

Experimental Effects of Atomic Oxygen on the Development of an Electric Discharge Oxygen Iodine Laser

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ABSTRACT

As the development of the electric discharge iodine laser continues, the role of oxygen atoms downstream of the discharge region was found to be very significant. One of the largest uncertainties is the rate of quenching of I^* by O atoms. We have taken a series of measurements of $O_2(^1\Delta)$ emission, I^* emission, O-atom titrations, gain/absorption, and $O_2(^1\Delta)$ yield to explore the significant positive and negative roles that O atoms play in the kinetics of the system that influence the gain. An estimate of the reaction rate for $I^* + O$ is provided. This investigation of the effects of atomic oxygen led to the measurement of positive gain on the 1315 nm transition of atomic iodine where the $O_2(a^1\Delta)$ was produced in a flowing electric discharge. Excess atomic oxygen was scavenged by NO_2 to minimize the deleterious effects. The discharge production of $O_2(a^1\Delta)$ was enhanced by the addition of a small proportion of NO to lower the ionization threshold of the gas mixture. The electric discharge was followed by a continuously flowing supersonic cavity, which was employed to lower the flow temperature.

Keywords: chemical oxygen-iodine laser, COIL, ElectriCOIL, RF excitation of oxygen, singlet-delta oxygen, DOIL

1.0 INTRODUCTION

The classic chemical oxygen-iodine laser (COIL) system¹ operates on the $I(^2P_{1/2}) \rightarrow I(^2P_{3/2})$ [hereafter denoted as I^* and I, respectively] electronic transition of the iodine atom at 1315 nm. The population inversion is produced by the near resonant energy transfer between the metastable excited singlet oxygen molecule, $O_2(a^1\Delta)$ [denoted $O_2(a)$ hereafter], and the iodine atom ground state I. Conventionally, a two-phase (gas-liquid) chemistry singlet oxygen generator (SOG) produces the $O_2(a)$. Early attempts to implement electric discharges to generate $O_2(a)$ and transfer energy to iodine to make a laser by Zalesskii² and Fournier³ did not result in positive gain. Several investigations have been conducted into the possibility of a continuous flow hybrid electrically powered oxygen-iodine laser with electric discharges to produce the $O_2(a)$.⁴⁻⁹ These studies have shown that flowing electric discharges through oxygen containing mixtures, typically diluted with a rare gas, can produce useful quantities of $O_2(a)$. Recent studies have demonstrated $O_2(a)$ yields greater than 15% using electric discharges,^{6,7,9} and modeling results^{4,7,8,10} have indicated that such a system may produce a viable laser. In this paper, we detail the investigation that led to our recently reported measurements of positive gain¹¹ in our ElectriCOIL system.

2.0 EXPERIMENTAL SETUP

A block diagram of the flow tube setup is shown in Fig. 1. A radio frequency (rf) discharge between two internal hollow cathode electrodes (each 13 cm long) operating at 13.56 MHz was used as the excitation source. The plasma zone is approximately 4.9 cm in diameter and 25 cm long. Details of the performance of a similar electric discharge with capacitive external electrodes can be found in Carroll *et al.*⁵ The subsonic diagnostic duct has four windows through which simultaneous measurements are made of the optical emission from $O_2(a)$ at 1268 nm, $O_2(b^1\Sigma)$ [denoted $O_2(b)$ hereafter] at 762 nm, I^* at 1315 nm, and the gain/absorption proportional to $\{[I^*] - 0.5 \cdot [I]\}$. A Roper Scientific Optical Multi-channel Analyzer (OMA-V) was used for the spectral measurements at 1268 nm and 1315 nm. A Santa Barbara Instruments Group, Inc. ST-6 CCD camera coupled to a Jarrell Ash M10023100 monochromator was implemented to measure the emission of $O_2(b)$ at 762 nm. The supersonic diagnostic cavity is a Mach 2 nozzle with view port windows.

