

Progress Toward an NCl_3 -Fueled Iodine Laser

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The NCl–I laser has been demonstrated by using HN_3 as a fuel. We discuss the possibility of constructing a $\text{NCl}(a^1\Delta)$ –I transfer laser by using NCl_3 as a fuel. Not only is NCl_3 more stable but it also may eliminate the requirement for a combustor. We present kinetic modeling and the results of experiments designed to understand the basic physical processes in this system. Experiments have included determination of the time profile history of $\text{NCl}(a)$, $\text{NCl}(b)$, I^ , and chlorine recombination. The efficiency of production of chlorine atoms in a microwave discharge has been measured. We have also shown that the autodecomposition of NCl_3 can be initiated by modest heating of the NCl_3 flow, which supports our belief that a combustor will not be required. The NCl–I laser operates on gas species, eliminating the need for heterogeneous gas–liquid reactions such as used for the production of COIL chemical lasers. The lasing species is the same as in COIL, simplifying the scaling process since many optical, tracking, and propagation problems have been demonstrated in the ABL program. This work is supported by the JTO through the AFOSR-administered MRI program.*

KEYWORDS: Chemical laser, NCl–I transfer laser, NCl_3 reactions

1. Introduction

The level structure of the $\text{NCl}(a^1\Delta)$ molecule is identical to the structure of $\text{O}_2(^1\Delta)$ since the two molecules are isoelectronic. As such, the molecule would be expected to be metastable and capable of transferring its energy to the iodine atom as does $\text{O}_2(^1\Delta)$ in the chemical oxygen iodine laser. In fact, lasers have been demonstrated by using the energy transfer from $\text{NCl}(a^1\Delta)$ to iodine atoms.^{2,3} These lasers produce $\text{NCl}(a^1\Delta)$ from the reaction of chlorine atoms and hydrogen azide. Not only are chlorine atoms difficult to produce (requiring a combustor), but hydrogen azide is in itself extremely unstable. We reviewed the development of this laser in previous papers.⁶ Our approach is to look at the possibility of using NCl_3 as a fuel replacing HN_3 and perhaps eliminating the need for a chlorine atom source. At Denver University, we have shown that the combustion of NCl_3 by hydrogen atoms produces $\text{NCl}(a^1\Delta)$ in high yield.¹ We used a microwave discharge to produce hydrogen atoms in those studies. A more recent study at Physical Sciences, Inc., has observed the pumping of iodine atoms by $\text{NCl}(a^1\Delta)$ and a resulting decrease in the optical absorption in the H-atom-initiated system.⁴ In this study, we are looking at the

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Table 1. Typical operating conditions

Species	Concentration (1/cm ³)	Pressure (torr)	Mole fraction
Ar	5.62E+16	1.73	73.20%
Cl ₂	1.18E+14	0.00	0.15%
Cl	7.86E+13	0.00	0.10%
NCl ₃	4.09E+13	0.00	0.05%
HI	0.00E+00	0.00	0.00%
H ₂	2.03E+16	0.63	26.49%
Total	7.67E+16	2.37	

chlorine-atom-initiated decomposition of NCl₃ as a source of NCl(a¹Δ). We are comparing the time profiles of various species to model predictions to evaluate the kinetic model.

2. Experimental Setup

The experimental apparatus has been described in previous papers.⁶ Briefly, we have a flexible flow system that allows us to inject reactants in several places and measure the emissions from various species as a function of time from the injection points. Typical operating conditions without the addition of HI are given in Table 1.

The flow velocity is about 900 m/s. The NCl₃ is produced in a hood under several layers of protection and carried with argon to the experimental apparatus. The concentration of NCl₃ is measured by absorption at 254 nm (Hg pen lamp) and recorded by using LabView. The amount of argon and NCl₃ admitted to the flow system is usually measured by replacement of a small auxiliary flow of argon. That is, the argon makeup flow is decreased by the desired flow rate, and then argon and NCl₃ are introduced to return to the original pressure. This procedure allows flow measurement without risking the decomposition of the NCl₃ in the flow meter. When HI is flowed to produce I atoms, the HI is added from a bulb diluted to about 5% in argon. The total flow is measured with a flow meter and typically results in an HI concentration of about 8×10^{13} cm⁻³.

