Preliminary yield measurements in the ElectriCOIL system


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ABSTRACT

Preliminary measurements of the yield of O$_2$(1$\Delta$) as a function of power absorbed in an RF discharge are presented. The yield is deduced from measurements of gain/absorption using the PSI Iodine Scan diagnostic coupled with a data reduction technique originally developed by PSI. A more formal presentation of the method of deducing the yield is provided. Atomic oxygen titration experiments are presented along with gain as a function of power input to the system.

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

1. INTRODUCTION

The classic chemical oxygen-iodine laser (COIL) system [McDermott, 1978] operates on the electronic transition of the iodine atom at 1315 nm, I$^*(2P_{1/2})$ $\rightarrow$ I(2P$_{3/2}$) + hν. The population inversion is maintained by the near resonant energy transfer between the excited singlet oxygen O$_2$(1$\Delta$) [also denoted O$_2$(a)] molecule and the I atom ground state I(2P$_{3/2}$). Traditionally, this pumping reaction has been fed by a liquid chemistry singlet oxygen generator (SOG). Over the past several years researchers around the world have been investigating the possibility of a hybrid electrically powered oxygen-iodine laser [Carroll, 2001; Schmiedberger, 2001; Hill, 2001; Ionin, 2003]. To date there have been many encouraging modeling results [Hill, 2001; Zimmerman, 2003; Carroll, 2003b; Carroll, 2003c; Frolov, 2003; Stafford, 2003] that indicate that such a system should produce a viable laser. A number of papers have presented experimental results demonstrating O$_2$(a) yields of greater than 15% with electric discharges [Hill, 2001; Schmiedberger, 2001; Verdeyen, 2002; Savin, 2003; Rakhimova, 2003], however these were absolute intensity measurements that often have a high degree of uncertainty. As such Rawlins et al. [Rawlins, 2003] introduced a method for using the PSI Iodine Scan system [Davis, 1996] to deduce with higher accuracy the O$_2$(a) yield from gain measurements and/or gain measurements coupled with spectral measurements of the O$_2$(a) and I$^*$ lines.

2. METHOD OF DEDUCING O$_2$(a) YIELD

There have been many papers reporting yields from many different types of discharges in O$_2$ and rare gas mixtures with O$_2$. The most common technique has been absolute intensity measurements of the radiation in the band around 1268 nm. As is well known, there are many pitfalls to this technique, e.g., one needs a calibrated source to calibrate a detector with stable and repeatable sensitivity, and a well characterized geometry for definition of the effective field of view.

Recently, Rawlins et al. [Rawlins, 2003] introduced a method using the PSI Iodine Scan system [Davis, 1996] to deduce the O$_2$(a) yield from its measurements alone, and/or coupled with relative measurements of the I$^*$ and O$_2$(a) emissions. A more formal mathematical formulation of these techniques, originally developed by Hager, Davis, and Rawlins et al. [Hager, 2002; Rawlins, 2003], is detailed below. The essence of the techniques is contained in identifying the unknowns and the most convenient independent measurements leading to a determination of those unknowns. For instance, the Iodine Scan system immediately determines the peak gain coefficient at line center γ (ν$_0$) (cm$^{-1}$), with its clairvoyance that is described in detail in [Hager, 2002; Rawlins, 2003].
sign and the temperature from the spectral width of the scan. This leads to a definitive equation for the population difference in terms of the known temperature dependent stimulated emission cross-section,

\[
\frac{12}{7} \frac{\gamma(v_0)}{\sigma_{ST}(T)} = [I^*] - \frac{1}{2}[I] = G
\]

where \(\gamma(v_0)\) is positive for gain and negative for absorption and is a known experimental value (note that \(G\) carries its own sign).

\[
\sigma_{ST} = \text{stimulated emission cross-section for the } F' = 3 \rightarrow F'' = 4 \text{ hyperfine transition of iodine}
\]

\[
= A_{21} \frac{\lambda^2}{8\pi} g(v_o) = 1.293 \times 10^{-17} \left(\frac{300}{T}\right)^{1/2} \text{cm}^2 \quad \text{[Bruins, 2002]}
\]

\[
g(v_o) = \text{line shape function evaluated at line center}
\]

\[
= \left(\frac{4\ln 2}{\pi}\right)^{1/2} \frac{1}{\Delta v_D} \quad \text{for Doppler broadening}
\]

where

\[
\Delta v_D = \left(\frac{8kT\ln 2}{Mc^2}\right)^{1/2} v_o = 252 \left(\frac{T}{300}\right)^{1/2} \quad \text{[Bruins, 2002]}
\]

\[
A_{21} = 5.0 \text{ s}^{-1}; \lambda = 1.315 \mu\text{m}
\]

Thus, from the scan system alone, one knows if one is above or below optical transparency, the temperature and the population difference.