A variety of flow meters were used to accurately measure the flow rates of the gases. A diagnostic developed by Physical Sciences Inc. (PSI) that is based upon the continuum absorption of molecular iodine at 488 nm was used to measure the I_2 flow. Details of this diagnostic are described by Rawlins *et al.*¹² Pressures in the subsonic and supersonic flow regions were measured by capacitance manometers. Measurements of gain (or absorption) were made with the Iodine-Scan diagnostic (ISD), developed by PSI.¹³ The ISD is a diode laser based monitor for the small signal gain in iodine lasers. Since the ISD uses a narrow band diode laser, the measured lineshapes can also be used to determine the local temperature from the Voigt profile.

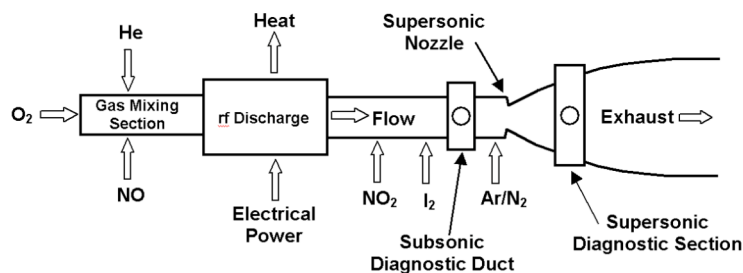


Figure 1: Schematic of the experimental apparatus.

Wedged anti-reflection coated windows were used on the sides of both the subsonic diagnostic section and the supersonic cavity for the gain diagnostic to minimize etalon effects. A 2-pass configuration (10 cm path length) was used in the subsonic section and a 4-pass configuration (20 cm path length) was used in the supersonic section. Yield measurements of $O_2(a)$ were made from the gain diagnostic based upon the techniques originally developed by Hager,¹⁴ Davis and Rawlins.¹²

3.0 EXPERIMENTAL RESULTS

During the course of this research, it was determined that electric discharge stability and temperature control are critical parameters to obtaining positive gain. Electric rf discharges sustained in moderate pressures (many to 10s of torr) of oxygen are prone to instabilities. The discharge production of O atoms, O_3 and other excited species adds higher levels of complexity to the downstream kinetics when the iodine donor species are added to the flow which are not encountered in a purely chemical generation system. The critical aspect of temperature control results from the equilibrium of the pumping reaction,



where the forward rate is $7.8 \times 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{s}$,¹⁵ with the equilibrium rate constant ratio of the forward to backward reactions being $K_{eq}=0.75 \exp(403/T)$,¹⁶ where T is the gas temperature. The threshold yield of $O_2(^1\Delta)$ for positive I^* to I inversion as a function of temperature can be written as $Y_{th}=1/[1+1.5 \exp(403/T)]$.¹⁷ Note that K_{eq} is larger and Y_{th} lower as T is decreased.

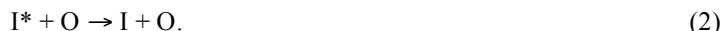
We had previously been unsuccessful in attaining positive gain (as had other groups, see Section 1) despite having achieved yields of $O_2(a)$ with an electric discharge that were, in principle, high enough to do so. Recently we conducted experiments that have led to the attainment of positive gain and we describe these experiments below. We were observing absorption in the supersonic region with temperatures of approximately 240 K, despite having yields that we believed were approximately 15%, which should have been well over the required threshold yield of $O_2(a)$ required for positive gain. As such we began a rigorous investigation of the effects of iodine in the subsonic flow region without the added complication of the supersonic cavity. To perform these experiments we moved the iodine injection point upstream (approximately 20 cm) of a diagnostic section in the subsonic flow tube, Fig. 1; previously we had been injecting the iodine just upstream of the nozzle throat as in traditional COIL geometries.

