

Studies of an Advanced Iodine Laser Concept

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Studies of an advanced iodine laser concept

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ABSTRACT

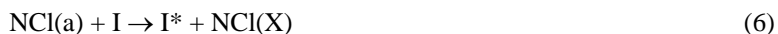
We discuss experimental results from spectroscopic and kinetic investigations of the reaction sequence starting with $\text{NCl}_3 + \text{H}$. Through a series of abstraction reactions, $\text{NCl}(a^1\Delta)$ is produced. We have used sensitive optical emission diagnostics and have observed both $[\text{NCl}(a^1\Delta)]$ and $[\text{NCl}(b^1\Sigma)]$ produced by this reaction. Upon addition of HI to the flow, the reaction of $\text{H} + \text{HI}$ produced iodine atoms that were pumped to the excited $\text{I}(^2\text{P}_{1/2})$ state, and we observed strong emission from the I atom $^2\text{P}_{1/2} \rightarrow ^2\text{P}_{3/2}$ transition at 1.315 μm . With a tunable diode laser we probed the I atom transition and observed significant transfer of population from ground state ($^2\text{P}_{3/2}$) to the excited state ($^2\text{P}_{1/2}$) and have observed optical transparency within the iodine atom energy level manifold.

1. INTRODUCTION

The chemical oxygen iodine laser (COIL) was the first in a unique class of atomic transition lasers pumped by energy transfer from a metastable partner.¹ In COIL, the $^2\text{P}_{1/2}$ state of iodine is excited by energy transfer from singlet molecular oxygen ($\text{O}_2(a^1\Delta)$) that is produced by a two phase (gas, liquid) chemical reaction. The reaction of Cl_2 with a basic hydrogen peroxide evolves gaseous singlet oxygen that is then used to excite the atomic iodine. COIL represents a unique class of gas phase lasers that has undergone tremendous development since it was first demonstrated in 1978 by McDermott et al.¹ The chemistry to produce singlet molecular oxygen has been very successful and has produced impressive power scaling.

However, the relatively complex liquid-gas chemistry involved with COIL has led to interest in developing alternate systems that use the iodine atom as the laser species but employ different energy transfer partners.

In 1992 Yang, Gyls, Bower, and Rubin² produced the first definitive evidence for the potential of an atomic iodine laser transfer laser pumped by $\text{NCl}(a)$. They used an intracavity method to infer a population inversion between the iodine $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ levels. Yang et al. used the following reaction sequence listed in Eqs. (1) through (6).



Ray and Coombe^{3,4} demonstrated the first NCl/I laser using photolytic production of $\text{NCl}(a)$ and I. While this was not practical as a laser system, these results proved the NCl(a)/I laser concept.

Subsequent to these promising results, researchers at the Air Force Research Laboratory measured small signal gain on the $F'=3 \rightarrow F''=4$ line of the atomic iodine $^2\text{P}_{1/2} - ^2\text{P}_{3/2}$ transition at 1.3152 μm ⁵ with the chemistry of reactions (1)

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through (6) but with HI as the iodine source. They used a tunable diode laser to probe this transition directly. In 2000, Henshaw et al. demonstrated the first cw atomic iodine laser pumped by chemically produced NCl(a) using all gas-phase reactants.⁶ This system was named the all gas-phase iodine laser (AGIL) and was a significant step in the development of short wavelength chemical lasers with potential for significant power scaling. Manke⁷ recently described a multi-watt AGIL system. AGIL offers a chemical iodine laser without the heterogeneous chemistry complexities present in COIL.

Coombe and co-workers^{8,9} developed an amine-based chemistry for producing NCl(a) that may offer some advantages over the azide-based process described above. This alternate process uses the following reactions to produce NCl(a).



This reaction sequence is similar to the $\text{NF}_2 + \text{H}$ chemistry that has been previously shown to produce high concentrations of NF(a) via sequential F atom abstraction reactions with H.^{10,11} Coombe et al.⁸ also demonstrated efficient energy transfer to I atoms from the NCl(a) produced by reaction (8). The amine chemistry offers an attractive alternative to the azide based chemistry used in the original AGIL laser because NCl_3 is inherently more stable than HN_3 .

We have been investigating aspects of this potential chemical laser system with a particular emphasis on the measurement of the energy transfer to the I atom manifold. McDermott et al.^{12,13} are also exploring this potential laser system. We are investigating whether this system can provide sufficient NCl(a) to produce small signal gain on the iodine $^2\text{P}_{1/2} - ^2\text{P}_{3/2}$ transition using the reaction sequence described in reactions (7) and (8) as the NCl(a) source. Our approach has been to develop ultra-sensitive diagnostics to probe whether the fundamental chemistry can produce positive small signal gain.