3. Results

Our typical experimental setup mixes chlorine atoms (and undissociated chlorine molecules) into a flow of argon and NCl₃. After 5 μs, H₂ or a mixture of H₂ and HI is added to the flow. The initial reaction between Cl atoms and NCl₃ should dissociate the NCl₃ into NCl₂. Reaction of H₂ with excess Cl atoms produces H atoms (and HCl). The H atoms then react with the NCl₂ to produce NCl(a¹Δ). To quantify the chlorine atom concentration, we measured the dissociation of chlorine by titrating the flow from the microwave discharge with HI and observing the excited HCl produced on an IbSb detector fitted with a filter that passes the HCl fundamental emission. The HI and Cl atom reaction is fast, and so monitoring the HCl emission at a point a few microseconds downstream of the mixing point is adequate. A typical titration experiment is shown in Fig. 1.

The average dissociation fraction was about 25%, in good agreement with the work of Manke and Setser.⁵ The discharge was coupled to the chlorine flow (5% chlorine in

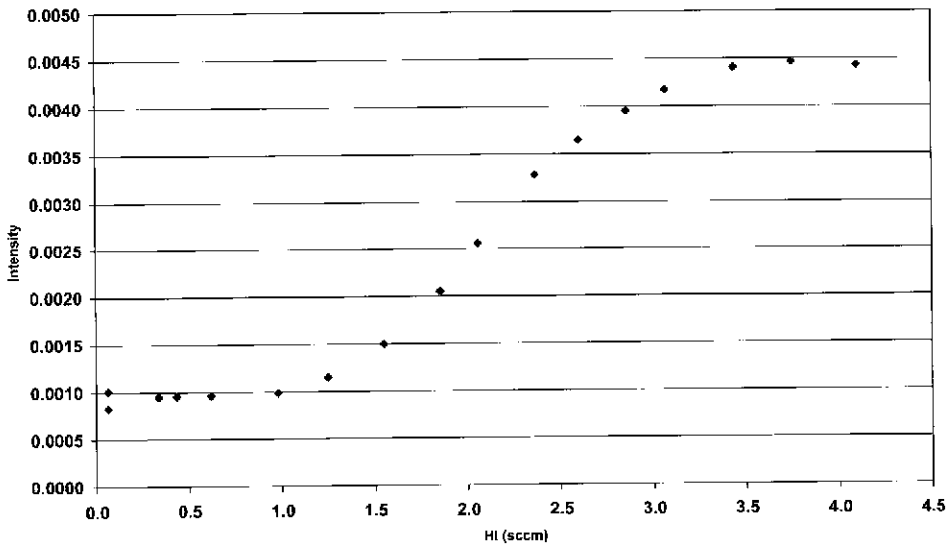


Fig. 1. HCl fundamental emission as a function of added HI.