We made simultaneous measurements of the optical emission from $O_2(a)$ at 1268 nm, $O_2(b)$ at 762 nm, I^* at 1315 nm, and the absorption through the optical windows in the subsonic diagnostic section. Two important things were immediately apparent from these data. First, for the zero iodine case there was a drop in the 1268 signal that begins at around 500 W. This drop in signal is believed to be a consequence of instabilities and thermal constriction that visibly develop in our existing discharge under these flow conditions. We are presently investigating the discharge stability issues in an effort to improve the performance and yield of the discharge, but will not discuss this issue further in this paper. The second and more troubling observation was that when very small amounts of molecular iodine were added to the flow, the level of $O_2(a)$ emission at 1268 nm dropped dramatically, by a factor of more than 5 at 500 W. The flow rate of O_2 was 4 mmol/s with an estimated $O_2(a)$ yield of 15% at 500 W of rf power, therefore there should be approximately 0.6 mmol/s of $O_2(a)$. The iodine flow rate was approximately 0.006 mmol/s, i.e., only 1% of the $O_2(a)$ concentration. Given that the molecular iodine was only 1% of the $O_2(a)$ and that the O atoms should rapidly dissociate it,⁴ the dramatic drop in 1268 signal could not be explained by the classic COIL iodine dissociation process. Further, the concentration of atomic iodine, approximately 2% of the $O_2(a)$, was far too low to explain a significant drop in $O_2(a)$ from the pumping reaction. These facts lead us to the suggestion that whatever phenomenon is causing this dramatic drop in $O_2(a)$ may also be the primary reason why we (and others) have been previously unsuccessful in attaining positive gain with such electrically pumped systems. Further, it leads to the point that while measurements of high yields in pristine environments of a rare gas plus O_2 and the various other oxygen species from a discharge are encouraging, the issue of greater significance is the yield in the presence of iodine at high enough densities to be of interest.

Given the successful history of COIL where the change in yield in the presence of iodine is negligibly small, the different character with this electrically pumped system is related to products of the discharge that are not present in classic COIL, i.e., products other than $O_2(a)$ and $O_2(b)$. Since the loss behavior occurs only with iodine

present, it is believed that the loss must be through the I* channel, i.e., energy transfers through I* from O₂(a) to some other species or into heating the gas. Various candidates are: O atoms, O₃, charged species, ultra-violet (UV) or vacuum ultra-violet (VUV) radiation. All could play a negative role and none appear in classic COIL. The most obvious candidate is atomic oxygen as it is present in number densities on the order of the O₂(a). Modeling predicts that ozone is in quantities of two to three orders of magnitude lower than O₂(a),^{4,10} and the charged species become negligible within a few cm downstream of the exit of the discharge,¹⁰ so these candidates seem less likely to be the major cause of the observed O₂(a) loss. The fact that our discharge and flow tube sections are co-linear allows radiation emitted in the discharge to be observed downstream, so it is conceivable that UV and VUV are playing some role, but the magnitude of this effect seems less likely to be a major contributor. As such, we focused on oxygen atoms as being the major contributor to the deleterious loss of O₂(a) when iodine was present.

Oxygen atoms play a positive role as well as a potentially detrimental role in the kinetics downstream of the discharge region with iodine present. Their beneficial role is that they rapidly dissociate molecular iodine through the processes I₂ + O → IO + I and IO + O → O₂ + I with reaction rates of 1.4 x 10⁻¹⁰ cm³/molecule-s,¹⁸ and 1.5 x 10⁻¹⁰ cm³/molecule-s,¹⁸ respectively. The potentially harmful role of oxygen atoms was first postulated by Heaven¹⁹ to be



Han et al.²⁰ have recently estimated this rate to have an upper bound of 2 x 10⁻¹² cm³/molecule-s; this is considerably smaller (an order of magnitude or more) than both the forward and backward rates of reaction (1) and hence this reaction was originally thought to be of limited importance in reasonably fast flowing systems such as our set up. However, of the candidate processes listed for the dramatic loss of O₂(a) in the presence of iodine, atomic oxygen seemed the most likely culprit and as such experiments were performed to test its effects.

