperature dependent, it is sensible that the hotter,  $NF_3$  case would reach the peak  $NCl(a^1\Delta)$  density at an earlier position (i.e., earlier time) in the reactor. All attempts to measure power at  $x = 6.5$  cm downstream were unsuccessful, even with a low threshold cavity (i.e.,  $OC = 99.97\%$  reflectivity). This result is consistent with the small-signal gain measurements that gave very low or no gain at  $x = 7.5$  cm (see Figs. 4 and 5). Clearly, the gain is strongly dependent on

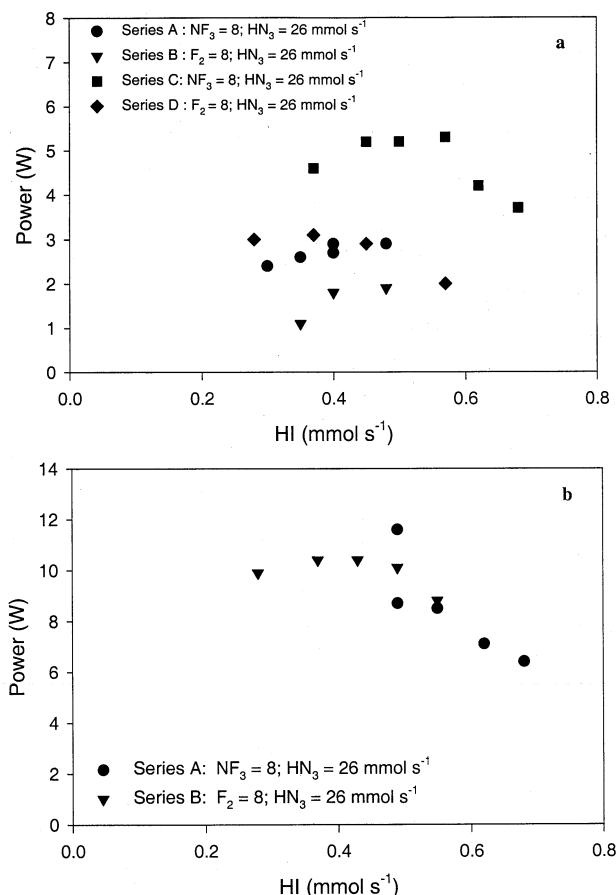


Fig. 6. AGIL power extraction versus HI. (a) Power extraction versus HI for  $x = 1.5$  cm downstream of the HI/ $\text{HN}_3$  injection block. Series A and B were collected on the same day, using a He:Ne laser to optimize the alignment. Series C and D were measured on a different day and an auto-collimating alignment telescope was used to optimize the alignment. The resonator consisted of two 2" concave (5-m radius of curvature) mirrors with measured reflectivities of 0.9999 and 0.998. (b) Power extraction versus HI for  $x = 4.0$  cm downstream of the HI/ $\text{HN}_3$  injection block. Series A and B were collected with the resonator centered 4.0-cm downstream of the end of the HI/ $\text{HN}_3$  injection block. The reagent flow conditions are as indicated in the figure.

the reaction time. A full explanation of this behavior requires additional analysis by computational fluid dynamics.

Table III summarizes the effect of varying the output coupler reflectivity for  $x = 4.0$  cm, and constant reagent flow rates of  $\text{NF}_3 = 8$ ,  $\text{HN}_3 = 26$ ,  $\text{DCI} = 25$ , and  $\text{HI} = 0.5$  mmol s<sup>-1</sup>. The mirror reflectivities for the various outcouplers were estimated from total transmission measurements and assuming  $R = 1.0 - T$ . The power versus reflectance data can be used to confirm the directly measured small-signal gain values. The  $x$ -intercept of a  $1 - R_2$  versus power plot gives the mirror reflectivity ( $R_2$ ) value for the threshold condition

$$g_0 = g_{\text{th}} = \frac{-\ln(R_1 R_2)}{2L}. \quad (8)$$

A crude extrapolation of the data in Table III gives  $R_2 \sim 0.993$ . For  $R_1 = 0.9999$  and  $L = 20$  cm the estimated threshold gain,  $1.8 \times 10^{-4}$  cm<sup>-1</sup>, is in good agreement with the directly measured value ( $2.0 - 2.5 \times 10^{-4}$  cm<sup>-1</sup>). The  $x = 4.0$  cm data suggests that even higher outcoupled power may be possible for

$0.9999 < R_2 < 0.998$ . Further enhancements to the extracted power may be realized by changing the mirror size ( $x_c$ ), moving the mirror position ( $x$ ), or increasing the F atom flow rate.

#### IV. DISCUSSION AND CONCLUSIONS

The fundamental performance characteristics of AGIL 2 have been examined. F + HI and F + HCl titrations have been used to determine the F atom production efficiency of the dc discharges. Optimum conditions for the production of  $\text{NCl}(a^1\Delta)$  and  $\text{I}(^2\text{P}_{1/2}) - \text{I}(^2\text{P}_{3/2})$  gain have been identified for a moderate range of reactor conditions. To date, the highest observed small-signal gain for AGIL 2 is  $2.5 \times 10^{-4}$  cm<sup>-1</sup>, essentially equivalent to the highest gain measured in AGIL 1. The highest observed power was 15 W.