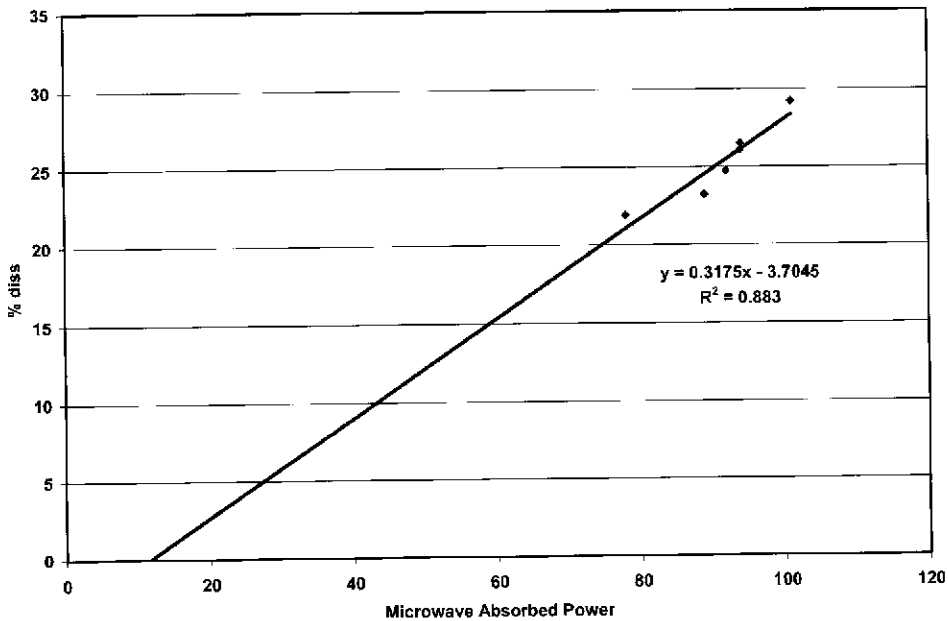


Fig. 2. Fraction of chlorine dissociated versus absorbed power.

argon) with a McCarron cavity and a ceramic discharge tube. Titrations were done at high microwave power (~100 W, <5 W reflected). There appeared to be a suggestion of microwave power dependence (Fig. 2). The microwave absorbed power is the difference between forward and reflected power.

In our previous paper, we noted that the rise time of the NCl(a¹Δ) emission seemed slower than predicted. We measure the NCl(a¹Δ) by using an intrinsic Ge detector with a 1.08-μm

narrow-band-pass filter. At early times, we noted the appearance of $\text{Cl}_2(\text{B-X})$ radiation in the visible, which might contribute to the signal at $1.08 \mu\text{m}$ since the recombination radiation extends well into the near IR. To evaluate this contribution, we measured the $\text{Cl}_2(\text{B-X})$ in the visible by using a $0.85\text{-}\mu\text{m}$ long pass filter and a visible (GaAs) photomultiplier

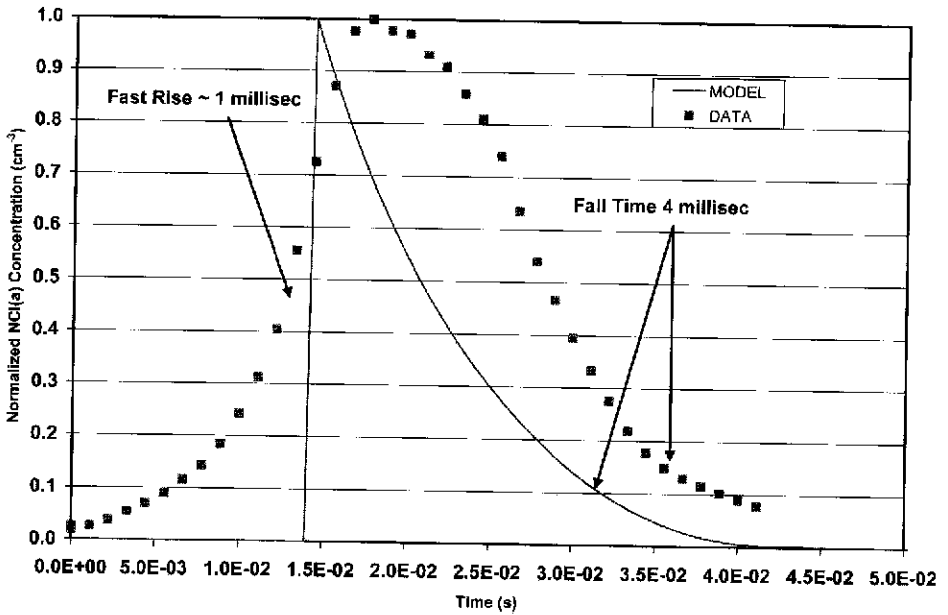


Fig. 3. Comparison of model and uncorrected $1.08\text{-}\mu\text{m}$ emission.