2. EXPERIMENT

2.1 NCl_3 generator

We used an NCl_3 generator based upon the previous work of Coombe and Gilbert.^{8,9} The generator was constructed with Teflon tubing, Nalgene bottles for the synthesis volume and overflow bottles, and a glass flow-through trap to isolate the reaction products (NCl_3 and Cl_2). A diagram of the NCl_3 generator is shown in Figure 1.

To produce NCl_3 , Cl_2 is diluted in Ar and flowed through an aqueous mixture of 1 N H_2SO_4 and NH_4Cl . During this process, NCl_3 is generated, and trapped at low temperature (dry ice – MeOH bath). At these temperatures, NCl_3 is a yellow liquid. During use, the NCl_3 was evaporated and the vapor mixed into the flow reactor. Atomic hydrogen was produced by flowing H_2 dilute in He through an Evenson microwave discharge cavity. In the flow tube, the H atoms react with NCl_3 via reactions (7) and (8) (above) to form NCl. This molecule is formed in two electronically excited states, NCl ($b^1\Sigma$), NCl ($a^1\Delta$) and perhaps also in the ground state (NCl ($X^3\Sigma$)), although correlation rules favor the formation of singlet states.

2.1.1. Description of flow reactor and diagnostics

The flow reactor and the locations of the diagnostics are illustrated in Figure 2. The positions of several optical diagnostics are indicated including: a fiber optic coupled Roper near-IR OMA for NCl(a) and I^* , a visible wavelength Ocean Optics OMA for NCl(b), and a Physical Sciences Inc. (PSI) IodineScan diode laser system for monitoring small signal gain or absorption on the (3,4) hyperfine line of the I atom. The near-IR OMA was calibrated for absolute spectral response using a limited field of view method combined with a blackbody radiator as described previously.¹³ A schematic of the flow reactor is shown in Figure 2.

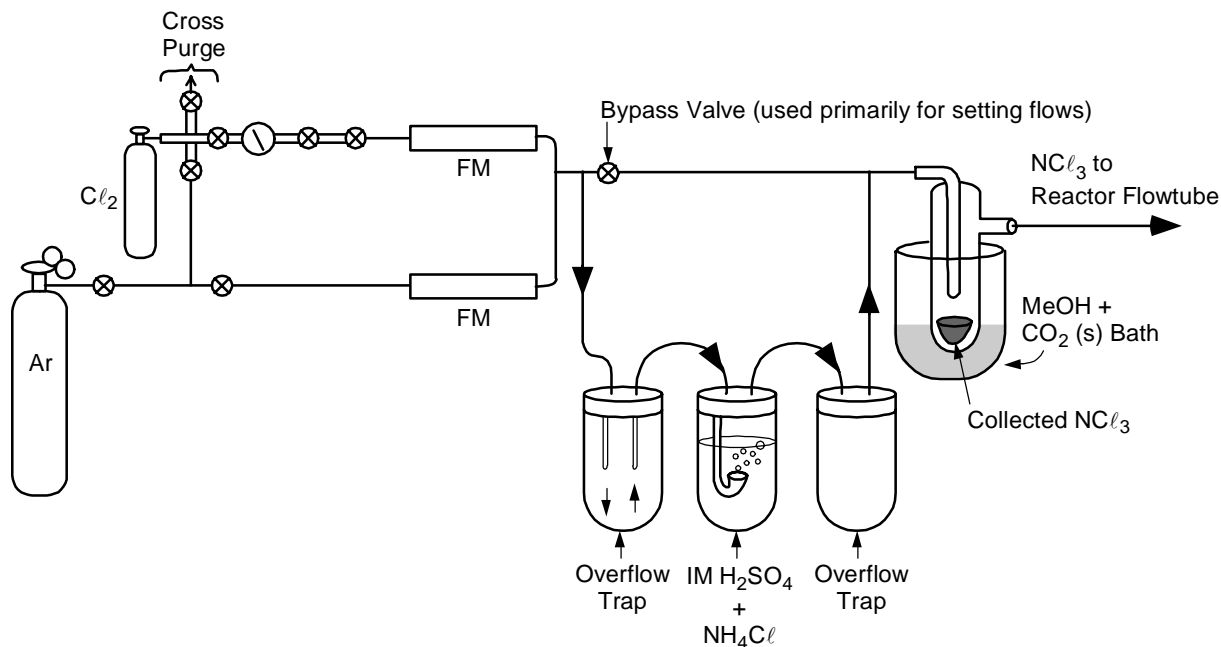


Figure 1. Diagram of NCl_3 generator.