If one also knows both the concentration of the iodine donor \(D_o\) and the fraction \(f\) of it that is dissociated from its parent \((I_2\text{ or CF}_2I)\), then the second equation comes from a conservation of atoms,

\[
fD_o = [I^*] + [I]
\]

Note that \([D_o] = 2[I] \text{ or } [CF_2I]\). Then, from Eqs. (1) and (2), it is just a matter of algebra to obtain the values of \(I\) and \(I^*\)

\[
[I] = 2/3 (f[D_o] - G) \quad \text{(3a)}
\]

\[
[I^*] = 1/3 (f[D_o] + 2G) \quad \text{(3b)}
\]

To convert these known quantities into yield one invokes the equilibrium relation:

\[
\frac{[I^*]}{[I]} = K_{eq} \frac{[O_2(a)]}{[O_2(X)]} = K_{eq} \frac{[O_2(X)] + [O_2(a)]}{[O_2(a)]} = K_{eq} \frac{Y}{1 - Y}
\]

\[
\text{(4)}
\]

where \(K_{eq} = 0.75 \exp(402/T)\) is the equilibrium rate constant due to the very fast transfer between \(I\) and \(O_2(a)\) and the reverse between \(I^*\) and \(O_2(X)\). The last equality of Eq. (4) presumes that one knows or measures the dissociation of \(O_2(X)\) by the discharge or neglects it in the first approximation as was done here, i.e., \([O_2(X)] = [O_2(X)]_0 - [O_2(a)]\) where \([O_2(X)]_0\) is the total concentration of all \(O_2\) species assuming no dissociation. Then one combines (4) with (3) and solve for \(Y\) to obtain

\[
Y = \frac{fD_o + 2G}{(2K_{eq} + 1)fD_o - 2G(K_{eq} - 1)}.
\]

\[
\text{(5)}
\]

Note that for \(G = 0\) (optical transparency – OT), \(Y_{OT} = 1/(2K_{eq} + 1) = 0.1486\) at 300 K. Eq. (5) represents “Technique #1” for determining yield from the gain diagnostic. The principal advantage of technique #1 is that it provides a relatively quick determination of yield requiring a single measurement. Note that the temperature needed for \(K_{eq}\) is also extracted from the gain measurement. However, the disadvantage is that it requires accurate knowledge of both the \(I_2\) flow rate and the dissociation fraction of the \(I_2\) at the measurement position, i.e., it requires accurate knowledge of \(fD_o\).
A second method, “Technique #2”, does not require the *a priori* assumption of the fractional dissociation of the iodine nor the flow of it. It does this by comparing the relative emission from I\(^*\) and O\(_2\)(a). We rewrite Eq. (4) so that excited states and thus spontaneous radiation from each are compared to each other:

\[
\text{Eq. (4) } \rightarrow \frac{[I^*]}{[O_2(a)]} = K_{eq} \frac{[I]}{[O_2(X)]]} = K_{eq} \frac{[I]}{[O_2(X)]_0(1-Y)}.
\]

(6)

The densities of I\(^*\) and O\(_2\)(a) are related to the integrated spectral emission from each band by:

\[
[I^*] = \frac{C}{A_I} \int [I^*(\lambda)]d\lambda
\]

(7a)

and

\[
[O_2(a)] = \frac{C}{A_\Delta} \int [O_2(a,\lambda)]d\lambda
\]

(7b)

where \(A_I = 7.87 \text{ s}^{-1}\), \(A_\Delta = 1/76 \text{ min} = 2.19 \times 10^4 \text{ s}^{-1}\) and the C’s are the same complex collection of geometric factors for each band. It is even debatable whether the different sensitivities at 1315 nm and 1268 nm of the OMA-V need be taken into account (note that we did not do so here since it is, at most, a few percent correction). Note that the \(A\) coefficient used in Eq. (7a) is the total \(A\) coefficient including all of the iodine hyperfine transitions that appear in the spectra, not just the 3 to 4 hyperfine transition as is used for the stimulated emission cross-section above.