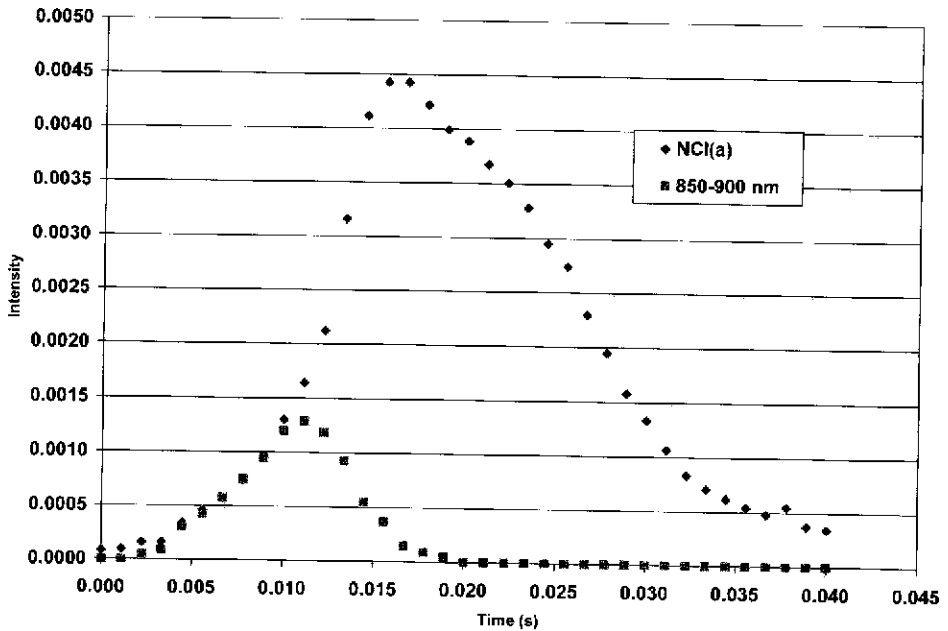


Fig. 4. $\text{NCl}(a^1\Delta)$ and $\text{Cl}_2(\text{B-X})$ normalized emissions.

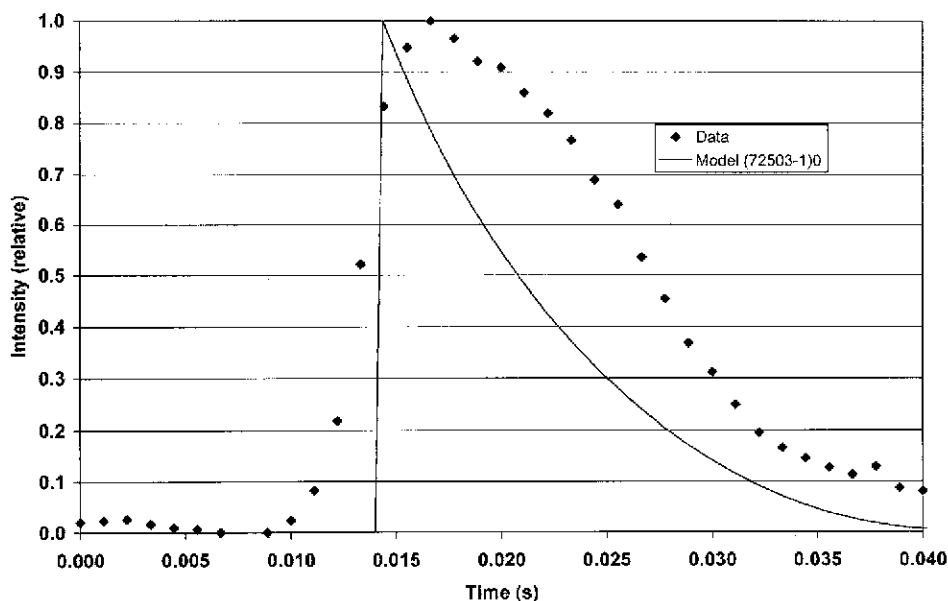


Fig. 5. NCl(a¹Δ) with Cl₂ (B-X) emission subtracted.