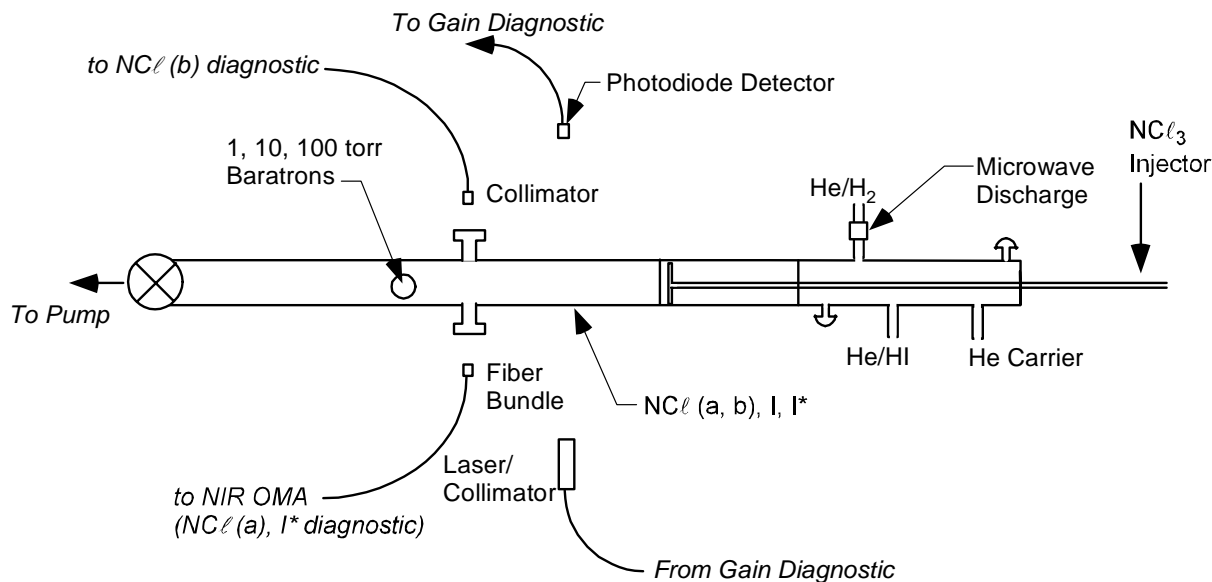


Figure 2. Schematic of flow reactor.

2.1.2. Measurements with IodineScan diode laser spectrometer

As shown in Figure 2, we used a PSI IodineScan diode laser spectrometer to probe the reactive flow for iodine atoms. We have extensively discussed this system previously¹³ and only briefly review this diagnostic here. The tunable diode laser probed the ($F'=3$ to $F''=4$) hyperfine levels in the $^2P_{1/2} \leftarrow ^2P_{3/2}$ transition of atomic iodine, the COIL output line. In the IodineScan unit, we used a PSI, balanced ratiometric detector that allows us to observe fractional absorptions as small as 1 part in 10^5 . With this ultra-sensitive diagnostic, we can probe for microabsorptions or exceedingly small signal gain.

We have used both a multipass Herriott cell and single pass configurations for the diode laser measurements. With the multipass configuration we obtained optical pathlengths exceeding 1.5 m. This provided excellent signal to noise absorption spectra. However, we identified problems with the multipass approach; the beams over-sample the off-axis regions of the flow and under sample the central core. Consequently, most of our diode laser measurements used a single pass configuration.

Several types of experiments were completed. We measured absorptions for I-atom concentrations with and without the presence of NCl(a). We also monitored the I-atom absorption as the NCl₃ and HI flows were systematically varied.

The flow reactor contained a 5.6 cm diameter cylindrical test section that contained eight windows and was Teflon coated to minimize NCl(a) quenching. We have used this test section in past experiments for kinetic and spectroscopic measurements,¹³ and it is well suited for the NCl(a)/I transfer laser experiments. The reactor contains all the diagnostics that we used in the long path system.

