ElectriCOIL: Preliminary Experiments of Excited Oxygen Generation by RF Discharge

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ABSTRACT

Engineers at CU Aerospace (CUA) and The University of Illinois at Champaign-Urbana (UIUC) have developed an innovation to the classical chemical oxygen-iodine laser (COIL) singlet oxygen generator (SOG) based on discharge excitation of molecular oxygen. A number density of ~2.1x10^15 of O2(1D) was measured for a total O2 flow rate of 7 mmol/s and an O2 partial pressure of 3.0 Torr. Theory indicates that O2(1D) concentrations should be 4-10 times the O2(1S) concentrations.

I. INTRODUCTION

The classical chemical oxygen-iodine laser (COIL) operates on the electronic transition of the Iodine atom at 1315 nm, I*(2P1/2) → I(2P3/2) + hν. The population inversion is provided and maintained by the nearly resonant energy transfer between the excited singlet oxygen O2(1D) molecule and the I atom ground state I(2P3/2) as follows: O2(1D) + I(2P3/2) → O2(1S) + I(2P1/2). Historically, this pumping reaction has been fed by a liquid chemistry singlet oxygen generator (SOG). It is desired to supplant this liquid loop with an all-gas-phase SOG system. Recent research by the Air Force Research Laboratory (AFRL) has demonstrated the feasibility of an NCl(1D) all gas phase chemical system [Henshaw, 2000]. CUA and UIUC believe that another method of energy donor generation may be obtained purely by electrical means.

A new kind of continuous wave COIL device is proposed: an Electrically assisted Chemical Oxygen Iodine Laser (ElectriCOIL) [Carroll, 2000]. ElectriCOIL operates on gaseous oxygen and iodine sources, as well as a to-be-determined diluent gas as flow conditions merit. The energy donor, O2(1D), is created by a combined ac/RF discharge generator surrounding the flow tube. Fujii [Fujii, 1994] reported a 17% yield in a small RF generator. More recently, the Japanese demonstrated 21% yield with a microwave [Itami, 1999] and improved their RF number to 32% [Fujii, 2000; Schmiedberger, 2000]. It is hoped that the ElectriCOIL concept will achieve a yield number of 30% or higher.

CUA and UIUC have taken preliminary steps in the experimental development of this device. A 2" glass flow tube experiment was constructed to demonstrate generation of O2 (1D) by electrical means. Key flow and electrical parameters were varied to characterize the system performance. Several diluents, such as N2, He, Ar, and NO were investigated. The accuracy associated with the O2(1D) measurement is severely limited by the extremely low level of signals due to the 0.276x10^3 s⁻¹ radiative transition rate. However, the O2(1D) → O2(1S) emission at 760 nm was measured with high confidence. Figure 1 depicts one configuration of the experimental setup. The flow tube is constructed of 2" glass, supported by oak standoffs and connected to flow, temperature, and pressure ports by 1/4" Ultra-Torr slip-on fittings. Axial measurements are made possible by 1 1/2" windows present in each of the flow elbows. Two configurations of this experiment were investigated. The first configuration placed the primary elbow approximately 10 inches downstream of the end of the RF coil, leading into a ~30-inch straight section, Figure 1a. A second configuration relocated the straight section just aft of the RF discharge, allowing the flow to proceed in a straight path after exiting the RF coil for some 30 inches, Figure 1b.

RF power is transferred to the flow through a resonator via a 9.7 MHz signal driven by an ENI A-300 RF power amplifier. The baseline case consisted of the above RF input signal, 7 mmol/s of oxygen flow, no diluent, and an AC discharge of 35.4 mA (rms) between 2 electrodes spaced 41 cm apart, as measured by a Pearson 110 current transformer. This discharge has been dubbed the pre-ionization discharge (PIX). Typical incident and reflected RF power levels for this case were 150 and 50 watts, respectively, as measured by a Bird Thruline model 43 wattmeter.
II. THEORY