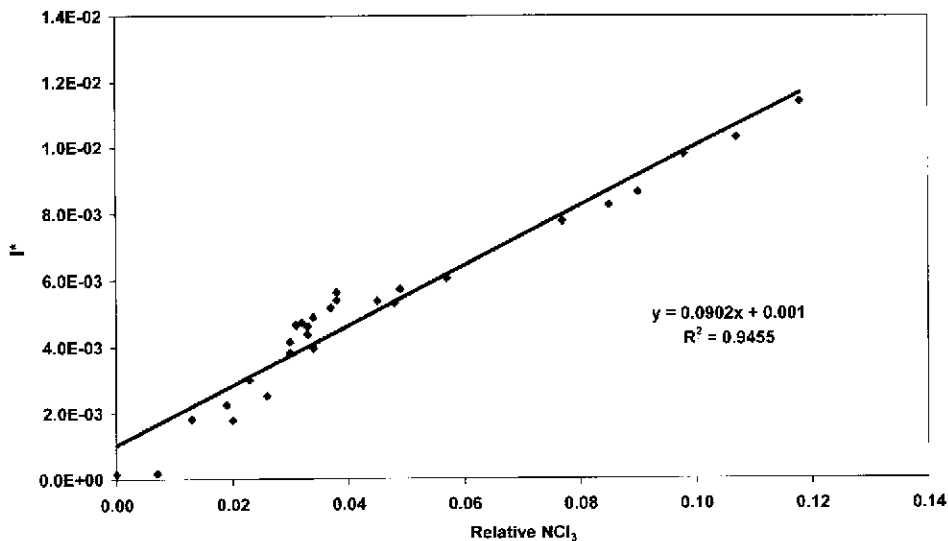


Fig. 6. Variation of I* signal with NCl₃ flow rate.

tube (PMT). This combination acted as a broadband (0.85–0.90 μm) filter because the PMT sensitivity drops off sharply at around 0.90 μm. Figure 4 compares these two emissions. The appearance of recombination radiation at an early time makes the NCl(a¹Δ) rise time look much slower than it is. Figure 5 compares the kinetic model with the corrected NCl(a¹Δ) emission. Although the production rate of NCl(a¹Δ) is slower than predicted, the fall time agrees well with model predictions.

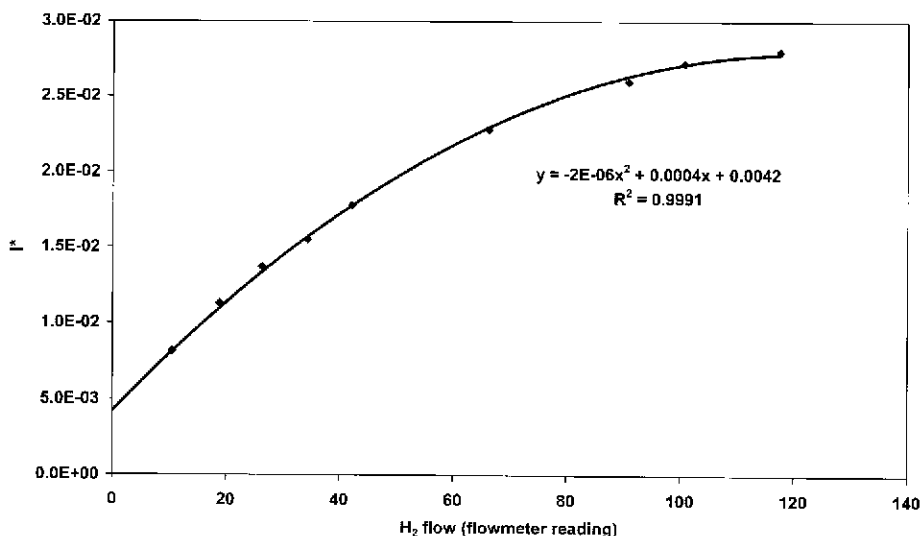


Fig. 7. Variation of I^* signal with H₂ flow rate.