As shown in Figure 3, NCl₃ was added through a circular injector. This arrangement more uniformly fills the flow reactor with NCl(a) and ground state I atoms will be pumped in the mixing region. We conducted similar experiments with the diode laser with the goal of observing small signal gain on the I atom manifold. A photo of the apparatus is shown in Figure 4. The red glow from NCl(b) extended more than 15 cm and visually filled both sets of windows on the flow reactor.

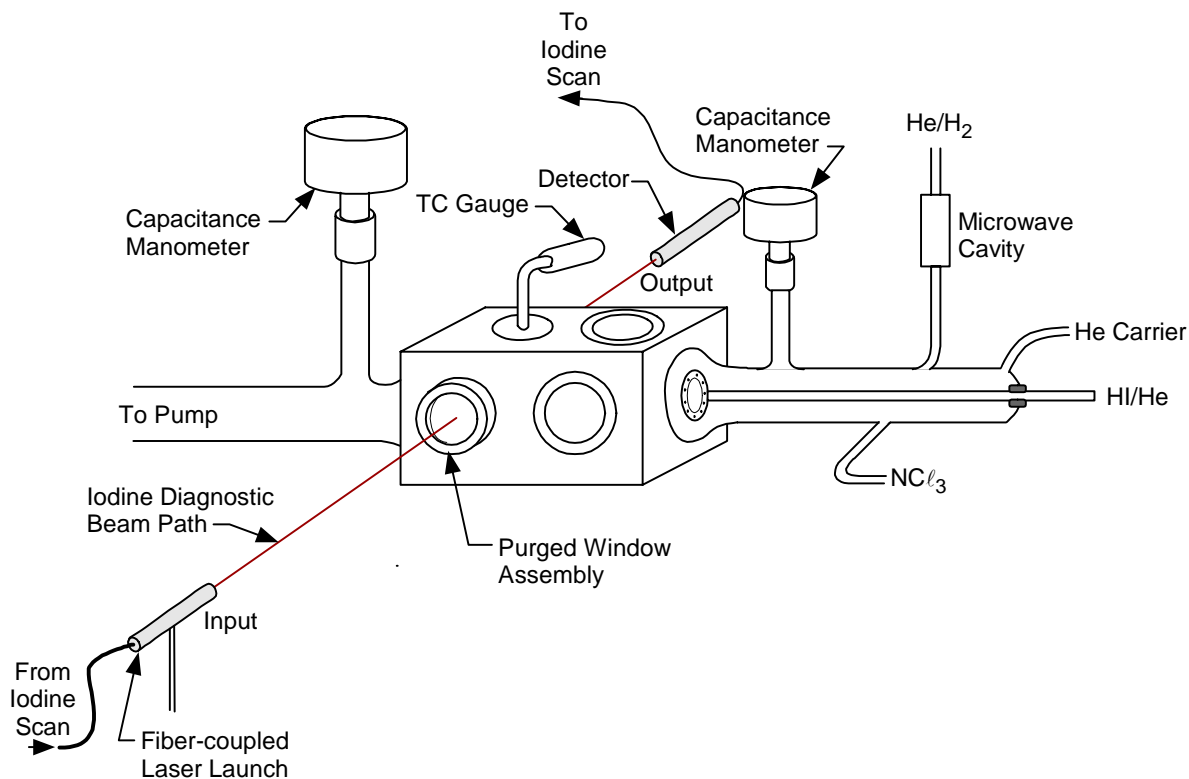


Figure 3. Details of flow channel for NCl(a)/I transfer laser studies.

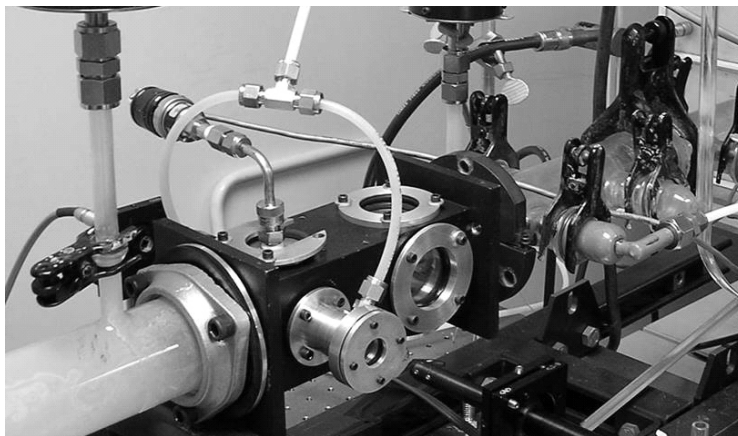


Figure 4. Photo of flow reactor.