The most critical experiments that directly address the scalability of AGIL remain to be completed. In particular, it has yet to be shown conclusively that  $[\text{NCl}(a^1\Delta)]$  and gain scale with increasing  $[\text{Cl}]$ . The AGIL 1 and AGIL 2 data strongly suggest that increases in  $[\text{NF}_3]$  (which leads to higher  $[\text{F}]$  and thus, higher  $[\text{Cl}]$ ) leads to higher gain and higher extracted power. However, the range of  $\text{NF}_3$  and  $\text{F}_2$  flow rates tested by AGIL 1 and AGIL 2 is rather limited. Significantly higher F and Cl atom flow rates can be generated by chemical combustors or high power microwave devices [30]. An AGIL device employing these technologies is currently in the planning and design stages.

#### ACKNOWLEDGMENT

The authors wish to acknowledge helpful discussions with Profs. M. C. Heaven (Emory University) and R. D. Coombe (Denver University) regarding AGIL chemistry.

#### 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] M. C. Heaven, "Chemical dynamics in chemical laser media," in *Chemical Dynamics in Extreme Environments, Advanced Series in Physical Chemistry*, R. A. Dressler, Ed. Singapore: World Scientific, 2001.
- [3] A. C. Becker and U. Schurath, "Matrix-isolated NCl: Radiative rates for  $b^1\Sigma^+ - a^1\Delta$ ;  $b^1\Sigma^+ - X^3\Sigma^-$  and  $a^1\Delta - X^3\Sigma^-$  in solid argon," *Chem. Phys. Lett.*, vol. 160, pp. 586-590, 1989.
- [4] D. R. Yarkony, "On the radiative lifetimes of the  $b^1\Sigma^+$  and  $a^1\Delta$  states in NCl," *J. Chem. Phys.*, vol. 86, pp. 1642-1643, 1987.
- [5] M. Bettendorff and S. D. Peyerimhoff, "Electronic-structure of the radicals-NF and NCl I. Potential-energy curves for NF," *Chem. Phys.*, vol. 99, pp. 55-72, 1985.
- [6] K. B. Hewett, G. C. Manke II, D. W. Setser, and G. Brewood, "Quenching rate constants of  $\text{NCl}(a^1\Delta)$  at room temperature," *J. Phys. Chem. A*, vol. 104, pp. 539-551, 2000.
- [7] K. Y. Du and D. W. Setser, "Quenching rate constants of  $\text{NF}(a^1\Delta)$  at room-temperature," *J. Phys. Chem.*, vol. 94, pp. 2425-2435, 1990.
- [8] J. M. Herbelin and R. A. Klingberg, *Int. J. Chem. Kinet.*, vol. 16, p. 849, 1984.
- [9] G. A. Capelle, D. G. Dutton, and J. I. Steinfeld, *J. Chem. Phys.*, vol. 69, p. 5140, 1978.
- [10] D. J. Benard, *J. Appl. Phys.*, vol. 74, p. 2900, 1993.
- [11] D. J. Benard and B. K. Winker, *J. Appl. Phys.*, vol. 69, p. 2805, 1991.
- [12] D. J. Benard, B. K. Winker, T. A. Seder, and R. H. Cohn, *J. Phys. Chem.*, vol. 93, p. 4790, 1989.
- [13] D. J. Benard, E. Boehmer, H. H. Michels, and J. J. A. Montgomery, *J. Phys. Chem.*, vol. 98, p. 8952, 1994.
- [14] E. Boehmer and D. J. Benard, *J. Phys. Chem.*, vol. 99, p. 1969, 1995.
- [15] D. J. Benard and E. Boehmer, *Appl. Phys. Lett.*, vol. 65, p. 1340, 1994.
- [16] D. J. Benard, *J. Phys. Chem.*, vol. 100, p. 8316, 1996.