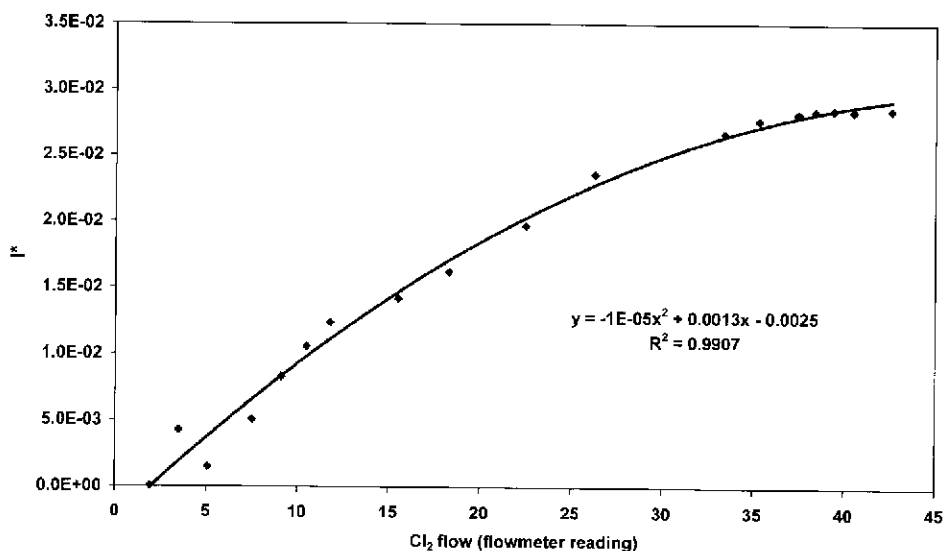


Fig. 8. Variation of I^* signal with Cl₂ flow rate.

Recently, we have conducted experiments adding HI to the reaction mixture. The HI is added (carried in argon) into the H₂ flow. Figure 6 shows that the I^* signal is linear in the NCl₃ flow rate. Variation of the hydrogen (Fig. 7) and chlorine (Fig. 8) are linear at lower concentrations and reach a peak at higher additions. This indicates that NCl₃ is probably the limiting reactant in these experiments.

The time profile of the I^* signal was unusual. It appears to reach a peak I^* value about 20 ms after HI injection, which agrees with the location of the maximum NCl(a¹Δ) concentration (see Fig. 5). The time profile includes a substantial contribution from Cl₂(B-X) at an early time (Fig. 9).

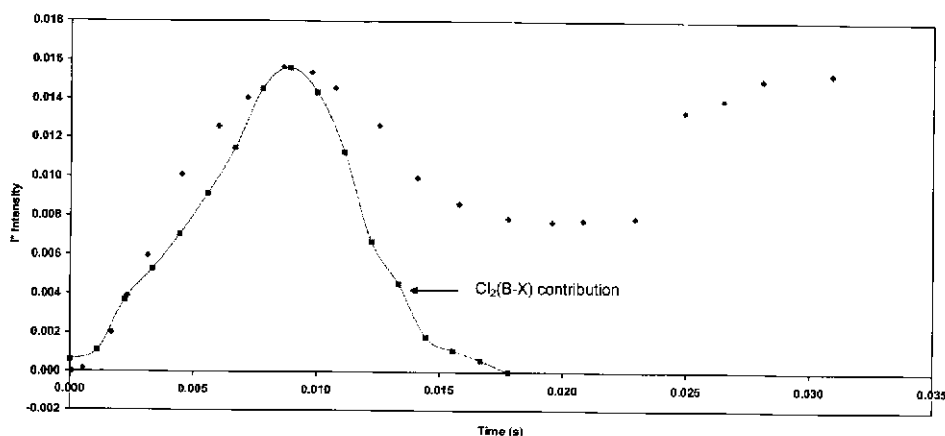
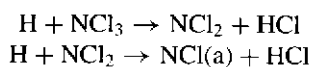


Fig. 9. Time profile of I*. Data are indicated by the points. The Cl₂ emission is scaled.

We see a similar trend in the emission at 1.315- μ m when HI is absent. This emission is much smaller than the I* emission and is also likely due to chlorine recombination.

4. Model Calculations

Our kinetic model currently includes 29 rate constants. They are detailed in Ref. 7. We have updated our model to include the recent work at Emory University,⁸ which gives new quenching rate constants for H₂, HCl, Cl₂, and O₂. A reinvestigation of these rates was necessary since earlier studies using ClN₃ as a source assumed that NCl(a¹ Δ) was a primary product of the photodissociation of ClN₃. It was recently shown that the primary product channel is fragmentation to Cl + N₃ and production of NCl(a¹ Δ) occurs as a subsequent reaction.⁹ In all cases, the new quenching rate is significantly slower than the old rate. The rise time of the NCl(a) emission is determined by the rate of the two production reactions:



The fall time is governed by the quenching of NCl(a). The assumed rates for each of these processes are given in the reference cited above. Absolute densities are not available in the flow system due to the difficulties in absolute intensity measurements. We plan to use an infrared optical multichannel analyzer in future experiments to measure the relative yield of I*(²P_{1/2}) from NCl(a).

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