Typical results are presented in Figures 5 through 9. Figure 5 shows the dependence of the atomic iodine emission at 1.315 μm as a function of NCl_3 added through the injector ring. Figure 6 shows the atomic iodine emission produced by the $\text{HI}+\text{H}$ reaction in the absence of any $\text{NCl}(\text{a})$. This spectrum implies an excited iodine atom concentration of $[\text{I}^*] \sim 1.4 \times 10^9 \text{ cm}^{-3}$. In Figure 7 we show a spectrum from the $\text{NCl}(\text{a}-\text{X})$ system from which we calculate $[\text{NCl}(\text{a})] \sim 1.2 \times 10^{12} \text{ molecules/cm}^3$. Under these conditions we also recorded the I^* emission shown in Figure 8. This translates to a concentration of $[\text{I}^*] \sim 5 \times 10^{11} \text{ cm}^{-3}$. Comparison of this I^* concentration to that without $\text{NCl}(\text{a})$ present implies an enhancement of the I^* population by a factor of 326. Combining these data with the IodineScan absorption measurements imply that in the presence of $\text{NCl}(\text{a})$, $[\text{I}^*]/[\text{I}] \sim 0.3$. While not inverted, we are clearly approaching the inversion ratio of 0.5. These results also show that we have pumped $\sim 5 \times 10^{11} \text{ cm}^{-3}$ I atoms to I^* via the transfer from $\text{NCl}(\text{a})$ produced by the amine based chemistry described in reactions (7) and (8) above. We note that these data imply $[\text{I}^*]/[\text{NCl}(\text{a})] \sim 0.42$. This compares favorably with Coombe's estimate of 0.6 and implies efficient transfer to I^* from the amine-derived $\text{NCl}(\text{a})$.

Finally, for one set of conditions we were able to increase the $\text{NCl}(\text{a})$ production to further enhance the I^* concentration. Single pass diode laser absorption measurements on the I atom are shown in Figure 9. The left panel shows the absorption trace produced with the $\text{HI}+\text{H}$ reaction present, but with no $\text{NCl}(\text{a})$. We also show a Gaussian fit to the absorption trace. The line center absorption is $\sim 3.5 \times 10^{-5}/\text{cm}$. The large, slowly varying features are due to etalons caused by the flow reactor windows. In the right panel we show the same trace, but with NCl_3 is added to the flow which produces $\text{NCl}(\text{a})$. The position of the line center for the iodine atom absorption is indicated. Within our ability to measure the absorption, the medium is transparent to the iodine atom (3,4) wavelength ($[\text{I}^*] - [\text{I}]/2 \sim 0$). We are presently attempting to produce higher concentrations of $\text{NCl}(\text{a})$ to produce a measurable positive small signal gain.

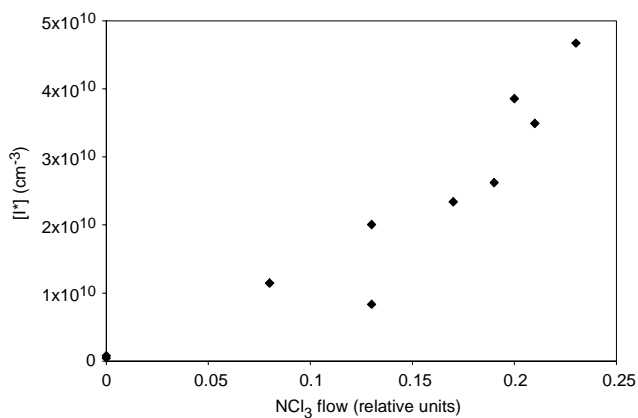


Figure 5. The dependence of I^* on NCl_3 flow rate.

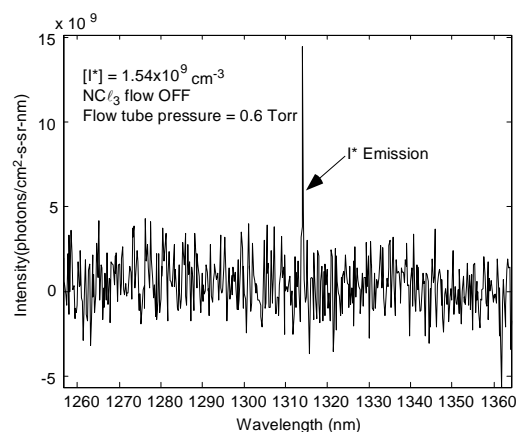


Figure 6. I^* spectrum without the addition of NCl_3 .