We established the O atom production from the discharge as a function of power into the discharge by titrating with NO₂ using a well established technique first developed by Kaufman.²¹ For these experiments the NO₂ was injected 50 cm downstream of the downstream electrode. A mixture of 4 mmol/s of O₂ and 16 mmol/s of He was run through the rf discharge at a pressure of approximately 10 torr (O₂ partial pressure of 2 torr). We found an approximately linear dependence of O atom production with discharge power; this linear behavior is consistent with previous modeling work in the range in which we are operating.¹⁰ At 300 W of system power, an O atom flow rate of 0.25 mmol/s was measured, or approximately an O atom yield of 6.3%.

We then added NO₂ upstream of the iodine ring injector and monitored the emission at 1268, 1315 and 762 nm at the subsonic diagnostic section. Figures 2 and 3 show the dramatic changes that occur as the flow rate of NO₂ is increased. Note that as NO₂ was added the pressure in the discharge region was maintained at approximately 10 torr by adjusting a downstream flow rate of Ar, see Fig. 1. Figure 2 clearly shows how increasing the NO₂ flow raises the 1268 signal in the presence of iodine progressively to approximately the signal with no iodine in the flow, i.e., by scavenging O atoms from the flow there is a progressively lesser effect from process (2). (Note that rf system power is presented; electrical measurements indicate that approximately 80-90% of the system power is actually absorbed by the plasma for the O₂:He=1:4 mixtures we ran in these experiments.) However, the situation is more complex than just that. Note that the point where we are almost back to the nominal 1268 signal occurs at an NO₂ flow rate of 1.0 mmol/s, yet the O atom flow at 770 W is only approximately 0.59 mmol/s. This result was unexpected since the NO₂ flow rate is well beyond the full titration point, i.e. where [NO₂] = [O] at the highest system power level. Since our mixing appears to be visibly complete within a few cm and the O+NO₂ reaction rate is fairly fast, approximately 1 x 10⁻¹¹ cm³/molecule-s at room temperature,²² we presently do not understand why we must significantly over-titrate the atomic oxygen to regain the majority of the O₂(a) signal; we suspect that there may be some other process(es) occurring that we have not yet identified nor understood.

Figure 3 illustrates the progressive rise in the I* emission with increasing NO₂ flow rate. This rise is consistent with the increasing O₂(a) signal shown in Fig. 2. It is of considerable interest that the location of the peak signal shifts to higher powers with higher NO₂ flow rates. Two simultaneously occurring effects can explain this. First, as the NO₂ flow rate increases the O₂(a) peak increases (and equivalently the yield) and shifts towards higher powers, Fig. 2; as the yield of O₂(a) increases/decreases then so should the observed I* signal via the equilibrium of reaction (1). Second, at higher NO₂ flow rates the atomic oxygen is severely over-titrated (especially at lower powers) and thus the iodine dissociation fraction (and available atomic iodine) is reduced.

A dramatic increase of the O₂(b) emission was also observed when NO₂ was added (not shown for brevity). We believe that this is due to a combination of atomic iodine formed by reactions with O atoms along with reaction (1) to produce I* followed by the process I* + O₂(a) → I + O₂(b), which has a reaction rate of 1.0 x 10⁻¹³ cm³/molecule-s.²³ While this is a negligible loss to O₂(a) it is a significant production rate of O₂(b). Such a phenomenon is not observed in classic COIL because the water vapor quenches O₂(b) rapidly; there is no water vapor in ElectricCOIL and thus the aforementioned reaction is observed.