The role of the $O_2(^1\Sigma_g^+)$ state is essential for the pumping of the upper state of the Iodine laser via:

$$O_2(a^1\Pi_g) + \overset{2}{1}I_{3/2} \rightarrow O_2(x^1\Sigma_g^+) + \overset{2}{1}I_{1/2}$$  \hspace{1cm} (1)

While (1) leads directly to the upper laser level, many of the $O_2(a^1\Pi_g)$ molecules are used to dissociate the iodine molecules.
\[
\begin{align*}
\text{O}_2(a^1\text{D}) + \text{I}_2 & \rightarrow \text{I}_2^* + \text{O}_2(x^3\text{S}) \quad k = 7 \times 10^{-15} \text{ cm}^3/\text{s} & (2a) \\
\text{O}_2(a^1\text{D}) + \text{I}_2^* & \rightarrow 2\text{I} + \text{O}_2(x^3\text{S}) \quad k = 3 \times 10^{-10} \text{ cm}^3/\text{s} \quad (2b)
\end{align*}
\]

Estimates are that approximately 5 \text{O}_2(a^1\text{D}) molecules are used in this process for each iodine molecule. However the \text{O}_2(b^1\text{S}) state can dissociate \text{I}_2 in one step:

\[
\text{O}_2(b^1\text{S}) + \text{I}_2 \rightarrow 2\text{I} + \text{O}_2(x^3\text{S}) \quad k = 4 \times 10^{-12} \text{ cm}^3/\text{s} \quad (3)
\]

For the classic chemically excited COIL, the \text{O}_2(b^1\text{S}) state is only present in very small quantities relative to the singlet-delta and ground state oxygen. In the ElectriCOIL concept, because of significant quantities the \text{O}_2(b^1\text{S}) state may assist in the dissociation process in a more significant way than in the classic COIL. Regardless, the iodine must be dissociated, either with a discharge or by the neutral chemistry route (2) enhanced by (3). The advanced ElectriCOIL system [Carroll, 2000] would also incorporate a pre-dissociation scheme for the iodine prior to injection into the \text{O}_2(b^1\text{S}) flow.

The justification for the use of an electrical discharge for the production of \text{O}_2(a^1\text{D}) and \text{O}_2(a^1\text{S}) states is provided by Figures 2 and 3. These are the predictions from a Boltzmann Equation solver (by Prof. M. Kushner) which tracks the fraction of electrical power utilized for each electron energy loss process. Shown here is the fraction used to excite the \text{O}_2(a^1\text{D}) state (0.977 eV/exc.) and the fraction used to excite the \text{O}_2(a^1\text{S}) state (1.627 eV). In both the pure \text{O}_2 and 1:1 mixture of Helium and \text{O}_2, nearly 50% of the electrical power can be used to produce \text{O}_2(a^1\text{D}) molecules and 20% can be used for the production of the \text{O}_2(a^1\text{S}) state at an E/N of about 8 \times 10^{-17} \text{ volt-cm}^2.

![Figure 2: Results of Boltzmann Calculation for Pure O2](image1)

![Figure 3: Results of Boltzmann Calculation with mix of He:O2 = 1:1](image2)

Obviously, the efficiency of the discharge in the production of the \text{O}_2(a^1\text{D}) state is critically dependent on the electric field-to-gas density ratio, E/N, with the optimum being ~10^{-16} \text{ V-cm}^2 for pure \text{O}_2 and slightly lower, 8 \times 10^{-17} \text{ V-cm}^2 for the 1:1 mixture of \text{He}:\text{O}_2. The total collisional power deposition and electron drift velocity as a function of E/N is shown in Figure 4 for a gas density of 10^{17} \text{ cm}^{-3} (p = 3.11 \text{ torr} @ 298\text{K}) and 3 electron densities in the range of our experiments.