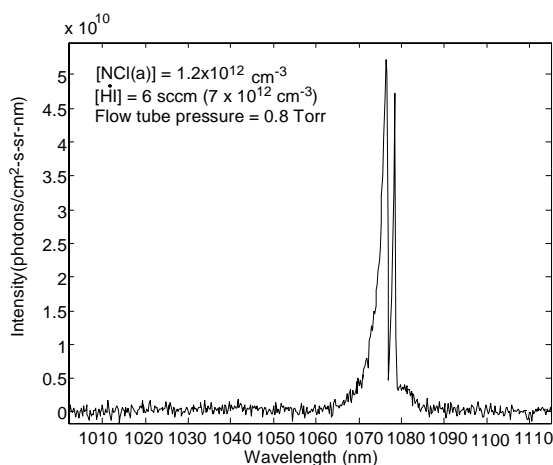


Figure 7. NCL(a) emission

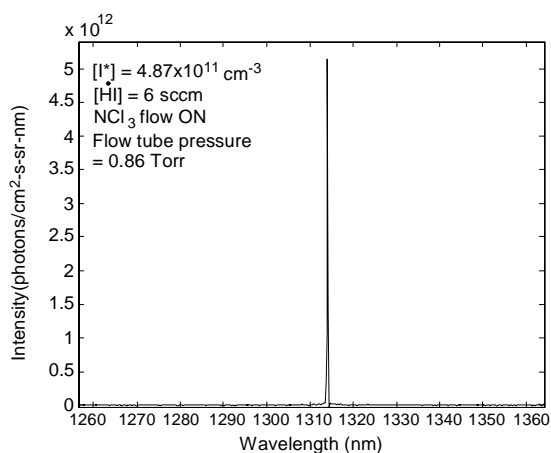


Figure 8. I* emission afetr the addition of NCL₃.

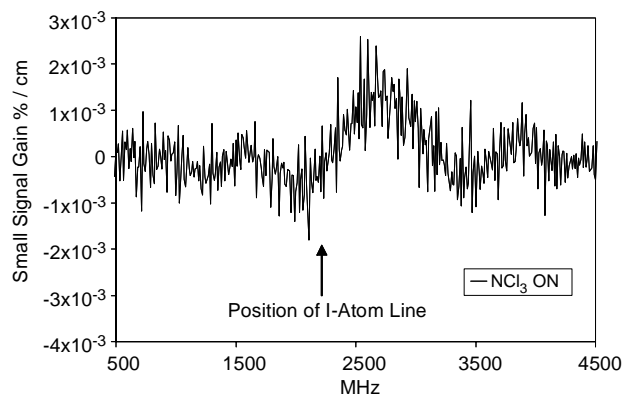
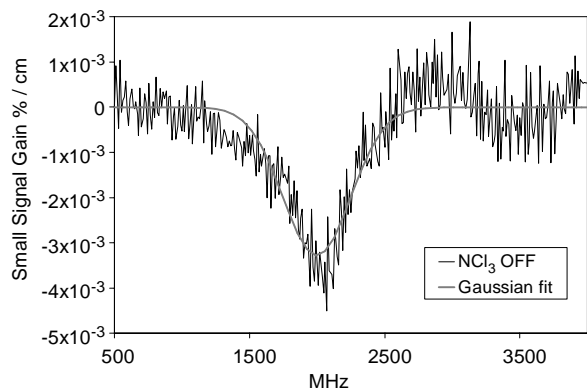


Figure 9. Diode laser absorption lineshapes of (3,4) lines in $I(²P_{1/2}) \leftarrow I(²P_{3/2})$ transition with and without the NCl(a) present. See text for explanation of the two traces.

3. SUMMARY

In these initial experiments we have demonstrated production of NCl(a) via the $\text{NCl}_3 + \text{H}$ reaction sequence and efficient energy transfer to the I atom manifold. The production of NCl(a,b) and transfer to atomic iodine is consistent with the original work of Coombe and co-workers.^{8,9} The diode laser experiments have shown a significant reduction (including optical transparency) in the measured I atom absorption due to NCl(a) pumping of the iodine atom manifold. These promising results encourage us to pursue this system further as a novel atomic iodine chemical laser. They also reported enhanced production of NCl(a) and I^* using D_2 in place of H_2 . We plan to repeat our experiments using deuterium.

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