We define \(r\) to be the ratio of the integrated counts,

\[
r = \frac{\int [I^*(\lambda)]d\lambda}{\int [O_2(a,\lambda)]d\lambda} = \frac{\text{# counts under I}^*\text{ spectra}}{\text{# counts under O}_2\text{(a) spectra}}.
\]

(8)

Then Eq. (6) becomes,

\[
K_{eq} \frac{[I]}{[O_2(X)]_0(1-Y)} = \frac{A_\Delta}{A_I} r.
\]

(9)

Now one can combine (9) with (3) and (5) to obtain \(fD_o\)

\[
fD_o = \frac{1}{(2K_{eq} + 1)} \left\{ \frac{3A_\Delta}{A_I} r \cdot [O_2(X)]_0 + 2G(K_{eq} - 1) \right\}
\]

(10)

and use (10) in (5) to obtain the yield

\[
Y = \left( \frac{1}{2K_{eq} + 1} \right) \left[ 1 + \frac{A_I}{A_\Delta} \cdot \frac{2GK_{eq}}{r \cdot [O_2(X)]_0} \right].
\]

(11)

Thus, the principle advantage of using Technique #2 is that \(fD_o\) becomes a measured quantity, Eq. (10), thereby reducing some uncertainty regarding the dissociation fraction and the flow rate measurement of small I\(_2\) flows (discussed below). Therefore, in principle Technique #2 should be a more accurate technique. Another advantage of Technique #2 is that if \(D_o\) is accurately known, then it is possible to compute the dissociation fraction \(f\). The primary disadvantage of this technique is that it requires additional spectral measurements of \(O_2(a)\) and I\(^*\), which requires movement of diagnostic equipment (to get spectral and gain measurements in the same position) and long integration times in the lower density supersonic cavity region, i.e., Technique #2 is a considerably more time consuming measurement.

Note that when \(G\) is negative the yield is less than that for optical transparency. Note too that \([O_2(X)]_0\) is just the sum of \([O_2(X)]\) and \([O_2(a)]\) which is less than the input \(O_2(X)\) density by the sum of the dissociation, \([O]/2\), the \(O_2(b)\) density, \(3/2\) of the \(O_1\) density, and the density of any other such state or molecule. Since the yields that we have measured are on the order of 10\%, the correction for anything other than the dissociation is not warranted. Indeed, even the dissociation is, at most, a 5-10\% correction, which is probably within the statistical accuracy of measuring \(G\) and \(r\) and the knowledge of \(A_\Delta/A_I\). If the correction were included it would represent a reduction in the denominator of yield, and
hence a 5-10% increase in the reported value of yield. Hence, measurements of yield from these techniques presented in this section will ignore dissociation and set $O_2(X)_0 = \text{input density of } O_2$ (at the location of the measurement).

Nominally the spectral measurement would require taking two separate spectra, one for the 1268 $O_2(a)$ emission and one for the 1315 $I^*$ emission, because the strength of the $I^*$ emission is several orders of magnitude larger than that from the $O_2(a)$. The process of taking data with Technique #2 was sped up considerably by using a 1268 narrow band-pass filter, which would reduce the 1315 emission to a level such that the 1268 and 1315 spectra could be observed on the same scan without saturating the detector. Figures 1a-1d illustrate this procedure. Results from this technique are shown later in Section 3.

![Spectral traces](image)

Figures 1a-1d: Spectral traces taken with the OMA-V of the 1268 $O_2(a)$ and 1315 $I^*$ emission lines, with and without a 1268 filter. The 1268 filter is seen to filter out most of the P and R branches of the 1268 spectra and to reduce the magnitude of the 1315 line by roughly 5 orders of magnitude.