As of this writing, we have not yet measured the electron density, but the V-I characteristic of the pre-ionization discharge suggests that an E/N of 1.5 \times 10^{-16} \text{ V-cm}^2 and an electron density of ~1 \times 10^{10} \text{ cm}^{-3} is a reasonable estimate for it (12 watts). Thus, this same value is a reasonable estimate for the 100 watt RF discharge with an increased electron density of ~8 \times 10^{10} \text{ cm}^{-3}.
For this E/N, 28.9% of the total 112 watts (32.4 watts) is used to produce \( \text{O}_2(\alpha_1 \text{D}) \) state (0.9775 eV/state) and 11.3% (12.7 W) is used to produce \( \text{O}_2(\beta_1 \text{S}) \) (1.627 eV/state). A typical mass flow rate of 7 mmol/s yields a peak laminar flow velocity of 3.78\( \times \)10\(^3\) cm/s and thus the average lifetime due to flow through the RF coil is 12 ms.

Thus, if one uses the fractional power deposition mentioned above, one can obtain a first order estimate of the densities of the excited states: \([\text{O}_2(\alpha_1 \text{D})]\) and \([\text{O}_2(\beta_1 \text{S})]\). The production rate for \((\alpha_1 \text{D})\) is:

\[
\frac{d[\alpha_1 \text{D}]}{dt} = + \frac{32.4W}{\text{Vol.} = 192.6\text{cm}^3} \frac{1}{0.9775\text{eV}} \frac{1}{1.6 \times 10^{19} \text{j/eV}} = 1.08 \times 10^{18} \text{cm}^3 / s
\]

Setting this production equal to the loss due to flow: \( \text{O}_2[\alpha_1 \text{D}]^* \) yields \( \text{O}_2[\alpha_1 \text{D}] = 1.37 \times 10^{16} \text{ cm}^{-3} \).

Doing the same calculation for the \((\beta_1 \text{S})\) state yields:

\[
\frac{d[\beta_1 \text{S}]}{dt} = + \frac{12.7W}{\text{Vol.} = 192.6\text{cm}^3} \frac{1}{1.627\text{eV}} \frac{1}{1.6 \times 10^{19} \text{j/eV}} = 2.53 \times 10^{17} \text{ cm}^3 / s
\]

and thus the exit density is: 3.2\( \times \)10\(^{15}\) cm\(^{-3}\)/s. This latter number is in good agreement with the fluorescence measurement of the \( ^5 \text{D} \) \( ^3 \text{S} \) radiation at 761.9 nm (see Figure 9, position 1").

There is a very simple reason for the exit ratio of \([\alpha_1 \text{D}]/[\beta_1 \text{S}] \sim 4.2\) predicted by the above theory. This is shown in Figure 5, where the cross-sections for the production of these two states are plotted as a function of energy. For virtually all electron energies of significance, the cross-section for the production of \([\alpha_1 \text{D}]\) is at least 4 times that for the production of \([\beta_1 \text{S}]\).

![Figure 4: Collisional Power and Drift Velocity versus E/N Compared for Pure Oxygen Gas and 1:1 Oxygen:Helium Mixture](image-url)
III. EXPERIMENTAL RESULTS

The primary measurement made on the ElectriCOIL flow tube experiment is a spectrographic analysis at 760 nm. A Santa Barbara Instruments Group, Inc. ST-6 CCD camera coupled to a data acquisition (DAQ) computer (through a monochromator), and employing KestrelSpec software, provides peak count levels as viewed across the 2” flow cross-section. Flow rates, RF and ac power levels, and diluent gas species and flow rates are all varied independently. The camera is translated along the flow axis (denoted the x axis) to obtain maps of O$_2$(^1S) versus x position. A typical scan exposure of five seconds yielded the baseline trace seen in Figure 6a; a theoretical calculation is shown in Figure 6b. Note that the agreement between experiment and theory is excellent.