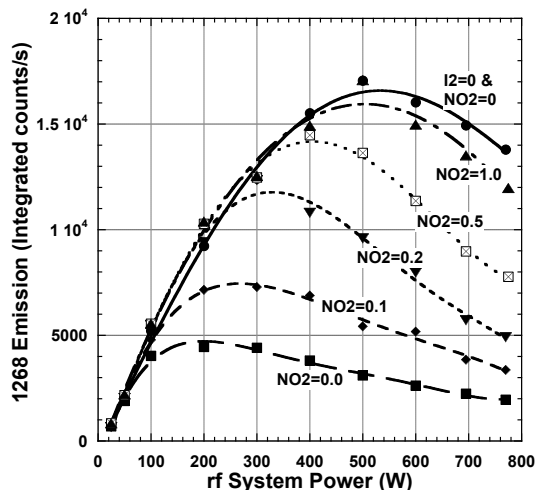


Figure 2: $O_2(a)$ emission at 1268 nm with and without iodine at the subsonic diagnostic port as a function of system power and the NO_2 flow rate, for a flow of 4 mmol/s of O_2 mixed with 16 mmol/s of He at a pressure of 10 torr. NO_2 flow rates are in mmol/s.

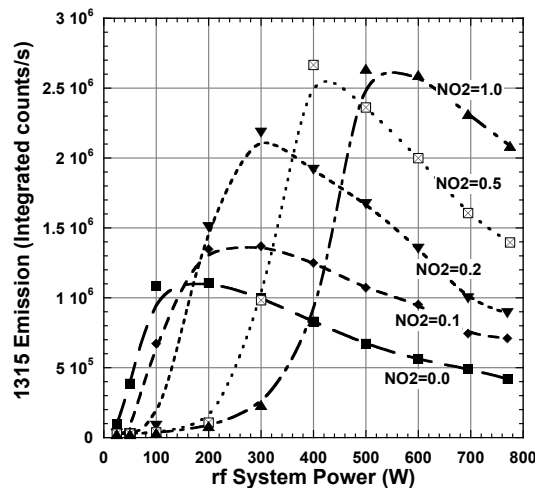


Figure 3: I^* emission at 1315 nm at the subsonic diagnostic port as a function of system power and the NO_2 flow rate, for a flow of 4 mmol/s of O_2 mixed with 16 mmol/s of He at a pressure of 10 torr. NO_2 flow rates are in mmol/s.

In an effort to establish a better estimate for the rate constant for reaction (2), the emissions of $O_2(a)$ and I^* were monitored as a function of the distance from the plane of the I_2 injection and is presented in Fig. 4. The data show that the two signals exponentially decay by a significant amount. Both appear to have the same approximate spatial decay rate, which is an indication of the near equilibrium between $O_2(a)$ and I^* via the forward and backward rates associated with reaction (1).

One can obtain a first order estimate of the rate coefficient for the deactivation of I^* to I to be,²⁴

$$k_2 = (u_f / L) [O_2(a)]_0 / [O]_0 [I^*]_0, \quad (3)$$

where u_f is the flow velocity and the subscript "0" indicates the concentration of the various species at the plane of iodine injection (with the assumption that the molecular iodine is dissociated immediately by the O atoms) with spatial variation of $O_2(a)$ and I^* being $\exp(-z/L)$ in agreement with Fig. 4. For the 10 torr case illustrated in Fig. 4 having an estimated $O_2(a)$ yield of 15% (at the I_2 injection point), a temperature of 375 K from the gain diagnostic and hence an equilibrium constant $K_{eq}=2.19$, an oxygen atom density of $3.72 \times 10^{15} \text{ cm}^{-3}$, an $O_2(a)$ concentration of $6.70 \times 10^{15} \text{ cm}^{-3}$, $[I]+[I^*]$ of $1.86 \times 10^{14} \text{ cm}^{-3}$ and thus $[I^*]$ of $4.60 \times 10^{13} \text{ cm}^{-3}$ [from K_{eq} and an $O_2(a)$ yield of 15%], a flow velocity of 2633 cm/s and L of 30.5 cm from Fig. 4 gives