### 3. EXPERIMENTAL MEASUREMENTS

A capacitive discharge was used for these experiments. Details of the discharge and its characteristics can be found in Carroll et al. [Carroll, 2003a]. Spectral measurements of the $O_2(1\Delta) \rightarrow O_2(1\Sigma^+$) emission at 1268 nm and of the $1^e \rightarrow 1$ emission at 1315 nm were made using a sensitive Princeton Instruments OMA-V LN$_2$-cooled InGaAs array detector. Atomic oxygen titration measurements were made in the supersonic flow tube and gain (yield) measurements were made in a supersonic diagnostic cavity, Fig. 2. The $I_2$ flow diagnostic was developed and built by PSI and is based upon the continuum absorption of molecular iodine from the ground electronic state ($X^1\Sigma^+$) to both the repulsive $1\Pi_u$ and the bound $B\Pi_v$ states (note that our $I_2$ diagnostic is only a 12-bit system, which is not as accurate as PSI’s newer 20-bit system [Rawlins, 2003]). Wedged AR coated windows were used on the sides of the cavity for the gain diagnostic to minimize etalon effects. Window purges were implemented to insure that the gain region sampled did not include any recirculation regions containing atomic iodine. The supersonic diagnostic cavity is a Mach 2 nozzle derived from the VertiCOIL configuration [Rittenhouse, 1999].
The high sensitivity Iodine Scan diagnostic [Davis, 1996] developed by Physical Sciences Inc. was incorporated into the experimental setup to make measurements of gain/absorption. The Iodine Scan diagnostic is a diode laser based, sensitive monitor for the small signal gain in iodine lasers. The system uses a single mode, tunable diode laser to access all six hyperfine components of the atomic iodine ($^{3}\text{P}_{1/2} \rightarrow ^{3}\text{P}_{3/2}$ transition near 1.315 microns). The Iodine Scan is frequency calibrated for automated operation only for the (3,4) hyperfine transition, the lasing transition in COIL. The unit is configured as a stand alone, automated system that is controlled via a Pentium Class PC. Fiber optic cables are used to deliver the diode laser probe beam to the COIL device, and a reference channel is used to normalize the absorption signals. A third channel is provided either for a second COIL location or for a user provided heated molecular iodine cell. Iodine gain/loss at line center and inferred temperature are displayed at a rate greater than 5 Hz. The user can also store lineshapes for later, more detailed analysis. Since the system uses a narrow band diode laser, the recorded lineshapes can be used to determine the local temperature from the Doppler width along a line of sight. System sensitivity for absorption or gain with this diagnostic is $< 0.01\%$/cm assuming a 10 cm path. For more details about this diagnostic see Davis et al. [Davis, 1996].

An operational problem encountered with the Iodine Scan system is that it was susceptible to electrical noise, in part through the detector and in part through the ILX laser controller. It was found early in its implementation that the RF signal shifted the frequency of the laser; the higher the RF power, the larger the shift. This problem was partially solved by shielding and grounding the capacitive RF discharge to a copper cylinder placed around the discharge section; the cylinder was then grounded to the table.

Oxygen atom titrations using NO$_2$ (a 1:1 titration technique developed by Kaufman [Kaufman, 1958]) were performed for the O$_2$:He = 5:20 mmol/s case as a function of discharge power and discharge pressure. As expected, Fig. 3 shows that the O atom yield increases with discharge power. Figure 3 also shows that the O atom yield drops significantly as pressure is increased. Modeling results (not discussed here) suggest that this is only in part due to O atom recombination [Stafford, 2003] and that a larger fraction of the drop is due to some unknown source.
O$_2$(a) yield measurements were made from the gain diagnostic based upon the techniques outlined in Section 2. Figure 4 shows measured yields of 12% for the He:O$_2$:Ar = 5:20:0 mmol/s, 6.4 torr case, and 11% for the He:O$_2$:Ar = 10:40:0 mmol/s, 10.5 torr case. The result with argon diluent was approximately 7% for the He:O$_2$:Ar = 5:0:15 mmol/s, 9.7 torr case, which supports previous findings that yields with argon diluent in the discharge are not as good as with helium diluent [Carroll, 2003a]. Corresponding measured temperatures in the subsonic region are illustrated in Fig. 5. Flow temperature with helium diluent is observed to be lower than with argon, consistent with previous findings [Carroll, 2003a]. Temperatures measured by the gain diagnostic in the supersonic cavity were in the range of 220-280 K. However, because the gain signal was weak for these cases there was a lot of scatter in the temperature measured by the gain diagnostic and as such is not shown here. The trend was higher temperature for higher absorbed power.
By implementing both techniques 1 and 2 discussed in Section 2, it was possible to deduce the dissociation fraction of donor species I$_2$ or CF$_3$I (some experiments were run with CF$_3$I because it is easier to quantify the flow rate of this iodine donor species than that of I$_2$). Figure 6 illustrates that there is poor dissociation when using CF$_3$I and at higher flow rate/pressure situations; even at 500 W the dissociation is not complete. The CF$_3$I+O dissociation rate is $5.8 \times 10^{-12}$ cm$^3$/molecule-s [Atkinson, 1999], whereas the I$_2$+O dissociation rate is $1.4 \times 10^{-10}$ cm$^3$/molecule-s [Payne, 1998], which is very fast by comparison. The high flow/pressure case also exhibited poor dissociation at lower discharge powers; this is believed to be a consequence of lower O atom yields at higher pressure, Fig. 3. Since a higher pressure system is ultimately desired for scaling reasons, it may be necessary to implement an iodine donor pre-dissociation scheme.