Studies were performed to investigate the effect of oxygen flow rate, diluent type and flow rate, system pressure, and axial flow position. The results of the major trade studies are presented in Figures 7-12. Axial distance is measured from the end of the ac discharge section. For a given power deposition level (typically ~100 watts), increasing the molar flow rate of the O$_2$ yielded a decrease in the O$_2$(^1S) measurement, Figure 7; this is most likely an energy density issue. Differing diluent species yielded considerably different behaviors on the O$_2$(^1S) production
level, Figure 8. Helium was seen to produce the strongest favorable response, while Nitrogen was observed to be a
detriment to the O_2[^1] reading at any level whatsoever. Figure 9 depicts the results of an experiment where the
CCD was translated downstream perpendicular to the flow axis. It is seen that the O_2[^1] level drops exponentially
in the flow direction. The data fits in Figure 9 are direct exponential fits. It is of interest that the amount of Helium
diluent added does not effect only the level of the O_2[^1] reading, it also alters the slope of the exponential fit to the
data. The overall exponential decay in signal is attributed to wall effects. The flattening of the fit slope with added
Helium suggests a flow velocity effect.

Figure 7: Effect of Oxygen Flow Rate on Peak O_2[^1] Level for a Fixed RF Input Power and Fixed Position of x=7'', Configuration 2

Figure 8: Effect of Diluent Gas Species and Partial Pressure for 7 mmol/s Oxygen, Fixed Position of 10'' downstream, Configuration 1

Figure 9: Effect of Helium Flow Rate (1.2 mmol/s of He per 1 Torr He) on O_2[^1] Level with Varying Position for 7 mmol/s Oxygen Flow, Configuration 2.
Figures 10 and 11 present the effect of the Pre-Ionization Discharge (PIX) as a function of the different flow rates of oxygen. This effect is particularly significant at high flow rates of oxygen, e.g. the 20 mmol/s case. For the lower flow rates of 2 mmol/s and 10 mmol/s the effect of the PIX was minimal.

Figures 10 and 11: Comparison of Distance Effect on Detected Peak Count Level for Varying Oxygen Flow Rates. Figure 10 (left) Has PIX Turned Off. Figure 11 (right) Has PIX On. (Both tests were performed in Configuration 1)

The next key measurement is that of the $O_2^{(1D)} \to O_2^{(3S)}$ emission at 1268 nm. As of this date, all measurements of $O_2^{(1D)}$ have been performed using a thermoelectrically-cooled germanium photodiode, filtered by a Coherent 42-6338 IR narrow bandpass filter and chopped at 159.8 Hz. Our signal with this setup was extremely weak because this particular narrow bandpass filter had a peak transmission at 1258 nm and less than 10% transmittance at 1268 nm. Typical peak signal levels, as measured by a Stanford Research lock-in amplifier, were ~45 mV for a typical scan length of 12”. Figure 12 illustrates the improvement in $O_2^{(1D)}$ signal as a function of absorbed RF power.

Figure 12: $O_2^{(1D)}$ Signal from Germanium Photodiode as a Function of Absorbed RF Power.
IV. SUMMARY

Advanced chemical iodine laser technology will logically include novel all gas phase generation techniques for an iodine energy donor and the injection of atomic rather than molecular iodine. A candidate method, RF excitation in conjunction with an ac discharge, has been investigated in this paper. It is seen that both the singlet sigma O$_2$ (1$^\Sigma_g^+$) and singlet delta O$_2$ (1$^\Delta_g$) excited states of the oxygen molecule may be readily created via electrical excitation in the laboratory. Both ac discharge and RF absorption are employed in tandem to bring about this excitation; this is a very important factor for higher flow rates. We believe that it may be possible to successfully supplant the two-phase elements (liquid BHP and a chlorine/helium/nitrogen gas mixture) of the classical COIL SOG using the ElectriCOIL prototype system.

ElectriCOIL will reduce weight and simplify both military and commercial chemical iodine laser systems. Potential cost and weight savings are also envisioned as the massive quantities of liquid chemicals will be completely eliminated from the device operation. Difficulty will certainly be encountered when searching for a yardstick to predict ElectriCOIL performance. Typical measures such as chemical efficiency must be redefined (or eliminated) to account for changes in the chemistry and parameters like the electrical power absorbed by the flow from the RF discharge. A set of diagnostics and analysis are planned to take advantage of the current development effort.

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