$$k_2 = 3.4 \times 10^{-12} \text{ cm}^3/\text{molecule-s}, \quad (4)$$

which is higher than the upper bound of $2 \times 10^{-12} \text{ cm}^3/\text{molecule-s}$ estimated by Han et al.²⁰ The simple exponential deactivation of $O_2(a)$ and I^* suggests a simple deactivation process as expressed by reaction (2). Based upon our experiments and analyses, the rate for $I^* + O$ appears to be approximately $3.4 \times 10^{-12} \text{ cm}^3/\text{molecule-s}$. Since the measurement by Han et al. is a more direct measurement of the rate, it is currently believed that the estimate of $3.5 \times 10^{-12} \text{ cm}^3/\text{molecule-s}$ determined in this work may be representative of a more global loss mechanism that is still not fully understood. Other possible quenchers of I^* that have been considered are NO_2 , NO, IO, and O_3 , but all would appear to have lesser effects. It is possible that the sum of the effects of lesser quenchers is adding up to a level that competes with the O atoms; further studies need to be conducted to validate or refute this possibility. Regardless of the quenching mechanism, our data clearly indicate that it is important to control the quantity of atomic oxygen in the flow prior to injecting iodine into the flow.

As discussed in prior works^{2-5,7-9} it is important to lower the parameter E/N such that it is close(r) to the optimal excitation cross-section value to attain maximal yields of $O_2(a)$. One way to lower E/N is to introduce a gas with a lower ionization threshold. NO has an ionization threshold of 9.26 eV, which is significantly lower than the 12.07 eV threshold of O_2 . Experiments were conducted by adding NO to the flow. It was found that NO additions of approximately 1-10% of the O_2 flow rate produced the largest increases of ~33% in the production of $O_2(a)$ and typically around 4-5% was optimal.

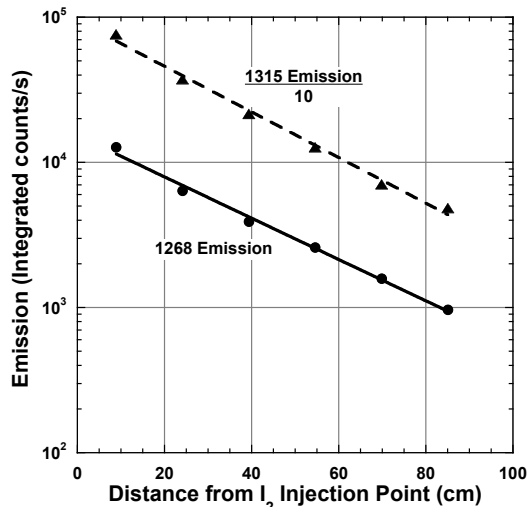


Figure 4: O₂(a) (1268 nm) and I* (1315 nm) emission versus distance from the I₂ injection point for a primary discharge flow of 4 mmol/s of O₂ mixed with 16 mmol/s of He at a pressure of 10 torr. A secondary flow of 0.008 mmol/s of I₂ and 2 mmol/s of He was injected at x=0. The rf power was 400 W.

broadening due to He, Ar, and O₂ to obtain the Doppler width according to the procedure outlined by Whiting.²⁵ From the resulting Doppler width, we obtain a temperature of ≈210 K at 100 W and ≈240 K at 400 W in the supersonic region. To our knowledge, these were the first measurements of positive gain in a continuously flowing iodine system with O₂(a) being provided by an electric discharge.¹¹

By adding pre-cooled Ar upstream of the nozzle throat and raising the upstream pressure to 13 torr we were able to make further improvements to the gain by lowering the total temperature and increasing the density. Figure 6 shows both a positive gain trace in the supersonic cavity and the corresponding absorption trace in the subsonic cavity. The flow conditions were the same for this case as discussed above with the exception of raising the Ar flow rate to 38 mmol/s of Ar to raise the upstream total pressure to 13 torr. The gain in the supersonic cavity was measured to be ≈0.005% cm⁻¹ at 400 W of rf discharge power. From the digitally filtered traces and the homogeneous broadening correction, we obtain temperatures of ≈220 K in the supersonic cavity and ≈375 K in the subsonic region.