Measurements of gain (absorption) as a function of system input power to the discharge were taken, Figs. 7 and 8. Figure 8 illustrates the measured gain vs. frequency as a function of system power. Initially the magnitude of absorption increases as you increase the system power from 0 to 150 Watts; this is caused by much of the initial energy going into the dissociation of the molecular iodine. Beyond 150 Watts the magnitude of the absorption decreases and heads towards positive gain. Due to system limitations and discharge instabilities at higher powers and higher pressures we have not yet attained positive gain, however we are encouraged by the data and believe that improvements to discharge will ultimately lead to a demonstration of positive gain in the ElectriCOIL system.
4. SUMMARY

Rawlins et al. [Rawlins, 2003] introduced and outlined a method to deduce the O\textsubscript{2}(a) yield from gain measurements and/or gain measurements coupled with spectral measurements of the O\textsubscript{2}(a) and I* lines. A more formal mathematical formulation of this technique is provided in this paper. Using this technique, we measured yields of 12% for the He:O\textsubscript{2}:Ar = 5:20:0 mmol/s, 6.4 torr case, and 11% for the He:O\textsubscript{2}:Ar = 10:40:0 mmol/s, 10.5 torr case. The result with argon diluent was approximately 7% for the He:O\textsubscript{2}:Ar = 5:0:15 mmol/s, 9.7 torr case, which supports previous findings that yields with argon diluent in the discharge are not as good as with helium diluent. Oxygen atom titrations using NO\textsubscript{2} were performed for the O\textsubscript{2}:He = 5:20 mmol/s case as a function of discharge power and discharge pressure. The O atom yield increases with discharge power (as expected) and the O atom yield drops significantly as pressure was increased (the magnitude of this drop with pressure was not expected). Modeling results (not discussed here) suggest that this is only in part due to O atom recombination and that a larger fraction of the drop is due to some unknown source, possibly related to discharge instability issues at higher pressure.

By implementing the techniques discussed above, it was possible to deduce the dissociation fraction of donor species I\textsubscript{2} or CF\textsubscript{3}I. It was found that there was poor dissociation when using CF\textsubscript{3}I and at higher flow rate/pressure situations; even at 500 W the dissociation was not complete. The CF\textsubscript{3}I+O dissociation rate is 24 times slower than the I\textsubscript{2}+O dissociation rate, so it is not unreasonable that better dissociation of the I\textsubscript{2} than of the CF\textsubscript{3}I was observed. The high flow/pressure case also exhibited poor dissociation at lower discharge powers; this is believed to be a consequence of lower O atom yields at higher pressure. Since a higher pressure system is ultimately desired for scaling reasons, it may be necessary to implement an iodine donor pre-dissociation scheme.

Measurements were made of gain as a function of power input to the discharge. Initially the magnitude of absorption increases as the system power was increased from 0 to 150 Watts; this is caused by much of the initial energy going into the dissociation of the molecular iodine. Beyond 150 Watts the magnitude of the absorption decreases and heads towards positive gain. Due to system limitations with existing equipment and discharge instabilities at higher powers and higher pressures we have not yet attained positive gain. However, a great deal of critically important data and information has been accumulated for this extremely complex problem. Further, we have assembled an excellent suite of diagnostics to aid in analyzing and understanding the experimental data. There are still unresolved questions related to the ElectriCOIL processes, but with further effort it is felt that complex processes can be unraveled and detrimental
processes controlled. Ultimately we believe that continued research and development on this concept will lead to a successful gain and lasing demonstration.

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REFERENCES