- [17] K. Y. Du and D. W. Setser, "Quenching reactions of  $\text{NF}(a^1\Delta)$  by  $\text{Cl}_2$ ;  $\text{ClF}$ ;  $\text{Br}_2$ ;  $\text{ICl}$ ;  $\text{IF}$ ; and  $\text{I}_2$ ," *J. Phys. Chem.*, vol. 96, pp. 2553–2561, 1992.
- [18] H. Cha and D. W. Setser, "NF( $b^1\Sigma^+$ ) quenching rate constants by halogens and interhalogens and the excitation rate-constant for IF(B) formation," *J. Phys. Chem.*, vol. 91, pp. 3758–3767, 1987.
- [19] A. J. Ray and R. D. Coombe, "Energy-transfer from  $\text{NCl}(a^1\Delta)$  to iodine atoms," *J. Phys. Chem.*, vol. 97, pp. 3475–3479, 1993.
- [20] T. L. Henshaw, S. D. Herrera, and L. A. V. Schlie, "Temperature-dependence of the  $\text{NCl}(a^1\Delta) + \text{I}(^2\text{P}_{3/2})$  reaction from 300 to 482 K," *J. Phys. Chem. A*, vol. 102, pp. 6239–6246, 1998.
- [21] T. L. Henshaw, G. C. Manke II, T. J. Madden, M. R. Berman, and G. D. Hager, "A new energy transfer chemical laser at  $1.315\ \mu\text{m}$ ," *Chem. Phys. Lett.*, vol. 325, pp. 537–544, 2000.
- [22] G. C. Manke II and D. W. Setser, "Kinetics of  $\text{NCl}(a^1\Delta)$  and  $b^1\Sigma^+$  generation: The  $\text{Cl} + \text{N}_3$  rate constant, the  $\text{NCl}(a^1\Delta)$  product branching fraction, and quenching of  $\text{NCl}(a^1\Delta)$  by F and Cl atoms," *J. Phys. Chem. A*, vol. 102, pp. 7257–7266, 1998.
- [23] —, "Measuring gas-phase chlorine atom concentrations: Rate constants for  $\text{Cl} + \text{HN}_3$ ;  $\text{CF}_3\text{I}$ ; and  $\text{C}_2\text{F}_5\text{I}$ ," *J. Phys. Chem. A*, vol. 102, pp. 153–159, 1998.
- [24] G. C. Manke II, T. L. Henshaw, T. J. Madden, and G. D. Hager, "Temperature dependence of the  $\text{Cl} + \text{HN}_3$  reaction from 300 to 480 K," *Chem. Phys. Lett.*, vol. 310, pp. 111–120, 1999.
- [25] 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  $1.315\ \mu\text{m}$  transition of atomic iodine in a subsonic flow of chemically generated  $\text{NCl}(a^1\Delta)$ ," *Chem. Phys. Lett.*, vol. 299, pp. 583–588, 1999.
- [26] R. D. Bower and T. T. Yang, " $\text{I}(^2\text{P}_{1/2})$  produced by the energy-transfer from  $\text{NCl}(a^1\Delta)$  to  $\text{I}(^2\text{P}_{3/2})$ ," *J. Opt. Soc. Amer. B*, vol. 8, pp. 1583–1587, 1991.
- [27] A. J. Ray and R. D. Coombe, "An  $\text{I}^*$  laser-pumped by  $\text{NCl}(a^1\Delta)$ ," *J. Phys. Chem.*, vol. 99, pp. 7849–7852, 1995.
- [28] 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 J.*, vol. 39, pp. 447–454, 2001.
- [29] G. C. Manke II, T. L. Henshaw, C. B. Cooper, and G. D. Hager, "Recent progress in the development of a multi-watt all gas-phase iodine laser (AGIL)," presented at the 33rd AIAA Plasmadynamics and Lasers Conf., Maui, HI, 2002.
- [30] S. J. Davis, D. B. Oakes, M. E. Read, and A. H. Gelb, "Atomic fluorine source for chemical lasers," in *Proc. SPIE, Gas and Chemical Lasers and Intense Beam Applications III*, San Jose, CA, 2002.

**Gerald C. Manke, II** received the B.A. degree in chemistry from Wartburg College, Waverly, IA, in 1992 and the Ph.D. degree in physical chemistry from Kansas State University, Manhattan, in 1997.

He is a Research Chemist in the Directed Energy Directorate (Gas and Chemical Lasers Branch) of the Air Force Research Laboratory, Kirtland AFB, NM. He is the principal investigator and co-inventor for the all gas-phase iodine laser (AGIL).

**Chris Cooper** received the B.S. degree in chemical engineering (*cum laude*) from the University of New Mexico, Albuquerque, in 1997.

He is a Chemical Engineer with Boeing-Rocketdyne, Kirtland AFB, NM. He is the Project Engineer for the all gas-phase iodine laser and has worked as a contractor for the Air Force Research Lab for almost three years.

Mr. Cooper received the Reibosomer Award for Excellence in Chemistry in 1993.

**Shiv C. Dass** received the M.S. degree in physics and the Ph.D. degree from University of New Brunswick.

He is a Senior Scientist with Boeing-Rocketdyne, Kirtland AFB, NM, where he works in the high-energy laser research area of the Air Force Research Laboratory. He has been working in the field of lasers and laser electrooptical systems for the past 25 years. He previously worked in a number of laser manufacturing industries in North America. He has published more than 15 research papers in scientific journals and holds one U.S. and international patent.

**Timothy J. Madden**, photograph and biography not available at the time of publication.

**Gordon D. Hager** received the Ph.D. degree in chemical physics from Washington State University, Pullman, in 1973.

He has been a Research Scientist with the U.S. Air Force Research Laboratory, Kirtland AFB, NM, since 1982. His area of expertise is high-power gas phase and chemical lasers.