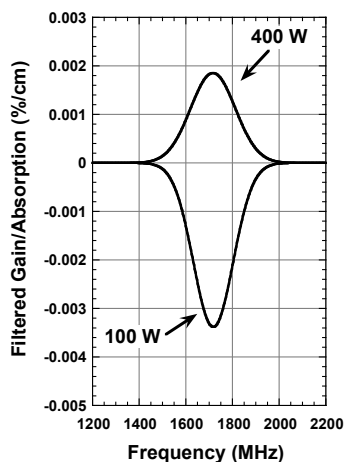


Figure 5: Digitally filtered signal of gain in the supersonic cavity as a function of frequency. Positive gain was observed at 400 W rf discharge power and absorption was observed at 100 W.

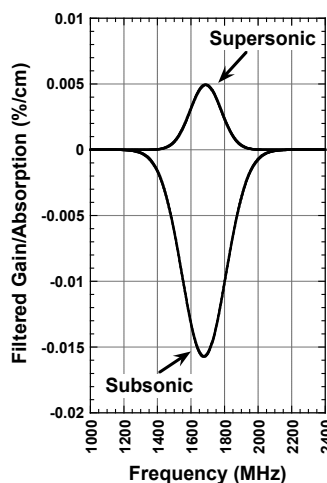


Figure 6: Digitally filtered signal of gain in the subsonic diagnostic section and the supersonic cavity as a function of frequency at 400 W rf discharge power with cooled N₂ injected upstream of the throat. Positive gain was observed in the supersonic section and absorption in the subsonic section.

4.0 CONCLUDING REMARKS

In conclusion, conditions for positive gain were established on the I* → I electronic transition of the iodine atom at 1315 nm pumped by a near resonant energy transfer from O₂(a) produced in an electric rf discharge. A

Several flow conditions were found that resulted in positive gain using the configuration shown in Fig. 1. A typical set of conditions is 4 mmol/s of O₂ mixed with 16 mmol/s of He and 0.2 mmol/s of NO flowing through a 400 W rf discharge. An additional 0.2 mmol/s of NO₂ was added downstream to scavenge some of the excess O atoms, followed by injection of a secondary stream of 0.008 mmol/s of I₂ with 2.0 mmol/s of secondary He diluent. To raise the pressure for more ideal nozzle performance with our vacuum system, 20 mmol/s of Ar was injected further downstream. The pressures in the subsonic diagnostic duct and in the supersonic diagnostic cavity were 10.6 torr and 1.6 torr, respectively.

Absorption in the subsonic region for these conditions was -0.009% cm⁻¹, with a temperature of 400 K, and an O₂(a) yield of approximately 15% (as computed from the technique outlined by Rawlins *et al.*¹²). Based on these measurements, positive gain could be expected if the gas temperature could be sufficiently reduced. As such, gain measurements in the supersonic cavity were made for the above flow conditions, Fig. 5. With 100 W of rf discharge power, only absorption was observed. Upon raising the discharge power to 400 W, positive gain of ≈0.002% cm⁻¹ was measured. The measured lineshapes were digitally filtered and then corrected for homogeneous

supersonic cavity was employed to lower the temperature of the flow and shift the equilibrium of atomic iodine more in favor of the I* state. This produced sufficient population inversion to observe a small, but easily identifiable positive gain of approximately $0.005\% \text{ cm}^{-1}$. The critical issues that needed to be addressed to attain positive gain were improvements to the discharge flow and stability, along with a significantly more complete understanding of the gas phase kinetics. Atomic oxygen was found to play both a positive role and a deleterious role in this system, and as such the excess atomic oxygen was controlled to minimize the harmful effects. The discharge production of $\text{O}_2(\text{a})$ was enhanced by the addition of a small proportion (4-5% of the O_2 flow rate) of NO to lower the ionization threshold of the gas mixture.

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